

NATIONAL AND KAPODISTRIAN UNIVERSITY OF ATHENS DEPARTMENT OF HISTORY AND PHILOSOPHY OF SCIENCE PROGRAM OF GRADUATE STUDIES

Ph.D. RESEARCH THESIS

"The penetration of thermodynamics into chemistry: The birth

of chemical thermodynamics in Europe and America"

Photis Dais

Athens April 2021



ΕΘΝΙΚΟ ΚΑΙ ΚΑΠΟΔΙΣΤΡΙΑΚΟ ΠΑΝΕΠΙΣΤΉΜΙΟ ΑΘΗΝΏΝ ΤΜΗΜΑ ΙΣΤΟΡΙΑΣ ΚΑΙ ΦΙΛΟΣΟΦΙΑΣ Της ΕΠΙΣΤΗΜΗΣ ΠΡΟΓΡΑΜΜΑ ΜΕΤΑΠΤΥΧΙΑΚΩΝ ΣΠΟΥΔΩΝ

ΔΙΔΑΚΤΟΡΙΚΗ ΔΙΑΤΡΙΒΗ

"Η διείσδυση της θερμοδυναμικής στη χημεία. Η γέννηση της χημικής θερμοδυναμικής στην Ευρώπη και την Αμερική"

Φώτης Νταής

Αθήνα, Απρίλιος 2021

Ph.D. RESEARCH THESIS

"The penetration of thermodynamics into chemistry: The birth of

chemical thermodynamics in Europe and America"

Photis Dais

ADVISORY COMMITTEE

Theodore Arabatzis, Professor of the Department of History and Philosophy of Science, National and Kapodistrian University of Athens (supervisor)

Aristotle Tympas, Professor of the Department of History and Philosophy of Science, National and Kapodistrian University of Athens

Kostas Gavroglu, Professor Emeritus of the Department of History and Philosophy of Science, National and Kapodistrian University of Athens

SEVEN MEMBERS EXAMINATION COMMITTEE

Theodore Arabatzis Professor, UoA

Eystathios Arapostathis, Assistant Professor, UoA

Efthymios P. Bokaris Associate Professor, Uol

Kostas Tampakis Associate Researcher, EIE Aristotle Tympas, Professor, UoA

Andreas Koutselos Professor, UoA

Efthymios Nicolaidis Research Director, EIE

Examination Date 04/23/2021

ΔΙΔΑΚΤΟΡΙΚΗ ΔΙΑΤΡΙΒΗ

"Η διείσδυση της θερμοδυναμικής στη χημεία. Η γέννηση της

χημικής θερμοδυναμικής στην Ευρώπη και την Αμερική″

Φώτης Νταής

ΤΡΙΜΕΛΗΣ ΣΥΜΒΟΥΛΕΥΤΙΚΗ ΕΠΙΤΡΟΠΗ:

Θεόδωρος Αραμπατζής, Καθηγητής, Τμήμα Ιστορίας και Φιλοσοφίας της Επιστήμης, Εθνικό και Καποδιστριακό Πανεπιστήμιο Αθηνών (επιβλέπων καθηγητής)

Αριστοτέλης Τύμπας, Καθηγητής Τμήμα Ιστορίας και Φιλοσοφίας της Επιστήμης, Εθνικό και Καποδιστριακό Πανεπιστήμιο Αθηνών

Κώστας Γαβρόγλου, Ομότιμος Καθηγητής Τμήμα Ιστορίας και Φιλοσοφίας της Επιστήμης, Εθνικό και Καποδιστριακό Πανεπιστήμιο Αθηνών

ΕΠΤΑΜΕΛΗΣ ΕΞΕΤΑΣΤΙΚΗ ΕΠΙΤΡΟΠΗ

Θεόδωρος Αραμπατζής Καθηγητής, ΕΚΠΑ

Αριστοτέλης Τύμπας Καθηγητής, ΕΚΠΑ

Ευστάθιος Αραποστάθης, Επίκουρος Καθηγητής, ΕΚΠΑ Ανδρέας Κούτσελος Καθηγητής, ΕΚΠΑ

Ευθύμιος Μπόκαρης Αναπληρωτής Καθηγητής, Παν/μιο Ιωαννίνων Ευθύμιος Νικολαΐδης **Διευθυντής Ερευνών, ΕΙΕ**

Κώστας Ταμπάκης Συνεργάτης Ερευνητής, ΕΙΕ

Υποστήριξη διατριβής 23/04/2021

Abstract

The first volume of the Zeitschrift für Physikalische Chemie appeared with important articles by van t 'Hoff, Ostwald and Arrhenius. Their publications in the journal, founded in 1887 by Ostwald and van 't Hoff, formed the theoretical basis of the new science of chemical thermodynamics. They succeeded in introducing thermodynamics into chemistry and providing the new science with a comprehensive theory of solutions based on the osmotic pressure and the dissociation of electrolytes in aqueous solutions. The latter approach was the cause for their sobriquet "the ionists." As in every science, the formulation of chemical thermodynamics presupposes the development and integration of a specific scientific background of theories and experiments that preceded and was made available to the ionists. This dissertation deals with the development of chemistry and thermodynamics has deeper roots that go back to the works of the natural philosophers of the eighteenth and early nineteenth centuries.

The first part of this dissertation deals with the development of chemical thermodynamics during the first half of the nineteenth century. This period could be characterized as the prehistory of chemical thermodynamics or the period of classical chemical thermodynamics. This part contains the endeavors of natural philosophers to understand the formation and decomposition of substances. The nature of forces that bind the particles together or make them fall apart. In short, they sought to find explanations for the chemical affinity. The discovery of the effect of concentration of substances on chemical affinity by Claude Berthollet in the early nineteenth century posed new questions

for philosophers. This time, about the equilibrium conditions in chemical reactions. The discovery of the electric battery by Volta in 1799 and the study of the phenomenon of electrolysis lead prominent natural philosophers, such as Davy, Grotthuss, Faraday, Ohm, Becquerel, Berzelius, and others, to search for the causes of the decomposition of substances and the mechanism of propagation of electricity in liquid conductors.

During the period 1830-1850, twelve natural philosophers, working independently, discovered simultaneously the first law of thermodynamics. In the 1850s, three eminent physicists Rudolf Clausius, William Rankine, and William Thomson (the late Lord Kelvin) enunciated the second law of thermodynamics. Chemists understood only the first law and used it in their laboratories, signaling the beginning of a new branch of chemistry, thermochemistry. The first part of the dissertation concludes with a brief description of the evolution of the law of the conservation of energy in chemistry and physiology.

The second part of this dissertation describes the evolution of chemical thermodynamics at a higher level of development. During this period, fragmentary and unconnected theories and experiments of the first half of the century began to systematize and integrate complex systems, both in electrochemistry and thermodynamics. Chemical thermodynamics benefited greatly from several scientific developments. First, two great electrochemists, Wilhelm Hittorf and Friedrich Kohlrausch presented experimental methods, innovative instrumentation, and a plethora of experimental results. Second, the discovery of the battery of constant current intensity by John Daniell and William Grove. This innovation significantly improved the accuracy of electrochemical measurements. Third, Rudolf Clausius and Hermann von Helmholtz elaborated on the phenomenon of

electrolysis and polarization of the electrodes, respectively. Fourth, Josiah Willard Gibbs, Pierre Duhem, and Hermann Helmholtz advanced the thermodynamic theory.

Hittorf measured the relative velocities of the ions (anions and cations) of the electrolytes and their transference numbers (percentage of the total electrical charge that each ion carries into the solution). In contrast, Kohlrausch employed the technique of electrical conductivity to examine the ability of electrolytic solutions to conduct electricity. From the multitude of measurements of the electrical conductivity of solutions of acids, bases, and salts, he derived the two laws of the electrolyte solutions that carry his name. Also, during the second half of the nineteenth century, Helmholtz proposed his electrical double-layer as an adequate theoretical model that explained the origin of electrode polarization.

Josiah Willard Gibbs and Pierre Duhem were two physicists whose theoretical approaches to thermodynamics significantly fostered the development of chemical thermodynamics. The two scientists followed a different path from the molecular mechanics of Maxwell and Boltzmann. Their thermodynamics had characteristics of an abstract, phenomenological methodology. They also showed differences in their theoretical approaches to thermodynamics. Gibbs examined the stability (or instability) of equilibrium states in homogeneous and heterogeneous multi-component systems in the context of rational mechanics, while Pierre Duhem aimed at integrating thermodynamics with the principles of rational dynamics. Duhem attempted to give a dynamic character to thermodynamics using the analytical mechanics of Lagrange. He believed that Lagrangian mechanics was the proper means to introduce time and motion into thermodynamics.

Х

The second part of this thesis involves an extensive analysis of Gibbs and Duhem's work in thermodynamics. It deserves to emphasize Duhem's relentless attempts to unify physics with chemistry, two sciences, which developed in parallel for almost the entire nineteenth century. This part ends with a thorough examination of the impact of Gibbs and Duhem's approach to thermodynamics on the development of chemical thermodynamics.

The third part of this dissertation considers the various internal and external factors that influenced the development of chemical thermodynamics in Europe during the nineteenth century. The analysis of these factors led to a parallel investigation of the conditions that paved the way for the emergence of a new technological branch of chemistry, chemical engineering.

The penetration of thermodynamics into chemistry is the subject of the following three chapters of the third part of the dissertation. During the last two decades of the nineteenth century, the three ionists, Arrhenius, van 't Hoff, and Ostwald, succeeded in integrating various uncorrelated studies and presenting a compact theoretical and experimental whole, which constituted their theory of solutions. The thesis describes the programs chosen by each ionist, his methodological approaches, and interpretations, the empirical methods he used, the influences from his immediate and international scientific environment, and the cultural and scientific traditions of his country. The same chapter includes a brief account of the contribution of Ostwald's collaborator Walther Nernst to ionists' chemical thermodynamics. Also, the chapter refers to the theoretical elaboration of the theory of solutions by Max Planck.

The thesis examines how the ionists communicated their results to the scientific community and each other and their struggle to defend their theory of solutions,

XI

particularly the electrolytic dissociation theory of Arrhenius, against the strong opposition and sometimes hostile criticism, especially from the British organic chemists.

The last chapter of this dissertation examines some aspects of the transfer and the development of chemical thermodynamics in America during the first two to three decades of the twentieth century. It is known that this transfer was realized by the American chemists, who trained in Germany, and in particular in Ostwald's laboratory at Leipzig. When the first generation of American chemists returned to America, they strove to establish a new science. However, American chemists were not mere carriers of the ionists' ideas, but they appropriated this knowledge. Except for Wilder Bancroft, who adopted a research program based exclusively on Gibbs' phase rule, most American chemists set forth research programs to investigate the anomalies observed in the ionists' theory, for example, the abnormal behavior of strong electrolytes. One of the most interesting figures of the first generation of American chemists was Gilbert Newton Lewis, whose personality and research program serve as a case study in this dissertation.

Subject Area: History of Science/The development of the chemical thermodynamics during the nineteenth century/the genesis of chemical thermodynamics in Europe and its transfer to America.

Key words: thermodynamics, chemistry, physics, electrochemistry, chemical kinetics, chemical affinity, chemical equilibrium, chemical engineering, galvanic cells, electrolytes, ions, electrolysis, ionic mobility, transference number, electrical conductivity, electrode polarization, electromotive force, first and the second law of thermodynamics, phase rule,

potentials, rational thermodynamics, chemical potential, thermodynamic potential, Gibbs-Duhem equation, Gibbs-Helmholtz equation, ionic dissociation, osmotic pressure, strong electrolytes, fugacity, activity, activity coefficient, ionic strength, free energy.

Περίληψη

Ο πρώτος τόμος του περιοδικού Zeitschrift für Physikalische Chemie εμφανίστηκε με σημαντικά άρθρα των van t' Hoff, Ostwald και Arrhenius. Οι δημοσιεύσεις τους στο περιοδικό, το οποίο ίδρυσαν το 1887 οι Ostwald και van 't Hoff, αποτέλεσαν τη θεωρητική βάση της νέας επιστήμης της χημικής θερμοδυναμικής. Κατάφεραν να εισαγάγουν τη θερμοδυναμική στη χημεία και να προσφέρουν στη νέα επιστήμη μια ολοκληρωμένη θεωρία των διαλυμάτων με βάση την ωσμωτική πίεση και τη διάσταση των ηλεκτρολυτών σε υδατικά διαλύματα. Η θεωρία της ηλεκτρολυτικής διάστασης ήταν η αιτία για το υποκοριστικό τους, οι «ιοντιστές». Όπως συμβαίνει σε κάθε επιστήμη, η διατύπωση της χημικής θερμοδυναμικής προϋποθέτει την ανάπτυξη και ολοκλήρωση ενός συγκεκριμένου επιστημονικού υποβάθρου θεωριών και πειραμάτων που προηγήθηκαν και τέθηκαν στη διάθεση των ιοντιστών. Η διατριβή ασχολείται με την ανάπτυξη της χημείας και της θερμοδυναμικής τα προηγούμενα χρόνια πριν τη διατύπωση των θεωριών των ιοντιστών. Η χημική θερμοδυναμική έχει βαθύτερες ρίζες που πηγαίνουν πίσω στα έργα των φυσικών

Το πρώτο μέρος της διατριβής ασχολείται με την ιστορία της χημικής θερμοδυναμικής κατά το πρώτο μισό του δέκατου ένατου αιώνα. Αυτή η περίοδος θα μπορούσε να χαρακτηριστεί ως η προϊστορία της χημικής θερμοδυναμικής, ή αλλιώς, η περίοδος της κλασικής χημικής θερμοδυναμικής. Το πρώτο μέρος περιγράφει τις προσπάθειες των φυσικών φιλοσόφων να κατανοήσουν τον τρόπο με τον οποίο σχηματίζονται και διασπώνται οι χημικές ενώσεις. Να κατανοήσουν τη φύση των δυνάμεων που συνδέουν τα συστατικά στοιχεία των ουσιών και τον τρόπο που αυτές αποσυντίθενται. Εν συντομία, οι φυσικοί φιλόσοφοι προσπάθησαν να βρουν εξηγήσεις για

XIV

την προέλευση της χημικής συγγένειας. Η ανακάλυψη της επίδρασης της συγκέντρωσης των ουσιών στη χημική συγγένεια από τον Claude Berthollet στις αρχές του δέκατου ένατου αιώνα, έθεσε νέα ερωτήματα στους φυσικούς φιλόσοφους. Αυτή τη φορά, σχετικά με τις συνθήκες ισορροπίας στις χημικές αντιδράσεις. Η ανακάλυψη της ηλεκτρικής μπαταρίας από τη Volta το 1799 και η μελέτη του φαινομένου της ηλεκτρόλυσης οδήγησαν εξέχοντες φυσικούς φιλόσοφους της εποχή, όπως οι Davy, Grotthuss, Faraday, Ohm, Berzelius, Becquerel και άλλους να αναζητήσουν τις αιτίες της διάσπασης των ουσιών και του μηχανισμού διάδοσης του ηλεκτρισμού στους υγρούς αγωγούς.

Την περίοδο 1830-1850, δώδεκα φυσικοί φιλόσοφοι ανακαλύπτουν σχεδόν ταυτόχρονα και ανεξάρτητα ο ένας από τον άλλο τον πρώτο νόμο της θερμοδυναμικής, ενώ στη δεκαετία του 1850 τρεις επιφανείς φυσικοί Rudolf Clausius, William Rankin και William Thomson (Lord Kelvin) διατυπώνουν τον δεύτερο νόμο της θερμοδυναμικής. Οι χημικοί αντιλαμβάνονται μόνο τον πρώτο νόμο και τον χρησιμοποιούν στο εργαστήριό, σηματοδοτώντας έτσι την έναρξη ενός νέου κλάδου της χημείας, της θερμοχημείας. Το πρώτο μέρος της διατριβής ολοκληρώνεται με μια σύντομη περιγραφή της εξέλιξης του νόμου της διατήρησης της ενέργειας στο πλαίσιο της χημείας και της φυσιολογίας.

Το δεύτερο μέρος της διατριβής περιγράφει την εξέλιξη της χημικής θερμοδυναμικής σε υψηλότερο επίπεδο ανάπτυξης. Κατά τη διάρκεια αυτής της περιόδου, αποσπασματικές και ασύνδετες θεωρίες και πειραματισμοί του πρώτου μισού του δέκατου ένατου αιώνα αρχίζουν να συστηματοποιούνται και να ενσωματώνονται σε σύνθετα συστήματα, τόσο στην ηλεκτροχημεία, όσο και στη θερμοδυναμική. Η χημική θερμοδυναμική ωφελήθηκε σημαντικά και από άλλες επιστημονικές εξελίξεις. Πρώτον, οι πειραματικές μέθοδοι, η καινοτόμος οργάνωση και η πληθώρα πειραματικών

XV

αποτελεσμάτων από δύο μεγάλους ηλεκτροχημικούς, τους Wilhelm Hittorf και Friedrich Kohlrausch. Δεύτερον, η ανακάλυψη της μπαταρίας σταθερής έντασης ρεύματος από τους John Daniell και William Grove. Αυτή η καινοτομία βελτίωσε σημαντικά την ακρίβεια των ηλεκτροχημικών μετρήσεων. Τρίτον, η θεωρητική επεξεργασία του φαινομένου της ηλεκτρόλυσης και της πόλωσης των ηλεκτροδίων στα γαλβανικά στοιχεία από τους Rudolf Clausius και Hermann von Helmholtz, αντίστοιχα. Τέταρτον, οι προηγμένες προσεγγίσεις στη θερμοδυναμική θεωρία που αναπτύχθηκαν από τους Josiah Willard Gibbs, Pierre Duhem και Hermann Helmholtz.

Ο Hittorf μέτρησε τη σχετική ταχύτητα (ευκινησία) των ιόντων (ανιόντα και κατιόντα) των ηλεκτρολυτών και τους αριθμούς μεταφοράς (ποσοστό του ολικού ηλεκτρικού φορτίου που κάθε ιόν μεταφέρει μέσα στο διάλυμα), ενώ ο Kohlrausch χρησιμοποίησε την ηλεκτρική αγωγιμότητα για να δώσει ποσοτική έκφραση στην ικανότητα των ηλεκτρολυτικών διαλυμάτων να άγουν τον ηλεκτρισμό. Από το πλήθος των μετρήσεων της ηλεκτρικής αγωγιμότητας των διαλυμάτων οξέων, βάσεων και αλάτων, ο Kohlrausch προχωρεί στη διατύπωση των δύο νόμων των ηλεκτρολυτικών διαλυμάτων σξέων, βάσεων και αλάτων, ο Helmholtz προτείνει το θεωρητικό μοντέλο της ηλεκτρικής διπλής στοιβάδας για να εξηγήσει το φαινόμενο της πόλωσης των ηλεκτροδίων.

Ο Josiah Willard Gibbs και ο Pierre Duhem ήταν οι δύο φυσικοί, των οποίων η θερμοδυναμική είχε σημαντικό αντίκτυπο στην ανάπτυξη της χημικής θερμοδυναμικής. Οι δύο επιστήμονες ακολούθησαν μια διαφορετική πορεία από τη μοριακή μηχανική των Maxwell και Boltzmann. Η θερμοδυναμική τους είχε χαρακτηριστικά αφηρημένης, φαινομενολογικής μεθοδολογίας. Έδειξαν, ωστόσο, και μεταξύ τους διαφορές στη

XVI

θεωρητική προσέγγισή της θερμοδυναμικής. Ο Gibbs εξετάζει τη σταθερότητα (ή την αστάθεια) καταστάσεων ισορροπίας σε ομοιογενή και ετερογενή συστήματα πολλών συστατικών στα πλαίσια της ορθολογικής μηχανικής, ενώ ο Pierre Duhem στοχεύει στην ενοποίηση της θερμοδυναμικής με τις αρχές της ορθολογικής δυναμικής Ο Duhem προσπαθεί να δώσει ένα δυναμικό χαρακτήρα στη θερμοδυναμική χρησιμοποιώντας την αναλυτική μηχανική του Lagrange. Θεωρεί ότι η Λαγκρασιανή μηχανική είναι το καταλληλότερο εργαλείο για να εισάγει το χρόνο και την κίνηση στη θερμοδυναμική. Αξίζει να τονιστεί η ακούραστη προσπάθεια του Duhem να ενοποιήσει τη φυσική με τη χημεία, δύο επιστήμες που αναπτύχθηκαν παράλληλα για σχεδόν ολόκληρο τον δέκατο ένατο αιώνα. Το δεύτερο μέρος της διατριβής περιλαμβάνει μια εκτενή ανάλυση των εργασιών τους στη θερμοδυναμική και ολοκληρώνεται με την διεξοδική εξέταση της επίδρασης των θεωριών των Gibbs και Duhem στην περαιτέρω ανάπτυξη της χημικής θερμοδυναμικής.

Το τρίτο μέρος της διατριβής ξεκινά με την εξέταση των διαφόρων εσωτερικών και εξωτερικών παραγόντων που επηρέασαν την ανάπτυξη της χημικής θερμοδυναμικής στην Ευρώπη κατά τον δέκατο ένατο αιώνα. Η ανάλυση αυτών των παραγόντων οδήγησε σε μια παράλληλη διερεύνηση των συνθηκών που άνοιξαν το δρόμο στην εμφάνιση ενός νέου τεχνολογικού κλάδου της χημείας, τη χημική μηχανική.

Η διείσδυση της θερμοδυναμικής στη χημεία, η οποία σηματοδοτεί τη γέννηση της σύγχρονης χημικής θερμοδυναμικής, αποτελεί το αντικείμενο των επόμενων τριών κεφαλαίων του τρίτου μέρους της διατριβής. Κατά τις δύο τελευταίες δεκαετίες του δέκατου ένατου αιώνα, οι τρεις ιοντιστές, οι Arrhenius, van 't Hoff και ο Ostwald επιτυγχάνουν να ενοποιήσουν διάφορες, ασύνδετες μεταξύ τους μελέτες και να

XVII

παρουσιάσουν ένα συμπαγές θεωρητικό και πειραματικό σύνολο. Τη θεωρία των διαλυμάτων, τη θεωρητική βάση μιας νέας επιστήμης, της φυσικής χημείας. Η διατριβή αναφέρεται στα προγράμματα που επιλέγουν οι ιοντιστές, στις μεθοδολογικές προσεγγίσεις και ερμηνείες τους, στις πειραματικές μεθόδους που χρησιμοποιούν, στις επιρροές από το άμεσο και διεθνές επιστημονικό περιβάλλον και στην επίδραση των πολιτισμικών παραδόσεων των χωρών τους. Μικρή σε έκταση, αλλά ουσιαστική έμφαση δίνεται στο επιστημονικό στυλ και στον τρόπο σκέψης του κάθε ιοντιστή. Στο ίδιο κεφάλαιο γίνεται μια σύντομη αναφορά της συνεισφοράς του συνεργάτη του Ostwald, Walther Nernst στη χημική θερμοδυναμική των ιοντιστών και στην θεωρητική επεξεργασία της θεωρίας των διαλυμάτων από τον Max Planck.

Η διατριβή εξετάζει τον τρόπο με τον οποίο οι ιοντιστές κοινοποιούν τα πειραματικά αποτελέσματα στην επιστημονική κοινότητα, αλλά και μεταξύ τους. Τον αγώνα τους να υπερασπιστούν τις θεωρίες τους και ειδικότερα τη θεωρία της ηλεκτρολυτικής διάστασης του Arrhenius, εναντίον της ισχυρής αντίδρασης και μερικές φορές εχθρικής κριτικής, ιδιαίτερα από τους Βρετανούς οργανικούς χημικούς.

Το τελευταίο κεφάλαιο της διατριβής εξετάζει ορισμένες πτυχές της μεταφοράς και της ανάπτυξης της χημικής θερμοδυναμικής στην Αμερική κατά τις πρώτες δύο έως τρεις δεκαετίες του εικοστού αιώνα. Είναι γνωστό ότι αυτή η μεταφορά πραγματοποιήθηκε από τους Αμερικανούς χημικούς, οι οποίοι εκπαιδεύτηκαν στη Γερμανία, και ιδιαίτερα στο εργαστήριο του Ostwald στη Λειψία. Όταν επιστρέφει στην Αμερική η πρώτη γενιά των Αμερικανών χημικών, προσπαθεί να καθιερώσει μια νέα επιστήμη, τη φυσική χημεία. Εφοδιασμένοι με τις γνώσεις που απόκτησαν στην Ευρώπη, οι Αμερικανοί φυσικοχημικοί επιχειρούν να βρουν νέες απαντήσεις σε παλιά προβλήματα. Οι Αμερικανοί χημικοί δεν είναι απλοί φορείς των θεωριών των ιοντιστών, αλλά οικειοποιούνται αυτήν τη γνώση. Με εξαίρεση τον Wilder Bancroft, ο οποίος υιοθέτησε ένα ερευνητικό πρόγραμμα βασισμένο αποκλειστικά στον κανόνα των φάσεων του Gibbs, οι περισσότεροι Αμερικανοί χημικοί συγκροτούν ερευνητικά προγράμματα με στόχο την διερεύνηση των αδυναμιών της θεωρίας των ιοντιστών, για παράδειγμα, την ανώμαλη συμπεριφορά των ισχυρών ηλεκτρολυτών. Μία από τις πιο ενδιαφέρουσες μορφές της πρώτης γενιάς των Αμερικανών χημικών είναι ο Gilbert Newton Lewis, του οποίου η προσωπικότητα και το ερευνητικό

Θεματική περιοχή: Ιστορία της επιστήμης/Ιστορία της ανάπτυξης της χημικής θερμοδυναμικής κατά τον δέκατο ένατο αιώνα / Η γέννηση της χημικής θερμοδυναμικής στην Ευρώπη και η μεταφορά της στην Αμερική.

Λέξεις κλειδιά: θερμοδυναμική, χημεία, φυσική, ηλεκτροχημεία, χημική κινητική, χημική μηχανική, χημική συγγένεια, χημική ισορροπία, ηλεκτρολύτες, ιόντα, ηλεκτρόλυση, γαλβανικά στοιχεία, ηλεκτρεγερτική δύναμη, ευκινησία ιόντων, αριθμός μεταφοράς, ηλεκτρική αγωγιμότητα, πόλωση ηλεκτροδίων, πρώτος και δεύτερος νόμος της θερμοδυναμικής δυναμικά, κανόνας των φάσεων, ορθολογική θερμοδυναμική χημικό δυναμικό, εξίσωση Gibbs-Duhem, εξίσωση Gibbs-Helmholtz, θεωρία ηλεκτρολυτικής διάστασης, ωσμωτική πίεση, ισχυροί ηλεκτρολύτες, πτητικότητα, ενεργότητα, συντελεστής ενεργότητας, ιοντική ισχύς, ελεύθερη ενέργεια.

To my wife, Despina

•

•

•

and to my daughter, Ioanna

ACKNOWLEDGMENTS

Special thanks belong to the Department of History and Philosophy of Science of the National and Kapodistrian University of Athens for giving me the opportunity and full support to conduct this dissertation.

The author of this dissertation happens to be Professor Emeritus of the Department of Chemistry of the University of Crete. A chemist's mentality and scientific reasoning are far different from those of a historian of science. Thus, the task of the thesis supervisor becomes much more complicated than directing a younger graduate student from the Department of History and Philosophy of Science. I am fortunate because Professor Theodore Arabatzis undertook this task. I am grateful to him for having introduced me to the climate of new science. I learned from him the way of doing research in the history of science. I learned how to approach historical facts by posing the right questions, reading between the lines and finding hidden interpretations, or deciphering those words that facilitate understanding complex historical texts. The interaction between philosophy and science was another vital lesson that I learned from him. I am grateful to Professor Arabatzis for directing my thesis, for help, and encouragement.

The second person I would like to thank is Kostas Gavrogu. Professor Gavroglu was the first person in the Department, who received me with courtesy and willingness, and listened carefully to my interest in the history of science. I had from him the first substantial information about the Department and the possibilities of doing research there. I am indebted to him for discussions, encouragement, and advice. Both Professors Arabatzis and Gavroglu were the inspirers of the original idea of this dissertation. The author is also indebted to Professor Aristotle Tympas for his valuable suggestions in the early stage of this study. I owe many thanks to the members of the examination committee for their constructive criticism, recommendations for improvements, hints of new ideas for future development, and for the wonderful conversation during the defense of my dissertation.

At the various stages of research, I presented my progress reports and the future schedule of my study to the meetings of the graduate students of the Department. I benefited greatly from the many suggestions, and I am indebted for this experience.

I would like to acknowledge the Secretary of the Department Mrs.Maria Gika for her valuable assistance with all procedural matters of the Department.

I express my appreciation to the staff of the Departmental library for their assistance in finding the various sources of information needed in my research.

Above all, I would like to thank my wife Despina who supported me all these years and showed remarkable patience when I spent many hours a day bent over a book or writing in front of the computer.

List of Publications

Photis Dais, 2019. The double transfer of thermodynamics: from physics to chemistry and from Europe to America. *Studies in History and Philosophy of Science* 77: 54-63.

Photis Dais, 2021. The impact of Gibbs' and Duhem's approaches to thermodynamics on the development of chemical thermodynamics. *Archive for the History of the Exact Sciences* 75: 175–248.

Content

Introduction1
PART I. The history of chemical thermodynamics during the first half of the nineteenth
century
Chapter 1. The prehistory of chemical thermodynamics16
Section 1. Chemistry during the first decades of the nineteenth century
1.1 Elective affinities17
1.2 The beginning of chemical kinetics
1.3 The beginning of electrochemistry24
Humphrey Davy,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
Jöns Jacob Berzelius27
Theodore von Grotthuss
André Marie Ampère
Michael Faraday
Georg Simon Ohm40
Antoine César Becquerel
John Frederic Daniell and William Robert Grove. The construction of batteries of constant
current intensity45
Section 2. Theories of heat and applications
Section 3. Mathematics in chemistry

Chapter	2.	The	development	of	thermodynamics	in	the	context	of	physics:	The
establishr	nen	t of th	e first law of th	ern	nodynamics	••••			• • • • •		56
Section 1	. Sa	ıdi Ca	rnot and the or	igin	of classical therm	ody	nam	ics			56

1.1 The beginning	56
1.2 The caloric theory versus the mechanical theory of heat	64
1.3 The <i>Reflexions</i> in oblivion	
Section 2. The first law of thermodynamics. A comparative study	72
2.1 Julius Robert Mayer	77
2.2 Ludwig August Colding	82
2.3 James Prescott Joule	86
2.4 The mechanical equivalent of heat	92
2.5 Hermann von Helmholtz	103

Chapter 3. The development of thermodynamics in the context of physics: Entropy and
the second law of thermodynamics109
Section 1. The origin of the second law111
Section 2. The first approach to the second law112
2.1 William Thomson (Lord Kelvin)112
2.2 Rudolf Clausius
2.3 William John Macquorn Rankine122
Section 3. Thomson resolves his ambiguities and enunciates the second law of
thermodynamics124
Section 4. The discovery of entropy

Chapter	4. The	e develo	opment	of	thermodynar	nics	in	the	context	of	chemistry	and
physiolog	gy: The	law of co	onservat	tion	of energy	•••••				• • • • •	• • • • • • • • • • • • • • •	.143
Section 1	. Electi	rochemic	cal cells	and	the correlation	on of t	for	ces				.144

Section 2. The origin of the animal heat154
2.1 Theories of respiration
2.2 Other sources of animal heat: Metabolism and nutrition
2.3 <i>Vital force</i> and the conservation of energy168
2.3.1 Justus Liebig and the <i>vital force</i> 169
2.3.2 Robert Mayer and the exclusion of <i>vital force</i> 173
2.3.3 Hermann von Helmholtz and the muscle contraction
Conclusions of Part I185
PART II. The second half of the nineteenth century: The advancement of electrochemistry
and thermodynamics
Chapter 5. The second generation of electrochemists
Section 1. Johann Wilhelm Hittorf: The migration of ions and their transference
numbers191
Section 2. Friedrich Kohlrausch: The conductivity of electrolytic solutions196
Section 3. Hermann von Helmholtz: The electric double layer and the introduction of the
charged ions
Section 4. From the kinetic theory of gases to the application of Ohm's law to electrolysis.
The Clausius-Williamson hypothesis217
Chapter 6. Gibbs' approach to thermodynamics
Section 1. Thermodynamic diagrams231
Section 2. Equilibrium states: Chemical potential and fundamental functions

Section 4. Effect of a diaphragm (Equilibrium of osmotic forces)	267
Section 5. Gibbs on irreversibility	269

Chapter 7. Duhem's approach to thermodynamics	276
Section 1. Thermodynamic potential	
Section 2. Toward a rational dynamics	295
Section 3. Unification of physics and chemistry	309
Section 4. Friction systems and permanent alterations	315

Intermezzo I. Die Thermodynamik Chemisher Vergänge: Helmholtz's free energy......322

Chapter 8. Impact of Gibbs and Duhem's approaches to	o thermodynamics on chemical
thermodynamics	
Conclusions of Part II	

PART III. The double transfer of thermodynamics from physics to chemistry and from
Europe to America
Chapter 9. Internal and external factors that favored or impeded the transfer of
thermodynamics into chemistry
Section 1. The domination of organic chemistry
Section 2. Industry and chemistry
2.1 Mass production and the emergence of chemical engineering
Section 3. The two traditions of thermodynamics and their reception from the scientific
community

Chapter 10. The ionists and the development of the theory of solutions: The	origin of the
modern chemical thermodynamics	404
Section 1. Svante August Arrhenius	408
1.1 A dissertation full of novel ideas	409
1.2 Arrhenius postulates the ionic dissociation theory	419
Section 2. Jacobus Henricus van 't Hoff	427
2.1 The Tetrahedral carbon atom	428
2.2 Ansichten über die organische Chemie	430
2.3 Études de Dynamique Chimique	433
2.3.1 The kinetics	433
Leopold Pfaundler's molecular collision theory	439
August Horstmann's dissociation theory	442
2.3.2 The analogy between ideal gases and dilute solutions	448
2.3.3 The principle of mobile equilibrium	450
2.3.4 Affinity	453
2.4 Towards a theory of solutions	457
Section 3. Friedrich Wilhelm Ostwald. The great organizer	465
3.1 The research work of Ostwald	467
Intermezzo II. Arrhenius' equation and the activation energy	472
Chapter 11. The ionists come together	475
Section 1. Arrhenius and Ostwald	477

Section 2. Ostwald and van 't Hoff	.483
Section 3. Arrhenius and van 't Hoff	.485
3.1 Ionic dissociation theory: The proof	.489
3.2 Ostwald's dilution law	.491
Section 4. Walther Nernst: The fourth ionist	.493
Section 5. Max Planck: The ionists' theory of solutions as seen by a physicist	.497

Chapter 12. Opposition to the ionists' theory of solutions	
Section 1. Reasons of the opposition	521
Section 2. The British opposition 1887-1888	523
Section 3. The hydrate theory and Arrhenius' reaction	531
Section 4. The meeting of the British Association at Leeds in 1890	536

Chapter 13. The development of chemical thermodynamics in America	
Section 1. The struggle for recognition	
Section 2. What was the science that transferred to America? Chemical the	ermodynamics
or physical chemistry?	556
Section 3. Gilbert Newton Lewis: A talented American physical chemist	
Section 4. Lewis' chemical thermodynamics	564
4.1 Escaping tendency, fugacity, activity, and activity coefficient	
4.2 The puzzling behavior of strong electrolytes	
4.3 Chemical free energies	
Section 5. Lewis' work in physical organic chemistry	596
5.1 The structure of the chemical bond	597

5.2 Studies on deuterium nucleus (heavy hydrogen)	598
5.3 The electronic theory of acids and bases	599
5.4 Phosphorescence and the Triplet state	600
Section 6. Lewis' missing Nobel Prize	602
Conclusions of Part III	608
General Conclusions	613

List of Figures (with captions)	
Appendix (Über die Erhaltung der Kraft)	665
List of Abbreviations	705
List of sources	

Introduction

The available historiography does not give an adequate account of the history of chemical thermodynamics. A thorough examination of the literature reveals few studies dealing with the essence of chemical thermodynamics. These studies are usually brief, incomplete, topical, or monothematic. Other essays and monographs focus on different aspects of physical chemistry and include only short fragments for the history of chemical thermodynamics. The history of the development of physical chemistry has overshadowed that of chemical thermodynamics. The scientific community of Europe accepted the new discipline of physical chemistry thanks to the persistent efforts of the Baltic German chemist Friedrich Wilhelm Ostwald (1853-1932) assisted by Jacobus van 't Hoff (1852-1911) from the Netherlands, and Svante August Arrhenius (1859-1927) from Sweden, the so-called ionists. According to the current historiography, these three men were able to transfer thermodynamics from physics to chemistry in a way acceptable to chemists. Application of thermodynamics to chemical problems in the laboratory occurred only after formulating van 't Hoff's theory of the osmotic pressure and Arrhenius' electrolytic dissociation theory. Walther Hermann Nernst (1864-1941), a disciple of Friedrich Wilhelm Georg Kohlrausch (1840-1910) and a coworker of Ostwald further expanded the ionists' chemical thermodynamics to electrochemistry. Historically, the birth of chemical thermodynamics is placed in the decade of 1880, when the ionists spread out their theories through the Zeitschrift für Physikalische Chemie, the journal that van 't Hoff and Ostwald established in 1887. The first volume of this journal contained the articles of the ionists that constituted the core of modern chemical thermodynamics. Perhaps, the first stage of the establishment of chemical thermodynamics in Europe ended in 1889, when Nernst, the fourth ionist, presented his theory on the concentration cells.

However, the system of chemical thermodynamics invented by the ionists had deep roots in earlier research works of a large number of natural philosophers of the eighteenth and the nineteenth centuries. For this reason, a detailed historical account of chemical thermodynamics is not an easy task for historians of science. The recognized kineticist Keith Laidler gave the following explanation for the intricacies involved in the historical development of chemical thermodynamics: "The story of how chemical thermodynamics is developed is somewhat confusing since several investigators worked along different lines and quite independently of one another".¹ Chemical thermodynamics presupposes the development of theories and experimentation that came at the ionists' disposal when they formulated their ideas. For instance, van 't Hoff could not have written his Études de Dynamique Chimique without acknowledging the work of Claude Louis Berthollet (1746-1822), Cato Maximillian Guldberg (1836-1902) and Peter Waage (1833-1900), Leopold Pfaundler (1839-1920), August Friedrich Horstmann (1842-1929), and other chemists and physicists. Arrhenius resorted to the help of the great electrochemists Wilhelm Hittorf (1824-1914) and Friedrich Kohlrausch, the physicist Rudolf Clausius (1822-1888), and the organic chemist Alexander William Williamson (1824-1904) to find scientific support in his theoretical innovations elaborated in his dissertation.

It is beyond the scope of this dissertation to present a comprehensive account of the history of chemical thermodynamics. Current literature has detailed information, although incomplete and discontinued, on the various aspects of chemistry development, particularly

¹ Laidler, 1993, p. 107.

physical chemistry. The interest here is to trace the main stages of the historical development of chemical thermodynamics, briefly present the theory's central concepts and the people involved in this crusade. The ionists were familiar with previous theoretical accomplishments of thermodynamics, experimental findings in chemical and physical processes, and studies on electrochemistry. They had well-developed ideas about what kinds of literature, problems, and scientists were or were not important to them. They selected earlier theories as sources of inspiration and used concrete experimental results to support their theoretical ideas.

The history of chemical thermodynamics until the advent of the ionists is the content of the first two parts of this dissertation. The first chapter of this dissertation involves attempts of natural philosophers to understand the nature of forces that keep together the elements of substances and how they decompose under external influences. The first kind of studies led to theories of chemical affinity explained by invoking Newtonian or electric forces. At the beginning of the nineteenth century, the effect of concentration on the change of the chemical affinity by the French chemist Claude Louis Berthollet raised questions about the equilibrium conditions in chemical processes. On the other hand, the problem of decomposition of substances remained unresolved until the invention of the voltaic cells and the study of the phenomenon of electrolysis. However, the natural philosophers called to solve two major problems concerning the operation of galvanic cells. Such problems were the decomposition mechanism of substances and the conduction of the electric current through the electrolytic solutions. They quickly recognized that the two phenomena were interrelated. And several theoretical approaches to the decomposition and conduction mechanism sprang from eminent electrochemists'

minds during the first three decades of the nineteenth century. These primitive theories greatly impacted the amelioration of the batteries and increased their power and stability for performing demanding experiments. These innovations turned electricity from a qualitative into a precise quantitative science, the science of electrochemistry.

In parallel with the experimentation and exploitation of electricity for industrial purposes, for example, the construction of electric motors, the European industry required efficient steam engines to satisfy its transportation needs. The eighteenth century had left a great legacy in a steam engine that worked well enough to drive machinery. Still, its low efficiency limited its use far from heavy applications, let alone to carry railway tractions. The challenge for engineers and physicists was great, but it was left to the young French engineer Sadi Carnot to solve the problem dealing with the heat engines. The first principle of thermodynamics, the conservation of energy, remained unnoticed for about a quarter of a century until several talented chemists, physicists, and amateur scientists provided the necessary theoretical and experimental shreds of evidence. The German medical doctor Julius Robert von Mayer (1814-1878), the German physiologist Hermann Ludwig Ferdinand von Helmholtz (1821-1894), the Danish physicist Ludwig August Colding (1815-1888), and James Prescott Joule (1818-1889), an amateur with a mechanical bent and a flair for measurement, had independently discovered the principle of the conservation of energy and measured the rate at which work could be converted into heat. It remained for Rudolf Clausius, William Thomson, 1st Baron Kelvin (1824-1907), and William John Macquorn Rankine (1820 -1872) to build the second law of thermodynamics. Chapters 2 and 3 refer to the perseverance of these men to discover the two laws of thermodynamics that played a decisive role in the development of chemical thermodynamics.

Each of the four men who discovered the first law of thermodynamics had different external influences, inspirations, and motivations to pursue their goals. A comparative study in chapter 3 reveals their distinct differences as exposed in their different scientific styles and scientific reasoning to discover the first law. For Mayer and Helmholtz, the road to finding the principle of conservation of energy passed through their observations in the field of physiology. Several physiological factors, such as the dispute regarding the influence of the *vital force* as the principal regulator of life processes, the origin of the animal heat, and the muscle contraction, sparked their interest in a possible relationship between mechanical work and heat production. The amateur scientist Joule came to the formulation of the first law when he decided to use electricity and build small electric motors for transporting the products and the various objects in the family brewery. Metaphysical concerns and the adherence to the philosophy of nature (Naturfilosophie) significantly influenced the thinking of Colding toward the conservation of forces. Chapter 4 gives a short account of the development of the conservation of energy in the more general framework of chemistry and physiology. These four chapters constitute the first part of the dissertation that describes the period that could be referred to as classical chemical thermodynamics.

The second part of the dissertation involves the advancement of the fields of electrochemistry and thermodynamics during the second half of the nineteenth century. Chemical thermodynamics benefited greatly from novel experimental methods and advanced instrumentation introduced by the great electrochemists Hittorf and Kohlrausch. The measurements of the ions migration in solutions, and the percentage of the electricity they carried out, the search for the ability of the electrolytic solutions to conduct electricity according to Ohm's law through the measurements of the electrical conductivity provided the ionists with a valuable quantitative tool to examine the reactivity of substances. Chapter 5 gives an extensive account of the research achievements of these two electrochemists.

Alongside the development of experimental electrochemistry, thermodynamics received a great impetus from Josiah Willard Gibbs (1839-1903) in America and Pierre Duhem (1861-1916) in France. They built a unified theory of thermodynamics that involved the study of equilibrium and non-equilibrium processes. Their work, which introduced the rigor of mathematics in chemical thermodynamics, had a poor reception from chemists. Chemists did not find any benefit from these theories in their practical work in the laboratory. Chapters 6 and 7 give a detailed account of Gibbs and Duhem's approaches to thermodynamics, whereas chapter 8 describes the impact of their work on the development of chemical thermodynamics. As an intermezzo between these two chapters, I will discuss the development of the free energy state function by Helmholtz.

The birth and the development of chemical thermodynamics did not take place in a vacuum. The nineteenth-century witnessed three different but closely related developments that generally influenced chemistry and physics, which facilitated or impeded the emergence of chemical thermodynamics in Europe, depending on the circumstances. The hitherto studies have omitted to explore the influence of external and internal factors on the development of chemical thermodynamics in Europe and America. Factors related to institutional, social, and economic conditions appeared to have a significant role in the transfer of thermodynamics into chemistry. This dissertation explores the scientific, educational, and cultural traditions of Europe by the time the ionists began their research from 1872 until the foundation of their theories by the end of 1880. Identifying these factors
and their impact on the development of chemical thermodynamics is the content of chapter 9 of this dissertation. The application of thermodynamics to chemical problems in the laboratory occurred only after the formulation of the solution theories of the ionists. That the edifice of chemical thermodynamics had an impact on the way chemists perceive the transfer of thermodynamics into chemistry suggests some plausible questions: what needs of chemists did chemical thermodynamics serve? Did that theory satisfy those needs? What were the methodological approaches used by the ionists to transfer thermodynamics to chemistry? This chapter provides answers to these questions.

The third part of this dissertation is devoted to developing the ionists' chemical thermodynamics, which is the main issue of this dissertation. These men were the first scientists who attempted to introduce thermodynamics in practical chemistry. The ionists were the first to show the benefits of using thermodynamics to solve crucial problems that occupied chemists since the beginning of the nineteenth century. The ionists, finally, showed that the collaboration between chemists and physicists was essential, not only for the mutual benefits of the two sciences but also a significant step for the consolidation of the chemical thermodynamics and its evolution into a new discipline, physical chemistry. I will give a detailed account of the work of the ionists in chapter 10.

Another aspect of the development of chemical thermodynamics that has not been explored adequately was how the ionists succeeded in combining various theories, apparently independent among themselves, and presented them as a compact theoretical and experimental whole. Each ionist worked separately and did not know what the other ionist had achieved. Ostwald's genius and talent recognized the value and the perspective of a research work that acted as a connecting thread between the ionists. But most of all, it

was the common research problems that brought the ionists together. Ostwald, who had done extensive research on chemical reactivity, found Arrhenius' dissertation to connect electrical conductivity with chemical reactivity. Van 't Hoff and Arrhenius felt an unexpected satisfaction when they realized that the ionic dissociation theory supported unambiguously the theory of the osmotic pressure and vice versa. In chapter I1, I will try to answer questions, such as what was the connecting thread that brought together these diverse theories? Under what conditions and influences did they come together and develop their chemical thermodynamics? Was this association of ideas motivated by intellectual reasons or by other factors at play? What did they get from thermodynamics? Whose thermodynamics did they use? The thermodynamics of Gibbs, Duhem, and Helmholtz, or the classical thermodynamics of Clausius, Thomson, and Rankine? What concepts from classical thermodynamics did they use, and how did they accommodate these principles in their theories? I conclude this chapter with a short account of the contributions of Nernst and Max Karl Ernst Ludwig Planck (1858-1947) to chemical thermodynamics. Planck's approach to van 't Hoff's osmotic pressure and Arrhenius' ionic dissociation gave a rigorous theoretical justification of the chemical thermodynamics. Unfortunately, this remarkable work remained unnoticed by chemists. It remained as an academic exercise of a practical theory rather than as an extension of the ionists' chemical thermodynamics. This remarkable theoretical edifice is utterly absent from today's textbooks.

History teaches us that new theories have to overcome serious obstacles before being recognized and accepted by the scientific community. Old views decline to make room for new ideas and discoveries that could provide solutions to problems that old theories cannot offer. On the other hand, old theories resist new theories' invasion and try to construe unexpected experimental results with some *ad hoc* modifications. The ionists' chemical thermodynamics did not escape from this unpleasant situation. Intense and sometimes hostile criticism broke against the ionists' theory of solutions and, in particular, on the theory of the electrolytic dissociation. In chapter 12, I will discuss the reasons for this criticism, which are not solely scientific. Strong opposition came almost exclusively from the British chemists and physicists through the meetings of the electrolysis committee of the British Association for the Advancement of Sciences (BAAS) and culminated in the meeting that took place in 1890 at Leeds. In this meeting, van 't Hoff and Ostwald gave a decisive battle defending their theories.

The last chapter of this study will focus on the knowledge transferred from Europe to America. From 1890 to1910, many American chemists traveled to Europe and trained in the new discipline of physical chemistry. The majority of the American students and post-doctoral fellows visited the physical chemistry laboratory of Ostwald at the University of Leipzig, fewer the laboratory of Nernst in Göttingen, and even fewer the laboratory of van 't Hoff in Amsterdam. Interestingly, American scientists did not simply transfer or diffuse the new knowledge from Europe to America. They instead appropriated and expanded this knowledge in accord with each individual's aspirations, interests, and talent. In this part of my study, I will seek to document this view by providing an overview of the development of chemical thermodynamics in America in the early years from 1890 to the mid-1920s and investigating the following critical questions. What was really transferred to America? Was it physical chemistry, or was it chemical thermodynamics? Who were the leading scientists involved in this process of appropriation? How did they use and extend the new knowledge? Was there any opposition to their efforts to establish the new discipline in their country? As a typical example of these questions, I will give an account of the research work on chemical thermodynamics of the American chemist Gilbert Newton Lewis (1875-1946). Lewis was the central figure of the transfer and the development of chemical thermodynamics in America.

Furthermore, I intend to clarify some rudimentary issues related to chemical thermodynamics. For instance, when and by whom had chemical thermodynamics been recognized as such and received the current name? Was this name originated from the historians, or were the scientists themselves who adopted this name? What was the ionists' chemical thermodynamics content, and whether it has changed with time and location? Before them, neither ionists nor researchers in chemistry or physics had given the name chemical thermodynamics to their theories. Perhaps, the only reference to this denomination appears in the introduction of the famous textbook *Thermodynamics and the Free Energy of Chemical Substances* published by Lewis in collaboration with his disciple Merle Randall (1888-1950) in 1923. However, not as chemical thermodynamics, but as thermodynamic chemistry.²

Apart from the name given to the ionists' theory (by whom?), the content of their chemical thermodynamics plays a central role in the development and the subsequent propagation of this theory among the chemists. The content of chemical thermodynamics becomes essential for three reasons: the first reason is the question posed previously: what has precisely been transferred to America by the American chemists who graduated from Ostwald's and van 't Hoff's laboratories. Secondly, to distinguish between chemical

² Lewis & Randall, 1923a, p. 2.

thermodynamics and physical chemistry and to understand how the contemporaries had conceived this distinction. Thirdly, to compare the content of the ironists' system of chemical thermodynamics with that currently taught at higher education institutions. This comparison will give us an idea of changes that eventually occurred in the content of chemical thermodynamics. Changes reflected in textbooks and the contributions made to chemical thermodynamics by scientists other than the ionists.

Understanding the development of chemical thermodynamics at the hands of the ionists, its impact on contemporaries, and why the ionists became the main characters to this development requires the historian to concentrate on personal perception and scientific style (in the general sense of the word). Answers to questions, such as why and in what way were the ionists interested in thermodynamics, while at the same time, previous generations of chemists showed strong resistance to allowing physical theories in their laboratories? How thermodynamics is implemented in their research programs? Had the opposition to ironists' theory originated from a methodological resistance to an invasion of new methods into chemistry, or matters of detail, like ignoring the effect of the solvent on the theory of the solution of salts? What was the role of nationalism in this opposition? What methodological approaches had the ionists' attitude concerning atomic theory in relation to the concept of ions? Are they critical for the perception of differences in their scientific styles and their style of reasoning?

To understand why the thermodynamics of Gibbs had a more significant impact on the development of chemical thermodynamics than Dujem's *Mechanique Chimique*, or why the ionists were considered by their contemporaries as the prominent personalities of this development, requires the historian to study the original writings of these scientists. Also, the investigation of other primary and secondary sources other than their scientific work is necessary. Their correspondence and recollections by themselves or by their students and colleagues are valuable sources to allow historian to understand their personalities, scientific styles, and scientific reasoning that affected the development of chemical thermodynamics.

In writing this dissertation, I examined and analyzed the work of several different investigators. Therefore, I considered it necessary to adopt two conventions. The first convention concerned the symbols of the various quantities in equations and functions. I avoided standardizing the symbols of the physical quantities used by each author in his original work. I preferred using the set of symbols that appeared in the original papers of each individual. Besides the loss of the historical value that the original symbols carry, their standardization requires the presentation of pertinent reference tables. Frequent reference to such tables creates difficulties for the reader to have a smooth and interrupted reading. In any case, the meaning of the original symbols is clearly explained when they first appear in the text.

The second convention concerns the numbering of equations. Two numbers separated by dot denote each equation. The first number corresponds to the number of each new chapter, and the second number indicates the increasing order of the equation in the text. Thus, the first equation in each new chapter has the number one. For the interested reader, who desires a thorough investigation of the importance given to particular equations by the authors, reference is made to the corresponding page of the original article. This method avoids any complicated double numbering system.

PART I. The history of chemical thermodynamics during the first half of the nineteenth century

The American physical chemist Gilbert Newton Lewis, in his well-known to historians textbook Thermodynamics and the Free Energy of Chemical Substances, co-authored with his disciple Merle Randall had distinguished three periods in the development of chemical thermodynamics:³ (1) The establishment of the basic principles of the theory of energy owing to the work of Black, Rumford, Hess, Carnot, Mayer, Joule, Clausius, Kelvin, and Helmholtz; (2) the building up from these principles the vast body of theorems as the result of the work of many men, making particular reference to Gibbs and van 't Hoff; and (3) the design of more specific thermodynamic methods and their applications to particular chemical processes leading to the systematic accumulation and quantification of a vast number of old and new experimental data of chemical thermodynamics. Lewis mentioned several examples of this nature: the specialized research of Henri Étienne Saint-Claire Deville (1818-1881), who gave the phenomenon of dissociation its modern name. The entropy usage by Horstmann to quantify the dissociation reaction of substances using the concept of entropy. The published thermodynamic data by Fritz Haber (1868-1934) were used to calculate energy changes of chemical reactions. The remarkable contribution of Nernst to the electrochemical theory and practice, and the studies of Johannes Nicolaus Brönsted (1879-1949) on chemical affinity using thermodynamics.⁴

Lewis' three periods could be widened to include subjects and people in the context of (a) the prehistory of chemical thermodynamics, where the beginning of the development

³ Lewis and Randall, 1923a.

⁴ Lewis and Randall, 1923a, pp. 5-6.

of the equilibrium and the kinetics of chemical reactions and the electrochemistry of solutions was occasioned; (b) the establishment of the two laws of thermodynamics; (c) the application of these laws to the theory of chemical affinity and chemical equilibrium; (d) the penetration of mathematical methods into chemistry. These scientific subjects played a significant role in developing new methodologies, tools, and experimentation that paved the way to the foundation of the ionists' chemical thermodynamics and later physical chemistry.

A puzzling question concerns the origin and the use of the expression of chemical thermodynamics. The name chemical thermodynamics implies the application of principles of classical or advanced thermodynamics to chemistry. However, even after this period, no one of the chemists used this denomination for his research, let alone the great thermodynamicists of the first and the second half of the nineteenth century. Before the ionists, chemists did not make use of thermodynamics in their research for several reasons.⁵ Horstmann and Pfaundler, who employed thermodynamics to explain the anomalies observed in dissociation reactions, were the sole exceptions to the rule. But even these two chemists and the ionists, ten years later, who founded the modern chemical thermodynamics, did not explicitly use the term chemical thermodynamics. The ionists preferred to name physical chemistry the new system of theories, methods, and experimentation that linked the two significant disciplines of physics (in the form of thermodynamics) and chemistry in the service of chemists.

Duhem called very often his generalized thermodynamics as *Chemical Mechanics* (Méchanique Chimique). However, this description had a wider content than the chemical

⁵ See chapter 9 of this dissertation.

thermodynamics of the ionists. Méchanique Chimique signified for Duhem generalized thermodynamics; the introduction of the analytical mechanics of Joseph-Louis Lagrange (1736-1823) into classical thermodynamics to remove the static description of physical and chemical phenomena. The expression *thermodynamic chemistry* adopted by Lewis in one of his publications, *Outlines of a New System of Thermodynamic Chemistry*,⁶ appears to be closer to the conception of modern chemical thermodynamics. It seems that the name chemical thermodynamics is a product of the twentieth century. By the turn of the nineteenth century, the work of Gibbs, Duhem, Helmholtz, Planck, and ionists showed that the scope of thermodynamic concepts could be expanded into chemical systems and chemical transformations. Consequently, during the first half of the twentieth century, thermodynamics progressively permeated all aspects of chemistry and flourished as a recognizable entity on its own, the chemical thermodynamics. For instance, Lewis and Randall's book was responsible for supplanting the chemical affinity and chemical equilibrium with free energy in the English-speaking world. The second book that contributed to the establishment of chemical thermodynamics was the textbook Modern thermodynamics by the methods of Willard Gibbs,⁷ written in 1933 by the brought together theories and application of thermodynamics to chemistry. In this manner, Lewis, Randall, and Guggenheim could be considered the founders of the modern chemical thermodynamics of the twentieth century.

⁶ Lewis, 1907.

⁷ Guggenheim, 1933.

Chapter 1. The prehistory of chemical thermodynamics

Modern chemical thermodynamics has given quantitative solutions to the problems of chemical affinity and chemical equilibrium. Today, the chemical affinity is quantified by measuring the oxidation and reduction potentials of the chemical elements that constitute the well-known electrochemical series of chemical elements tabulated in modern textbooks, secondly, by the free energies of formation (or decomposition) obtained from calorimetric measurements or specific electrodes. In turn, the free energies are used to calculate the equilibrium constants that proved to be a significant quantitative measure of the equilibrium state in chemical processes. Also, the sign and the magnitude of the free energy of a reaction, calculated from the individual free energies of the reactants and products, is a secure qualitative indicator of the spontaneity of the chemical process.

It took more than a century for chemists and physicists to determine these thermodynamic quantities, to classify them according to the physical state and the chemical composition of compounds, and therefore to be able to conclude at a glance about their relative stability and their behavior in chemical and physical changes. This fascinating journey that lasted from near the end of the eighteenth century until the beginning of the twentieth century is the subject of this study.

Section 1. Chemistry during the first decades of the nineteenth century

The present historiography dealing with the development of chemical thermodynamics has focused its attention mainly on events after introducing thermodynamics into chemistry. However, the historian cannot achieve a unified framework to explain the origin of chemical thermodynamics without the significant innovations in chemical theories of affinities, which were published between 1800 and 1803. His studies are incomplete without studying the forces involved in the dynamics of chemical reactions and the new concepts derived from the investigation of the electrical processes occurring in the galvanic and electrolytic cells during the first three decades of the nineteenth century. This chapter briefly discusses some of the most fundamental ideas that influenced chemical thermodynamics and led sixty years later to formulate the fundamental equations of chemical affinities and chemical equilibrium.

1.1 Elective affinities

Attempts of natural philosophers to explain the chemical affinity that is, how different chemical species were capable of forming compounds and conditions of equilibrium between reactants and products of chemical reactions, may be considered the prehistoric development of chemical thermodynamics. Both terms are old, and their origins, especially for affinity, go back to the seventeenth century when Newton thought of the formation of substances due to gravitational forces exerted between particles. However, the term affinity and its conceptual interpretation have somewhat modified during the eighteenth century in *elective affinities* or *elective attractions*. The usage of this phrase seemed to be rapidly widespread across Europe, and in particular, in France. On the other hand, Claude Louis Berthollet had advanced the concept of chemical equilibrium at the turn of the nineteenth century. Berthollet invented the *law of mass* or the *mass action law* using the present terminology, and through this law, interpreted the chemical equilibrium. However, he

proportions proposed by Joseph Louis Proust (1754-1826). Nevertheless, the law appeared to be useful since it had elucidated apparent anomalies observed in chemical reactions upon varying the mass of the reactants. Both concepts of elective affinities and the law of mass vindicated the role of the precursors in the development of chemical thermodynamics.

Elective affinity was the name chemists gave to attractive, special forces exerted between the substances causing chemical reactions. For a given free substance, the strength of the elective affinity is constant. It determines the ability of this substance to combine preferentially with another substance in a mixture, excluding thus a third substance. Also, elective affinity expresses the power of a free substance to replace an equivalent amount of another substance in a compound if the former substance has a higher elective affinity than the substance of the compound. The reactions in which the theory of elective affinity was applied were mainly reactions between acids, bases, and salts. Thus, according to the theory of elective affinities, one free base or one free acid substitutes another acid or another base, respectively, in salt, if the elective affinity of the free substance is stronger than the substance which had already formed the salt in question. Otherwise, if the original substance of the compound had stronger elective affinities than the free substance, no reaction occurs. In the case of mixing two salts, double displacement reactions may occur upon exchanging the constituent substances of the two salts, depending on their relative affinities.

Based on single and double displacement reactions, chemists classified substances according to their elective affinities. Tables illustrated qualitatively the order in which acids replace one another in combination with a base and a series of bases in combination with an acid.⁸ Nicolas Lémery (1645-1715) built the first tables of elective affinities, and Etienne-François Geoffroy (1672-1731) in the first three decades of the eighteenth century. Their solution chemistry concerned the selective dissolution of metals in acids or the replacement of metals in metallic salts. Geoffroy did not refer to the phrase *elective affinity*, but in his Table, he published it in 1718. Geoffroy did not use the word affinity. He preferred to use the word *rapport* (relationship).⁹

By the mid-eighteenth century, chemists pursued the elucidation of chemical affinity more systematically. By the 1770s, affinity had become the frontier of theoretical chemistry among the leading chemists in Europe. Several affinity Tables had been proposed during the eighteenth century. The most prominent figures in this regard were Louis-Bernard Guyton de Morveau (1737-1816), a lawyer who became the first author of the French nomenclature reform. In 1787, Torbern Bergman (1735-1784), a Swedish professor of chemistry who produced the most elaborate affinity Table of the time in 1775,¹⁰ and Richard Kirwan (1733-1812), a British interlocutor of chemistry between 1767 and 1777, and one of the last supporters of the phlogiston theory. These three natural philosophers constituted the foremost chemical authorities in European science in the mid-1780s. Their experimental and theoretical work in solution chemistry paved the way to the last phase of the eighteenth-century Chemical Revolution.¹¹

⁸ For a detailed account of theories of elective affinities and affinity Tables, see Kim, 2003, pp. 111-146 and 222-275.

⁹ Geoffroy, 1718, p. 37. It has been suggested that Geoffroy's preference the word *rapports* indicating his decision to maintain neutrality on the theoretical issues that devided Newtonians from Cartesians who prevailed in French science (Golinski, 2008, p. 384).

¹⁰ Kim, 2003, p. 259. Bergman's Table was divided into two parts for wet and dry reactions., with thirty-four columns and twenty-seven substances listed in each column.

¹¹ Historians of chemistry had examined the cognitive status of the affinity Tables. However, no consensus has arrived from this discussion. It is uncertain whether affinity Tables are merely a collection of facts, or provide a comprehensive framework, a conceptual structure, or a theoretical system (Kim, 2003, pp. 141-146; Golinski, 2008, pp. 384-388).

1.2 The beginning of chemical kinetics

Soon, anomalies in elective affinities were observed in chemical reactions that did not fit the predicted order in the Tables.¹² The influence of solubility, volatility, and the formation of solid residues or the evolution of gases in the products of the reactions were severe interfering factors that occasionally altered the order of affinities in the Tables. Furthermore, incomplete reactions or reactions occurring with high speed did not allow effective chemical analysis of the constituents of the reactions. These factors led some chemists to doubt whether cohesive forces may be more critical than affinities. Other chemists considered alternative methodological approaches to remedy anomalies and overcome external disturbances. Berthollet shared the general conviction that elective affinities were crucial to the formation of compounds. He offered experimental evidence that the affinities in the Tables have possibly been modified because of the formation of insoluble or volatile substances. However, he noted another anomaly that he found very difficult to deal with. The influence of the quantity of a substance in the course of a reaction. The excessive amount of a substance seemed to offset or even reverse the elective affinity of the participating substances. He recognized that changing the proportions of two bases or two acids in a displacement reaction could weaken or even reverse the order of displacement, thereby the order of affinities. He demonstrated that by increasing enough the mass of a substance, it could displace a small amount of another substance of a compound with a stronger affinity than the first substance. He then reinterpreted elective affinities upon considering *chemical mass* as the driving force of the attractive forces or chemical activity of a substance. He proposed a new doctrine, the law of mass, in which

¹² Holmes, 1962, pp. 107-108.

the *chemical mass* of a substance is a product of its affinity and the quantity of the substance in contact with a given second substance. Berthollet published the *Essai de Statique Chimique* in 1803. He gave experimental evidence and a theoretical explanation for the effect of the mass of the various constituent substances on the equilibrium of a chemical reaction.¹³ This two volumes book contained several experimental results that supported the validity of the law of mass and lengthy discussions of his general ideas about the universal attractions between particles in the form of gravitational forces that determined affinities.¹⁴ However, his conclusion was unfortunate because he asserted the formation of a substance upon mixing its components in any proportion. After discovering the law of definite proportions of Proust and the atomic theory of John Dalton (1766-1844), Bertollet's law of indefinite or variable proportions proved wrong.

The influence of the mass on a chemical reaction continued to be an active research program until the mid-nineteenth century. Relevant studies undertaken by several chemists, such as Joseph Louis Gay-Lussac (1778-1850), Jöns Jacob Berzelius (1779-1848), John Hall Gladstone (1827-1902), and Marcellin Berthelot (1827-1907), Léon Péan de Saint-Gilles (1764-1829) kept this subject alive.¹⁵ Berthelot and Saint-Gilles, in 1862 and 1863, conducted the most successful investigations. They chose to perform experiments in organic reactions, such as those between an alcohol and a carbonic acid to form ethers,¹⁶ because they experienced that inorganic reactions between bases, acids, and salts are

¹³ Berthollet, 1803.

¹⁴ The increasing chemical effect of a substance of low affinity with increasing its mass provides the analogy between Newtonian forces and chemical affinity. Newton had shown that gravity is proportional to the mass of the body.

¹⁵ Holmes, 1962, pp. 129-140; Lindauer, 1962.

¹⁶ This essay has been published in four parts between 1862 and 1863. Berthelot and Saint-Gilles, 1862; 1863; Berthelot 1862.

unsuitable for equilibrium studies.¹⁷ Such responses are so rapid that almost any analytical technique destroys the equilibrium. The reaction itself proceeds in one direction and never reaches equilibrium (one-way reactions or irreversible reactions).

Affinity Tables did not involve mathematics. Also, no equations were used to express the law of mass. Wilhelmy formulated the first mathematical relationship between the reaction velocity and the mass of the reactants in 1850. The introduction of time in a chemical process was a hallmark and signified the beginning of chemical kinetics. However, equilibrium initially had a static character. Wilhelmy speculated that equilibrium had a mechanical character as the result of two opposing forces. Cato Maximillian Guldberg and his brother-in-law Peter Waage presented an advanced treatment of chemical equilibrium as a static process in three articles published between 1864 and 1879.¹⁸ They discovered that the ratio of the active masses¹⁹ of the products to the active masses of the reactants of the reaction in equilibrium was to a good approximation stable and equal to a constant, the equilibrium constant, characteristic of the particular reaction. Since the chemical reaction should retain its equilibrium state, any external disturbance, such as adding an extra quantity of a reactant or removing an amount of the product, the reaction will proceed in a direction such that the equilibrium constant will assume the initial calculated value. However, the mass action law of Guldberg and Waage does not consider rates. The two Norwegians considered forces supposed to act at both sides in opposite

¹⁷ Berthelot and Saint-Gilles, 1863, pp. 132-135.

¹⁸ In 1864, Guldberg and Waage published the first article in Norwegian, thus attracting very few scientists' attention. They issued a second article written in French three years later but in an obscure Norwegian journal. Finally, in 1879, they decided to publicize their ideas in a more widely distributed journal. Ostwald translated the last two articles in German and published thein in his Klassiker. For a short presentation of Guldberg-Waage's work, seeLund, 1965.

¹⁹ The term active mass adopted by Guldberg and Waage had the meaning of concentration of substances, not the masses considered by Berthollet.

directions for a reversible reaction. The two opposing forces become equal at equilibrium. In other words, Guldberg and Waage described a static and not a dynamic equilibrium.

In this respect, historians and kineticists do not consider the two Norwegian scientists as the precursors of modern chemical kinetics.²⁰ Nevertheless, their model explained the possible change in the direction of the reaction towards the fixed equilibrium constant by increasing or decreasing the concentration of a reactant as discovered by Berthollet about sixty years before. Guldberg and Waage published their work in Norwegian and thus inaccessible to the large readership. Few were interested in their work, which passed largely unnoticed, except perhaps by the ionists. Ostwald had used Guldberg and Waage's mass action law and carried out a large number of experiments with acid solutions. He confirmed the validity of the mass action law and found that the acids' strength (chemical affinity) goes in parallel with their reaction velocity. In other words, how fast the reaction proceeds. Furthermore, Ostwald based its dilution law for the weak electrolytes on the Guldberg-Waage equation of equilibrium. Arrhenius used in his dissertation this law to describe the equilibrium between the active and inactive molecules until finally, van't Hoff replaced the forces of Guldberg and Waage's theory with the rate constants of the reversible reactions²¹

The exact relationship between masses of reactants and products had been used in 1973 by August Horstmann, professor extraodinarius of chemistry at the University of Heidelberg, to calculate the equilibrium constant of chemical reactions.²² The innovations

²⁰ Laidler, 1993, p. 115.

²¹ See Part Iii, chapters 10 and 11 of this dissertation.

²² The work of Horstmann on the dissociation of gases and liquids will be discussed in chapter 10.

introduced by Hortsmann were: (a) the proof of the validity of Avogadro's law,²³ which has been questioned due to the apparent variation of the density of certain gases caused by their variable dissociation degree at different temperatures, and (b) the application of Clausius' entropy and disgregation of substances to chemical reactions occurring in the gas and liquid phase.²⁴ Horstmann preferably used the concept of disgregation because he thought it was the only factor contributing to the variation of entropy in these reactions. However, the employment of disgregation in chemistry was somewhat premature since Hortsmann could not determine this function experimentally. He virtually had abandoned disgregation and entropy in his following publications.²⁵

1.3 The beginning of electrochemistry

With the advent of galvanism and the construction of voltaic cells, another chapter opened for investigations related to chemical affinity.²⁶ The use of the voltaic or galvanic cells was twofold, depending on the background of the investigator. The experimenters preferred to use batteries (several voltaic cells connected in a series or parallel) to investigate the effect of the electric current on substances (bodies). In other words, to exploit the phenomenon

²³ Avogadro's law states, "equal volumes of all gases have the same number of molecules at the same temperature and pressure". This empirical relation derives from the kinetic theory of perfect (ideal) gases. The law is approximately valid for real gases at sufficiently low pressures and high temperatures. Van der Waals proposed a consistent description of the properties of the real gases through his famous equation that bears his name.

²⁴ Van 't Hoff had Horstmann in high regard and published four of Horstmann's papers in Ostwald's Klassiker series shortly after the turn of the century and before Horstmann's death. He published a biographical note of Horstmann (van 't Hoff, 1903, p. 67). Horstmann's physics eclipsed after the appearance of the thermodynamics of Gibbs, Duhem, and Helmholtz. Current textbooks do not refer to Horstmann at all. He became known much later when historians linked his work with van 't Hoff's chemical thermodynamics. ²⁵ Jensen, 2009, p. 87.

²⁶ The experimental determination of the chemical equilibrium had to wait until 1889 when Nernst published his famous equation that related the electromotive force (cell potential) with the equilibrium constant of an electrochemical reaction.

of electrolysis for practical investigations. The theorists, on the other hand, sought to understand the working of the voltaic cell itself.²⁷ By the turn of the nineteenth century, chemists and a few amateur scientists split into those who observed the effect of electricity and those who were more inclined to mathematize it. Both trends endeavored to explain the decomposition of substances under the influence of the electric current and the process by which electric current propagates through the solutions from one pole (electrode) to the other pole. This difference in investigations precisely distinguished André-Marie Ampère (1775-1836) and Jean-Baptiste Biot (1774-1862) in connection with the object of their studies. Biot focused on the battery and endeavored to explain its electric action by the arrangement of its constituents, while Ampère sought to find the working conditions of the battery. For Biot, the battery was an object of study in its own right, while Ampère confined itself to considering it a simple electricity source. Ampère was more interested in the investigation of the process of electrolysis than Biot.²⁸ The investigation of the electrolysis process was the type that led to valuable conclusions about the affinity of substances. The chemical affinity between substances was not the result of gravitational forces but mediated by electrical forces. In any event, the results obtained in these studies did not go further than the qualitative arguments. The reader might acquire a better picture of these electrochemical investigations upon examining briefly some of the achievements of the protagonist natural philosophers at that time.

²⁷ Here, it is necessary to clarify the distinction between a voltaic or galvanic cell and an electrolytic one. A galvanic cell is an electrochemical cell that produces an electric current through the progress of a spontaneous chemical reaction. An electrolytic or decomposition cell is the cell in which electrolysis occurs. An electric current passes through the cell by an external battery (usually composed of a series of voltaic cells), causing an otherwise nonspontaneous chemical reaction to proceed. Resulting in the decomposition of the substances that take place in the reaction.

²⁸ Petit, 2013, p. 71.

Humphrey Davy

In 1806, Humphrey Davy (1778-1829) presented his results to the Royal Society from many experiments conducted on various bodies in the neat state or solutions (basalt, zeolite, lava, salts, and acids). These investigations concerned the examination of the effects produced by electricity on these media.²⁹ Explaining the propagation of electricity in solutions, Davy concluded that the decomposed parts of the bodies during the action of the battery undergo a transfer from one pole to the other. The layer of water that penetrates the decomposed bodies probably hampers this process. As far as the phenomenon of decomposition is concerned, he concluded that electricity is capable of eradicating or neutralizing the chemical affinity of the bodies. In other words, chemical affinity and the intensity of the electric current are of the same order. There are, therefore, different degrees in the combination of bodies that electricity can reveal. Whenever electricity afforded by the given battery cannot decompose the body, the chemical affinity is especially strong, and decomposition may require a battery offering more intense electricity.

In some cases, changing the polarity of the battery, Davy observed weakening or even reversal of the tendency of bodies to combine one another. This observation led him to the conviction that electricity can modify the affinity between two bodies. However, Davy did not comment on how the bodies carry electricity or the reasons leading to the phenomenon of decomposition.

²⁹ Davy, 1807.

Jöns Jacob Berzelius

Berzelius advanced Davy's electrochemistry through his dualistic theory.³⁰ He agreed with Davy that the chemical affinity of bodies is electrical, but he had a different view regarding electrochemical decomposition.³¹ Berzelius advanced Davy's electrochemistry through his dualistic theory. He agreed with Davy that the chemical affinity of bodies was electrical but had a different view regarding electrochemical decomposition. The electric current from the battery overcomes the chemical affinity and separates the combined bodies; that is to say, it overcomes or cancels the forces by which the bodies unite. Berzelius divides the bodies into two categories: electropositive and electronegative bodies. Electropositive bodies carry a positive charge and are attracted by the negative pole of the electrolytic cell. Berzelius published his electrochemistry and the dualistic hypothesis of the formation of substances through the intervention of electrical forces in two essays published in 1811 and 1819.³²

Berzelius's most significant contribution to the concept of chemical affinity was his electrochemical system, in which he classified several bodies according to their relative electrical state.³³ Bodies are electropositive towards those that precede them and electronegative towards those who follow them. The reference of the scale is oxygen. Berzelius considers oxygen as endowed with *absolute negativity* because it never combines

³⁰ For a short account of Berzelius' achievements in chemistry, see Wisniak, 2000, 345-350.

³¹ Berzelius and Davy had a personal, social, and scientific relationship. Both knew each other's research. They had established an epistolary relationship communicating their work outside the editorial circuit. However, this mutual respect appeared to be superficial, and soon these two eminent scientists stood out from one another (Petit, 2013, pp. 48-51).

³² Berzelius, 1811; 1919.

³³ Berzelius classified 50 elements according to their electrochemical properties. Oxygen is placed at the top of the series. (Berzelius, 1819, pp. 77-79, and 156-157).

with a body more negative than that. On the contrary, all the other bodies can be positive or negative depending on the body they combine. Sulfur, for example, is negative towards oxygen and positive towards metals. This electrochemical scale of bodies allowed Berzelius to classify the hitherto known chemical elements according to their reactivity with oxygen. Furthermore, his decomposition experiments concluded that, unlike electronegativity, there is no absolute electropositivity. Berzelius initially considered hydrogen as an electropositive reference. However, hydrogen proved to be electronegative in its combination with potassium metal.

The position of bodies in the scale signifies the intensity of their polarity and explains their differences in affinity. The more intense the polarity of two bodies, the stronger the chemical affinity is, and the stronger their tendency to combine. Utilizing this classification system, Berzelius gave an electrical explanation for the double displacement reactions. In contrast, he strove to provide a convincing reason for the electrochemical indifference observed for some compounds, the third class of electrochemical relations, as he called this category of compounds.³⁴ Furthermore, Berzelius determined the weight of each element in its compounds with oxygen and verified the law of the definite proportions proposed by Dalton.³⁵ Thus, Berzelius discovering that the atomic weights are integer multiples of the weight of oxygen overthrown hydrogen and concomitantly disproved Prout's hypothesis that elements are built up from hydrogen atoms.

Berzelius attempted to theorize on the question about the origin of electricity in bodies. He proposed a corpuscular theory, in which he made an analogy between the macroscopic electrified body and the microscopic electrical polarity of each of the atoms

³⁴ Berzelius, 1819, pp. 81-83.

³⁵ Ibid, pp. 122-151.

in their union.³⁶ "Do we imagine that in the molecules of a body, electricity of one of the poles is either predominant or more concentrated in a certain point than the electricity of the other pole, in much the same way that one of the poles of a magnet can be much stronger than the other".³⁷ Besides, the intensity of the polarity of each body explains the observed differences in affinity. However, Berzelius warns the reader that this analogy is only speculation, "if even our conjectures were correct, they would always remain doubtful [...] because any experimental evidence does not accompany it".³⁸

Theodore von Grotthuss

The German chemist Freiherr (Baron) Christian Johann Dietrich Theodore von Grotthuss (1785-1822) published in 1805 a memoir in which he described a mechanism of decomposition of water molecules and the propagation of electricity. The first chapter of the memoir describes several electrolysis experiments on several acids and metallic salts.³⁹ The second chapter of this essay gives a short account of Grotthuss' research.⁴⁰ Using acidified water, Grotthuss seeks to explain the evolution of hydrogen and oxygen gases at the negative and positive poles of the cell, respectively. Since hydrogen gas evolves in the negative pole only, an attractive force is in operation for the hydrogen. The English surgeon Anthony Carlisle (1768-1840) and the English chemist William Nicholson (1753-1815) first observed this phenomenon known as the *Nicholson Paradox* shortly after Volta discovered the pile.

³⁶ Ibid, pp. 85-86.

³⁷ Ibid, p. 86.

³⁸ Ibid, p. 84.

³⁹ Grotthuss, 1805, pp. 1-11.

⁴⁰ Ibid, p. 12-18.

Grotthuss' model for the decomposition of water molecules and the propagation of electricity in acidified water solutions is remarkable and is used today as a guide to explain the much higher mobility of the hydrogen ions over common cations. According to this model, the electric current of the galvanic cell induces an electrical polarity between the water molecules. All the oxygen molecules (the notion of ions was unknown at that time) represented by a positive sign will tend to go towards the positive pole, while all the molecules of hydrogen represented by a positive sign situated on the same route, will tend, to reach the negative pole. He assumed that water molecules "will appear to constitute the complement of the battery in action."41 They form an array along the direction of the current between the poles (Figure 1.1). Molecules at the vicinity of the poles will split, separating themselves into hydrogen at the negative pole and oxygen at the positive pole. Hydrogen and oxygen are set free from two different molecules in immediate contact with the poles. The remaining components of these two molecules unite at once with the opposite parts of the following adjacent molecules of water. In other words, each oxygen atom simultaneously passes and receives a single hydrogen ion.⁴² "J'en déduis que, s'il était possible d'établir un courant d'électricité galvanique dans de l'eau, de façon qu'il décrivit dans celle-ci une ligne parfaitement circulaire, toutes les molecules du liquide situées dans

⁴¹ Grotthuss, 1805, p. 16,

⁴² Grottthuss' theory seems extraordinary since, at that time, the water formula was thought to be HO and not H₂O, and the concept of ions was still confusing. Nevertheless, this mechanism has proven to be correct with the current standards. This proton-hopping propagation mechanism was not a simple transfer. It was described instead as a jumping hydrogen atom from one oxygen to the next one. Chemists have invoked this mechanism to explain the unusual high velocity of the proton under the influence of an electric field relative to the velocities of other common cations. Biochemists used the same mechanism to explain possible defects in the hydrogen bonding networks of proteins. For an account of Grotthuss' propagation mechanism, its modern versions, and its significance in the biochemistry of proteins, see Cukierman, 2006.

ce cercle, seraient décomposées, et à l'instant recomposées: d' où il suit que cette eau, quoique subissant l'effet de l'action galvanique, resterait toujours eau".⁴³

In summary, Grotthuss considered that electric conduction originated from electric forces exerted by the poles and inducing molecular motions in two opposing directions only, the decomposition progressing from molecule to molecule. Grotthuss' theory provided a model that applied not only for the decomposition of water molecules but also for the electrolysis of other substances dissolved in water pro. The polar arrangement, such as it exists in the elementary molecules of water traversed by the galvanic current, must establish itself equally between the elementary molecules of any other liquid body For example, for the decomposition of metallic compounds, the metallic component is deposited at the negative pole of the cell provided instead of oxygen, whereas the nonmetallic component on the negative pole.⁴⁴ Furthermore, he observed that metals have different affinities⁴⁵ perceived later by Davy and Berzelius. These two men and Faraday (see below) were influenced by Grotthuss' theory of decomposition and propagation. However, neither Davy nor Berzelius cited Grotthuss in their papers.⁴⁶ On the contrary, Faraday mentioned very often Grotthus in his work on electrolysis.

⁴³ Grotthuss, 1805, p. 17.

⁴⁴ Grotthuss, 1805, pp. 20-21.

⁴⁵ Grotthuss stated clearly "Tous les métaux en dissolution ne sont pas décomposés par l' électricité galvanique . Du nitrate de manganese, j'obtins des bulles gazeuses au pôle négatif (1), au lieu d'un dépôt métallique; et il paraît que, lorsque dans les mêmes circonstances le métal en dissolution a plus d'affinité pour l'oxigène,que n'en a l'hydrogène pour ce principe, c'est l'eau qui doit subir seule la decomposition". (Grotthuss, 1805, pp. 3-4).

⁴⁶ Jaselskis, et al., 2007, p. 123.

André Marie Ampère

André Marie Ampère (1775-1836) made an essential contribution to chemical affinity and the effect of electricity on the decomposition of bodies in the electrolytic cell. Ampère worked with Davy and Grotthuss regarding the propagation of the electric current and presented a theory of chemical affinity analogous to Berzelius's. He developed, however, his theories proposing original ideas arguing between chemistry and geometry with electrochemistry. After a visit to Ampère's laboratory in Paris, the Danish physicist and chemist Hans Christian Ørsted (1777-1851), who contributed to the theory of electromagnetism, had noted once that Ampère was a gifted theoretician and a mediocre experimenter.⁴⁷

In 1822, Ampère published a memoir in which he introduced new ideas about dynamic electricity. He replaced Charles Augustin de Coulomb's (1736-1806) electrostatics with electrodynamics.⁴⁸ He thought that the electricity in motion in the voltaic conductor caused the phenomena of attraction and repulsion, and therefore the electrodynamic action is a better explanation for their occurrence. He changed the name *pole* of the batteries with the names *current-holder* or *rheophore*. He thought that the name pole imparts false analogies with the same word attached to the fields of geometry and astronomy. Besides, he asserted that the poles do not signify the extremities of the battery.⁴⁹

Ampère developed his theory on electrochemistry in a second memoir that read in front of the Academie des Sciences in January of 1824. He published this work in its entirety much later, in 1847. The French scientist began posing the question: if the particles

⁴⁷ Petit, 2013, p. 74

⁴⁸ Ampère, 1822, p. 200.

⁴⁹ Petit, 2013, pp. 71-72.

constituting the bodies are electrified (according to Berzelius dualistic theory), why did the same bodies not show any sign of electricity macroscopically?⁵⁰ To remove this paradox, he imagined that each particle has an electric atmosphere of the opposite sign of its electricity, which masks the *potential action* of the internal electricity (**Figure 2**). He assimilated each particle as a microscopic bottle of Leyden. Ampère designed the particle and its atmosphere and explained geometrically how the bodies show an excess of electricity negative or positive upon decomposition.

Further on, based on this geometrical model, Ampère attempted to give an account of the chemical affinity of bodies through the process of their combination between them to form compounds. This combination occurs by merging the electric atmospheres of the constituting particles of the two bodies characterized by opposing electricity (**Figure 2**). The total electricity of the two bodies is neutralized when the opposing electricities of the two atmospheres are equal and produce what Ampère called a *neutral fluid*. The internal electrics of the molecules are no longer masked by the outer atmospheres and can therefore interact and form a new molecule. Otherwise, the newly formed body shows an electronegative or electropositive character depending on the dominance of the negative or the positive electricity of the respective atmospheres.⁵¹ At any rate, decomposition and propagation of bodies in an electrolytic cell occurs by the same mechanism proposed by Davy and Grotthuss, i.e., by consecutive decompositions and recompositions of the water molecules linked in a chain along the direction of the electric current.⁵² **Figure 1.2** shows Ampère's model for the decomposition/recombination of the water molecules.

⁵⁰ Ampère, 1847, p. 172.

⁵¹ *Ibid*, 1847, 178-179.

⁵² *Ibid*, 1847, pp. 179-180.

Michael Faraday

Michael Faraday (1791-1867) made an extraordinary contribution to electrochemistry during the decade of 1830. He reconsidered the theory of decomposition and redefined the propagation of electricity. He invented the two laws of electrolysis. The English physicist was an excellent experimenter and inventor of new devices for conducting his experiments. Upon exchanging views with the polymath Rev William Whewell (1794-1866) and his friend and personal physician Whitlock Nicoll (1786-1838), he proposed new terminology in electrochemistry. The words electrolyte, electrodes, anode, cathode, ion, cation, and anion are new concepts associated with Faraday's research on electricity in solutions.⁵³

Faraday was a positivist, and he was skeptical of theories and hypotheses. He relied on experiments as a means to find new evidence for resolving ambiguities and comprehend electrical phenomena. Faraday trained near Davy, and although he did not have a formal degree, he managed to prove himself scientifically. His first publications were about electromagnetism, and there is no doubt that these types of experiments had a substantial impact on his future research to understand the electrochemical phenomena.⁵⁴

Faraday realized that the battery provides a considerable amount of electricity but is very low intensity due to very low voltage. Low-intensity electricity does not allow a higher degree of decomposition and, therefore, a new insight into this process. Faraday abandoned the arrangement of voltaic cells and invented the electric friction machine that provided higher voltage and, thus, the higher intensity emission of an electric current.⁵⁵

⁵³ Faraday, 1834, p.79, §665, and pp. 77-78, § 662 For the story concerning Faraday's attempts to invent the proper terminology of his new electrochemistry, see Petit, 2013, pp. 92-95 and Ross, 1961, pp. 188-189.

⁵⁴ Petit, 2013, pp. 85-86.

⁵⁵ In 1801 the English physiologist, chemist, and physicist William Hyde Wollaston (1766-1828) performed an experiment showing that the electricity from friction was identical to that produced by voltaic piles. He

The high voltage of the new electrical device allowed the performance of *remote decomposition* of bodies.⁵⁶ In this respect, Faraday was able to obtain decomposition upon varying the distance between the poles of the electric machine with similar results. He concluded that the decomposition of bodies is internal and occurred within the decomposing body in solution and not at the poles of the apparatus.⁵⁷ This internal decomposition was due to the electric forces of the current. "They [the experiments] indicate at once an internal action of the parts suffering decomposition, and appear to show that the power which is effectual in separating the elements is exerted there, and not at the poles."58 His reasoning stemmed from Coulomb's law. The electric forces should have been weakened with increasing distance between the poles, resulting thus in a less effective decomposition, which was not what he observed in the experiments. Internal decomposition may recall the dissociation theory invented by Svante Arrhenius, which constitutes an inseparable part of modern chemical thermodynamics. However, as we shall discuss later, in Arrhenius' dissociation theory, the electric current does not affect the separation of the electrolyte into ions. The electrolyte dissociates instantly upon its dissolution in the solvent.

The decomposition procedure suggested by Faraday (and his predecessors) assumes the influence of the electric forces, "....may perhaps best perceived, like an axis

used ordinary friction electricity to decompose water (Wollaston, 1864). Interestingly, Ampère considered friction machines less effective for electrodynamic applications because electricity propagates much more rapidly by contact than through liquids (Petit, 2013, p. 117).

⁵⁶ Faraday, 1933a. pp. 31-33, §290-307, and pp. 34-37, §309-321; Faraday, 1833b, p. 676, §453-454.

⁵⁷ Faraday gave a short description of the theories concerning the electrochemical decomposition as viewed by the eminent experimenters Davy, Biot, Auguste Arthur de la Rive (1801-1893), and Henri Victor Regnault (1810-1878). All of them concluded that decomposition of bodies took place at the poles of the electrolytic cell (Faraday, 1833b, pp. 682-687, §480-492).

⁵⁸ Faraday, 1833b, p. 680, §471.

of power having contrary forces, exactly equal in amount, in contrary directions.⁵⁹ He linked these forces with the propagation of electric current. The propagation consisted of a step-by-step mechanism of decomposition and recombination of the body constituents in opposite directions. It appears that the propagation mechanism suggested by Faraday is not practically different from that proposed earlier by Ampère. Both men refused that decomposition occurred at the poles.

However, Faraday differed from Ampère because he assumed that the current's propagation was primarily dependent on the affinity of the bodies. He advocated that a higher affinity between bodies favor a better transfer of electricity. Faraday's explanation for this mysterious hypothesis (the opposite hypothesis could have been expected) is related to the ease by which the two elements of the body that are present after decomposition transfer the electricity to the poles due to their strong opposing power of combination.⁶⁰ This hypothesis was clarified when Faraday adopted the terms ions, cations, and anions. "If one ion be combined in right proportions with another strongly opposed to it in its ordinary chemical relations, i.e., if an anion be combined with a cation, then both will travel, the one to the anode, the other to the cathode, of the decomposing body."⁶¹

Thus, the combination of the influence of the electric current and the mutual chemical affinity of the bodies provides the mechanism of propagation suggested by Faraday. "Passing to the consideration of electro-chemical decomposition, it appears to be the effect is produced by an *internal corpuscular acti*on, [emphasis by Faraday) exerted according to the direction of the electric current, and that it is due to a force either

⁵⁹ Ibid, p. 695, §517.

⁶⁰ Faraday, 1833b, pp. 706-707, §549-550.

⁶¹ Faraday, 1834. pp. 111-112, §827.

superadded to or giving direction to the ordinary chemical affinity of the bodies present. [...] and it is because the ordinary chemical affinity is relieved, weakened, or partly neutralized by the influence of the electric current in one direction parallel to the course of the latter, and strengthened or added to the opposite direction, that the combining particles tend to pass in opposite courses".⁶² A particle cannot travel from one pole towards the other unless it finds a particle of the opposite kind ready to pass on the contrary direction. Faraday presented schematically the process of decomposition/ recombination accompanying the propagation of the electric current (**Figure 1.3**).⁶³

The *seventh series of researches* published in January 1834 contained experiments and calculations that enounced the two well-known laws of electrolysis. Under a variety of conditions upon changing the size of electrodes, the intensity of the current, and the concentration of sulfuric acid in aqueous solutions, he measured the weight of the oxygen and hydrogen gases deposited on the electrodes of the decomposition cell upon the passage of a known quantity of electricity. Once the decomposition process is accomplished, the amount of gas is measured using a device of his invention, which he calls a voltaelectrometer. He uses it to determine the amount of electricity passed through the instrument (**Figure 3**). He performed similar decomposition experiments with various substances other than acidified water. He observed that none of these three variations affected the experimental results in all cases, which connected the measured weight of the elements deposited on or liberated from the electrodes to the quantity of electricity. Faraday found a proportionality relation between the two quantities. This relationship described the

⁶² Faraday, 1833b, y. 696, §518.

⁶³ Faraday, 1951, pp. 69-70. This book is a collection of the series III-VII and XVI, XVII of the original Faraday's Experimental Researches in Electricity. It contains plates and figures.

law of the *electrolytic action*. He stated that "I consider the foregoing investigation as sufficient to prove the very extraordinary and important principle with respect to WATER (capital letters denoted by Faraday), that when subjected to the influence of the electric current, a quantity of it is decomposed exactly proportionate to the quantity of electricity which has passed".⁶⁴ This statement represents the first law of electrolysis. It holds for the electrolysis of any substance, including water. The formulation of this law is as follows:

$$m = ZQ \tag{1.1}$$

Here, *m* is the mass deposited at the electrode, and *Q* is the charge of the electricity passing through the solution. The proportionality constant *Z*, known as the *electrochemical equivalent*, expresses the body's mass deposited/liberated per unit charge. Faraday did not use atomic weights computed on the basis of Dalton's atomic theory to define the weight of the decomposed materials. Faraday wanted to avoid any reference to atoms in his calculations and used the equivalents⁶⁵ proposed by William Wollaston. The latter shared the same skepticism with Faraday about the atomic weights and, in general, about Dalton's atomic theory.⁶⁶ Adding the concept of electrochemical equivalents, Faraday completed his law of *electrolytic action*. This result is, in essence, the second law of electrolysis. It states that when the same quantity of electricity passes through several electrolytes, the mass of the substances deposited is proportional to their respective chemical equivalent or equivalent weight.

⁶⁴ Faraday, 1834, p. 91, §732. For criticism and recognition of the laws of electrolysis by Faraday's contemporaries, see, Ehl and Ihde, 1954, pp. 229-232; Petit, 2013, pp. 135-136.

⁶⁵ Faraday considered the notions of the lectrochemical equivalent and chemical equivalent as identical, and always consistent for a given substance.

⁶⁶ Wollaston, 1814, p. 7.

Faraday calculated the *electrochemical equivalent of matter*, and Joule calculated the mechanical equivalence of heat. Both researchers compared their equivalent values with those measured in ordinary chemical reactions performed in the laboratory outside the galvanic or the electrolytic cell. They hoped that this comparison of the electrochemical reactions with neat chemical reactions would offer the means to categorize these reactions. The result was somewhat disappointing; they observed quantitative discrepancies of the measured heat between the electrochemical and the ordinary reactions. Careful examination of this anomaly led Faraday and then Joule to recognize the existence of two general categories for reactions occurring in the cells: the primary reactions, which were the electrochemical reactions that occurred at the poles, and the secondary reactions, which resulted as byproducts of the primary reactions. Polarization of the electrodes and the dissolution of metal oxides in acids in the cells are phenomena owing to such secondary reactions. Faraday used the argument of secondary reactions when he observed that the electrolysis of certain substances deviated from the low of the *electrolytic action*.⁶⁷ John Frederic Daniell (1750-1845) has thoroughly investigated the complexity introduced in the law of electrolysis by secondary reactions.

After articulating the two laws of electrolysis, Faraday summarized eleven points that ions, electrolytes, and electrochemical equivalents must obey.⁶⁸ These theoretical considerations allowed Faraday to deduce the identity of a cation on the anode from its associated anion in the cathode. This conclusion is essential when secondary reactions obscure the products deposited on or liberated from the electrodes. Furthermore, the

⁶⁷ Petit, 2013, p. 97.

⁶⁸ Faraday, 1834, pp. 111-113, §826-836.

equivalent of a compound (complex) body could be determined if the nature of the substance collected to one of the electrodes is available.⁶⁹

Faraday set forth a Table of electrochemical equivalents determined from electrolytic methods.⁷⁰ These values are then compared with the chemical equivalents obtained by other scientists. He adjusted the values of the latter to fit the experimental results. He appraised the Table of electrochemical equivalents, the equivalents of ions, as a powerful utility tool in developing the intimate relation of ordinary chemical affinity to electrical action. Although Faraday was aware of the low precision of the values in the Table, he stressed that these values were real, not theoretical. These values helped him to decide what was the exact chemical equivalent, the definite proportion, or the atomic number of a body.⁷¹ However, Faraday did not go further to calculate the atomic weight of the element

Georg Simon Ohm

Early in 1830, Faraday's electrochemistry found an unfavorable context in the German Empire. The dominance of Volta's contact theory obscured any research on electrochemical decomposition. Eminent philosophers, including the physician Cristopher Heinrich Pfaff (1773-1852), the editor of the *Annalen der Physic und Chimie* Johann Christian Poggendorff (1796-1877), and the professor of experimental physics at the University of Munich Georg Simon Ohm (1789-1854) were fervent followers of the contact theory. Ohm showed interest in investigating and analyzing the characteristics of

⁶⁹ *Ibid*, p. 113, §137-140.

⁷⁰ *Ibid*, pp. 114-115.

⁷¹ *Ibid*, p. 115, §851.

the contact theory to cope with the opponents of this theory.⁷² In 1827, Ohm published his major essay Die galvanische Kette, mathematisch bearbeitet (The galvanic circuit investigated mathematically):⁷³ When Ohm first published his memoir he faced unprecedented hostile criticism. They called his work a web of naked fancies. The German Minister of Education proclaimed that, "a professor who preached such heresies was unworthy to teach science.⁷⁴ Ohm presented his theory based on three laws that expounded within the context of the contact theory.⁷⁵ The first law expresses the mode of distribution of the electricity within the one and the same body; the second relates the mode of dispersion of the electricity in the surrounding atmosphere, and the third expresses the mode of development of the electricity at the point of contact of two heterogeneous bodies. The last two laws are purely experimental, whereas the first is, in part at least, theoretical. However, none of these laws and their treatment takes into consideration the chemical effects of electricity. For Ohm, when they occur, chemical reactions within the batteries are just boring manifestations that must be neglected as much as possible.⁷⁶ In this respect, he used solid conductors to avoid perplexed, second-order effects induced by electricity. In his experiments, Ohm initially used voltaic piles to measure tensions across the soli

⁷² According to the contact theory, the contact of two conducting metals explains the electrical conduction. The phenomenon is thought of as the consequence of discharges between contiguous particles of the two metals. The chemical theorists rejected the idea of the contact force and claimed that chemical processes played a much more central role, and they were the very cause of the cell's activity. The supporters of the contact force reacted rapidly to the chemists' claims advocating that the chemical reaction was a secondary factor, and its role was to assist the primary cause of electricity, that is, the exchange of electricity between the two metallic conductors. For more details about this long-lasting dispute, see Kipnis, 2000, pp. 121-151; Kragh, 2000, 33-157; Kragh and Bak, 2000, pp.84-85. Reference to the dispute between chemists and contactists will be made on several occasions tin he following chapters of this dissertation.

⁷³ Ohm, 1827. Ohm's memoir was transladed into English by in 1891 by ThpmasD. Lockwood and re-edidet in 1969. The 1891 edition was used here.

⁷⁴ Davis, 1980.
⁷⁵ Ohm, 1891, p. 12.

⁷⁶ Ibid, pp. 17-18.

conductors. He replaced it later with a thermocouple seeking a more stable voltage. He used a galvanometer to measure the electric current. He performed several experiments with wires of varying lengths, diameters, and material.⁷⁷ In each case, Ohm presented graphically the fall of the electric current intensity across the wire of the circuit. He modeled his measurements through the following empirical equation:

$$x = \frac{a}{b+l} \tag{1.2}$$

Where *x* is the reading from the galvanometer, *l* is the length of the wire *a*, is a constant that depends on the thermocouple junction temperature, and *b* is a constant of the entire setup.⁷⁸ From this equation, Ohm determined his law of proportionality. "The electromotive force acting between the extremities of any part of a circuit is the product of the strength of the current and the resistance of that part of the circuit."⁷⁹

Ohm's law was the first mathematical expression in early electrochemistry. As a veritable contactist, Ohm did not think about any application of his law to electrolytic solutions. Nevertheless, the formation of ions through the action of the electric current proposed by Faraday brought Ohm's theory in harmony with the electrolytic solutions.⁸⁰

Faraday's electrochemistry did not find suitable ground in France either. This disinterest among French electrochemists resulted partly from the difficult of the French chemists to comprehend the theory behind the electrochemical concepts proposed by Faraday, and partly because they were indifferent occupied by different research interests. Organic chemistry obscured electrochemistry in France. At about the same period, organic

⁷⁷ Ibid, pp. 20-35.

⁷⁸ In modern notation, *x* is the measured intensity of the electric current, *a* is the electromotive force of the thermocouple, *b* is the internal resistance of the thermocouple, and *l* is the resistance of the wire. ⁷⁹ Ohm. 1827, p. 181.

⁸⁰ Electrochemists had to overcome another obstacle in order to apply safely Ohm's law to electrolysis, the polarization of the electrodes.
chemists appeared to have an active interest in electrochemistry. Faraday's theory on the degradation of substances into ions in the electrolytic cell contradicted the traditional theories of substitution reactions. Faraday's theory could explain effectively the formation of new compounds by substituting atoms or groups of atoms in compounds. The theory was better suited to the electronegative and electropositive nature of bodies. For instance, it offered a better explanation for substituting the electropositive hydrogen with the electronegative chlorine atom.

Antoine César Becquerel

After Ampère's significant contribution to electrochemistry, the latter seemed to decline in France. It appears that no vital research was conducted in the field until the appearance of Antoine César Becquerel (1788-1878). Becquerel was one of the few French scientists working on electricity and appeared to be the main guarantor of electrochemical culture in France. Becquerel was the author of five of the seven electrochemistry dissertations published in *des Annales de Chimie et de Physique* in 1826-1835. He was almost the only electrochemist who published memoirs (nearly thirty) on electrochemistry between 1798 and 1878.⁸¹ Notwithstanding, Becquerel met at the beginning of his career with a scientific environment indifferent in his work. He felt isolated by a strong group of scientists whose research interests focused on other fields of science but electrochemistry.

The graduate of the École Polytechnique was aware of the scarcity of experimental data regarding electrical phenomena. "The electric phenomena are so enveloped still of darkness that one cannot say immediately if the results obtained are simple or come from

⁸¹ Petit, 2013, p. 121, note 381.

composite effects. It is by multiplying the experiments and varying them to clarify the electrochemical theory".⁸² Under the influence and support of Ampère, he began a thorough investigation of electrical phenomena. He conducted his first experiments in mineralogy. The research on minerals led him to electrical experiments through which he explained the appearance of electricity in crystals under compression. He showed that this phenomenon (today is known as the piezoelectric effect) is general and occurred with crystals deprived of the center of symmetry. He generalized the action of liquids on metals, and he experimented with very low currents and tensions. He studied many other causes of the development of electricity by bodies (heat, contact, and friction).⁸³

Unlike Faraday's skepticism on the relation between atom and electricity, Becquerel speculated the connection between electricity and the constitution of matter. However, Becquerel did not give the ontological meaning of a charged atom, i.e., an ion. Becquerel paid attention to Faraday's electrochemistry, whose view was comparable with his own. However, he exposed his disagreement with Faraday in some respects. For instance, Becquerel did not find helpful the properties ascribed to ions, anion, and cation. He preferred the electropositive and electronegative bodies that expressed the duality of electricity. Both Faraday's ions and Becquerel's electropositive and electronegative bodies obey the law of the electrolytic action and explain the propagation of electricity in solutions. On the other hand, Becquerel accepted the terms electrodes and electrolytes proposed by Faraday.

Early in 1830, after many years of careful observation and accumulation of experimental facts, Becquerel expressed general opinions on the phenomena of

⁸² Becquerel, 1824a, p. 176.

⁸³ Becquerel, 1824b, p. 5.

electrochemical decomposition and the propagation of the electric current. He assumed that the electric forces produced by the electric current of the pile polarized the molecules.⁸⁴ He conceived polarization⁸⁵ induced by the two poles of the electrolytic cells similar to that of small magnetic bars subjected to the action of an external magnetic field. Becquerel, thus, had an opinion for the propagation of current similar to that proposed by Ampere. However, he argued that the remote actions of the pile could not alone explain the electrochemical decomposition. He found that the use of an *ethereal* interpretation was beneficial as an explanation. The propagation step-by-step mechanism in the form of an uninterrupted chain of polarized molecules explains the displacement of bodies at the poles and opens up new perspectives on the chemical combination. The latter description is not very different from that proposed by Faraday (except, of course, the propagation through an ethereal medium). Thanks to numerous publications, either alone or in cooperation with Ampère, Biot, and his son Alexandre Edmond Becquerel (1820-1891), who succeeded Becquerel at the Musèum d'Histoire Naturelle received an excellent reception in France and England.

John Daniell and William Grove: batteries of constant current intensity

Unlike Germany and France, Faraday's electrochemistry had a better chance in England. The recognition of Faraday's concept of ions was an advantage for Faraday to expand his ideas to scholars outside the Royal Institution and an opportunity for the science of electrochemistry to advance new experimental and theoretical approaches and to enrich its

⁸⁴ Becquerel, 1833, pp. 583-584.

⁸⁵ This type of polarization is different from the polarization of electrodes. The term polarization was used initially to describe electrolysis, which was then called polarization liquid. As more electrochemical processes were invented, the term polarization evolved to denote any potential mechanical side-effects that occur at the interface between electrolyte and electrodes.

arsenal with more effective instrumentation. The professor of King's College London, John Frederic Daniell, and the Welsh lawyer William Robert Grove (1811-1896)⁸⁶ invented new batteries to provide electric current with constant intensity. The hitherto batteries provided electric current with fluctuating intensity due to secondary reactions at the electrodes that led to polarization. The varying current intensity was a nuisance for the experimenters and often led to unprecise results. Both Grove⁸⁷ and Daniell constructed such batteries of constant intensity. Grove's battery⁸⁸ was sixteen times more powerful than Daniell's battery,

William Daniell⁸⁹ was a skilled experimenter and an ingenious inventor of several meteorological instruments. He devised barometers to measure the water pressure, hygrometers to estimate the water content, and pyrometers to measure the temperature of furnaces. He entered the field of electrochemistry when he began in 1835, the construction of the voltaic cell, which carried his name.⁹⁰ Daniell's batteries were well-known for their constancy conveying electric current devoid of intensity fluctuations shown by most batteries of the time. He investigated and solved the *reverse polarization* caused by the liberation of hydrogen gas during electrolysis by separating the compartment of the zinc

⁸⁶ For a short biography of Grove, see Scott, 1981, pp. 559-561.

⁸⁷ Grove's most important work was summarized in the lengthy memoir Traité expérimental de l'électricité et du magnétisme naturelles published in seven volumes between 1834 and 1840.

⁸⁸ Grove, galvanic cell consisted of two electrodes of amalgamated zinc and platinum immersed in diluted nitric acid and diluted muriatic acid (hydrochloric acid), respectively, using a porous diaphragm in between the two solutions (Grove, 1839a). In other experiments, he replaced muriatic acid with dilute sulfuric acid and nitric acid with concentrated nitro-sulfuric acid (Grove, 1939b, pp. 287-289). In his second paper, Grove discussed the theory behind the battery (Grove, 1939b, pp. 289-291).

⁸⁹ For a short biography of the man, see Thackray, 1981, pp. 556-558.

⁹⁰ Daniell's cells consisted of a container divided into two compartments by a membrane permeable to ions. In one compartment, a zinc electrode was dipped in a zinc sulfate solution and, in the other compartment, a copper electrode in a copper sulfate solution. Daniell described the tests and the construction of the battery in his two memoirs of 1836 and 1837. For the story of the construction of Daniell's battery, and the priority dispute that broke between Grove and Edmond Becquerel against Daniell, see Owen, 2001.

electrode, and the attendant dilute sulfuric acid from that of the copper electrode immersed in a copper sulfate solution with a porous diaphragm (**Figure 4**). This arrangement effectively prevented the formation of hydrogen gas at the copper electrode and thus enabled the battery to function unimpaired for long periods. Daniell's cell and its functioning conditions were described in 1836 and 1837 in the *Philosophical Transactions*.⁹¹ For this achievement, Daniell received in 1837 the Copley Medal, the Royal Society's highest award. The use of several Daniell's cells coupled in a chain formed a durable battery that provided a large electromotive force. This battery was suitable for commercial applications, such as electroplating or gilding, thus giving electrochemistry a tremendous impetus for research. Joule benefited in his experiments by using batteries consisting of a series of Daniell's⁹² and Grove's cells (see below). Apart from experiments and inventions, Daniell published a large number of theoretical papers in electrochemistry. In 1831, he was appointed as professor of chemistry in King's College, London.

Ohm's reaction to the announcement of the invention of Daniell's constant intensity battery was at the height of the upheavals it brought in the electrical practice in the laboratory. He wrote to Danniell: "Allow me, Sir, [...] to acknowledge to you the high satisfaction and delight, which I feel in having become connected with a gentleman, who, by way of his scientific investigations, has derived the discovery of constant galvanic apparatuses, by means of which the experimental constitution of the laws of the galvanic

⁹¹ Daniell, 1836; 1837; Partington, 1964, pp. 128-130.

⁹² Daniell used to send his papers to Joule, where he clarified several aspects of electrochemistry, including the elucidation of the nature of primary and secondary reactions, Forrester, 1975, pp. 278 and 303. Joule expressed his debt explicitly to Daniell (Joule's scientific papers, 1884, p. 104).

circuit also on such chains, which have taken fluids as ingredients, was so much facilitated".⁹³

Daniell made extensive investigations of the possible effects of the decomposition of secondary compounds to assess the decomposition of water in the presence of dissolved salts. In this respect, he wrote to Faraday: "I have no doubt that you will agree with me in thinking that the decomposition of secondary compounds by the voltaic current, particularly in connection with water, has not yet received all the attention which it deserves, and that the subject is worthy of further experimental research".⁹⁴ He performed a series of seventeenth experiments varying the type of the electrodes of the constant current cells, the type and the concentration of salt solutions, and the nature of the porous diaphragms. He observed that the decomposition of an equivalent of water caused the decomposition of an exact equivalent of the salt. The electricity carried by the ions of the dissolved salt caused, in turn, the decomposition of water. Any deviation from these observations is ascribed to the formation of secondary compounds collected at the poles. These compounds resulted not from the electrochemical action but secondary reactions of decomposition products with other bodies in solution. For instance, sulfuric acid is formed at the anode by the secondary reaction of one equivalent of hydrogen (resulting from the decomposition of water) with one equivalent of sulfate anion coming from the decomposition of sodium sulfate. Similarly, the formation of soda at the cathode was due to the action of one equivalent of sodium with one equivalent of oxygen.

⁹³ Quoted in Petit, 2013, p. 134.

⁹⁴ Daniell, 1939, p. 97.

In 1844, Daniell and his assistant William Allen Miller (1817-1870) published a paper in which they proposed their mechanism of the propagation of the electric current during electrolysis. According to this model, each ion equivalently moves towards the corresponding electrode: "the release of whole equivalents of ions at the electrodes is accompanied only [...] by the effective transfer of a half equivalent on each side".⁹⁵ They, therefore, envisioned that on each side of the diaphragm, the transfer of cations and anions takes place in a perfectly identical way [**Figure 1-4**). However, further quantitative measurements indicated the opposite behavior from this hypothesis. The process of the ions' transportation towards the electrodes appeared to be far too heterogeneous to support the hypothesis that anions and cations move at the same rate during electrolysis. Unable to explain the reasons for the discrepancy between their theory and the experimental results, Daniell and William Miller left the question open: "we shall therefore prefer leaving them to the elucidation of further investigation, to adding one more to the already too numerous list of hasty generalizations".⁹⁶

In summary, at the beginning of the nineteenth century, several natural philosophers turned their attention to the electrochemical decomposition observed with the Volta cell. The first electrochemists studying the phenomenon of electrolysis sought to find answers to questions of how substances decompose during the process of electrolysis and how the electric current propagates through the electrolytic solutions. The answers were frequently varied, depending on each electrochemist's tradition and cultural environment that affected his scientific style and reasoning. The invention of Grove and Daniell's constant current batteries reached the electrochemists and facilitated the collection of more accurate

⁹⁵ Daniell and Miller, 1844, p. 2.

⁹⁶ Ibid, p. 19,

experimental data. Furthermore, these observations specific to voltaic and electrolytic cells revealed the close relationship between electricity and matter leading to the reformulation of the concept of chemical affinity. Between the third and fourth decades of the nineteenth century, electrochemistry began to acquire a theoretical basis with the definition of the ion by Faraday. In the same period, Ohm formulated his law of electrical conduction although applicable solely to solid conductors. Since this law was inappropriate for electrolytic solutions, it was not considered a universal law, despite the ambitions nurtured by its author. Clausius, Kohlrausch, and Helmholtz achieved this generalization when they were interested in electrochemistry.

Section 2. Theories of heat and applications

The prevalent heat theory during the first half of the nineteenth century was the doctrine that heat was a special kind of substance or fluid (caloric) capable of penetrating all space and flowing in and out of all bodies. In accord with the law of the conservation of mass, first proposed by Antoine Laurent Lavoisier (1743-1794), heat should be indestructible. This theory was the precursor for the development of experimental calorimetry by Lavoisier and Laplace. The success of the calorimetric experiments was, in return, the proof of the material nature of heat.⁹⁷ Experiments and analytical expressions by Lavoisier, Joseph Black (1728-799), and Pierre-Simon Laplace (1749-1827) consolidated the explanatory context for the caloric model.⁹⁸ The rise and fall of the temperature of bodies, the thermal expansion of gases, the dependence of the specific heats of gases on pressure

⁹⁷ There are opposite views on this matter, claiming that the law of the conservation of heat did not arise from the calorimetric measurements but from the calorimetric set-up itself, which was thermally insulated. In other words, calorimetry did not directly support the materiality of heat (Psillos, 1994, pp. 168-169).

⁹⁸ For the caloric theory, see Fox, 1971; Mendoza 1961; Brown, 1950.

and volume, the adiabatic phenomena of heat⁹⁹ observed by Laplace and Gay-Lussac, the latent heat, and the change of state (vaporization and freezing of liquids) were better explained by the caloric theory.

On the other hand, the experiments of Benjamin Thompson (the late Count Rumford) (1753-1814) and Humphry Davy on frictional heat seemed to render questionable the caloric theory. Count Rumford suggested that heat could not be a material substance. Friction cannot produce heat in an inexhaustible manner. Therefore, no material substance can be inexhaustible. The generation of heat by friction could be better explained as a kind of motion advocated by the new theory, the so-called mechanical or the dynamical theory of heat. According to this theory, heat is a kind of motion of the particles constituting matter. As such, it cannot disappear following the conservation of matter.

Most calorists ignored this explanation. Though not convincing, their primary claim was that heat production by rubbing two bodies together did not produce inexhaustible heat, as Count Rumford suggested. At any rate, Rumford and Davy's experiments on frictional heat were not the reason for the abandonment of the caloric theory. Apart from the difficulty of explaining frictional heat, the calorists were aware of other challenges that troubled the caloric theory. These included shaky experimental verifications, inaccuracy in experimental results, and, most importantly, the unsuccessful efforts to determine the weight of caloric, a property that it should have had as a material substance.

On the other hand, the calorists were familiar with the advantages of the mechanical theory of heat, which could expound on heat production by friction and, in particular, radiant heat. In this respect, most eminent scientists working within the caloric theory,

⁹⁹ For the historical development of adiabatic phenomena and their connection with the caloric theory, see Kuhn, 1958.

including its originators Lavoisier, Laplace, and Black, were very cautious in exposing their theoretical commitments. Nonetheless, the mechanical version of heat was physically and mathematically undeveloped. It did not attract any significant attention amongst physicists until the emergence of the second law of thermodynamics. Clausius, William Thomson, and Rankine showed that such a theory of heat was compatible with the assumptions of Nicolas Léonard Sadi Carnot (1796-1832) and the mathematical formalism of Benoît Paul Émile Clapeyron (1799-1864) based on the caloric theory. Under these circumstances, both approaches were in use, especially after the first quarter of the nineteenth century, to explain similar or different phenomena of heat. Early in the nineteenth century, this was the situation concerning the development of the two theories of heat when the young engineer Sadi Carnot wrote a theoretical account on the proper operation of steam engines. This study might be considered as the first application of the caloric theory to practical problems.

Section 3. Mathematics in chemistry

Although Newton and the great French mathematicians of the eighteenth century had pointed out the advantages of explaining natural phenomena, including chemistry, it took more than a hundred years to apply mathematics to chemistry. In chapter 9, I will discuss why chemists avoided using advanced mathematics in the laboratory most of the nineteenth century. Even though chemists experienced the discoveries of the beginning of the nineteenth century, such as the atomic theory of Dalton, the mass action low of Berthollet, and the establishment of stoichiometry in chemical reactions by Jeremias Benjamin Richter (1862-1807), the application of mathematics to chemistry was limited to most practical work. Influenced by the expansion of organic chemistry, chemists continued to ignore the usefulness of mathematics since their needs did not surpass simple arithmetic for the calculations of weights, volumes, and composition of reacting substances. The neglect of mathematics in the education of a chemist was more or less the usual practice and expressed the general disposition of chemists towards mathematics.¹⁰⁰

It appears that mathematics entered chemistry when chemists began a thorough study of chemical processes to investigate the length of time needed to complete chemical reactions required for chemical manufacturing. In other words, time is used to measure the duration for the completion of a chemical reaction. A further step was introducing the differential equations over time employed to mathematize the speed of chemical reactions in terms of reaction rates. Ludwig Ferdinand Wilhelmy (1812-1864) was the first chemist who introduced time in his studies of the inversion of sucrose in acidified aqueous solutions in 1850. Wilhelmy set forth a differential equation connecting through a proportionality constant the change of sugar concentration (the loss of sucrose with the element of time) with the initial quantity of sugar and the quantity of the sulfuric acid (the acid concentration remains constant throughout the reaction since the acid plays the role of a catalyst). The proportionality constant was the rate constant of the reaction. He applied this equation to fit the experimental data obtained by the technique of polarimetry.¹⁰¹ In 1864, the two Norwegian scientists Cato Guldberg and Peter Waage, mentioned above, used reaction

¹⁰⁰ The following incident is characteristic of this disposition. Professor of chemistry and botany at Oxford University C. G. B. Daubeny (1795-1867) issued in 1853 a pamphlet, which was an enlightened statement for better education. However, the pamphlet included the following proposal: "It would manifestly be quite foreign to the purpose and fatal to the genius, of a School of Physical Science, to encourage the introduction of any subjects that are treated mathematically" (Laidler, 1985, p. 46).

¹⁰¹ Wilhelmy, 1850. Wilhelmy first deduced the mathematical expression of the reaction law of a monomolecular reaction, and then he verified this law from the experimental data. The formulation of Wilhelmy's reaction law has nothing to envy from the analogous law proposed by van 't Hoff 25 years later.

kinetics data and differential rate equations to establish the equilibrium conditions in chemical reactions. As we shall see later, van 't Hoff shared the most significant contribution to mathematical foundation in his chemical kinetics.¹⁰²

Mathematical methods became apparent in chemistry when chemists employed thermodynamics to elaborate the unsolved problems of chemical affinity and chemical equilibrium. This stage of development characterizes the beginning of modern chemical thermodynamics. Physicists, who were familiar with the mathematical apparatus, established classical thermodynamics. However, the need for physicists to verify their theories in practical problems turned their interest to chemistry. Clausius applied thermodynamics to chemistry when he introduced the term chemical equilibrium and expounded the phenomenon of electrolysis on a molecular basis. During the second half of the nineteenth century, James Clerk Maxwell (1831-1879), Ludwig Boltzmann (1844-1906), Josiah Willard Gibbs, Hermann von Helmholtz, and Pierre Duhem used complex mathematics (algebra, differential calculus, Lagrangian analytical mechanics, etc.) to treat chemical problems in the form of microscopic and macroscopic theories. This type of chemical thermodynamics developed on a theoretical basis took quite a long time before chemists recognized its utility, and exploited its potential in their research. The ionists have used mathematical methods in their system of chemical thermodynamics, although with a milder mathematical language. The ionists bypassing the intricacies of theorists' mathematical formality, proposed simple equations that fitted properly the experimental data obtained in the laboratory. When training in mathematics entered into the chemistry

¹⁰² See chapter 10, section 2 of this dissertation.

curricula of the institutions of mid and higher education by the end of the nineteenth century, mathematics began to be part of the chemical skill.

Chapter 2. The development of thermodynamics in the context of physics: The establishment of the two laws of thermodynamics

The first half of the nineteenth century was a critical period in which the theoretical structure and the basic concepts of classical thermodynamics emerged. Both laws of thermodynamics were formulated during the decades of the 1840s and 1850s. Together with the concepts of energy and entropy, these laws formed the basis of the next generation of thermodynamicists of the 1970s and 1880s. In this chapter, I will attempt to give a detailed account of great scientists' work made in thermodynamics. This account will serve as the preamble of the issues I will discuss in the following chapters.

Section 1. Sadi Carnot and the origin of classical thermodynamics

The year 2024 marks the hundredth anniversary of Carnot's memoir *Reflexions sur la Puissance Motrice du Feu*. In this short book of 102 pages, Sadi Carnot at 28 described the reversible cycle for an ideal heat engine and paved the way for the correct formulation of the second law of thermodynamics by the triumvirate of physicists Clausius, Thomson, and Rankine. This little book changed physics in the nineteenth century and laid the foundations for the new science of thermodynamics. It was a private publication, just 200 copies, most of which were lost or burned along with all Carnot's belongings, who died at the age of 32 from cholera. William Thomson became acquainted with Carnot's work through Clapeyron's memoir, who first studied Carnot's writing. Thomson has described Carnot as the "most profound thinker in thermodynamic philosophy in the first thirty years of the nineteenth century." Forty years after, Carnot, Clausius, Thomson, and Rankine

reformulated the second law with precise definitions. The formulation of Thomson seems to be closer to Carnot's conception of the second law of thermodynamics. Thomson's doctrine of the dissipation of energy described non-equilibrium conditions in accord with Carnot's interest in the concept of temperature regardless of conditions that were far from or close to equilibrium. Carnot stated in his *Reflexions* that the diminution of temperature "is the only cause and the only measure of power generation." On the contrary, the concept of entropy by Clausius emphasized to a certain degree states of equilibrium.

1.1 The Beginning

The origin of classical thermodynamics goes back to the third decade of the nineteenth century when the French engineer Sadi Carnot published in 1824 his single memoir entitled *Reflexions sur la puissance motrice du feu.*¹⁰³ Carnot, a graduate of the *École Polytechnique*, was interested in finding the optimum working conditions of the heat engines for obtaining the highest efficiency, i.e., the motive power obtained from a given quantity of heat. As an expert on the commerce and industries of different European countries, Carnot was acquainted with these problems early in his career as an engineer. As a well-trained engineer in physics, mathematics, and economics, he had the necessary theoretical background to deal with them.¹⁰⁴ However, his treatise proved to be more

¹⁰³ Carnot, 1824; Carnot 1878. There are several translation of the *Reflexions* together with introduction, commentary and bibliography: *Thurston, 1897; Mendoza, 1960; Fox, 1986.* All references and quotations used below were taken from R. H. Thurston's edition of 1897. For comparison, the corresponding pages of the original French editions of 1824 are given in parenthesis.

¹⁰⁴ Shin, 1980, pp. 185-189, and 191-193. During the first half of the nineteenth century, engineers in France coming from the lower social strata graduated from the Écoles d'Arts et Métiers. This institution established during the early nineteenth century did not possess any theoretical learning and advanced knowledge of applied science. The situation was improved with the creation of the École Central des Arts et Manufactures, mainly by the industrialists themselves, where engineers began to have some contact with physical sciences. Contrary to these institutions, the graduates of the École Polytechnique, the so-called corps of engineers, were state engineers with technical and administrative duties but had no tangible

ambitious than a one-sided study. Throughout his memoir, condensed propositions and assertions were distributed concerning relationships of heat and the motive power (mechanical work) and the thermal properties of gases. One of his essential theorems concerned the production of motive power in an ideal heat engine as long as a difference of temperatures existed between two reservoirs but without any heat loss.

In this process, the heat is conserved. The heat is transported undistractedly from the furnace (boiler) to the condenser (refrigerator) of the engine. The spontaneous direction of the heat flow from a warm body to a cold body was a relatively straightforward statement of the second law of thermodynamics. The presence of the cold body was vital to produce motive power. Thomson, Clausius, and Rankine later reformulated this fundamental insight as to the second law of thermodynamics. Carnot further concluded that the production of motive power was not unlimited and strove to find the conditions of its maximum value. This condition is achieved if a heat engine's working occurred in a reversible process of four steps between two different temperatures; An isothermal and adiabatic compression in the forward direction.¹⁰⁵ The whole process was carried out by a gas (e.g., atmospheric air or water steam) constituting the agent through which the heat transferred from the boiler to the condenser. Besides, Carnot ascertained that the heat flow from the hot to the cold reservoir produced motive power if the engine functioned by

contact with the industry. Nevertheless, they were well educated in physical sciences and mathematics, but, with few exceptions, they were not involved in research or the development of technological innovation. The majority of these men were the descendants of privileged social origins.

¹⁰⁵ Mendoza, 1981, p. 77; Fox, 1970. Carnot described a three-stage cycle for a steam engine in a recently found brief assay Recherche d'une formule prope à rèpresenter la puissance mortice de la vapeur d'eau. The same three-stage cycle is mentioned in the *Reflexions*, before its final version of a four-step reversible cycle. The three-stage cycle neglects the adiabatic process, and therefore the temperature difference between the boiler and the condenser of the heat engine was finite.

volume changes through alternating the gas expansion and compression in the reversible cycle. Otherwise, the transfer of heat alone from a hot to a cold body, that is, simple conduction of heat, cannot produce useful mechanical work. Carnot did not say explicitly about the lost work in the *Reflexions*, albeit he must have noticed this effect. He advised the engineers to avoid the useless contact of the steam with the metallic parts of the engine, acquiring different temperatures than that of the condenser¹⁰⁶. He concluded, "The necessary condition of maximum [motive power] is therefore that in the bodies employed to realize the motive power of heat there is no change in the temperature which is not due to the change of volume".¹⁰⁷

No heat engine operating between a given temperature difference can have a greater motive power than "Carnot's engine".¹⁰⁸ In other words, *the maximum quantity of work can be produced when and only when a substance undergoes transformations in a Carnot cycle*. Any heat engine working differently than Carnot's reversible cycle would produce less motive power than Carnot's perfect engine. This statement is Carnot's fundamental theorem for heat engines' maximum obtainable motive power for a given amount of heat. The mathematical proof of *maximum efficiency*, *u*, for perfect engines was delivered in a

¹⁰⁶ Thurston, 1897, pp. 56-58 (*Reflexions*, 1824, pp. 22-24).

¹⁰⁷ Thurston, 1897, p. 57 (*Reflexions*, 1824, p. 23).

¹⁰⁸ However, Carnot realized that the inverse process could not apply to real heat engines, particularly the fourth step of the adiabatic compression from the lower to the higher temperature. The inverse process of vaporizing water by compression without the input of heat was physically unimaginable. Moreover, redistribution of heat from the condenser to the boiler for the preparation of the next cycle would cause a further loss of motive power. He attempted to solve this difficulty by considering an infinitesimal temperature difference between the warm and cold bodies. This theoretical contraption satisfied achieving the necessary adiabatic condition in the cycle (Thurston, pp. 59-60; Reflexions, pp. 26-27). Later, Carnot thought that he could extent his cycle to an engine working in temperatures differing by a finite amount by employing an infinite series of bodies whose temperatures exhibit a gradual fall from the initial to the final temperature (Thurston p. 60; Reflexions, p. 27). Nevertheless, this theoretical artifice proved unsatisfactory (Barnett, 1978, pp. 341-342). At any rate, this rather technical problem was left to skillful engineers after Carnot.

lengthy footnote in his *Reflexions* in terms of the so-called *Carnot's function* or *Carnot's coefficient*, F(t), namely u = F(t)dt.¹⁰⁹ Thus, Carnot proved that the efficiency of a perfect engine working reversibly was maximum, but he did not know the value of this efficiency.¹¹⁰ The knowledge of F(t) would allow the determination of the maximum efficiency of Carnot's engine.

The proof of this thesis led Carnot to confirm the law of perpetual motion for thermal processes.¹¹¹ However, the condition of maximum motive power and avoiding perpetual motion should apply to any heat engine that may use different working substances as carriers of the heat from the warm to the cold reservoir. Carnot showed that the use of permanent gases or air, or even the vapor of a volatile liquid, such as alcohol, produces the same motive power (at a given temperature difference) with an equal or lesser heat input than the vapor of water. He established the following general proposition, *the motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperatures of the bodies between, which is effected, finally, the transfer of the caloric.*¹¹² This passage is the *principle of Carnot*, which along with the fundamental theorem, was the most significant result of his analysis. To assess the validity

¹⁰⁹ Thurston, Note E, 1897, pp. 244-251 (*Reflexions*, 1824, pp. 73-79).

¹¹⁰ Emil Clapeyron emphasizes the importance of Carnot's function in his memoir published in 1834. However, he was unable to measure or calculate this function. Carnot's function was a basic constituent of William Thomson's definition of the absolute temperature scale in 1848. Nevertheless, the method chosen to calculate F(t) as a function of temperature was not convincing. Finally, F(t) was determined by Clausius in 1850. In 1851, William Thomson proved that the maximum efficiency was the same for all substances at the same temperature range, verifying thus the validity of Carnot's theory. No modification of F(t)expression is required upon replacing the material theory of heat adopted by Carnot with the dynamical theory of heat. For an account of the properties, the use, and the limitations of Carnot's function, see Potter, (1963). Current textbooks of physical chemistry express the efficiency of a heat engine in terms of the absolute temperatures of the cold (T_c) and hot (T_h) reservoirs (e = (1 - T_c/T_h)

¹¹¹ The proof of the impossibility of the perpetual motion appeared in two places in the *Reflexions*. The second was the most rigorous and achieved through his reversible cycle. Thurston, 1897, pp. 54-55, 66-67 (*Reflexions*, 1824, pp. 20-22, 56).

¹¹² Thurston, p. 68 (*Reflexions*, 1824, p. 38).

of his principle, he selected three different agents: atmospheric air, the vapor of water, and the vapor of alcohol and measured the motive power of the engine.¹¹³ For example, the value of 1 cal = 370 Kg that he obtained for the equivalent of heat and work was only five units higher than the value of 1 cal - 365 Kg calculated by Mayer between 1840 and 1842.

However, the process for obtaining the motive power in engines by utilizing different substances or using the same substance in two different states, for instance, a gas at two different densities, led Carnot to examine the properties of perfect gases.¹¹⁴ Since the amount of heat transferred by the air or the vapor is strictly dependent on their heat capacities or the specific heats, the study of the properties of the specific heats of gases was another subject of his investigations. Some of these properties were rediscovered after his death. Neglecting the two adiabatic processes (as being infinitesimal) in his cycle and using the laws of Robert Boyle (1627-1691) and Gay-Lussac,¹¹⁵ he stated the general theorem; *When the gas passes without change of temperature from one definite volume and pressure to another volume and another pressure equally definite, the quantity of caloric absorbed or relinquished is always the same, whatever may be the nature of the gas chosen as the subject of the experiment.¹¹⁶ Using the above theorem and the experimental results of Siméon Denis Poisson (1781-1840) and those by Nicolas Clement (1779-1841) and*

¹¹³Thurston, pp. 98-106 (*Reflexions*, 1824, pp. 80-88). The values of the motive power equivalent to heat calculated by Carnot are tabulated as a function of the nature of the heat carrier and temperature difference (Barnett, 1978, p. 355),

¹¹⁴ Thurston, 1897, pp. 68 (*Reflexions*, 1824, p. 20).

¹¹⁵ As deduced from the *Reflexions*, Carnot was well aware of the contemporary scientific literature regarding gas laws (Boyle, Mariott, Gay Lussac, Dalton, and Poisson). He was familiar with the experimental results of François-Étienne Delaroche (1781-1813) and Claude Berard (1813-1878) on specific heats of gases, and those of Clement and Desormes on compressed air, and various other experiments.

¹¹⁶ Thurston, 1897, p. 72 (*Reflexions*, 1824, p. 41-42).

Charles Bernard Desormes (1777-1862), he estimated the ratio of $(C_p / C_v)^{117}$ of the specific heats at constant pressure C_p and constant volume C_v . This ratio was found to be equal to a constant value for all perfect gases. He concluded, *the difference between specific heat under constant pressure and specific heat under constant volume is the same for all gases*.¹¹⁸ Through his cycle, Carnot confirmed the famous law of Pierre Louis Dulong (1785–1838) and Alexis Thérèse Petit (1791-1820) that the specific heats of gases were dependent on temperature. Carnot considered that the change of specific heats of gases with temperature within a broad temperature range could be significant for the variation of the motive power of heat.

Furthermore, he proved that the heat absorbed in an isothermal expansion was dependent on the logarithm of the ratio of the initial over the final volume. It is interesting to note that in his studies on the properties of gases, Carnot did not consider microscopic conceptions inherent in the dynamical theory of heat. He used the macroscopic measurable quantities of pressure, volume, and temperature.

In the last 30 pages of the *Reflexions*, Carnot turned his attention to practical problems akin to pure engineering. He assessed the benefits and limitations of the various kinds of heat engines (between the mono-cylinder, double-cylinder, or between low- and high-pressure engines). Carnot found the relationship between the temperature scale applied to the heat engines and the quantity of the motive power produced and estimated the exact motive power performed by an amount of heat during the operation of an ideal

¹¹⁷ This ratio proved to be very useful for the mathematical expression of an ideal gas undergoing a reversible adiabatic process, i.e. $PV^{\gamma} = constant$, where $\gamma = \frac{C_P}{C_V}$.

¹¹⁸ For perfect gases, $C_P - C_V = R$, where R is the universal gas constant, Thurston, 1897, p. 72 (*Reflexions*, 1824, p. 46).

engine. Furthermore, he evaluated the advantages and disadvantages of the heat carriers other than water steam. Finally, he estimated the motive power produced by a fixed amount of burnt coal and concluded that in addition to the economy, other factors (safety, durability, strength, dimensions) should be taken into account for the construction of a heat engine.

Some authors thought that Carnot's *Reflections* is correct if only one replaces the French terms *calorique* with entropy and *chaleur* with heat (energy). In this respect, the germane verbal and mathematical formalism of Carnot in the Reflexions could coincide with the first and the second law of the thermodynamics for a reversible process.¹¹⁹ The interest in unearthing an analogy between modern thermodynamics principles and Carnot's theory renewed in the 1970s.¹²⁰ These attempts to present Carnot as a "modern" scientist met the intense opposition of the historians of science Thomas Kuhn and F. O. Koenig. Both answered conductively to this "unsound historical hypothesis" (Kuhn's words).¹²¹ As Kuhn had pointed out, "attempts to present Carnot as a scientist hundred years after his time does not coincide with the historians' efforts to understand the development of the scientific concepts". Carnot found it unnecessary to distinguish *calorique* from chaleur, as noted in a footnote on page 15 of his *Reflections* of 1824. "Nous jugeons inutile d'expliquer ici ce que c'est que quantité de calorique ou quantité de chaleur (car nous employons indifférement les deux expressions), ni de décrire comment on mesure ces quantités par calorimeter".

¹¹⁹ La Mer, 1954. Wilhelm Ostwald was the first to remark the different meanings of the words calorique and chaleur in Carnot's *Reflexions*. He proposed replacing calorique with entropy. Ostwald was sympathetic to Carnot and translated the *Reflexions* into German, thus disseminating Carnot's ideas. ¹²⁰ Gillispie, Pisano, 2013, pp. 191-225; Lervig, 1972.

¹²¹ Kuhn, 1955; Koening, 1959, pp. 57–111.

1.2 The caloric theory versus the mechanical theory of heat

Although Carnot wrote the *Reflexions* in the context of the caloric theory, doubts about its validity must have troubled his mind about the materiality of heat. There are passages in the *Reflexions* that might reflect Carnot's reservations about the cogency of the caloric theory.¹²² After utilizing the principle of the impossibility of perpetual motion, he stated that, "perpetual motion would amount to unlimited creation of motive power without consumption either of caloric or any other agent whatever".¹²³ This statement implies that heat is consumed across the thermal cycle, during which work is produced. Thus, this statement suggests that the impossibility of perpetual motion is at odds with the principle of conservation of heat. Reconciliation of his ambivalent attitude towards the two theories of heat is the following passage, which is part of another footnote of the *Reflexions*; "To deny [the conservation of heat] it would be to overthrow the whole theory of heat to which it serves as a basis. For the rest, we may say in passing, the main principles on which the theory of heat rests require the most careful examination. Many experimental facts appear almost inexplicable in the present state of this theory".¹²⁴ A clear indication of the change that occurred in Carnot's conceptions evidenced in his posthumously published Notes sur les Mathématiques, la Physique et autre Sujets appended to the 1878 edition of the Reflexions edited by his brother Hippolyte Carnot (1801-1888).¹²⁵ Scrutiny of the notes, show that Carnot started to have doubts about the uniqueness of the caloric theory, "Lorsqu'une hypothèse ne suffit plus á l'explication des phenomènes, elle doit être

¹²² Klein, 1974, p. 24; Elkana, 1974, p. 90; Mendoza, 1961, pp. 32-36 describe the way by which Carnot accepted the caloric theory of heat.

¹²³ Thurston, 1897, p. 55 (Reflexions, 1824, p. 21).

¹²⁴ Ibid, pp. 67-68 (*Reflexions*, 1824, p. 37).

¹²⁵ Carnot, 1878, pp. 89-102.

abandonée. C'est le cas où se trouve l'hypothèse par laquelle on conisidère le calorique comme une matière, comme un fluide subtil. Les faits d'experience qui tendent a la detruire sont les suivant".¹²⁶

Carnot suggested five experimental facts that may constitute supportive evidence against the caloric theory. Carnot began to realize that all of his theorems and presentations in *Reflexions* might be wrong. His consideration about the indestructibility and convertibility of the motive power (energy) and his vague thoughts about the first law of thermodynamics evidenced his turn against the caloric theory. "Heat is simply motive power, or rather motion which has changed form. It is a movement among the particles of bodies. Wherever there is a destruction of motive power, there is, at the same time, production of heat in quantity exactly proportional to the quantity of motive power destroyed. Reciprocally, wherever there is a destruction of heat, there is a production of motive power",¹²⁷ and finally defined the mechanical equivalent of heat that had been calculated in *Reflexions* using the method of Clément–Desormes".¹²⁸

It is unknown when Carnot wrote the *Notes* (this holds as well for the *Reflexions* for which only the publication date is known). There are speculations that he wrote it while he was thinking and writing his book.¹²⁹ Unfortunately, the lack of any direct connection between the *Reflexions* and the *Notes* does not allow us to draw a safe conclusion on Carnot's twist from the caloric to the motion theory of heat, particularly regarding his

¹²⁶ "When a hypothesis no longer suffices to explain phenomena, it should be abandoned. This is the case with the hypothesis that regards caloric as matter, as a subtle fluid." (Carnot, 1878, p. 90). ¹²⁷ Thurston, 1897, p. 225. (*Reflexions*, 1878, p. 94.

¹²⁸ Ibid, p. 226 (*Reflexions*, 1878, p. 95).

¹²⁹ At about that time, Carnot had started to lose confidence in all that he had written. Mendoza has suggested that many of the notes were probably written at virtually the same time as the *Reflexions*, or at least by the time he came to correct the proofs (or to write the very final draft, if there was one). Mendoza, 1959, p. 389.

speculation on the energy conservation law. There was a long unconnected jump between the *Reflections* and the *Notes*. Nevertheless, Carnot's hesitation concerning the correctness of the caloric theory expressed in his *Reflexions* may well be understood as the normal reaction of the scientist willing to provide evidence in favor of his theory by performing experiments. We must not forget that experimental data needed for numerical computations of applications of Carnot's theorems and principles were inaccessible at the date of his writing. What seems to be more likely to affect Carnot's thinking in favor of the mechanical theory of heat was the influence of the new theory of heat that has begun to demand its place at the forefront of nineteenth-century science. It is unlikely that the experiments of Count Rumford and Davy on frictional heat and the speculations accompanying the radiant heat could have escaped from Carnot's attention, knowing his interest in being updated from the scientific literature of his time.

The following passages from the *Notes* sound less caloric-minded than those he quoted so far. It concerns heat produced by the expenditure of motive power by percussion or friction of bodies. "Thus heat is produced by motion. If it is matter, it must be admitted that the matter is created by motion".¹³⁰ Furthermore, after discussing the nature of heat from radiation, he posed the striking question: "Could a motion (that of radiating heat) produce matter (caloric)?" giving immediately the answer that rejects the caloric theory: "No, undoubtedly; it can only produce a motion. Heat is then the result of a motion. Then it is plain that the consumption of motive power could produce it, and that it could produce this power."¹³¹ Presumably, these were the key questions that played a significant role that

¹³⁰ Thurston, 1897, p. 220 (*Reflexions*, 1878, p. 91).

¹³¹ Ibid, p. 222 (*Reflexions*, 1878, p. 92).

made Carnot reflect that the real solution to the problem might exist within the realm of an alternative operational theory. Twenty years after the *Reflexions*, Joule provided sufficient experimental evidence that heat was not matter that transferred by the caloric from one place to another, but that is generated by mechanical forces (work). If so, there must be some kind of equivalence of heat and work. Despite the controversial arguments underlying Carnot's thoughts about the nature of heat (matter or motion) in the *Reflexions*, the heat engines did not require any specific theory for their operation. Carnot's cycle for perfect engines holds independently of any hypothesis of the nature of heat or mechanism by which heat transmitted or transformed into motive power.¹³²

Before concluding this section, it is legitimate to comment on Carnot's motivation and possible influences that inspired him to write his little book In almost all articles and books written for Sadi Carnot's work and life, there is an inference to the influence of Lazare Carnot (1753-1823), Sadi's father, on his son. Lazare Carnot was indeed a prominent figure of the French Revolution and during the Napoleonic era. A competent scientist and an excellent mechanical engineer. He wrote several books on rational mechanics. He studied the hydraulic machines aiming at establishing the best conditions for their operation at maximum efficiency. In his analysis, he implied the conservation of energy expressed as the conservation of *vis-viva* and used the mechanical work to measure the efficiency of the hydraulic machine, i.e., the product of the force imposed by the machine times the height from which water drops.¹³³ It is not difficult for someone to

¹³² Barnett claims that the subject of heat engines as treated by Carnot in the *Reflexions* is not clear; to a certain extent, Carnot's acceptance of the caloric hypothesis, invalidates his theory (Barnett, 1978, p. 337). However, as demonstrated by Clausius and Rankine, Carnot's reversible cycle could be expounded equally well by the adoption of the dynamical theory of heat.

¹³³ For the life and achievements of Lazare Carnot see Gillispie, 1971; Gillispie, 1981; Gillispie, and Pisano, 2013, pp. 1-132.

imagine that Sadi Carnot had extended some of his father's ideas on mechanics to thermal processes. Indeed, Sadi Carnot was aware of the mechanical principles governing the functioning of hydraulic machines and windmills, e.g., the production of mechanical work at maximum efficiency and the impossibility of perpetual motion as a necessary condition to avoid irreversibility processes, etc. However, Sadi Carnot recognized that the modeling of the mechanical work for the hydraulic machines was utterly different from that needed for the construction and function of heat engines. The hydraulic work is modeled on the ground of well-developed laws of Newtonian mechanics. Thermodynamics, on the other hand, deals with the transformation of heat into other forms of energy and *vice versa*, and how heat affects matter. The new theory of heat requires the extension and generalization of the laws of physics.¹³⁴ It is quite probable that Carnot was aware of his father's work on mechanical theories, although never cited his father in the *Reflexions*. Sadi Carnot followed a completely different path to construct the theory he presented in his book.

Influences and motives for Carnot appear to have come from two sources: The good knowledge Carnot had for the contemporary literature regarding the physics of gases and specifically the work of Alexis Petit and his personal friend and collaborator Nicolas Clement. Both are mentioned in the *Reflections*. Petit had estimated the motive power of the heat engine working with air and the vapor of water. In his analysis, Petit did not consider any reversible operation as Carnot did, but he employed the living force presumed to be necessary to overcome the engine's resistance.¹³⁵ Carnot obtained the value for the motive power of 1 kg of steam expressed as a function of temperature by employing

¹³⁴ Thurston, 1897, p. 44, 61 (*Reflexions*, 1824, pp. 8, 28-29)

¹³⁵ Thurston, 1897, footnote on p. 105. More, about the contribution of Petit to this subject and Carnot's comments on Petit's memoir, see Gillispie, and Pisano, 2013, pp. 93-96.

Clément's law for the pressure of saturated vapors.¹³⁶ The motivation that led Carnot to compose his memoir was in the first few pages of the *Reflections*. It was his interest in the heat engines; "The study of these engines is of the greatest interest, their importance is enormous, their use is continually increasing, and they seem destined to produce a great revolution in the civilized world".¹³⁷The construction and operation of heat engines were the subjects of professional engineers, technologists, and inventors. However, few engineers in the early nineteenth century had sufficient scientific knowledge to make heat engines more efficient through a theoretical analysis of their working conditions. Instead, they followed the so-called *systematic evolutionary improvement*. By keeping every component of the engine constant except for one, they varied it systematically until they obtained the best performance. They repeated this procedure for every other component. This procedure resulted in most of the time in poor performance since the successive modifications of the various engine components did not work synergistically.

Carnot's intention to propose solutions for the best performance of the heat engines based on a thorough theoretical analysis of the problems was the primary motivation that propelled him to compose his remarkable memoir. As noted above, he had the appropriate scientific background to meet this challenge. Apart from the purely scientific interest, Carnot considered this study critical for the economy and the industry of France facing the problem of a coal shortage and rendering; thus, the cost of coal per amount of heat produced a decisive factor for the French industry.

¹³⁶ Thurston, 1897, p. 105 (*Reflexions*, 1824, p. 86).

¹³⁷ Thurston, 1897, p. 38 (*Reflexions*, 1824, p. 2). See also, Barnett, 1978, p. 336.

1.3 The Reflexions in oblivion

Carnot's *Reflections* passed unnoticed by the scientific literature of the time. Although it contained novel and fresh ideas that would have been very useful for engineers and physicists, it passed to oblivion for almost ten years after its publication. It was revived by the French engineer Emile Clapeyron, another graduate of the École Polytechnique. Clapeyron published a memoir in which he presented Carnot's cycle in the form of an indicator diagram.¹³⁸ The famous Scottish engineer James Watt (1736-1839) invented this type of presenting engineering data, which rendered Carnot's cycle easy to comprehend and thereby very useful for contemporary engineers. In addition to the graphical explanation of Carnot's cycle, Clapeyron contributed to thermodynamics by treating Carnot's theory in a mathematical and analytical form and discovering the famous *Clapeyron's equation* derived from his studies on vapors.

Nevertheless, Clapeyron, like Carnot, was a calorist, thereby supporting Carnot's notion of the conservation of heat. Another fifteen years elapsed until William Thomson and Rudolf Clausius rediscovered Carnot's *Reflexions*. They did not read the original *Reflexions* but learned about it from Clapeyron's memoir. Nevertheless, the question remains. Why was Carnot's *Reflexions* forgotten so quickly? Why was Carnot's work, written by an engineer primarily for steam engineers, entirely neglected by them? The prevailing view amongst the historians of science is as follows:¹³⁹ For engineers, the *Reflexions* were of no practical use. It was a theoretical assessment for the operation of heat

¹³⁸ Clapeyron, 1834, p. 190.

¹³⁹ Gillispie and Pisano, 2013, pp. 142-143.

even though it was written in a straightforward language with simple calculations, lacking any intriguing mathematics.

On the other hand, physicists did not avoid their prejudice and considered the *Reflexions* an unworthy work written by an army engineer. From their point of view, the *Reflexions* were too practical and hence less valuable for theoretical physics in general. The attitude of the scientific community concerning Carnot's work did not differ substantially. In a meeting of the Academie des Sciences, Pierre Simon Girard (1765-1836), a distinguished mining engineer, presented a favorable review for *Reflexions*. However, not one of the prominent French scientists, such as Jean-Baptiste Joseph Fourier (1768-1830), Laplace, Ampère, Gay-Lussac, Dulong, and Adrien-Marie Legendre (1752-1833) paid attention to Carnot's ideas or referred to his work.¹⁴⁰ Amongst the engineers, only Jean-Victor Poncelet (1788-1867), another graduate of the Ecole Polytechnique, made a short notice for Carnot's treatise in a footnote in one of his early works.¹⁴¹ Even Clapeyron, who discovered Carnot, did not refer to him, but very briefly in his scientific biography of 1847 prepared to support his candidacy for election to the French Academy of science.¹⁴²

As we shall see below, the next generation of physicists, who founded the first law of thermodynamics, did not mention Carnot, except perhaps Joule in one of his articles in 1844. However, Joule did not conceive the gist of Carnot's theorems, and even though proved experimentally the equivalence of heat and work he missed the chance to approach the idea of the second law of thermodynamics. Nevertheless, Joule was not the sole

¹⁴⁰ Klein, 1974, p. 25; Barnett, 1978, p. 25.

¹⁴¹ Kerker, 1960, pp. 264-265.

¹⁴² Ibid, p. 264.

philosopher who paid little attention to Carnot's *Reflections*. All the great thinkers who articulated the first law of thermodynamics and calculated the mechanical equivalence of heat kept the same attitude. They spoke exclusively of the equivalence of forces and the interconversion of forces into different forms. The mechanistic model that all changes in nature were a manifestation of a conserved entity, the force, prevailed among philosophers of the first half of the nineteenth century. Therefore, the Second Law, unlike the first law, appeared foreign and unnatural to them.

Section 2. The first law of thermodynamics: A comparative study

The law of conservation of energy (hereafter conservation law) is an intellectual product of the first half of the nineteenth century. It is one of the most fundamental laws of nature. The law was discovered practically in the 1840s, not by a single scientist but by a dozen engineers and natural philosophers. The scientists involved in the formulation of the conservation law had different motivations and influences and different lines of thinking. The first serious attempt to investigate the complex and confusing scientific process leading to the conservation law was effected by Thomas Kuhn in his classical paper *Energy conservation as an example of simultaneous discoveries* published in 1977.¹⁴³ Upon examining primary sources alone, Kuhn concluded that in a relatively short period of 20 years (1830-1850), twelve European engineers and natural philosophers arrived at the same time in the pronunciation of the conservation law. This coincidence belongs to the so-called multiple and simultaneous discoveries. According to Kuhn, three external factors were the criteria for the selection of the twelve natural philosophers and engineers. These factors

¹⁴³ Kuhn, 1977, pp. 66-104.

depended on the specificity of the period, the frequency of occurrence, and the impact of these factors on the private research of each discoverer. These influential factors suggested by Kuhn were,¹⁴⁴ first, energy conversion processes in laboratories or other private spaces,¹⁴⁵ second the philosophy of nature, the *Naturphilosophie*, that flourished during the first third of the nineteenth century, especially in Germany,¹⁴⁶ and third the interest in heat engines that contributed resolutely to the mechanization of production and transportation during the first and the second industrial revolution in England (1760-1830) and in the European Mainland (1830-1914), respectively.

Moreover, Kuhn concluded that these three factors did not affect to the same degree the twelve scientists. Kuhn divided the twelve scientists into three groups according to their contribution to the conservation law. The first group of four scientists computed the mechanical equivalent of heat, but they did not make any general statement for the conservation law.¹⁴⁷ The second group of four co-discoverers enunciated such a general statement but did not make any numerical calculation of the equivalence between work and heat. And the third group is considered the primary discoverers because they articulated the conservation law and provided evidence for its quantitative applications and, therefore,

¹⁴⁴ Disagreements have been raised for some of these factors. Also, methodological differences were expressed to some points of Kuhn's analysis. Most of them are of minor importance, see for instance, Kipnis, 2014; Elkana, 1970.

¹⁴⁵ Private laboratories existed during the first half of the nineteenthcentury. Joule carried out his pioneering experiments in his private laboratories installed in the family brewery.

¹⁴⁶ Natural philosophy suggested the unity of all forces in nature. It was a product of German idealism and related to the philosophical work of Fichte, Hegel, and especially of Schelling.

¹⁴⁷ Between 1842 and 1878, several natural philosophers and engineers calculated the mechanical equivalent of heat (Kipnis, 2014, p. 2028, Table 3). It is interesting to note that the tabulated results in this reference ranged considerably depending on the experimental method used, the experimental errors, and the approximation involved in the calculations. The uncertainty in the experimental results in the early years of thermodynamics rendered unclear whether the mechanical equivalent of heat had a constant value. The constancy of this conversion factor was proved later by the detailed experiment performed by Joule.

acquired the largest share in its recognition by the scientific community.¹⁴⁸ The latter group belonged to the two Germans Robert Mayer, Hermann Helmholtz, the Englishman James Joule, and the Danish Ludwig August Colding (1815-1888). P. M. Heimann objected to Kuhn's argument to portray Helmholtz as a typical discoverer of the conservation law.¹⁴⁹ Hermann asserted that the grouping of Helmholtz, according to certain general features, implied the risk of distorting Helmholtz's conceptual approach to the conservation law, which was not parallel to those of the other three scientists of this group. Kuhn claims that Helmholtz's force was an expression of energy. Hermann argues that in formulating his essay, Über die Erhaltung der Kraft (on the conservation of force), Helmholtz does not express the conservation law because forces in nature do not have constant intensity. Helmholtz adopted, late in 1856, the expression conservation of energy suggested in 1853 by William Rankine.¹⁵⁰ Helmholtz thought that energy embodies the overall result or the power of the various processes occurring in nature. Heimann's argument prompts further investigation. I decided to perform a comparative study of the work of the four scientists. This comparison perhaps would offer the opportunity to go deeper and disclose the range of incentives, influences, methodological approaches, and research styles characterizing each philosopher in his endeavor to achieve his goal.

Among the four scientists, Mayer and Colding arrived at discovering the conservation law before determining the mechanical equivalent of heat. Their interest in

¹⁴⁸ Several historians expressed similar opinions for this third group (Kipnis, 2014, p. 2009; Schirra, 1991, pp. 155-157). Schirra refuses any credit at all to the other eight contributors. Opposite views expressed by others: Elkana, 1970. Brush, 1970, p. 161.

¹⁴⁹ Heimann, 1974a, p. 205-206.

¹⁵⁰ Rankine distinguished two forms of energy. The actual energy (kinetic energy) and potential energy. He formulated the conservation law as follows: "The law of the conservation of energy is already known, viz. that the sum of the actual and potential energies in the universe is unchangeable". (Rankine, 1853, p. 106)

this subject derived, at least initially, from metaphysical and religious beliefs regarding the indestructibility of forces of nature. In 1842, Mayer made the following statement "Heat is a force; it may be transformed into mechanical effect," and about a steam engine, "the work done by the machine is inseparably bound to a consumption of heat". However, these statements do not express a general formulation of the conservation law.¹⁵¹ Joule followed the opposite course; via a series of experiments of increasing accuracy, he determined the amount of heat generated in solid and liquid conductors by electric currents or during chemical processes occurring in galvanic cells, wherefrom gradually came to the idea of the conservation law. Helmholtz never measured or calculated the mechanical equivalent of heat. However, he joined Joule and Mayer in recognizing that the mechanical equivalent of heat held the key to demonstrating the conservation of force.¹⁵²

Helmholtz performed very few experiments and those in the field of physiology. His experimental work on the origin of putrefaction and fermentation and muscle contraction was performed after the publication of *die Erhaltung der Kraft*. In *Erhaltung der Kraft*, Helmholtz succeeded at unifying existing empirical laws derived from hitherto experiments and observations into a theoretical framework associated with the conservation of force and *vis viva*. He applied it to interpret the interconversion of natural forces. Nevertheless, Helmholtz's interest in the theoretical approach to the conservation of forces must be seen in his research on animal heat and muscle contraction problems, which made him, think about the possibility of formulating such a theory of the conservation of forces. Contrary to Helmholtz, Mayer, and Joule lagged in mathematical

¹⁵¹ Truesdell, 1980, p. 155.

¹⁵² Helmholtz in his Bericht of 1845 (vide infra) had noticed Carnot and Clapeyron's calculations of the work produced by a certain quantity of heat, which was virtually the mechanical equivalent of heat.

skill, they never attempted to offer serious mathematical formulation to their speculations and experiments. Any attempt made by Joule, primarily to provide some theoretical explanations for his experimental results, was a loan from other philosophers. On the other hand, Colding showed the necessary mathematical skills that evolved from his training as an engineer and were involved in fluid dynamics, hydrology, and other engineering material during his regular activities.

Another feature of the work of these four scientists has to do with the term force and its interpretation by each philosopher. . Mayer, Colding, and Helmholtz repeatedly refer to the concept of force, albeit with a different interpretation; Mayer and Colding approached force from a metaphysical and theological point of view, whereas Helmholtz used Newtonian forces of attraction and repulsion in his conservation principle. Joule did not introduce any philosophical perspective in his experiments. Whenever he used the term force, he meant natural forces, such as mechanical, chemical and electrical, or electromagnetic forces, and not its metaphysical conception. However, he left the indestructibility of forces at the disposal of the Creator. "The grand agents of nature as expressed by the various kind of forces are, by the Creator's fiat, indestructible; and that wherever mechanical force is expended, an exact equivalent of heat is always obtained".¹⁵³ He used different terminologies, such as work, duty, or other words coming from the engineering language. Nevertheless, all four scientists had a common feature: they were outsiders. None of them was trained formally as a physicist. Mayer and Helmholtz trained as medical doctors. Joule was an amateur scientist never formally educated. Colding was

¹⁵³ Joule expressed this belief in several of his articles collected in the *Scientific papers of James Prescott Joule,* henceforth abbreviated as JSP (1884, pp. 58, 158, 189, 269, 273).

heavily occupied with technical, administrative duties, and other official responsibilities as an engineer.

2.1 Julius Robert Mayer

The historiography has not yet illuminated all aspects concerning the external factors that influenced Mayer's work towards the conservation law. Kuhn asserted that *Naturphilosophie* was a significant cause that affected Mayer's thinking, but he did not explain how and to what extent this factor had preoccupied Mayer's thoughts. There are accounts that Mayer's journey to India was the beginning of inspiration that led him to formulate the conservation law.¹⁵⁴ However, they cannot detect a reasonable route from observing the color of venous blood to the conservation law¹⁵⁵. Other accounts suggest that Mayer's interest in the conservation law stimulated by the ship's sailors' talks about the storms that were heating the seawater.

In contrast, other reports claim that Mayer reached the conservation law in proportion to the law of conservation of matter to justify the connection of force as the

¹⁵⁴ While letting the blood of European sailors who had recently arrived in Java in July 1840, Mayer was astonished by the unusual redness of their venous blood and the fast coagulation of fibrin, which were characteristics of the arterial blood. He attributed this redness to the tropical climate (high temperature and humidity). As a physiologist did pay attention to these factors, but how far these observations alone led him to pursue the conservation law is hard to say. However, in his first two papers in 1841 and 1842, Mayer did not mention this physiological observation.

¹⁵⁵ Mayer, in a letter to his friend the physician Wilhelm Griesinger (1817-1868) on 14 June 1844, admitted that his theory was not concocted at the writing table but arose from observations of the "changed physical condition" in the tropics, and to his reflections on "the conditions of the blood [which] directed my thoughts primarily to the production of animal heat by the respiratory process (Quoted in Heinemann, 1976, p. 280). However, this statement does not prove whatsoever that the Java trip was the cause to formulate his version of the energy conservation. Mayer said nothing of how he moved from physiology to the idea of the conservation of force (Kremer, 1984, pp. 219-220). Teresa Rocha-Homem gives a medical explanation whether Mayer really saw a red venous blood color. She explains that in the tropics, there is generally less food consumption and therefore lower glucose metabolism during the Krebs cycle; there is a smaller difference in temperature between the organism and the environment. These are all venous hyperoxemia conditions and they can theoretically corroborate Mayer's observation. They do not corroborate, however, Mayer's explanation (Rocha-Homem, 2015).

cause and force as the effect. This analogy is accompanied by a paradigm from chemistry related to water formation from oxygen and hydrogen. The cause is the combination of these two elements, and the effect is water. It appears that all these factors may have a role in Mayer's formulation of the conservation law, though it is not clear how these factors converged to affect its discovery efficiently.

It appears that Mayer made his first thoughts about conservation law through philosophical and conceptual considerations away from physics. However, this inclination is not the sole influence on Mayer's thinking. He turned into physics only when he realized that he could find in it a more straightforward process to express the conversion of forces, the transformation of heat into force, and subsequently to calculate the mechanical equivalent of heat. Another route that led him toward conservation law was physiology. As a medical doctor,¹⁵⁶ Mayer's interest in physiological problems and, in particular, in the role of the *vital force* as a factor governing life processes picked his thinking in the direction of forces and heat. In the last chapter of this part, I will return to this point when discussing the connection of animal heat with the conservation law.

Chemistry was an indispensable part of the discovery of the conservation of forces. Mayer had extensively studied chemistry at Tübingen and had received the highest marks. Therefore, he was familiar with the law of the conservation of matter. Mayer defined chemistry as the science of matter and physics as the science of forces and just as matter is conserved, so too are forced. "Chemistry, whose problem is to outline in equations the causal connection existing between the different kinds of matter, teaches us that matter, as a cause has matter for its effect; but we are equally justified in saying that to force as a

¹⁵⁶ For Mayer's biographies, see Turner, 1981, pp. 235-240.; Caneva, 1993, pp. 3-17.
cause, corresponds force as effect".¹⁵⁷ He used an example from the chemistry when he argued about the relationship between cause and effect. "[...] we prefer the assumption that heat proceeds from motion, to the assumption of a cause without effect and of an effect without a cause,--just as the chemist, instead of allowing oxygen and hydrogen to disappear without further investigation, and water to be produced in some inexplicable manner, establishes a connection between oxygen and hydrogen on the one hand and water on the other".¹⁵⁸

Mayer's ideas about forces were summarized in his very first article *Bemerkungen über die Kräfte der unbelebten Natur* published in 1842 in Justus von Liebig's (1803-1893) journal *Annalen der Chimie und Pharmacie*. Although the magazine was well known, Mayer's work went unnoticed. His next three articles published from 1845 until 1848 were equally indifferent to the scientific community. The intricate style of the paper with many hypotheses, metaphysical terms, and the absence of any experiment were some of the reasons for the poor reception of Mayer's first appearance in the scientific literature. Nevertheless, this first paper contained Mayer's basic philosophy about the nature of force and its transformations, and in addition, the calculation of the mechanical equivalent of heat¹⁵⁹. He noted that in contrast to matter that implied specific properties, including conservation quality, the term force conveyed something unknown, unreachable, and hypothetical. Mayer defined force fully applying the metaphysical principle *causa aequat*

¹⁵⁷ Mayer, 1842, p. 234-235.

¹⁵⁸ Mayer, 1842, p. 235.

¹⁵⁹ Mayer expressed his thoughts several times privately through his correspondence with his friends. One of them, Wilhelm Griesinger (1817-1868), with liberal ideas, urged Mayer to abandon *Naturphilosophie* and use physics as a weapon against vitalism and as a positive knowledge to introduce purely physical views of the living phenomena (Kremer, 1984, pp. 225-.226).

effectum (cause corresponds to the effect).¹⁶⁰ He integrated this principle in his reasoning as follows: Forces are causes, which are mutable phenomena and must appear in effect and remain preserved in it until the effect again becomes a cause that, in turn, generates another effect. This process must guarantee that the cause is lost during the transformation into the effect. In other words, cause and effect are both forces, and their totality is preserved.

Furthermore, Mayer defined causes (forces) as imponderable, indestructible, convertible entities. They must conserve in proportion with the matter. They differ from matter only because they are imponderable.¹⁶¹ The example corroborating the conservation of force was taken from physics and concerned with the transformation of motion or falling force¹⁶² (here motion and force coincide) into heat as observed during the processes of friction and percussion. Here motion is the mechanical work (the cause) that transformed into heat (the effect).¹⁶³ Falling force, motion, and heat were different manifestations of one indestructible force, and therefore they must maintain a definitive quantitative relationship among themselves. The calculation of the amount of heat, which corresponded to a given quantity of motion or falling force, that is, the calculation of the mechanical equivalence of heat, was the final step. He stated that this value is 365-kilogram meters per kilocalorie. The force required to raise a mass of one kilogram to a height of 365 meters is equal to the heat needed to raise the temperature of one kilogram of water one degree Celsius. Mayer gave details of the calculations in his second article. A memoir of 112

¹⁶⁰ René Descartes used the sentence *causa aequat effectum* for a proof of God. Leibniz used the same phrase as a metaphysical law in his theory of motion, which demanded not only the proportionality, but equality of cause and effect. For further discussion on the meaning and features of this phrase in science, see Bunge, 2009, pp. 203-216.

¹⁶¹ Mayer, 1962, p. 372.

¹⁶² Mayer did not consider gravity as a force but rather as a characteristic of matter. He thought that if gravity were a force, it would constantly produce an effect without itself consumed, violating the principle of the conservation of force.

¹⁶³ Mayer, 1862, pp. 374-375.

pages, entitled *Die organische Bevengung in irhem Zusammenhange mit Stoffwenchsel ein Beitrag sur Naturkunde (The organic movement in its connection with the metabolism contributes to natural history*),¹⁶⁴ which was his most original and comprehensive article. It was published in private since Liebig refused publication in his *Annalen der Chimie und Pharmacie* because the paper did not correspond to the journal's scope. He considers the paper as an account of bridging physics and mathematics to physiology. Furthermore, it did not contain experimental data. In this article, Mayer sets out the physical basis of his theoretical considerations extending the idea of conservation to magnetic, electric, and chemical forces. Moreover, he continued giving further quantitative estimates regarding other aspects of the heat transformation into mechanical power, such as heat engines, locomotives, and paper mills.

In the second half of this memoir, Mayer explored the physiological aspects of the conservation law in the plant and the animal kingdom. He sought to unravel the qualitative and quantitative relationship between the chemical and mechanical forces in animals mediated by the necessary heat produced upon the combustion of food. He focused his investigations on the plants and vegetable life, particularly on whether the force of light is the cause of the production of the chemical tension. In plants, the production of mechanical effects plays a lesser role, and therefore only the conversion of matter and force are of interest. In conclusion, he sought to establish the conservation of force in the context of physiology and to refute views held by some organic chemists, such as the claim of the existence of *vital force*. Mayer's denied explicitly any role of the *vital force* in life

¹⁶⁴ Mayer, 1845; Weyrauch 1893a, pp. 45-138. This article was translated into French in 1871. There is no complete translation in English. John Tyndall provided partial translation for the first half of this article (Tyndall, 1864)..

processes while discussing the origin of the animal heat and attacking Liebig's use of the *vital force* to explain muscle action. I shall examine these two subjects in the last chapter of this part in conjunction with exploring the contribution of chemistry to the formulation of the first law of thermodynamics.

Mayer did not perform any experiment himself, probably because he did not have the means. His calculations, including that for the mechanical equivalent of heat, relied on experimental data taken from the literature. In particular, for the mechanical equivalent of heat, he used the experimental data of de la Roche and Berard for the specific heat of the air and the value of Dulong's ratio of the respective heats under constant volume and constant pressure. Although these data were of low accuracy, Mayer was the first who calculated an adequate number for the mechanical equivalent of heat in the context of the conservation of force.

2.2 Ludwig August Colding

Ludvig Colding is the least known of the four scientists who discovered the conservation law¹⁶⁵. His first article *Nogle Sztninger om Krzfterne (Theses about forces*), read in the Danish Society of Sciences in 1843, was published only in 1856 and in the Danish language, not understood beyond the Scandinavian countries.¹⁶⁶ The same fate had his following three articles published in Danish. Finally, he decided to publish abroad his last paper in English.¹⁶⁷ Colding considered this publication important "to be understood [his work] and placed in that position in relation to this discovery to which I have a claim"¹⁶⁸.

¹⁶⁵ For Colding's biography, see Dahl, Per, 1972; Caneva, 1997a. Dahl, Per, 1981, 84-87.

¹⁶⁶ Colding, 1856. For the reasons of this huge delay see, Dahl Per, 1963, p. 181.

¹⁶⁷ Colding, 1864.

¹⁶⁸ Ibid, p. 57.

This memoir is of value since it is a summary of his various contributions to this subject. Although Colding had been recognized as one of the founders of the first law of thermodynamics, his delayed appearance in European science did not allow him to stand at the same scientific level as the other three co-discoverers. This distance from the periphery to the center did not prevent him later from claiming his share in the discovery of the conservation law.¹⁶⁹

The motivation of Colding to pursue the conservation law reflected various influences. According to Colding himself, his acquaintance with the principle of active and lost forces of Jean Le Rond d' Alembert (1717-1783) was the starting point¹⁷⁰ for his speculations about the *imperishable forces*. However, the imperishability of forces may not be the direct product of his reading of D' Alembert's *Traité de Dynamique*. It may have been the outcome of his prior religious and metaphysical beliefs about the nature of forces.¹⁷¹ "As the forces of nature are something spiritual and immaterial entities of which we are cognizant only by their mastery over nature, these, entities must, of course, be very superior, to everything material in the world; and as it is obvious that it is through them only that the wisdom we perceive and admire in nature expresses itself, these powers must be in relationship to the spiritual, immaterial, and intellectual power itself that guides nature in its progress; but if such is the case, it is consequently quite impossible to conceive of

¹⁶⁹ Colding was involved in a priority dispute with Mayer to establish himself as an independent discoverer. For more information, see Kragh, 2009. pp. 11-18.

¹⁷⁰ Colding, 1864, p. 58.

¹⁷¹ Kragh claims that the religious sentiment in the new conception of energy was particularly keen to Colding but it can also be found in other scientists at the time. Kragh mentioned Mayer, Joule, and William Grove (2009, pp. 5-6.).

these forces as anything naturally mortal or perishable. Surely, therefore, the forces ought to be regarded as absolutely imperishable".¹⁷²

Kuhn classified Colding under the influence of *Naturphilosophie* and the doctrine *vis viva* never perishes. Kuhn reached this conclusion because Colding was a protégé¹⁷³ of Hans Ørsted. The latter is recognized as a passionate Kantian and a Naturphilosophe. and secondly because of his acquaintance with D' Alembert's sense of force.¹⁷⁴ Whatever was the origin of the influence on Colding, the enunciation of the conservation law embodies the crux of his philosophical and religious convictions for the natural forces: "As no power is lost in nature, so no power can grow up in nature except at the expense of some other power".¹⁷⁵ Colding strove to explain the origin of material life as the result of the generation of *vis viva* which is equal to the work done by the force of gravity in accord with this principle. In contrast, the emergence of intellectual life, independent of matter, commenced with God's creation of human beings.

Colding was an engineer who graduated from the Copenhagen Polytechnic, and he had a succession of technical, administrative, and academic positions in his country. In addition to the burden of his official responsibilities, Colding found time to pursue an impressive range of scientific research.¹⁷⁶ Following the advice of his mentor Ørsted, in parallel with his religious and metaphysical predispositions, he carried out the proper

¹⁷² Colding, 1864, pp. 57-58

¹⁷³ Dahl Per, 1963, pp. 175-177.

¹⁷⁴ D' Alembert in his Traité de Dynamique ascribed three meanings of force: (I) [dead force], where a body tends to move itself with a certain velocity, but the tendency is arrested by some obstacle; (2) [quantity of motion], in which the body moves uniformly with this certain velocity; and (3) [living force], where the body moves with a velocity which is consumed and annihilated little by little by some cause.

¹⁷⁵ Colding, 1864, p. 61.

¹⁷⁶ Dahl, Per, 1981, p. 81.

experimental verification of his theories. Kenneth Caneva argues¹⁷⁷ that it is disputable whether Colding's experimental work is firmly connected to his philosophical context in general or to D' Alembert principle of lost forces in particular. I think Colding himself answers this question. "In my first treatise of 1843, the title of which is "Theses concerning Force". I presented my idea to the Royal Society (of Copenhagen) that most likely would hereafter be found to be a general law of nature but, after stating that the only trustworthy decision of the question was to be got from the experimental investigation of nature; itself."¹⁷⁸

Colding conducted experiments in 1843 on the heat produced by the friction of solid bodies. Although these experiments justified his preconceived conviction that the heat evolved from the friction was strictly proportional to the work expended, he did not calculate at that time the mechanical equivalent of heat. Later in the 1847 meeting of the Scandinavian Association in Copenhagen, he presented experiments that were more accurate. The description of the apparatus and the results of this study were published in 1850 in a local journal.¹⁷⁹ However, this study remained unknown to most foreign scientists.

Colding showed his mathematical skill in his second article on conservation law, translated by Peter Tait (1831-1901) and published in the *Philosophical Magazine* in 1871.¹⁸⁰ In this article, Colding obtained general mathematical expression for the total internal energy (*vis-viva*) contained in the particles constituting the body and the relation between the heat q produced by the friction and the mechanical work expressed in terms

¹⁷⁷ Caneva, 1997b, p. 70.

¹⁷⁸ Colding, 1864, p. 58

¹⁷⁹ Colding, 1850.

¹⁸⁰ Colding, 1871.

of the resistance *P* during friction and space *s* passed through, i.e., q = Ps, following his previous experiments. He further examined the variation of the internal energy of fluids (gases and liquids) upon compression, producing heat. The expressions derived from the mathematical treatment of his findings, in combination with Dulong's formula for specific heats of gases, allowed him to conclude that the specific heats of fluids are practically constant within a small range of temperatures. Finally, he calculated the mechanical equivalent of heat using the exact expression of the specific heats under the constant volume and pressure of one atmosphere. He found it 1204 foot-pound per degree Celsius. This value is to be compared with the average value of 1185 units of work obtained from the experiments on friction.

2.3 James Prescott Joule

The work of Mayer lacks experimental quantification of the conservation law and that of Colding was based on meager experimental results. On the contrary, Joule determined the equivalence between heat and force through a series of demanding experiments. Mayer and Colding were mainly theoreticians. Joule was a capable experimenter, and therefore, he did not trouble himself with metaphysical questions regarding the concept of force. He focused on constructing sophisticated devices to minimize systematic errors and performing accurate experiments to disclose the laws governing heat on metallic conductors or electrical circuits owing to the circulation of electric current. These rigorous experiments and observations were the main argument of Joule and his supporters on the priority dispute with Mayer. Mayer was the first who enunciated the law of the conservation of energy in 1842 and calculated the mechanical equivalent of heat. However, Joule as Mayer lacked

relevant mathematical skills, and thus he was unable to formulate a rigorous theory for his experimental findings. Helmholtz later formulated the relevant theory. Nevertheless, Mayer and Joule shared the common view concerning the indestructibility of force This conviction was strengthened by the religious belief that only the Great Creator has the power to destroy forces, the grand agents of nature.

Joule's interest in electricity originated from his studies of the works of William Sturgeon (1783-1850),¹⁸¹ Faraday, and Berzelius. Sturgeon introduced Joule into electromagnets, Faraday motivated Joule's research program of heat and electricity,¹⁸² whereas Berzelius provided Joule with ideas about the electrical nature of the chemical affinity. Joule received further assistance from Daniell and Grove's ideas on the interconversion of chemical forces into electricity and found practical aid from their batteries of constant current intensity.

Joule trained as a chemist taking private lessons in chemistry and mathematics by Dalton and the private teacher of mathematics and chemistry John Davies (1816-1850). Dalton was another influential person for Joule's methodological approach in designing his experiments. Joule owes to Dalton the belief that simple laws govern natural phenomena. His carefully designed experiments interpreted simple laws expressed with simple linear or at most quadratic mathematical relationships. Furthermore, Dalton infiltrated to Joule his atomistic convictions that affected Joule's theoretical models when he strove to explain the electrical nature of chemical affinity.

¹⁸¹ William Sturgeon was a typical amateur scientist whose significant achievement concerned the construction of electromagnets and other apparatuses for displaying electromagnetic phenomena. He lectured on science and electromagnetism to schools and other groups (Finn, 1981, p. 126).

¹⁸² Joule followed the same research program as Faraday. He also adopted Faraday's methods and presentation style and the audience he addressed (Forester, 1975, p. 277).

Joule's research work can be divided into three periods, although it is somewhat difficult to sort out the order in which Joule did his work and developed his ideas. His habit of adding second thoughts to papers on entirely different subjects makes it somewhat difficult for the historian to unravel the origin of Joule's thinking. Nevertheless, the first period runs from 1838 to 1840. The young Joule undertook a series of experiments concerned with electromagnets and testing the efficiency of electromagnetic devices (electric motors). In the second period, from 1841 to 1843, Joule studied the thermal effects of voltaic electricity and electrolysis. In the last period, starting in 1844 and lasting until 1849, Joule endeavored to determine the mechanical equivalent of heat.

During the decade of the 1830s, nearly the end of the first industrial revolution in England, attention focused on the production of electricity by mechanical means. And then its exploitation to manufacture and transportation. After the discovery by Ørsted in 1820¹⁸³ that the electric current produces magnetism and the reverse process, i.e., the generation of electric current by moving a magnetic bar through a metallic spiral by Faraday eleven years later, electricity and magnetism began to attract the industrial interest. These two interrelated dynamic phenomena seemed to find practical applications by constructing electromagnetic engines, or electric motors in which electric currents produce magnetic fields (magnetic energy), and the design of magneto-electric machines (the precursors of the dynamo) generate electricity from magnetism. In short, the former devices use electricity, while the latter produces electricity. The main constituent of the electric motor

¹⁸³ Ørsted observed that a compass needle was deflected from magnetic north by a nearby electric current, confirming a direct relationship between electricity and magnetism (Ørsted, 1820). This phenomenon was not incidentally discovered during Ørsted's lecture as often reported. Ørsted had investigated the connection between electricity and magnetism since 1818, but he was slow to publish because he was quite confused by the results he was obtaining (For more about this discovery, see Martins, 2003).

was the electromagnet invented by Sturgeon, who had already published details of its properties in 1925. In 1836, Sturgeon established the first international scientific journal on electricity the *Annals of Electricity*, which accepted articles from both scientific and practical interests. Joule submitted his first articles to this journal. The establishment of the London Electrical Society was another visible sign of the advent of the new electrical power.

Beginning the decade of 1830, the idea of replacing steam with electricity in the industry and why, not in transportation was slowly maturing. The first electric motors pioneered in the same period were designed as efficient machines. In 1935, the rotative electrical motor was proposed as an alternative mechanical device to replace heat engines.¹⁸⁴ The law cost of electrical motors and their simple operation without the necessary piston rods, boilers, condensers, cranks, etc., of the heat engines, corroborated the belief that electricity might successfully apply to the working of the machinery of any kind.¹⁸⁵ Joule described these expectations in one of his papers entitled *On a new class of magnetic forces* published in 1844. "At that period, the expectations that electro-magnetism would ultimately supersede steam, as a motive force, were very sanguine. There seemed to be nothing to prevent an enormous velocity of rotation, and consequently an enormous power, except the resistance of the air, which it was easy to remove, the resistance of iron to the induction of magnetism, which I had succeeded in overcoming to a great extent by

¹⁸⁴ Cardwell, 1976, pp. 675-676.

¹⁸⁵ These plans were delayed to put into practice. The transfer of knowledge from the laboratory's smallscale research to the plant's large-scale production involved many practical problems. The technology of the time was unable to deal with these problems. The competition from heat engines, the indifference of engineers to tackle these problems, and the absence of scientific studies to make the electric current a cheap alternative to steam engines prohibited the applications of electricity for more than fifty years after Faraday's discovery. Exceptions were Joule in Manchester, Moritz Hermann von Jacobi (1801-1874) in St. Petersburg, and Thomas Davenport (1802-1851) in the United States.

annealing the iron bars very well, and the inertia of the electric fluid".¹⁸⁶ In short, this was the enthusiasm for electricity that young Joule felt during the first half of the nineteenth century in Manchester. This city was one of the most important industrial centers in England.

Joule's documents cover his creative work from 1838 to 1850, from his first experiments on electric motors to the enunciation of the principle of the conservation of energy and the consolidation of the mechanical equivalent of heat as a constant quantity. In this context, it is worthwhile to discuss a few of Joule's interesting experiments published in the literature.¹⁸⁷

Joule's first applications of electricity had a practical purpose. He scheduled his first research efforts to ease the working conditions in the family brewery. He pursued constructing an electromagnetic machine to convey goods from place to place in the brewery. In the same space, Joule established his first laboratory to perform experiments. He studied the working conditions of electromagnets and electromagnetic machines and proposed pertinent modifications aimed at higher efficiency. Despite his initial optimism that electromagnets could replace steam engines in small-scale operations, both the efficiency and the cost of running such electromagnetic apparatuses were inferior to machines working with steam.

¹⁸⁶ JSP, 1884, p. 47. On the same page, Joule mentioned the Prussian'Russian physicists Moritz Hermann von Jacobi (1801-1874), who had showed the existing obstacles against the increasing velocity of the rotation of the electromagnet.

¹⁸⁷ See, for instance, Reynolds, 1892; Fox, 1969, pp. 72-103; Forrester, 1975; Cropper, 1988; Forrester provides an analysis of the work of Joule in the context of electrochemistry. Fox discusses the various stages of Joule's research in the context of physics. Cropper gives a modern interpretation of an electrochemistry paper of Joule published in 1852. Reynolds offers a full biography of Joule in the various stages of his life, a detailed account on his research work, and his struggle for recognition.

Nevertheless, Joule's three-year work in this field did not seem to have been in vain. He found that the passage of the electric current through a metallic rod resulted in the development of heat, a phenomenon known to most physicists at the time. In a series of accurate experiments, he confirmed the proportionality between the amounts of heat produced in the metallic conductor and the intensity of the electrical current. The proportionality factor was the resistance of the conductor. The latter was the cause of heat creation. He then discovered that the same law between heat and electricity applies to batteries and whole electric circuits.

During these experiments, Joule observed chemical changes in the compartments close to the electrodes of the electrolytic cell. The production of hydrogen and oxygen gases on the negative and positive electrodes respectively caused the deterioration of the cell operation and limited its lifetime. Joule performed several demanding experiments under different conditions trying to eliminate or reduce this phenomenon, namely the polarization of the electrodes. The study of the electrode polarization ensued two significant achievements—first, the electrical explanation of the chemical affinity of substances, almost fifty years before Nernst. The second accomplishment is the interpretation of the evolution of heat during the passage of electricity through the solution of the electrolyte. These important experiments linked three forms of energy (*vis viva*), namely electrical, chemical, and thermal energy. The link between the three forms of energy made Joule's research differ from Faraday and the other contemporary electrochemists. More importantly, it opened the road towards conservation law.

Until then, Joule had suggested that the cause of heat production was the resistance of the solid or the liquid conductor, and in addition, he deemed that heat was transferred from the source (battery) to the conductor. However, it was surprising that the heat transferred from the battery to the conductor did not bring about a drop in the battery's temperature as expected. With a series of sophisticated experiments, including the famous paddle-wheel experiment, he showed that heat in the solid or liquid conductors is not conveyed but generated by transforming the mechanical work into heat. This discovery was the hallmark in Joule's experiments, which allowed him to calculate the mechanical equivalent of heat and finally to enunciate the first law of thermodynamics.

2.4 The mechanical equivalent of heat

The early studies of Joule had included electromagnets and electromagnetic machines. Unlike most inventors, Joule approached electromagnetic devices from a scientific and systematic way. He strove to design a powerful electric motor and then to put it to practical tests. Very early, during 1838-1839, Joule published in Sturgeon's Journal *Annals of Electricity* a series of papers expressing his hope that electromagnetism will ultimately replace the steam with proper machinery.¹⁸⁸ In the first and the last paper of this series, he gave the description and the sketches of two types of such electromagnetic engines (**Figure 5**). However, he had the scientific wisdom to note that this expectation depends on the economy resulting from the machine's operational duty, i.e., the quantity of electricity produced over the cost of working the electromagnetic engine.¹⁸⁹ In a lengthy paper *On electromagnetic forces* published in 1840,¹⁹⁰ Joule analyzed the factors that improved the

¹⁸⁸ These papers and letters to the editor were: *Description of an Electro-Magnetic Engine* (JSPP, 1884, pp.1-3 and 16-19); *Description of an Electro-magnetic Engine, with Experiments* (JSP, 1884, pp. 4-6); *On the use of Electro-magnets made of Iron Wire for the Electro-magnetic Engine* (Joule, 1852a; JSP, 1884, pp. 6-10), *Investigations in Magnetism and Electro-magnetism* (JSP, 1884, pp. 10-14 and 15-16). ¹⁸⁹ JSP, 1884, p. 14,

¹⁹⁰ JSP, 1884, pp. 19-39.

lifting power of an electric motor. These factors were the length, the sectional area, the thickness of the electromagnet coil, the size of the voltaic cell, and other physical characteristics of the conductor. In 1842, he published another paper *On a new class of magnetic forces*,¹⁹¹ where he examined the properties of electromagnets. He proposed a new theory on the phenomenon of magnetism to comprehend the magnetic attraction, the magnetic saturation, and the electrostriction (the lengthening of the magnetic bar upon its magnetization).¹⁹² This theory presupposes material particles surrounded by clouds of magnetism and electricity, reminiscent of his instructor's atomic theory (Dalton). **Figure 6** depicts the model that Joule proposed to explain the magnetization of a piece of iron metal.¹⁹³

Despite his efforts to improve the electromagnetic engines and the exhaustive tests targeted at augmenting their duty, the latter proved to be much lower than that of the steam engines. Joule gave precise scientific details and quantitative results for the mechanical and economic factors that reduced the efficiency of his electric machines compared to steam engines.¹⁹⁴ He concluded, "For although my machine is by no means perfect, I do not see how the arrangement of its parts could be improved so far as to make the duty per lb. of zinc superior to the duty of the best steam-engines per lb. of coal. And even if this were attained, the expense of the zinc [electrode] and exciting fluids of the battery is so great,

¹⁹¹ JSP, 1884, pp. 46-59.

¹⁹² JSP, 1884, 51-52.

¹⁹³ Although his theory regarding the origin of magnetism and electricity of iron came from Ampère's hypothesis on phenomena of magnetism, he based his model on the notion of atoms surrounded by two concentric atmospheres of magnetism and electricity. Nevertheless, he was not satisfied wondering whether this model existed in nature. In particular, he could not find convincing answers to the possibility of saturation due to the accumulation of quantities of magnetism. "Such a theory seems to afford a natural and complete expression of facts. It supposes nothing which we cannot readily comprehend, except the existence and elementary properties of matter, which are necessarily assumed by every theory, and which the Great Creator has placed utterly beyond the grasp of the human understanding (SP, 1884, pp. 50-53). ¹⁹⁴ JSP, 1884, p. 47.

when compared with the price of coal, as +to prevent the ordinary electro-magnetic engine from being useful for any but very peculiar purposes".¹⁹⁵ In 1843, in his well-known paper *On the Calorific Effects of Magneto-Electricity, and on the Mechanical Value of Heat*,¹⁹⁶ where he determined for the first time the mechanical equivalent of heat by using an electromagnet,¹⁹⁷ he compared the duty of the magneto-electric circuit with that of the Cornish steam engine. He found that the duty of the steam engine was more than ten times greater than that achieved by the magneto-electric machine.¹⁹⁸

No pure evil good. Electric motors could not compete with steam engines, but Joule's work during these first three years did not go in vain at all. These experiments on electric motors have revealed heat in the voltaic cells (batteries) used to provide electric currents to motors and electromagnets. Most importantly, he ascertained that heat could be produced in an entire electric circuit. Engineers had already noticed the heat evolved upon the passage of electric current to motors. However, the elucidation of the reasons for this heat production had not attracted any particular scientific attention. Accordingly, Joule decided to investigate this phenomenon. He ascertained that apart from the known proportionality between the resistance of the conductor and the heat produced, there was an additional factor that determines the quantity of heat evolved. Through a series of standard resistances, he proved the quantitative relationship between the heat produced and the resistance and the intensity of the current.¹⁹⁹ The heat *Q* is proportional to the resistance *R* and the square of the intensity of the current for a time *t*, i.e.

¹⁹⁵ JSP, 1884, p. 48.

¹⁹⁶ Joule, 1843a; JSP, 1884, pp. 123-159.

¹⁹⁷ JSP, 1884, p. 151, 153, 156.

¹⁹⁸ JSP, 1884, p. 157.

¹⁹⁹ As noted by Joule himself, "M. Ed. Becquerel and M. Lenz had separately confirmed that the heat evolved by voltaic electricity was proportional to the resistance to conduction and the square of the current". He

$$Q = RI^2 t. (2.1)$$

He generalized this important law for the batteries and a whole electrical circuit involving decomposition cells.²⁰⁰ These studies demonstrated that the heat law was valid for solid bodies and liquid conductors. Using the above formula, he calculated the resistances of batteries and circuits by measuring the heat evolved upon the passage of a current of a given intensity.²⁰¹ He made measurements and calculations of equivalences relating to chemical, electrical, and thermal effects. He reported this research, which covered the second stage of his studies in electrochemistry, in five papers starting from 1841 and ending in 1846.²⁰² His attention focused on developing an electrochemical theory based on a large number of experiments in galvanic and electrolytic cells, carefully designed and accurately performed.

The observation that oxygen gases accumulated in the negative electrode's compartments of various voltaic cells led Joule to develop his theory of combustion.²⁰³ The oxygen reacted with the metal (zinc, iron, or silver) of the negative electrode and formed a very thin metal oxide film. A similar film of hydrogen gas was created on the positive electrode (platinum or copper). Although Joule did not designate the phenomenon as

considered, however, that his experiments on this subject were more accurate to make the results of these experiments worthy of confidence by the employment of a galvanometer and thermometers of great delicacy and accuracy (Joule, 1852b, p. 485; JSP, 1884, p. 211).

²⁰⁰ A large part of these interesting studies is the subject of a paper entitled *On the heat evolved by metallic conductors of electricity and in the cells of battery during electrolysis* published early in 1841 (Joule, 1841; JSP, 1884, 60-81).

²⁰¹ JSP, 1884, p 71.

²⁰²Joule's last paper was submitted in 1846 in a competition for a prize offered by the French Academy of Science in thermochemistry (JSP pp.298-328). The paper was published six years later (Joule, 1850).

²⁰³ The results of these experiments were communicated to the literary and Philosophical Society of Manchester in 1841 under the title *On the electric origin of the heat of combustion* (Joule, 1842; SP, 1884, pp. 81-109).

polarization,²⁰⁴ he ascertained that the action of the cell deteriorated with time. This failure resulted in a decrease in the intensity of the electric current provided by the cell. The formation of gases obstructed the access of the reactants to the metallic electrodes, thereby increasing the cell's resistance. The removal of hydrogen and hence the elimination of polarization was achieved by either the influx of oxygen through the electrolytic solution or by disrupting the cell operation and moving the metal in the fluid or exposing the electrode in the atmospheric air. In both cases, the liberated hydrogen was removed, and polarization was annulated. The metal oxides are removed by adding a small quantity of acid to the solution. These experiments allowed the assessment of the electric current intensity required for the combustion of hydrogen and various metals (or for the decomposition of oxides during electrolysis).²⁰⁵ In other words, to measure the resistance to the electric current associated with these secondary reactions. This observation was verified when he compared the heat evolved in the cell reaction with the heat evolved from a similar reaction taking place outside the cell (in a calorimeter). The latter quantity was less than the former, indicating that the extra heat arose from the resistance during combustion (Figure 7).

Furthermore, Joule generalizing Berzelius' suggestion that heat and light of combustion arise from the discharge of electricity between the particles of the combustible substances and oxygen, he pictured the combustion within the electrolytic cell as a result of the interaction of the electric current with the reacting atoms of the metals or hydrogen.

²⁰⁴ Much later. In 1872, Joule read a paper on polarization in front of the Manchester Literary and Philosophical Society. The experiments performed at that time were described in a note in 1883 entitled, *On the polarization of platina plates by frictional electricity* (JSP, 1884, pp. 620-622). Nevertheless, this experiment concerned the discharge of a condenser (capacitor) rather than the phenomenon of polarization in voltaic or electrolytic cells.

The heat evolved by the union of the two particles is proportional to the intensity of the current passing between them. In other words, to the strength of their chemical affinity. The heat evolved from this reaction due to the resistance of the reacting particles to the current obeying the *heating law* $Q = RI^2t$. The chemical affinity of the particle determined the intensity of the current passing from oxygen to combustible during their union. Since the quantity of heat is proportional to the current intensity, the latter is proportional to the chemical affinities of certain metals and hydrogen for oxygen. Joule succeeded in measuring the affinities of the voltaic apparatus.²⁰⁶ He thus succeeded in establishing relations between heat and chemical affinity. "The quantities of heat are evolved by the combustion of the equivalents of bodies are proportional to the intensities of their affinities for oxygen".²⁰⁷

In a subsequent paper, *On the electrical origin of chemical heat*,²⁰⁸ Joule sought to avoid any possible side effects in his experiments in order to calculate the affinities of the elements in oxides. He corrected the theoretical values of affinity by eliminating the forces affecting the electrolysis current, interfering with the affinity forces of the oxide elements. Joule considered three kinds of forces in operation, of which two acted against and one in favor of the electric current used for the electrolysis of the solution of the sulfate of metallic oxide. The first two forces are the affinity of the elements of the oxide for one another and the affinity of the oxide for the acid (usually sulfuric acid) used for the elimination of polarization. The third force is the affinity of water for the acid, which has the opposite direction to the two others and is generally less than either. Joule corrected the affinity

²⁰⁶ Jlbid, pp. 97-100.

²⁰⁷ Ibid, p. 100.

²⁰⁸ Joule, 1843b; JSP, 1884, pp. 102-107.

values by subtracting the current intensity resulting from the difference of the affinities of sulphuric acid for the metallic oxides and hydrogen from the electrolysis current intensity. Joule corrected the theoretical values of affinity for the oxides of three metals (zinc, copper, and iron) and hydrogen. For each case, he proposed the pertinent experimental method for the elimination of disturbing forces.²⁰⁹

The sequel of Joule's electrochemical investigations involved electrolysis, and the origin of heat evolved upon the passage of the electric current through the decomposition (electrolytic) cell.²¹⁰ Joule intended to compare the *experimental heat*, Q_{exp} evolved upon the passage of an electric current supplied by a battery to the electrolytic cell with the *theoretical heat* obtained from the law $Q_{th} = RI^2 t$. He found that the experimental heat evolved during the electrolysis of water was greater than the theoretical value. He attributed the difference of heats $Q_r = Q_{exp} - Q_{th}$ to the resistance of the decomposition reaction to the current. i.e., to the resistance due to the separation of water into its elements hydrogen and oxygen. According to Joule, Q_r became latent and dissipated to the circuit. The calculated resistance R_r from Q_r is the extra resistive obstacle to the circulation of the electric current across the decomposition cell.²¹¹ Joule did not interpret his experimental results in the framework of the conservation law. However, Joule's subsequent experiments indicate that he might have in mind that heat and work are connected, already in 1843.

²⁰⁹ JSP, 1884, pp. 105-107.

²¹⁰ These studies summarized in the 1844 article *On the heat evolved during the electrolysis of water* (JSP, 1884, pp. 109-123).

²¹¹ Cropper claims that the difference $Q_r = Q_{exp} - Q_{th}$ represents the mathematical expression of the first law of thermodynamics. He considered Q_r as the enthalpy ΔH_r (heat at constant pressure) of the electrochemical reaction, and Q_{th} as the electrical work W_{el} done by the voltaic cell. Therefore, the difference of heats can be replaced by $\Delta H_r = W_{el} - Q_{exp}$, which is the formal statement of the conservation law (Cropper, 1988, p. 6). Joule did not interpret his experimental results in the framework of the conservation law. Howhever, his subsequent experiments might indicate that he had in mind the conception that heat and work are connected already in 1843.

The third stage of Joule's chemical-electrical-thermal studies concerned the calculation of the mechanical equivalent of heat. In 1849, Joule read to the Royal Academy of London the article On the mechanical equivalent of heat.²¹² This article published a year later in Philosophical Transactions of the Academy was a repetition of previous experiments performed in 1845 and 1847. These articles entitled On the existence of an equivalent heat and the ordinary forms of mechanical power²¹³, and On the mechanical equivalent of heat, as determined by the heat evolved by the friction of fluids,²¹⁴ respectively. He employed his previous paddle-wheel experiment to exert fluid friction and obtain values of the mechanical equivalent of heat from the friction (agitation) of the fluid (water, mercury, or cast iron) contained in a metallic vessel (Figure 8). He repeated these experiments aiming at greater accuracy by improving the experimental device, the measuring instruments, and the experimental methodology, avoiding systematic errors (temperature differences between the fluid in the vessel and the surroundings, the velocity with which the leaden weights dropped to the ground, etc.).²¹⁵ He mentioned the pioneering work of Count Rumford, Davy, Dulong, Faraday, Grove, and Mayer. He advanced the idea that heat was motion and that the calorific effects developed by the friction of fluids were proportional to the force expended under certain conditions.²¹⁶ He gave a short outline of

²¹² Joule, 1850; JSP. 1884, pp. 298-328.

²¹³ Joule, 1845a; JSP, 1884, pp. 202-205.

²¹⁴ Joule, 1847; JSP, 1884, pp. 277-281.

²¹⁵ Joule did not estimate whatsoever random errors in his experiments. He gave only averaged values (arithmetic mean) for his experimental observations, even though relevant statistical quantities had been proposed for error analysis by the end of the 18th century, beginning of the 19th century, such as the mean square error. Carl Friedrich Gauss (1777-1855) had published two books in Latin [*Theoria Motus* (1809) and Theoria Combinationis (1823)], where he applied the least-squares and error analysis to astronomical observations. The second book, *Theory of the Combination of Observations Least Subject to Errors,* was the most popular and has become classic in applied mathematics: This book has been translated in English (Stewart, 1995). For a historical account of error analysis, see Sheysnin, 1979, pp. 39, 45, 49.

his earlier experiments to determine the mechanical equivalent of heat by various methods, which were in progress from year to year, lasting more than seven years. From the value of 838 foot-pounds in 1843, he had reduced the equivalent factor to 781.5 in 1847 and 772.7 foot-pounds in 1849, which is essentially the same number (772) we use today.

When did Joule begin to think about the mechanical equivalent of heat? The journey began in the year 1843. Joule was aware of Peltier's experiment²¹⁷ and thought that this experiment proves to a great deal that the heat evolved by thermo-electricity is transferred from the heated solder, not heat being *generated*.²¹⁸ Also, Joule ascertained that if a large battery were connected by thick conducting wires with a coil of very thin wire, nearly the whole of the heat due to the chemical changes taking place in the battery would be evolved by that coil, while the battery itself will remain cool.²¹⁹ Again, heat was transferred not generated. Joule wondered why the heat transferred from the battery to the electromagnet (or the latent heat in the electrolysis reaction) did not induce any cold to the battery, or why the coils of the magneto-electric machine did not become cold while the heat was transferred. From the coils? Was the heat in both cases transferred or generated?

In an article read before the Chemical Section of Mathematical and Physical Science of the British-Association meeting at Cork on the 21st of August 1843, Joule clarified his inquiry. Heat is generated on the conductor by mechanical means and not being transferred from the battery. Electricity is still the essential intermediate agent for the interconversion between the heat produced and the chemical changes in the battery. "[...]

²¹⁷ JSP.1884, pp. 79, 124, When a current is made to flow through a junction between two metals, e.g., antimony and bismuth, heat may be absorbed or removed at the junction. This effect is named after French physicist Jean Charles Athanase Peltier (1785-1845), who discovered it in 1834 (Peltier, 1834).
²¹⁸ JSP.1884, p. 124,

²¹⁹ Jlbid, p. 120.

hitherto no experiments have been made decisive of this very interesting question for all of them refer to a particular part of the circuit only, leaving it a matter of doubt whether the heat observed was generated, or merely transferred from the coils in which the magnetoelectricity was induced, the coils themselves becoming cold".²²⁰

He proceeded to resolve this ambiguity by setting forth a general experimental plan that involved a small compound electromagnet, immersed in a glass vessel containing water and rotated between the poles of a powerful magnet (magneto-electric effect). He then measured the arising electricity by an accurate galvanometer. He ascertained the calorific effect on the electromagnet coil by the change of temperature in the water surrounding the small electromagnet (**Figure 9**).²²¹ The idea was that if heat is transferred from the rotating coil to the rest of the circuit, then the coil must become colder. No such outcome was observed. Instead, the water temperature rose, and the heat evolved in the coil obeyed the standard law $Q = RI^2t$. Once Joule realized that the generated heat in the circuit derived from the work done by the permanent magnet for the rotation of the coil, he proceeded to find whether there was a constant relationship between the quantity of the generated heat and the external work done on the rotating coil.

Henry J. Steffens has suggested an alternative possibility that led Joule towards the discovery of the mechanical equivalent of heat.²²² Based on the translated 1842 paper of Robert Mayer's *Bemerkungen über die Krafte der umbelebten Natu*,*r*²²³ found it in Joule's laboratory notebook, Steffens claims that Joule may have read Mayer's paper as early as 1843. Therefore his discovery of the mechanical equivalent of heat may not have been

²²⁰ Ibid, p. 123.

²²¹ Ibid. pp. 124-125.

²²² Steffens, 1979, pp. 217-219.

²²³ See section 2, paragraph 2.1 of this dissertation.

entirely independent after all. Due to this fact, Steffens asserts that Joule's ideas for the relationship between work and heat went through an abrupt modification, and his experiments showed a sudden change of direction between mid-1843 and mid-1844.²²⁴

Mendoza and Cardwell responded to Steffens' claims through an article published two years later.²²⁵ Their principal argument against Steffens' allegations emanated from a PS added by Joule in his paper discussing the generation of heat by mechanical work, which was the essential evidence of Steffens' disagreement. The crucial passage invoked by Mendoza and Cardwell reads: "I have lately proved experimentally that *heat is evolved by the passage of water through narrow tubes* [emphasis by Joule]. My apparatus consisted of a piston perforated by a number of small holes, working in a cylindrical glass jar containing about seven lb. of water. I thus obtained one degree of heat per lb. of water from a mechanical force capable of raising about 770 lb. to the height of one foot, a result which will be allowed to be very strongly confirmatory of our previous deductions. I shall lose no time in repeating and extending these experiments, being satisfied that the grand agents of nature are, by the Creator's fiat, *indestructible* and that wherever mechanical force is expended, an exact equivalent of heat is *always* obtained".²²⁶

The last phrase of this passage is an indirect approach to the conservation law, although the truth of this law is attributed to God's will. In a letter sent to William Thomson in 1848 mentioned by Mendoza and Cardwell,²²⁷ Joule stated that he owed nothing to Mayer. However, he did not deny Mayer's contribution to the discovery of the conservation

²²⁵ Mendoza, and Cardwell, 1981.

²²⁴ Steffens' book received negative criticisms in four reviews that appeared between 1980 and 1981, (a) Trevor, W. 1980. *Endeavour* 4: 130, (b) Burchfield, J. O. 1980. *Isis* 71: 183; (c) Smith, *C. 1980. Ambix* 27: 142, (d) Gooding, D. 1981. *BJHS* r 14: 217.

²²⁶ JSP, 1884, pp. 157-158.

²²⁷ Mendoza & Cardwell, 1981, p. 179.

law by saying in that letter, "the merit will belong to all those who have worked out the doctrine". This passage comes from 1843 Joule's paper *On the Calorific Effects of Magneto-Electricity, and on the Mechanical Value of Heat*. The experiment of the narrow tubes was never published. Joule mentioned this experiment twice in his papers. The first time in his 1845 paper, when he measured the mechanical equivalent of heat using the paddle-wheel apparatus.²²⁸ The second time in his 1850 paper *On the Mechanical Equivalent of Heat* published.²²⁹ However, Joule used this unpublished experiment in his lengthy discussion with William Thomson to convince him that Carnot's principle was incorrect and that mechanical work is produced only by transforming a certain quantity of heat.

2.5 Hermann von Helmholtz

Helmholtz was one of the most remarkable scientists of the nineteenth century. He participated in the development of medicine, physics, chemistry, and philosophy of science and achieved an impressive number of scientific results. The physicist Helmholtz played a significant part in the formulation of the law of the conservation of energy, the vortex equations for fluid dynamics, significant theoretical contribution to electrodynamics, advancement of electrochemistry through his theory on polarization, the discovery of the free energy, and the bound energy in chemical thermodynamics, the study of monocyclic and polycyclic systems, and the principle of least action in mechanics. The medical researcher Helmholtz contributed to the physiological aspects of human perception,

²²⁸ Joule, 1845a; SP, 1884, p. 204.

²²⁹ JSP, 1850, p. 302.

including sign theory, spatial perception, optics, acoustic, and the invention of the ophthalmoscope. His constant interest in the epistemology of science guaranteed his enduring significance for philosophy. In this paragraph, I will focus on his contribution to the foundation of conservation law in physics. As a matter of fact, in his famous essay *Über die Erhaltung derKraft* (on the conservation of force).²³⁰ Helmholtz did not use the term energy. He formulated his mathematical approach to this subject in terms of natural forces, raising thus a controversial discussion among the historians and philosophers of science about the real meaning of Helmholtz's word *Kraft*.²³¹

Due to financial reasons, Helmholtz studied medicine despite his inclination for physics. Studies in physics required financial support from his family, which he was unable to afford. On the other hand, the state provided a stipend for five years of study at Friedrich-Wilhelm-Institut's medical school in Berlin with Helmholtz's obligation to serve the army for eight years after graduation.²³² The curriculum of the medical school did not require courses in physics and mathematics. However, Helmholtz read privately mathematics, namely, the works of the famous French mathematicians and physicists Laplace, Biot, Daniel Bernoulli (1700-1782), D' Alembert, Lagrange, and the Swiss Leonhard Euler (1707-1783). He completed his education by reading the philosophical works of Immanuel Kant (1724-1804) and Georg Wilhelm Friedrich Hegel (1770-1831).²³³ His mathematical expertise will become apparent later when he is involved in problems related to physics.

²³⁰ Helmholtz, 1847a; translated in English by Tyndall, 1853.

²³¹ Elkana, 1974, pp. 132-138.

²³² For Helmholtz's biography, see Turner, 1981, pp. 241-253; Helmholtz's autobiography, 1893; Koenigsberger, 1906, pp. 1-26, and the most recent biography, Cahan, 2018.

²³³ Helmholtz was a man of impressive spiritual culture. He played exceptionally well classical piano; he had the talent for reading poems aloud, made his verses, and acted comedy almost like a professional. He once participated as an actor in a play called *Lodgings to Let*, which performed on December 23, 1846, (Koenigsberger, 1906, p.36).

Especially during the year 1871, when he will begin his second career as a physicist at the University of Berlin.

Notwithstanding, his research conducted for his doctoral dissertation in sensory physiology in the laboratory of Johannes Peter Müller's (1801-1858), professor of physiology at Humboldt University of Berlin, was the line thread for Helmholtz's acquaintance with physics. The cause had a name *vital force*. The influence of Justus Liebig, particularly his famous book *Animal Chemistry* that appeared just as Helmholtz was completing his medical studies, and his acquaintances with liberal students at the university motivated Helmholtz to turn into physics.²³⁴ These men organized the circle of Müller's students and collaborators in which dominant figures were: Ernst Wilhelm von Brücke (1819-1892),²³⁵ Emil du Bois-Reymond (1818-1896),²³⁶ Carl Ludvig (1816-1895),²³⁷ and Rudolf Virchow (1821-1902).²³⁸ These four men and Helmholtz innovated the science of medicine in several of its branches, both in theory and in practice. However, the motives that incited Helmholtz to reveal his inclination in physics and finally writing

²³⁴ Lenoir, 1982, p. 196; Heimann, 1974a, p. 209.

²³⁵ Brücke was a physician and physiologist. He did research on the nature of cells, work dealing with the physiology of language, investigations on the effect of electricity on muscles, and studies on the protein albumin. He also made significant contributions to the fields of physics, plant physiology, microscopic anatomy and experimental physiology.

²³⁶ du Bois-Reymond became a successful physician and physiologist. He discovered the nerve action potential, and he demonstrated the electrical nature of nerve signals and created the new discipline of the experimental electrophysiology.

²³⁷ Ludwig was a physician and physiologist. Ludwig worked on several topics such as the physiology of blood pressure, urinary excretion, and anesthesia. In 1842, he became professor of physiology in Zurich, and in 1846 professor of comparative anatomy in Vienna. He went in 1865 to the University of Leipzig and developed there the Physiological Institute, designated today after him: Carl Ludwig Institute of Physiology. He received the Copley Medal in 1869; he was elected a foreign member of the Royal Swedish Academy of Sciences. He is credited for inventing the stromuhr, i.e., an instrument for measuring the velocity of blood flow, like a rheometer.

²³⁸ Virchow made significant contribution in several field of medicine, such as pathology, anatomy, cell biology, theory on cancer origin, autopsy, forensic, and others. He was forceful opponent of the vital force and an impassionate advocate for social and political reforms. His ideology involved social inequality as the cause of diseases that requires political actions to remedy this injustice: He was a dedicated political activist, participating in the social-liberal revolution of 1848 in Germany.

the *Erhaltung* were more than those rooted in the conviction that the development of science is due solely to its esoteric logic. External factors related to the social and political environment at the German States in Helmholtz's time played a role in Helmholtz's decision to participate actively in the circles of young scientists who sought reforms in science at the universities.²³⁹

In 1845, Brücke, du Bois-Reymond, Ludvig, and a few other physicians founded the *Berlin Physikalische Gesellschaft* to perform experimental and theoretical work to free physiology from the *vital force*.²⁴⁰ They argued that the production of animal heat did not need the function of a metaphysical force, but it was a matter of metabolism. Apart from the need for experimental work, they realized that a theory was required to consolidate the experimental findings. They thought it appropriate to infuse physics into physiology. This relation could facilitate the reconstruction of physiology on a more exact basis. They knew that fitting the conclusions of physiology to physics required mathematical skills for formulating relevant problems and finding appropriate solutions methods. In this, Helmholtz had a decided advantage over the rest. He joined the *Gesellschaft* in 1845. In 1846, Helmholtz prepared two important review articles (Berichte), one for his mentor Johannes Müller and the other for his friend Du Bois-Raymond. Both reviews are

²³⁹ In the first half of the nineteenth century, three waves of revolutions broke out in mainland Europe. Social strata of the bourgeoisie and petit-bourgeoisie claimed political, economic, and social reforms from the autocracy and the landowners. The last wave of uprisings erupted in 1848 and had the most significant impact on the German states. The central ideology of the rebellious individuals was liberalism and, secondly, socialism. The latter ideology being less influential at that time. Although there were differences within the ideology of liberalism (democratic, conservative, or moderate trends of liberalism), it flourished in the universities. Those who formulated the liberal ideology and spread out its demands were intellectuals and students at universities. The revolutionary atmosphere at that time penetrated by the liberal ideology had significant implications for education and research. It was reflected on the demands for freedom and reforms. More about liberalism in German universities in McClelland, 1980. pp. 151-232.

²⁴⁰The *vital force* was an extra force of unknown origin that was supposed to control the physical and chemical forces of the organs of the living body.

considered as the prelude of his famous memoir *Über the Erhaltung der Kraft*. The two reviews had provided the historians with helpful information to delineate the methodological approach and the conceptualization model used by Helmholtz to formulate the conservation law in his *Erhaltung*.

In the more extensive article for Müller, Helmholtz reviewed the empirical research on animal heat from 1800 onwards. Helmholtz claimed that the material theory of heat is no longer tenable because it cannot explain the creation of heat in friction. He adopted the *undulatory theory of heat*,²⁴¹ although this theory raised problems regarding the origin of animal heat. The same review contradicted the respiratory theory of heat with the theory of metabolism as the fundamental source of heat. It attacked the *vital force* as violating the principle of perpetual motion.²⁴² In the second Bericht, Helmholtz outlined more explicitly the subjects that would treat later in *Erhaltung*. He commented on the relations between heat and motion, chemical processes and heat, and electricity and heat. He once rejected the respiratory theory that heat originated not from the combustion of carbon and hydrogen but mainly from the nutrients.²⁴³ However, Helmholtz did not make any reference to the role that the work –equivalent to heat would play in explaining the relation between heat and metabolism. Physiology was the battleground where the conservation law emanated, but physics had the simplicity, the methodology, and the mathematical tools to express what Helmholtz called the conservation of force. The *Erhaltung* differed significantly from

²⁴¹ The undulatory or wave theory of heat has been considered as the intermediate stage of the development of the theory of heat, between the caloric theory and the mechanical rheory of heat. According to the wave theory of heat, heat is the vibrations of an ethereal fluid that fills all space, and which transmits vibrational motion from one atom to another.

from one atom to another

²⁴² Helmholtz, 1847b; Kremer, 1984, pp. 244-252.

²⁴³ Helmholtz, 1846; Kremer, 1984, pp. 252-253.

the two *Berichte*. It was a theoretical study in physics, in which physiology was a minor fragment discussed briefly at the end of the memoir. It was physics that provided Helmholtz the theoretical framework for the conservation of force. The old doctrine of the impossibility of the Perpetuum mobile and the Newtonian central forces provided the necessary theoretical argument for the conservation of force as explained and applied by Helmholtz in the Erhaltung. The appendix contains a detailed analysis of the *Erhaltung*.

Nevertheless, Physiology was the battlefield on which Helmholtz fought against the old doctrine of *vital force*. In 1847, while still writing the *Erhaltung*, Helmholtz conducted his unique experiments seeking to link the mechanical work produced by the muscle action of frogs with the chemical changes that occurred in the muscle fibres. His understanding and evaluation of the mechanical equivalent of heat are probably connected to his research, as we shall see in chapter four.

Chapter 3. The development of thermodynamics in the context of physics: Entropy and the second law of thermodynamics

The equivalence of heat and mechanical work constituted the first law of thermodynamics. The direction of a spontaneous process in nature was the subject of the second law of thermodynamics (henceforth the second law). The formulation and experimental verification of the first law took less than two decades. In contrast, the theoretical development of the second law and its application to physics and chemistry lasted beyond the turn of the twentieth century. Physicists and chemists found it highly challenging to apprehend new terms and related concepts (especially the concepts of entropy and energy dissipation). Reinterpretations, misinterpretations, and hesitations were debated on these matters in the scientific communities of Europe and America. It is worthwhile to mention that the founders of the second law had to admit the truthfulness of the first law, the mutual transformation of mechanical work and heat, and the mechanical equivalent of heat. Then, abandon the caloric theory and Carnot's principle for the heat engines to reconstruct the physical processes upon another foundation. The course towards the second law was a real challenge for William Thomson, as I shall discuss below.

Each of the three contributors to the second law, namely William Thomson, Rudolf Clausius, and William Rankine, followed different approaches towards the constitution of the second law. Clausius recognized rather quickly the weak point of Carnot's principle that heat produced work in a heat engine, and at the same time, its quantity was conserved. Clausius managed to modify this weak point of Carnot's theory by adopting Joule's discovery that heat is never conserved but transformed into work. However, Clausius did not initially grasp the implications of the irreversibility inherent in Carnot's theory. He neglected temporarily this weak point by adopting the notion of entropy. William Thomson had recognized much earlier the irreversible process occurring in the conduction of heat from a hot to a cold body. However, he entangled in the contradiction between heat generated by friction or percussion and the hypothesis of heat as a preserved substance, according to Carnot-Clapeyron theory. Thomson's efforts to resolve this ambiguity took him several years, from 1847 when he first met Joule until 1851 when he published the first of a series of papers under the general title *on the dynamical theory of heat*. He strove to perceive and reconcile the two contradictory processes of producing heat from mechanical effects and vice versa.²⁴⁴

On the other hand, Rankine agreed with Joule and Clausius' views on thermodynamics, although in a different theoretical context related to a microscopic structural model of heat transportation via the so-called molecular vortices. He accepted the concepts of the equivalence of heat and mechanical work and irreversibility. In this respect, he exerted additional pressure on Thomson's fundamental conflict on the issue of the conduction of heat and the lost work and the indestructibility of the living force (*vis viva*). Rankine did not enunciate any version of the second law. On the other hand, Clausius quickly realized the cause of this contradiction and managed to reconcile Carnot's theory with Joule's inter-convertibility of heat and work by adding a second statement to Carnot's principle. However, according to the opinions of Thomson and Rankine, Clausius'

²⁴⁴ Thomson preferred the term mechanical effect instead of work or other equivalent terms following the vocabulary of James Watt, and Thomson's friend, Lewis Gordon (1815-1876), professor of Civil Engineering at the University of Glasgow. This term was not generally used in Britain. It is occasionally used by the British Association of the Advancement of Science (Smith, and Wise, 1989, pp. 291-293).

modification of Carnot's theorem had a rather qualitative character lacking a profound quantitative proof.

Section 1. The origin of the second law

The origin of the second law undoubtedly is credited to Sadi Carnot. As noted previously, Carnot saw the production of mechanical work in a heat engine as the result of the transportation of heat (calorique) from the boiler to the condenser of the engine, not heat being lost. In other words, he presumed that exactly as much heat received from the boiler, it entered the refrigerator of the engine. The steam of the liquid (water or alcohol) or the air was employed to transfer the caloric. Furthermore, the heat transfer agent liquefied by contact with the cold water of the refrigerator of the engine in simultaneous production of motive power. Apart from the conduction of heat from high to lower temperatures, a change in the volume of the transporting agent was equally crucial to obtain mechanical work. The availability of gas expansion and compression in the engine's pistons led Carnot to discover the proper condition through a reversible cycle that allowed a heat engine to achieve its maximum motive power. Carnot calculated the motive power of the doublecylinder engines used to drainage Cornwall's tin and copper mines and found only 1/20 of the theoretical value. He noticed emphatically, "We have, nevertheless, selected our example from among the best steam engines known. Most engines are greatly inferior to these".²⁴⁵ Where did the lost work go, since the heat is conserved according to Carnot's principle? While the heat transfer from a hot body to a cold one affected the motive power, the communication of heat from the hot to the cold body by mere conduction or radiation

²⁴⁵ Thurston, p. 125 (*Reflexions*, p. 117)

produced no work, or if work had been done, where did it go?. Carnot had noticed this case in the context of the optimum operation of heat engines and advised the engineers to avoid the useless contact of the steam with the metallic parts of the engine acquiring different temperatures than that of the condenser.²⁴⁶ He did not discuss this subject further, at least in his *Reflexions*. This question attracted the attention of the three founders of the second law. Clausius and Rankine found solutions rather quickly although employing different methodological approaches, while took Thomson one year to resolve the ambiguity of the lost work.

Section 2. The first approach to the second law

In the mid-nineteenth century, three physicists, under different circumstances, came in contact with both Carnot's theory for the effective operation of the steam engines and the experiments of Joule. They observed that the theory was inconsistent with the conclusions of the experiments. Based on the caloric theory of heat, Carnot concluded that the heat provided by the engine's boiler was conserved, while Joule's experiments showed that a portion of the heat was converted into work. Closing the gap between theory and experiment was at the forefront of the efforts of the three thinkers.

2.1 William Thomson (Lord Kelvin)

To understand Thomson's thinking and his methodological approach to thermodynamics, one must examine the influences and perceptions that shaped his views towards the

²⁴⁶ Thurston, pp. 56-58 (*Reflexions*, pp.22-24). Refer to earlier discussions on his subject.

dynamical theory of heat.²⁴⁷ His studies on Joseph Fourier's physics and, in particular, Carnot's *Reflections*, the frequent discussions and exchange of letters with his brother James Thomson (1822-1892), and the debates between him and Joule formed in general William Thomson's thinking towards the second law that finally he enunciated in 1851. Nonetheless, Thomson was not convinced about the truth of this law. The final reconciliation between the conservation of energy and the dissipation of the mechanical effect, that is, the gap between reversible and irreversible processes reflected on Thomson's cosmological views, was left to his theological beliefs.

Early in the 1940s, Thomson read Fourier's treatise. *The analytical theory of heat which* was an account of the theory of heat viewed by Fourier as an autonomous branch of physics.²⁴⁸ The perusal of Fourier's theory of heat transfer was decisive for Thomson's ambivalence regarding the nature of heat. Fourier's demarcation of heat from any mechanical view was interesting since "these effects [heat and work] thought to be irrelevant to the principles of movement and equilibrium"²⁴⁹ as expressed by the phenomena of heat conduction. Fourier regarded the conduction of heat in solid bodies as a dual process linking interior and exterior conductivity. The latter is expressed in terms of the radiation of heat. He manipulated the whole process of heat conduction through the concept of the flux of heat across a surface in two ways: a direct flow on the surface and as a flow of heat radiated immediately above the surface. He proceeded to the mathematical

²⁴⁷ For Thomson's biography and work on thermodynamics, see Thompson, 1910; Smith, and Wise, 1989; Buchwald, 1981, pp. 374-388.

²⁴⁸ Fourier, 1822; translated in English by Freeman, 1878.

²⁴⁹ Joseph Fourier belongs to the French school of the great mathematicians and physicists of the eighteenth and nineteenth century, including Laplace, Biot, D'Alembert, and Poisson. However, his work on heat conduction had little influence on his contemporaries and successors, despite its originality, importance, and influence on the various aspects of the subject. For an analysis of Fourier's work, including biographical details, see Herivel, 1975.

treatment of this model of heat conduction by adopting various boundary conditions.²⁵⁰ However, Fourier's demarcation of heat from mechanical theories prevented him from recognizing any implicit or explicit connection between heat and mechanical work. He concentrated on an abstract mathematical description of the empirical laws that controlled the phenomena of heat conduction and radiation in solid bodies and, to a lesser extent, in fluids. Whether Fourier's theory on conduction had affected William Thomson's views on heat conduction before the meeting with Joule is not clear. Crosbie Smith claims²⁵¹ that Thomson had primarily appealed by the simplicity of Fourier's mathematics and the exactness and rigor. At any rate, Fourier's theory on heat transfer had left open the question of the nature of heat. Thomson considered that the distinction between the material and the dynamical nature of heat was one of the most important characteristics of the theory. He published in 1842 a memoir *on the linear motion of heat*,²⁵² which was an alternative mathematical solution for the linear motion of heat along the lines of Fourier.²⁵³

Carnot's theory of the conservation of heat exerted a strong influence on Thomson's view on thermodynamics. It seems that Thomson was inspired by the work of Carnot during his stay in Paris in 1845 when he visited the laboratory of Victor Regnault. Regnault had a strong reputation as a very skillful experimenter, and in this respect, Thomson decided to visit his laboratory to obtain experimental skills. Thomson read Carnot's *Reflections* in the prototype three years later in 1848 because he could not find a

 ²⁵⁰ For a heuristic presentation of Fourier's method of deriving the equations for the propagation of heat and further on Laplace's, Biot's, and Poisson's criticisms on this model, see Herivel, 1975, pp. 180-190.
 ²⁵¹ Smith, 1976, p. 305; Herivel, 1975, pp. 216-217. Herivel contended that Fourier's mathematics were more influential than his physics.

 ²⁵² He published the memoir in two parts, in 1842 and 1843 (Thomson, 1882, pp. 10-15, and 16-20.)
 ²⁵³ Thompson, 1910, pp. 41-42.
copy of it in Paris.²⁵⁴ Thomson heard about Carnot's theory on heat through Clapeyron's memoir that he probably read while in Regnault's laboratory. Others gave an alternative explanation of when and how Thomson heard about Carnot for the first time.²⁵⁵ Indeed, Carnot's principle had no conflict with Thomson's natural philosophy of heat, and on this, his brother James Thomson had a decisive role. James Thomson trained as an engineer, but his inclination was towards theoretical scientific issues rather than practical details. However, as an engineer, he was familiar with hydraulic and heat engines' theoretical and practical aspects. He had a better knowledge to expound the transfer of heat in the context of Carnot-Clapeyron theory in analogy with the transfer of water in waterfalls. He expressed these views during several discussions and exchanging a long series of letters with William Thomson.²⁵⁶ William Thomson had a wide range of research interests, as reflected in the vast number of papers published in various fields. An essential factor that directed William Thomson's interest in the theory of heat was his brother. James Thomson made William interrupt his research in other areas of physics and focused his attention on Carnot's theory.

²⁵⁴ In 1846, Lewis Gordon gave to Thomson a copy of the *Reflexions*.

²⁵⁵ In August 1844, a year before the visit to Paris, William Thomson received a letter from his brother. The latter inquired of his brother, who proved that a definite quantity of mechanical effect given out during the passage of heat from one body to another. This letter might indicate that the two brother had discussed Clapeyron's memoir (Smith, 1976, p. 307; 1977, pp. 235-236). However, this allegation casts some doubts about its validity. James Thomson made no explicit reference to Clapeyron's memoir in his letter, nor could the passage quoted by Smith be attributed solely to Clapeyron's paper. It is well known that several engineers, such as Comte de Pambour, Carl von Holtzmann (1811-1865), Karl Friedrich Mohr (1806-1879), Marc Seguin (1786-1875), to name a few, were involved in theoretical and practical aspects of the working of heat engines. In particular, Holtzmann had heard of Carnot's ideas through reading Clapeyron's paper (Cardwell, 1971, pp. 224-229). Therefore, it cannot be excluded that the two brothers discussed recent developments on heat engines reported by contemporary engineers.

²⁵⁶ For a detailed discussion concerning James Thomson' interest in Carnot's theory of heat and the exchange of ideas with his brother, see for instance Smith, 1977, pp. 233-241.

Thus, William Thomson was well prepared before the Royal Society of Edinburgh meeting on 2 January 1947. He attended Joule's short presentation on heat production upon steering a quantity of water mechanically in a vessel (the paddle-wheel experiment). From this time on, Thomson entered a dramatic mental conflict between two different relationships of work and heat; Carnot's theory suggesting the proportionality between heat and work provided that heat flowed from higher to lower temperature and, on the other hand, the transformation of heat into work advocated by Joule's experiments.

Why did not Thomson admit Joule's new explanation that heat was developed by the friction of fluids at the expense of mechanical work (the paddle-wheel experiment)? First, he doubted the accuracy of the very experiments performed by Joule; Thomson knew from the waterfall analogy and the heat developed in a conductor upon the passage of electric current that the quantity of heat produced via the mechanical effect must be proportional to the intensity of the current squared. Considering the minimal temperature differences recorded by Joule, errors in the measurements propagated in the calculations of the equivalents of heat and work seemed unavoidable.²⁵⁷ Second, Joule's experiments led Thomson to conclude that work is converted into heat, but not vice versa. Thomson thought that the conversion of heat into mechanical effect was probably impossible, undoubtedly undiscovered. He stated clearly about this hidden transformation in letters sent

²⁵⁷ Joule made tremendous efforts to eliminate the constant (systematic) errors resulting from measuring instruments' imperfections and methodological inefficiencies. However, he did not estimate random errors from temperature or pressure fluctuations, and environmental instabilities. Laplace, Johann Heinrich Lambert (1728-1777), Bernoulli, and especially Gauss had proposed statistical methods for estimating random errors early in the nineteenth century. The probable error, mean square error, median, and variance were some of these statistical measures of accuracy. Joule used only the mean values of his experimental data. As an exercise, I applied modern statistics to Joule's data obtained from the paddle-wheel experiments to have an idea about the breath of random errors in his measurements. The calculated mean values, standard deviations, variances, and medians of the experimental data indicated that Joule had made a splendid work, considering the enormous experimental difficulties that he had to overcome in order to achieve reliable values for the mechanical equivalent of heat.

to his brother²⁵⁸ and his father. Furthermore, he mentioned the same problematics in an appended footnote of a paper he published in 1848. He calculated the absolute temperature scale based on Carnot's cycle and Regnault's experimental data of latent heat and pressures of saturated vapor.²⁵⁹

The third reason that made Thomson skeptical about Joule's deductions from his experiments (in the meantime, Thomson had received two of Joule's original papers published in 1943 and 1844) was that Joule said nothing about heat conduction. This issue was precisely the concept which occupied Thomson's mind since his first reading on Fourier's treatise, i.e., the question, if mechanical work is produced, where does it go? Carnot stated clearly in his *Reflexions* that mechanical work was lost when heat passed through the cylinders and the other metallic parts of the engine. In a letter sent to Thomson in 1848, Joule admitted that he had not yet read Carnot's theory sufficiently "to enter into a discussion of this theory of motive power of heat".²⁶⁰ The lack of a serious study of Carnot's theory led probably Joule to focus his criticism on Carnot's theory merely on the question of the interconversion of energy and heat. Thus, he failed to conceive the notion of the irreversibility inherent in Carnot's principle.²⁶¹ On the other hand, several circumstances seemed to favor Carnot's theory in Thomson's thinking. The attainment of an optimum mechanical effect for the Stirling hot air engine in 1847, the explanation of the

²⁵⁸ Smith, 1977, p. 241. Thompson, 1910, p. 266.

²⁵⁹ Thomson, W., 1848, p. 102; Thompson, 1910, pp. 268-269; Smith, 1977, pp. 245-246.

²⁶⁰ Quoted in Smith, 1977, p. 251.

²⁶¹ Joule commented on Carnot's theory through Clapeyron's paper at the end of his 1845 paper *On the changes of temperature produced by the rarefaction and condensation of air* (Joule, 1845b, pp. 382-383; JSP, 1884, pp. 188-189.). He rejected both Carnot's and Clapeyron's views on the lost work on the ground that no work (force) can be annihilated, "Believing that the power to destroy belongs to the Creator alone, I entirely coincide with Roget and Faraday in the opinion, that any theory which, when carried out, demands the annihilation o [force, is necessarily erroneous".

lowering of the freezing point of ice under pressure in 1848, and the discovery of the absolute temperature scale all through Carnot's cycle had demonstrated theoretically and experimentally the validity of Carnot's theory.²⁶²

Entangled between two opposing interpretations of the relationship between heat and mechanical effect, Thomson had communicated, in 1849, an account of Carnot's theory.²⁶³ He intended to answer two fundamental questions: first, the precise nature of the thermal agency (heat) that produced the mechanical effect, and second, the equivalence between heat and work. He gave answers in the context of Carnot's theory and the reversible operation of Carnot's perfect engine. Calorimetric measurements offered significant evidence to support Carnot's principle of the conservation of heat. "This is a fact which has never been disputed; it is first assumed without investigation and then confirmed by various calorimetric experiments. To deny it would be to reject the entire theory of heat, which forms the principal foundation".²⁶⁴ As discussed previously, calorimetric measurements did not confirm the conservation of heat but the insulation of the experimental setup. Thomson proceeded to calculate Carnot's coefficient for a wide range of temperatures. He based these calculations on the mathematical analysis of the Carnot-Clapeyron reversible cycle in combination with Victor Regnault's experimental data on pressure, latent heat, air density, and water vapor. The new aspect in this paper was Thomson's characterization of heat as a state function, modifying thus Carnot's principle.²⁶⁵ As a result, the work obtained from a cyclic change of state derives from the

 ²⁶² For a full account of the lowering of the freezing point of ice and the Stirling hot air engine, see. Thomson,
 W., 1847; 1850; Thomson, J., 1849; Smith, 1977, pp. 237-241; Smith, and Wise, 1989, pp. 295-300
 ²⁶³Thomson, W., 1849.

²⁶⁴ Thomson, W., 1849, p. 115.

²⁶⁵ In thermodynamics, a state function is the property of a system (entropy, enthalpy, internal energy, Gibbs and Helmholtz's free energy are state functions, but not heat) whose change does not depend on the

only change that occurs during the cycle, i.e., the transfer of heat (without loss) from high to low temperature. Nevertheless, Thomson appeared hesitant in accepting Carnot's theory beyond any doubt. Although he rejected Joule's experimental evidence for the *generation* of heat upon liquid friction²⁶⁶ on the ground of the lost work,²⁶⁷ he did not preclude the idea that heat may not be a substance (caloric). Since "several experimental facts appear nearly inexplicable in the actual state of this [Carnot's] theory".²⁶⁸ He repeatedly suggested (in various locations of the paper) that "although it [Carnot's principle] and with it, every other branch of the theory of heat may ultimately require to be reconstructed upon another foundation, when our experimental data are more complete".²⁶⁹

2.2 Rudolf Clausius

A year later, in 1850, Clausius published the paper, *On the moving force of heat, and the laws regarding the nature of heat itself which are deducible therefrom*, which announced that Carnot's theory on steam engines could be modified to agree with Joule's experimental findings.²⁷⁰ He read Carnot's theory presumably through Clapeyron's memoir and Thomson's *Account of Carnot's theory* of 1849. In the 1850 paper, Clausius stated that,

path by which the system arrives at its present equilibrium state. The value of a state function can be determined only from its values of the initial and final states of the system. Thomson's characterization of the quantity of heat in a reversible cyclic process (Carnot's cycle) as a state function ensured its transportation through the engine without loss.

²⁶⁶ Thomson, W., 1849, footnote p. 116.

²⁶⁷ Ibid, footnote pp. 118-119.

²⁶⁸ Ibid, p. 116.

²⁶⁹Ibid, p. 117.

²⁷⁰Clausius 1850. T. A. Hirst translated and edited this paper in English along with several other papers of Clausius. Hirst collected nine of Clausius' memoirs and published them in 1887 under the general title: *The mechanical theory of heat with its applications to the steam engines and the physical properties of Bodies*. This collection has useful mathematical appendices and explanatory notes added by Clausius himself (Clausius 1887). These papers were published first in Poggendorff's *Annalen der Physik* between 1850 and 1865 and later in the *Philosophical Magazine* but without appendices and notes.

"he did not imagine that the difficulties were that great as Thomson considered them to be". He thought that "*no* heat is lost: for it is quite possible that in the production of work both may take place at the same time; a certain portion of heat may be consumed, and another portion transmitted from a warm body to a cold one; and both portions may stand in a certain definite relation to the quantity of work produced".²⁷¹ This statement had the place of a maxim, which constituted the prelude of the second law of thermodynamics. As Clausius stated, "in all cases where work is produced by heat, a quantity of heat proportional to the work done is expended; and inversely, by the expenditure of a like quantity of work, the same amount of heat may be produced".²⁷²

In 1854, Clausius published the article *Über eine veränderte Form des zweiten Hauptsatzes der mechanischen Wärme theorie* (on a modified form of the second fundamental theorem in the mechanical theory of heat). This essay was the fourth memoir in Hirst's collection. Clausius stated the second law of thermodynamics, as it is known today: "heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time".²⁷³

Clausius' discovery of 1850 was regarded as not creative, although not deprived of imagination. Clausius succeeded in resolving the conflict between Carnot and Joule's two approaches by merely eliminating from Carnot's theory the view that heat is conserved and incorporating Joule's view on the equivalence of heat and work. This combination appeared to be relatively trivial. Others expressed favorable views and praised the creativity of Clausius. They argued that Clausius' theory was not a simple combination of

²⁷¹ Clausius, 1887, p. 17.

²⁷² Ibid, p. 18.

²⁷³ Ibid, p. 117.

Carnot and Joule's experiments.²⁷⁴ "This memoir marks an epoch in the history of physics," wrote Gibbs in an obituary of Clausius in 1889. "...it might have been said at any time since the publication of that memoir, that the foundation of the science [of thermodynamics] was secure, its definitions clear, and its boundaries distinct".²⁷⁵ In his book *Thermodynamics and chemistry*, Pierre Duhem wrote, "It was Clausius who, in an imperishable memoir, reconciled Carnot's theorem with the principle of equivalence. However, Clausius did not limit himself to the realization of this work, which alone would have assured him the admiration of physicists. He generalized and transformed Carnot's theorem into one of natural philosophy's most important and fruitful principles. It is with justice that the name of Principle of Carnot and Clausius is given to the great law that they established".²⁷⁶

This article provides much other information. It signifies the beginning of the remarkable intellectual journey from the conservation of energy of bodies to the increasing entropy of the universe. In this first memoir, Clausius concludes that (a) the internal energy is a state function, but not the work and heat being dependent on the path of contiguous changes of the body, (b) the internal energy is a function of temperature, but independent of volume (for perfect gases), (c) the specific heats of gases are independent of temperature (this conclusion was proven later to be wrong at high temperatures), (d) based on this assumption, he examines the isothermal and adiabatic processes, although he does not apply these results to Carnot's cycle, and (e) the difference and the ratio of the specific heats under constant pressure and constant volume, respectively, are constant quantities. In

²⁷⁴ See, for instance, Meheus, 1999, pp. 90, and 92-94.

²⁷⁵ Quoted in Klein, 1969, p. 129.

²⁷⁶ Duhem, 1903, pp. 75-76.

addition, Clausius exposed the first law of thermodynamics analytically and defined internal energy²⁷⁷ as the sum of the heat content of the body and the portion consumed by performing interior work.²⁷⁸ Nevertheless, Clausius' analysis of the second law did not reach anything like entropy. Clausius introduced entropy fifteen years later, in 1865, as described in his ninth memoir of the collection.

2.3 William John Macquorn Rankine

William Rankine made his appearance during the conflict for priority that broke up between Clausius and Thomson in 1850. He read to the Royal Society of Edinburgh the paper *On the Mechanical Action of Heat, especially in Gases and Vapours*.²⁷⁹ Rankine revealed his motivation for writing this article in a letter sent to the editor of the *Annalen der Physik und Chemie*, J. C. Poggendorff:²⁸⁰ "...I have arrived at conclusions respecting the specific heat of gases and vapors, and the latent heat of evaporation, agreeing with those of M. Clausius and deduced from principles, and using a method, which, although differing in some details from those employed by him, are the same in their essential points". He introduced a molecular theory, modeling the transportation of heat through the hypothesis of molecular vortices.²⁸¹ This model was similar to assumptions put forward by others,

²⁷⁷ Thomson was first to propose the term internal energy adopted by Clausius. However, in his attempt to indicate the two constituents of the internal energy separately, Clausius invented two new terms, namely *thermal* and *ergonal* content for the free heat and the interior work, respectively (Clausius, 1887, p. 254.) ²⁷⁸ Clausius, 1887, pp. 29, and 78. Clausius gave a deeper analysis of the first law in the fourth memoir of the collection (Clausius, 1887, pp. 112-116). In the sixth memoir, he considered the effect of the interior work on the thermodynamic state of the body (see below).

 ²⁷⁹ Rankine, 1850. The same paper was published in a collection of Rankine's papers, the *Miscellaneous Scientific Papers* in 1881, although with a slightly different title than the German article (1881, pp. 234-284). Rankine gave a short account of this paper in a letter sent to J. C. Poggendorff, the editor of the *Annalen der Physic and Chemie* (Rankine, 1851a). This letter has been translated into English (Rankine, 1851b).
 ²⁸⁰ Rankine, 1851b, p. 172.

²⁸¹ Rankine, 1850, pp. 234-243.

including Davy and Joule. However, Rankine's treatment was different because he had formulated this theory in a rigorous mathematical language. Through this model, Rankine explained the mechanism of changing the elasticity of bodies produced by heat and explained the cause of absorption and radiation of heat. Nevertheless, the obscurity of the physical details and metaphysical explanations involved in this molecular model of vortices and the lack of an accurate statement for the second law deprived Rankine of full credit as one of the founders of the second law of thermodynamics.

Rankine was aware of the experiments performed by Joule and noted in his paper of 1850 the variability of the values obtained by Joule for the mechanical equivalent of heat. He ascribed these discrepancies to "the smallness of the differences of temperature measured in those experiments renders the numerical results somewhat uncertain, it appears to me that, as evidence of the convertibility of heat and mechanical power, they are unexceptionable".²⁸² He thought that the values of the mechanical equivalent of heat must be lower than the values calculated by Joule. The Scottish mechanical engineer proposed the measurements of the velocity of sound as an alternative method, which appears to be a valid experiment independent of any sophisticated apparatus. However, he changed later his view about the accuracy of Joule's experiments and calculations. He sent a statement of corrections and modifications of the results to the Royal Society of Edinburgh, giving this time full credit to the accuracy of Joule's results. "That the agreement amongst the results from substances so different,²⁸³ shows that the error by unknown losses of power is insensible, or nearly so." and he refers to the dynamical

²⁸² Rankine, 1850, p. 244.

²⁸³ Joule performed experiments on the heat of friction using thermal carriers steam, mercury and cast iron.
Moreover, Rankine recognized the large number of repetitions that Joule conducted for each experiment.

equivalent being close to Joule's figures. Thus, by the end of 1850, Rankine had fully adopted Joule's framework of mutual convertibility of heat and work and his figure for the dynamical equivalent of heat.

Rankine had read the 1850 paper of Clausius Über die bewegende Kraft der Wärme and agreed with Clausius' opinion regarding the correctness of the equivalence of heat and work calculated by Joule. However, he thought that Clausius did not wholly express it in the language of mutual convertibility of heat and work. Furthermore, Rankine had some doubts about the completeness of the proof regarding the second law offered by Clausius. It seemed to him somewhat unsatisfactory, "I always thought the principle of Clausius [the second law statement] to which you [Thomson] refer had an appearance of probability; but I was not satisfied with his mode of proving it."²⁸⁴ Thomson had sent Rankine the 1850 Clausius paper about *the moving power of heat*. Therefore, Thomson was aware of the work of Clausius before the publication of his famous series of articles on the new theory of heat under the general title *On the dynamical theory of heat*. Contrary to Thomson and Clausius, Rankine did not raise any priority claim and did not involve in the Clausius-Thomson dispute.

Section 3. Thomson resolves his ambiguities and enunciates the second law of thermodynamics

In March 1851, Thomson published the first paper of five contiguous articles in the *Transactions of the Royal Society of Edinburgh*. Later, in 1952, the same article was published in the *Philosophical Magazine*.²⁸⁵ With this paper, Thomson came to accept

²⁸⁴ Letter from Rankine to William Thomson in 17th of March 1851 (Quoted in Smith, *1977*, p. 260).
²⁸⁵ Thomson, W., 1851.

formally the dynamical theory of heat and the conclusions derived previously by Joule, Rankine, and Clausius regarding the mutual transformation of heat and work. Thomson had the honesty to ascribe to them (as well as to Mayer) the credit for discovering the two laws of thermodynamics.²⁸⁶ Thomson made clear that his intention in this article was to communicate a new theory of heat, the dynamical theory of heat. Thomson sought to reconcile Carnot's theorem of a perfect thermodynamic engine and Joule's mutual convertibility of heat to work. To strengthen the significance of the dynamical theory, he made a complete reinterpretation of his previous calculations presented in his 1949 article based on Regnault's observations on steam engines. Recall that this article was an account of Carnot's theory. This study led to a fundamental axiom, which constituted an alternative statement for the second law of thermodynamics, namely, "It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects".²⁸⁷ He founded the dynamical theory of heat in two propositions, the validity of which demonstrated accordingly through applying the new theory to physical and chemical processes. In the first proposition, Thomson adopted Joule's principle of mutual convertibility of heat and mechanical effect (work).

Proposition 1. When equal quantities of mechanical effect are produced by, whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or generated.

²⁸⁶ Ibid, pp. 175-176.

²⁸⁷ Thomson, W., 1851, p. 179. Thomson explained the consequence of this statement in a footnote. "If this axiom be denied for all temperatures, it would have to be admitted that a self-acting machine might be set to work and produce mechanical effect by cooling the sea or earth, with no limit but the total loss of heat from the earth and, or, in reality, from the whole material world".

The confirmation of this proposition signified Thomson's abandonment of the caloric theory in favor of heat as a motional process. In the proof of this proposition, he concluded that, "the heat which a body emits or absorbs will be the thermal equivalent of the work done upon it by external forces, or done by it against external forces".²⁸⁸ In the second proposition, Thomson dealt with the state of reversibility as expressed by Carnot and modified by Clausius in 1850.

Proposition II. If an engine were such that, when it is worked backwards, the physical and mechanical agencies in every part of its motions are all reversed, it produces as much mechanical effect as can be produced by any thermodynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat.

He based the proof of the second proposition on the truth of the axiom stated above and demonstrated by a thought experiment. He assumed two adjustable thermodynamic engines, for example, B and A. The engine B works reversibly in a cycle. At the same time, A is more efficient than B, and both are sharing the same boiler and refrigerator. The engine B runs backward and restores heat at the hot reservoir regardless of the quantity of heat that A had extracted. Recall that A is more efficient than B; then A will transport less heat to the refrigerator than B had extracted. Also, A will produce more work than is required to operate B. The operation will end up with engine A powering B and, at the same time, delivering work. Thomson concluded, "We should thus have a self-acting machine, capable of drawing heat constantly from a body surrounded by others at a higher temperature and converting it into mechanical effect. But this is contrary to the axiom, and therefore we

²⁸⁸ Ibid, pp. 178-179.

conclude that the hypothesis that A derives more mechanical effect from the same quantity of heat drawn from the source than B is false".

The first proposition was also a query of the lost work that tormented his mind since 1842 when he made his acquaintance with Fourier's treatise on heat conduction and later in 1848 while reading Carnot's *Reflexions*. He felt that mechanical work that did not appear in direct thermal conduction or the remaining work that left in a perfect engine after the small portion of mechanical work obtained by the heat transformation was "irrecoverably lost to man, and therefore wasted, although not annihilated".²⁸⁹

Later, in 1852, Thomson published a short paper, *On a universal tendency in nature* to the dissipation of mechanical energy.²⁹⁰ He clarified the notion of the lost work and explained what he had meant by the abstruse term dissipation of energy. He made his intentions clear from the first paragraph of the paper. "**The** object of the present communication is to call attention to the remarkable consequences which follow from Carnot's proposition, that there is an absolute waste of mechanical energy available to man when heat is allowed to pass from one body to another at a lower temperature, by any means not fulfilling his criterion of a *perfect* thermo-dynamic engine, established, on a new foundation, in the dynamical theory of heat".²⁹¹ He further used the axiom of the second law (vide supra) and classified the different sources of the "*dissipation* of mechanical energy". He placed the transformation of mechanical work into heat in reversed thermal engines next to the irreversible processes of friction, thermal conduction, and thermal radiation, in which the dissipation of energy made the complete restoration of the

²⁸⁹ Ibid, p. 189.

²⁹⁰ Thomson, W., 1852.

²⁹¹ Ibid, p. 304.

mechanical work impossible.²⁹² Friction and conduction were the two processes utilized by Thomson to estimate the loss of mechanical work upon dissipation experienced by a perfect steam engine. In the end, he draws the following general conclusions relating to his central concept of dissipation.²⁹³

1. There is, at present in the material world, a universal tendency to the dissipation of mechanical energy.

2. Any restoration of mechanical energy without more than an equivalent of dissipation, is impossible in inanimate material processes, and is probably never effected by means of organized matter, either endowed with vegetable life or subjected to the will of an animated creature.

3. Within a finite period of time past the earth must have been, and within a finite period of time to come to the earth must again be, unfit for the habitation of man as at present constituted, unless operations have been, or are to be performed, which are impossible under the laws to which the known operations going on at present in the material world are subject.

So far, I have discussed Thomson's views on the second law, the lost work, and the dissipation of energy basically from primary sources (Thomson's scientific papers). It is worthwhile at this stage to explore the reasons that prompted Thomson to abandon the caloric theory of heat in favor of the motion theory of heat. Why Thomson was so slow to accept the dynamical theory and its implications, while scientists like Rankine and Clausius, who were not so close to Joule as Thomson was, assimilated much easier Joule's experiments? It is plausible to assume that the long debate with Joule, the exchange of

²⁹² TIbid, pp. 304-305.

²⁹³ Ibid, p. 306.

illuminating letters with Rankine, and the 1850 article of Clausius must have exerted intense pressure on Thomson's mind. Undoubtedly, these men influenced Thomson's dramatic shift from a broad-minded uncertainty about interconversion in 1849 to the uncompromising assertion of irreversible dissipation in 1851 and 1852. Thomson's inmate meticulous methodology of investigating scientific issues and his admiration for Carnot's theory on steam engines cannot be ruled out as steady convictions that affected his views. Furthermore, the replacement of the caloric theory by a new theory did not make it necessary since the former theory was adequate to explain many aspects of thermal phenomena satisfactorily, as noted previously. Besides, the physical process in which heat is transformed into work still lacked experimental evidence although the thermoelectric effect discovered by Thomas Johann *Seebeck* (1770-1831) in 1821 was such an example.²⁹⁴

The answer behind Thomson's bend into the dynamical theory is twofold and founded in the realms of mechanics and philosophy. Thomson noted that if heat transformation into work explained the work produced in steam engines as Joule supported, then the heat was not a state function. In a closed system of states, the body had to absorb more heat along one portion of the cycle than it emitted along the return portion of the same cycle. This procedure meant that since heat change depends on the path from an initial to a final state, it could not be conserved. Heat is not a state function. In this respect, a new view for the theory of heat than the caloric theory is required, and the dynamical theory

²⁹⁴ Seebeck rediscovered independently Alessadro Volta's (1745-1827) observation in 1894, that an electric potential difference is developed across the junction of two electrically conducting materials (metals) when a temperature difference is applied between them. Seebeck observed that a compass needle would be deflected by a closed loop formed by two different metals joined in two places, with an applied temperature difference between the joints. Howeve, Seebeck did not recognize that an electric current was involved in this effect. Thus he called the phenomenon *thermomagnetic effect* (Seebeck, 1922). Ørsted reexamined the phenomenon and coined the term *thermoelectricity* (Ørsted, 1823).

satisfies this need. The second piece of evidence that made Thomson feels an inclination towards the dynamical theory of heat has its origin in the notion of the body's internal energy, identified as the body's vis viva. What is the relationship between vis viva and heat? The answer to this question was of great importance for Thomson. The answer to this question was of considerable significance for the nature of heat. Heat might be related to the vis viva of a body. It could be a state of motion that originated from intermolecular forces within the body, for example, during heat conduction from one part of the body to another. "the propagation of heat consists in the communication of vis viva from molecules in motion to contiguous molecules of the body, and unless any portion of the vis viva be lost in producing changes in the dimension, or the arrangement of the body against a resistance, or some be gained [...] by the reverse process, the quantity of heat remains constant. Thus the ordinary method of estimating quantities of heat is consistent with the dynamical theory".²⁹⁵ In these remarks, conservation of vis viva during conduction replaces the older doctrine of the conservation of caloric. In contrast, the loss of vis viva would be equal to the lost work.

However, more profound issues lay behind Thomson's thinking to espouse the new theory of heat. Thomson's reflection stems from his theology and philosophy of nature rooted in the fundamental beliefs of his time. Thomson and other scientists like Joule, or Faraday, vigorously supported the belief that the power to annihilate mechanical effect was the privilege of God alone. As a result, "Energy has here clear theological associations, being an indestructible entity, created, sustained, and destructible only by God's power.

²⁹⁵ This passage was taken from Thomson's draft of his 1851 paper. Transcripts of the draft were published in Smith, *1877*, p. 284.

Creation and annihilation of energy concerning human beings are impossible".²⁹⁶ In other words, Thomson, following the voluntarist tradition for the natural philosophy that had prevailed in Scotland, since the eighteenth century placed energy conservation within this theological perspective,²⁹⁷ "all created things must be sustained' or 'the continual presence of God is necessary to preserve as to create".²⁹⁸ Thomson saw the lost work and the dissipation of energy within the context of the voluntarist philosophy of nature. He spoke about them in terms of belief. He argued that the problems arose from the loss of useful work in friction and conduction, resulting in a necessary energy diffusion, which only God Himself could restore to its original concentration. Dissipation had finally become an issue independent of conservation, "God alone could create or annihilate energy, and God alone could restore the original distribution or arrangement of energy in the created universe".²⁹⁹ Thomson resolved the principle of the dissipation of energy within the realm of theology.

²⁹⁶ Thomson's draft of his 1851 paper; Smith, 1977, p. 264

²⁹⁷ From Thomson's notebook, we know that he attended the introductory lecture in the senior natural philosophy class at Glasgow College given by William Meikleham (1771–1846), professor of astronomy at the University of Glasgow. In his lectures, Meikleham put forward three general reasons for the study of natural philosophy. First, it "extends our power over nature by unfolding the principles of the most useful arts". Second, "it gratifies the mind by the certainty of its conclusions, by its great extent and by explaining phenomena". And third, "above all it leads us to view the Creator as the Great First Cause, and as maintaining the energies of nature". Thomson's 1846 introductory lecture advocated a study of natural philosophy for much the same reasons: practical benefits, intellectual satisfaction, and, most importantly, the approach to God by obtaining knowledge of the laws of nature established by Him "for maintaining the harmony and permanence of his Works". The intimate connections suggested here between Gods, man, and nature characterizes the role of natural philosophy in Glasgow College. William Thomson, Notebook of Natural Philosophy class, 1839-40, NB9, ULC; Introductory lecture [1846]', in Thompson, 1910, pp. 239-251. ²⁹⁸ Quoted in Smith, and Wise, 1989, p. 84.

²⁹⁹ Ibid, p. 332.

Section 4. The discovery of entropy

As noted, Clausius had supplemented Carnot's principle to agree with Joule's experiments on the mutual inter-convertibility of heat and work. In his approach to reconciling these two divergent directions of heat transfer, Clausius considered two kinds of transformation, i.e., transformation of heat into work (transformation of the first kind) and the transformation due to the passage of heat from a warmer to a colder body.³⁰⁰ Both transformations co-occurred during a cyclical process similar to Carnot's reversible cycle. The occurrence of one transformation presupposes the incidence of the other. In other words, these two transformations are equivalent in the sense that the transformations of the first kind can replace the second transformation. It means that the transformation of heat into mechanical work at the higher temperature can be transformed back into heat at the lower temperature. Clausius sought to find the relation between these two transformations and the magnitude of their equivalent values. He first decided to separate the two transformations, find appropriate mathematical expressions for their equivalent values, and finally define the total effect (total sum) of the equivalent values of both transformations. He achieved the first goal through a circular process of six steps,³⁰¹ in which he denoted with Q, the quantity of heat of the first transformation of heat into work at a temperature t_1 and Q_1 , the quantity of heat associated with the second transformation, that is, the heat flowing from temperatures t_1 to t_2 . The equivalent values of these two transformations were the product of the quantity of heat responsible for the respective transformation multiplied by a function of temperature f(t). Accordingly, the equivalent value for the first

³⁰⁰ Clausius discussed this issue in the fourth memoir, Clausius, 1887, pp. 111-135, and in his 1854 publication in *Annalen der Physik* (Clausius, 1854).

³⁰¹ Clausius, 1887, pp. 119-120. See also Cardwell, 1971, pp. 264-265.

transformation at the temperature t_1 takes the form $Q \cdot f(t_1)$. The quantity of heat Q released by the system is transformed into work. Therefore, its value $Q \cdot f(t_1)$ is negative.³⁰² Accordingly, the second transformation from temperature t_1 to temperature t_2 is represented by the product

 $Q_1 \cdot f(t_1, t_2; t_1 > t_2)$. The equivalent value of the total transformation is the sum of the individual transformations, which come about concurrently, i.e., $Q \cdot f(t_1) + Q_1 \cdot F(t_1, t_2)$. For constant temperature, the function f(t) takes the convenient form of 1/T,³⁰³ where *T* is the absolute temperature. This function is independent of the nature of the process by which the transformation is achieved.

At this stage, Clausius articulated the first fundamental theorem of the equivalence of the transformations.³⁰⁴ If two transformations which, without necessitating any other permanent change, can mutually replace one another, be called equivalent, then the generation of the quantity of heat Q of the temperature t from work has the equivalencevalue $\frac{Q}{T}$, and the passage of the quantity of heat Q from the temperature t_1 to the temperature t_2 , has the equivalence-value, $Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$, wherein T is a function of the temperature, independent of the nature of the process by which the transformation is effected. In this case, when $Q_{T_2} = Q_{T_1}$, it is evident that the passage of the quantity of heat Q, from the temperature t_1 to temperature t_2 , has the same equivalence value as a double transformation of the first kind, that is to say, the transformation of the quantity Q, from the heat at the temperature t_1 into work, and from work into heat at the temperature t_2 .

³⁰² Ibid. p. 124.

³⁰³ Ibid, p. 125.

³⁰⁴ Ibid, pp. 125-126.

Next, Clausius generalized the problem assuming that several bodies K₁ K₂, K₃, etc., may serve as reservoirs of heat at t temperatures t_1 , t_2 , t_3 , etc., have received during the process the quantities of heat Q_1 , Q_2 , Q_3 , etc., then the total equivalent value N of all the transformations that might be taking place in a circular process, whatever complex could be, will be given by³⁰⁵

$$N = \frac{Q_1}{T_1} \pm \frac{Q_2}{T_2} \pm \frac{Q_3}{T_3} \pm \dots = \sum_{i=1}^{i} \frac{Q_i}{T_i}$$
(3.1)

The ratio $\frac{Q_i}{T_i}$ (i = 1, 2, 3, etc.) is the *equivalent values for each transformation of both kinds*. Eq. (3.1) represents an algebraic summation of equivalent values dependent on the sign of the quantities of heat absorbed or evolved upon the transformation.³⁰⁶ Furthermore, Eq. (3.1) holds for constant or nearly constant temperature. When the temperature of one or more bodies changes considerably during the process, the summation of Eq. (3.1) should be replaced by an integral, namely

$$N = \int \frac{dQ}{T} \tag{3.2}$$

dQ is the element of heat (an infinitesimal quantity of heat), indicating the body's temperature when receiving it. The area inside the circular path traced according to Watt's indicator for the steam engines used by Clapeyron to represent Carnot's cycle graphically estimates the integral in Eq. (3.2). For a reversible cycle of operations or a *compensated transformation* of Clausius' terminology, Eqs. (3.1), and (3.2) equals zero. In this case, the transformations that occur during the reversible cycle must cancel each other so that their

³⁰⁵ Ibid, p. 127.

³⁰⁶ The work induced or done to the body or a system of bodies upon absorbing a quantity of heat is conventionally negative in sign. In contrast, the absorbed quantity of heat has a positive sign. The work expended or done by the body or a system of bodies upon emitting a quantity of heat is positive in sign, whereas the heat given off is negative (Clausius, 1887, p. 329).

algebraic sum becomes zero. For an irreversible process or an *uncompensated transformation*, according to Clsusius' denomination, such as friction, percussion, or heat conduction from one body to another of different temperatures, these equations take a positive value.³⁰⁷ Values other than zero mean that the positive and the negative equivalent values of irreversible transformations are not equal, as in the reversible processes.³⁰⁸ Still, the net effect is positive, i.e., the positive transformations dominate the negative ones. The theorem respecting the equivalence-values of the transformations may accordingly be stated thus: *The algebraic sum of all the transformations occurring in a cyclical process can only be positive, or, as an extreme case, equal to nothing*". The following general form combines both processes,

$$\int \frac{dQ}{T} \ge 0 \tag{3.3}^{309}$$

Equation (3.3) consists of the general mathematical expression of the *theorem of the equivalence of transformations*.³¹⁰ Furthermore, Eq. (3.3) is the mathematical expression of the entropy, a fundamental quantity, which underscores the second law of thermodynamics. The entropy is a quantitative measure that shows the direction followed by spontaneous (irreversible) processes occurring in nature. The inequality (3.3) explains the famous Clausius' statement nicely: "The entropy of the universe tends to a maximum",

³⁰⁷ Ibid, pp. 127-131, and 138. Cardwell, 1971, pp. 265-267.

³⁰⁸ In an irreversible circular process, the quantity of heat flowing from the higher to lower temperature is greater than the quantity of heat transformed into work. Engineers of steam engines knew this effect and tried to diminish heat loss by a mere transfer from the boiler to the refrigerator. Furthermore, due to the second law of thermodynamics, the net effect of the equivalent transformations associated with heat flow must be positive. This conclusion is supported by the fact that the work produced at the higher temperature O1 / T1 is negative and lower than the work expended at the lower temperature, which is positive, O2 / T2. (T1 >T2)

³⁰⁹ Modern textbooks of physical chemistry and thermodynamics write this integral equation as $\oint \frac{dQ}{T} \ge 0$. The cyclic or contour integral sign \oint denotes in general a cyclical process. ³¹⁰ Clausius' sixth memoir, 1887, pp. 218-219.

which is another way of expressing the second law of thermodynamics. At constant temperature, The change of the entropy of a system transformed at constant temperature T from the initial state 1 to the final state 2 in a cyclic process is equal to

$$S_2 - S_1 = \int_1^2 \frac{Q}{T}$$
(3.4)

dQ is the element of heat that the system receives or liberates to the environment. S_1 and S_2 are the entropies of the system in states 1 and 2, respectively. When the system undergoes a reversible process and receives heat from the environment, then its entropy increases by $\int_1^2 \frac{Q}{T}$, while the entropy of the environment decreases $-\int_1^2 \frac{Q}{T}$. The total result is zero, i.e. $S_2 - S_1 = 0$, or $S_2 = S_1$. When the system undergoes an irreversible change (spontaneous process) from a state 1 to a state 2, its entropy change is no longer equal to $\int_1^2 \frac{Q}{T}$. According to Thomson's theorem of the dissipation of energy, less work is obtained from the system in an irreversible change than in a reversible one; the heat absorbed is also less, and therefore

$$S_2 - S_1 > \int_1^2 \frac{Q}{T}$$
, or $S_2 - S_1 - \int_1^2 \frac{Q}{T} > 0$ (3.5)

In other words, the total entropy change of the system and its surroundings is positive, i.e., when an irreversible change takes place, the entropy of the universe increases, the latter being considered an isolated system.

The double valued entropy (zero for reversible and positive for irreversible changes) is well known to physicists of later generations, it survived intact until our days. However, it took Clausius eleven years to define and publish the quantity he called entropy. The few pages in current textbooks of thermodynamics and physical chemistry referring to entropy and its applications do not reveal the long and hard road it took for entropy to enter higher education. Clausius had first to solve the puzzle of the transformations associated with the body's internal work and then express its equivalent value since the theorem of the equivalence of transformations concerned only with the external work owing to exterior forces exerted on or by the body under consideration. Filling this gap Clausus delayed publishing his theory of the equivalence of transformations in its complete form for some eight years. Reference to entropy in current textbooks of physical chemistry retains only the general idea of this physical quantity.

Clausius had described in a concise form in his sixth memoir the long process of the evolution of his thoughts towards the definition of entropy and the mathematical expression of the second law of thermodynamics.³¹¹ Clausius separated entropy into components in order to deal with the inherent properties of this thermodynamic quantity that characterized the spontaneous changes in the physical system and its surroundings. He asked, what were the changes induced in the state of a body while absorbing heat from an external thermal source? Part of this heat (energy) is transformed into exterior work dW to overcome external forces, the same way as the work expended by gases to overcome the external pressure upon expansion. Another part of the heat is transformed into interior work denoted by *I* required to overcome existing interactions between the particles (atoms or molecules) of the body and a third part is stored within the body. The last component is the thermal content *H* or the internal heat of the body. The change of the body's internal energy, dU may be expressed as dU = dH + dI

$$\mathrm{d}U = \mathrm{d}H + \mathrm{d}I \tag{3.6}$$

³¹¹ Clausius, 1887, pp. 215-266.

Clausius proceeded to define the last two components and express their equivalent values. and connect these values with the increments of the absorbed heat, which was the origin of their existence. The determination of the quantity of the thermal component denoted by Hand its change by dH presented no trouble whatever the amount of heat present in the body. However, the definition of the interior work I, and its change denoted by dI, was not an easy task, since no one knew about the nature of the particles of the body and, in particular, the nature of the intermolecular forces.³¹² Only the sum of dI and the exterior work dW can be estimated. i.e. the total work dL,³¹³

$$dL = dI + dW \tag{3.7}$$

Clausius avoided this difficulty introducing the new concept of *disgregation* Z of the body and its infinitesimal change dZ, the latter being considered proportional to the total work, dL, i.e.,³¹⁴

$$dL = JTdZ \text{ or } dZ = \frac{dL}{JT}$$
(3.8)

J is the mechanical equivalent of heat. The *disgregation* adopted by Clausius describes the degree of dispersal or the disorder of the particles constituting the bodies without reference to their velocities. *Disgregation* denotes the alteration of the state of aggregation of bodies by heating. The strength of the intermolecular interactions determines the degree of molecular rearrangement and thereby the magnitude of *disgregation*. It is more significant for gases than that for liquids. The *disgregation* of liquids is greater than that of a solid

³¹² The magnitude of the internal energy, dU may be expressed as dU = dH + dI. dI cannot be determined. Only the sum of dI and the exterior work dW, i.e. the total work dL = dI + dW is estimated (Clausius, 1887, footnote, pp. 225-226).

³¹³ Clausius, 1887, footnote, pp. 225-226.

³¹⁴ Clausius, 1887, pp. 227.

(following the entropy order).³¹⁵ Using the mathematical expression of the first law of thermodynamics and making the appropriate substitution, Clausius obtained

$$dQ = dU + JdW = dH + JdI + JdW = dH + dL = dH + TdZ$$
(3.9)

or, dividing by *T*, and upon integration,

$$\int \frac{dQ}{T} = \int \frac{dH}{T} + \int dZ \tag{3.10}$$

The last term of the expression (3.10) is the equivalent value of the *disgregation* representing the third transformation, in theory, describing the change of the rearrangement of the constituent molecules. For finite reversible cyclic processes, the expression (3.10) equals zero, since each equivalent value of the transformations in this expression goes to nothing for a reversible circular change, namely

$$\int \frac{dQ}{T} - \int \frac{dH}{T} - \int dZ = 0 \tag{3.10a}$$

After rearranging, Clausius obtained Eq. (3.11)

$$dS = \int \frac{dQ}{T} = \int \frac{dH}{T} + \int dZ \tag{3.11}$$

Clausius denoted the equivalent value of the left-hand side of Eq. (3.11) by dS and called the quantity S entropy.³¹⁶ From Eq. (3.11), Clausius concluded that the entropy depends first on the heat content of the body dH and secondly on the disgregation. Thus, *disgregation* may be thought of as the precursor of the entropy used today in physical chemistry textbooks. Therefore, the entropy constitutes a measure of the dispersal of

³¹⁵ The order Z(gas) > Z(liquid) > Z(solid) is justified by the fact that the strength of the intermolecular interactions decreases progressively from the gas phase to the liquid and solid phases. The gas molecules move freely at high velocities, and they have more room and more positions in which they can be arranged than the liquid and solid molecules.

³¹⁶ The symbol S initially designated the *transformational content* of the body. Later, Clausius thought it better to use the word entropy originated from the Greek word $\tau \rho \sigma \pi \dot{\eta}$, meaning *transformation*. As he said, "I have intentionally formed the word entropy to be as similar as possible to the word energy" (Clausius, 1887, p. 357).

matter, or, more accurately, its capacity to assess the degree of disorder of a body or several bodies that compose a physical system. An ordered system has low entropy, whereas a higher entropy characterizes a disordered system and vice versa. Highly disordered states are distinguished by a higher entropy associated with a greater magnitude of *disgregation* discussed above.

The size of the entropy for an irreversible or uncompensated process is equally important because it indicates the direction of spontaneous processes (such processes are all irreversible) occurring in nature. From the inequalities (3.3) and (3.5), Eq. (3.11) can have a positive value,

$$dS = \int \frac{dH}{T} + \int dZ > 0 \tag{3.11a}$$

Consequently, an irreversible process is accompanied by an increase in entropy according to the property of entropy to designate the direction of physical or chemical changes.³¹⁷ This conclusion is in accord with current observations for irreversible processes, such as the free expansion of a gas or a chemical reaction in a voltaic cell producing electricity. Nevertheless, entropy in inequality (11a) is decomposed into two integrals, and therefore, it is expedient to discuss the contribution of each component to the magnitude of the entropy. A prerequisite to assess the contribution of each such component is the study of the specific conditions under which an irreversible change occurs. For instance, it is known that a perfect gas undergoes free expansion without the production of wor. The absence of

³¹⁷ The state of increasing entropy holds for isolated systems that cannot exchange either energy or matter outside the system's boundaries (with the surroundings of the system). In contrast, in closed systems, the entropy may decrease due to heat transfer beyond their boundaries. In this case, the entropy of the surroundings will increase. The increase of the entropy of the surroundings will compensate for the decrease in the entropy of the system. The result will be a net increase in the entropy of the pair systemenvironment. Eleven years later, Willard Gibbs clarified this situation with his two renowned statements on equilibrium (chapter 6, section 2 of this dissertation).

intermolecular forces in an ideal gas ensues no change in its internal energy, i.e., no heat is evolved (d*H*/*T* remains constant). However, the volume increase during expansion disturbs the arrangement of the gas particles, thus increasing the disgregation and inducing an increase in entropy. On the other hand, when the gas receives external heat under constant volume, the *disgregation* cannot possibly change (dZ remains constant) because there is no molecular rearrangement—however, the heat content $\int \frac{dH}{T}$ increases, leading to an increase in the entropy of the system (Eq. (9.11a)).

The sixth and the ninth memoirs of Clausius' collection contain the analytical formulation of the theorem of the equivalence of transformations that led to entropy. The sixth memoir, *On the application of the theorem of the equivalence of transformation to interior work*, was published in 1962. The ninth memoir *On the determination of energy and entropy of a body* was published in 1865.³¹⁸

The concept of entropy had a great cosmological application, as noted by Clausius, and seemed to be a valuable tool for resolving theoretical problems in chemistry, such as chemical affinity and chemical equilibrium. However, Clausius' contemporaries ignored entropy. Thomson never mentioned entropy in his work, and even Clausius himself did not give entropy any prominent place in his research. Chemists did not understand this new concept, let alone its use in their laboratory. An exception was August Horstmann, who employed disgregation and entropy in 1869 and 1873 as a guide to study the dissociation of chemical substances. The founders of the new discipline of physical chemistry (Ostwald, Arrhenius, Van 't Hoff) chose to avoid any reference to entropy. In contrast, Planck, who

³¹⁸ Clausius, 1887, pp. 366-376.

contributed to the development of modern chemical thermodynamics, applied entropy in his theoretical treatment of the dissociation/osmotic pressure theories of the ionists.

The next generation of chemists was familiar with entropy, but they preferred to use alternative measures for the chemical affinity and chemical equilibrium. Gibbs used primarily the chemical potential and the free energy at constant pressure, Helmholtz the free energy at constant volume, and Duhem his thermodynamic potentials. The entry of entropy in research and education began decades after the First World War, especially by the American chemists.³¹⁹

³¹⁹ Kragh, and Weininger, 1996 give an excellent historical account for the tortuous process of entropy assimilation in chemical research and education.

Chapter 4. The development of thermodynamics in the context of chemistry and physiology: The law of conservation of energy

The laboratory practice of classical thermodynamics by chemists proved to be a slow process. For several reasons, thermodynamics in chemistry laboratories began relatively late, during the last two decades of the nineteenth century. Despite this fact, chemists have made significant contributions to the first law of thermodynamics. Chemists were those who established the new specialty of thermochemistry based on conservation law. Chemists formed a new perception of the conservation law by extending its application to multi-component systems being in a state of equilibrium. Willard Gibbs had thoroughly studied conditions of equilibrium of multicomponent systems using examples from chemistry. Pierre Duhem offered new interpretations of irreversible processes by combining thermodynamics with chemistry and employing Lagrange's analytical mechanics. Their work in thermodynamics will be examined in the second part of this dissertation. In this chapter, I will give a short account of the conditions in which chemistry functioned as a medium for the discovery of the first law. In particular, I will look into the theoretical and experimental efforts of several scientists of different disciplines, including chemists, electrochemists, and physiologists who worked alone or in collaboration or even in competition to one another to solve specific problems in their research fields. Efforts from men of different traditions, cultures, scientific styles, and interests converged to the discovery of the conservation law either as the result of a carefully scheduled experimentation or as an unintentional outcome disconnected with any prior arrangement. Electricity and experimental physiology were two preferential scientific media where

chemistry had a significant role in formulating the first law. The galvanic cells were the virtual devices that served chemists to study the interconversion of chemical, electrical, thermal, and mechanical forces. The galvanic cells produced electricity, and new substances are formed in electrolytic cells upon the passage of direct electric currents. The quantitative relationship between heat and mechanical work expressed as the conversion factor, the mechanical equivalent of heat, led to the articulation of the law of the conservation of energy. On the other hand, the search for the reasons that caused the animal heat and its possible equivalence with (mechanical) muscular actions made chemistry an essential tool for elucidating the intermediate processes within the living organisms.

Section 1. Electrochemical cells and the correlation of forces

From 1830 to 1850, several prominent British chemists, namely Faraday, Grove, Daniell, Richard Phillips (1778-1851), Joule, and others, made significant contributions to electricity, emphasizing the universal importance of the interconversions of forces. These men published papers and gave lectures on the heat of combustion, determination of the exact relations among the electric currents, chemical forces, and heating effects, being persistently interested in chemistry. The universal conversion factor of the mechanical equivalent of heat emerged out of these investigations. As noted previously, Joule observed that the quantity of heat Q, generated in the closed circuit of the galvanic cell at a total time t, was proportional to the square of the current intensity, I, with proportionality constant, the resistance R of the circuit to the current, ($Q = RI^2t$). He observed the same phenomenon (heating law) in the electrolytic cell, where the decomposition reaction was the source of the resistance for the electric current. Joule used the heating law to determine the heat produced by different chemical reactions in the galvanic cells and compared these values with the heat evolved in combustion reactions outside the cell, quantifying in this way the chemical affinity of the substances. What remained for Joule was to establish the quantitative relationship between the generated heat by chemical means and the mechanical work produced and *vice versa*. He achieved this relationship by performing the historical experiment on electromagnetism; the conversion of chemical force (chemical reaction) producing electricity in the battery, which generated heat on the electromagnetic machine. In a series of experiments of this kind, he evaluated the mechanical value of heat. He published this work in 1843 under the title On the calorific effects of magneto-electricity and on the mechanical value of heat. The year 1843 marks the turning point of Joule's scientific activity. His research interests changed direction from chemistry towards physics. However, his audience and readers of his papers continue to be within the scientific community of chemists. Joule's relationship with the community of chemists ceased in 1847 when he entered the field of physics due to his acquaintance and discussions with William Thomson. Electricity was no longer essential in his experiments. Neither the chemical combinations were a necessary ingredient for his experimentation. Joule's subsequent experiments to consolidate the accuracy and the constancy of the mechanical equivalent of heat extended to include different kinds of mechanical forces, such as frictional forces exerted on fluids.

Joule measured the intensity of current and the quantity of heat produced subsequently in the electrical circuit from which he managed to derive the chemical affinity of the elements. His predecessor, Faraday, performed famous experiments that led to the reformulation of electrochemistry. Faraday redefined the propagation of electricity, and proved through a series of ingenious experiments that the decomposition of substances is internal and occurred in solution and not at the poles (electrodes) of the apparatus caused by the electric forces of the current. The English amateur scientist measured the weight of the element deposited on the electrodes of the decomposition cell upon the passage of a known quantity of electricity. He intended to derive the relationship between the mass of the element deposited on the pole and the quantity of electricity that caused this particular decomposition. In other words, Faraday strove to determine the electrochemical equivalent of that element. This finding constituted the first law of electrolysis. Faraday did not further investigate thermal and mechanical effects produced during the electrolysis process and, therefore, examine likely relations between these two phenomena. He concentrated strictly on the chemical decomposition effected by the electric current and the propagation of electricity in solution via the mechanism of decomposition. It left to Joule to compute the mechanical equivalent of heat and enunciate the conservation law. As noted above, the discrepancy observed between the equivalent values obtained from the electrochemical reactions within the cells and those measured in ordinary chemical reactions performed in the laboratory outside the galvanic or the electrolytic cell led the two scientists to conclude that secondary reactions eventually occurred at the electrodes of the cells apart from the primary reactions. Primary reactions were the electrochemical reactions directly involved in the chemical change within the cells. The secondary reactions were the ordinary chemical reactions that resulted as byproducts of the primary reactions. Polarization³²⁰ of

³²⁰ Polarization creates two mechanical side effects: first, the evolution of gases or the deposition of other products at the interface between electrode and electrolyte (as seen by Joule), and second, the so-called *concentration polarization* manifested by uneven depletion of reagents near the region of the electrodes causing concentration gradients at the boundary layer. Both effects isolate the electrode from the electrolyte, impeding the electrochemical reaction, and charge the transfer of the electricity between the two electrodes. Concentration polarization has escaped classical electrochemistry. This kind of polarization

the batteries electrodes or the dissolution of metal oxides by acids in electrolytic cells were phenomena owing to such secondary reactions. Faraday did not move further to study the phenomenon of polarization. Faraday hoped that comparing the electrochemical reactions with neat chemical reactions would offer the means to categorize the former reactions. The result was disappointing, and quantitative discrepancies were observed in the measured heats between the electrochemical and the ordinary reactions. On the other hand, Joule conducted several experiments to investigate the origin of the phenomenon of polarization as a possible cause of the deterioration of the action of the cells.

John Daniell and Richard Phillips,³²¹ both professional chemists, and Faraday's friends, turned into electrochemistry in the late 1830s following Faraday's researches of 1833 to1838. Recall that John Daniell was the inventor of the constant current intensity of batteries, which contributed decisively to obtaining electrochemical measurements of high accuracy. Daniell was a capable experimenter, but a mediocre theoretician. He was not involved in theoretical pursuits in the context of electrochemistry. He instead employed the battery as a source of constant electric current than as a medium for theoretical research.

Contrary to Daniell (and Faraday), another influential figure in mid-nineteenth century science. Grove became the first professor of experimental philosophy at the London Institution in 1841. The London institution affiliated with the Royal Institution of Brittain was founded in 1840 to promote industrial interests. Grove's inaugural lecture in

has been exploited as an inherent component to all types of membrane separation processes, e.g., gas separations, pervaporation, membrane distillation, reverse osmosis, and separations at a microscopic scale as nanofiltration, ultrafiltration, and microfiltration.

³²¹ Richard Phillips (1778–1851) was one of the founding members of the Chemical Society of London in 1841 and became its president in 1849, holding the position until his death. He was also prominent in the British Association for the advancement of sciences. He became an editor at the *Annals of Philosophy* and later joint-editor of the *Philosophical Magazine*. He published papers in both journals. (https:// en.wikisource.org/wiki/1911 Encyclopedia Britannica/Phillips,William).

1842 was the first announcement of what Grove called the *correlation of physical forces* (see below). Grove did not strictly state the conservation law, and he did not measure or calculate the mechanical equivalent of heat. Kuhn has grouped Grove with Faraday, Mohr, and Liebig considering that the line thread that connected the four men was the existing network of conversion processes. Furthermore, Kuhn discussed Grove's approach to the conservation of energy as well as his philosophical views for science on equal terms as those of Joule, Faraday, Mayer, Helmholtz, Colding, and Carnot, indicating in this respect Grove's notable contribution to the philosophy of science and the experimental electrochemistry.³²² However, Kuhn did not give a definite answer to whether the conversion processes or Grove's philosophical beliefs were the igniting sparks that led him to discover the conservation of force. Furthermore, it is not clear whether Grove enunciated the principle of the conservation of force in a qualitative manner or through the calculation of the mechanical equivalent of heat. As to the first question, Kuhn reconsiders his opinion expressed in the first part of the paper regarding Grove's approach to the conservation concept. He eluded that both conversion processes and the Naturphilosophie may have affected his road to the conservation of energy.³²³ Grove could not have been included in the twelve pioneers of the conservation of force, mainly for two reasons: first, Grove did not enunciate the conservation law. Also, he did not perform any experiment or calculation for the mechanical equivalent of heat. Second, he did not have any influence from the *Naturphilosophie*, which always sought a single unifying principle for all-natural forces.

³²² Grove appears in Kuhn's paper as an influential figure of equal caliber with Faraday, Joule, and the other prominent pioneers (Kuhn, 1977 pp. 68, 76, 78-80, 82, 98-100, 103).

³²³ Kuhn, 1977, p. 99. Morus deemed Grove as a massive influential figure in the Victorian era moving in the same intellectual and social circles as Faraday, Herschel, Lyell and Darwin (Morus, 1991, p. 589; Scott, 1981, pp. 559-561).

Grove participated in the network of the conversion processes by constructing batteries and performing studies in electrochemistry. However, he used these experiments as an interpretative basis of his philosophy of *the correlation of forces* (not conservation of forces), making the latter visible and available to the readers.

As noted, Grove presented his first thoughts about the doctrine of correlation of forces in the inaugural lecture in 1842 as a professor of the London Institution. He then proceeded with a series of six lectures delivered in 1843. These lectures, incorporating a collection of experimental papers in electrochemistry (mainly batteries constructions), were the subject of a volume entitled *The correlation of physical forces* first published in 1846.³²⁴ Grove's philosophical views regarding the correlation of forces did not refer only to science. He extended his thoughts to other spheres of social and political life. He discussed the correlation of forces in a broader and more complex context but always outside the conservation of force. Apart from the physical forces (the affections of matter as he called them)³²⁵ involved economic, social, political, and moral correlations. On page 165 of the last version of his memoir, Grove clarified the meaning of correlation as follows: "The term Correlation, which I selected as the title of my Lectures in 1843, strictly interpreted, means a necessary mutual or reciprocal dependence of two ideas, inseparable even in mental conception". He continually reminded the reciprocal function of the science magneto-electricity and electromagnetism due to the mutual correlation of the forces of magnetism and electricity.

³²⁴ The first publication followed by five subsequent editions. The sixth edition appeared in 1874. I have used the last published version of Grove's paper (Grove, 1974).

³²⁵ "The affections of matter were qualities or properties of matter, which cannot be separated from it. Motion, heat, light, electricity, magnetism and chemical affinity were the six affections of matter, which were essentially separate from one another, although they were correlated or connected by a reciprocal relation" (Quoted in Cantor, 1976, p. 279).

There is no historical evidence to ascertain that Grove had any contact with the German ideology of the *Naturphilosophie*. The philosophical tradition of the Scottish Common Sense School of philosophy³²⁶ seemed to affect Grove when he came into contact with this philosophy as a student at Oxford University. Presumably, Grove found in this tradition the philosophical resources he utilized to construct his theory of the correlation of forces in science and other fields of human life. Grove confirmed his association with this school of philosophy asserting that, "our knowledge of the normal course of nature is derived from experience". Grove approached the correlation of forces through the empirical doctrines of the School that reflected the positivism and phenomenalism of John Locke, George Berkeley, and David Hume. At the same time, he rejected Francis Bacon's (1561-1626) opinion that scientists have to find the causes of the phenomena in nature by observation and experimentation. From this position, Grove denied the causality and the relationship between the cause and the effect. He claimed that one could not distinguish between cause and effect, and any attempt to do so is a matter of convenience rather an adequate interpretation of the natural phenomena. He called attention to the paradox of the discoveries of Oersted and Faraday. Magnetism produces electricity (Oersted), and electricity produces magnetism (Faraday). He noted, "if electricity causes magnetism, and magnetism causes electricity, why then electricity causes electricity, which becomes, to speak, a reductio ad absurdum (reduction to absurdity) of the doctrine".³²⁷

³²⁶ The Scottish School of Common Sense was a realist philosophy that flourished in Scotland in the late 18th and early 19th centuries during the Scottish Enlightenment. It is originated in the ideas of Scottish philosophers Thomas Reid (1710-1796), Adam Ferguson (1723-1816), James Beattie (1735-1803), and Dugald Stewart (1753-1828). Its roots can be found in responses to the writings of such philosophers as John Locke(1632-1704), George Berkeley (1685-1763), and David Hume (1711-1776). One central concern of the School was to defend common sense against philosophical paradox and skepticism (Broadie, pp. 235-300, 2008)

³²⁷ Grove, 1874, p. 9.
The second example is Grove's construction of the gaseous battery (today the most efficient *fuel cell*). The cause is the reaction of oxygen and hydrogen gases in the platinum electrodes of the cell and the formation of water. The result (effect) is the production of electric current. Cause and effect are inseparable. Grove subsequently used this battery to electrolyze acidified water. The cause was the electric current of the gaseous battery, and the effect was the electrolytic decomposition of water and the production of the gases oxygen and hydrogen. He concluded in his publication: "This battery establishes that gases in combining and acquiring a liquid form evolve sufficient force to decompose a similar liquid and cause it to acquire a gaseous form. This is to my mind the most interesting effect of the battery; it exhibits such a beautiful instance of the correlation of natural forces".³²⁸

These two examples show that Grove's philosophical views about the correlation of physical forces are related explicitly to experimental practice in his laboratory, which in turn it might be regarded as the vehicle carrying over his philosophical discovery. Grove used experiments from various divisions of physical sciences to reject causality and to demonstrate the conformity of the six *affections* of matter with the principle of correlation of forces. Since the *affections* interacted with matter, they constituted forces. His conclusions justified his expectations about the lack of any relationship between cause and effect: "Light, Heat, Electricity, Magnetism, Motion, and Chemical-affinity, are all convertible material affections; assuming either as the cause, one of the others will be the effect; thus heat may be said to produce electricity, electricity to produce heat; magnetism to produce electricity, electricity magnetism: and so of the rest. Cause and effect, therefore, in their abstract relation to these forces, are words solely of convenience: we are

³²⁸ Grove, 1842, p. 420.

unacquainted with the ultimate generating power of each and all of them, and probably shall ever remain so".³²⁹ Several of his experimental papers evidenced the theory of correlation of forces as a guide in Grove's laboratory work. For instance, he exploited the direct correlation between the chemical reaction in the voltaic cell and the produced electricity to improve and increase the efficiency of the cell. He replaced the dilute sulfuric acid with dilute nitric acid and contrary to the usual method of opposing polarization. He added the polarizing force to the initial force of the battery. In the published paper, he described several experiments seeking the same methodology to increase the efficiency of the constructed batteries.³³⁰ The diminution of polarization resulted in the supply of constant current intensity. Scientists of various horizons adopted Grove's pile; as Ostwald affirmed, "scientific journals of those days are filled with reports recognizing the power and constancy of Grove's cells. Many research projects would have been impossible without the help of Grove's battery".³³¹

Grove recognized that steam engines were superior to his nitric battery from the fuel economy point, but contrary to Joule, he refused to set batteries aside. He asserted that the fuel within the battery was expended only when the machine was in action, unlike the steam engines that wasted fuel in warming up before producing any useful work, apart of course, of their characteristic law efficiencies. He suggested using the electric power of batteries in cases where the function of the steam would be inapplicable. The frequent use of today's batteries to drive the operation of small-scale machines seems to justify Grove's expectations.

³²⁹ Grove, 1874, p. xiv.

³³⁰ Grove, 1843.

³³¹ Ostwald, 1896, p. 593.

At this stage, it is legitimate to ask why Grove preferred to develop a theory that correlated the physical and other phenomenal forces. Why he did not attempt to interpret his observations quantitatively in terms of the principle of the conservation of force? This principle was not alien to Grove, and he mentioned it in his work on the correlation of physical forces. Grove knew about Mayer and Joule's calculations of the mechanical equivalent of heat, as well as Thomson's theory on the dissipation of heat.³³² However, he decided to refute both theories because they contradicted the principle of the correlation of forces. Grove's arguments against the conservation of force were not philosophical but purely scientific. First, he doubted the accuracy of the values for the mechanical equivalent of heat determined by Mayer, Joule, and others. He stressed the inherent lack of constancy for this conversion factor; "other investigators have given numbers [of the mechanical equivalent of heat] more or less discordant, so that, without giving any opinion on their different results this question may be considered at present far from settled".³³³ Second, he offered possible explanations for the observed discrepancy. He claimed that the heat evolved in compressing a gas isothermally might be less than, equal to, or greater than the equivalent of the work spent since this work might produce other effects on the gas other than heat; for instance, by molecular rearrangements³³⁴ or molecular vibrations¹⁸⁴ which neutralize some of the heat produced. Comparing the heat produced by the so-called arrested motion (e.g., percussion), where all mechanical work converted into heat, with that obtained by other mechanical means (expansion, friction, electricity), Grove asserted that the equivalence of heat and work for the latter processes has yet to attain.¹⁸⁴ He

³³² Grove, *1874*, pp. 60-64, and 67-68.

³³³ Ibid, p. 61.

³³⁴ Ibid, p. 63.

concluded that "it may turn out that in some cases it is a correct expression to say that mechanical force produces a disturbance of the equilibrium of temperature than that it produces heat".¹⁸⁴

Section 2. The origin of the animal heat

Strictly speaking, physiology has not promoted a theoretical and experimental framework for establishing the principle of conservation of energy. Still, it stood as the borderline between chemistry and physics, which contributed to the discovery of the conservation of force. Physiology and *vital force* paved the way towards the formulation of conservation law. The search for the origin of animal heat, the functioning of the controversial *vital force* in animal and vegetable life influenced the thinking of prominent scientists of the era. However, a closer examination of the research performed at that time for the causes of heat in living systems reveals that questions concerning the mechanism of muscle contraction began to transform the hitherto static thinking into "thermodynamic" theories.

In this section, I will try first to describe the contribution of chemistry to physiology and discuss the connection of these researches to the principle of conservation law. Numerous great thinkers have contributed to the conservation of force on the battleground of chemistry and physiology. They explained almost everything from the respiration mechanism, animal heat, nutrition, chemical constitution of nutrients, metabolism, muscular exhaustion, and many others.³³⁵ This chapter will focus, in particular, on the efforts of Liebig, Mayer, and Helmholtz for two reasons. First, because they were among

³³⁵ For a comprehensive study of th evolution of the conservation of energy in the context of physiology and the way by which ideas, concepts, and experimental techniques from physical sciences infused into physiology, see Kremer, 1984.

Kuhn's discoverers of the conservation law working in the field of physiology, and second, because they have provided the most precise physiological framework for the foundation of the conservation law. Liebig was a chemist, whereas the other two were physicians. Helmholtz turned into a physicist when he was appointed professor at the University of Berlin. It is fruitful to start with the theories of respiration, which mark the origin of physiology.

2.1 Theories of respiration

The search for the origin of animal heat has its origin in the controversy against the phlogiston chemistry of respiration connected with animal heat. Joseph Priestley (1733-1804) in 1776 and Adair Crawford (1748-1795) in 1779 provided respiration theories based on phlogiston chemistry. Priestley suggested that blood in the lungs gives off phlogiston to the inhaled air, exhaling as phlogisticated air (air exhausted of oxygen). Crawford's theory was interesting because it associated the process of animal respiration with animal heat and determined heat by calorimetric measurements of heat capacities pioneered by himself.³³⁶ Both Priestley's and Crawford's rather speculative theoretical approaches to the production of animal heat upon respiratory process could be summarized to the following equation (reaction): (air + heat) + blood + phlogiston) = (air + phlogiston) + (blood + heat). According to this process, heat conveyed by atmospheric air entering the lungs is exchanged with the phlogiston carried out by the blood flowing into the lungs from the other parts of the organism. The phlogiston combines with the atmospheric air in the lungs.

³³⁶ Crawford, 1788. Kremer, 1984, pp. 48-52.

of the organism.³³⁷ However, as noted later by Dulong and the French physical scientist Cèsar Mansuète Despretz (1792-1863), Crawford's imperfect method of determining specific heats of gases and heats of combustion made his results unreliable.³³⁸

Lavoisier, having started the attack against the foundation of the phlogiston theory, disagreed with both theories. To refute Crawford's phlogiston theory of respiration, he collaborated with Laplace on a series of painful experiments on animal respiration using an ice calorimeter. Laplace performed these experiments using an ice calorimeter of his design. This apparatus functioned at law temperature (0° C) to overcome the ordinary calorimeters' limitations and ensure the safety of the tested small animals, usually sparrows and guinea pigs (**Figure 10**). The results of the experiments reported in his *Mémoire sur la Chaleur*³³⁹ in 1783 were interpreted more or less in the same way as the interpretation offered by Crawford with one important difference: the phlogiston had no place in Lavoisier's respiratory process and the transfer of heat. The transformation of the atmospheric air (or oxygen) into the fixed air (carbonic acid or carbon dioxide) in the lungs was the cause of the animal heat that was transferred to the rest of the body by the arterial blood.

Nevertheless, a comparison of the quantitative measurements of the exhaled carbon dioxide in the ice calorimeter with those obtained by combusting the carbon in foods and charcoal in separate experiments under the same temperature, pressure, and same quantity of air showed a rather large discrepancy of 20%, which attributed to systematic errors of the measurements. Further experiments on animal respiration published in 1784-1785 were

³³⁷ Kremer, 1984, p. 50.

³³⁸ Ibid, pp. 151-152.

³³⁹ Lavoisier and Laplace, 1783.

primarily dedicated to correcting systematic errors. Lavoisier realized that a small quantity of air was consumed to burn hydrogen originated from a small amount of water residing in the lungs. In analogy with hydrogen oxidation in foods, the latter finding improved somewhat the accuracy of the experimental results since the new source of combustion increased the amount of heat produced by the respiratory gases. Interestingly, Lavoisier knew nothing about the relative proportions of carbon and hydrogen in the material he combusted. He had no information about the presence of oxygen as a molecular constituent like alcohol. Since no thermochemical data existed at that time, he probably used specific heats to calculate the amount of heat produced. However, he did not give details of the methodology he used to reach his conclusions. Besides, the experimental results obtained were not reproducible and changed dramatically with changes in the ambient temperature and the animals of the same kind. Lavoisier and Laplace and later, with Lavoisier's second collaborator Armand Jean François Sèguin (1767-1835), had never assumed that oxygen somehow produced heat and work, thereby making a first reference to the conservation law as alluded by some historians.³⁴⁰ They instead explained the origin of the animal heat within the context of caloric theory and the conservation of heat; that is, the amount of heat given off by the animal should equal the heat entered the animal body by external sources. This explanation required discovering the heat sources and the quantitative assessment of the balance between these two forms of heat. The solution to this problem was attempted in the mid-nineteenth century by Liebig and Helmholtz.

³⁴⁰ Lavoisier and Seguin's observation that the quantity of the inhaled oxygen was proportional to the rate of respiration as long as the animal breathes normally has raised by some historians the possibility that Lavoisier and his collaborators made some kind of contribution to the conservation law or at least to the correlation of forces. Kremer had discussed this point and had the opinion that Lavoisier gave no indication of the relation between the oxygen intake and mental or physical work, (Kremer, 1984, pp. 74-75.).

No significant study appeared to advance the hitherto theory on animal heat after Lavoisier's death until approximately 1830. This period was characterized by the intention to defend and preserve Lavoisier's legacy. Francois Delaroche and the chemist Jacques Etienne Bèrard made some interesting experiments of this period. These two physicians performed respiratory experiments on cold and warm-blooded animals upon changing the ambient temperature. They found that the oxygen intake was higher in cold-blooded animals than that inhaled by warm-blooded animals. However, they found the *Respiratory Quotient*, *RQ*,³⁴¹ to be less than one in both cases. However, they were very cautious about concluding that their results could have supported any particular theory. Furthermore, Delaroche confirmed Crawford's observation that the color of venous blood became increasingly red like that of arterial blood at high ambient temperatures. This finding was what Mayer had observed thirty years later in the sailor's venous blood during his trip to Java. Delaroche interpreted this observation as a decrease of the chemical action of respiration, whereas the same observation led Mayer to the first law of thermodynamics.

The Academy of Franc played a major role in this strategy. Under the influence of its senior member Berthollet, the Academy announced in 1821 a contest for the causes (chemical or physiological) of the animal heat. The prize question of the contest was formulated in such a way as to restrict the problem of animal heat to Lavoisier's method ignoring any objections raised by contemporary physiologists. The contest did not lead to any new conclusion even though two of the most talented experimenters of France took

³⁴¹ The respiratory quotient or respiratory coefficient (RQ) is a dimensionless number indicating the ratio of the carbon dioxide produced by the body to oxygen consumed by the same body. At that time, they believed that RQ must have been equal to unity for perfect animal respiration. Today, RQ measures the metabolic rate, and its value depends on the kind of the ingested nutrient and ranges between 0.70 (for lipids) and 1.0 (for carbohydrates).

part in this context: the chemists Dulong and Despretz. They used nearly identical water calorimeters. Dulong employed Rumford's method to eliminate heat losses from the calorimeter (**Figure 11**), whereas Despretz rejected this method and used Newton's law for radiant cooling. He claimed that with this method, he was able to measure heat losses.³⁴² Dulong concluded that the "fixation of the oxygen absorbed during respiration is insufficient to furnish all the heat lost by animals in natural conditions of life." Thus, another cause of heat must exist. "of what nature is this other cause? This is that perhaps never will know with certainty".³⁴³ The other contestant did not offer more satisfactory results (in all experiments he performed, the calculated RQ was steadily lower than unity) than Dulong's. Despretz speculated about other sources of animal heat. The most interesting of them was his suggestion that the movement of blood and the friction of different animal parts can produce the small remaining portion of heat. However, no connection of heat with mechanical work is mentioned in all these studies.

2.2 Other sources of animal heat: Metabolism and nutrition

Since Dulong and Duspretz, refuted Crawford and Lavoisier's static method experimentally to reveal the cause of the respiration and animal heat, most physiologists and chemists turned their attention to alternative sources explaining the life phenomena. The years following the failure of the contest on animal heat witnessed many changes regarding the methodological approaches and the interpretation of respiration and animal heat. First, an impressive collection of new data was accumulated. Data were gathered by

³⁴² Kremer has compared these two calorimeters in terms of their structure, methods of measurements, and accuracy (1986, pp. 56-60).

³⁴³ Quoted in Kremer, 1984, p. 158.

measuring the exchange of gases in animals lungs and blood and studying the influence of various external factors and internal conditions on respiration and body heat, for example, changes in the ambient temperature, the state of animal transpiration, nutrition, and digestion, the different species (cold or warm-blooded animals), the physical state of the animal undergone various tests (starvation, sleep, muscular exercise, fear, etc.). Second, the development of experimental dynamic methods replaced the static methods adopted by Lavoisier and experimenters of earlier decades. These methods included the comparative measurements of the body temperature, the construction of highly precise respiratory apparatuses to measure gases in the circulating blood, and placing devices to hold the whole animal body for more than 24 hours to avoid slight daily variations. The development of the quantitative analysis in organic chemistry, for which I will refer below, was another discovery that provided physiologists and chemists with a potential tool for studying the process of animal heat. Third, the various theories and assumptions suggested for interpreting the phenomenon of animal heat.

The Swiss-Russian chemist Germain Henri Hess (1802-1850) was considered one of the founders of thermochemistry. Besides the discovery of the law of *the summation of heats*,³⁴⁴ Hess observed that a combustible compound like hydrocarbon would evolve less heat than expected by summing up the heats of combustions of its elements separately.³⁴⁵ Hess correctly noted that the extra heat must be produced upon combining the elements to form the substance (today, this excess heat is called the heat of formation). This conclusion

³⁴⁴ The law of summation of heats states that the total heat developed in a chemical process (formation or decomposition of substances,) is constant, regardless of whether the process goes directly, or through intermediate steps. This law is a consequence of the first law of thermodynamics. However, Hess did not connect this law with the conservation of energy...

³⁴⁵ Hess, 1840a; 1840b; 1842.

can partly explain the discrepancy observed between the *in vivo* respiratory heat and the *in vitro* heat of the combustion of substances.

Notable scientists, such as the skillful experimenter Victor Regnault continue favoring the chemical theory or the combustion theory of respiration and animal heat. Regnault claimed that respiratory and heat phenomena are closely connected to chemical reactions in the animal body. However, these phenomena were too complex to precisely calculate the heat from the quantity of oxygen consumed. He introduced the oxidation of nutrients as an additional source of heat. Still, he could not compute the heat resulting from this source due to the lack of relevant heats of combustion and the identity of the substances excreted by the animal. Regnault, in collaboration with the French agricultural chemist Jules Reiset (1818-1896), was able to compare the amount of consumed oxygen as determined directly using a respiratory apparatus of his design (Figure 12) with the amount absorbed, the latter being estimated indirectly from the carbon dioxide and the water produced.³⁴⁶ Regnault debated the alternative physical theory of respiration, which was proposed for a time by biological theorists. The latter claimed that all the exchanges of gases between the lungs and blood and between blood and tissues were a matter of diffusion following either the law of partial pressures of Dalton, Henry's law, or Graham's diffusion law. However, by excluding any chemical character of respiration, the diffusion theory

³⁴⁶ Regnault, and Reiset, 1849. In a long introduction, Regnault and Reiset gave a detailed account of relevant researches on animal heat and respiration theories performed by Lavoisier, Laplace, Liebig, Dulong, Despretz, and others. Then, they described the apparatus, the method of experimentation adopted, and discussed the results obtained. Regnault was a great experimenter in chemistry and a capable artist with several innovations in photography. He is nowadays conspicuously absent from all the textbooks and reviews dealing with experimental chemistry. Fortunately, his legacy in chemistry was saved thanks to historians, who referred to him through their research papers and monographs. (see for instance Poncet, and Dahlberg, 2011).

could not explain the formation of carbonic acid in the blood, the effect of nutrients on heat, and the compounds excreted by the animal.

Chemistry and physiology found common research ground when nutrition came into play as a possible source of animal heat. These researches were culminated in the 1840s and 1850s, combining physiological and chemical experimental methods to solve nutritional questions *in vivo* and *in vitro*. The examination of nutrition led inevitably to theories of metabolism as closely related to animal heat. Respiration moved to the background and became a separate research subject or associated with the process of nutrition. Prominent scientists as the physiologists Francois Magendie (1783-1855) and Johannes Müller, the chemists and physician William Prout (1785-1850), the anatomist and physiologist Friedrich Tiedemann (1781-186), and the chemists Jacob Berzelius and Leopold Gmelin (1788-1853) made some interesting, but somewhat speculative contributions to animal heat.³⁴⁷ Despite the experimental developments, the vast number of chemical and physiological processes comprising nutrition and metabolism, in general, did not allow a full explanation of the animal heat.

The development of practical, though the tedious method of elementary analysis by Gay-Lussac and Louis Jaques Thenard (1777-1857) in 1810 marked a new era in the research for the physiological processes during nutrition. This new technique was promising since it made it possible to determine the percentage composition of the nutrients and, eventually, the various metabolites. Nevertheless, at its initial stage, the analysis was relatively slow and laborious requiring extraordinary skill; more importantly, it was of low accuracy to provide convincing information about physiological processes. Therefore, the

³⁴⁷ Kremer, 1984, pp. 180-186. Coley, 1996, pp. 171-174.

quantitative analysis in this period was necessarily confined to the determination of the composition of isolated compounds in the laboratory (*in vitro*) than obtaining quantitative results for the substances in the living organisms during metabolism (in vivo). It was impossible to identify the hundreds of substances in nutrients and metabolites at an atomic or molecular level. In this respect, the chemists decided to group the various substances. Criteria for this classification were first the specific properties of the substances in each group, e.g., fats, carbohydrates, proteins. The second characteristic of the substances of each family was their specific function in the animal organism, and third their possible interactions and interconversions. Although very useful, this methodology required considerable improvements to handle the complexity characterizing the research of animal heat. The vague and inconclusive results obtained sometimes led to hypotheses and theories of limited scope. For instance, they had explained the presence of nitrogen in animal tissues by invoking the so-called animalization theory. Herbivorous animals, which certainly consumed nitrogenous plants, could supply nitrogen to carnivorous animals. However, this explanation was hard to stand alone when physiologists perceived that the overall proportion of nitrogen in vegetable nutrients was much smaller than that found in animals.³⁴⁸ Physiologists abandoned this explanation and turned their attention to the possibility that animals absorbed nitrogen from the air³⁴⁹. Notwithstanding, the animalization theory survived amongst physiologists and biologists for about forty years. In any case, the new technique of elementary analysis caused a shift of the chemical and

³⁴⁸ In 1837, the Dutch organic chemist Gerardus Johannes Mulder (1802-1880) performed chemical analysis for specific proteins (albuminous substances) common to animals and vegetables. He showed that the assimilation of organic vegetable substances by animals did not alter their basic elementary composition (Holmes, 1963, pp. 73-74.).

³⁴⁹ Holmes, 1963, pp. 62-63.

physiological research on animal heat from respiration to nutrition and processes involved in nutrition.³⁵⁰ Furthermore, nutrition was the motive that made the two disciplines come closer so that some researchers referred to a new discipline of *physiological chemistry* or *chemical physiology*.

The German chemist Justus Liebig was among the scientists who applied elementary analysis to determine the composition of substances participating in the nutritional processes in living organisms. Liebig made the elemental analysis much simpler and more accurate than before. Between 1830 and 1840, Liebig and his students analyzed many organic compounds in the nutritional and respiratory processes. These substances constituted animal and plant tissues, inherent in natural products used as nutrients or substances secreted by the organism. The calculated percentage compositions of these compounds allowed Liebig to deduce many physiological explanations much more comprehensively than his predecessors. In 1842, Liebig published his famous treatise *Animal Chemistry or Organic Chemistry in its Application to Physiology and Pathology*,³⁵¹ considered the best account of applying quantitative organic chemistry to physiology.

³⁵⁰ Today, the subject of nutrition comprises primarily dietary requirements, as well as the exchange of matter between the organism and the environment. However, in the nineteenth century, this term was more complicated. It involved several contingent processes, such as mastication, digestion, absorption, chylification (medical term, meaning qualification of chyle), the formation of blood, decomposition, and secretion. In other words, earlier nutrition resembled metabolism (Holmes, 1975, p. 136).

³⁵¹ Liebig, 1842. I have used the Eglish traslation.

³⁵² The Animal Chemistry contains three parts and a large number of appendices and notes. The first part (pp. 1-99) is a compilation of theories and hypotheses given in short accounts or reports. Liebig explained almost all aspects of nutritional, respiratory, and biochemical processes occurring in plants and animals (carnivore and herbivore). The second part (pp. 105-191) of the treatise deals with the metamorphoses (growth and decomposition) of tissues within the living organisms and the transformations of foods during metabolism. He describes these changes through his famous equations in a quantitative manner, although erroneously, these transformations. Finally, in the third part of animal chemistry (pp. 195-271), Liebig describes the properties and the manifestations of the vital force and those of chemical forces and their relationship towards the production of heat and mechanical force. The scrutiny of this study discloses the vitalist attitude of Liebig. Because of this, Kuhn classified Liebig into the group of scientists involved in the formulation of the principle of the conservation of energy. Several authors had thoroughly analyzed Animal Chemistry (Holmes, 1964; Hall, 1980; Rosenfeld, 2003).

The tabulated data of his analyses and those of other chemists³⁵³ and the calculated composition of almost all known substances in nutrients and those involved in nutritional and physiological processes in animals and plants allowed Liebig to develop the most comprehensive theory regarding the chemical processes and the physiological functions of nutrition. The formation and decomposition of animal tissues and the biochemistry of respiration were some examples of these theories.

The introduction of chemistry to physiology began with nutrition. In particular, Liebig strove to figure out the chemical transformations that nutrients undergo within the animal body. Liebig developed a new theory of chemical processes in living organisms. He depicted his ideas through hypothetical chemical equations derived from the molecular formulae of the participating compounds. He treated physiological processes like chemical reactions subject to the laws of chemistry.³⁵⁴ Liebig thought that he could demonstrate how organic chemistry could apply to problems of physiology that physiologists had failed to achieve. Liebig's equations and hypotheses were never confirmed *in vivo*, during the physiological processes in living systems. Liebig's ideas did not go without criticism from chemists and especially from physiologists. The opposition pointed out that his conclusions were simply hypotheses, although some of his ideas proved to be correct at a later time.³⁵⁵

Metabolism, the oxidation of nutrients, was another subject where chemistry contributed to physiology. Liebig considered metabolism as the source of the manifestation of life every movement, every manifestation of force, every activity in the animal. The

³⁵³ The French chemist Jean-Baptist Dumas (1800-1884) made a substantial contribution to elementary analysis of organic compounds to elucidate their composition and understand their chemical behavior. Dumas shared very similar ideas to those of Liebig (Kremer, 1984, p. 193).

³⁵⁴ Liebig, 1842, pp. 121-191;

³⁵⁵ Holmes, 1963, pp. 78-80. Rosenfeld, 2003, pp. 1701-1702.

animal needs the heat produced by the oxidation of nutrients by the inhaled oxygen to replace the heat lost from the body's activity. He rejected the effect of other causes as alternative heat sources, for example, the nervous system or mechanical theories ascribing animal heat to friction or elastic stretching. He considered these theories as a manifestation of the vital force, "as if movements themselves could originate without a certain expenditure of kraft (force) which is consumed in these movements".³⁵⁶ This statement implies Liebig's reflection on the conversion of forces. Liebig refuted any previous experimental approach to Lavoisier's theory of heat. To support his views against Lavoisier's respiratory interpretation of the animal heat, Liebig reported one of his few physiological studies. He recorded the amount of food prepared in a month for 28 soldiers and determined the average daily consumption and excretion of carbons. He hoped to calculate the daily heat generated by the consumption of nutrients through the experimental heat of combustion of carbon. The calculated calories were more than enough to sustain a constant body temperature, allow for heat radiation, and warm the exhaled air and excrements. However, he did not consider the expenditure of heat for mechanical motion. These calculations were subjected to severe errors that would make the results meaningless. There were based on erroneous heats of combustion as measured by Dulong and Despretz's in 1821 and on undetermined effects of several external factors (movements, temperature fluctuations, foods eaten, clothing, and time of the day).³⁵⁷

Liebig speculated about another source of heat. The oxygen in certain foods is sugars, starches. As a result, the chemically engaged oxygen in substances can produce

³⁵⁶ Liebig, 1842, p. 32.

³⁵⁷ Ibid, p. 35 and 290-295. Kremer provided a historical account of the failed experiment (1986).

additional heat. These substances could convert to body fats, and the liberated oxygen might not leave the organism as a gas. Still, it could participate in further oxidation of nutrients to form more carbonic acid and water. ³⁵⁸ Nevertheless, Liebig seems to abandon this heat source rapidly when he discovers that metabolism is not a static process but rather a dynamic characteristic. He thought it could be more convenient to refute the challenge of the theory of respiration if he considers metabolism as a means of the conversion of forces.

Liebig proposed a *principle of correlation of forces* that expressed a conversion of forces with constant coefficients, i.e., a relationship equating the heat ingested and that liberated by living bodies. However, the equation lacked the work done by the animals. Therefore, it cannot express the mathematical formulation of the conservation law. It was simply a law of heat conservation, similar to Carnot's theory, although it resulted from a different cause.

As noted earlier, the calorimetric measurements of the heat produced by the oxidation of food did not agree with the heat obtained *in vitro*; a large discrepancy of 20% was observed—this discrepancy ascribed to systematic errors of the measurements. Liebig, confident for his analytical data, claimed that the old Dulong's and Despretz's heats of combustion were incorrect. He expected to eliminate the heat discrepancy by correcting the heats of combustion for carbon and hydrogen. Liebig used Dulong's 1838 data as he thought it to be more accurate. He confirmed their accuracy by comparison with Hess' similar measurements. However, the entire procedure that Liebig used to correct combustions' heat, especially for carbon, was unorthodox.³⁵⁹ Liebig engineered the data to obtain convenient values for his calculations. With the manipulated heats of combustion,

³⁵⁸ Ibid, pp. 84-95; Kremer, 1984, pp. 208-209.

³⁵⁹ Kremer, 1984, pp. 210-213.

Liebig computed all calorimetric data published by Dulong and Despretz. Thus, the discrepancy between the ingested and released heat ranging from 15% to 30% dropped to 3%. In the light of new experimental findings for the combustion heats of hydrocarbons reported in 1846, Liebig's calculations became precarious. Liebig admitted the dubious data tacitly. The 1846 edition of *Animal Chemistry* neglected all references to the animal heat investigations.³⁶⁰

2.3 Vital force and the conservation of energy

The analysis of Liebig's various experiments, hypotheses, and theories in his Animal Chemistry goes beyond the scope of this dissertation. Instead, I will examine Liebig's attitude towards the role of the *vital force* that played in the physiology of living systems, I will discuss whether the vital force was a major factor that led Liebig to approach the principle of the conservation of force. With this connection, it is interesting to review the involvement of the other two medical scientists, Helmholtz and Mayer, in problems regarding the role of the vital force in animal life. The vital force was the scientific and philosophical matter that occupied intensively the minds of physiologists and chemists in the mid-nineteenth century. I will examine whether the vital force was one of the factors that have led Helmholtz and Mayer to the enunciation of the principle of conservation of force.

The idea of *vital force* (life force) overwhelmed German physiology during the first half of the nineteenth century. Chemists and physiologists considered *vital force* as an extra

³⁶⁰ Liebig, 1842, pp. 37-39; 1846, p. 44; Kremer, 1984, pp. 214-215.

force that controlled the physical and chemical forces of the organs of the living body.³⁶¹ Vital force stimulated the decomposition of food and governed the growth and function of the living tissues. While the physical and chemical forces were free to act in producing decomposition during life and after death during the process of putrefaction, their action is continually being controlled or at least supplemented by the vital force.³⁶² Such a **vital force** does not exist in the non-living, inorganic world. In other words, the doctrine of vitalism was a characteristic trait that distinguished living organisms from the physicochemical world. Ernst Heinrich Weber (1795-1878), a distinguished physician and psychologist, argued that the so-called vital force was, in fact, a physical force. He found it necessary to explain the vital force in physical terms in his attempts to banish vitalism. Weber did not deny the vital force, but he sought a different interpretation of its function in the context of physics.

2.3.1 Justus Liebig and the vital force

Justus Liebig, who established chemistry as a science in Germany, was initially uncertain, vacillating between Weber's interpretation of vital force and the difficulty to explain the origin of the heat produced by the action of muscles. He accused the Naturphilosophen of using the vital force to expound phenomena they do not understand or explain results not obtained from experiments. Still, on the other side, he did not reject all the concepts underscoring the v*ital force*.³⁶³ He stated that, "no other way

³⁶¹ Liebig gave an extended definition of the *vital force* (*vis vita* or *vitality*) in his book *Animal Chemistry* (Liebig, 1842, p. 1)

³⁶² Kremer, 1984, pp. 237-238.

³⁶³ Liebig, at one point, resorted to the vital force to protect animal tissues from decay due to oxidation by the atmospheric oxygen (Liebig, 1842, p. 221-224). Mayer refuted this explanation. He argued that the site

is possible or conceivable to gain insight into the essence of vital force other than the way of the physical research".³⁶⁴ In the third part of his Animal chemistry, discussing the phenomena of motion in the animal organism, he favored the vital force's major role as a cause of growth and decomposition of the plant and the animal tissues. Liebig described three manifestations of vital force in living organisms:³⁶⁵ (a) a force breaking down the cohesive forces holding together the nutrient substances resulting, either in a complete decomposition or in a rearrangement into other substances, "the vital force appears as a moving force or cause of motion when it overcomes the chemical forces (cohesion and affinity) which act between the constituents of food, and when it changes the position or place in which their elements occur; it is manifested as a cause of motion in overcoming the chemical attraction of the constituents of food, and is, further, the cause which compels them to combine in a new arrangement and assume new forms";³⁶⁶ (b) a cause of resistance to the decay of the living tissues, "the vital force is manifested in the form of resistance, inasmuch as by its presence in the living tissues, their elements acquire the power of withstanding the disturbance and change in their form and composition, which external agencies [e.g., the oxygen of the atmosphere] tend to produce"; 367 (c) the only force for the movement of the animal body, "the vital force further manifested itself as a cause of motion and of change in the form and structure of material substances by the disturbance and abolition of the state of rest".³⁶⁸ After a lengthy discussion in which he compared vital force

of oxidation in the animal organism must be the circulating blood rather than the tissues (Kremer, 1984, pp. 228-229).

³⁶⁴ Quoted in Kremer, 1984, p. 341. Kremer offers an extensive discussion for Liebig's contradicting deliberations for the *vital force* (Kremer, 1984, pp. 341-344).

³⁶⁵ Liebig, 1842, pp. 204, 210-215, and 2219-221.

³⁶⁶ Ibid, p. 204.

³⁶⁷Ibid, p. 198.

³⁶⁸ Ibid, p. 196.

with mechanical, electrical, and chemical forces in related processes, Liebig questioned the existence of vital force.

"In what form or in what manner the vital force produces mechanical effects in the animal body is altogether unknown and is as little to be ascertained by experiment as the connection of chemical action with the phenomena of motion we can produce with a galvanic battery. All the explanations which have been attempted are only representations of the phenomenon; they are more or less, exact descriptions and comparisons of known phenomena with those whose cause is unknown. [...] We do not know how a certain something, invisible and imponderable in itself (heat) gives to certain bodies the power of exerting enormous pressure on surrounding objects; we do not know even how this something itself is produced when we burn wood or coals. [...] So is it with the vital force and the phenomenon exhibited by the living bodies".³⁶⁹

Finally, he noted, "Motion, by whatever cause produced, it cannot in itself be annihilated; it may indeed become inappreciable to the senses, but even when arrested by resistance (by the manifestation of an opposite force), its effect is not annihilated".³⁷⁰ This is a statement in accord of the old doctrine "from nothing no force can be generated".

Liebig attempted to theorize on muscle contraction. He deemed that the muscle tissues undergo oxidation only after the muscle has produced mechanical force. Oxidation induces chemical changes, but it does not cause motion. At this stage, Liebig invokes the vital force as the driving force of mechanical effects on the animal muscles, or the *vital*

³⁶⁹ Ibid, pp. 231-232.

³⁷⁰ Ibid, p. 204.

force is consumed as a mechanical force. Vital force enables muscle tissues to move.³⁷¹ However, Liebig could not say how the vital force produces mechanical motion; how are the chemical forces influenced by the vital forc*e* to produce mechanical motion? Liebig finding himself unable to resolve this contradiction concluded

"In what form or in what manner the vital force produces mechanical effects in the animal body is altogether unknown and is a little to be ascertained by experiment as the connection of chemical action with the phenomena of motion we can produce with a galvanic battery. All the explanations seem to be representations of the phenomenon. They are more or less exact descriptions and comparisons of known phenomena with these, whose cause is unknown. In this respect, we are like an ignorant man, to whom the rise and fall of an iron rod in a cylinder, in which the eye can perceive nothing, and its connection with the turning and motion of a thousand wheels at a distance from the piston-rod appear incomprehensible".³⁷²

However, this confession terminated with Liebig's declaration about the potential of the vital force. The last paragraph of the first section of the third part of his *Animal Chemistry* could answer the question: Was Liebig not a vitalist.

"So it is with the vital force and with the phenomenon exhibited by living bodies. The cause of these phenomena is not chemical forces; it is not electricity, nor magnetism; it is a force that has certain properties in common with all causes of motion and change in form and structure in material substances. It is a peculiar force because it exhibits manifestations which are found in no other force".³⁷³

³⁷¹ Ibid, 1842, pp. 230-231.

³⁷² Ibid, 1842, pp. 231-232.

³⁷³ Ibid, p. 232.

2.3.2 Robert Mayer and the exclusion of vital force

One of the influences that motivated Mayer's involvement in physiology was his deliberations about the production of animal heat in respiration.³⁷⁴ Liebig's Animal *Chemistry* attracted his attention to this subject. Mayer agreed with Liebig's considerations that the origin of the animal heat results from food metabolism and the oxidation of nutrients, but he strongly disagreed with Liebig's metaphysical vital force and its participation in the final explanation of life phenomena. Mayer claimed that the cause of all forces produced in animals, including heat and movement, originated from metabolism and chemical interaction between nutrients and the inhaled atmospheric oxygen. He differentiated his theory from that of Liebig's in three aspects: first, he considered that all forces in the animal were the result of metabolism that occurred in blood and not from the decomposition of organized animal tissues; second, he refuted the vital force categorically as an explanation for the muscle action or as a protection to the decomposition of tissues; third, he established a system of physics as a weapon against vitalism. Mayer's method of physics in which he employed mathematics appeared in his published paper of 1845, as noted earlier.³⁷⁵ "During the life process, the only conversion of matter or force occurs, but never a creation of one or the other". For animals, this statement leads to the formulation of the correlation of forces, as did Liebig and Helmholtz, the latter in the earlier stages of his investigation. Mayer proposed a thermodynamic equation correlating the chemical

³⁷⁴ Heiman argues that the first motivation for Mayer's interest in respiration and animal heat was the Java trip (see chapter 2, section 2, and paragraph 2.1 of this dissertation). Mayer confessed in a letter to his friend Griesinger two years after the trip (in 1844) that the light color of the venous blood and the process of acclimatization process after which venous blood became dark again led his thought to the production of animal heat in respiration. However, Mayer did not say how he had concluded from the physiology of blood the idea of the conversion of heat into work and vice versa (Heiman, 1974b, 279-281; Kremer, 1984, p. 220).

³⁷⁵ Chapter 2. Section 2, paragraph 2.1 of this dissertation.

force in the uptake of the nutrients and inhaled oxygen with the mechanical force and heat (chemical force = work + heat). As Helmholtz, Mayer added a separate explanation for the discrepancy observed in the correlation equations of Liebig. He argued that some organic substances in the animal body might break down and release heat without the intervention of inhaled oxygen, and he cited fermentation as an example.³⁷⁶

Mayer began his attack against the vital force in the context of Liebig's theory in his 1845 essay on muscle contraction resulting from the decomposition of muscle tissues. Mayer first noted the existing contradiction between the first two parts and the third part of Animal chemistry. In this third part, Liebig invoked the vital force to explain muscle contraction, whereas, in the first two parts, metabolism was the cause of the body movement.³⁷⁷ He suggested replacing the metaphysical vital force of Liebig's theory presented in the third part of the Animal chemistry with experimental facts. As noted earlier, Mayer did not perform experiments by himself. He used instead analogies and quantitative arguments to exclude the vital force from physiology. Mayer compared the metallic parts of the engine with the fibres of the animal muscles. As the metallic parts of the engines do not provide mechanical work and therefore are untouched during the engine's operation, so too the components of the muscle, the fibres, are the structural support of the muscles. Hence, they remain intact during the generation of force.³⁷⁸

The second Mayer's weapon against the vital force was logic. He posited rhetorical questions to certain points of Liebig's theory of muscle contraction regarding the cause that the vital force was supposed to serve. If, for example, the *vital force* is consumed

³⁷⁶ Kremer, 1984, pp. 227-228.

³⁷⁷ Ibid, p. 357.

³⁷⁸ Mayer, 1845; Weyrauch, 1893, p. 88; Kremer, 1984, p. 355.

protecting the muscle from decomposition, where does it go after death? If vital force is annihilated after death without producing mechanical force or any other kind of force, it violates the principle of the conservation of force.³⁷⁹ Furthermore, Mayer argued that animal tissues resist the direct attack of oxygen. Based on physiological findings, he contended that tissues at ordinary temperatures show a slight tendency to react directly with oxygen. Even if this weak tendency for oxidation of the organic matter exists, the oxygen affinity will be much higher for the fluid than for the solid tissues. It would combine with the more accessible circulating arterial blood than with the muscle tissues. He rejected altogether the hypothesis of tissues oxidation, asking if this hypothesis is correct, why then the muscle tissues are not quickly oxidized.³⁸⁰ Mayer considered that the improper use of the conservation principle offered another argument against Liebig's theory for vital force and muscle contraction. Liebig asserted that the sum of voluntary and involuntary movements of the animal in a given period is constant. However, Mayer noted that this is not possible since pulse and respiratory rates increase rather than decrease, as required by Liebig's theory during strenuous physical effort.³⁸¹

Mayer used quantitative arguments to reject Liebig's assertion that the muscle decomposes by oxygen in proportion to the mechanical work performed. However, Liebig presented no experimental facts to support his arguments. Mayer claims that if according to Liebig, the muscle tissues undergo oxidation and the resulting carbonic acid is

³⁷⁹ Mayer rejects Liebig's explanation that the vital force transforms into chemical force after death during the putrefaction. Mayer explains that the rapid putrefaction immediately after death results from the physical spread of the rotting material and not from the transformation of the vital force. Mayer proved to be correct. In the 1850s, Louis Pasteur (1822-1895) showed that the cause for fermentation and putrefaction were organisms in the air. In the 1860s, Joseph Lister (1827-1912) revolutionized surgical practice by utilizing carbolic acid (phenol) to exclude atmospheric germs and thus prevented putrefaction in compound fractures of bones.

³⁸⁰ Mayer, 1845; Weyrauch, 1893, p. 136; Kremer, 1984, pp. 357-358.

³⁸¹ Mayer, 1845; Weyrauch, 1893, pp. 137-138; Kremer, 1984, p. 156.

proportional to mechanical work produced, then the muscle of a man, who performs work equal to 32,810 kg per day (equivalent to the quantity of heat of 77,200 cal will have been wholly disintegrated in thirteen weeks. Working at the same rate, the heart muscle would have been oxidized in four days. In both cases, there is a very short time for muscle recovery. In this respect, muscles cannot burn their tissues.³⁸²

After the criticism on Liebig's theory on muscle contraction, Mayer presented his theory for the same subject in his 1845 assay, which, as noted earlier, appeared in 1893. Briefly, this theory ascribes the ability of the muscle to act due to arterial blood circulation through the muscle tissues. The blood oxygen combusts the carbon in blood from the ingested nutrients the latter received in the lungs. Oxidation of the carbon in the blood provides the tissues with heat, the necessary energy to produce mechanical motion.³⁸³ In other words, muscles use combustible materials for producing mechanical work independently of any vital force.

Mayer validated his theory by explaining some physiological phenomena. For example, he attributed muscle fatigue to the temporary depletion of the arterial blood supply in the muscle. The muscle recovers as the blood replenishes the vessels of its tissues. Mayer completed his theory on muscle contraction by explaining why the blood is oxidized only during muscle contraction.³⁸⁴ Mayer had used the analogy that muscles work like steam engines (see above). He perceived the muscles as machines that transform the chemical energy into heat and mechanical energy. As the ordinary steam engines, muscles are not efficient. Mayer attempted to provide some estimation of the efficiency of the

³⁸² Mayer, 1845, Weyrauch, 1893, pp. 89-90; Kremer, 1984, pp. 355-356. Kremer erroneously quoted 300,000 Kg. of work.

³⁸³ Mayer, 1845; Weyrauch, 1893, pp. 108, 114; Kremer, 1984, pp. 358-359.

³⁸⁴ Kremer, 1984, p. 360.

mechanical work performed by the human body. By taking into account measurements of the carbon intake from Liebig, he computed the body efficiency in mechanical work produced from the body heat. He found that the work produced from the heat provided by the circulating blood was about 18%.³⁸⁵

In 1851, Mayer wrote an article³⁸⁶ entitled *Bemerkungen über das mechanische Aequivalent der Wärme* that was published about forty years later. This article discussed the importance of the mechanical equivalent of heat already calculated in his 1845 essay, reflecting the equivalence between the muscle contractions and the working force produced and the heat obtained by physiological/chemical means.

2.3.3 Hermann von Helmholtz and the muscle contraction

As seen, Helmholtz approached the law of conservation of energy through the field of physiology, although he expressed the law in the context of physics. His first independent research in physiology after the completion of his dissertation was rather mediocre. He selected an intensively debated topic dealing with the causes of fermentation and putrefaction.³⁸⁷ One side of the debate represented by physiologists having as forefront Theodor Schwann (1810-1882) supported the position that microorganisms were the cause of decomposition in these processes.³⁸⁸ The side of chemists represented by Liebig

³⁸⁵ Mayer, 1845; Weyrauch, 1893, p. 86; Kremer, 1984, p. 160,

³⁸⁶ Mayer, 1851, pp. 1-56; Weyrauch, 1893, pp. 235-245.

³⁸⁷ Helmholtz, 1883, pp. 726-734; Kremer, pp. 239-240.

³⁸⁸ Theodor Schwann was a German physician and physiologist with an essential contribution to biology. He studied muscle contraction and developed an experimental method to calculate the contraction force of the muscle (Kremer, 1984, pp. 316-325). He discovered the enzyme pepsin as the physiological agent of digestion. His most significant contribution was establishing the structure and the functioning of plant and animal cells and their products. He formulated his cell theory from these studies, which became the basis for modern cell biology (histology). Furthermore, Schwann introduced the term "metabolism", which he first used in German science. For a short discussion about Schwann's contribution to biology, see Thomas, 2017.

attributed the cause solely to motions of atoms. No life is involved in these processes. Helmholtz seemed to favor Schwann's interpretation. However, his experiments on the conditions governing fermentation and putrefaction were ambiguous. In this first appearance, Helmholtz did not mention vital force and, in general, forces and anything related to animal heat. Despite his first unsuccessful appearance in the field of experimental physiology, he began to thrust deeply into the heart of this field.

Helmholtz approached the issue of vital force in the context of the old doctrine of the impossibility of the *Perpetuum mobile* (perpetual motion) and the Newtonian central forces.³⁸⁹ In their theories for the heat engines, Carnot and Clapeyron had already used these philosophical and mechanical doctrines known for almost a hundred years. However, the doctrine of perpetual motion seems to favor the concept of vital force. Nevertheless, scientists excluded perpetual motion from any physical or chemical process. Helmholtz thought that the role of vital force as the unique and continuous source of animal heat violates the reciprocity of the cause (heat ingested) and the effect (heat emitted), leading to a constant energy supply. The new field that Helmholtz chose to battle vital force was animal heat and metabolism.

In his first Bericht, Helmholtz criticizes the idea that heat results from the combustion process in the lungs. He emphasizes the discrepancy observed between the amount of heat evolved in the combustion of compounds *in vitro* and the heat produced by the nutrients in animals (*in vivo*). He rejected the view that oxygen contained in substances,

³⁸⁹ Elkana argues that perpetual motion was not one of the premises of Helmholtz. He claims that this doctrine was known well before the formulation of the conservation law; it was for Helmholtz the implication of the conservation law and not vice versa (Elkana, 1974, pp. 123, 130). Regardless of this detail, what is important in this case is that Helmholtz built his *Erhaltung* on the doctrine of perpetual motion and the concept of central forces. Helmholtz mentioned both premises already in the introduction of the *Erhaltung*.

such as alcohols and organic acids, did not participate in the heat released by combustion inside the organism. Helmholtz invoked the experimental data provided by Liebig and other chemists to strengthen his criticism against the theory of respiration.³⁹⁰

Following Liebig's conviction, that metabolism was the prime source of the heat produced in an organism. Helmholtz adopted Liebig's principle of the correlation of forces. He pursued the confirmation of this principle. In this respect, he scheduled the reformulation of the correlation equation introducing new equivalents between the animal action and the heat developed.³⁹¹ Shortly, he had to cope with two methodological problems. Liebig's theoretical determination of animal heat based on the combustion of foods did not agree with measurements performed by Dulong and Despretz. This discrepancy might be supportive of the presence of the vital force. Therefore, Helmholtz decided to choose an alternative conceptual model of heat that would allow him to interpret the correlation of forces that produced heat.

Since Liebig's correlation equation equaled the heat ingested with that liberated by the living body, the caloric theory of heat was the most appropriate to refute the vital force provided that the experimental data supported the equivalence of heat in both sides of Liebig's equation (ingested vs. emitted heat). Here Helmholtz faced the second methodological problem, the widespread conceptual model of heat as motion. This theory precluded the conservation of heat, advocating thus the vitalist origin of heat. Helmholtz had rejected the caloric theory in favor of the mechanical equivalent of heat.³⁹² Finally, to

³⁹⁰ Kremer, 1984, pp. 249-250.

³⁹¹ Helmholtz published this study in 1846 by the medical faculty of the University of Berlin (Helmholtz, 1846, pp. 542-566).

³⁹² In his Bericht of 1846, Helmholtz states without hesitation that the material theory of heat is no longer tenable, and that a kinetic theory must be substituted for it (Helmholtz, 1846, p. 542; Koenisberger, p. 34).

remove the discrepancy between theoretical predictions and experimental findings and eliminate the vital force for heat production, he adopted the caloric theory as a methodological approach. He obtained a theoretical reformulation of Liebig's equation. Helmholtz achieved this goal by the introduction in both sides of the equation, additional terms representing sources of the heat absorbed by animals through the oxidation of foods and the heat emitted not only from the respiratory channels but also from other organs of the living body. This modified equation gave physicians a well-defined theory that satisfied the experimental results.³⁹³

In addition, Helmholtz found that, on average, the quantity of heat generated by an animal is about eleven percent greater than that liberated by respiration. He concluded, therefore, that metabolism of nutrients alone might account for almost the entire quantity (within one percent) of the animal heat. "Hence we must be temporarily satisfied with the fact that at least very nearly as much heat is generated through chemical processes in the animal as we find in it and its output and that we must regard it as experimentally demonstrated that by far the greatest part of organic heat is a product of chemical processes".³⁹⁴ Nonetheless, the equation lacked the decisive component of the work done by animals and thereby the perspective for a mechanical equivalent of heat. At any rate, the exclusion of vital force from physiology was Helmholtz's determination at this stage.

In 1845, Helmholtz published an experimental paper entitled *Über den Stoffverbrauch bei der Muskelaction*. Helmholtz investigated whether the mechanical force and the heat generated in organisms resulted from the material exchange. He strove to find

³⁹³ Helmholtz, 1846, p. 544; Bevilacqua. 1993, 299).

³⁹⁴ Hemholtz, 1846, pp. 547.

possible relationships between mechanical muscle action and chemical changes manifested by the decomposition of muscle tissues. By doing this, he expected to exclude the vital force. "One of the most important questions of physiology, one immediately concerning the nature of the vital force, is whether the life of organic bodies is the effect of a special self-generating, purposive force or whether it is the result of forces active in inorganic nature which are specially modified through the manner of their interactions".³⁹⁵ Despite his exhaustive experimental efforts, he was unable to verify this view experimentally. He found that some minor breakdown of muscle fibres occurred, but his experiments could not decide this issue directly.³⁹⁶ Later, he abandoned the idea of chemical decomposition. However, it was reasonably evident that chemical changes, heating, and mechanical force occur concurrently during the muscle action. "I must leave unresolved one of the most important questions, namely, whether the muscle fibre participates in the reaction. This seems a priori highly probable, for we find that protein compounds are universally the bearers of the highest vital energies; and especially in our case, the appearance of an increased quantity of sulfates and phosphates in the urine after strenuous muscle activity speaks for a breakdown of phosphoric and sulfuric compounds. [...] Against a breakdown of the muscle fibre, however, speaks the fact that for the most part the quantity of water extract lost corresponds to the increase in spiritous extract".³⁹⁷

In this study of muscle contraction, Helmholtz had not attempted to correlate the mechanical work of the muscle contraction and the produced heat, since he could not have detected significant heating of active nerves in his experiments. Nevertheless, he did not

³⁹⁵ Helmholtz, 1845, p. 735

 ³⁹⁶ Helmholtz, 1845, pp, 737-743; Kremer, 1984, pp. 242-243; Lenoir, 1982, pp. 200-202.
³⁹⁷ Helmholtz, 1845, p, 743-; Lenoir, 1982, p. 202.

exclude the possibility that the nervous system provided some portion of the total quantity of bodily heat. Assuming that a small portion of heat has developed in the nervous system, the next question was crucial: Where did this heat come from? The answer to this question was crucial. If the heat in the muscle was so small that it is practically unnoticed by the experiment, then one could have argued that a portion of the heat would be transferred from the nervous system. This fact leads to the loss of bodily thermal constancy resulting from depressing the activity of the central nervous system, and therefore to resort to vital force for the recovery of the muscle activity. Helmholtz had to investigate the various causes that might give rise to the heat present in the tissues. Respiration, the influx of blood, the activity of the nerves were some of these sources of heat including the generated heat directly in the tissues themselves through the chemical process of material exchange.³⁹⁸

To give a definite answer to this critical question, Helmholtz had to measure the amount of heat of the muscle tissues. The task appeared impossible with existing measuring devices of temperature. Helmholtz decided to devise by himself an instrument capable of measuring such tiny amounts of heat. He did so by combining a thermocouple with DuBois-Reymond's astatic galvanometer. The device was indeed ingenious and allowed Helmholtz to measure temperatures differences as low as 0.037 °C per unit of the electric current. In 1848, Helmholtz published details for the construction and the calibration of the measuring device. He used as a model the frog legs as in the experiment of 1845.³⁹⁹ He measured temperature differences as small as 0.14 to 0.18 °C, corresponding to very small

³⁹⁸ This question reminds Joule's question while seeking to demonstrate that heat is not transported from the battery to the rotative electromagnet but is generated by the transformation of the work performed by the electromagnet.

³⁹⁹ Helmholtz, 1848. Timothy Lenoir provided a detailed description of Helmholtz's efforts to avoid possible systematic errors and construct an accurate device (1982, pp. 207-208).

quantities of heat. The result of this test was highly significant to his theory. He found that the amount of heat generated in the nerve would deflect the galvanometer needle no more than about 0.5 °C. This finding meant that the temperatures generated in the nerve could only be a few thousandths of a degree, which was an infinitesimal contribution to the temperature generated by the muscle contraction. Helmholtz derived two important conclusions from the experiment regarding the heat generated by the muscle action. First, the heat is generated directly in the muscle tissue itself, and its origin is due to chemical processes occurring in the muscles. Second, the heat is produced independently of the nerve stimulation, and the contribution of the nervous system to the total quantity of animal heat is negligible. With these two results, Helmholtz had effectively destroyed the possibility of the vital force intervention in muscle contraction and, in general to physiology.

Furthermore, in doing these muscle experiments, Helmholtz probably did not observe the relationship between the chemical forces represented by the chemical changes in the muscle tissues and the heat developed by the muscle action. Chemical reactions produced heat, which in turn induced a current in a thermocouple, giving rise to the deflection of an indicator in the magnetic field produced by the electric current of his apparatus. Helmholtz began to think about the conversion of forces.

Under the influence of Du Bois-Raymond and his colleagues in the *Berlin Physikalische Gesellschaft*, Helmholtz began to write his famous essay *Über die Erlhaltung der Kra*ft. As discussed in the previous chapter,⁴⁰⁰ Helmholtz applied the conservation of force to the principles of several physical phenomena of his time. In the last section of the *Erhaltung*, Helmholtz applied his two premises: the impossibility of the

⁴⁰⁰ Chapter 2, section 2, paragraph 2.5. A thorough analysis of the *Erhaltung* was nade in the Appendix of this dissertation.

perpetual motion and the Newtonian forces to life phenomena. Helmholtz attempted to discover the equivalence of the tension forces inherent in the chemical processes (chemical tensions) and the vis-viva in the form of heat and mechanical work. For the kingdom of plants, he admitted that insufficient experimental data and lack of appropriate methodological approaches precluded the precise application of the principle of the conservation of force to life phenomena. He could say that the stored tension forces were chemical in origin and that the only absorbed heat (vis-viva) was the chemical solar rays.⁴⁰¹ For the animal world, the theoretical treatment was more fordable. The conservation of force is possible since animals utilize a certain quantity of chemical tensions and generate heat and mechanical forces. He considered the production of work from the transformation of heat, but he alluded that the mechanical work was small compared with the quantity of heat evolved. He suggested eliminating mechanical work from the equivalence.⁴⁰² The experiments of Dulong and Despretz corroborate this suggestion. In the sense that the heat generated by the combustion and the transformation (metamorphosis) of nutrients were equal to the heat given out by the animals. That is the perseverance of the principle of the conservation of force.

Summarizing the contribution of Liebig, Helmholtz, and Mayer to the conservation of force, physiology provided the context, but not necessarily the source of the ideas of the three men concerning the conservation of force. In the context of physiology, these scientists attempted to correlate the calorimetric experiments of Dulong and Despretz with a chemical theory of heat (respiratory or else).⁴⁰³ The conservation of force became clear

⁴⁰¹ *Tyndall, 1853,* p.160.

⁴⁰² *Ibid,* p.161.

⁴⁰³ Other physiologists and chemists followed this line. For instance, physiologist Hermann Nasse (1807-1892) alleged that the blood pumping creates frictional heat that should be taken into account in the

when chemistry, physics, and mathematics entered the field of physiology. The employment of physics and chemistry allowed Helmholtz and Mayer to reject the vital force and realize that conversion processes occurring in the animal body by metabolism or other chemical processes should include the work done by the muscles. Only Helmholtz and Mayer succeeded in transcending the threshold of the conservation of matter to enter the conservation of force. Liebig did not go beyond the correlation or conversion of forces, although he resorted to examples from physics and chemistry to support his chemical theory.⁴⁰⁴ On the other hand, the very research for muscle contraction to exclude the vital force inspired Mayer to articulate the law of the conservation of force and Helmholtz to write the *Erhaltung*.⁴⁰⁵

Conclusions of part I

The first half of the nineteenth century is perhaps one of the most important periods for the subsequent development of chemical thermodynamics. The early experiments and theories of the natural philosophers of the eighteenth century were transformed during the

generation of heat other than respiration and oxidation of foodstuffs. Using Joule's mechanical equivalent of heat estimated that the heart could generate about one-tenth of the heat produced by the animal through respiration (Nasse, 1850; Kremer, 1984, p. 256).

⁴⁰⁴ Liebig described different physical phenomena in relation to the origin of forces and heat in animal bodies. He presented analogies between the bodily heat and the heat produced in a galvanic cell, during friction and light absorption. It was characteristic the example of the battery connected to a wire conductor. Liebig compared his theory of the correlation of forces in living systems with the chemical, electrical, and magnetic phenomena correlated via a mutual interconversion (Liebig, 1842, pp. 31-32).

⁴⁰⁵ Kremer supports the view that Helmholtz did not write the *Erhaltung* to reject the *vital force*. He doubts that Helmholtz succeeded in bringing heat and work into a thermodynamic equation (1984, pp. 237-238). Koenisberger, on the other hand, favors the opposite view in his official biography for Helmholtz. He considers vital force a significant cause that led Helmholtz to his famous essay (1906, pp. 25-26, 50). Lenoir shares Koenisberger, opinion (1982, p. 213-215). Regardless of these opposite views, Helmholtz hints at his *Erhaltung* that vital force does not exist (Helmholtz, 1847a, p. 4; Tyndal, 1853, p. 116). Besides the reformulation of the experimental physiology that preached by the group of the Berlin Physikalische Gesellschaft would be meaningless without attacking the vital force.

nineteenth century into principles and laws of physics and chemistry. At the same time, the seed of new sciences other than thermodynamics, such as electrochemistry and chemical kinetics, found prolific soil to grow. The studies of the first electrochemists Grotthuss, Berzelius, Faraday, Grove, Daniell, Becquerel, and others, contributed to the rapid growth of electrochemistry during the second half of the nineteenth century. Hittorf and Kohlrausch unravel the properties of ions and electrolytes, paving the way for developing the modern theory of electrolytic dissociation. On the other hand, the early experiments of Berthollet, Guldberg and Waage, Wilhelmy, Berthelot, and the Danish chemist Hans Peter Jørgen Julius Thomsen (1826-1909) led to the discovery of the mass action law, and the introduction of time and the concepts of the reaction rates and the equilibrium constant laid the foundation for the field of chemical kinetics.

The discovery of the first two laws of thermodynamics was one of the more significant results of the research activity of prominent physicists in the first half of the nineteenth century. The first law was the result of a simultaneous scientific and philosophical activity. Energy conversions studied in the laboratory that sought to improve the efficiency of steam engines, and the influence of the philosophical doctrines of the *Naturphilosophie*, which advocated the unity of all physical forces, were significant factors that led to the formulation of the conservation law. On the other hand, the combined efforts of physiologists and chemists enunciated the first law or the principle of correlation of forces from another perspective. The study of life processes and the controversy over the existence or absence of the indestructible vital force as the regulating force of chemical and physiological processes in living bodies led Mayer and Helmholtz to articulate the first
law of thermodynamics. However, the two physicians were able to do so, only upon introducing physical and chemical considerations to explain their findings in physiology.

The second law of thermodynamics began along with the industrial need to construct efficient steam engines. The necessity to improve their efficacy motivated the young French engineer Sadi Carnot to reevaluate their performance and propose new working conditions to enhance their effectiveness. Only through a reversible cycle, steam engines acquire the highest degree of efficiency and cost-effectiveness. Along with the practical results in engines, Carnot established some theoretical considerations that led him very close to the enunciation of the second law, known as Carnot's theorem. However, his theoretical treatment was inconsistent with the new conceptions concerning the nature of heat. The new theory that considered heat as motion replaced the old doctrine that viewed heat as a material substance. Although the old theory of heat did not prevent the engines from working reversibly, increasing thus their efficiency, the physicists sought to reconstruct the physical processes upon another foundation. Clausius was the first physicist who appreciated the value of Carnot's theorem. He immediately adapted this principle to the new kinetic theory of heat. This simple correction of Carnot's theorem constituted the second law of thermodynamics. Rankine formulated the same law based on a different theoretical context related to a microscopic structural model. The third physicist of this group, William Thomson, tormented by the question of where the heat would go, for example, after percussion or friction, hesitated to accept Joule's experiments that proved the equivalence between heat and work. Finally, a year after Clausius' statement, Thomson articulated the second law of thermodynamics differently but equivalent to that of Clausius.

PART II. The second half of the nineteenth century: The advancement of electrochemistry and thermodynamics

The modern⁴⁰⁶ chemical thermodynamics invented by the ironists did not develop in a vacuum. In the last quarter of the nineteenth century, the development of electrochemistry, solution chemistry, chemical kinetics, and thermodynamics provided a prolific soil of new ideas, theories, and methods for the ironists. The theoretical interpretation of experiments in chemical equilibrium, rates of reaction, electrochemistry, and thermochemistry showed progress. However, these theories were fragmentary, occasioned for separate experiments. With the exception perhaps of thermochemistry, these investigations did not constitute an integrated theoretical system. Yet, during the second half of the nineteenth century, theoretical approaches "escaped" the blockage of organic chemistry and offered a proper understanding of the physical, chemical, and electrochemical phenomena. The second part of this dissertation is dedicated to advanced experiments and explanations for galvanic and electrolytic cell processes and new theoretical models of thermodynamics that emerged during the last quarter of the nineteenth century. Gibbs, Duhem, and Helmholtz developed new approaches to thermodynamics. They were changing the fate of chemistry from a purely experimental and classificatory science into a dynamic, theoretical science. Some historians considered the thermodynamics of these three physicists to constitute the

⁴⁰⁶The term "modern" has been used to characterize the chemical thermodynamics that developed during the last two decades of the nineteenth century may not be justifiable. Since then, chemical thermodynamics has been enriched with new concepts, methods, theories, and experimental findings, whereas older concepts have been eliminated. For instance, the technique of reversible cycles introduced by Clausius and adopted by van 't Hoff and Lewis had been replaced by Gibbs' chemical potential and free energy. The thermodynamics of dilute solutions has been extended to concentrated solutions, the so-called real solutions.

beginning of the development of chemical thermodynamics during the nineteenth century. Their theories had a significant impact on the subsequent development of the ionists' chemical thermodynamics. Indeed, several of their propositions could have offered earlier than expected, solutions to the long-standing problems of chemical affinity and chemical equilibrium and the elucidation of the laws that governed non-equilibrium processes. However, several reasons delayed the penetration of their approaches to thermodynamics into chemistry. At any rate, the ionists were the scientists who achieved the transfer of thermodynamics into chemistry.

This chapter is devoted to the study of the progress of electrochemistry, and thermodynamics for conceptual and historical reasons. For a long time during the nineteenth century, energetics, thermodynamics, and electrochemistry were inseparable. Thermodynamics and electrochemistry have developed in parallel. Gibbs and Duhem used experiments from galvanic cells to exemplify their theories. Helmholtz entered thermodynamics investigating the phenomenon of polarization) the functioning of different kinds of galvanic cells (e.g., concentration cells), and calculated the electromotive force.

Chapter 5. The second generation of electrochemists

From 1850 onwards, science instilled two methodological approaches: the mathematization of natural processes and the development of advanced instrumentation requiring great skillfulness. Regarding electrochemistry, one can trace two innovations that gave a new impetus to this field. The first innovation was theoretical and concerned with applying the kinetic theory of gases to electrolytic solutions by Clausius. The second innovation involved the construction of sophisticated instrumentation to study the properties of the electrolyte solutions. Wilhelm Hittorf measured the velocity of ions in solutions, and the fraction of the electrical charge transferred by each ion to the electrolytes to conduct electricity. The ionists, Nernst, and other electrochemists signaled the second innovation.

The development of electrochemistry stepped on the outstanding achievements of the previous generation of electrochemists. Hittorf's research on the transference numbers, Kohlrausch's measurements of the electrical conductivity of electrolytic solutions, and Clausius's theory on the structure of solutions linked the scientific past with the scientific future underscored by the formulation of the theory of solution by the ionists. The invention of new instrumentation, the methodological approaches, and the collection of a vast number of measurements by the two electrochemists facilitated both Arrhenius and Ostwald in their undertakings. Arrhenius established the theory of electrolytic dissociation, and Ostwald performed conductivity measurements to correlate the chemical reactivity with the electrical conductivity and to derive the dilution law of the electrolytes. Arrhenius and Ostwald considered Kohlrausch's device for measuring electrolytic conductivities far more accurate than any other instrument they have used previously. David Cahan remarked that Kohlausch's work between 1869 and 1880 played a crucial role in establishing chemical thermodynamics and later physical chemistry.⁴⁰⁷

Section 1. Johann Wilhelm Hittorf: The migration of ions and their transference numbers

Wilhelm Hittorf was a *privatdozent* at the Royal Academy of Münster. He appointed professor when the academy became a university.⁴⁰⁸ He investigated the way the ions move in solution under the influence of the electric current during electrolysis. Hittorf was aware of the electrolytic decomposition mechanisms proposed by Davy, Grotthuss, and Faraday. He found the theory of Faraday more appropriate to explain his experiments. The decomposition of bodies into ions is an internal process. It occurs in solution upon the electric current's action and not the result of the attractive and repulsive forces of the electrodes. He appraised Faraday's action law as the single quantitative measure of the electrodes, provided that the current of electricity is inconstant quantity.⁴⁰⁹ Hittorf used this law to measure the concentrations of ions around the electrodes when he attempted to determine the ratio of the transference numbers expressed by the amount of the ions in the areas around the two electrodes.

⁴⁰⁷ Cahan, 1989, p. 167, 182.

⁴⁰⁸ For a short biography of Hittorf, see Drennan, 1981, pp. 438-440.

⁴⁰⁹ Contrary to the usual practice, Hittorf dedicated the introduction of one of his four papers on electrochemistry (first published in Ostwald's *Klassiker* and translated in English in 1899) to discuss the theories of previous investigators (Hittorf, 1899, pp. 49-51). The journal's editor, in which this paper appears, provides a short biographical note of Hittorf (Hittorf, 1899, pp. 80-81).

Hittorf presented graphically the decomposition process of electrolytes in solution and the propagation of the electric current. He combined Berzelius' dualistic theory of affinity (as electropositive and electronegative forces) and Faraday's notion of the ions. He considered the ions as a hybrid of these two theories. More importantly, for him, was the accurate description of the movement of the ions in solution. Hittorf believed that the elucidation of the exact nature of migration of the ions between the two electrodes under the influence of the electric current would shed light, not only in the decomposition process but also in the way by which the ions combine in the molecule. In other words, a possible relation between the velocities by which the ions move in solution and their chemical affinity. The propagation process, he suggested, was similar to the step-by-step action envisaged by Faraday. However, he adopted a graphical representation of propagation identical to that of Berzelius, placing the two ions one below the other supposedly moving in a horizontal direction (Figure 1-5).⁴¹⁰ This arrangement avoids the rotation of the molecules and allows the process to continue undisturbed. However, most importantly, this arrangement depicts the distance covered by the ions during their transference to the electrodes, "it seems possible to determine by experiment the relative distances through which the two ions move during electrolysis".⁴¹¹ He found that these distances are analogous to the relative velocities⁴¹² of the two ions moving towards the two electrodes. For equal velocities, both ions traverse equal distances. After electrolysis, the "borders" near the anode and cathode will contain equal numbers of equivalents of anions and cations,

⁴¹⁰ Figures 2 and 3 in Hittorf, 1899, pp. 52-54.

⁴¹¹ Hittorf, 1899, p. 52.

⁴¹² Kohlrausch first introduced the term mobility. Today, the term ionic mobility has replaced the words velocity or the rate of an ion in solution. The ionic mobility expressed in $m^2/(V \cdot s)$ depends on the intensity of the electric current, the ion's nature, the electrolyte's concentration, and the properties of the solvent (dielectric constant, lack of reactivity with the electrolyte).

respectively. On the same electrodes, e. g., the anode, the number of equivalents of anions will be greater by the same amount as the number of equivalents of the cations is less. The inverse relationship exists between the equivalents of the anions and cations in the area around the cathode. For unequal velocities, the concentration of the ions in the compartment around the electrodes must be different. If, for example, one ion moves through distance 1/n, and the other ion at a distance equal to $(\underline{n}-1)/n$, then, after electrolysis, 1/n more equivalent of the former ions will be discharged on the respective electrode and (n-1)/n, fewer equivalents of the latter ions.⁴¹³

After theoretical considerations, Hittorf worked out an experimental program to determine the relative ionic velocities by using a measuring device of his design. This device ensures "the exact separation of the electrolyte without introducing a diaphragm"⁴¹⁴ that may obstruct the progress of the ions. He constructed an apparatus in a glass cylinder divided into two parts, accommodating the anode (lower part) and the cathode (higher part).⁴¹⁵ The cylinder has a vertical position to disturb the smooth running of the electrolysis. The anode has a circular perforated plate. The cathode has a different shape to prohibit metal deposits during electrolysis (**Figure 13**). The deposit of the electrolysis was collected below the electrode. Hittorf found that the conic shape of the electrode is more suitable for preventing the accumulation of metal ions near the electrode; hence, the compartment of the anode is somewhat larger than the compartment of the cathode. Both compartments are filled with the same electrolyte. During electrolysis, the liquid around the anode becomes more concentrated and remains in the lower compartment, whereas the

⁴¹³ Hittorf, 1899, p. 54.

⁴¹⁴ Ibid, p. 57.

⁴¹⁵ Ibid, pp. 57-60, Figs. 4 and 5.

solution around the cathode is diluted. The solutions in both compartments were analyzed to determine the quantity of the metal deposits. The determination of the deposited metal is necessary for the computation of the transference numbers.⁴¹⁶ The transference numbers are defined as the ratios of the percentage of the amounts of anions and cations deposited in the electrodes during electrolysis⁴¹⁷. Hittorf associated the velocities of the ions' migration with their transference number. He did not consider independent the ions velocities; Experimenting with salts having a common ion, he observed that "If we glance at the values [of transference numbers] obtained with the three silver salts, it is at once evident that the same cation migrates by different amounts when in combination with different anions, the condition of the solutions remaining otherwise the same".⁴¹⁸ Interpreting Hittorf's reasoning on the transference numbers and velocities *u* and *v* of the cations and cations, respectively, a reciprocal relationship between these two quantities hold:

Decrease of the concentration in the compartment of the anode $\underline{}$	(5, 1)
Decrease of the concentration in the compartment of the cathode $\frac{1}{v}$	(3.1)
transference number of cation, $n = u/(u + v)$	(5.2a)
transference number of anion, $(1 - n) = v/(u + v)$	(5.2b)
Hittorf performed a large number of experiments with several salts containing different	
combinations of ions by varying the strength of the electric current, the concentration of	

the electrolyte in solution, and the temperature (Figure 13). He sought to determine

⁴¹⁷ The contemporary definition of the transference number is the ratio of the electric current derived from the cation or the anion to the total electric current. In other words, the transference number is the fraction of current carried by the ions. The transference number is connected to the ionic velocities. ⁴¹⁸ Hittorf, 1899, p. 76

⁴¹⁶ Ibid, pp. 59-61. It was Hittorf who introduced the term transference number and not Kohlrausch as stated elsewhere (Petit, 2013, p. 167).

whether the transfer of ions depends on these factors. The results of experiments were expressed as the percent concentration of the ions near the respective electrodes. He concluded from these results:⁴¹⁹

- The strength of the electric current does not affect the transference number of the ions. The transference numbers of the ions remain constant.
- The transference number increases with the dilution of the electrolyte. There exists a lower limit of concentration, below which the ionic transference remains constant. This limit is not common and depends on the nature of the electrolyte.
- The temperature does not affect the ionic transference number between certain limits, ranging from 4 to 21 °C. However, these experiments provide no information as to whether this range of temperature holds for all electrolytes. Neither justifies the cause of this limited temperature range in which the transport of the ions remains constant.

• The type of anion influences the transference number of the cation and vice versa. Hittorf performed several experiments with solutions of different concentrations and determined the transference numbers of the silver cation in silver sulfate, silver acetate, and silver nitrate; these were 44.6%, 62.6%, and 47.4%, respectively. In contrast, the transference number of the anions sulfate, acetate, and nitrate of the same salts were 55.4%, 37.4%, and 52.6%, respectively.⁴²⁰ In these numbers, Hittorf saw a relation with chemical affinity; "The farther apart two substances stand from each other in the voltaic series, the stronger appears their chemical affinity. We might, therefore, look for a measure of

⁴¹⁹ I, pp. 63, 67, 68, 73.

⁴²⁰ Hittorf, 1899, pp. 61-76.

chemical affinity in the distances through which the anions migrate during electrolysis".⁴²¹ Nevertheless, he was quite prudent to denote, "At present, however, I am far from ready to assign this significance to the above figures".⁴²²

As often happens, Hittorf's contemporaries did not immediately accept his experimental results and interpretations. An exception was Kohlausch, who praised the work of Hittorf.⁴²³ Kohlausch used Hittorf's results in his electrical conductivity experiments to advance the emerging discipline of electrochemistry. Hittorf continued his research on conductivity, but this time in the gaseous state. He began a series of demanding experiments on phenomena observed after the passage of electricity through rarefied gases and the unusual behavior of cathode rays.⁴²⁴ These investigations led to the brilliant discovery of the gas discharged tubes and the exploration of the properties of cathode rays by several investigators including William Crookes (1832-1919).

Section 2. Friedrich Kohlrausch: The conductivity of electrolytic solutions

Hittorf used diagrams to illustrate the migration of the ions in solutions. At the same time, Kohlrausch used a combination of experiments and mathematical formalism to describe the effects of the invisible ions on the macroscopic properties of the electrolytic solutions. Kohlrausch, however, had to overcome the obstacle of polarization that caused systematic errors in electrical conductivity measurements. Several electrochemists had observed the

⁴²¹ Ibid, p. 77.

⁴²² Ibid

⁴²³ Kohlrausch mentioned in his publications Hittorf 's success in giving his results a surprising measure of certainty through an admirable skill in the arrangement of his devices and the appropriate care in his determinations and analyses,

⁴²⁴In 1869, Hittorf published the first paper on a long-term project in gas discharge research (Hittorf, 1869). In the following years, he published several articles, where he combined the gas discharge phenomena with the definition and precise measurements of physical properties (Müller, 2011).

phenomenon of polarization of electrodes during electrolysis. They had applied *ad hoc* measures to obviate the phenomenon without great success. Polarization disturbs the process of electrolysis and distorts experimental results. Polarization is manifested as an electrical side-effect. It appeared as a bias-current that opposes the electric current of electrolysis from the battery or as chemical complexity in the form of secondary chemical reactions that occur at the interface between electrolyte and electrodes. Kohlausch began an ambitious research program that involved the measurement of the electrical conductivity of electrolytic solutions. The prerequisite for achieving this goal was the measurement of the resistance of the solution, which seems impossible or highly inaccurate due to polarization. Furthermore, his decision to measure the electrical resistance of solutions led him to test the validity of Ohm's law for conducting liquids. Nevertheless, to achieve both research targets, Kohlrausch had to eliminate first the effect of polarization.

He attempted to remove this obstacle with two innovations: one mechanical and the other electrical. He described his instrumentation and methodological innovations in detail in an article published in 1869 in collaboration with his teaching assistant Wilhelm August Nippoldt (1843-1904).⁴²⁵ Preliminary experiments and calculations have shown that the polarization was proportional to the current density at the electrodes. The first measure they had applied was the increase in the size of the electrodes. They expected that larger electrode plates would reduce the current density at the surface and thereby the phenomenon of polarization.⁴²⁶ The next step to rid the polarization was alternating current, i.e., an electric current (AC), which periodically reverses direction, in contrast to the direct

⁴²⁵ Kohlrausch, and Nippoldt, 1869. Abstract of this article in English has been translated and published in the *Philosophical Magazine*.

⁴²⁶ Ibid, pp. 296-297; Cahan, 1989, p. 172; Petit, 2013, pp. 51-53.

current (DC), which flows only in one direction. They thought that two opposing electric currents having the appropriate intensity value could, during the electrolysis, separate the two constituents of the electrolyte in chemically equivalent amounts, assuming that they immediately reunite to form the original chemical bond. They hoped that the alternate current could retain each electrode in the initial state after the two opposing currents have passed through each electrode.⁴²⁷

The next step was the construction of the apparatus to apply this method. Kohlrausch invented a device constituted of three indispensable units: an induction unit, which gave alternating currents, a second unit which controlled and measured these currents; the third unit was a rheostat to compensate for the resistance of the solvent. Once the compensation was achieved, it was clear that polarization disappeared, and the rheostat measured the resistance of the electrolytic solution solely.⁴²⁸ The memoir continues with determining the resistances of a series of aqueous solutions of sulfuric acid of various concentrations, all measurements at the same temperature. The results confirmed the validity of Ohm's law. An important observation made by the two experimenters was that concentrated solutions did not obey Ohm's law strictly. In 1874, Kohlrausch constructed a new induction apparatus that provided a *sine-shaped* alternating current more accessible way, more regularly, and more quietly than when the induction machine supplied a siren. Kohlrausch's new device is depicted in **Figure 14**.⁴²⁹

⁴²⁷ Ibid, 1869, p. 282-283. Kohlrausch admitted that the method of the alternating current had been employed by other scientists (he mentioned de la Rive, Lenz, Poggendorff, de Heer). However, he insisted that these attempts did not destroy the polarization. For the complete annulation of this phenomenon, he proposed the diminution of the duration of the two components of the alternate current.

⁴²⁸ Ibid, 1869, pp. 285-288.

⁴²⁹ Kohlrausch, 1874; Cahan, 1989, p. 175.

Equipped with the new instrumentation, Kohlrausch advanced his research program to determine the electrical conductivity of electrolytes.⁴³⁰ This time in collaboration with a new assistant Otto Grotrian (1847-1921), at the University of Darmstadt. He completed this study and established his theory on electrolytic conductivity at the University of Würzburg during the second half of the 1870s. In Darmstadt, the two collaborators performed a series of exhaustive experiments measuring the resistances and conductivities of thirty-five different solutions of strong electrolytes, mostly chlorides of alkalis and alkaline earths, to varying concentrations from 5% to 62% at three different temperatures, 0 °C, 18 °C, and 40°C. They observed first, the conductivity of all solutions increases with the increasing concentration of the added salt. However, the conductivity curves do not show the same behavior with concentration for all electrolytes.⁴³¹ The conductivity curves showed a linear dependence in the range of small concentrations, which was more extended for the univalent salts, e.g., NaCl, KCl, than for the bivalent salts, e.g., CaCl₂, MgCl₂ at the same concentration range. At much higher concentrations, the electrolytic curves of the bivalent electrolytes showed a maximum.⁴³² The linear dependence of the conductivity of strong electrolytes observed in dilute solutions is known as Kohlrausch's law.⁴³³ Second, the temperature affected nearly uniformly the electrical conductivity of the electrolytes in question. Despite that, the dependence of conductivity on temperature coefficient as a

⁴³⁰ Current textbooks of physical chemistry use the word conductace instead of conductivity. However, there is a substantial difference between these two terms. Conductivity is the inherent property of the material. The degree to which the material conducts electricity, in this case, the electrolytic solution. On the other hand, conductance is the measured value that relates the conductivity with the geometry of the material (shape, area). The absolute value of conductance is given as the reciprocal value of the resistance of the electrolytic solution.

⁴³¹ Kohlrausch and Grotrian, 1875, pp. 231-233, and Figure 1.

⁴³² Ibid, p. 232, and Figure 1.

⁴³³ Kohlrausch did not investigate the electrical conductivity of weak electrolytes in this study and, therefore, he was unaware of their different behavior compared to strong electrolytes.

function of the electrolyte concentration did not follow the same trend. The univalent electrolytes demonstrated, in general, a decrease of their conductivity values with the temperature coefficient, whereas the conductivity of the bivalent electrolytes showed the reverse trend.⁴³⁴

Kohlausch thought that his earlier measurements were inadequate to have a clear interpret the conductivity of electrolytic solutions fully. He felt that comprehensive experiments were needed to escape superficial observations and, in particular, quantify the results. In 1876, he published a long memoir *Das Elektrische Leitungsvermogen der Chlor*, *Brom- und Jod-Wasser- stoffsaure, der Schwefel-, Phosphor-, Oxal-, Wein- und Essigsaure in wassrigen Losungen.*⁴³⁵ He presented new results for many aqueous solutions of inorganic monobasic and polybasic acids, including weak organic acids (oxalic acid, tartaric acid, acetic acid), discussing unique aspects of conductivity. He correlated the conductivity behavior of acids with their properties (acid strength, specific weight, molar mass), their physical state (e.g., fumed vs. diluted sulfuric acid or neat vs. diluted acetic acid), and the influence of external variables, including concentration, and temperature. Three comprehensive Figures showed these correlations graphically. These correlations observed in this study are shown in **Figure 15**:

A few results in this study have been brought in connection with his earlier work in collaboration with Grotrian and the results obtained by other researchers. These results have been further discussed in the context of the electrolytic transference numbers proposed by Hittorf that have given a clear expression of the conductivity of many diluted

⁴³⁴ Ibid, pp. 228-231, and the insert in Figure 1.

⁴³⁵ Kohlrausch, 1876a.

aqueous solutions. The conductivity behavior of the various electrolytes of this study can be summarized as follows:

Figure 15a shows the dependence of the absolute electrical conductivity (see below) with the concentration (expressed in percentage of the substance dissolved in water) at $18 \,^{\circ}$ C.

- At small concentrations, the behavior of the electrical conductivity of all inorganic acids (Hydrochloric acid, hydrobromic acid, nitric acid, phosphoric acid, and hydrogen iodide) is linear.—The same behavior is observed for the strong bases and the salt of strong electrolytes (ammonium chloride, ammonium nitrate, potassium bromide, potassium chloride, caustic soda, ammonium sulfate, sodium chloride, and potassium carbonate). The range of concentration where linearity is observed depends on the nature of the acid, and in general of the nature of the electrolyte.
- As the concentration increases (limited only by the solubility of the acid in water), the electrical conductivity curve reaches a maximum and then decreases. Sulfuric acid nitric acid and hydrochloric acid show the highest conductivity maxima and phosphoric acid the lowest.
- The organic acids (tartaric, oxalic, and acetic acid) conduct electricity much lower than inorganic acids, with the least conductivity indicated by the weakest acetic acid. Their maxima are lower in comparison with the maxima of the inorganic acids, the smallest shown by the acetic acid.

Figure 15b, shows the temperature dependence of the monobasic and polybasic acids.

• The monobasic inorganic acids HCl, HI, HBr, and HNO₃ form a separate group, the conductivity of which indicates similar behavior concerning the effect of temperature.

Their temperature coefficients are the same, and almost independent of the concentration. This is shown clearly in **Figure 15c** in which the temperature coefficients are plotted in a shorter range of concentrations.

- The temperature coefficients of polybasic acids, sulfuric, and phosphoric acids, show a differential behavior among themselves and to those of monobasic acids. In particular, the dilute phosphoric acid has the smallest temperature change. On the other extremity lies the acetic acid, which shows much less variability with temperature.
- Sulfuric acid shows the most unusual behavior. The temperature coefficient starts from a small value, grows fairly evenly, and then rises faster, reaching a maximum, decreasing again until it increases at a much higher concentration, reaching a second minimum.

Kohlrausch proceeded to quantify the conductivity behavior of the acids in dilute solutions fitting the experimental results with an empirical quadratic equation of the form:⁴³⁶

$$k = xp + x'p^2 \tag{5.3}$$

Here, k is the absolute conductivity (it is the reciprocal of the resistance. Today is called specific conductance) of the solution, and p is the concentration of the acid, using Kohlrausch's notation. The coefficients x and x' are determined from the measured electrical conductivity of solutions of known concentrations of the particular substance. The coefficient x denotes the specific conductivity (today is called resistivity) of the electrolyte. In dilute aqueous solution, the specific conductivity shows a linear behavior with acid concentration (in this case, x' becomes zero). In general, the linear dependence of the absolute electrical conductivity of strong electrolytes (strong acids, strong bases, and

⁴³⁶ Ibid, p. 266.

salts) with concentration represents the first law of Kohlrausch. At higher acid concentrations, the conductivity declines from the proportionality with the concentration.⁴³⁷ In the higher concentrations, the quadratic term in Eq. (5.3) is required to fit the experimental data. In other words, Eq. (5.3) describes both cases. Kohlrausch expressed the generality of this equation as follows: "the two constants *x* and *x*' make the conductivity properties [of electrolytes] numerically comparable at least for dilute solutions".⁴³⁸ However, none of the above quantities had concrete units. Kohlrausch converted the specific conductivities of acids into electrochemically equivalent quantities. That is, weights decomposed by the same amount of electricity (Faraday's law) by multiplying the specific conductivities by the corresponding equivalent weights. The electrochemical equivalents were the same for monobasic acids but considerably smaller for polybasic acids.

As noted, the electrical conductivity is temperature-dependent. Kolhrausch employed a second-order equation to describe the influence of the temperature on the conductivity of the acids, namely⁴³⁹

$$k_{\rm t} = k_0 (1 + \alpha t + \beta t^2) \tag{5.4}$$

 k_0 , α , and β are constants determined by fitting the experimental data to Eq. (5.4). The consistency of this equation has been already tested in **Figure 15**.

The second law of Kohlrausch concerned the independence of the velocities of the ions in solutions. Kohlrausch was aware of the link between the transference numbers of the components of the electrolyte and their velocities proposed earlier by Hittorf. He sought

⁴³⁷ Ibid, pp. 266-267.

⁴³⁸ Ibid, p. 266.

⁴³⁹ Ibid, p. 249.

to connect the velocities of the ions with conductivities. His reasoning was based on Faraday's law that water was a poor conductor of electricity and acted only as a medium in which electrolysis of the dissolved electrolyte occurs. The displacements of the constituents of the electrolyte as they migrate in solution impart an electrical resistance. This resistance is due to the frictional resistance that the migrating ions experienced against the water molecules and to each other. Therefore, the electrical conductivity must have a connection with the velocities of the ions. Kohlrausch enunciated this idea in a rather short article Uber das Leitungsvermbgen der in Wasser Gelhsten Elektrolyte im Zusammenhang mit der Wanderung ihrer Bestandteile published in 1876.440 He concluded from this idea that "in a dilute solution every electrochemical element has a perfectly definite resistance pertaining to it, independent of the compound from which it is electrolyzed". ⁴⁴¹ It took three years for Kohlraush to confirm this hypothesis and hence the relationship between the electrical conductivities and transference numbers of electrolytes. In other words, the validity of Hittorf's Eq. (5.2). The denominator of this equation gives the sum of the velocities of the electrolyte's two components (ions). Therefore, for Kohlrausch to obtain the sought relationship between conductivities and transference numbers, will suffice to derive an expression that connects the ratio of the conductivities of two electrolytes, which have a common ion, with the ratio of the transference numbers of the same electrolytes. He chose two electrolytes with a common ion, e.g., chlorine in the salts NaCl and KCl, and measured their electrical conductivities, l_{NaCl} and l_{KCl} , respectively. Denoting the velocities of sodium and potassium ions as u_{Na} and u_K , respectively, and u_{Cl} the velocity

⁴⁴⁰ Kohlrausch, 1876b.

⁴⁴¹ Ibid, p. 215.

of chlorine ion, he wrote the transference numbers of the common ion n_{Cl} and n'_{Cl} in the two electrolytes:

$$n_{Cl} = \frac{u_{Cl}}{u_{Cl} + u_{Na}} \tag{5.5a}$$

$$n'_{Cl} = \frac{u_{Cl}}{u_{Cl} + u_K}$$
 (5.5b)

After a little algebra, Kohlrausch managed to establish the relationship between the ratio of the electrical conductivities of two electrolytes and a common ion to the ratio of their transference numbers, namely,

$$\frac{l_{NaCL}}{l_{kCl}} = \frac{u_{Cl} + u_{Na}}{u_{Cl} + u_{K}} = \frac{\left(\frac{u_{Cl}}{u_{Cl} + u_{K}}\right)}{\left(\frac{u_{Cl}}{u_{Cl} + u_{Na}}\right)} = \frac{n_{Cl}'}{u_{Cl}}$$
(5.6)

He then concluded that, "the conductivity of electrochemically equivalent solutions of two electrolytes, having a component in common, shall vary inversely as the transference numbers of the common component".⁴⁴² The proportionality between the conductivity and the sum of the velocities of the ions has mechanical and electrical explanations. Kohlrausch preferred the electrical explanation. His hypothesis originated in Faraday's law and the relationship between the electric current and the sum of the ions' velocities. Both the mechanical and the electrical explanations are equivalent, although they differ in their origin.⁴⁴³

In 1879, Kohlrausch published another highly extended essay in order "to obtain a complete picture of [the conductivity] of a larger group of bodies". He divided the memoir

⁴⁴² Ibid, pp. 216-217.

⁴⁴³ According to mechanical explanation, the conductivity of an electrolyte is manifested as an electrical resistance originated from the frictional resistance of the solution to the displacements of the ions. Since the anion and cation displacements are proportional to the sum of their velocities, the conductivity must be proportional to the sum of the two velocities.

into two parts: The first part was purely experimental and practical,⁴⁴⁴ and the second part was theoretical.⁴⁴⁵ He investigated 158 solutions of 40 different substances. Combining the experimental data from previous work, Kohlrausch had data on 260 aqueous solutions of over 50 different substances at his disposal. He measured electrical conductivities as a function of concentration and temperature. He expected to obtain a clear overview of the conductivity behavior of inorganic and organic acids and bases and salts of light and heavy metals or salts and acids with ions consisting of groups of atoms (complex ions). He exercised special care to obtain accurate results in dilute solutions and concentration changes and confirm the law of conductivity in dilute solutions.

The experimental part consisted of nine paragraphs. They dealt with the description of the substances he used, the preparation of electrolytic solutions, the description of the apparatus and peripherals, the experimental conditions, the method of measurements, and the measured electrical conductivities. The conductivity data compared with previous results obtained in his laboratory or with experimental data of the literature. The practical part constituted of five paragraphs, where Kohlrausch evaluated several aspects of the tabulated experimental data, e.g. accuracy and. Reproducibility. Then comes the theoretical part with twenty-two paragraphs. Kohlrausch discussed Hittorf's hypotheses on the migration of ions and criticized the accuracy of the transference numbers, "Even if Hittorf succeeded in giving his results a surprising measure of certainty through an admirable skill in the arrangement of his devices, and the appropriate care in his current determinations and analyses, the third decimal of a determination of n [the transference number] by several

⁴⁴⁴ Kohlrausch, 1879, pp. 1-51.

⁴⁴⁵ Ibid, pp. 145-210.

units was probably everywhere uncertain; often the second decimal will no longer be hidden".⁴⁴⁶ The inaccuracies become higher in concentrated solutions. He noted that the transference numbers at these high concentrations showed significant fluctuations, and therefore it was one of the reasons why Hittorf avoided measuring transference in that high concentration range.

Kohlrausch attempted to offer an explanation for the failure of the conductivity laws at higher concentrations. One plausible reason why measurements at high concentrations fail is that the electrical resistance generated from the friction of the ions exerted by the water molecules is intermingled with the additional friction of the ions against each other. In dilute solutions, the water molecules predominate over those of the electrolyte. Therefore, the conduction of electricity emanates from the migrating ions and is independent of their mutual frictional interactions. It appears that the condition of dilute solutions ensures, to a high degree of accuracy, the independence of the ion velocities.⁴⁴⁷ This ions independence was the basic assumption made by Kohlrausch in his efforts to confirm the law of independent ion migration in solutions that he had expressed three years ago. He stated clearly, "According to this [hypothesis], every electrochemical elemente.g., H, K, Ag, NH₄, C1, I, NO₃, $C_2H_3O_2$ - in dilute aqueous solution have a certain resistance, regardless of the electrolyte from which the component is separated. From these resistances, which must be determinable for each element once and for all, the conductivity of each (diluted) solution can be calculated".448

⁴⁴⁶ Ibid, 1879, p. 161.

⁴⁴⁷ Arrhenius must have been aware of the work of Kohlraush (he spent one year in Kohlrausch's laboratory) , and therefore he began his conductivity measurements directly in dilute solutions. It appears that this choice was not the result of luck, as Arrhenius used to say, but the consequence of acquiring prior knowledge (see chapter 10, section 1 of this dissertation).

⁴⁴⁸ Kohlrausch, 1879, p. 168.

Kohlrausch endeavored to quantify the law of independent migration of ions through a series of mathematical definitions. In the 1876 essay, Kohlrausch asserted that the conductivity of an electrolyte is proportional to the sum of the ion velocities. The proportionality constant was the number of the chemical equivalents, or as he called it, the *molecular number*, *m*. i.e.⁴⁴⁹

$$k = (u + v)\mathbf{m} \tag{5.7}$$

He called the sum of the velocities of the ions as the *absolute molecular conductivity*, λ , in the dilute solutions, i.e.,

$$\lambda = u + v \tag{5.8}$$

Here, Kohlrausch renamed the velocity of the ion as *mobility*.⁴⁵⁰ The factor λ is determined experimentally from the concentration dependence of the electrical conductivity. From the values of λ and the transference numbers, he calculated the absolute velocities of the migrating ions via the combination of Eqs. (5.2) and (5.8), i.e.,⁴⁵¹

$$u = (1-n)\lambda$$
 and $v = n\lambda$ (5.9)

From Eqs. (5.7) and (5.9), Kohlrausch obtained the following relationships:

$$u = (1 - n)\frac{k}{m}$$
, and $v = n\frac{k}{m}$ (5.10)

Finally, Kohlrausch decided to change the units of the measured conductivity. He chose to express all measured quantities in terms of the Gauss-Weber *absolute measuring units*,⁴⁵²

⁴⁴⁹ Kohlrausch discussed the derivation of Eq. (5.8) i1879, p. 152, 170).

⁴⁵⁰ This term is in use in current textbooks of physical chemistry.

⁴⁵¹ Kohlrrausch, 1879, pp. 170-171.

⁴⁵² Gauss first demonstrated in 1832 the link between electromagnetic units and the customary units of length, mass, and time employing his measurement of the Earth's magnetic field. Franz Ernst Neumann (1798-1895). in 1845 extended this principle to electrical measurements. Weber proposed a complete system of electrical and magnetic metric units in 1851. Weber had the idea to define the electrical units solely concerning absolute units of length, mass, and time, expressed in millimeter, milligram, and second, respectively (Weber, 1851; Jungnickel and McCormmach, 1985, pp. 70-73.

i.e., milligram (mg) for the mass, millimeter (mm) for the length, and second (sec) for the time or using the gram (g), centimeter (cm), and second (sec). Using this metric system, Kohlrausch replaced the relative conductivity λ with the *absolute molecular conductivity* Λ in dilute solution expressed as $\Lambda = (1.08/10^7) \lambda (\text{mm}^3 \cdot \text{mg}^{-1}).^{453}$ Accordingly, he expressed the *ionic mobility* in mm/sec or cm/sec using the values of the absolute molecular conductivity.⁴⁵⁴ Kohlrausch confirmed the law of the independence of the ions' mobilities in dilute solutions using the samples mentioned in the experimental part.

Section 3. Hermann von Helmholtz: The electric double layer and the introduction of the charged ions

As noted in previous sections, the phenomenon of polarization of the electrodes was a significant problem that deteriorated the output of the electrochemical cells and the efficiency of electrolysis. The proponents of early electrochemistry have proposed various methods to deal with the problem. Most of the suggested solutions were empirical and based on macroscopic observations. Consequently, the results were limited to specific electrolytic systems, including Daniell's and Grove's constant current batteries.

The polarization phenomenon occurring during electrolysis became a significant field of research in the fourth decade of the nineteenth century. Several physicists of the time, including Faraday, Christian Friedrich Schönbein (1799-1868), Johann Wilhelm Ritter (1776 -1810), and others, contributed to the research efforts on this subject. Apart from the complications in electrolysis, polarization had another implication regarding the generation of electricity in the electrochemical cells. Chemists used polarization to oppose

⁴⁵³ Kohlrausch, 1879, p. 199.

⁴⁵⁴ Ibid, pp. 202-203.

the contact theory. It seems that polarization favored the explanation of electrolysis in the framework of the chemical approach.⁴⁵⁵ What was lacking in these studies was the knowledge of the origin of the problem on a microscopic scale. Among the various researchers who focused on the polarization phenomenon was Helmholtz. Helmholtz's implication in this kind of research led to a theoretical explanation of polarization through a comprehensive description of the causes that gave rise to this phenomenon. Helmholtz proposed in 1879 a microscopic model known as the *electric double layer* formed in the interface between the electrolytic solution and the metallic electrode.

Helmholtz's first approach to the problem of polarization was in his memoir published in 1847, *Über die Erhaltung der Kraft*. Based on a few experimental results of Faraday, Emil Lenz's (1804-1865), and Poggendorff, Helmholtz gave a preliminary theoretical explanation of the qualitative characteristics of polarization. He demonstrated its impact on the electromotive force of the battery and the intensity of the electric current. However, he did not miss to point out that the hitherto few experimental results did not allow rigorous quantitative conclusions. Since I have given a detailed analysis of this memoir in the appendix of this dissertation referring in particular to polarization, I will present, here, just a few points of Helmholtz's theory.

For a galvanic cell with no polarization, Helmholtz applied Ohm's law, and the fact that the heat evolved by voltaic electricity was proportional to the resistance to conduction and to the square of the electric current as confirmed by Lenz and Joule.⁴⁵⁶ Helmholtz

⁴⁵⁵ According to the contact theory, the mere contact between two different metals (conducting metals) generates electricity, for example, silver and tin. The chemical theorists rejected the idea of the contact force. They claimed that chemical processes played a much more central role, and they were the very cause of the cell's activity (chapter 2, section 2, and paragraph 2.5 of this dissertation; Kragh, 2000, p. 149).
⁴⁵⁶ See Chapter 2, section 2, paragraph 2.3 of this dissertation.

derived the amount of heat Q generated at time t in the circuit of the galvanic cells, and the heat Q' evolved by the chemical reaction occurring in the cell. The following equations give these two quantities

$$Q = RtI^2 = nAIt \tag{5.11}$$

and

$$Q' = nI(\alpha_z - \alpha_c)t \tag{5.12}$$

In these equations, *I* is the current intensity, *R* is the resistance of the circuit of the battery, and *A* is the electromotive force (electrical potential difference) of the galvanic cell. The quantities α_z and α_c are the heats of the half-reactions occurring in the negative and positive electrodes of the cell, respectively. Upon application of Ohm's law, the intensity of the electric current is given by

$$I = \frac{A}{R} = \frac{\alpha_z - \alpha_c}{R} \tag{5.13}$$

Helmholtz considered an additional resistance, μ , in the interface between the metal and the solution for a galvanic cell with polarization. Adding this residual heat due to polarization to the reaction heat given by Eq. (5.11), Helmholtz obtained the conservation law

$$I(a_z - a_h)t = nI^2Rt + I\mu t$$
(5.14)

Simplifying Eq. (5.14), Ohm's law for the cell with polarization is written as

$$I = \frac{a_z - a_h - \mu}{R} \tag{5.15}$$

Comparison of Eq. (5.13) with Eq. (5.15) illustrates the change of the current intensity when polarization is in operation. He concluded that the resistance μ due to polarization should depend on the type of the electrode and the electric circuit in general. Furthermore, he pointed out that so far, there are no consistent observations regarding the dependence of this quantity on the current intensity. Here Helmholtz cited Joule's relevant experiments, not to support his theory, but to criticize and judge Joule's results and methods as unreliable, even though they corroborated some aspects of his theory.⁴⁵⁷

Five years later, in 1853, Helmholtz published two articles in *Annalen der Physik und Chemie*, where he described for the first time a microscopic model for the phenomenon of polarization in galvanic and decomposition cells. According to this *electric double layer* model,⁴⁵⁸ charged electrodes immersed in electrolytic solution repel charged bodies (co-ions) carrying the same charge while attracting those with opposite charges (counter-ions). As a result, two layers of opposite polarity form at the interface between the surface of the metal of the electrode and the electrolyte. This model ensured the neutrality of the solution. This arrangement that resembles a capacitor (a diaphasic layer of opposite charges between two metals) stores the work that expended for its formation in the form of an electric potential.

No further research followed the idea of forming an electrical double layer as the cause of polarization. Helmholtz devoted his time to physiology and his professional duties as a medical doctor in the army. He resumed his electrochemical studies ten years later when he published two papers dealing with the investigation of galvanic polarization using a Daniell's cell with a platinum electrode.⁴⁵⁹ He discussed the double layer in real-time, considering the occlusion of hydrogen and oxygen gases, the electrolysis products of water, as bubbles, penetrating the surface of the platinum plates. Helmholtz perhaps got the idea that hydrogen and to a much lesser extent, oxygen can diffuse into certain metals from a

⁴⁵⁷ Helmholtz, 1853a, p. 151.

⁴⁵⁸ Helmholtz, 1853b.

⁴⁵⁹ Helmholtz, 1872; 1873.

process examined by the Scottish chemist Thomas Graham (1805-1869) in 1858. Graham demonstrated a similar effect for palladium.⁴⁶⁰

In 1879, he laid the theoretical foundations for an original model of the distribution of charges on the surface of an electrified element. His theory is based on the following principle: if two bodies carrying different charges are brought into contact, they keep their electrical states. He believes that this idea applies to any type of contact, including that established between an electrode and an electrolyte during the decomposition processes. He then focused his attention on the contact area itself and attempted to explain how the charges of metals are distributed on their surface. He used as a model Daniell's cell with copper and zinc electrodes. The solid copper plate has a potential $P_{\rm C}$ during electrolysis while zinc carries a potential P_Z , the first potential being superior to the second. He then considers that when the two plates approach each other, the electric bodies on the surface of the zinc are positive while those carried by the copper are negative. By bringing the two plates together in closed contact, the positive and negative bodies face each other. According to Helmholtz, they do not attach because the number of charged particles increases when the distance decreases (due to the attraction exerted by the body charged with opposite electricity). If the distance between the plates is zero, the number of charged bodies on the metal surfaces becomes infinite. To avoid this paradox, he considers that the distance cannot be zero. The assumption of a very tiny space between the metal surfaces allowed Helmholtz to assume that the positive and negative bodies on the two metal plates

⁴⁶⁰ Kragh, 1993, p. 411. Thomas Graham is known to chemists and physicists for his diffusion law, the "Graham's Law." He studied the behaviour of gases in two cases; the first regarding gas diffusion, and the second regarding gas effusion. Graham's law states that *the rate of diffusion or of effusion of a gas is inversely proportional to the square root of its molecular weight*. Therefore, for a mixture of gases, the heavier the gas, the slower is its rate of diffusion through a porous plug or the rate of escape through a small pinhole in a vessel.

that face each other form an electric double layer. The two metal plates do not touch because a kind of molecular capacitor is interposed between them. He estimated that the minimum thickness of this capacitor is about one-thirty millionth of a millimeter.⁴⁶¹ He then applied this idea to the contact zone between a platinum electrode and a solution of acidulated water. He estimated that the thickness of the capacitor formed between the metal surface and the solution is approximately 1/2,475,000ths of millimeters (**Figure 13**).⁴⁶²

Helmholtz defined by K_C the potential energy of the attraction of the copper metal for a positive unit of electricity, and by K_Z , the potential energy for the zinc metal that attracted the negative unit of electricity. The gain of the potential energy due to the passage of the electricity d*E* from the copper at electrical potential P_C to the zinc at electrical potential P_Z is $dE(K_Z - K_C - P_C + P_Z)$. At the static equilibrium, this work must equal zero, and hence,⁴⁶³

$$K_Z - K_C = P_Z - P_C (5.16)$$

This equation offers the mathematical expression of the mechanism that ensures the stationary condition of equilibrium in the electrical double layer that is formed between the fluid-charged layer and the metallic charged surface.

In 1881, Helmholtz refined his conception of the electrical distribution on the surface of the electrodes. He was convinced, in particular, that the chemical reactivity of the charged bodies that constituted the electrolyte proved their implication in polarization.⁴⁶⁴ The accumulation of charged bodies on the surface of the electrodes was the cause of the appearance of opposite electrical currents to that imparting decomposition.

⁴⁶¹ Helmholtz, 1879, p. 339.

⁴⁶² Ibid, p. 340.

⁴⁶³ Ibid, pp. 340-341.

⁴⁶⁴ Helmholtz, 1881, p.263.

It did not take long for Helmholtz to connect these charged bodies and the Faraday's ions and considered them the cause of polarization. Helmholtz's electric double layer model formed in solutions of electrolytes (**Figure 16**) survived for quite a long time, despite its main drawback, since it did not take care of the instability of the layer of the ions caused by thermal motion. The French physicist <u>Louis Georges Gouy</u> (1854-1926) in 1910, and the English physicist <u>David Leonard Chapman</u> (1869-1958) in 1913, proposed an improved model of the electric double layer (known as the Gouy-Chapman layer), taking into consideration the diffusion of the ions and the instability of the layer.⁴⁶⁵ Several other improvements were available since. Otto Stern (1888-1969) in 1924 improved, even more, the theory for the double-layer introducing the size of the ions in the properties of Helmholtz and Gouy-Chapman's models.⁴⁶⁶ He considered two parts of the double layer: (a) compact or rigid layer of ions at distance of closest approach (Helmholtz's layer), (b) diffuse layer (Gouy-Chapman's layer).

In 1877, Helmholtz performed new electrochemical research that could be considered the prelude of his studies on thermodynamics and the discovery of the concept of free energy. His study was concerned with the function and the calculation of the electromotive potential of the concentration cells.⁴⁶⁷ Regarding the operation of the cell, Helmholtz considers two primary processes- an electric and an evaporation process.⁴⁶⁸ The first process involves the transport of ions from the compartment of the concentrated

⁴⁶⁵ Gouy, 1910; Chapman, 1913.

⁴⁶⁶ Stern, 1924.

⁴⁶⁷A concentration cell is a form of galvanic cell with two equivalent compartments (half-cells) that contain the electrolyte solution of the same composition differing only in their concentrations. One compartment contains the electrode of the anode, and the other compartment the electrode of the cathode. Due to the different concentrations, the cell gives rise to a small voltage until the cell reaches the state of equilibrium, in which the concentration of reactant in both half-cells becomes equal. Because concentration cells produce small amounts of energy, they are not typically used for energy storage. ⁴⁶⁸ Helmholtz, 1877, pp. 203-204; Kragh, 1993, pp. 412-414.

aqueous solution of the electrolyte to the compartment containing the dilute solution. This process gives rise to an electric current and tends to dilute the most concentrated solution. The second process involves water evaporation, leading to the equalization of the electrolyte concentration in both compartments. Neglecting secondary effects (e.g., forces of attraction and repulsion, polarization) as unimportant, he assumed that the operation of the concentration cell was reversible. Then, he applied the second law of thermodynamics and set forth a relationship between the vapor pressure of the electrolytic solution, *P*, and electromotive force, *E*, that depended only on the final stage of the process.⁴⁶⁹

$$E = P_k - P_a = \int_k^a q(1-n) \frac{\mathrm{d}W}{\mathrm{d}p} dp$$
(5.17)

Here P_k and P_a are the electric potentials of the cathode and the anode, respectively. q is the mass of water that combines with one electrolytic equivalent of the salt. n is the transference number of the cation, and W is the evaporation work. Helmholtz taking from the literature the information that the change of the vapor pressure is directly proportional to the salt concentration obtained the electromotive force of the concentration cell as a function of the dilution (the reciprocal of concentration) of the electrolyte in the two compartments:⁴⁷⁰

$$E = P_k - P_a = bV_0(1 - n)\log\frac{s_a}{s_k}$$
(5.18)

 S_a and S_k are the dilutions of the electrolyte in the compartments of the anode and cathode, respectively. Helmholtz and his student James Moser tested this equation experimentally and found it to be approximately valid. Nernst simplified Eq. (5.18), introducing the ionic mobilities of the anion and cation and removing any association with the vapor pressure of

⁴⁶⁹ Helmholtz, 1877, p. 208.

⁴⁷⁰ Ibid, p. 211.

the solution.⁴⁷¹ Studying the concentration cells, Helmholtz did not take into consideration changes in temperature. He calculated the electromotive force of the concentration cell at a constant temperature. Temperature changes would complicate the mathematical manipulations since the calculation of the electric potential, as a function of temperature comprises integration constants whose temperature dependence is unknown. At this stage, Helmholtz, still influenced by the doctrine of the central forces of the *Erhaltung*, found it unnecessary to deal with temperature effects. Central forces, which are forces of gravity, do not depend on temperature. Helmholtz dealt with temperature effects in 1882 when he developed his thermodynamic theory.

Section 4. The Clausius-Williamson hypothesis

Clausius' theory on electrolysis, known as the *Clausius hypothesis*, inspired Arrhenius to corroborate his work on the dissociation of electrolytes in solutions. Clausius' involvement in electrochemistry aimed at solving the problem of applying Ohm's law to liquids. This law applied well to solid conductors but failed to explain the conducting behavior of conducting fluids owing to the passage of the electric current. Clausius' electrochemical hypothesis originated from his studies on the kinetic theory of gases.⁴⁷² He stated that the gas molecules were able to move freely by translations and rotations. These motions that generate intermolecular collisions and collisions between molecules and the walls of the container are responsible for the manifestation of macroscopic phenomena such as temperature and pressure. Claudius thought that this idea could apply to liquids. However,

 ⁴⁷¹ Nernst, 1889, pp. 136-139 and 154-155. Nernst compared his methodology for the derivation of the electromotive force of concentration cells with that of Helmholtz. (Nernst, 1889, pp. 162-165).
 ⁴⁷² Clausius, 1857, pp. 111, 115.

he expected that interactions between molecules in liquids should take a different qualitative form.⁴⁷³

Concerning Ohm's law, he considered that all previous hypotheses about the conduction of electricity were in the wrong direction. The mechanisms of decomposition and the propagation of the electric current without free changes in solution prohibited the perfect proportionality of the current intensity with the tension applied. He distinguished the electrolyte molecules into two classes, the intact molecules and the partially decomposed molecules. He called the first *complete molecules* and the second *partial* molecules. None of these two types of molecules starts moving in solution because of the effect of electrical action.⁴⁷⁴ He argued that these two kinds of molecules were in incessant motions within the solution well before the passage of the electric current. In other words, the molecules alternatively decompose and recompose without the application of the electric current. This ceaseless motion ensures the validity of Ohm's law. Otherwise, one concludes that decomposition of the complete molecules occurs before the solution carries partial molecules. This static view of decomposition would have required an electric current of higher intensity than that predicted by Ohm's law, "....that so long as the force acting within the conductor does not possess this requisite intensity, no decomposition whatever can take place; but that, on the other hand, as soon as the force has attained this intensity, a great many molecules must be simultaneously decomposed, since all are exposed to the influence of the same force, and have almost the same relative positions to

⁴⁷³ Ibid, p. 119.

⁴⁷⁴ Clausius did not use, whatsoever, Faraday's terminology of ions, anions, and cations. He preferred Berzelius' dualism of the electropositive and the electronegative bodies, slightly paraphrased as positive and negative partial molecules. In any case, Clausius did not claim in his theory that the partial molecules were free ions.

each other ", and continues his reasoning about the falsification of previous theories of static decomposition: "So long as the moving force acting within the conductor is below a certain limit, it causes no current whatever; so soon as it attains this limit, however, a powerful current is suddenly produced".⁴⁷⁵

The static view of electrolysis had another consequence. An excess of partial molecules charged with the same electricity could accumulate in any part of the electrolytic solution. Thus, any molecule would repel any other molecules with similar electricity in the congregation. As a result, these repulsive forces would create a significant resultant force acting from within the solution outwards. Secondly, the electricity adhering to all other molecules would make a certain tension that could prevail in the electric conditions of the solution. In short, the formation of electrical charge gradients within the solution would limit the efficiency of electrolysis, On the contrary, when both kinds of partial molecules are of equal numbers and are everywhere uniformly distributed in any given space of the solution, the forces exerted by the electricity of the surrounding partial molecules cannot occasion any resultant force. The uniform distribution of partial molecules will eliminate the tendency of such resultant electricity to move in a definite direction independently of the electricity adhering to each molecule and thus impeding the motion of that molecule.⁴⁷⁶ Clausius learned from a conversation with a chemist⁴⁷⁷ that the British chemist Alexander Williamson expressed similar views for the motional behavior

⁴⁷⁵ Clausius, 1858, p. 99.

⁴⁷⁶ Ibid, p. 97.

⁴⁷⁷ The chemist was Clausius' colleague Georg Städeler (1821-1871) at the Polytechnicum. Städeler informed Clausius that the British had already written a hypothesis of molecular movement in liquids (Petit, 2013, p. 157).

of molecules in the liquid and gaseous states. Williamson expressed these views independently in a study concerned with a new method of synthesizing alcohols.

In 1850, Williamson attempted to synthesize longer chain alcohols from the ordinary ethyl alcohol (ethanol or simply alcohol) using a method analogous to the substitution method of the German organic chemist August von Hofmann (1818-1892). To his surprise, the product of the reaction was not alcohol, but "nothing else than common ether". He decided to interrupt his attempt to synthesize alcohols and devote his research to elucidating the mechanism that led to the formation of ethers. He asserted that the interaction between alcohol and sulfuric acid, the two reactants of the etherification reaction, was a substitution process of one hydrogen of one molecule of alcohol by the carbon radical of a second alcohol molecule, sulfuric acid acting as a catalyst facilitating the chemical process. Williamson gave a dynamic explanation for the etherification reaction. He postulated that atoms were constantly moving particles, the dancing molecules as he called them, and their collisions were a necessary precondition for chemical transformation without the help of chemical affinity. Atoms or groups of atoms (radicals) constantly moved and exchanged from one molecule to another and strongly opposed the static view, which dominated chemistry. However, he did not explain the cause of this motion. This dynamic picture of an organic reaction was in severe contradiction with the hitherto static perception in organic chemistry. However, Williamson did not explore possible causes that made atoms move from molecule to molecule or find any conceivable relation between chemical affinity and molecular substitution.⁴⁷⁸

 ⁴⁷⁸ For a thorough discussion of the organic synthesis of ethers and Williamson's hypothesis, see Williamson,
 1850; Petit, 2013, pp. 157-159; Petit, 2016, pp. 365-370; Paul, 1978, pp. 23-25.

Clausius, probably willing to avoid any dispute of priority, did not fail to acknowledge the work of Williamson, emphasizing, however, that he had arrive "in a manner different from and independent of that of Williamson" at the same conclusion.⁴⁷⁹ At the same time, his reference to Williamson's novel synthesis of ethers and the accompanying explanation of the mechanism of the chemical process legitimized his theory since the scientific community had already accepted the hypothesis of Williamson. The idea of molecular dynamics was common to both hypotheses, but the similarity between their works stops here. Both scientists wrote about atoms and molecules in the context of a dynamical framework, but their theoretical approaches were different in the details. *Williamson's hypothesis* refers to organic substitution reactions, where one atom replaces another atom, or it is replaced by a third atom. This replacement takes place under the constant movement of atoms and molecules in space. The cause of their movement is undetermined and does not appear to have any direct relation to affinity.

Similarly, *Clausius' hypothesis* espouses the continual motion of partial molecules and complete molecules in solution. However, Clausius keeps a distance from Williamson by asserting that the number of collisions between the molecules is much smaller than that predicted by Williamson's theory. The existence of only a small number of free ions is sufficient to explain the conductibility of the electrolytic solution and the application of Ohm's law, "As I arrived at the conclusions concerning the interchanges which take place amongst the partial molecules of a liquid in a manner different from, and independent of that of Williamson, I thought it advisable, even after becoming acquainted with his memoir, to communicate my views of the subject unchanged, since, by so doing, I shall best render

⁴⁷⁹ Clausius, 1858, pp. 103-104.

manifest how far these two methods of viewing the subject serve mutually to corroborate each other".⁴⁸⁰ Furthermore, Clausius was able to offer a mechanical explanation of the electrolytic conductivity. He was thus connecting the microscopic behavior of the ions with the macroscopic properties of electrolysis. Clausius' explanation showed the inherent link between thermodynamics and electrochemistry.

Clausius and Williamson did not communicate, although their hypotheses on molecular dynamics had a common ground. Each scientist continued to work in their discipline as, in general, did physicists and chemists during the more significant part of the nineteenth century. It was a time when physicists did not understand chemistry, and chemists were suspicious of physicists. It will take another thirty years before chemists and physicists start recognizing that cooperation could solve several of their research problems.

Clausius's theory on electrolytic conduction and Williamson's studies on the etherification process, known as the *Clausius-Williamson hypothesis*, influenced Arrhenius' efforts to develop the theory of electrolytic dissociation. Kohlrausch was another important source of inspiration for Arrhenius. The Swede chemist learned from Kohlrausch's work on the conductivity of electrolytes while he was visiting Kohlrausch's laboratory and had with him an immediate contact. This close relationship with Kohlrausch was valuable assistance for Arrhenius, who strived to find his way in the field of electrochemistry.

The second generation of electrochemists in Europe, particularly in Germany, endeavored to generalize Ohm's law in solutions in a more detailed manner than the electrochemists of the first half of the century. They share the decomposition of molecules

⁴⁸⁰ Ibid, p. 104.
as the leading cause of the propagation of electricity, but now, their propagation schemes of electricity have no abstract characteristics; they specifically ascribe it to the existence of ions. These entities are considered as charged molecules that carry electricity. The German physicists used new and more effective methodologies and accurate instrumentation to investigate the physical properties of ions in solutions. Hittorf established the laws for the ionic mobility of the ions in solutions and quantified the percentage of electric charge carried out by moving ions from one electrode to the other. Kohlrausch investigated the conductivity of electrolytes as a function of their nature, concentration, and temperature. Clausius offered specific theoretical consideration for the decomposition and the kinetics of ions in solutions.

Furthermore, Helmholtz was the first physicist who introduced mathematics in electrochemistry as early as 1847. Through the concept of ions, Helmholtz attacked systematically the problem of electrodes polarization that reduced battery life. Helmholtz finally gave a satisfactory explanation through his model of the double-layer of charges between the electrode's surface and the electrolyte's ions. Thus, in the late 1870s, the concept of ion and electric conduction in solutions had received a different theoretical and experimental approach. The new trend paved the way for the mathematization of electrochemistry and the investigation of electrolysis at a microscopic scale. The second generation of electrochemists left behind a rich scientific legacy on which Arrhenius stepped in and developed his electrolytic theory of dissociation.

Chapter 6. Gibbs' approach to thermodynamics

The foundation of the two fundamental laws of thermodynamics was followed by the development of several theoretical systems spread all over the European continent. These thermodynamic systems may be grouped into two general trends. The first trend, the so-called mechanical-molecular or merely mechanical, or molecular mechanics, was associated with great physicists, such as Rudolf Clausius, Ludvig Boltzmann, and James Clerk Maxwell. The second stream of theoretical physics was the so-called analytico-positivist or simply positivist with several representatives including Gibbs, Duhem, Helmholtz, Planck, Arthur Joachim von Oettingen (1836-1920), and François Jacques Dominique Massieu (1832-1896). These two traditions differed radically in interpreting the physical laws derived from their studies of natural phenomena. The mechanical approach stressed the importance of dynamics (the imposition of Newtonian or electrical forces in nature) and considered the intermolecular attractions as the driving force for the formation of matter. The theoretical physicists of this group used probabilistic procedures and statistical mechanics as mathematical tools.

On the other hand, positivism rejected molecular attraction. It suggested that the laws of nature should be derived directly from observations and experiments, rejecting thus any search for hidden causes that may explain the fundamental laws of nature. In their theoretical quest, they espoused macroscopic approaches to interpreting natural phenomena. Among the prominent physicists of the second trend of thermodynamics, Gibbs, Duhem, and Helmholtz had a significant impact on the development of chemical thermodynamics. These three men had no direct influence on the transfer of thermodynamics from physics to chemistry for reasons that will be discussed later. As noted, the representatives of positivism did not participate directly in the genesis of chemical thermodynamics. Nevertheless, they gave a new impetus to the new science when their work was recognized by the scientific community. Their theories penetrated chemical and physical research and education and therefore, it is expedient to give an outline of their approach to thermodynamics. I will begin with Josiah Willard Gibbs.

When Gibbs entered thermodynamics in 1873, "thermal" physics was divided into two camps. On the one hand, developing thermodynamics governed the thermal properties of substances and theories based on general macroscopic principles. On the other hand, thermochemistry sought to measure the chemical affinity of substances from the heat released in chemical reactions.⁴⁸¹ The Danish chemist Julius Thomsen in the 1850s and the French chemist Marcellin Berthelot in the 1860s, guided by the first law of thermodynamics, developed the new science of thermochemistry. Performed experiments by these two scientists corroborated the thermochemical conception that chemical affinity depended on reaction heats. Therefore, not surprisingly, this theory was strongly attracted by chemists. Thomsen and Berthelot formulated independently, in slightly different terms, the principle of maximum work. This principle relied on the conviction that the heat evolved in chemical reactions could be used to measure the chemical affinity of substances. Berthelot postulated that chemical reactions always proceeded in the direction that would produce the greatest amount of work. In other words, chemical reactions always release heat, and the reaction that gives off the greatest amount of heat is the reaction that preferentially will occur. Subsequent theoretical and experimental investigations

⁴⁸¹ For an account of the state of thermodynamics in the second half of the nineteenth century, see Darrigol2018a, 42-68; Darrigol 2018b, pp. 4-11.

(spontaneous chemical processes that absorb heat, the occurrence of reversible reactions, and the existence of chemical equilibrium) indicated that the theory of thermochemical affinity is not correct or limited in scope. While Thomsen admitted the limitations of the principle, Berthelot insisted that the theory needed some modifications in the light of new experiments. At the same time, he considered that all physical transformations, such as fusion and vaporization, need heat to occur as an exception from his principle. To explain that endothermic reactions need heat to take place, he invoked the concomitant occurrence of physical transformations that absorb more heat than the chemical reaction can give. Berthelot's insistence to make his theory work lasted until the beginning of the twentieth century, even though the second law of thermodynamics and Helmholtz's free energy worked against his principle.

Concurrently with the beginning of thermochemistry, Clausius, William Thomson, and Rankine formulated the second law of thermodynamics. From the first day of its appearance, even after 1870, the interpretation of the second law was disputed. Based on the available energy (Thomson) or the disgregation (Clausius), the two main concepts of the law were surrounded with much confusion. The concept of entropy, introduced in 1865, created further ambiguities in thermodynamics' interpretation and possible future applications. Entropy appeared to be an unnecessary ingredient of thermodynamics, and even its inventor paid relatively little importance to this concept. Clausius was uncertain about its meaning and significance. Thomson never used entropy. Maxwell misinterpreted entropy attributing the available energy to this quantity. He printed these remarks on entropy in his book the *Theory of Heat* and misinterpreted Clausius in two subsequent publications.⁴⁸² He finally corrected this error when he had read Gibbs' work on thermodynamics.⁴⁸³ In the 1860s and 1870s, thermodynamics was still a young, incompletely understood theory. Its basic concepts and methods were still in flux; its scope was not fully appreciated (especially by chemists), and there were still dreams of perpetual motion of the second kind.⁴⁸⁴

The study of the nature of phase transitions, notably the phase transition between the gaseous and liquid states, was a fruitful application of thermodynamics that attracted the attention of physicists in the 1860s and 1870s. In 1862, James Thomson, the brother of William Thomson, used graphical methods to interpret the experimental work of his friend Thomas Andrews (1813-1885) on the rarefaction of gases. Andrews reported his results On the Effect of Great Pressures Combined with Cold on the Six Non-condensable Gases to the British Association in 1861. The graphical representation of experimental results of liquid-to-gas phase transitions culminated in the 1870s, when Andrews presented to the Royal Society his results and experiments on the continuity of phases and the critical point for carbonic acid in graphical form. Several physicists attempted to interpret these experiments graphically and define the critical point of the gas-liquid phase transition. The graphical method found its most significant utility in this kind of research. By introducing the second law of thermodynamics, Gibbs generalized the problem, succeeded in establishing the conditions of transitions between the three phases of a substance and defined unambiguously the critical point as the point of tangency of two surfaces.

⁴⁸² Maxwell, 1872.

⁴⁸³ Garber 1969, p. 150.

⁴⁸⁴ Horstmann's work was an exception to the general attitude of perceiving the new ideas in the field of thermodynamics.

Gibbs' motivation to initiate research in thermodynamics is not clear. Gibbs did not leave any writing or verbal evidence for his decision.⁴⁸⁵ However, what is certain is that Gibbs perceived the value of the second law of thermodynamics and used it systematically in his approach to thermodynamics. He introduced entropy to describe graphically the properties of homogeneous substances, including the recently discovered critical point and the chemical equilibrium of multi-component systems.

Gibbs was born on February 11, 1839, and grew up in New Haven, a small city of Connecticut. He never left his hometown, except for a three-year stay in Europe for studies. He studied engineering in the new graduate school at Yale University. In 1863, he received the first Ph.D. degree granted in the United States. In 1871, he was appointed professor of mathematical physics at the same university. Gibbs never married and lived together with the family of one of his sisters in the family home. He died on April 28, 1903.

Gibbs' main work in thermodynamics is composed of three essays, which are closely related to each other, although they are presented in different forms. The first two, namely *Graphical Method in thermodynamics of liqu*ids⁴⁸⁶ and the second *A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces*,⁴⁸⁷ are restricted to the geometrical representation thermodynamic equilibria. These two papers are not developed with the variety and generality of the third and more important essay *on the equilibrium of heterogeneous substances*.⁴⁸⁸ The two geometrical papers appeared m the second volume of the *Transactions of the Connecticut Academy of*

⁴⁸⁵ Martin Klein conjectures that the historical Tait-Clausius entropy dispute on the pages of the *Philosophical Magazine* arouse Gibbs' interest in thermodynamics (Klein 1989, p. 6).

⁴⁸⁶ Gibbs, 1873a.

⁴⁸⁷ Gibbs, 1873b.

⁴⁸⁸ Gibbs, 1876; 1878.

Arts and Sciences issued in December 1873, whereas the heterogeneous substances appeared in two parts in the third volume of the same journal; the first part issued in June 1876, and the second part in July 1878. Gibbs wrote no other significant papers on thermodynamics. He restricted himself in some minor applications as the treatise On the vapor-densities of peroxide of nitrogen. formic acid, acetic acid, and perchloride of phosphorus,⁴⁸⁹ which was appeared in 1879 in the American Journal of Science, an abstract of the *Heterogeneous substance* entitled *Abstract of the "Equilibrium of heterogeneous* substances" published in the same journal in 1878, In 1886, and 1888, he submitted two letters to the British Association for the Advancement of Science about the application of his potential functions to galvanic cell, and two short articles in *Nature* concerning the semipermeable films and the osmotic pressure, published in 1897. These writings on thermodynamics, along with some unpublished fragments of a supplement to the heterogeneous substances, were collected and published in 1906 by his former student Henry Andrews Bumstead (1870-1920) and R. G. Van Name, in a volume entitled the Scientific papers of J. W. Gibbs (noted as GSP, 1906 henceforth), which I have used as a reference in the present study.

Looking through the second paper of the series, one finds remarkably few diagrams or figures that would help the reader comprehend Gibbs' thinking on the various thermodynamic processes he describes. The limited visual details accompanying the nature of the three-dimensional surfaces and tangent planes had proved a formidable challenge for those who have studied his graphical work. Historians have given a concise analysis of these papers focusing primarily on details concerning Gibbs' personality and scientific

⁴⁸⁹ Gibbs, 1879.

reasoning, the conditions connecting his work to the scientific environment of his time, and the interaction of this work with new challenges in physics and chemistry.⁴⁹⁰ Much earlier, physicists had attempted to get deeper into Gibb's work in light of the current understanding of thermodynamics. W. P. Boynton, in a series of three publications,⁴⁹¹ recognized the inherent problems in reconstructing Gibbs' surface. He was finally able to discuss the thermodynamic surfaces and Gibbs' two-dimensional projections based on van der Waals' equation. Paul Saurel, who conducted his dissertation with Duhem on systems in equilibrium,⁴⁹² approached Gibbs' second graphical paper from a strictly mathematical point of view.⁴⁹³ He demonstrated the conditions that must be satisfied by a one-component system in a critical state, and he deduced the most important of Gibbs' theorems. Edwin Bidwell Wilson (1879-1964), another former student of Gibbs, who attended his course in thermodynamics at Yale University during the period 1899-1900, reconstructed those lectures.⁴⁹⁴ Although the reconstruction of a course through students' notes gives a vague idea about oral lectures, it provides valuable information about the development of Gibbs' thinking on thermodynamics. Gibbs taught his students the properties of the thermodynamic surfaces, the tangent planes, the derived surfaces, the loci of stability, and the critical point. He completed the general discussion on surfaces in parallel with van der Waals' equation. He afforded thus conceptual but unrealizable isothermals through the critical point.495

⁴⁹⁰ Martin Klein's two papers (1984) and (1989) and Lynde Wheeler's biography of Josiah Willard Gibbs (1962) are useful references for a historical perspective of Gibbs' thermodynamics. Klein's article of 1989 reappeared slightly modified in *Physics Today* 1990, 43: 40-48.

⁴⁹¹ Boynton, 1900a; 1900b; 1905.

⁴⁹² Saurel defended his dissertation in 1900 on a subject related to Gibbs and Duhem's work on the equilibrium of chemical systems (Jaki, 1984, pp. 136-137).

⁴⁹³ Saurel, 1902.

 ⁴⁹⁴ Wilson used the notes of another Gibbs' student, because he lost his notes (1936, p. 19).
 ⁴⁹⁵ Wilson, 1936, pp. 19-59.

Recent reviews on Gibbs' second graphical paper concentrate on cases that Gibbs did not predict or mention in his thermodynamic models.⁴⁹⁶ Others have used analytical and graphical methods or even computerized methods to generate images of Gibbs' surfaces and to examine various aspects of equilibrium processes in homogeneous and heterogeneous phases.⁴⁹⁷ My intention in this section is to elucidate a few points related to the two graphical papers, particularly for the second one, by scrutiny of the original papers. For this purpose, I will present a few figures to assist with my analysis. Furthermore, I will attempt to answer questions, such as - how and in what way was Gibbs interested and used diagrams in his first appearance in the literature.

Section 1. Thermodynamic diagrams

Gibbs entered thermodynamics in 1873, when he published two papers in the *Transactions* of the Connecticut Academy, with only four months distance in between. Both articles dealt with the study of the thermodynamic properties of states in equilibrium. However, Gibbs did not use the analytical method. Instead, he preferred graphical representations that would allow him to demonstrate general theorems of thermodynamics and the solution of particular problems, for example, phase equilibria and the critical state of substances. The second innovation introduced in these papers was the employment of energy, entropy, and volume as coordinates of the diagrams. These variables contrasted the traditional graphical forms with coordinates the pressure, temperature, and volume. In other words, the geometrical representations adopted by Gibbs did not deal explicitly with classical processes of heat taken in or given out by the system with the concurrent connection with

⁴⁹⁶ Fisher, 1989.

⁴⁹⁷ Clark and Katz 1939; Jolls, 1989a, 1989b; Coy, 1993.

the work done or received by the system. Instead, he treated the problem in terms of the state functions of the system.

In his two graphical papers, Gibbs started describing the movement of a body from one state to another using five variables: the energy ε (actually the internal energy), the entropy η , the volume v, the pressure p, and the temperature t (for each variable, I have used Gibbs' notation). He expressed the relationship among these variables by the following fundamental equation:

$$d\varepsilon = td\eta - pdv \tag{6.1}$$

The differentials indicate infinitesimal changes for these quantities. Under constant entropy and constant volume (denoted by subscripts), the following expressions for the pressure and temperature hold:

$$\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}\upsilon}\right)_{\eta} = -p \tag{6.2}$$

$$\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}\eta}\right)_{\upsilon} = t \tag{6.3}$$

Eq. (6.1) results from the elimination of heat and work of the first law of thermodynamics, $d\varepsilon = dQ - dW$, and keeping the state functions of energy and entropy. However, the heat absorbed and the work done by the system are retained implicitly in Eq. (6.1) through the equalities $dQ = td\eta$ and dW = -pdv. Eq (6.1) allowed Gibbs to replace the symmetric variables v, -p, and -W with the variables η , t, and Q, respectively, without changing the aforementioned qualities. Therefore, because of the existing symmetry between these two groups of variables, an entropy-temperature diagram is equivalent to the conventional volume-pressure diagram in the analysis of thermodynamic processes.⁴⁹⁸

⁴⁹⁸ GSP, 1906, p. 9.

Eqs. (6.1) to (6.3) could describe a three-dimensional diagram, in fact, a surface in a Cartesian coordinate system. However, Gibbs preferred in the first paper to use twodimensional diagrams to represent thermodynamic processes. He left the thermodynamic treatment of multi-phase systems for his second paper published four months later.

In the first diagram of the first paper, Gibbs preferred to illustrate the change of the state of the system mapped continuously on the points of a plane constructed from values of the entropy and temperature at constant pressure and volume. Gibbs thought that the entropy-temperature diagram offered a greater potential in the analysis of thermodynamic phenomena as compared to the classical pressure-volume diagram. For instance, the former representation allowed a much easier evaluation of the work done to the system and the heat absorbed by the system during reversible cycles than those obtained from the traditional pressure-volume plot and subsequent comparison of real processes with Carnot's perfect engine. Furthermore, introducing entropy would enable students and engineers to familiarize themselves with the second law of thermodynamics. "This inconvenience is perhaps more than counterbalanced by the advantages of a method which makes the second law of thermodynamics so prominent and gives it so clear and elementary an expression",⁴⁹⁹ wrote Gibbs having in mind the difficulty of chemists and most physicists to assimilate the concept of entropy.

The second diagram of the first paper proved to be more convenient than the entropy-temperature diagram because it provided a clear interpretation of the coexistence of phases partly as solid, partly as a liquid, and partly as vapor at a particular set of values for the pressure and temperature. This ability is because the two variables entropy and

⁴⁹⁹ GSP, 1906, p. 11.

volume are extensive variables and, therefore, proportional to the amount of substance, while pressure and temperature as intensive properties are not connected with the size of the system. Thus, the entropy-volume plot can determine the quantity of the substance in each state, while the pressure-volume diagram cannot, since pressure and volume remain constant at any point inside the system. In the entropy-volume diagram, the three in contact phases occupy the interior of a triangle. The vertices of the triangle indicate the values of the volume and entropy of the substance in the three perfectly defined states (L for liquid, S for solid, and V for vapor). The three sides of the triangle represent pair of phases, liquid-vapor (LV), liquid-solid (LS), vapor-solid (VS), that exist in equilibrium.⁵⁰⁰ Since entropy and volume are extensive variables, the sums of the entropies and the volumes of the particular phase define the position of the vertices of the triangle LVS. Gibbs has defined the position of the triangle in terms of the extensive state properties of entropy and volume via the following equations:

$$v = \mu v_V + v v_L + (1 - \mu - v) v_S \tag{6.4}$$

$$\eta = \mu \eta_V + \nu \eta_L + (1 - \mu - \nu) \eta_S \tag{6.5}$$

where μ , v, and (1-v- μ) are the masses of the substance in the vapor, liquid and solid phases, respectively; subscripts denote the entropies and volumes in each phase. Pressure and temperature are both fixed within the triangle. Gibbs denoted that the entropy-volume representation conveyed more information than in any other diagram. For example in the pressure-temperature diagram, the three different states in equilibrium are crowded in a single point (the triple point). In contrast, the entropy-volume diagram gives more space to

⁵⁰⁰ GSP, 1906, p. 24, Fig. 9.

distinguish gradual changes or reversible processes between physical states. The extensive nature of the entropy-volume diagram facilitates the precise tracking of the portion of the substance in each state and the gradual passage of the substance from one state to another state until the occurrence of the complete transformation. For example, the transformation from the metastable states⁵⁰¹ of superheated liquid to partial vaporization or the transformation of a supercoiled liquid to partial crystallization.⁵⁰²

In the second paper, Gibbs introduced a third extensive variable, energy. Together with the entropy and volume, the energy defines the three axes of a rectangular coordinate system. The importance of this paper lies in the explanation offered for the nature of the equilibrium state of a system that can be solid, liquid, or gas (vapor) or some combinations of these three phases. Through constructing three-dimensional representations in the form of surfaces, Gibbs provided a theoretical explanation for the geometrical characterization of the critical point and the continuity of phases at or near this point.

Gibbs was familiar with diagrams. He was aware of the experimental pressurevolume diagram presented in 1869 by the Irish chemist and physicist Thomas Andrews when he attempted to liquefy the carbon dioxide gas. Andrews discovered that the gas could not liquefy above a specific temperature despite the application of high pressures.⁵⁰³ However, below that specific temperature, the so-called *critical point*, liquefaction was possible. The stable vapor phase of the substance subsists above the critical point. In

⁵⁰¹ A metastable state is a nonequilibrium state characterized by higher energy than that of the equilibrium state attained by the system. Its lifetime is short and transforms very quickly to the stable equilibrium state either by itself or by external disturbances. The superheated liquid exists at the maximum temperature or the minimum attainable pressure after which the liquid must boil. Accordingly, the supercooled liquid exists as a liquid at a (negative) temperature below its freezing point. A liquid at the supercooled state will crystallize in the presence of a seed crystal or nucleus around which a crystal structure can form.

⁵⁰³ Andrews, 1869.

contrast, below the critical point, the gas splits into two phases, the liquid, and the vapor phase, that coexists in equilibrium.

Andrews constructed the pressure-volume diagram for the carbonic acid (carbon dioxide) from experimental measurements at various temperatures ranging from 13.1 °C up to 48.1 °C (Figure 17). The isothermal curves above 31.1 °C are continuously approaching Boyle isotherms of an ideal gas, while those below 31.1 °C break in two points. When condensation begins with a subsequent diminution of volume, the pressure remains constant until the second point at which the entire mass has become liquid, and the pressure increases rapidly as the volume continues to decrease. The segment of the curve between these two points, representing the condensation of the gas, is a straight line parallel to the axis of volume. This behavior is different from that of the isotherm of 31.1 °C, which seems to exhibit a simple point of deflection, which coincides with the critical point of the carbonic acid. As a pure experimenter, Andrews was unable to give any theoretical explanation for his observations except perhaps a detailed description of the experiments.⁵⁰⁴ Thus, he could not accurately define the position of the critical point on the isotherm of 31.1 °C nor the behavior of the other isotherms at temperatures below the critical point.

Gibbs was aware of another diagram, the diagram by which James Thomson strove to explain Andrews' experiment theoretically.⁵⁰⁵ In his publication of 1871, Thomson claims that the straight lines, which appear in Andrews' diagram, must extend

⁵⁰⁴ In 1876, Andrews published a second paper with a higher degree of accuracy, in which the temperature range extended by three more series of measurements at 6.5 °C, 64 °C, and 100 °C. He did not offer any theoretical explanation for the critical point, except perhaps, some vague statements about the action of internal attractive and resistive molecular forces (Andrews 1876, pp. 448-449). It seems that Andrews was unaware of Gibbs' graphical papers.

⁵⁰⁵ Gibbs cited both Andrews' and Thomson's studies in his *Graphical Method*.

continuously, for some distance at least, into the area of lower pressures in some way representing a gradual transition from the gaseous to the liquid state.⁵⁰⁶ He constructed a three-dimensional curve called a pressure-volume-temperature coordinate system and then considered indefinite, closely spaced sections on the curve parallel to the pressure-volume plane. The theoretical isotherms sketched freehand were similar to the theoretical isotherms calculated by van der Walls in his dissertation based on the famous equation of state for real gases that carries his name.⁵⁰⁷ In other words, Thomson replaced Andrews' straight line with two curved lines (below and above the straight line) (Figure 18a). Thomson did not give any theoretical explanation for the behavior of the isotherms below the critical point. Also, the drawing of the curved lines cannot accommodate unstable intermediate states occurring from the stable gas to the liquid phase of carbonic acid. Accordingly, these curved lines cannot represent the exact behavior of the substance. Thomson admitted that, "Such an experiment as that sketched out here would not be easily made, and unless it was conducted with very great precautions, there could be no reasonable expectation of success in its attempt".⁵⁰⁸

Neither Thomson nor van der Waals succeeded in giving definite answers to questions: what is the proper location of the straight line segment of the isothermal curve parallel to the axis of volume? What condition specifies the pressure and the temperature at which vapor and liquid coexist in equilibrium? Van der Waals' equation for real gases failed to reproduce Andrews' experiments, even by altering the values of the two constants of the equation that corrected the repulsive and attractive intermolecular forces of carbonic

⁵⁰⁶ Thomson, J., 1871, p. 281.

⁵⁰⁷ Van der Waals 1873, pp. 56, 80-81, and Figure 6.

⁵⁰⁸ Thomson, 1871, p. 285.

acid. Van der Waals left this problem open.⁵⁰⁹ Four years later, in a lecture delivered at the Chemical Society on February 18 Maxwell provided a solution to the problem. He tackled Andrews ' experiment by discussing the relationship between pressure and density of real gases resulting from the competition of molecular motion and intermolecular forces. He constructed a model known as *Maxwell's construction*, in which he defined the straight line as the line which cuts off equal areas above and below the curved line of Thomson's model.⁵¹⁰ However, Maxwell did not specify the exact position of the critical point. Concluding his lecture, Maxwell did not forget to mention Gibbs, "who has given us a remarkably simple and thoroughly satisfactory method of representing the relations of the different states of matter by means of a model. By means of this model, problems which had long resisted the efforts of others and myself may be solved at once".⁵¹¹

As in the first graphical paper, Gibbs thought that the development of an adequate geometrical representation of substances in phase changes would be an appropriate strategy to approach the problem. In this respect, he represented the equilibrium states of a

 $^{^{509}}$ Clausius put forward a detailed account of why van der Waals' equation deviates from Andrews' experiments. He proposed modifying the van der Waals equation to contain four constants (van der Waals' equation contains two constants). Clausius tested his equation with Andrews' experimental data taken from his pressure-volume diagram of carbonic acid. This modified equation reproduced the experiments at low densities of the gas but failed at high densities near the point where pressure increases rapidly. The modified Clausius equation was unable to reproduce Andrews' straight-line segment. However, it predicted the metastable states of the supersaturated vapor or the superheated liquid (Clausius 1880, pp. 398-400). ⁵¹⁰ Van der Waals' equation for real gases cuts the horizontal line of the isothermal curve (at p = constant) in three real points corresponding to three real solutions of the equation (Figure 18b). It follows that the gas, instead of performing a continuous transformation along the isothermal curve, it will go through a discontinuous change of state. In the former case of the continuous transformation, the curve is expected to descend towards the axis continually, p =constant, as the volume increases. This transformation is similar to that observed when a gas is compressed at a temperature above its critical temperature. In the latter case of the discontinue transformation, the substance will undergo a discontinuous change from the segment FE to the segment CB (Figure 18b). The result will be the sudden liquefaction of the gas. The discontinuous transformation will vanish when the isothermal line has a unique inflection point with a horizontal tangent. This point of inflection is the critical point. Its coordinates determine the critical pressure, volume, and temperature.

⁵¹¹ Maxwell 1875, pp. 358-359.

substance as points on a surface, the so-called *thermodynamic surface*,⁵¹² located on a rectangular coordinate system with its three axes denoting changes of the extensive functions of the energy (ε) , entropy (η) , and volume (v). A point on the surface has a specific set of values for these thermodynamic properties. Figure 19a depicts schematically part of the *primitive surface*, actually the *energy surface* ε (η , v) on the rectangular coordinate reference that contains points located by the entropy η and volume v. This figure shows that the projection of this part of the surface on the (η, v) plane is equivalent to the two-dimensional entropy-volume plot that Gibbs discussed in the first graphical paper. This projection indicates that thermodynamic processes described on the (η, v) plot partially reflects processes on the associated energy surface ε (η, v) . The slopes of the tangent plane in the entropy direction (Eq. (6.2)) and the volume direction (Eq. (6.3)) for a point P of the tangency shown in **Figure 19a** represents the pressure and temperature of the state, respectively. The arrows in the figure emphasize the inclinations of the tangent planes visually. One of the arrows is parallel to the v axis for a fixed value of entropy, and therefore $d\eta = 0$, whereas the other arrow is parallel to the η axis for a fixed value of volume, and hence dv = 0. The value of the vertical coordinate (dotted line in the figure) gives the energy of the material. Since the pressure is always positive, the energy must decrease when the volume increases at constant entropy, as deduced from Eq. (6.2). According to Eq. (6.3), the energy must increase with increasing entropy at constant volume since the temperature is a positive quantity reckoned from absolute zero. This

⁵¹² Gibbs divided the thermodynamic surface into two parts, of which one represents homogeneous phases and the other mixtures of heterogeneous phases. Gibbs called the first part *primitive surface*, and the second part *derived surface* (GSP, 1906, pp. 35-36). Gibbs pointed out that none of these surfaces exists when the system is not in a state of thermodynamic equilibrium.

behavior means that the entire thermodynamic surface must lie on the positive side of the plane at v = 0. However, Gibbs noted that the values $\eta = 0$ for the entropy and $\varepsilon = 0$ for the energy have no meaning whatsoever since they result from the integration of Eq. (6.1).⁵¹³ Furthermore, it contains arbitrary integration constants. Therefore, adjusting these constants is required to bring these state functions to the origin of the coordinate system.

One point on the tangent plane of the primitive surface identifies a homogeneous phase, two points that have a common tangent plane (called double tangent plane) on the surface represent two phases or states in contact, say liquid (L) and vapor (V). Gibbs was the first to propose the condition of equilibrium of two phases in contact. Since the points representing coexistent phases are on the same tangent plane, they must have the same temperature (t' = t'') and pressure (p' = p''). Furthermore, the common tangent plane cuts the energy axis at the same point, i.e., they have the same intercept, which is⁵¹⁴

$$\varepsilon' - t'\eta' + p'v' = \varepsilon'' - t''\eta'' + p''v''$$
(6.6)

The primes and the double primes denote the energies, entropies, and volumes of the two points P' and P'' of the respective coexistent phases on the primitive surface. In other words, the two points in the straight line joining the center of gravity of two masses of the substance represent the two phases. Rearranging Eq. (6.6), Gibbs obtained the following equation:

$$\varepsilon'' - \varepsilon' = t' (\eta'' - \eta') + p' v'' - v')$$
(6.7)

This equation defines a double tangent plane at the two points (primed and double primed) of the surface, and then it follows that these two points have a common tangent plane.

⁵¹³ GSP, 1906, pp. 34-35.

⁵¹⁴ GSP, 1906, p. 37.

Furthermore, Eq. (6.7) connects the properties of the primitive surface with the second law of thermodynamics since the left-hand side of the equation represents the difference of energies of the two states. In contrast, the first term on the right-hand side represents the heat received, and the second term the work done by the system.⁵¹⁵

Gibbs imagined that a curvature forms when the tangent plane changes position on the primitive surface. This rolling motion of the tangent plane upon the surface creates a secondary or a *developable surface*,⁵¹⁶ which forms a part of the envelope of the successive positions of the rolling plane. **Figure 19b** shows schematically a developable surface that may result from the rolling motion of the tangent plane in **Figure 19a**.

As the tangent plane rolls on the primitive surface, there is a position in which it touches the primitive surface in a third point in the solid phase (S) of the substance. The three-point tangency (a triple tangent plane) forms a plane triangle (SLV), the vertices representing the three phases of the substance, solid, liquid, and vapor. These three phases are in equilibrium at the same constant temperature (t' = t'' = t''') and pressure (p' = p'' = p'''). Gibbs gave the condition of equilibrium for three coexistent phases.⁵¹⁷

$$\varepsilon' - t'\eta' + p'v' = \varepsilon'' - t''\eta'' + p''v'' = \varepsilon''' - t'''\eta''' + p'''v'''$$
(6.8)

The primes, double primes, and triple primes denote the energies, entropies, and volumes of points at the triangle's vertices of the respective coexistent phases on the primitive surface. A point within the triangle represents three states in equilibrium, consisting of the

⁵¹⁵ GSP, 1906, p. 37-38.

⁵¹⁶ A *developable surface* is the type of surface that a tangent plane creates. The surface generated by a straight line or by a straight line tangential to a space curve is a *ruled surface*. A developable surface could be a ruled surface, but the opposite does not hold. Gibbs described the surfaces obtained from the rolling planes as developable surfaces. However, these surfaces are in fact ruled surfaces spanned by lines joining corresponding points of common tangent planes (Lawrence, 2011). ⁵¹⁷ GSP. 1906, p. 37.

center of gravity of masses proportioned to the masses of the three phases. This triple tangent plane forms a triangle that, according to Gibbs' definition, represents values of the three variables (entropy-energy-volume) at unique temperature and pressure values.⁵¹⁸ The plane triangle SLV is Gibbs' *derived surface*.

After establishing the criteria for phase equilibrium, Gibbs examined the geometrical properties of the surface, indicating the stability or the instability of a given phase. To answer this question, he proposed a thought experiment in which the substance under study is surrounded by a much larger mass of the same material. Therefore, the mass and temperature of the system are considered constant. A diathermal envelope separates the substance and the surrounding medium.⁵¹⁹ The envelope is a poor conductor of heat and does not yield any osmotic pressure on its surface. The whole system is placed in isolation. The initial energy, entropy, and volume of the substance is ε' , η' , υ' and in its final state after the interaction with the medium, assumes values ε'' , η'' , υ'' . The corresponding values for the medium are E', H', V' and E'', H'', V''. Gibbs applied to the medium equation (6.1) and integrated between the initial and final states under constant pressure P and the temperature T; he obtained

$$E'' - E' = TH'' - TH' - PV'' + PV'$$
(6.9)

Because of the diathermal envelope separating the substance and the medium, the sum of the energies may decrease. They will never increase, and the sum of the entropies will never decrease. Finally, the volume of the system remains constant, namely

⁵¹⁸ This triangle is similar to that presented in Gibbs' first graphical paper and discussed above. ⁵¹⁹ A diathermal wall between two thermodynamic systems allows heat transfer from one system to the other, but does not allow transfer of matter between the two systems. A diathermal envelope encloses a closed system.

$$\varepsilon'' + E'' \le \varepsilon' + E' \tag{6.10}$$

$$\eta'' + H'' \ge \eta' + H' \tag{6.11}$$

$$v'' + V'' = v' + V' \tag{6.12}$$

Rearranging and adding Eqs. (6.10) to (6.12), Gibbs obtained the following inequality, which expresses the criterion of stability of a pure substance maintained at a fixed temperature and pressure.⁵²⁰

$$\varepsilon'' - T\eta'' + P\upsilon'' \le \varepsilon' - T\eta' + T\upsilon' \tag{6.13}$$

The expressions on both sides of this inequality represent the intercepts of the tangent planes of the two states. They denote the vertical distance of the points (ε' , η' , υ') and (ε'' , η'' , υ'') at the points of tangency that are above the fixed plane passing through the origin and representing the pressure p and temperature t. The equation (6.13) expresses that the ultimate distance is less or at most equal to the initial one. Hence, any change of the state that results in a diminution of the distance of the points (ε' , η' , υ') and (ε'' , η'' , υ'') favors a state of stability; otherwise, it results in a state of instability.

Gibbs considers that the primitive curve is not a smooth curvature but contains convex and concave sections; he affords the following geometrical criteria for equilibrium and stability. "If the form of the surface lies such that it falls above the tangent plane except at the single point of contact, the equilibrium is necessarily stable"; in other words, the primitive surface is concave upwards. "On the other hand, if the surface has such a form that any part of it falls below the fixed tangent plane, the equilibrium will be unstable"; here, the surface is concave downwards. Finally, Gibbs defined a limiting state between

⁵²⁰ GSP, 1906, p. 40.

those of stability and instability as the neutral state, "although the surface does not anywhere fall below the fixed tangent plane, but meets the plane in more than one point, as we might anticipate from its intermediate character between the cases already considered, and is neutral".⁵²¹ Although the neutral state is, a limiting state is stable in regards to absolute stability provided that the temperature and the pressure of the complex system surroundings remain constant and disregarding the distinction between continuous and discontinuous change. In this paper, Gibbs gives a geometrical representation of stability and the instability of states and the definition of a neutral state. In his memoir, *the heterogeneous substances*, Gibbs offered algebraic expressions for the concept of stability and equilibrium.

Gibbs considered the relation between the primitive and the derived surfaces to specify the limits of equilibria and stability of homogeneous and heterogeneous phases of the substance. In this respect, he imagined the derived surface containing the three tangential vectors (the three sides of the triangle) to roll over the primitive surface in three directions, in each direction touching the surface at two points. As a result, three envelopes of the derived surface are obtained. The first envelope connects the solid and liquid states, the second envelope the liquid and the vapor states, and the third envelope the vapor and solid states. The composite surface is made up of the surface, which represents essentially stable phases. The three developable surfaces that connect the points of contact of double tangent planes representing the two phases together with the triangle of the derived surface constitute the surface *dissipated energy*.⁵²² **Figure 20** depicts a heuristic picture of the

⁵²¹ GSP, 1906, pp. 42.

⁵²² GSP, 1906, p. 48.

surface of the dissipated energy and its projection onto the entropy-volume plane.⁵²³ The stability of the state is determined relative to its position (represented as a point) to the surface of the dissipated energy. For a given volumes and entropies, the surface of the dissipated energy represents the locus of all points at which the energy is at a minimum. This situation is in accord with the thermodynamic properties of the substance. Above that surface, of the dissipated energy the equilibrium is stable, whereas, below the surface, the equilibrium is unstable or neutral when the points are on the surface. Presumably, Gibbs used the term surface of dissipated energy for the equilibrium surface to pay tribute to William Thomson. Recall that William Thomson introduced the concept of dissipation of heat (energy) or the loss of energy when he strove to figure out the equivalence between heat and work in the context of the second law of thermodynamics.

Gibbs noted that the surface of dissipated energy had important application to certain problems, which refer to the theoretically possible results with a given body or system of bodies in a given initial condition.⁵²⁴ He discussed the conditions under which the body has a certain amount of available energy and the conditions that affect the amount of the body's entropy or as Gibbs put it, the *capacity of the entropy* or the *available entropy*. In both circumstances, a point on the surface of the dissipated energy represents the initial state of a body, being in stable equilibrium. There are cases in which the body might move outside the surface of the dissipated energy where the equilibrium is unstable, or the body is solid with different values of the tensions along with different directions, or if different

⁵²³ In case of more than three coexistent phases, for example, with the sulfur that exists at high pressure in four allotropic forms and has three triple points, the surface of the dissipated energy will include three triple tangent planes and six different developable surfaces connecting the various allotropic phases (Bryan, 1907, p. 179)

⁵²⁴ GSP, 1906, pp. 49-54.

parts of the body are in different states. All these discontinuous changes can produce a certain amount of available energy that is capable of producing work. One cannot exclude the case in which the body has a sensible motion. The body's *vis viva* constitutes available energy.⁵²⁵

The second problem that Gibbs discussed in relation to the surface of the dissipated energy was the change of the body's entropy being initially in equilibrium on the surface of the dissipated energy. He sought to find the conditions under which the body's entropy increases without changing the system's energy or increasing its volume, excluding thus the possibility for the body to perform work. Heat is allowed to pass from the body to external bodies, and vice versa, only because the algebraic sum of all heat which thus passes in and out shall be zero. Gibbs asserted that this could be realized by finding the greatest amount by which it is possible to diminish the entropy of an external body under these conditions. This amount of entropy decrease will be, evidently, equal to the amount by which the body's entropy can be increased without changing the body's energy or increasing its volume.⁵²⁶ Gibbs graphically represented the relationship between the available energy and the available entropy and the surface of dissipated energy, as shown in Figure 21. This figure is similar to Figure 3 of Gibbs' article. ⁵²⁷ This figure shows the change of the energy and the entropy of the body represented by the distance of the point denoting the initial state from the surface of dissipated energy, measured parallel to the axes of the energy ε and the entropy η , respectively.

⁵²⁵ Ibid, p. 50

⁵²⁶ Ibid, pp. 50-51.

⁵²⁷ Ibid, footnote on p. 51.

In the second problem, Gibbs dealt virtually with the concept of the unavailable energy, which imparted to the body from the surroundings. However, he talked only of the entropy, not of the availability or the unavailability of energy. Gibbs did not identify the entropy with the measure or the factor that determines the unavailable energy.⁵²⁸ Nevertheless, he referred implicitly to it when he commented on Peter Tait's misinterpretation of Clausius' definition of entropy.⁵²⁹ According to Gibbs, Tait defined entropy in the opposite sense to that in which Clausius has employed it. He subsequently appeared to use the entropy to denote available energy. "Professor Maxwell", Gibbs continues, "uses the word entropy as synonymous with available energy, with the erroneous statement that Clausius uses the word to denote the part of the energy which is not available (Theory of Heat, pp. 186 and 188). The term entropy, however, as used by Clausius does not denote a quantity of the same kind (i.e., one which the same unit can measure) as energy, as is evident from his equation, cited]S = Q/T] in which ..., S and Q are evidently measured by different units".⁵³⁰ When Maxwell read Gibbs' second geometrical paper, he realized his errors and accused Tait of leading him astray. Maxwell managed to correct this error in a subsequent edition of his Theory of Heat.⁵³¹

Focusing on **Figure 20**, we observed the parallel straight lines ("tie-lines") traced on the three envelopes. The tie-lines connect any pair of points at which the plane cuts the

⁵²⁸ In thermodynamics, the portion of the total internal energy of the system, which is not capable of performing mechanical work, i.e., the unavailable energy, is connected with the entropy. Entropy is the factor or the measure which determines the unavailability of energy of a thermodynamic system. The entropy η multiplied by the temperature t of the system represents the unavailable energy lost to the system. Eq. (6.1) explicitly gives the two portions of the unavailable ($td\eta$) and available energy constituting the total internal energy $d\varepsilon$. The available energy is given in terms of the mechanical work pdv.

⁵²⁵ GSP, 1906, footnote on p. 52.

⁵³⁰ Ibid.

⁵³¹ Daub, 1970, pp. 322-323; Garber, 1969, pp. 149-150.

primitive surface and describe the coexistence of two distinct phases, each characterized by the values of energy, entropy, and volume corresponding to the endpoints of the contact line. Several two-phase systems in equilibrium can be determined on the tie-lines. The temperature, pressure, and masses all change along these lines. If the change between two phases occurs not through the tie-line but along the primitive curve, then for each of these two-state systems, Eqs. (6.2) and (6.3) continue to hold. Such curves are the isothermal and the isopiestic curves on the primitive surface. The edges of these straight lines trace six lines (vertical lines designated by the letter l in Figure 20) on the surface. A tangent plane at any point of the primitive surface outside the loci of the vertical lines lies either on the tangent plane or else lies above it. These six lines together define the *limit of absolute* stability. The surface outside these lines, which has the form of a con-nodal or bimodal curve, is the surface of absolute stability.⁵³² The projection of the surfaces on the entropyvolume plane (Figure 20) depicts the three-phase region of the derived surface SLV and the two-phase regions of the unstable mixture of states along with the tie-lines intersecting the curves separating the coexistent phases.

As the three tangent planes of the derived surface roll along the primitive surface, the latter may change from concave upwards to concave downwards. In other words, the primitive curve will change from a bimodal curve to a *spinodal curve*,⁵³³ leading to a violation of the criterion of stability. The dividing line between the two parts of the primitive curve, representing stable and unstable equilibrium states, defines the *limit of*

⁵³² GSP, 1906, pp. 43-44.

⁵³³ Gibbs did not use the terminology bimodal and spinodal. Maxwell describing Gibbs' thermodynamic curve used the terms *convexo-convex curve* and *spinode curve* for the bimodal and spinodal surfaces, respectively.

essential stability.⁵³⁴ The region between the *bimodal* and *spinodal* curve represents *metastable states* of the substance.

Figure 22 shows the various lines and curvatures on the primitive surface projected on the entropy-volume plane.⁵³⁵ Full lines represent lines on the primitive surface, while dotted lines are those of the derived surface. The points S, L, and V have a common tangent plane and represent the solid, liquid, and vapor phases that coexist in equilibrium. The pairs of lines LL' - VV', SS" - VV", and SS'" - LL'" are the six lines traced by the rolling double tangent, which lies the derived surface as depicted in **Figure 20**, and represent the *limit of* absolute stability. Between LL' and VV' is a liquid-vapor mixture. Between SS" and VV" is a solid-vapor mixture, and between SS'" and LL'" is a solid-liquid mixture. L"'LL', V'VV", and S"SS" are the boundaries of the surfaces which represent, respectively, the stable states of liquid, vapor, and solid. Straight lines connecting points representing the pure phases and running through all possible associated mixed-phase could be drawn in each of the above three regions. A few dashed lines in the liquid-vapor mixtures (Figure 22) illustrate the definite answer that Gibbs gave to the question posed by Andrews, as to where the straight line segment of the isothermal curve below the critical point, parallel to the axis of volume, must be drawn. The volume, entropy, and energy at each point on the tie-lines could be calculated from the corresponding values of the points of two coexistent phases of the substance, considering the masses of the substance in the two phases.⁵³⁶ The line

⁵³⁴ GSP 1906, p. 45.

⁵³⁵ This figure is similar to Figure 2 of Gibbs' article (GSP, 1906, p. 44), except for identifying the various sections of the diagram for clarification. Maxwell presented a more detailed diagram in his textbook *Theory of heat* (1902, p. 207).

⁵³⁶ If m' and m" represent the masses of the substance in the two coexistent phases, the volume, entropy, and the energy of the mixture at a point x on the tie-line can be calculated by an expression of the form: x = m'x' + m''x''. The primes and the double primes denote the entropies, energies, and volumes of points of the two pure phases (**Figure 22**). Similarly, for a mixture of masses m', m", m"' of three coexistent phases

ll'Cuv'ss' in **Figure 22** represents the *limit of essential stability*. This line touches the surface of the *limit of absolute stability* at critical point C. The *bimodal* curve is tangent to the *spinodal* curve at the critical point. However, the coincidence of the two lines is not accidental.⁵³⁷ Gibbs proposed the following physical property for the critical point: "Although this is a limiting state between those of stability and those of instability in respect to continuous changes, and although such limiting states are in general unstable in respect to such changes, yet the critical state is stable regarding them". Following this statement, Gibbs proposed four equivalent sets of crucial criteria representing first and second-order temperature and pressure variation near the critical point.⁵³⁸ Gibbs revisited the subject of critical phases in *heterogeneous substances*, where the criteria for phase stability are expressed in the form of the second-order and higher-order variations of the chemical potentials concerning the variation of the quantity of the coexistent phases.⁵³⁹

Very few scientists, at his time, would have been able to understand Gibbs' work and even fewer to show an interest in the geometrical model proposed by this "unknown" American Physicist. The first to visualize Gibbs' three-dimensional surface was James Clerk Maxwell, who in the 1870s was Head of the Cavendish Laboratory at Cambridge University. He devoted a thorough discussion of Gibbs' thermodynamic surface in his textbook on the *Theory of Heat*.⁵⁴⁰ He furnished a detailed drawing of the energy-entropyvolume diagram for water. He then sent a plaster model to Gibbs, who was flattered and

⁽in the derived surface), the values of entropy, energy, and volume at the triple point is the center of masses at the respective vertices of the triangle (the *centroid*).

⁵³⁷ Paul Saurel studied the condition for the tangenial relationship between the *bimodal* and *spinodal* curves (1902, pp. 483-484).

⁵³⁸ GSP, 1906, p. 46.

⁵³⁹ Ibid, pp. 129-131.

⁵⁴⁰ Maxwell 1902, pp. 195-208.

pleased, but with his typical modesty, told students who asked about it that the model came from a "friend in England".⁵⁴¹ Copies of Maxwell's three-dimensional model are kept at the University of Cambridge, in Clark University at the National Museum Scotland, while Gibbs' copy is displayed at the Sloane Physics Laboratory of Yale University (**Figure 23**).

Why did Gibbs use the graphical representation in his first appearance in thermodynamics and not the analytical method he applied extensively in his third paper?⁵⁴² Gibbs did not leave any information clarifying his decision to use diagrams. There are claims that Gibbs deemed the geometric representation primarily for didactic purposes.⁵⁴³ Perhaps, Gibbs found it appropriate to use geometry to disseminate among his students the value of the second law of thermodynamics and to make intelligible the concept of entropy. A passage from Gibbs' first paper might justify this conclusion. "it is, however, nothing more nor less than a geometrical expression of the second law of thermodynamics in its application to fluids, [...] it is more important for purposes of instruction and the like to familiarize the learner with the second law than to defer its statement as long as possible, the use of the entropy-temperature diagram may serve a useful purpose in the popularizing of this science".⁵⁴⁴

However, Gibbs' training as an engineer may have partly influenced his decision to enter thermodynamics by using geometric representations. Gibbs had an interest in engineering.⁵⁴⁵ He worked on an engineering dissertation (the first Ph.D. conferred in the

⁵⁴¹ Cropper 2004, p. 118.

⁵⁴² Duhem, who considered Gibbs an algebraist, alleged that the geometrical demonstrations of these papers did not play almost any role in the study of thermodynamic properties. They rather constitute the algebraic analysis in the form of Cartesian algebra (1908, p. 17).

⁵⁴³ Klein 1984, p. 148.

⁵⁴⁴ GSP, 1906, p. 11.

⁵⁴⁵ According to Professor Walters of Yale, who commented on Gibbs' dissertation, Gibbs showed his predilection for mechanics and skill in the use of the geometrical approach (Wheeler 1962, p. 28).

US). Later, he completed the manuscript of a paper (never published) on analytical mechanics and obtained a patent for an invention that improved the brake for railway cars of engineering interest.⁵⁴⁶ His interest in applied mechanics and inventions was manifested in two more circumstances. First, in his studies in Europe from 1866 to 1868, he was attracted to articles connected with his earlier design of the railway brake. Second, he was involved in improving the Watt conical pendulum governor for steam engines.⁵⁴⁷ From these facts, it is reasonable to assume that Gibbs was familiar with Watt's indicator diagrams, which engineers used to deal with various kinds of heat engines' performance compared to the ideal behavior. Therefore, the diagrams in the two articles of 1873 might have been due to Gibbs' inclination to the applied mechanics. From the three diagrams of these two articles, the temperature-entropy diagram seems to be more beneficial for engineers. It offered an easier way to obtain the relative amount of work done and the heat absorbed during the operation of the heat engine than the traditional pressure-volume diagram.⁵⁴⁸

Probably, both events played a role in Gibbs' start in graphic research. However, a statement in the introduction of Gibbs' first graphical paper might explain less dramatically his decision to enter thermodynamics using graphical methods. "So far as regards a general graphical method, which can exhibit at once all the thermodynamic properties of a fluid concerned in reversible processes, and serve alike for the demonstration of general

⁵⁴⁶ Wheeler 1962, pp. 32, 34-37.

⁵⁴⁷ Ibid, pp. 43, 55-56.

⁵⁴⁸ Gibbs contrasted Watt's indicator to his graphical representations to emphasize the usefulness of the proposed entropy-temperature diagram. "The method in which the coordinates represent volume and pressure has a certain advantage in the simple and elementary character of the notions upon which it is based, and its analogy with Watt's indicator has doubtless contributed to render it popular" (GSP, 1906, p. 11).

theorems and the numerical solution of particular problems, it is the general if not the universal practice to use diagrams in which the rectilinear co-ordinates represent volume and pressure".⁵⁴⁹

Gibbs' two papers of 1873 modeled the thermodynamic equilibrium as a function of five variables in two and three dimensions. In the third and longest paper *On the equilibrium of heterogeneous substances*, he dealt with additional variables as great as the number of the components constituting a heterogeneous mixture. Gibbs studied conditions for stability of equilibrium states of material systems, ranging from phases of homogeneous fluids to heterogeneous systems and other complex systems from solids to chemical reactions, from osmotic and electromotive forces to material films and surfaces of discontinuity. He proposed several alternative criteria of stability and equilibrium that led him to establish the famous phase rule and define critical phases of complex systems. His work *On the equilibrium of heterogeneous substances* written almost entirely in analytical form appears as a plausible approach due to the complexity of the examined systems.⁵⁵⁰ The first part of this essay has influenced most of the science of chemical thermodynamics, and therefore, I will focus my attention on this part.

⁵⁴⁹ GSP, 1906, p. 1.

⁵⁵⁰ Nevertheless, Gibbs used geometrical representations in *heterogeneous substances* to interpret the thermodynamic behavior of pure and multi-component systems. He recognized, however, that the Cartesian coordinate system tused in the first two papers was unsuitable when the system had more than three independent variables. He thought that he could overcome this obstacle by reducing the number of variables to two or three. He used the temperature, pressure, and the ζ function (see below) by making the total mass of the system constant, equal to unity. Through this line of reasoning, he studied the conditions of equilibrium of homogeneous substances, the binary and ternary systems. He adopted a different representation method for ternary systems, changing the Cartesian coordinate system into a two-dimensional equilateral triangle or a three-dimensional prism. (GSP 1906, pp. 115-129). The first diagram is currently in use by physicists and engineers to illustrate phase transformations in multicomponent and multi-phase systems.

Section 2. Equilibrium states: Chemical potential and fundamental functions

The starting point of the *heterogeneous substances* was Gibbs' attempts to find the true meaning of entropy and define simply and precisely the criteria of equilibrium, bringing to an end in this way the vagueness and the conflict around the interpretation of the concept of entropy. Using the state equation (6.1), he clarified the conditions of equilibrium and stability of an isolated system,⁵⁵¹ following a reversible change in terms of the state functions of entropy and energy. He considered two different but equivalent criteria for equilibrium expressed by the following inequalities.⁵⁵²

$$(\mathrm{d}\eta)_{\varepsilon} \le 0 \tag{6.14}$$

$$(\mathrm{d}\varepsilon)_{\eta} \ge 0 \tag{6.15}$$

The first inequality implies that for the equilibrium of any isolated system, it is necessary and sufficient that in all possible variations of the state of the system which does not alter its energy. The variation of its entropy shall either vanish or be negative. The second inequality entails that for the equilibrium of any isolated system, it is necessary and sufficient that in all possible variations of the state of the system, which does not alter its entropy, the variation of its energy shall either vanish or be positive.⁵⁵³ The first inequality follows directly from the two laws of thermodynamics. According to the first law, the energy of an isolated system is constant.

⁵⁵¹ An isolated system is a thermodynamic system enclosed by rigid, immovable walls (for instance, a Dewar's vessel) through which neither mass nor energy (heat) can pass. An isolated system obeys the conservation law, that is, its total energy and mass stay constant. The isolated system is an idealized model system away from common experience. In the *heterogeneous substances*, Gibbs considered a particular idealized system to apply the second law. The scenario of an isolated system (called the total system or universe) comprises two parts: a sub-system of interest and the sub-system's surroundings or simply the surroundings to be so large that they can be considered an unlimited heat reservoir at temperature *T*. No matter how much heat is transferred to (or from) the sub-system, the temperature of the surroundings will remain constant.

⁵⁵² GSP, 1906, p. 56.

⁵⁵³ Ibid.

In contrast, the second law states that the entropy of such a system increases, reaching its maximum value in equilibrium. Perturbation of the system from the state of equilibrium entails a decrease of the entropy, thus verifying the criterion of Eq. (6.14). The second inequality is the consequence of the first, and therefore any violation of the first results in a violation of the second and *vice versa*. If the system is perturbed from the state of equilibrium in a way in which its entropy increases (e.g., by receiving heat), i.e. $(d\eta)_{\varepsilon} > 0$, then the return of the system to the initial equilibrium state requires the entropy to decrease towards its initial unperturbed value. The decrease in entropy can only be possible by reducing its energy, violating Eq. (6.15).

However, the chemical equilibrium for a system composed of several different substances, the conditions of equilibrium and stability should take into consideration the influence of the masses of the various substances on the internal energy of the system. It is here where Gibbs introduced his beloved chemical potential.⁵⁵⁴ This thermodynamic quantity replaced entropy in almost every material system in the *heterogeneous substances* subjected to theoretical treatment. Let Gibbs define the chemical potential. "If to any homogeneous mass we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the potential for that substance in the mass considered".⁵⁵⁵ The chemical potential is

⁵⁵⁴ Gibbs never used the term chemical potential in *heterogeneous substances*. Instead, he simply used the word potential in his writings. The term chemical potential has been attributed to the American chemist Wilder Dwight Bancroft (1867-1953), who renamed Gibbs' potential in a letter sent to Gibbs in 1899 (Baierlein 2001, p. 431). It appears that Gibbs accepted the new terminology tacitly, as can be deduced in his reply letter to Bancroft in May 1899. (GSP, 1906, p. 425). In the current textbooks of physical chemistry, this state function refers to as chemical potential.

symbolized by the Greek letter μ . Gibbs generalized Eq. (6.1) by adding the new terms dm_i that signified an infinitesimal change of the mass m_i of the ith substance of the system. The change in the mass of each substance contributes to the change in the total internal energy of the material system. Let S₁, S₂, ..., S_n be the various substances with masses $m_1, m_2, ..., m_n$, respectively. The substances of the system could be contiguous or mixed. The differential equation below expresses the change of the internal energy of the system.⁵⁵⁶

$$d\varepsilon = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_n dm_n = td\eta - pdv + \sum_i^n \mu_i dm_i$$
(6.16)

This equation tells us that the energy of the system changes by dz when the mass of each constituent changes by an infinitesimal amount, dm_i provided that the entropy and volume of the system remain constant ($d\eta = 0$, dv = 0). The differential coefficients $\mu_1, \mu_2, ..., \mu_n$ of the respective masses are the chemical potentials of the substances S₁, S₂, ..., S_n of the mixture, respectively, with corresponding masses $m_1, m_2, ..., m_n$. Each chemical potential μ_i in Eq. (6.16) describes *the intensity of the energy change upon changing the mass of a particular substance*. The chemical potential expresses *the energy of the system per molecule or per mol of the particular substance that participates in the availability of the system to do work*. It applies to any physical and chemical process as in chemical reactions, osmotic or electrochemical phenomena, phase equilibria, dissociation processes in the gas and liquid phases, dilutes and non-dilute solutions, etc. According to Gibbs' definition, Eq. (6.16) gives the chemical potentials with respect to each of the masses considered as independent variables, i.e.,

$$\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}m_i}\right)_{\eta,\nu,m_{j\neq i}} = \mu_i \tag{6.17}$$

⁵⁵⁶ GSP, 1906, p. 63.

The subscripts in Eq. (6.17) denote the physical quantities that remain constant, indicating that the energy change of the system is attributed solely to the change in the amount of the particular substance S_i. Generalizing Eqs. (6.2) and (6.3) for a multi-component system, Gibbs defined its temperature and pressure as follows:

$$\left(\frac{d\varepsilon}{dv}\right)_{\eta,m_{j\neq i}} = -p \tag{6.18}$$

$$\left(\frac{d\varepsilon}{d\eta}\right)_{v,m_{j\neq i}} = t \tag{6.19}$$

Eq. (6.17) offers another definition of the chemical potential μ_i . It manifests the rate of change of energy of the multi-component system upon addition of an infinitesimal quantity of dm_i of the substance S_i , when the entropy η , the volume v, and the remaining quantities m_j ($j \neq i$) are held constant. The condition of equilibrium of the multicomponent system in a single phase (homogeneous) requires the chemical potential of each substance to be constant throughout the total mass of the system at constant temperature and pressure, i.e.,

$$t_1 = t_2 = t_3 = \dots = t_n = t$$
 (thermal equilibrium) (6.20)

$$p_1 = p_2 = p_3 = \dots = p_n = p \qquad (\text{mechanical equilibrium}) \qquad (6.21)$$
$$\mu_1 = \mu_2 = \mu_3 = \dots = \mu_n = \mu \qquad (\text{chemical equilibrium}) \qquad (6.22)$$

Eq (6.22) denotes that "the potential for each component substance must be constant throughout the whole mass".⁵⁵⁷ Eqs. (6.20) to (6.22) hold equally well for a multi-phase system. Integration of Eq. (6.16) between the limits of integration $0-\varepsilon$, $0-\eta$, 0-v, and keeping constant the intensive parameters t, p, and μ_i , gives the internal energy of the system: $\varepsilon = t\eta - pv + \sum_{i}^{n} \mu_i m_i$ (6.23)

⁵⁵⁷ Ibid, p. 65.

Eqs. (6.23) indicate that the number of independent variables to be determined to characterize the multicomponent system is 2n+5: n+2 from Eq. (6.16) ($t, p, \mu_1, \mu_2, ..., \mu_n$), n+2 from Eq. (6.23) (ε , υ , $m_1, m_2, ..., m_n$) and including Eq. (6.16) which is an additional independent variable. On Eq. (6.16) or (6.23) depend a very large class of variables from which the properties of the system can be considered. In general, all the thermal-mechanical, and chemical properties of the system can be obtained, Gibbs called Eq. (6.16) or (6.23) a *fundamental equation* for the substance in question, because all these properties were deduced from a single equation. Gibbs proposed other equations which possessed the same properties, as we shall see below.

By differentiation of Eq. (6.23) and subtracting Eq. (6.16), the well-known *Gibbs-Duhem equation* is obtained, namely.⁵⁵⁸

$$tdt - vdp + \sum_{i}^{n} m_{i} d\mu_{i} = 0 \tag{6.24}$$

Eq. (6.24) provides a relation between the variations of the n + 2 quantities, t, p, m_1 , m_2 , ..., m_n . If the variations of n + 1 of these quantities take any arbitrary values, the changes of the remaining quantity can be determined. A single homogeneous mass is therefore capable of only n + 1 independent variations of state. At constant temperature and pressure, Eq. (6.24) becomes:

$$\sum_{i}^{n} m_{i} \mathrm{d}\mu_{i} = 0 \tag{6.25}$$

This simplified form of the Gibbs-Duhem equation indicates how the chemical potential could change for a given composition while the system maintains its equilibrium. Furthermore, it denotes that the chemical potential of a particular substance in a multicomponent system is a dependent variable and can be determined when the chemical

⁵⁵⁸ Ibid, p.88.
potentials of the remaining substances of the system are available. Eqs. (6.24) and (6.25) play an important role in the study of the equilibrium and stability of several systems in *heterogeneous substances*, for example, the definition of the ideal gas mixture and the equilibrium of the coexistent phases (the phase rule).

Gibbs regarded equations (6.16) and (6.24) as *fundamental equations*, since they can afford all the independent variables they contain. Gibbs had introduced three other *fundamental equations*.⁵⁵⁹ The equations are expressions of the functions χ , ψ , and ζ .

$$\chi = \varepsilon + pv \tag{6.26}$$

$$\psi = \varepsilon - t\eta \tag{6.27}$$

$$\zeta = \varepsilon - t\eta + pv = \psi + pv \tag{6.28}$$

Eqs. (6.26) – (6.28) hold for an isolated system of a homogeneous substance and acquire a generalized form by adding the summation term $\Sigma \mu_i m_i$ as in Eq. (6.23). Hence, differentiation of functions χ , ψ , ζ over mass afford alternative definitions for the chemical potential.⁵⁶⁰

$$\left(\frac{\mathrm{d}\chi}{\mathrm{d}m_i}\right)_{\eta,p,m_{j\neq i}} = \left(\frac{\mathrm{d}\psi}{\mathrm{d}m_i}\right)_{t,v,m_{j\neq i}} = \left(\frac{\mathrm{d}\zeta}{\mathrm{d}m_i}\right)_{t,p,m_{j\neq i}} = \mu_t \tag{6.29}$$

As before, the subscript letters denote the quantities which remain constant upon differentiation of the equations (6.26) to (6.28) with respect to the individual masses m_i and compare with Eq. (6.17). These definitions reflect the possibility of measuring the chemical potential under different experimental conditions. The function ζ is experimentally more favorable for measuring the chemical potential since the pressure is constant. Experiments under constant pressure (e.g., atmospheric pressure) are more accessible to perform than

⁵⁵⁹ Ibid, p. 85-92.

⁵⁶⁰ Ibid, p. 89.

experiments under constant volume. The latter requires the implementation of a closed vessel as in calorimetric measurements. Gibbs' chemical potential survived until our days in current physical chemistry textbooks and represents a reliable measure to assess the equilibrium of chemical and physical processes. Gibbs considered that functions ψ and ε might be taken as equal to the work W done by the system at constant temperature and constant entropy when a quantity of heat Q is absorbed in a reversible process, i.e.

$$d\varepsilon = W - Q \tag{6.30}$$

$$-\mathrm{d}\psi = W \tag{6.31}$$

Gibbs regarded $-\psi$ and $-\varepsilon$ as *force functions* at constant temperature and constant entropy, respectively.⁵⁶¹ In like manner, he considered ζ function as the work done by the system at constant temperature and pressure less the work done by the change of the volume (mechanical work). In other words, ζ may represent the net work performed by the system in a reversible process. Therefore, this fundamental function could be defined as a net work function. Furthermore, Gibbs defined the equilibrium state at constant temperature via the ψ function and at constant temperature and pressure in terms of the ζ function, respectively, i.e.

$$(\mathrm{d}\psi)_t \ge 0 \tag{6.32}$$

$$(\mathsf{d}\zeta)_{t,p} \ge 0 \tag{6.33}$$

Gibbs showed that these equilibrium conditions were equivalent to each other and to that expressed by the inequality (6.15).⁵⁶² Therefore, conditions (6.32) and (6.33) might be used instead of (6.15) to determine the equilibrium states with evident advantage in respect to the brevity of the formulae. However, the former conditions show the same limitation as

⁵⁶¹ Ibid, p. 89.

⁵⁶² Ibid 6, pp. 89-91.

condition (6.15) expressed by their subscripts in formulae (6.32) and (6.33) that diminishes by one (temperature) in (6.32), and two (temperature and pressure) in (6.33) the number of independent variations in the state of the system considered. On the other hand, the four conditions of equilibrium stated above might give to the experimenter the choice to see in each case the form which he would take into consideration to determine the equilibrium under concrete experimental conditions. For example, if the experimenter adopts inequality (6.32) as the general condition of equilibrium, he has chosen in effect to take the thermal condition of equilibriums that is an experiment under constant temperature.

Gibbs recognized the significance of the ζ function as a measure of the state equilibrium at constant pressure and temperature. The minimum value of this function indicates that the chemical process has reached the state of equilibrium, i.e., in equilibrium, $d\zeta = 0$. The decrease of the ζ function towards its minimum value determines the condition for a spontaneous chemical or physical process. Today, the function ζ has been replaced by Gibbs' free energy, symbolized by *G* with the same mathematical and physical properties.

Gibbs appeared to be a scholastic reader of the literature. He knew in detail almost everything that had been published regarding mechanics and thermodynamics. He had read the papers of the founders of classical thermodynamics. Also, he had read the two papers of the French physicist François Massieu,⁵⁶³ published in 1869.⁵⁶⁴ Massieu had derived two functions Ψ and Ψ' analogous to Gibbs' ψ and ζ functions, respectively. Massieu called

⁵⁶³ François, Massieu was born in 1832 in Vatteville-la-Rue (today Seine-Maritime). After his father's death, he was able to continue his studies in Rouen, and entered the Ecole Polytechnique in 1851. He completed his training through courses at the Ecole des Mines and trainings in the railways, Mining and industry. He became an Engineer at the Mines Corps and in 1857 was appointed Professor at the Ecole de Mines in Saint-Étienne. For a short biography and analysis of Massie's work, see Ballian, 2017. ⁵⁶⁴ Massieu, 1869.

these functions characteristic functions.⁵⁶⁵ Massieu justified the name characteristic functions by showing that several thermal and mechanical properties of material systems could directly be obtained from these functions. From the partial first derivatives of Ψ , the internal energy, entropy, and pressure could be obtained, and through its partial second derivatives specific heats, expansion coefficients, and compressibility factors could be determined. Alternatively, the second characteristic function Ψ' incorporated all thermodynamic properties of the material systems. Massieu stressed that, by relying on characteristic functions, one could; on the one hand, use theory to determine some quantities not yet measured, and, on the other hand, check the consistency with thermodynamics of experimental data, and prove or disprove the compatibility of empirical formulae. Gibbs recognized the merit of the generalization of thermodynamics to mechanics proposed by the French engineer and cited Massieu's Ψ and Ψ' functions in a footnote of his *Heterogeneous substances*.⁵⁶⁶ However, Massieu did not examine whether these two functions could have played the role of potential in the case of equilibrium. It was Gibbs and in particular, Duhem who recognized that Massieu's two functions played this role.

Most interesting regarding the evolution of the concept of the chemical potential was the postscript of a letter from Maxwell to George Gabriel Stokes (1819-1903) on August 3, 1875, a full year before the publication of the *heterogeneous substances*.⁵⁶⁷ In connection with Andrews' experiments on the condensation of mixed gases, Maxwell sent a draft of a whole theory that would explain Andrews' experimental results by using a

⁵⁶⁵ In 1876, Massieu published an extended memoir, in which he showed the various properties and the applicability of the functions denoted this time as H and H' (Massiei, 1876).

⁵⁶⁶ GSP, 1906, pp. 86-87.

⁵⁶⁷ Stokes 1907, pp. 33-35.

provisional term called *reaction* for the quantity, which Gibbs invented soon afterward and named it potential. Maxwell defined *reaction* as Gibbs defined the potential in Eq. (6.17). Perhaps, Maxwell's insight into the significance of Gibbs' two papers on the geometrical representation of thermodynamics of fluids led him to anticipate some of Gibbs' thoughts developed in *heterogeneous substances*. Maxwell planned to do further research on the conditions of equilibrium of heterogeneous systems, but he stopped looking at this subject after the appearance of Gibbs' memoir. Nevertheless, he managed to derive the equilibrium conditions for a mixture and the effect of chemical combinations on equilibrium states. At any rate, Maxwell's thermodynamics touched a small part of what Gibbs had achieved.

Maxwell, who received the *heterogeneous substances* from Gibbs, was one of the very few physicists who understood what Gibbs had written in this essay. He felt admiration for Gibbs' work and especially for this new concept of potential, which indicated for the first time the association of the energy with any constituent substance through its proportionality to the mass of the constituent. In a paper where Maxwell gave a short account of the first portion of *heterogeneous substances*, he provided his explanation for Gibbs' potentials in Eq. (6.16) together with the other variables.

"These n + 2 new quantities, the pressure, the temperature, and the *n* potentials of the component substances, form a class that differs in kind from the first group of variables. They are not quantities capable of combination by addition but denote the intensity of certain physical properties of the substance. Thus, the pressure is the intensity of the tendency of the body to expand, the temperature is the intensity of its tendency to part with heat, and the potential of any component substance is the *intensity* with which it tends to expel that substance from its mass. We may, therefore, distinguish between

these two classes of variables by calling the volume, the entropy, and the component masses the *magnitudes*, and the pressure, the temperature, and the potentials the *intensities of* the system".⁵⁶⁸ Today, Maxwell's intensities and magnitudes correspond to intensive and extensive functions that determine the state of the system under study.

Gibbs did not state explicitly the analogy of his fundamental functions with the potentials of rational mechanics although the three functions χ , ψ , and ζ fulfill the criteria of the potential of rational mechanics regarding the corresponding pairs of independent variables. For the χ function, the independent variables are the entropy and the pressure; for the function ψ , the independent variables are the temperature and the volume, and for the function ζ , the temperature and the pressure are the independent variables. Gibbs expressed this analogy tacitly when he considered the decrease of the functions ψ as equal to the work done by external forces at a constant temperature according to Eq. (6.31). In rational mechanics, when the work of external forces, applied to a system is equal to the decrease undergone by a certain quantity whose value depends only on the state of the system, then the forces admit a potential. This potential is the function, the decrease of which represents the work done. Therefore, function ψ justifies the role of potential in thermodynamics. Similarly, function ζ is a potential, since its change is equal to the work done under constant temperature and pressure as noted previously.

Gibbs used chemical potential as a primary criterion to study the equilibrium and stability of homogeneous and heterogeneous systems. Some examples are the coexistence of phases that led to the famous phase rule, the equilibrium state characterizing phenomena of osmosis through a diaphragm and the effect of the osmotic pressure on the equilibrium,

⁵⁶⁸ Maxwell, 1876, p. 821

the interpretation of critical phases of fluids, the solubility of fluids, and the specific conditions for equilibrium of chemical reactions, the assessment of the electromotive force from the liberated heat in galvanic cells, the equilibrium conditions for dissociation processes in the gas phase and solution.⁵⁶⁹ He employed scarcely the other fundamental functions (potentials) and usually as an ancillary application.

In summary, the formulation of general criteria for the equilibrium of isolated systems in terms of energy and entropy offered a great service to classical thermodynamics. These equilibrium conditions ceased the confusion and the conflict around the interpretation and use of the concept of entropy.

Section 3. Coexistent phases: The phase rule⁵⁷⁰

In *heterogeneous substances*, Gibbs devoted two pages⁵⁷¹ under the heading *On coexistent phases of matter*, presenting the conditions for which a number of different phases of a substance are in equilibrium. These conditions constitute what today we call the phase rule. The phase rule provides the conditions of stability for a multi-component system in coexistent phases. Gibbs provided the mathematical relation between the possible numbers of phases, *r*, the number of components, *n*, and the number of independent variations or degrees of freedom, *F*, in a chemical system.

F = n + 2 - r

(6.34)

⁵⁶⁹ Scrutiny of today's physical chemistry textbooks reveals that the chemical potential has several applications on mixtures of substances and solutions, phase rule, the law of mass action, semipermeable membranes, osmosis, Raoult's law, galvanism, etc.). These applications, including Gibbs' paradox and its measurement method, are presented by Ingo Müller (2006).

⁵⁷⁰ The German chemist Wilhelm Meyerhoffer (1864-1906) working with van 't Hoff at the University of Amsterdam used for the first time the name phase rule. He published a paper entitled *Die Phasenregel und ihre Anwendungen* (The phase rule and its applications) (1893), ⁵⁷¹ GSP, 1906, 96-98.

Degrees of freedom are the intensive variable pressure, temperature, and chemical potential. The equation holds even when a component present in one phase is absent from another. This equation, however, does not hold when the concentration of a component in the phase changes, for example, through the occurrence of a chemical reaction. This procedure alters the composition of the phase or favors the formation of a new component. In this case, as established by Gibbs, the phase rule is not adequate to explain the equilibrium of such systems.⁵⁷² Gibbs devoted a few lines to offer a short, not rigorous proof of the phase rule upon considering that each component's intensive variables temperature, pressure, and chemical potential in the various phases should be constant. Thus, in equilibrium, a system of *n* components will have n + 2 independent variables given by Eq. (6.24), that is, the temperature, the pressure, and the *n* chemical potentials. Upon consideration that an equation of state relating n + 2 variables is written for each of the r phases, a simple subtraction of the number of equations from the number of variables gives the number of degrees of freedom.⁵⁷³ Furthermore, Gibbs established the differential equations that express the relation of the variations of temperature and pressure in a system of n + 1 coexistent phases (as before, n is the number of components). The treatment of a

⁵⁷² For the system of pure water with its vapor, there are two phases (liquid and vapor), then r = 2. If we treat water as a single component, n = 1, the phase rule predicts one degree of freedom. We can change the temperature under constant pressure or the pressure under constant temperature and maintain the system in equilibrium without changing the number of phases or the components in each phase. If we consider the dissociation of water, the number of components in the liquid phase is not one but three: neutral water molecules, hydronium ions, and hydroxyl ions. In this case, r is still two, but the number of components is now three. The phase rule predicts three degrees of freedom, which is absurd. In this case, the conditions of neutrality and the dissociation reaction should be considered in the phase rule equation to determine the correct number of degrees of freedom.

⁵⁷³ Gibbs deduced the phase rule far more concisely by the following reasoning, "A system of r coexistent phases, each of which has the same n independently variable components is capable of n + 2 - r variations of phase. The temperature, the pressure, and the potentials for the actual components have the same values in the different phases, and the variations of these quantities are by [equation] [97] subject to as many conditions as there are different phases. Therefore, the number of independent variations of the phase of the system, will he n + 2 - r'' (GSP, 1906, p. 96).

single component in a two-phase system leads to an equation analogous to the Clausius-Clapeyron equation. Gibbs generalized this equation for *n* components and n + 1 coexistent phase for known relations among various chemical potentials.⁵⁷⁴

The chapter on the equilibrium in the coexistent phases of material systems was largely ignored. It was in print for nearly ten years at the moment, when the Dutch chemist Hendrik Willem Bakhuis Roozeboom (1854-1907) discovered it. He sought a theoretical explanation for the puzzling behavior of the HBr-H₂O system. Roozeboom, who was appointed professor of chemistry at the University of Amsterdam in 1897 when van 't Hoff moved to Berlin, asked the assistance of van der Walls. Van der Waals, a competent mathematician, found a proper solution for the problem by employing Gibbs' phase rule.⁵⁷⁵ The phase rule and its applications were a major factor for the recognition of Gibbs' work on thermodynamics; especially when the American physical chemist Wilder Bancroft used it extensively in his research program at Cornell University.

Section 4. Effect of a diaphragm (Equilibrium of osmotic forces)

In 1887, the Dutch chemist Jacobus Henricus van 't Hoff published in the *Zeitschrift für Physikalische Chemie*, which was established by Ostwald and himself, a paper entitled *Die Rolle des Osmotischen Druckes in der Analogie Zwischen Lösungen und Gasen* (The role of osmotic pressure in the analogy between solutions and gases).⁵⁷⁶ Van 't Hoff presented a new theory for dilute solutions. He showed the importance of semi-permeable membranes

⁵⁷⁴ GSP, 1906, p. 99-100.

⁵⁷⁵ For informative discussions on Roozeboom;s experiments on the system HBr-H₂O and van der Waals' theoretical trearment of the problem, see Daub,1976, pp. 747-748; Wisniak 2003, pp.425-427; Duhem 1908, pp. 23-25.

⁵⁷⁶ van 't Hoff, 1887.

and osmotic pressure in studying solutions. He also established surprising analogies between the laws of the very dilute solutions and the laws which govern perfect gases. However, he had simply rediscovered results published by Gibbs about ten years before contained in the *heterogeneous substances* under the heading *Effect of a diaphragm* (*Equilibrium of osmotic pressure*).⁵⁷⁷ It seems van 't Hoff did not know about Gibbs' discovery.

Gibbs did not comment on the reversible cycles, nor did he ever use them, as van 't Hoff did in his work on the osmotic pressure. Gibbs in his theoretical treatment of phase equilibria used the chemical potential as the primary tool.⁵⁷⁸ He used the chemical potential to study the equilibrium of two homogeneous fluids separated by a diaphragm, which is permeable to some components and impermeable to others, and sufficiently strong to withstand the excess pressure on either side. The conditions of equilibrium for the components S_a, S_b, ... etc. that can pass the diaphragm under constant temperature are t' = t'',

$$\mu'_a = \mu''_a, \ \mu'_b = \mu''_b, \quad \text{etc.},$$
(6.35)

but not necessarily p' = p''. The prime and the double prime indicate the presence of the same component in the two phases separated by the diaphragm. The first condition indicates thermal equilibrium, closely related to the chemical equilibrium expressed by the chemical potentials. Different chemical potentials characterize components that do not pass

⁵⁷⁷ GSP, 1906, pp. 83-85.

⁵⁷⁸ Duhem rejected the method of reversible cycles first introduced by Clausius on the ground that it was a lengthy and painful procedure for studying physical and chemical processes. Alternatively, he proposed using the thermodynamic potential as a more accessible and effective tool (see below). Contrary to Gibbs, Duhem, and Max Planck, van 't Hoff considered reversible cycles the most suitable method to study thermodynamic systems instead of using abstract physical conceptions and mathematical functions, such as entropy.

the diaphragm in the two phases, and the pressures exerted on the two sides of the diaphragm are different, i.e., $p' \neq p''$. So, the resultant force per unit area on the membrane will be equal to the difference between the pressures of the two phases, that is, equal to the osmotic pressure.

Section 5. Gibbs on irreversibility

There are reservations whether Gibbs' work belongs to the field of thermodynamics. His theory in thermodynamics, as manifested in the graphical papers and the *heterogeneous substances*, does not involve any reference to any irreversible processes.⁵⁷⁹ Gibbs' theory refers almost exclusively to virtual changes, not to thermodynamic processes. Gibbs avoids commitments to equations of motion and deals entirely with states of equilibrium and conditions of stability. Gibbs' thermodynamics bears features of thermostatics.⁵⁸⁰ It is closer to rational mechanics than to rational dynamics.⁵⁸¹ Gibbs never referred to the kinetic theory founded by Boltzmann or Maxwell, let alone Boltzmann's papers on irreversibility. However, this does not necessarily mean that Gibbs was unaware of Boltzmann or Maxwell's theories. Alternatively, Gibbs may have avoided commenting on these theories because he was very cautious about the validity of the molecular models and

⁵⁷⁹ Clifford Truesdell (1984, p. 22) stressed that in the whole *heterogeneous substances* he found one, and only one passage, where Gibbs hinted the state of irreversibility. Gibbs discussed the case of an imperfect electrochemical apparatus in which Clausius' inequality $d\eta \ge dQ/t$ for the irreversible process may hold, leading to a lower electromotive force as compared to that measured when the cell operates under conditions of reversibility (GSP, 1906, pp. 338-339).

⁵⁸⁰ Pierre Duhem thoroughly studied Gibbs' thermodynamics and considered this work a manifestation of thermostatics (statique chimique). Arguing Gibbs' reference to equilibrium processes, he posed the following question: "suppose the original condition of a body satisfies Gibbs' criterion of equilibrium. If its condition is then forcibly altered, will that body upon release tend to resume or at least remain near its original condition"? Duhem considered that equilibrium in nature is not realizable; it is a virtual equilibrium since any physical process presupposes the departure from the equilibrium state accompanied by dissipation (loss) of energy as in viscous fluids and deformable solids.

⁵⁸¹ Dunn, and Fosdick 1980; Truesdell 1986, pp. 101-113.

kept a distance from them. As noted, Gibbs did not utterly oppose the perception of molecules and atoms and conceived their use in theories that would better understand the experiment than the phenomenological theories did. Gibbs often referred to atoms, molecules, and molecular structures in *heterogeneous substances*.⁵⁸² At any rate, it seems that Gibbs did not set aside the question regarding irreversibility. He attempts to meet this challenge, not in his papers on thermodynamics but in his book on statistical mechanics. Indeed, Gibbs summarizes his thoughts about irreversibility in Chapter XII of his book of Elementary Principles in Statistical Mechanics⁵⁸³ with a special reference to The Rational Foundation of Thermodynamics in the subheading of the book. This book was published after a long delay.⁵⁸⁴ Gibbs published this book in 1902, one year before his death, and at the time, he enjoyed an international reputation for his work on thermodynamics. In this book, Gibbs discusses his novel ideas about the canonical, micro-canonical, and grand canonical assembly of independent mechanical systems in the phase space. Although he prefers to express his ideas using general terms like systems or particles forming the ensembles, he does not evade referring clearly to molecules in the book's last chapter. Gibbs stated epigrammatically the objectives of this work in the book's subtitle and explained them clearly in the preface.

"But although, as a matter of history, statistical mechanics owes its origin to investigations in thermodynamics, it seems eminently worthy of independent

⁵⁸² GSP, 1906, pp. 138-144, 167-168, 171, 185.

⁵⁸³ Gibbs 1902.

⁵⁸⁴ Gibbs was slow to publish. He was not easily satisfied with his intellectual product, and some of his publications remained on the shelf for several years before becoming available to the readers. He had completed the book *Elementary Principles in Statistical Mechanics* in 1892. The bool appeared ten years later, even though his notes on this subject had been distributed among the students who attended his lectures (Klein 1989, p. 14).

development, both on account of the elegance and simplicity of its principles, and because it yields new results and places old truths in a new light in departments quite outside of thermodynamics. Moreover, the separate study of this branch of mechanics seems to afford the best foundation for the study of rational thermodynamics and molecular mechanics". ⁵⁸⁵

Also, in the preface, Gibbs touched on other items like the link between the statistical mechanic and thermodynamics, the analogies between these two sciences, and emphasizes their mutual benefits. "The laws of thermodynamics, as empirically determined, express the approximate and probable behavior of systems of a great number of particles, or, more precisely, they express the laws of mechanics for such systems as they appear to beings who have not the fineness of perception to enable them to appreciate quantities of the order of magnitude of those which relate to single particles, and who cannot repeat their experiments often enough to obtain any but the most probable results. The laws of statistical mechanics apply to conservative systems of any number of degrees of freedom and are exact. [...] This does not make them more difficult to establish than the approximate laws for systems of a great many degrees of freedom, or for limited classes of such systems (...) The laws of thermodynamics may be easily obtained from the principles of statistical mechanics, of which they are the incomplete expression, but they make a somewhat blind guide in our search for those laws. This is perhaps the principal cause of the slow progress of rational thermodynamics, as contrasted with the rapid deduction of the consequences of its laws as empirically established".586

⁵⁸⁵ Gibbs, 1902, p. viii.

⁵⁸⁶ Ibid, pp. viii-ix.

Chapter XII of the *Elementary Principles* entitled On the motion of systems and ensembles of systems through a long time is devoted to studying two subjects related to the dynamics of an ensemble of independent systems that distributed in phase space.⁵⁸⁷ The first question raised here is under which conditions will a general mechanical system return with time to its initial phase? Or, if not, will it do so to any required degree of approximation?⁵⁸⁸ In the second subject, Gibbs investigates the question as to whether an ensemble of isolated systems, i.e., not interacting with other ensembles of systems, has any tendency over time towards a state of statistical equilibrium.⁵⁸⁹ In both cases, Gibbs referred to statistical equilibrium, or at least to the evolution of the phase space than towards a rigorous explanation of the irreversibility characterizing the ensemble of mechanical systems. He does not present a complete theory of irreversibility, and the proofs of various propositions were in the form of qualitative, although plausible, arguments. Unlike the remaining fourteen chapters of the book, chapter XII was written in Gibbs's usual condensed writing style, and surprisingly, it was devoid of mathematics; the eleven pages of this chapter have not even one equation or an algebraic function. Gibbs is probably not satisfied with the treatment of irreversibility, as it was evidenced in the book's preface. Over the six-page prologue, where Gibbs presents his objectives, describes his methods, and gives the outlines of the chapters, he avoids mentioning the results of chapter XII. Gibbs was reluctant to publish any of his work unless he was satisfied with his intellectual

⁵⁸⁷ The phase space describes the mechanical state of the bodies that are distributed in the ensemble. The coordinates and momenta of the bodies in the ensemble determine the degrees of freedom of the phase space. The dimensions of the phase space depend on the number of degrees of freedom. For n coordinates and n momenta, the dimensions of the phase space are 2n. The graphical representation of the phase space is the *phase plane* that contains the number of points, each with its own coordinate and momentum.

⁵⁸⁸ Ibid, p. 139.

⁵⁸⁹ Ibid, p. 143.

product. Chapter XII seems to be an exception to his strict discipline for publication. A possible reason for the sketchy appearance of this chapter might be due to Gibbs' hastiness to finish this book promptly for Yale College's Bicentennial celebrations.⁵⁹⁰

Returning to the first question mentioned above, Gibbs has to investigate the dynamical nature of the assembly of systems. In other words, to find the fraction of systems that leaves the phase and will not return to it with time. In this respect, he had to prove the following theorem: "If we imagine an ensemble of identical systems to be distributed with a uniform density throughout any finite extension-in-phase,⁵⁹¹ the number of the systems which leave the extension-in-phase and will not return to it in the course of time is less than any assignable fraction of the whole number".⁵⁹² The sole assumption associated with this theorem is that the energy of the systems of the ensemble assumes two finite values being less or greater than any of the energies of the phase they lie. Gibbs illustrates the free motion of a rigid body having one point fixed to assimilate the distinction among three parts of the independent systems of the canonical ensemble. The part that never passes out the ensemble, that which will pass out and all return within it, and the part that passes out, never returns, exactly or approximated to their original phase.⁵⁹³ Gibbs does not prove the rigid body problem essentially. He provided a more straightforward, deductive explanation in the case of a micro-canonical ensemble for the theorem concerning the return of the

⁵⁹⁰ Ibid, p. 15.

⁵⁹¹ Gibbs extended the simple phase space to the complex extension-in-phase. He considered that all possible phases could form an extension of 2n dimensions. The single element (phase) of this extension has been defined by the product of the differentials of the momenta (*p*) and coordinate (*q*), namely $dp_1 dp_2 \dots dp_n dq_1 dq \dots dq_n$.

The number of all phases of an ensemble that fall within the extension-in-phase will be represented by the integral, which is taken within any limit.

 $[\]int \dots \int \mathrm{d} p_1 \mathrm{d} p_2 \dots \mathrm{d} p_n \mathrm{d} q_1 \mathrm{d} q \dots \mathrm{d} q_n$ (Gibbs, 1902, pp. 6-10)

⁵⁹² Ibid, p. 139.

⁵⁹³ Ibid, pp. 140-141.

systems to the original ensemble. This proof can be easily extended to any arbitrary statistical equilibrium.⁵⁹⁴

The second question on the assumption that an ensemble not in equilibrium tends towards a state of equilibrium raises the following contradiction. The tendency towards the condition of statistical equilibrium presupposes that the average probability index of the ensemble should take its minimum value at the state of equilibrium. In contrast, this particular index must be constant, representing the permanent distribution or the average density of the systems in the ensemble. To solve this dilemma, Gibbs investigates the analogy with a familiar phenomenon related to the effect of stirring on mixing an incompressible liquid. A coloring, non-diffusible matter adds (for instance, ink). The analogy with the statistical problem stems from the fact that the greatest degree of mixing upon stirring develops when the mean square of the density of the coloring matter attains a minimum.

Nevertheless, the mean square of the density of the coloring matter cannot change from its initial value. The density of each of its particles remains virtually constant regardless of the motion of the liquid during stirring. The presence of the coloring matter does not change the liquid's hydrodynamic properties, probably due to the liquid's incompressibility. Nevertheless, it is common to observe that a liquid initially is not uniformly colored, becomes so after a simple stirring. Gibbs elaborates on the solution of this problem, exploring the elementary density (the ratio of the mass to volume of each particle) of the coloring matter. He does that through the choice of the element of the volume in different ways. He concludes that the element of volume can be fixed in phase

⁵⁹⁴ Ibid, p. 142.

space and be finite in size (this condition ensures the constancy of the mean square density of the coloring substance). Then stirring would result in the diminution of the mean square of the density of the coloring matter. "Whether the time required for this result would be long or short depends upon the nature of the motion given to the liquid and the fineness of our method of evaluating the density".⁵⁹⁵

In the following three pages of the chapter (146-148), Gibbs investigates a particular case of a fluid motion upon considering the rotational motion of a cylindrical mass of liquid around the cylinder's axis, of which one quadrant is black, and the rest is white. In the last pages of the chapter, he discusses the analogy between statistics and hydrodynamics, which clarifies the apparent contradiction between the requirement for a permanent, uniform distribution of the ensemble of systems in the phase space and its tendency towards statistical equilibrium.⁵⁹⁶

⁵⁹⁵ Ibid, p. 146

⁵⁹⁶ Gibbs 1902, pp. 148-151.

Chapter 7. Duhem's approach to thermodynamics

Duhem was born in Paris on June 9, 1861. He finished the Collège Stanislas, a state lycée in Paris, where Duhem continued his schooling after a short period in a private school. In 1882, Duhem passed the entrance examinations of the École Normale Superieure. In 1885 presented a doctoral dissertation in physics, which the examiners rejected. Duhem was convinced that behind this decision was Marcelin Berthelot, who was at that time the indisputable star in French chemistry and a strong political figure. In his thesis, Duhem described his new concept, the thermodynamic potential, and questioned Berthelot's principle of *maximum work*. Duhem defended a second thesis, and finally, he received his doctorate in 1888. Due to his dispute with Berthelot, he was never appointed in a chair of physics in Paris. He was "exiled" for the rest of his life in provincial universities at Lille, Rennes, and finally at Bordeaux, where he died on September 14, 1916.

Reconstructing thermodynamics, Duhem rejected the two views of molecular mechanics regarding the interpretation of heat as the result of rapid motion of particles (atoms or molecules) that composed ordinary bodies and the identification of temperature with the average kinetic energy of the body. This interpretation based on the hidden movements of atoms and molecules was the subject of intensive studies initially by Clausius, and later by Maxwell and Boltzmann. Duhem thought that this theory might be successful in dealing with the principle of the conservation of energy but failed to deduce Carnot's law in a thoroughly satisfactory manner in the context of dynamics. The second view, associated with Clausius⁵⁹⁷ and Kirchhoff in Germany, Rankine in Britain, Gibbs in

⁵⁹⁷ Clausius, and Rankine, contributed to both theoretical trends of thermodynamics. They both based the development of thermodynamics on a molecular interpretation, although using different concepts. Even

America, and Jonas Ferdinand Gabriel Lippmann (1845-1921) in France, sought to make thermodynamics independent of all hypotheses about the nature of heat. These scientists attempted to establish thermodynamics on its principles away from theories of molecular mechanics. Duhem considers both approaches unacceptable since they overlook the analogies between these two trends, for instance, the conditions of equilibrium and irreversibility. According to Duhem, none of these theoretical methodologies can interpret irreversible processes, and any relevant attempt constitutes a rather qualitative description. Time as a variable of the state of the system is absent in these theories.⁵⁹⁸ Duhem outlines his strategy to reconcile thermodynamics with dynamics as follows: "We have tried in the present work to suggest a third position of dynamics to thermodynamics. We have made dynamics a particular case of thermodynamics. Or rather, we have constituted, under the name thermodynamics, a science, which embraces in common principles all the changes of state of the bodies, including both changes of place and changes in physical qualities".⁵⁹⁹

Gibbs employed analogies between thermostatics and rational mechanics in his *heterogeneous substances*, whereas Duhem pursued a form of generalized thermodynamics elaborating classical thermodynamics with the principles of rational mechanics in its static and dynamic character. He derived his thermodynamic potentials in analogy with rational mechanics, whereas he employed the principle of virtual velocities and the theorems of Lagrange's analytical mechanics to describe non-equilibrium processes. He deemed that

when he worked in a phenomenological register, Clausius relied on kinetic-molecular intuition, for examp;e, the free heat and disgregation. For Clausius' motivation to develop the molecular theory in the context of thermodynamics, see Garber 1970; Darrigol, 2018a, pp. 58-60.

⁵⁹⁸ Scrutiny of the main traditions in thermodynamics may reveal a finer classification of theoretical approaches. Stefano Bordoni discerns five streams sorted according to their conceptual distance from molecular mechanics (2013, pp. 618-619).

⁵⁹⁹ Duhem, 1894, p. 285.

the change of place in space in mechanics was a transformation as straightforward as a temperature change in thermodynamics or some other physical quality.

Rational dynamics⁶⁰⁰ is the theoretical branch of physics that deals with problems concerning complex movements of bodies, i.e., processes occurring in time, and belongs to the general context of dynamics like equilibrium in the frame of statics. Conditions for statics require the absence of external forces exerted to the system, which is in equilibrium. In this case, the system is considered isolated. In cases where external forces are acting on the system, the resultant force is zero so that the system attains its equilibrium state. Rational dynamics has its origin in Newton's physics but was developed in the eighteenth century by the French physicists and mathematicians Bernoulli, Euler, D' Alembert, and advanced by Lagrange.

Furthermore, Duhem sought to bridge the gap between physics and chemistry in the context of his generalized thermodynamics. Chemistry and physics convey many analogies concerning the interpretation and mathematization of various physical and chemical phenomena and processes. Dilatation, contraction, fusion, vaporization, dissociation reactions, variations in electricity, and magnetism are analogous phenomena to calorific phenomena and can be treated within the context of generalized thermodynamics. In a word, Duhem sought to embrace together all physical and chemical

⁶⁰⁰ A rational dynamical system could be defined by the Hamiltonian system of differential equations: $\frac{dq_{r=}}{dt} = \frac{dU}{dp_{r}}, \quad \frac{dp_{r=}}{dt} = \frac{dU}{dq_{r}} = P_r$. The energy of the system U is a known function of the dependent variables q_r called the position coordinates, and an equal number of dependent variables p_r the generalized momenta coordinates of the system. The only independent variable is the time t. The state of the system, therefore, is defined when the values of the time and the 2n variables q_r and p_r are known. The energy of the system is the sum of the kinetic energy and the potential energy. As a matter of fact, the kinetic energy is a homogeneous quadratic function of the momenta coordinates (or velocities), whereas the potential energy is independent of these coordinates. The definition of the generalized force P_r coordinates depends on the particular mechanical problem. When $P_r = o$, then the system is considered as isolated (Bryan 1907, pp. 29-30).

transformations, and this was the formidable task that he had undertaken starting from Gibbs and Helmholtz's equilibrium thermodynamics. Duhem used to call his generalized thermodynamics *Energetics*⁶⁰¹ or *chemical mechanics*. Duhem's thermodynamics was developed in parallel with the chemical thermodynamics proposed by the ionists (van 't Hoff, Arrhenius, Ostwald). As we shall see later, these two approaches to chemical thermodynamics had a completely different reception from the scientific community and, in particular, from chemists.

Duhem reformulated thermodynamics following the conventional language of analytical mechanics. He built new mechanics on the principles of thermodynamics. He was aware of the difficulty that would cause to the reader the formal language of his work. In this respect, in founding his energetics, he used a dual methodology.

"One, the most perfect in itself, is to unfold this link in the logical order, starting from the principles and hypotheses, following the long and minute deductions, until we reach the conclusions. This method, applied to chemical mechanics, requires the use of continual mathematical analysis; if we had followed it, our book would have repelled most of those to whom we address it. The other method consists in exposing the truths in their invention; we understand better the contents of a physical law when we know by what efforts it generated what errors it was necessary to discard to bring it to light".⁶⁰²

He adopted the first method in most of his essays and monographs when he considered the cross-fertilization among mechanics, thermodynamics, physics, and chemistry. He applied the second method with mild mathematical formulation to three

⁶⁰¹ This name was first introduced by Rankine. The same term was also used by Ostwald and Georg Helm (1951-1923) but in a completely different context than Duhem's.

⁶⁰² Duhem, 1893a, p. vi.

memoirs: his first dissertation published in 1886, *Le potentiel thermodynamique et ses applications à la mécanique*, and in *l'étude des phénomènes électrique*,⁶⁰³ the treatise *Introduction à la mécanique chimique*,⁶⁰⁴ and the sole book he wrote in English, *Thermodynamics, and chemistry*.⁶⁰⁵ My analysis will follow both modes of exposition to provide the reader with a better acquaintance of Duhem's generalized thermodynamics.

Section 1. Thermodynamic potential

Duhem began his scientific work early, in 1882, while he was in the last year of his studies at the Collège Stanislas. He read Gibbs' writings on thermodynamics and the first part of Helmholtz's *Die Thermodynamik Chemisher Vergänge*, (thermodynamics of Chemical Processes) translated by the French physicist Clément Georges Lemoine (1841-1922). These works referred to the *characteristic functions* Ψ and Ψ' (later renamed as H and H') invented by François Massieu in 1869. These functions took the form of Gibbs' ψ and ζ fundamental equations and Helmholtz's free energy.⁶⁰⁶ Duhem realized that these functions should play an important role in thermodynamics analogous to the potential in rational mechanics. He was one of the first to see real promise in this, calling such functions *thermodynamic potentials*.

He was still an undergraduate student at the École Normale Supérieur when he published a brief note entitled *Sur le potentiel thermodynamique et la théorie de la pile voltaïque*. He introduced the *thermodynamic potential* as a general criterion to study

⁶⁰³ Duhem 1886.

⁶⁰⁴ Duhem 1893a.

⁶⁰⁵ Duhem 1903.

⁶⁰⁶ Duhem included the German speaking physicists Arthur von Oettingen, professor at the Dorpart University in Estonia, among the physicists who viewed thermodynamics in a remarkable generalized context. Stefano Bordoni gives a short account on Oettingen's thermodynamics (2013, pp. 635-640).

equilibrium states of stable systems at a given temperature.⁶⁰⁷ The minimum value of the thermodynamic potential indicated the condition of equilibrium attained by the system. He gave a lengthy list of applications in which the newly proposed thermodynamic potential could replace the method of reversible cycles. However, since "these results are too numerous to be summarized, even succinctly, in this Note",⁶⁰⁸ he treated explicitly only the voltaic pile as an example in this study.

Duhem presented the complete derivation of the thermodynamic potential and its extensive applications to several chemistry and physics problems in his first treatise, *Le potentiel thermodynamique*. This book was his first dissertation written in a little more extended form, which was published with his expenses. The thesis was rejected by a committee of three scholars whose president was the physicist Gabriel Lippmann as "not worthy of being defended as a thesis before the Faculty of Science of Paris".⁶⁰⁹ Duhem claimed that behind this decision was the chemist Marcellin Berthelot, a prominent chemist within the French scientific community with a strong political influence.⁶¹⁰ In his dissertation, Duhem questioned Berthelot's "third principle" of thermochemistry, the principle of *maximum work*. For Berthelot, this principle had a broad generality for chemical reactions.⁶¹¹ Duhem published the rejected thesis for one more reason: he wanted

⁶⁰⁷ Duhem, 1884.

⁶⁰⁸ Duhem, 1884, p. 1113.

⁶⁰⁹ For a thorough discussion of the events that took place during Duhem's presentation, see Jaki, 1984, pp. 50-53.

⁶¹⁰ Berthelot was regarded as one of the most famous chemists in the world. Upon being appointed to the post of Minister of Foreign Affairs for the French government in 1895, he was considered the most influential living chemist in France. In 1901, he was elected as one of the Forty Immortals of the Académie française.

⁶¹¹ Miller, 1966, pp. 49-50; 1981, pp. 225-233.

to vindicate Jules Moutier (1829-1895),⁶¹² his physics teacher at Collège Stanislas. Duhem regarded Moutier as one of the principal founders of chemical mechanics whose work Berthelot had slighted.

In the introductory part of the book, Duhem presented a rather extensive historical account of the efforts made by physicists to establish the principles of chemical mechanics that may play the same role as the virtual velocities and Lagrange's Mécanique Analytique play in all mechanics, rational and dynamics.⁶¹³ He mentioned Berthelot's principle of maximum work as the first attempt to identify energy with the potential of a chemical system. The inadequacy of this principle to explain heat absorption by endothermic reactions undermined the proposition that energy could play the same role as the potential in mechanics. On the other hand, entropy could not play the role of force function either. At this stage, Duhem mentioned Horstmann's suggestion in 1873 that entropy cannot decrease during a physical or chemical change of an isolated system contrary to any natural force; it can only increase or at least becomes constant at a given temperature.⁶¹⁴ Therefore, physicists were obligated to seek, among other thermodynamic quantities, a function that could describe chemical equilibria.⁶¹⁵ As noted, Massieu had introduced in 1869 two characteristic equations, Ψ and Ψ' . Duhem commented that Massieu did not examine whether these two functions could have played the role of potential in the case of equilibrium. Gibbs recognized that Massieu's two functions could play this role. Gibbs had

⁶¹² Jules Moutier was a professor of physics and chemistry at Collège Stanislas. Duhem had great respect for Moutier as a teacher and physicist and learned from him the new thermodynamics of Gibbs (Jaki, 1984, pp. 29-30 and 260-263). In 1872, Moutier published the *Eléments de thermodynamique*, and in 1885, the textbook *La thermodynamique et ses principales applications*.

⁶¹³ Duhem 1886, pp. II-VII.

⁶¹⁴ Horstmann 1873, p. 192.

⁶¹⁵ Duhem 1886, pp. III-V.

proposed two functions corresponding to Massieu's Ψ and Ψ' functions, namely the ψ and ζ function, respectively. In 1882, Helmholtz distinguished two kinds of energies that constituted the internal energy of the bodies, *free energy*, and *bound energy*. Helmholtz claimed that the free energy could be transformed into mechanical or electrical work by the system. In contrast, the bound energy appears as heat within the body.⁶¹⁶ The free energy is identified with Massieu's Ψ function and Gibbs' ψ function.⁶¹⁷ In short, the works of Massieu, Gibbs, and Helmholtz showed Duhem that energy and entropy could play the role of potentials and be helpful for the study of the properties of physical and chemical systems.

The dissertation *Le potentiel thermodynamique* consists of three parts. The first part contains seven chapters. The first chapter presents the derivation of the thermodynamic potential.⁶¹⁸ In the remaining six chapters, Duhem applied his potential to questions in thermodynamics that have been studied earlier by alternative methodologies. He treated, for example, Gibbs' dissociation of compounded gases, Helmholtz's results on voltaic cells, and Kirchhoff's examination of the heat liberated on saline solutions (the heat evolved upon neutralization of an acid by a base forming a salt plus water). The following

⁶¹⁶ In rational mechanics, the free enegy is identified with the available energy of the system and the bound energy with the unavalable energy. As we shall see later, measure of the unavailable energy is the entropy. ⁶¹⁷ In 1853, the Navy engineer and director of the École du Genie Maritime, Ferninand Reech (1805-1884) sent a long essay entitled *Théorie generale des effets dynamiques de la chaleur* to the *Journal de Mathématiques Pures et Appliquées*, in which he introduced four functions (Reech called them *Formules generales*) that were similar to Gibbs' fundamental functions, Massieu's characteristic functions, and Duhem thermodynamic potentials. Reech wrote these functions in a complete different style than those presented by Gibbs, Messieu, and Duhem. Reech proved that these functions had the properties of potentials because they were functions of pairs of independent variables in accord with rational mechanics (Reech, 1853, pp. 407-408). Clifford Truesdell and S. Bharatha edited a book in 1977 dedicated to the memory of the great French thermodynamicists Carnot, Reech, and Duhem. The two emphasized the role of Reech in the development of thermodynamics and analyzed the reasons that led Reech's work to pass in oblivion (Truesdell and Bharatha, 1977, pp. 57-65 and 119-125). Also, Truesdell, 1980, pp. 277-301). ⁶¹⁸ Duhem 1886, pp. 1-10.

two parts of this memoir involved novel applications of the thermodynamic potential to chemical mechanics, such as solutions and mixtures, and static and dynamic electrical phenomena. Duhem repeated the derivation of the thermodynamic potential in his textbook *Thermodynamics and chemistry* written in English,⁶¹⁹ and his memoir *Introduction à la mécanique chimique*.⁶²⁰ In the last derivation, Duhem demonstrated explicitly the analogies between thermodynamics and rational mechanics, and between thermodynamics and rational mechanics, and between thermodynamics and rational mechanics. This memoir will be used to demonstrate Duhem's methodology in deriving his internal and total thermodynamic potentials.

Duhem began using Carnot's theorem as modified by Clausius' principle of the equivalence of heat and work. But first, Duhem found it necessary to establish the notion of the reversible transformation (he used repeatedly the word modification). He claimed that a state of reversible transformation does not exist. It is a virtual transformation. The system when passes from an old state to a new state through a series of intermediate states, infinitely close to each other, is forced to immediately leave each state to the next one. Thus, the state in which the system was for a moment was not a state of equilibrium.

Duhem considered the process during which a system passes from state 1 to state 2, under the influence of external forces, by crossing the intermediate states A, B, C, D.... He claimed that one cannot support the view that the system placed in the same conditions, subject to the same forces can return from state 2 to state 1 by going through the same in reverse order, i.e., ...D, C, B, A, but through the states ...D', C', B', A' different to the states ...D, C, B, A. He thought that it is feasible for this transformation to become reversible and the system to go back from state 2 to state 1. It will suffice, for example, to

⁶¹⁹ Duhem, 1903, pp. 94-103.

⁶²⁰ Duhem, 1893a, pp. 93-113.

increase for a suitable time the external forces acting on the system. However, this reverse transformation will not occur under the action of the same external forces as the direct transformation; the system cannot go through the same intermediate states crossed in the opposite direction. The system might return to its initial state by the inverse series of transformations passing through the states ...D', C', B', A', different from states D, C, B; A. Duhem defined this transformation as a *realizable transformation*. "Thus", Duhem concluded, "the reversible modification is a series of states of equilibrium; it is essentially unachievable. It is never except by thought that one can make such a modification undergo a system".⁶²¹

Duhem imagined a system passing through a closed cycle, during which it experiences a succession of a series of infinitely small transformations $M_1, M_2, ..., M_n$, which bring it back to the same state from which it started. During each infinitely small transformation M_i (i = 1, 2, ..., n), the system releases an infinitely small quantity of heat Q_i at an absolute temperature T_i . Clausius defined each transformation by the respective quotient Q_i/T_i . The total transformation that the system undergoes in traversing the closed cycle is given by Clausius as

$$\sum_{1}^{n} \frac{Q_{i}}{T_{i}}$$

If all the transformations that make up the cycle are reversible, this sum is equal to 0.

$$\sum_{i=1}^{n} \frac{Q_i}{T_i} = 0 \tag{7.1}$$

If the transformations in the cycle are all realizable or if some of them are realizable and the others reversible, then

⁶²¹ Duhem, 1893a, pp. 93-95.

$$\sum_{i=1}^{n} \frac{Q_i}{T_i} > 0 \tag{7.2}$$

Clausius defined a quantity *S* such that, for any reversible transformation bringing the system from state 1 to state 2. In this case, the sum $\sum_{i=1}^{n} \frac{Q_i}{T_i}$ might be given as

$$\sum_{i=1}^{n} \frac{q_i}{r_i} = S_1 - S_2 \tag{7.3}$$

The quantity *S* is the entropy of the system. It has the value S_1 in state 1 and the value S_2 in state 2. For a cycle, in which all transformations are reversible, $S_1 = S_2$ through Eq. (7.1). For a closed cycle where some or all transformations are realizable, $S_1 > S_2$, according to inequality (7.2). In other words, the sum $\sum_{i=1}^{n} \frac{Q_i}{T_i}$ relative to any reversible transformation is equal to the reduction that the entropy of the system undergoes by the effect of this transformation. Eq. (7.3) can be written as

$$\sum_{i=1}^{n} \frac{Q_i}{T_i} + S_2 - S_1 = 0 \tag{7.4}$$

And for a cycle consisting of one or more realizable transformations, the following inequality is obtained

$$\sum_{i=1}^{n} \frac{Q_i}{T_i} + S_2 - S_1 > 0 \tag{7.5}$$

or else, by denoting by N a quantity which is certainly positive

$$\sum_{1}^{n} \frac{Q_{i}}{T_{i}} = S_{1} - S_{2} + N \tag{7.6}$$

There is no information about the nature of the quantity N, except that it is positive. Clausius gave N the name of *uncompensated transformation* relating to the transformation which makes the system pass from state 1 to state 2. Comparing Eqs. (7.4) and (7.6), one concludes that a reversible transformation is characterized by an uncompensated transformation equal to 0. The quantity ($S_1 - S_2$) in Eq. (7.6), which reduces to zero for any closed reversible cycle, received by Clausius the name of *compensated transformation* relating to the transformation which makes the system pass from state 1 to state 2.

For an isolated system from the surroundings, the heat exchange between the system, and the exterior, becomes 0. In other words, $Q_i = 0$, for any reversible or realizable transformations. Consequently $\sum_{i=1}^{n} \frac{Q_i}{T_i} = 0$ and from Eq. (7.6) one has

$$S_1 - S_2 + N = 0$$
 or $S_2 - S_1 = N$ (7.7)

When N = 0, all transformations are reversible or *compensated transformations*, whereas when N > 0, at least one of the transformations is realizable or *uncompensated transformation* as defined by Clausius. In the latter case, S_2 is greater than S_1 ; therefore, in the considered transformation, the entropy of the system increases. As a corollary, Duhem defined the equilibrium state of an isolated system. "A system of bodies, absolutely isolated in space, is in equilibrium if none of the changes which may occur in it causes its entropy to increase".⁶²²

The following equality expresses the equivalence of heat and work or the law of the conservation of energy, namely

$$EQ = E(U_1 - U_2) + \tau_e \tag{7.8}$$

Where, *E* is the mechanical equivalent of heat; Q is the amount of heat released during the transformation, τ_e is the work carried out by the external forces, U_1 and U_2 are the initial and final values of the internal energy, respectively. For an isolated system, Q = 0, and $\tau_e = 0$, since no external body interacts with the system. The preceding equality therefore becomes $U_1 - U_2 = 0$ or $U_1 = U_2$.

⁶²² Duhem, 1893a, p. 104.

In other words, the internal energy of the system has the same value at the end of the transformation as it had at the beginning. In summary, an isolated from its environment system in which one or more transformations are realizable transformation presents the following two characteristics: (a) it keeps its energy constant, and (b) it increases its entropy.

Clausius assimilated the whole universe to a similar system, isolated in the middle of space, and he stated the following two famous propositions:

Die Energie der Welt ist constant (the energy of the universe is constant).

Die Entropie der Welt strebt einem Maximum zu (the entropy of the universe tends towards a maximum).

Gibb used these two propositions as the epigraph of the most important of his memoirs on thermodynamics *on the equilibrium of heterogeneous substances*.

Duhem realized that the previous thermodynamic treatment and its conclusions did not clearly show the analogy between thermodynamics and rational mechanics. In other words, the equivalence of the heat and the work produced. He examined the effect of an isothermal transformation to the equality (7.6); that is to say to a transformation during which the temperature of the system has everywhere the same constant value T (i.e., $T_1 = T_2 = ... = T_n = T$). Then, this equality becomes

$$\frac{Q}{T} = S_1 - S_2 + N \tag{7.9}$$

and

$$Q = T(S_1 - S_{2}) + TN \tag{7.10}$$

Here, Q represents the sum of the quantities of heat released by the system during the various elementary transformations $M_1, M_2, ..., M_n$ which make up the total transformation.

N is the sum of all isothermal uncompensated transformations undergone by the system passing from state 1 to state 2.

The two terms of the right-hand side of Eq. (7.10) represent magnitudes of the same kind as a quantity of heat. Duhem called the term $T (S_1 = S_2)$ the amount of compensated heat released during the isothermal transformation, and the second term *TN* the amount of *uncompensated heat* released in the same transformation. These two quantities of heat are distinguished by two essential properties: the amount of compensated heat has a magnitude determined when the initial state 1 and the final state 2 are known. It is not the same with the second term; the uncompensated heat can only be determined if we know not only the two extreme states 1 and 2 but also all the intermediate states that the system has passed through and the external forces which forced the system to pass from each of these states to the next. The second character that distinguishes these two kinds of heat is the sign of their magnitudes. The sign of the compensated heat is positive or negative depending on whether heat is released or absorbed by the system, respectively. On the contrary, the amount of uncompensated heat released by any realizable isothermal transformation is substantially positive.

Multiplying both members of Eq. (7.10) with the mechanical equivalent of heat *E*, one obtains a relationship that connects three kinds of work performed in an isothermal transformation.

$$EQ = E(S_1 - S_{2}) + ETN (7.11)$$

The left-hand side of this equality is the work produced by the system equivalent to the amount of heat Q absorbed by the system during the isothermal process. The first term of the right-hand side of the equality is the equivalent work produced by the amount of the

compensated heat. The second term of the right-hand side of the same equality is the equivalent work produced by the amount of the uncompensated heat. Duhem gave the first term the name *compensated work* C accomplished in the isothermal transformation considered

$$C = ET(S_1 - S_2) \tag{7.12}$$

He named the second term *uncompensated work*, namely

$$\tau = ETN \tag{7.13}$$

In the uncompensated transformation, N is positive. Therefore, the uncompensated work must be positive alike. Duhem concluded, "Any realizable isothermal transformation generates positive uncompensated work".⁶²³ This proposition is another criterion to ascertain whether a system is in equilibrium. If the uncompensated work is zero or negative, the transformation is not realizable; the system cannot leave the state, where it is; it necessarily remains in equilibrium. Duhem enunciated the following theorem,

"A system, taken in a given state, at a given temperature, is in equilibrium if all the virtual isothermal modifications of this system correspond to zero or negative uncompensated work".⁶²⁴

With this theorem, Duhem exposed the analogy between thermodynamics and rational mechanics. The proposition of rational mechanics which serves to determine the conditions of equilibrium of any mechanical system is expressed through the principle of *virtual velocities* or the *principle of the virtual work*,

⁶²³ Duhem, 1893a, p. 108.

⁶²⁴ Ibid.

"A mechanical system, taken in a given state, is in equilibrium if all the virtual modifications of this system correspond to a zero or negative work of the forces, which applied to it".⁶²⁵

The uncompensated work plays, in thermodynamics the same role as the work of forces in rational mechanics. This analogy was not evident in Massieu, Gibbs, and Helmholtz's thermodynamics.

By comparing equations (7.11) and (7.13) with each other, one obtains

$$\tau = EQ + E(S_1 - S_2) \tag{7.14}$$

The principle of the equivalence of heat and work expressed by the equality (7.8) combined with equality (7.14) gives

$$\tau = E(U_1 - TS_1) - E(U_2 - TS_2) + \tau_e \tag{7.15}$$

This equation shows that for the determination of the uncompensated work generated in an isothermal transformation, it is not necessary to evaluate separately the variation of the internal energy and the variation of entropy. It suffices to calculate the variation undergone by the equality

$$\mathbf{F} = E(U - TS) \tag{7.16}$$

Duhem recognized the fundamental role of this quantity in thermodynamics. Knowledge of the values that quantity F takes for the various states of the system allows the calculation

⁶²⁵ The idea of virtual work was invoked by many notable physicists of the 17th century in varying degrees of generality when solving problems in statics. The principle was systematized by Bernoulli in 1715 who made explicit the concept of *infinitesimal displacement* (it is considered as an alternative definition of the virtual velocities). D'Alambert in his *Traité de Dynamique* of 1743 extended the principle of virtual work to rational dynamics. Finally Lagrange in his *Mécanique Analytique* of 1788 generalized the principle to apply to all mechanics.

of all mechanical or thermal properties of the system. Taking into consideration the expression of the quantity F in Eq. (7.16), Eq. (7.15) becomes

$$\tau = (F_1 - F_2) + \tau_e \tag{7.17}$$

As noted, the second term on the right-hand side of this equation is the work of the external forces. The first term $(F_1 - F_2)$ depends on the change undergone by the internal state of the system. It is independent of the external forces. Therefore, the calculation of this difference does not require the knowledge of the existence of foreign to the system bodies, nor the forces which these bodies exert on the system. According to Duhem, this term represents the *internal uncompensated work*. It is equal to the decrease of the quantity *F*, which takes a well-defined value when the system is in a determined state.

In rational mechanics, when the work that a group of forces, applied to a system, affects a transformation of the system, it is equal to the decrease undergone by a certain quantity whose value depends only on the state of the system. In this case, this group of forces admits a potential. This potential is the function, the decrease of which represents the work done.⁶²⁶ Duhem saw the analogy between his function F and the potential of rational mechanics. "There is an absolute analogy between the laws of equilibrium established in thermodynamics and the statics of a mechanical system in which the internal forces admit a potential; the same role is played, in this theory, by the potential of internal forces and, in thermodynamics, by the internal thermodynamic potential".⁶²⁷ Duhem espoused the quantity *F* as an analogous to mechanics term and gave it the name of *internal thermodynamic potential*. This function is just Massieu's Ψ function, Helmholtz's free

⁶²⁶ Duhem, 1903, pp. 14-15.

⁶²⁷ Duhem, 1893a, p. 111.

energy, and Gibbs' ψ function. Eq. (7.17) indicates that the total uncompensated work is the sum of the work of the external forces and the *uncompensated internal work*. Duhem offers two concrete examples, in which the work of external forces is equal to the reduction undergone by a certain physical quantity during the transformation.⁶²⁸ This group of external forces admits a potential, the value of which depends on the state of the system alone. Duhem defines this potential by the general form $\Omega = F + W$, which modifies the work of the external forces for an isothermal transformation from state 1 to state 2, namely

$$\tau_{\varepsilon} = \Omega_1 - \Omega_2 \tag{7.18}$$

Combining Eqs. (7.17) and (7.18), Duhem obtained the expression for the *total uncompensated work*.

$$\tau = (F_1 + \Omega_1) - (F_2 + \Omega_2) \tag{7.19}$$

Thus, the total uncompensated work performed during a transformation of the system from state 1 to state 2 is equal to the decrease that a quantity undergoes as a result of this transformation. This quantity, the value of which depends on the state of the system is

$$\Phi = F + \Omega \tag{7.20}$$

Duhem gave this quantity the name of *total thermodynamic potential*. Therefore, the total uncompensated work performed during the isothermal transformation from the initial state 1 o the final state 2 is given by

$$\tau = \Phi_1 - \Phi_2 \tag{7.21}$$

Recall that any isothermal transformation which generates zero or negative uncompensated work is not realizable. The application of this proposition to a system that admits a total thermodynamic potential, allowed Duhem to define the conditions for equilibrium. "A

⁶²⁸ Duhem, 1893a, pp. 111-112.

system is in stable equilibrium if the value of the total thermodynamic potential of this system is a minimum of all the values that the same quantity can take at the same temperature".⁶²⁹ This theorem emphasizes the structural analogy between mechanics and thermodynamics as an intermediate stage, advancing the structural analogy between physics and chemistry.

Duhem's thermodynamic potential had important consequences from a theoretical and practical point of view. In two specific instances for external mechanical work, i.e., W = pv, the thermodynamic potential takes two different values, depending on the constancy of the volume or the pressure of the process. In the first case, when the volume is constant, then W = 0, and $\Omega = E (U-TS) + W = E (U-TS) = F$. In this case, the thermodynamic potential becomes equivalent to Helmholtz's free energy and Gibbs' ψ function. In the second case, when pressure is constant, then $\Omega = E (U-TS) + pv$, and the thermodynamic potential becomes Gibbs' ζ function or Gibbs' free energy. Duhem expresses entropy and volume in terms of the derivatives of the total thermodynamic potential Φ . This result allowed him to deduce other mechanical properties of the system, such as the coefficient of dilatation under a constant volume or constant pressure, the coefficient of compressibility, and the specific heat at constant pressure.

The thermodynamic potential proved to be a powerful tool in Duhem's hands. He used it systematically to interpret equilibrium and non-equilibrium processes in chemistry and physics. It had become part of his applications to the explanation of old and new experiments. This thermodynamic quantity gave a new unity to hydrodynamics, viscosity,

⁶²⁹ Duhem, 1893a, p. 112.
vaporization, and dissociation, replacing the intangible constructions of reversible cycles and the one-sided principle of maximum work.

In 1888, Duhem finally received his doctoral degree while being *Maître de Conférences* in the Faculty of Science of the University of Lille. He presented the second dissertation entitled *L'aimantation par influence* (magnetization by induction) in the Department of Mathematics (not in Physics). The title of the dissertation did not include the word thermodynamics to avoid another conflict with Berthelot. However, its content was essentially thermodynamics, with its very backbone the thermodynamic potential. Meanwhile, Duhem published many papers on electromagnetism, thermoelectricity, thermochemistry, capillarity, osmosis, and chemical solution properties.

Section 2. Towards a rational dynamics

Duhem derived his thermodynamic potential in the context of rational mechanics. He followed the tradition of the second half of the nineteenth-century thermodynamics dealing with equilibrium states. However, Duhem planned to remove this limitation and give a dynamic character to his thermodynamics. Between 1891 and 1894, Duhem published four important papers. He attempted to reform thermodynamics beyond the doctrines of rational mechanics. These papers were a consequence of his attempts to build the structural analogy between analytical mechanics and thermodynamics. The paper *Sur les Équations Générals de Thermodynamique* contains contains several equations describing a system's thermal and mechanical properties in equilibrium under the influence of external forces. These equations and the logic behind their derivation proved to be very helpful for his subsequent articles regarding the infusion of the principles of rational mechanics into thermodynamics.

The state of the system is completely specified by a set of λ independent variables (normal variables) α , β ,, λ , and the temperature ϑ . These variables are associated with $\lambda + 1$ functions, R_{α} , R_{β} ,, R_{λ} , C, the so-called *thermal* or *calorific coefficients*, except the function C, which stands for the *thermal capacity* of the system. The external forces that keep the system in equilibrium are represented by the quantities \underline{A} , B,, L, Θ , which are finite, uniform and continuous functions of the variables α , β ,, λ , ϑ . Any departure from equilibrium manifested by an infinitesimal change of the normal variables, namely $\delta \alpha$, $\delta \beta$,, $\delta \lambda$, $\delta \vartheta$, is compensated by the external forces to maintain equilibrium. The virtual work, τ_{e} , of these forces is expressed in terms of the quantities \underline{A} , B,, L, Θ , and the displacements $\delta \alpha$, $\delta \beta$,, $\delta \lambda$, $\delta \vartheta$:

$$d\tau_e = A\delta\alpha + B\delta\beta + \dots + L\delta\lambda + \Theta\delta\vartheta$$
(7.22)

The liberated or absorbed heat, Q, during this change is given in terms of the thermal coefficients R_{α} , R_{β} , ..., R_{λ} , C:

$$dQ = R_{\alpha}\delta\alpha + R_{\beta}\delta\beta + \dots, + R_{\lambda}\delta\lambda + C\delta\theta$$
(7.23)

Duhem derives the sufficient and necessary conditions under which the system obeys the two fundamental principles of thermodynamics.⁶³⁰ Furthermore, he gives the relations among the functions, A, B,, L, Θ , indicating that these functions do not assume arbitrary values. He also gives the expressions of these functions that describe the equilibrium of the system. The calorific coefficients and the thermal capacity can be calculated as long as the equilibrium equations are known. In the next chapter, Duhem follows the opposite procedure. He derives the equilibrium equations for the same system under the same equilibrium conditions, whose thermodynamics have already been studied. While in the

⁶³⁰ Duhem, 1891, pp. 234-236.

first chapter, he began from the mechanical interpretation of functions A, B, \dots , L, Θ , and calculated the calorific quantities, in this second chapter starts from known equations of equilibrium for the coefficients $R_{\alpha}, R_{\beta}, \ldots, R_{\lambda}$. Subsequently, he estimates the generalized forces A, B, ..., L, Θ . According to this procedure, the coefficients R_{α} , R_{β} , ..., R_{λ} , C, have a double interpretation reflecting the alliance between mechanics and thermodynamics; they have the property of *generalized coefficients* as well as *generalized forces*. In chapter three of the article, Duhem presents once more the derivation of the internal and total thermodynamic potential of the system, taking this time into account explicitly the effect of the external forces on the system. In chapter four, Duhem describes the use of the internal thermodynamic potential in determining the energy, the entropy, the calorific and the mechanical coefficients, and the equilibrium conditions of the system. In contrast, in the last chapter, he showed how to calculate the values of the change of the normal variables, the internal energy, the entropy, and the calorific coefficients when the system remains in equilibrium at a constant temperature under the action of the external forces A, B, ..., L. In this paper, Duhem does not take time as a variable, although time seems to play the role of an essential implicit parameter.

Duhem introduced time and motion in a series of three articles published in a series of three parts, this time not in a journal of physics, but a journal of mathematics, *theJournal Mathématiques Pures et Appliquées*. These papers had the general title *Commentaires aux Principes de la Thermodynamique*. The first part of this trilogy appeared in 1892. In the next two years, Duhem published the second and the third parts of the *Commentaires*. Les *Commentaires* edited and translated by Paul Needham.⁶³¹

⁶³¹Needham, 2011.

The first *Commentaire*⁶³² begins with a burst of definitions about a collection of bodies. Each body (called the system) is considered to be isolated in space. At an instant t, the system's nature and state are defined by the independent magnitudes A, B, ..., L and $\alpha, \beta, \dots, \lambda$, respectively. The first magnitudes preserve the values of mass or electrical charge of the system, whereas the second magnitudes change their values upon a physical or chemical transformation. Both groups of variables are independent of time. When the system moves within a certain lapse time t, the direction and the magnitudes of the velocities are defined as the derivatives of the variables α , β , ..., λ , namely $d\alpha/dt$, $d\beta/dt$, ..., $d\lambda/dt$).⁶³³ However, not all variables are independent of time. Duhem regarded the set *a*, *b*, \dots , *l* as the variables dependent on time and able to undergo any variation with time. Nevertheless, at equilibrium, both sets of variables α , β , ..., λ , and a, b, ..., l are independent of time. The temperature was a special variable determining the state of the system. The magnitude of temperature is determined arbitrarily as a single-valued, continuous, and monotonous function of the variable ϑ of the form $\Theta = F(\vartheta)$. In the second chapter, using the concepts and definitions discussed in the first chapter, Duhem attempts to define the mechanical work and the energy of a system under the influence of external bodies. He derives the appropriate mathematical expression of the mechanical work and the energy of the system. The system's energy is the sum of two kinds of energy: *internal* energy or potential energy and kinetic energy or actual energy. Duhem clarifies the relationship between the kinetic energy, velocity, and the mechanical work done by the external bodies on the system and makes it move. Finally, he determines the form of the kinetic energy of the moving system. The last short paragraph of this chapter refers to the

⁶³²Duhem, 1892a.

⁶³³ Ibid, p. 278.

principle of the conservation of energy, "when a material system isolated in space, undergoes any transformation, the total energy [kinetic energy plus internal energy] of the system remains unchanged by the effect of this transformation".⁶³⁴ He warns that this proposition is simply a physical hypothesis, and its verification depends on the experience. In the third and last chapter of the 1892 paper, the system's interaction with external bodies takes an analytical form. He considers an isolated space system Σ composed of two independent subsystems, S and S'. He examines changes imparted to the internal energy and the kinetic energy and the mechanical work of the system Σ due to possible interaction of these two independent subsystems S and S'. He concludes that the kinetic energy of Σ is the sum of the subsystems S and S' kinetic energies, whereas the total internal energy contains interaction terms. He formulates these terms as forces exerted by the system S' on the system S and as *influences* exerted by the system S on the system S'. He calls *mutual* actions the ensemble of forces and influences. He defines the virtual work of the influences and *actions* that are performed by the system Σ . Duhem expresses the following theorem to emphasize the possibility of heat exchange between the interacting subsystems S and S': "In all real changes of a complex isolated system comprising two independent systems S and S', one of these systems releases as much heat as the other system absorbs".⁶³⁵ Duhem generalized and extended the mechanical/t thermodynamic evaluation of the work and energy changes and the heat exchange in complex systems constituted of n isolated independent systems. This treatment allowed Duhem to delineate the features of complex systems.

⁶³⁴ Ibid, p. 307.

⁶³⁵ Ibid, p. 319.

As in the 1892 paper of the *Commentaires*, the first chapter of the second part of the series contains preliminary definitions, equations, and remarks.⁶³⁶ He takes into account real and virtual changes occurring via real and virtual closed thermodynamic cycles. Duhem offers the following proposition for a real cycle: "A real closed cycle can be exactly reproduced indefinitely PROVIDED THAT IT IS POSSIBLE TO ARBITRARILY ARRANGE THE BODIES EXTERNAL TO THE SYSTEM".637 He further defines and demarcates various thermal transformations, such as adiabatic, exothermic, and endothermic changes. He studies isothermal changes in complex systems that occur through continuous and independent Carnot's cycles; changes that occurred as a sequence of equilibrium states, and finally as reversible changes. These transformations represent one of the most subtle problems of thermodynamics: the distinction between the commonly used term reversible and the term real or virtual reversible transformation. He concludes that reversible transformation is not realizable, but it is instead an entirely virtual change. He calls this process a realizable transformation. Duhem justifies this conclusion by mechanical and thermodynamic means. Finally, he proposes two hypotheses for the isothermal and adiabatic reversible transformations.⁶³⁸ The second chapter is devoted to the study of Carnot's cycle and Carnot's theorem.⁶³⁹ In this chapter, Duhem distinguished and compared the various reversible and irreversible Carnot's cycles in terms of their efficiency. To achieve this goal, he combined the principle of conservation of energy, the

⁶³⁶ Duhem, 1893b, pp. 293-309.

⁶³⁷ Ibid, p. 297. Duhem used Capital letters.

⁶³⁸ Ibid, pp. 305-309.

 $^{^{639}}$ Recall from chapter 2, section 1, Carnot's fundamental theorem deals with the maximum obtainable motive power in heat engines for a given amount of heat. Carnot provided the proof of the maximum efficiency *u* for a perfect engine in a lengthy footnote in his *Reflexions*. He demonstrated that the efficiency of a perfect engine working reversibly was at a maximum, but he did not know its value.

two hypotheses of Clausius and William Thomson for the conditions of exothermic and endothermic changes during a real Carnot's cycle, and the third hypothesis for athermic changes (any process not receiving or releasing heat) he additionally proposed.⁶⁴⁰ The third and final chapter deals with Clausius' theorem⁶⁴¹ and entropy. He demonstrates the validity of Clausius' theorem using thermodynamics and geometry. He imagines a line in an *n*dimensional space representing a series of equilibrium states of the system maintained by external actions of the surrounding bodies. He concludes that for every reversible transformation, the integral $\int \frac{dq}{F(\vartheta)}$ has the same value and vanishes in the case of reversible cycles. Duhem defines this integral as the entropy of the system. He further considers the case in which the system undergoes solely isothermal changes, i.e., for all reversible changes, dQ = 0, or the athermal case for which the temperature is neglected. Conditions of a constant temperature or no temperature are important for rational mechanics, which does not involve heat changes. Duhem completed this chapter using thermodynamics to derive proper mathematical expressions for the principles of mechanics.⁶⁴²

In the last *Commentaires* of 1894, Duhem explicitly introduces time in dealing with the motion of a thermodynamic system and utilizes Lagrange's analytical mechanics to derive the second law of thermodynamics. However, the word motion has, for Duhem a more general meaning than a simple change of position in space. He approaches in this regard the Aristotelian doctrine that motion is a change of the quality (state) of the system,

⁶⁴⁰ Duhem 1893b, pp. 310-328.

⁶⁴¹Recall from chapter 3, section 4, Clausius' theorem states that a system exchanging a quantity of heat Q with external reservoirs and undergoing a cyclic process is one that ultimately returns a system to its original state. The theorem was expressed mathematically by the so-called Clausius inequality for a cyclic process, i.e., $\oint \frac{dQ}{T} \ge 0$, T is the absolute temperature of the external reservoir. ⁶⁴²Duhem, 1893b, pp. 357-358.

"the word *motion* does not stand in opposition to the word *rest*, but to the word *equilibrium*".⁶⁴³ In a footnote, he remarks that the content of the first chapter is simply a limited exposition of the properties of the system necessary for the reader to understand the following chapters.⁶⁴⁴ Indeed, he had already described in detail the material of the first chapter in the 1891 paper Sur les équations général de thermodynamique. Having at his disposal the proper mathematical formalism, Duhem proceeds to examine the properties of a complex system formed by two distinct parts 1 and 2, independent of one another, under the influence of external bodies. The state of the system is determined by two sets of independent variables $\alpha_1, \beta_1, \dots, \lambda_1, \vartheta_1$ and $\alpha_2, \beta_2, \dots, \lambda_2, \vartheta_2$. As in the 1892 Commentaires, he calculates the internal energy, the entropy, the calorific coefficients, and the condition of equilibrium of the combined system (1, 2) by employing the internal thermodynamic potential of this system. The latter quantity is the total internal thermodynamic potential consisting of the sum of the separate internal thermodynamic potentials of systems 1 and 2. This summation includes the potential of the mutual actions of subsystems 1 and 2 as described previously with the subsystems S and S'. The novelty here is the introduction of terms representing the system's interaction (1, 2) with the external bodies. Furthermore, he proves that the total entropy is equal to the sum of the individual entropies of the two independent parts 1 and 2 of the system.⁶⁴⁵

In the second chapter, Duhem explicitly enters the realm of irreversibility and the thermodynamics of complex systems. He examines the laws of motion of a system under the action of external bodies. He sets forth the known equations that describe the system in

⁶⁴³ Duhem, 1894, p. 222.

⁶⁴⁴Ibid, p. 207.

⁶⁴⁵Ibid, pp. 210-218.

equilibrium and attempts to generalize them according to conditions of non-equilibrium that characterize circumstances of viscosity or friction. For this reason, he introduces a group of new functions $f_{\alpha}, f_{\beta}, \dots, f_{\lambda}$, the so-called *passive resistances* which represent the resistance that the system should overcome to attain an equilibrium. Cases of viscous fluids or friction exerted between two solids, two liquids, or between solid and liquid, and cases of electromagnetic hysteresis are examples of this kind. The passive resistances depend uniquely on the variables α , β , ..., λ , ϑ , the velocities $\alpha' = d\alpha/dt$, $\beta' = d\beta/dt$, ..., $\lambda' = d\lambda/dt$, and time t. In other words, the passive resistances depend on the system's position and motion relative to the external bodies. These resistances, which are resistances of the usual mechanical term, induce a disturbance to the system associated with a corresponding work called the *elementary work of the passive resistances*, namely $f_{\alpha}d\alpha + f_{\beta}d\beta + \dots, + f_{\lambda}d\lambda$. The work of passive resistances is either zero or negative. This property allowed Duhem to identify the work of the passive resistances with the non-compensated work of Clausius. Furthermore, using the axiomatic character of the passive resistance, Duhem succeeds to confirm Clausius' inequality for a real closed cycle. For systems without viscosity or friction, the inequality sign disappears as expected. Duhem shows that no real transformation of an isolated system can decrease the system's entropy, a theorem that Clausius was first to establish. However, unlike Clausius, Duhem demonstrates the validity of this theorem taking into account explicitly the system's kinetic energy, Duhem further affirmed the generality of Clausius' inequality for complex systems with *n* independent parts, each having either the same or distinct but uniform temperatures⁶⁴⁶.

⁶⁴⁶Ibid, pp. 234, 238.

In previous chapters, Duhem studied the equilibrium conditions of independent moving systems that may or may not interact with each other. In the third chapter of the third *Commentaire*, he examines equilibrium conditions for the displacement of dependent systems in motion. Duhem defines the connecting requirements of what he calls bilateral and unilateral connections of a system with its parts (subsystems) 1 and 2 brought into contact by a continuous displacement. If the virtual displacements of the two subsystems 1 and 2 with normal variables $\alpha_1, \beta_1, ..., \lambda_1$, and $\alpha_2, \beta_2, ..., \lambda_2$, do not change their contact, then the system is subject to the so-called *bilateral connections*. In this case, all the virtual displacements of the system are reversible. If these contacts do change during the displacements, then the system is subject to *unilateral connections*. In this case, the virtual displacements are no longer all reversible.

Furthermore, Duhem defines the *connecting conditions* for the system subject to bilateral connections and the conditions that exclude displacements tending to make the two bodies penetrate one another.⁶⁴⁷ Next, Duhem calculates the limiting values of the internal energy, entropy, and internal thermodynamic potential for a system with several connections (two or more). After manipulating the normal variables α , β ,, λ , and the action variables A, B,, L, of the composite system (1, 2), he derives equations for the quantities mentioned above. These values are limiting values towards which these quantities tend when parts 1 and 2 touch one another. The limits of these quantities are controlled by the restrictions of the actions that part 2, acting against part 1, and similarly, the limits of the actions that part 1 exerts on part 2. Mutual actions of the two systems 1 and 2 have not been defined since this type of action only holds when these systems are

⁶⁴⁷ Ibid, pp. 239-242.

independent, which is not the case here.⁶⁴⁸ In the sequel, Duhem seeks to describe the condition of equilibrium for systems in bilateral connections for two cases: first when the system of the two parts, 1 and 2, departs from equilibrium by a virtual isothermal displacement, and second when the external actions exerted between the two parts of the system perform the virtual work dW. He used the change of the internal thermodynamic potential d*F* of the system which undergoes the variation. He proves that the necessary and sufficient condition for the system to be in equilibrium is the equality dF = dW that holds for all virtual isothermal displacements. Duhem expresses the external work dW and the internal thermodynamic potential d*F* of the system as a function of the normal variables and the actions, obtaining explicit formal conditions in terms of these variables. Duhem did not establish conditions of equilibrium for unilateral connections since these connections do not preserve the contact between the two parts.

Having examined the properties and the equilibrium conditions for a system with bilateral connections between its parts and with nearby bodies, Duhem proceeds to calculate the heat absorbed or released by the system. He proves that the quantity of heat released/absorbed by the system in any change is the algebraic sum of the quantities of heat released/absorbed during the same change by the various parts of the system. Regarding the exchange of heat in a real or virtual change among the different parts of the system under bilateral connections, he concluded that the quantity of heat released by one part of the system is equal to the quantity of heat absorbed by the other part.⁶⁴⁹

Duhem completed this section dealing with the properties of a system consisting of dependent parts studying its motion with uniform and non-uniform temperature and subject

⁶⁴⁸Ibid, 242-244.

⁶⁴⁹ Ibid, pp. 256-259.

to bilateral connections with external bodies. The equation that expresses the law of motion connects the virtual work of the external forces, dW, the isothermal variation of the internal thermodynamic potential, dF, the virtual work of the forces of inertia, d τ , and the virtual work of the passive resistance, d ϕ :

$$\mathrm{d}W + \mathrm{d}\phi - \delta F = \mathrm{d}\tau \tag{7.24}$$

This equation expresses the principle of the equivalence of heat and work for a system subjected to bilateral connections with neighboring bodies and remains true even when the temperature of the various parts of the system is not uniform. For uniform temperature, the equations that define the system's calorific coefficients, together with the equations of motion and those of the internal energy and the internal thermodynamic potential, are similar to equations obtained for a system with independent parts. However, for a system formed from n parts at different temperatures exhibiting bilateral connections between one another, Duhem arrived at the following general inequality

$$\int \left[\frac{dQ_1}{F(\theta_1)} + \frac{dQ_{21}}{F(\theta_2)} + \dots + \frac{dQ_n}{F(\theta_n)}\right] \ge 0$$
(7.25)

This inequality represents an extension of the Clausius inequality over the various parts of the system.⁶⁵⁰

In chapter four, Duhem examines the displacement of equilibrium caused by a variation of temperature. First, he defines the equilibrium conditions at constant temperature in terms of the total thermodynamic potential, which takes a minimum value at equilibrium. Then, Duhem seeks to find the conditions of equilibrium when temperature variation induces the displacement of the body from equilibrium. Whenever the system's temperature increases, the normal variables that characterize the state of the system

⁶⁵⁰ Ibid, p. 262.

undergo the necessary changes for the system to establish a new equilibrium state, which is different from the initial equilibrium state. Duhem supposed the case in which these variables undergo the same variations but at a constant temperature. In that case, the virtual change imposed on the system entails absorption of heat.⁶⁵¹. Lavoisier and Laplace had anticipated this law, which was stated clearly by van 't Hoff.⁶⁵²Duhem discusses van 't Hoff's law of displacement of equilibrium with temperature which marks the difference between exothermic and endothermic compounds in connection with the effect of temperature changes on equilibrium. He contrasts once again this thermodynamic law with the doctrine of the maximum work of Berthelot.

Duhem further considers the cases of isothermal and isentropic displacement from equilibrium. In the first case, he adopts a system in equilibrium under constant external actions and constant temperature as manifested by the minimum of its thermodynamic potential. Utilizing his thermodynamic potential, Duhem explored changes in the system's equilibrium induced by external actions. He demonstrated that in the passage from the old state of equilibrium to the new one, the external actions always produce positive work.⁶⁵³Henri Louis Le Chatelier (1850-1936) has articulated a particular case of this law. Duhem proves the generality of this law. Nevertheless, he did not omit to mention Le Chatelier's proposition in this *Commentaire*, although without further discussion. Similarly, Duhem found that positive work is performed by the external actions disturbing the equilibrium of a system under constant entropy⁶⁵⁴.

⁶⁵¹Ibid, pp. 263-268.

⁶⁵²See below, chater 10, section 2, paragraph 2.3.3 of this dissertation

⁶⁵³ Duhem 1894, p. 268-271.

⁶⁵⁴lbid, pp. 271-273.

Concluding this chapter, Duhem examines conditions for stability and displacement of equilibrium at constant temperature and constant entropy. To accomplish these studies, he uses his total internal thermodynamic potential. He demonstrates that the condition for stability of an equilibrium state at a constant temperature and constant entropy is reflected on the total thermodynamic potential which attains a minimum of all values that the system can take at the same temperature and entropy.⁶⁵⁵ Duhem notes emphatically that the thermodynamic potential at constant entropy (E*U*+ Ω) differs from that at constant temperature (*F* + Ω).

Duhem went deeper in thermodynamics and examined the relationship between isothermal and isentropic stability. In this respect, he sought to answer the question: If the equilibrium of a system is stable for all the isothermal changes imposed on it, is it also stable for all isentropic changes? He showed explicitly that the isothermal stability of equilibrium entails isentropic stability.⁶⁵⁶ Finally, Duhem provided pertinent formal conditions for the isentropic displacement of the system from equilibrium ensued by the influence of external actions. He demonstrated that the system undergoing isentropic changes reached a new state of equilibrium following the same route as that of the isothermal changes. In the passage from the old to the new equilibrium state, the external actions always perform positive work.⁶⁵⁷

Concluding this trilogy, Duhem contrasted his dynamic mode of explanation of thermal phenomena with attempts made by the founders of classical thermodynamics to establish their theories independently of all hypotheses about the nature of heat. However,

⁶⁵⁵Ibid, p. 268-273.

⁶⁵⁶Ibid, pp. 274-27.

⁶⁵⁷lbid, p. 276-281.

Duhem emphasized, these very capable physicists had tried to formulate their thermodynamics, not on theorems obtained from rational mechanics but on their principles. He mentioned the progress that was made in this direction (using principles of rational mechanics in thermodynamics) first by Clausius and then by Massieu, Gibbs, and Helmholtz, into an analytic form like that Lagrange gave to mechanics, and concluded referring to his work presented in the *Commentaires*: "We have tried in the present work to suggest a third position of dynamics in relation to thermodynamics. We have made dynamics a particular case of thermodynamics, or rather; we have constituted, under the name thermodynamics, a science which covers in shared principles all the changes of state of bodies, including both changes of position and changes in physical qualities"⁶⁵⁸.

Section 3. Unification of physics and chemistry

One year before the appearance of the third part of the *Commentaires*, and in the same year of the publication of the second part of the *Commentaires*, Duhem gave his readers another memoir, the *Introduction à la Mécanique Chimique*. Duhem's motivation to write this book is given plainly in the introduction of this memoir: "The new chemical mechanics, the result of these efforts, are little known to chemists; the courses, the treatises, the textbooks still teach today theories condemned; whoever wishes to know the theory now admitted is obliged to look for it in a crowd of memoirs scattered in French, German, and English journals; bristling with algebraic formulas; cluttered with detailed discussions that make it difficult to follow the sequence of general ideas".⁶⁵⁹ Duhem wrote the *Introduction* almost

⁶⁵⁸ ⁶⁵⁸ Ibid, p. 285.

⁶⁵⁹ Duhem 1893a, p. v.

devoid of mathematics to be understood by his fellow chemists. Most importantly, this book is an opportunity for Duhem to overcome the distinction between physics and chemistry raised by Berthelot's principle of the *maximum work* and establish through his thermodynamic potential the physical and chemical processes, which have a common theoretical interpretation. As noted, Berthelot's doctrine of the maximum work postulates that the amount of heat evolved in chemical reactions determines the work produced. This principle concedes that all chemical reactions are exothermic, releasing heat. However, several examples of endothermic reactions and physical processes, such as fusion and evaporation, require heat. Berthelot ignored endothermic reactions and considered physical processes as an exception to the rule, separating practically physics from chemistry. Duhem thought that properly formulated mechanics had to treat physical and chemical changes alike in a single theory for state changes. "No chemical mechanics could be viable unless it embraces in the same system of laws both changes of physical state and chemical reactions," wrote Duhem in an article of 1897⁶⁶⁰ while keeping opposing Berthelot's principle of maximum work. And elsewhere, he posed the question; "Is it not to be expected that physical mechanics and chemical mechanics do not constitute separate sciences, proceeding by different methods based in different principles, but a single science, the mechanics of changes of state"?661

The *Introduction* is a historical rather than a strictly scientific account of the development of chemistry during the nineteenth century (even though it refers to several experimental findings to support premises and propositions). He has arranged the

⁶⁶⁰ Duhem, 1897a, p. 373.

⁶⁶¹ Duhem, 1902a, p. 168.

experimental and theoretical achievements in twelve chapters and chronological order, starting from the Newtonian forces of attraction as the mechanical explanation of chemical affinity to the contrast between the true equilibrium and the so-called *false equilibrium* of physical and chemical processes. He further notices, "Chemical mechanics consists almost entirely of the opposition between endothermic and exothermic reactions; it is to find the exact meaning of this opposition that, from Newton to our day, the most eminent minds have devoted their efforts".⁶⁶² He distinguishes three successive stages of the evolution of these efforts related to the effect of temperature on the formation or the decomposition of exothermic and endothermic substances. A comprehensive outline of the gist of the *Introduction* appears in the literature,⁶⁶³ which is helpful as a first acquaintance with Duhem's memoir. However, the concept of *false equilibrium* tackled by Duhem in the last chapter of the *Introduction* deserves further discussion. One might contrast false equilibrium with the preceding chapter of the *Introduction*, which copes with the displacement of true equilibrium in chemical and physical processes with temperature.

In the third part of the *Commentaires*, Duhem describes the true displacement from equilibrium, induced by temperature change or by the effect of external actions under isothermal and isentropic conditions. There is a change in equilibrium from the old to the new state, in which the system produces positive non-compensated work. Thermodynamics does not allow changes with the production of zero or negative non-compensated work. These transformations are virtual and do not occur. Thus, whenever, according to theory, a system has to be in equilibrium, it is, in fact, in equilibrium. Duhem further examines the

⁶⁶² Duhem, 1893a, p. vi.

⁶⁶³ Bordoni, 2012, pp. 233-236.

displacement of equilibrium with temperature and pressure or other factors, such as the mass of the substance and the medium's acidity. This study is a compilation of experimental results to account for the theory and demarcate the endothermic and exothermic physical and chemical processes concerning their ability to change their equilibrium state in absorbing or releasing heat following temperature changes. In this treatise, Duhem found the opportunity to contrast thermodynamics with thermochemistry and his thermodynamic potential with Berthelot's principle of *maximum work*.

However, this is not always the case, and experience shows that a system can remain in equilibrium even if, according to the theory, it should not be in that state. Conversely, theory declares that a physical or chemical change must occur, but experience does not necessarily show it to be realizable, or it happens under conditions that theory does not predict. Duhem distinguishes two kinds of equilibria as follows: "Let us call a state of true equilibrium a state of equilibrium which is at once foreseen by theory and realized by experience; and a state of *false equilibrium* any state of equilibrium which the experiment realizes, whereas the preceding theory declares it impossible". And then he posed the question, "How is it that there are *false equilibrium* states? Such is the objection to which we must answer if we do not want to be compelled to give up the speculations that we have developed in the previous chapters".⁶⁶⁴ For instance, a mixture of oxygen and hydrogen at room temperature remains at a state of equilibrium, contrary to the theory that requires water formation. This state is a state of *false equilibrium*. If the temperature gradually increases under constant pressure and composition, no chemical reaction occurs; then, suddenly, when the temperature reaches about 500 °C, a part of the gaseous mixture

⁶⁶⁴ Duhem, 1893a, p. 159.

will pass with an explosion into the state of water vapor. The system enters a new state of equilibrium, which is unique under the given conditions of temperature, pressure, and composition. This state is the real state of equilibrium that conforms with the laws of classical thermodynamics. Below the temperature of 500 °C, the system remains in a state of *false equilibrium*. No work is produced in a state of *false equilibrium*. Later Duhem exploited cases of false equilibrium to describe friction systems in which equilibrium is only apparent and not reversible. Furthermore, Duhem used false equilibrium to oppose the static and dynamic equilibrium of Gibbs and Helmholtz, respectively, in favor of new mechanics of non-reversible processes.

Duhem applies his internal thermodynamic potential to study the conditions of false equilibrium observed during the vaporization of liquids. According to classical thermodynamics, the liquid remains in equilibrium in contact with its vapor at each temperature and specific pressure. For pressures below the tension of the saturated vapors, the liquid vaporizes, whereas, at higher pressures than the tension of the saturated vapors, the vapor condenses. Duhem confirms that the general law for vaporization applies when the masses of liquid and vapor are large. Consequently, the total internal thermodynamic potential is a function of liquid and vapor's individual internal thermodynamic potentials. When this condition is not respected, and the mass of the vapor is much less than the mass of the liquid as manifested by the presence of a tiny bubble in the interior of the liquid mass, the total internal thermodynamic potential requires an additional term representing the effect of the surface separating the liquid from the vapor phase. The presence of this additional term will completely change the conclusions obtained from the study of potential. Although the value of this extra term in the thermodynamic potential is unknown, the laws of equilibrium appear to be very different from those of classical thermodynamics.⁶⁶⁵ Duhem will treat false equilibrium more rigorously three years later in his essay *Théorie Thermodynamique de la Viscosité, du Frottement et des Faux Équilibres Chimiques*.⁶⁶⁶ False equilibrium is related to endothermic and exothermic reactions associated with the dissociation and formation of material substances. A specific section of this essay is devoted to the structural analogy between false equilibrium and mechanical friction.

The *Introduction* is the treatise in which Duhem explicitly exposed his thoughts about the unification of physics and chemistry. He considers that this unification could be achieved by investigating the development of ideas long elaborated by great thinkers from Lavoisier and Laplace up to Gibbs and Van 't Hoff and a host of other theorists and experimenters. These physicists and chemists contributed to constructing a broad synthesis of ideas, by their theoretical speculations or their experimental investigations. Duhem did not exclude erroneous theories from these efforts. The system has abandoned incorrect theories, but "the current building is built largely from the debris of those theories [...] One cannot drive a false idea out of science when one is content to demonstrate its falsehood; it is also necessary to create the right idea, it must replace it". The second building block for the manifestation of this unification was thermodynamics. Duhem recognized the importance of thermodynamics to chemistry and the unification of physical and chemical processes under a common theory. Unfortunately, Duhem never succeeded in fulfilling this aim. Fragments of his thermodynamics found a proper place in chemical thermodynamics.

⁶⁶⁵ Duhem 1893a, pp. 161-169.

⁶⁶⁶ Duhem, 1896.

Section 4. Friction systems and permanent alterations

Gibbs and Helmholtz's thermodynamics dealt with reversible processes. Duhem's thermodynamics dealing with irreversible processes could be considered as the negation of reversible transformations or at least as limited cases of the reversible changes upon elimination of time and velocity from relevant equations. Duhem designs his generalized thermodynamics to embrace all physical and chemical phenomena that have undergone irreversible transformations. He agrees with Gibbs' description that reversible transformations are a continuous succession of states of equilibrium between two groups of transformations taking place in two directions inverse to each other. These transformations should occur by a succession of infinitesimal changes that do not disturb the system from the state of equilibrium. As pointed out by Duhem, the problem arises when these states differ little from the states of equilibrium upon the action of external disturbances, e.g., changes of temperature, pressure, and composition, or the action of the surrounding bodies. "It is clear," Duhem concludes, "that a continuous sequence of such states of equilibrium cannot be a reversible transformation; for another succession of states, infinitely close to the first, will still be a series of states of equilibrium; it cannot be a real change. Therefore, a system that offers a similar peculiarity does not present the recognizable characteristics of systems subjected to Mechanics of Gibbs and Helmholtz; it requires the creation of another Mechanics".⁶⁶⁷ The new mechanics linked to thermodynamics appeared in his memoir *L'Évolution de la mécanique*.⁶⁶⁸ This work is a

⁶⁶⁷ Duhem, 1905, p. 298.

⁶⁶⁸ L'Évolution de la mécanique was published in seven parts in *Revue Générale des Sciences*. As a book, it appeared in 1903 by A. Joanin, Paris. The edition of 1905 has been used in this study. There exists an English

simplified overview of rigorous theoretical analyses of the thermodynamic/mechanical properties of complex systems that had been published in preceding single papers and essays in *Revue Générale des Sciences*. The importance of *L'Évolution* is twofold: First, it is written almost devoid of mathematics (the second method of Duhem's style of writing), and second, it gives rise to queries that raise answers for the future.⁶⁶⁹The main question that occupied Duhem's thinking when he wrote the *L'évolution* was "which route will it [mechanics] follow? Where is the one who leads to the desired end, which will one day become the royal road"? The answers he gives in this essay clearly show his concern and anxiety with this matter. He responded to this challenge with no hesitation, making clear once more his intention to follow a different road from that of his predecessors in the field of thermodynamics. "By enumerating the various paths which, in turn, solicit the preferences of Mechanics, by calculating the chances that each of them will lead to the solution of the problems possessed by physics, I will not pretend to be impartial. Among these roads, there is one that I have been working on for twenty years, devoting all my efforts to prolonging it, smoothing it out, clearing it, making it straighter and safer".⁶⁷⁰

The first part of the book, entitled *Les Explications Méchaniques*, consists of fifteen chapters that constitute a historical overview of the evolution of mechanics from the Aristotelian, Cartesian, Newtonian and Leibnizian interpretation of mechanics towards the recent views of Gibbs and Helmholtz on equilibrium thermodynamics. Several chapters are devoted to analytical mechanics and the virtual velocities, all due to Lagrange,

translation, *The evolution of mechanics* by Sijthoof and Noordhoff, published in 1980, andto which I have no access. English translation of portions of chapter VII is available in Maugin's book (2014, pp.176-183). ⁶⁶⁹Duhem, in writing *l'Évolution* used material of several of his previous publications. Therefore, this book may be taken as an overview of Duhem's philosophical, historical, and scientific deliberations on thermodynamics.

⁶⁷⁰ Duhem, 1905, p. 2-3.

D'Alembert, Poisson, Claude-Louis Navier (1785-1836), Augustin-Louis Cauchy (1789-1857), and Gauss's contribution to rational dynamics. Other chapters are dedicated to theories of the electromagnetism of Faraday, Helmholtz, and Maxwell; others to classical thermodynamics pointing out the contribution of the founding fathers of the first and the second law of thermodynamics. Duhem does not neglect to attack atomism, and what he calls a return to Cartesianism; he cites William Thomson, Maxwell, Boltzmann, and Heinrich Rudolf Hertz (1857-1894) as the main contributors to molecular mechanics.

The second part of *L'Évolution* entitled *Les Théories Thermodynamiques*, contains fifteen chapters. In the first two chapters, Duhem unfolds his philosophical views about the role of mathematics in physics as an abstract representation of qualitative and quantitative properties of bodies, and the esoteric connection of the theory, the experiment, and the measuring instruments and processes as a necessary precondition for the development of physics. The next chapters include Duhem's views on thermodynamics, presented in his previous published work. Those are now given in a different writing style more appealing to readers with poor knowledge of mathematics, and therefore unable to follow the rigor mathematical language of the original papers. In particular, chapters XIII and XIV focus on new mechanics suitable for irreversible processes related to friction, viscosity, and permanent alterations. In the first of these two chapters, entitled Le Frottement et les Faux Équilibres Chimiques, Duhem proposes chemical and physical systems that demonstrate the phenomenon of false equilibrium, in which a continuous sequence of equilibrium states is observed. These states differ little upon altering the pressure, the temperature, or the composition of the reactants to an infinitesimal degree. The system remains in equilibrium, but it is not a reversible transformation. He uses a mixture of hydrogen and oxygen gases

and vapor of water to support his argument. Based on existing experimental data, he asserts that the equilibrium is maintained at low temperatures, whatever the mixture's composition is. On the other hand, at a constant temperature, one obtains a succession of equilibrium states upon increasing the composition of the vapor successively in the mixture, from that which corresponds to the complete absence of water vapor. This state is a state of false equilibrium, and it is not a reversible transformation. There is a movement from equilibrium, but it is so slow that practically no transformation is observed. Nevertheless, at high temperatures, the reaction occurs irrespective of the external action, and in this case, the false equilibrium converges to the true equilibrium.⁶⁷¹ Duhem extended the concept of false equilibrium to infinite other material systems subject to friction, "whose statics is not Gibbs' statics, whose dynamics is not Helmholtz's dynamics, and that among these systems range precisely systems endowed with friction".⁶⁷² Friction systems served Duhem as a guide to formulate new thermodynamics embodied by the mechanics of non-reversible transformations. In his mechanics of friction system, false equilibrium is associated with friction in its general interpretation, including mutual friction between solids, between solid and liquid (viscous fluids), and between two liquids. He studied the latter systems in his hydrodynamic article *Recherches sur l'Hydrodynamique*.⁶⁷³ Several treatises and memoirs give details of his theoretical approach to thermodynamics of friction systems. Traité Élémentaire de Méchanique Chimique, fondée sur la Thermodynamique,⁶⁷⁴ Thermodynamique et Chimie, Leçons Élémentaires à l'Usage des Chimistes,⁶⁷⁵ Théorie

⁶⁷¹Ibid, pp. 299-300.

⁶⁷²Ibid, p. 304.

⁶⁷³Duhem, 1901a.

⁶⁷⁴Duhem, 1897b.

⁶⁷⁵Duhem, 1902b.

Thermodynamique de la Viscosité, du Frottement et des Faux Équilibres Chimiques.⁶⁷⁶ The following equation, which connects the internal thermodynamic potential F with the external action A, the force of inertia, *J*, the action of friction, *f*, and the action of viscosity *v*, is a simple outline of this theory. For simplicity, a single normal variable α defines the state of the system apart from the temperature and pressure.⁶⁷⁷

$$A + J + v \pm f = \frac{\partial F}{\partial \alpha}$$
(7.26)

This equation describes non-equilibrium states since the action of friction does not become zero when the generalized velocity $\alpha' = \frac{d\alpha}{dt}$ of the system tends to zero; instead, it will tend to a positive value g. Equality (7.26) stands for two cases depending on the sign of the coefficient of friction f. The latter is added when the generalized velocity is positive and subtracted when the generalized velocity is negative. The non-equilibrium condition will no longer be represented by the sign of equality but by a double inequality, expressing the fact that the absolute value of the difference $A - \frac{\partial F}{\partial \alpha}$ does exceed the value of a constant g, i.e.

$$-g \le \mathbf{A} - \frac{\partial \mathbf{F}}{\partial \alpha} \le +g \tag{7.27}$$

The equality holds for the equilibrium condition. In other words, in equilibrium, the difference $A - \frac{\partial F}{\partial \alpha}$ becomes zero, in accord with Gibbs' statics. Between -g and +g, the states are characterized by true equilibrium. However, there exists an infinity of other states of equilibrium, which are states of false equilibrium. Depending on the external actions, the magnitude of *g* determines how close to true equilibrium is the false equilibrium. II *g*

⁶⁷⁶Duhem, 1896.

⁶⁷⁷ Duhem, 1905, p. 305.

is large, states of false equilibrium spread out on both sides of states of true equilibrium. The states of false equilibrium come so closer to the states of true equilibrium the smaller becomes the value of the constant g. Finally, suppose this value to become sufficiently weak. In that case, the states of the false equilibrium will deviate so little from the states of true equilibrium, so that the experiment will no longer be able to distinguish between them.⁶⁷⁸

Besides the friction systems, irreversible transformation occurs in systems, which show permanent changes. However, the analogy between these two systems concerning the governing rules of thermodynamics stops here. Essential differences separate these two categories of irreversible processes. Friction systems are supposed to reach equilibrium via exceptional equilibrium states in a transformation of extreme slowness. In contrast, systems that have undergone permanent alteration would never reach the initial state by simply reversing the first transformation. Deformation of solids manifested on their plasticity and elasticity; electromagnetic hysteresis⁶⁷⁹ are a few systems capable of permanent transformations. Duhem suggests the formation of a new branch of thermodynamics for these systems different from frictional systems and distinct from Gibbs and Helmholtz's thermodynamics. As in friction, Duhem constructs the new mechanics for systems with permanent alteration by generalizing the theory of reversible systems. He considers the latter systems as limiting cases of very weak permanent alteration systems.⁶⁸⁰ In chapter

⁶⁷⁸ Duhem, 1905, p. 308.

⁶⁷⁹Under the name hysteresis, Duhem refers to a number of systems that suffer permanent alterations, e.g., dielectric, chemical, elastic hysteresis, or alterations imposed on metals by the effect of temperature, such as annealing, hardening, etc. (Duhem, 1905, pp. 318-319).

⁶⁸⁰ Duhem has described the theoretical analysis of these complex phenomena of deformable solids as a function of one and two variables in seven memoirs published between 1895 and 1902 under the general title *Les Déformations Permanentes et l'Hystérésis* (Duhem, 1895, 1898, 1902)

XVI of *L'évolution*, Duhem adopts a simplified approach to study the deviation from equilibrium for systems that show hysteresis. He formulates an equation that expresses the variation from equilibrium as a function of a single variable α (e.g., the length of a wire), the external action A (e.g., the weight of a wire or the effect of the temperature), and an additional factor that represents the phenomenon of permanent alteration:

$$d\mathbf{A} = d\frac{\partial \mathbf{F}}{\partial \alpha} \pm h d\alpha \tag{7.28}$$

Here, *h* is the *coefficient of the permanent alteration*⁶⁸¹and reflects the degree of the alteration. The sign of the coefficient depends on the sign of the normal variable, reflecting the direction of the transformation without changing its absolute value. For infinitely small deformations (when, $h \rightarrow 0$), the double equation merges to one and becomes $dA = d \frac{\partial F}{\partial \alpha}$. This equality expresses a reversible transformation, in which the external action A equals the variation of the normal variable α . However, for permanent alterations, the magnitudes of the coefficient *h* are not zero and the two equalities of Eq. (7.28) differing in the sign of the second term are distinct from each other. In this case, the effect of the external action on the normal variable produces two distinct states. For example, small oscillation induced by the external action separates these states. Then, the system maintains a permanent alteration, according to Duhem. Further oscillations of the normal variable of different magnitudes, sometimes in one direction and sometimes in another direction, accumulate new residual alterations resulting in a gradual and notable deformation.⁶⁸² In the sequel,

⁶⁸¹ Duhem calls this coefficient, the *coefficient of hysteresis* when he refers the phenomena of hysteresis within the context of his theory on permanent alteration (1905, p. 320).
⁶⁸² Duhem, 1905, pp. 321-322.

Duhem discusses applications of the new mechanics, including permanent alterations formed by elastic deformations (e.g., quenching, annealing, and hardening of metals), the polarization of dielectric bodies, and phenomena of hysteresis (e.g., elastic, chemical, electromagnetic hysteresis).

In a sense, the studies concerning the behavior of friction and deformable systems constitute the final stage of Duhem's outstanding work on his generalized thermodynamics. He completed it through the complex net involving analytical mechanics, thermodynamics, physics, and chemistry. As we shall see below, Duhem's sophisticated studies of friction and permanent alteration paved the way to a new branch of mechanics that flourished by the mid-twentieth century, especially in America.

Intermezzo I. Die Thermodynamik Chemisher Vergänge: Helmholtz's free energy

Helmholtz appeared in the field of thermodynamics about eight years after Gibbs and studied the same subject. As Gibbs, Helmholtz was a great mathematician of his time, but still, one must say, that he attained only a small portion of what Gibbs had achieved in thermodynamics. Unfortunately, Helmholtz's work had the same fate as Gibbs'. He wrote in a very abstract manner, and very few paid attention to that work in his time.

Helmholtz's motivation to develop his theory of thermodynamics has not any contact with the work performed by his predecessors. He was unaware of Massieu's characteristic functions of 1869, Horstmann's two papers of 1869 and 1873, and their implication to chemistry. Also, he seemed to be unfamiliar with Gibbs' *heterogeneous*

substances of 1876.⁶⁸³ Until 1882, when he published the first two parts of his famous trilogy *Die Thermodynamik Chemisher Vergänge*, Helmholtz did not refer to Gibbs and Massieu. As soon as he acknowledged their work in thermodynamics, he did not neglect to give credit to both physicists in the third part of his *Chemisher Vergänge* published in 1883.

Presumably, his contact with thermodynamics was motivated by his work in electrochemistry and his studies on polarization and concentration cells. In 1882, he stated, "In fact, I myself have been led to the theory of free chemical energy, about to be set forth here, by the question of the connection between the electromotive force of such a battery and the chemical changes going forward within it".⁶⁸⁴ Helmholtz's views on thermodynamics are contained in his memoir *Die Thermodynamik Chemisher Vergänge*, which was published in three parts in 1882 and 1883.⁶⁸⁵ In the first part of this series published in 1882, Helmholtz described the concept of free energy and derived its mathematical expression. He distinguished two parts of the heat content of a body. One part appears only as heat, and the second part could be freely converted into other kinds of work (mechanical or electrical). He named the former part *bound energy* and the latter part *free energy*.

The calculation of the bound and free energies required a system that should work reversibly in a thermodynamic sense. Helmholtz found such a system in the concentration cell, a system that was familiar to him from earlier studies as described earlier. He knew

⁶⁸³Gibbs has sent reprints of his memoir to Helmholtz, whereas Horstmann attended some of Helmholtz's lectures in Heidelberg.

⁶⁸⁴Helmholtz, 1882, p. 24.

⁶⁸⁵These three parts have been translated into English: Helmholtz, von H. F. The thermodynamics of chemical processes. (1888). *Physical memoirs selected and translated from foreign sources*, London: Taylor and Francis, vol. 1, Part I, pp. 43-62, Part II, pp. 63-75, and Part III, pp. 76-97.

that this galvanic cell worked with an electric current intensity so vanishingly small that heat development in the circuit can be neglected. This very small quantity of heat allowed the process in this system to be perfectly reversible.⁶⁸⁶ Helmholtz wondered about the connection between the electromotive force of the galvanic cell and the chemical changes taking place within the cell. This specific question led Helmholtz to investigate the more general subject as to what portion of the energy in a body can be converted to other forms of work. He starts his analysis from Clausius' two fundamental equations that hold under reversible conditions. The first equation expresses the change of the entropy at a constant temperature when a body receives or liberates heat, i.e.,⁶⁸⁷

$$\oint \frac{\partial Q}{\partial t} d\theta = 0 \tag{I.1}$$

The cyclic integral denotes a reversible cycle; θ is the absolute temperature according to Helmholtz's notation. The second equation derives by combining Eq. (I.1) and the mathematical expression of the first law of thermodynamics, namely,

$$\frac{\partial S}{\partial \theta} = \frac{1}{\theta} \frac{\partial U}{\partial \theta} \tag{I.2}$$

S and *U* are the entropy and the total internal energy of the system, respectively. Helmholtz considers a mechanical or electrical system that is described by temperature and an arbitrary finite number of other independent parameters p_x , such as volume, density, electric charge. Then, he applies the first law of thermodynamics to this system

$$JdQ = \frac{\partial U}{\partial \theta} d\theta + \sum_{x} \left[\left(\frac{\partial U}{\partial p_{x}} + P_{x} \right) dp_{x} \right]$$
(I.3)

⁶⁸⁶ Helmholtz, 1882, pp. 23-24.

⁶⁸⁷Helmholtz used partial derivates, indicating that apart from temperature, any other variable is kept constant. In a wide variation of temperature, Helmholtz used standard differentials.

J denotes the mechanical equivalent of heat. P_x could be the pressure or an electric potential difference, and $P_x \cdot dp_x$ is the whole freely convertible work produced by the variation of p_x . Through a series of mathematical manipulations, Helmholtz arrives at the mathematical representation of the *free energy*, the *ergal*, as he called it.

$$\mathbf{F} = U - J\theta S \tag{I.4}$$

Helmholtz ascribed to the free energy function properties of potential energy.⁶⁸⁸ Since U is the total internal energy, the difference $U - F = J\theta S$ signifies what Helmholtz calls the *bound energy*.⁶⁸⁹ The internal energy and the entropy are obtained from the free energy. By differentiating Eq. (I.4) with respect to θ , one obtains

$$\frac{\partial F}{\partial \theta} = \frac{\partial U}{\partial \theta} - JS - J\theta \frac{\partial S}{\partial \theta}$$
(I.5)

From Eq. (I.2), Eq. (I.5) is simplified to

$$\frac{\partial F}{\partial \theta} = -JS \tag{I.6}$$

Whence, in consideration of Eq. (I.4), it follows

$$U = F - \theta \frac{\partial F}{\partial \theta} = F + J\theta S \tag{I.7}$$

Equations (I.6) and (I.7) give the values of the two functions S (entropy) and U (total internal energy), respectively, in terms of the differential coefficient of F (free energy). Substituting the entropy from Eq. (I.4) to Eq. (I.6), Helmholtz obtained the famous *Gibbs-Helmholtz equation* that has a widespread application within the context of chemical thermodynamics.

$$-\theta \frac{\partial F}{\partial \theta} = U - F = J\theta dS \tag{I.8}$$

⁶⁸⁸ Helmholtz, 1882, p. 30.

⁶⁸⁹The bound energy identified earlier with the latent heat. However, no distinction existed between the latent heat and the heat transformed into external work.

All the parameters in Eqs (I.1) - (I.8) other than temperature remain constant. With Eq. (I.3)

$$dQ = J\theta S \tag{I.9}$$

This equation determines the *bound energy*, which expresses the mechanical equivalent of the quantity of heat which must be conveyed to the body at temperature θ to raise entropy to the value *S*. Helmholtz' bound energy is identical to the unavailable energy of the rational mechanics, Clausius proposed an analogous terminology in thermodynamics when he defined entropy as the uncompensated transformation. In his second graphical paper, Gibbs, when referring to the properties of the surface of the dissipated energy, confirmed the role of the entropy as the measure or the factor that determines the unavailable energy.⁶⁹⁰

Continuing his thoughts, Helmholtz derives the expression of the work done by the system and the heat received by the system in a cyclic process, namely⁶⁹¹

$$dW = -dF - JSd\theta \tag{I.10}$$

and

$$JdQ = dU - dF$$
 or using Eq. (I.5), $dQ = \theta dS$ (I.11)

For the isothermal process ($d\theta = 0$), Eq. (I.10) confirms that the external work is produced at the expense of free energy. On the other hand, Eq. (I.11) indicates that the bound energy changes at the expense of the incoming or outgoing heat. It increases in the former case and decreases in the latter case. For adiabatic processes (dQ = 0), work is produced at the expense of both free energy and bound energy to keep the entropy constant. Eq. (I.10) leads

⁶⁹⁰Chapter 6, section 1 of this dissertation.

⁶⁹¹Helmholtz, 1882, p. 35.

to another significant conclusion. When the temperature rises, the bound energy increases at the cost of free energy, which decreases by the same amount.⁶⁹²

For irreversible isothermal processes, for example, spontaneous chemical processes from state 1 to state 2, the work performed by the free energy is given by integration of Eq. (I.10).⁶⁹³

$$W = F_1 - F_2 \tag{I.12}$$

Eq. (I.12) implies that the work produced by the free energy of a chemical process determines the direction of the chemical change. Integration of Eq. (I.11) provides the heat produced or absorbed by the chemical change.

$$JQ = U_1 - U_2 (I.13)$$

Thomsen and Berthelot were devising their thermochemistry erroneously considered this quantity as a measure of the chemical affinity. Helmholtz wrote, "Assuming the unlimited validity of Clausius's law, and it would be the value of free energy, not that of the total energy that is manifested by the development of heat that decides in what sense chemical relationships can be active".⁶⁹⁴ Furthermore, Helmholtz defines the condition of chemical stability as⁶⁹⁵

$$\delta F \ge 0 \tag{I.14}$$

Therefore, stability is not determined by the work produced in a chemical reaction according to the principle of maximum work—the combination of Eqs. (I.8) and (I.14) show immediately that a spontaneous chemical process may occur by heat absorption

⁶⁹²Ibid, p. 36.

⁶⁹³Ibid, p. 37.

⁶⁹⁴Ibid, p. 23.

⁶⁹⁵Ibid, p. 38.

favoring, thus endothermic reactions. If the quantity $\theta \frac{\partial F}{\partial \theta}$ is more prominent than F, then U would be negative, and the system (the reaction) absorbs heat.

Helmholtz differentiates the *vis viva* or actual energy (kinetic energy) of the body from the work-equivalent to heat. He proposes to call the first as *vis viva of regular or ordered motions* and the second as *irregular or disordered motions*. Disordered motions differed from ordered motions in that "the motion of every single particle [molecule] need not bear any kind of similarity to that of its neighbor".⁶⁹⁶ With this vague statement, Helmholtz sought to distinguish the quantity of entropy as the measure of irregularity or disorder. "We have every reason to believe that the movement of heat is of the latter kind, and in this sense, the size of the entropy can be called the measure of disorder".⁶⁹⁷

One question that needs clarification is how did Gibbs and Helmholtz get their names on Eq. (I.8), the so-called *Gibbs-Helmholtz equation*? There is much confusion about the origin of this equation, which has been ascribed to both Gibbs and Helmholtz.⁶⁹⁸ Helmholtz has derived this equation in his 1882 paper. Gibbs did not describe such an equation in the bulk of his thermodynamics. Gibbs' first connection with this equation was through a letter sent in 1887 to Oliver J. Lodge (1851-1940), the secretary of the Electrolysis Committee of the British Association for the Advancement of Science (BAAS).⁶⁹⁹ Gibbs showed how Helmholtz's earlier result could be derived from the

⁶⁹⁶Ibid, p. 34.

⁶⁹⁷Ibid, pp. 33-34.

⁶⁹⁸ Mathias, 2016, p. 1085.

⁶⁹⁹Gibbs sent two letters to Oliver Lodge wgo read both letters in front of the members of the electrolysis committee. The letters dealt with electrochemical thermodynamics in reversible galvanic cells. In the first letter dated January 8, 1887, Gibbs referred to the connection of the electromotive force with the heat of the electrochemical reaction. Gibbs claimed that this relationship allows predicting both the electromotive force and the reversible heat without setting up the cell at all (Lodge 1887a, pp. 388-389; GSP, 1906, pp. 406-408). In the second letter dated November 21, 1887, Gibbs proceeded to ramify the content of the first letter. Using Carnot's isothermal reversible cycles and applying the second law of thermodynamics, he

equation of his ζ function that he had already proposed in his *heterogeneous substances*.⁷⁰⁰ Gibbs rederived Eq. (I.8) five years after Helmholtz, while he was fully aware of Helmholtz's earlier result.⁷⁰¹In his letter to Lodge, Gibbs desired to show that the problem of the determination of the relation between the heat evolved in an electrochemical reaction taking place in a voltaic cell and the electromotive force produced had been solved in the last pages of his *heterogeneous substances*. The spirit of this letter was a rather gentle warning to the committee to avoid useless labor rather than a priority claim. On the other hand, Helmholtz was unaware of Gibbs' *heterogeneous substances* and the identity of Gibbs' ψ function with his free energy function. He hastened to recognize Gibbs' priority with this matter as soon as he became aware of Gibbs' essay.⁷⁰²

Neither Gibbs nor Helmholtz suggested or thought to give a name to this equation. The credit for naming this equation goes to the scientific community. Nernst, in his textbook *Theoretische Chemie vom Standpunkte der Avogadroschen Regel and der Thermodvnami*k ascribed Eq. (I.8) to Helmholtz and applied it to galvanic cells to measure the chemical affinity of chemical substances.⁷⁰³ Nernst mentioned both Gibbs and Helmholtz as the inventors of the equation in 1911 in the third edition of his textbook *Theoretical Chemistry*. He tested the validity of this equation and, in general, the heat

derived an algebraic relationship between electromotive force and energy and the system's entropy (actually the ζ function). He easily obtained from this equation the Gibb-Helmholtz equation (Lodge, 1889, pp. 343-346; GSP, 1906, pp. 408-412). It is worth noting that the theory presented in the second letter was taken from his *heterogeneous substances* (FSP, 1906, pp. 338-339). The new in the letter was the derivation of the Gibb-Helmholtz equation.

⁷⁰⁰GSP, 1906, p. 411.

⁷⁰¹Ibid

⁷⁰²Helmholtz discussed that Gibbs' force function and Massiei's H function corresponded to his free energy function in the Third Part of the trilogy Die Thermodynamik Chemisher Vergänge published in 1883. I had no access to the original paper. I referred to the English translation (Helmholtz 1888), pp. 77-78).
⁷⁰³ Nernst, 1893, pp. 709-713.

theorem on several physical and chemical systems.⁷⁰⁴ From the second decade of the twentieth century, textbooks began referring to the Gibbs-Helmholtz equation as a significant innovation in thermodynamics and physical chemistry. Also, Gibbs and Helmholtz are cited in James Riddick Partington's (1886-1965) textbook of 1913 and Lewis and Randall's textbook of 1923.

What differentiates Helmholtz from Gibbs, Massieu, Duhem is that only Helmholtz explored the significance of free energy in chemistry. He tested the equation experimentally⁷⁰⁵ and applied it to several chemical problems. Gibbs did not establish the Gibbs-Helmholtz equation. He discussed what he called "Helmholtz's equation" in the 1887 letters without any further consideration. William Thomson proposed a similar equation to Eq. (I.8) in 1855 but failed to it any chemical significance. It was with Helmholtz that the equation got paramount importance in chemical thermodynamics.

Helmholtz published the second and third parts of *Die Thermodynamik Chemisher Vergänge* in 1882 and 1883. He applied his theory to several chemical problems including calculations for the heat and the free energy of salts solutions and galvanic polarization. He revisited the issue of polarization he had initiated in 1873 in the light of his new theory of thermodynamics, indicating thus the importance he ascribed to this phenomenon. Helmholtz assumed in 1873 that the formation of the oxygen and hydrogen gases during the electrolysis of water had a significant influence on the intensity of the electric current. The building of the electric double-layer explained the microscopic equilibrium obtained

⁷⁰⁴(Nernst 1918.

⁷⁰⁵Helmholtz's student Siegfried Czapski supervised by Helmholtz provided experimental support to the Gibbs-Helmholtz equation in 1884 (Czapski, 1884). These experiments also offered qualitative arguments in favor of Helmholtz's theory. Observed deviations between theory and experiment explained in 1888 by Nernst, who by 1889 verified the validity of the Gibbs-Helmholtz's equation thoroughly(Nernst, 1889).
at the surface of the electrodes. However, he was unable to explain these two processes quantitatively. The dissolution of gases and the metal-liquid interfacial layer could not explain the unlimited duration of the polarization current obtained with low electromotive force as in the concentration cells. Neither the increase of the polarization forces by increasing the electromotive force of the cell. The removal even of the last traces of the dissolved gases did not remedy the problem of polarization.⁷⁰⁶ Using his thermodynamic theory, Helmholtz confirmed that the resistance of the chemical forces to the electric current increases steadily with the amount of the gases given off at the electrodes during the electrolysis of water. Using his thermodynamic theory, he calculated the free energy of the gas bubbles formed after the saturation of the layers next to the electrodes and the work corresponding to the diffusion of the gases through the liquid. He proposed "a tolerably complete analytical theory of polarization-currents, the deductions from which appear to agree with the phenomena in all essential particulars".⁷⁰⁷

⁷⁰⁶Joule was the first, who undertook this measure. Helmholtz used more advanced methods and instrumentation for the removal of the dissolved gases and the air from the atmosphere. ⁷⁰⁷Helmholtz, 1883, p. 95.

Chapter 8. Impact of Gibbs and Duhem's approaches to thermodynamics on chemical thermodynamics

How successful were Gibbs and Duhem's projects on thermodynamics? To what degree has their contribution to thermodynamics influenced the development of chemical thermodynamics? Answers to these questions presuppose the exploration first, the reception of their thermodynamics by the contemporary scientific community inside and outside their country. Second, the way Gibbs and Duhem's ideas began to penetrate chemical thermodynamics. Third, the emergence of their thermodynamics in University textbooks and monographs. Fourth, the possibility that their theories might have found other outlets for recognition and application.

Gibbs formulated and studied conditions, which he took to signify the stability of equilibrium states of material systems. As noted, Gibbs dealt with phases of homogeneous fluids to mixtures of complex systems, from solids to chemical reactions, and from osmotic and electromotive forces to material films and surfaces of discontinuity. On the other hand, Duhem studied equilibrium and non-equilibrium processes through his thermodynamic potential. However, his major work on energetics was devoted to the theoretical study of the non-equilibrium processes in fluids and solids. Both Gibbs and Duhem's thermodynamics incorporated the necessary methods and tools to solve chemical affinity and chemical equilibrium problems that engaged chemists for almost a century. Nevertheless, the reception of their work from the scientific community did not take place quickly and smoothly. Neither Gibbs nor Duhem's theories had an immediate impact on the new system of chemical thermodynamics. The transfer of thermodynamics from physics to chemistry was the work of the so-called ionists, namely, the three chemists van 't Hoff from the Netherlands, Svante Arrhenius from Sweden, and Friedrich Wilhelm Ostwald from Germany. Their work, which marked the birth of chemical thermodynamics in Europe achieved practically during the last two decades of the nineteenth century. Shortly after, the German chemist, who turned physicist, Walther Hermann Nernst, extended the solution theories of the ionists in the field of electrochemistry. Several reasons explain the indifference showed by contemporaries regarding Gibbs and Duhem's works.⁷⁰⁸ Some of these reasons are common for both scientists. In contrast, others are distinct, reflecting either the personality of the men or external factors, for example, the unfriendly and, in some cases, the hostile attitude against Duhem from some of his colleagues within the French scientific community.

Some common reasons have been ascribed to (a) the lack of interest on Gibbs and Duhem's part in attracting attention to their work, (b) the lack of concern from their students and colleagues to disseminate the work of their mentors and coworkers, (c) the style of their writings, and (d) the significant differences between their theoretical approaches and competing scientific schools of the period, such as the chemical thermodynamics set in motion by the ionists. As shown below, the first two allegations did not constitute significant factors to delay the general appreciation of their work. The charge that the writing style was a deterrent to their prompt recognition may have affected the

⁷⁰⁸Gibbs and Duhem were honored by the Scientific Academies of their countries and abroad. And by some of their colleagues, at least from those who had an understanding of their work. For Gibbs' recognition, see Wheeler, pp. 83-93, and 97-99; for Duhem's recognition, see Jaki, 1984. pp. 141-147. However, personal recognition does not necessarily mean a wide reception of their work.

reception of their work. Gibbs's terse and condensed writing style, which made it difficult for the readers to apprehend his work, has been underlined as a major obstacle to attaining recognition. However, the criticism of Gibbs' writing style has been somewhat overemphasized. However, it is not necessarily correct for Duhem, whose talent for presenting his work was evident. The complex mathematics they used in their work was accused as the major cause for the impediment of their recognition. However, the use of mathematics by Gibbs and Duhem was not their primary concern. It came as a logical consequence from their very general principles and the necessity of applying particular physical methods to express their ideas, for example, the algebra in Gibbs' *heterogeneous substances* and Lagrange's analytical mechanics in Duhem's energetics. The last allegation has some weight. It delayed the dissemination of their contribution to thermodynamics but not to the same extent.

For Gibbs, the publication of his work in the relatively unknown journal *The Transactions of the Connecticut Academy of Arts and Science* seems to contribute to the inadequate circulation of his work.⁷⁰⁹ However, the librarian of the Connecticut Academy claimed that the *Transactions* circulated in 170 learned societies, of which 140 were in foreign lands.⁷¹⁰ For Duhem, however, the situation was more intricate, mainly because of his contentious character and the unfavorable social, political, and scientific beliefs during his academic life in France. His highly conservative religious and political views against

⁷⁰⁹ Gibbs distributed reprints of his *heterogeneous substances* to a large number of contemporary physicists, chemists, mathematicians, and astronomers, who, according to him, might have some interest in his work. The extensive mailing list of the individuals that received reprints is reported in Wheeler, 1962, pp. 235-248. However, most of the recipients of Gibbs' reprints showed characteristic indifference to his work, probably due to their difficulty in understanding his concise writing style or because Gibbs was unknown to his colleagues in Europe. Amongst the few, who indicated an immediate interest in Gibbs' thermodynamics was Maxwell.

⁷¹⁰Wheeler, 1962, p. 96); the release of a scientific journal does not necessarily imply that it will have a wide readership. It depends on the quality of the journal and the level of research reflected on its pages.

those of the liberals that dominated French science and the aggressive nature of his writings on various controversial scientific subjects made personal enemies of many of his contemporaries. As a result, the combined opposition blocked his career and partially suppressed his work, which is rarely cited in contemporary French literature. Duhem's work met another serious obstacle to achieve recognition: his extreme anti-atomism that affected the whole of his work. Duhem's resentment of molecular mechanics and molecular models as an explanation of physical and chemical phenomena persisted stubbornly until the end of his life. His Traité Élémentaire de Méchanique Chimique, fondée sur la *Thermodynamique*⁷¹¹ which was a complete account of his ideas on chemical mechanics, and the treatise L'Évolution de la Mechanique did not include even one word for atoms or molecules. Duhem shared with positivism the belief that physical theory should be based on precise experimental results. He pointed out that it must not introduce chemical mechanics at any time, especially at its theoretical base, the slightest parcel of hypotheses. Otherwise, it will collapse when new facts appear, forcing science to abandon old hypotheses for new ones recognized as more effective in explaining the experiment. He insisted that atomism was only one hypothesis, among many others, and however ingenious, it could be, it was a somewhat dangerous way of representing the constitution of matter. His views on atomism have been expressed clearly in several places of his scientific and philosophical publications. Duhem has exerted criticism on several subjects, of atomism including Dalton's law of constant proportions, the symbols of the elements, chemical combinations (mixtures), molecular formulae, isomerism, isomorphism, and atomic valence. Duhem provided a critique of atomism as early as 1892 in the last section

⁷¹¹ It was published in four large volumes of 1430 pages in total, from 1897 to1899.

of the article *Notation Atomique et Hypothèse Atomistique*.⁷¹² He further elaborated this idea in his article *L'Ècole Anglaise et les Théories Physiques: Á Propos d'un Livre Récent de W. Thomson*,⁷¹³ and in his memoir *Le Mixte et la Combinaison Chimique*.⁷¹⁴ On the other hand, without being an ardent follower of atomism, Gibbs gave more room to the microscopic theories concerning the interpretation of physical or chemical phenomena whenever macroscopic theoretical approaches failed to give convincing answers or no answers at all.

Indeed, the concept of atoms and their participation in forming molecules was unclear to scientists during the nineteenth century. Despite the pronunciation of the laws of constant and multiple proportions, the introduction of a molecule was instead a confusing concept. Chemists had no idea how atoms form molecules or how molecules decompose into atoms. Nevertheless, younger scientists than Duhem, such as William Crookes, Joseph John Thomson (1856-1940), and Jean Baptiste Perrin (1870-1942), performed by the end of the nineteenth century-beginning twentieth-century experiments the interpretation of which called for the presence of atoms and molecules. Duhem never stopped believing that elusive hypotheses, axioms, and postulates not given by commonsense observations, could not preoccupy his energetics. It was a solid construction without breaking or separating parts. "The use of disparate models cannot be regarded as a physical theory, for it lacks what is the very essence of a theory, unity, which links in a rigorous order the laws of the various groups of phenomena".⁷¹⁵ He insisted that energetics did not search to explain the constitution of matter but only to interpret the matter in a

⁷¹²Duhem, 1892b.

⁷¹³Duhem, 1893c.

⁷¹⁴ Duhem, 1902a, pp. 143-161.

⁷¹⁵ Duhem, 1905, p. 195.

mathematical language based on the fundamental laws of nature, and therefore had nothing to fear from the atomists. He firmly believed that energetics could flourish, ignoring atomism. He had in mind that the new physics was in conflict with other physical theories, particularly rational mechanics, and contradicted with common sense. However, he believed that molecular mechanics would not retreat, and as if he felt the inevitable prevalence of the new physics and atomism over the abstract concepts of rational mechanics, he predicted the defeat of his energetics: "For my part, I must admit that I have remained attached to this last mode of representation [energetics] so far and that I am more assured of it than of any other; but I cannot raise any objection in principle against a method followed by such great physicists".⁷¹⁶

Duhem tried to keep a distance from several discoveries. The theory of relativity, X-rays, radioactivity, the interpretation of the Brownian motion by Einstein's theory and the verification by Perrin's experiments, and light quanta were some of the discoveries for which Duhem was either silent or whenever he referred to them; he did it with relentless criticism. He questioned the notion of the inseparability of time and space. He considered the principle of relativity as a creation of geometry. One could not give proper account to this theory without recourse to purely algebraic formulae.⁷¹⁷

Maxwell's electromagnetic theory was another target of Duhem's severe criticism. It was accompanied by an extended historical analysis of the development of electrostatics and electromagnetics.⁷¹⁸ Although Duhem recognized Maxwell as a genius, he objected to

716Ibid

⁷¹⁷Duhem, 1915, pp. 134-135; Jaki, 1984, p. 312.

⁷¹⁸Duhem criticized Maxwell's electromagnetic theory in his essay *Les théories électriques de J, Clerk Maxwell. Étude historique et critique*. This essay was published in two parts in 1900 (Duhem, 1900) and 1901 (Duhem, 1901b) in *Annales de la Societe Scientifique de Bruxelles*. These articles were republished as a single book translated into English (Duhem, 1902c),

his theory in certain respects. According to Duhem's opinion, Maxwell's theory, while algebraically rigorous, was inconsistent with mechanics. It violated the principle of virtual displacements. He asserted that Maxwell postulated the so-called displacement current and introduced *ad hoc* electrodynamic energy to overcome inconvenient obstacles. These methodological flaws prohibited the subsequent development of the theory. Duhem preferred the theory of electromagnetics given by Helmholtz, who, in addition to the transverse radiation flux suggested by Maxwell, proposed the inclusion of a longitudinal flux. The introduction of that second flux made easier the interpretation of the electromagnetic waves detected by Hertz. Duhem claimed that Helmholtz's theory developed according to consistent logic and in agreement with experiments.⁷¹⁹ Furthermore, Duhem contributed to the improvement of Helmholtz's version of the electromagnetic theory.⁷²⁰

There are allegations that Duhem, the great savant, did not have the insight to understand the rise of atomism in the scientific scene and insisted on proclaiming its collapse. However, this statement does not tell the whole story. The triumph of views that bitterly opposed his phenomenological theories, such as the atomic theory, Maxwell's electromagnetic theory, the photoelectric effect, the notion of electrons and photons, Planck's hypothesis of quanta, and Einstein's relativity removed any interest in his work. Nevertheless, much of Duhem's energetics was not overlooked solely because of the rise of the new physics. Atomism was not the only factor for the poor reception of Duhem's

⁷¹⁹ Jaki 1984, pp. 276-278, 301, 394-305.

⁷²⁰Criticism of Maxwell's classical electromagnetic theory was widespread among French physicists in Duhem's time. But it was relatively shallow compared to the detailed and rigorous analysis of it given by Duhem. Nevertheless, Duhem's treatise on Maxwell's electromagnetic theory was eliminated from contemporary French reviews, articles, and monographs (Jaki, 1984, pp. 283-284).

work. Social factors and Duhem's scientific style played their role in keeping his thermodynamics away from the foreground of science. In general, the rise of the new theories and applications in modern physics did not significantly retard the development of phenomenological theories. These theories persisted in offering realistic interpretations of microscopic phenomena at a macroscopic level. Even at a later time, the merit of the phenomenological approach did not decrease. Good examples are Planck and Ostwald's early works in thermodynamics and thermochemistry, which were very well received despite the anti-atomism of their authors.⁷²¹ Atomistic and phenomenological theories each followed a different way in the study of physical and chemical phenomena. However, these different theoretical approaches seem to meet each other at the interpretation level.

Gibbs' writing style was a deterrent to his prompt recognition.⁷²² Several eminent scientists expressed complaints about *heterogeneous substances*. They found this work hard to read due to its concise and abstract style, with no examples, no references, and applications. This writing style contrasts with Duhem's lucid style with the lengthy enlightening introductions. Unlike Gibbs, who, in his writings, barely had the usual introduction, in which scientists referred to previous works related to the subject they deal with, On the other hand, Duhem was revealing in his practice of writing books and articles.

⁷²¹Ostwald was an ardent opponent of atomism. His energetics rejected any reference to the structure of matter and displaced matter with energy. However, when experimental evidence for the particulate nature of matter became dramatic, Ostwald changed his attitude and converted to atomism (Hiebert, 1981a, p. 463).

⁷²² Duhem, who studied thoroughly Gibbs' work in *heterogeneous substances* and exposed Gibbs' thermodynamics among his contemporaries in France, made once the following ironic comment regarding Gibbs' dense writing style: "Il semble parfois qu'en publiant ses travaux, Gibl)s eût été possédé du désir de les voir passer inaperçus; s'il en fut ainsi, il fut bien souvent servi à souhait; bien souvent, ses idées demeurèrent ignorées de ceux-là mêmes qui auraient eu le plus grand intérêt à les connaitre." (It sometimes seems that by publishing his works, Gibbs would have been possessed of the desire to see them go unnoticed; if this was the case, his wishes were often fulfilled; very often, his ideas remained ignored to those who would have had the greatest interest in knowing them) (Duhem, 1908, p. 14).

Almost all of his writings were a detailed historical reconstruction of the achievements made by previous researchers in the field. This type of presentation gave the reader a complete picture of the historical development of the scientific subject he put forward. Despite the enlightening introductions accompanying almost all of his publications, Duhem's work faced a negative response from the scientific community. Therefore, the writing style is not the decisive factor that caused the slow or negative reception of their thermodynamics. It was probably the lack of a deeper understanding of their content due to the unprepared mental soil for these works, especially for chemists.⁷²³\

The key factor that essentially impeded the introduction of their theories into experimental chemistry must be sought in the many laws, axioms, corollaries, and the rigorous mathematical language of Gibbs' *heterogeneous substances* and the majority of Duhem's papers and memoirs. This factor delayed the birth of the new specialty of chemical thermodynamics. Few physicists may have had the skill in mathematics to understand Gibbs and Duhem's thermodynamics.⁷²⁴ The majority of chemists had no adequate knowledge of thermodynamics and no sufficient mathematical knowledge to comprehend the theories invented by Gibbs, let alone the more demanding analytical mechanics used by Duhem.⁷²⁵ Chemists were familiar with the first law of thermodynamics reformulated in Thomsen and Berthelot.'s thermochemistry, which could easily apply to

⁷²³ Duhem commenting on Gibbs' writing style, concluded: "If therefore, Gibbs has left his discoveries of chemical mechanics in an abstract and purely algebraic form, it is not that he was incapable of presenting them in a language more concrete and more accessible to experimenters, it is because of his intellect." (Duhem, 1908, p. 26).

⁷²⁴Maxwell, van der Waals, Helmholtz, J.J. Thomson, and Hertz were among Gibbs' few contemporary physicists who understood the heterogeneous substances. However, only Maxwell spoke enthusiastically to his fellow physicists in Britain about Gibbs and included Gibbs' graphical representations in his textbook *Theory of Heat*. Maxwell's premature death in 1879, at the age of 48, put an end to his excellent work in physics, while Gibbs lost a keen supporter of his thermodynamics.

⁷²⁵For a thorough discussion of the various factors that delayed the transfer of thermodynamics into chemistry, see chapter 9 of this dissertation.

their experiments. It was complicated for chemists to comprehend what entropy meant, how it could be used, and how it could be measured.⁷²⁶ As far as mathematical skill is concerned, chemists had little need for sophisticated mathematics.⁷²⁷ They needed to know how to weigh out stoichiometric quantities, measure densities, record melting, and boiling points, and determine the correct atomic ratios in combustion and other reactions. Simple arithmetic was sufficient for these operations.

On the other hand, many physicists were deficient in analytic abilities and, therefore, unable to grasp the practical aspects of chemical changes. Gibbs and Duhem repeatedly stressed the weakness they felt to test their theories due to the lack of pertinent experimental data. In contrast to Gibbs in America, Duhem found a prolific soil in France. Experimental chemistry was flourishing in the laboratories of competent French chemists. The excellent work of Sainte-Clare Deville, Regnault, François-Marie Raoult, (1830-1901), Le Chatelier, Berthelot, and others provided theoreticians with a multitude of experimental data confirming existing theories or contributing to the generation of new ones. For instance, in the rejected dissertation *Le potentiel Thermodynamique*, Duhem presented or rederived using his thermodynamic potential several known results on the

⁷²⁶Not only chemists but also the majority of physicists had difficulty accepting or assimilating the concept of entropy. As noted, William Thomson never mentioned the entropy in his work, and even its creator, Clausius, did not give entropy any prominent place in his research. The founders of the discipline of physical chemistry chose to avoid any reference to entropy. The next generation of chemists was familiar with entropy, but they preferred to use alternative measures for the chemical affinity and chemical equilibrium. Gibbs made use of the chemical potential and free energy under constant pressure, Helmholtz used the free energy under constant volume, and Duhem the thermodynamic potentiasl. Hortsmann was one of the few who attempted to use entropy in interpreting dissociation recations, but woth minimal success. Reconciliation of entropy and chemistry was achieved during the decades after the First World War, especially by the American physical chemists (Lewis, Randall, Trevor, Noyes, and others). The "tortuous" course of entropy to enter research and education is the subject of an excellent paper by Kragh and Weininger, 1996.

⁷²⁷ In a letter to Gibbs in 1887, Ostwald proposed the translation of the *heterogeneous substances*, admitted that "I cannot deny that at present the study of your work is pretty difficult, particularly for the chemist, who is usually not at home in a mathematical treatment" (quoted in Moore et al., 2002, p. 115).

vapor pressure of pure liquids and solutions, dissociation of gases, and heterogeneous systems, and heat effects on voltaic cells. He obtained new results on solubility and freezing points of complex salt solutions and electrified systems. Despite the scarcity of experimental data, Gibbs used what he had at his disposal to test some of his equations.

This attitude changed during the last two decades of the nineteenth century when physics and chemistry were finally unified through chemical thermodynamics. As noted above, the ionists van 't Hoff, Arrhenius, and Ostwald were the group of scientists who made thermodynamics accessible to chemists. Although more limited in scope than Gibbs and Duhem's thermodynamics, their theories were simpler, had a clear experimental orientation, and were more attractive to chemists. The ionists developed new concepts and experimental methods to describe the properties of aqueous solutions of substances. They considered several old and new problems comprising chemical affinity, the effects of mass and temperature on chemical equilibria, reaction rates, phenomena of osmotic pressure, and electrolytic dissociation.⁷²⁸ However, Gibbs had elaborated many of the ionists' ideas earlier in the *heterogeneous substances*, except perhaps the properties of the electrolytic solutions. By the end of the 1880s, the ionists had successfully unified various unconnected studies and presented a compact theoretical and experimental whole that constituted the modern chemical thermodynamics, the theoretical basis of the new discipline of physical chemistry. However, the ionists theory of solutions lost much significance for physicists and chemists when they grasped Gibbs' and Duhem's potentials, which treated many of the ionists' results in a more penetrating and elegant way.

⁷²⁸ For the development of the ionists' chemical thermodynamics and the foundation of physical chemistry, see chapters 10 and 11 of this dissertation.

The ionists recognizing the deficiency of chemists in mathematics advised them of the necessity of physical and mathematical training if they wished to go beyond the purely practical side of science. The general situation changed slowly and took more than three decades, well after World War I, until the education of chemists in mathematics at higher education institutions reached a satisfactory level. The young physical chemists appeared better prepared in mathematics, capable of applying thermodynamic methods to solve technical problems in their laboratories.

At this stage, I shall examine the events that occurred in Europe and America, which facilitated the recognition and acceptance of Gibbs and Duhem's ideas. Second, the penetration of their work in chemical thermodynamics and later in the new discipline of physical chemistry.

The recognition of Gibbs' thermodynamics did not go so quickly. It took several steps before it attracted the attention of chemists in Europe and America. The concise writing style noted before was hardly intelligible by chemists, although it made some contact with chemical experiments. Gibbs referred to some twenty experimental results related to solutions, dissociation of gases, thermochemistry, galvanic and electrolytic processes in *heterogeneous substances*. He demonstrated his interest in comparing his theories with experiments in his publication of 1879, *On the Vapor-Densities of Peroxide of Nitrogen, Formic Acid, Acetic Acid, and Perchloride of Phosphorus*.⁷²⁹ In this study, Gibbs explained the abnormal variations of the densities of the vapors of substances by comparing the experimental densities with those calculated through his algebraic formulae expressing the density of an ideal gas mixture.

⁷²⁹ Gibbs, 1879; GSP, 1906, pp. 372-403.

Gibbs' ideas attracted the physicists primarily. The first who paid attention to Gibbs' thermodynamics was Maxwell. As discussed previously, Maxwell was familiar with thermodynamics and had ample knowledge in mathematics, and thus he was able to grasp what Gibbs was doing. He immediately saw the importance of this work for chemistry and physics, and he privately advocated Gibbs' ideas within the scientific community of his country. He would have done much more if he had not died early, just one year after the formal publication of Gibb's *heterogeneous substances*. The death of Maxwell signified practically an impediment for any possible interest in Gibbs' diagrams and surfaces, and with it, the chance for an earlier application of the entropy and the second law of thermodynamics to chemical problems. The introduction of the entropy as a variable in diagrams was forgotten.

After Maxwell, several physicists in Europe and America elaborated on Gibbs' ideas. Helmholtz and Planck in Germany, van der Waals, Rozeboom, and Franciscus Antonius Hubertus Schreinemakers (1864-1945)⁷³⁰ in the Netherlands, Georges Lemoine, Duhem, and Le Chatelier in France, Frederick Donnan (1870-1956) in Britain, Arthur Amos Noyes (1866-1936), Theodore William Richards (1868-1928), Gilbert Newton Lewis, Wilder Dwight Bancroft, and Gibbs' former students Edwin Wilson and Henry Bumstead in America were some of those who were more influential in propagating Gibbs' thermodynamics in their countries, although not with the same ease and the same

⁷³⁰ The Dutch physical chemist. became a professor at the University of Leiden in 1901. His research dealt mainly with heterogeneous phase equilibria in and multicomponent systems. He proposed the residue method, which made possible the determination of the chemical composition of solid phases in ternary systems without separating these phases from the mother liquor. He developed methods for depicting the equilibriums in ternary and quaternary systems. He established phase diagrams for many ternary and quaternary aqueous salt systems. Schreinemakers' contributions are widely used in physicochemical analyses, petrography, and metallurgy.

efficiency. Their reference to Gibbs' work was often fragmentary and connected with their research or teaching of chemical thermodynamics. The exception was Duhem, who had read Gibbs' papers and was impressed by the multitude of ideas that sprang from these writings. He referred to Gibbs' memoir *heterogeneous substances* as "one of the most significant events in the history of science during the last three centuries".⁷³¹ He compared Gibbs' *heterogeneous substances* to Lagrange's famous treatise *Analytical Mechanics*.

Duhem was so impressed by Gibbs' *heterogeneous substances* that he sat down and wrote a study on Gibbs's work just one year after the publication of his rejected dissertation. Duhem sent a nearly fifty-page long essay in two installments to the *Bulletin des Sciences Mathématiques*.⁷³² Duhem focused on two phenomena, which heavily occupied the physicists and chemists at that time: The dissociation of gases, and the electromotive force of galvanic cells. Gibbs interpreted these phenomena using his theory of potentials.⁷³³ 1n 1908, Duhem wrote a review on Gibbs' work and life as a whole.⁷³⁴ This review was initially published in the *Bulletin des Sciences Mathématiques*, in 1907. Duhem's research career was deeply influenced by Gibbs' ideas, not passively but energetically. Duhem appropriated Gibbs' thermodynamics. He clarified it, criticized it, enriched it, and disseminated it all over France through his lectures and publications.

⁷³¹ Quoted in Klein, 1990, p. 57.

⁷³² Dugem, 1887.

⁷³³ Duhem discussing Gibbs' contribution to the theory of the galvanic cells came to the conclusion that Gibbs had the priority over Helmholtz concerning the fundamental rule of voltaic piles. This achievement had been referred to as Helmholtz's theorem. Duhem admitted his failure to recognize Gibbs as the true founder of the new theory of battery due to "an incomplete knowledge of the works of Mr. Gibbs [...] we will therefore only be fulfilling a duty of justice here by rectifying it and proclaiming the undeniable priority of Mr. Gibbs" (Duhem, 1887, p. 174).

⁷³⁴ Duhem, 1908

What gave tremendous impetus to recognizing Gibbs' chemical thermodynamics were first, the translation of the heterogeneous substances in German by Ostwald in 1892, and certain important chapters of the memoir in French by Le Chatelier, which were published in 1898. Second, the establishment of the *Gibbs-Helmholtz equation* and its use to calculate the free energies of substances by thermal means. Third, the applications of the phase rule in research and industry. In 1889, Ostwald decided to ask permission from Gibbs to publish a German translation of the *heterogeneous substances*. The translation was finished in 1892 and finally published in Ostwald's new series Klassiker der exacten *Wissenschaften*.⁷³⁵ The two translations in German and French allowed many physicists and chemists to come closer to the original thermodynamics of the American physicist and find a rich source of novel ideas and propositions that could apply to their research. On the other hand, the training of chemists in mathematics in Europe and America during the first decades of the twentieth century advanced their knowledge to comprehend the usefulness of thermodynamic formulae and functions and to apply them, when possible, to chemical reactions and other physical processes in their studies.

A second step in widening Gibbs' recognition was the *Gibbs-Helmholtz equation*. This equation is one of the essential formulae in thermodynamics and finds numerous applications in physical chemistry. As noted previously, Helmholtz was the first who derive this equation in 1882. The Gibbs-Helmholtz equation relates the free energy change (expressed either using Gibbs' free energy d*G* under constant pressure, or Helmholtz's free energy dA or dF under constant volume) to the change in the heat content or the enthalpy

⁷³⁵ The correspondence between Gibbs and Ostwald when the latter asked Gibbs' permission to translate the *heterogeneous substances* reveals traits of Gibbs' character and scientific style. For instance, he refused to write a short introduction in the German translation and delayed to provide a personal portrait for the same publication (Moore et al., 2002).

dH and the entropy change dS. Using Helmholtz's free energy, the Gibbs-Helmholtz equation was given earlier by Eq. (I.8) derived in Intermezzo I. It can be written with a different notation as⁷³⁶

$$dF = dH + T \left(\frac{dF}{dT}\right)_p \tag{8.1}$$

T is the absolute temperature. The entropy enters Eq. (8.1) through the relation $\left(\frac{dF}{dT}\right)_p = dS$. Gibbs derived this equation much later in a letter sent on January 8, 1887, to Professor Oliver Lodge, the secretary of the Electrolysis Committee of the British Association for the Advancement of Science.⁷³⁷ Equation (8.1) was the precursor of the formulation of the *Heat Theorem* by Nernst, widely known as the *third law of thermodynamics*.

However, the Gibbs-Helmholtz equation came on the surface and attracted the interest of physicists for a different reason. Physicists thought that they could use the free energy suggested by Helmholtz to measure the chemical affinity of substances and the equilibrium constants K_{eq} of chemical processes via the relationship⁷³⁸

$$dF = -RT \ln K_{eq} \tag{8.2}$$

More importantly, thermal data can be used alone to obtain information about chemical affinity and chemical equilibrium through Eq. (8.1). Heats of reactions, specific heats, thermal coefficients, and other thermal quantities could be measured using calorimetric methods. These methods are much easier to implement than constructing selective electrochemical cells.⁷³⁹ Working backward and determining the free energy from the

⁷³⁶ Helmholtz derived the equation in his 1882 famous paper *Über die Thermodynamik Chemischer Vorgänge* (1882). (On the thermodynamics of chemical processes) dealing with free and the bound energies (see Intermezzo 1).

⁷³⁷ GSP 1906, p. 411: Mathias 2016, p. 1085.

⁷³⁸ A rigorous account of this equation is given in chapter 13, section 4, paragraph 4.3.

⁷³⁹ In 1889, the twenty-four-year-old Nernst showed that the free energy of a chemical reaction could be measured by making the reaction the source of a galvanic cell and measuring the electrochemical potential

equilibrium constant is another possibility.⁷⁴⁰ The calculation of the free energy requires the integration of Eq. (8.1), i.e.

$$\Delta G = -T \int_{T_0}^T \left(\frac{\Delta H}{T^2}\right) dT + JT$$
(8.3)

 ΔH can be obtained from the experimental value of the specific heat C_p under constant pressure, i.e., $\Delta H = C_p T$. However, the use of Eq. (8.3), as such, presents two severe obstacles that one should overcome to allow an accurate calculation of the free energy. First, the definition of the lower limit of integration T_0 is taken as the lowest possible temperature of the measurements, which was initially unknown. The second and more challenging is the evaluation of the integration constant *J* that depends on temperature and cannot be determined calorimetrically.

The challenge for the determination of the integration constant advanced the importance of the equation as a valuable tool for quantifying chemical affinity and chemical equilibrium. At the same time, it attracted the research interest of the scientific community in Europe and America. From the mid-1880s until the final formulation of Nernst's heat theorem in 1906, the integration constant dilemma drew several investigators' attention. There were at least six attempts to integrate Eq. (8.1) by prominent scientists of the time: Le Chatelier in1888, Lewis in 189), Richards in 1902, van 't Hoff in 1904, Fritz

⁽electromotive force). Nernst showed that there was a simple proportionality between the electrochemical potential and the free energy. This relationship was recognized as the *Nernst's equation*. However, this methodology has practical difficulties. Each chemical process requires a specific galvanic cell, which is not feasible for all cases. Furthermore, it requires very dilute solutions to directly use concentrations in Nernst's equation).

⁷⁴⁰ This procedure requires the measurement of the concentrations of all components of the chemical reaction at equilibrium. The measurements are repeated with increasing dilution. Extrapolation to infinite dilution allows the calculation of the equilibrium constant and the free energy. However, this method is laborious and prone to experimental errors, especially at low concentrations in which the equilibrium may be disturbed by extracting and measuring the concentrations of the reaction components.

Haber in 1905, and Nernst in 1906.⁷⁴¹ Haber came closer to a solution and perhaps nearer the formulation of the heat theorem before Nernst. However, Nernst (1906) was the one who found the answer. The basic flaw of all previous attempts was the consideration of gas-phase reactions. In such reactions, the specific heats of the reactants are not in general equal to those of the products. Therefore, it was not possible for the total heat capacity of the reaction to approach zero as the temperature approaches absolute zero.

In contrast, heat capacities should approach zero as *T* approaches zero for reactions in the condensed phase (solids or liquids). The problem was solved with an excellent approximation by setting the absolute zero as the lower limit of the integration in Eq. (8.3). Determination of the lower integration limits of this equation allowed the evaluation of the integration constant provided that F is known at some other temperature *T*. Nernst published the solution of the problem in 1906.⁷⁴²

Gibbs could not have obtained recognition from the derivation of the equation alone. Besides, Helmholtz preceded in the derivation of the equation. Furthermore, none of the scientists who attempted to calculate the free energy from Eq. (8.3) mentioned Gibbs' name. Gibbs benefited indirectly from the solution of this equation. He gained recognition when his name was associated with this equation and when the latter was introduced in research and education. In the third edition of his textbook *Theoretical Chemistry* published

⁷⁴¹ There are several accounts on these scientists' efforts to solve the integration problem (Nernst 1907, pp. 39-76; 1918, pp. 1-14 and 227-231; Hiebert 1981b, pp. 437-439; Cropper 1987, pp. 5-6; Coffey 2006, pp. 371-382).

⁷⁴² Nernst, 1906, pp. 5-8. The important point of Nernst analysis was that the difference $\Delta F - \Delta H$ goes to zero, i.e., ΔF tends to become equal to ΔH as the temperature goes to zero. Also, the limiting values of the temperature coefficient of free energy $d\Delta F/dT$ and the heat content $d\Delta H/dT$ are zero, as $T \rightarrow 0$. The integration constant becomes zero at the absolute zero for all reactions involving pure liquid and solid substances. At the absolute zero, Berthelot's principle of the maximum work is valid, since in this case, the heat of the reaction represents the maximum useful work produced.

in 1911, Nernst mentioned Gibbs and Helmholtz as the inventors of the equation, while he tested the validity of this equation and the heat theorem in several physical and chemical systems.⁷⁴³ From the second decade of the twentieth century, textbooks began referring to the Gibbs-Helmholtz equation as a significant innovation in thermodynamics and physical chemistry. The early textbook of James Partington⁷⁴⁴ and that of Lewis and Randall⁷⁴⁵ are cited as examples.

The phase rule originated from the short subsection on the equilibrium of coexistent phases of matter in his heterogeneous substances had a double effect on Gibbs' reputation. First, Gibbs' name became known within the European scientific community, and then in his country. Second, it had a significant impact on physical chemistry and other sciences, such as geology, mineralogy, metallurgy, petrology, ceramics, and industrial manufacturing. The application of the phase rule in phase diagrams for specific systems became an unprecedented display for students, researchers, engineers, and technologists to obtain at a single glance valuable information about the solubility, freezing points, melting points, and other physical characteristics. In complex cases, the phase rule in the form of diagrams provided detailed information and opportunities for further research for transformations induced upon changes in physical conditions. One may recall that Gibbs presented the coexistent phases with no rigorous proof and with the absence of any likely implications. Several physicists in Europe and America, including Duhem, delivered formal proof of the phase rule. The phase rule was perceived and used first in Europe, in the Netherlands, by Roozeboom, van 't Hoff, and his student Wilhelm Meyerhoffer, and

⁷⁴³ Nernst, 1918.

⁷⁴⁴ Partington, 1913.

⁷⁴⁵ Lewis and Randall, 1923a.

afterward in America mainly by Bancroft. The phase rule predicted the formation of a new phase, namely the phase HBr.2H₂O, in the system HBr-H₂O investigated by Roozeboom. Roozeboom published this significant result in 1886, and one year later, he proposed to his fellow chemists to adopt Gibbs' phase rule. Roozeboom probably convinced Ostwald of the importance of Gibbs' thermodynamic theory to make *heterogeneous substances* available to the broader scientific community in Germany.⁷⁴⁶ Duhem praising the chemists from the Netherlands for applying so successfully the phase rule in their research activities, remarked "in less than twenty years, the ideas contained in the formulas of the Professor of New Haven had prodigiously increased and transformed what the chemists had known hitherto, the alloys and the isomorphic mixtures; Consequently, they had revolutionized the theories of metallurgy and mineralogy".⁷⁴⁷ Van 't Hoff, influenced by Meyerhoffer, decided to use Gibbs' phase rule to systematically study the mineral equilibria associated with the marine potash and magnesite deposits in Stassfurt near Magdeburg. Van 't Hoff published about fifty papers for the Stassfurt salts with his collaborators.⁷⁴⁸

When Bancroft was at the University of Leipzig working for his dissertation in Ostwald's physical chemistry laboratory, the German prepared the translation of Gibbs' *heterogeneous substa*nces. Bancroft presumably learned at that time about the phase rule, which became his main research interest when he returned to the United States. After unsuccessful efforts, while he was at Harvard, to interpret solubility relations quantitatively in ternary systems using *ad hoc* empirical equations, Bancroft turned into Gibbs' phase

⁷⁴⁶ Daub 1976, p. 748.

⁷⁴⁷ Duhem 1908, p. 24.

⁷⁴⁸ A report for Stassfurt deposits involving Van 't Hoff experimental findings issued in the 1991 *Data in Geochemistry. Bulletin-United States Geological Survey*, issue 491, pp. 210-217. This survey did not include phase diagrams due to the limited space of the journal.

rule as an alternative way to find correct answers. Since then, the phase rule and its applications constituted Bancroft's main research program. The appeal of the phase rule to Bancroft was so influential that he undertook to reconstruct much of physical chemistry around the principles governing the phase rule.⁷⁴⁹ He argued that the phase rule should serve as the cornerstone for instruction and research. Bancroft began writing a book to inform the American scientific community of the significance of their fellow citizen's work. The publication of this book in 1897, and all of Bancroft's books and articles about the phase rule publicized in the next twenty years, mainly through the *Journal of Physical chemistry* (founded by Bancroft in 1896), expanded the recognition of Gibbs' work in America, even though Bancroft's career faced an unprecedented failure.⁷⁵⁰

The recognition of Gibbs' work is one thing; its penetration into the chemical thermodynamics is another. Van 't Hoff indeed ignored Gibbs' ideas incorporated in the *heterogeneous substances*. He did not exploit the simplicity of the chemical potential and insisted on using Carnot and Clausius' method of reversible cycles. Van 't Hoff was a practical chemist with insufficient mathematical skills and little interest in using rigorous thermodynamic methods. He was not interested in advancing thermodynamics as an important field of science. Upon realizing the strength of thermodynamics that would solve practical problems in chemistry, he took from it whatever he thought to be useful for consideration of chemical facts. He selectively used thermodynamics as a tool in his studies, similarly as the physicist uses mathematics in his research. His object was

⁷⁴⁹ Servos 1990, pp. 168-201; 1982.

⁷⁵⁰ Bancroft's research program based on the phase rule had a limited scope and finally collapsed, unable to compete with the advancement of physical chemistry. In later years, however, the phase rule became the central research subject of engineers. John Servos has provided details for the bankruptcy of Bancroft's research program (Servos, 1982).

chemistry, not physics. His opinion about thermodynamics formulated by physicists in the second half of the nineteenth century was expressed when he compared the method of the reversible cycles with the state functions, such as entropy and free energy.

"I shall suggest as to the choice of the most suitable form of this [Carnot-Clausius] principle. It may be applied either by carrying out the so-called reversible cycles of operations or by the introduction of abstract physical conceptions and mathematical functions, such as entropy, as is done by physicists like Gibbs, Planck, and Duhem. I am convinced that, for the chemist, the first form, in which reversible cycles are employed, is the most advantageous". ⁷⁵¹

This statement reveals van 't Hoff's alienation from the concept of entropy that he never used it.

The distance between Gibbs' chemical potential and van 't Hoff's semipermeable membrane⁷⁵² constituted a characteristic example of the dualistic development of chemical thermodynamics until they merged in the new discipline of physical chemistry. Contrary to van 't Hoff, Ostwald recognized the significance of the *heterogeneous substances* and managed to translate them into German. Still, he did not attempt to enhance the ionists' chemical thermodynamics by introducing Gibbs' ideas. As Ostwald admitted, following what Gibbs had written in the *heterogeneous substances* was complicated. He hoped that upon translating the memoir could be easier for him to approach Gibbs' work. Walther Nernst was the scientist who enriched the ionists' chemical thermodynamics, including some of Gibbs' concepts in his textbook *Theoretische Chemie vom Standpunkte der*

⁷⁵¹ van 't Hoff 1903, p. 21.

⁷⁵² A semi-permeable membrane is an imaginary device known as the equilibrium box. Van 't Hoff invented this thought experiment to study concentrations changes in gas mixtures or solutions. (van 't Hoff 1912, p. 54; Kipnis 1991, p. 215).

Avogadroschen Regel and der Thermodvnamik (first edition in 1893).⁷⁵³ There are several pages of Nernst's textbook devoted to Gibbs' ideas.

The controversy among the physicists regarding the use of one or the other approach to describe the thermodynamic phenomena led perhaps Arnold Johannes Wilhelm Sommerfeld (1868-1951) to write. "In method, there is a certain rivalry between cyclic processes and the method of thermodynamic potentials. The former is preferred for their immediacy, especially in engineering. We shall use the latter almost exclusively. They make possible a much shorter treatment, without any of the caprice attached to the artificially thought out cyclic processes".⁷⁵⁴ However, prominent physical chemists of the nineteenth and twentieth century, such as Gilbert Newton Lewis, found nothing artificial or inconsistent in treating cyclic processes and used them carefully in their research.

New scientific ideas are generated and incubated in a scientist's mind. Formulated in scientific laws and axioms and expressed in mathematical formulae, they are consequently tested and confirmed in the laboratory. Sometimes, nature takes responsibility for the approval or the rejection of the expected confirmation. But without a doubt, the new ideas survive whenever they become part of the teaching process in the classroom when they constitute a separate section in textbooks used by the students of a particular scientific field. This process is one of the most influential and prolific stages of the transfer of knowledge. Nernst included specific ideas of Gibbs' thermodynamics in his textbook, as mentioned before. The popularity of this textbook amongst physics and chemistry students was unprecedented. It became the regular textbook in physical

⁷⁵³ The book was translated in English from the fourth German edition (1895) by Lehfeldt, R. A. (Nernst, 1904).

⁷⁵⁴ Quoted in Truesdell, and Bharatha, 1977, p. 148,

chemistry until 1926, which was the publication date for its fifteenth edition. One of the main assets of the book appealing not only to chemistry students but also to students attending sciences other than physical chemistry was the efforts of the author to merge the two sciences of physics and chemistry that hitherto were developed independently of one another. Nernst noted in the introduction of his textbook: "And the essential contents of this [textbook] will invariably imply so much of chemistry as shall be indispensable for the physical investigator, and so much of physics as shall be indispensable for the chemical investigator; and in all of this the physicist must conduct himself as a specialist of physics, and the chemist as a specialist of chemistry".⁷⁵⁵

The merger had a name: Physical Chemistry, which was created as a particular branch of chemistry. Several pages of this textbook were devoted to Gibbs's ideas.⁷⁵⁶ The equilibrium of homogeneous and heterogeneous systems (p. 462), the simultaneous evaporation of the solvent and the dissolved substances (p. 483), the thermodynamic treatment of the dissociation reactions of gaseous substances (pp. 608-609 and 655-658), and most of all the phase rule with a short but rigorous proof were some of Gibbs' valuable propositions. Detailed examples of applications (pp. 609-630), and finally, the study of reactions equilibria and the calculation of the equilibrium constant using Gibbs' chemical potential (pp. 668-669) are prominent chapters in this textbook. At the same time, when Nernst propagated Gibbs' ideas in his textbook, Gibbs' original work was barely known in his country. The *heterogeneous substances* were distributed to the American students after his death. In the meantime, the interested scientists used the German translation.

⁷⁵⁵ Nrnst, 1904, p. xii.

⁷⁵⁶ Ibid.

After Nernst, several textbooks of physical chemistry in Europe and America contained on their pages topics referring to the phase rule and the chemical potential along with examples and applications. Two textbooks deserve to be mentioned. The first textbook, Modern thermodynamics by the methods of Willard Gibbs was written in 1933 by the British physical chemist Edward Guggenheim. This book was devoted to Gibbs' work on thermodynamics. Lewis and Randall were the authors of the second textbook, Thermodynamics and the Free Energy of Chemical Substances, published in 1923, which became a classic textbook in America. However, Lewis preferred to use Clausius and van 't Hoff's reversible cycles than Gibbs or Duhem's potentials. In 1903, Duhem circulated a textbook, Thermodynamics and chemistry that advocated recognizing Gibbs' work, this time in America. Duhem wrote this book devoid of advanced mathematics specifically for American students. He wrote in the introduction: "One of the objects which I had in mind when writing it was to make the work of J. Willard Gibbs known and admired; I like to think it will contribute to enhancing, within your active universities, the glory of your illustrious countryman".757 Duhem's introduction was a hymn to the author of the *heterogeneous substances* and the phase rule.

Unlike Gibbs, Duhem did not significantly affect the development of chemical thermodynamics formulated by the ionists, Nernst, and Gibbs. Duhem has gained eternity with the eponymy⁷⁵⁸ of two important equations: the *Gibbs-Duhem equation*⁷⁵⁹ describing

⁷⁵⁷ Duhem, 1903, p. iii.

⁷⁵⁸ Eponymy in science is the praxis of affixing the name of the scientist to all or part of his achievents as, for example, Copernican system, Avogardo's number, Hooke's law. Planck's constant or Halley's comet. It is a kind of eternal reward. In this way Scientists leave their signatures in history. Their names are mentioned in all scientific languages of the globe. For an analysis of the system of eponymy rewarded in various sciences and disciplines see Merton, 1957, pp. 642-644.

⁷⁵⁹ It is unknown when and by whom added the name of Duhem to this equation. Duhem had derived an analogous equation) in his first dissertation for two components, and later for the general case, when he

a fundamental law of solution and the *Duhem-Margules*⁷⁶⁰ equation. The Gibbs-Duhem equation allows us to calculate the chemical potential of a system under different conditions. It applies to a variety of chemical and physical processes. This equation is used today as a criterion for thermodynamic consistency. It finds some applications to phase equilibrium and chemical equilibrium, for example, as a test for the thermodynamic consistency of the vapor-liquid equilibrium, which is a powerful check on the apparent accuracy of the experimental data. It is also helpful in calculating the partial molar quantities of a binary mixture by measuring its composition, for example, the activity coefficients and the partial vapor pressures. The Duhem-Margules equation yields an elegant formulation of Raoult and Henry's laws for ideal and real solutions.⁷⁶¹ Also, Duhem's false equilibrium has survived in physical chemistry, although under different names, such as metastable or quasi-stable equilibrium state. Catalytic reactions may be

considered the effect of the masses of substances on his thermodynamic potential. (Duhem 1886, pp. 32-35 and 140-143). The same topic reappeared in his *Traité Élementaire de Méchanique Chimique Fondée sur la Thermodynamique* (1897b, Vol. 3, pp. 1-4); Miller 1963). Duhem thought that the total thermodynamic potential Φ under constant pressure and temperature was a homogeneous function of the first degree of the masses of the various substances of the system. Using Euler's theorem, he derived an equation analogous to Eq. (6.25) of chapter 6 of this dissertation.

⁷⁶⁰ Max Margules (1856-1920) was a mathematician, physicist, and chemist. In 1877 he joined the Central Institute of Meteorology and Geodynamics in Vienna as a volunteer. He received his Ph.D. in electrodynamics in Berlin. During his doctoral studies, he worked as a privatdozent. He lost this teaching position upon refusing to convert from Judaism. In 1882, he returned to Viena and the Institute of Meteorology. He focused on electro- and hydrodynamic problems and devoted his free time to physical and physicochemical problems. The Duhem–Margules equation and the Margules' Gibbs free energy equation exemplify his free-time devotion. In 1900 he switched to meteorology and developed his thermodynamic knowledge. In 1919 the Austrian Society for Meteorology awarded him the silver Hann Medal of Acknowledgement. Margules accepted the medal but rejected the money. Margules lived in extreme poverty and died from starvation (Wisniak, 2003).

⁷⁶¹ The Duhem-Margules equation, sometimes called Gibbs-Duhem-Margules equation, describes the relationship between the mole fraction N_i (expression of composition) with partial pressure P_i of the irth component of a liquid mixture expressed by the relation, $\sum_{i=1}^{n} N_i \text{dlogP}_i = 0$. Integration of this equation gives Raoult's law for the partial pressures of the mixture, whereas Henry's law results when the mole fraction of the solute goes to zero ($N_i \rightarrow 0$). and consequently N_i becomes equal to P_i . In other words, the concentration of the solute dissolved in the solvent, is proportional to the partial pressure of the vapor above the solution.

considered as specific examples of false equilibrium. Duhem's concept of the thermodynamic potential described above is absent in today's physical chemistry textbooks, overwhelmed by Gibbs' chemical potential and Gibbs' free energy, and in cases when the volume is constant by Helmholtz's free energy.

Duhem's four volumes of his *Traité Élémentaire de Méchanique Chimique, fondée* sur la Thermodynamique, and the Thermodynamique et Chimie influenced French physics and provided a whole generation of French physicists and chemists with their knowledge of chemical thermodynamics. However, as physical knowledge progressed during the twentieth century and a new physics emerged with novel discoveries, Duhem's chemical thermodynamics began to decline. Almost no one reads the four volumes of his *Traité élementaire* altogether, except perhaps Bancroft, who reviewed these volumes in three continuous reports. Bancroft's first comments on *Traité Élementaire* were enthusiastic. This enthusiasm moderated when Bancroft realized Duhem's chemical thermodynamics with the dozens of axioms and corollaries, and hundreds of equations could not apply to the laboratory. In evaluating the last volume, he wrote:

"These four volumes of Duhem's are monumental work and will be of immense service. On the other hand, it would be easy to overestimate their value. What we have is an exhaustive study of chemical equilibrium put into a mathematical form and expressed in terms of thermodynamic potential. This application of mathematics to chemistry is, unfortunately, more ornamental than useful. There are myriads of formulas, but very few can apply to any concrete case. The book is only a mathematical outline of theorems and mathematical equations that contain unknown functions. For the experimental theorist, the book is a joy and a sorrow, and a joy because it points out so much and a sorrow because it always stops short of becoming practical".⁷⁶²

Bancroft's reaction towards *Traité élementaire* reveals a significant cause for the poor reception of Duhem's theory. American physicists and physical chemists, for example, Joseph Ellis Trevor (1864-1941), professor at Cornell University, and Harry C. Jones (1865-1916), associate professor of chemistry at John Hopkins University, both disciples of Ostwald, showed the same ambivalent attitude towards the thermodynamics of the professor at the Bordeaux University. Others, as the physicist Edgar Bachingham (1867-1940), professor at Bryn Mawr College, had Duhem in high regard. On the other hand, Duhem received favorable criticism in Germany from Ostwald and Georg Helm, professor of physics at the Technical Institute in Dresden. Ostwald accepted Duhem's articles in the Zeitschrift fur Physikalische Chemie founded by Ostwald and van 't Hoff in 1887 and conducted most often reviews of Duhem's books in the same medium. Helm gave proper credit to Duhem's work. Helm and Ostwald developed their energetics as a new trend in physics, which had different content and aims from Duhem's energetics. Also, in a lengthy article included in a massive dictionary of chemistry, Planck mentioned the thermodynamic potential amongst the four most important consequences originating from the entropy function.⁷⁶³

With few exceptions, Duhem's work on thermodynamics received negative criticism in his native country. Duhem's work was not reviewed in French journals or mentioned in monographs in many instances. And this, although Duhem's work appeared superior to other major French articles and books published previously. For example, Louis

⁷⁶² Bancroft 1899, p. 82.

⁷⁶³ Jaki 1984, pp. 281-283.

Marcel Brillouin (1854-1948), professor of Mathematical Physics at the Collège de France, found no room in his two-volume monograph on elasticity to mention Duhem, whose competence in this field was well-known in the scientific community. However, the silence on Duhem's work in major French publications had deeper roots. It is hardly attributed solely to the incomprehensible formal language of his writings. Social reasons seemed to surpass the professional jealousy that made several contemporary French scientists unwilling to recognize the value of the contribution of potential competitors to the development of science. Academic politics, personal enmities, and scientific patronage, all arranged from behind the scenes, played their role in prohibiting Duhem's work to appear in French literature.⁷⁶⁴

After his death, the deliberate slighting of Duhem's work persisted in France. Surveys of the French science history, chapters in physics, mechanics, mathematics, and thermodynamics in dictionaries and monographs omitted any reference to Duhem or presented him as a fervent anti-atomist who has lost his cause once and for all. While Gibbs-Duhem equation and Duhem-Margules equation made their first appearance abroad and used for over one decade,⁷⁶⁵ they found no place in French literature.⁷⁶⁶ The Duhem-Helmholtz electromagnetic theory met the same negative attitude from French historians,

⁷⁶⁴ Jaki has given a detailed account on the reception of Duhem's work by the French community and abroad during his lifetime. Few French physicists, including Jules Tannery (1848-1910), Henri Poincaré (1854-1912), and Paul Langevin (1872-1946), gave support or at least were sympathetic to Duhem's publications. Others, like Le Chatelier, Perrin, Brillouin, Berthelot, and several others of lower caliber avoided citing Duhem's name in their work (Jaki 1984, pp. 279-302).

⁷⁶⁵ Jaki has provided a list of early textbooks and other writings, published abroad, in which the Gibbs-Duhem equation was mentined (Jaki, 1984, p. 308).

⁷⁶⁶ Yves-André Rocard (1903-1992), professor at the Sorbonne and director of the physical laboratories at the École Normale Superieure, seems to have been the first French author to refer in print to Gibbs-Duhem equation in his *Thermodynamique* in 1952 (Jaki 1984, p. 308),

Duhem's influence on the chemical thermodynamics of reversible processes had been overlooked. Still, his contribution to the thermodynamics of irreversible processes proved crucial for developing the new field of continuum mechanics. His contemporaries' interest in Duhem's generalized thermodynamics was relatively low, but it was not absent altogether. The first favorable reference to Duhem's work was made a year after his death, in 1917, by the French engineer Émile Jouguet (1871-1943).⁷⁶⁷ Jouguet had great respect for Duhem and his work and regarded him as the founding father of irreversible thermodynamics. He commented on Duhem's exceptional work on irreversible phenomena like viscosity, friction, and hysteresis not touched by anyone before. He appreciated the ability of Duhem to realize that the description of these phenomena required the development of a new physics, expressed in specific differential equations of motion of the first order corresponding to variables with or without inertia. Jouguet praised Duhem's energetics, but also, he was aware of Duhem's place in French science: "Duhem had a very peculiar place in French science: he had not taken part in the building up of recent theories, his method contradicted some habits, and his theories could be understood at the price of efforts which some people were not able to make".⁷⁶⁸ Ten years later, in 1928, another of Duhem's colleagues at Bordeaux University, the physicist Octave Manville, published a detailed analysis of Duhem's thermodynamics in two volumes, which remained the sole study for many decades on Duhem's theoretical physics.⁷⁶⁹ Duhem's colleagues and

⁷⁶⁷ Émil eJouguet was a graduate of the *École Polytechnique* and from 1920 to 1939 professor at *l'École des mines de Paris*. He had collaborated with Duhem at Bordeaux, and thus he was able to evaluate Duhem's physics and his overall theoretical achievements. Jouguet has created the theory of detonation waves with application to high explosives continuing his mentor's efforts on this subject. Duhem had considered the explosives as a side effect of the false equilibrium. Jouguet credited Duhem with 'having laid the theory of explosives on especially solid foundations (Jaki 1984, p. 305).

⁷⁶⁸ Quoted in Bordoni 2012, p. 245.

⁷⁶⁹ Manville 1928.

students made short analyses of his work in physics and mathematics during the decades of the 1920s and 1930s. Pierre Hubert, professor of physics at the University of Montpellier, Émile Picard (1856-1941), professor of mathematics at l'Ècole Normale Supérieur and Secretary of the Academie des Sciences, Jacques Hadamard (1865-1963), professor of mathematics at the University of Bordeaux, and several other physicists mainly from the provinces of France referred very often to Duhem's work.⁷⁷⁰

Duhem's work on thermodynamics for complex systems gained great impetus after the mid-twentieth century, especially in America, when physicists initiated studies concerning irreversible processes and the description of the complexity of real systems. Plasticity, viscoelasticity, creep, damage, phase transformations, magnetic and electric hysteresis were amongst the phenomena, which attracted the attention of physicists and material engineers that had their origin in Duhem's theory of non-reversible alterations Duhem's work began to be cited in relevant investigations concerning continuum mechanics.⁷⁷¹

Duhem's original ideas were instrumental to the development of the mechanics of the twentieth century. Some of his ideas were the normal variables of the state incorporated in thermostatics, the internal variables fully exploited in non-linear fields of mechanics, the internal degrees of rotation in the area of deformable solids, the notion of homogeneous functions in thermodynamics, and the notion of non-local continua in the field of continuum mechanics. The influential series of papers of C. Eckart on irreversible thermodynamics published in 1940 and 1948 brought some of Duhem's ideas on irreversible processes back to their existence. Clifford Truesdell devoted several pages

⁷⁷⁰ Jaki 1984, pp. 241-244 and 304-307.

⁷⁷¹ Truesdell 1952.

discussing Duhem's thermodynamics of irreversible processes. Focusing in particular on the Clausius-Duhem inequality, which is the mathematical expression of the second law of thermodynamics for irreversible processes, namely (1) heat never flows against a temperature gradient, and (2) deformation absorbs energy but cannot release it.⁷⁷² Also, references to Duhem's contribution to mechanics and related fields are scattered in various chapters of Gerard Maugin's book on continuum mechanics.⁷⁷³

In summary, Duhem's tremendous work in physical chemistry assisted a whole generation of French physicists and chemists, enriching their knowledge of chemical thermodynamics. Still, by the mid-twentieth century, it was utterly forgotten. On the contrary, Duhem's contribution to the development of the new field of continuum mechanics proved to be more fruitful.

Conclusions of Part II

The second half of the nineteenth century witnessed the rapid development of electrochemistry and thermodynamics. The new generation of electrochemists showed with clever experiments the existence of charged particles as the minuscule carriers of the electric current in galvanic and electrolytic cells. The fact that salt solutions conducted electricity was supportive to Arrhenius' theory of the electrolytic dissociation he presented in the second half of the 1880s. Furthermore, the investigation of the polarization of the electrolytic the electrolytic distorted the electrolytic that caused disturbing effects on the process of electrolysis and distorted the experimental results in electrical conductivity measurements offered the theoretical explanation of the phenomenon and thereby an effective remedy for the problem.

⁷⁷² Truesdell 1984, pp. 38-44.

⁷⁷³ Maugin 2014.

Gibbs and Duhem had built their thermodynamics on the second law of thermodynamics. Although Gibbs hesitated to reject the atomic theory altogether, both scientists considered the second law and entropy irreconcilable with atoms and molecules. Both characterized entropy as the building block of the second law.

Gibbs used entropy as an essential variable in his first two geometric articles in 1873, in which he described the properties of equilibrium systems in two- and threedimensional diagrams. Also, he used entropy to describe three-dimensional surfaces. Gibbs interpreted and determined - without a doubt - the critical point of the carbonic acid that Thomas Andrews has experimentally identified since 1869. Yet, Gibbs had not explicitly used entropy in his theoretical treatment of the various thermodynamic systems in his *heterogeneous substances*. Entropy entered indirectly in his analysis through his chemical potentials.

Similarly, entropy played no significant role in Duhem's generalized thermodynamics. Duhem, in his theoretical approach, employed analytical mechanics, whereas Gibbs relied on the algebraic methodology. This difference in their methodological approaches reflects the orientation of their thermodynamics. The study of irreversible processes, which was the main subject of Duhem's generalized thermodynamics, required Lagrange's analytical mechanics as a necessary tool to introduce time-dependent equations. Therefore, mechanics had a more comprehensive application for Duhem than for Gibbs. Duhem did not confine mechanics solely in his thermodynamic potentials. He extended its use in complex systems characterized by irreversible transformations. Gibbs used the chemical potential to a lesser extent, and the fundamental functions to study equilibrium processes. Duhem was trained as a physicist; however, he used examples from chemistry more frequently than Gibbs did to test his theories or to exert his polemic against atomism. Chemistry was the vehicle he employed to confirm his theory of false equilibrium. And through the false equilibrium, he built a new chemical theory on explosive reactions.

During the last two decades of the nineteenth century, a group of chemists, the socalled ionists, successfully transferred thermodynamics into chemistry. This achievement marked the birth of modern chemical thermodynamics. Although this theory was of limited scope, it appealed to chemists because of its simplicity and mild mathematical language. But most of all, it had a concrete orientation towards experimentation.

Gibbs did not participate in the transfer of thermodynamics to chemistry. However, after the translation of his essay *On the equilibrium of heterogeneous substances* in German and French and the use of some of his ideas, as the phase rule, by European and American chemists, Gibbs' theories gave a new impetus to chemical thermodynamics. Gibbs' ideas began to enter education and research and enriched the new discipline of physical chemistry. Gibbs' chemical potential and free energy (the ζ function) replaced the methods of analogies and the reversible cycles proposed by van 't Hoff. The chemical potential, the Gibbs-Duhem, and the Gibbs-Helmholtz equations are used exclusively to study the equilibrium of chemical and physical processes. The Gibbs-Helmholtz equation, the point of departure for a competitive international investigation to calculate chemical equilibrium from thermal data, was the beginning of the broad recognition of his work. The Gibbs-Helmholtz equation became one of the most recognized equations of chemical thermodynamics.

Duhem's prodigious work in thermodynamics was essentially forgotten for reasons discussed in the last chapter of this part. Duhem's thermodynamics did not leave any significant trace in today's textbooks of physical chemistry. Only two equations, Gibbs-Duhem and Duhem-Margules, remained in chemical thermodynamics as a blurred glimpse of his past great work. His efforts to unify physics and chemistry in the context of his energetics had no practical implication with few exceptions; it was left to Ostwald and the American chemists to achieve this goal by establishing a new discipline, the physical chemistry. Nevertheless, Duhem's energetics had an impact on the so-called *nonsensical sciences* many decades later.⁷⁷⁴ In the second half of the twentieth century, irreversibility and complexity became more generally interesting to physicists and engineers. Only then, Duhem's work began to appear in closely related studies.

⁷⁷⁴ The rather eccentric expression of the *nonsensical branches of mechanics* indicates fields of physics, mechanics, and electromagnetism. The list of these fields includes the so-called false equilibria, friction, viscosity, hysteresis phenomena, and electromagnetic theory of materials. These are precisely dissipative phenomena such as thermodynamically irreversible reactions, plasticity, viscoelasticity, memory effects, etc.
PART III. The double transfer of thermodynamics from physics to chemistry and from Europe to America

The transfer of knowledge between scientific disciplines, such as physics and chemistry, is common in modern times. The discipline of physical chemistry, an indispensable part of any Department of Chemistry curriculum, verifies this trend. Unlike the last and the present centuries, the diffusion of knowledge between the two sciences was very slow to negligible, at least until the end of the nineteenth century. Beginning the nineteenth century, chemists who prevailed in European science, particularly in France and Britain, had delineated the area of their research interests. Their research programs encompassed all matters exclusive to chemistry: chemical affinity and chemical equilibrium, determination of chemical composition, and physical and chemical properties of substances. Chemists neglected the thermodynamic theories and, in general, physics and physicists for reasons that will be examined in the following chapter.

The second half of the nineteenth century witnessed the advancement of electrochemistry and thermodynamics. Clausius' hypothesis for the electrolytic solutions was widely known amongst electrochemists and physicists. Clausius' application of the kinetics of gases to ions in solutions had already gained supporters and critics. Hittorf and Kohlrausch contributed significantly to expanding the electrochemistry founded by the great electrochemists of the first half of the century introducing innovations in experimentation to measure the velocity of ions in solutions, the percentage of the electric charge they transported in solution (transference numbers), and the measurement of the electrolytic conductivity.

Gibbs and Duhem expanded classical thermodynamics introducing the notion of potentials in the study of reversible and irreversible physical and chemical processes. Most importantly, these two physicists attempted to test their theories using experimental findings from chemistry that were available at the time. Although their theories were considered much too general to be directly transferred to experimentally investigated processes, Gibbs and Duhem's potentials and functions provided chemists with practical tools to evaluate affinity and establish criteria for equilibrium. Gibbs and Duhem's thermodynamics was too theoretical and too mathematical to attract chemists' interest to search for the treasures hidden on the pages of the memoirs of these two great theorists.

It remained for the ionists to transfer the thermodynamics into chemistry in a manner acceptable to chemists and thus achieve the interaction between physics and chemistry.

Chapter 9. Internal and external factors that favored or impeded the transfer of thermodynamics into chemistry

The nineteenth century witnessed three different, but closely related, developments that influenced the course of chemistry and facilitated or impeded, depending on the circumstances, the emergence of chemical thermodynamics in Europe: First, the increasing influence of organic chemistry on chemical research and education, especial in Germany and France; second, the transfer of the industrial activity from Britain to the European mainland that marked the beginning of the second industrial revolution in Belgium, France, and Germany; third, the development of thermodynamics and the way chemists received and accommodated its theories in their experimental work. Each factor had a distinctive effect on the development of chemical thermodynamics. At times, these factors had a combined (synergistic) effect increasing or decreasing the speed of its development and occasionally altering its direction.

Section 1. The domination of organic chemistry

In the mid-nineteenth century, the research interests of chemists in Europe had shifted to organic chemistry. Organic chemistry exhibited a dynamic development as a result of a series of changes that began in the decades of the 1830s and 1840s due to the research achievements of the founding generation of chemists. Namely, Jöns Berzelius in Sweden, Jean-Baptiste Dumas, Charles Adolphe Wurtz (1817-1884), Auguste Laurent (1807-1853) and Charles Frédéric Gerhardt (1816-1856) in France. Friedrich Wöhler (1800-1882), Robert Wilhelm Eberhard Bunsen (1811-1899), and Justus Lebig in the Germanic states. Organic chemistry assumed an explosive growth in the second half of the century with the

burgeoning industrialization of the European mainland along with the advancement of synthetic organic chemistry, and the development of the structure theory. The inventors of the chemical structures sought to organize the anarchy that existed in the recognition and classification of the thousand organic compounds synthesized in the organic laboratories or isolated from natural sources. The increasing knowledge to discern the internal arrangement of atoms within molecules went hand in hand with the new and powerful ability to synthesize known and novel organic substances. Amongst the influential contributors of the second stage of the development of organic chemistry were the German chemists Friedrich August Kekulé (1829-1896), Hermann Kolbe (1818-1884), Johann Friedrich Wilhelm Adolf von Baeyer (1835-1917), Emil Erlenmeyer (1825-1909), the British chemists' Alexander William Williamson, Edward Frankland (1825-1899), Archibald Scott Couper (1831-1892), the French, chemists Marcelin Berthelot, and Louis Pasteur, and the Russian chemist Alexander Mikhaylovich Butlerov (1828-1886).

For many years, organic chemistry had been an auxiliary science at the medicine service to prepare pharmaceuticals and other medical recipes. Academic organic chemists used to work at the German and French universities in medical schools even when organic chemistry began to acquire the reputation and stature of an independent discipline. The transfer of the organic chemistry institutions and research laboratories from the medical faculty to the school of philosophy took place in the second half of the nineteenth century. Even then, organic chemistry was a subordinate branch of inorganic chemistry. Most chemists preferred to work with inorganic materials because the methods of preparation and isolation of inorganic substances had been more accessible and more comfortable to handle. Few or no byproducts at all accompanied the formation of the target substances in the respective chemical reactions. Most inorganic compounds did not require intricate purification procedures, thus facilitating any subsequent determinations of their physical and chemical properties. Unlike inorganic compounds, the isolation and purification of natural and synthetic organic substances was a complicated process and occasionally unrealizable with current methods or produced with low yields of little value.

The process of organic chemistry as an independent discipline took place during the first half of the nineteenth century. Its dominance in the science of chemistry in Europe was completed after 1865 when first, organic chemists invented novel experimental techniques for effectual isolation and purification of organic substances. These experiments were crucial for the identification of isolated substances. The discipline of organic chemistry as an assertive discipline further progressed, first by the discovery of the elemental analysis conducted on an apparatus invented by Liebig in 1830;⁷⁷⁵ second, by new models of chemical education and research created in the form of the laboratory-based training of students, and third when autonomous chemical institutes built in the philosophical faculties of the universities.

Another significant role in the split of organic chemistry from other disciplines was the theoretical and experimental undertakings of these sciences that were diverse compared to those adopted by organic chemists. An example is electrochemistry, which was developing simultaneously with organic chemistry, and characterized by entirely different concepts, methods, and notations. Organic chemists did not use electricity in their synthetic methods, nor were they interested in deepening their knowledge in subjects like chemical affinity and chemical equilibrium. The great electrochemist Faraday was too preoccupied

⁷⁷⁵ See chapter 4, section 2, paragraph 2.2 of this dissertation.

with other matters to study the effect of the electric current on organic compounds. Organic synthesis (electro-synthesis) through electrolysis required selective control of the electric potential at the electrodes, which was not an easy task at that time. By the end of the 1840s, the organic chemist Hermann Kolbe employed the electric current to produce free radicals of very high reactivity.⁷⁷⁶ Chemists developed electro-synthesis by the end of the nineteenth century as an effective method for preparing industrial products.⁷⁷⁷

The pedagogical reform in German universities during the decade of 1830 allowed students for the first time to enter a research laboratory and perform experiments⁷⁷⁸—even conducting research combined with lectures anticipated by the university curriculum.⁷⁷⁹ This laboratory-based training attracted a large scientific clientele for chemistry. It consisted of chemistry students and students from other disciplines, especially students from medicine and pharmacy, who considered the training in the chemical laboratories a vital factor to promote their professional careers—for example, medical students who decided to undertake studies in physiology. A sizeable segment of clientele for chemistry was students who sought careers outside the traditional professions at the universities and technical schools, or teachers in gymnasia, and colleges, for example, in mining, agriculture, or industry.⁷⁸⁰ This elusive clientele for chemistry increased dramatically after

⁷⁷⁶ Kolbe, 1948 and 1949; Rocke, 1993, pp. 182-184. An example of electro-synthesis is Kolbe's electrolytic process of the decarboxylative dimerization of two carboxylic acids (or carboxylate ions). For a short story of the organic electrosynthesis, see Baizer, 1989, pp. 172-175.

⁷⁷⁷ Baizer, 1980; Cardoso, 2017.

⁷⁷⁸ In France, this process was much slower due to the high degree of centralization of the French academic system.

⁷⁷⁹ Before the start of the laboratory-based practice, the institutionalized academic laboratories were for the personal research of professors and the preparation of lectures and demonstrations. Two to three students might be allowed to work there, usually selected through patronage. For the development and the performance of laboratory-based instructions in French and German universities, see Rocke, 1993, pp. 26-34; Levere, 2001, pp. 121-135.

⁷⁸⁰ For the chemistry's clientele see, Turner, 1982, pp. 139-157.

1865 when the industrialization of the European mainland began to flourish, and the enthusiasm showed for studies in chemistry was a good reason for the establishment of the second-generation institutes in organic chemistry. Students enrolled in chemical institutes looked at the chemical industry as a significant employment market during the nineteenth century.

Consequently, this laboratory-based education acquired an international reputation. By the mid-nineteenth century, a large number of students from Europe and abroad, especially from America, flocked into the laboratories of Wöhler's at Göttingen,⁷⁸¹ Liebig's at Giessen,⁷⁸² and to a lesser extent at the laboratory of Bunsen located first at the University of Marburg and later at the University of Heidelberg.⁷⁸³ The influx of students from abroad did not surprise the German Professors since there was no such practical training in Britain and America. The German laboratories were the only outlet for international students to learn their craft. For example, the Royal Institution was an excellent center for chemical studies in London but did not provide practical classes.

The building of second-generation chemistry institutes in German states fostered the scientific leadership of Germany in organic chemistry. It came to dominate German science until the eve of World War I.⁷⁸⁴ Furthermore, the foundation of the second-

⁷⁸¹ Wöhler used to acknowledge in his publications the names of students who showed independence, persistence and originality in their work. In some cases, the student allowed to publish with his name alone (Rocke, 1993, p. 19).

⁷⁸² Liebig insisted that all students in his chemical laboratory spend an entire semester working all day every day in the laboratory (Rocke, 1993, p. 22).

⁷⁸³ Bunsen ended his career as an organic chemist in 1841 and never returned to this profession when he thought that organic chemistry lost its experimental orientation and became theoretical. In contrast to Wöhler and Liebig, Bunsen never founded a research school. He was indifferent to skillful students and showed interest only for beginners (Rocke, 1993, p. 25).

⁷⁸⁴ The establishment of the chemical institutes in German universities began before the flourishing of the German chemical industry. However, they were small with cheap facilities, low official budgets, and rarely accepted students for training like Liebig and Wöhler. These two chemists were the exceptions in this chaotic situation for organic chemistry. Most of the first-generation institutes became obsolete after 1866,

generation institutes coincided with the age of classical organic chemistry. Chemists used valence and structure theories to resolve practical issues related to identifying and classifying the ever-increasing number of organic substances that tormented organic chemistry and afflicted organic chemists for about half a century. Structure theory prevailed in all previous models⁷⁸⁵ proposed to classify the vast number of substances, either isolated from plants and animals or synthesized in the laboratory. Structure theory elucidated molecular formulae for carbon compounds and organized them into two broad categories of aliphatic (chain) and aromatic (ring) compounds. The consensus amongst organic chemists for the dominance of previous classification models and gave way to prolific experimentation.⁷⁸⁶ Synthetic organic chemistry⁷⁸⁷ benefited from the structure

and the demand for trained industrial chemists led to the emergence of second-generation chemical institutes. However, the transition from classical chemistry to modern chemistry around the turn of the century required a reformulation of research methods, training, and organization of the chemical institutes. These changes led to the formation of third-generation institutes for chemistry. For the development of the German academic institutes in 1866-1914 and their impact on the development of organic chemistry, see Johnson 1985, pp.503-510.

⁷⁸⁵ Several authors review the various classification theories proposed by French, German, and British chemists and report the fierce quarrels between German and French chemists, which sometimes reached the limits of chauvinism, especially during the Franco-Prussian war. See, for instance, Rocke, 1993, chapters 3, 4, 6-8; Fisher, 1973 and 974; Levere, 2001, Chapters 8 and 11.

⁷⁸⁶ Unlike organic chemistry, inorganic chemistry had not any relation with structure theory. Inorganic compounds formed ionic crystals held together by electrostatic forces, which disrupted upon dissolution in water. Therefore, classical organic methods of analysis were fruitless for the inorganic substances, leading thus to erroneous structures. The physical chemistry theory of ionic dissociation proposed in the 1880s introduced the concept of ions and broke with distinct molecules. This interpretation opens the way for the formulation by Alfred Werner (1866-1919), the coordination chemistry that was the corresponding structure theory of the inorganic substances.

⁷⁸⁷ The idea of organic synthesis dates back to 1828 when Friedrich Wöhler synthesized for the first time an organic substance (urea) from an inorganic one (ammonium cyanate). This synthesis has considered a first step to freeing organic chemistry from the mysterious vital force. To others, this reaction was the link between organic with inorganic chemistry. However, contemporary chemists doubted this discovery claiming that the ammonium cyanate used by Wöhler had been prepared from cyanides, manufactured from animal materials. Hermann Kolbe and Marcelin Berthelot, who effectively synthesized organic compounds from inorganic materials, were the chemists who had substantiated the efficacy of organic synthesis. Kolbe synthesized acetic acid from inorganic carbon and water, while Berthelot synthesized formic acid from carbon monoxide (Kolbe, 1993, p. 241). Also, Berthelot prepared methane, ethylene, and acetylene from inorganic materials (passing crude coal gas through an iodine solution). In the second step,

theory because of the tremendous predictive capacity of the latter concerning the synthesis of new organic compounds. Thus, whereas in 1860, there existed some 3.000 carbon compounds, by 1899, this number increased to 74.000, with millions more still open to investigation.⁷⁸⁸ Also, the application of structure theory required pure substances with the correct stoichiometric constitution, which in turn dictated the development of efficient analytical techniques, as noted above.

The remarkable growth of organic chemistry manifested on several quantitative indicators, such as the number of academic and industrial positions occupied by organic chemists, the ever-increasing enrollment of students in organic chemistry institutes, the appearance of new organic chemistry journals. The number of research papers published in organic chemistry was far more than that in any competing discipline.⁷⁸⁹ As a result, organic chemistry dominated German education and research and thus attracted the interest, not only of the German students but also of students from abroad.⁷⁹⁰ The keen interest of chemists in the powerful ability to synthesize novel organic substances, combined with the innovative theoretical investigations on taxonomy and molecular structure had weakened their attention to the old problems of chemical affinity and chemical equilibrium.

The dominance of organic chemistry through the more significant part of the nineteenth century retained the boundaries created between chemistry and physics since the scientific revolution. Some early endeavors to explain stable chemical combinations

alcohol from ethylene and acetylene, formic acid, aldehyde, and benzene from acetylene (Armstrong, 1927, pp. 158-160). ⁷⁸⁸ Johnson, 1985, p. 504

Johnson, 1985, p. 504

⁷⁸⁹ Rocke, 1993, pp. 2-3.

⁷⁹⁰ Jones, 2012, pp. 15-16.

and the feasibility of chemical reactions using physical methods were often controversial and ineffective. Affinity either defined by physical terms (Newtonian type of attractive forces, electric forces) or became the physics subject. Physicists used statistical mechanics' mathematical language to formulate affinity at a microscopic level or particular physical methods.⁷⁹¹ The genesis of chemical thermodynamics and the new discipline of physical chemistry in the 1880s brought about a link between physics and chemistry. As a unique domain of investigation, physical chemistry established general laws for chemical processes and introduced novel quantitative methods and experimentation.

However, the transition from general chemistry to physical chemistry was arduous to incorporate mathematical expressions and the conviction that chemistry should function as a theoretical discipline. The task was not easy. The leading founders of physical chemistry (Ostwald, van 't Hoff, and Arrhenius) had to battle for social and institutional support with well-entrenched organic chemistry over the next two or three decades. Organic chemists resented having their lovely science depicted as a mere compounding of novelties. They were not prepared to accept or even share their laboratory-oriented values with physical chemists themselves. As a result, the continuous growth of organic chemistry during the second half of the nineteenth century and the beginning of the next, particularly in Germany and Britain, was a severe obstacle to developing other sub-disciplines of

⁷⁹¹ The German-British physicist Franz Arthur Friedrich Schuster (1851-1934), a professor of applied mathematics in Manchester, presented in 1884 a dissociation theory of gases subjected to an electric discharge in vacuum tubes. J.J. Thomson) aware of these experiments and, in collaboration with Schuster, performed several experiments with diatomic gases, such as nitrogen, hydrogen, and oxygen. He concluded that the decomposition of the gaseous molecules did not depend on the current of discharge. Still, it was a consequence of the chemical affinity, that is, how strongly did the atoms bind within the molecules. Furthermore, Thomson contended that chemistry was unable to explain affinity of bodies. He believed that physics was best suited to resolve this great question (Petit, 2013, pp. 214-217 and 220-221). The ionists, on the other hand, saw physics as a helpful tool for the advance of chemistry (see Chapters 10 and 11 of this dissertation).

chemistry as physical chemistry. Usually, the hegemony of a single discipline impedes the progress for disparate disciplines and sometimes could hinder scientific progress in general. Organic chemistry had procured strong roots in America, as well. The transfer of organic chemistry to America had commenced gradually since the beginning of the second half of the nineteenth century with ambassadors the American students who had trained in the research laboratories of Wöhler, Liebig, Bunsen, Kolbe, Fischer, and other great organic chemists.

Organic chemistry benefited when industrial activities were transferred from the British isles to the rest of Europe, the so-called second industrial revolution.⁷⁹² Organic chemistry provided a large body of organic materials, obtained either from nature (e.g., gelatin, fats, collagen, sugars) or prepared in the laboratory, such as dyes, pharmaceuticals, and other products of the expanding chemical industry.⁷⁹³ To satisfy the need to obtain synthetic materials on a large scale, chemists had to reconsider vital questions concerning the percentage of yield and cost per unit material. Answers to these questions revitalized the old interests in reversibility and spontaneity of chemical reactions. Solutions to these problems required radical intellectual changes and innovative approaches. The following section deals with the relationship between the development of organic chemistry and the industrial production of chemicals during the nineteenth century until the Great War of 1914-1918.

⁷⁹² Kranzberg, 1982, pp. 209-230.

⁷⁹³ Sherwood Taylor, 1957, pp. 228-274.

Section 2. Industry and chemistry

The first industrial revolution occurred in Britain in the period between 1760 to sometime between 1820 and 1840. It was characterized by the transition from the land manufacturing processes and production methods to machines, iron production processes, the increasing use of steam power, and the rise of the development of the factory system. Technology entered industrial production, although not in an organized and scientific manner. Technology relied basically on studies regarding various factors determining production processes, construction of machines (e.g., textile machinery. paper machines, machine tools), methods used by inventors and skillful apprentices, and sometimes by the entrepreneur himself. The adopted scheme for these production activities depended on improvised methods, such as trial and error. Trained engineers from middle and higher education institutions (technical schools and universities) made their appearance during the last quarter of the nineteenth century. The results were impressive in any event, especially in the construction of steam engines and machinery, transportation achievements (locomotives, canals, waterways, roads), and the mechanization of textile production.⁷⁹⁴

Concerning chemical manufacturing, the industry of inorganic materials prevailed during the period of the first industrial revolution. The manufacturing of alkalis, mineral acids, and bleaching powders constituted the most significant materials of the period. The alkali industry (potassium carbonate, sodium carbonate, ammonia soda, caustic soda) and bleaching powders found importance. The growing textile industry, and later in the 1830s, the glass industry both demanded new and better alkalis. The acid industry tailored to the production of sulfuric acid had several applications, mainly in the manufacturing of other

⁷⁹⁴ The bibliography of the first and second industrial revolution is quite extensive. For the first revolution, see for instance Allen, 2009, pp. 233-275.

inorganic chemicals, such as sodas, metal sulfates, and bleaching agents (chlorine, calcium hypochlorite), acetic acid, nitric acid, and other mineral acids. The manufacturing of various chemicals used in several metallurgical processes, such as extracting pure metals from minerals and ores or producing cast iron and steel, was another branch of industrial activity related to chemistry. The metallurgical industries expanded vastly during the first industrial revolution. However, the change in methods was slight compared with the significant advances in the second half of the nineteenth century during the second industrial revolution when science entered industrial production.

The second industrial revolution signified the industrialization of continental Europe. France, Germany, and Belgium were the first countries that received the benefits of the first industrial revolution transferred from the British isles. It began around 1860 and concluded at the threshold of the war of 1914-18. During this period, the relationship between science and industry changed dramatically, especially during the last two decades of the nineteenth century. The industry started exploiting the inventions.⁷⁹⁵ Research industrial laboratories were components in the organizational plans of the firms.⁷⁹⁶ Scientists on a salaried permanent basis replaced the consulting scientists and individual scientific entrepreneurs. For instance, chemists replaced foremen and managers as the directors of the process of production. The link between the companies and universities and technical schools of mid and higher caliber strengthens: First, by cooperations with outstanding academic research chemists, usually leading professors, through contracts; second, by engaging postdoctoral fellows to work for one or two years at the university

⁷⁹⁵ Rosenberg, 1984, pp. 231-250.

⁷⁹⁶ Perusal of the historiography reveals about a dozen of titles that refer to industrial research laboratories. The following references provide extensive information about this topic: Beer, 1958; Meyer-Thurow, 1982; Homburg, 1992; Marsch, 1995; Reinhardt, 1998, pp. 239-260.

research laboratories on research projects related to the company's production problems; third, by pressing the universities and technical schools to organize their curriculum in such a way as to include specific industrial training. The triangle industry/research/education worked satisfactorily for the leading European industrial countries. However, the industrialization of these countries acquired different traits and forms depending on the social and institutional conditions prevailing in each country.⁷⁹⁷

Before 1850, the organic chemistry industry was in its infancy. Some natural products were isolated and purified, and very few new compounds were synthesized, primarily in academic research laboratories and small private laboratories by individual chemists and other inventors. The chemicals were produced in small quantities with processes that remained the same for years, and thus they could be carried out by skillful craftsmen without any previous specific training. The mutual benefits of organic chemistry and the chemical industry became apparent when complicated substances were produced in large quantities. Industrial areas of mass production like the textile industry, steel industry, and the manufacture of products of the twentieth century (petrochemicals, rubberlike products, automobiles, etc.) needed chemicals such as dyestuffs, drugs, explosives, plastics, and the like. The chemical industry's expansion was impressive, particularly in Germany and later on the other coast of the Atlantic. The rise of industrial organic chemistry coincided with the synthetic dyestuffs industry between 1860 and 1880 and the synthetic drug industry, which did not begin before 1880. Mass production chemicals required different organizational processes. More skillful personnel of well-trained chemists, more effective chemical methods for the synthesis of new substances or

⁷⁹⁷ Shinn, 2001, pp. 133-153; Homburg et al., 1998, pp. 9-120.

chemicals already in nature, upgrading the instrumentation, and the innovation of the infrastructure, The research organization in the most important chemical plants constituted basically of three small units were separated from the production performing specific tasks of scientific and technical nature. These were the unit for the analysis of raw materials, the unit for the quality control of the final product, and the unit or the research laboratory, the heart of the factory.⁷⁹⁸ There, chemists conducted scientific investigations for concrete research projects involved in discovering new products of commercial interest. Organizational research models emerged during the last two decades of the nineteenth century and were adopted by the most successful German, British, and French chemical industries.⁷⁹⁹ This research activity in major firms stimulated a market whereby knowledge of organic chemistry was appealing. Chemists were employed heavily in well-defined positions within the research structure of the company, ranging from the chemist as analyst and sometimes as a manager to a well-trained research chemist.

Did the industrialization of science have an impact on the development of chemical thermodynamics? Was it recognized by the founders of chemical thermodynamics the necessity of applying their knowledge to problems of industrial interest? Could the ionists' experimental tools be turned into industrial use? Why did European and American companies seek to employ the first and later generations of the ionists? In its first steps, chemical thermodynamics found a non-fertile ground to thrive due to the overwhelming

⁷⁹⁸ Today, the nineteenth century industrial research laboratory turned into the R&D Department, with multitasking undertakings related to developing new services or products or improving existing services or products. As in the industrial research laboratory, the Research and Development section of the company constitutes the first stage of the development of possible new services or production processes. The R&D department is staffed with engineers or industrial scientists (chemists, physicists, biologists) or even a mixture of both experts.

⁷⁹⁹ Companies as AEG, BASF, Hoechst, and Bayer in Germany, the United Alkali Co, in Britain, du Pont, Eastman Kodak, General Electric, and Westinghouse in America are mentioned as examples (Homburg, 1992, p. 103).

influence of organic chemistry and, to a lesser extent, inorganic chemistry.⁸⁰⁰ The introduction in industrial applications was a chance for the new science to demonstrate its potential for innovations and escape from the sway of organic chemistry. The involvement of physical chemists in the industry would foster the new discipline of physical chemistry in Europe and America. Physical chemistry may not be considered as profitable for the invention of new products as organic chemistry, it has, however, the potential to suggest more efficient methods and processes to obtain better yields and low costs (getting larger profit with the same cost or getting the same yield at a lower cost).⁸⁰¹ Problems involving the effect of concentration, temperature, volume, and pressure upon the solubility of substances, the yield of chemical reactions, the minimization, and the separation of byproducts are common problems in the industry. Almost all the procedures involved in the *unit operations* (see below) belong to the arsenal of physical chemistry.

The ionists, especially Ostwald, quickly recognized the benefits that the newformed discipline of physical chemistry could obtain upon integrating industrial production with its theories. Ostwald claimed that "good practice is founded on good theory, and when a man's theory does not have a good practice, it is because his particular theory is a bad or insufficient one, not because he has a theory".⁸⁰² The principal leaders of physical chemistry, Nernst, Haber, Ostwald, Van 't Hoff, were involved in industrial work by the turn of the century.⁸⁰³ Ostwald, in 1894, tried to establish a link between physical chemistry

⁸⁰⁰ On the contrary, chemical thermodynamics benefited by the development of electrochemistry (see below).

⁸⁰¹ Bancroft, 1899, pp. 1102-1104; Rittman, 1914.

⁸⁰² Quoted in Donnan, 1909, p. 215.

⁸⁰³ Servos, 1990, p. 69. Gilbert Newton Lewis in an article published in 1905, he reviewed several technical achievements of physical chemists. He described attempts to to construct fuel cells. One reads, "Many attempts have been made to construct a galvanic cell, which will consume at one electrode the oxygen of the air, at the other some kind of fuel (coal or carbon monoxide) (Lewis, 1906, pp. 893-894). Historians

and industry by helping the foundation of the *Deutsche Electrochemishe Gesellschaft*.⁸⁰⁴ In 1900, Ostwald applied his knowledge in catalysis to a large-scale industrial chemical project concerning the synthesis of ammonia by catalyzing the reaction of hydrogen and nitrogen gases with heated iron wire. He patented the process and made connections with the industry to develop this method commercially.

Nonetheless, the project did not have the success that Ostwald hoped for. Technical problems resulted in an unprofitable small yield of the produced ammonia.⁸⁰⁵ A year later, Ostwald returned with a new synthetic approach of industrial interest. This time, he went through the catalytic oxidation of ammonia to nitric acid.⁸⁰⁶ With his private assistant Otto Eberhard Herrmann Brauer (1875–1958), Ostwald oxidized ammonia with air in the presence of platinum wire acting as a catalyst. Ostwald patented his discovery in 1902. After the small-scale experiments in the laboratory, in 1904, Ostwald and Brauer proceeded to a large-scale production developing a pilot plant. This plant was brought into operation in 1906 and fully proved the feasibility of the process. A larger-scale plant was then designed and built, and by the end of 1908 was producing some three tons of 53 percent nitric acid per day. Several of Ostwald's successors strove to prove his method to increase the yield of nitric acid. Progress was slow for a time, and numerous experimental plants failed. Still, the outbreak of war gave a much greater urge to the project since nitric acid was the basic material for manufacturing explosives needed in the war. By 1916, the picture

know that the first fuel cells were invented by William Grove in 1838. The first commercial use of fuel cells came more than a century later following the invention of the hydrogen–oxygen fuel cell by Francis Thomas Bacon (1904-1992) in 1932. The alkaline fuel cell, also known as the Bacon fuel cell after its inventor, has been used in NASA space programs since the mid-1960s to generate power for satellites and space capsules. ⁸⁰⁴ Servos, 1990, p. 68.

⁸⁰⁵ Ostwald, 2017, pp. 296-299.

⁸⁰⁶ Ibid, pp. 299-305.

had changed radically. The industrial chemists increased the yield of the reaction by improving the effectiveness of the catalyst.⁸⁰⁷

Not the ionic theory of solution, but electrochemistry developed by the ionist Walther Nernst, one of the most talented disciples of Ostwald, was the specialty that interested the most in the industrial business with light bulbs. The efficiency of the ionic conduction in the solid filament of an incandescent lamp was the subject of intensive research that interested the competing companies of General Electric (GE) in America and the Allgemeine Electrizitatsgesellschaft (AEG) in Germany. The most effective material for the filament or the conduction medium was the primary target for both companies.⁸⁰⁸ Nernst himself patented, in 1897, his light bulb by using sticks of specially prepared ceramic and showed that his bulb could produce light 50% more efficiently than the carbon filament used previously.⁸⁰⁹

However, the success of elaborating a connection with industry before World War I was relatively meager. Even though the founders of chemical thermodynamics and their disciples were experimenters and their research programs and publication practices were suitable for industrial applications, they found it very difficult to carry over into the industry. It often proved very difficult to convert scientific knowledge into technology than anticipated. For example, the process of the ionic conduction in solution was practically impossible to apply as such to the ionic conduction in the solid-state or in the gas phase (through the electric discharge in vacuum) that interested most manufacturers of batteries and light bulbs. The entry of physical chemistry into the industry was not quick and smooth.

⁸⁰⁷ Hunt, 1958, p. 133.

⁸⁰⁸ Wise, 1983.

⁸⁰⁹ Wise, 1983, p. 12. Diana Barkan provides detailed information about Nernst's efforts to invent his light bulb (Barkan, 1999, pp. 91-109).

Ionists penetrated the industry very slowly, and after transforming their scientific practice to harmonize with the working conditions, they found in the industry. Closer liaisons between physical chemistry and industry have interwoven during the interwar years. Several causal conditions inside and outside Academia had to be overcome to allow the entrance of physical chemistry into the industry and to facilitate the industrial careers of physical chemists. Some of them were: (a) The reluctance of most academics in chemistry to implement applied training for students in higher education institutions. This attitude conflicted with physical chemists who found it necessary to link physical chemistry with industry. They proposed specific programs where chemists could acquire knowledge in mathematics, physics, laboratory training for large-scale processes emulating those occurring in the industry, and other engineering practices; even courses in economics and management had suggested.⁸¹⁰ However, these academic trends did not wish to degrade the core of the curriculum courses concerning scientific chemistry.⁸¹¹ At its extremes, this disagreement has led some universities to establish well-implemented education programs and laboratory training that paved the way to establishing a new discipline, chemical engineering (examples are the MIT in America and UCL in England). (b) Chemists in Academia hesitated to accept work offers in the industry, where the working and research conditions were completely different from those they had as university scholars. They found or thought they found elements, such as tools or techniques, and processes of low value to their previous research at their laboratories. Some found that the institutionalization of patent rights restricted the publication of their research results and prohibited their identities as contributors to science. They thought they had to abandon the

⁸¹⁰ Bancroft, 1899; Donnan, 1909; Walker, 1905.

⁸¹¹ Bancroft, 1899, p. 1105; Donnan, 1909, p. 277.

research program they had trained in and adopt a new way of looking at the scientific problems. Thus, many academics insisted on keeping their academic positions and working part-time in the industry. Others considered another form of co-operation with the industry by implementing industrial research programs at the university or acting as consultants. This attitude changed slowly with the establishment of the industrial research laboratories. (c) Chemical thermodynamics and physical chemistry later confronted a severe obstacle: the dilute (ideal) solutions. The whole chemical thermodynamics, almost all relevant scientific papers published every year, dealt with solutions containing less than one to two percent of the dissolved substance. This limitation would lead to inaccurate conclusions in quantitative calculations in real solutions using the hitherto principles of chemical thermodynamics. Practically, the quantitative directions of chemical thermodynamical could not be found application in technical works.

The situation changed drastically after the war of 1914-18 when the government policy changed towards the enforcement of academic-industry relations at a national level. The cessation of raw materials and industrial products from Germany during the war and the subsequent destruction of the German industry created a severe shortage of raw materials for the American industry and commodities from the American market. As a result, the American government was forced to promote through financial assistance (grants from the Research Council) the direct research work to benefit industry and the subsequent industrial manufacturing of raw materials.⁸¹² The latter could have been obtained either by using methods invented in Germany, for example, the Haber-Bosch process for ammonia manufacture, or by contributing to the development of new materials

⁸¹²Roberts, 1997, pp. 301-302.

and new production methods in the American research laboratories in particular raw materials from petrol. The petrochemical industry that flourished in America more than anywhere else was one of the leading causes that favored the recognition and consolidation of methods and processes of physical chemistry in industry and led to the establishment of chemical engineering as a separate discipline from electrical engineering and other branches of engineering. Chemical engineers adopted most of the basic principles and methodologies of physical chemistry.⁸¹³ Furthermore, the transfer of the ionists' chemical thermodynamics to America by the turn of the century and the subsequent development of physical chemistry by the American chemists allowed the conversion of the tide and the application of the ionists' solution theory to higher concentrations with acceptable accuracy. This matter will be discussed in the following chapter.

2.1 Mass production and the emergence of chemical engineering

By the end of the century, when the increase in production became a crucial factor, the process of producing commercially potential new organic substances (dyestuffs, drugs, etc.) in the research laboratory was inadequate. The small-scale laboratory processes had to transform into large-scale production processes of the plant. Furthermore, the conversion of laboratory processes to plant scale required a different plant design and operation. These new activities were distinct from discovery and investigation in the research laboratories. They needed scientists with mixed qualifications of a chemist and an engineer, in other words, a chemical engineer. The historiography for the emergence of the new discipline affirms that chemical engineering developed in Britain and the United States around 1900.

⁸¹³ Donnan, 1936, pp. 73-74.

However, the origin of the fundamental concept of *unit operations*, which would differentiate chemical engineering as an independent discipline from chemistry, is still open to discussion.⁸¹⁴ Practical problems of exploiting vast oil fields and exploration for petrochemicals production played a decisive role in the genesis of chemical engineering in the US.

On the other hand, British historians claimed that the conceptual framework of chemical engineering, the *unit operations* first introduced by George E. Davis (1850-1906), an English consultant who called himself a chemical engineer.⁸¹⁵ The subject of unit operations became widely known in a series of lectures given in Manchester Technical School in 1887 and described in his two volumes *Handbook of chemical engineering*, which was published in 1901. Clive Cohen had tried to reconcile the different views when he suggested that chemical engineering developed in the US, while its ground concept was a British brainchild.⁸¹⁶

The content of Davis' lectures was a plant manufacturing catalog. It described the machinery (boilers, heat exchangers, pressurized vessels, instruments to measure and control pressure and temperature) and guides for their applications, various industrial methods and processes, design of plant sectors, and other pieces of industrial interest. Consultants and early chemical engineers had the opportunity to select the parts of the plant from this catalog, which they believed would be best to meet their needs or the needs of their clients. The catalog in his Handbook included chapters, such as fitting a technical laboratory, materials used in plant construction, production and supply of steam, and

⁸¹⁴ Cohen, 1996, pp. 172-174; Divall and Johnston, 1998, pp. 199-214.

 ⁸¹⁵ For Davis' biographical sketch, see Cohen, 1996, pp. 174-176.
⁸¹⁶ Cohen, 1996, p. 175.

chapters on separating soluble from insoluble materials, evaporation, and distillation others. This latter group of chapters in the second volume of the handbook has led writers to attribute the concept of unit operations to Davis.

Arthur Dehon Little (1863-1935), an engineering consultant, used first the term unit operations in 1915. He defined unit operation as discrete unitary processes operating sequentially to obtain the final industrial product. These processes employed in chemical manufacturing were physicochemical and mechanical conduct, such as distillation, roasting, filtering, and condensation. The basic operations were further enriched with additional steps, such as grinding, mixing, separating solids, crystallization, heat transfer procedures, electrolysis, and other processes. At the same time, the order and the total number of units may differ from one product to another and the manufacturing process. Plant operations had extended in the production of raw materials, the exploitation of intermediate substances, and the manufacture of consumer goods. Plant operations applied particularly to industrial sectors, such as coal, petroleum, minerals, metallurgy, chemical and cellulose industries, food production, breweries, and the design and construction of apparatuses.

Furthermore, the concept of unit operations that developed in Britain and America from 1880 onwards (although not at the same time and the same pace) was the medium that reconciled the controversy between supporters of pure research in chemistry and those who favored the applied chemistry. Reconciliation was realized through the modification of the teaching programs of the British and American universities and the cooperation between the higher education institutions and the chemical industry. The supporters of pure chemistry did not finally deny an industrial link, although they believed that fundamental principles of pure science (physics, chemistry) could have better advanced industrial performance. In contrast, the supporters of applied science insisted that a pure chemical engineering approach would better serve the future of the industry.⁸¹⁷

In contrast to Americans and Britons, the process of unit operations failed in Germany. The petrochemical industry and large coalfields were negligible in Germany to allow a combined mechanical and chemical operation. The severe restrictions in raw material resources forced the German chemical industry to solve the problem by synthesizing necessary materials, such as ammonia, acetone, synthetic rubber, in contrast to the US industry, which obtained the required raw materials from petroleum, the well-known petrochemicals. On the other hand, the Germans were obsessed with dyestuffs chemistry. Complex chemical syntheses dominated the dyestuffs and pharmaceutical industries. As a result, the industrial practice had organized around specific industrial products and their manufacturing processes. Chemical plants were designed and maintained by a combination of chemists and mechanical engineers with a strict division of labor. The tasks of chemists and chemical engineers were distinct in the German industrialists considered chemical engineering as an unnecessary hybrid.⁸¹⁸ They thought that pure chemists were the expert to focus their research on

⁸¹⁷ The rivalry between Arthur Noyes and William Hultz Walker (1869-1934) at the Department of Chemistry of Boston University regarding the scientific orientation of MIT (known as Boston Tech until 1916) is an example of the atmosphere encountered in designing and organizing the educational program in American universities. Noyes, who regarded MIT as a vehicle for a science-based university with graduate school directed towards basic research, lost the battle due to the popularity of chemical engineering over the chemistry degree. Noyes left Boston University, and MIT flourished as an applied science school (Servos, 1980, pp. 534-535). A similar situation happened at the Central institution in London, although not the result of conflict between two opposing views of scientific orientation. Henry Edward Armstrong's (1848-1937) chemistry courses that involved scientific methods and approaches were abandoned in favor of John W. Hinchley's new unit operations course (Cohen, 1996, p. 182). Unlike Walker and Hinchley, Noyes and Armstrong did not have any significant industrial experience, while their research interests focused on pure science.

⁸¹⁸ Hougen, 1977.

substances, their properties, and their chemical transformations. In contrast, they considered chemical engineers as the technical apparatus through which the various processes invented by chemists could become operational under both chemical and economical optimum conditions.⁸¹⁹

The establishment of chemical engineering as a discipline was progressed upon its institutionalization in the mid and higher institutions (technical schools or colleges, universities, and academics) as well as by the foundation of professional associations that promoted and consolidated chemical engineering as a distinct and independent discipline from chemistry and mechanical engineering. From 1870 until the beginning of the next century, several attempts were made to introduce university curricula courses to train students in industrial or technical chemistry. All these efforts failed, or at best, they were short-lived. Several reasons prohibited the establishment of engineering training in higher education. Structural changes, the fracturing of knowledge, authority hierarchies among various groups of confusing professional status, e.g., between chemists working as analysts and chemists occupied in production, between academic and industrial chemists. Disagreements between chemists and entrepreneurs, conflicts between universities and industry, even conflicts between firm owners, i.e., between those who favored chemists in plant operation and those who considered university chemists technically incompetent to deal with practical problems in the industry and resented their interference.

Nevertheless, institutions of higher education under the pressure of the industrial sector (this pressure was more vigorous from the chemical industry) and the menace exerted by existing technical institutions started exploring the possibility of scheduling

⁸¹⁹ Buhholtz, 1979, pp. 38-39.

curricula of technical knowledge. Under these circumstances, several attempts were made to convert institutes of pure science into technical schools or simply to introduce courses in technical subjects offering knowledge of engineering and chemistry.⁸²⁰ As noted, these efforts proved to be short-lived; they did not have any chance to survive before the beginning of the twentieth century. The introduction of applied science in curricula of higher education institutions began after 1910 when Hinchley taught unit operations in the Imperial College.⁸²¹ After 1910, unit operations appeared in the curricula of British and American universities. University courses on chemical engineering started to become increasingly popular to students willing to study the new discipline of chemical engineering, professional chemists, and employers who planned to advance their position in the industry or increase their managerial capacity. Around 1920, unit operations began to organize systematically and, for the first time, appeared in a textbook, Principles of Chemical Engineering, published in 1923 and remained in print in three editions over fifteen years.⁸²² The book provided powerful mathematical tools and engineering data, making it possible for chemical engineers to routinely design various equipment units to meet specific performance requirements and improve industrial efficiency by analyzing their work into small units. Finally, the program of unit operations was used as an alternative device for chemical engineers to differentiate themselves from the more extensive and well-established chemistry and mechanical engineering disciplines. By the early 1920s, the unit operations was an essential part of chemical engineering teaching at MIT and a growing number of other American colleges and the Imperial College, London.

⁸²⁰ Donnelly, 1986, pp. 213-217.

⁸²¹ Ibid, p. 218.

⁸²² Cohen, 1996, p. 184.

A further example of the institutionalization of engineering education was the department of chemical technology at Imperial College, where Hinchley taught his course in chemical engineering. As a result, he managed to increase its research program steadily throughout the 1930s. When (in 1938) Imperial College offered an undergraduate program for the first time since Armstrong's course was wound up in 1911, they were able to advertise the existence of no fewer than twenty-six research topics (there had been none in 1920) in which postgraduates could work for the M.Sc. or Ph.D. dissertations.⁸²³ Postgraduate courses in chemical engineering started in England in 1932, and chemical engineering was a special undergraduate course of study in 1937.⁸²⁴

Despite differences in the education system and industrial organization in Britain and the United States, professional societies of chemical engineering embraced unit operations. They regarded it as an essential element for chemical engineering and actively sought to influence the chemical engineering curricula offered by university departments. The American Institute of Chemical Engineers (AIChemE) was founded in 1908 and the Institution of Chemical Engineers in England (IChemE) in 1922. The first attempts for the foundation of AIChemE appeared when the editorial of the journal *Chemical Engineer*, founded in 1907, called for a professional society.⁸²⁵ A large number of engineers and chemists working in the industry responded favorably to the call. AIChemE was established one year later despite the vehement opposition from the powerful American Chemical Society (ACS). Within months after installing AIChemE, ACS reacted by creating the promised Division of Industrial Chemistry and Chemical Engineering, the

⁸²³ Cohen, 1996, p. 190.

⁸²⁴ Buhholtz, 1979, p.43.

⁸²⁵ Reynolds, et al., 1983.

Division of Fertilizer Chemistry, and several other divisions to prevent the defection of further splinter groups. Furthermore, ACS announced a new engineering journal, the *Journal of Industrial and Engineering Chemistry*.⁸²⁶

AIChemE was initially weak because of its elitist attitude towards academics (only chemists with high qualifications and experience in the industry were allowed to become members of the institute, thus precluding most academics). Much later, during the depression years of the 1930s, when the membership declined considerably, AIChemE decided to relax the strict criteria for the enrollment and as a result, the enrollment doubled. A few months after the foundation of AIChemE, a relevant committee was set up to promote chemical engineering education by forming respective departments at universities to increase the competence of chemical engineering graduates. The committee recommended that the principle of unit operations should represent the core of the curricula of chemical engineering courses. In this way, AIChemE succeeded in playing a pivotal role in the institutionalization of unit operations, locating thus the discipline firmly within faculties of engineering, and differentiating the profession from its neighboring disciplines. AIChemE was developed into a strong organization providing further engineering education. By 1959, it brought itself into the United Engineering Trustees and the engineering specialties of Mechanical and Electrical engineering and Mining, while it established its headquarters.

IChemE in Britten followed a parallel way of development as its American counterpart to promote chemical engineering in academic institutions. It acted as a mediator of the industrialists to negotiate with academics to achieve a mutually acceptable

⁸²⁶ Cohen, 1996, p. 186-187.

undergraduate curriculum. By 1922, the chemical engineering course held at MIT was a model in London, although they believed that the course was inspired by Davis as noted above, and not by MIT. However, IChemE's road to reach its destination appeared to be more challenging mainly for economic reasons. Stringent economic conditions made it difficult for British universities to apply unit operations contrary to American universities, assisted financially by philanthropic organizations such as the Rockefeller Foundation.⁸²⁷ Unit operations required complex and costly installations for practical training. At any rate, after 1930, British universities managed steadily to establish chemical engineering courses and chemical engineering programs for graduate studies.

Section 3. The two traditions of thermodynamics and their reception from the scientific community

In chapters two and three of this dissertation, classical thermodynamics, formulated by the founding fathers Carnot, Clausius, William Thomson, Rankine, Joule, Helmholtz, Colding, and Mayer, was thoroughly discussed. The foundation of classical thermodynamics was followed by the development of several theoretical thermodynamic systems that spread out in Europe during the second half of the nineteenth century. These thermodynamic theories are grouped into two general trends. The first trend, the so-called mechanical/molecular or simple mechanics (later became known as a molecular mechanic), was associated with great physicists like the German Rudolf Clausius, the Austrian Ludvig Boltzmann, the Britons James Maxwell, George Francis FitzGerald (1851-1901), J. J. Thomson, and

⁸²⁷ However, the crucial point for running unit operation courses was cost, since the machinery and materials for the installation of unit operations at the university premises were expensive and of short duration, and consequently few universities could afford the necessary expenses.

Oliver Lodge, and the Dutch Hendrik Antoon Lorenz (1853-1928). In France, this trend appeared as having traditional roots associated with the great French physicists and mathematicians Laplace, Poisson, and Ampère. These prominent natural philosophers developed theoretical physics during the eighteenth beginning of the nineteenth century followed by the newer generation of physicists, although of lower caliber, including Joseph Louis François Bertrand (1822-1900) and Émile Verdet (1824-1866). The second stream of theoretical physics, the so-called analytico-positivist or simply positivist, was associated with physicists such as Gibbs, Ernst Mach (1838-1916), Planck, Helmholtz, and Rankine, and in France with physicists such as Jean-Baptiste Joseph Fourier, Augustine-Jean Fresnel (1788-1827), and later by François Massieu, Pierre Maurice Duhem, and the majority of experimental physicists and chemists, including Gay-Lussac, Regnault, and Dumas. These two traditions differed radically in the way they interpreted the physical laws while studying natural phenomena. The mechanical approach stressed the importance of dynamics (i.e., the exertion of gravitational or electrical forces in nature) and considered the inter-molecular attractions as the driving force for matter formation. The theoretical physicists of this group used probabilistic procedures and statistical mechanics as mathematical tools. Positivism rejected molecular attraction as an explanation of the properties of matter and suggested that the laws of nature should be derived directly from observations and experiments, denying thus any search for hidden causes that may explain more efficiently the fundamental laws of nature. The first trend led to the development of statistical thermodynamics, while the second branch of physics formed rational thermodynamics and irreversible processes.

Neither of these thermodynamic theories had any immediate impact on chemistry during the nineteenth century. They did not participate in the genesis of chemical thermodynamics. Despite numerous successful results after Maxwell and Boltzmann's contribution, the kinetic theory of gases and Boltzmann's probabilistic theories were never widely accepted by physicists, let alone the chemists. Significant conceptual difficulties involved in these theories hardly ever surmounted by chemists and a large part of physicists. Many understood the atomic and molecular constitution of matter, which was fundamental for these theories, no more than a working hypothesis. The inability to convincingly explain the irreversibility observed in physical and chemical processes was another obstacle that these molecular theories had to overcome. Other difficulties were experimental, such as the marked discrepancy between the measured heat capacity of polyatomic gases and the corresponding theoretical prediction. On the other hand, the phenomenological theories of the second tradition supposedly founded on the experience and observation had not a different reception by chemists owing to their macroscopic and more abstract approaches using rigorous mathematical language.

Two more reasons seem to contribute to the aversion that chemists felt for thermodynamics: First, most chemists were occupied heavily by organic chemistry and structural theories and, therefore, felt no need to go beyond their usual research subjects. Second, they had no sufficient mathematical skills to comprehend the thermodynamic theories invented by physicists. Chemists were more familiar with the first law of thermodynamics, as reformulated in thermochemistry by Thomsen and Berthelot. Chemists found it much easier to apply in their laboratories the laws of thermochemistry and use its much simpler mathematical language in their calculations. It was complicated for them to comprehend what entropy meant, how it could be used, and how it could be measured. As far as mathematical skills are concerned, chemists had little need for sophisticated mathematics. They needed to know how to weigh out stoichiometric quantities, measure densities, record melting points, and boiling points, and determine the correct atomic ratios in combustion and other reactions. Simple arithmetic was sufficient for these operations.⁸²⁸

The reception of thermodynamics by physicists and chemists differs. An intense dispute broke up with the community of physicists as to which of the two trends of thermodynamics was superior in explaining the physical phenomena. The molecular theory was able to explain natural phenomena taking into account the constitution of matter. They claim that the heat and temperature of bodies can be better understood as the result of more or less strongly interactions of moving particles (atoms or molecules) with one another. On the other hand, the followers of the macroscopic theory of the second trend argued that molecular mechanics relied on simple but temporary hypotheses that either fail to explain certain phenomena or be replaced by new ones. Duhem, who considered the elusive of premises, strongly opposed theories based on atoms and molecules. He claimed that these theories could reconstruct the first law of thermodynamics but failed to account for the second law qualitatively. He considered that none of these mechanical models was able to give a clear interpretation of irreversible processes. Time as a variable of the state of the system was absent in these theories.

⁸²⁸ Characteristic is the statement of Friedrich Wöhler, comparing mathematics and observation: "My imagination is fairly active, but I am somewhat slow in my thinking. No one is less oriented to be a critic than I. The organ for philosophical thought is entirely missing in me, as you know so well, just as that for mathematics. Only for observation do I imagine that I have a passable facility in my brain, which may be connected with a sort of instinct to be able to predict empirical relationships" (Rocke. 1993, p. 34).

The attitude of chemists concerning physics and physicists was ambivalent. On the one hand, some chemists safeguarded the traditional domains of chemistry against physics and mathematics. On the other hand, some chemists considered the methods of physics and thermodynamics necessary instruments for solving chemical problems and thus viewed physicists as potential collaborators. Chemists of the first group, primarily organic chemists, felt that mathematical equations are counterproductive since they do not inform the chemist about the physical processes associated with particular chemical properties. These chemists, such as Henry Edward Armstrong in London and Hermann Kolbe in Leipzig, opposed the thermodynamic approach to chemistry.⁸²⁹ Organic chemists were reluctant to share the chemical institutes or university chairs with physicists or chemists who had abandoned organic chemistry's intricate and beautiful science and devoted their research to a mixture of chemistry and physics.⁸³⁰ They were reluctant to share state and private funding allocations.⁸³¹ Even the American physical chemist Wilder Bancroft resented his colleagues who considered physics to be the fundamental science. As he once told his students: "[a chemist] must be a chemist rather than a physicist".⁸³² Very few organic chemists pursued the study of relations between physical properties of substances and chemical identity, chemical affinity, or chemical reactivity. The attitude of chemists

⁸²⁹ Kolbe protested against the appointment of the physicist Gustav Heinrich Wiedemann (1826-1899) to the position of professor ordinarius (professor with a chair) for physical chemistry at the University of Leipzig, the first such position in Germany, because he was a physicist (Rocke, 1993, p. 269).

⁸³⁰ The response of the great sugar chemist, Emil Fischer (1852-1919), when Ostwald told him that organic chemists should thank physical chemists for developing new methods of measuring molecular weights, was characteristic: "I do not need your methods"; quoted in Servos, 1990, p. 331.

⁸³¹ In Germany, the ministries had begun to control growth in various institutions by checking the duplication of facilities and distributing resources selectively. As a result, the funding and chairs for new scientific fields, including physical chemistry, were restricted. In 1904, the twenty one universities of Germany supported only four institutes of physical chemistry (Servos, 1990, pp. 50-51). ⁸³² Servos, 1990, p. 323.

concerning thermodynamics changed somewhat when the training in mathematics and physics began to enter the curricula of higher education institutions and technical schools, which began to establish departments in technical chemistry and chemical engineering, and later in physical chemistry.

The foundation of the theory of chemical thermodynamics signaled the interaction between physics and chemistry. It began in Europe during the last two decades of the nineteenth century. It evolved significantly in America, especially after World War I when it constituted the theoretical basis of a new discipline, physical chemistry. However, the ionists, van 't Hoff, Arrhenius, and Ostwald selectively used thermodynamics. Van 't Hoff, for example, did not intend to contribute to the development of thermodynamics as such. Upon realizing its capacity to solve practical problems in chemistry, van 't Hoff took from it whatever he thought to be useful for consideration of chemical facts. He selectively used thermodynamics as a tool in his studies, similarly to the physicist's use of mathematics in his research. His object was chemistry, not physics. He treated thermodynamics as a method, not a theory with its principles and subjects, aiming at achieving immediate practical results. He was interested in understanding chemical reactions and solutions' properties. He was less concerned with scientific rigor in arriving at simple relationships applicable to the needs of chemists in their laboratories. Even in the derivation of the osmotic law, he did not use thermodynamics, but the Avogadro law of the ideal gases extended into the dilute solutions. He believed in the ability of an experiment to produce a clear and definite answer to a problem than seeking elegance and accuracy. The experiment was a tool for testing, not a step for further investigation or discovery. However, he rarely performed experiments by himself. He was in love with ideas and emphasized the imagination to discover things in nature.⁸³³ His opinion about thermodynamics formulated by physicists in the second half of the nineteenth century expressed as follows: "I shall make a suggestion as to the choice of the most suitable form of this [Carnot-Clausius] principle. It may be applied either by carrying out the so-called reversible cycles of operations or by the introduction of abstract physical conceptions and mathematical functions, such as entropy, as is done by physicists like Gibbs, Planck, and Duhem. I am convinced that, for the chemist, the first form, in which reversible cycles are employed, is the most advantageous".⁸³⁴

None of the ionists mentioned or employed the concept of entropy. They ignored Gibbs' thermodynamics, let alone Duhem's generalized thermodynamics with its severe mathematical language.⁸³⁵ The new trends in thermodynamics, as manifested in the works of Gibbs, Duhem, and Helmholtz were appreciated much later by the American physicists and chemists when they struggled to establish the new discipline of physical chemistry in their country. The American chemists realized that Gibbs' thermodynamics was a treasure of novel ideas that could give an impetus to chemical thermodynamics. On the other hand, mostly physicists who were involved in studies related to irreversible processes occurring in deformable solids and viscous liquids discovered Duhem's rational dynamics. The new discipline of continuum mechanics that began to develop in the mid-twentieth century has its roots in Duhem's energetics.

⁸³³ Root-Bernstein, 1980. pp. 241-242

⁸³⁴ Van 't Hoff 1903, p. 21.

⁸³⁵ Even Ostwald, who translated Gibbs' memoir *On the equilibrium of Heterogeneous substances*, did not attempt or suggest any further to enhance the quality of the ionists' chemical thermodynamics, introducing some of Gibbs' ideas, as for example, the phase rule.

Traditionally, scientists strive to secure their disciplinary authority within the scientific community, and in particular within the institutional framework of their country. Attempts for the dominance of a discipline over related disciplines or specialties do not always have a scientific fervor. These efforts aim to gain a privileged reception by the state, secure governmental or private funding allocations, widen the perspective of its members in the job market, and acquire benefits from other social and economic tangible and intangible outlets. Thus, the appearance of a new rival discipline is confronted with irony and contempt, regardless of whether the newborn discipline has to offer new product ideas, practical methods, and prolific processes that would contribute to the advancement of science. Instead, the established discipline strives to invalidate the new discipline's fundamental doctrines and refute the usefulness of its existence. Therefore, it is no wonder why the ionists' chemical thermodynamics in Europe and America had been met with scorn and hostility, mainly by organic chemists.

The battle for supremacy between conflicting disciplines is usually limited to the academic cycles. However, the struggle for dominance is heavily influenced when the disciplines pursue a share in the industrial making. Additional factors, mainly economic ones, seem to play a significant role in the outcome. In this case, the rivalry goes beyond the narrow academic context. It is guided by new rules depending on each country's social, economic, and cultural context. In the new environment, the rules changed, and the new discipline acquires the freedom to expand and show its potential for scientific and economic growth. Thus, chemical engineering, as an applied science in the industrial sector succeeded to overcome the resistance of organic chemistry. It took its share in the technical schools and Universities as an independent discipline with a temporary rival the pure
chemistry and in particular organic chemistry. On the contrary, physical chemistry, which had no access to the industry, at least in its infancy, faced strong opposition from the dominant organic chemistry.

Chapter 10. The ionists and the development of the theory of solutions: The origin of the modern chemical thermodynamics

The transfer of knowledge between scientific disciplines, especially physics and chemistry, is a typical process in modern times. The discipline of physical chemistry, which is an indispensable part of any university curriculum, provides a characteristic example. The diffusion of knowledge between the two sciences was very slow to negligible almost during the nineteenth century. Beginning the nineteenth century, chemists who prevailed in European science, particularly in France and Britain, had delineated the area of their research interests. Their research programs encompassed all matters exclusive to chemistry. Chemists are preoccupied with research subjects, such as the synthesis of new compounds for industrial and pharmaceutical use, the improvement of old synthetic methods to increase the reaction yield, the invention of effective methods to isolate natural products, the discovery of laws that governed chemical affinity and chemical equilibrium, the determination of the chemical composition of substances and specify their physical and chemical properties. Chemists neglected thermodynamic theories, which began to grow during the first decades of the nineteenth century, and advanced in the second half of the same century by the efforts of physicists. As discussed in chapter 9 of this dissertation, the description of thermodynamic laws engaged a rigorous mathematical language that was difficult for chemists to comprehend and use in the laboratory.

On the other hand, many physicists were deficient in chemical skills and, therefore, unable to grasp the general notion of chemical substances and chemical changes. Furthermore, physicists failed to comprehend the practicalities involved in the chemical experiments and, therefore, were not able to t evaluate the efficacy of detailed experimental data for testing their theories. This attitude changed slowly and culminated during the last two decades of the nineteenth century when physics and chemistry met each other through chemical thermodynamics. Physics offered chemistry explanations about the nature of chemical affinity and chemical equilibrium or criteria to assess the spontaneous course of chemical reactions. Furthermore, physics provided chemists with advanced scientific instruments, new experimental techniques, and methods, giving thus a great impetus to quantitatively analysis. Thermodynamics enriched chemistry with a unique pattern of thinking and practicing. The introduction of mathematics and combining chemical experiments with theoretical interpretation gave a new functional image to chemistry as an independent experimental and theoretical science.

chemists employed classical thermodynamics Whenever (this happens occasionally), its methods proved valuable tools in dealing with chemical reactions. Berthollet, Guldberg and Waage, and later Thomsen, Berthelot, Horstmann, and Leopold Pfaudler (1839-1920) showed how the first and the second law of thermodynamics could help determine the direction of chemical reactions (although Thomsen and Berthelot in a way of limited scope). Gibbs, Duhem, and Helmholtz provided the tools (potentials, free energies) to quantitate the equilibrium and non-equilibrium states in physical and chemical processes. However, the transfer of thermodynamics from physics to chemistry and the exploitation of the benefits that this science could offer chemists in their work occurred only during the last two decades of the nineteenth century. What is surprising in this case is the fact scientists working at the periphery of Europe accomplished the transmission of thermodynamics into chemistry. Arrhenius in Sweden, van 't Hoff in the Netherlands, and Ostwald in Estonia working independently, away from the scientific centers of Europe, France, Britain, and Germany, where science flourished during the nineteenth century, were the men who embodied chemistry with the doctrines of thermodynamics.⁸³⁶ The science of electrochemistry founded during the first decades of the nineteenth century still progressed in the second half of the nineteenth century in the center. Hittorf, Kohlrausch, and Helmholtz kept the concept of ions alive.

On the other hand, Faraday's conviction that ions were produced in electrolysis persisted amongst electrochemists. Recall that Faraday suggested that the application of an electromotive force was necessary for the formation of ions.⁸³⁷ The international reputation of the German electrochemists was a major reason that the ions and their role as carriers of electricity in solutions gained attention outside Germany. Arrhenius, who founded the electrolytic dissociation theory, spent several months in Kohlrausch's laboratory. Therefore, it is not surprising that some of the research findings in this laboratory were integrated by scientists working in peripheral universities located in Uppsala, Amsterdam, and Riga. These universities were less prestigious compared to those in Berlin, Göttingen, or Würzburg, but they were also less subject to the constraints of the authority. There, original research took place to elucidate the properties of the electrolytes in solutions.

The reception of thermodynamics of Gibbs, Duhem, and Helmholtz was much slower and had to overcome severe obstacles to penetrate chemistry. Their work was absent

⁸³⁶ The relationship between the center and periphery regarding the transfer of scientific ideas, practices, and technology is a historiographical issue that has extensively occupied historians in later years. It is customary to ascribe the transfer of new knowledge from the geographical center to the periphery. In the case of chemical thermodynamics, however, the opposite procedure took place, a fact that underlines the complexity of the subject (Gavroglu et al., 2008).

⁸³⁷ The novelty of Arrhenius' ionic dissociation theory is summarized in the following sentence: even in the absence of an electric current, aqueous solutions of salts contain ions due to the spontaneous dissociation of the electrolytes. He thus proposed that chemical reactions in solution were reactions between ions.

in chemical thermodynamics established by three chemists originating from the periphery of Europe. These three men, the so-called ionists,⁸³⁸ made thermodynamics accessible to chemists. Although more limited in scope than Gibbs and Duhem's thermodynamics, the ionists' theories were mathematically simpler and had a clear experimental orientation; therefore, they were more appealing to chemists. The ionists developed new concepts and experimental methods to describe the properties of aqueous solutions of substances. They were committed to the view that electrolytes in water break into ions without the action of the electric current as contended by the previous generation of electrochemists. They considered several old and new problems comprising chemical affinity, the effects of mass and temperature on chemical equilibria, reaction rates, phenomena of osmotic pressure, and electrolytic dissociation.⁸³⁹ By the end of the 1880s, the ionists unified various unconnected studies and presented a compact theoretical and experimental whole that represented the theoretical basis of the new discipline of physical chemistry.⁸⁴⁰ Two questions arise at this stage: What was the connecting thread that brought together these diverse theories? What motivated these three chemists to espouse thermodynamic methods in their solution theories, while earlier chemists had felt such resistance to physic?

Each ionist had a unique scientific style in devising his scientific program. He defined the problems, chose the proper experimental methods, and interpreted and

⁸³⁸ The nickname ionists, derives apparently from tArrhenius' ionic dissociation theory. It is attributed to Horstmann. Horstmann reviewing an article by Lothar Meyer (1830-1895) on osmotic pressure refers ironically to the "wild army of the Ionists" that opposed the attack of organic chemists on their dissociation theory (Crawford, 1996, p. 96). Patrick Coffey has used the same phrase as a chapter heading of his book dealing with some features of the work of the ionists (2008, p. 23).

⁸³⁹ For the ionists' biographies and information about their work, see Cohen, 1912; Root-Bernstein, 1980; Servos, 1990, pp. 20-45; Laidler, 1993, pp. 114-128, and 209-214; Crawford, 1996; Petit, 2013, pp. 196-206. Walker, 1928.

⁸⁴⁰ The ionists' theory of solutions lost much of its significance for physicists when the former became aware of Gibbs' papers, which treated many of the ionists' results in a more penetrating and elegant way.

communicated the experimental results to his country's scientific community under the influence of the educational and cultural traditions characterizing each social milieu.

Section 1. Svante August Arrhenius

Arrhenius was born on 19 February 1859 in the ancient state of Vik (Wijk) near Uppsala. After attending the Cathedral School in Uppsala, he entered the University of Uppsala at seventeen. He studied mathematics, chemistry, and physics and passed the candidate's examination in 1878. He chose physics as the principal subject for his doctoral dissertation. He completed his dissertation in 1884, in which he put forth 56 theses. Most of these doctrines would still be accepted today unchanged or with minor modifications. Arrhenius wrote his dissertation in French.⁸⁴¹ It is not clear why he preferred the French language. Luckily, this choice was beneficial for him when he sought recognition from abroad. His dissertation received proper credit only when Ostwald read a copy of it. Arrhenius received the Nobel Prize for Chemistry in 1903, becoming the first Swedish Nobel laureate. In 1905, he became director of the Nobel Institute and kept this position until his death in Stockholm on 2 October 1927.⁸⁴²

⁸⁴¹ The thesis' title was *Recherches sur la conductibilité galvanique des électrolytes*. (1884) Bihang till K. Svenska retenskaps akademiens handlingar (Appendix to K. The Swedish Academy of Sciences' documents), vol. 8, no. 13 and 14; reprinted in Ostwalds Klassiker, no 160 (Leipzig, 1907).

⁸⁴² For biographical information and analysis of Arrhenius' work, see Harrow, 1920, pp. 111-133; Walker, 1928; Root-Bernstein, 1980, pp. 16-111; Snelders, 1981a, pp. 296-302; Servos, 1990, pp. 20-45; Laidler, 1993, pp. 114-128; Crawford, 1996; Petit, 2013, pp. 196-206.

1.1 A dissertation full of novel ideas

Arrhenius began his dissertation at the University of Uppsala under the guidance of Per Theodor Cleve (1840-1905), a professor of chemistry at the University of Uppsala, and Tobias Robert Thalén (1827-1905), a Professor of Physics at Stockholm Technical School, and in 1874, professor of physics at the University of Uppsala. Arrhenius commenced his studies to perform electrical conductivity measurements to determine the molecular weight of substances dissolved in water.⁸⁴³ He chose this subject because he wanted to create new knowledge in science rather than synthesizing new organic or inorganic substances. However, due to the limited space in Thalén's physics laboratory,⁸⁴⁴ Arrhenius did his experiments at the Högskola Research Institute in Stockholm with Eric Edlund (1819-1888), a professor of physics of the Académie des sciences, and Sven Otto Pettersson (1848-1941), a professor of chemistry at the Institute.⁸⁴⁵

At Högskola, Arrhenius started in 1882 gathering conductivity data on different electrolytes in a series of different dilutions of the added sugar whose molecular weight strove to determine.⁸⁴⁶ He soon realized that the electrical conductivity depended as much

⁸⁴³ Arrhenius was unaware that the French chemist François Raoult had found in the spring of 1882 that molecular weights of dissolved non-volatile substances in water, such as sugars, could be measured by the depression of the freezing point of the solvent.

⁸⁴⁴ Thalén was an eminent and competent experimental physicist. His research interests pertained to spectroscopy.

⁸⁴⁵ The Högskola Research Institute did not confer doctoral degrees, and Arrhenius still had as instructors Cleve and Thalén. The latter, for some reasons, disliked Arrhenius, possibly because Arrhenius preferred to conduct his dissertation in electrochemistry and not synthesizing substance for spectroscopic analysis. Thalén asking Edlund to provide Arrhenius with laboratory facility warned him that Arrhenius was lazy and clumsy (Coffey, 2008, p. 11). Arrhenius got along with both Edlund and Peterson, who became his immediate directors. Social reasons may have been another reason for Cleve and Thalén's antipathy to Arrhenius. The professors in Uppsala (a small city north of Stockholm) were the social elite, while Arrhenius came from a lower-middle-class background. On the other hand, Edlund, whom worked productively at the Högskola, was the son of a peasant (Root-Bernstein, 1980, p. 29).

⁸⁴⁶ His decision to start his experimenting with cane sugar was probably due to Cleve's statement that the formula of cane sugar was some unknown multiple of the formula C₁₂H₂₂O₁₁ (Arrhenius, 1912, p. 358).

on the concentration of the electrolyte as it did on the molecular weight of the added sugar. He decided that he first had to examine the conductivity dependence on electrolyte concentration to understand the problem. The first electrical conductivity data were somewhat confusing, making thus Arrhenius put away his original research project and turn his attention to the dependence of electrical conductivity upon electrolytes' concentration that seemed more interesting to examine. This decision proved to be a hallmark in the development of the electrolytic dissociation theory that constituted an integral part of the theory of chemical thermodynamics.

In the beginning, he placed his investigation under the authorities of Kohlrausch and Hittorf. From the first, he borrows the conductivity measurements, the conductivity laws, and the mathematical formulae, and from the second, the mobility of ions in solutions. Arrhenius considered that the solvent molecules do not play a significant role in the conductivity of the electrolytes. Any change in their electrical conductivity is the result of their concentration change. Arrhenius used highly dilute solutions at the beginning, so he avoided any irregularities caused by the concentrated solutions (**Figure 24**). He confessed later that, "my great luck was that I investigated the conductivity of the most dilute solutions. In these dilute solutions, the laws are simpler compared with those for concentrated solutions, examined before. It was then easy to find that the irregularities, which came in every step with concentrated solutions, disappeared".⁸⁴⁷ He concluded that the ions of a weakly concentrated solution move more quickly compared to those of a very concentrated solution. He concluded, therefore, that the electrical conductivity of solutions of electrolytes increases with dilution.

⁸⁴⁷ Arrhenius, 1912, p. 358.

Furthermore, he asserted that the size of the ions affected their conductivity and exemplified this rather qualitative hypothesis with his observation that the acids had an excellent conductivity. The relative size of the electrolyte ions determines the frictional resistance imposed on their rotational motion and, therefore, the magnitude of their velocity. The small size of the hydrogen ions of acids would explain their high electrical conductivity.⁸⁴⁸

The first part of his thesis was experimental, and up to this point, Arrhenius' theoretical explanations on the electrical conductivity of electrolytes did not differ significantly from the earlier work of Kohlrausch and Hittorf. Pettersson was not entirely satisfied with it. He demanded a more advanced theory and probably advised Arrhenius to read more carefully the existing literature.⁸⁴⁹ Arrhenius came across Clausius's hypothesis of the incessant motion (translation and rotation) of the complete and partial molecules within the liquid well before the electrolysis. These two types of molecules engendered upon collisions alternatively decompose and recompose electrolytes without applying the electric current.⁸⁵⁰ The second encounter of Arrhenius during his search of the literature was the *Williamson hypothesis*.⁸⁵¹

In the *Clausius-Williamson hypothesis*, Arrhenius saw the link between the electrolytic theories and the chemical reactivity. Williamson's version described the

⁸⁵⁰ Chapter 5, section 4 of this dissertation.

⁸⁴⁸ Arrhenius, 1884a, pp. 55-56.

⁸⁴⁹ Following Pettersson's advice, Arrhenius studied memoirs and treatises carefully on chemistry and electricity. He read Wiedemann, Maxwell, Lothar Meyer', and Berthelot. From Meyer, he borrowed Guldberg and Waage's mass action law. From his reading of Wiedemann, he learned about the Clausius-Williamson hypothesis. From Maxwell, he cited the principle of the incompressibility of electricity to support the idea of circular currents (his proposition on the electric current circulation mechanism in solution). Finally, he agreed with the analogy between chemical dissociation and vaporization of liquids that Berthelot exposed in his *Essai de Mécanique Chimique*, vol 2. (Petit, 2013, p. 206).

dynamics in chemical reactions, whereas Clausius's hypothesis pertained to electrolysis. The idea that dynamics was the common characteristic that linked the electrolytic theory and the chemical theory led Arrhenius to imagine the existence of two sorts of electrolyte molecules in solution. According to Williamson's hypothesis, the active molecules participate in chemical reactions and conduct the electrical current as described by Clausius. The other type of molecules the *inactive molecules*, do not decompose and do not participate in chemical reactions or electricity conduction. "La solution aqueous d'un hydrate quelconque se compose, hors l'eau, de deux parties, d'une active (électrolytique), l'autre inactive (non-électrolytique). Ces trois parties constituants, l'eau, l'hydrate actif, et l'hyhydrate inactif, forment un équilibre chimique, tel qu'à une dilution la partie active augmente et la partie inactive diminue".⁸⁵². However, Arrhenius found difficulties to define exactly the nature of the active and inactive molecules, "A quel égard, ces deux parties différentes, reste à élucider". He assumed that the active molecules might have resulted from the inactive molecules by pairing with the solvent molecules (e.g., HCL with H₂O).⁸⁵³ Whatever the nature of the active molecules, Arrhenius led by the Clausius-Williamson hypothesis, asserted that the active molecules constantly exchange their atoms with other molecules of the same kind or with foreign molecules, giving rise to double decomposition and ordinary chemical reactions. Thus, Arrhenius connected electrical conductivity with chemical reactivity, a fact that attracted Ostwald's attention when he received a copy of Arrhenius' dissertation.

⁸⁵² Arrhenius, 1884b, p. 5.

⁸⁵³ Arrhenius led to this conclusion from the behavior of liquid acids and bases, such as ammonia, acetic acid, sulfuric acid, and the gas hydrogen chloride. These electrolytes conduct electricity only after their dissolution in water.

Furthermore, Arrhenius identified the portions of active and inactive molecules through his *activity coefficient*. He initially defined the activity coefficient as the ratio of the active to inactive molecules. Since the absolute conductivity of the electrolyte declines with dilution, Arrhenius redefined the activity coefficient α as the ratio of the active molecules to the total number of the electrolyte molecules (active + inactive) in the solution.

$$\alpha = \frac{n}{n+m} \tag{10.1}$$

Here, *n* is the number of active molecules, and *m* is the number of inactive molecules.⁸⁵⁴ The greater the activity coefficient, the greater the proportion of the active molecules and the greater the conductivity of the electrolyte. Heating and dilution increase the activity coefficient indicating that these external factors increase the proportion of the active molecules, which intensifies at the same time the electrical conductivity of the electrolyte. Arrhenius considered the activity coefficient a new measure of chemical affinity and the means of expressing a compound's reactive capacity. Chemical affinity was inversely proportional to the activity coefficient. The larger the activity coefficient, the greater the number of the active molecules in solution and thereby the smaller the chemical affinity of the ions constituting the electrolyte. In other words, the chemical reactivity is proportional to the activity coefficient must increase as the number of decomposed molecules of the electrolyte increases with increasing temperature and dilution.

⁸⁵⁴ Arrhenius defined the activity coefficient in terms of the ions conducting electricity: "Le coéfficient d'activité d'un électrolyte est le nombre exprimant le rapport du nombre d'iones qu'il y a reéellement dans l'électrolyte, au nombre d'iones qui y seraient renfermés, si l'électrolyte était totalrment transformé en molécules électrolytiques simples" (Arrhenius, 1884b, pp. 5-6). Arrhenius considers as ions the entities proposed by Clausius. He clarified the nature of the ions by the time he postulated his ionic dissociation theory.

In the theoretical part of his dissertation, Arrhenius proposed his model for the electric current propagation that explained the mechanism of the formation of the active molecules and indirectly the relationship between electrical conductivity and reactivity. He borrowed this model from Hittorf's mechanism of propagation. However, Arrhenius gave it a dynamical character suggesting a combination of longitudinal and rotational molecular motions. These two kinds of motions resulting from the interchange between the active and inactive molecules create a circular current that propagates through the electrolytic solution and passes in between the molecules, e.g., the two molecules AB and A_1B_1 , that are separated by a surface mm₁n of constant electricity enclosing the molecule A₁B₁ (Figure **1.6**). The ions A, A_1 are the positive ions, and B, B_1 are the negative ions. By the action of circular current running, A passes from B to B_1 and A_1 passes from B_1 to B (Figure 1.6). The total quantity of electricity contained within the surface mm_1n must remain the same after the process as before.⁸⁵⁵ The conduction of electricity through the circular currents would depend on temperature, and therefore, according to Williamson, should be directly proportional to chemical reactivity exhibited by the electrolyte. However, Arrhenius noted a scarcity of experimental results to confirm the proportionality between electrical conductivity and chemical reactivity safely.⁸⁵⁶

Why did Arrhenius choose the concepts of active and inactive molecules and not the well-established notion of ions? Adopting the idea of the active molecules, Arrhenius probably evaded the contact of potassium or sodium with water. It was well-known to chemists that solid potassium and sodium react very strongly with water evolving large

⁸⁵⁵ Arrhenius, 1884b, pp. 8-9; Root-Bernstein, 1980, pp. 81-82.

⁸⁵⁶ Arrhenius classified the acids, bases and salts into different groups of reactivity (weak and strong) according to the magnitude of their electrical conductivity (Arrhenius, 1884b, pp. 14-19).

quantities of heat that may cause a fire. This situation is true for metallic potassium or metallic sodium. It is not true for the electrolyte potassium chloride or sodium chloride, which decomposes into inert to water potassium and sodium ions. Potassium and sodium ions do not react chemically with water. However, water molecules hydrate these ions.

Arrhenius chose the concepts of active and inactive molecules for one more reason. In his electrolytic theory, Arrhenius shared the idea of the freely moving active molecules with molecules in a state similar to partial molecules described by Clausius. Arrhenius believed that connecting his conceptions of electrolyte decomposition with the authority of Clausius could give some kind of protection to his theory against controversies. However, sharing his idea about the active and inactive molecules and their properties in solution with Clausius, he endangered the originality of his work.

Arrhenius thought that the formation of active and inactive molecules through collisions was analogous to a chemical equilibrium between two types of compounds. In other words, the reaction between the ions and the neutral molecules of the electrolyte can produce new ions as substances AB and CD can form substances AC and BD. Thus, he could be able to affirm that electrolytes obey the same physical principles as ordinary chemical compounds. Arrhenius imagined that the application of the equilibrium law of Guldberg and Waage to electrochemistry was the proper device to determine the equilibrium state between the dissociated and the undissociated molecules.⁸⁵⁷ In accord with the Clausius-Williamson hypothesis, Arrhenius succeeded in relating the electrolytic theory with chemical equilibrium. The equilibrium was measurable by the electrolytic conductivity of the solution. As a result, he correlated the activity coefficient obtained from

⁸⁵⁷ Arrhenius, 1884b, pp. 82-86; Petit, 2013, p. 205; Rroot-Bernstein, 1980, pp. 97-99.

conductivity measurements with the chemical reactivity as expressed by the active mass of Guldberg and Waage's theory. The consideration that molecules active in conducting the electrical current are also chemically active opened a great perspective in physicochemical research undertaken by the ionists in the following years.

However, the Guldberg-Waage equilibrium scheme was consistent only with weak electrolytes like acetic acid or oxalic acid. It failed for strong electrolytes (strong acids and bases, and salts). This observation caused a great deal of trouble for Planck and van 't Hoff. They were unable to figure out what caused the disagreement between their calculations and the law of equilibrium. But not for Ostwald, who was familiar with the electrolytic behavior of the weak and strong electrolytes through the thousand experiments he had conducted using these materials. This experience allowed Ostwald to discover the dilution law before van 't Hoff and Planck (see below).

Arrhenius' dissertation was a compilation and synthesis of many scattered knowledge in electricity and chemistry. He attempted to reconcile chemistry with physics, (but not with thermodynamics in particular) that developed separately in the nineteenth century with his dissertation. He realized that such a reconciliation required the rapprochement between chemistry and the ideas of Clausius, Williamson, and the Guldberg and Waage equilibrium law. In the context of his theory, Arrhenius had compared methods and ideas from different fields that developed independently, and at the same time, he used them to legitimize his investigation. He stated, "All these propositions and all these laws are taken from the most different parts of chemical science; but as the theory agrees so well with reality in these various points, it seems likely that it must also do so in the intermediate

regions".⁸⁵⁸ He built a complex and well-documented theory of electrochemistry, but on the other hand, exposed himself to criticism from all sides.

Based on his theory, Arrhenius deduced a number of electrochemical laws, such as those of Faraday and Hittorf. Assuming that every electrolyte has a constant composition, Arrhenius proved the necessity for equivalent weights of every substance playing the part of an ion. The experimental data of the variations of electrical conductivity and solubility by dilution, heating, and addition of foreign bodies indicated the origin of several phenomena that occurred in systems at equilibrium. He observed that the Guldberg-Waage mass law showed irregularities for certain electrolyte systems. This anomaly concerns the strong electrolytes, for which the mass action law is not applicable, as it was recognized by van 't Hoff and confirmed quantitatively by Ostwald through the dilution law.

I will discuss in a separate section the opposition to the theory of electrolytic dissociation. However, it is interesting at this stage to find out what was the opinion of Arrhenius' professors about his dissertation. Arrhenius' dissertation did not impress Cleve and Thalén. They considered the experimental work not precise, as Arrhenius had not controlled temperature, water quality, or concentration carefully, and in addition, he had studied only a small number of compounds.⁸⁵⁹ They pointed out that he had chosen a topic on the borderline between physics and chemistry that they had not encouraged. At the same time, Arrhenius has abandoned the subject he had set for himself: the determination of molecular weights by the method of electrical conductivity. Also, Cleve and Thalén adversely criticized the theoretical part of Arrhenius' thesis. They found that the concept

⁸⁵⁸ Quoted in Petit, 2013, p. 206.

⁸⁵⁹ Oliver Lodge expressed similar doubts about the quality of the experimental part when Arrhenius asked Lodge's opinion about his dissertation (see chapter 12 of this dissertation).

of activity coefficient was not well documented and that he had proposed a theory that contradicted the established views of electrochemistry.⁸⁶⁰ The two professors completely ignored that the author of the dissertation founded his dissertation on prominent scientists' renowned ideas, such as Hittorf, Kohlrausch, Clausius, Williamson, Guldberg, and Waage. They gave Arrhenius' dissertation a barely passing grade *non sine laude approbatur* (not without credit approval) that would not allow him to teach at any university of his country.⁸⁶¹ His prospects seemed limited to teaching at a gymnasium. On the graduation day, Cleve and Thalén showed their contempt by walking out of the examination room without even stopping to congratulate him.⁸⁶²

van 't Hoff's memoir *Études de dynamique chimique* (see below) was published in the same year when Arrhenius defended his dissertation. Van 't Hoff's book and Arrhenius' dissertation marked the beginning of the long road that led to the genesis of modern chemical thermodynamics. Their work came at the right time to strengthen the link between physics and chemistry that has started during the last quarter of the nineteenth century, as Ostwald had imagined.

⁸⁶⁰ Cleve and Thalén questioned the validity of Arrhenius' theory in three points. The first is the difficulty of comprehending how sodium chloride, customarily considered as an exceptionally stable material, to split into its components by merely dissolving it in water. The second question was equally crucial for chemists: How is it possible for free sodium to be present in an aqueous solution when metallic sodium violently reacts with water? Third, how can free chlorine be present in the odorless solution since a water solution of chlorine is yellowsh and has a penetrating odor? (Root-Bernstei, 1980, p. 117). These puzzling questions were plausible since the electrochemists, including Arrhenius, did not explicitly differentiate the properties between atoms and ions, except perhaps the fact that ions carry electricity.

⁸⁶¹ Pettersson had a different opinion and considered Cleve and Thalén's decision unfortunate. He reviewed Arrhenius' dissertation in the Swedish journal *Nordisk* and praised it very highly. In particular, he stressed Arrhenius' discovery of the relation between electrical conductivity and reaction rates (Snelders, 1981a, p. 297; Crawford, 1996, pp. 41-43).

⁸⁶² Root-Bernstein, 1980, p.108-109; Crawford, 1996, p.43; Coffey, 2008, p. 14;

1.2 Arrhenius postulates the ionic dissociation theory

In his dissertation, Arrhenius postulated that electrolytes decomposed into inactive and active molecules. He assumed that the active molecules produced by hydration of the inactive molecules were the carriers of electricity. However, he did not explain the nature of these two types of molecules, except perhaps of the vague statement that the inactive molecules are complex, probably hydrates of the active molecules.

In December of 1887, Arrhenius finally published his ionic dissociation theory, in which he made clear that the electrolytes in solutions dissociate into ions. However, the idea of the dissociation of electrolytes into charged entities had grown in Arrhenius' mind much earlier. What had it been the origin of his thinking that led him to postulate his dissociation theory? Several reasons might have caused Arrhenius's thinking to shift from the old dissociation theory expounded in his dissertation to the germs of the ionic dissociation theory.⁸⁶³ His photochemical studies on gases were among the various factors that had the greater influence upon Arrhenius' theoretical views of the dissociation process into electrically charged atoms (i.e., ions).⁸⁶⁴

What made Arrhenius turn his attention to the study of the effect of light on reaction rates? Root-Bernstein connected Arrhenius's photochemical research with his reading the section of van 't Hoff's *Études de dynamique chimique*. The Swede discussed various photochemical results for gases and performed his photochemical experiments.⁸⁶⁵ Also, Arrhenius was familiar with Edlund's research on the active states of gaseous electrolytes.⁸⁶⁶ In general, the photochemical research, which was available at that time,

⁸⁶³ Root-Bernstein, 1980, pp. 375-377.

⁸⁶⁴ Ibid, pp.367, 378-379.

⁸⁶⁵ Ibid, p. 369.

⁸⁶⁶ Ibid, p. 370. However, Edlund did not use light but electricity to perform his experiments (Edlund, 1884).

concerned mostly the exploration of the mechanism by which light stimulated an initial induction or an initial acceleration of the rate of chemical reactions. The reaction between chlorine and hydrogen was a well-known experiment of this type of research. However, van 't Hoff did not distinguish inactive or active states in the photochemical experiments. From his photochemical experiments and the literature data, van 't Hoff concluded that "the chemical induction or initial acceleration may be referred to secondary actions, and therefore the phenomenon may be of service in investigations relating to chemical dynamics, since it indicates, in a way which is not to be undervalued, that some necessary precaution has been omitted".⁸⁶⁷

In December 1886, Arrhenius sent to Ostwald a brief letter describing his project to measure the conductivity of the halide gases under various light conditions. He intended to determine whether the light-induced activity of gases correlated with the corresponding variation in conductivity.⁸⁶⁸ However, his initial experiments did not involve photochemical reactions but conductivity measurements of gaseous electrolytes by passing a current of electricity through rarefied gases.⁸⁶⁹ In other words, Arrhenius performed some kind of discharge experiments in gases.

What did Arrhenius expect from these experiments? Arrhenius' intuition in performing these experiments can be summarized as follows: Arrhenius was familiar with the investigation of Horstmann, van 't Hoff, Berthelot, and Sainte-Claire Deville in the gas phase at high temperatures. These experiments demonstrated the dissociation of gases as shown by an increase in their density or pressure. Since in the gas phase no solvent exists,

⁸⁶⁷ Van 't Hoff, 1884, p. 82.

⁸⁶⁸ Root-Bernstein, 1980, p. 370.

⁸⁶⁹ Ibid p. 371.

hydration is not necessary for the accomplishment of dissociation, as he proposed in his dissertation. In the absence of hydrated molecules, the atoms would be the sole carrier of electricity. Therefore, the dissociated atoms in gases should be charged entities. Through the analogy between gases and dilute solution entrenched by van 't Hoff, and Horstmann, Arrhenius concluded that hydration was not a necessary condition for the transfer of electricity by the ions of electrolytes in solution. In other words, Arrhenius sought to correlate electrical conductivity in solution with the dissociation of gases into charged atoms.

Nonetheless, Arrhenius had to prove this logic experimentally, and hence he changed the direction of his research to photochemistry. Experiments conducted in the gas phase in a high vacuum ensure the absence of any gas contact with foreign bodies. In January 1887, Arrhenius reported to Ostwald that he had performed some exciting experiments.

The German-British physicist Franz Arthur Friedrich Schuster, a professor of applied mathematics at the University of Manchester, performed electric discharge experiments as early as 1881. In 1884, he was able to present a theory of the discharge through gases. He postulated that the gas subjected to an electric discharge is the medium of the electrolytic action. He assumed that conduction in gases takes place by the dissociation of molecules.⁸⁷⁰ He proposed to verify this idea by examining the effect of electric discharge on mercury vapor. His subsequent experiments focused on the conduction of nitrogen, oxygen, hydrogen, and carbon derivatives, all of which were compounds. Through spectroscopic analysis of the discharge tubes, he concluded that

⁸⁷⁰ Schuster, 1884, p. 318, Petit, 2013, p. 217.

dissociation occurred, but the state of dissociation of the molecules was not homogeneous in the tube. Schuster's spectral analysis became an effective means of measuring the dissociation state of gases subjected to electric discharge. However, never during his presentation did he use the word "ions". He preferred to use the expression *positively electrified particles*.⁸⁷¹ At the meeting of the British Association held in September of 1885 in Aberdeen, Schuster presented his old and new results on the electric discharge of gases.⁸⁷² Another important aspect noted by Schuster was the analogy between gases and electrolytes concerning the surrounding medium. The discharge experiment of gases required the achievement of the highest possible vacuum. The absence of any other body is prohibited as interfering with the accuracy of the experiment. To avoid any water disturbance in the process of electrolysis, Schuster considered water an inert medium. In contrast, the surrounding medium of electrolysis in solutions is the water molecules. Thus, the vacuum of the discharge is analogous to the water of electrolysis. It was, therefore, more convenient for Schuster to perform experiments in gases independently of any solvent.

Another physicist, who used discharge experiments to formulate a theory of dissociation in the gas phase, was J. J. Thomson, a student of Shuster. He probably became interested in this field after discussing the gas discharge with Shuster when both worked at the Cavendish Laboratory in Cambridge. During this informal collaboration, they convinced themselves of the relevance of the analogy between electrolytic and gas conduction.⁸⁷³ J. J. Thomson began to discuss molecular dissociation early in 1883. He saw

⁸⁷¹ Schuster, 1884, p. 327.

⁸⁷² Petit, 2013, p. 219.

⁸⁷³ Petit, p. 220.

it as a consequence of the Clausius-Williamson hypothesis.⁸⁷⁴ In a Bakerian Lecture in the Royal Society, delivered in May 1887, J. J. Thomson expressed his intuition that an electric discharge induces dissociation of gas molecules.⁸⁷⁵ In the meeting of the British Association of the Advancement of Sciences held in September 1887 in Manchester, Oliver Lodge, the secretary of the electrolysis committee, reported J. J. Thomson's work on electrolytic conduction. Thomson rejected the classical explanation that the electric current caused dissociation of the salt in solution. Instead, he supported the view that the salt dissociates upon its dissolution in water and before the application of the electric field. He offered three pieces of evidence in favor of this explanation. The third argument was an extension of van 't Hoff's work on osmotic pressure.⁸⁷⁶ His conclusion in the report put forward the analogy between gases and solutions regarding the conduction of electricity. Electrolytes dissociate before the flow of the electric current regardless of whether they are in the gaseous state or in solution.877 Schuster878 and other members of the committee opposed the idea of free ions without the action of the electric current.⁸⁷⁹ Thomson defends his position by assuming that Schuster and the others physicists did not fully understand his interpretation of the Clausius-Williamson hypothesis.⁸⁸⁰ In 1887, Thomson's research seemed closer to the ionic dissociation theory of the ionists than to the British physicists and chemists. Thomson at that timer appeared as an exception of the strong opposition of British scientists against Arrhenius' ionic dissociation theory. But not for long.

⁸⁷⁴ Thomson, J.J., 1883.

⁸⁷⁵ Ibid, 1887.

⁸⁷⁶ Petit, 2013, p. 223.

 ⁸⁷⁷ The letter sent to the Committee of Electrolysis has been reproduced in Thomson's book of mathematical physics *Applications of Dynamics to Physics and Chemistry* (Thomson, J.J., 1888, pp. 293-295).
⁸⁷⁸ Schuster, 1890, p. 539, and 557-559.

 ⁸⁷⁹ For the opposition against Arrhenius' ionic dissociation theory, see chapter 12 of this dissertation.
⁸⁸⁰ Thomson, J.J., 1890, p. 295.

How close was Arrhenius' electrolytic dissociation theory to Schuster's discharge experiments and Thomson's intuition about the existence of free ions in the gas and the liquid state? Was Arrhenius familiar with Schuster and J.J. Thomson's research before he began his photochemical experiments? Root-Bernstein avoids giving a clear answer to this question. He attributes the discovery of the electrolytic dissociation of gases to a simultaneous discovery by Arrhenius, Shuster, Thomson, and W. Giese.⁸⁸¹ He further mentioned a report to the electrolysis committee in which Lodge refers to Shuster's discharge experiments.⁸⁸² And then he concludes that neither Lodge, Schuster, nor Arrhenius seems to have been aware of each other's work.

Axel Petit, on the other hand, describes two cases in which J.J. Thomson exchanged views with Ostwald and Arrhenius with regard to scientific matters. The first contact was a short controversy between J. J. Thomson and Ostwald. Ostwald criticized⁸⁸³ how J. J. Thomson attempted to describe the chemical combination through a mathematical equation.⁸⁸⁴ Thomson's reply was rather crude, questioning Ostwald's credibility. In addition, he took the opportunity to address a scathing attack on the reliability of Ostwald's *Lehrbuch*.⁸⁸⁵ Ostwald felt despised by this answer, but he managed to respond politely within the context of scientific ethics.

It was not until 1890 when Arrhenius and J. J. Thomson exchanged views on the dissociation of electrolytes. Arrhenius had resumed his investigation into the electrical

⁸⁸¹ Root-Bernstein, 1980, p. 371-172. For Thomson and Giese, Root-Bernstein referred to Partington's *History of Chemistry*. However, Partington does not give any information on this subject. He just mentions in one line statement Shuster and Thomson's names and the type of research they performed (Partington, 1972, p. 929).

⁸⁸² Root-Bernstein, 1980, pp. 371-372.

⁸⁸³ In his textbook *Lehrbuch der Allgemeinen Chemie*, 1887a, p. 747; Petit, 2013, p. 224.

⁸⁸⁴ Thomson, J.J., 1884, p. 267; Petit, 2013, p. 221.

⁸⁸⁵ Petit, 2013, p. 225.

conduction through gases. He used these experiments to demonstrate the existence of ionic dissociation in gases. His objective was to confirm that ionic dissociation was a unified theory applied equally to gases and solutions. He measured the conductivity variation of vaporized solutions with the concentration and found a proportionality between the two parameters.⁸⁸⁶ Having read Arrhenius' article, Thomson disagreed with rather technical problems involved in the photochemical method than with the essence of the paper's content. Arrhenius, in turn, noted the vagueness of the results obtained by Thomson.⁸⁸⁷ Despite these minor disagreements, the two scientists agreed on the analogy between electrolytic and gas conduction. No further discussion between Thomson had terminated abruptly when Thomson removed his interest from the physicochemical interpretations of the discharge phenomena. He moved to other research fields of physics. Nevertheless, as a member of the electrolysis committee of BAAS, J. J. Thomson had participated in debates and raised doubts about the ionists' electrolytic dissociation theory.⁸⁸⁸

The information on photochemical studies from van 't Hoff *Études* is not the sole influence of Arrhenius to initiate photochemical experiments. It was mainly the emulation created with the British physicists and, in particular, with members of the electrolysis committee of the British Association that led him to reconsider his old dissociation theory. Arrhenius had made contact with the secretary of the committee Oliver Lodge since 1886 when he sent to him his dissertation asking for his opinion.⁸⁸⁹ Also, Arrhenius had read

⁸⁸⁶ Arrhenius, 1891. Petit, 2013, p. 252; Root-Bernstein, 1980, pp. 412-413

⁸⁸⁷ Petit, 2013, pp. 255-256.

⁸⁸⁸ See chapter 12, section 2 of this dissertation.

⁸⁸⁹ Lodge replied favorably for the theoretical part of Arrhenius' thesis. He found the experimental part badly performed (see Chapter 12, section 2 of this dissertation).

Lodge's 1885 report on electrolysis, in which Lodge described discharge experiments in gases. Among the various propositions, Lodge suggested continuing studies that promoted the rapprochement between the discharge and electrolytic conduction.⁸⁹⁰ This suggestion was not emerged by chance, inasmuch Lodge was aware of the work of Schuster on gas conduction.⁸⁹¹ Therefore, Arrhenius could have taken into consideration the research suggested (along with J. J. Thomson) the analogy between gas and liquid conduction.⁸⁹² "The experiments reported by Prof. Thomson on the changes in the properties of electrolytic solutions induced by the electric current are of particular interest to me. In particular, the precise determination of the depression of the freezing point, if a current passes through the liquid, or not would be very promising".⁸⁹³ The latter sentence of this letter indicates that Arrhenius had information about the work performed by members of the electrolysis committee on various aspects concerning electrolytes.

Photochemical experiments had made it possible for Arrhenius to postulate that the dissociation observed in both the gas and the liquid state resulted in the formation of ions. The concept of ions allowed a reformulation of the dissociation theory of his dissertation. It allowed him to rethink the validity of the old interpretation of several properties of electrolytic solutions related to this entity; to reexamine his theory based on such notions as electrical conductivity, chemical reactivity, activity coefficient, and the Clausius-Williamson hypothesis. As we shall see in later sections, van 't Hoff's papers where he described his solution chemistry and the colligative properties of the solutions of the

⁸⁹⁰ Lodge, BAAS Report, 1885, p. 633; Petit, 2013, p. 214.

⁸⁹¹ Shuster was a member of the committee, and very often, he reported his work to its members.

⁸⁹² Petit, 2013, p. 255.

⁸⁹³ Letter of Arrhenius to Lodge, November 1887. Quoted in Petit, 2013, p. 252.

electrolytes paved the way for Arrhenius to reach his dream; the articulation of the ionic dissociation theory.

Section 2. Jacobus Henricus van 't Hoff.

Van 't Hoff was born on 30 August 1852 and raised in Rotterdam, the Netherlands.⁸⁹⁴ After completing his elementary and secondary schooling in Rotterdam, he passed the final examination in 1869 and intended to study chemistry. However, following his father's advice, he spent two years at the Polytechnic School at Delft to study applied chemistry.⁸⁹⁵ However, his practical training in a local sugar factory convinced the young man that theoretical chemistry, not applied chemistry, was his interest. He decided to study pure chemistry and enrolled at the University of Leyden. Soon realized that Leyden did not offer special facilities for chemistry and left Leyden soon after he passed examinations as a candidate for a doctoral thesis. In 1872, van 't Hoff visited the laboratory of the eminent organic chemists August Kekulé at the University of Bonn, where he spent almost a year. It was there where van 't Hoff learned about the two-dimensional structural formulae of compounds suggested by Kekulé and possibly imagined that these formulae would be extended in space. Van 't Hoff probably imagined the concept of the tetrahedral carbon atom in 1873, while visiting the laboratory of Adolph Würtz in Paris.⁸⁹⁶ There, being in solitude and free from practical research, he had ample time to imagine the threedimensional problem. Interestingly, in Würtz's laboratory, he met Joseph Achille Le Bel

⁸⁹⁴ For van 't Hoff's biography and detailed analysis of his work, see Cohen, 1912; Harrow, 1920, pp. 79-109; Snelders, 1981b, pp. 575-681; Root-Bernstein, 1980, pp. 182-350-; Servos, 1990, pp. 20-45; Laidler, 1993, pp. 209-214; Walker, 1913.

⁸⁹⁵ The program at the Polytechnic School was three years. The young van 't Hoff managed to finish it in two years.

⁸⁹⁶ Root-Bernstein, 1980, p. 191.

(1847-1830), who shared credit with van 't Hoff for the tetrahedral carbon atom. Le Bel postulated independently the tetrahedral carbon atom later that year.⁸⁹⁷ Van 't Hoff published his theory on the tetrahedral carbon atom immediately upon his return to Holland in 1874. On 22 September of the same year, he obtained his doctoral degree at the University of Utrecht, conducting his dissertation on the synthesis of cyanoacetic acid and malonic acid under the supervision of Edward Mulder (1832-1924). His dissertation was of little significance. In 1876, he was appointed lecturer of physics at the State Veterinary College of Utrecht, and in 1877 lecturer in theoretical and physical chemistry at the University of Amsterdam. From 1878 until 1896, he served as professor of chemistry, mineralogy, and geology and head of the chemistry department. In 1896 moved to Berlin and became a professor at the Prussian Academy of Sciences in Berlin, rejecting offers from the University of Leipzig and the University of Amsterdam. He continued his research until his death on 1 March 1911. He was awarded many honorary titles and medals. In 1901, he became the first Nobel laureate in chemistry for his work on osmotic pressure in solutions and on the laws of chemical dynamics.

2.1 The tetrahedral carbon atom

In the same year, when van 't Hoff received his Ph.D. He published a twelve-page pamphlet that marked the origin of a new specialization in organic chemistry, stereochemistry. This novelty raised severe criticisms and little support from contemporary chemists.⁸⁹⁸ Van 't Hoff's biographers do not fail to refer to the scathing comments of Kolbe for the tetrahedral carbon atom. Van 't Hoff has mentioned Kolbe's statement in his

⁸⁹⁷ Root-Bernstein, 1980, p. 190.

⁸⁹⁸ Van 't Hoff, 1967, pp. 6-7; Snelders, 1981b, p. 577; Root-Bernstein, 1980, pp. 191-192.

speech *Imagination in Science*. In this speech, van 't Hoff included the whole of Kolbe's statement.⁸⁹⁹ I present a quite extended citation of this statement, for two reasons: first, because Kolbe made this statement in the context of a general criticism for the decline of science in Germany, and second, to point out that even great scientists may not have the talent to evaluate the perspective of discovery.⁹⁰⁰ Ostwald had such a talent. Ostwald saw earlier than anyone the merit of Arrhenius' dissertation and van 't Hoff's thermodynamics, as we shall see below.

A year later, van 't Hoff published his discovery in a more extended version with the title *La chimie dans /'espace*.⁹⁰¹ This little book was translated into German and in English. Van 't Hoff rejected the perpendicular arrangement on the same plane of the four affinities of one carbon atom (the carbon valence) as not existent. He supposed that the four affinities (chemical bonds) of the carbon atom are equivalent and directed to the corners of a tetrahedron, the carbon atom situated at the center of the tetrahedron.⁹⁰² In

⁹⁰¹ Van 't Hoff, 1875.

⁸⁹⁹ Van 't Hoff, 1967, pp. 6-8.

⁹⁰⁰ "As a consequence of this, there is an overgrowth of the weed of the seemingly learned and ingenious but in reality trivial and stupefying natural philosophy. This natural philosophy, which had been put aside by exact science, is at present being dragged out by pseudoscientists from the junk-room which harbors such failings of the human mind, and is dressed up in modern fashion and rouged freshly like a whore whom one tries to smuggle into good society where she does not belong. One who considers this apprehension to be exaggerated should read, if he can manage it, the recently published pamphlet, "The arrangement of the atoms in space", by Messrs. Van 'T HOFF and HERRMANN, [assistant at the Agricultural Institute in Heidelberg who prepared the German edition of La chimie daps l'espace], which teems with fantastic trifles. I would ignore this paper as so many others!, if it were not for a renowned chemist who protected this nonsense and recommended it warmly as meritorious accomplishment (Kolbe meant Johannes Wislicenus (1835-1902) Professor of Chemistry at the University of Wtirzburg who recommended van 't Hoff's brochure). A Dr. J. H. V AN'T HOFF who is employed at the Veterinary School in Utrecht appears to find exact chemical research not suiting his taste. He deems it more convenient to mount Pegasus (evidently loaned from the Veterinary School) and to proclaim in his "La chimie dans l'espace" how, to him on the chemical Parnassus which he ascended in his daring flight, the atoms appeared to be arranged in the Universe".

⁹⁰² The necessity for a space formula became increasingly felt by other chemists before van 't Hoff. However, he gave it the proper three-dimensional shape, the carbon atom at the center of the tetrahedron and attached to four different groups that explained the optical isomerism (Walker, 1913, p. 1131-1132).

such a tetrahedron, a compound of the type $CR_1R_2R_3R_4$ with four different substituents, R, is possible to construct two spatial or stereochemical structures, which are nonsuperimposable images of one another (like an object and its mirror image, or the left and the right hands). In this case, there is no center or plane of symmetry for the tetrahedron. The concept of the asymmetric tetrahedral carbon atom would explain many cases of isomerism, which current models could not explain. More importantly, van 't Hoff explained the origin of the optical activity (the rotation of the polarized light by a solution or a crystal due to molecular asymmetry) demonstrated by Louis Pasteur experimenting with crystals of tartaric acid. Van 't Hoff also discussed the relationship between the asymmetric carbon atom and the number of isomers. He demonstrated that the number of possible isomers of a compound with n non-equivalent asymmetric carbon atoms is 2^n . He explained how these isomers decrease as one or more of the asymmetric carbon atoms become equivalent. In 1878 and 1881, he completed the two volumes of his first book, Ansichten über die organische Chemie (Views on organic chemistry),⁹⁰³ his last service to organic chemistry, and the beginning of his research endeavors in the realm of physics.

2.2 Ansichten über die organische Chemie

In *Ansichten*, van 't Hoff attempted to link the chemical and stereochemical formulae with the chemical and physical properties of substances. He believed that the chemical structure did not simply symbolize the composition of a substance, but also the intrinsic properties of the matter that constituted the chemical compound. He thought that the chemical formula should reflect changes in the properties of that matter. In the first volume of the *Ansichten*,

⁹⁰³ Van 't Hoff, 1878-1881.

van 't Hoff introduced a simplistic and naive mathematical analysis of the chemical affinity. He invoked the old tradition concerning the nature of force. He contended that affinity is the manifestation of attractive gravitational forces between atoms as they move and approach one another to form molecules. But he was unable to apply this theory to real cases. The absolute mass and size of the atoms were unknown at that time, and in addition, he could not define the type of motion of the atoms.

Furthermore, as we have seen, most chemists were unprepared to understand and assimilate the mathematics involved in his theory. Unable to calculate and apply the chemical affinity in the formal language, van 't Hoff decided to approach the problem from another angle; he defined affinity as a manifestation of valency and reactivity. He hoped that this way would allow him to compare the chemical properties (composition) with physical properties (valency and reactivity)⁹⁰⁴, which was his initial target in writing this book, after all.⁹⁰⁵

In the second book of the *Ansichten*, van 't Hoff presented a classification of organic substances based on carbon and its valency as expressed by the number and type of substituents, X. In this classification, he excluded the hydrogen atoms. In the first category, he classified the compound CH₄ (the structure of the gas methane), in the second class, compounds of the form HCX₃ (X = Cl, Br, OH, etc.), in the third class H₂CX₂, in the fourth class HCX₃, and the last, compounds of the form CX₄. He then compared the chemical composition of compounds in each class with the rate at which they tend to undergo a particular chemical change at the same experimental conditions (pressure, and

⁹⁰⁴ One definition of reactivity is the rate at which a chemical substance tends to undergo a chemical reaction.

⁹⁰⁵ Root-Bernstein, 1980, pp. 217-228.

temperature); for example, oxidation and reduction reactions or other substitution reactions. At any rate, van 't Hoff's attempt to correlate the chemical composition of substances reflected on their molecular structure with their chemical reactivity could not be considered as a novelty. Earlier experiments performed by organic chemists had attempted to compare the variation of the reactivity of compounds with chemical structure.⁹⁰⁶

The questionable theory of affinity and the illegibility of the book made *Ansichten* unappealing to the interested reader. Van 't Hoff himself lessened the book's quality with the words "it is hardly worth knowing," referring, however, to the origin of the book.⁹⁰⁷ This statement presumably made most of his biographers evaluate *Ansichten* as a work of low merit. Although van 't Hoff had some concrete results in his attempt to integrate the chemical composition with the affinity and reactivity of compounds, he failed to provide general principles of affinity applicable to substances' chemical and physical properties. The *Ansichten* received a poor reception from the scientific community. However, one should approach the *Ansichten* with a different perspective, away from evaluating its scientific merit. *Ansichten* should be seen in the context of van 't Hoff's future studies and goals. *Ansichten* should be viewed as the prolific soil that sustained van 't Hoff's interest in connecting chemical and physical properties, bringing him closer to physics and thermodynamics. Van 't Hoff's tendency to change his scientific horizon will become apparent in his next work, the *Étude de Dynamique Chimique*.

⁹⁰⁶ Ibid, pp. 229-231.

⁹⁰⁷ Quoted in Root-Bernstein, 1980, p. 198.

2.3 Études de Dynamique Chimique

Van 't Hoff devoted three years to complete the *Études*, which appeared in 1884 when Arrhenius defended his thesis in Uppsala. The *Études* contained van 't Hoff's ideas about reaction rates, the theories of equilibrium, and affinity. These subjects constituted a significant part of the ionists' chemical thermodynamics. Van 't Hoff published in1896 a second edition of the *Études* translated in English. However, this edition did not contain the introduction of the first edition. In the introduction van, 't Hoff revealed his motivation for writing the book and paid tribute to several physicists who inspired him to pursue research in physics, particularly in the fields of kinetics and thermodynamics.

2.3.1 The kinetics

The first part of the *Études* dealt with the molecularity of the reactions. Van 't Hoff has not changed its scope that had in *Ansichten*; to establish the connection between the chemical constitution and the physical properties of substances. His intention in writing the *Études* becomes apparent from the first paragraphs of the introduction:

"General progress, made in science, goes through two distinct phases: originally, all scientific research is descriptive or systematic; it later becomes a rational or philosophical order. [...] Rational research in chemistry has been characterized in recent times by a marked tendency to relate the formula for constituting a body to its properties. This direction is justified by the fact that the formula for constituting a body is not only the symbolic expression of its composition but reveals, although still in an imperfect way, the intimate nature of the matter of which this body is

composed. Since all the properties of a body result from this intimate nature of matter can be easily foreseen that one day the constitutive formula will be able, by further development, to indicate to us exactly and in all their extent the properties of the body which it represents".⁹⁰⁸

What van 't Hoff had changed in *Études* was the mode of the classification of the reactions that brought chemistry more closely to the side of physics. He classified the normal reactions according to the number of molecules participating in the corresponding chemical reaction process. He discerned the reactions as monomolecular reactions involving the change in only one molecular structure (today, they are called unimolecular reactions, and usually involve processes of decomposition or isomerization), bimolecular reactions, and termolecular reactions depending on whether two molecules or three molecules participate in the reaction, respectively. He then connected the rate or velocity of the reactions with the concentration of the reactants or the products of the reaction (quantity in unit volume). Van 't Hoff used the velocity of the reaction because he was not interested in examining the end products at the equilibrium as in his Ansichten. He preferred to study the development of the reaction with time to examine how the reaction reached the state of equilibrium. Van 't Hoff's interest has shifted from the static analysis of forces (as Guldberg and Waage) to the dynamical rates of reactions. Taking into account, as an example, the general form of a regular (elementary or single-step) chemical reaction, in which the substance A gives under certain conditions two new substances B and Γ , one can write the following reaction scheme,⁹⁰⁹

⁹⁰⁸ Van 't Hoff, 1884, pp. 1-2.

⁹⁰⁹ Van 't Hoff did not use Eq. (10.2) for his kinetic analysis. I have adopted this general equation to facilitate the subsequent discussion of the various forms of the rate law and in particular to distinguish between molecularity and order of the reaction.

$$A = 2B + \Gamma \tag{10.2}$$

The differential equation that expresses the relationship of the rate of the reaction and the concentration of the substance A that undergoes the chemical transformation is as follows:⁹¹⁰

$$-\frac{dC_A}{dt} = k_1 C_A \tag{10.3}$$

Eq. (10.3) describes the decrease (negative sign) of the concentration C_A of the reactant A with time, which is proportional to its concentration. The proportionality constant, k_1 is the *rate constant* of the reaction.⁹¹¹ If one considers the reaction process may hold from right to left, i.e., the substances B and Γ react with each other and produce the substance A, then the rate equation for the formation of substance A could be written as

$$\frac{dC_A}{dt} = k_2 C_B^2 C_\Gamma \tag{10.4}$$

or, it may be written as

$$\frac{dC_A}{dt} = k_3 C_B^2 \tag{10.5}$$

If the substance Γ does not participate in the formation of substance A. The increase (positive sign) of the concentration of A with time in the rate laws (10.4) is proportional to the square of the concentration C_B of substance B, and the concentration C_{Γ} of substance Γ . k_2 is the rate constant of the reverse reaction. On the other hand, in the rate law (10.5), B is the only substance consumed in the reaction to give A. k_3 is the new rate constant. The molecularity of the reaction (10.2) from left to right is one (one molecule of A decomposes to give substances B and Γ). The rate of the reaction is proportional to the concentration of A, only. The molecularity of the reaction (10.2) from right to left is three (two molecules

⁹¹⁰ The current name of this equation is *rate equation* or the *rete law*.

⁹¹¹ Vant 't Hoff, 1884, p. 13.

of B react with one molecule of Γ to give one molecule of A. In all the three rate laws, the exponents of the concentrations correspond to the reaction's stoichiometry of (10.2). The summation of these exponents defines a new kinetic quantity, the *order of the reaction*.

Thus, the order of the rate law (10.3) is one that of the rate law (4) is three, and for the rate law (10.5) is two. Now, the molecularity in the rate law (10.3) coincides with the order of the reaction. Both are equal to one. The same is true for the rate law (10.4). The molecularity and the order are equal to three.⁹¹² In contrast, the reaction order in the rate law (10.5) is two, while the molecularity is three. It implies that the molecularity does not always coincide with the order of the reaction. Which of the two rate laws (10.4) and (10.5)is the correct one? This question finds no answer without proper experimentation. It suggests that a given reaction's order and rate equation cannot be reliably deduced solely from the reaction's stoichiometry and must be determined experimentally. Van 't Hoff did not explicitly define the reaction order, but he found the difference between molecularity and order in his *Études* experimentally. He discovered that the order of the thermal decomposition of arsine and phosphine did not follow the expected chemical equation of a quadrimolecular reaction (involving four molecules). Upon determining the rate law of the decomposition experimentally, he found that the reaction was of the first order.⁹¹³ Using various experimental methods, Van 't Hoff determined the molecularity, the rate law, and the order of more complicated reactions under different activity factors, reaction conditions (pressure, effects of the medium), and the movement of the molecules.⁹¹⁴ The methods

⁹¹² The order of the reaction can also be specified separately for each constituent in the rate law. Thus, the order of the reaction with respect to component B in the rate law (10.5) is two and zero for the constituent Γ , whereas the order of the reaction is two for B and one for Γ in the rate law (10.4).

⁹¹³ Van ' t Hoff, 1884, pp. 83-87.

⁹¹⁴ Ibid, pp. 83-123.

used by van 't Hoff to study the kinetics of the reaction, are effective only in cases in which the transformation of the reactants to products was slow. Fast reactions were not amenable to kinetic studies, at least with the experimentation of the time. Furthermore, fast reactions are one-sided reactions leading to completion and therefore unsuitable models for studying chemical equilibrium.

Van 't Hoff's interest in studying the dynamics of chemical reactions led him to investigate the principles of chemical equilibrium. One of the most important innovations in chemical equilibrium was its symbolism with two anti-parallel arrows (\rightleftharpoons) that still holds today in textbooks. According to Van 't Hoff, the symbol of equality in reaction (10.2) does not reflect what is happening during this process. The sign of equality presents a static image for the reaction. It indicates that the reaction has just one direction to completion (usually from left to right). In contrast, the symbol (\rightleftharpoons) provides a dynamic picture of the chemical reaction. Thus, following the new symbolism, reaction (10.2) writes:

$$A \rightleftharpoons 2B + \Gamma \tag{10.2a}$$

This reaction proceeds not in one direction but in two opposite directions. The two reactions occur simultaneously, not necessarily at the same rates and in competition until the completion of equilibrium. Which of the two opposing reactions will prevail, so that the equilibrium shifts to one or the other direction? Towards the reactants or to the reaction products? The result of this competition depends on the magnitudes of the rate constants of the forward and the backward reactions, which in turn depends on the nature of the reaction and the conditions under which the reaction takes place. In any case, the answer requires experimental verification.

Van 't Hoff had in mind the "kinetic" theory of Guldberg and Waage. Also, he had studied Berthollet's theory of incomplete reactions. Van 't Hoff knew that in these reactions, reactants and products coexisted in the equilibrium state. Also, he knew that any change in the concentrations of selected compounds participating in the reaction might affect the reaction equilibrium. These investigators inflicted to him the idea of forward and backward reactions. However, van 't Hoff rejected the static nature of Guldberg and Waage.'s theory. As we have seen in the first chapter, Guldberg and Waage believed that the equilibrium of reactions taking place in two opposite directions was the result of the balance between two opposing gravitational forces. Van 't Hoof adopted the views of Pfaudler⁹¹⁵ and Horstmann for a dynamical equilibrium process. These scientists had a significant influence on van 't Hoff's work on kinetics and thermodynamics. The Dutch chemist did not omit to mention their names in his *Études* and praise their work. However, the two Norwegian scientists provided van 't Hoff with the mathematical definition for the equilibrium constant, as we shall see below.

Both Pfaudler and Horstmann studied dissociation reactions in the three forms of matter (gas, liquid, and solid). However, they approached this subject from a different perspective. Pfaudler used the kinetic theory of heat and applied the mass action law in terms of molecular collisions. Horstmann, on the other hand, used the second law of thermodynamics to explain the chemical equilibrium in the thermal decomposition of molecules. Pfaundler was influenced by Clausius' paper of 1857 on the mechanical theory of heat and the experiments on dissociation performed by

⁹¹⁵ For Leopold Pfaundler's life and work, see Jensen and Kuhlmann, 2012, pp. 35-36. T
Saint-Claire Deville. The entropy introduced by Clausius in 1865 provided Horstmann with the necessary conceptual foundation. At this stage, it seems appropriate to interrupt the flow of the discussion concerning van 't Hoff's *Études* and make the acquaintance with the dynamics of Pfaundler and the thermodynamics of Horstmann that influenced the entire work of van 't Hoff.

Leopold Pfaundler's molecular collisions theory

Pfaundler developed his theory on dissociation in a paper published in 1867.916 He considered that polyatomic molecules have internal and external modes of motion. Internal rotations and vibrations constitute the internal motions, whereas the molecules possess an external translational motion. He considered that internal motions have an upper limit, and dissociation occurs if they exceed this limit. Internal motions overcome this limit by exchanging energy with the translational motion (vis-viva) through molecular collisions. Not all collisions are adequate to induce dissociation. The magnitude of the translational motions does not have a constant value which is common to all molecules. The distribution of translational modes of motions (velocities and vis viva) does not equally affect each molecule's critical limit of internal motions. Therefore, there is a mixture of dissociated and non-dissociated molecules at a constant temperature in the gas phase or solution. The greater the temperature is, the greater the number of molecules that exceed the upper limit of their internal motions. In other words, as the temperature increases, the frequency of the effective collisions increases, which in turn leads to a greater degree of dissociation. A state of equilibrium is established between the dissociated molecules (the products of the

⁹¹⁶ The title of this article *Beiträge zur chemischen Statik* (Contributions to chemical statics) seems strange, since the whole treatment of dissociation by Pfaundler lies on molecular dynamics (Pfaudler, 1867).

reaction) and the undissociated molecules (the reactants of the reaction). Pfaundler used the thermal decomposition of the solid calcium carbonate as an example to apply his theory of dissociation. The decomposition of calcium carbonate produces the solid lime (calcium oxide) and the gas carbonic acid (carbon dioxide) according to the following reversible reaction

$$CaCO_3 \text{ (solid)} \rightleftharpoons CaO \text{ (solid)} + CO_2 \text{ (gas)}$$
 (10.6)

The CO₂ molecules collide with each other and with the surface of the solid CaCO₃ leading to a redistribution of their translational motions. At each temperature, a portion of CO₂ molecules loses sufficient *vis viva* and recombines with CaO molecules to reform calcium carbonate. In accord with Berthollet and Saint-Claire Deville's experiments, Pfaundler observed that by changing the temperature of removing CO₂ molecules from the space above the solid CaO, the equilibrium of the reaction (10.6) is disturbed. ⁹¹⁷

Pfaundler extended his theory seeking to explain the mechanism of decomposition/ reassociation of molecules in displacement reactions. He based his conceptual model on an intermediate molecular complex formed through molecular collisions of the reactant molecules. He imagined a reaction of the following type

$$AB + C \rightleftarrows [ABC] \rightleftarrows A + BC \tag{10.7}$$

Depending on how the *vis viva* of collisions redistributed among the internal modes of motion of the complex ABC, it could be either decomposed back to the original reactant molecules AB and C or into the new product molecules A and BC. The net result is the establishment of an equilibrium state between reactant and product molecules.⁹¹⁸ Pfaundler

⁹¹⁷ Pfaundler, 1867, p. 76. Pfaundler did not explicitly use the chemical reaction (10.6). He explained the chemical process verbally.

⁹¹⁸ Ibid, pp. 67-70; Jensen and Kuhlmann, 2012, p. 32.

devoted the second part of his paper to the intermediate complex theory.⁹¹⁹ In the third part of his paper, Pfaundler discussed the mechanism of collisions for the double displacement reactions.⁹²⁰ Also, Pfaundler was able to explain the mass action law in terms of his collision theory.

Pfaundler defended his theory against the earlier kinetic theory of Williamson. Recall that Williamson invoked limited molecular motions displayed by atoms or radicals exchange between nearest neighboring molecules. Williamson's theory lacked the concepts of collisions and the collision complex, which constituted the core of Pfaundler's kinetic theory. Pfaundler devoted the third part of his paper to opposing Williamson's hypothesis with his collision theory. He repeatedly explained the difference between Williamson's exchange theory of reactions and his theory of molecular collisions and that the former was inconsistent with the experiment.⁹²¹ Clausius had noted this inconsistency already in 1858. Unfortunately, Pfaundler found his efforts largely wasted. His fellow chemists considered his theory a mere application of Williamson's theory and gave credit to Williamson as the originator of the current molecular theory of the chemical reaction.⁹²² Van 't Hoff gave

⁹¹⁹ Pfaundler's theory of the molecular complex may be considered as the predecessor of two theories of the modern chemical kinetics, which explain the effect of temperature on the reactions rates; the first is the *collision theory* and the second the theory of the *activated complex* or the *transition state theory* (Lund, 1968.). The collision theory deals with the frequency and the energy of the effective collisions that lead to dissociation. In contrast, the activation complex theory takes care of the energy and the geometry of the intermediate complex. For the simple case of the reaction scheme (10.7), the old bond AB is breaking, and at the same time, the new bond BC is forming. The intermediate configuration ABC has partial reactant and partial product character. Also, the activated complex has a potential energy usually expressed by the Gibbs' energy that corresponds to the exact configuration of the activated complex at the transition state that has an equal probability of forming either the reactants or products of the given reaction. The reaction to proceed from the reactants to products.should overcome this potential energy.

⁹²⁰ Pfaundler, 1867, pp. 79-81; Jensen and Kuhlmann, 2012, p. 33.

⁹²¹ Pfaundler, 1867, pp. 72-84.

⁹²² Ibid, pp. 77-78, and 82-84: Jensen and Kuhlmann, 2012, pp. 34-35, and 37-38. Root-Bernstein has a different opinion. He considers Pfaundler as a proponent of the Clausius-Williamson hypothesis (1980, p. 251).

credit to Pfaundler as being the first to show that chemical equilibrium results from the equalization of the velocities of the forward and the reverse reaction. Van 't Hoff associated Pfaundler's dynamic collision theory with Guldberg-Waage's static theory through the equilibrium constant. He extended the expression of the equilibrium constant in the form of the ratio of active masses to the rate constants of the forward and backward reactions. For the reaction (10.2a), one obtains⁹²³

$$K_{eq} = \frac{C_B^2 C_\Gamma}{C_A} = \frac{k_1}{k_2}$$
(10.8)

Depending on the relative magnitude of the two rate constants, the equilibrium shifts to the left or the right, When $k_1 > k_2$ ($K_{eq} > 1$) the equilibrium shifts towards the products, whereas it shifts to the reactants when $k_1 < k_2$ ($K_{eq} < 1$).

August Horstmann's dissociation theory

Horstmann approached the subject of dissociation of substances by observing that the determination of the molecular weight of substances using vapor pressure measurement was not valid for several substances.⁹²⁴ Horstmann assumed that, for some reason, Avogadro's law for determining the molecular weights did not apply to certain cases. Experimental findings showed that the molecular weight changes with temperature, corresponding to different molecular structures at different temperatures.⁹²⁵ Horstmann investigated the problem in 1868 and 1869 and proposed that the deviation from Avogadro's law was due to the dissociation of molecules, a phenomenon that Saint-Clair

⁹²³ Van 't Hoff, 1884, pp 125-127.

 ⁹²⁴ For an analysis of Horstmann's contribution to thermodynamics, see Kipnis, 1997; van 't Hoff, 1902;
 Jensen, 2009; Darrigol, 2018b, pp. 6-7; Root-Bernstein, 1980, pp. 156-268.
 ⁹²⁵ Root-Bernstein, 1980, pp. 259-263

Deville, Pfaundler, and others had studied earlier.⁹²⁶ Therefore, the number of molecules in a given volume of gas should increase, leading to an apparent deviation of Avogadro's law. Horstmann realized that the previous hypothesis that all molecules in the body show the same resistance to decomposing forces of heat and, therefore, must all decompose at the same temperature do not fit the experimental results. This hypothesis, although plausible, contradicted the kinetic theory of gases developed by Clausius and Maxwell. Consequently, he assumed that the molecules in a body do not have all the same average energy. At any given temperature, there are a few molecules with sufficient energy to dissociate. He further contended that the number of molecules that dissociate (the degree of dissociation) increases with increasing temperature.

Horstmann investigated this viewpoint further in an article published in 1871. In this article, he compared the experimental results of Saint-Claire Deville on the oxidation of iron in the presence of water with those calculated by applying thermodynamics reasoning. He concluded that the kinetic theory of Maxwell was incapable of explaining the results of Saint-Claire Deville.⁹²⁷ He chose the road of thermodynamics, using Clausius-Clapeyron's equation and the first law of thermodynamics.

$$\frac{dp}{dT} = \frac{Q}{AT\delta y} \tag{10.9}$$

Q is the amount of heat for decomposition. A is the mechanical equivalent of heat, p is the pressure of dissociation, and δv is the difference between the volumes of the vapor v and the liquid v' (here Horstmann approximated δv with the much larger volume of the vapor).

⁹²⁶ Horstmann, 1868 and 1869; Root-Bernstein, 1980, pp, 263-265.

⁹²⁷ Horstmann, 1871, p. 635.

He further assumed that the gases obey Avogadro law, pv = RT. Substituting the volume in Eq. (10.9), he obtained

$$\frac{dp}{dT} = \frac{pQ}{AT^2} \tag{10.10}$$

Eq. (10.10) can be rearranged as

$$\frac{d\ln p}{dT} = \frac{pQ}{AT^2} \tag{10.11}$$

Eqs. (10.10)) and (10.11) describe the change of pressure of the gas and thereby its density with the temperature. Integrating Eq. (10.11), Horstmann obtained the expression

$$R\ln\frac{p_1}{p_2} = -\frac{Q}{AT} + C \tag{10.12}$$

C is the integration constant. The final equation, which holds for the water vapor and the hydrogen gas, describes the dependence of the pressure of the dissociated molecules upon the heat of dissociation for the equilibrium case. In particular, in the reaction of the iron oxidation, he equated the ratio $\frac{p_1}{p_2}$ with the ratio of the partial pressures of the dissociated molecules of the water vapor and hydrogen gas. Horstmann observed that the dissociation pressures of the hydrogen gas and water vapor that evolved in the reaction increase with temperature. This increase was faster for the water molecules than for the hydrogen molecules.⁹²⁸ He explained this behavior according to the dissociation pattern suggested by Pfaundler. The decomposition of the intermediate compound of the iron oxidation provides a larger number of water molecules than the hydrogen gas.⁹²⁹ These results and, in particular, Eq. (10. 12) proved to be of great importance for van 't Hoff.

⁹²⁸ Ibid, p. 637.

⁹²⁹ The oxidation of iron (rusting of iron) in the presence of water or air moisture is a complex chemical process. It provides two types of intermediate iron hydroxides. In this respect, it is amazing that Saint-Claire Deville succeeded to isolate and identify the two gases, and measure their partial pressures as a function of temperature.

Horstmann's paper of 1873, which appeared in the same year as the two graphical papers of Gibbs, does not have any immediate relevance to what van 't Hoff had written in *Études*. Van' t Hoff mentioned nowhere on the pages of his *Études* the concept of entropy.⁹³⁰ However, the 1873 Horstmann's paper deserves further discussion because it is the first bold attempt by a physicist to apply thermodynamics to chemical processes during a period in which the confusion about the interpretation of the second law persisted among the physicists. These two approaches, thermodynamics and kinetics, developed by Horstmann and Pfaundler, respectively, to explain dissociation reactions reflected the two competitive trends of theoretical physics, that is, between molecular mechanics, and rational thermodynamics.

Right at the beginning of the 1873 paper, Horstmann addressed the critical question concerning the phenomenon of the chemical dissociation "A complete theory of dissociation has to explain in general why an equilibrium state, rather than a complete reaction, is possible and, for each case, which circumstances can influence the degree of dissociation. I believe I can demonstrate the basis for such a theory in the following".⁹³¹ Clausius introducing the concept of entropy claimed that the entropy increases towards a maximum value for an isolated system. The attainment of this maximum signifies the fact that the system has reached the equilibrium state. Horstmann asserted that the same principle holds for dissociation reactions approaching the limited state of equilibrium: "The cause of the limiting state for dissociation phenomena is, in my opinion, identical with the physical phenomena; it occurs when the entropy has become as large as possible for the

⁹³⁰ Entropy was mentioned only once in the English edition of the *Études*. A footnote on p. 150 of the book, van 't Hoff informs the reader that the formula, which describes the temperature dependence of the equilibrium constant, has also been deduced from the principle of the entropy increase.
⁹³¹ Horstmann, 1873, p. 76.

change in question. Hence our problem is solved if we know by what circumstances and in what manner the entropy of the process in question may be altered".⁴⁹ To achieve this goal, he correlated the entropy with the arrangement of the particles in the bodies. He made this connection by adopting the concept of disgregation Z, which, according to Clausius, expresses the arrangement of the particles in the bodies. Eq. (3.9) in chapter three relates the entropy with the disgregation. Thus, the entropy can be calculated as long as the disgregation is known. Horstmann found it plausible that the arrangement of the particles in the bodies changes the dissociation.

Horstmann imagined that several causes during the decomposition of a gaseous substance increase or decrease the entropy of the reaction. For instance, entropy decreases during the conversion of heat into chemical work and increases because the non-dissociated molecules expand.⁹³² However, the net result of all these contributions by the individual processes should increase the entropy of the reaction. The reaction must therefore stop whenever the entropy decrease starts becoming larger than the entropy increase. At this moment, the dissociation reaction has reached the condition of equilibrium, in which dS = 0. Horstmann expressed the condition of equilibrium in terms of the degree of the dissociation, *x*, as follows:

$$dS = \left(\frac{dS}{dx}\right)dx = 0 \tag{10.13}$$

Using Eq. (3.9) of chapter three and defining the heat required for the decomposition as a fraction of the dissociated species, namely xQ, the entropy of dissociation could be calculated explicitly from the equation⁹³³

⁹³² Ibid, p. 77.

⁹³³ Ibid, p. 78.

$$\frac{\mathrm{d}s}{\mathrm{d}x} = \frac{\left[Q + x\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)\right]}{T} + \frac{\mathrm{d}Z}{\mathrm{d}T} \tag{10.14}$$

Horstmann had further elaborated this equation for various cases, including cases in which a single substance in the gaseous, in solution, or the solid is decomposed into two other substances. Horstmann had extended his theory to more complex cases that involved double displacement reactions. In each case, the disgregation takes a particular form. For instance, the disgregation o the dissociation of the solid calcium carbonate according to reaction (10.6) is composed of the disgregations of the two solids (CaCO₃ and CaO), and the disgregation of the gas carbon dioxide. In other words, the total disgregation of the dissociation reaction (10.6) is the algebraic summation of the individual disgregations.

The dissociation theory of Horstmann, described in his 1873 paper, offered some qualitative explanations for the most important internal and external factors that influence the reaction processes: The temperature, the volume of the reacting substances, and the pressure to which they are subjected, especially when changes in these quantities affect the disgregations of the individual substances depending on their physical state (gas, liquid, solid), or their natural morphology (e.g., allotropic forms). Also, Horstmann's theory predicts the effect of the mass action law on the degree of dissociation and its modification upon changing the experimental conditions.⁹³⁴ When a substance is selectively added or removed from the reaction mixture, such modifications are always observed with gaseous and dissolved reactants but never with immiscible solids and liquids. In an immiscible system, substances may be removed from the reaction without affecting the disgregation of the whole system. Nonetheless, this situation contradicts the experiment and the theory

⁹³⁴ Ibid, pp. 80-81.

of the random fluctuations that allowed some molecules to deviate from the average arrangement, and thereby undergoing dissociation.

Horstmann's approach was able to describe qualitatively the conditions (pressure, temperature, volume, and the nature of substances) that favored dissociation. He explained the alteration of the bodies' internal molecular arrangement (disgregation) during decomposition but encountered severe difficulties to provide quantitative results for these observations. He found insurmountable difficulties to calculate the disgregation of the various substances of the dissociation reactions. Horstmann felt unable to proceed further because "The theory of dissociation developed here may require yet further testing and verification, though it is in keeping with the examples that have been cited".⁹³⁵

2.3.2 The analogy between ideal gases and dilute solutions

Van 't Hoff accepted both the kinetic and the thermodynamic theories of Pfaundler and Horstmann. From the German chemist, van 't Hoff gained something equally important with the dynamical view of dissociation, which played a decisive role in the development of his solution theory: the analogy between the thermodynamics of the perfect gases and that of the dilute solutions of salts. Horstmann expressed this analogy in terms of the similar behavior of the disgregation of the molecules constituting these two phases.⁹³⁶ The analogy between gases and dilute solutions allowed van 't Hoff to draw an analogy between the vapor pressure of gases and the concentration of solutes in the solution. Without any

⁹³⁵ Ibid, p. 81.

⁹³⁶ This similarity is expressed by Horstmann as follows: "I want to mention that our theory would lead us to a relationship of this kind if one assumes that in dilute solutions the disgregation of a salt depends on the separation of its particles in a manner similar to that of a permanent gas, an assumption which is highly probable" (Horstmann, 1873, p. 195).

rigorous derivation, Van 't Hoff equated the ratio of the partial pressures in Eq. (10.12) with the ratio of the concentrations.

$$R\ln\frac{p_1}{p_2} = \frac{c_1}{c_2} = K_{eq} \tag{10.15}$$

Equation (10.15) holds for dilute solutions of substances. The ratio of the concentrations in Eq. (10.15) is equal with the equilibrium constant K_{eq} , which in turn is equal to the ratio of the rate constants of the forward and backward reactions according to Eq. (10.8). Substituting in Eq. (10.12), the ratio of the vapor pressures with the equilibrium constant, he obtained

$$\ln K_{eq} = -\frac{Q}{AT} + C \tag{10.16}$$

Q is the heat content of the reaction (today, the enthalpy of the reaction). Eq. (10.16) applies to any homogeneous reversible reactions. Van 't Hoff differentiating and rearranging Eq. (10.16), derived the well-known expression for the temperature dependence of the equilibrium constant.

$$\frac{\mathrm{dln}K_{eq}}{\mathrm{d}T} = \frac{Q}{2T^2} \tag{10.17}$$

This equation⁹³⁷ is true for homogeneous and heterogeneous equilibrium in gases and dilute solutions.⁹³⁸

The kinetic studies of van 't Hoff continued with the thermodynamic theory of equilibrium. However, the study of the effect of temperature on the reaction velocity preceded the thermodynamics of equilibrium. He thought this study should be presented

⁹³⁷ In all formulae with logarithms, Van 't Hoff employed the symbol of the base10 logarithm (log10). Instead, I have used the natural logarithm (In), which is widespread in current physical chemistry textbooks. The choice of any of the two symbols does not change the equations' form and meaning since these logarithms are arithmetically related.

⁹³⁸ Van 't Hoff, 1884, p. 127. In the 1896 edition of the *Études*, van 't Hoff presented a rigorous proof of Eq. (10.17).

here as a continuation of the chapter dealing with his kinetics. The substitution of the ratio k_1/k_2 to K_{eq} , gives⁹³⁹

$$\frac{\mathrm{dln}k_1}{\mathrm{d}T} - \frac{\mathrm{dln}k_2}{\mathrm{d}T} = \frac{Q}{2T^2} \tag{10.18}$$

As before, Q is the quantity of heat of the chemical transformation. However, Eq. (10.18) does not directly give the dependence of the absolute rate constant on temperature. In this respect, van 't Hoff proposed an empirical equation of the form⁹⁴⁰

$$\frac{\mathrm{dln}k}{\mathrm{d}T} = \frac{A}{T^2} + B \tag{10.19}$$

The quantities A and *B* are treated as constants. Depending on the chemical reaction, the constants **A** or *B* may be negligible compared to each other, and Eq. (10.19) may be split into equation (10.20) when *A* is set equal to zero, or Eq. (10.21) when *B* is set equal to zero.

$$\frac{\mathrm{dln}k}{\mathrm{d}T} = B \tag{10.20}$$

$$\frac{\mathrm{dln}k}{\mathrm{d}T} = \frac{A}{T^2} \tag{10.21}$$

Van 't Hoff completed this part of kinetics with several applications. Integration of Eq. (10.21) gives the exponential form of the dependence of the rate constant on temperature,

$$k = (constant)e^{-A/T}$$
(10.22)

Arrhenius has further elaborated the second approximation described by Eq. (10.21) in 1889, leading to the well-known Arrhenius' equation (see below, Intermezzo II).

2.3.3 The principle of mobile equilibrium

⁹³⁹ Ibid, p. 115.

⁹⁴⁰ Ibid, p. 116.

Pierre Duhem discusses in his *Commentaires* the displacement of true equilibrium in physical and chemical processes imposed by a change of temperature. He referred to van 't Hoff's law of displacement of equilibrium with a temperature as expressed by the aforementioned equations. This temperature dependence of the equilibrium constant marks the difference between exothermic and endothermic compounds. Based on his observation of different forms of equilibrium in homogeneous and heterogeneous systems, Van 't Hoff articulated the *principle of mobile equilibrium*. "Every equilibrium between two different conditions of matter (systems) is displaced by lowering the temperature, at constant volume, towards that system the formation of which evolves heat".⁹⁴¹ In a footnote, Van 't Hoff clarified the content of this principle,

"This principle applies to every possible case, both of chemical and physical equilibrium. It indicates the effect of an elevation and a depression of the temperature; finally, if no system is present, the formation of which evolves heat, a change of temperature will not displace the equilibrium. Only one circumstance has been implied, namely the constancy of the volume occupied by matter; however, in applications, it does not generally have to be taken into account ".⁹⁴²

Van 't Hoff reminded that the principle of mobile equilibrium did not include the effect of other external factors on equilibrium, for example, pressure and concentration. Henry Le Chatelier and Karl Ferdinand Braun (1850-1918)⁹⁴³ independently formulated this principle more broadly, including temperature, pressure, volume, and concentration. *When any system at equilibrium for a long period of time is subjected to a change in*

⁹⁴¹ Ibid, p. 161.

⁹⁴² Ibid.

⁹⁴³ Karl Ferdinand Braun was a German electrical engineer, inventor, physicist and Nobel laureate in physics (1909). He discovered the mobile equilibrium independently.

concentration, temperature, volume, or pressure, the system changes to a new equilibrium, which partly counteracts the applied change.

Van 't Hoff, in his *Études*, studied reversible reactions. He distinguished between cases in which the quantity of heat Q in Eq. (10.17) is positive and those in which it is negative. When Q is positive, that is, when heat is evolved (exothermic reaction) by the formation of the product, the equilibrium constant K_{eq} will increase with falling temperature, and hence the concentration of the products will increase at the expense of the reactants. The reverse reaction is favored with increasing temperature (endothermic reaction). Since the total concentration of reactants and products is constant, the volume remains invariable. Therefore, any temperature change at constant volume will favor one or the other direction of the reaction. When Q is negative, products are formed with the absorption of heat. The products' concentration will be formed at the expense of the reactants when the temperature increases. In contrast, the depression of temperature always increases the quantity of the system, which evolves heat.

Van 't Hoff presented in his *Études* several examples showing the application of the principle of mobile equilibrium. One example is the dissociation of the dinitrogen tetroxide (N_2O_4) into nitrogen dioxide (NO_2).⁹⁴⁴

$$N_2O_4 \rightleftarrows 2 NO_2 \tag{10.23}$$

The reaction from left to right is exothermic, and therefore the formation of N_2O_4 is favored at low temperatures. Compound N_2O_4 is formed at a lower temperature at the expense of NO_2 . The fraction of N_2O_4 which exists in equilibrium will be very considerable. In

⁹⁴⁴ Ibid, p. 168.

contrast, the reaction from right to left is endothermic, and the association of the NO_2 molecules will occur at higher temperatures.

The use of the principle of mobile equilibrium makes it possible to predict the direction in which any given chemical equilibrium will be displaced at higher or at lower temperatures. On lowering the temperature, the equilibrium is displaced towards those compounds formed with the evolution of heat, while compounds formed with absorption of heat will predominate at higher temperatures.⁹⁴⁵ Through the principle of mobile equilibrium, Van 't Hoff criticized the inadequacy of the principle of maximum work proposed by Thomsen and Berthelot and proved that the only condition under which the principle of maximum work is "rigorously true" at the absolute zero.⁹⁴⁶

2.3.4 Affinity

The last chapter of the *Études* is devoted to chemical affinity. This chapter indicates that van 't Hoff constantly desired to express affinity in analytical form, which started a few years ago with the *Ansichten*; this time, using thermodynamics. Van 't Hoff considers affinity as a force that produces changes in a chemical reaction. Furthermore, he defined the transition point in a reversible chemical reaction as the temperature at which the reactants and the products exist in equilibrium. Take, for instance, the double substitution reaction below

$$KI + NaCl \rightleftharpoons KCl + NaI$$
 (10.24)

The transition point is the temperature at which the affinity that generates potassium iodide (KI) and sodium chloride (NaCl) is equal to the affinity that produces potassium chloride

⁹⁴⁵ Ibid, p. 169.

⁹⁴⁶ Ibid, p. 174.

(KCl) and sodium iodide (NaI). In other words, the difference in affinities of the two systems is equal to zero at the transition point. Above or below the transition point, the resultant force of affinity acts in the opposite direction, which is only the expression of a change of sign in the difference in affinities passing through this point.

Right at the beginning of the chapter, van 't Hoff defined the work produced by the affinity, A, and its analytical form, i.e.,⁹⁴⁷

$$A = q \frac{P-T}{P} \tag{10.25}$$

In other words, Eq. (10.25) states that "the work of the affinity (A) is equal to the heat produced by the transformation {q}, divided by the absolute temperature of the transition point [P] and multiplied by the difference of this and the temperature (T)".⁹⁴⁸ Considering that the maximum quantity of work that affinity can perform equals the amount of work done by the change when reversibly takes place, van 't Hoff thought it would be possible to obtain equation (10.25) through thermodynamics.⁹⁴⁹ Eq. (10.25) shows that when the temperature of the reaction coincides with the transition point, i.e., P = T, then A = 0, in accord with the definition of the transition point.

This study had one more significant purpose for van 't Hoff: demonstrating the validity of the connection between perfect gases and dilute solutions that preoccupied his mind since his acquaintance with Horstmann's work. This analogy became evident when van 't Hoff attempted to measure the magnitude of the affinity. The driving force of this

⁹⁴⁷ Van 't Hoff proveed Eq. (10.25) using thermodynamic reasoning (Ibid, pp. 190-192).

⁹⁴⁸ Ibid, p. 177. Van 't Hoff gave the second definition of affinity expressed by Eq. (10.25) as follows: "the work, expressed in calories, in wliich the affinity in a given chemical reaction can perform, when the reaction takes place at a given temperature, is equal to the quantity of heat evolved by the reaction, divided by the absolute temperature of the transition point, and multiplied by the difference between the temperature of the transition point and the temperature at which the reaction occurs" (Ibid, pp. 192-193). ⁹⁴⁹ Ibid, pp. 190-192.

pursuit seems to be the experiments of the German chemist Eilhard Mitscherlich (1794-1863), who measured the magnitude of the affinity of the water molecules of crystallization with sodium sulfate in the decahydrated sodium sulfate salt ($Na_2SOS_4 \cdot 10H_2O$). The measurements performed by Mitscherlich using the increase of the pressure in a vacuum due to the evaporation of the crystallization water did not satisfy van 't Hoff, who found the obtained value much smaller than that he regarded as plausible. Regardless of the experiment's accuracy, Mitscherlich showed the connection between the magnitude of the attraction (affinity) of the salt to the water of hydration and the diminution of the vapor pressure. The lowering of the vapor pressure demonstrates that the equilibrium shifts towards the hydrated salt, which in turn indicates an increase in the affinity between the water and sodium sulfate molecules. The opposite trend is expected when the vapor pressure increases.

Van 't Hoff chose another method to measure affinity. This method was invented by the German botanist and plant physiologist Wilhelm Friedrich Philipp Pfeffer (1845-1920). Pfeffer based his mode of measurement on the osmotic pressure developed between two salt solutions of different concentrations or between a salt solution and pure water separated by a semipermeable diaphragm, This diaphragm allowed the passage of water molecules but prohibited the salt molecules from doing so. The water passing through the membrane in consequence of the attraction of the salt solution increased the pressure on the porous diaphragm. After some time, a condition of equilibrium was attained because the pressure in the porous cell of the diaphragm increasingly resists the inflow of water, finally stopping it entirely. The magnitude of the resulting final pressure, the osmotic pressure, is a measure of the salt and pure water affinity. The measured osmotic pressure by the osmometer invented by Pfeffer was much higher than the vapor pressure measured in Mitscherlich's experiment. However, neither Pfeffer nor other plant physiologists like Hugo de Vries (1848-1935) and Mauritz Traube (1826-1894), who studied the phenomenon of osmosis in plants, had published a theoretical explanation for the osmotic pressure.

We have seen that the papers of Pfaundler, Horstmann, and Guldberg-Waage were a source of inspiration for van 't Hoff in developing his kinetic theory in solutions. In the *Études*, van 't Hoff succeeded in systematizing, exemplifying, and applying the field's principles and left a theory of chemical dynamics as a guide for future development. On the other hand, the studies of Mitcherlich on the vapor pressure of solutions and Pfeffer's measurements of the osmotic pressure caused by the affinity of solutes for water across a semipermeable membrane had a far-reaching effect on van 't Hoff subsequent research. The conceptual analogy between the perfect gases and dilute solutions that van 't Hoff exploited in the *Études* facilitated his theory on osmotic pressure. This theory, combined with the electrolytic dissociation of Arrhenius, constituted a significant part of modern chemical thermodynamics.

The reception of *Études* was $poor^{950}$. Only two reviews for it appeared in the literature. Both reviews were favorable, but they did not spread knowledge of van 't Hoff's achievements. Besides, the reviews were published in journals of somewhat limited

⁹⁵⁰ Root-Bernstein puts forward six reasons why *Études* did not resonate with chemists' interests (Root-Bernstein, 1980, pp. 282-283). However, some of the quoted reasons would be better suited to chemists' difficulty in comprehending the thermodynamics of Gibbs and Duhem, but not so much concerning the *Études*. The wording in *Études* was much simpler and the mathematics not severe as in the *heterogeneous substances*. It is true, however, that during the period 1883-1884, chemists were not yet prepared to conceive a new theory, where physics began to enter chemistry and offer solutions to problems, such as chemical affinity and chemical equilibrium. It took more than two decades for the ionists' theory of chemical thermodynamics to become a commonly used theory by chemists.

circulation. The second reviewer was Arrhenius himself.⁹⁵¹ He found the book very interesting and wrote an enthusiastic review published in a University review, the *Nordisk Revy*.⁹⁵² Arrhenius directed his criticism to the results that had a direct relationship with his research. He addressed the author's attention to those results that confirmed or contradicted his findings and thoughts. In this sense, Arrhenius offered a review for the *Etudes* hardly objective. In any case, this review is very important for the historian because it signifies the initial contact between the two men.

2.4 Toward a theory of solutions

Van 't Hoff had exploited the analogy between the perfect gases and the dilute solutions to formulate his kinetic theory and to study in his *Études* the affinity and the equilibrium of chemical reactions. However, van 't Hoff espoused this analogy not from solid theoretical deliberations but from the 1873 paper of Horstmann, as well as from the experiments of Mitscherlich and Pfeffer. Mitscherlich measured the affinity of the solute for the water vapor, whereas Pfeffer had directly measured the solute's attraction for the liquid water. In other words, the results of Mitscherlich came from vapor pressure measurements, while Pfeffer obtained his results from the osmotic pressure of water. The vapor pressure measured by Mitscherlich was much lower than the osmotic pressure measured by

⁹⁵¹ The first reviewer was van 't Hoff's former teacher Antoine Corneille Oudemans (1831-1895), a professor at the Technical University of Delft. He published his review in the *Recueil de Travaux Scientifiques des Pays* Bas a journal with a rather limited readership to disseminate van 't Hoff's innovations in the *Études* (Root-Bernstein, 1980, pp. 283-284).

⁹⁵² Root-Bernstein, 1980, pp. 285-289.

Pfeffer.⁹⁵³ Van 't Hoff ascribed the discrepancy between the two data sets to differences in the two experimental techniques.

Nevertheless, van 't Hoff thought that he had to find analytical forms to express this analogy. To derive the properties of solutions, van 't Hoff employed the laws of perfect gases, the first and the second law of thermodynamics. Subsequently, he focused his investigation on the properties of dilute solutions to derive the laws of chemical equilibrium. ⁹⁵⁴ He published the results of this investigation in a long paper in 1885.⁹⁵⁵

In this paper, van 't Hoff obtained several significant results. He showed that the laws of Boyle,⁹⁵⁶ Gay-Lussac,⁹⁵⁷ and the combined laws of Boyle and Gay-Lussac⁹⁵⁸ apply to dilute solutions. Second, he derived the mass action law of Guldberg and Waage from thermodynamic principles for both dilute gases and dilute solutions at a constant temperature.⁹⁵⁹ Third, he showed that the change of the equilibrium constant with temperature is related to the heat of the chemical reaction.⁹⁶⁰ Fourth, he related the equilibrium constant to the electromotive force of galvanic cells.⁹⁶¹ Van 't Hoff had introduced these subjects in his *Études but* without proof.

⁹⁵³ The vapor pressure measured by Mitscherlich was the 1/200 of the atmospheric pressure, while the osmotic pressure obtained by Pfeffer was the 2/3 of the atmospheric pressure (Root-Bernstein, 1980, p. 307).

⁹⁵⁴ Van 't Hoff avoided using the concept of entropy. The core of his approach in thermodynamics was the properties of perfect gases and Carnot reversible cycles from which he developed analytical expressions with geometrical methods.

⁹⁵⁵ Van 't Hoff, 1886. This paper was first published in the French journal *Recueil Travaux Chimie de Pays Bas* in 1885. The article appeared in 1886 in the Dutch journal *Archives Néerlandaise des Sciences Exactes et Naturelles*. The second publication is my source of information regarding van 't Hoff's work on solutions. ⁹⁵⁶ Van 't Hoff, 1886, pp. 247-250.

⁹⁵⁷ Ibid, pp. 251-254.

⁹⁵⁸ Ibid, pp. 255-257.

⁹⁵⁹ Ibid, pp. 257-265.

⁹⁶⁰ Ibid, pp. 265-268.

⁹⁶¹ Ibid, pp. 297-301.

Van 't Hoff had to find the expression that could be used as a standard to compare (or connect) the experimental data. He adopted the *perfect (ideal) gas law*⁹⁶²

$$PV = nRT \tag{10.26}$$

P and *V* are the gas pressure and gas volume, respectively, *T* is the absolute temperature, *n* is the number of moles of the gas, and *R* is the universal gas constant. The pressure in Eq. (10.26) could represent the vapor pressure of water in Mitscherlich's experiments to a good approximation. To connect the two data sets, van 't Hoff "equated" the osmotic pressure Π with the gas pressure *P* in the formula

$$\Pi V = nRT$$
 or $\Pi V = RT$ (for one mole) (10.27)

This time, *V* is the volume of the dilute solution,⁹⁶³ *T* is the absolute temperature, *n* is the number of moles of the dissolved substance (solute), and *R* is as before the universal gas constant. Eq. (10.27) expresses the mathematical form of the analogy between perfect gases and dilute solutions. It tells us that the osmotic pressure Π , which the solute would exercise in the gaseous state, occupies a volume equal to the volume of the solution. Pfeffer had shown that the osmotic pressure⁹⁶⁴ was proportional to the concentration of the solute in

⁹⁶²The *ideal gas la*w, also known the *general gas equation*, is the equation of state of a hypothetical ideal gas. Émile Clapeyron was first to state this law in 1834 as a combination of the empirical Boyle's law, Charles' law, Avogadro's law, and Gay-Lussac's law.

⁹⁶³ How much dilute should a solution be to conform to Eq. (10.27)? A standard state could be delineated when the concentration of the solute assumes its limited value of zero ($c \rightarrow 0$). In this ideal state, the solution is called infinitesimally dilute or ideal solution in analogy with the ideal gas. The ideal state of gas or solution presupposes the absence of any intermolecular interactions. As long as the gas' pressure or the solute's concentration is such that the interactions between the molecules can no longer be neglected, deviations from Eqs. (10.26), and (10.27) are observed (van 't Hoff, 1886, p. 256).

⁹⁶⁴ Van 't Hoff assumed that the osmotic pressure is the effect of collisions of the solute molecules on the semipermeable membrane, in analogy with the gas pressure due to the collisions of its molecules on the walls of the container. A second model of the osmotic pressure suggested again by van 't Hoff is based on the affinity of the solute for the water molecules. The solute molecules attract the molecules of the pure solvent on the other side of the semipermeable membrane (van 't Hoff, 1886, p. 247). At osmotic equilibrium, the hydrostatic pressure between the solution and the pure solvent compensates for this attraction. The osmotic pressure is a measure of this attraction and is proportional to the solute concentration according to Eq. (10.28).

dilute solutions. Taking into account that the ratio n/V is equal to the concentration c of the solute, Eq. (10.26) becomes

$$\Pi = cRT \tag{10.28}$$

. Eq. (10.28) indicates that the osmotic pressure is proportional to the solute concentration at a given temperature. Equations (10.26) to (10.28) assimilate the following conceivable picture: the solute particles are present in the volume of the solution as a gas rather than in a dissolved state. They exert the minimum pressure which needs to be applied to a solution to prevent the inward flow of its pure solvent across a semipermeable membrane.

Van 't Hoff wished to validate Eq. (10.28) experimentally using solutions of different concentrations. To carry out these experiments, he asked the aid of his colleague Hugo de Vries, a professor of chemistry and physiology at the University of Amsterdam and director of Amsterdam's Botanical Institute and Garden.⁹⁶⁵ De Vries had studied the phenomenon of osmosis in plants and had invented isotonic solutions.⁹⁶⁶ Based on isotonic preparations, de Vries measured the change in the osmotic pressure resulting from the different concentrations of solutions on the two sides of the semipermeable membrane. De Vries responded to van 't Hoff's inquiry and suggested to him the papers of Traube and Pfeffer as valuable sources for measuring the osmotic pressure. Traube had developed highly resistive permeable membranes to water, restricting the access of the dissolved substance. Pfeffer, on the other hand, using Traube's membranes, invented an effective

⁹⁶⁵ De vries was a Dutch botanist and one of the first geneticists. He is known chiefly for suggesting the concept of genes, rediscovering the laws of heredity in the 1890s and for developing a mutation theory of evolution.

⁹⁶⁶ An isotonic solution is one that has the same solute concentration, as another solution. Isotonic solutions separated by a semipermeable membrane have in equilibrium at a given temperature the same osmotic pressures or the resultant osmotic pressure is zero. Using Gibbs' theory, the solutes in isotonic solutions have the same chemical potentials.

osmometer. In 1877, Pfeffer reported his method of experimentation and the first measurements of osmotic pressures. These data attracted van 't Hoff's attention, who found them extremely useful for the validation of his theory. Van 't Hoff used Pfeffer's data and de Vries' isotonic data to corroborate the validity of Eq. (10.28). In particular, Pfeffer's measurements for sugar solutions allowed van 't Hoff to calculate the constant R of solutions. Van 't Hoff found to his surprise, that the value of R in dilute solution was identical with that of the gas constant.⁹⁶⁷ However, van 't Hoff recognized that the volume of data he collected was extremely limited. Besides, van 't Hoff f did not perform any experiment by himself.

Nonetheless, despite this limitation, van 't Hoff observed that for certain substances, the calculated figures from Eq. (10.28) deviated from the experimental data, specifically, for solutions of electrolytes. The calculated osmotic pressures were larger than could be expected from theory. He once advised Horstmann's papers and discovered that Horstmann observed similar deviations from Avogadro's law for certain gases. From these discrepancies, Horstmann concluded that the theory and the experiment would converge only when dissociation is considered. Van 't Hoff, unable to explain this anomaly, introduced in Eq. (10.28) an *ad hoc* variable or factor *i* as a measure of the abnormality shown by the substance.⁹⁶⁸ This factor is also known as *van Hoff's coefficient*. Van 't Hoff never attempted to explore the theoretical background of factor *i*.

$$\Pi = icRT$$

(10.29)

⁹⁶⁷ When *P* is expressed in kg/m² and V in m³, the value of *R* is 845 in Eq. (10.26), and 840 in Eq. (10.27) at the same temperature of 273 K (Ibid, p. 256). ⁹⁶⁸ Ibid, pp. 257, 272.

Eqs. (10.28) and (10.29) are identical, if i = 1. This case was true for non-electrolyte substances, like sugars, alcohols, benzene, naphthalene, but for acids, bases and salts, *i* was larger than one. The factor *i* appear to be a major obstacle in establishing the analogy between perfect gases and dilute solutions. Van 't Hoff felt that his theory was incomplete.

Nevertheless, he continued his efforts to substantiate the presence of factor *i*. He proposed four different methods for the determination of *i*: using (a) the law of solubility of gaseous bodies,⁹⁶⁹ (b) the lowering of the vapor pressure,⁹⁷⁰ (c) the osmotic pressure,⁹⁷¹ and (d) the depression of the freezing point.⁹⁷² Van 't Hoff employed cycles of reversible transformations under the appropriate conditions to obtain the relations that connected the factor *i* with the parameters involved in each method he proposed. For instance, to derive Avogadro's law for dilute solutions (Eq. (10.27)) he performed a series of reversible transformations (presented in the form of a Clausius-Clapeyron cyclical diagram) on a virtual osmometer equipped with a piston.⁹⁷³ He further elaborated all four methods and provided pertinent formulae for calculating the factor *i*. Van 't Hoff calculated the factor i with the method of the osmotic pressure using Eq. (10.29). The following equation gives factor *i* in terms of lowering the water vapor pressure upon adding the solute.⁹⁷⁴

$$i = 5.6 \frac{P_0 - P}{P_0} m_1 \tag{10.30}$$

⁹⁶⁹ Van 't Hoff, 1886, pp. 268-270.

⁹⁷⁰Ibid, pp.270-271.

⁹⁷¹ Ibid, pp. 271-273.

⁹⁷² Ibid, pp. 273-274.

⁹⁷³ van 't Hoff used reversible cycles to derive the laws of Gay-Lussac and Boyle for solutions analogous to those found for gases (Van 't Hoff, 1886, pp. 245-252; Root-Bernstein, 1980, pp. 320-322). ⁹⁷⁴Ibid, p. 271.

 P_0 and P are the pressure of the pure water and that of the solution, respectively. Here, m_1 is the molecular weight of the solute. The factor *i* is determined with the aid of the freezing-point depression by mean of the equation⁹⁷⁵

$$i = \frac{T_0 - T}{18.2} m_1 \tag{10.31}$$

 T_0 and T are the temperatures of the pure water and the solution, respectively.

The French chemist Francois Marie Raoult published in 1882 a method for determining the molecular weights of substances soluble in various solvents, including water. He observed that the freezing point (the transition temperature at which a liquid becomes solid) of the solvent is reduced upon the addition of a small amount of a substance. He discovered that in a multitude of cases, the depression of the freezing point of the solvent depended only on the ratio of the number of molecules of the dissolved substance and the solvent molecules; it was independent of the nature, the number, and the arrangement of the atoms which make up the dissolved molecules, i.e., on the structure of the substance.⁹⁷⁶ Furthermore, he specified that in an aqueous solution containing one mol of solute per 100 mol of solvent, the freezing point be reduced by 0.63 ° C, regardless of the nature of the solute.⁹⁷⁷ Five years later, Raoult published another crucial paper to determine the molecular weight of substances in solutions. He observed that the vapor pressure of the solvent decreased upon the addition of a certain quantity of the solute.⁹⁷⁸ However, this reduction in vapor pressure had been predicted, via thermodynamic calculations, by Guldberg in 1870 and van 't Hoff in the 1886 paper.

⁹⁷⁵ Ibid, pp. 273.

⁹⁷⁶ Raoult, 1882a. p. 189.

⁹⁷⁷ Raoult, 1882b. p. 1033.

⁹⁷⁸ Raoult, 1887. Raoult presented some results for the lowering of the vapor pressure earlier (Raoult, 1878). Van 't Hoff has used these data to compare the calculated factor *i*.

Since for sugar, i = 1, van 't Hoff adopted a 1:100 aqueous sugar solution as a standard and calculated the factor *i* for a 1:100 aqueous solution of any other substance by simply measuring the depression of the freezing point of water for this particular substance. He found that for non-electrolyte substances, the freezing point depression was the same as that of the sugar; therefore, i = 1 for these substances. However, for most electrolytes, the freezing point depression was higher than that of the sugar. In this case, *i* was larger than unity. Van 't Hoff tabulated the values of *i* for several non-electrolytes and electrolytes. The same tables contained the corresponding values obtained from the measurement of the osmotic pressure performed by Pfeffer and Mitscherlich.⁹⁷⁹ For example, for the gaseous bases and acids, H₂S. NH₃, and SO₂, i = 1, whereas for HCl, i = 1.98. For the salts, NaCl, i = 1.89, and for CaCl₂, i = 2.52. Van 't Hoff completed this piece of the investigation by comparing the calculated values of *i* with the tabulated experimental data of Pfeffer, de Vries, Raoult, and others.⁹⁸⁰

Having obtained values for the factor i, van 't Hoff realized that he had to derive the law of Guldberg and Waage for dilute solutions to reinforce the analogy between perfect gases and dilute solutions. He derived this law employing his favored method of reversible cycles. Performing a reversible cycle of six isothermal operations for the general reversible chemical reaction⁹⁸¹

$$a_1 M_1 \rightleftarrows a_2 M_2 \tag{10.32}$$

van 't Hoff obtained the standard form of the equilibrium condition at constant temperature for this reaction.⁹⁸²

⁹⁷⁹ Van 't Hoff, 1885, pp. 275-278.

⁹⁸⁰ Ibid, pp. 272, and 274-278.

⁹⁸¹ Ibid, pp. 257-265.

⁹⁸² Ibid, p. 263.

$$K_{eq} = \frac{c_2^{a_2 i}}{c_1^{a_1 i}} \tag{10.33}$$

As before, K_{eq} is the equilibrium constant; C_1 and C_2 are the concentrations of the species M_1 and M_2 , respectively; a_1 and a_2 are the stoichiometric coefficients of the reaction, respectively. Van 't Hoff had used Eq. (10.33) to calculate the factor *i* for dilute solutions of electrolytes.⁹⁸³

Under the prism of thermodynamics and the reversible cycles, Van 'T Hoff proved several results that he had tackled in his *Études*, including the temperature dependence of the equilibrium constant,⁹⁸⁴ Taking into consideration factor *i*, the temperature dependence of the equilibrium constant is written as⁹⁸⁵

$$\frac{\mathrm{dln}K_{eq}}{\mathrm{d}T} = \frac{Q}{2iT^2} \tag{10.34}$$

Van 't Hoff used Eq. (10.34) to calculate *i* for several temperatures and compare its values.⁹⁸⁶ While the equilibrium constant increases with temperature, the factor *i* remains constant. Finally, Van 't Hoff derived the relationship between the equilibrium constant and the electromotive force, E.⁹⁸⁷

$$\ln K_{eq} = \frac{E}{2iT} \tag{10.35}$$

⁹⁸³ Ibid, pp. 279-290.

⁹⁸⁴Ibid, pp. 265-368.

⁹⁸⁵ Ibid, p. 291.

⁹⁸⁶Ibid, p. 291-297.

⁹⁸⁷ Ibid, pp. 197-301. In 1886, van 't Hoff wrote three papers in the Dutch journal *Archives Neerlandaises*. These papers contained most of the materials of the 1886 paper and a few new theoretical treatments. In the third paper of the series, van 't Hoff discusses the theory behind Eq. (10.34). Van 't Hoff sent these papers to Pettersson for publication in a Swedish journal. Arrhenius became aware of these papers from Pettersson. He showed vivid interest in their content, although at the beginning was unwilling to suggest a publication for papers that already published in another journal. These papers, especially the third one, sparked Arrhenius's imagination to articulate the ionic dissociation theory and explained the origin of factor i (Root-Bernstein, 1980, pp. 332-340 344).

It seems that every formula presented in *Études* required the factor i to apply for any substance in solutions, which shows an anomalous depression of the freezing point or higher osmotic pressure compared to solutions of other non-electrolytes. Van 't Hoff was able to find an explanation for this intricacy when he related his solution theory to the electrolytic dissociation theory of Arrhenius.

Section 3. Friedrich Wilhelm Ostwald: The great organizer

Ostwald was born ethnically Baltic German in Riga. His parents were descendants of German immigrants. He was educated in Riga. Ostwald graduated from the University of Dorpat, Estonia (now Tartu) in 1875. He studied chemistry and physics. The following year he was awarded the master's degree and appointed Privatdozent at the University of Dorpat. During his time at Dorpat, Ostwald had significant exposure to the humanities, the arts, and philosophy, which became a focus of his endeavors after his 1906 retirement from academic work. He completed his Ph.D. at the University of Dorpat in 1878, with Carl Ernst Heinrich Schmidt (1822-1894), as his thesis advisor. His doctoral thesis was entitled *Volumetric and Optical-Chemical Studies*. He also studied at the university's physics institute with Arthur von Oettingen.

In Schmidt's laboratory, Ostwald learned many of the basics of analyzing inorganic compounds and measurements of equilibria and chemical reaction rates. These lessons formed part of the subjects of Ostwald's later research efforts. In 1881, he was appointed professor of chemistry at the Riga Polytechnic Institute, where he quickly proved to be an outstanding teacher. He remained there until 1887, and subsequently, he became Professor of Physical Chemistry at Leipzig University. In 1898 Ostwald celebrated the official dedication of the new physical chemistry institute of the University of Leipzig, which became a famous training center of physical chemistry for generations of students from Germany and abroad, especially from America. After being appointed as the first German exchange professor to Harvard University, Ostwald remained on the faculty at Leipzig University until his retirement in 1906. Following his retirement, Ostwald became active in philosophy, politics, and other humanities. He died in 1932 following a short illness. Ostwald published more than 500 original research papers for the scientific literature and approximately 45 books during his academic career.⁹⁸⁸

3.1 The research work of Ostwald

Ostwald was an excellent experimenter but a poor theorist. He did not make any significant contribution to solution theory from a theoretical point of view. Ostwald admitted his minor contribution to solution theories. In his autobiography, he wrote, "It has become customary in the history of science to combine with the names of van 't Hoff and Arrhenius that of Wilhelm Ostwald, though this name was not conspicuous for an equivalent discovery at that time. This prominence is attributable to the fact that in my person the organizing factor was represented, and without this, rapid and far-reaching development of a new field of science could not have been accomplished".⁹⁸⁹

The work of Ostwald may be distinguished schematically in two stages. The work that was performed before his acquaintance with Arrhenius and van 't Hoff, and the research that was undertaken after his acquaintance with the other two ionists and the formulation of the electrolytic dissociation theory. Ostwald as a young scientist devoted

⁹⁸⁸ For Ostwald's work and biographical information, see Hiebert, 1981a, pp. 455-469; Mi Gyung 2006; Ostwald' autobiography, 1909; 2017.

⁹⁸⁹ Ostwald, 2017, p. 155.

his master and doctoral dissertations to studies of chemical affinity. Upon examining Thomsen's calorimetric measurements, Ostwald realized that measurements of physical parameters are more accurate. They could be applied for determining affinity, replacing thus thermochemical methods. He correctly thought he could calculate the chemical change in any reaction via the measurable change of physical properties of the substances participating in a chemical reaction. Ostwald invented the more effective volumetric method⁹⁹⁰ determining the volume changes during the neutralization of acids by bases in dilute solutions.⁹⁹¹ This methodology that encompassed many experiments with acids and bases allowed Ostwald to determine the chemical reactivity of these compounds. He compared the volumetric method with an optical method based on the measurement of the refractive index. He determined a large group of acids and bases and other double decomposition reactions and specified the reactivity in terms of refraction coefficient. He found that the optical methods were less accurate than the volumetric method. At any rate, these physical methods allowed Ostwald to offer numerical values for the chemical affinity usually assigned by qualitative and often arbitrary terms.

⁹⁹⁰ The volumetric method invented by Ostwald was far different, laborious, and less accurate than the present volumetric method used in analytical chemistry. Ostwald used pycnometers to determine specific volumes before and after the reaction, at a constant temperature, and take their difference to evaluate affinity.

⁹⁹¹Today, the volumetric method (called titration) is a process in which the quantity of some constituent of a sample in solution is determined by adding (titrate) to the measured sample a precisely known quantity of another solution of a substance (called the titrant) of known concentration with which the constituent of the sample reacts in a definite, known proportion. The process is carried out by gradually adding the titrant from a burette. A specific substance called indicator is added in the sample solution before the titration to mark the end-point of the titration by changing its color at an exactly equivalent amount of the titrant that has been added to the sample. The end-point of the titration signifies the termination of the reaction. In 1891, Ostwald formulated a theory for the base-acid indicators using the principle of ionic equilibrium. In 1906, he examined several organic substances as potential indicators and determined the structural changes undergone in acid and basic solutions, which caused the change of their color.

Furthermore, these experimental methods by measuring the concentrations of various components of chemical reactions facilitated the application of the mass-action law. More importantly, the physical methods do not disturb the course of the reaction. In contrast, the chemical methods require the interaction of the reaction and measuring the concentration of one or more reaction constituents. This procedure shifts the equilibrium state of the transformation during the analysis. Ostwald used another method to measure the relative affinities of acids and bases; the study of the kinetics of the acid-catalyzed reactions, such as the hydrolysis of the cane, sugar and other esters and the saponification of acetamides. These acid-catalyzed reactions are slow reactions and easier to apply physical methods for monitoring the progress of the reaction and determining reaction rates. The calculated affinity coefficients agreed very well with those obtained by other methods. The general conclusion from these studies is that each acid and base has a particular affinity coefficient independent of the nature of the chemical reaction in which the acid or base participates. Furthermore, these studies constituted a credible reference for comparison with subsequent research findings in the context of the dissociation theory of electrolytes.

In 1884, Ostwald designed a research program to reinforce the validity of Arrhenius' electrolytic dissociation theory, and to relate, if possible, the chemical affinity to electrical conductivity. He aimed to correlate these substances' chemical activity (rates of reactions) to their electrical activity (electrical conductivity) and compare the affinities of acids and bases determined earlier by other chemical and physical methods to those obtained by the conductivity method.⁹⁹² He concluded that the conductivity method was

⁹⁹² Ostwald's experiments, the use of Kohlrausch's conductivity apparatus, and the data analysis have been described elsewhere (Root-Bernstein, 1980, pp. 153-159). It is worthwhile to mention that the more

easier to perform and more elegant than his previous method of specific volumes. Ostwald submitted these experiments to the *Journal für Practische Chemie* in July 1884.⁹⁹³ This paper was significant for three reasons: first, Ostwald showed the proportionality between the reaction velocities of acids-catalyzed reactions and the electrical conductivities of the acids; second, he verified Arrhenius' theory correlating chemical affinity with the conductivity of the electrolytes; third, referring to Arrhenius' dissertation theory, he made known Arrhenius' priority in this area of research, Ostwald facilitated the acquaintance of the German scientific community with the Swede's work.

Nevertheless, this paper did not involve other essential aspects of Arrhenius's theory, for example, the electrical conductivity behavior at extreme dilution, the application of the mass action law, or the exploration of the nature of the active and inactive molecules. It appears that Ostwald focused his attention on the correlation between chemical reactivity and electric conductivity.⁹⁹⁴ Even after the collaboration with Arrhenius, Ostwald still did not refer to these issues in his second publication in 1885; Ostwald conducted some 2000 experiments involving 120 acids to verify and extend the correlation between chemical and electrolytic activity.⁹⁹⁵

Arrhenius and Ostwald extended their studies in electrolytes from another perspective. They used the obtained values of the heats of the dissociation/formation to calculate the heat of neutralization of the acids with bases. They observed that at the same

straightforward conductivity technique he used and the various modifications that Ostwald brought about to the apparatus allowed him to produce vastly more data in six months than Arrhenius had obtained in three years.

⁹⁹³ Ostwald, 1884.

⁹⁹⁴ Root-Bernstein claims that Ostwald had not fully understood the electrolytic theory of Arrhenius exposed in his dissertation (1980, p. 160). Ostwald found it difficult to accept the dissociation of the electrolyte into free ions by simply dissolving in water. As we shall see later, this argument was propounded repeatedly by those who opposed the ionic dissociation theory of Arrhenius.

⁹⁹⁵ Ostwald, 1885; Root-Bernstein, 1980, p. 168.

temperature, (a) the heat of neutralization of strong acids by strong bases is the same, equal to 13.7 Kcal, irrespective of the nature of the strong base or the strong acid; (b) the heat of neutralization of weak acids with strong bases, or weak bases with strong acids, or weak acids with weak bases are lower than that of the strong acids and bases; (c) for some weak acids the heats of neutralization were higher than that of the strong acids with strong bases.

In addition to his remarkable skill as an experimenter, Ostwald excelled at constructing his working apparatus. Among other instruments, he invented the first simple, chemically regulated thermostat to control the temperature of his kinetic experiments and the viscometer carrying his name. The thermostat became the regular instrument of chemical laboratories over the next few decades. The viscometer is still being used in current physical chemistry laboratories. Arrhenius made use of the Ostwald viscometer to study the internal friction of electrolytes.⁹⁹⁶ The author of this dissertation had used in his chemistry laboratory a modern version of Ostwald's viscometer and method to measure the viscosity of polymers solutions.

During the last decade of the nineteenth century, Ostwald made significant contributions to other research fields, including catalysis. Important experimental work on catalytic processes was carried out in his newly founded Institute of physical chemistry at Leipzig in 1897. His catalytic measurements became the best way to measure the strength of weak acids in acid-catalyzed reactions that gave impetus to Arrhenius' theory. Apart from the chemical catalysis performed in the laboratory, Ostwald extended his investigations in applied catalysis upon manufacturing nitric acid using metal catalysts.⁹⁹⁷ Other studies involved processes of autocatalysis, inhibition phenomena (poisoning),

⁹⁹⁶ Root-Bernstein, 1980, p. 142, 168.

⁹⁹⁷ See chapter 9, section 2 of this dissertation.

contact and surface effects, and enzymes produced by living systems. The 1909 Nobel Prize in chemistry rewarded this intensive research in catalysis.⁹⁹⁸

Ostwald proved to be a competent organizer of facts, theories, people, and institutions, among other virtues. His ability as a prominent scientific organizer played a decisive role in developing the new discipline of physical chemistry.

The previous paragraphs described in short the research programs of the ionists; their theories in solution chemistry and their applications, such as the thermodynamics of physical and chemical phenomena, the kinetics of chemical reactions, the dissociation of electrolytes in solutions, and the electrical conductivity-chemical reactivity relationship. It is worth noting that none of these men was aware of one another or met each other before 1884. Each ionist thought that he worked alone in his particular field. The situation changed rapidly after 1884, as we shall see below.

Intermezzo II. Arrhenius' equation and the activation energy

In 1889, Arrhenius published a paper in the *Zeitschrift fur Physikalische Chemie* dealing with the inversion of cane sugar in acidic solutions. In this paper, he presented his account of the temperature dependence of the reaction rates. Arrhenius had already published his theory of electrolytic dissociation and sought to consolidate it, especially after the success of Ostwald's dilution law issued in 1888. He decided to deal with the kinetics of chemical reactions because he thought that the nature of the connection between the number of active ions and the reaction rate is of significant theoretical interest that has not been appropriately

⁹⁹⁸ For an account of Ostwald's research work on catalysis, see his Nobel lecture on catalysis (Ostwald, 1909). "Uber Katalyse . Nobelpreisvortrag, gehalten in Stockholm am 12 . Dezember 1909," in Les Prix Nobel en 1909 (Stockholm, 1910), 63-88 .

studied. "Since the question of the nature of the connection between the number of active ions and the rate of reaction is of significant theoretical interest, I have tried to answer this question for one of the most studied cases, the inversion of cane sugar by acids, taking into account the many that have already been asked, and try to give a uniform answer to some of the new ones I mentioned especially for the discussion".⁹⁹⁹ He noted that the influence of temperature on chemical reaction rates is much too large than expected if one considers only the effect of the temperature on the frequency of collisions or the decrease of the viscosity of the medium with increasing temperature. He suggested that a possible cause could be an equilibrium between two kinds of cane sugar ".¹⁰⁰⁰ He assumed that the active molecules are an isomeric form of the cane sugar's normal molecules, forming the products. The equilibrium condition between the active M_a and inactive M_i cane sugar molecules may be described with the following general scheme

$$M_i \rightleftharpoons M_a$$
 (II.1)

He further assumed that the amount of the active cane sugar molecules is approximately proportional to the inactive molecules, i.e., $M_a = kM_i$. Arrhenius did not take into account the energy difference between active and inactive molecules and simply considered the shift of the equilibrium towards the active molecules. Therefore, he used van 't Hoff's Eq. (10.18), namely

$$\frac{\mathrm{dln}k}{\mathrm{d}T} = \frac{Q}{2T^2} \tag{II.2}$$

which integrates to

⁹⁹⁹ Arrhrnius, 1889a, p. 226.

¹⁰⁰⁰ Ibid, pp. 231-233.

$$k(T_1) = k(T_0)e^{q(T_1 - T_0)2T_1T_0}$$
(II.3)

An analogous equation to (II.3) holds for the rate constant of the reverse reaction. Arrhenius did not give any formal proof for Eqs. (II.2), or (II.3), nor did he explicitly justify the remarkably rapid increase of the rate constant with temperature. Instead, he tested the validity of these equations by comparing eight sets of published experimental data on the effect of temperature on reaction rates with those calculated by using Eq. (II.3). All cases he studied or found in the literature showed the generality of this equation. He demonstrated that in each set of reactions, he could use a value of the heat of the reaction q, such that $k(T_1)$ was represented adequately by Eq. (II.3). Arrhenius extended this equation to include the dissociation process of electrolytes. He equated the heat evolved with the heat of the electrolyte molecule dissociated into its ions or the heat required to form the molecule from its ions.

On the other hand, van 't Hoff used Eq. (10.20) (chapter 10, Section 2, paragraph 2.3.2) to explain the influence of the temperature on the rates of reactions at high temperatures. He obtained a linear relationship of the logarithm of the rate constant with temperature. Current chemical kineticists recognize Arrhenius as the inventor of the exponential relationship of the rate constant of the chemical reactions with temperature. However, the exponent and the equation's pre-factor $k(T_0)$ have received a new interpretation.¹⁰⁰¹ Van 't Hoff did not react to Arrhenius's publication, although he did not know about the study of his colleague on a subject that originated from his *Études*.¹⁰⁰²

¹⁰⁰¹ The pre-factor is identified with the *frequency of collisions* that lead to active molecules, e.g., for dissociation; the exponent, called *activation energy*, is the energy that the molecules should overcome to become active. For a historical development of the Arrhenius equation, see Laidler, 1984.

¹⁰⁰² However, there are still two opposing opinions as to the name of this equation. In one view, Arrhenius was the first to give explicitly the exponential form of this equation, i.e., Eq. (II.3), and asserted its general applicability to all reactions, while van 't Hoff using equation $\frac{d\ln k}{dT} = \frac{A}{T^2} + B$, admitted the possibility that A
Chapter 11. The ionists come together

In this section, I will try to answer the following questions: what was the connecting thread that brought these diverse theories together? Under what conditions and influences did the ionists come together and develop chemical thermodynamics? Was this association of ideas motivated by intellectual reasons or by other factors at play? How have these three chemists turned into physics to find solutions in opposition to chemists' general, negative attitude against physicists and physics, particularly thermodynamics? What did they get from thermodynamics? Whose thermodynamics did they use? Gibbs', Duhem's, Helmholtz's thermodynamics or Clausius, Thomson and Rankine's classical thermodynamics? What is a concepts from classical thermodynamics did they use, and how did they express these ideas in their theories?

Collaboration between scientists is a beneficial practice that began essentially in the last two decades of the nineteenth century and flourished during the next century. In earlier years, individual researchers preferred to work alone, even in the same country. The limited communication media, journals, international meetings, and the distance were, most of the time, severe restrictions to collaboration. The lack of cooperation and the inadequacy of exchanging ideas and information before publication led to unpleasant situations, such as the repetition of discoveries or heated disputes about priorities. The

might be zero and B non-zero, i.e., Eq. (10.20). This possibility leads to the linear logarithm of the rate constant being a linear function of temperature. Therefore, the equation is justly named after Arrhenius, although he did not originate this relationship (Logan, 1982, pp. 279-280). According to the an alternative view, Arrhenius derived this equation using van 't Hoff's treatment as his starting point. Furthermore, Arrhenius did not consider a temperature dependence of the exponent of the equation and therefore adopted van 't Hoff's more straightforward equation (10.21) or (10.22). Therefore, this equation should be attributed to van 't Hoff (Laidler, 1993, pp. 240-241).

following passage reproduced from Ostwald's autobiography expresses precisely the problem of the absence of collaboration between scientists in the nineteenth century: "All of these things were completely new at the time and lay in an area far from the centre of contemporary scientific research with its emphasis on the investigation of organic chemistry. The handful of researchers interested in chemical affinity struggled to solve individual problems, but their results did not permit the elaboration of general rules. The only other scientists who like me pursued the general problems were J. H. van 't Hoff in Amsterdam and S. Arrhenius in Stockholm, and they had either not started their work, or at least not published their results so that neither I nor the rest of the world was aware of what they were doing".¹⁰⁰³ The reader might conclude that this statement utters a concern for the prevalence of organic chemistry, which hinders the elaboration of other general problems in chemistry.

Collaboration in science is fruitful when the two parties have common interests in a particular research subject or collaborate on a subject of overlapping interest, regardless of whether they have expert knowledge in different research areas. Overlap involves the contribution of a particular theory to solve problems of another space, in another laboratory, or even of another field—overlap in collaboration between scientists of similar or different fields or specialties. Physical chemistry is such a medium that allows a common ground between various experts (manly physicists and chemists) on various specialties that could cover a greater area of the possible knowledge on specific questions. There is much to be gained by bridging together isolated researchers.

¹⁰⁰³ Ostwald, 2017, p. 86.

There are cases where younger scientists seek collaboration with eminent scientists hoping to gain support for learning from their knowledge and experience and promoting their careers (as Arrhenius sought cooperation and support by sending copies of his dissertation to prominent scientific figures of his time). However, making such collaborations is not always beneficial to the younger scientist. Often graduate students become miniature versions of their advisors and continue to be the scientific executives (privatdozents or postdoctoral fellows in our times) working for years in projects set forth by others. Nevertheless, some of these talented young scientists become conscious of the feedback they had received from their advisors expounded their independent research program (as happened by the American disciples of Ostwald or when Arrhenius decided to change the subject of his dissertation despite the discontent of his instructors).

Also, collaboration provides a broader array of methods and techniques and better and more concrete local and international networks (through such a network, the ionists transmitted their ideas on chemical thermodynamics in Europe and America and succeeded in establishing the new discipline of physical chemistry). Finally, cooperation seeks to synthesize scientific objectives to pursue financial resources, especially needed by the experimenters.

Section 1. Arrhenius and Ostwald

Arrhenius, frustrated by the adverse evaluation of his dissertation, decided to seek support from abroad. He sent a copy of his dissertation to all those he had cited in his thesis and trusted that they were capable of recognizing its value. Clausius, Ostwald, Thomsen, Lothar Meyer received copies of the manuscript during the summer of 1884. Also, van 't Hoff received a copy of the dissertation, probably after the suggestion of Pettersson, who had contact with van 't Hoff.¹⁰⁰⁴ Only Ostwald, then a professor of chemistry at the Polytechnikum of Riga, responded supportively to Arrhenius' letter.¹⁰⁰⁵ On the other hand, van 't Hoff sent his response more than a year later, in August 1885. We must recall here that Arrhenius had previously contacted van 't Hoff when he sent his review on the *Études*.

Ostwald had the talent to foresee the perspective that a new theory, method, or advanced experiment could have for scientific development. Ostwald was a born leader, enjoying teaching and encouraging others. However, Ostwald's interest in the Arrhenius dissertation had another stronger motivation lacking from the other recipients of Arrhenius' dissertation. As mentioned earlier, Ostwald was involved in studies concerning the determination of the reactivity of various acids in chemical reactions in solutions. He achieved this goal by measuring the reaction rates employing multiple chemical and physical methods. Ostwald considered in 1884 in extending his research to include electrochemical methods. In this respect, Arrhenius' dissertation dealing with the relationship between the reactivity of chemical substances in solutions and their electrical conductivity attracted immediately his interest. Although Ostwald perfectly understood the experimental part of Arrhenius' thesis, he found it difficult to perceive the theoretical explanations for the decomposition of electrolytes into the active and inactive molecules of the second part of the dissertation. He was the first person outside the Uppsala University who expressed doubts about some of Arrhenius' conclusions of the electrolytic dissociation theory of 1884. Ostwald expressed his

¹⁰⁰⁴ Root-Bernstein, 1980, p. 130; Petit, 2013, p. 206.

¹⁰⁰⁵ Arrhenius recalled that "I received friendly answers from most of these scientists and they were very glad to make my acquaintance, and so on, but it was not very much more" (Arrhenius, 1912, p. 360).

objections regarding the behavior of the electrical conductivity of electrolytes with dilution. He expected to observe a decrease in the conductivity with increasing dilution (decreasing concentration) since the number of molecules would become increasingly rare. rare. Thus, the collisions that imparted decomposition were less effective as the distance distance between the molecules decreased with dilution. "Experiment showed exactly the opposite. The molecular conductivity increased as one diluted the solution and tended towards a maximum, which could be found at measurable dilutions for many salts".¹⁰⁰⁶ Arrhenius was unprepared to give a convincing answer to this question. He clarified this point three years later when he completed his theory of ionic dissociation. Also, Ostwald had expressed his confusion about the nature of the active and inactive molecules. The explanation given by Arrhenius was revealing and deserves special mention. Arrhenius is explicit about the model adopted for his dissociation theory of 1884. He wrote to Ostwald that the molecules of the electrolyte did not dissociate themselves. They constituted, per se, the inactive molecules, which combined with the solvent molecules to form the active molecules.¹⁰⁰⁷ For example, the inactive molecule HCl and the active molecule, the combination HCl, H_2O , or referring to bases, the inactive ammonia, NH_3 and the active hydrated molecule NH₄OH (NH₃, H₂O). Arrhenius had already expressed this hypothesis in his dissertation.¹⁰⁰⁸ Also, he did not deny in his letter to Ostwald his dependence on the Clausius-Williamson hypothesis. He continues, "the active molecules find a way, probably through collisions with other molecules or other combinations, to transform into inactive

¹⁰⁰⁶ Ostwald, 1916, p. 180; Root-Bernstein, 1980, pp. 145-146.

¹⁰⁰⁷ The formation of the inactive molecules reminds the complex molecules of the hydrates theory proposed by the British chemists and the Russian chemist Dimitry Mendeleev (1834-1907) in opposition to the ionic dissociation (see chapter 12).

¹⁰⁰⁸ Chapter 10, Section 1, paragraph 1.1 of this dissertation; Arrhenius, 1884b, p. 13.

molecules and vice versa. Only the dissociation and re-association of these combinations takes place in solution".¹⁰⁰⁹ This explanation raises the question of whether Arrhenius formulated his theory of ionic dissociation in 1884. However, Ostwald appreciated Arrhenius' demonstration of the validity of mass action law in electrolytes and was excited with the theory of chemical reactivity.

Ostwald performed preliminary experiments with some spare acids he had in his laboratory using Arrhenius' methodology and found that the acids' chemical reactivity measured before by other methods was nicely correlated with the method of electrical conductivity. Ostwald was impressed with the rapidity in obtaining results with the methodology of electrical conductivity. "The end result was that I had here a means of determining in just a few minutes the chemical affinities which, using my old methods, had taken as many days".¹⁰¹⁰ In the fall of the same year, Ostwald visited Arrhenius in Uppsala. This meeting proved to be decisive, not only for Arrhenius' scientific future but also for chemistry. These men discussed the particularities of their research and the perspective of their collaboration. They made plans regarding the progress of the whole chemistry "the need to reform chemistry," as noted by Ostwald. The need to focus on the study of chemical reactions rather than synthesizing and categorizing new substances. These plans were, of course, a hint against organic chemistry, which dominated chemistry in the nineteenth century.¹⁰¹¹

During his stay in Uppsala, Ostwald visited Cleve and convinced him about the value of Arrhenius' dissertation. After this visit, Arrhenius nominated

¹⁰⁰⁹ Quoted in Root-Bernstein, 1980, pp. 149-151;

¹⁰¹⁰ Ostwald, 2017, p. 115.

¹⁰¹¹ Chapter 9, section 1 of this dissertation.

privatdozent in the new field of physical chemistry in November 1884. Arrhenius had found a great partner and an ardent supporter. To increase the morale of the unemployed young Swede, Ostwald offered him a position in his laboratory in Riga. Also, this move restoring Arrhenius' true worth as a scientist was a political message to the authorities of the University of Uppsala.¹⁰¹² With Ostwald's help, Arrhenius received a travel grant to study abroad for a year. He planned to travel across Europe and visit all the experts in electrolytes. Arrhenius visited Ostwald in Riga to perform precise conductivity measurements and van 't Hoff in Amsterdam to discuss the application of thermodynamics to chemistry. He visited Kohlrausch in Würzburg to improve his experimental skill and study molecular properties, such as diffusion, capillarity, thermal conduction, correlating them with their electrical properties¹⁰¹³ Also; Arrhenius visited Boltzmann in Graz.¹⁰¹⁴

Needless to say that the collaboration between Arrhenius and Ostwald was successful. In conjunction with van 't Hoff, both scientists demonstrated that their joint efforts ended up establishing new science. However, one could ask, what would be the characteristics that signaled a good collaboration between Arrhenius and Ostwald? A first, remark is the fact that this collaboration began between a Professor and a student. This type of collaboration seems at least unorthodox in our days.

Nevertheless, at their first meeting, Ostwald showed signs of a good collaborator for Arrhenius. Ostwald discussed and made plans together with Arrhenius for future research on an equal basis. Ostwald probably realized that Arrhenius was in a very bad position and sought to give him encouragement and faith for his capacity. Ostwald was

¹⁰¹² Root-Bernstein, 1980, p. 163.

¹⁰¹³ Crawford, 1996, pp. 60-61; Petit, 2013, pp. 208-209

¹⁰¹⁴ Arrhenius, 1912, p. 161; Ostwald, 2017, pp. 115-116; Root-Bernstein, 1980, pp. 168-169.

impressed by Arrhenius' dissertation, but at the same time, he was candid and skeptical. He had the right judgment to discern Arrhenius' ideas from his enthusiastic temperament that led him in vague and sometimes obscure discourses. Another factor that guaranteed a successful future collaboration was their complementary skills. Arrhenius was more on the theoretical side rather than an experimenter with the ability to extrapolate his ideas and invent new ones. In contrast, Ostwald was an experimenter with the unparalleled skill to perform highly accurate experiments and invent novel instrumentation. Finally, both scientists had a broadly shared vision beyond the narrow space of their laboratories. They both perceived the current problems of chemistry and agreed on the way they could approach these problems.

The excellent collaboration between these two men did not harm their completely different characters. Arrhenius was argumentative and graceless. He showed a defensive attitude and an excessive rigor to people reminiscent of the signs that left the wretched behavior of his advisors in his character. These psychological remnants were reflected in the ironic comments he made in several instances.¹⁰¹⁵ On the other hand, Ostwald was sanguine and aggressive and had a rapid reaction speed. He thinks and works very quickly, and he was a source of new ideas and projects. According to his classification of the scientific geniuses between classicists and romanticists, Ostwald belonged to the romantic type of intellectuals.¹⁰¹⁶ The third ionist, van 't Hoff belonged to classicists according to Ostwald's "taxonomy", although his character did

¹⁰¹⁵ See for instance, Arrhenius, 1912, p. 356, 360.

¹⁰¹⁶ In his *Grosse Männer*, Ostwald sought to classify great scientists according to their temperament. About the criteria of this classification (Deltete, 1996, pp. 290-291). This reference includes a thorough study of the characters and scientific styles of Gibbs and Ostwald.

not comply with all characteristics defined by Ostwald for the classicists. Van 't Hoff was an introvert and a bit of a recluse personality. He worked slowly and needed time to think about any novelty in science before expressing his opinion. This trait of his character was presumably one of the reasons that he delayed his comments on Arrhenius' dissertation. This is how Arnold Frederik Holleman (1859-1853), a former van 't Hoff's laboratory assistant¹⁰¹⁷ portrays the Dutchman. "He was by nature cautious and uncommunicative; current topics, literature, etc., were not considered. Queries addressed to him were rarely answered on the spot, but one could be sure that he would return to the subject matter in a day or two. I never saw him lose his temper, get angry, or annoyed. He even remained calm when some of his students allowed a water bath to dry up, let one of his sealed tubes explode, or, worse yet, tore out of the "Berliner Berichte" the page which he badly needed".¹⁰¹⁸ Van 't Hoff preferred to work alone as a classicist, but he shared his discoveries with others as a romanticist and left his ideas in the open for any subsequent development.

Section 2. Ostwald and van 't Hoff

Ostwald never had a close collaboration with van 't Hoff as he had with Arrhenius. Each man developed his research program independently of one another. Ostwald had his first contact with van 't Hoff after reading the *Études* suggested to him by Arrhenius. Arrhenius held van 't Hoff in high esteem and undoubtedly had praised the work of the Dutchman to Ostwald. Ostwald read the *Études* in 1886, while he was getting the last part of his textbook

 ¹⁰¹⁷ Holleman was van 't Hoff's assistant in 1887. In 1893, he was appointed professor of chemistry in the University of Groningen and in 1905 he was called to Amsterdam as professor of organic chemistry.
¹⁰¹⁸ Holleman, 1952, p. 380.

Lehrbuch der Allgemeinen Chemie (Textbook of General Chemistry). He planned to describe the current state of the research concerning chemical affinity. Ostwald's first reaction to the *Études* was critical. "It was entitled *Études de Dynamique Chimique* and had been written by a completely unknown researcher whose name, according to the title page, was J. H. van 't Hoff. It described both theoretical and experimental studies of the laws governing the rates of chemical reactions. It deferred neither to past, nor present researches and ended with some confusingly written paragraphs which suggested that the author had made considerably greater advances in the application of thermodynamics to chemistry than had Horstmann—or I".¹⁰¹⁹ However, this first impression did not last long. Ostwald realized that van 't Hoff's theory of solution combined with the electrolytic dissociation theory of Arrhenius constituted the starting point for the subsequent development of new chemistry. He believed that these two complementary theories would lead to the development of many diverse discoveries that would extend chemistry beyond the limits of conventional science.

The second contact with van 't Hoff occurred when Ostwald considered that an important step to promote the new science was a written basis for disseminating new methods and theories of chemists and physics. The establishment of a new journal would help emerge the new science as an independent entity within the broad field of chemistry. In 1887, Ostwald with van 't Hoff founded the new journal; they called it *Zeitschrift für Physikalische Chemie, Stöchiometrie und Verwandtschaftslehre* (Journal of physical chemistry, stoichiometry and affinity studies). Ostwald considered it important to get van 't Hoff's support for the journal and accepted his conditions to be named co-editor in the

¹⁰¹⁹ Ostwald, 2017, p. 123.

journal, adding that he had no wish to interfere in the journal's running. Still, he would be satisfied with a formal appointment. "It seemed to me to be so important to link the journal to the name of this brilliant researcher that I unreservedly agreed to his conditions. I never regretted this decision and am convinced that the rapid success of the journal was to a large extent due to having van 't Hoff on board".¹⁰²⁰ Ostwald and van 't Hoff succeeded in attracting a large group of collaborators/contributors from all over Europe, giving an international reputation for the journal.¹⁰²¹ The first issue of the Zeitschrift appeared in February of 1887. It contained two articles, which, according to Ostwald, formed the basis for the subsequent development of the new branch of science, physical chemistry: Arrhenius' Über die Dissociation der in Wasser gelösten Stoffeand, and van 't Hoff's Die Rolle des osmotischen Druckes in der Analogie zwischen Aösungen und Gasen, Arrhenius' paper articulated the final form of ionic dissociation theory, whereas van 't Hoff's article clarified the analogy between the perfect gases and dilute solutions in the context of the osmotic pressure. In the opening pages of volume number one of the journal, Ostwald made clear to its readers and the international scientific community the scope of the ionists to pursue the foundation of new science, the physical chemistry. In the meantime, the University of Leipzig offered van 't Hoff an academic position in physical chemistry, the only professorship in Germany. Van 't Hoff, who had already spent eighteen years in the University of Amsterdam, preferred to continue his stay there. He refused the call, which Ostwald eventually filled.

¹⁰²⁰ Ostwald, 2017, p. 128.

¹⁰²¹ Some of the collaborators and participants in the editorial board were Thomsen, Massieu, Le Chatelier, Saint-Claire Deville, Duhem, Horstmann, Mendeleev, Lothar Meyer, Lodge, Goldberg, and others, in total twenty-two chemists and physicists, including Ostwald, Arrhenius, and van 't Hoff. Gibbs wrote to Ostwald that he did not have time to participate in this endeavor (Root-Bernstein, 1980, pp. 358-360).

Section 3. Arrhenius and van 't Hoff

The first contact of the two men was held in 1884 when Arrhenius sent a copy of his dissertation to van 't Hoff and in the same years his review on the *Études*. It took more than a year for van 't Hoff to respond. He finally wrote to Arrhenius in August 1885. In the meantime, van 't Hoff had worked out his physical theory of solutions, and thus he was able to relate his theory to Arrhenius electrolytic investigation. As Ostwald, van 't Hoff appreciated the connection between electrical conductivity and chemical reactivity but found himself compelled by some of Arrhenius' ideas that could not be adjusted to his research program. The most crucial objection concerned the electrical origin of affinity adopted by Arrhenius. Affinity for Arrhenius was a manifestation of electrical attraction that was prevented by the decomposition of the electrolytes. Also, Arrhenius asserted that reactivity originated from the electrical properties of the substance.

Contrary to Arrhenius, van 't Hoff explained affinity as the result of universal gravitational forces. He did not deny the existence of the electric forces, but he considered that these forces had a secondary modifying influence on the affinity. Questioning the primary importance of the electrical nature of affinity in electrolytes, van 't Hoff inevitably raised the argument: decomposition could not occur in solution without the expense of work; where did this work come from?¹⁰²² Arrhenius had already proved that this argument was wrong, and no work needed to perform by any means for the decomposition of the electrolytes.¹⁰²³

¹⁰²² This argument was raised by a physicist named Hans Jahn (1853-1906). Jahn attacked the Clausius-Williamson hypothesis (Root-Bernstein, 1980, p. 121).

¹⁰²³ Arrhenius, 1884c; Root-Bernstein, 1980, pp. 126-128.

Arrhenius had read van 't Hoff's Swedish papers. He realized that van ' Hoff was wrong and prepared to write to him about this matter. This letter was of great value because Arrhenius explained several facets of his new theory of ionic dissociation. More importantly, he explicitly discussed the connection of his activity coefficient α with factor *i*. Therefore, he was aware of this factor, which made the fine theory of solution look incomplete.

Furthermore, Arrhenius had postulated the second version of his ionic theory of dissociation in terms of ions that replaced the active molecules of his dissertation. Therefore, he felt prepared to proceed with the final step to consolidate his theory with the most convincing piece of evidence. He explained to van 't, Hoff that if sodium chloride remains in normal condition, its factor i should be 1. "The *i* is, however, much greater; therefore, the natural expedient is to explain this by saying that NaCl is dissociated into its parts in the same way that one says that I₂ is dissociated by high temperature".¹⁰²⁴ He continued proposing the method by which the factor *i* could be determined. "From the preceding hypothesis [the existence of dissociated ions of Na and Cl] one can even calculate the value of *i* from the conductivity, and this *i* shall probably attempt in the near future".¹⁰²⁵

Recall that Arrhenius had based his new theory of ionic dissociation on the analogy between the dissociation of gases and the dissociation of the electrolytes in dilute solutions. Arrhenius considered further that his theory could explain the abnormal behavior of the colligative properties of electrolytes. Nonetheless, he had not published anything about this

¹⁰²⁴ Cohen, 1912, p. 240; Root-Bernstein, 1980, 399.

¹⁰²⁵ Cohen, 1912, p. 241; Root-Bernstein, 1980, p. 400.

theory; presumably because he understood that he needed more soundproof to legitimize its validity. The paper of van 't Hoff seemed to meet this objective.

Van 't Hoff replied to Arrhenius very quickly (in eight days), something under normal circumstances. It has been said that van 't Hoff required much time to study and digest any new idea before communicating his opinion. Nothing strange with this behavior. As Ostwald was interested in Arrhenius's dissertation, and Arrhenius's expressed his enthusiasm for the *Études*, van 't Hoff was eager to hear Arrhenius's ideas to resolve the factor *i* and eventually complete his solution theory. In response to the letter, van 't Hoff confirmed Arrhenius's observations and favored experimental proof. "That which bears on your observations concerning this is that the value of *i* increases at just about the same pace as the number of ions and that the conductivity increases with the value of *i*. This is evident of well-known cases [he mentioned experiments performed in his laboratory]".¹⁰²⁶

Nevertheless, van 't Hoff could not overcome the authority of Clausius and his dissociation theory, according to which a very small number of molecules decomposes. This hypothesis, of course, contradicts the increasing dissociation of the electrolytes with increasing dilution inherent in Arrhenius' theory. "I nevertheless think that the activity is covered by Clausius' interpretation of the socalled dissociation of electrolytes in an extremely small portion of the salt. Then the reason for the increase in i is no longer evident; and yet, for all that, I see, so

¹⁰²⁶ Cohen, 1912, p. 243; Root-Bernstein, 1980, pp. 401-402.

far, no serious reasons not to consider a continuous dissociation".¹⁰²⁷ The last sentence of this quotation reveals van 't Hoff's dilemma. Who was right to follow? The renowned Clausius and his hypothesis of the limited dissociation, or the young Arrhenius whose extensive dissociation rationalized the increase observed for the factor *i* of the electrolytes. Van 't Hoff avoided further discussion asking some more time to think about it. Arrhenius sent a second letter to van 't, Hoff. He admitted that all chemists and physicists follow Clausius because they have a strong insight against dissociation, although there is no evidence against it.¹⁰²⁸ In any case, Arrhenius must have realized from the correspondence with van 't Hoff that a theory could not survive for long without experimental verification.

3.1 Ionic dissociation theory: The proof

In the last letter to van 't Hoff, Arrhenius wrote about his plans to compare the results of the electrical conductivity measurements with the literature data of the colligative properties¹⁰²⁹ of substances in aqueous solutions. He counted, especially, on Raoult's data obtained from the freezing-point depression experiments, which Arrhenius considered the most accurate. In particular, he wanted to calculate the factor *i* from his and Ostwald's electrical conductivity data and compare these values with those obtained by van 't Hoff using the data of Pfeffer and Mitscherlich. This comparison is crucial for Arrhenius' theory. If the two values agree, it is highly probable that dissociation occurs and that the resulting

¹⁰²⁷ Cohen, 1912, p. 243; Root-Bernstein, 1980, p. 403.

¹⁰²⁸ Cohen, 1912, p. 244; Root-Bernstein, 1980, p. 404.

¹⁰²⁹ Colligative properties in physical chemistry are properties of solutions that depend on the number of solute particles (molecules or ions), but not upon the identity of the solute. Colligative properties include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure.

entities (ions) for each substance are inherently charged. If not, and the two values differ from each other, then Arrhenius and his theories are in trouble.

One might imagine the agony of the researcher in front of the crucial moments while expecting the results of an experiment that might or might not corroborate his theory.

To proceed, Arrhenius needed a mathematical relationship connecting the term *i* with some quantity representative of the electrical conductivity. Arrhenius used his activity coefficient α . After a little algebra using Eq. (10.1) (on page 413) and assuming that dissociation occurred, Arrhenius related the two coefficients through the following simple equation.

$$i = 1 + (k - 1)\alpha \tag{11.1}$$

This equation is valid on the assumption that each molecule of the electrolyte dissociates into *k* ions. For instance, for NaCl, which dissociates into two ions, k = 2; for H₂SO₄, which dissociates into three ions (two single charged cations H⁺ (protons) and one double-charged anion SO_4^{2-}), k = 3. Arrhenius used Eq. (11.1) to compare the electrical conductivity data and the osmotic and freezing-point depression data of twelve non-electrolyte substances, fifteen bases, twenty-three acids, and forty salts. The theory, the tabulated experimental, and calculated values were published in the first issue of the *Zeitschrift für Physikalische Chemie* in December 1887.¹⁰³⁰ Arrhenius finally found the experimental evidence for his theory. The factor *i* obtained from different sources confirmed that there should be only dissociated molecules in infinitely dilute solutions, that is, ions and that van 't Hoff's laws apply to all bodies. In the remainder of his paper, Arrhenius discussed various technicalities

¹⁰³⁰ Arrhenius had disseminated his ideas about electrolytic dissociation through the BAAS report of May 1887 (see chapter 12, section 2 of this dissertation). Also, he published his results in two Swedish journals in June and November 1887. Therefore, he had ensured the priority of his research for the electrolytic dissociation theory (Root-Bernstein, 1980, p. 481).

and explained the causes of some inconsistencies observed between experimental and calculated values. The articulation of the final version of the ionic dissociation theory offered a new interpretation for almost all aspects related to the properties of electrolyte solutions. Among others, it provided explanations for the activity coefficient. He explained the behavior of the molecular conductivity that increases to a maximum depending on the nature of the electrolyte and the number of dissociated ions. He justified the complete dissociation of the strong electrolytes, and that of the weak electrolytes at infinite dilution, and demonstrated the connection of his theory with the Clausius-Williamson hypothesis.

However, Arrhenius' ionic dissociation theory accounts for the behavior of dilute solutions. It hardly applies to concentrations in the range from 0.05 M to 0.10 M or higher. Furthermore, Arrhenius' ionic dissociation theory is inadequate to explain the behavior of strong electrolytes in solutions. The generalization of the electrolytic dissociation theory for concentrated solutions and strong electrolytes will be the subject of investigation of the twentieth century.

3.2 Ostwald's dilution law

In January of 1888, Ostwald announced the results of his investigation regarding the application of mass action law to binary electrolytes, the famous *dilution law*.¹⁰³¹ Ostwald used the well-established van 't Hoff's proportionality to derive this law between the pressure of perfect gases and the osmotic pressure of dilute solutions. The theory now leads to the formula valid for gases and dilute solutions in the simplest case, where a

¹⁰³¹ Ostwald, 1888a, and 1888b. The first paper contained the theory, and the second one the results and discussion.

molecule splits into two ions. Ostwald combined Eqs. (10.15), and (10.16) (on page 449) from van 't Hoff's *Études*, and obtained the following equation (Ostwald's notation).

$$R\ln\frac{p}{p_1p_2} = \frac{\rho}{T} + \text{const.}$$
(11.2)

 $p \ \tau is the heat of dissociation, p$ is the osmotic pressure of the undecomposed molecules of the electrolyte, and p_1 , p_2 are the partial osmotic pressures of the two ions of the binary electrolyte. For constant temperature, assuming that none of the decomposition products is excessively present, (otherwise the neutrality of the solution is questionable). Therefore, the two osmotic pressures are equal ($p_1 = p_2$). Under these conditions, Eq. (11.2) simplifies to

$$\frac{p}{p_1^2} = const \tag{11.3}$$

Following the proportionality law mentioned above, the pressure in the solution could be set proportional to the existing concentrations u and u_1 of the undissociated and dissociated molecules of the electrolyte, respectively, and inversely proportional to the volume v of the solution; Eq. (11.3) becomes

$$\frac{p}{p_1^2} = \frac{u_{/\nu}}{\left(\frac{u_{1/\nu}}{2}\right)^2} = C \tag{11.4}$$

Here, the constant C is the dissociation constant (the equilibrium constant K_{eq} in van 't Hoff's theory). Ostwald proposed Arrhenius' electrical conductivity method to measure the quantities of the undecomposed and decomposed electrolyte. He defined with μ_v the molecular conductivity of the electrolyte at volume v and μ_0 the limit value of the molecular conductivity at infinite dilution. Since the conductivity is proportional to the amount of the dissociated electrolyte, the mass action law can be written in terms of the measurable molecular conductivity as follows

$$C = \frac{\mu_{\infty}(\mu_{\infty} - \mu_{\omega})}{(\mu_{\nu})^2} \tag{11.5}$$

Eq. (11.5) expresses the famous Ostwald's dilution law. According to this law, only at infinite dilution, the weak electrolytes undergo complete dissociation. This conclusion was precisely what Ostwald observed in his dilution experiments. The molecular conductivity of weak acids and bases increased with increasing dilution (decreasing concentration) and reached a maximum at infinite dilution (at zero concentration limit). The dilution law does not hold for strong electrolytes. For weak electrolytes, it is approximately correct at higher concentrations.

In February of 1888, Planck applied the principles of thermodynamics and gave an elegant theoretical derivation of the dilution law in one month's distance.¹⁰³² Six months later, van 't Hoff published his results that confirmed the dilution law.¹⁰³³ His results were more accurate and consistent than Ostwald's hasty results.¹⁰³⁴ The formulation of dilution law by Ostwald and van 't Hoff completed the ionists' theory of solutions and the first phase of the development of modern chemical thermodynamics. The second phase has been ascribed to a group of scientists who had been trained as physicists. To mention a few, Pierre Duhem, Max Planck, Walther Nernst, and Oliver Lodge were very deeply involved in early chemical thermodynamics. Nernst's electrochemical studies and Planck's theoretical treatment of van 't Hoff' and Arrhenius' results in dilute solutions were central to the enrichment of the new discipline.

¹⁰³² Planck, 1888.

¹⁰³³ Van 't Hoff, 1888.

¹⁰³⁴ Root-Bernstein discussed the complications behind the scene that led to the simultaneous discovery of the dilution law (1980, pp. 501-511.

Section 4. Walther Nernst: "The fourth ionist"

Walther Nernst was the scientist who examined the mechanism responsible for the appearance of potential in galvanic cells. Through experimental and theoretical work, he developed a new theory for the thermodynamic processes in galvanic cells. Nernst published his theory in 1889 and laid the foundations of theoretical electrochemistry. The thermodynamic theory and the experimental setup allowed Nernst to measure the free energy and the equilibrium constant of electrochemical reactions. Nernst conducted his experiments in Leipzig when he worked as an assistant at Ostwald's physical chemistry laboratory and later in his laboratory at the University of Göttingen. He began there as a lecturer in 1891, and three years later, he was promoted to the rank of full professor. Nernst was in Leipzig when he worke the celebrated textbook *Theoretical Chemistry*, translated into English, French, and Russian.

Nernst succeeded for the first time in calculating the diffusion coefficient for dilute solutions and in demonstrating the relationship between ionic mobility, diffusion coefficient, and electromotive force in concentration cells. Nernst realized early that the study of the mobility of ions in solution is not as easy as his predecessor electrochemists imagined. The phenomenon is far more complicated. Apart from electric and frictional forces, there are gravitational forces, electromagnetic forces, paramagnetic and diamagnetic forces, electrostatic forces, and forces due to osmotic pressure. He thought that the problem could not be solved by performing conductivity measurements alone. He had to combine experiments with mathematics. This research led him to investigate further the relationship between electromotive force (the electrical potential difference between the two electrodes in a galvanic cell) and the ionic concentrations. He sought to find an electromotive force capable of opposing the diffusion of the ions in solution. He coined a thought experiment. A galvanic cell of two solutions of the same electrolyte but of different concentrations. He then related the electromotive force produced by the system with the osmotic pressures exerted by the two solutions through the following equation¹⁰³⁵

$$E_1 - E_2 = E = \frac{u - v}{u + v} p_0 \ln \frac{P_1}{P_2}$$
(11.6)

 E_1 and E_2 denote the electrical potential of the two solutions of different concentrations; P_1 and P_2 are the osmotic pressures that each of the solutions exerts on each other; u and v are the mobilities of the cations and the anion of the electrolyte, respectively, and p_0 is a constant, specific for each electrolyte. If u = v, i.e., the ionic mobilities are equal, the electromotive force is zero. This assumption is absurd since the generated electromotive force in the cell could not be eradicated. Nernst concluded that the generation of the anion and cation. Once Nernst derived Eq. (11.6), he constructed several cells with different electrolyte concentrations to verify this equation. Since the osmotic pressure is proportional to the concentration of the electrolyte, Eq. (11.6) can be written as

$$E = \frac{RT}{NF} \ln \frac{C_1}{C_2} \tag{11.7}$$

R is the gas constant, *T* is the absolute temperature, *N* represents the gram equivalents of the electrolyte that reacted, 1036 and *F* is the Faraday's constant. The number *NF* corresponds

¹⁰³⁵ Nernst, 1889, pp. 136-138; Petit, 2013, pp. 235-237.

¹⁰³⁶ A concentration cell is a voltaic cell that is comprised of two half-cells (assembled as the left and right half cell in the voltaic apparatus and connected by an electrolytic bridge) with the same electrodes but differing in concentrations. A concentration cell acts to dilute the more concentrated solution (through the deposition of metal cations from the solution to the solid electrode) and concentrate the more dilute solution (through the formation of metal cations from the solid electrode to the solution), creating thus a voltage at the galvanic cell. Imagine, for example, that the two half cells are composed of zinc electrodes immersed in two solutions of zinc sulfate (ZnSO₄) of different concentrations. Suppose that the concentration of the left half cell is 0.1 M and that of the right half cell is 1.0 M. In the left half cell with the

to the passage of electricity measured in coulombs. Helmholtz has shown already that the electromotive force of a galvanic cell is directly proportional to the free energy of the cell reaction. Therefore, Eq. (11.7), better known as Nernst's equation, constitutes a vital link between thermodynamics and electrochemical solution theory. This equation is widely used in cell physiology and neurobiology.¹⁰³⁷

A quick look at Eq. (11.7) shows that the ratio of the concentrations is proportional to the equilibrium constant of the reaction that takes place within the galvanic cell. Nernst was familiar with this relationship and the connection between the equilibrium constant and Helmholtz's free energy of the reaction, thereby connecting the free energy with the electromotive force. This line of reasoning led Nernst to propose that the free energy of a chemical reaction could be measured by making the reaction the source of energy for a battery and then measuring the voltage across the battery terminals as Helmholtz had suggested. Many chemical reactions can afford the proper energy required for a battery to function, although there are often practical difficulties constructing the appropriate cells. Also, the Nernst equation cannot overcome the problems associated with determining the ionic concentrations of strong electrolytes. The validity of the method depends on the degree of dilution. The measurements of the electromotive force become increasingly accurate only as the solutions approach infinite dilution. Nernst's equation is not applicable

smaller concentration, zinc cations are formed from the zinc metal and transferred to the solution, increasing thus its concentration. In the right half cell with the higher concentration, the opposite reaction occurs; zinc cations from the solution are deposited on the solid electrode, hence decreasing its concentration. These opposite reactions will continue until the system reaches its equilibrium state. The calculated electromotive force of the aforementioned voltaic cell at temperature 25 °C using Eq. (11.7) and taking into account the values of the various constants, is 0.0296 volts. Equilibrium is obtained when the concentration of the electrolytesolutions in the two half cells becomes equal. In that case, $C_1 = C_2$ and E = 0 from Eq. (11.7).

¹⁰³⁷ For an account on Nernst's research work on electrochemistry, see Bartel and Huebener 2007, pp. 43-51, 62-68, and 150-154; Barkan 1999, pp. 41-90.

for concentrated solutions for all electrolytes. The American physical chemist Gilbert Newton Lewis confronted this problem by introducing the concepts of activity and activity coefficient.¹⁰³⁸

Another significant Nernst's contribution to the dissociation of electrolytes is the symbols he used to represent the ions in the solution. He designated the ions as having exponents (for the cations) and - (for the anions). For example, the dissociation of ammonium chloride (NH₄Cl) takes the form:

$$\mathrm{NH}_{4}\mathrm{Cl} \to \mathrm{NH}_{4}^{+} + \mathrm{Cl}^{-} \tag{11.8}$$

Instead of $NH_4Cl \rightarrow NH_3+HCl$

Indeed, Nernst's idea was symbolic, but it was crucial to remind chemists of the concept of ions as an inherently charged entity. This notation prevails today.

Section 5. Max Planck: The ionists' theory of solutions as seen by a physicist

Although the ionists had developed a comprehensive research program, van 't Hoff's new ideas on osmotic pressure in solutions and Arrhenius's theory of the ionic dissociation were still semi-empirical. They did not arise from the first principles of thermodynamics. Both van 't Hoff and Arrhenius used thermodynamics selectively. The two ionists were not concerned with the rigorous derivation of the various equations and functions used to express the laws of their theories. They rather were interested in connecting natural phenomena with chemical phenomena and the practical applications of their theories to the problems of chemical affinity and chemical equilibrium, which was the overriding demand for chemists.

¹⁰³⁸ See Chapter 13, section 4, paragraphs 4.1 and 4.2 of this dissertation.

It is interesting to examine the way by which the physicists approached the dissociation of electrolytes in solutions. Max Planck was the physicist who independently derived a rigorous theoretical version of van't Hoff and Arrhenius' results. In a series of three monographs, from February to December of 1887, Planck used the second law of thermodynamics and the concept of entropy to derive the law of the osmotic pressure and the relevant equations that described the colligative properties of solutions. Also, Planck attempted to eliminate on a theoretical basis the factor *i*, which van 't Hoff had arbitrarily used in his equations to fit the experimental data.

Rudolf Clausius was the physicist who influenced the most Planck in the first steps of his scientific career. Planck studied the writings of Clausius, the man who first distinguished and formulated the two laws of thermodynamics. Planck was impressed by Clausius' clarity of expression of his thoughts. Clausius' writings introduced Planck into the second law of thermodynamics and entropy who came to call it *the principle of the increase of entropy*.

Planck devoted the first fifteen years of his research to clarifying, expounding, and applying the second law of thermodynamics, especially the concept of irreversibility, to physical and chemical phenomena.¹⁰³⁹ However, his excellent work on thermodynamics did not give him the satisfaction that he deserved. He learned too late that some of his results had been anticipated by Josiah Willard Gibbs in his *heterogeneous substances*. He found himself in the same unpleasant situation when he discovered that Arrhenius had already formulated the theoretical treatment of electrolytic dissociation. He had solved the problem of van 't Hoff's factor *i* some months before Planck. Arrhenius' theory on

¹⁰³⁹ Klein, 1966, p. 24.

electrolytic dissociation was included in the 1887 report of Oliver Lodge submitted to the electrolysis committee of the British Association for the Advancement of Science (BAAS).¹⁰⁴⁰

Planck admired the genius of Clausius in describing the second law, but he thought that the law lacked the generality characterizing the first law of thermodynamics. He argued that the second law failed to take into account the entropy of the surrounding medium. In other words, he considered that Clausius' second law had not applied to a closed system in which energy exchange allowed between the system and the surroundings. He began then to reformulate the second law. He gave entropy a central role in the theory presented in his dissertation. Despite the innovation that characterized his work, contemporary physicists largely ignored it. As Gibbs and Arrhenius did before, Planck distributed copies of his dissertation to several eminent physicists of his time without, however, receiving any response from them. Among the great men who received Planck's dissertation, Clausius, and Helmholtz ignored the work of the young physicist, whereas Kirchhoff expressed his disappointment for its content.

The context in which Planck developed his theory was the *principle of the increase of entropy*, as he called the modification he planned to introduce in the second law of thermodynamics.¹⁰⁴¹ Formulating this principle, he emphasized not the intermolecular interaction but the properties that share all compounds, such as temperature, pressure, energy, and entropy. Planck had rejected molecular mechanics, at least during the first

¹⁰⁴⁰ See chapter 12 below, section 2 of this dissertation.

¹⁰⁴¹ Planck developed the theory of the entropy increase in three articles published in December 1886 (Planck, 1887a), February 1887 (Planck, 1887b), and July 1887 (Planck, 1887c). In the second article, Planck applied his theory on the dissociation of gases and derived van 't Hoff's equations for the colligative properties of solutions in the third article.

period of his research career dealing with classical thermodynamics. He deemed that any reference to composition was an acceptance of the atomic hypothesis that led to metaphysics. Planck claimed that dealing with equilibrium needed not any assumption for the molecular constitution. He had defined equilibrium not as a function of forces (gravitational or electrical) but in terms of entropy. His limited knowledge of chemistry and his lack of familiarity with experimental work was a factor, making Planck dislike the atomic theory.

Three years after he discovered the preponderance of Gibbs in some issues of thermodynamics, Planck reappeared in the literature in 1887. During these three years of silence, Planck probably contemplated his stature in physics and planned the new direction that his research should take. He published a series of three papers entitled *Über das Princip der Vermehrung der Entropie* (on the principle of the increase of entropy), which constituted his attempts to extend the thermodynamic theory beyond the work of Gibbs. It appears that these three papers, and especially the third one, brought him closer to the research performed by the ionists. Ostwald facilitated Planck to espouse this approach by encouraging him to continue his theoretical work on thermodynamics. He introduced Planck into almost all of the fundamental works of Gibbs, Guldberg and Waage, Lothar Meyer, Arrhenius, and van 't Hoff.¹⁰⁴² However, Ostwald omitted or forgot to tell Planck that Arrhenius had already solved the problem with van 't Hoff's factor *i* some months ago.¹⁰⁴³ The implication to Planck's work on the dissociation theory caused by Ostwald's oversight was another disappointment for Planck.

¹⁰⁴² Root-Bernstein, 1980,, p. 431.

¹⁰⁴³ Ibid, pp. 433-434.

In the first paper of the series,¹⁰⁴⁴ Planck produced a theory of the dissociation of gases based on the second law. His treatment was an extension of the thermodynamic results of Horstmann, Berthelot, Gibbs, and Thomsen based on the second law and entropy considerations. As Gibbs, Helmholtz, Duhem, and van 't Hoff, Planck attacked the principle of the maximum work of Berthelot and Thomsen demonstrating that the final state of the system did not depend on the heat evolved in a physical and chemical process but the tendency towards the maximum of the entropy. Despite the important theoretical results, Planck presented in this paper, it passed almost unnoticed by both physicists and chemists.

Before Planck postulated his dissociation theory, he first approached van 't Hoff's results formulated in 1886, which was finally published in February 1887. Planck introduced *the principle of the increase of entropy* via the following general inequality applied to a closed system¹⁰⁴⁵

$$\sum dS_{system} + dS_{surroundings} \ge 0 \tag{11.9}$$

The first term of Eq. (11.9) denotes the change of the system's entropy, and the second term is the change of the entropy of the surrounding medium. Also, Eq. (11.9) indicates the direction of the increase of the entropy of the closed system, and thereby the direction in which the system will vary with a temperature change. The entropy of the surrounding medium is a function of heat Q and is given by the well-known Clausius inequality $-(Q/T) \ge 0.^{1046}$ The equal sign in Eq. (11.9) shows that the closed system is in

¹⁰⁴⁴ Planck, 1887a.

¹⁰⁴⁵ Planck, 1887c, p. 468.

¹⁰⁴⁶ Planck, 1887a, p. 568.

equilibrium. Planck expressed the direction of the variation of the closed system through a function Φ . This function is defined by¹⁰⁴⁷

$$\Phi = S - \frac{U + pV}{T} \tag{11.10}$$

 Φ is a work function that Planck had found to be equal to $\Phi = \text{TW}$ (*W* being the work) in an earlier paper¹⁰⁴⁸. The function Φ is similar to Gibbs' function ζ and Duhem's total thermodynamic potential. At constant temperature and pressure, the inequality (11.9) for a closed system consisting of several substances will change as¹⁰⁴⁹

$$\sum \frac{\mathrm{d}\Phi}{\mathrm{d}n} \mathrm{d}n + \frac{\mathrm{d}\Phi}{\mathrm{d}n_1} \mathrm{d}n_1 + \frac{\mathrm{d}\Phi}{\mathrm{d}n_2} \mathrm{d}n_2 + \dots > 0 \tag{11.11}$$

Here, *n* is the mass of the solvent, and n_1 , n_2 , ...etc. are the masses of the dissolved substances. Each differential $d\Phi/dn_i$ represents the potential of the substance n_i in the system under constant pressure and temperature. The left-hand side of the inequality (11.11) without the first term that represents the solvent molecules is similar to Gibbs' ζ fundamental equation at constant temperature and pressure.¹⁰⁵⁰ Eq. (11.11) denotes the direction in which a process takes place within a closed system. This direction of the process is such that a change of one or more of the masses *n* produces a positive change of the function Φ .¹⁰⁵¹

The condition of equilibrium implies that,¹⁰⁵²

$$\sum \frac{d\Phi}{dn} dn + \frac{d\Phi}{dn_1} dn_1 + \frac{d\Phi}{dn_2} dn_2 + \dots = 0$$
(11.12)

¹⁰⁴⁷ Planck, 1887c, p. 469.

¹⁰⁴⁸ Planck, 1887a.

¹⁰⁴⁹ Ibid ¹⁰⁵⁰ GSP, 1906, p. 87, Eq. 92.

¹⁰⁵¹ Planck, 1887c, p. 469.

¹⁰⁵² Ibid, p. 470.

When the derivative of Φ with respect to *n* reaches a maximum, the value of Φ is at a maximum as well, which corresponds to the maximum value of the entropy, in agreement with the principle of the increase of entropy. To demonstrate a connection of his theory and that of van 't Hoff, Planck had to determine the function Φ in such a way as to make its connection with the various properties of substances participating in physical and chemical processes (affinity, reactivity, concentration).

Using the thermodynamic principle of increasing entropy, Planck succeeded to derive the Avogadro law for gaseous solutions as a necessary precondition to shift from the isotropic systems (pure gases and liquids) to heterogeneous systems (solutions). In the fourth chapter of the third paper of 1887, Planck derived all the important results of van 't Hoff: the colligative properties of solutions, i.e., the osmotic pressure, the lowering of the vapor pressure, and the freezing-point depression.¹⁰⁵³ Also, Planck demonstrated the strength of his theory upon deriving the Guldberg-Waage mass action law and the equations that expressed the effect of temperature and pressure on the equilibrium constant.¹⁰⁵⁴

Planck observed that both the vapor pressure and the freezing point depended on the molecular weight of the dissolved salt. He thought that deviation from theory is an indication that the molecules of the salt in solution are not those that are commonly regarded as such. The salt in the solution has undergone some kind of alteration. Following Ostwald and Arrhenius, Planck deemed that the molecular weight change was due to some sort of decomposition, although Planck was not specific about the nature of this

¹⁰⁵³ Ibid, pp. 495-499.

¹⁰⁵⁴ Ibid, pp. 485-494. Recall that van 't Hoff presented for the first time the temperature effect on the equilibrium constant in his *Études*. However, Planck presented its derivation through his theory of the entropy increase in an elegant way.

decomposition. Such a chemical change of the salt in the solution could modify the theoretical relation between the molecular weight of the salt and the vapor pressure and freezing point of the solvent. Assuming that the salt molecules are not all of the same types, he considered that there exist molecules of the type n_1 with molecular weight m_1 , molecules n_2 with molecular weight m_1 , and so on. The system in question would be described as:

$$nH_2O, n_1m_1, n_2m_2, n_3m_3, \dots, +n'H_2O$$
 (11.13)

In this sequence n and n' correspond to the number of solvent molecules in the liquid state (solution) and gas state (vapor) or the liquid state and solid phase (ice), respectively. The comma indicates components in the same phase (liquid) and the plus sign, components in another phase (solid or vapor). For a single substance (solute) dissolved in water (solvent), the notation (11.13) simplifies to

$$nH_2O, n_1m_{1,1}, +n'H_2O$$
 (11.14)

Expressing the concentration of the solute with the ratio n_1/n , and connecting this ratio with the molecular weights of the solute and the solvent, Planck obtained the following expression for the lowering of the vapor pressure, which compares with the analogous equation derived by van 't Hoff, namely¹⁰⁵⁵

$$\frac{n_1}{n} = \frac{p_0 - p}{p_0} = m_1 \cdot 5.6 = 1 \tag{11.15}$$

¹⁰⁵⁵ Planck, 1887c, p. 497. Planck obtained the connection between the ratio n_1/n and the molecular weight of the solute m_1 and water m taking into account a standard solution of one part by weight of solute in one hundred parts of weight of water. Then, $n \cdot m = 100n_1m_1$., and using the molecular weight of water equal to 18, he obtained the relation 5.6 $\frac{n_1}{n}m_1 = 1$.

Here, p_0 is the vapor pressure of pure water, p is the pressure of water upon the addition of a small amount of the solute to the solvent and the difference $(p_0 - p)$ represents the lowering of the vapor pressure of the solvent.

Planck followed the same procedure for the derivation of the expression describing the freezing point depression of water. He obtained the following relationship¹⁰⁵⁶

$$\frac{n_1}{n} = \left(\vartheta_0 - \vartheta\right) \frac{Q_0}{T^2} \tag{11.16}$$

Here, ϑ_0 is the freezing point of pure water (solvent) under the atmospheric pressure, ϑ is the temperature of the solvent upon the addition of a small amount of the substance and the difference $(\vartheta_0 - \vartheta)$ represents the depression of the freezing point of the solvent. Q_0 measured in calories is the heat of fusion (internal energy plus extra work) of a molecule of ice. Planck had to eliminate the dependence of his equation on the parameters Q_0 and nto obtain a comparable to van 't Hoff equation. Furthermore, Planck had to introduce somehow in Eq. (11.16) the molecular weight of the solute. He followed the same procedure as in the vapor pressure with one more step: the conversion of the heat Q_0 into its mechanical equivalent and finding a numerical value (adjusting properly the various units) for the ratio $\frac{Q_0}{T^2}$.¹⁰⁵⁷ This conversion at the freezing point gave the numerical value for the ratio

$$\frac{Q_0}{T^2} = \frac{1}{102} \frac{1}{^{0}\text{K}} \tag{11.17}$$

He finally obtained the desired equation for the depression of the freezing point of water, namely

¹⁰⁵⁶ Ibid, p. 499. ¹⁰⁵⁷ Ibid.

$$\frac{n_1}{n} = \frac{18}{100m_1} = \frac{(\vartheta_0 - \vartheta)}{102} \quad \text{or} \qquad \frac{(\vartheta_0 - \vartheta)}{18.2} = 1 \tag{11.18}$$

In all of his derived equations, Planck did not include the factor *i*, (the van 't Hoff's coefficient as Planck called it) which was indispensable for van 't Hoff's equations. Planck needed *i* to fit the mass action law and the colligative properties of the electrolytes to experimental results. The decomposition of the electrolytes in dilute aqueous solutions makes the left-hand side of Eqs. (11.15) and (11.18) for the vapor pressure and the freezing point by no means equal to one, but usually acquired larger values. However, the factor i had no theoretical basis in Planck's thermodynamics. After all, the factor *i* was an empirical parameter introduced by van 't Hoff only to fit the experimental data of Mitscherlich, Pfeffer, and Raoult. Planck was a theoretical physicist with minimal knowledge of chemistry. His motivation to derive van 't Hoff's equations of solution chemistry appeared as a mental exercise rather than a chemical problem. His thermodynamics in treating dilute solutions differed significantly from that of van 't Hoff. Planck saw the link between the ideal gases and dilute solutions as a phase change, a transition from the gas to the liquid phase,¹⁰⁵⁸ while van 't Hoff saw this link via the analogy between ideal gases with ideal solutions. Planck sought to find solutions for the anomaly manifested on factor *i* based on the theoretical ground of thermodynamics. On the other, van 't Hoff with the aid of Arrhenius' activity coefficient was satisfied with the use of this factor which reconciled the theoretical values obtained from his equations with the experimental data. However, Planck needed to find ways to justify the addition or the elimination of factor *i* in each equation. Otherwise, he may lose the link with van 't Hoff's theory, hence the correlation between

¹⁰⁵⁸ This consideration discloses the limited knowledge of Planck in chemistry since his theoretical approach does not apply to the solute at all. The phase transition, for example, from solution to its vapor or from solution to ice concerns only the solvent since the dissolved solid substance will remain intact.

theory and observations that was important for the ionists. Planck dealt with this problem in the last section of his third paper of 1887 entitled *Scheinbare Abweichungen von der Theorie* (Apparent deviations from the theory).¹⁰⁵⁹

Planck found it extremely difficult to reconcile the theory of the entropy increase with the empirical factor *i* in his equations. Since the theory of increasing entropy was not amenable for solving this rather empirical problem, Planck focused his attention on more practical solutions. He thought that the proper theoretical treatment, in this case, would concern the molecular weight of the solute, since its experimental value has been observed to deviate from that obtained from the molecular formula. "In other words, any apparent deviation from theory is an indication that the salt in solution has undergone a chemical change".¹⁰⁶⁰ Planck proceeded to modify his theory and find new theoretical relations in a form to confirm the experiment without reference to molecular weight. Using the sequence (11.13) above and the logic behind it, he obtained the relation between the lowering of the vapor pressure and the depression of the freezing point of water containing one percent of an added substance, namely

$$\frac{p_0 - p}{p_0} = \frac{\vartheta_0 - \vartheta}{102} = \frac{n_1 + n_2 + n_3 + \dots}{n}$$
(11.19)

Planck interpreted Eq. (11.19) as follows: "For any dilute aqueous solution, the lowering of the vapor pressure or the freezing point depression divided by 102 is equal to the ratio of the number of all molecules of the dissolved substance (regardless of whether they are similar or dissimilar) to the number of water molecules. This formula claims exact

¹⁰⁵⁹ Planck, 1887c, pp. 499-503.

¹⁰⁶⁰ Ibid, p. 501.

numerical validity; for most substances, it gives a larger number of molecules than is usually assumed, i.e., partial or complete chemical decomposition of the substances in the solution".¹⁰⁶¹ Planck believed that Eq. (11.19) expressed the modification he sought for the hitherto accepted theory of the ionists, i.e., the elimination of factor *i* from the expressions that quantitate the depression of the vapor pressure and the freezing point of water. In other words, Planck thought that he corrected van 't Hoff's theory from the need of the empirical parameter without neglecting decomposition (the way he meant decomposition) of the solute. However, a simple comparison of the vapor pressure and the depression of the freezing point shows that his equations were not different than those of van 't Hoff.¹⁰⁶² They simply changed forms. Comparison of van 't Hoff's Eq. (10.30) and Eq. (10.31) (on page 462) for the lowering of the vapor pressure and the freezing point depression, respectively with Planck's final expressions (11.19), one finds the following relationship for both additivity properties,

$$5.6\frac{n_1 + n_2 + n_3 + \dots}{n}m_1 = i \tag{11.20}$$

This comparison demonstrates that Planck was far from eliminating the factor *i*. He simply replaced it with another expression which was a function of the factor he attempted to rid of it.

Planck was a very capable theorist but with poor knowledge of chemistry. Root-Bernstein had the opinion that Planck was not capable of understanding the implications of his results to the ionic dissociation focusing his attention on an alternative derivation of

¹⁰⁶¹ Ibid, p. 502.

¹⁰⁶² Root-Bernstein, 1980, pp. 469-471.

van 't Hoff's equations, demonstrating perhaps the superiority of the mathematical rigor and logic versus empirical considerations. In this respect, Planck missed the opportunity to give a useful perspective of his findings relating van 't Hoff's coefficient with the molecular constitution expressed in Eq. (11.19).¹⁰⁶³ Planck's theory of decomposition failed to remove van 't Hoff's factor *i*. Notwithstanding, Planck was able to connect this factor to the composition of the solute although he failed to discuss this important discovery. According to Root-Bernstein, Planck's theory of dissociation has two relatively serious drawbacks compared to Arrhenius's relevant theory. First Planck abstractly discusses decomposition. His theory does not refer to the nature of the entities that resulted from the dissociation of the electrolyte molecules. There is no statement for the existence of ions, or at least for some kind of active molecules.¹⁰⁶⁴ Second, although Planck has derived [indirectly] the factor *i*, he was unable to understand the significance of the results of his theory concerning the experimental facts. His limited knowledge in chemistry did not allow him to understand the more profound value of factor *i*, which undoubtedly reflected the electrolyte's dissociation. Instead, Planck presented his theory as a culmination of logic independently of any other view, except perhaps the second law of thermodynamics and Avogadro's law. In short, Root-Bernstein concludes, Planck's theory was disconnected from the experiment and would hardly have been survived if Arrhenius' theory had not been recognized. Still, chemists did not pay much attention to theories not connected with what they were doing in the laboratory. Planck's solution theory was

¹⁰⁶³ Root-Bernstein, 1980, p. 470.

¹⁰⁶⁴ It is not surprising that Planck failed to understand the nature of the ion, or even to admit its existence in solution. This attitude was widespread not only among physicists but also among several chemists, as we shall see in the next chapter. At that time, confusion surrounded the concept of ion and a strong tendency formed to questioning its existence.

virtually forgotten. At best, it was remembered as a theoretical confirmation of Arrhenius' ionic dissociation theory.

Two months after the paper of Arrhenius of December 1887, in which the Swede communicated the final version of his ionic dissociation theory and eight months from his last paper, Planck published in February 1888 in the *Annalen der Physik* another article on his decomposition theory. This time, Planck used experimental data to com[are with his theory. In this paper entitled *Das Chemische Gleichgewicht in verdünnten Lösungen* (the chemical equilibrium in dilute solutions), Planck approached the subject of ionic dissociation with a different perspective than that in his previous paper. He must have read Arrhenius' paper of December 1887 because he was seemingly convinced about the necessity of factor *i* (he called it this time decomposition coefficient) in explaining the decomposition of the salts in water solutions. Also, Planck referred to the decomposed molecules, not as atoms or molecules but as ions. "Namely, if n_1 designates the number of undecomposed molecules, n_2 the number of the molecules each split into two ions".¹⁰⁶⁵

Planck began with the distinction between the *real molecules* and the *normal molecules*. The real molecules are responsible for the additivity properties of solutions, whereas the normal molecules are obtained from the usual molecular weight of the dissolved substance (determined by its molecular formula). This distinction originated from his previous paper, where he considered that molecular weight is the parameter that deviates from theoretical predictions. For aqueous solutions of salts and acids, the number of real molecules n is usually higher than the number of normal molecules N. On the other hand, for solutions of substances like benzene, alcohol, sugars, etc., n is often less or at

¹⁰⁶⁵ Planck, 1888, p. 142, 143, 154.
least equal to *N*. He set i = n/N, and defined decomposition for i > 1, and a chemical compound of the normal molecules in the solution for i < 1.¹⁰⁶⁶ At this stage, Planck wondered whether the real molecules were hydrated or not. He recognized that experiment could not resolve such a situation in which the dissolved substances are chemically combined with individual molecules of the solvent. However, he thought that hydration did not change the total number of dissolved molecules. The ratio of the number of the real molecules to the normal molecules is not altered essentially by hydration, since the water molecules are very large compared to the molecules of the substance.¹⁰⁶⁷ Therefore, Planck concluded, "All attempts to explain the deviation from the molecular law of freezing point or vapor pressure of dilute solutions by the formation of hydrates are in principle futile; the only possible explanation leads to a chemical change between the dissolved molecules". This statement is a direct answer to those who favored the hydration theory of dissociation (see the following chapter 12).

Planck linked the factor i with the expressions of the vapor pressure and freezing point of the previous paper through the following relationship

$$i = \frac{n}{N} = \frac{n_1 + 2n_2}{n_1 + n_2} = \frac{n_0}{N} \cdot \frac{q_0 \left[\vartheta_0 - \vartheta \right]}{\vartheta_0^2} = \frac{n_0}{N} \cdot \frac{p_0 - p}{p_0}$$
(11.21)

 n_0 represents the number of the solvent molecules, n_1 designates the number of the undecomposed molecules, n_2 is the number of molecules that decompose into two ions each. Planck denoted that in aqueous solutions of alcohol, sugar, ammonia, hydrogen sulfide, formic acid, the sulfates of copper, zinc, iron, $n_2 = 0$, whereas for the complete dissociation in

¹⁰⁶⁶ Ibid, p. 141.

¹⁰⁶⁷ Ibid. This conclusion is not always correct. It depends on the size of the dissolved substance. In any case, the size of the hydrated ions does not change the equilibrium condition. The concentration of water in the mass action law is very large compared to the concentrations of the various substances; it is considered constant, and is incorporated in the equilibrium constant.

an aqueous solution of hydroxides of potassium, sodium, lithium, the halogen acids, sulfuric acid, nitric acid, many salts, $n_1 = 0$. Eq. (11.21) can be used to calculate the values of n_1 and n_2 uniquely from N and *i*.

After the preliminaries concerning the new concepts of the type of molecules in a solution of substances and the connection of i with his theoretical equations of the vapor pressure and freezing point, Planck examined the variability of i (this time, he called it the degree of decomposition). He considered the state of equilibrium between the decomposed and the undecomposed molecules for a system of a 1:1 salt in solution, symbolized as

 n_0m_0 , n_1m_1 , n_2m_2 , n_3m_3

 n_0 is the number of solvent molecules, n_1 is the number of the undecomposed) molecules as before, and n_2 and n_3 ($n_2 = n_3$) are the numbers of the two ions that originated from the decomposed molecules. m_0 , m_1 , m_2 , m_3 , are the respective molecular weights. Following the procedure developed in his previous paper, he calculated the numerical concentrations, i.e. the ratios of the individual number of molecules to the total number of molecules, and taking into account the stoichiometry of the dissociation reaction, he obtained the condition of equilibrium in terms of the equilibrium constant *K*.

$$\frac{n_2^2}{n_0 n_1} = K \tag{11.22}$$

He expressed n_1 and n_2 in terms of *N* and *i*, and setting 2/K = K', Planck linked the factor *i* with the equilibrium constant

$$i = 1 + \frac{\sqrt{1 + 2K' \cdot \frac{N}{n_0} - 1}}{K' \cdot \frac{N}{n_0}}$$
(11.23)

This equation shows that the degree of decomposition *i* generally varies with temperature and pressure (through the equilibrium constant), and in a specifiable way with *the normal*

concentration, i.e. the known ratio of the normal molecular number N of the dissolved substance to the molecular number n_0 of the solvent.

Planck further examined the nature of the variability of factor *i* with the dilution. He saw correctly that the variability of *i* is governed by the constant *K'*, which provides a measure of the chemical strength of the normal molecules in the solvent concerned, which is independent of the degree of predilution. Then, for K' = 0 ($K = \infty$), i = 2, i.e., complete dissociation; for $K' = \infty$ (K = 0), i = 1, i.e., no dissociation at all. This analysis gives the two limits of *i*. He concluded that only for these limiting cases is *i* independent of the dilution.¹⁰⁶⁸ Next Planck sought to test the concentration dependence of *i* with the experiment.¹⁰⁶⁹ He introduced the percentage *P* of the dissolved substance in solution and rewrote Eq. (11.21) in terms of the known normal molecular weight of the solute M, and that of the solvent m_0 .¹⁰⁷⁰

$$i = \frac{M[\vartheta_0 - \vartheta]}{18.5 \cdot P} = \frac{5.56 \cdot M(p_0 - p)}{M \cdot p_0} = 1 + \frac{\sqrt{1 + 2KP} - 1}{KP}$$
(11.24)

Planck found that the values of *i* calculated from the theoretical formula (11.24) were in a direct contradiction with the experimental data; *i* instead of decreasing with increasing percentage, on the contrary usually increases, i.e., the degree of decomposition increases with the concentration of the solution - a result which is *a priori* incompatible with the theory. Planck gave a rather scanty explanation for this discrepancy upon comparing the ionic dissociation in an aqueous solution with the slow dissociation of the hydrogen iodide

¹⁰⁶⁸ Ibid, p.144.

¹⁰⁶⁹ Ibid, pp. 144-146.

¹⁰⁷⁰ Ibid, p. 144.

molecules in the gas phase.¹⁰⁷¹ Then, Planck decided to combine the decomposition coefficient *i* with Arrhenius' activity coefficient α . obtained through electrical conductivity experiments, a method that Planck considered as most accurate and consistent for many diverse measurements. He derived an empirical linear equation for the absolute electrical conductivity k with two fitting parameters a and b, namely

$$k = const. (i - 1) \cdot P = a \cdot \sqrt{1 + bP} - 1$$
 (11.25)

and compared the values of conductivity observed by Kohlrausch with the values calculated from the above formula for i. He observed that Eq. (11.25) fits the experimental data noticeably better than the quadratic interpolation formula of Kohlrausch (Eq. (5.3) on page 202).

It should be noted here that Planck has used the factor i with a double interpretation; as a decomposition coefficient (Zersetzung Coëfficient) and as a degree of dissociation (Zersetzung Grades). As decomposition coefficient, i do not change with concentration (and temperature) Planck had determined correctly the two limits of i using its relationship with the equilibrium constant, i.e., Eq. (11.22). What does change with concentration is the degree of dissociation; it increases with increasing dilution.

In the second and last section of his paper, Planck sought to correct the general formula of equilibrium for solutions. He thought that the equation of chemical equilibrium given by van 't Hoff and Guldberg-Waage did not express the real equilibrium in the solution. It can no longer suffice if the necessity of i is not taken into account. Planck deemed that the equilibrium law retains its validity under all circumstances, provided the real molecular numbers (the number of real molecules as defined above) and the real

¹⁰⁷¹ Ibid, p. 146.

molecular weights for all substances are to be taken into account. However, only the number of normal molecules, as defined above, is accessible from the experiment. Therefore, the formula of equilibrium expressed by the number of real molecules and the real molecular weight is generally not useful for direct application, because all the substances occurring in solution have their normal molecular weight. Consequently, Planck thought that the number of normal molecules N should replace the number of real molecules n in the equilibrium formula.

Furthermore, Planck remarked that the size of the water molecules in the liquid state is not identical to that of the isolated molecules of the vapor state. Water molecules in the liquid could be in any multiple of a vapor molecule.¹⁰⁷² Therefore, Planck extended the distinction between real molecular numbers n_0 and normal molecular number N_0 to the solvent itself. N_0 is always known. On the other hand n_0 is known only for the gaseous state from Avogadro's law. For a 1:1 salt in aqueous solution, the system solute-solvent is symbolized as before by

n_0m_0 , n_1m_1 , n_2m_2 , n_3m_3

The number of real molecules of water n_0 and the real numbers n_2 and n_3 ($n_2 = n_3$) of the two ions that originated from the decomposed molecules should be replaced by the number of the normal molecules N_0 , for the solvent, $n_1 = N(2 - i)$ and $n_2 = N(i - 1)$ for the solute¹⁰⁷³ Then, the general equilibrium condition of a system that is valid for the real molecular numbers must change into the normal conditions. The formula of equilibrium instead of the real molecular numbers and the corresponding concentrations, the normal

 ¹⁰⁷² This remark for the aggregation of the water molecules from a physicist at that time is astonishing.
 Today, we know that water molecules form clusters of various sizes through hydrogen bonding.
 ¹⁰⁷³ Planck, 1888, p. 150,

molecular numbers, and the normal concentrations must be used. Furthermore, Planck divided the transformation from the real to normal conditions into two classes.¹⁰⁷⁴ The first type of transformation is a physical transformation, such as evaporation, fusion, freezing of a solution in which none of the molecular numbers of the dissolved substances undergo any change. In this case, the real molecules of the dissolved substances enter into the expression of equilibrium with their total number *n*; their concentrations are to be replaced by the sum of the products *iN* (recall that i = n/N). For the solvent molecules the replacement of n_0 by N_0 is required to complete the transformation. In the second type of transformation, the molecular number of the solute is changed, since dissociation occurs. As in the first type of transformation, N_0 can be put instead of n_0 for the molecular number of the solvent without changing the meaning of the equilibrium. Regarding the decomposed molecules of the substance, Planck suggested the aforementioned theoretical treatment to achieve the expression for the equilibrium state under normal conditions.

Planck concluded his study with the following general statement: "If the molecules of a substance in a dilute solution are not all of the normal composition, then one has to proceed in setting up the equilibrium formula as if only the most numerous molecules of the substance were present in the solution. The other molecular species are not taken into account at all".¹⁰⁷⁵ Planck claims that this theorem reflects the advantage of his equilibrium formula over that of van 't Hoff, because it takes into account the variability of i.¹⁰⁷⁶

Planck's article of 1888 presented here in some detail is revealing, in the sense that it shows Planck's endeavors to ensure validity for his theory upon comparing his results

¹⁰⁷⁴ Planck, 1888, pp. 151-152.

¹⁰⁷⁵ Ibid, p. 153.

¹⁰⁷⁶ Ibid, p. 154.

with experiment. As a theoretical physicist, Planck had indeed insufficient knowledge of chemistry but he had realized as many physicists before him, that chemistry is the proper medium for testing theories. Planck presented little evidence to support his assumptions about the chemical equilibrium between the different types of molecules of the same substance in dilute solutions. But, on the other hand, he indicated that his theory is not disconnected from practical use as reflected on the variability of the degree of decomposition with dilution.

Planck's theory of solution was forgotten not only because its creator showed insufficient understanding of the chemistry involved in the ionic dissociation. Other reasons seemed to play their role in the unfortunate outcome of his theory. First, Planck's work faced the same problems that Gibbs and Duhem had in presenting their thermodynamics; His article of 1887 was written in an abstract form extremely difficult for chemists to comprehend its mathematical language. Planck himself complained about the mathematical shortcomings of even reasonably well-trained chemists like Ostwald.¹⁰⁷⁷ Second, Planck was not an ionist. He did not even belong to the cycle of the ionists. The only contact he had with this milieu, before the publication of his 1887 article, was the two letters he exchanged with Ostwald. The first letter was sent in May 1887, when he asked Ostwald's advice on his intention to study affinity, in which he discovered a lacuna in existing theories. The second letter was written in June 1887, in which Planck expressed his thanks to Ostwald for the information and the literature on affinity he received from him. Planck had no contact with van 't Hoff, neither before nor after the announcement of his version on the dissociation theory, whereas he felt the pressure of the rival theory of

¹⁰⁷⁷ Quoted in Root-Bernstein, 1980, p. 430.

Arrhenius. Planck had discussed with Arrhenius when the latter dropped at Kiel before visiting van 't Hoff in Amsterdam. Plank stressed the difficulty he had to apply the law of Guldberg. and Waage to the solution of copper sulfate. "I agree wholly with you, but there is a difficulty. If I consider the conductivity of copper sulfate, I may calculate how great a part of that salt is dissociated, and then this part must conform to the law of equilibrium which was announced by Guldberg and Waage. The difficulty is that my calculations do not agree with that law". ¹⁰⁷⁸ Planck asked Arrhenius whether it was possible to suppose that this discrepancy was due to the circumstance that the equilibrium was not reached immediately after the solution. Arrhenius replied, "I supposed there was no hope to help it out by such a hypothesis".¹⁰⁷⁹

Planck's theory did not find proper support from the ionists and especially from Ostwald who silenced on this issue. The ionists were heavily occupied to defend their theory from the opposition, disseminate its virtue among the chemists, and establish the new science of physical chemistry. They did not think that there was a place for Planck's theoretical treatment of the theory of solutions. Today, Planck is better known for his contribution to quantum physics than to the thermodynamics of solutions.

Planck demanded priority of the theory of ionic dissociation from Arrhenius. However, Arrhenius was the first who communicate this theory. In May 1887, Arrhenius sent a letter to Oliver Lodge in which he gave the first account of his theory. Although

¹⁰⁷⁸ Arrhenius, 1912, pp. 361-362. Copper sulfate is a strong electrolyte for which the Guldberg-Waage equilibrium law does not apply.

¹⁰⁷⁹ Arrhenius, 1912, p. 362. Arrhenius was probably aware of this difficulty because later when he discussed the same subject with van 't Hoff, he suggested to him the use of acetic acid. "Yes, that is as you say [van 't Hoff remarked that the law of Guldberg and Waage did not apply to potassium chloride), but you ought to try the calculation with acetic acid; for with acetic acid you can change the degree of dissociation in the proportion of I to 100, but with the salt you cannot change it more than in a proportion of 3 to 4. Of course, you must, if you want to see if a rule is true, take the greatest variation possible". (Arrhenius, 1912, p. 362)

Lodge was reluctant to admit the increasing dissociation with dilution, he nonetheless read Arrhenius' letter to the members of the electrolysis committee of the British Association for the Advancement of Science (BAAS). In June and November 1887, the theory appeared in two Swedish journals. Finally, in December 1887, the final version of the theory was published in the *Zeitschrift*.¹⁰⁸⁰ Arrhenius' letter of 1887 was unknown to Planck, who published his version of the ionic dissociation theory in July 1887.

Ostwald's intervention played an overbearing role in the development of the dispute between Arrhenius and Planck over the priority of the ionic dissociation theory. Ostwald advises Planck to deal with the theoretical elaboration of solution theory, providing him with all the information about the hitherto results obtained by Arrhenius and van 't Hoff and the pertinent literature about this subject. However, Ostwald acted superficially and did not inform Planck about Arrhenius' letter to the electrolysis committee of BAAS. Also, Ostwald failed to inform Arrhenius of the discussion he had with Planck. Presumably, Arrhenius learned about the decomposition theory of Planck later in December 1887. Ostwald never explained or admitted any role in this dispute. He did not say a word about this event in his autobiography. The conflict for priority ended in favor of Arrhenius and van 't Hoff's solution theory.¹⁰⁸¹ Thus, Planck was left with the impression that he had the priority in formulating the ionic dissociation theory, when in fact he experienced another disappointment losing for a second time the priority of discovery.

Ostwald never discussed or mentioned this event. In his autobiography, we read the following passage for Planck's contribution to the ionic dissociation theory: "Unexpected help [over the objections expressed by Eilhard Ernst Gustav Wiedemann (1852-1928), the

¹⁰⁸⁰ Root-Bernstein, 1980, pp. 389, 481.

¹⁰⁸¹ Root-Bernstein gives an account on Arrhenius-Planck's conflict for priority (1980, pp. 474-477).

son of physicist Gustav Wiedemann, on the dissociation theory] came from the brilliant mathematical physicist Max Planck. From a completely different starting point, he had arrived at general laws governing chemical equilibria whereby he had reached the same results as earlier workers but had made progress in important points. He compared the ability of salts to reduce the freezing point of a liquid with the theory and demonstrated that this required that more molecules be present than the normal chemical formulae allowed. He had, however, did not suggest as to where the extra molecules might come from. He joined in the discussion and showed that E. Wiedemann's explanation of polymerized water would not serve, because the molecular size of water was not an element in the equation and hence was irrelevant".¹⁰⁸²

¹⁰⁸² Ostwald, 2017, p. 160.

Chapter 12. Opposition to the ionists' theory of solutions

When Arrhenius asked the organic chemist Emil Fischer for his opinion about his ionic dissociation theory, Fischer warned him that most chemists would not favorably see his ideas on the dissociation of electrolytes into ions.¹⁰⁸³ Kohlrausch thought that Arrhenius went too far, whereas Gustav Wiedemann, the physics professor at the University of Leipzig, found Arrhenius' theory fantastic in the extreme¹⁰⁸⁴. Recall that Lodge had his reservations for certain aspects of the Arrhenius' theory.

Section 1. Reasons of the opposition

Intense and sometimes hostile criticism broke against the ionists' theory of solutions and, in particular, on the theory of the electrolytic dissociation. This criticism was partly due to the resistance of chemists to thermodynamics and mathematics¹⁰⁸⁵ and, in part, to objections raised on several aspects of the dissociation hypothesis. A third reason seems to play an additional role in the hot discussions between the British scientists and their followers on the one hand and the ionists on the other. The nationalism that sprang stronger in the late nineteenth century had its share in this struggle for scientific supremacy.¹⁰⁸⁶ This social trend appeared in industrialized countries, such as France, Germany, and England, and to a lesser extent in the periphery states (Netherlands, Sweden, Austria, Russia, etc.).

¹⁰⁸³ Ibid, p. 287.

¹⁰⁸⁴ Ibid, pp. 287-288. According to Arrhenius, Wiedemann's response was as follows: "It is very interesting, of course, but you have not found the real cause of the things in question. I know what this cause is, it is the internal friction, and I hope to show it to you" (Arrhenius, 1912, p. 363). Arrhenius claimed that Wiedemann did not keep his promise.

¹⁰⁸⁵ See chapter 9, of this dissertation.

¹⁰⁸⁶ Crawford, 1992, pp. 28-46.

The transfer of the industrial activity from England to the European mainland in the decade of 1860 onwards created national competition in manufacturing commodities, trade, and in general in every aspect underlining the economic growth. National industrialization certainly affected science and scientists, both taking part in its development. The government involvement in this competition was direct when scientific activities were perceived as promoting trade and commerce. Physicists and chemists participated in their countries' efforts for industrialization and provided theoretical and practical knowledge. For instance, physicists contributed to the growth of the electrical industry, while chemists provided new processes and products in chemical industries. The physical sciences were the sources of knowledge, instrumentation, methods, and trained workers in the industry, mechanics, transportation, and trade. Physicists and chemists played another important role in the national integrity of their country. In the newly created scientific organizations (Academies, associations), institutions (Universities, technical schools, and laboratories) worked not only in research programs or reported new scientific results, but they also endeavored to establish a national scientific culture that could prevail in the European center and periphery. The journal Zeitschrift für Physikalische Chemie is an example. Its editors (Ostwald and van 't Hoff) issued the journal only in the German language, despite its international character.¹⁰⁸⁷ This cultural infusion of knowledge and values into the cultural life of the citizens culminates in periods of the formation of new states. The physicist and physiologist Hermann von Helmholtz and the physician Emil du Bois-Reymond (1818-1896) actively supported the national power. However, it should not be

¹⁰⁸⁷ Duhem asked once Ostwald to allow publications in French on the ground that the German language was not widespread among the French scientists. Ostwald refused Duhem's request.

forgotten that they were cases in which scientific nationalism extended to its extremes and changed into its most virulent form of chauvinism.

Nationalism in science did not deny its coexistence with internationalism. Nationalism and internationalism coexisted in the period between 1880 and 1914.¹⁰⁸⁸ Although nationalism and internationalism in science appear to have a contradictory conceptual relationship, in reality, they have common roots; national industrialization and economic growth. Despite the strong competition in almost all fields of science, governments realized that scientific competition could continue to proceed in the context of international meetings, conferences, and congresses. The competition was intense in conventions and congresses regarding the standardization of the metric system of weights and measures and electricity.¹⁰⁸⁹ Alongside the competition, internationalization through organized scientific meetings (sometimes financially assisted by governments) would allow scientists from different countries to be aware of the progress in particular fields they were behind or intended to begin. Also, they could have the chance to share new ideas, methods, and experimentation that could be useful for their research, oppose competitive theories, or defend their priorities in discoveries. This ambiguous atmosphere prevailed at BAAS meetings and became apparent during the debates for the ionic dissociation theory.

Section 2. The British opposition, 1887-1888

The main battlefield between the British scientists and the ionists was the electrolysis committee of the British Association for the Advancement of Science (BAAS), held in

¹⁰⁸⁸ Crawford, 1992, p. 43.

¹⁰⁸⁹ The International Congress on Metric Standards in France in 1875 is an example of this kind (Crawford, 1992, p. 42).

various cities of Great Britain since 1831. On the pages of the reports of the electrolysis committee, Arrhenius and the British scientists expressed their opinions or opposition about various theories on electrolysis; how electrolytes decompose and carry electricity. Ideas, experiments, criticisms were presented, either directly by the authors in the meetings or through letters and articles sent to the committee. Oliver Lodge, the secretary of the British Association, presented to the members of the committee the various letters and articles; he organized the agenda of the meetings and prepared general reports concerning the progress of the various subjects.

On May 17 and June 8 of 1886, Arrhenius sent to Lodge two letters.¹⁰⁹⁰ Arrhenius commented on the ions' velocity resulting from the dissociation of double salts that are free to move within the solution and explained the electrolysis of the double salts MgSo₄ and CuSo₄ in dilute and concentrated solutions. Also, Lodge commented on an Arrhenius' paper published in Wiedemann's *Annalen der Physik und Chemie*.¹⁰⁹¹ Arrhenius discussed the effect of the friction exerted by the solvent and explained why the ions H and OH have greater velocities than the ions from salts in dilute solutions. Arrhenius sent these letters contributing to the discussion (through the pages of the BAAS report) between him, Kohlrausch, and the French physicist Edmond Marie Léopold Bounty (1846-1922) on the nature of electrolytic conductivity, especially under the simplifying circumstances of extreme dilution.

Lodge had received from Arrhenius a copy of his dissertation, and in 1886, during the 56th meeting of BAAS held in Birmingham; he reported his opinion for this work.¹⁰⁹²

¹⁰⁹⁰ Lodge, 1887a, pp. 310-312.

¹⁰⁹¹ Lodge, 1887b, pp. 315-318.

¹⁰⁹² Lodge, 1887c, pp. 357-384.

Lodge was critical of the experimental part of the dissertation as inadequately performed. He was more appreciative for the second part of the dissertation, in which Arrhenius presented his theory but was not committed to it.

"I must express my regret to the author for the adverse opinion and trust that my appreciation of a great deal in the second part will compensate for it to some extent. It sometimes seems as if the author allowed himself occasionally to indulge in an exploded type of reasoning, wherein, by manipulation of imaginary data, a confusion is produced, out of which emerge several laws more or less in agreement with experience, which is thenceforth labeled and referred to as theoretical deductions. It may be, however, that the italicized and numbered statements throughout the paper are not intended for strict statements of deduced law, but are merely summaries of more or less probable truth. In that case, it is their form only which is misleading, and one would judge them by a different standard".¹⁰⁹³ Lodge seemed confused by the inactive and active molecules. "How the inactive and active portions differ is not certain, perhaps only physically; perhaps the active part is a compound of hydrate and solvent".¹⁰⁹⁴

On the other hand, he found important Arrhenius' activity coefficient. He thought that this "dissociation ratio", as he called the activity coefficient, consisted of a helpful measure of the chemical activity of the electrolyte. Arrhenius replied to Lodge's criticism in the same report.¹⁰⁹⁵

The most sophisticated criticism of the solution chemistry of the ionists came from Great Britain and, in particular, from London. The organic chemist Henry Edward

¹⁰⁹³ Ibid, p. 358.

¹⁰⁹⁴ Ibid, p. 364.

¹⁰⁹⁵Arrhenius, 1987c, pp. 384-387.

Armstrong, a member of the electrolysis committee of BAAS, exerted the toughest criticism of all. He was a fierce opponent of the ionists' theory of solutions. He did not miss any opportunity for a tenacious opposition to almost anything from the solution theory.¹⁰⁹⁶ He targeted the weak point of the ionic dissociation theory concerning its incapacity to offer a convincing explanation of why an electrolyte molecule such as sodium chloride dissociates in aqueous solutions. Where could the salt get the required energy from to split into positive and negative ions? Furthermore, he did not find likely the absence of water in the process of dissociation. He felt that water molecules must be involved as active components of the solution. He refused to accept that the dissociated atoms of the electrolyte were the active species, while the water was merely the mechanical means of separating the ions. In a paper published in the Proceedings of the Royal Society in 1886, Armstrong presented an alternative to dissociation theory, the so-called theory of *residual* affinity.¹⁰⁹⁷ He modified Berzelius' dualism and considered that an exact equivalence between the electropositive and the electronegative atoms does not exist. The electronegative element has an unsatisfied or residual affinity ready to cling to new atoms or other molecules instead of affinity saturation through charge saturation. The result of this residual affinity of unsaturated atoms would be the formation of complex molecules or molecular aggregates in solution. Each of these aggregates is saturated and therefore inert. The effect of dilution, i.e., the addition of solvent molecules, is to break up these aggregates into simpler molecules. In a highly dilute solution, the aggregates are further decomposed in much simpler molecules reaching those in the gaseous state. The electric current in an electrolytic cell assists the separation of aggregates into simpler molecules.

¹⁰⁹⁶ De Berg, 2003, p. 414.

¹⁰⁹⁷ Armstrong, 1886.

In other words, the applied E.M.F. in the cell induces disruption and interchange and brings about the same result as the Clausius-Williamson dissociated condition. In other words, the action of the electromotive force of the cell is the driving force for dissociation.

Oliver Lodge objected to Armstrong's decomposition model in a report presented to the electrolysis committee in August-September 1887 during the 57th meeting of BAAS held in Manchester.¹⁰⁹⁸ In this report, Lodge compared the views of Arrhenius and Armstrong on electrolysis. Lodge's criticism of Armstrong's views was severe. He pointed out that whatever the nature of molecular complexes, the supposition that the decomposition occurred through the applied E. M. F, instead of an independent process, was fatal for the theory of the residual affinity. He claimed that the role of the applied electrical potential is to redirect the random motion of the ions towards the electrodes of the electrolytic cell. With this statement, Lodge defended the foundation of the Clausius-Williamson hypothesis.

Regarding the chemistry involved in Armstrong's theory, he stressed that any chemical approach assuming that the electromotive force produces the changes necessary for the passage of electric current should explain why a minimal electromotive force is sufficient for the initiation of the electrolysis. Lodge's reference to Arrhenius' theory was not critical as that of Armstrong. His opinion was that Arrhenius had provided a perfectly orthodox view of the nature of electrolysis, which was of particular interest in its application to chemistry. Lodge identified Arrhenius' active molecules with the dissociated molecules of Clausius.¹⁰⁹⁹ However, this statement does not necessarily mean that Lodge took Arrhenius' part in this argument.

 ¹⁰⁹⁸ Lodge, 1888, pp. 351-353. Dolby, 1976, pp. 317.
 ¹⁰⁹⁹ Ibid, p. 351.

Armstrong sent a quite lengthy but unconvincing answer to Lodge's report, which turned out to be a harsh criticism of Arrhenius's ionic dissociation theory.¹¹⁰⁰ Armstrong, like most of the British chemists, was unfamiliar with mathematics and physics. He had difficulties comprehending the physicochemical laws associated with the dissociation process in the electrolyte solutions before and during electrolysis. Armstrong feeling his inadequacy in going through the heart of the problem ended his letter to Lodge with internal grief: "In conclusion, I would add that I urge these pleas on behalf of my hypotheses with the greatest diffidence, feeling that I am unfortunately unable to fully appreciate the force of the mathematical and physical arguments. I do think, however, that in framing our conceptions we may perhaps have been too much guided by statistical principles; it is quite open to questions whether the atoms in molecules are in that state of unrest- are perpetually changing places in the manner in which our fancy has allowed us to picture them to be".¹¹⁰¹ Armstrong stressed the importance to understand the complexity of the inter-atomic and intra-atomic structures and recognized the difficulty for the chemist to quantify the various peculiarities and relationships involved in dissociation, and he stressed that "for this reason, it is all-important that chemists and physicists should cooperate".

Arrhenius sent a detailed reply to Armstrong's comments on the ionic dissociation theory. Arrhenius' article published in the 1889 issue of the BAAS report, summarized the conclusions of the meeting held in Bath in September of 1888.¹¹⁰² Arrhenius attacked Armstrong's residual affinity in two points: the role of water in the dissociation of the electrolytes and the asserted significance of the formation of complex molecules

¹¹⁰⁰ Armstrong, 1888, pp. 354-358.

¹¹⁰¹ Ibid, p. 357.

¹¹⁰² Arrhenius, 1889b, pp. 352-355.

(aggregates) due to the unsaturated affinity. Arrhenius emphasized that water was necessary as a medium in which electrolytes dissociate, but it did not dissociate itself and did not participate in the conduction of electricity. Experiments show that the extent of the dissociation of pure water is extremely small and is impossible to detect.¹¹⁰³ Strong and weak acids dissolved in equal volumes of water show differences in their dissociation degree, thereby different molecular conductivities. But this behavior is attributed solely to their chemical structure (actually to the chemical bonding). The aggregates, which are supposed to break up by the water in simpler molecules, do not carry an electrical charge as the ions, and therefore cannot be directed towards the electrodes by the applied E.M.F.¹¹⁰⁴ In his reply, Arrhenius takes the opportunity to stress the fact that the laws of the ionic theory of dissociation do not apply to the concentrated solution. In this range of concentrations, the behavior of electrolytes deviates from the regularities observed in dilute solutions, which are analogous to those obtained in the case of gases¹¹⁰⁵. Finally, Arrhenius commented briefly on the new theory of hydrates introduced by the Russian chemist Dimitri Mendeleev. I will discuss below the features of this theory and Arrhenius's disposition to it.

Regardless of the impact that the ionic dissociation theory had on the members of the electrolysis committee, Arrhenius' contribution to discussions about the various aspects of the process of electrolysis allowed him to obtain contacts with the British scientific community and the chance to propel the recognition of his theory.

¹¹⁰³ Arrhenius, 1889b, p. 353. Ordinary distilled water in equilibrium with carbon dioxide of the air has a very small conductivity of the order of $10^{-6} \Omega^{-1} m^{-1}$. This scale of measurements requires very sensitive instruments that apparently was not available in the physical chemistry laboratories at that time. ¹¹⁰⁴ Ibid, p. 354. ¹¹⁰⁵ Ibid, p. 252.

Armstrong was not alone in contrasting Arrhenius' ionic dissociation. He was supported by the chemist Spencer Umfreville Pickering (1858-1920),¹¹⁰⁶ the Irish physicists George FitzGerald, and J.J. Thomson, though the latter was more careful in his criticism.¹¹⁰⁷ Lodge's stance was ambivalent. FitzGerald, a strong anti-ionist, considered the dissociation theory premature and believed that the truth was more complicated than Arrhenius recognized. J.J. Thomson was skeptical about the dissociation theory, arguing that all so-called dissociations could be explained by the attractive forces between solute and solvent.¹¹⁰⁸ Even the dilution law of Ostwald was attacked as an inadequate mathematical simplification of the more complex phenomena of chemical changes.¹¹⁰⁹ Furthermore, the opponents of the ionic dissociation law argued that this law does not seem to apply to the case of strong electrolytes. The inadequacy of Arrhenius' theory to explain the behavior of strong electrolytes was the weak point of the dissociation theory that was exploited by its opponents the most.

The osmotic pressure theory did not escape their attacks. The main argument against it derived from its molecular interpretation. Although the analogy between the gas pressure and the osmotic pressure was not denied (and thereby the application of the Avogadro law to both states), FitzGerald claimed that the supposed molecular similarity in the gas and liquid phases revealed the danger of assuming that the physical conditions are all alike.¹¹¹⁰

¹¹⁰⁶ Well-off and not forced to look for a job, Pickering performed most of his research at home (Dolby, 1976, 319)

¹¹⁰⁷ Recall that J.J. Thomson was in favor of the free dissociation of the electrolytes in solutions in analogy with the dissociation of gases in discharge experiments (Chapter 8, section 1 of this dissertation).
¹¹⁰⁸ Thomson, J.J., 1888, p. 213; Hiebert, 1981c, p. 104. Five years earlier, Thomson had supported the idea that electrolytes dissociate when dissolved in water and before the passage of the electric current.
¹¹⁰⁹ De Berg, 2015, p. 37.

¹¹¹⁰ Ibid, p. 36.

Section 3. The hydrate theory and Arrhenius' reaction

In 1886, Pickering came against the ionic dissociation proposing an alternative theory. Independently of Armstrong, Pickering developed a theory employing residual valencies to explain such molecular aggregates as hydrated salts and double salts.¹¹¹¹ He plotted the heat of dissolution against concentration for hydrated salts at various temperatures. The observed irregularities of the curves led him to conclude that different hydrates were formed in solutions at various temperatures. Subsequently, Pickering gave a concrete picture of his hydrate theory of solutions.¹¹¹² He argued that solutions contain molecular compounds of indefinite proportions, held together by residual valencies. He further asserted that when a solid dissolved, the molecular aggregates of the solid-state were broken down into simpler forms (which absorb heat) and replaced by aggregates with the liquid (which evolve heat). Pickering's solution theory combines Armstrong's residual affinities and the hydrate theory developed in 1887 by Mendeleev. However, his reasoning on the disruption of the molecular aggregates into simpler forms upon its dissolution in water and the consequent replacement of these simpler entities with a new formation of aggregates with water is a blurry image of today's theory of the ions solvation.¹¹¹³

The theory on hydration received a strong impetus from the Russian chemist Dimitri Mendeleev. In 1887, he published a short article in the journal of the Russian

¹¹¹¹ Pickering, 1886a; Dolby; 1976, pp. 318-321.

¹¹¹² Pickering, 1886b.

¹¹¹³Today we know that ionic solids form crystals in which the ions of opposite charge are held together with electrostatic forces (the ionic bond). For instance, sodium cations and chloride anions are arranged in a cubic lattice in sodium chloride salt. When the solid salt dissolves in water, the water molecules disrupt the lattice and surround (hydrate) each positive or negative ion via ion-dipole forces. The energy required for the dissociation of the electrolyte molecules into ions in water is compensated by the energy released by the hydration of ions by the water molecules. This scheme, however, does not justify the followers of the hydrate theory, whose major point was the compulsory participation of water in the process of dilution. The difference is that the hydrate theory did not accept the formation of ions.

physicochemical society aiming at discrediting the theory of ionic dissociation. Mendeleev argued that all water in the solution is combined with the dissolved substance. There will be changes in the solution properties at different concentrations as one such complex molecule (a hydrate) is replaced. He further considered equilibrium between the formed and decomposed hydrates according to the laws of chemical equilibrium. He chose the specific gravity of aqueous solutions of ethyl alcohol to test his hypothesis. Plotting the specific gravity of the solution as a function of the percentage of the composition of the dissolved alcohol, he obtained a parabola of the second order. But when he plotted the first derivative of the specific gravity with the percentage concentration, he observed a series of discontinued straight lines with increasing concentration. He claimed that each straight line represents the varying proportions of two hydrates in equilibrium. He interpreted the point of discontinuity as the point in which a higher hydrate is replaced by another hydrate containing a lower proportion of water molecules. Mendeleev observed three such points of discontinuity for the alcohol-water solutions, of the general type $xC_2H_6OH + yH_2O$,¹¹¹⁴

$C_2H_6OH + 12H_2O$	17.56% of alcohol
$C_2H_6OH + 3H_2O$	46.00% of alcohol
$6C_2H_6OH + H_2O$	88.46% of alcohol

At the concentration of 88.46%, a single hydrate forms. In other words, as the concentration increases still further, an increasing amount of the next lower hydrate appears in the solution. Furthermore, Mendeleev contended that his hydrate theory applied without exception to several solutions of a hundred different salts, such as H_2SO_4 , NH_3 , HCL, and other electrolytes. Mendeleev emphasized that van 't Hoff's factor *i* rarely achieves an

¹¹¹⁴Mendeleev, 1887, p. 780.

integer value, and in several cases, it assumed different values for the same electrolyte at different concentrations. He deduced from this observation that it is important to check the dependence of i with the concentration before postulating free ions' existence.¹¹¹⁵

Some British chemists received Mendeleev's hydrate theory enthusiastically, especially by Armstrong and Pickering. It appeared as a credible alternative to the ionic dissociation theory, and contrary to this theory, it was applicable at higher concentrations. Armstrong welcomed Mendeleev's theory as a general method for demonstrating the nature and significance of hydration in solution. However, he made no use of Mendeleev's experimental approach. On the other hand, Pickering realized the importance of the method, and he decided to perform experimental work to validate it.¹¹¹⁶

Arrhenius attacked Mendeleev's theory in a paper published in 1889 in the *Philosophical Magazine*. He did so because he wanted to convey his arguments against the hydrate model to the English audience. "As many English chemists (Armstrong, Crompton, Pickering) have in recent publications accepted and defended Mendeleev's views. I take the opportunity of offering a few observations in an English scientific journal on Mendeleev's paper".¹¹¹⁷ Arrhenius began his paper by contrasting the applicability of his theory to that of Mendeleev's. He listed seventeen "branches of the physical sciences" that could be explained, one by one, by the ionic dissociation and the study of osmotic pressures. He added that this was not the case for the hydrate theory and remarked wittingly, "Are we to assume that the view that hydrates exist in solutions can render such service? So far as I am aware not a single numerical datum has hitherto been deduced from

¹¹¹⁵ Mendeleev 1890.

¹¹¹⁶ Dolby, 1976, p. 328; Petit, 2013, p. 242.

¹¹¹⁷ Arrhenius, 1889c, p. 30.

this hypothesis".¹¹¹⁸ He then questioned the heart of Mendeleev's theory, the graphical evidence for the existence of Mendeleev's hydrates. He pointed out that every property represented with such curves was usually not very simple. These representations were not useful without a theoretical framework for their explanation.

Furthermore, he noted that the property of the specific gravity used by Mendeleev was not a proper choice to prove the existence of hydrates. Arrhenius invoked Ostwald's reasoning that the specific gravity could not be used for setting forth stoichiometric laws. Arrhenius depicted two diagrams of the change of the specific gravity of sulfuric acid with the concentration obtained by Mendeleev. In the first diagram, he plotted the empirical data against concentration. The plot was a parabola as expected (Figure 25). In the second diagram, he plotted the first derivatives of the same data (Figure 26). The two plots differed markedly, not only in their appearance but also in the number of the breakpoints.¹¹¹⁹ Arrhenius was wondering a second time, "Who would be likely to discover that these two curves are identical?"¹¹²⁰ He concluded that "when, exceptionally, a sudden break occurs in a series of phenomena, it must be verified with the greatest care both theoretically and practically before its existence is finally accepted".¹¹²¹ Arrhenius did not exclude entirely the existence of some kind of hydration of the ions in the solution. What he rejected was the replacement of the ionic dissociation with the hydrate theory, the ions with the hydrates He affirms that the ionic dissociation theory accepts that a small degree of hydration of ions exists in very dilute solutions. Still, the composition of this hydration did not alter with

¹¹¹⁸ Ibid, p. 31.

¹¹¹⁹ Ibid, pp. 33-34.

¹¹²⁰ Ibid, p. 33.

¹¹²¹ Ibid, p. 34.

concentration they do not influence the ionic equilibrium between decomposed and undecomposed molecules and certainly disagreed with Mendeleev's views.

Mendeleev's model of hydrates did not last long, at least in the form in which was proposed by his originator. After his first enthusiasm, Armstrong began to expose some doubts about the explanations given by Mendeleev for his hydrate theory. He thought that a wide range of properties should be investigated as a function of concentration and temperature until solid evidence of the existence of hydrates had been obtained. Armstrong also remarked that the method was far from conclusive, as more than two hydrates could be present in a solution at a given concentration.¹¹²² Pickering also agreed with Armstrong that there might be more than two hydrates of a solute present in a solution of a given concentration. Soon, Pickering expressed severe reservations about Mendeleev's method. Especially when the data Mendeleev had used were not reproducible. They did not lead to Mendeleev's graphical results when replotted.¹¹²³ Pickering was convinced that the breakpoints of Mendeleev were not present in the density curves for solutions of sulfuric acid.

Nonetheless, Pickering did not abandon the idea of the hydrates. He thought that the basic idea that solutions are composed of hydrates must be correct. He sought to find singular points on the curves by plotting the second derivatives of Mendeleev's data (specific gravity of sulfuric acid) against concentration. Indeed, he found these points, but as Arrhenius and Ostwald criticized, this broken curve cannot explain the laws of chemical equilibrium, which require continuous changes.¹¹²⁴ Furthermore, Pickering did not justify

¹¹²² Dolby, 1976, pp. 328-329.

¹¹²³ Ibid, p. 329.

¹¹²⁴ Ostwald, 2017, pp. 216-217.

using the second derivative and not higher-order derivatives or at least indicating the limit to differentiation. Pickering did not explain why he obtained different numbers of straight lines (he observed 17 straight lines corresponding to 16 hydrates) in his second derivative plot compared to the number of lines in Mendeleev's first derivatives, and therefore different types of hydrates.¹¹²⁵ Nonetheless, Pickering felt that he had achieved a major triumph for his theory when he succeeded in isolating by crystallization a hydrate of sulfuric acid, namely H₂SO₄.4H₂O.¹¹²⁶

The crucial battle between the ionists and the British anti-ionists took place at Leeds, where the BAAS meeting was held in September of 1890.

Section 4. The meeting of the British Association at Leeds in 1890¹¹²⁷

The meeting had the title *on the theory of solution and its connection with osmotic pressure*,¹¹²⁸ and it was held at Leeds, from Saturday 6th to Monday 8th of September 1890. Leading experts from Europe were invited. Ostwald and van 't Hoff were invited and attended the meeting, whereas Arrhenius was absent. He sent a letter read by Ostwald's British student, the Scottish chemist James Walker (1863-1935). Ostwald considered this invitation as a great opportunity to "carry the new gospel to the heathens".¹¹²⁹ The British participants were almost all opposing the ionic dissociation theory. Some considered it

¹¹²⁵ Arrhenius commented on Pickering's second derivative curve in a note in his paper of 1889c, pp. 36-38.

¹¹²⁶ Pickering, 1890; Dolby, 1976, p. 331.

¹¹²⁷ For an outline of the debate during the meeting, see Dolby, 1976, pp. 331-338; Petit, 2013, 247-252. For a detailed account of the formal presentations and discussions in the various sessions of the meeting, see BAAS report of the electrolysis committee, 1991, pp. 142-144, 185-216, 310-338.

¹¹²⁸ Ostwald in his autobiography claims "that the discussion in the meeting was not to be restricted to the question of the theory of solutions. It was to extend particularly to Arrhenius's dissociation theory, which seemed to conservative British minds to be nothing short of scandalous" (Ostwald, 2017, p. 217). ¹¹²⁹ Ibid.

scandalous. The Scottish chemists William Ramsay (1852–1916) and James Walker both were convinced ionists. They had repeatedly supported ionists' dissociation theory in the electrolysis committee.¹¹³⁰ It appears that Walker had mediated in the committee to send invitations to the ionists. Ramsay played an important mediating role between the ionists and the British to approach each other's views. The chairman of the meeting was Francis FitzGerald, who was also the chairman of the electrolysis committee for that year.

Ostwald and van 't Hoff found it extremely difficult to convince the opponents of the ionic dissociation theory, who were represented basically by the three organic chemists Armstrong, FitzGerald, and Pickering. Ostwald had another difficulty with his imperfect knowledge of the English language. The meeting had two formal sessions on Saturday and Monday and a formal discussion period on Sunday. These sessions ran more or less in the usual organizational pattern of recent conferences. The participants presented or read papers followed by relevant discussions. The formal discussion period looked like a round table held in today's conferences. However, the informal discussions brought the ionists in intimate contact with the British scientists, and the two ionists tried to understand each other. It was the informal discussions in which the ionists and the followers of the Ostwald's school strived to convince the British chemists and physicists about the logical consequences of their theory.

FitzGerald opened the Saturday session reading a paper entitled *Electrolytic Theories*.¹¹³¹ This paper was an introduction to the following discussion regarding the controversy between the British views on electrolysis and the extreme dissociation theory

¹¹³⁰ Root-Bernstein, 1980, pp. 517-518. For this reason, Ramsay's work seemed to be hardly appreciated by the London Chemists, and received the offensive comments of Armstrong who developed a strong aversion to him (Petit, 2013, p. 247).

¹¹³¹ FitzGerald, 1891, pp. 142-144.

of solutions supported by the recent investigations of the ionists. To explain the electrolysis process without free ions, FitzGerald suggested a modification of Grotthuss' hypothesis in the direction of Clausius. He supposed that if the molecules drew one another apart at a rate proportional to the applied electromotive force, the relation between electric force and the decomposition becomes linear, satisfying Ohm's law in the case of small currents. This theory also agrees with Clausius' hypothesis in that it explains electrolysis and double decomposition as properties of the same kind.

FitzGerald contrasted Arrhenius' theory, which assumes that molecules in a liquid will occasionally be arranged by accident in the proper polarized condition in a closed circuit for drawing one another apart. If the circuit includes molecules of different kinds, there will result in double decomposition.¹¹³² He pointed out the severe difficulties in supposing that uncombined atoms are free to move in solution for a finite time. He stressed rather ironically that the free atoms assume by their own accord a specific arrangement that is required before exchanges take place leading to electrolysis and double decomposition. He considered as likely the hypothesis of Armstrong's suggestion that the proper arrangement for double decomposition might be a double molecule and one that should be investigated from the chemical rather than the physical side.¹¹³³ He insisted that the dissociation of electrolytes is an unnecessary condition to explain their colligative properties. He thought it more plausible to think about the electrolyte's nature rather than the number of its molecules in solution. "In this connection, it is well to state that some bodies may be much better able to produce pressure than others, because of their being more easily polarized, i.e., turned into an effective direction. A molecule which could be

¹¹³² Ibid, p. 143. ¹¹³³ Ibid easily turned into an effective direction would be about twice as effective as a molecule which went about in a higgledy-piggledy way; and one would consequently expect electrolytes to produce more, nearly double, the osmotic pressure that other bodies did. As to the changes of boiling and freezing points, they seem explicable by exactly the same hypothesis. The reduction of vapor pressure by the molecular affinity of dissolved salt would depend only on the number of molecules of salt if all salts have the same molecular affinity for water, and the same would apply to the change in freezing point". Therefore, FitzGerald concluded, "All these phenomena are explained without assuming free atoms, and they are all explained by what can hardly avoid being a [*v*]*era causa*, namely, whatever affinities they are that cause solution, which latter is an unexplained phenomenon on the dissociation hypothesis".¹¹³⁴

On Saturday, W. N. Shaw also presented a lengthy paper entitled on the Present State of our Knowledge in Electrolysis and Electrochemistry¹¹³⁵. The article was a review of the literature. Shaw made a thorough report on Arrhenius's dissociation theory and its applications explaining various physical and chemical phenomena.¹¹³⁶ Also, he referred to the dilution law of Ostwald¹¹³⁷ and the Arrhenius equation of the temperature dependence of the dissociation constant. He calculated the heat of formation of molecules from the corresponding values of their ions and the heat of neutralization of acids with bases.¹¹³⁸

The formal discussion started with a paper by Pickering, *the present position of the hydrate theory of solution*.¹¹³⁹ This paper expounds on his hydrate theory and scathing

¹¹³⁶ Ibid, pp. 210-216.

¹¹³⁴ Ibid.

¹¹³⁵ Shaw, 1891, pp. 185-223.

¹¹³⁷ Ibid, pp. 217-219.

¹¹³⁸ Ibid, 1891, pp. 220-222.

¹¹³⁹ Pickering, 1891, pp. 311-322.

criticism of ionists' solution theory. Pickering began by presenting evidence for the formation of hydrates in solutions. He mentioned Mendeleev's hydrate theory, his experiments on the change of the properties of various substances (electrolytes and non-electrolytes) with concentration, and finally, the isolation of hydrates by crystallization, for example, the hydrate of sulfuric acid with water molecules.

In the second part of his paper, he refuted the theories of van 't Hoff and Arrhenius. Based on the existence of hydrates in solutions, he rejected the analogy between the ideal gases and the dilute solutions of substances which was the fundamental principle on which van 't Hoff built his osmotic pressure. Due to the presence of the solvent, the hydrates could not have the same freedom as if they were genuinely gaseous and would therefore obey the imperfect laws of gases.¹¹⁴⁰ He used the same argument by referring to the freezing point depression of the solvent and described the tests which may be applied to ascertain whether, in producing this depression, the dissolved substance behaves as a perfect gas or not. He grouped these tests under three principal headings:¹¹⁴¹ All three concerned with the freezing point depression constant.

1. Is the molecular depression (i.e., that produced as calculated for one molecule dissolved in 100 molecules) constant, independent of the nature of the solvent?

2. Is it independent of the strength [concentration] of the solution, so long as this strength does not exceed the limits ('gas' strength) mentioned above? (Boyle's law)?

3. Is it independent of the nature of the dissolved substance? (Avogadro's law)?

In all cases, Pickering provided experimental evidence that the depression of the freezing point is not a constant (0.63 °C for aqueous solutions) as anticipated by the theory

¹¹⁴⁰ Ibid, p. 315. ¹¹⁴¹ Ibid

of the osmotic pressure. This property was dependent on the nature of the dissolved substance, the nature of the solvent, and the concentration. He found that the change of solvent for a given substance caused a considerable variation of the depression of the freezing point ranging from 100 to 35,600 percent compared to the value in water solutions (0.63 °C). Thus, the solvent has a very significant influence on the results obtained.¹¹⁴² By plotting the freezing points of sulfuric acid and the nitrate and chloride salts of calcium in water solutions with concentration, he observed an anomalous behavior of this property very far from the expected regular constancy. The dissolved alcohol has shown the same irregular behavior in water.¹¹⁴³ From his previous experimental data, Pickering was able to examine the effect of the nature of the dissolved substance on the solvent freezing point depression. Taking solutions of concentrations corresponding to their hypothetical gas states, the values obtained with sulfuric acid, calcium nitrate, chloride salts, and alcohol showed 30% or more variation for the freezing-point depression (0.63 °C). He concluded that these data denied the idea of absolute constancy of the freezing point and questioned the validity of the theory of osmotic pressure.¹¹⁴⁴

He finalized his criticism by stressing the usual argument spoken against the free dissociation of the electrolytes in solutions. "...how can we regard it probable that compounds of such stability and compounds formed with such a development of heat as sulfuric or hydrochloric acid should be thus entirely dissociated by water; still less that these, and all the most stable compounds which we know, should be thus demolished, while

¹¹⁴² Ibid.

¹¹⁴³lbid, pp. 316-317.

¹¹⁴⁴ In these experiments, Pickering presumably measured the constant of the freezing point depression of the solvent. This constant, which today is called *cryoscopic constant*, depends on the properties of the solvent, but not the solute. For example, this constant is 1.86 for water, 3.90 for acetic acid , 20.2 for cyclohexane.

all the less stable ones—such as hydrocyanic, sulfurous, boric acids, &c.—remain intact? How can we admit that the more stable a body is the more prone is to undergo dissociation? [...] Indeed, the theory of dissociation into ions is altogether unintelligible to the majority of chemists. It seems to be quite irreconcilable with our ideas of the relative stability of various bodies, and with the principle of the conservation of energy".¹¹⁴⁵ Pickering devoted a long discussion to this matter, striving to refute any possible argument that could justify the formation of ions from the dissociation.¹¹⁴⁶ In this paper, Pickering better than anyone else expressed the theory of hydrates and exposed the defects involved in the ionic dissociation theory.

Arrhenius sent a letter to the meeting read by James Walker in the discussion period.¹¹⁴⁷ Arrhenius replied to Pickering in some points raised in his paper. (a) He mentioned that several times had stressed that the ionic dissociation theory is applicable to dilute solutions only. Therefore, observations at higher concentrations do not have to do with the dissociation theory. (b) Depression of the freezing- point per gram molecule that decreases with increasing concentration is not a deduction from the law of osmotic pressure; Pickering's statement for the analogous case of highly compressed gases has been proved to be false by the research Regnault.¹¹⁴⁸ (c) As far as the change of the freezing point depression of sulfuric acid in dilute solutions is concerned, Arrhenius remarked that this observation did not contradict the dissociation theory because sulfuric acid is an electrolyte.¹¹⁴⁹ Using Pickering's experimental data of sulfuric acid in a concentration

¹¹⁴⁵ Ibid, p. 319.

¹¹⁴⁶ Ibid, pp. 318-320.

¹¹⁴⁷ Walker, 1891, pp. 323-325.

¹¹⁴⁸ Ibid, p. 323.

¹¹⁴⁹ Ibid, p. 324.

range from 0.002 to 1.00 normal solutions¹¹⁵⁰ and the corresponding degree of dissociation from conductivity measurements, Arrhenius calculated remarkably good results for the van 't Hoff's factor *i*, in particular at low concentrations.¹¹⁵¹ Arrhenius concluded in his letter, "The agreement, in fact, is so extremely good as to lead one to put more faith in the calculated than in the observed values".¹¹⁵² Ostwald noted in his autobiography, "Arrhenius had recalculated the results of a large number of Pickering's own data on the reduction of the freezing point of solutions of sulfuric acid using the equations of the dissociation theory and had found an astonishingly good agreement which showed that Pickering's experiments were a good deal better than his theories.."¹¹⁵³

In the subsequent formal discussion, FitzGerald gave the most extended account on electrolysis.¹¹⁵⁴ He criticized both Arrhenius's dissociation theory and van 't Hoff's osmotic pressure. His presentation was interesting as an example of some scientists' boldness and imaginative creation in proposing new theories. FitzGerald rejected Arrhenius's term dissociation and Armstrong's residual affinity as vague representations of the solution. He suggested the term *measure of ionization*, "whose meaning requires further investigation".¹¹⁵⁵ Undoubtedly, ionization did not mean dissociation. He objected that the ions, after dissociation, traveled the solution independently of one another. "As

¹¹⁵⁰ Normality is an expression of concentration for solutions. A normal solution contains a quantity of solute expressed in gram-equivalent weight per liter of solution.

¹¹⁵¹ Ibid, pp. 324-325.

¹¹⁵² Ibid, p. 325.

¹¹⁵³ Ostwald, 2017, p. 220.

¹¹⁵⁴ FitzGerald, 1891, pp. 326-330.

¹¹⁵⁵ Ibid, p. 327. After the meeting, FitzGerald explained to Lodge his motivations and his conception of ionization. "I am beginning to think that if we call the state of these electrolytes an" ionization "of the substance and in consideration of the prejudices of Armstrong & Co attitude this ionization to a continuation of the salt and the water and say that in this big molecule the ions can meander about and exchange by the breaking up of this bloated water-salt molecule the Germans & English will all be satisfied" (quoted by Petit, 2013, p. 250).

long as there is any link connecting the elements of molecules together which essentially prevented one of them getting away without the others following, I would not agree to say that the elements were dissociated. Hence, I object to the term dissociation as applied to the ions in an electrolyte. All agree that one cannot escape or diffuse without the other following; it may be due to electrical forces between them, it may be for other causes, but in either case, I would refuse to call them dissociated".

Furthermore, FitzGerald was very critical regarding the energy required for the dissociation. He rejected explanations, such as the formation of an ionic state, something like an allotropic form of the atoms, characterized by different internal energy from the energy of the atoms in the neutral molecule. Also, he rejected the explanation that the cause for dissociation is the affinity of the atoms to electricity.¹¹⁵⁶

His opposition to the term dissociation and the independent movement of the dissociated ions manifested in how he understood the Clausius-Williamson hypothesis. He imagined that the ions were paired in their own chinks, moving independently between the solvent molecules. The chinks were small compared with the variation of force between the ions. This condition afforded sufficient independence for any theory of electrolysis. In addition, whenever two molecules were found within the same chink, there would be adequate independence to exchanging partner ions. Therefore, FitzGerald concluded there was no need to invoke any process of dissociation into free ions. The process mediated by the formation of chinks was what FitzGerald called ionization.

Regarding the osmotic pressure theory of van 't Hoff, FitzGerald criticized the Swede's suggestion that the kinetic pressure of solute particles, unable to penetrate the

¹¹⁵⁶ Ibid, p. 329.

semipermeable membrane, produced the osmotic pressure of dilute solutions. He thought that the solvent had a role to play in the osmotic pressure, and he suggested that part of the osmotic pressure could have come from the difference of pressure in the solvent near and far from the salt. He believed that the water molecules could press very hard even on a membrane permeable to them.¹¹⁵⁷

Armstrong, who was undoubtedly the leading chemist in opposition to the ionists' theory, did not develop his position significantly at the Leeds meeting. In the published formal discussion, he concentrated on just a few of the difficulties of the theory that he had previously set out.¹¹⁵⁸ In his intervention, the London chemist complained that the discussions were only about physical considerations. He then chose to advance a chemical counter-argument to the theory of ionic dissociation. He put forth the following reaction of neutralization,

 $KOH + HCl \rightarrow KCl + HOH$

He commented that the "dissociationists" would think that the reaction between hydrogen chloride and potassium hydroxide would produce only one new compound, namely water. Consequently, the main action that would have occurred upon mixing the base and the acid could be a reaction between ions. In this case, the reaction of neutralization writes

 $H + Cl + K + OH \rightarrow K + Cl + H_2O$

For Armstrong, this leads to considering hydrogen chloride and water as very different from each other. The first would dissociate almost entirely, while the second would be very stable. However, chemists have long perceived these two compounds as chemically analogous; "the facts of chemistry appeared to afford the strongest evidence that hydrogen

¹¹⁵⁷ Ibid, p. 328.

¹¹⁵⁸ Armstrong, 1891, pp. 325-326.

chloride and oxide were in all ways comparable compounds. Furthermore, the behavior of the two compounds at high temperatures afforded no grounds for such a belief in the instability of the one and the stability of the other". Armstrong defined them as hydrides of two elements, chlorine, and oxygen, with similar chemical properties. Therefore, there was a contradiction between the ionist's ideas and classical chemistry, which he defended.

Lodge intervening in the discussion tried to reconcile the ionists and the British opponents.¹¹⁵⁹ However, he was one more British scientist who denied the ionists' theory of solution. Lodge considered the dissociation of the electrolytes as an abhorrent idea and questioned van 't Hoff's analogy between perfect gases and dilute solution. He found it like to commit the fallacy called by logicians "the illicit process of the major".¹¹⁶⁰ Lodge made an awkward remark while he was trying to reconcile the two theories. "Moreover, it is not quite apparent why (in Mr. Pickering's paper, for instance) the antithesis of the hydrate theory is supposed to be the dissociation theory. Free molecules in solution, rather than free atoms,¹¹⁶¹ would seem to be the opposite to the formation of definite chemical hydrates".¹¹⁶²

Ostwald and van 't Hoff participated in the discussion after the British have presented their views. They had anticipated that they would be the British attack target and had prepared their intervention to defend their solution theory. Ostwald first read a paper *On the electrical behavior of semi-permeable membranes*.¹¹⁶³ Then van 't Hoff defended

¹¹⁶¹ British chemists and physicists in the meeting at Leeds, and elsewhere avoided using the word ion invented by their British fellow Faraday.

¹¹⁵⁹ Lodge, 1891, pp. 330-331.

¹¹⁶⁰ Ibid, p. 331.

¹¹⁶² Lodge, 1891, p. 331.

¹¹⁶³ Ostwald, 1891, pp. 331-335
the theory of osmotic pressure against the criticisms of Fitzgerald and Pickering.¹¹⁶⁴ Ostwald discussed in his paper a series of experiments that, in his opinion, evidenced the existence of ions and the role they played in the osmotic pressure through a semipermeable membrane. In the subsequent discussion, Lodge asked him whether these experiments were real or thought experiments. Ostwald advised Lodge to read a paper published by Nernst in 1889, in which Nernst described these experiments. To convince Lodge, Ostwald described another experiment that, according to him, demonstrated the existence of free hydrogen ions. Ostwald described this experiment first in a letter sent to Ramsay in January 1889 accompanied by an illustration of the experimental setup. In the same year, he published it with Nernst in the *Zeitschrift*.¹¹⁶⁵

The British scientists were hesitant to accept the *crucial experiment* as Ostwald used to call it and questioned its effectiveness. Ostwald's paper did not convince Lodge, nor was FitzGerald. Others contended that this experiment revealed nothing new but the establishment of the transport of electricity through an electrolyte accompanied by electrolysis,¹¹⁶⁶ which is perfectly in agreement with all known relevant experiments. They argued that Faraday had previously observed the electrolysis produced by the discharge of a capacitor. Even its originators quickly forgot the crucial experiment. Ostwald did not

¹¹⁶⁴ Van 't Hoff, 1891, pp. 335-338.

¹¹⁶⁵ Briefly, the experiment is conducted as follows: A large glass jar containing dilute aqueous sulfuric acid is covered on the outside with tinfoil. The neck of the jar is connected with a siphon with a vessel also containing dilute sulfuric acid. In the vessel, a capillary electrode, i.e., a short Lippmann electrometer, is immersed. The electrode is grounded. Suppose the outer covering of the jar is connected with a source of positive electricity. In that case, the negative SO₄ ions are attracted a form a layer in the interior of the jar. In contrast, the positive hydrogen ions are repelled and directed toward the electrode of the vessel. The appearance of hydrogen bubbles around the capillary tube indicates the discharge of hydrogen ions on the capillary electrode leaving behind molecular hydrogen gas (Ostwald, and Nernst, 1889, pp. 121; Root-Bernstein, 1980, p. 519). Root-Bernstein provides a sketch of the apparatus, which is absent in Ostwald and Nernst's paper.

¹¹⁶⁶ Root-Bernstein, 1980, p. 523.

mention it in his autobiography, while he reproduced the paper in his huge history of electrochemistry with no further comment.¹¹⁶⁷ Partington, in his history of chemistry, simply mentioned that Ostwald and Nernst described in 1889 an experiment to demonstrate the existence of free ions by their motion in an electrostatic field.¹¹⁶⁸ A flaw in the experiment made it either a mistake, or newer, more effective results obtained by the ionists made the crucial experiment unnecessary to convince scientists of the validity of the dissociation-osmotic theory.¹¹⁶⁹

In the sequel of his intervention, Ostwald responded to questions and remarks made by FitzGerald, Pickering, and Armstrong during their discussion period. In particular, FitzGerald's problematic was the usual question for the energy source required to separate, e.g., Cl and H by dissolving HCl in water. Pickering's remark that the dissociation of electrolytes into frees ions violates the first law of thermodynamics; Armstrong's question is why water does not split into ions, while hydrogen chloride, a body similar to water, does.¹¹⁷⁰ Ostwald did not hesitate to argue in a stern tone with Armstrong's remark that one should distinguish between chemical facts and chemical feelings.¹¹⁷¹ The facts, Ostwald replied, supported his colleagues' theory, and the feelings would change quite easily. "Chemists will speak in a year or two as quietly of free ions as they now speak of the uncombined mixture of hydrochloric acid and ammonia in the gaseous state [of ammonium chloride] ".¹¹⁷²

¹¹⁶⁷ Ostwald, 1896, p.1124-1130.

¹¹⁶⁸ Partington, 1972, p. 634.

¹¹⁶⁹ Root-Bernstein, 1980, pp, 523-524.

¹¹⁷⁰ Ostwald, 1891, pp. 333-335.

¹¹⁷¹ Here, Ostwald hinted Armstrong assertion that the dissociation theory was against the feelings of chemists (Ostwald, 1891, p. 334).

¹¹⁷² Ibid, p. 334.

Van 't Hoff had a relatively short contribution to the formal discussion. He commented on FitzGerald's objection as to the importance of the solvent in exerting significant pressure through a semipermeable membrane and on Pickering's insistence to link the constancy of the depression of the freezing point with the theory of the osmotic pressure. van 't Hoff pointed out that he approached the subject of the osmotic pressure, not from an attitude to popularize it but to prove the laws that governed the phenomenon using thermodynamics and kinetics. He stressed that he had simplified the problem reckoning the analogy between the ideal gases and dilute solutions. From a kinetic point of view, the law of Avogadro and the law of the osmotic pressure stood on the same basis. But, if someone wants to do a rigorous analysis (towards the more concentrated solutions); he has to resort to the last kinetic grounds. "He must take everything into account movement of the molecules of the two substances mixed, action on themselves and each other using the very complicated formula recently developed by van der Waals".¹¹⁷³

Van 't Hoff invoked experimental findings and Raoult's suggestion to refute Pickering's insistence that the invariability of the freezing point depression constant was derived from the theory of the osmotic pressure. "Mr. Pickering commits a fundamental error in supposing that the osmotic pressure theory arrives at 0.63 as the number with which we had to multiply the solvent's molecular weight in order to get the so-called constant of depression. Such a conclusion was never drawn from the theory in question; it was the formula $0.02T^2/W$ (*W* is the molecular latent heat) that was deduced. The value 0.63 was an empirical one introduced by Raoult. This difference has urged Professor Eijkman¹¹⁷⁴ to

¹¹⁷³ Van 't Hoff, 1891, p. 336.

¹¹⁷⁴ Christiaan Eijkman (1858-1930) was a Dutch physician and professor of physiology whose demonstration that beriberi disease is caused by poor diet led to the discovery of the vitamin thiamine

a very extensive experimental research, the conclusion of which was so evident that in the July number of the *Annales de Chimie et de Physique*, Raoult openly accepts the value $0.02T^2/W''$. Van 't Hoff continues, "No one now defends the value 0.63, and a good deal of the objection which Mr. Pickering directs against it has no bearing on the osmotic pressure theory itself".¹¹⁷⁵

It has been suggested¹¹⁷⁶ that the real contact between Ostwald and van 't Hoff and the British adversaries was made during the informal discussion outside the meeting rooms, during the party organized by Arthur Smithells (1860-1939) professor of chemistry at the University of Leeds. At the Fountains Abbey situated in the park of Studley Royal, the gests of the party felt free to discuss the various issues of their disagreement and break down some cultural and disciplinary barriers. Smithells' detailed recollections gave a vivid picture of the atmosphere held at the party, and the intense discussions alternated with hilarity.¹¹⁷⁷ Nonetheless, neither the formal debate described in the BAAS report nor the informal contact between the participants at the party could reconcile the opposite views. It appears that neither side triumphed at the Leeds meeting on theories of solution.

The formal meeting concluded with John Gladstone's remark that there had been a rapprochement and increased mutual understanding between the two sides.¹¹⁷⁸ Ostwald was satisfied that he was able to make his voice heard in Britain. He remarked, "I do not think I am wronging our hosts in supposing that the invitation had been given first of all with the friendly intention of persuading us that we were in error and of sending us back

⁽vitamin B₁). Together with Sir Frederick Hopkins, he received the Nobel Prize for Physiology or Medicine in 1929 for the discovery of vitamins.

¹¹⁷⁵ Van 't Hoff, 1891, p. 336.

¹¹⁷⁶ Dolby, 1976, pp. 333-334; Petit, 2013, pp. 248-249.

¹¹⁷⁷ ibid

¹¹⁷⁸ BAAS report, 1891, p. 338.

home again after a good lesson. And during the first few days, our adversaries alone held the floor so that one might have thought up to a certain point that we were already scientifically dead. But when, after long and lively personal discussions, the representatives of the modern ideas finally had a chance to speak, even at the public sessions, the appearance of things was not slow in changing, and we were able to separate from our hosts amiably and not without triumph".¹¹⁷⁹

Nonetheless, the British opposition continued through the 1890s, arguing against the new theories, particularly Arrhenius's electrolyte dissociation theory. The British scientists were not convinced of the two major principles of the dissociation/osmotic pressure theory. They insisted on two points: the absence of active participation of the solvent in both the dissociation of electrolytes and the pressure exerted on a semipermeable membrane and the analogy between the gaseous state and the dilute solution. On the other side, the ionists could not convincingly answer the argument that there is insufficient energy in the solution to create dissociation. The attraction between ions is too great to overcome. The crucial experiment proposed by Ostwald failed to shed light on the existence of ions. Nevertheless, the ionists' theory was at its beginning and had more to know about the physical chemistry of solutions and more to gain in the following years.

¹¹⁷⁹ Quoted by Dolby, 1976, p.337.

Chapter 13. The development of chemical thermodynamics in America

It is well-known that the American scientists who studied abroad and returned to their country afterward have transferred the thermodynamics to America. However, to understand how thermodynamics was transferred from Europe to America and its subsequent development during the first two to three decades of the twentieth century, one must examine several aspects of this process. What were the reasons for American chemists' migration to European laboratories (mainly to Germany and less to Netherlands and Sweden) during the two decades of 1890 and 1900? Why had most American students and chemists preferred to undergo training in physical chemistry rather than organic chemistry or inorganic and analytical chemistry that flourished in Germany at the same time? How did chemical thermodynamics develop conceptually and practically in America? What were the research interests of the first American physical chemists?? This question seems equally important because it signifies the new science content that reached the American continent. What was really transferred in America? The ionists' solution theory formulated in the decade of 1880, or the new discipline propagated by Ostwald and the other two ionists? Was it chemical thermodynamics, or was it physical chemistry? ¹¹⁸⁰ Finally, what resistance did physical chemistry feel from other branches of chemistry, and how had it been established and flourished in academia and industry?

Section 1. The struggle for recognition

¹¹⁸⁰ The literature on the subject is scarce. John Servos has undertaken the most important study in his book Physical Chemistry, from Ostwald to Pauling (Servos 1990), with a few more scattered, brief references.

I have already discussed the contribution of each ionist to the transfer of thermodynamics from physics to chemistry. The next step of the ionists was much more difficult. First, they had to convince chemists about the interpretative potential of their theory to various chemical problems and, second, to establish their work as a new discipline in chemistry. Ostwald contributed the most to this task. He began this course as soon as he became a professor at the institute of physical chemistry at the University of Leipzig in 1887. There, he founded his laboratory of physical chemistry. Ostwald had to struggle to overcome many obstacles. The first obstacle was the tradition and the power of organic chemistry, which had dominated German universities since 1830. Influential organic chemists, such as Liebig in Giessen, Wöhler in Göttingen, Bunsen in Heidelberg, and Kolbe in Leipzig, had established famous laboratories in which students from all over Europe and America gathered either for doctoral studies or for postgraduate training. Organic chemists would not look favorably at a competitor science. The strong opposition to Arrhenius' theory of ionic dissociation by the British organic chemists originated from this competition.¹¹⁸¹ Ostwald also had to find sufficient funding allocations for his laboratory's operation, acquire appropriate equipment, and staff it with competent collaborators. Most importantly, he had to find an innovative research program and an attractive title for the new science to present it to the scientific community with claims as a separate branch of chemistry. He considered van 't Hoff's thermodynamics for solutions and Arrhenius' theory of electrolytic dissociation as the basis for the new science. This research program was essentially the content of the chemical thermodynamics. Nevertheless, Ostwald gave the new science the name physical chemistry to denote that the new discipline sprang from the

¹¹⁸¹ See chapter 9 of this dissertation.

unification of physics and chemistry. With the theory of solution of van 't Hoff and Arrhenius in his arsenal, Ostwald launched an international campaign to inform the scientific community about the potential of the new science. Having as a crossing-point his physical chemistry laboratory in Leipzig, Ostwald established an international network of acquaintances with influential chemists and physicists of the time. Most of these eminent scientists willingly participated in the journal's editorial board that Ostwald established together with van 't Hoff in 1887. The journal had the characteristic title Zeitschrift fur Physikalische Chemie reflecting Ostwald's intentions to use it as a medium to disseminate the work conducted in the field of physical chemistry. The journal was international and accepted research and review articles from all over the world. However, the journal's language was German despite the reservations expressed by scientists from other countries. The journal proved to be an effective channel for disseminating the new science with many articles outside Germany. At the same time, Ostwald wrote and published books, review articles, laboratory manuals, translations of scientific papers, and even introductory textbooks for other sciences (e.g., physiology, geology, agriculture, medicine) to show that the new science could provide answers to more specific issues. He organized seminars in Leipzig and participated in international conferences aiming at publicizing the new science. After seven years of work, he published in 1887 an epitome of chemistry in these days, the Lehrbuch der Allgemeinen Chemie, which went through many reprints. This book could be considered as the first textbook in chemical thermodynamics.

Ostwald's excellent reputation as an outstanding teacher and researcher, which had spread as far as the other side of the European continent, the fully equipped laboratory he set up in Leipzig, brought great distinction to him and his laboratory. His laboratory soon became an international research center for foreign students. From 1889 until 1906, 44 doctoral students and postdoctoral fellows from England, Canada, and the US, 38 from various American Universities, were trained in Ostwald's laboratory.¹¹⁸² American scientists became the best ambassadors of the new science in America and brought with them intact the research program of Leipzig upon returning to their country.

Besides the reputation of the German physical chemist, several other reasons motivated the American students to travel abroad and study physical chemistry at Ostwald's laboratory. First, graduate studies in America were not well organized, and very few graduate schools in physical sciences subsisted in American universities. Schools of organic and inorganic chemistry and, to a lesser extent, physics and mathematics overwhelmed the American Universities. None in physical chemistry. The high tuition fees, which a student had to pay for his studies in the American university, forced the Americans to travel abroad to get a degree in physical sciences. The total costs, including the travel expenses for studying in a German university, were less than that required in an American university. The third reason was subjective and concerned the personal preference for someone who wished to study a young science, whose future development promised a better professional career.

Section 2. What was the science that really transferred to America? Chemical thermodynamics or physical chemistry?

¹¹⁸² Dolby, 1977, pp. 291-292; Servos, 1990, pp. 54-55.

Upon returning to their country, the American scientists and those appointed in academic positions and set up physical chemistry laboratories conducted research programs originated basically from elements involved in the ionists' theories. Issues of chemical affinity and chemical equilibrium (measurements of free energies and heats of chemical reactions), measurements of atomic and molecular weights by physicochemical methods, studies of electrolytic solutions, osmotic phenomena were some of their research projects. Perhaps, the only exception was Wilder Bancroft at Cornel University, who set up a whole research program based on Gibbs' phase rule. Later, he extended his research program to include colloidal solutions.

Historians have a consensus that the knowledge transferred to America by Ostwald's students was almost unchanged the ionists' physical chemistry. Dolby, discussing the transmission of the new science to America in the late nineteenth century, consents to the idea that the ionists' body of knowledge was transferred whole, as it were. Still, he specifies the new specialty as physical chemistry in accord with the name given by Ostwald in his attempt to advance this new science to the rank of a discipline.¹¹⁸³ I argue that what was transferred in America was not the new discipline of physical chemistry but chemical thermodynamics. Physical chemistry had a multifaceted content, which was formulated in subsequent years. Chemical thermodynamics was the ionists' theory of solutions developed in the 1880s with elements derived from the electrochemistry of Nernst.

In my opinion, it is the content that characterizes the identity of a branch of science and not solely its name. Although the content has changed over time, the gist of the new

¹¹⁸³ Dolby, 1977, p. 298.

science in the 1890s consisted of theories and experiments formulated and designed basically on the old scientific questions of chemical affinity and equilibrium, which, as suggested earlier, were answered when chemists practiced thermodynamics. Therefore, the new science that arrived in America at the end of the nineteenth century was chemical thermodynamics, even though Ostwald endeavored to present it as physical chemistry. In other words, Ostwald's physical chemistry was what chemists called later chemical thermodynamics.

Physical chemistry became a separate discipline much later and characterized by a change in its content. Apart from chemical thermodynamics, which was its theoretical basis, it began to incorporate systematically other established specialties from chemistry and physics. Experimental and theoretical branches of physics and chemistry, such as chemical kinetics, photochemistry, electrochemistry, thermochemistry, radiochemistry, statistical thermodynamics, spectroscopy (e.g., optical spectroscopy, nuclear magnetic resonance spectroscopy, electron paramagnetic resonance spectroscopy, mass spectroscopy, laser spectroscopy, microscopy), crystallography, surface chemistry, physics and chemistry of colloids and polymers, and several other areas of specialization that enriched the physical chemistry textbooks, education, and research. With time, some of these specialties became independent and constituted separate disciplines in the European and American educational systems. Individual research laboratories and research programs were established in the universities' physical chemistry and physics departments, and new professions appeared in academia. Physical chemistry emerged later as a discipline, whereas chemical thermodynamics was its generative cause. Physical chemistry has always been open to new theories and methods from chemistry and physics. It has never been a coherent discipline but a disunified corpus of theoretical knowledge and various practices and theories. As taught and practiced today, physical chemistry appears to have fulfilled Ostwald's dream for the chemistry of the future. In the editorial preface of the first issue of the *Zeitschrift* in February 1887, Ostwald defined physical chemistry as Emil Du Bois-Reymond had defined it five years earlier: He began with this phrase: "The undersigned does not know how to explain the purpose and content of the present new journal better than by speaking from the speech with which Mr. E. du Bois-Reymond in the Leibnitz meeting of June 29, 1882, welcomed Mr. H. Landolt as a new member of the Royal Prussian Academy"; and then continues with the following lines of Du Bois-Reymond's speech.

"In contrast to modern chemistry, physical chemistry can be called the chemistry of the future. [...] And yet what Kant said of the chemistry of his time still applies to this modern chemistry: It is a science, but not a science; not at least, in the sense in which there is only science at all, namely, in the sense of the knowledge of nature which has developed into mathematical mechanics. [...] When will this goal be achieved, who can say? Perhaps that Newton is already practicing somewhere, on school benches when he is young. Forces: perhaps even after a hundred years our successors are still just as perplexed about the transformation of chemistry into mechanics, like us. Certainly, however, the means to initiate this transformation is, in addition to the further development of structural chemistry, the zealous cultivation of the field of physical chemistry, in a somewhat broader sense. Mathematical, physical, and optical crystallography; the doctrine of refraction and dispersion, natural and magnetic circular polarization of light; Spectroscopic analysis; Thermochemistry with the mechanical theory of gases and dissociation theory; electrochemistry, since electrochemical dualism does exist; finally, the science of diffusion, to which belong absorption and solution. We must combine all of this and many others to form a complete picture of molecular processes This must all be accomplished before we can say that what the alchemists called "the great work" is done".¹¹⁸⁴

Since 1882, when Du Bois-Reymond gave his speech, the ionists of the first and subsequent generations in Europe and America had done a great deal to establish many of these fields of knowledge. The first seeds of the new discipline were planted in the first issue of *Zeitschrift* and Ostwald's editorial. Arrhenius and van 't Hoff accomplished the first stage of the "great work" by publishing in the first issue of the journal the final versions of their theories of solutions.

But why did American scientists regard the acquired knowledge from Europe as physical chemistry and called themselves physical chemists? American scientists shared Ostwald's ambitions and transferred chemical thermodynamics to America using the label physical chemistry according to Ostwald's strategy. They acted as ambassadors of a new science upon their arrival to America. There was another, a perhaps more significant reason to do so. They needed the new discipline as a scientific background to repel strong opposition and establish themselves in American higher education institutions.¹¹⁸⁵ Presenting chemical thermodynamics as the new specialty of physical chemistry was a suitable choice. They believed that physical chemistry was a dynamic science with great

¹¹⁸⁴ Oswald, 1887b, pp. 1-2.

¹¹⁸⁵ As in Europe, Organic chemistry prevailed in American science. Recall that during 1830-1860, the first stream of American students and chemists, who sought further education abroad, traveled to Germany and studied organic chemistry in the laboratories of Wöhler, Liebig, Bunsen, and others (chapter 9, section 1).

potential, competitive with other chemistry specialties, such as organic chemistry and inorganic chemistry. American chemists found ionists' theory easy to understand and functional for their research. Moreover, novel experimental techniques invented mostly by Ostwald and Nernst, friendly experimental methodologies, and highly accurate devices that equipped the physical chemistry laboratories were all suitable to research concerning analytical chemistry. Physical chemists hoped that a new science would satisfy the needs of the growing American industry and find its share in funding from government, industry, and private foundations.

The investigation of the overwhelming majority of scientists, who obtained professorial chairs and establish laboratories, was inspired, in the beginning, by the research programs of the laboratories where they had worked before. However, the American scientists did not use the new science from Europe as a commodity or as a passive transmission of knowledge. Chemical thermodynamics was not an issue of a simple transfer process or diffusion in America but as one of the instances in which scientific knowledge was the subject of appropriation. American scientists arriving in their country from Ostwald's laboratory and elsewhere appropriated¹¹⁸⁶ the knowledge obtained there in the sense that ideas and techniques were advanced in unexpected and sometimes startling ways. The most talented soon became independent and researched other or related subjects of the specialty. These American physical chemists challenged the underlying assumptions of ionists' theory. They modified and extended the theory to familiar topics, seeking new answers to old problems. The less talented continued to perform experiments, gathering

¹¹⁸⁶ The concept of appropriation of scientific ideas, acquired from the center and transferred to the periphery, is more general and signifies the transformation of the acquired knowledge according to the periphery's social, cultural, and educational context (Gavroglu et al. 2008, pp. 159-161).

data and pursuing to consolidate existing theories.¹¹⁸⁷ Careful examination of the research work of prominent American physical chemists, such as Arthur Noyes, Theodore Richards, Irving Langmuir (1881-1957), Joseph Trevor, and Gilbert Lewis, to name a few, shows that they were not passive recipients of the ionists' chemical thermodynamics. Instead, they used it as the beginning for advancing new knowledge, the content of which was contingent upon each individual's research interests and expertise. The theory of solutions of the ionists and Nernst (electrolytic dissociation, electrical conductivity, osmotic pressure, and electrochemical processes), chemical affinity (measurements of the free energies of formations), and chemical equilibrium (measurements of the free energies of advanciant advanced physicochemical methods of high precision were, among others, the starting points of their investigations. One deviation from the ionists' research program was the work of Wilder Bancroft at Cornell. He employed the phase rule invented by Gibbs and the properties of colloidal solutions as the basis of his research.¹¹⁸⁸

The fact that most of the research work of the first generation of American physical chemists was rooted in the ionists' theory of solutions is additional evidence that the science transferred to America was chemical thermodynamics. American scientists attained academic positions in American universities and other institutions (much fewer in the industrial research laboratories). At these positions, and even though they were confronted with tremendous difficulties, they managed to establish research laboratories

¹¹⁸⁷ This type of research accumulating data and other facts in the context of a well established theory without questioning or chalenging its fundamental assumptions constitutes the so-called normal science according to Thomas Kuhn.

Kuhn explained normal science as slowly accumulating detail in accord with established broad theory, without questioning or challenging the underlying assumptions of that theory. ¹¹⁸⁸ Servos, 1982; 1990, pp. 166-201.

similar to Ostwald's, or even whole departments of physical chemistry, contributing thus decisively to the dissemination of the new discipline, to the training of new generations of physical chemists, and the advancement of new knowledge in chemical thermodynamics. In brief, they managed to create a research tradition in physical chemistry. Perhaps the most recognized personality among the chemists of the time was Gilbert Newton Lewis.

Section 3. Gilbert Newton Lewis: A talented American physical chemist

Lewis was born in Weymouth, Massachusetts, in 1875.¹¹⁸⁹ Lewis was home-schooled entirely through elementary school and attended high school only briefly. He received a broad education that included Latin, Greek, French, German, history, and algebra. However, he did not have the chance to socialize in a schooling environment. The lack of close relations with young people of his age influenced his character as an adult. Lewis began his undergraduate education at the University of Nebraska, but in 1892 transferred to Harvard when his family returned to the Boston area. He graduated from Harvard with a bachelor's degree in chemistry in 1895. He excelled in mathematics, physics, and both experimental and theoretical chemistry. After graduation, he taught for a year at Phillips Andover Academy. He then returned to Harvard in 1896 as a Ph.D. candidate under the instructions of the physical chemist Theodore Richards, a 1916 Nobel laureate in chemistry, who was only seven years older than Lewis. Unlike his mentor, Lewis had an excellent grasp of mathematics, physics, and thermodynamics. Lewis had read Gibbs' and Duhem's papers and was familiar with the work of the European physicists on thermodynamics. He completed his graduate studies in 1899, defending his thesis entitled

¹¹⁸⁹ On Lewis' life, and career, see Lachman 1955; Hilderbrand, 1958; Servos, 1984; Branch, 1984; Lewis, 1998' Coffey, 2008; Calvin, 2010;

A general equation for free energy and physicochemical equilibrium, and its application.¹¹⁹⁰ Lewis's dissertation consists of a careful experimental study of the properties of zinc and cadmium amalgams as electrodes and an entirely theoretical study of an equation he had derived to determine free energies. Lewis published two papers from his thesis with Richards as a joint author.

After remaining one year at Harvard as an instructor, in late 1902, he went abroad on a traveling fellowship. He spent one semester at Leipzig with Ostwald and another at Gottingen with Nernst. Nernst and Lewis developed a lifelong enmity that seemingly affected his nomination for the Nobel Prize. He returned to Harvard as an instructor of thermodynamics and electrochemistry for three years. After the job at Harvard, Lewis accepted the position of Superintendent of Weights and Measures in the Philippine Islands and Chemist at the Bureau of Science in Manila.¹¹⁹¹ He returned to Cambridge, Massachusetts, when the Massachusetts Institute of Technology (MIT) appointed him to a faculty position. There, he had a chance to join a group of outstanding physical chemists under the direction of Arthur Amos Noyes. He remained at MIT from 1905 to 1912, during which time he started his exceptional contribution to chemical thermodynamics. The results of his research appeared in over thirty papers that laid the foundation for the future development of physical chemistry. In 1912, Lewis was appointed Chairman of the

¹¹⁹⁰ In his Biographical Memorial of Lewis (1958, p. 210), Joel Hildebrand suggests the title "Some electrochemical and thermochemical relations of zinc and cadmium amalgam". Patrick Coffey, on the other hand, in his book "Cathedrals of Science" (2008, p. 45), gives another title, "The development and application of a general equation for free energy and physicochemical equilibrium". The first title coincides with Lewis' and Richards' first paper published in 1898, whereas the second title is the same as the second paper published in 1899, Lewis being the sole author. Both papers derived from Lewis' dissertation, whose title, according to the Library of Harvard and the ProQuest database for published dissertations, is *A general equation for free energy and physico-chemical equilibrium* (Lewis, 1899a).

¹¹⁹¹ It is not clear why Lewis left Harvard and "immigrated" to Manila. In later life, he boasted that he was fired (Branch, 1984, p. 18).

Department of Chemistry and Dean of the College of Chemistry at the University of California, Berkeley. He held these positions until he was 65. He continued as professor and professor emeritus until he died while working in his laboratory on March 23, 1946. Lewis' last graduate student, Michael Kasha (1920-2013), found his lifeless body under a laboratory workbench. There is confusion regarding the cause of his death. One possibility was that Lewis was poisoned. He had been working on an experiment with liquid hydrogen cyanide, and deadly fumes from a broken line had leaked into the laboratory. The coroner, however, ruled that the cause of death was coronary artery disease because of a lack of any signs of cyanosis. Some others believe that it may have been a suicide,¹¹⁹²

Section 4. Lewis' chemical thermodynamics

The ionists and Nernst's theories suffered from two serious shortcomings: first, they did not apply to concentrated solutions, and secondly, they failed to describe the solution properties of strong electrolytes. At concentrations greater than 0.001 M, or 0.01 M (M stands for molarity, a measure of concentration), severe deviations were observed between theoretical and experimental results depending on the electrolyte's nature. Salts such as potassium chloride (KCl) or sodium chloride (NaCl), strong bases such as sodium hydroxide (NaOH), and strong acids such as hydrochloric acid (HCl) showed a high degree of dissociation even at high concentrations. Furthermore, these strong electrolytes did not obey Ostwald's dilution law. The ionists were familiar with these anomalies, but they

¹¹⁹² Coffey, 2008: 310-315.

preferred to cover them with silence. Laidler contended that Arrhenius himself refused to discuss any proposed modification of his theory.¹¹⁹³

Arthur Noyes was one of the first American physical chemists who stressed the inadequacy of Arrhenius' dissociation theory to explain the behavior of strong electrolytes. Noyes had received his Ph.D. working at the Ostwald's physical chemistry laboratory. When he returned to his native country, he continued his work and founded a physical chemistry laboratory at MIT.¹¹⁹⁴ Initially, the prestige of organic chemistry attracted Lewis, who devoted two years of his research work to this field. Finally, he interrupted his links with organic chemistry and adhered to the ionists' physical chemistry. The significance of his role in the institutionalization of physical chemistry in the United States was great, as he became the teacher of a new generation of American physical chemists. Noves envisaged a bold hypothesis: Wouldn't strong electrolytes be fully dissociated, even at high concentrations? This idea involved imagining a difference in the strength that binds strong electrolyte molecules from the so-called weak electrolytes. For Noyes, weak electrolytes are bonded by chemical forces, while electrical forces bond strong electrolytes. This conceptualization of bonding reminds the present considerations of ionic and covalent bonding of the strong and weak electrolytes, respectively.

Gilbert Newton Lewis was the leading figure among the American physical chemist who tackled these undoubtedly difficult problems. Lewis' investigations on the behavior of the electrolytes in concentrated solutions and that of strong electrolytes amount to a good

¹¹⁹³ Laidler, 1993, p. 216. Arrhenius, however, admitted that his theory was not suitable for concentrated solutions. Recall that Arrhenius mentioned in his letter sent to the convention held at Leeds that the ionic dissociation theory was applicable to dilute solutions only (chapter 12, section 4 of thisdissertation). He found himself lucky because he started by chance his experiments in his dissertation with dilute solutions. ¹¹⁹⁴ Servos 1990), p.58-59, and p.110-114.

example of how the American physical chemists appropriated the ionists' chemical thermodynamics.¹¹⁹⁵

Lewis knew about these problems. Furthermore, he was aware that the theory behind thermodynamics had followed two discreet paths. The ionists inherited the first, and Gibbs, Helmholtz, and Duhem developed the second. He considered the first as unsystematic and often inexact, involving a large number of disconnected and approximate in character equations, whereas the second, although rigorous and exact, was rather suitable for mathematicians and physicists than for chemists.¹¹⁹⁶ Lewis, venturing into a new ground of thermodynamics, decided to adopt an intermediate route, trying to reconcile these two approaches. However, he was cautious to preserve the work of the ionists while adding to this theory the necessary rigor. Throughout his chemical thermodynamics, the methodology he followed was the development of exact equations and the unambiguous identification and separation of various approximations, filling the gap between the earlier accounts and his investigations devoted to real systems.

Lewis derived exact equations, i.e., equations suitable for tangible systems. He replaced the pressure and concentration of substances with the new concepts of fugacity and activity, respectively. These two innovative thermodynamic quantities embodied the non-ideal behavior of the chemical and physical systems. Fugacity for real gases, such as the vapor pressure, and activity for the concentrated solutions of electrolytes and non-

¹¹⁹⁵ Continuing the work of the ionists, several physical chemists in Europe have tackled the problem of strong electrolytes, as manifested in a review article published by Lewis in 1906. Lewis reviewed the work done in foreign lands, referenced theories and experiments performed in Europe to explain the observation that strong electrolytes deviate from Ostwald's dilution law. It is worthwhile to mention that Lewis reviewed conductivity studies of strong electrolytes in non-aqueous solutions with interesting findings (Lewis, 1906, pp. 903-905).

¹¹⁹⁶ Lewis, 1907, p. 259.

electrolytes. The new concepts of activity and activity coefficient both sprang from his endeavors to resolve the problematic behavior of strong electrolytes. A few aspects of Lewis' theories have been outlined briefly in the literature.¹¹⁹⁷ The following presentation of Lewis' work on electrolytes is more extensive and extracted from a careful reading of his original papers. Furthermore, Lewis's contribution to the measurement and classification of free energies of chemical reactions will be discussed as well.

Besides the purely scientific work, Lewis had the talent to invent and use words that conveyed as accurately as possible the meaning of the chemical and physical phenomenon he described. The terms *escaping tendency*, *fugacity*, *activity*, *activity coefficient*, and *ionic strength* are given as examples of his efforts to describe as accurately as possible the deviation of solutions from the ideal behavior. Another characteristic feature of Lewis' scientific style was the relatively long introductions accompanying most of his research papers with a historical purpose. The detailed assessments of previous processes and approaches related to his investigation facilitated the reader to acquire prior knowledge on the subject.

4.1 Escaping tendency, fugacity, activity, and activity coefficient

Lewis published two papers on the escaping tendency. He published the first paper when he was working as an instructor at the University of Harvard.¹¹⁹⁸ He sent the second paper for publication while he was visiting Ostwald's laboratory in Leipzig.¹¹⁹⁹ He discussed the

¹¹⁹⁷ For a brief account on the escaping tendency, fugacity, activity, and activity coefficient, see Gavroglu, and Simoes 2012, pp. 50-52; Servos, 1990, pp. 139-141. For strong electrolytes, see Pitzer 1984; Servos 1990, pp. 142-145; Laidler 1993, p. 218.

¹¹⁹⁸ Lewis, 1900.

¹¹⁹⁹ Lewis, 1901.

concept of escaping tendency in his first paper, while his second paper introduced the concept of fugacity. It seems that initially, Lewis did not define clearly the meaning of fugacity. It appeared that the term fugacity simply replaced the concept of escaping tendency.¹²⁰⁰ Nevertheless, these two terms had completely different meanings. The escaping tendency describes the property of a substance, whereas fugacity, denoted by f, is the measure of this property.¹²⁰¹ Lewis describes the escaping tendency as the tendency of the molecules of a substance in one phase to escape into some other phase brought in contact with the first under the influence of some external perturbation. Two general laws underline the escaping tendency: (1) if the escaping tendency of a given substance is the same in the two phases, then the substance will not pass from one phase to the other. In this case, the two phases are considered to be in equilibrium. (2) If the escaping tendency of a given substance is greater in one phase than in the other one, the substance will pass from the phase of higher escaping tendency into the phase of lower escaping tendency when the two phases are brought in contact. As a measure of the escaping tendency, Lewis made use of the fugacity. Lewis defined fugacity by the following conditions: (1) the fugacity of a molecular species in two phases is the same when these phases are in equilibrium regarding the distribution of that species. (2) The fugacity of gas approaches the gas pressure as a limiting value if the gas is indefinitely rarefied. In other words, the escaping tendency of a perfect gas is equal to its gas pressure.¹²⁰² It is evident from this

¹²⁰⁰ Patrick Coffey contended that Lewis changed the concept of the escaping tendency into fugacity between his first and second papers to avoid confusion with Richards's paper, which was published in between Lewis's two papers. In a letter sent to Lewis, Richards claimed a share to credit the idea of the escaping tendency. Richard had confused his concept of "outward tendency" or "driving tendency" or "reaction tendency" with Lewis' escaping tendency. For this story, see Coffey, 2006, pp. 382-390; 2008, pp. 48-51.

¹²⁰¹ Lewis and Randall, 1923a, p. 190.

¹²⁰² Lewis, 1901, p. 54.

definition that fugacity has, in general, the dimensions of pressure. Adopting this measure, Lewis rid of the limitations of the vapor pressure of a gas. Fugacity embodies the non-ideal behavior of gases. Replacement of the vapor pressure P by fugacity ensures the validity of the laws of thermodynamics. The new concept of fugacity (and activity) proved to be the refuge of chemical thermodynamics, averting the collapse of its entire structure. The ratio of fugacity to the vapor pressure, i.e., f/P, expresses now the degree of the non-ideality or the deviation from the ideal behavior of the gas system. For f/P = 1, the fugacity equals the vapor pressure of a perfect gas (another proof that fugacity has the pressure units). For the non-ideal behavior, the ratio f/P starts deviating from unity, and this deviation becomes larger, the larger the divergence of the vapor pressure from the ideal behavior. In 1907, Lewis published a critical paper for his version of chemical thermodynamics. He widened the significance of fugacity, introducing another thermodynamic quantity that embraces the non-ideal behavior of all chemical systems. He calls this quantity activity denoted by the letter ξ . The activity follows the same laws as fugacity: (1) when the activity of a substance is the same in two phases, that substance will not pass from one phase to the other. (2) When the activity of a substance is greater in one phase than in the second phase, the substance will pass from the first to the second phase when they are brought together. The following equation relates activity and fugacity:¹²⁰³

$$\xi = \frac{f}{RT} \tag{13.1}$$

Activity shares the same properties with fugacity with the exception that it has the dimensions of concentration.

¹²⁰³Lewis, 1907, p. 262-263.

On the other hand, the activity of the solute in a solution at constant temperature and pressure is proportional to its concentration, c, *i.e.*,¹²⁰⁴

$$\xi = \rho c \tag{13.2}$$

Arthur Noyes referred later to the proportionality constant ρ as the *activity coefficient*. ρ tends to unity ($\rho \rightarrow 1$) for dilute solutions (when $c\rightarrow 0$) and becomes smaller than unity ($\rho < 1$) for concentrated solutions. Therefore, ζ and ρ incorporate the non-ideal behavior of solutions. The replacement of concentration with activity renders the laws of solutions valid (exact) for dilute and concentrated solutions. Using activity, Lewis derived several important thermodynamic equations, which had the same form as the approximate equations of the ideal systems but turned out to be exact when expressed in terms of activity. One of these equations describes the equilibrium constant,¹²⁰⁵

$$K_{\xi} = \frac{\xi_k^{n_k} \xi_{k+1}^{n_{k+1}} \dots \xi_{r_r}^{n_r}}{\xi_1^{n_1} \xi_2^{n_2} \dots \xi_{k-1}^{n_{k-1}}}$$
(13.3)

For the following general chemical reaction scheme

$$n_1 A_1 + n_2 A_2 + \dots + n_{k-1} A_{k-1} \longrightarrow n_k A_k + n_{k+1} A_{k+1} + \dots + n_r A_r$$
(13.4)

Eq. (13.3) represents the true thermodynamic equilibrium constant of the reaction (13.4) at a constant temperature, which remains constant independently of the concentration of reactants and products. The familiar van 't Hoff's equation gives the effect of temperature on K_{ξ} , i.e.,

$$\frac{d\ln K_{\xi}}{dT} = \frac{Q}{RT^2} \tag{13.5}$$

Q is the heat of the reaction, and T is the absolute temperature. For practical reasons, Lewis proposed several methods for the determination of activities.

¹²⁰⁴ Ibid, p. 265.

¹²⁰⁵ Ibid, p. 285.

The concepts of fugacity and activity signify a measure expressing the non-ideality of physical systems. However, these concepts do not explain how and why the system deviates from the ideal behavior. These abstract constructs do not favor further investigation for obtaining an immediate analytical description of the inherent causes responsible for the non-ideal behavior of concentrated solutions and gases under high pressures and low temperatures.

4.2 The puzzling behavior of strong electrolytes

Around 1900, several European and American physical chemists were involved in intensive research to explain the strange behavior of strong electrolytes. The general idea derived from Arrhenius ionic dissociation theory was that strong electrolytes dissociate entirely in almost all concentrations and that the dilution law invented by Ostwald was not applicable for them. Furthermore, physical chemists could not explain the electrolytes' anomalous behavior at higher concentrations, only a few percent higher than the extreme dilution. Some qualitative arguments associated with the internal and external friction exerted on the mobility of the ions within the solution did not find any verification from experimental data. American physical chemists directed a large part of their investigation towards experiments of increasing accuracy to demonstrate in the first place that this anomaly was real and it was not due to severe experimental errors.

At that time, the leading figure in physical chemistry in America was Arthur Noyes. He established one of the most influential physical chemistry laboratories globally, following the philosophy of Ostwald's laboratory in Leipzig. Noyes was one of Ostwald's students and had received his doctoral degree in 1890 from him. The efforts of Noyes and his bright collaborators did not solve the problem of strong electrolytes. However, a number of their working hypotheses, mainly their experimental results, paved the way for the German physicists, Peter Debye (1884-1966) and Erich Hückel (1896-1980) to develop a theoretical explanation of the behavior of strong electrolytes in dilute solutions in 1923.

Among Noyes' young collaborators was Lewis, who participated actively in the restructuring and extension of the dissociation theory of Arrhenius. In 1909, he published an overview of Arrhenius' dissociation theory.¹²⁰⁶ Lewis admitted that the theory was incomplete and suggested ways to tackle the problem of strong electrolytes. It is true that Lewis did not offer a strict theoretical explanation of the anomalous behavior of strong electrolytes. Still, he shed light on several obscure aspects of the subject through his fine experimental work. Lewis perceptively pointed out that the critical problem associated with strong electrolytes was the degree of dissociation and its proper measure. This quantity is important because it represents the quantitative measure of the extent of dissociation. It is expected to offer a specific answer as to whether strong electrolytes dissociate completely, and if so, at which limiting concentration. The degree of dissociation, *a*, could be a major cause for the failure of Ostwald's dilution law. Lewis expressed Ostwald's dilution law in terms of the concentration, *c*, of the electrolyte in solution and the degree of dissociation, namely

$$K_{\rm d} = \frac{\alpha^2 c}{1 - \alpha} \tag{13.6}$$

 K_d is the dissociation equilibrium constant. K_d is reasonably consistent for weak electrolytes, even at higher concentrations, but varied enormously with concentration for strong electrolytes. Lewis derived Eq. (13.6) assuming that if *c* is the total salt

¹²⁰⁶ Lewis, 1909.

concentration of the salt CH₃COONa, α c is the concentration of the sodium cation Na+ and the acetate anion concentration CH₃COO⁻, and $(1 - \alpha)c$ is the concentration of the nondissociated salt. He used these concentrations in the mass action law applied to the dissociation process CH₃COONa \rightarrow Na⁺ + CH₃COO⁻. Based on the literature data and his carefully conducted experiments, Lewis concluded that electrical conductivity measurements, commonly used at the time for the determination of the degree of dissociation, were not reliable. Following Kohlrausch' suggestion, Lewis calculated the degree of dissociation α from the ratio of the molecular conductivity of the electrolyte Λ_m at concentration *m* and Λ_0 the molecular conductivity at infinite dilution, *i.e.*¹²⁰⁷

$$\alpha = \frac{\Lambda_m}{\Lambda_0} \tag{13.7}$$

He found that the degree of dissociation Λ_m/Λ_0 of all strong electrolytes was lower, roughly by a factor of two than the value calculated from the much more accurate technique of the depression of freezing point. Lewis attributed this inconsistency to the limitation of Kohlrausch's law of conductivity, according to which the mobility of the ions and their corresponding transference number¹²⁰⁸ are independent of the concentration.¹²⁰⁹ Therefore, the deviation of strong electrolytes from the dilution law could be attributed largely to this cause. Lewis estimated the relative degree of dissociation of forty-four univalent electrolytes at the same temperature and concentration (0.1 M). He chose the mobility and

¹²⁰⁷ Lewis, 1912. Lewis used the symbol Λ for molecular conductivity. The symbol m stands for molality, which is an expression of concentration. The concentration may be expressed in molality, m. (number of mol of a substance in 1000 grams of the solvent), or in molarity, M (number of mol of a substance in 1000 liters of solution). Lewis preferred molality because this expression of concentration does not change with temperature. In contrast, the concentration expressed in molarity changes with temperature (Lewis, 1913, p. 5.).

 ¹²⁰⁸ According to Hittorf's definition in 1853, the transference number denotes the fraction of the total current transferred by each ionic species in solution (see chapter 5, section 1 of the present dissertation).
 ¹²⁰⁹ Lewis, 1912, pp. 638-639; Lewis and Linhart, 1919.

transference number of the hydrogen ion as a standard to calculate the mobilities and the transference numbers of the other ions in the various salts. Consequently, from HCl, he calculated the mobility and the transference number of chlorine anion; from chlorine anion, he calculated the sodium cation in NaCl, and so on; for every two salts having a common ion, he calculated the two dissimilar ions.

From the tabulated data of the *corrected degree of dissociation*, as Lewis called the relative degree of dissociation,¹²¹⁰ and those obtained from the ratio Λ_m/Λ_0 , he concluded notable discrepancies between these two groups of data. For example, while the degree of dissociation ordinarily measured through the conductivity ratio showed wide variations among the univalent alkali halides, the corrected degree of dissociation showed that all salts dissociated in a solution of 0.1 m to practically the same extent. He observed significant differences for the higher valence electrolytes.¹²¹¹

In 1921, Lewis published a lengthy article,¹²¹² where he tried to explain the behavior of strong electrolytes through the concepts of activity and activity coefficient. For practical reasons, Lewis utilized the relative activity α , defined in terms of the activity ξ , namely, $\alpha = \xi/\xi^0$, where ξ^0 is the activity of the electrolyte in a chosen standard state.¹²¹³ This ratio indicates that α is a dimensionless quantity. With activities, the mass action law for a 1:1 electrolyte becomes¹²¹⁴

$$K_d = \frac{\alpha_+ \alpha_-}{\alpha_2} \tag{13.8}$$

¹²¹⁰ Lewis, 1912, p. 1631.

¹²¹¹ Ibid, p. 1640.

¹²¹² Lewis and Randall, 1921a.

¹²¹³ Lewis, 1913, p. 17.

¹²¹⁴ Lewis and Randall, 1921a, p. 1113.

Here, α_+ and α_- are the activities of the cation and the anion, respectively, and α_2 is the activity of the electrolyte as a whole. Eq. (13.8) represents the exact equation of the dissociation constant as expressed in terms of activities. Lewis defined the equilibrium constant given by Eq. (13.8) as the true or exact thermodynamic equilibrium constant. Activities are proportional to each ion's concentration (expressed in terms of molality m) with a proportionality constant, the active ty coefficient γ of each ion (e.g., $\alpha_+ = \gamma_+ m_+$ for the cation and $\alpha_- = \gamma_- m_-$ for the anion). Since there was no experimental method for determining the individual ion activities, Lewis proposed another concept, the geometric mean of activities. For the general type of electrolyte $A_{\nu^+}X_{\nu^-}$ with ν_+ the number of cations and ν_- the number of anions released in solution, the mean activity is given by¹²¹⁵

$$\alpha_{\pm} = \left(\alpha_{\pm}^{\nu_{\pm}}, \ \alpha_{\pm}^{\nu_{\pm}}\right)^{1/\nu} = \alpha_{2}^{1/\nu}$$
(13.9)

In this equation,¹²¹⁶ $v = v_+ + v_-$. Furthermore, Lewis defined the mean activity coefficient, γ_{\pm} , so that in dilute solutions can be regarded as a thermodynamic degree of dissociation:¹²¹⁷

$$\gamma_{\pm} = \frac{\alpha_{\pm}}{m(\nu_{+}^{\nu_{+}}, \nu_{-}^{\nu_{-}})^{1/\nu}}$$
(13.10)

At infinite dilution γ_{\pm} becomes equal to unity. Furthermore, following the geometrical mean quantities, Lewis defined the mean molality of the ions and wrote it as

$$m_{\pm} = m \left(\nu_{+}^{\nu_{+}}, \nu_{-}^{\nu_{-}} \right)^{1/\nu}$$
(13.11)

Substituting the denominator of Eq. (13.10) with its equal in Eq. (13.11), Lewis obtained the corrected mean activity coefficient

$$\gamma_{\pm} = \frac{\alpha_{\pm}}{m_{\pm}} = \left(\gamma_{+}^{\nu_{+}}, \gamma_{-}^{\nu_{-}}\right)^{1/\nu}$$
(13.12)

¹²¹⁵ Ibidl, 1921a, p. 1113.
¹²¹⁶ Ibid, 1921a, p. 1114.
¹²¹⁷ Ibid

Employing Eq. (13.12), Lewis redefined the activity coefficient as the *thermodynamic* degree of dissociation¹²¹⁸ and replaced the degree of dissociation used in the older approximate equations. Lewis using these concepts determined the activity coefficients of strong electrolytes as a function of their concentrations. To obtain these results, he employed several experimental methods, such as the vapor pressure for volatile electrolytes, the electrical conductivity, the distribution ratio of the concentrations of the electrolyte between water and some nonionizing solvent, the lowering of the vapor pressure, and the freezing point depression of solvent, and the electromotive force of specific cells, such as H₂ / HCl // AgCl / Ag (or HgCl / Hg) at 25 °C. The range of the concentration measurements depends on the experimental method. For example, very low concentrations, in the range between 0.01 and 0.0001 m, were achieved for the lowering of the vapor pressure and the freezing point depression, whereas higher concentrations (4-11 m) are allowed for the measurement of the solute vapor pressure. In all cases, the thermodynamic activity coefficient decreases with increasing concentration reaching a minimum and then increases as the concentration further increases. The concentration at which the minimum of the activity coefficient occurs depends on the nature of the electrolyte.

Lewis compared the results obtained with the method of the freezing point depression with the values of Λ_m/Λ_o and found that the ratio Λ_m/Λ_o diverged from the thermodynamic degree of dissociation. The latter appeared more noticeable for the salts of the higher valency (bivalent and trivalent salts). For instance, at a concentration of 0.01 m, the thermodynamic activity coefficient for NaCl obtained from the freezing point

1218 Ibid

depression method was 0.992, whereas that obtained from the ratio Λ_m/Λ_0 was found to be 0.941. For the bivalent and trivalent electrolytes, the discrepancy was even higher. For the bivalent barium chloride, BaCl₂, these values were 0.716 and 0.850, respectively; for the trivalent electrolyte lanthanum nitrate La(N0₃)₃, the values of the thermodynamic degree of dissociation and that of the ordinary degree of dissociation were 0.571 and 0.750, respectively.¹²¹⁹

From 1912 until 1921, Lewis had published his first paper elaborating the problem with the strong electrolytes and the effect of the concentration on the electrolytic dissociation. Furthermore, he desired to compare the accuracy of the various experimental method in measuring the degree of dissociation. He strove to find a mathematical expression to connect the activity coefficient explicitly with concentration. Elaborating the theory behind the method of the freezing point depression, he obtained a simple empirical equation that linked a function, *j*, with molality m:¹²²⁰

$$j = \beta m^{\alpha} \tag{13.13}$$

a and β are constants determined graphically from the experimental data. The fitting procedure for all univalent electrolytes resulted in an exponent *a* taking the approximate value $\frac{1}{2}$, whereas, for other types of electrolytes, this value ranged between 0.3 and 0.4. Further treatment of the freezing point depression data resulted in an expression relating the mean activity coefficient of univalent electrolytes with concentration:

$$\ln\gamma_{+} = -3\beta m^{1/2} \tag{13.14}$$

¹²¹⁹ Lewis and Randall, 1921a, p. 119, 1121.

¹²²⁰ Lewis and Randall, 1921a, p. 1122. In a previous publication with Linhart, Lewis derived an analogous equation (Lewis, Linhart, 1919, p. 1958).

Though limited to the univalent electrolytes, this equation was one of the earliest expressions for the dependence of the activity coefficient on the concentration in a dilute solution. It could be considered a precursor to the relevant equation derived theoretically by Debye and Hückel.¹²²¹

Reviewing the literature and his experimental data for the activity coefficient of a particular electrolyte in a mixture of electrolytes with various types of valence (or charge) at constant total concentration, he concluded that *in any dilute solution of a mixture of strong electrolytes of different valence types, the activity coefficient of each electrolyte depends upon the total concentration (molality) and the valence types of all the electrolytes present in the mixture.¹²²² In this respect, a new quantitative measure was required to determine the activity coefficient in mixed electrolytes of various valence types. This quantity was the <i>ionic strength* μ , given by the following expression:

$$\mu = \frac{1}{2} \sum_{i} m_{i} z_{i}^{2} \tag{13.15}$$

In eq. (13.15), m_i is the molality, and z_i is the charge for the i^{rth} ion in the mixture. The summation runs over all the ions. From the definition of the ionic strength, Lewis expressed the following corollary. In dilute solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.¹²²³ Peter Debye and Erich Hückel later confirmed this empirical rule. Eq. (13.15) holds good for dilute solutions irrespective of the added salt. For concentrated solutions, however, the determined activity

¹²²¹ For dilute aqueous solutions, the law of Debye-Hückel is expressed, as $\ln \gamma = -0.509[z_j][z_-]m^{1/2}$. Here, z_j and z_- denote the charges of the cation and the anion, respectively. In later expressions of concentration, the ionic strength replaced molality. The theory of Debye-Hückel is valid for dilute solutions up to 0.01 m or less. For higher concentrations, several equations exist, such as the extended Debye-Hückel equation. However, these equations do not give the same results in identical solutions.

¹²²² Lewis and Randall, 1921a, p. 1137.

¹²²³ Ibid, p. 1141

coefficient is unpredictable since its value depends on the nature of the added salt in the mixture.

Eq. (13.12) expresses the activity coefficient of the electrolyte in terms of the geometric mean of coefficients of the individual ions. For example, for the potassium chloride (KCl), γ_+ is the activity coefficient of potassium ion K⁺, and γ_- that of the chlorine ion, Cl⁻ Therefore, if the activity coefficient of each ion is known, then the mean activity coefficient the salt could be calculated or vice versa. However, no experimental method exists to measure the activity coefficient of individual ions separately.¹²²⁴ From his numerous experiments and literature data, Lewis knew that the activity coefficient for extremely dilute solutions $(c \rightarrow 0)$ is the same for all ions and becomes equal to unity for infinite dilution (zero concentration). As the concentration increases, it might be expected that the activity coefficients of two ions of similar type would remain approximately the same, up to a moderately concentrated solution. Furthermore, from the definition of the ionic strength and the subsequent corollary mentioned above, Lewis knew that in dilute solutions, the activity coefficient of a certain electrolyte is independent of the particular character of any other strong electrolytes present but depends solely upon the total ionic strength. These two hypotheses allowed Lewis to calculate the activity coefficient of a particular salt using known activity coefficients of other salts with common ions. For example, a solution that contains the salts KCl, KIO₃, BaCl₂, and Ba(IO₃)₂, each at an ionic strength of 0.01 m;¹²²⁵ According to Eq. (13.12), the activity coefficient of KCl, $\gamma_{KCl}^2 =$ γ_{K^+} , γ_{Cl^-} ; the activity coefficient of BaCl₂, $\gamma_{BaCl_2}^3 = \gamma_{Ba^{2+}} \gamma_{Cl^-}^2$, and similarly for the other

¹²²⁴ The activity coefficient of individual ions can be calculated from the Debye-Hückel equation (for ionic strength less than 0.1) or from Eq. (13.12) using as a reference the activity coefficient of the hydrogen ion. In the second case the relative ion activity coefficient is calculated.

¹²²⁵ Lewis and Randall, 1921a, p. 1145.

two salts. Considering that, the activity coefficient for each common ion is the same in these four salts and with a bit of algebra, Lewis obtained the following relation for the four activity coefficients.

$$\left(\frac{\gamma_{KCl}}{\gamma_{KIO_3}}\right)^4 = \left(\frac{\gamma_{BACl_2}}{\gamma_{B\alpha(IO_3)_2}}\right)^3 \tag{13.16}$$

Eq. (13.16) tells us that the activity coefficient of any of the four salts can be calculated if the activity coefficients of the other three salts are known. Lewis's work on strong electrolytes and concentrated solutions is a very good example of what appropriation meant regarding the appropriation of the ionists' science by the American physical chemists.

In summary, from his numerous experiments, the introduction of theoretical concepts and hypotheses, and the thermodynamic calculations, Lewis evidenced that the concentration is an inadequate measure for describing the various processes, especially at high pressures for gases and high concentrations of solutions. The introduction of fugacity as a measure of the escaping tendency of substances in the gas phase instead of the vapor pressure described the non-ideality of the gaseous mixtures. The activity of the ions instead of the hypothetical concentration is of value, referring not only to strong electrolytes but also to weak electrolytes at higher concentrations. Furthermore, Lewis provided several methods for measuring the activity coefficient of various types of electrolytes. He examined thoroughly each method upon comparing their accuracy and the concentration limits of solutions for reliable measurements. However, Lewis' achievements in physical chemistry are not confined solely to the properties of imperfect gases and strong electrolytes. His contribution to thermodynamics, particularly the determination of the free energy from the heat of reactions, deserves a separate discussion.

4.3 Chemical free energies

Lewis extracted the first paper from his dissertation. The paper entitled *Some Electrochemical and Thermochemical Relations of Zinc and Cadmium Amalgam* was published in 1898. It was a purely experimental work in which Lewis proposed a novel methodology of measuring accurately the heat evolved in the formation of zinc and cadmium amalgams. He used electrochemical cells that had two electrodes of amalgams (a solid mixture of the metal with mercury) immersed into two separate vessels containing the same electrolyte but of different concentrations. He tested the accuracy of measurements based on the Nernst equations suitable for concentration cells. The authors of this paper were Richards and Lewis.¹²²⁶

Lewis published the second paper from his dissertation in 1899. The paper entitled *The development and application of a general equation for free energy and physicochemical equilibrium*.¹²²⁷ Lewis was very ambitious, and in this paper, wished to derive a single equation from the first principles of thermodynamics and the laws of gases, which should enable one to predict almost anything, including the calculation of the free energy. Recall the inherent difficulties in measuring the free energy using galvanic cells and the pursuit for other more convenient methods to do so.¹²²⁸ Thermochemical methods appeared to be much easier than using the electromotive force. The Gibbs-Helmholtz equation offered a route to free energies from thermochemical measurements. However, the integrated form of this equation used for the calculation included an undetermined constant.¹²²⁹ Le Chatelier was the first who strove to solve the problem of integration in

¹²²⁶ Richards and Lewis, 1898.

¹²²⁷ Lewis, 1899b.

¹²²⁸ See chapter 8 of this dissertation.

¹²²⁹ Ibid

1888, although unsuccessfully.¹²³⁰ Five e eminent physicists and chemists followed Le Chatelier in attempting to solve the problem, and Nernst was the one who finally found the solution.

Using his generalized equation, Lewis derived expressions for several thermodynamic properties of solutions and gases including an equivalent formula for van der Waals' equation for the non-ideal gases. In the summary of his paper, Lewis appended a list of fifteen subjects (conditions, formulae, laws) derived from his general equation, which, according to him, "systematize a part of the hitherto knowledge of physical chemistry perhaps point out new laws".¹²³¹ Nonetheless, Lewis did not arrive at his scope of calculating the free energy through thermochemical means. The dissertation was not well received by Wilder Bancroft, who at that time was a professor of chemistry at Cornell University and editor of the *Journal of Physical Chemistry*. Bancroft reviewing Lewis' paper, wrote, "The author deduces a single equation which should enable one to predict anything; but which does not lead the author to anything new. He even discusses the distribution of a substance between two liquid phases without any reference to the increased miscibility of the two phases. What we need in physical chemistry is a closer adherence to facts and less approximation theory".¹²³²

Lewis did not abandon the idea of free energy. He recognized the tremendous value of this thermodynamic quantity in determining chemical affinity, chemical equilibrium, and hence the direction of a spontaneous chemical reaction. He returned to the subject with a significant paper published in 1913. In the introduction, he wrote, "Hence a complete free

¹²³⁰ Le Chatelier, 1888.

¹²³¹ Lewis, 1899b, p. 3.

¹²³² Bancroft, 1901, p. 405.
energy table for all common substances will not only serve as a table of chemical affinities, but it will enable the chemist to predict the amount of work that can be furnished under conditions of highest efficiency by each chemical reaction and will show as well the direction in which the reaction will proceed, and the extent of the yield".¹²³³ Lewis introduced two important concepts regarding the composition of any solution or mixture of substances. The first concept is the *mole fraction*, defined as the number of moles of a substance in a solution divided by the number of mol of all constituents.¹²³⁴ The benefit of using this dimensionless concentration is the fact that it does not change with temperature, while the concentration expressed in mol per liter of solution (molarity) does. The second expression of the composition of a solution constituent is the partial molecular or molal *volume*. In general, the partial molal volume \tilde{V} of a substance X in a solution or a mixture is the change in volume per mol of X added to the mixture under constant temperature and pressure. In a solution containing n_1 mol of substance X₁, n_2 mol of substance X₂, the partial molal volume of X₁ is defined analytically by the equation,¹²³⁵

$$\frac{\partial V}{\partial n_1} = \tilde{V}_1 \tag{13.17}$$

V is the total volume of the solution or the mixture. An analogous equation holds for the partial volume of substance X_2 . In other words, the partial molal volume of the substance X_1 or X_2 in a given solution is the increase in the volume of a very large amount of this

¹²³³ Lewis, 1913, p. 1.

¹²³⁴Ibid, p. 5.

¹²³⁵ Lewis, 1913, pp. 5-6. Eq. 13.18 can be expressed in terms of a standard differential, in which the constant parameters are denoted as subscripts, i.e., $\left(\frac{dV}{dn_1}\right)_{t,p,n_2}$. In terms of thermodynamics, the partial molal volume is defined as the rate of change of the total volume of solution with the change in the amount of a particular solute component.

solution when one mol of X_1 or X_2 is added to it. The change of volume *V* of the solution upon the addition n_1 mol of X_1 and n_2 mol of X_2 is given by the following equation¹²³⁶

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \tag{13.18}$$

Unlike the molal volume of a pure substance (volume of one mol), the partial molal volume of a substance in the solution may be either positive or negative depending upon the nature of the intermolecular forces between the particular substance and the other components in the solution. This means that at a constant temperature, the volume of the solution may increase or decrease upon the addition of the substance. The partial molal volume approaches the molar volume in dilute solutions and becomes equal at infinite dilute solutions. The partial molal volume's definition and properties may be expanded to other extensive thermodynamic quantities, such as partial molal heat capacity at constant pressure, partial molar energy, partial molal entropy, or partial molar free energy.¹²³⁷

Of particular interest is the comparison between the *molal Gibbs' chemical potential* or the *molal Gibbs' free energy* for a single component μ , or *G*, respectively, and *the partial molal Gibbs' chemical potential* $\overline{\mu}_t$ in a multicomponent system. Both quantities are expressed by the differential of the ζ function in Eq. (6.29) (page 259) for j = 0, and $j \neq 0$, respectively. The partial molal quantities play the same role as the volume, the heat capacity, the heat content, and the chemical potential or the free energy of a pure substance. They are used in equations of identical form with those used for a pure substance. Lewis used the partial molal heat content, the partial molal free energy, and partial molal activity to study the thermodynamic properties of concentrated solutions.¹²³⁸

¹²³⁶ Ibid.

¹²³⁷ Lewis aptly remarked that the partial molal free energy is a potential as defined by Gibbs (Lewis, 1913, p. 15).

¹²³⁸ Lewis and Randall, 1921b, pp. 234-236.

The second novelty introduced by Lewis in the 1913 paper is the symbols that indicated the physical state of the substances participating in a chemical reaction. For liquid substances, he used the symbol (l), for solids (s), for gases (g), and aqueous solutions, the symbol (aq). For example, the reaction Fe (s) + 2HCl (aq) \rightarrow FeCl₂ (aq) + H₂ (g) takes place between the solid iron and an aqueous solution of HCl. It gives the products of an aqueous solution of FeCl₂, while gas hydrogen is evolved. The remainder of the 1913 paper concerns the properties, calculation, and application of free energy.

Lewis defined free energy according to Helmholtz's definition as the maximum amount of work that can be utilized for any external purpose, for example, the operation of an electrical motor. However, Lewis used neither Helmholtz's symbol A for the free energy nor his exact mathematical definition Lewis formulated the free energy denoted by *F* following Gibbs' ζ function, or Duhem's total thermodynamic potential. Helmholtz's free energy *A* corresponded to Gibbs' ψ function or Duhem's internal thermodynamic potential.¹²³⁹ Lewis probably preferred *F* to *A* because the former definition implied measurements at constant pressure, which are much easier to perform than measurements at constant volume for the latter. Furthermore, Lewis defined the conditions of equilibrium and the spontaneity of a chemical process through the following inequality

$$\Delta F \le 0 \tag{13.19}$$

The equal sign signifies the state of equilibrium.

Lewis resumed his efforts for the determination of the integration constant resulting from the Gibbs-Helmholtz equation, in which he had been involved about fifteen years ago. He devoted a brief discussion about the efforts of the scientists to solve this problem,

¹²³⁹ Lewis, 1912, p. 14; Lewis and Randall, 1923a, p. 158.

starting from Le Chatelier who first tackled the problem in 1888 until 1906 when Nernst found a solution based on reactions that involved substances in the condensed state.¹²⁴⁰ He admitted that it was important to calculate in advance the integration constant, either by a theoretical approach or through some other experimental method, and then use it to evaluate the free energy by using thermochemical means. However, Lewis noted that one could go in the opposite direction: to calculate the integration constant from the experimental free energy at one temperature and use this value to calculate the free energy at another temperature.¹²⁴¹ In other words, Lewis solved the problem of integration experimentally rather than theoretically.

Based on the transformation of sulfur from the rhombic to monoclinic allotropic form, Lewis demonstrated the utility of free energy for chemical processes. These two forms of sulfur differ in the arrangement of atoms in their crystals.¹²⁴²

S (rhombic) = S (monoclinic)

The equation below gives the temperature dependence of the free energy of this transformation over the temperature range from 0 $^{\circ}$ C to 100 $^{\circ}$ C.

 $\Delta F = 120 + 0.50T \ln T - 0.00125T^2 + JT \tag{13.20}$

J is the integration constant. Substituting the value $\Delta F = 0$ cal at 368 °C, the value of the constant is J = -2.820, whence the free energy at any other temperature could be calculated. Thus, at 25 °C (or at 298 Kelvin), the free energy is $\Delta F = 18$ cal. The positive value of the free energy implies that the rhombic form is more stable at this temperature.¹²⁴³

¹²⁴⁰ Lewis, 1913, pp. 28-30.

¹²⁴¹ Lewis, 1913, pp. 26-28; Lewis and Randall, 1923a, pp. 172-173.

¹²⁴² Ibid, p. 15.

¹²⁴³ Lewis and Randall, 1923a, p. 174.

The additivity of free energy (free energy is an extensive function) allows the calculation of the free energy of chemical reactions as the difference between the free energies of the products and reactants. The sign of the calculated free energy indicates the spontaneous direction of the reaction at the given temperature. Furthermore, Lewis considered the possibility to write reactions analogous to thermochemical reactions and apply the Hess law for the free energies. Such equations may be combined by addition and subtraction to calculate the free energy of a chemical reaction without performing any experiment. Lewis gave the following example.¹²⁴⁴

$$H_2 + S \text{ (rhombic)} = H_2 S \text{ (g)}^{1245}$$
 $\Delta F = -7830 \text{ cal}$ (13.21)

S (monoclinic) = S (rhombic) $\Delta F = -18$ cal (13.22)

Both reactions occur at 25 °C. Hence, by addition, he obtained the free energy of the formation of the hydrogen sulfide

$$H_2 + S \text{ (monoclinic)} = H_2 S \text{ (g)}$$
 $\Delta F = -7848 \text{ cal}$ (13.23)

The above equations give at once the free energy of hydrogen sulfide. In general, this simplistic procedure allows the calculation of the free energy of formation of compounds. This is very important information since the absolute free energy of a substance cannot be determined experimentally. Today, physical chemistry textbooks have tabulated the (standard) free energies of formation for many compounds at 298 K.

Apart from reactions in the gas and solid phase, Lewis dealt with reactions in solutions. The theoretical treatment and relevant equations are similar to those discussed previously, except perhaps for the fact that partial molal free energies are calculated. Furthermore, Lewis showed the relationship between the free energy and the functions of

¹²⁴⁴ Lewis, 1913, p. 15; Lewis and Randall, 1923a, p. 171.

¹²⁴⁵ Lewis did not use arrows in the chemical reactions. He used the equal sign.

fugacity and activity and derived the relationship that connected the free energy change with the equilibrium constant of the reaction.¹²⁴⁶ If one mol of a perfect gas passes at a constant temperature from pressure p_1 to pressure p_2 , one may write the first relationship between the free energy change ΔF and the fugacity as follows:¹²⁴⁷

$$\Delta F = RT \ln \frac{p_2}{p_1} = RT \ln \frac{f_2}{f_1} = RT \ln \frac{\xi_2}{\xi_1}$$
(13.24)

 f_1 and f_2 are the fugacities which are proportional to pressures p_1 and p_2 , respectively. Eq. (13.24) may be used in cases where a substance, whose vapor is considered as a perfect gas, exists in any two states, e.g., as a pure liquid or solid, or a solution and the vapor pressures of the substance above those two states are p_1 and p_2 . For the real case, when the vapor is not considered as a perfect gas, the fugacities replace the pressures via a proportionality constant as discussed previously. Similarly, ξ_1 and ξ_2 are the activities of the two states in question. Activities are proportional to fugacities through Eq. (13.1) shown above. Whenever, therefore, the fugacity or the activity of a substance in any two phases is known, the change in the free energy may be calculated using Eq, (13.24). However, Lewis recognizes that is not always easy to determine separately the numerical values of these functions for each phase. Alternatively, he suggested as more practical the calculation of the ratio between the activities or fugacities of a substance in two different states at the same temperature.

To relate the equilibrium constant of a chemical reaction with the change of the free energy of the reaction, Lewis had to derive analogous expressions to Eq. (13.24) in terms of the pressures of substances in the gas phase or concentrations in solution. However, in

¹²⁴⁶ Lewis, 1913, pp. 16-20.

¹²⁴⁷ Ibid, p. 17.

a chemical reaction, ΔF represents the difference in the molal free energies or the partial molal free energies of the substances involved in the reaction. For the general reaction

$$dD + eE + . = gG + hH + ...$$
 (13.25)

The change of the free energy of this reaction is given as the difference of the free energies of the reactants from those of the products, namely

$$\Delta F = (gF_G + hF_{h+\cdots}) - (dF_D + eF_E + \cdots)$$
(13.26)

At equilibrium, $\Delta F = 0$, then

$$(gF_G + hF_{h+\dots}) - (dF_D + eF_E + \dots) = 0$$
(13.27)

At this stage, Lewis defined the condition of *the standard state* such that if F is the free energy of the substance in any state¹²⁴⁸

$$F = RT \ln a \quad \text{or} \quad \overline{F} = RT \ln a \quad \{13.28\}$$

where *a* is the relative activity given as $\alpha = \xi/\xi^0$ (page 574). Then

$$\Delta F = F_2 - F_1 = RT \ln \frac{a_2}{a_1} \tag{13.29}$$

whose form is similar to that of Eq. (13.24). Substitution of the free energies F from Eq. (13.28) into Eq. (13.27) and after a little algebra, the following equality is obtained

$$\Delta F = RT \ln \frac{a_g^g a_H^h \dots}{a_D^d a_E^e \dots} \tag{13.30}$$

The quotient of this equation is called the *activity quotient* of the reaction. At equilibrium, this equation equals zero. If all substances are gases or dissolved in solutions, the relative activities may be replaced with sufficient accuracy by pressures p and concentrations c, respectively. The pressure or the concentration of each substance is multiplied by a

¹²⁴⁸ Ibid, p. 18.

constant, which is the proportionality constant of the transformation. Consequently, at equilibrium, Eq. (13.30) may be rewritten as

$$RT \frac{p_G^g p_{H\cdots}^h}{p_D^d p_E^e \cdots} = 0 \quad \text{or} \quad RT \frac{c_G^g c_H^h \cdots}{c_D^d c_E^e \cdots} = 0$$
(13.31)

These expressions equal the respective equilibrium constants, K_p and K_c , which by definition collect the various proportionality constants mentioned above, namely¹²⁴⁹

$$K_p = \frac{p_G^g p_H^h \dots}{p_D^d p_E^e \dots} \quad \text{and} \quad K_c = \frac{c_G^g c_H^h \dots}{c_D^d c_E^e \dots} \tag{13.32}$$

Equations (13.32) can be used in all cases except reactions involving concentrated solutions, or gases under high pressure. Eqs. (13.32) are approximate and become exact as the gases approach the ideal state and the solutions the infinite dilution.

Finally, Lewis obtained a relationship between the change in free energy of a reaction in which all the substances are under normal conditions (standard state),¹²⁵⁰ and the equilibrium constant of the reaction.¹²⁵¹ He denoted the change of the normal free energy as F^0 . He considered the reaction (13.25). The change of the free energy in this reaction when the substances are in any given state is expressed by Eq. (13.26). When the substances are in the standard state, then Eq. (13.26) is rewritten as

$$\Delta F^{0} = (gF_{G}^{0} + hF_{H}^{0} + \dots) - (dF_{D}^{0} + eF_{E}^{0} + \dots$$
(13.33)_

Taking into consideration the activities of each substance of the reaction in the nonstandard state, then for each substance one has

$$F_i - F_i^0 = RT \ln a_i \tag{13.34}$$

¹²⁴⁹ Ibid, p. 19.

 ¹²⁵⁰ Each substance of the reaction is in the standard state whent is at unit activity, or, in other words, dealing with a pure substance (i.e. having a fixed composition in any phase) under constant pressure).
 ¹²⁵¹ Lewis, 1913, pp. 19-20; 1923a, pp. 291-294.

The index i runs for all substances in the reaction. Combining equation (13.26), (13.33), and Eq. (13.34) for each substance, one obtains¹²⁵²

$$\Delta F - \Delta F^0 = RT \ln \frac{a_G^g a_H^h \dots}{a_D^d a_E^e \dots}$$
(13.35)

By determining the activity quotient, the change of the free energy in the standard state ΔF^0 is calculated when ΔF is known and vice versa. At equilibrium $\Delta F = 0$, and from Eq. (13.35) the equilibrium constant under standard conditions is obtained.

$$\Delta F^0 = -RT \ln \frac{a_G^g a_H^h \dots}{a_D^d a_E^e \dots} = -RT \ln K$$
(13.36)

Lewis concluded his paper by showing how one could calculate the free energy change of a chemical reaction conducted in an electrolytic cell. And through the sign of the resulting free energy, he discovered a suitable convention for the sign of an electromotive force.¹²⁵³ This convention is very useful since the sign of the electromotive force indicates the tendency of the current to run from left to right, or vice versa.

Parenthetically, it is interesting to note that Lewis proposed another innovation; the short notation of the chemical cell. Instead of writing the chemical reaction explicitly. This notation, in addition, shows at a glance the construction of the cell. For instance, the following reaction that takes place in the electrolytic cell,¹²⁵⁴

Cd (12.5% amalgam) + Hg₂SO₄ (s) = CdSO₄ (s) + 2Hg (1) (13.37)

can be written as (Lewis notation)

Cd (12.5% amalgam),
$$Hg_2SO_4$$
 (s) // CdSO_4 (s), Hg (1) (13.38)

¹²⁵² Lewis, 1923a, p. 293.

¹²⁵³ Lewis,, 1913, pp. 20-25.

¹²⁵⁴ Ibid, p. 20.

The E.M.F of the above cell at 20° is +1.0183 volts. The double slash in the notation separates the cell into two parts, the left and the right *half cells*. Each half cell has its potential. The algebraic sum of the two single potentials equals the experimental determined E.M.F. According to Lewis' notation, the two half cells can be depicted as

Cd (12.5% amalgam),
$$Hg_2SO_4 : E = \chi$$
 (13.39a)

CdSO₄, Hg (1):
$$E = \psi$$
 (13.39b)

 χ and ψ are the single potentials of the half cells, and $\chi + \psi = +I.0183$ volts is the total potential or the E.M.F. of the cell. Lewis attempted to write the equations of the *half-reactions* that take place in the half cell. He strikingly referred to the transfer of positive and negative electricity from one half-reaction to the other, which little differs conceptually from the current knowledge of the transfer of electrons in redox reactions.¹²⁵⁵

For the cell H₂, HCl (0.1 M), Cl₂ of an electrical potential of +1.4881 volts, and considering 76% the degree of dissociation of HCl in water, Lewis wrote the reactions of the half cells in the form

$$\frac{1}{2}$$
 H₂ + $+$ = H⁺(0.076 M : E = x (13.40a)

$$\frac{1}{2} \operatorname{Cl}_2 = \mathcal{Cl}^-(0.076 \text{ M}) + \quad (+) : E = y$$
 (13.40b)

The symbol (\div) in the reactions (13.40) represents one equivalent of positive electricity. The reactions are written in such a way as to demonstrate the direction of the passage of the electric current. The positive current passes the half cell H_2 , H^+ from left to right when the reaction (13.40a) runs from left to right. In the other case, the positive current passes through the half cell Cl_2 , Cl^- from left to right when the reaction (13.40b) runs from left to right. Adding these reactions together, one obtains the reaction for the whole cell

¹²⁵⁵ Ibid, p. 21.

A very interesting part of Lewis' 1913 paper that was reproduced in his textbook of 1923 is the application of thermodynamics to the operation of the voltaic cells. He considered a cell working reversibly with an electromotive force *E*. If the chemical reaction in the cell occurs upon the passage of *n* Faraday equivalents, then the electrical work done by the cell is *nFE*. If the reaction takes place at constant pressure, then according to Helmholtz the free energy must be equal to the useful electrical work, i.e.¹²⁵⁶

$$\Delta F = -nFE \tag{13.41}$$

Eq. (13.41) tells us that the electromotive force *E* multiplied by the amount of electricity passing through the cell measures the maximum of the output work of the cell. Eq. (13.41) tells us something more. A positive *E* implies that $\Delta F < 0$, and therefore the reaction as written is spontaneous (Eq. (13.19) on page 585). As a result, the reaction (13.37) runs spontaneously from left to right since the E.M.F. of the cell is positive.

The Nernst's equation for the reaction 13.25) in terms of activities may be written as¹²⁵⁷

$$E = E^{0} - \frac{RT}{nF} ln \frac{a_{G}^{g} a_{H}^{h} \dots}{a_{D}^{d} a_{E}^{e} \dots}$$
(13.42)

Similar equations can be written taking into account the pressure of gases or the concentrations of the substances in solution multiplied by constants. These proportionality constants are collected in the term E^0 . When all the activities (concentrations or pressures) are unity, the last term of Eq. (13.42) vanishes. In this case, E^0 represents the E.M.F. of the cell under normal conditions (standard state), and represents the normal E.M.F., that is, $E = E^0$.¹²⁵⁸ As shown earlier, at equilibrium, the quotient in Eq. (13.42) is equal to the

¹²⁵⁶ Ibid, p. 22; 1923a, p. 168.

¹²⁵⁷ Ibid, p. 22-23; 1923a, p. 293-294.

¹²⁵⁸ The normal E.M.F., is very important, not only for predicting the direction of the electrochemical reaction, but also for calculating all the normal thermodynamic quantities (enthalpy, entropy, free energy) of the reaction. Values of E^0 are tabulated in current textbooks for a large number of chemical reactions.

equilibrium constant. Therefore, the equilibrium constant can be calculated by measuring the E.M.F., of the cell in which the reaction takes place provided that the normal potential is known. Alternatively, the equilibrium constant can be calculated directly from the normal E.M.F. by using Eq. (13.43) below:

$$\ln K = \frac{nF}{RT} E^0 \tag{13.43}$$

This equation results by combining Eqs. (13.36) and (13.41). It should be stressed once more that all previous discussions and derived relationships are valid for dilute solutions. They fail for concentrated solutions or gases at high pressure. Nevertheless, Lewis proposed a preliminary solution to the problem based on the Gibbs-Duhem equation expressed in terms of the partial molal free energies.¹²⁵⁹

Apart from the measurement of the free energy using galvanic cells, Lewis proposed an alternative methodology based on calorimetric measurements. By examining the influence of temperature on the free energy of a chemical or physical process, Lewis arrived at the Gibbs-Helmholtz equation.¹²⁶⁰ Using a reversible cycle of four steps, he calculated the total work produced by the system against a constant external pressure and applying the second law of thermodynamics rederived the well-known Gibbs-Helmholtz equation for the change of the free energy.

$$T\frac{d(\Delta F)}{dT} = \Delta F - \Delta H \tag{13.44}$$

 ΔH , here, is the change of the enthalpy (heat content) of the system. The calculation of ΔF requires the integration of this equation, and the evaluation of the integration constant. As discussed in chapter 8, the determination of this constant was not possible because of its

 ¹²⁵⁹ Ibid, pp. 25-26. It is interesting to note that Lewis mentioned only the name of Duhem as the creator of this equation. He referred to both physicists later in his textbook of 1923.
 ¹²⁶⁰ Ibid. pp. 26-30.

unknown behavior with temperature. Lewis gave a brief account of the efforts of six investigators, including himself, who inquired the determination of the integration constant in advance before any measurement of free energy, relying on known physical and chemical properties of the substances involved in the reaction.

Lewis thought that he could have bypassed the problem upon calculating the integration constant from the experimental free energy at one temperature and using this value to calculate the free energy at another temperature. By using the method of the separation of variables of the differential calculus, Lewis gave another form of the Gibbs-Duhem equation, namely¹²⁶¹

$$\frac{\frac{\mathrm{d}(\Delta F)}{\mathrm{d}T}}{\mathrm{d}T} = -\frac{\Delta H}{T^2} \tag{13.45}$$

This equation is suitable for the calculation of ΔF by direct integration provided that one knows ΔH as a function of temperature. Such a temperature dependence may be expressed in an analytical form. For the enthalpy change, the following equation gives better results.¹²⁶²

$$\Delta H = \Delta H_0 + \Delta \Gamma_0 T + \frac{1}{2} \Delta \Gamma_1 T^2 + \frac{1}{3} \Delta \Gamma_3 T^3 + \cdots$$
(13.46)

The quantities $\Delta\Gamma_i$ are constants characteristics for the particular reaction. Usually, terms no greater than T^2 are required for good accuracy. Substitution of the last equation in Eq. (13.45) and integrating, the following expression for the temperature dependence of the free energy is obtained

$$\Delta F = \Delta H_0 - \Delta \Gamma_0 T \ln T - \frac{1}{2} \Delta \Gamma_1 T^2 - \frac{1}{6} \Delta \Gamma_3 T^3 - \dots + IT$$
(13.48)

¹²⁶¹ Ibid. p. 27; 1923a, p. 173. ¹²⁶² Ibid.

The quantity I is the integration constant, which may be evaluated when the free energy is known at some temperature. An example of the utility of this equation has been given by Eq. (13.20) on page 586 dealing with the calculation of the change of the free energy of the transformation of sulfur from the rhombic to monoclinic allotropic form,

As noted earlier, in collaboration with his assistant Merle Randall,¹²⁶³ Lewis published one of the most successful physical chemistry textbooks of the twentieth century. The title of the book is *Thermodynamics and the free energy of chemical substances*.¹²⁶⁴ The title reflects Lewis' devotion to thermodynamics and the usefulness of free energy. Lewis and Randall measured standard free energies of formation for several organic and inorganic substances. They tabulated these results in an appendix of their textbook.¹²⁶⁵ Randall continued research on the free energies and in 1830 contributed 81 pages of enthalpy, entropy, and free energy data to the seventh volume of the International Critical Tables.¹²⁶⁶

Section 5. Lewis' work in physical organic chemistry

Besides his contribution to chemical thermodynamics, Lewis excelled in four other fields of chemistry and physics. After 1920, Lewis oriented his research almost exclusively to the newly developed field of physical organic chemistry. By the end of the second decade

¹²⁶³ Randall graduated from the Chemistry Department of the University of Missouri. He received his B.S. in 1907 and M.S. in 1909. He obtained his Ph.D. from MIT in 1912. His thesis, entitled *Studies in Free Energy*, was based on work done under the supervision of Lewis. He collaborated with Lewis at Berkeley, initially serving as Lewis' private assistant. In 1917, Randall was officially appointed to the position of Assistant Professor of Chemistry at Berkeley, where he continued to teach and do research on thermodynamics until his retirement in 1944.

¹²⁶⁴ For a short description of this textbook, see Jensen, 2005.

¹²⁶⁵ Lewis and Randall, 1923a, pp. 607-608.

¹²⁶⁶ Jensen, 2005, p. 6.

of the twentieth century, Lewis showed a preference to problems related to organic chemistry, particularly the elucidation of the nature of chemical bonding.

5.1 The structure of the chemical bond

Lewis suggested his cubic atom following the accepted idea that chemical bonds are formed by sharing electrons between atoms to a complete set of eight. This *cubic atom* explains the cycle of eight elements in the periodic table (Figure 27). Molecules are built up by a concentric series of cubes with electrons at each corner and the nucleus at the center—two cubes with a shared edge form a single bond. Two cubes with a common face represent the double bond (Figure 28). Lewis recognized later that the cubic structure could not represent the triple bond and suggested its replacement by van 't Hoff's tetrahedral atom. Lewis published his model in 1916 in the article The Atom and the Molecule, almost simultaneously with the German physicist Walther Ludwig Julius Kossel (1888-1956), who dealt with the same general subject.¹²⁶⁷ An extensive treatment of the topic appeared in 1923 in a volume entitled Valence and the structure of atoms and molecules published as a monograph of the American Chemical Society.¹²⁶⁸ In this monograph, Lewis presented his ideas from several of his previous publications on the chemical bond and elaborated on *Abegg's rule*¹²⁶⁹ regarding the significance of an outer octet of electrons of an atom.¹²⁷⁰ The idea of pairing electrons as a manifestation of the

¹²⁶⁷ Linus Pauling compared Lewis and Kossel's papers on chemical bonds and found Kossel's paper much inferior To Lewis, representing no significant contribution to the subject (1984, p. 201). ¹²⁶⁸ Lewis, 1923b.

 ¹²⁶⁹ The German chemist Richard Abegg (1869-1910) stated this concept in 1904. Lewis was one of the first to refer to the concept as "Abegg's rule" when he used it to base the argument in the 1916 article.
 ¹²⁷⁰ Jensen (1984) offered detailed information on the development of the octet rule.

chemical bond paved the way for the covalent bond concept¹²⁷¹ and its subsequent quantum mechanical treatment.

Lewis's chemical bond theory is one of the most important contributions to structural theory and physical organic chemistry. In his classic book *The Nature of the Chemical Bond*, Linus Pauling detailed Lewis's theory on the chemical bond. In 1984, Pauling published a short article to a reminiscence of Lewis' contribution to the chemical bond. He ended the article by saying, "Gilbert Newton Lewis showed himself to be one of the great chemists of the 20th century through his work in chemical thermodynamics and other fields, as well as through his formulation of the basic principle of the chemical bond—the idea that the chemical bond consists of a pair of electrons held jointly by two atoms".¹²⁷²

Ironically, Lewis and van Hoff, two eminent physical chemists, the first with his theory on chemical bond and the second with the stereochemistry of the carbon atom have made significant contributions to organic chemistry. At the same time, organic chemistry became a severe obstacle to establishing the discipline of physical chemistry.

5.2 Studies on deuterium nucleus (heavy hydrogen)

¹²⁷¹ Langmuir, a former student of Lewis, popularized Lewis' electron-pair bond, while the latter served in the army during the First World War. Langmuir extended the electron pair bonding introducing the partially ionic bonding mechanism. Adopting this mechanism, Langmuir sought to distinguish between non-polar and polar bonding of homonuclear and heteronuclear substances, respectively. To emphasize the difference between the two bond types, Langmuir introduced the terms electrovalent and covalent bonding. Lewis was unhappy with Langmuir's initiatives because he thought the chemical bond mechanism was his research area. Through Langmuir's notebook, Robert Kohler described the development of Langmuir's electron pair model, the so-called *Octet theory of valence* (Kohler, 1974). Langmuir was the Nobel Prize winner in 1932 but for another subject related to the physicochemical properties of surfaces. ¹²⁷² Pauling, 1984, p. 203).

Between 1933 and 1934, Lewis published more than 26 papers dealing with the separation and study of the properties of deuterium and its compounds. Deuterium is an isotope of the hydrogen atom, known as heavy hydrogen because it has a mass of two since it carries one proton and one neutron in its nucleus. Harold Urey (1893-1981), another student of Lewis, discovered the deuterium spectroscopically in samples of liquid hydrogen that had been isotopically enriched via fractional evaporation. Using the fractional electrolysis of water, an approach independently suggested by Edward Wight Washburn (1881-1934), a disciple of Arthur Noyes, Lewis succeeded in preparing a macroscopic quantity of deuterium and began studying its properties. The result was 26 papers in sixteen months.¹²⁷³

5.3 The electronic theory of acids and bases

Lewis continued with his classic work on the electronic theory of acids and bases. This study lived until our days as *the Lewis acid-base definitions*. These concepts define an acid as an electron-pair acceptor and a base as an electron-pair donor. This definition is more general than the definition of the two physical chemists, the Danish Johannes Nicolaus Brönsted (879-1947) and the English Thomas Martin Lowry (1874-1936), and enlarged the number of substances that behave as acids and bases. Lewis noted the definition of acids and bases in just a few pages in his 1923 monograph on the chemical bond. Much later, in 1938, he gave a popular lecture on the subject at the Franklin Institute in Philadelphia. This lecture was published in the journal of the institute with a rather poor readership.¹²⁷⁴ Lewis sought to find a solid base of experimental evidence for the definition of the acids and bases first mentioned in 1923. In collaboration with his research, assistant

¹²⁷³ Coffey, 2008, pp. 212-216.

¹²⁷⁴ Lewis, 1938.

Glenn Theodore Seaborg (1912-1999), a 1951 Nobel laureate in chemistry, Lewis started a research program on generalized acids and bases. Later, Lewis with his student Michael Kasha demonstrated the existence of two types of acids and bases: the primary and the secondary acids and bases. This distinction was based on their behavior during the neutralization of bases with acids. Furthermore, they examined the behavior of organic acids and bases as indicators and the effect of the solvent and tempera on their color in solutions. The change of the color of the solution is due to a structural change in the indicator's molecule depending on the acidic, neutral or alkaline environment in the solution. An acid-base indicator is a weak acid or weak base that dissociates in water to yield two species (ions) with different colors. Acid-base indicators are a significant component in quantitative measurements using volumetric analysis.¹²⁷⁵ Lewis and Kasha's work appeared in three papers published in the *Journal of the American Chemical Society* between 1939 and 1940.¹²⁷⁶

5.4 Phosphorescence and the Triplet state

In the last years of his life, Lewis and his graduate student Michael Kasha recognized that phosphorescence of organic molecules involved the emission of light from one electron in an excited triplet state (a state in which two electrons in different orbitals have their spin vectors oriented in the same direction). They assigned and interpreted the triplet state in organic molecules.¹²⁷⁷ Lewis got this idea from his previous fluorescence research and the notion that fluorescent compounds in a solvent cooled to a glass-like solidity can show

¹²⁷⁵ See footenote 992 on page 468.

¹²⁷⁶ Seaborg has given a detailed account on his collaboration with Lewis, and the experiments performed in Lewis' laboratory (1984).

¹²⁷⁷ Lewis, and Kasha, 1944, p. 214.

phosphorescence. The two authors demonstrated that despite many earlier statements to the contrary, each substance has a unique phosphorescent state. In this respect, the pattern of the phosphorescence bands could serve for the identification of substances. From this basis, Lewis and his last student Michael Kasha have attacked the connection between color and molecular structure on a broad front. Furthermore, they showed the dependence of the lifespan and the energy of the phosphorescent state on certain substituent groups (auxichromes), the solvent used, and the temperature.¹²⁷⁸

During his stay at MIT, Lewis made other research contributions. He was involved heavily in physics and chemistry, and between 1909 and 1912, Lewis and his collaborators published three papers on relativity. He derived the famous mass-energy relationship differently from Albert Einstein's (1879-1955) derivation; He combined this method with special relativity. He presented a major work in mathematical physics. Lewis applied synthetic geometry to the study of space-time and noted the identity of a space-time squeeze mapping and a Lorentz transformation.¹²⁷⁹

In 1928, Lewis sent a letter to James Partington relative to his possible nomination for a Nobel Prize. Lewis summarized his achievements as follows:¹²⁸⁰

"While I have flirted with many problems, I was for many years pretty loyal to the main task which I had set for myself, namely, to weave together the abstract equations of thermodynamics and the concrete data of chemistry into a single science. This is the part of my work in which I feel the greatest pride, partly because of its utility, and partly because it required a considerable degree of experimental

 ¹²⁷⁸ For a detailed story of the triplet state structure of molecules studied by Lewis, see Kasha 1984.
 ¹²⁷⁹ Coffey, 2008, pp. 187-188, 242, 305, Servos, 1984, p, 8.

¹²⁸⁰ Quoted in Jensen, 2005, p. 7.

skill ... That part of my work, therefore, which has given me the greatest amount of personal satisfaction was the study of the free energy of formation of the most important compounds and, in particular, the electrode potentials of the elements".

Section 6. Lewis' missing Nobel Prize

Several historians and biographers in the past puzzled with the absence of Lewis in the Nobel Awards. Many believed that Lewis must have been received the Nobel Prize for his excellent work in several fields that gave an impetus to the new specialty of physical organic chemistry that involved several theoretical and experimental methods of physical chemistry into organic chemistry. The most thorough discussion of this issue occurs in the monograph by Patrick Coffey dealing with early twentieth-century American physical chemists.¹²⁸¹ The most recent account on this issue summarizing the hitherto literature is a short paper by William B. Jensen.¹²⁸² It has been suggested that Lewis deserved the Nobel Prize for any one of the five achievements mentioned above, including his chemical thermodynamics discussed extensively. Lewis was nominated for the prize virtually every year between 1922 and 1944, in total, thirty-five times.

Most of the first reports issued by the Nobel committee between 1924 and 1934 concerned Lewis's work on chemical thermodynamics. Svante Arrhenius, in 1924, wrote the first report to evaluate Lewis' chemical thermodynamics. A relatively unknown Swedish electrochemist named Wilhelm Palmaer (1848-1942) wrote the subsequent three reports for 1932, 1933, and 1934. Theodor Svedberg (1884-1971) wrote the second report

¹²⁸¹ Coffey, 2008, pp. pp. 192-207, 217-221, 298-304, 322. ¹²⁸² Jensen 2017.

in 1926. Svedberg was a Swedish chemist active at Uppsala University. He received the Nobel Prize for his research on colloids and proteins using the ultracentrifuge.¹²⁸³

Arrhenius dismissed Lewis's theory of the chemical bond in one sentence: "It is rather insignificant, and the major part was done by Langmuir, and it is in opposition to the theory of Bohr, which is probably correct".¹²⁸⁴ Arrhenius was more favorable for Lewis' thermodynamics but criticized Lewis because he did not come up with an equation for strong electrolytes as van der Waals did for the real gases. Arrhenius entirely omitted in his report to mention Lewis' formula of the ionic strength, which is precisely what Arrhenius required in his report.¹²⁸⁵ It is not clear why Arrhenius neglected the ionic strength from his report and in general for his opposition to Lewi's work.¹²⁸⁶ However, it is true, that Lewis exerted severe criticism on the ionists' solution theory in one of his articles published in 1907.¹²⁸⁷ However, in a subsequent publication, Lewis' criticism was milder and recognized the value of Arrhenius' ionic dissociation theory.¹²⁸⁸

Svedberg's report in 1926 was much more positive than that of Arrhenius. Svedberg began with a description of the theory behind Lewis's formulation of chemical

¹²⁸³ Ibid, pp. 2-3.

¹²⁸⁴ Coffey, 2008, p. 192.

¹²⁸⁵ Ibid, pp. 192-193.

¹²⁸⁶ ibid, pp. 193-194.

¹²⁸⁷ Lewis, 1907, pp. 259-260.

¹²⁸⁸ Lewis, 1909, p. 6. Lewis referred to three kinds of evidence that Arrhenius brought forward to justify his dissociation theory; first, the various methods based on the colligative properties in solutions of determining the molecular concentration of the salts gave identical results, indicating that the number of dissolved molecules is greater than the number calculated from the simple chemical formula of the salt; second, in an aqueous solution of a strong electrolyte, the properties are purely additive. For instance, a solution of hydrogen chloride does not show the properties of the pure gas, but the distinct properties of the hydrogen cations and chloride anions. In other words, the solution of hydrochloric acid in water behaves as a mixture of hydrogen and chloride ions which are present in all acids and all chloride salts, respectively; third, the solution of electrolytes show electrical properties in solution as manifested by Kohlrausch's law of the additivity of conductivities at infinite dilutions, the agreement between conclusions drawn from conductivity and transference experiments, and the coincidence in the degree of dissociation calculated from conductivity and freezing point depression. support to the theory of ionic dissociation (Ibid, pp. 1-2).

thermodynamics and pointed out the importance of Lewis' work on strong electrolytes. "The area of which we are speaking is totally inaccessible to numerical calculations if we stay on the ground of the classical theory. But with the aid of Lewis's methods [of ionic strength], and by using the table that he has assembled, calculations are now possible with great exactitude. From the above investigations, it should be clear that the service that Lewis has made to chemical science through the creation of exact methods to determine the changes of free energy in chemical reactions has to be acknowledged as of the greatest value. [...] So it seems to the undersigned [Svedberg] that Lewis's work on chemical affinities is of such importance that it would deserve to be honored with a Nobel Prize in chemistry". However, Svedberg felt that "Several important points will become clearer in the near future because some of the ongoing or expected work will have been completed. It seems to me that it may be advisable to postpone the award of the prize for a few years".¹²⁸⁹ And with this conclusion, Svedberg blocked Lewis from the award. In the same year, Svedberg received the Nobel Prize in chemistry.¹²⁹⁰

As said, Palmaer, the secretary to the Nobel chemistry and physics committees, wrote the reports of 1932, 1933, and 1934. Palmaer made a cruel attack on Lewis's work on chemical thermodynamics in a crude attempt to deny him a Nobel Prize explicitly. So blatant were his efforts in this direction that Coffey became convinced that this was done on purpose. ¹²⁹¹ Palmaer was a close friend of Nernst,¹²⁹² with whom Lewis had an

¹²⁸⁹ Quoted in Coffey, 2008, p. 194.

¹²⁹⁰ Ibid, p. 195; Jensen, 2017, p. 3.

¹²⁹¹ Coffey gives a detailed account on this sad story (2008, pp. 197-200).

¹²⁹² Palmaer, a Swedish electrochemist, was active in supporting Nernst's Nobel candidacy. In 1920, he led a rebellion on the Royal Swedish Academy of Sciences, submitting a thirteen-page report on behalf of Nernst, opposing the recommendation of the Nobel Committee for Chemistry to reserve the Nobel prize for that year (Coffey, 2008, p. 158).

enduring enmity, since 1901 when he was working as a postdoctoral fellow in Nernst's laboratory in Göttingen. In addition, Lewis repeatedly exerted acute criticism on Nernst's work and noted the errors and weaknesses of his electrochemistry. Something that Nernst disliked, and did not forget.¹²⁹³

Special reports for Lewis' achievements in the theory of chemical bonding were written twice in 1932 and 1940 on behalf of the Nobel committee. In the 1932 report, Svedberg avoided making the errors and misinterpretations of Arrhenius's earlier comments. After a short description of Lewis' theory of electron paired bonding, Svedberg continues, "Without doubt, Lewis's discovery of the role of electron pairs in molecular structure, and his identification of an electron pair with a chemical bond, must be considered an outstanding achievement". However, he concluded, "There is every reason to admire the intuition which led Lewis to the idea of the concept of the electron pair as being responsible for the chemical bonding; but on the other hand, one should not be blind to the fact that Lewis's hypothesis has not had much significance for later research. Spectroscopy and wave mechanics together go far beyond Lewis's idea". Svedberg finally concluded, "As a concluding judgment, it seems justified to say that Lewis's theory of valence neither has been nor can become of such importance for chemistry that an award of a Nobel Prize should be motivated".¹²⁹⁴ Svedberg's assessment of Lewis' theory on chemical bonding was based on his paper of 1916, and in hindsight, advances in quantum physics and chemistry that had begun after Lewis left the field in 1923. On the other hand,

 ¹²⁹³ Jensen, 2017, p. 3. Coffey is revealing regarding Svedber's and Palmaer's involvement in the 1932 Nobel
 Prize (2008, pp. 202-203, and 204-296).
 ¹²⁹⁴ Ibid, pp. 200-201.

the Lewis-Langmuir electronic theory was popular amongst organic chemists from the 1920s to 1950s and became the basis for newly reformulated ideas of the chemical bond.

The last nomination of Lewis for the Nobel Prize on his theory of the electron pair occurred in 1840. This time, the Nobel committee asked Ludwig Ramberg (1874-1940) to prepare the report. Ramberg was a member of the chemistry committee and a professor of organic chemistry at Uppsala University. He was well known for his dislike of "the so-called electronic theory of organic chemistry". His report on Lewis's electron paired theory was essentially a replica of Svedber's report written about nine years ago. In the letter submitting his 1940 report to the chemistry committee, Ramberg wrote, "I submit my report on Lewis's valence theory. It has become a long story, but this is mainly because I discovered Svedberg's report of 1932, which both he and I had forgotten about. It contained everything that could be stated briefly, and therefore I had nothing to do but to put into writing that which could not be stated briefly".¹²⁹⁵ Ramberg's report ended with the rather contemptuous phrase: "From a pedagogical point of view, Lewis's theory undeniably holds quite a few advantages, perhaps mostly on an elementary level".¹²⁹⁶

Many believed that Lewis deserved to share the Nobel Prize of 1934 with Harold Urey. Lewis contributed to the separation and study of deuterium and its compounds, which had been of more direct chemical interest than Urey's discovery.¹²⁹⁷ Svedberg was again requested to prepare a report for the Nobel committee. Svedberg recommended sharing the

¹²⁹⁵ Ibid, pp. 298-299.

¹²⁹⁶ Ibid, p. 299.

¹²⁹⁷ The newspaper of Oakland, California, *Post-Enquirer*, published an article on 25 October 1934, in which speculated that "Dr. Gilbert Newton Lewis of the University of California, and Dr. Harold Clayton Urey, a former student at the university, were mentioned today in Stockholm dispatches as likely recipients of this year's Nobel Prize in Chemistry" (Coffey, 2008, p. 208)

prize between Urey and Lewis. However, later, Svedberg changed his mind and recommended Urey as the sole candidate for the prize. He rejected Lewis' candidacy on the ground that other workers were beginning to purify heavy water, and Lewis's monopoly on the chemical characterization of deuterium compounds was vanishing. Svedberg.¹²⁹⁸

In 1934, Lewis resigned from the National Academy of Sciences, in which he was elected in 1913. The reason for this resignation is not apparent since Lewis refused to state the real cause for his resignation. There are speculations about his resignation. The dispute over the internal politics of the institution or the failure of the candidates he had nominated to be elected might be some of the reasons. Another cause that led him to his decision to resign may have been sparked by resentment over the award of the 1934 Nobel Prize for chemistry to his student, Harold Urey. Lewis almost certainly felt he should have shared the Prize for his work on purification and characterization of heavy water.¹²⁹⁹

The last nominations of Lewis for the Nobel Prize occurred in 1944. This time on his phosphorescence research. The author of the 1944 Nobel report was Arne Fredga (1902-1992), an organic chemist and one of Ramberg's students. He was elected in 1943 as a member of the Royal Swedish Academy of Sciences, and in 1944, he became a member of the Nobel Committee for Chemistry. Fredga set aside two nominations, which referred to Lewis's collective scientific work, and wrote his report for a third one that referred to his nine publications on the luminescence of organic molecules during the past two years. Fredga's report was quite encouraging for Lewi's work. However, he expressed some reservations: "Definite and decisive results do not seem to me to be won yet, but his work

¹²⁹⁸ Ibid, p. 217-219. Jacob Bigeleisen (1919-2010), Lewis's student and research associate from 1941 to 1943, agreed with Svedberg's decision (Coffey, 2008, p. 220). ¹²⁹⁹ Ibid, pp. 221-222.

even without this is of definite interest".¹³⁰⁰ The committee judging the work of Lewis presented by Fredga sent its report to the Royal Swedish Academy of Sciences by saying: "The committee however wishes to wait for further development in this area and does not consider itself ready to award the prize to Lewis".

Prejudices, enmities, wrong evaluations, and hesitations were reasons that drifted Lewis away from the Nobel Prize. An additional cause for the failure of Lewis to receive the prize, especially in the last nominations, was the refusal of the committee to consider the collective scientific work of Lewis. Lewis had been nominated many times for the Nobel Prize, each time in separate areas of his work. However, the theory of chemical bonding, the acid-base theory, and photochemistry are components of a single theory that enriched the new branch of organic chemistry, the physical organic chemistry.

Conclusion of Part III

The third part of this dissertation describes the development of chemical thermodynamics at the hands of the three ionists, Nernst and Planck, and the subsequent transfer of this theory from Europe to America. Several internal and external factors have been examined which contributed to the formulation of this theory. External factors, such as the dominance of organic chemistry during the nineteenth century, the second industrial revolution, and the need for cooperation between physicists and chemists, were the most important. Classical thermodynamics and Gibbs, Duhem, and Helmholtz's advanced thermodynamics had little or no influence on the development of chemical thermodynamics by the ionistrs. Physicists, who had some knowledge in chemistry and chemists with some skill in

¹³⁰⁰ Ibid, p. 300.

mathematics, began to think about possible mutual benefits that might result from such a cooperation. The former confirmed their theories with the experiments that only chemistry could offer, and the latter found new interpretations for old chemical problems, such as chemical affinity and chemical equilibrium. It is worthwhile to recall that the pioneers of this tendency were Gibbs, Horstmann, and especially Duhem. However, the ionists were the scientists who achieved this goal. They succeeded in unifying physics and chemistry by using idiosyncratic thermodynamics for the formulation of their theories. The ionists developed their thermodynamics basically on two methodological approaches. The proportionality between ideal gases and dilute solutions, and the empirical reversible cycles. These modes of investigation allowed the ionists to use an easier way to explain physical and chemical processes and derive mathematical equations rather than through the strict application of the principles of classical thermodynamics, let alone the thermodynamics of the second half of the nineteenth century.

Ironically, each ionist found his way to physics through subjects related to organic chemistry. Arrhenius initiated his doctoral dissertation by determining the molecular weight of cane sugar using electrical conductivity measurements. Van 't Hoff suggested the tetrahedral stereochemistry of the carbon atom and illustrated the structure of organic molecules in three dimensions. Ostwald studied the acid catalysis of organic reactions, and in the larger part of his research dealt with the chemical and physical properties of organic substances. Arrhenius' experiment with cane sugar was unsuccessful but not useless. It allowed him to realize that specific chemical problems might be solved by electrical means. Under the influence of his supervisor, the physicist Eric Edlund, an expert on electrical theory who taught him practical matters in electrical research, he started conductivity measurements of electrolytes in aqueous solutions in the context of his doctoral dissertation. He realized quickly that electrical conductivity might be related to the chemical properties of electrolytes through their ability to conduct electricity. He then devoted his studies to revealing the relationship between chemical reactivity and the electrical conducting power of electrolytes (acids, bases, and salts) to determine the mass action law. Conductivity measurements brought him closer to the related theories of Hittorf, Kohlrausch, Clausius, and the two Norwegian chemists Cato Guldberg and Peter Waage and smoothly to thermodynamics.

Van 't Hoff abandoned his research on the stereochemistry of carbon and focused his attention on another subject, still within organic chemistry. He thought that the chemical formulae of organic compounds could have a more advanced role than being used as simple symbols for taxonomy. Molecular formulae of substances could be correlated with their properties. Van 't Hoff sought to explain organic chemistry within a physical and mathematical contour. The result of these studies was the two volumes book, the Ansichten *über die organische Chemie.* The merit of this book was not its content, which anyhow had a poor reception, but the influence exerted on van 't Hoff's thinking. The Swedish chemist investigated the inherent relationship between the chemical and physical properties of substances that brought him closer to physics and thermodynamics. This tendency became apparent in his next work, the *Étude de Dynamique Chimique*. During the period 1885-1886, van 't Hoff using thermodynamics inquired into several problems already hinted in his books that led him to correlate osmotic pressure with gas pressure, the dissociation theory of Arrhenius with the colligative properties of dilute solutions, and invent the kinetic principles of chemical reactions.

Ostwald was an excellent experimenter, but he did not significantly contribute to solution theory from a theoretical point of view. His work is somewhat related to physical organic chemistry, and his acquaintance with thermodynamics was made through his collaboration with Arrhenius and especially with van 't Hoff. Among the three ionists, Van 't Hoff relied the most on thermodynamics dealing with his theoretical pursuits. Still, Planck was the man who advanced the ionists' solution theory to a strictly theoretical basis from the first principles of thermodynamics.

The ionists' theory emerged as a byproduct of their efforts to deal with chemical problems. Ostwald's students originally transferred this theory to America in a similar pattern to that in Leipzig. Most of the first generation of American physical chemists appropriated this knowledge and struggled to find solutions to problems that the ionists' chemical thermodynamics had been unable to resolve. Since the ionists formulated their theory of solutions in analogy with the laws of ideal gases, it was incapable of describing the properties of real systems. Their theories did not apply to concentrated solutions and specifically, the ionic dissociation theory failed to explain the strange behavior of strong electrolytes. In this regard, most American chemists devoted their research endeavors to finding solutions for the description of non-ideal systems. The process of appropriation involved several scientists grappling to overcome local resistances and prejudices. These efforts successfully led to the propagation of chemical thermodynamics and eventually to a new discipline, the physical chemistry. Within the insecure scientific environment in which organic and inorganic chemistry dominated, the first generation of American physical chemists strived to establish themselves and the new science in their country. They started seeking new answers to old problems; they directed their efforts to construe the strange behavior of concentrated solutions and solutions of strong electrolytes. The measurement and application of free energies was another field of interest for a few American scientists. The most interesting figure amongst the first generation of American physical chemists was Lewis, whose research program served as a case study in this chapter.

Lewis endeavored to fill the gap between the rigorous thermodynamics of physicists and the practical but inexact thermodynamics of the ionists. Lewis introduced the term "exact" in equations that described the behavior of non-ideal systems (e.g., concentrated solutions, vapor pressure, and strong electrolytes). These equations incorporated quantities, such as the fugacity, activity, activity coefficient, ionic strength that embraced the properties of real systems. Furthermore, with his systematic study of the free energy of chemical reactions, Lewis provided new quantitative methods of measurements and applications to physicochemical systems, strengthening thus the hope of furnishing soon a table of free energy data as complete as the existing tables of thermochemistry in current textbooks of physical chemistry, and thermodynamics.

General Conclusions

This dissertation is a first attempt to outline the historical development of chemical thermodynamics, which led to modern chemical thermodynamics. By modern, I am not referring to the chemical thermodynamics taught today alone or within the context of physical chemistry. Instead, I am implying the science that Arrhenius, van 't Hoff, Ostwald, and Nernst developed during the late 1880s and by the American physical chemists during the first two to three decades of the twentieth century, having Lewis as the representative figure of this development. The core of current chemical thermodynamics is the ionists' solution theories corrected by Lewis to account for the irregularities of strong electrolytes, enriched by Gibbs, Duhem, and Helmholtz's theoretical considerations.

The present dissertation is divided into three parts. The first part contains a brief account of the early chemical thermodynamics or its prehistoric development that appeared during the first half of the nineteenth century. During this period, the seeds of new branches of chemistry were cultivated, while physicists formulated the two laws of thermodynamics. New fields of chemistry, such as electrochemistry, chemical kinetics, the chemistry of solutions, thermochemistry, and thermodynamics, were the building blocks of the earlier chemical thermodynamics. The emergence of the new branches of chemistry occurred in parallel with the organic and inorganic branches, which dominated, especially the first, during the whole nineteenth century. Thermodynamics, in particular, was the recipient of a hostile attitude from organic chemists. Organic chemists had excluded any contact with physicists and the products of their work. Therefore, in the early stages of the development of the new branches of chemistry and thermodynamics, there was no contact between chemists and physicists, let alone cooperation. The two leading sciences of chemistry and physics had a parallel growth that lasted until the 1880s. Chemists, rejecting any alliance with physicists, proceeded to synthesize new compounds (organic and inorganic), determine their physical and chemical properties, and find rules for the classification of old and new organic substances.

On the other hand, physicists studied the conditions under which chemical compounds are generated and destroyed in the electrolytic cells. Davy, Grotthuss, Faraday, de la Rive, Becquerel, and others disclosed the laws according to which chemical substances split when subjected to an electric current. They inaugurated the new science of Electrochemistry, which at one time, especially with Berzelius, had nearly absorbed the whole of chemistry. Hess, Dulong, Berthelot, and Thomsen measured the amounts of heat released or absorbed during chemical reactions and created Thermochemistry. Numerous thermochemical experiments conducted by Thomsen and Berthelot led these two chemists to propose a system in chemistry, which became very popular and long-lived. The principle of maximum work, in which all chemical changes occurring without the intervention of outside energy tend toward the production of bodies that liberate heat. However, this theory of chemical reactions could not anticipate changes in the physical state, such as fusion, vaporization, dissolution. These physical changes occurred spontaneously by absorbing heat. The inventors of thermochemistry, especially Berthelot, had to distinguish physics and chemistry to regard physical chemistry as an illusion. The final blow to this interpretation for the heat evolved in chemical reactions was given by the discovery that several spontaneous chemical reactions required absorption of heat to occur or by the consideration of reversible chemical reactions reaching the equilibrium state.

As established by Thomsen and Berthelot, thermochemistry was based on the first law of thermodynamics. The discovery of the law of the equivalence between heat and work by the "great four" (Mayer, Joule, Colding, Helmholtz) prepared the thermodynamic doctrine of the transformation of heat into work and vice versa. The young thermodynamics was created from all the existing experimental and theoretical pieces. The theories of the physical state changes, Clausius' deductions on vaporization phenomena, J. J. Thomson's experiments on fusion and Kirchhoff's explanation of dissolution formed the first material for the preparation of the second law of thermodynamics. Due to these observations and Carnot's theorem derived from his studies on heat engines, Clausius, William Thomson, and Rankine formulated the second law of thermodynamics using different methodological approaches. Fifteen years later, Clausius introduced the concept of entropy that was initially obscured by dubious disgregation.

In the second half of the nineteenth century, electrochemistry and thermodynamics entered a second, higher stage of development. Hittorf and Kohlrausch's investigations in electrochemistry and Raoult's in solution chemistry extended the primitive studies conducted by the first electrochemists. From the speculative description of the electrolysis process, electrochemistry reached the establishment of quantitative measures for the properties of the microscopic carriers of electricity in solutions. Hittorf studied the velocity of the ions and the fraction of the electricity they carried over the electrodes of the electrolytic cells. Kohlrausch investigated the electrical properties of the various classes of electrolytes and their dependence on concentration and temperature. However, none of these great electrochemists attempted to link the electrical properties of the electrolytes with their chemical reactivity. Raoult's experiments in aqueous solutions and various organic solvents established a simple relation between the dissolved substance's molecular weight and the solution's freezing point. Later he extended his investigations with regard to other properties of solutions known as colligative properties.

By the end of the third quarter of the nineteenth century, the two Norwegian chemists Guldberg and Waage presented an advanced chemical equilibrium and kinetics treatment. They discovered that the ratio of the active masses of the products to the active masses of the reactants of a chemical reaction in equilibrium was to a good approximation stable and equal to a constant, the equilibrium constant, which was unique for the particular reaction. Although historians and kineticists deny the work of the two Norwegians is the precursor of modern chemical kinetics, their contribution to the development of chemical thermodynamics is significant. The ionists had extensively used Guldberg and Waage's mass action law and carried out many experiments with solutions of weak electrolytes. Guldberg and Waage's theory inspired Ostwald's dilution law. Van 't Hoff brought this law closer to modern kinetics introducing the concept of reaction rates.

However, the concepts of thermodynamics were absent as interpretative tools for these experimental investigations. The sole exception was Horstmann, who employed the second law of thermodynamics. He used Clausius' concepts of entropy and disgregation to explain the equilibrium of the dissociation reactions at high temperatures. Horstmann gave some qualitative explanations for this chemical phenomenon but failed to obtain quantitative results. The limited experimental data precluded the calculation of the substances' disgregation in the various physical states. Apart from his boldness to use the second law of thermodynamics when confusion about the interpretation of this law persisted, Horstmann showed an essential property of dilute solutions: their analogy with the perfect gases, as manifested by the similar behavior of the disgregation of molecules in these two phases. This proposal played a critical role in the development of van 't Hoff's solution theory.

The approaches of Gibbs and Duhem to thermodynamics gave a new perspective in chemical thermodynamics. Their work revealed a treasure of new ideas that could have provided definite answers to chemists' problems in their laboratories. However, the rigor of their mathematics expressed in hundreds of equations, functions, axioms, and corollaries repelled chemists from reading their work. Besides, chemists were notorious for their lack of mathematical skills. Hittorf and Kohlrausch had used mathematics to formulate the laws derived from their experiments. However, their mathematics was simple and, therefore, applicable to the experiments performed in the laboratory.

The scrutiny of Gibbs and Duhem's thermodynamics discloses another essential feature, their tendency to use examples from chemistry to confirm their theories. This propensity to use empirical facts to confirm theories was observed more often amongst physicists than for chemists. When physicists realized the existing scarcity of experimental results, they started complaining. The dominance of organic chemists in the institutions of higher education, who resented mathematics and physics in general, prevented chemistry from accepting the products of physics. Organic chemists considered equations and functions as "contaminants" that threatened the "purity" of organic chemistry.

Concurrently with the deceleration imposed on the development of chemical thermodynamics by organic chemists, other factors seemed to favor the progress of this science. The second industrial revolution from England to the European mainland established new industries that demanded raw materials and other commodities. Research

617

began to shift from the small-scale production of the laboratory to the mass production in the factory. Therefore, it became necessary to develop new methods, experimentation, and structures adapted to industrial production needs. Chemists embarked on a new process of applying physical methods to increase the efficiency of chemical reactions to the desired direction and control the various stages of production. Thus, a new discipline emerged as a necessary transformation of pure chemistry to practical chemical engineering. The emergence of the new branch of chemical engineering with the new profession of the chemical engineer began to compete with pure chemistry and vindicate a share in the curricula of higher education institutions. Now, chemists and physicists began to work together. Physical methods applied to chemical problems gave a new impetus to industrial production, culminating in establishing industrial research laboratories. The process of unit operation applied to the chemical industry is a good example of this direction. Unit operation, involving a series of physical and chemical operations from the starting materials to the final products, required the cooperation between physicists and chemists.

The third part of this dissertation describes how thermodynamics was transferred to chemistry that marked the genesis of chemical thermodynamics, which is the central thesis of this dissertation. The research program and the scientific style of each ionist emerged from different influences, and their countries' scientific traditions were one of the subjects of this part. These very different traditions and influences from the immediate scientific environment in their countries led each scientist to undertake his particular investigation. In his dissertation, Arrhenius eschewed the directions of Thalèn and Cleve in Uppsala for a trivial subject in organic chemistry and began a physicochemical research program in mixing the theoretical and the electrical programs of Edlund and Pettersson at
Stockholm. To secure his primitive dissociation theory in his thesis, he invoked the expertise of a physicist (Clausius) and an organic chemist (Williamson). However, he did not avoid the negative criticism of his instructors who downgraded his dissertation. Van 't Hoff's chemical thermodynamics arose from translating the chemical structure of substances into their physicochemical properties and mixing his research with the German tradition of Horstmann, Pfaundler, Traube, Mitscherlich, and Pfeffer. Ostwald's research began in Latvia, a country with a limited research tradition. Ostwald sought to escape from this backward environment and formulate a research program making chemistry less empirical and more scientifically oriented. To achieve this program, Ostwald desired to move from Riga to a German University. He knew that he would have the opportunity to complete his research program studying with leading figures in chemistry in Germany.

Each ionist took a different path in formulating his particular theories. He chose his scientific area of investigation, his methodology to approach problems, and his tools to accomplish his research. Arrhenius sought to disclose the laws that governed the electrolytic dissociation; van 't Hoff strove to explain the osmotic pressure in dilute solutions by introducing Avogadro's law for the ideal gases based on the analogy with dilute solutions. In contrast, Ostwald compared various methods to study the reactivity of substances (mainly acids and bases) in chemical reactions with or without catalysts. The connecting thread that brought the three men together was the synthesis of several favorable events. First, the distribution of Arrhenius's dissertation by himself to scientists abroad, one copy of which reached Ostwald, second, Ostwald's talent to assess the value of Arrhenius' dissertation, and third, the interest of each ionist in the work of the others. This mutual interest arose from the need of each ionist to find solutions to specific problems

encountered in his work. Arrhenius's ionic dissociation explained the mysterious factor *i*, which appeared in almost every equation of van 't Hoff's solution theory. At the same time, this achievement confirmed the truthfulness of Arrhenius' dissociation theory. Ostwald perceived that the electrical properties of compounds suggested by Arrhenius nicely accorded with his experiments on the reactivity properties of substances performed by his volumetric and optical methods. On the other hand, Arrhenius saw that Ostwald's experiments affirmed his hypothesis connecting electrical conductivity with chemical reactivity.

The three ionists never used the term chemical thermodynamics to characterize the whole of their theories. They probably thought that chemical thermodynamics was termlimited in scope, restricting the prospects of advancing their work at the stage of a new discipline. Thus, they chose to label their theories with the more general and perhaps more convincing physical chemistry. After all, the future organization of the new discipline would incorporate thermodynamics as a separate chapter in the textbooks together with other conceptions of physics and chemistry. But, what sort of thermodynamics did the ionists employ in formulating their solution premises? The second law of thermodynamics and the concept of entropy were absent in ionists' work, let alone the potentials of Gibbs and Duhem and the free energy of Helmholtz. Although van 't Hoff was familiar with Horstmann's work, which inspired the analogy between perfect gases and dilute solutions, he neglected the German physicist's theoretical treatment of the dissociation reactions of substances based on Clausius' entropy and disgregation. In his analysis of the osmotic pressure, Van 't Hoff focused on Avogadro's law and the physical properties of ideal gases. In contrast, his research on chemical equilibrium was a byproduct of his chemical kinetics.

We saw that van 't Hoff was one of the scientists who actively participated in developing kinetics. A tremendous amount of experimental work had been performed, and suitable differential equations were set up and solved in a few decades around the turn of the century. The relationship between equilibrium constants and rate constants was well established at that time. Today, chemical kinetics and equilibrium and non-equilibrium thermodynamics are two well-defined branches of physical sciences. Phenomenological theories of the reaction rates belong to chemical kinetics, whereas the study of equilibrium states, energy dissipation, or entropy production in chemical reactions pertains to thermodynamics. Current textbooks of physical chemistry describe the principles of both sciences.

Arrhenius, on the other hand, never used thermodynamics in the strict sense described in previous chapters. His electrolytic dissociation theory needed not the aid of thermodynamics to develop. The tension for priority between the experimentalist Arrhenius and the theorist Planck, who derived the electrolytic dissociation and the osmotic pressure from the first principles, shows the gap between the methodological approaches of these two scientists. A theorist who explicitly used the second law of thermodynamics and an empiricist who based his theory on experimental facts. Root-Bernstein claims that even Nernst had not used thermodynamics in his electrochemistry. He asserts that electrochemistry developed as a separate specialty of chemistry in parallel with thermodynamics¹³⁰¹. However, as Lewis had shown, the electromotive force of the galvanic cell was closely connected with Gibbs or Helmholtz's free energy and the equilibrium constant. Chemists and physicists had used galvanic cells to measure the free

¹³⁰¹ Root-Bernstein, 1980, pp. 552-553.

energies and equilibrium constants for chemical reactions. Electrochemistry and thermodynamics were separated as distinct branches of physical chemistry much later. When electrochemistry extended its scope to electrodynamic and quantum phenomena.

The objectives of the ionists were beyond the simple formulation of new laws in solution chemistry. They wanted to establish the domain of their theories as a new, autonomous, academic discipline and profession in parallel with organic and inorganic chemistry. Ostwald was the most enthusiastic and inventive proponent of this idea. Ostwald skillfully organized and administered an efficient plan to achieve this goal. His physical chemistry laboratory established at the University of Leipzig, his exciting experimental research program, his fame as an ingenious experimenter and an excellent teacher, and his massive scientific work, together with his exuberant character, were the best credentials to make his dream come true. During the last two decades of the nineteenth century, Ostwald was the most recognizable chemist, and his star shone in the scientific constellation. Ostwald's campaign to promote the new discipline brought an excellent reputation to him and his laboratory, soon becoming an international research center for foreign students. From 1889 until 1906, 44 doctoral students and postdoctoral fellows from England, Canada, and the US, 38 were from various American Universities, were trained in Ostwald's laboratory.¹³⁰² The American chemists became the best representatives of the ionists' new discipline of physical chemistry. Another step forwarding the promotion of the new discipline was the publication of a journal devoted to physical chemistry carrying this name. In February of 1887, Ostwald with van 't Hoff as a coeditor circulated the first volume of Zeitschrift für Physikalische Chemie, Stöchiometrie und Verwandtschaftslehre,

¹³⁰² Dolby, 1977, pp. 291-292; Servos, 1990, pp. 53-69.

which amongst others contained articles by van 't Hoff, Arrhenius, Ostwald, Lothar Mayer, Mendeleev, Guldberg, Thomsen, Le Chatelier, Raoult, Ramsey, and Planck. In the same year, Ostwald published his book *Lehrbuch der Allgemeinen Chemie* (textbook of general chemistry), which was an epitome of chemistry in these days, and the first textbook in chemical thermodynamics. This book became popular amongst chemistry students and for students of other disciplines. Ostwald admitted that "these two events were crucial for the emergence of physical chemistry as an independent entity within the group of sister sciences and permitted its further and ever more rapid development".¹³⁰³

In addition to writing articles and editorials for the *Zeitschrift*, Ostwald published numerous original articles, essays, and memoirs of great scientists from all over the globe. Ostwald aimed at "correcting" the "lack of knowledge of those great works on which the building of science rests". The German essays and translated into German works of foreign authors from all areas of the physical sciences were collected and published in a series of books, under the general title *Klassiker der exakten Wissenschaft*en (classics of the exact sciences). The first volume in 1889 contained Helmholtz's *Die Erhaltung der Kraft*. In 1894, the physicist Arthur von Oettingen took over the publication and remained the editor until 1920, when the son of Ostwald, Wolfgang Ostwald (1883-1943), took over the task. Ostwald initially continued to publish the chemistry volumes until his replacement by Richard Abegg. 195 volumes had appeared by 1915, before the first interruption due to the First World War until 1919.¹³⁰⁴

¹³⁰³ Ostwald, 2017, pp. 154-155.

¹³⁰⁴ For the historical development of the series, see Dunsch and Müller, 1989.

Nevertheless, the transformation of chemical thermodynamics into something bigger as the new discipline of physical chemistry was not an easy task. Its reception from the scientific community was very slow and under severe tensions and opposition. Tensions between theorists and experimenters, interdisciplinary tensions for academic supremacy, and professions, especially in the industrial sector. An apparent tension between a theorist and an experimenter was manifested in the priority dispute between Arrhenius and Planck over the ionic dissociation theory and the relative merits of Planck and van 't Hoff's formulation of the osmotic theory. However, the tension between theorists and experimenters could not be generalized between chemists and physicists. Many physicists sided with Arrhenius, whereas several chemists objected to Arrhenius' ionic dissociation theory. As we have seen, the most vigorous opposition came from the British organic chemists.

On the other hand, most physical chemists and even physicists in Germany and the US espoused the ionists' chemical thermodynamics to successfully integrate theory in the experiment. Several physical chemistry laboratories were established in Germany. In 1890, Nernst directed the first department of physical chemistry at Göttingen instituted by the Prussian Government. Physical chemistry and electrochemistry held a prominent place in the chemistry departments at the University of Würtzbourg, since 1875 when Kohlrausch was appointed as a physics professor. In 1896, the Berlin Academy of Science bestowed on van 't Hoff, the chair of physical chemistry at the local University. Wherever physical chemistry departments or laboratories were not anticipated, individual chemistry and physics professors taught physical chemistry courses preparing their students for practical work. The young universities in America were much more interested in physical chemistry

than were their European counterparts. They considered physical chemistry as fundamental science. Bancroft and Trevor, for instance, established at Cornell University a department of physical chemistry. When he returned from Ostwald's laboratory to his native country, Noyes founded a physical chemistry laboratory at MIT. Similarly, Richards and Lewis inaugurated their physical chemistry laboratories, the first at the University of Harvard and the second at the University of California, Berkeley. Furthermore, following the example of Ostwald and van' t Hoff, Bancroft established the first American journal of physical chemistry in 1896. Noyes was the editor of the journal in the period of 1952-1964. He was the chief editor of the *Journal of Physical Chemistry* until 1932. In 1997, the journal split into *Journal of Physical Chemistry A* (containing articles on molecular theoretical and experimental physical chemistry) and *The Journal of Physical Chemistry B* (containing articles on solid-state, soft matter, liquids, etc.) due to the ever-growing amount of research in this area. A further split occurred in 2007.¹³⁰⁵

Physical chemistry in France was poorly developed. Prominent French chemists, like Berthelot, Le Chatelier, or Brillouin, focus on their research programs. Their way of thinking was nurtured by the French tradition. In contrast to their American colleagues, they were less receptive to the ideas of the ionists. An exception to this tendency was Pierre Duhem. Duhem had conceived the merits of physical chemistry and sought to convince his fellow chemists, emphasizing the achievements of the new science and the benefits that French chemistry would have obtained by adopting the theories, the methods, and the experimentation of physical chemistry. "Prenons-y garde si la mème routine, si la même haine de tout ce qui renferme une idée neuve, la mème horreur de tout ce qui exige un

¹³⁰⁵ Barbara, 1996, pp. 12695-12696/

nouvel effort intellectuel, arrêtaientplus longtemps, en France, l'essor de la chimie physique et de l'électrochimie, la vérité, outragée par ceux qui ont pour mission de la servir, se vengerait encore une fois en nous infligeant un nouveau désastre" industriel et, cette fois, l'industrie des grands produits minéraux serait sans doute frappe".¹³⁰⁶

In 1903, the *Société de Chimie Physique* launched the French journal of physical chemistry, *Journal de Chimie Physique*. The scope of the journal was "to cover all the major fields in which French physical chemists and chemical physicists are active: theoretical chemistry, chemical kinetics, electrochemistry, catalysis, organized media (supramolecular chemistry), spectroscopy, thermodynamics, and polymers". The journal ended its publication in 1999, because "of a general trend in Europe to replace national publications with international ones to better compete with American publications".¹³⁰⁷

Ostwald thought that another way to raise physical chemistry to a higher status within the scientific community was to demonstrate that physical chemistry can give definite answers to problems of other sciences. Therefore, he strove to integrate methods, theories, and experimentation of physical chemistry into the educational system and the research programs of other sciences. Thus, in addition to the *Lehrbuch*

¹³⁰⁶ Duhem, 1899. pp. 273-274. "Let us beware: if the same routine, if the same hatred of everything that contains a new idea, the same horror of everything that requires a new intellectual effort, were to arrest any longer the launch of physical chemistry and electrochemistry in France, then the truth, outraged by those whose mission is to serve it, would once more take revenge on us, inflicting a new industrial disaster. This time, the industry for the large scale production of mineral products would undoubtedly be struck". ¹³⁰⁷ The French journal was incorporated into a new journal resulting initially from a cooperation between the French and the German Chemical Societies. This new journal, called *ChemPhysChem* launched in 2000 and covered both Chemical Physics and Physical Chemistry. ChemPhysChem is currently part of Chemistry Europe, an association of 16 chemical societies from 15 European countries. It publishes a family of academic chemistry journals. https://chemistry-europe.onlinelibrary.wiley.com/doi/full/10.1002/cphc. 201900937; Bebensee et al., 2020, p. 4.

der Allgemeinen Chemie, he began writing manuals for students attending disciplines other than chemistry. He placed physical chemistry as a dynamic alternative to inorganic chemistry and analytical chemistry. In this task, Ostwald found assistance from van 't Hoff. The latter taught chemistry, mineralogy, and geology, and thus, he was aware of the objectives of these sciences. Little information is available on whether Ostwald's attempts to influence the curricula of disciplines other than chemistry were successful. Also, the lack of information regarding the intrusion of physical chemistry into scientists' research activities of different disciplines does not allow a safe conclusion about interdisciplinary tensions (however, see below).

Eventually, the theories of the ionists were generally accepted, and they turned themselves to other scientific topics. Van 't Hoff and Arrhenius began to investigate interdisciplinary problems in terms of physical chemistry theory. Ostwald followed another road. In late 1890 or early 1891, he began explicitly to formulate his version of a theory of energy. In his energetics (utterly different in spirit and content from Duhem's energetics), Ostwald abandoned the second law of thermodynamics and the concept of entropy and focused his attention on constructing a world view exclusively from energetic material without using the concept of matter. This theory was based solely on the first law of thermodynamics and considered that every object or system is constituted of energy of different forms. Energy is characterized by two distinct factors, its intensity, and capacity.¹³⁰⁸

¹³⁰⁸ Robert Deltete has done a thorough study on Ostwald's program on energetics. He examined the chemical origin of Ostwald's energetics, his attempts to develop a consistent and coherent theory of energetics, the opposition to this work and Ostwald's replies, and finally the fall of energetics (Deltete, 1983).

Arrhenius became active in geology (the origin of ice ages), astronomy, physical cosmology, and astrophysics, accounting for the solar system's birth by interstellar collision. He considered radiation pressure accounting for comets, the solar corona, the aurora borealis, and zodiacal light. Arrhenius, in 1896, was the first to use basic principles of physical chemistry to assess the extent to which increases in atmospheric carbon dioxide will increase Earth's surface temperature through the greenhouse effect. Through his spectroscopic observation of the infrared radiation absorbed by the carbon dioxide of the Earth's atmosphere, and using the Stefan–Boltzmann law (which describes the total energy radiated from a black body (hated body) in terms of its temperature), he calculated the change in the rate of heating Earth's surface.¹³⁰⁹ He concluded that "if the quantity of carbonic acid increases in geometric progression, the augmentation of the temperature will increase nearly in arithmetic progression".¹³¹⁰ This statement, known as *Arrhenius' rule* for the climatic change, is still in use today.

Using physical chemistry, Arrhenius contributed to geological science, attempting to explain the cause of the eruption of volcanoes. He considered that water at high temperatures (1000 to 2000 °C) of the magma becomes a stronger electrolyte than silicic acid and thus decomposes the silicate salts. The magma expands and penetrates the crevices of the volcano. When the magma is cooled, the reverse process takes place. Water is liberated and exploded violently under low pressure.¹³¹¹ Arrhenius published this interesting hypothesis in a Swedish journal. However, he was unable to confirm this hypothesis, which was soon forgotten.

¹³⁰⁹ Arrhenius, 1896.

¹³¹⁰ Arrhenius, 1897, p. 15..

¹³¹¹ Arrhenius, 1900.

The issue that raised interdisciplinary tension between physical chemistry and biology was the toxin-antitoxin (or antibody-antigen) relation in living systems. Arrhenius working with the Danish bacteriologist Thorvald Madson (1870-1957), claimed that the reciprocal action of toxin and antitoxin is of the same nature as a chemical reaction. The German wining the Nobel Prize, bacteriologist Paul Ehrlich (1854-1915), seemed to corroborate this hypothesis. Ehrlich specified the type of the chemical reaction as a possible neutralization process of toxin by antitoxin. Using the mass action law, Arrhenius attempted to quantitate the toxin-antitoxin reaction as a chemical equilibrium linked to the interaction of a weak acid and a weak base. Arrhenius and Madson successfully applied the mass action law to a large number of quantitative observations of toxins-antitoxins reactions found in the literature. In 1903, Ehrlich invited Arrhenius to Germany to exchange views about the issue of toxin-antitoxin interaction. To the astonishment of the Swedish, Ehrlich had abandoned the chemical interpretation and inclined towards the biological side of the problem based on his old side-chain theory. For Ehrlich, neutralization had now a completely different meaning. He interpreted the toxin-antitoxin interaction as a binding procedure in which the antitoxin binds to the toxin through unique chemical structures. Borrowing a concept used by Emil Fischer to explain the interaction between an enzyme and its substrate, Ehrlich proposed that the toxin-antitoxin binding was like the fit between a lock and key. He called this theory a *side-chain theory*. He published the first part of his sidechain theory in 1897 and its full form in 1899 in a lecture he delivered to the Royal Society in London.¹³¹² In a lecture of 1904 entitled Mutual relations between toxins and

¹³¹² Ehrlich, 1899.

antitoxins Physical chemistry versus biology in the doctrines of immunity,¹³¹³ Ehrlich launched a scathing attack on the physicochemical approach. Arrhenius responded with a book published in 1907 having the symbolic title *Immunochemistry*.¹³¹⁴ The book was a collection of six lectures delivered at the University of California, in Berkeley, during the summer session of 1904. The object of the lectures was to criticize Ehrlich's biological approach to immunity and to illustrate the application of the methods of physical chemistry to the study of the theory of toxins and antitoxins.

An interdisciplinary tension, this time, between physical chemistry and inorganic chemistry, occurred, although this tension was personified by Alfred Werner's resignation from the editorial board of the *Zeitschrift für Inorganische Chemie*. The founder of the coordination chemistry in a letter of June 23, 1904, to Richard Lorenz, editor of the journal, announced his resignation because "it [the journal] has gradually developed so strongly in the physicochemical direction that it no longer meets the needs and expectations of the pure inorganic chemist".¹³¹⁵ At that time, the methods of physical chemistry gained preponderance in the educational system, and courses of general chemistry were gradually transformed into elementary physical chemistry courses.¹³¹⁶ When and to what extent is the conflict between inorganic chemistry, analytical chemistry, and physical chemistry for primacy at higher education institutions is not clear.

When van 't Hoff accepted the new position at the University of Berlin, he continued contributing to the development of physical chemistry for the benefit of the

¹³¹⁴ Arrhenius, 1907.

¹³¹³ Ehrlich, 1904. This lecture was given at the John Hopkins University.

¹³¹⁵ Quoted in Kauffman, 1966, p. 678.

¹³¹⁶ Ibid.

German industrial sector. He began to study the origin of oceanic deposits and the conditions of the formation of oceanic salt deposits, particularly those at the area of Stassfurt, using Gibbs's phase rule as more appropriate to tackle the subject. He investigated the phase equilibria of the various quantities of individual salts that formed from the Stassfurt minerals after the evaporation of water at a constant temperature. He also studied the form, the order, and the quantities of the salts and their development with time, temperature, and pressure. This important theoretical study was very beneficial for the German potash industry.¹³¹⁷

In summary, this dissertation is a first attempt to outline the historical development of chemical thermodynamics, emphasizing the period in which it became a distinct specialty within the science of chemistry. The period in which the ionists began to use theories systematically from physics to interpret their experimental findings.

. Two final sentences as an epilogue of this dissertation: As with any science, the formation of chemical thermodynamics presupposes the development and construction of a specific scientific whole of theories and experimentation that preceded and made available to ionists. Thus, the issues raised in thus dissertation acquire a dynamic character regarding the evolution of chemical thermodynamics, long before the historiographically accepted period of its birth as a new science.

¹³¹⁷ Snelders, 1981b, p. 580.

List of Figures (with captions)



Fig. 1.1. Propagation model of Theodore Grotthuss. When the water molecule represented by **oh**, yields its oxygen **o** to the wire filament (the pole) +, its hydrogen **h**, being along the route of the electric current, combines with the arriving oxygen **o'** of neighboring water molecules, of which the hydrogen **h'** recombines with oxygen **r**, etc. The same process occurs in the opposite direction. The water molecule **QP**, which, by yielding its hydrogen **Q** to the negative pole -, is immediately rehydrogenated by the arrival of the oxygen molecule **X**. This succession of decomposition and recombination of the water molecules will continue until it is completely decomposed. (Grotthuss, 1806, p. 72).



Fig. 1.2. Propagation model of André-Marie Ampère. A scheme designed for the decomposition/recombination of the water molecules. Here, o and h denote the oxygen and the hydrogen atom, respectively. The spheres indicate the electric atmospheres surrounding the internal electricity of the atoms. m, m^I, m^{II}, m^{III}, ... represent the chain of the water molecules oriented to the positive and negative pole of the battery (Ampère, 1824, p. 72).



Fig. 1.3. Propagation model of Michael Faraday. The propagation combines increasing and decreasing affinities between particles as and particles bb of the opposite type. (Upper row). Particle a can only move towards the pole P if it meets a particle b of moving towards the pole N. The movement is due to the increased affinity of the particle a to particle b in their path; at the same time, there is a decrease in affinity between the particle a, and the particle b, which has already met. (Lower row). Particle a now arrives at the pole P. it is set free because the particle b of the opposite kind, with which was the moment before in combination, influenced by the electric current, shows a more significant attraction for the particle a', which is before it in its course than for the particle a, towards which the affinity has weakened (Faraday, 1951, pp. 69-70).



Fig. 1.4. Propagation model of John Frederic Daniell and William Allen Miller. A, B, C., etc., are a series of particles of chlorine. a, b, c, etc., a series of particles of potassium. XY is a central line or a diaphragm. Z and P are the two electrodes. State 1 represents the arrangement of the particles before the passage of the electric current. The particles A, B, C., etc., combine with particles a, b, c, etc. to form molecules of potassium chloride. State 2 represents the arrangement of the ions after a single equivalent of each ion has been disengaged at the electrodes. Thus, each particle has moved half a step towards the respective electrode and combines with the next adjacent particle. The new molecules Ba, C_b, Dc, etc., would form a chain between the electrodes. State 3 represents the arrangement of the garticle from each chlorine and potassium has crossed the central vertical line, and therefore, one equivalent would thus be transferred, while two particles would have been disengaged (Daniell and Miller, 1844, p. 2).



Fig. 1.5. Propagation model of Wilhelm Hittorf. (Top) A raw of adjacent molecules (line a). The electric current decomposes each molecule into the cation turned towards the cathode and the anion towards the anode. Then (line b), the two ions separate and move in opposite directions until they meet a neighboring ion, itself migrating. This process requires an inversion of the position of the molecules to ensure that each cation and anion turned towards the same electrode. The two ions are represented one below the other and move horizontally (line c). The number of equivalents of the cations and the anions at the borders of the respective electrodes should be proportional to the distance traveled by each cation and anion moving in the opposite direction. (Middle) The result is when cations and anions each move at a 1/2 distance. (Bottom) The result is when the anion moves 1/3 and the cation 2/3 of the distance (Hittorf, 1889, pp. 52-54).



Fig. 1.6. Propagation and the dynamic molecular decomposition/recombination model of Svante Arrhenius. Molecules AB and A_1B_1 are separated by an imaginary surface mm_1n of constant total electricity enclosing the molecule A_1B_1 . A, A_1 are the positive ions, and B, B_1 are the negative ions (above) (Arrhenius, 1884b, pp. 8-9). Proposed reconstruction of the model for electrolytic conduction resulting from the interaction of his circular currents according to Clausius-Williamson hypothesis (below) (Root-Bernstein, 1980, p. 83).



Fig. 2. Formation of the molecule AB according to Ampère geometrical scheme. (1) The electronegative particle A and the electropositive particle B with the surrounding electrical atmospheres of opposite signs of electricity. (2) The atoms A and B approach and the two electrical atmospheres begin to overlap. (3) The final stage of the formation of the molecule AB, retaining their opposite partial charge (Ampère, 1824, p. 73).



Fig. 3. Various forms of volta-electrometers that was designed by Faraday. He constructed in total seven such apparatuses. Each volta-electrometer is used for a particular group of experiments. For instance, the volta-electrometer on the right is employed for a succession of experiments and the collection of large quantities of gases (Faraday, 1951, pp. 122-125).



Fig. 4. Daniell's voltaic cell. It produces an electric current of constant intensity (left). The battery consisted of several connected cells (right) (Daniell, 1836, pp. 106-107).





Fig. 5. Two electro-magnetic engines (electric motors) constructed by Joule in 1838 and 1839 (JSP, 1884, pp. 4-6, 16-17).



Fig. 6. Illustration of the magnetization theory of Joule. (a) Section of the magnetized iron bar with six atoms represented by black circles. (b) The shadowed circles around the atoms represent the atmospheres of electricity. (c) The shadowed ovals represent atmospheres of electricity moving in planes at right angles to the magnet's axis (JSP, 1884, pp. 50-53).



Fig. 7. Experimental setup of Joule for measuring the heat of combustion during electrolysis. (a) An individual voltaic cell consisted of a glass jar and the two electrodes immersed in a dilute solution of sulfuric acid. An air pump covers the jar to operate in a vacuum for more accurate results. (b)The pair of the platinum (p) and the zinc (z) electrodes. (c) An array of ten such jars connected in a series provide the necessary electric current for the electrolysis. The decomposition cell is connected on the one hand with the battery and on the other with a galvanometer. (d) The diagram of the measured quantity of electricity during ten consecutive time intervals in dilute sulfuric acid in the decomposition cell. (e) Results of the same type of experiments with a solution of sulfate of oxide of zinc in the cell. (f) The double glass jars were used to measure the heat of combustion outside the electrolytic cell. The combustible material is placed within the smaller jar reacting with an atmosphere of oxygen. The space left between the two jars contains water. (Joule, 1841, p. 98; JSP, 1884, pp. 88-96).



Fig. 8. Representation of the paddle-wheel apparatus of Joule to measure the mechanical equivalent of heat (JSP, 1884, p. 302-305).



Fig. 9. The revolving electromagnet constructed by Joule confirms that the calorific effect on the rotating electromagnet coil is not transferred from the permanent electromagnet but is generated from work done by the permanent electromagnet to the rotating coil (JSP. 1884, p. 125).



MÉMOIRE SUR LA CHALEUR

Fig. 10. Lavoisier's ice calorimeter. (f, bottom left) The inner chamber holds the animal; (a) the ice layer, which insulates the middle layer of ice (b). The amount of ice that melts is proportional to the amount of heat released in the animal chamber. Laplace constructe a similar ice calorimeter (Lavoisier and Laplace, 1783).



Fig. 11. Dulong's water calorimeter. Water flowing into the entry gasometer (left) is controlled at T to allow the ventilation of the chamber. Similarly, the rate of water is controlled at the exit of the gasometer by the siphon H so that the pressure in the chamber remains constant. Before leaving the chamber at EE', the exiting gases pass through a serpentine tube, giving heat to the water in the calorimeter (Dulong, 1841).



Fig. 12. Respiratory physiology apparatus of Henri Victor Regnault and Jules Reiset. In this closed-loop device, oxygen is supplied to the dog by a tube on the left. The tubes on the right are used to remove the carbon dioxide. Carbon dioxide is removed by an absorbent and then returned to the respiration chamber to be used again. Weighing of the absorption vessels allowed measurement of carbon dioxide produced. Oxygen is continually delivered to replace that used up by the animal. The oxygen consumption is measured by the amount required to maintain a constant pressure for the system (Regnault and Reiset, 1849).



Fig. 13. Hittorf's apparatus for measuring the velocities of ions. (a) The cylinder contains the solution of the electrolyte and the two electrodes. (b) The complete setup of the apparatus. The cylinder is mounted on a horizontal ground-glass plate and covered by a bell-glass to prevent evaporation of the solution, increasing thus its concentration (1899, pp. 57-60).



Fig. 14. Kohlrausch's sine-shaped alternating current electrical conductivity apparatus. Here, m is the magnetic plate and M, the multiplier (Kohlrausch, 1874, p.54).



Fig. 15. Kohlrausch's electrical conductivity experiments. Plots of the absolute electrical conductivity values (ordinate) against the concentration of electrolytes expressed in percentage of the dissolved electrolyte (abscissa). (a) Various univalent and bivalent electrolytes, as well as the weak acids oxalic acid, tartaric acid, acetic acid, (b) The temperature dependence of the absolute electrical conductivity of four strong monobasic and polybasic acids, HCl, HNO₃, H₂SO₄, and H₃PO₄, (c) The temperature dependence of the absolute electrical strong acids (Kohlrausch, 1876a).



Fig. 16. (a) Illustrations of Helmholtz's polarization model (Helmholtz, 1879) and (b) Gouy-Chapman's polarization model (Gouy, 1910; Chapman 1913). In both models, a double layer of opposite charges is formed at the interface between the metal of the electrode and the electrolytic solution. Helmholtz's double layer is a static construction. In contrast, the Gouy-Chapman model is dynamic, thus allowing the influence of the thermal motion of the ions of the electrolyte on the stability of the layer (reproduced from Gongadze et al., 2009).



Fig. 17. Andrews' Experiment on Carbon Dioxide. Pressure-volume curves (the volume increases from bottom to top, and the pressure increases from left to right) for carbonic acid (carbon dioxide) were measured by Thomas Andrews and reported in his 1869 paper. The isothermal curves above 31.1 °C (the critical point of carbonic acid) are approaching the ideal Boyle isotherms, while those below 31.1 °C break in two points. When condensation begins with a subsequent diminution of volume, the pressure remains constant until the second point at which the entire mass has become liquid, and the pressure increases rapidly as the volume continues to decrease. The segment of the curve between these two points, representing the condensation of the gas, is a straight line parallel to the axis of volume (Andrews, 1869, p. 583).



(a)

Fig. 18. (a) James Thomson's pressure-volume curves of Thomas Andrews experiment. Reproduced in his 1871 paper. Thomson argued that a minimum and maximum curve should replace the straight lines on the 21.5 °C and 13.1 °C isotherms (Thomson, 1871, p. 281). (b) The relation between pressure and volume of a real gas after van der Waals' equation. It depicts the change of the state of the real gas along the isothermal curve ABCDEFG. The horizontal coordinate represents the volume, and the vertical coordinate represents the pressure (van der Waals, 1875, p. 358).


Figure 19. (a) Schematic representation of Gibbs' thermodynamic surface, containing points located by the entropy η , the volume v, and the internal energy ε . Each point on the surface represents a state of the system characterized by unique values of energy, entropy, and volume. For a constant value of energy, a point in the figure represents a state as a function of η and v [ε (η , v)]. Arrows of a point on the surface measure the slopes of the tangent planes on the surface parallel to the direction of the axis of the entropy η for a fixed value of v, according to Eq. (6.2), or parallel to the direction of the axis of the volume v for a fixed value of η , according to Eq. (6.3). The tangent planes determine the temperature and the pressure of the state of the system at a particular point with coordinates η and v. (b) Schematic representation of the developable surface that has been traced by the rolling motion of the tangent plane depicted in the scheme (a).



Fig. 20. Schematic illustration of the flat derived surface (SLV) encircled by the envelope of the developable characters created by the rolling motion of three tangent planes over the primitive surface. The figure shows the regions of the coexistent phases of solid-vapor, solid-liquid, and vapor-liquid mixtures along with the tie-lines. The projection of the primitive surface on the entropy-volume plane depicts a heuristic representation of Gibbs' primitive surface. The three developable surfaces together with the triangle of the derived surface constitute the surface dissipated energy (see Chapter 6, section 1).



Fig. 21. The plane (ε , η) perpendicular to the axis of the volume v passes through point A, which represents the initial state of the body. MX is the section of the plane with the surface of dissipated energy. Q ε and Q η are sections of the planes at $\varepsilon = 0$ and $\eta = 0$, and therefore parallel to the axes of the energy ε and the entropy η respectively. AD and AE are the energy and entropy of the body in its initial state. AB and AC are its available energy and the available entropy, respectively. When cither the available energy or the available entropy of the body is 0, the other quantity has the same value. In this case, each quantity may be varied without affecting the other (GSP, 1906, p. 51).



Fig. 22. The horizontal projection of Gibbs' primitive surface (solid line) and the derived surface (dotted line) on the entropy-volume (η , υ) plane. Between LL' and VV' is a liquid-vapor mixture. Between SS" and VV" is a solid-vapor mixture, and between SS'' and LL''' is a solid-liquid mixture. L''LL', V'VV'', and S''SS''' are the boundaries of the surfaces which represent, respectively, the stable states of liquid, vapor, and solid. C is the critical point. The dashed lines in the area of the coexistent liquid-vapor phases represent the positions of Andrews' straight-line segments of the isothermal curves below the critical point, parallel to the axis of volume. (GSP, 1906, p. 44)





Fig. 23. Maxwell's plaster of Gibbs' three-dimensional surface was kept at the National Museum Scotland. The diagram on the left is the thermodynamic surface from Maxwell's book *Theory of Heat* (1902, pp. 195-208). The diagram is drawn roughly from the same angle as the photo on the right. It shows the three Cartesian axes e (energy, increasing downwards), ϕ (entropy, increasing to the lower right and out-of-plane), and v (volume, increasing to the upper right and into-plane).



(b)

Fig. 24. Arrhenius' experimental methodology for measuring the electrical conductivity of dilute solutions. (a) The apparatus is a parallel-walled vessel in which amalgamated zinc plates, E and E', are immersed very close to the opposite sides of the vessel. A layer of zinc sulfate solution is introduced, extending from the horizontal bottom of the vessel to line 1. The absolute electrical conductivity is measured to be k_1 . After this measurement, sufficient pure water is added so that after the solution has been stirred, the level reaches 2 doubling the solution layer from the bottom. Then the conductivity of the new (dilute) solution is measured and found to have increased and had a value of k_2 . The procedure repeated in the same way, doubling the volume of the previous layer by adding pure water, and each time the electrical conductivity is measured, k_4 , k_8 , etc. At each dilution, the conductivity increases but ultimately at a lower rate than at the beginning. A final value of k_{∞} is reached at infinite dilution. (b) The diagram shows the results of the conductivity measurements for some univalent salts. The abscissa of the diagram describes the dilution (concentration in gram-equivalents per liter) and the ordinate the absolute electrical conductivity (Arrhenius, 1903, pp. 48-50).



Fig. 25. Mendeleev's plot of the specific gravity (*s*) of aqueous solutions of sulfuric acid against their concentrations (*p*). The curve is a parabola of the second-order according to the equation: $s = C + Ap + Bp^2$. A, B, C are constants (reproduced in Arrhenius, 1889c, p. 33).



Fig. 26. Arrhenius using the data of Figure 25, plotted the first derivative of the specific gravities (*s*) of the aqueous solutions of sulfuric acid against their concentrations (p), $\left[\frac{ds}{dp} = A + 2Bp\right]$. Discontinued straight lines are observed in this plot (reproduced in Arrhenius, 1889c, p. 304).



Fig. 27. Lewis' cubic atoms for some chemical elements (from top to bottom: lithium, magnesium. aluminum, silicon, phosphorus, sulfur, fluorine, and chlorine). In these pictures, the circles represent the electrons in the outer shell of the central atom. (Gilbert N. Lewis' memorandum dated March 28, 1902, found in the JFK library California State University, Los Angeles). These figures have been designed to explain several important laws of chemical bonding (Lewis, 1916, p. 768).



Figure 28. Lewis' cubic construction of the covalent (a) single and (b) double bond

Appendix (Über die Erhaltung der Kraft)¹³¹⁸

In the first *Bericht*, a review discussing the theory of heat, Helmholtz had built his methodological approach to eliminate the *vital force* from physiology. In his memoir Über die Erhaltung der Kraft, Helmholtz performed as a physicist and addressed his essay to physicists.¹³¹⁹ He began the introduction of the memoir clarifying the methodology he adopted to approach theoretical and experimental physics. He described the interaction of his theoretical principles with empirical laws governing various physical phenomena as deduced from experience or using these principles as an agency to draw conclusions for imperfectly known laws. He based his theoretical structure on two propositions (maxims): The impossibility of the perpetual motion and the Newtonian forces of attraction and repulsion dependent solely on the distance of two interacting bodies. He further analyzed these two propositions in section I of the memoir. In section II, he derived the law of the conservation of force from these two assumptions. He dedicated sections III to VI of the memoir to the applications of the principle of conservation of force to various branches of physics: mechanics (section III), force equivalent of heat (section IV), a force equivalent to electrostatic and galvanism (section V), and a force equivalent to magnetism and electromagnetism (section VI). He concluded the last section with a short discussion about the applicability of the principle of conservation of force to physiological processes in living systems. This brief account on the force equivalent to heat in the plant and animal kingdom is the sole reference in the memoir devoted to physiology.¹³²⁰

 ¹³¹⁸ Helmholtz 1847a; translated by J. Tyndall, 1853. The translated version is used in this analysis.
 ¹³¹⁹ Tyndall, 1853, p.114.

¹³²⁰ Ibid, pp. 161-162.

Comparing the principles of conservation of force derived in sections I and II with the empirical laws of various phenomena, Helmholtz distinguished between experimental and theoretical physics. He claims that "the finding of these laws is the office of the experimental portion of science. The theoretical portion seeks, on the contrary. To evolve the unknown causes of the processes from the visible actions which they present; it seeks to comprehend these processes according to the laws of causality".¹³²¹ Although a physiologist, Helmholtz was the first who delineated theoretical and experimental physics.

Historians have noted that Helmholtz was the recipient of the Kantian philosophy. Yehuda Elkana, for example, has compared quotations taken from *Erhaltung* with germane expressions found in the works of Kant to show their similarity.¹³²² Fabio Bevilacqua asserts that Helmholtz evolved the law of causality. He was referring to a Kantian concept of cause, to a transcendental causality, but without abandoning a regulative causality, which is a necessary precondition for the possibility of explaining the natural laws.

The first pages of the introduction of *Erhaltung* might reflect this influence through his discussion about the principle of causality and the conceptions of matter and force. The ultimate causes must be unchangeable (constant) provided that the theoretician fully apprehends the natural phenomena. Helmholtz asserts that the problem of finding unchanging fundamental causes might be interpreted as the problem of finding constant forces. Therefore, causes and forces are inseparable and identify one another; force as a cause must produce an effect, which becomes visible to our senses when force is exerted on the matter. The effect is the motion of matter in space; forces produce the change of

¹³²¹Ibid, p. 115.

¹³²² Elkana, 1974, pp. 165-169.

matter in reference to space. Force has an effect that becomes apparent when exerted on the matter. It induces motion, which our senses perceive when a body changes position in space concerning another body. In other words, when a moving force is exerted between two bodies inducing alteration of their distance, it must be an attractive or repulsive Newtonian force, the intensity of which depends solely on distance. In this respect, matter and force must be inseparable. However, Helmholtz recognizes that problems arise upon confining the properties of forces solely to distance, ignoring the possibility of their dependence on time and velocity. "The solvability of the problem", he claims, is left to "the condition of the complete comprehensibility of nature".¹³²³ To justify this vague statement, he invokes examples of mechanical systems operating with unchangeable attractive and repulsive forces, such as the conservation of the motion of the centre of gravity. In contrast, for terrestrial matters, the principle of *virtual velocities* and the conservation of *vis viva* is regarded as a means to remove this limitation.¹³²⁴

It is interesting at this stage to compare Helmholtz's considerations and the methodological approach to the conservation of force with Mayer's contribution of 1842.¹³²⁵ Helmholtz did not quote Mayer in *Erhaltung*. Later, he claimed that he had no knowledge of Mayer's work. Both men used the Leibnizian principle of causality as reflected in the doctrine of cause and effect. However, Helmholtz had performed a much lengthier and systematic work on physiology before turning it into physics. Mayer remained a physiologist and used the principle of the conservation of force for his

¹³²³ Tyndall, 1853, p. 117.

¹³²⁴ Ibid, p. 117. However, Helmholtz recognized later that his Newtonian model of stable forces over time was not fully accepted and he abandoned this interpretation. Bevilacqua, 1993, pp. 308-309.
¹³²⁵ Chapter 2, section 2, paragraph 2.1 of this dissertation.

consequent studies on animal metabolism, combating the vital force. Helmholtz, on the other hand, left physiology and became a physicist.

Nevertheless, these two men showed distinct differences in the conceptualization of nature and force. Another similarity is that both inspired the conservation of force principle within physiology, and both used physics and chemistry to formulate this principle. Helmholtz adopted the mechanical description of nature, the mechanical theory of heat, the hypothesis of central forces, and the reduction of all forms of forces (mechanical, electrical, magnetic, and electromagnetic) to the basic central ones.

On the other hand, Mayer approached the conservation of force and derived the mechanical equivalent of heat through metaphysical reasoning rather than experimentation. Indeed, Helmholtz did not conduct extensive experiments, but he relied on experiments performed by others, especially those of Joule, as supportive evidence for his theory. Moreover, he did not work mechanical equivalents.

Section I. The principle of the Conservation of vis viva

In section I of the *Erthaltung*, Helmholtz sought to demonstrate the equivalence between his two maxims stated in the introductory section of the memoir, the impossibility of the perpetual motion and the Newtonian forces. In doing so, he started from the conservation of *vis viva* in the context of the engineering mechanics, and in particular, using the proposition of Lazare Carnot that the *vis viva* of a falling body of mass *m* is equivalent to the product of the vertical distance *h* and the weight *w* lifted. Carnot called the latter quantity "latent living force" while Helmholtz renamed it "work," introducing this term in physics. The work, or more precisely, the potential energy of the falling body, is w = mgh, g being the gravitational acceleration, and h is the initial height of the body. The equivalence of the potential energy and *vis viva* expressed by

$$wh = mgh = \frac{1}{2} mv^2 \tag{A.1}$$

Here, v is the velocity of the falling body. Equation (A.1) is the mathematical formulation of the conservation of *vis viva*, which is applicable only for specific forces, that is, forces that act along the line connecting two material points of the two bodies. The intensity of forces depends only upon the distance between the two material points. He calls these attractive or repulsive forces *central forces*. As a matter of fact

Section II. The principle of the Conservation of Force

Helmholtz widened the law of the conservation principle of *vis viva*, considering any number of material points that exert upon each other central forces. The total sum of the *vires vivae* at all times is conserved. Using Langrangian mechanics, Helmholtz proved that the necessary and sufficient condition for which the conservation of *vis viva* can be applied in all its generality, the forces acting on all material points must be central forces.¹³²⁶ However, the use of central forces restricts the generality of the conservation of vis viva principles and the impossibility of the perpetual motion, for non-central forces violate these two principles. To escape from this inconsistency, Helmholtz thought to remove the restriction imposed by the notion of the central forces showing that forces depending not only on position but also on time and velocity are in agreement with the conservation of *vis viva* to the principle of the conservation of force. Equation (A.2) replaces Eq. (A.1), namely

¹³²⁶ Tyndall, 1853, p. 120-121.

$$\frac{1}{2}md(q^2) = -\Phi dr \tag{A.2}$$

Here, q is the velocity of the body when the force acts along with the direction r in a Cartesian coordinate system. He called Φ the intensity of the force, which is the scalar measure of the corresponding Newtonian central force (force is a vector).¹³²⁷ To prove that the force in Eq. A.2 is a central force, he considers forces acting at distances r and R (from the origin of a Cartesian coordinate system, say a), and the body acquires velocities Q and q, Eq. (A.2 becomes

$$\frac{1}{2}mQ^2 - \frac{1}{2}mq^2 = -\int_r^R \Phi dr$$
(A.3)

The left-hand side of Eq. (A.2) represents the *vis viva* of the body with mass *m* and velocity q, whereas in Eq. (A.3) the difference of the *vires vivae* possessed by the body *m* at two different distances *r* and *R* (condition: R > r) from the origin of the Cartesian system with velocities Q and q, respectively. Therefore, the forces must be central forces.

Helmholtz described the expression of the right-hand side of Eq. (A.2) as *tension* and that of Eq. (A.3) as the summation of all *tensions* between distances R and r.¹³²⁸ He defined tensions as the forces that tend to move the body of mass m before the motion occurs. The potential of this force is in opposition to the *vis viva* of mechanics being considered the force inherent in the moving body. Helmholtz interpreted Eqs. (A.2) and (A.3) as follows: "the increase of *vis viva* of a material point during its motion under the influence of a central force is equal to the sum of tensions which correspond to the alteration of its distance".¹³²⁹ In simple physics, Eqs. (A.2) and (A.3) represent the

¹³²⁷ Scalar is the amplitude of a vector. It is a numerical value that does not have direction. Vector, on the other hand, has amplitude and direction. Central forces are vectors, designated by the same symbol Φ . ¹³²⁸ The integral in Eq. (A.3) does not represent a summation, but rather a surface area (see below). ¹³²⁹ Tyndall, 1853, pp. 122, 124.

equivalence between the kinetic energy (left-hand side) and the potential energy (righthand side) of the body, or the transformation of the potential energy into kinetic energy and *vice versa*. In the general case, of many bodies with masses $m_1, m_2, m_3, ..., m_n$, Eq. (A.3) becomes

$$\sum_{i=1}^{n} \left[\frac{1}{2} m_i Q_i^2 \right] - \sum_{i=1}^{n} \left[\frac{1}{2} m_n q_n^2 \right] = -\sum_{i=1}^{n} \sum_{j \neq i}^{n} \int_{r_{ij}}^{R_{ij}} \Phi_{ij} \, dr_{ij} \tag{A.4}$$

The term on the right-hand side is divided into two portions: one portion in which the index j is always greater than the index i, and the other in which j is always smaller than *i*. The right-hand side of Eq. (A.4) expresses the sum of the tensions (potential energy) consumed, and on the left-hand side, the increase of *vis viva* (kinetic energy) of the whole system. Finally, Helmholtz stated the conservation of force, stressing central forces as an important element of the law.

"In all cases of the motion of free material points under the influence of their attractive and repulsive forces, whose intensity depends solely upon distance, the loss in tension is always equal to the gain in vis viva, and the gain in the former equal the loss of the latter. Hence, the sum of the existing tensions and vires vivae is always constant. In this most general form, we can distinguish our law as the principle of the conservation of force".¹³³⁰

A few points regarding the conservation of force expressed by Eqs (A.2) to (A.4) need further considerations from a historical and physical point of view. First, these equations describe the equivalence of the variation of *vis viva* on the left-hand side with the tension(s), the quantity on the right-hand side of the equations. This equivalence means that the total

¹³³⁰ Ibid, p. 121.

force must be conserved in every transfer of tension into vis viva and vice versa. The quantity $\int \Phi dr$ has the dimension of work (force times distance). Helmholtz evaded using this term for tension, while he accepted the same terminology in treating the conservation of vis viva in Eq. (A.1). However, in accordance with the principle of the conservation of force as expressed by Eqs. (A.2) to (A.4)), an increase in vis viva inflicts an equivalent diminution for tension. Since vis viva could be equated with the body's kinetic energy,¹³³¹ tensions represent the potential energy noted above. The sum of these quantities must be conserved. Second, Helmholtz regarded the scalar Φ corresponding to the intensity of the central force as the ordinate of a point on the abscissa along which the central force is acting. In other words, the intensity of the force is measured perpendicularly to the vector of the central force. As the point of mass, m moves along the abscissa from r to R with increasing velocity, the vis viva increases at the expense of the intensity of the force, i.e., vis viva increases. At the same time, the tension decreases, and the whole (vis viva plus tension) is conserved at every point along the distance r-R. As a result, the scalar Φ does not have a constant value but decreases progressively from r to R. As a result, the integral¹³³² $\int \Phi dr$ represents the area of the curve with an upper and lower bound.

The third speculation regards Eq. (A.4), which describes the central forces exerted among n points (bodies). This problem is analytically unsolvable even for three bodies interacting mutually by central forces. This difficulty is mainly due to the large number of variables (actually 18) that entered the Lagrangian or the Hamiltonian equations. These variables show inseparable cross terms. The three-body problem (e.g., sun-moon-earth) has

¹³³¹ The conservation of *vis viva* was first designated as conservation of motion. Elkana, 1974, p. 31. ¹³³² Helmholtz erroneously interpreted the integral as the sum of forces. This is true only for the expression of tensions in Eq. (A.4).

been solved numerically. Quantum mechanics and other mathematical techniques obtain solutions for more complex systems with various approximations. Therefore, Eq. (A.4) has historical importance and reveals the originality, the sophisticated scientific plan, and the admirable talent of a twenty-seven-year young man.

Helmholtz concluded this section with three propositions.¹³³³ (1), the principle of conservation of force implies that the maximum quantity of work obtainable by a system is a finite quantity when the attractive or repulsive forces are independent of time and velocity; (2) if the forces depend on time and velocity, or they are not central forces, i.e., they act in different directions other than that joining the active material points, then force can be gained or lost infinitely (ad infinitum); the third proposition concerns with the equilibrium and the spontaneity of motion for a system of bodies, and has to do with the equilibrium between external and internal forces. (3) A system of bodies is considered to be in equilibrium whenever the tensions are in equilibrium with external forces. The bodies of the system cannot be displaced within the system, being at rest. However, if the system of bodies is in equilibrium, it could be set in motion under the influence of its internal (non-central) forces. It appears that the hypothesis of central forces depending on distances only was the basic to Helmholtz's conservation law.

In the following sections III-VI of the *Erhaltung*, Helmholtz compares or applies the two principles of conservation (*vis viva* and force) to mechanical, thermal, electrical, magnetic, and electromagnetic theorems. Helmholtz's tension is, by modern standards, a strange quantity. Regardless of its nature, force, work, or potential energy, it appears to be inexhaustible with a perpetual capacity, capable of producing never-ending *vis viva*.

¹³³³ Ibid, p. 126.

Therefore, applications to physical laws and phenomena were an essential prerequisite for Helmholtz to link the tensions to physical forces and to justify the principle of the impossibility of perpetual motion.

Section III. The application of the principle in Mechanical Theorems

This section applies the conservation of *vis viva* to mechanical theorems that involve motion caused by gravitational forces and the transmission of motion through the incompressible solid and fluid bodies in the absence of friction or concussion. Furthermore, he applies the conservation of *vis viva* to elastic collisions or in cases when *vis viva* is lost through friction or inelastic collisions. A significant part of this section is devoted to Fresnel's use of the principle of *vis viva* to derive the laws of light reflection, refraction, polarization, and the application of the principle to interference.

Section IV. The Force-equivalent of Heat

In section IV, Helmholtz dealt with the equivalence of heat and force and attempted to interpret thermal phenomena in his theoretical framework. In this section, as in the remaining sections of the *Erhaltung*, he treated the various problems of physics by adopting a mixture of qualitative description and mathematical formalism. His conclusions were scarcely supported by experimental data, as he admitted, mainly because he could not easily find such data in the literature. Helmholtz did not perform experiments in physics by himself, at least in the context of the *Erhaltung*. Helmholtz was recognized as a competent experimenter from his research in physiology, not in physics. The lack of

experimental activity in the *Erhaltung* might be attributed to the haste of the *Gesellschaft* to combat the *vital force*.¹³³⁴

Helmholtz began looking at classic phenomena, the non-elastic collision and the friction of bodies, seeking to find the compensation between the heat that develops during percussion and friction (friction also is produced in static electricity) the increasing tensions of the body. Going deeper to the subject, Helmholtz considered that apart from friction at the surface of two bodies, moving one against the other with a certain velocity, friction occurs also in the interior of the bodies. This internal friction causes small changes in the molecular constitution of the body, which, however, is compensated quickly after the cessation of friction. He rejects the old mechanical assumption that vis viva is completely lost during percussion or friction, thus disconnected from the increased tensions caused by rubbing or striking the body. He probably believed that heat could produce mechanical action from his acquaintance with Carnot's and Clapeyron's work. Similarly, electricity could create mechanical action through attractive and repulsive forces. In this context, neglecting molecular effects and the development of electricity, he posed two crucial questions: (a) What is the quantity of heat constantly developed for a specific loss of mechanical force (vis viva)? (b) How far can a quantity of heat correspond to a mechanical force?

Unaware of the research of Mayer and Colding, Helmholtz asserts that few experimental results exist to allow an efficient answer to the first question.¹³³⁵ He mentions Joule's measurements of the heat developed by the friction of water in narrow tubes and the heat created in vessels in which the water was set in motion by a paddle-wheel. He

 ¹³³⁴ Chapters 2, section 2, paragraph 2.5, and chapter 4, section 2, paragraph 2.3.3 of this dissertation.
 ¹³³⁵ Ibid, p. 131.

referred to his efforts to establish the mechanical equivalent of heat. Although these results were the only ones at his disposal, Helmholtz depreciated their significance ascribed to Joule's problematical methodology and hence their low accuracy.¹³³⁶ "Probably the above numbers are too high since in his proceeding a quantity of heat might have readily escaped unobserved, while the necessary loss of mechanical force in other portions of the machine is not taken into account".¹³³⁷ Fabio Bevilacqua speculates that Helmholtz asked severe criticism on Joule's experiments. He ignored Joule's subsequent and more accurate calculations of the mechanical equivalent of heat and sand because he did not trust Joule as an amateur scientist. He did not want to compare his theoretical physics with doubtful experimental data.¹³³⁸ Bevilacqua repeated the calculations for converting Joule's values of the mechanical equivalent of heat from the British to the continental units of the various physical quantities (temperature, weight, height) and found that Helmholtz systematically erred in using his conversion factors between the two systems of units. Consequently, the converted values of Joule's experiments were too high, imparting reasonable suspicion to Helmholtz for their accuracy.

The second question is more specific to Helmholtz's work and related to the nature of heat that is considered equivalent to mechanical force. He discusses the material theory (caloric) of heat used by Carnot in his studies on heat engines.¹³³⁹ He criticizes the interpretation given by William Henry (1774-1836) and Bethollet for the heat developed by friction using the caloric theory. He discredits Henry's assumptions as lacking any

¹³³⁶ Helmholtz referred to Joule's measurement of 1843, which was less accurate than his subsequent findings during the years 1945 and 1946.

¹³³⁷ Tyndall, 1853, p. 131.

¹³³⁸ Bevilacqua, pp. 322-323.

¹³³⁹ Helmholtz learned about Carnot's *Reflexions* from Clapeyron's memoir.

experimental proof. In contrast, he considers Berthollet's theory that the source of the heat produced by friction is the displacement of the caloric as not applicable to the friction of fluids. He invoked Davy's experiments of the melting of the ice by friction and the fact that the quantity of heat developed on a body by voltaic electricity is increased. Helmholtz regarded the caloric theory as lacking the capability to interpret his basic assumption of tensions and the conservation of force. Therefore, he inclined towards the mechanical theory of heat as an alternative theory to describe the heat produced by frictional and voltaic electricity. However, he recognized that frictional and voltaic electricity did not produce indisputable evidence against the caloric theory. One might very well claim that the development of heat could result from the caloric transfer from its original place.

"Passing by frictional and voltaic electricity –because it might be here suspected that by some hidden relation of caloric to electricity, the former was transferred in the heated wire- two other ways of producing electric tensions by purely mechanic agencies in which heat does not at all appear, are still open to us, namely by induction and by the motion of magnets".¹³⁴⁰

Regarding the application of the conservation of force to electrical conduction, he cited the process of charging a Leyden jar by the electrophorus (a negatively electrified device by friction). He also referred to magneto-electric machines, where electric currents are induced on an electric conductor by an external magnet when the magnet and the conductor are moved in opposite directions. In both cases, "heat can be developed *ad infinitum*, while nowhere disappears".¹³⁴¹ Furthermore, Helmholtz invoked Joule's experiments of 1843, evidencing that the electric current produced heat and not cold in the immediate neighborhood of the circuit directly under the influence of the magnet; no displacement of

¹³⁴⁰ Ibid, p. 132.

¹³⁴¹ Ibid, p. 133.

caloric was thus conceivable to the electrical circuit. Helmholtz concluded that the caloric theory must be rejected and replaced by the mechanical theory of heat. The latter theory allows the production of heat by mechanical forces. He proceeded to link his basic theoretical assumptions conceptually with heat, expressing first, the quantity of heat as the quantity of *vis viva* of the calorific motion, and, secondly, the quantity of those tensions between the atoms, which, by changing the arrangement of the latter, such a motion can develop. He used the old terminology free heat for the *vis viva* and latent heat for the quantity of tensions forces. He described free and latent heat adopting Ampère's hypothesis. He ascertained the production of heat due to motions of the first kind, i.e., translational and rotational motions of the body's atoms.

In contrast, he deemed the atoms' displacement of the subordinate particles (chemical elements, electricity, etc.) as the latent heat's origin. Forces of the neighboring atoms compensate for motions of the first kind. Motions of the second kind are tension forces and are compensated by elastic forces among the particles within the atoms.¹³⁴² Under certain circumstances, latent heat could be communicated to the surroundings and become free heat. However, a lack of experimental confirmation is an insurmountable obstacle for Helmholtz to substantiate the proposed qualitative and original model of heat as motion.

In the same section, Helmholtz attacked two more modes of heat manifestations. The heat developed during chemical processes and the disappearance or transformation of heat during mechanical, electrical, and chemical processes. He mentioned the old explanation of the origin of heat in a chemical process as the liberation of caloric, which

1342 Ibid.

was previously latent in the combined bodies. Then he proceeded to present his views on the subject, "the quantity of heat developed by chemical processes would be the quantity of *vis viva* produced by the chemical attractions, and the above law (Hess' law) would be the expression for the principle of the conservation of force in this case".¹³⁴³ In other words, Helmholtz conceived the heat produced¹³⁴⁴ in chemical reactions as *vis viva* generated by chemical forces of attractions that played the role of tension forces. This explanation did not contradict Hess' low. On the contrary, Helmholtz believed that this law is a confirmation of the conservation of forces.

Helmholtz's attempts to investigate the conditions and the laws that governed the disappearance of heat led him to formulate the conservation of force within the framework of his theoretical work. He assumed the transformation of heat into work and vice versa not simply an experimental finding but a necessary consequence of the conservation of force. Once more, Joule's results were the only source of experimental findings corroborating the law of conservation of force.¹³⁴⁵ Joule's experiments compared the temperature change of the compressed air when it was expanded in the atmospheric pressure in a vacuum. In the former instance, the compressed air was cooled because it had to exert mechanical force to overcome the resistance of the atmospheric pressure. In the second case, no temperature change was observed. The air rushing into the vacuum found no resistance and exerted no mechanical force, and therefore no change of temperature takes place.

¹³⁴³ Ibid, p. 134.

¹³⁴⁴ By the time Helmholtz was writing the *Erhaltung*, the view that heat was evolved during chemical processes prevailed amongst chemists. Chemical reactions requiring heat to occur were unknown or ignored.

¹³⁴⁵ Ibid, p. 135.

Helmholtz concluded this section by comparing the research of Clapeyron and Holtzmann with his views on the conservation of force.¹³⁴⁶ He ignored the fact that Clapeyron and Holtzman used the caloric theory in their work and focused his attention on their research in finding the force equivalent to heat. He noted the limitation of Clapeyron's law regarding the proportionality between the quantity of heat produced by the pressure exerted on different bodies and their expansibility. This law formulated in the context of the caloric theory was not general. It applied only to gases since only for this case, the law did not contradict the experiment. For solid or liquid bodies, no measurable evolution of heat was observed.

On the other hand, Holtzmann assumed that heating a gas either increases its temperature or expands. In the latter case, work is produced. From the experimental specific heats of Dulong, Holtzmann calculated the mechanical equivalent of heat, and he found 374 Kg-m. Helmholtz stressed that the laws of these two men and their calculations could be accepted when the entire *vis viva* transmitted as heat is converted into mechanical force. He rephrased the law according to his theory of the conservation of force. This law holds only when the sum of *vis viva* and tension forces of the expanded gas is the same as that of the denser gas at the same temperature. At this point, Helmholtz's views found support from Joule's experiments and compared Holtzmann's value of the mechanical equivalent of heat with those obtained by Joule, without any further comment.¹³⁴⁷ Helmholtz demonstrated the coincidence of the theoretical formula of Clapeyron to that of Holtzmann for the undetermined function of gases, C, whose reciprocal was equal to the

¹³⁴⁶ Helmholtz obtained his information about their work from Clapeyron's memoir of 1934 and Holtzmann's paper of 1945.

¹³⁴⁷ Ibid, p. 137.

value of the mechanical equivalent of heat. From this comparison, and using the law of Gay-Lussac for gases, he derived an expression for the calculation of the mechanical equivalent of heat, namely

$$\frac{1}{c} = \frac{a}{k(1+at)} \tag{A.5}$$

The denominator of Eq. (A.5) comes from the expression of the law of Gay-Lussac for the gases. a is the coefficient of expansion of gases. The values obtained from Eq. (A.5) were in good agreement with those calculated by Clapeyron from the velocity of sound and the latent heat of vapors.¹³⁴⁸

Section V. The Force-equivalent of Electric Processes

Helmholtz dedicated section V of the *Erhaltung* to apply the law of conservation of *vis viva* to static electricity and galvanism. He called the generation of heat or chemical decomposition upon the passage of electric current in galvanic (voltaic) and electrolytic cells, respectively.

Static electricity. Helmholtz treated static electricity in the context of Coulomb's law and Gauss' theory of static electricity, but without using Gauss's mathematical physics. His approach was germane to the description of the natural phenomenon of electricity rather than to mathematics. The use of physical concepts, such as equilibrium surfaces, equipotential surfaces, and free tensions, is an example of his approach to physics in his first theories. He identified Coulomb's force between electric elements e_I and e_{II} of opposite signs separated by a distance r with the intensity of the central force Φ (recall that the same symbol represents the scalar and the sectorial direction of force), i.e.,

¹³⁴⁸ Ibid, p. 127; see Table on p. 138.

$$\Phi = -\frac{e_I e_{II}}{r^2} \tag{A.6}$$

The summation of all *tensions* consumed by the motion of a charge e_{II} from the infinity to distances *R* and *r* from a fixed charge e_{I} generating the electric field is given by¹³⁴⁹

$$-\int_{R}^{r} \Phi dr = \frac{e_{I}e_{II}}{R} - \frac{e_{I}e_{II}}{r}$$
(A.7)

The right-hand side of Eq. (A.7) defines the difference of electric potentials of the two charges and represents the gain of *vis viva* during this transfer. According to Helmholtz, "the increase of *vis viva* is equal to the excess of potential at the end of the route over its value at the beginning".¹³⁵⁰ Since the electric potentials are scalar quantities, Eq. (A.7) applies to electrified bodies (conductors) as well, provided that the distribution of charges (electricity) does not change. In this case, he called that the bodies idio-electric. On the other hand, if the distribution of charges changes, the magnitude of the electric tensions in the body itself becomes altered, and the *vis viva* gained must then be different. Helmholtz gave a more general expression for the gain of *vis viva* during the exchange of electricity between two electrified bodies of opposite charges. He calculated the maximum of the *vis viva* generated and the quantity of tension gained by electrifying two bodies (conductors), A and B. He expressed the maximum of the generated vis viva and the quantity of tension gained by electrifying the two bodies.¹³⁵¹

¹³⁴⁹ Ibid, p. 139. The two expressions $\frac{e_I e_{II}}{R}$ and $\frac{e_I e_{II}}{r}$ are the electric potential energies of the system of the two electrical elements at distances *R* and r. In other words, the work done when the electric element e_{II} moves from *R* to *r*. The difference between these two quantities in the right-hand side of Eq. (A.7) represents the electric potential between the two charges at distances *R* and *r*. The electric potential of a single charge *q* is given by $V = \frac{q}{r}$. In modern terms, these equations include a constant, the *permittivity*, characteristic of the medium, where the motion of the two charges occurs. ¹³⁵⁰ Ibid. ¹³⁵¹ Ibid. p. 140.

⁶⁸²

$$-V + \frac{W_a + W_b}{2}$$

However, this expression holds for point charges since Helmholtz did not consider the geometrical characteristics of the two conductors.

Later, he approached the same problem from a different point of view using the concept of equilibrium surfaces. The potential of an electric charge possesses equal values all over the conductor's surface (e.g., an electrified spherical surface).¹³⁵² The equilibrium of electricity on the conductor's surface presupposes the resultant of the whole of the attractive forces of its own electricity and those exerted by outside conductors to be perpendicular to the surface.¹³⁵³ On the equilibrium surface, the gain of vis viva by an infinitely small electric particle is constant in its passage from one conductor to the other. Helmholtz derived the relationship for the gain C_a of vis viva of a particle, e, moving from an infinite distance to the equilibrium surface of the conductor A. He generalized this process considering the distribution of all electric particles on the equilibrium surface of conductors A and B. This distribution was given in terms of the quantities of electricity Q_a and $Q_{\rm b}$. These electricities must have opposite signs since conductors carry opposite charges. The opposite charges are better manifested when the two conductors A and B, are connected. Helmholtz assumed that Q_b and, therefore, C_b are negative quantities. He proposed the following relationships for the gain of *vires* vivae C_a and C_b for conductors A and B.

¹³⁵² Today, these surfaces are equipotential and are defined as the locus of all points of a given potential. No work is done on these surfaces since the potential of a moving charge on the surface does not change, and no gain for vis viva is obtained.

¹³⁵³ Perpendicular to the equilibrium surfaces is the direction of the magnetic field. For a point charge or a spherical conductor, the electric field is radial, and the directions of Helmholtz's central force coincide with the electric field's line of force. Therefore, the attractive or the repulsive forces exerted on a charge outside the equilibrium surface must be perpendicular.

$$-Q_a C_a = V + W_a \tag{A.9a}$$

$$-Q_b C_b = V + W_b \tag{A.9b}$$

V and *W*s are the potentials or the tensions of the conductors as defined previously.¹³⁵⁴ For equal quantities of electricity ($Q_a = Q_b = Q$), the tension of the two conductors is

$$-\left(V + \frac{W_a + W_b}{2}\right) = Q \frac{(C_a - C_b)}{2}$$
(A.10)

This equation is obtained by adding Eqs. (A.9a) and (A.9b) for equal electricities. As C_b is negative, the quantity in the right-hand side of Eq. (10), namely $C_a - C_b$, representing the total gain of the *vis viva* of the system of the two conductors, is positive.¹³⁵⁵ The left-hand side of Eq. (A.10) stands for the tensions of the two conductors.

The tensions of the left-hand side of Eq. (A.10) depend on the two conductors' relative discharge capacity, separation distance, and the modifications resulting when one or both of these factors change. For instance, when C_b is nearly zero, i.e., the discharge capacity of conductor B is very great, then Eq. (A.10) becomes

$$-\frac{W_a + W_b}{2} = \frac{QC_a}{2} \tag{A.11}$$

If the distance between the two conductors is also very great, the mutual tension V is almost zero, and the relationship (10) becomes

$$-\frac{W_a}{2} = \frac{QC_a}{2} \tag{A.12}$$

During the discharging process, the *vis viva* is lost, and heat Θ is developed, which is equal to the quantity Q, namely,

$$\Theta = \frac{1}{2\alpha} Q(C_a - C_b) \tag{A.13}$$

¹³⁵⁴ Ibid. p. 141.

¹³⁵⁵ *Ibid*, pp. 141-142. Since Ca is negative, Ca – Cb is equal to the absolute sum of both, i.e., a positive quantity.

In this equation, Helmholtz had introduced the mechanical equivalent of heat *a*. In batteries, whose external coating is not insulated, the capacity of discharge is very fast, and thus $C_b = 0$; Eq. (A.13) becomes

$$\Theta = \frac{1}{2a} Q C_a = \frac{1}{2a} \frac{Q^2}{S}$$
(A.14)

Where *S* is the capacity of discharge of the battery, which is related to *vis viva* and the quantity of electricity *Q* by the relationship: C = QS, with regard to the conversion factor *a*, Helmholtz claimed that no experimental data existed to verify the validity of Eqs. (A.13) and (A.14).

In the second part of section V of *Erhaltung*, Helmholtz put forward his ideas about galvanism. Helmholtz's galvanism must be seen in the context of the old controversy regarding the theory behind the action of the voltaic and the electrolytic cells. This dispute is traced back to the eighteenth century when Alessandro Volta (1745-1927) attempted to replace Galvani's animal electricity with metallic electricity. From 1790 to the 1850s, the question of which theory explained more satisfactorily the production of electric current in a voltaic and electrolytic cell divided the entire scientific community in Europe, especially in Germany, France, and Britain. Two camps were formed in each country—one supporting Volta's contact force theory¹³⁵⁶ and the other the chemical theory. Prominent physicists and chemists, including Christoph Heinrich Pfaff (1773-1852), Berzelius,

¹³⁵⁶ Volta had invented the first electrochemical series for metals (tension series), according to which metals that are easily oxidized occupy the positive end of this series. Metals with a small affinity to oxygen take up the negative end of the series. Later, Berzelius attempted to widen the idea of the electrochemical series to all other elements. This series of elements reflected qualitatively the chemical affinity of the atoms of the different elements coming into contact and form molecules. Faraday successfully made the third attempt to classify the elements according to their electrochemical equivalents through his experiments on the decomposition of electrolytes by the electric current.

Poggendorff, Ohm,¹³⁵⁷ and Carlo Matteucci (1811-1868), were keen followers of the trend of the so-called contactism. Wollaston, Ørsted, Becquerel. Faraday, de la Rive, and William Ritchie (1790-1837) were the natural philosophers who advanced the theory of chemistry.¹³⁵⁸ Contact theory considered that electricity was generated as a result of the mere contact between two different metals (conducting metals), for example, silver and tin. The phenomenon was thought of as the consequence of discharges between contiguous particles of the two metals. The chemical theorists rejected the idea of the contact force and claimed that chemical processes played a much more central role and were the very cause of the cell's activity. The formation of the various deposits on the electrodes made them think that chemical transformations occur in the wet part of the electrochemical cell. They further stressed the violation of the principle of the impossibility of the perpetual motion by an undefined contact force, which seems to produce an endless circulation of electricity (free electricity). According to them, Volta and his followers undervalued this claim, which played almost no role in the controversy. The construction of the voltaic cells (Daniell and Grove cells) with two metals immersed in an electrolytic solution seemed to favor the chemical perspective. Even this achievement did not change "contactists" opinion about the preponderance of the contact theory over chemical reactions. The supporters of the contact force reacted rapidly, advocating that the chemical reaction was a secondary factor, and its role was to assist the primary cause of electricity manifested by the exchange of electricity between the two metallic conductors. The controversy did not

¹³⁵⁷ Ohm invented experimentally that the intensity of the current is proportional to the electromotive force driving the current and inversely proportional to the resistance of the conductor. However, this law applied well to solid conductors but failed to explain the conducting properties of the liquids.

¹³⁵⁸ Faraday and later de la Rive affirmed that contact could not be the only source of electric current. They gave preference to chemistry as the leading cause of electricity in the electrochemical cells.

stop even after the 1840s when the law of the conservation of energy was established. Although with diminishing enthusiasm from the side of the contact theory.¹³⁵⁹

What side in this dispute did Helmholtz take in his *Erhaltung*? According to Fabio Bevilacqua, Helmholtz seemed not to accept the superiority of one or the other view.¹³⁶⁰ Helge Kragh also agreed that Helmholtz did not explicitly side with any of the parties in the controversy.¹³⁶¹ It appears that Helmholtz interpreted the cause of the production of electricity in electric circuits, adopting one or the other theory depending on the type of the conductor. Helmholtz chose to avoid taking a clear stand on this issue for two reasons. First, he figured out that none of these theories prevailed in giving a conclusive answer for the cause of the production of electric currents in all kinds of galvanic cells. The hitherto experiments performed to support one or the other theory either did not corroborate all electrical phenomena or offered different interpretations for the same phenomenon.

"The idea of the force of contact, the force which is active in the place where two different metals touch each other, and which develops and sustains the different electric tensions of the latter, has not hitherto been rendered more determinate than it is here, because the attempt to embrace the phenomena resulting from the contact of conductors of the first and the second classes were made at a time when the constant and distinguishing feature of the phenomena, namely the chemical process, was not yet properly recognized".¹³⁶²

Secondly, the two core premises of Helmholtz's memoir were not compatible with one or the other theory. The contact force seemed to favor the concept of the central forces in the form of attractive and repulsive forces. In contrast, the principle of the impossibility

¹³⁵⁹ For more details about this long lasting dispute, see Kipnis, 2000; Kragh, 2000.

¹³⁶⁰ Bevilacqua, 1993, p. 328.

¹³⁶¹ Kragh, 2000, p. 149.

¹³⁶² *Tyndall, 1853*, p. 144.

of perpetual motion contradicted the endless action of the contact force. Therefore he recognized the necessity of the chemical processes (however, see below). "The principle which we have thus far advocated [the impossibility of the perpetual motion] contradict the idea of such a force directly if it does not also recognize the necessity of the chemical processes".⁵⁹

He studied two classes of conductors, (a) metallic conductors, in which a mere contact of two metals produces electricity and follows the law of the tension series, and (b) those in which chemical decomposition occurs (electrolytic cells). The first class' conductors exhibited phenomena that were interpreted by employing the theory of the contact force in terms of the attractive and repulsive forces of two metals, which removed electrical charges in the contact area from one metal to the other. When an electric particle that passes from one to the other metal does not further gain or lose *vis viva*, the electrical equilibrium is achieved, and the conservation of *vis viva* is established. In other words, the same, the tensions of the two metals equal the change of the *vis viva* upon the passage of the electrical charge between the two metals.¹³⁶³

Following the conservation of force in the galvanic cells, Helmholtz focused on the phenomenon of polarization. The phenomenon of polarization, specifically during chemical decomposition, became a significant field of research in about 1835 and onwards—polarization used by chemists against the contact theory. Polarization favored the explanation of electrolysis in the framework of the chemical theory.¹³⁶⁴ Based on a few experimental results of Faraday, Lenz, and Poggendorff, Helmholtz gave an account of the qualitative characteristics of polarization and its impact on the electromotive force of the

¹³⁶³ *Ibid*, p. 145.

¹³⁶⁴ Ibid, p. 144.

battery and the intensity of the electric current. He pointed out that the hitherto few experimental results did not allow safe quantitative conclusions.¹³⁶⁵

He studied the effect of polarization on the current intensity of a circuit in two types of cells; those that stimulate polarization but not decomposition reactions and those that give rise to both (electrolysis). In the first class pertained the simple circuit of Faraday consisted basically of copper with positive electrodes made of silver, gold, platinum, and coal in common acidic solutions, such as aqueous sulfuric and nitric acids. He did not provide a concrete description of the circuits of the second class. Helmholtz offered two explanations for the phenomenon of polarization. The first is the macroscopic description, which is similar to that given by Joule in 1843. The formation of metal oxides in the negative electrode and the occlusion of hydrogen gas in the negative electrode. Both manifestations of polarization result in the diminution of the current intensity of the circuit. For the removal of polarization, Helmholtz suggested the same actions proposed by Joule. Renewal of the currents and the reworking of the battery after moving the metal in the fluid or removing the metal from the solution in the air for a few minutes until the complete oxidation of the liberated hydrogen. The second, the microscopic interpretation, was an overview of the present interpretation of the phenomenon of polarization. He considered that polarization was due to a modification of the equilibrium of fluid particles across the metallic surface induced by the chemical process occurring in the electrolytic solution. Here, Helmholtz made use of the dualist theory of Berzelius for the chemical affinity of substances. He claimed that the circuit's electric current separated atoms carrying electric charges $\pm E$ to the surface of the metal charged with the opposite electricity. The charged

¹³⁶⁵ Ibid, pp.148-149.

atoms are retained on the surface by electric attraction.¹³⁶⁶ This explanation for the partaking of the atoms of the electrolyte in the production of polarization, which seemed to favors the contact force theory, was found plausible to him since polarization could be destroyed by chemical means. He provided qualitative and quantitative information about the effect of polarization on the equilibrium potential and the variability of the current intensity in the circuit, especially for electrolysis. The current intensity variation was dependent on the nature of the metals used as electrodes, the size of the surface of the metal, and the intensity of the current initially applied to the circuit.

Helmholtz obtained the quantitative treatment of the modifications induced by polarization on the potential and the current intensity through his principle of conservation of force. He applied this principle to three types of circuits: (a) circuits not producing polarization, (b) those producing polarization but not decomposition, and (c) circuits producing both (electrolysis).¹³⁶⁷ His strategy was somewhat different from that used earlier in the interpretation of various physical phenomena. He applied the law of conservation to electrical, chemical, and thermal transformations in a non-mechanical rational and without any specific appraisal in terms of tensions and *vis viva*. As a prototype of electrical circuits, he used three kinds of batteries constructed using Daniell's, Grove's, and Bunsen's electrical cells. Helmholtz selected these galvanic cells because he presumed they worked with no polarization and thus provided constant current intensity. Helmholtz applied Ohm, Lenz, and Joule's laws to these electrical systems and derived the total

¹³⁶⁶ Helmholtz returned to the problem of polarization in 1879. He explicitly proposed his polarization model in the form of the electrical double layer at the surface of the electrode. See chapter 5. Section 3 of this dissertation.

¹³⁶⁷ Tyndall, 1853, pp. 148-152
amount of heat, Θ , generated at time *t* in the circuit of n cells due to a chemical reaction connected in parallel.

$$\Theta = I^2 R t = nAIt \tag{A.15}$$

R and *I* are the resistance and the current intensity of the battery, respectively. The resistance of the battery was calculated from the individual resistances of the *n* cells. *A* is the electromotive force (potential difference) of the electrical system. The heat is equivalent to the quantity of electricity *Q* produced by the chemical reactions occurring in the positive and negative electrodes of the battery consisting of n cells,¹³⁶⁸ i.e., Q = nIt. The equivalence between the heat Θ' of the reaction and the quantity of electricity *Q* requires a conversion factor. Taking into account Daniell's cell, Helmholtz supposed that the heat a_z liberated by an atom of zinc during its dissolution, and the heat a_c resulted from the precipitation of a copper atom on the positive platinum electrode offered this conversion factor in the form of the difference ($a_z - a_c$). Then the quantity of heat developed in the time t would be $I(a_z - a_c)t$. Thus, the heat of the reaction Θ' would be expressed as

$$\Theta' = Q (a_z - a_c) = nI(a_z - a_c)t \tag{A.16}$$

From Eqs. (A.15) and (A.16), he obtained the chemical and electrical equivalence,¹³⁶⁹

$$A = (a_z - a_c) \tag{A.17}$$

Eq. (A.17) implies that the electromotive force of the battery is proportional to the difference in the quantities of heat developed by the chemical reactions in the two metallic electrodes. The intensity of the constant current according to Ohm's law must be

¹³⁶⁸ The reactions that take place in the electrodes depend on the type of the cell. For instance, for the Daniell cell, oxidation and dissolution of zinc occur in the negative electrode (anode), whereas reduction and precipitation of copper occur in the positive electrode (cathode).

¹³⁶⁹ Earlier in 1841 and 1843, Joule had confirmed the equivalence between the heat of the chemical reaction and electricity experimentally. However, Helmholtz objected to the accuracy of Joule's experiments.

$$I = \frac{A}{R} = \frac{a_z - a_c}{R} \tag{A.18}$$

However, this is not the case when polarization occurs in systems with or without decomposition. For these systems, the current varies; it is stronger at the beginning and diminishes more or less quickly to the point that it remains pretty constant. This current must be equal to that due to chemical decomposition. In the latter case, the conservation of force requires the equivalence of the heat developed during the decomposition and the quantity of the electricity passing through the electrolyte.¹³⁷⁰ For variable current intensity resulting from the polarization, Helmholtz considered an additional constant resistance μ at the interface between the metal and the fluid (where aggregation of the fluid and metal particles occurs). This extra resistance to the electric current creates a quantity of heat ϑ , i.e., $\vartheta = \mu It$. Adding this residual heat due to polarization to the reaction heat given by Eq. (A.15) and applying the conservation law, Helmholtz obtained the following equality

$$I(a_z - a_h) = I^2 r + I\mu$$
 (A.19)

Ohm's law becomes

$$I = \frac{a_z - a_h - \mu}{r} \tag{A.20}$$

Helmholtz did not validate his conclusions derived from the conservation law, with and without polarization, and the equality of the heat developed chemically and electrically due to inadequate experimental data. Helmholtz cited Joule's relevant experiments, but only to criticize Joule's results and methods as unreliable rather than to verify some aspects of his theory of polarization^{,1371}

¹³⁷⁰ Joule had described polarization effects as early as 1941 and again in 1844 when he studied the heat evolved during the electrolysis of water, although using the term polarization at that time. He mentioned it clearly while looking at its effect on the heat evolved during the action of a voltaic pile in his article on the heat disengaged in chemical combustions, published in 1852.

¹³⁷¹ Tyndall, 1853, p. 151.

In closing the discussion regarding the polarization in electric circuits, Helmholtz endeavored to interpret polarization and chemical decomposition in terms of the contact force,¹³⁷² indicating once more his firm belief on the central line of his memoir regarding the attractive and repulsive forces. The reinterpretation of metal-fluid interactions with reference to the contact theory might indicate his preference for contact forces. For polarization in circuits where no reaction occurs, the two metals immersed in the solution attracted the component atoms of the dissolved substance depending on their electric charge, i.e., the negative meta attracts the positive component of the substance, and the positive metal attracts the negative component. In 1853, Helmholtz published two articles in Annalen der Physik und Chemie of Poggendorff, where he described for the first time a model for the phenomenon of polarization in galvanic and decomposition cells. According to this model,¹³⁷³ which was improved in 1879, charged electrodes immersed in electrolytic solution repel bodies (co-ions) carrying the same charge while attracting those bodies with opposite charges (counter-ions) to their surface. As a result, two layers of opposite polarity form at the interface between each electrode and the electrolyte, thus ensuring the solution's neutrality. This model, which supported the contact theory and Helmholtz's central forces, survived for quite a long time, despite its main drawback, since it did not consider the instability of the layer of the charged particles caused by thermal motion in solution. In 1910, Louis Georges Gouy (1854-1926) and David Leonard Chapman (1869-1958) 1in 913 proposed an improved model of the double layer, considering the diffusion of the ions and the instability of the instability the layer. Several other improvements were made available since.

¹³⁷² *Ibid,* p. 152.

¹³⁷³ Helmholtz, 1853b.

Section V of the *Erhaltung* concludes with a discussion concerning the thermal conduction and the origin of thermoelectric currents in an electrical circuit where the so-called Peltier effect is in operation.¹³⁷⁴ Helmholtz described a different manifestation of the thermoelectric phenomenon than that observed by the French physicist Jean Charles Athanase Peltier. Helmholtz described not the *Peltier effect* but the *Seebeck effect* observed in 1821 by the German physicist Thomas Johann Seebeck. In this process, electric current is generated owing to the creation of an electromotive force at the junctions of two electrically connected, dissimilar metals (conductors) maintained at different temperatures (e.g., heating one of the junctions and cooling the other). The reversible process, the production or absorption of heat at the junctions when electric charge flows through the circuit, was discovered by <u>Peltier</u> in 1834.¹³⁷⁵ At the atomic scale, an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side. William Thomson had predicted and later observed in 1851 this phenomenon (Thomson effect).

The device that creates a temperature-dependent voltage resulting from the Seebeck effect is the thermocouple consisting of two dissimilar electrical conductors forming an electrical junction. The voltage is used to measure temperature. Thermocouples are widely used as temperature sensors.

Helmholtz applied the law of conservation of force to a closed-circuit consisting of two metals A and B, soldered at two junctions and maintained at two different temperatures

¹³⁷⁴Tyndall, 1853, pp. 153-154.

¹³⁷⁵ The term thermoelectric effect encompasses three separately identified effects: the Seebeck effect (see footnote 293, p. 128), Peltier effect (footnote 216, p. 99), and Thomson effect. The Seebeck and Peltier effects are different manifestations of the same physical process; textbooks may refer to this process as the Peltier–Seebeck effect. The separation may be attributed to the independent discoveries by Peltier and Seebeck. The Thomson effect is an extension of the Peltier–Seebeck model and is credited to Lord Kelvin.

 t_A and t_B ($t_A > t_B$), respectively. The heat generated in the entire circuits with an electromotive force A at time t is AIt. The Joule's heating effect is I^2Rt . q_At is the quantity of heat developed by the metal A at one junction, and q_Bt is the quantity of heat absorbed by the metal B.at the other junction of the circuit. The net thermal conduction is $(q_A - q_B)t$. From the law of the conservation of forces, Helmholtz obtained the following equivalence

$$AI = I^2 R + (q_A - q_B)t$$
 (A.21)

Let the electromotive force induced at the junctions due to the temperature difference t_A - t_B of the two metals be $B_{t_A} - B_{t_B}$ (this local electromotive force produces the thermoselectric current, which opposes the current of the circuit), then the intensity of the resultant current for the entire circuit will be

$$I = \frac{A - B_{t_A} + B_{t_B}}{R} \tag{A.22}$$

when $t_A = t_B$, then $I = \frac{A}{R}$, and from Eq. (A.20) $q_A = q_B$. In other words, the temperature at both junctions is the same; the current intensity is constant, and the heat developed, and that absorbed must be equal, independently of the junction cross-section.¹³⁷⁶Any temperature difference at the junctions results in a modification of the current intensity of the circuit, as indicated by Eq. (A.22). From Eqs. (A.21) and (A.22), Helmholtz obtained the following relationship,

$$(B_{t_A} + B_{t_B})I = (q_A - q_B)$$
(A.23)

This equation describes the relationship between the electromotive force created at the two junctions of the metals and the forces generating heat. Helmholtz stated, "at constant

¹³⁷⁶ *Ibid*, p. 153.

current intensity, the force that generates and absorbs heat increases with the temperature, in the same proportion as the electromotive force".¹³⁷⁷ Eq. (A.23) holds as long as the current intensity is constant.

Section VI. Force-equivalent of Magnetism and Electromagnetism

Helmholtz treated the phenomena of magnetism and electromagnetism based on the central forces in the form of attractions and repulsions and the conservation of *vis viva*, and in analogy with galvanism. In this respect, he replaced the electric elements e_{I} and e_{II} in Eq. (A.6) with magnetic elements m_{I} and m_{II} of opposite signs at a distance *r*. Thus, the intensity of the central force within the context of magnetism is written as¹³⁷⁸

$$-\Phi = \frac{m_I m_{II}}{r^2} \tag{A.24}$$

Following the pattern of electrostatics, Helmholtz defined the quantity $-\frac{m_I m_{II}}{r}$ as the gain of *vis viva* during the passage of the magnetic elements from an infinite distance to the distance r. He concluded, in analogy with static electricity, that "the gain of *vis viva* during the motion of two magnetic bodies, whose magnetism does not change, for instance of steel magnets, when we subtract from the potential at the end of the motion its value at the commencement of the motion".¹³⁷⁹

Helmholtz introduced concepts of static electricity into the field of magnetism. He used the expression $(V + \frac{1}{2}(W_a + W_b))$, which in the present case denotes the increase of *vis viva* for two magnetized bodies A and B. *Wa*, and *W_b* are the two potentials of the

¹³⁷⁷ Ibid, p. 154.

¹³⁷⁸ Ibid.

¹³⁷⁹ Ibid, pp. 154-155.

individual magnetized bodies A and B, and V is the mutual potential, i.e., the potential of the two bodies approaching each other. When one of the two bodies, say B, cannot be magnetized, then the gain of the potential becomes $V + \frac{W_a}{2}$. An interesting implication of this case is the fact that if B is a permanent steel magnet, the approximation of a body A with variable magnetism generates a *vis viva* equal to the increase of the sum $V + \frac{W_a}{2}$. The gain of *vis viva* $-\frac{W_a}{2}$ equals the loss on the mechanical work expended for the magnetization of the Body A.

Helmholtz defined the potential of the magnetized body. He considered that the exterior of a magnet could be represented by a distribution of the magnetic fluid over its surface. Therefore, Therefore, he substituted the potential of the magnet with the potential of such a surface. The potential C of a body A magnetized by the magnet B is given in analogy with Eq. (A.9) by¹³⁸⁰

$$-Q_a Ca = V + W_a \tag{A.25}$$

Here, Q is the quantity of magnetism. Since the north and south poles of a magnet contain equal amounts of magnetism, Q in each equals zero. In this case, $V = -W_a$. For the magnetized body A by the magnet B, this relationship indicates that the mutual potential of the two bodies equals the negative individual potential of body A. In other words, the magnetism of body A is entirely bound by magnet B.¹³⁸¹

After the electrostatics, Helmholtz turned his investigations into the phenomenon of electromagnetism. He attempted to approach the new theory of electrodynamics. The latter was a new field of research that Helmholtz was destined to study closely in the years

¹³⁸⁰ Ibid, p. 155. ¹³⁸¹ Ibid to come. As in previous sections, he began discussing the research performed in this area. He gave a brief account of the theories of Ampère, Weber, Neumann, Hermann Günther Grassmann (1809-1877), and Lenz. The interpretation of electromagnetism was based on attracting and repulsive forces induced by the electric current. The intensity of the forces depended on the direction and velocity of the current. Weber agreed with this view and considered the acceleration of the current as an additional factor that influenced attraction and repulsion forces. Furthermore, Weber showed a better understanding of the induction current in circuits. Neumann extended Lenz's law for an entire electric circuit and developed the laws of the induced current for closed circuits. Neumann, Weber, and Grassmann had a common view on this subject, for which experiments were available.

Helmholtz treated electromagnetism, not in the context of constant central forces, but by employing the law of the conservation of force, "Up to the present time no hypothesis has been established by which these phenomena could be referred to constant central forces". Although he knew that the interpretation of electromagnetism was conducted by considering non-Newtonian forces exerted by the electric elements of current, he preferred using the conservation of force as his methodological approach. He hoped that using the principle of the conservation of forces, he could deduce empirical laws on this phenomenon. Because experimental data existed only for closed circuits, he

Helmholtz considered a system consisting of a magnet moving under the influence of the electric current circulating a conductor or an electric circuit. He further sought to calculate the current intensity on the conductor or the circuit modified by the induced current of the moving magnet. He derived a mathematical expression for the modified current intensity of the circuit by equating the mechanical work of the tension forces of the current expressed as *aAIdt* (*a* being the mechanical equivalent of heat, and the other quantities with their usual meaning), with the sum of the *vis viva aI*²*Rdt* generated in the circuit by the current, *R* being the resistance of the circuit, and the *vis viva I* $\frac{dV}{dt}dt$, gained by the magnet under the effect of the current (*V* is the potential of the magnet towards the conductor carrying the unit current), namely¹³⁸²

$$\alpha AIdt = \alpha I^2 R dt + I \frac{\alpha V}{dt} dt \tag{A.26}$$

Eliminating the current intensity in both sides of Eq, (A.26), he obtained Ohm's law for the circuit

$$I = \frac{A - \frac{1dV}{adt}}{R} \tag{A.27}$$

Helmholtz designated the quantity $\frac{1}{a} \frac{dV}{dt}$ as the electromotive force generated in the circuit. This electromotive force, in turn, induced an electric current, the intensity of which is given by Eq. (A.26). According to Lenz, this electromotive force acts against the force, which moves the magnet in the direction of increasing velocity. The electromotive force is practically independent of the current intensity since before the motion of the magnet, no current existed.

Helmholtz considered the case where the current intensity was changeable over time. He gave the following expression for the whole current intensity¹³⁸³

$$\int I dt = -\frac{1}{aR} \int \frac{dV}{dt} dt = \frac{1}{a} \frac{(V_I - V_{II})}{R}$$
(A.28)

¹³⁸² Ibid, p. 157. ¹³⁸³ Ibid. $V_{\rm I}$ denotes the potential at the beginning, and $V_{\rm II}$ at the end of the motion of the magnet. If the magnet approaches from a very great distance, $V_{\rm I}$ = 0. then Eq. (A.28) simplifies to

$$\int Idt = \frac{\frac{1}{a}V_{II}}{R} \tag{A.29}$$

Eq. (A.29) has a form consistent with Ohm's law. It indicates that the current intensity is independent of the route or the velocity of the moving magnet. Helmholtz formulated the following law: "The entire electromotive force of the induced current, generated by a change of position of a magnet relative to a closed conductor, is equal to the change which thereby takes place in the potential of the magnet towards the conductor when the latter traversed by the current -1/a''.¹³⁸⁴ Helmholtz notified that Neumann had arrived at the same conclusion, but instead of the concrete definition of the conversion coefficient 1/a, he had an undetermined constant ε .¹³⁸⁵

Helmholtz extended his theory on electrodynamics beyond what was known until then. He considered complex cases involving interactions of a magnet with more than one conductor or interactions between different conductors. Using the same reasoning as before, he calculated the intensity of the modified electric current that traversed the conductor induced by a moving magnet. Also, he calculated the current generated in a piece of iron magnetized by this conductor.¹³⁸⁶ Upon applying the conservation of force to this system, he obtained the following expression for the modified current intensity of the conductor.¹³⁸⁷

$$I = \frac{A - \frac{1}{\alpha} \left(\frac{\mathrm{d}\varphi}{\mathrm{d}t} + \frac{\mathrm{d}\chi}{\mathrm{d}t}\right)}{R} \tag{A.30}$$

¹³⁸⁴*Ibid*.
¹³⁸⁵*Ibid*, p. 158.
¹³⁸⁶ Ibid.
¹³⁸⁷ Ibid.

Here, φ is the conductor's potential for the unit current, and χ is the potential of the magnetism of the piece of iron for the unit current excited by the conductor. The electromotive force of the induced current due to the presence of the piece of iron is $-\frac{1}{\alpha}\frac{d\chi}{dt}$. Finally, Helmholtz calculated the intensity of the induced current through the magnetization of the piece of iron by the magnet.

In closing the section of electromagnetism, Helmholtz discussed the case of the interaction between two conductors 1 and 2 moving toward each other. One expects a modification of the current intensity in each conductor. He denoted A_1 the electromotive force of conduction of conductors 1 excited by conductor 2, A_2 the electromotive force of conduction of conductors 2 influenced by conductor 1. *V* is the potential towards each other. Helmholtz did not consider the geometry of conductors (e.g., spherical, cylindrical, or the shape of wires), nor the relative direction of the two currents (parallel or opposite). Using his methodology of applying the conservation of force for the tension forces of the two conductors A_1I_1 and A_2I_2 , irrespective of whether these forces were repulsive or attractive, and the *vires vivae* with the heat produced by the currents in the two conductors, namely, $I_1^2R_1$ and $I_2^2R_2$, Helmholtz obtained the following equation¹³⁸⁸

$$A_1 I_1 + A_2 I_2 = I_1^2 R_1 + I_2^2 R_2 + \frac{1}{a} I_1 I_2 \frac{\mathrm{d}V}{\mathrm{d}t}$$
(A.31)

Here, I_1 and I_2 are the modified current intensities of conductors 1 and 2, respectively, under their mutual influences. R_1 and R_2 are the resistances to the current flowing the conductors 1 and 2, respectively. The last term on the right-hand side of Eq. (A.31) expresses the *vis viva* of one conductor under the influence of the current circulating the

¹³⁸⁸ Ibid, p. 159.

other conductor. From this equation, the current intensity of one of the conductors can be derived, assuming that its current intensity is much less than the current intensity of the other conductor. If $I_2 \ll I_1$, the electromotive force A_1 vanishes compared to its value before the interaction. Helmholtz obtained the following equation for the current intensity of the conductor 2,

$$I_2 = \frac{A_2 - \frac{1}{a} I_1 \frac{dV}{dt}}{R_2}$$
(A.32)

An analogous equation holds for conductor 1. If the intensity I_1 is vanishingly small compared to I_2 , then

$$I_1 = \frac{A_1 - \frac{1}{a} I_2 \frac{dV}{dt}}{R_1}$$
(A.33)

From Eqs. (A.32) and (A.33), Helmholtz derived the following conclusions:¹³⁸⁹ first, the electromotive forces *V* of the conductors on each other are equal if the current intensities are the same, whatever the shape of the conductors could be. Second, the total electromotive force of induction, excited during a certain motion of the conductors towards each other, and furnishes a current that itself is unchanged by the induction, is equal to the change of the (mutual) potential towards the other conductor traversed by $-1/\alpha$. It is interesting to note that Ampère had studied the interactions between two parallel wires carrying electric currents and derived the force acted on the one by the other wire, known widely as the Ampère's law or Ampère's force law.¹³⁹⁰ However, Ampère did not recognize at that time the phenomenon of induced current.

¹³⁸⁹ Ibid, pp.159-160.

¹³⁹⁰ Ampère derived this law for two parallel wires in 1823. Maxwell in 1873 and Duhem in 1892 derived the general formulation of this law for conductors of arbitrary geometries.

It has been said¹³⁹¹ that Helmholtz's theory developed in section VI of the *Erhaltung* dealing with magnetic and electromagnetic phenomena did not add that much to the contemporary knowledge developed by scientists, such as those mentioned at the beginning of the section (including Faraday and Oersted). The novelty introduced by Helmholtz was the reinterpretation of these phenomena in the context of the conservation of force, extending this theory to new quantitative predictions. What was needed in Helmholtz's theory of electrodynamics was the experimental data that would give the necessary precision of the theoretical conclusions derived from his equations.

Helmholtz devoted the final chapter of the *Erhaltung* to applying the principle of conservation of force to physiological processes occurring in living organisms. This chapter, which covers the least space of *Erhaltung*, was the prelude of subsequent more extensive studies he performed in later years in the fields of physiology and physics. As we saw previously, Helmholtz was involved in studies pursuing the exclusion of the *vital force* in living organisms, trying to find the connection between the ingested and developed heat in living systems adopting Liebig's correlation theory. No attempt was made to formulate the force equivalent for the energy balance.

In *Erhaltung*, he attempted to discover the equivalence of the tension forces inherent in the chemical processes (chemical tensions) and the developed *vis viva* in the form of heat or mechanical work. For the kingdom of plants, he admitted that insufficient experimental data and a lack of appropriate methodological approaches precluded the precise application of the principle of conservation of force. He could say that the stored tensions forces were chemical in origin and that the only absorbed *vis viva* was the chemical

¹³⁹¹ Bevilacqua, p. 332.

solar rays.¹³⁹² For the animal world, the theoretical treatment was fordable. The application of the conservation of force seems possible since animals utilize a certain quantity of chemical tensions from the oxidation of foods received from their immediate environment and generate heat and mechanical forces. However, he thought that the mechanical work was small compared to the heat (*vis viva*). He doubted whether it was necessary to include the heat generated by the combustion and the nutrient transformation equal to that given out by the animals in the form of work. He suggested eliminating mechanical work from the equivalence relationship.¹³⁹³ Dulong and Despretz's experiments seemed to confirm this suggestion.¹³⁹⁴

Summarizing the previous pages of the Erhaltung, Helmholtz gave an account of his plan as outlined at the start of the *Erhaltung* and in what he had achieved by applying his two premises to the pertinent laws of natural phenomena.

"I believe I have proved that the law in question does not contradict any known fact in natural science, but in a great number of cases is, on the contrary, corroborated in a striking manner. I have endeavored to state in the most complete manner possible, the inferences which flow from a combination of the law with other known laws of natural phenomena and which still await their experimental proof".¹³⁹⁵

¹³⁹² *Ibid,* p.160.

¹³⁹³ Ibid, p. 161.

¹³⁹⁴ However, as we noted previously, Dulong and Despretz's experiment was characterized by a high degree of inaccuracy.

¹³⁹⁵ *Ibid*, p.162.

List of abbreviation

ACP	Annales de Chimie et de Physique
ACPh	Annalen der Chemie und Pharmacie
ACS	American Chemical Society
AHES	Archive for History of Exact Sciences
AIChemE	American Institute of Chemical Engineers
AJP	American Journal of Physics
AP	Annalen der Physik
APC	Annalen der Physik und Chemie
BAAS	British Association for the Advancement of Science
BHC	Bulletin of the History of Chemistry
BJHS	The British Journal for the History of Science
CR	Comptes Rendus
CRAS	Comptes Rendus (hebdomadaires) des séances de l'Académie des Sciences
DSB	Dictionary of Scientific Biography
ERE	Experimental Researches in Electricity
GSP	Scientific papers of J. W. Gibbs
HS	History of Science
HSPBS	Historical Studies in the Physical and Biological Sciences
HSPS	Historical Studies on the Physical Sciences

JACS	Journal of the American Chemical Society
JCE	Journal of Chemical Education
IChemE	Institution of Chemical Engineers
JCS	Journal of the Chemical Society
JMPA	Journal de Mathématiques Pures et Appliquée
JPC	Journal of Physical Chemistry
JRSA	Journal of the Royal Society of Arts
JSP	Scientific papers of James Prescott Joule
MIT	Massachusetts Institute of Technology
PAAAS	Proceedings of the American Academy of Arts and Sciences
PM	Philosophical Magazine
PRS	Proceedings of the Royal Society
РТ	Philosophical Transactions
PTRS	Philosophical Transactions of the Royal Society
RQS	Revue des questions scientifique
SHPS	Studies in History and Philosophy of Science
ZPC	Zeitschrift für Physikalische Chemie

List of sources

The following list of references comprises the sources cited in footnotes. Authors are listed alphabetically and their publications chronologically. Translations into English of primary sources, whenever they exist, are denoted explicitly in the corresponding references.

Primary sources

Ampère, A. M. 1822. Recueil d'observations électrodynamiques. Paris: Crochard.

Ampère, A. M. **1847**. Sur le mode de transmission des courants électriques et la théorie électrochimique. Revue scientifique et industrielle 31: 171-187.

Andrews, T. 1869. The Bakerian Lecture: On the Gaseous State of Matter. *PTRS* 159, 575–590.

Andrews, T. 1876. The Bakerian Lecture: On the Gaseous State of Matter. *PTRS* 166: 421-449.

Armstrong, H. E. 1886. Electrolytic conduction in relation to molecular composition, valency, and the nature of chemical Change: Being an attempt to apply a theory of residual affinity. *PTRS* 40: 268-291.

Armstrong, H. E. 1888. Comparison between the Views of Dr. Arrhenius and Professor Armstrong on Electrolysis. Reply to Professor Lodge's criticisms. In: *Report of the BAAS*, 57th meeting, Manchester, August-September 1887. London: John Murray.

Armstrong, H. E. 1891. *Report of the BAAS*, 60th meeting, Leeds. September 1890. London: John Murray.

Armstrong, H. E. 1927. Marcelin Berthelot and synthetic chemistry. A study and an interpretation. 1827 (Oct. 25)-1907 (March 18). *JRSA* 76: 145-171.

Arrhenius S. 1884a. Recherches sur la Conductibilité galvanique des electrolytes. Première Partie, Bihang till Kungliga Vetenskaps-Akademiens Handlingar, vol.8, n°13.

Arrhenius S. 1884b. Recherches sur la Conductibilité galvanique des Electrolytes. Deuxième Partie, Bihang till Kungliga Vetenskaps-Akademiens Handlingar, vol.8, n°14.

Arrhenius S. 1884c. Über die Göltigkeit der Clausius-Williamsonschem Hypothese. Beleuctung einiger von Herrn Dr. Hans Jahn gemachten Einwörf*e. Berichte der deutschen chemische Gesellschaft* 15: 49-52.

Arrhenius, S. 1887a. Über die Dissoziation der Wasser gelösten Stoffe. *ZPC* 1: 631-648. Arrhenius, S. 1887b. Translation of a letter received from Dr. Arrhenius respecting the above criticism. In: *Report of the BAAS*, 57th meeting, Birmingham, September 1886. London: John Murray.

Arrhenius, S. 1889a. Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren. ZPC 4: 226–248. Partial translation by Back, M. H., Laidler, K. J. 1967. In *Selected readings in chemical kinetics*, pp. 31-35. Oxford, Pergammon Press.
Arrhenius, S. 1889b. Reply to Professor Armstrong's Criticisms regarding the Dissociation Theory of Electrolysis. In: *Report of the BAAS*, 58th meeting, Bath, September 1888. London: John Murray.

Arrhenius S. 1889c. Electrolytic Dissociation versus Hydration. PM 28: 30-38.

Arrhenius S. 1891. La conductibilité des sels vaporisés dans la flamme d'un bec Bunsen. *La Lumière Électrique* 39: 501-509. Arrhenius, S. 1896. On the influence of carbonic acid in the air upon the temperature of the ground. *PM* 41: 237–276.

Arrhenius, S. 1897. On the influence of carbonic acid in the air upon the temperature of the Earth. *Publications of the Astronomical Society of the Pacific* 9: 14-24.

Arrhenius, S. 1900. Zur Physik des Vulkanismus. Geologiska Föreningen I Stockholm Förhandlingar 22: 395-420.

Arrhenius, S. 1903. Development of the theory of electrolytic dissociation. *Nobel Lecture*. pp. 45-58. https://www.nobelprize.org/prizes/chemistry/1903/arrhenius/lecture/

Arrhenius, S. 1907. Immunochemistry. The application of the principles of physical chemistry to the study of the biological antibodies. New York: The MacMillan Company.

Arrhenius, S. 1912. Electrolytic dissociation. JACS 34: 353-364.

Bancroft, W. D. 1899. The relation of physical chemistry to technical chemistry. *JACS* 21: 1101-1107.

Bancroft, W. D. 1901. Review of the development and application of a general equation for free energy and physico-chemical equilibrium, by Gilbert Lewis. *JPC* 5: 405.

Becquerel, A. C. 1824a. Développemens relatifs aux effets électriques observes dans les actions chimiques; et de la Distribution de l'électricité dans la pile de Volta, en tenant compte des actions électro-motrices des liquides sur les métaux. *ACP* 26:176-188.

Becquerel, A. C. 1824b. Des actions électromotrices de l'eau et des liquides en général sur les métaux. *ACP* 27: 5-19.

Becquerel. A. C. 1833. Considérations générales sur les décompositions électrochimiques et la réduction de l'oxyde de fer, de la zircone et de la magnésie, à l'aide de forces électriques peu considerable., *Mémoires de l'Académie des Sciences* 12: 583-597.

Becquerel, A. C. 1834-1840. *Traité expérimental de l'électricité et du magnétisme et de leur rapports avec les phénomènes naturelles*. Paris: Firmin Didot Frères.

Berthelot, M. 1862. Essai d'une theorie sur la formation des ethers. ACP 65: 110-128.

Berthelot, M., Péan de Saint-Gilles, L. 1862. Recherches sur les affinités. De la formation et dècomposition des èthers. *ACP* 65: 5-110.

Berthelot, M., Péan de Saint-Gilles, L. 1863. Recherches sur les affinités. de la formation et dècomposition des èthers. Troisieme and quatrieme partie. Paris: Mallet-Bachelier, Imprimeur-Libraire.

Berthollet, C. L. 1803. Essai de Statique Chimique. Paris: Firmin Didot.

Berzelius J. J. 1811. Essai sur la nomenclature chimique. *Journal de physique de chimie et d'histoire naturelle* 73: 253-286.

Berzelius, J. J. 1819. Essai sur la théorie des proportions chimiques et sur l'influence chimique de l'électricité, Paris: Méquignon-Marvis.

Carnot, S. 1824. *Reflexions sur la puissance motrice du feu et sur les machines propres a développer cette puissance*. Paris: Chez Bachelier, Libraire.

Carnot, S. 1878. *Reflections sur la puissance mortice du feu et sur les machines propres* a développer cette puissance: Extrait de note inédites de Sadi Carnot sur les mathématiques, la physique et autre sujets. Paris, Gauthier-Villars.

Chapman, D. L. 1913. A contribution to the theory of electrocapillarity. *PM* 25: 475–481.

Clapeyron, E. 1834. Mémoire sur la puissance motrice de la chaleur. *Journal de l'Ecole Royale Polytechnique* XIV: 153–190.

Clausius, R. 1850. Über die bewegende Kraft der Wärme und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen. *AP* 155: 368-397.

Clausius, R. 1854. Über eine veränderte Form des zweiten Hauptsatzes der mechanischen Wärme theorie. *AP* 93: 481–506.

Clausius, R. 1857. Über die Art der Bewegung welche wir Wärme nennen. *ACP* 100: 353-380. Translation in English, Clausius, R. 1857. On the nature of the motion, which we call heat. *PM, fourth Series* 14: 108-127.

Clausius, R. 1858. On the conduction of electricity in electrolytes. *PM*, *fourth Series* 15: 94-109.

Clausius, R. 1865. Über Verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie. *APC* 201: 352-400..

Clausius, R. 1880. On the behaviour of carbonic acid in relation to pressure, volume and temperature. *PM* 9: 303-408.

Clausius, R. 1887. *The mechanical theory of heat with its applications on the steam engine and the physical properties of bodies*. Hirst T. A. (Editor and translator). London: Taylor & Francis.

Colding, L. A. 1850. Unders¢gelse om de almindelige Naturkraefter og deres gjensidige Afhaengighed og isaerdeleshed om den ved visse faste Legemers Gnidning udviklede Varme (Study on the ordinary forces of nature and their mutual Dependence and, in particular, on the heat developed by the rubbing of certain solid bodies). *Det Kongelige Danske Videnskabernes Selskabs Skrifter, 5th series* 2: 122-146.

Colding, L. A. 1856. Naturvidenskabelige Betragtninger over Slaegtskabet mellem det aandelige Livs Virksomheder og de almindelige Naturkraefter (Scientific Considerations on the Relationship between the Enterprises of Spiritual Life and General Natural Powers).

Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger 4-6: 136-168.

Colding, L. A. 1864. On the history of the principle of the conservation of energy. *PM* 27: 56-64.

Colding, L. A. 1871. On the universal powers of nature and their mutual dependence. *PM* 42: 1-20.

Crawford, A. 1779. *Experiments and observations on animal heat, and the inflammation of combustible bodies being an attempt to resolve these phenomena into a general law of nature*. 2nd edition, 1788. London: Johson.

Czapski, S. 1884. Über die thermische Veränderlichkeit der elektromotorischenKraft galvanischer Elemente und ihre Beziehung zur frein Energie derselben. *AP* 21: 209-243.

Daniell, J. F. 1836. On voltaic Combinations. PTRS 126: 107-124.

Daniell, J. F. 1837. Further Observations on Voltaic Combinations. PTRS 127: 141-160.

Daniell, J. F. 1839. On the electrolysis of secondary compounds. PTRS 129: 97-112.

Daniell, J. F., Miller, W. A. 1844. Additional Researches on the Electrolysis of Secondary Compounds. *PTRS* 134: 1-19.

Davy, H. 1807. The Bakerian Lecture: On some chemical Agencies of Electricity. *PT* 97: 1-57.

Duhem, P. 1884. Sur le potentiel thermodynamique et la théorie de la pile voltaïque. *CRAS* 99: 1113–1115.

Duhem, P. 1886. Le potentiel thermodynA. amique et ses applications à la mécanique et à l'étude des phénomènes électriques. Paris: A. Hermann. **Duhem, P. 1887**. Étude sur les travaux thermodynamiques de 1. Willard Gibbs. Bulletin des sciences mathématiques 11: 122- 148, and 159-176.

Duhem, P. 1891. Sur les équations général de thermodynamique. *Annales Scientifiques de l'Ecole Normale Supérieure, 3e Série* VIII: 231–266.

Duhem, P. 1892a. Commentaire aux principes de la thermodynamique-premier Partie. *Journal de JMPA, 4e Serie* VIII: 269–330.

Duhem, P. 1892b. Notation atomique et hypothèses atomistiques. *RQS* 31: 391–457. Translated by **Needham, P. 2000**. Atomic Notation and Atomistic Hypotheses. *Foundations of Chemistry* 2: 127–180.

Duhem, P. 1893a. Introduction a la mechanique chimique. Paris: George Carré.

Duhem, P. 1893b. Commentaire aux principes de la Thermodynamique-Deuxième partie. *Journal de JMPA, 4e Serie* IX: 293–473.

Duhem, P. 1893c. L'Ècole anglaise et les théories physiques: Á propos d'un livre récent de W. Thomson. *RQS* 34: 345–378. Edited and translated by Ariew, R., and P. Barker, as

Duhem, P. 1996. The English School and Physical Theories: On a Recent Book by W. Thomson. In: *Essays in the History and Philosophy of Science*. Indianapolis: Hackett.

Duhem, P. 1894. Commentaire aux principes de la thermodynamique – Troisième partie: Les équations générales de la thermodynamique. *JMPA* 10: 207–285.

Duhem, P. 1895, 1898, 1902. Sur les déformations permanents et l'hystérésis. In: 4e and 5e mémoire de l'Académie de Belgique, tome. LIV, tome. LVI, tome. LXII.

Duhem, P. 1896. Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques, *Mémoires de la Société des Sciences physiques et naturelles de Bordeaux, 5e série* II: 99-126.

Duhem, P. 1897a. Thermochimie à propos d'un livre récent de Marcelin Berthelot. *RQS* XII: 361-392.

Duhem, P. 1897b. *Traité élémentaire\ de Mécanique chimique fondée sur la Thermodynamique*, Livre II; tome. I, Paris: Librairie Scientifique A. Hermann.

Duhem, P. 1899. Une science nouvelle la chimie physique. In: *Revue philomathique de Bordeaux et du Sud-Ouest*, 2e année, n°5, 1er mai et n°6, 1er juin, pp. 205-219 and 260-280. Bordeaux: Impr. Gounouilhou. Translated by Needham, P. 2002. *Mixtures and chemical combinations and related essays*. pp. 253-276. Dodrect: Kluwer.

Duhem, P. 1900. Les théories électriques de J, Clerk Maxwell. Étude historique et critique. *Annales de la Societe Scientifique de Bruxelles, Premiere Partie* 4: 239–253.

Duhem, P. 1901a. Recherches sur l'hydrodynamique. *Annales de la Faculté des Sciences de Toulouse, 2e Série* 3: 379–431.

Duhem, P. 1901b. Les theories electriques de J. Clerk Maxwell: Les electrostatiques de Maxwell. *Annales de la Societe Scientifique de Bruxelles, Deuxième Partie* 25: 1–90.

Duhem, P. 1902a. *Le mixte et la combinaison chimique*. Paris, C. Naud, Editeur; translated by **Needham, P. 2002**. *Mixtures and chemical combinations and related essays*, pp. 85-94, Dordrecht: Kluwer.

Duhem, P. 1902b. Thermodynamique et chimie, leçons élémentaires à l'usage des chimistes. Leçons XVIII. XIX et XX, Paris: Librairie Scientifique A. Hermann.

Duhem, P. 1902c. Les théories électriques de J. Clerk Maxwell. Étude historique et critique. Paris: A. Hermann. Edited and translated by **Aversa, A. 2015**. The electric theories of J. Clerk Maxwell. A historical and critical study. New York: Springer.

Duhem, P. 1903. *Thermodynamics and chemistry. A non-mathematical treatise for chemists and students of chemistry.* New York: John Wiley & Sons.

Duhem, P. 1905. L'évolution de la mécanique. Paris: Librairie Scientifique A. Hermann.

Duhem, P. 1908. Josiah-Willard Gibbs, à propos de la publication de ses mémoires scientifiques. Librairie Scientifique, A. Hermann.

Duhem, P. 1915. La science Allemande. Paris: A. Hermann et Fils.

Dulong, P. L. 1841. Mémoire sur la chaleur. ACP, 3d serie 1: 440-455.

Ehrlich, P. 1899. Observations upon the constitution of the diphtheria toxin. *Transactions* of the Jenner Institute for Preventive Medicine 1: 1-15.

Ehrlich, P. 1904. Physical chemistry versus biology in the doctrines of immunity. *Boston Medical and Surgical Journal* 150: 443-445.

Faraday, M. 1833a. ERE, Third Series, PTRS 123: 23-54.

Faraday, M. 1833b. ERE, Fifth Series, PTRS 123: 676-710.

Faraday, M. 1834. ERE, Seventh Series, PTRS 124: 77-122.

Faraday, M. 1951. Experimental Researches in Electricity. London: J. M. Dent & Sons Ltd.

FitzGerald, G. F. 1891. Electrolytic Theories. In: *Report of the BAAS*, 60th meeting, Leeds, September 1890. London: John Murray.

Fourier, J. 1822. Théorie analytique de la chaleur. Paris: Firmin Didot Père et Fils.

Gauss, C. F. 1809. Theoria Motvs Corporvm Coelestivm In Sectionibvs Conicis Solem Ambientivm. Hambvrgi: Svmtibvs F. Perthes et I. H. Besser.

Gauss, C. F. 1823. *Theoria Combinationis Observationum Erroribus Minimis Obnoxiae*. Göttingen: Apud Henricum Dieterich. **Geoffroy, E.-F**. 1718. Sur Les rapports de differences substances en Chimie. *Histoire* 35-37.

Gibbs, J. W. 1873a. Graphical Methods in the Thermodynamics of Fluids. *The Transactions of the Connecticut Academy of Arts and Science* 2: 309-342.

Gibbs, J. W. 1873b. A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces. *The Transactions of the Connecticut Academy of Arts and Science* 2: 309-342.

Gibbs, J. W. 1876. On the equilibrium of heterogeneous substances. *The Transactions of the Connecticut Academy of Arts and Science* 3: 108-248.

Gibbs, J. W. 1878. On the equilibrium of heterogeneous substances. The Transactions of the Connecticut Academy of Arts and Science 3: 343-524.

Gibbs, J. W. 1879. On the vapor-densities of peroxide of nitrogen, formic acid, acetic acid, and perchloride of phosphorus. *American Journal of Science, Series 3* 18: 371-387.

Gibbs, J. W. 1902. *Elementary Principles in Statistical Mechanics developed with special reference to the rational foundation of thermodynamics*. New York: Dover Publications.

Gouy, M, 1910. Sur la constitution de la charge électrique a la surface d'un électrolyte. *Journal de Physique Théorique et Appliquée* 9: 457–468.

Grotthuss, C. J. T. 1805. Sur la décomposition de l'eau et des corps qu'elle tient en dissolution à l'aide de l'électricité galvanique, pp. 1-39. Rome: Bayer. Staatsbibliothek. This paper has been republished with the same title. Grotthuss, C. J. T. 1806. Annals de Chimie 58: 54–73.

Grove, W. R. 1839a. Pile voltaïque d'une grande énergie électro-chimique. CRAS 8: 567-570. **Grove, W. R. 1839b**. On a small voltaic battery of great energy; some observations on voltaic combination and forms of arrangement; and on the inactivity of the copper positive electrode in nitro-sulphuric acid. *PM* 15: 287-293.

Grove, W. R. 1842. On a gaseous voltaic battery. PM 23: 417-420.

Grove, W. R. 1843. Experiments on voltaic reactions. PM 23: 443-446.

Grove, W. R. 1874. *The Correlation of physical forces*, pp. 1-180. London: Longmans, Green, and Co.

Helmholtz, H. F. 1845. Über den Stoffverbrauch bei der Muskelaction. *Wissenschaftliche Abhandlungen von Hermann Helmholtz*, 1888, zweiter band, pp. 735-744. LeipsigLJohann Ambrosius Barth.

Helmholtz, H. F. 1846. Wärme, Physiologisch. Encyklopädisches Wörterbuch der Medicinischen Wissenschaften. Members of the Berlin Medical Faculty (Eds.), Berlin: Verlag von Veit et Comp.

Helmholtz, von H. F. 1847a. Über die Erhaltung der Kraft; eine physikalische Abhandlung. Berlin: G. Reimer, pp. 1-72. This article was published in 1882 in the *Wissenrchaftliche Abhandlungen, erster band*. Leipzig: Johann Ambrosius Barth, pp. 11-75.

Helmholtz, H. F. 1847b. Bericht über die Theorie der Physiologischen Wärmeerscheinungen für 1845 In: *Fortschritte der Physik im Jahre 1845*, Berlin: Reimer, pp. 346-355. This artcle appeared as well in *Wissenrchaftliche Abhandlungen*, *erster band*, Leipzig: Johann Ambrosius Barth, pp. 3-11 (1882).

Helmholtz, von H. F. 1848. Uber die Wärmeentwickelung bei der Muskelaction. In: Wissenschaftliche Abhandlungen von Hermann Helmholtz, 1888, zweiter band, pp. 745-

763. LeipsigLJohann Ambrosius Barth. Also Helmholtz, von H. F. 1848 Archiv fur Anatomie und Physiologie pp. 158-164,

Helmholtz, von H. F. 1853a. The conservation of force. Translated by J. Tyndall: In: *Scientific Memoirs selected for the transactions of foreign Academies of Science and from foreign journals*, pp. 114-162. London: Taylor and Francis.

Helmholtz, H. F. 1853b. Über einige Gesetze der Vertheilung elektrischer Ströme in körperlichen Leitern, mit Anwendung auf die thierisch-elektrischen Versuche. *APC* 7: 211-233 and 353-376.

Helmholtz, von H. F. 1872. Über galvanische Polarisation des Platin. Halle, Zeitschrift fur die gesamten Naturwissenschaften 6: 186-188.

Helmholtz, von H. F. 1873. Über galvanische Polarisation in gasfreien Flüssigkeiten. *AP* 226: 483-495.

Helmholtz, von H. F. 1877. Über galvanische Ströme, verursacht durch Concentrations-Unterschiede; Folgerungen aus der mechanischen Wärmetheorie *Monatsberichte der Königlichen Preussische Akademie des Wissenschaften zu Berlin* 713-726. Also, it was published in. Helmholtz, von H. F. 1878. *AP* 239: 201-216.

Helmholtz, H. F. 1879. Studien über elektrische grenzschichten. APC 7: 337–382

Helmholtz, H. F. 1881, On the modern development of Faraday's conception of Electricity. In: *The Question of the Atom; From the Karlsruhe Congress to the first Solvay Conference 1860-1911*. Nye M. J. (Ed.), pp. 251-282. Los Angeles: Thomas Publishers.

Helmholtz, H. F. 1882. Die Thermodynamik Chemisher Vergänge. In: *Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin*, Erster Halbband, Januar bis Mai, pp. 22-39. Translated in English under the direction of the Physical Society

of London. **Helmholtz, H. F. 1888**. The thermodynamics of chemical processes In: *Physical memoirs selected and translated from foreign sources,* Vol. I. Part II, pp. 43-62. London: Taylor and Francis.

Helmholtz, von H. 1883. Uber das Wesen der Faulniss und Gahrung. In: *Wissenschaftliche Abhandlungen von Hermann Helmholtz*, vol. III, pp. 726-734. LeipsigLJohann Ambrosius Barth. Translated in English as **Helmholtz, von H. 2001**. On the Nature of Putrefaction and Fermentation. *Science in Context* 14: 499 – 504.

Helmholtz, von H. F. 1888. The thermodynamics of chemical processes. In: *Physical memoirs selected and translated from foreign sources*, Vol. I. Part III, pp. 76-97. London: Taylor and Francis.

Helmholtz, von H. 1893. Hermann Von Helmholtz, an Autobiographical Sketch: An Address Delivered on the Occasion of His Jubilee, 1891. London: Longmans, Green, and Company.

Hess, H. G. 1840a. Recherches sur les quantités de chaleur dégagées. CR 19: 759-763.

Hess, H. G. 1840b. Thermochemische Untersuchungen. AP 50: 385–404.

Hess, H. G. 1842. Thermochemische Untersuchungen. AP 26: 463 – 479.

Hittorf, W. J. 1869. Über die Electricitätsleitung der Gase. APC 212: 1-31.

Hittorf, J. W. 1899. On the migration of ions during electrolysis. In: *The fundamental Laws of electrolytic Conduction*. Goodwin H. M. (Ed.). New York: Harper & Brothers Publishers), p. 47-80. Translated from the orininal article **Hittorf J. W. 1853**. Über die Wanderungen der Ionen während der Elektrolyse. *APC* 89: 177-211.

Horstmann, A. F. 1868. Zur Theorie der Dissociacions-Erscheinungen. Berichte der deutschen chemische Geselschaft 1: 210-215.

Horstmann, A. F. 1869. Dampfspannung und Yerdampfungswärme des Salmiaks. Berichte der deutschen chemische Geselschaft 2: 137-40.

Horstmann, A. F. 1871. Zur Theorie der Dissociation. *Berichte der deutschen chemische Geselschaft* 4: 635-639.

Horstmann, A. F. 1873. Theorie der dissociation. *Liebig's ACPh* 170: 192-210. An English translation of this article appears in the *Bulletin of the History of Chemistry* 2009, 34: 76-82.

Joule J. P. 1841. On the heat evolved by metallic conductors of electricity and in the cells of battery during electrolysis. *PM* 19: 260-277;

Joule J. P. 1842. On the electric origin of the heat of combustion. PM 20: 98-113.

Joule J. P. 1843a. On the calorific effects of magneto-electricity, and on the mechanical value of heat. *PM* 23: 263-276.

Joule J. P. 1843b. On the electrical origin of chemical heat. PM 22: 204-208.

Joule J. P. 1845a. On the existence of an equivalent heat and the ordinary forms of mechanical power. *PM* 27: 205-207.

Joule J. P. 1845b. On the changes of temperature produced by the rarefaction and condensation of air. *PM* 26: 369-383.

Joule J. P. 1847. On the mechanical equivalent of heat, as determined by the heat evolved by the friction of fluids. *PM* 31: 173-176

Joule J. P. 1850. On the mechanical equivalent of heat. PTRS 140: pp. 61-82.

Joule, J. P. 1852a. On the use of electro-magnets made of iron wire for the electromagnetic engine. *Journal of the Franklin Institute* 53: 35–38.

Joule J. P. 1852b. On the heat disengaged in chemical combinations. PM 3: 481-504.

JSP. 1884. *The Scientific Papers of James Prescott Joule*, vol. 1. The Physical Society of London (Eds.). London, Taylor, and Francis.

Kolbe, H. 1848. Zersetzung der Valeriansäure durch den elektrischen Strom. *ACPh* 64: 339–341.

Kolbe, H. 1849. Untersuchungen über die Elektrolyse organischer Verbindungen. *ACPh* 69): 257–294.

Kohlrausch, F., Nippoldt, W. A. 1869. Uber die Gultigkeit der Ohmschen Gesetze fur Elektrolyte und eine numerische Bestimmung des Leitungswiderstandes der verdunnten Schwefelsaure durch alternierende Strome. *AP* 138: 280-298. Translated as an abstract,

Kohlrausch, F., Nippoldt W. A. 1870. On the Extension of Ohm's Laws to Electrolytes and on the Numerical Determination of the Resistance of dilute Sulphuric Acid by means of Alternate Currents. *PM* 40: 227-229.

Kohlrausch, F. 1874. Uber die Wirkung der Polarisation auf alternierende Strome und fiber einen Sinusinduktor. *Annalen der Physik* Jubelband: 290-303.

Kohlrausch, F., Grotrian, O. 1875. Das elektrische Leitungsvermogen der Chloride von den Alkalien und alkalischen Erden, sowie der Salpetersaure in wassrigen Losungen. *AP* 230:215-239.

Kohlrausch, F. 1876a. Das elektrische Leitungsvermogen der Chlor-, Brom- und Jod-Wasser- stoffsaure, der Schwefel-, Phosphor-, Oxal-, Wein- und Essigsaure in wassrigen Losungen. *AP* 235: 233-275.

Kohlrausch, F. 1876b. Uber das Leitungsvermbgen der in Wasser gelhsten Elektrolyte im Zu- sammenhang mit der Wanderung ihrer Bestandteile. *Nachrichten von der Königl. Gesellschaft der Wissenschaften und der Georg-Augusts-Universität*, Göttingen: No. 10,

pp. 213-224. Translated as **Kohlrausch, F. 1899**. On the conductivity of electrolytes dissolve in water in relation to the migration of their components. In: *The fundamental laws of electrolytic conduction*. Goodwin H. M. (Ed.), pp. 85-91. New York: Harper & Brothers Publishers.

Kohlrausch, F. 1879. Das electrische Leitungsvermögen der wässerigen Lösungen von den Hydraten und Salzen der leichten Metalle, sowie von Kupfervitriol, Zinkvitriol und Silbersalpeter. *APC* 6: 1-51 and 145-210.

Lavoisier, A. L., Laplace, P. S. 1783. *Mémoire sur la chaleu*r. Paris: Gauthier-Villars et Cie. Translated in English: 1994. Memoir on heat, *Obesity Research* 2: 189-202.

Le Chatelier, H. 1888. Recherches expérimentales et théoriques sur les équilibres chimiques. Paris: Dunond.

Lewis, G. N. 1899a. *A general equation for free energy and physicochemical equilibrium, and its application*. Ph.D. Dissertation. Ann Arbor: Harvard University.

Lewis, G. N. 1899b. The development and application of a general equation for free energy and physico-chemical equilibrium. *PAAAS* 35: 3-38.

Lewis, G. N. 1900. A new conception of thermal pressure and a theory of solutions. *PAAAS*36: 145-168

Lewis, G. N. 1901. The law of Physico-chemical change. PAAAS 37: 49-69.

Lewis, G. N. 1906. A review of recent progress in physical chemistry. JACS 28: 893-910.

Lewis, G. N. 1907. Outlines of a new system of thermodynamic chemistry. *PAAAS* 43: 259-293.

Lewis, G. N. 1909. The use and abuse of the ionic theory. Science 30: 1-6.

Lewis, G. N. 1912. The activity of the ions and the degree of dissociation of strong electrolytes. *JACS* 34: 1631-1643.

Lewis, G. N. 1913. The free energy of chemical substances. JACS 35: 1-30.

Lewis, G. N. 1916. The Atom and the Molecule. JACS 38: 762–785.

Lewis, G. N., Linhart, G. 1919. The degree of ionization of very dilute electrolytes. *JACS* 41: 1951-1960.

Lewis, G. N., Randall, M. 1921a. The activity coefficient of strong electrolytes. *JACS* 43: 1112-1154.

Lewis, G. N., Randall, M. 1921b. The thermodynamic treatment of concentrated solutions, and applications to thallium amalgams. *JACS y* 43: 233-254.

Lewis, G. N., Randall, M. 1923a. *Thermodynamics and the Free Energy of Chemical Substances*. New York: MacGraw-Hill Book Co. Second edition revised by K. Pitzer and L. Brewer in 1961.

Lewis, G. N. 1923b. *Valence and the structure of atoms and molecules*. New York: The chemical Catalog Co: Dover reprint 1966.

Lewis, G. N. 1938. Acids and Bases. Journal of the Franklin Institute 226: 293-313.

Lewis, G. N., Kasha M. 1944. Phosphorescence and the triplet state. *JACS* 66: 2100–2116.
Liebig, J. 1842. *Die organische Chemie in ihrer Anwendung auf Physiologie und Pathologie*. Braunschweig: Vieweg. Translated the original by Gregory W. Liebig, J. 1842. Animal Chemistry or Organic chemistry in its application to physiology and pathology. London: Taylor and Wanton.

Lodge, O. 1885. On the Influence of Marpietism on the Discharge of Electricity through Gases. In: *Report of the BAAS*, 54th meeting, Montreal. London: John Murray.

Lodge, O. 1887a. Electrochemical Thermodynamics (Letter from Professor J. Willard Gibbs). In: *Report of the BAAS*, 56th meeting, Birmingham, September 1886. London: John Murray.

Lodge, O. 1887b. Translation of a letter received from Dr. Arrhenius. In: *Report of the BAAS*, 56th meeting, Birmingham, September 1886. London: John Murray.

Lodge, O. 1887c. On the conductivity of mixtures of aqueous acid solutions. In: *Report of the BAAS*. 56th meeting, Birmingham, September 1886. London: John Murray.

Lodge, O. 1887d. Recherches sur la Conductihilité galvanique des Électrolytes. Par Svante Arrhenius. Mémoire presents a l'Academie des Sciences de Suede, le 6 Juin 1883. In: *Report of the BAAS*, 56th meeting, Birmingham, September 1886. London: John Murray.

Lodge, O. 1888. Comparison between the Views of Dr. Arrhenius and Professor Armstrong on Electrolysis. In: *Report of the BAAS*. 57th meeting, Manchester, August-September 1887. London: John Murray.

Lodge, O. 1889. Electrochemical Thermodynamics (Letter from Professor Willard Gibes to the Secretary of the Electrolysis Committee of the British Association). In: *Report of the BAAS*, 58th meeting, Bath, August-September 1888. London: John Murray.

Lodge, O. 1891. *Report of the BAAS*, 60th meeting, Leeds. September 1890. London: John Murray.

Manville, O. 1928. *L'Oeuvre scientifique de Pierre Duhem*. Memoires de la Societe scientifique des sciences physiques et naturelles de Bordeau. Paris: Blanchard.

Massieu, F. 1869. Sur les fonctions caractéristiques des divers fluides et sur la théorie des vapeurs. *CR* 69: 858–862, and 1057–1061.

Massieu, F. 1876. Thermodynamique: Mémoire sur les fonctions caractéristiques des divers fluides et sur la théorie des vapeurs. *Académie des Sciences de L'Institut National de France* XXII: 1-92.

Maxwell, J. C. 1872. Theory of Heat. London: Longmans, Green, and Co.

Maxwell, J. C. 1875. On the dynamical evidence of the molecular constitution of bodies. *Nature* 11: 357-359.

Maxwell, J. C. 1876. On the equilibrium of heterogeneous substances. PM 16: 818-824.

Maxwell, J. C. 1902. Theory of Heat. 3d Edition. London: Longmans, Green, and Co.

Mayer, J. R. 1842. Bemerkungen über die Kräfte der unbelebten Natur. ACPh 42: 233-240.

Mayer, J. R. 1845. *Die organische Bevengung in irhem zusammenhange mit Stoffwenchsel ein Beitrag sur Naturkunde*. Heilbronn: Verlag C. Drechsler.

Mayer, J. R. 1851. Über die Physiologische Bedeutung des Mechanischen Aequivalente der Wärme. Heilbronn: Verlag C. Drechsler..

Mayer, J. R. 1851. Bemerkungen über das mechanische Aequivalent der Wärme. Heilbronn: Verlag C. Drechsler.

Mayer, J. R. 1862. Remarks on the forces of inorganic nature. PM 24: 371-377.

Meyerhoffer, W. 1893. Die Phasenregel und ihre Anwendungen. Leipzig: Franz Deuticke.

Mendeleev, D. 1887. The compounds of ethyl alcohol with water. JCS 51: 778-782.

Mendeleev, D. 1890. Dissociation of Substances in Solution. JCS Abstracts 58: 326.

Nasse H. 1850. Über den Einfluss der Nahrung auf das Blut. Marburg: E I wert'sche Universitätsbuchhandlung.

Nernst, W. 1889. Die elektromotorische Wirksamkeit der Jonen. ZPC 4:.129-188.

Nernst, W. 1893. Theoretische Chemie, vom Standpunkte der Avogadroschen Regel und der Thermodynamik. Stuttgart: Verlag von Ferdinand Enke.

Nernst, W. 1904. *Theoretical chemistry from the standpoint of Avogadro's rule and thermodynamics*,-London: Macmillan and CO., Ltd.

Nernst, W. 1906. Über die Berechnung Chemischer Gleichgewichte aus thermischen Messungen1. *Nachrichten von der Gesellschuft der Wissenschalien zu Göttingen* 1-40.

Nernst, W. 1907. *Experimental and theoretical applications of thermodynamics to chemistry*. New York: Charles Scribner's Sons.

Nernst, W. 1918. *Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes*. Halle: Verlag von Wilhelm Knapp. Translated in English: **Nernst, W. 1969**. *The New heat theorem. Its foundation in theory and experiment*. New York: Dover Publications INC.

Nicholson, W., Carlisle, A., Cruickshank, W. 1800. Experiments in Galvanic Electricity. *PM* 7: 337-347.

Ohm, G. S. 1827. Die galvanische Kette: mathematisch bearbeitet. Berlin: Riemann. It has been translated, **Ohm, G. S. 1891.** The Galvanic Circuit Investigated Mathematically. New York: D. Van Nostrand Company.

Ørsted, J. C. 1820. Experiments on the effect of a current of electricity on the magnetic needle. *Annals of Philosophy* 16: 273–276.

Ørsted, H. C. 1823. Nouvelles expériences de M. Seebeck sur les actions électromagnetiques. *Annales de chimie*, 2nd series. 22: 199–201.

Ostwald, W. 1884. Notiz über das Elektrische Leitungsvermogen der Säuren. *Journal für Praktische Chemie* 30: 93-95.
Ostwald, W. 1885. Electrochemische Studien. III. Abhandlung. Uber den Einfluss der Zusamensetzung und Konstitution der Säuren auf ihre Leitfahigkeit. *Journal für Praktische Chemie* 32: 300-374.

Ostwald, W. 1887a. *Lehrbuch Der Allgemeinen Chemie*. Leipzig: Verlag von Wilhelm Engelmann.

Ostwald, W. 1887b. An die Leser. ZPC 1: 1-4.

Ostwald W. 1888a. Zür Theorie der Lösungen. ZPC 2:36-37.

Ostwald W. 1888b. Über die dissociationtheorie der Elektrolyse ZPC 2: 270-283.

Ostwald W., Nernst, W. 1889. Über Freie ionen. ZPC 3: 120-130.

Ostwald, W. 1891. *Report of the BAAS*, 60th meeting, Leeds. September 1890. London: John Murray.

Ostwald W. 1896. Elektrochemie, ihre Geschichte und Lehre. Leipzig: Veit & Comp.

Ostwald, W. 1909. *Nobel lecture on catalysis*. Nobel Prize. The Nobel Foundation. https://www.nobelprize.org/prizes/chemistry/1909/ostwald/lecture/

Ostwald, W. 1916. *L'Evolution d'une science*. *La chimie*. Translated by Marcel Dufour. Paris: Ernest Flammarion..

Ostwald, W. 2017. *The Autobiography*. Berlin: Springer International Publishing AG. Translated by Jack, R., Edited by Scholz, F., and Jack, R., from the original publication:

Ostwald, W. 1927. Lebenslinien: Eine Selbstbiographie. Berlin: Hofenberg.

Peltier, J. C. A. 1834. Nouvelles expériences sur la caloricité des courants électrique. Annales de Chimie et de Physique. 56: 371–386.

Pfaundler, L. 1867. Beiträge zur chemischen Statik, APC 131: 55-85.

Pickering, S. U. 1886a. The influence of temperature of the heat of chemical combination. *JCS* 49: 260-311.

Pickering, S. U. 1886b. On the nature of solutions. *Chemical News and Journal of Industrial Science* 54: 215-217.

Pickering, S. U. 1890. The nature of solutions, as elucidated by the freezing points of sulphuric acid solutions. *JCS* 57: 331-369

Pickering, S. U. 1891. The present position of the hydrate theory of solution. In: *Report of the BAAS*, 60th meeting, Leeds, September 1890. London: John Murray.

Planck, M. 1879. Über den zweiten Hauptsatz der mechanischen Wärmettheorie. Inaugural dissertation. Munchen: Th. Ackermann.

Planck, M. 1887a. Über das Princip der Vermehrung der Entropie. Erste Abhandlung.

Gesetze des Eintritts beliebiger thermodynamischer und chemischer Reactionen. *Wiedemann's Annalen der Physik* 30: 562-582. Republshed in *APC* 268: 562-582.

Planck, M. 1887b. Über das Princip der Vermehrung der Entropie. Zweite Abhandlung.
Gesetze des Eintritts beliebiger thermodynamischer und chemischer Reactionen.
Wiedemann's Annalen der Physik 31: 189-208. Republshed in APC 267: 189-208..

Planck, M. 1887c. Über das Princip der Vermehrung der Entropie. Dritte Abhandlung.
Gesetze des Eintritts beliebiger thermodynamischer und chemischer Reactionen.
Wiedemann's Annalen der Physik 32: 462-503. Republshed in APC 268: 462-503.

Planck, M. 1887d. Über die molekulare Konstitution verdünnter Lösungen. ZPC 1: 577-582.

Planck, M. 1888. Das Chemische Gleichgewicht in Verdünnten Lösung. APC 270: 139-154. Planck, M. 1890. Über den osmotischen Druck. ZPC 6:187-189.

Priestley, J. 1776. Observations of respiration, and the use of the blood. *Philosophical Transaction* 66: 226-248.

Rankine, W. J. M. 1850. On the Mechanical Action of Heat, especially in Gases and Vapours. *Transactions of the Royal Society of Edinburgh* 20: 147-190.

Rankine, W. J. M. 1851a. Über die mechanische Theorie der Wärme. APC 157: 172-176.

Rankine, W. J. M. 1851b. On the mechanical theory of heat. PM 2: 61-65.

Rankine, W. J. M. 1853. On the General Law of the Transformation of Energy. *PM* 5: 106-117.

Rankine, W. J. M. 1881. *Miscellaneous Scientific Papers*. Millar, (Ed.), London: Charles Griffin and Company.

Raoult, F. M. 1878. Sur la tension de vapeur et sur le point de congélation des solutions salines. *CR* 87: 167-169.

Raoult, F. M. 1882a. Loi de congélation des solutions benzéniques des substances neutres.*CR* 95: 187-189.

Raoult, F. M. 1882b. Loi générale de congélation des dissolvants. CR 95: 1030-1033.

Raoult, F. M.1887. Loi générale des tensions de vapeur des dissolvants. *CR* 104: 1430-1433.

Reech, F. 1853. Theorie gènèrale des effets dynamiques de la chaleur. *Journal de Mathematiques Pures et Appliquees* 18: 357-568.

Regnault, V., Reiset, J. 1849. Recherches Chimiques sur la Respiration des animaux des diverses classes. *ACP* 25: 299-519.

Richards, T. W., Lewis, G. N. 1898. Some Electrochemical and Thermochemical Relations of Zinc and Cadmium Amalgams. *PAAAS* 34: 87-99.

Saurel, P. 1902. On the critical state of a one-component system. JPC 6: 474-491.

Schuster A. 1884. The Bakerian Lecture, experiments on the discharge of electricity through dases. Sketch of a theory. *PRS* 37: 317-339.

Schuster A. 1890. Bakerian Lecture: The discharge of electricity through gases. *PRS* 45: 557-559.

Seebeck, T. J. 1822. Magnetische Polarisation der Metalle und Erze durch Temperatur-Differenz. In: *Abhandlungen der Königlichen Akademie der Wissenschaften zu Berli*n, pp. 265-273. Berlin: Royal Academy of Sciences.

Show, W. N. 1891. Report on the present state of our knowledge in electrolysis and electrochemistry. In: *Report of the BAAS*, 60th meeting, Leeds, September 1890. London: John Murray.

Stern, O. 1924. Zur Theorie der elektrolytischen Doppelschicht. Zeitschrift für Elektrochemie. 30: 508-516.

Stokes, G. G. 1907. *Memoir and scientific correspondence of the late Sir George Gabriel Stokes*. Vol. 2, Section III, Larmor J, (Ed.). Cambridge: Cambridge University Press.

Thomson, J. 1849. Theoretical considerations on the effects of pressure in lowering the freezing point of water. *Transactions of the Royal Society of Edinburgh* 16: 575-580.

Thomson, J. 1871. Considerations on the abrupt change at roiling or condensing in reference to the continuity of the fluid state of matter. *PRS* 20: 278-286.

Thomson J. J. 1883. On a theory of the electric discharge in gases. PM 15: 427-434.

Thomson J. J. 1884. On the chemical combination of gases. *PM* 18: 233-267.

Thomson J. J. 1887. The Bakerian Lecture: On the dissociation of some gases by the electric discharge. *PRS* 42: 343-345.

Thomson J. J. 1888. *Applications of Dynamics to Physics and Chemistry*. London: Macmillan and Co.

Thomson, J. J. 1890. The discharge of electricity through gases. *Nature* 42: .295.

Thomson, W. 1847. Notice of Stirling's air engine. *Proceedings of the Royal Philosophical Society of Glasgow* 2: 169-170.

Thomson, W. 1848. On an absolute thermometric scale founded on Carnot's theory of the motive power of heat and calculated from Regnaut's observations. *PM* 1: 100-106.

Thomson, W. 1849. An account of Carnot's theory of the motive power of heat; with numerical results deduced from Regnault's experiments on steam. *Transactions of the Royal Society of Edinburgh* 16: 113-155.

Thomson, W. 1850. The effect of pressure in lowering the freezing point of water, experimentally demonstrated. *PM* 37: 123-127.

Thomson, W. 1851. On the dynamical theory of heat, with numerical results deduced from Mr. Joule's equivalent of a thermal unit, and M. Regnault's observations on steam. *Transaction of the Royal Society of Edinburgh* 4: 174-210.

Thomson, W. 1852. On a universal tendency in nature to the dissipation of mechanical energy. *PM* 25: 304-306.

Thomson, W. 1882. On the linear motion of heat, part 1 and part II. In: *Mathematical and Physical papers of Sir William Thomson*. Art. IV and V, Vol. 1. Cambridge, Cambridge University Press. van der Waals, J. D. 1873. Over de continuiteit van den gas- en vloeistoftoestand, pp. 1-154, Leiden: Sijthoff, A.W.

van 't Hoff, J. H. 1875. La chimie dans l'espace. Amsterdam: Bazendijk

van 't Hoff, J. H. 1878-1881. Ansichten über die organische Chemie. vols 2. Brunswick:Druck und Verlag von Friedrich Vieweg und Sohn.

van 't Hoff, J. H. 1884. Etudes de dynamique chimieque. Amsterdam: F. Miller.
Translated by Ewan Thomson as Van 't Hoff, J. H. 1896. *Studies in chemical dynamics*.
Frederik Miller & Co.

van 't Hoff, J. H. 1886. L'Équilibre chimique dans les systemes gazenx on dissout a l'etat dilué. *Archives Néerlandaise des Sciences Exactes et Naturelles* 20: 239-302. A synopsis of this article was published in *Recueil Travaux Chimie de Pays Bas* 4 (1885) 424-427.

van 't Hoff, J. H. 1887. Die Rolle des Osmotischen Druckes in der Analogie Zwischen Lösungen und Gasen. ZPC 1: pp. 481-508. Translated as van 't Hoff, J. H. 1995. The role of osmotic pressure in the analogy between solutions and Gases. *Journal of Membrane Science* 100: 39—44.

van 't Hoff, J. H. 1888. Dissociationstheorie der Elektrolyte. ZPC 2: 781-786.

van 't Hoff, J. H. 1891. *Report of the BAAS*, 60th meeting, Leeds. September 1890. London: John Murray.

van 't Hoff, J. H. 1894. Wie die Theorie der Lösungen entstand. Berichte der deutschen chemischen Gesellschaft 27: 6 – 19.

van 't Hoff, J. H. 1902. Lebensbericht. A. Horstmann. Ostwald, W. (Ed.), *Klassiker der Exacten Naturwissenschaften*, Nr. 137. Leipsig: Engelmann,

van 't Hoff, J. H. 1903. *Physical chemistry in the service of sciences*. In: *The decennial publications, second series*, vol. XVIII. Chicago: The University of Chicago Press.

van 't Hoff, J.H. 1912. Die chemischen Grundbegriffe nach Menge, Mass und Zeit. Braunschweig: Vieweg, & Sohn.

van 't Hoff, J. H. 1967. *Imagination in science*. Translated with Notes and a General Introduction by Springer, G. F. Berlin Heidelberg: Springer-Verlag Berlin Heidelberg GmbH.

Walker, J. 1891. Dr. James Walker read the following translation of a communication from Dr. Arrhenius. In: *Report of the BAAS*, 60th meeting, Leeds, September 1890. London: John Murray.

Weber, W. E. 1851. Messungen galvanischer Leitungswiderstände nach einem absoluten Maaße. *APC* 82: 337–369. Translated in English: by Atkinson, E. as Weber, W. E. 1861.
On the Measurement of Electric Resistance according to an absolute Standard. *PM* 22: 261–269.

Wilhelmy, L. F. 1850. Über das Gesetz, nach welchem die Einwirkung der Säuren auf den Rohrzucker stattfindet. *APC* 81: 413–433, and 499–526. It was reprinted in Ostwald's *Klassiker der exacten Wissenschaften*, no. 29, Leipzig, 1891. This publication contains a complete list of Wilhelmy's ten papers. Portions of the paper were translated into English as **Wilhelmy, L. F. 1850**. The law by which the action of acids on cane sugar occurs. In: Source Book in Chemistry 1400–1900. Henry M. Leicester and H. S., Klickstein, A (Eds.), pp. 396–400. 1968, 4rth edition. New York: Harvard University Press.

Williamson, A. W. 1850. Theory of Ætherification. PM 37: 350-356.

Wollaston, W. H. 1814. A Synoptic Scale of Chemical Equivalents. *Philosophical Transactions of the Royal Society of London* 104: 1-24.

Wollaston, W. H. 1864. *Telegraphic journal: A weekly record of electrical and scientific progress*. Ser. 10, Vol. 1, p. 127. London: Truscott, Son & Simmons.

Secondary sources

Allen, R. C. 2009. *The British Industrial Revolution in Global Perspective*. pp. 233-275. Cambridge: Cambridge University Press.

Atkins, P. W., De Paula, J., James Keeler, J. 2018. *Physical Chemistry*, 11th Edition. Oxford: Oxford University Press.

Baierlein, R. 2001. The elusive chemical potential. AJP 69: 423-434.

Balian, R. 2017. François Massieu et les potentiels thermodynamiques. *Comptes Rendus Physique* 18: 526-530.

Baizer, M. M. 1980. Prospects for further industrial applications of organic electrosynthesis. *Journal of Applied Electrochemistry* 10: 285-290.

Baizer M. M. 1989. History of organic electrosynthesis. In: *Electrochemistry, Past, and Present*, Stock, J. T., Orna, M. V. (Eds.), ACS Symposium Series. Washington, DC: American Chemical Society.

Barbara, P. F. 1996. Brief History of Physical Chemistry in the American Chemical Society. *JPC* 100: 12694-12700.

Barkan, D. K. 1999. Walther Nernst and the transition to modern physical science. New York: Cambridge University Press.

Barnett, M. K. 1978. Sadi Carnot and the second law of thermodynamics. *Osiris* 13: 327-357.

Bartel, H.-G., Huebener, R. P. 2007. *Walter Nernst. Pioneer of Physics and Chemistry*. New Jersey: World Scientific.

Bebensee, F., Welter, K., Heydenrych, G. 2020. Forever young/ChemPhysChem 21: 4-6.

Beer, J. J. 1958. Coal Tar Dye Manufacture and the Origins of the Modern Industrial Research Laboratory. *Isis* 49: 123-131.

Bevilacqua, F. (1993). Helmholtz Ueber die Erhaltung der Kraft. In: *Hermann von Helmholtz and the foundations of nineteenth-century science*, Cahan, D. (Ed.), pp. 291-333. Berkeley, University of California Press.

Bordoni, S. 2010. *Taming complexity. Duhem's pathway to thermodynamics*. Doctoral Dissertation. Universita Deglis Studi di Bergamo.

Bordoni, S. 2012. Unearthing a buried memory: Duhem's third way to thermodynamics, Part 2, *Centaurus* 54: 232-249.

Bordoni, S. 2013. Routes toward an abstract thermodynamics in the late nineteenth century. *The European Physical Journal H* 38: 617-660.

Boynton, W. P. 1900a. Gibbs' thermodynamical model. Physical Review 10: 228-233.

Boynton, W. P. 1900b. Gibbs' thermodynamical model for a substance following van der Waals' equation. *Physical Review* **11: 291-303**.

Boynton, W. P. 1905. Thermodynamical potentials. *Physical Review* 20: 259-267.

Broadie A. 2009. *A History of Scottish Philosophy*. Edinburgh: Edinburgh University Press Ltd.

Branch, G. E. K. 1984. Appendix: Gilbert Newton Lewis, 1875-1946. JCE 61: 18-21.

Brown, S. C. 1950. The caloric theory of heat. AJP 18: 367-373.

Brush, S. G. 1970. The Wave Theory of Heat: A Forgotten stage in the transition from the caloric theory to thermodynamics. *BJHS* 5: 145-167.

Bryan, G. H. 1907. *Thermodynamics. An introductory treatise dealing mainly with first principles and their direct applications*. Leipzig: B. G. Tuber.

Buchwald, J. Z. 1981. Thomson, Sir William (Baron Kelvin of Largs). In: *DSB*, Gillispie,C. C. (Ed.), vol. 13, pp. 374-388. /New York: Charles Scribner Sons,

Buchholtz, K. 1979. Verfahrenstechnik (Chemical Engineering) - Its development, present state, and structure. *Social Studies of Sciences* 9: 33-62.

Bumstead, H. A., Van Name, R. G. 1906. *The Scientific Papers of J. W. Gibbs*. Vol. 1. New York: Longman, Green, and Co.

Bunge, M. 2009. *Causality and modern science* 4th edition. New Brunswick: Transaction Publishers,

Cahan, D. 1989. Kohlrausch and Electrolytic Conductivity. Instruments, Institutes, and Scientific Innovation. *Osiris* 5: 166-185.

Cahan, D. 2018. Helmholtz: A life in science. Chicago: The University of Chicago Press.

Calvin, M. 2010. Gilbert Newton Lewis: His influence on physical organic chemistry at Berkeley. In: *183rd National Meeting of the American Chemical Society*, Las Vegas, Nevada, March 30-31, 1981, pp. 1-36.

Caneva, K. L. 1993. *Robert Mayer and the Conservation of Energy*. Princeton New Jersey: Princeton University Press.

Caneva, K. L. 1997a. Colding, Øersted, and the meanings of force. HSPBS 28: 1-138.

Caneva, K. L. 1997b. Physics and Naturphilosophie: A reconnessance. HS 35: 35-106.

Cantor, G. N. 1976. William Robert Grove. The correlation of forces and the conservation of energy. *Centaurus* 19: 273-290

Cardoso, D. S. P., Šljukić, B., Santos, D. M.F., Sequeira C .A. C. 2017. Organic Electrosynthesis: From laboratorial practice to industrial applications. *Organic Process Research & Development* 21: 1213-1226.

Cardwell, D. S. L. 1971. From Watt to Clausius. The rise of thermodynamics in the early industrial age. London: Heinemann.

Cardwell, D. S. L. 1976. Science and technology: The work of James Prescott Joule. *Technology and Culture* 17: 674-697.

Chapman H. C., Albert P. Brubaker, A. P. 1891. Researches upon Respiration. Proceedings of the Academy of Natural Sciences of Philadelphia 43 13-44.

Clark, A. L., Katz, L. 1939. Thermodynamic surfaces of H₂0. *Transactions of the Royal Society of Canada*, 3rd series Sec. III 33: 59-71.

Coffey, P. 2006. Chemical free energies and the third law of thermodynamics. *HSPBS* 36: 365-396.

Coffey, P. 2008. *Cathedrals of Science. The Personalities and Rivalries That Made Modern Chemistry*. Oxford: Oxford University Press.

Cohen, E. 1912. *Jacobus Henricus rant Hoff: Sein Lehen and Werken*. Leipzig: Akademische Verlagsgesellschaft.

Cohen, C. 1996. The early history of chemical engineering a reassessment. *BJHS* 29: 171-194.

Coley, N. G. 1996. Studies in the History of Animal Chemistry and its Relation to Physiology. *Ambix* 43: 164-187.

Coy, D. C. 1993. *Visualizing thermodynamic stability and phase equilibrium through computer graphics*. Ph.D. Dissertation, Iowa State University.

Crawford, E. 1992. Nationalism and Internationalism in science 1880-1939. Cambridge: Cambridge University Press.

Crawford, E. 1996. *Arrhenius, From Ionic Theory to the Greenhouse Effect*. Canton, MA: Science History Publications.

Cropper, W. H. 1988. Joule's work in electrochemistry and the emergence of the first law of thermodynamics. *HSPBS* 19: 1-14.

Cropper, W. H. 2004. *Great Physicists. The Life and Times of Leading Physicists from Galileo to Hawking*. pp. 106-123. N Oxford: Oxford University Press.

Cukierman, S. 2006. Et Tu, Grotthuss! and other unfinished stories. *Biochimica et Biophysica Acta* 1757: 876–885.

Dahl, Per F. 1963. Colding and the Conservation of Energy. Centaurus 8: 174-188.

Dahl, Per, F. 1972. *Ludvig A. Colding and the Conservation of Energy Principle*. New York: Johnson Reprint Corporation.

Dahl, Per F. 1981. Colding, Ludvig Augusts. In: *DSB*, Gillispie, C. C. (Ed.), Vol. 15, Supplement 1, pp. 84-87. New York: Charles Scribner Sons.

Darrigol, O. 2018a. *Atoms, Mechanics, and Probability: Ludwig Boltzmann's Statistico-Mechanical Writings* - An Exegesis. Oxford: Oxford University Press.

Darrigol, O. 2018b. The Gibbs Paradox: Early History and Solutions. Entropy 20: 1-54.

Daub E. E. 1970. Entropy and dissipation. *Historical Studies in the Physical Sciences* 2: 321-354.

Daub E. E. 1976. Gibbs' phase rule: A centenary retrospect. JCE 53: 747-751.

Davis, B. 1980. A web of naked fancies? Physics Education 15: 57-61.

De Berg, K. C. 2003. The development of the theory of electrolytic dissociation. *Science* & *Education* 12: 397-419.

De Berg, K. C. 2015. Foundations of and challenges to electrolyte chemistry. *Foundations of Chemistry* 17: 33-48.

Delete, R. J. 1983. *The energetics controversy in late nineteenth-century Germany: Helm, Ostwald and their critics.* Ph.D. Dissertation, volumes I, and II. Yale University

Deltete, R. J. 1996. Josiah Willard Gibbs and Wilhelm Ostwald. A contrast of scientific styles. *JCE* 73: 289-295.

Deltete, R. J., Brenner, A. 2004. Review. Pierre Duhem: Mixture and Chemical Combination and Related Essays. *Foundations of Chemistry* 6: 203-230.

Divall, C. M., Johnston F. 1998. Scaling up: the evolution of intellectual apparatus associated with the manufacture of heavy chemicals in Britain, 1900-1939. In: *Determinants in the Evolution of the European Chemical Industry*, 1900-1939. Travis, A.

S., Schroter, H. G., Homburg, E., Morris, P. J. T. (Eds.), pp. 199-214. Dordrecht: Kluwer Academic Publishers.

Dolby, R. G. A. 1976. Debates over the theory of solution: A study of dissent in physical chemistry in the English-speaking world in the late nineteenth and early twentieth centuries. *HSPS* 7: 297-404.

Dolby, R. G. A. 1977. The transmission of two new scientific disciplines from Europe to North America in the late nineteenth century. *Annals of Science* 34, 287-310.

Donnan, F. G. 1909. The university training of technical chemists. *Journal of the Society of Chemical Industry* 28: 275-280.

Donnan, F. G. 1933. Ostwald Memorial Lecture. JCS 316-332.

Donnan, F. G. 1936. The chemist in industry: Some considerations about training and prospect. *Journal of Careers* 15: 73-77.

Donnan, F.G., Haas, A. 1936. *Commentary on the scientific writings of J. Willard Gibbs*. New Haven, Connecticut: Yale University Press.

Donnelly, J. F. 1986. Representations of Applied Science- Academics and Chemical Industry in Late Nineteenth-century England. *Social Studies of Sciences* 18: 195-234.

Drennan, O. J. 1981. Hittorf, Johann. Wilhelm. In: *DSB*, Gillispie, C. C. (Ed.), vol. 5, pp. 438-440. New York: Charles Scribner Sons.

Dunn, E., Fosdick, R. L. 1980. The Morphology and Stability of Material Phases." *Archive for Rational Mechanics and Analysis* 74: 1-99.

Dunsch, L., Müller, H. 1989. Ein Fundament zum Gebäude der Wissenschaften: Einhundert Jahre Ostwalds Klassiker der exakten Wissenschaften (1889-1989). Leipzig: Akademische Verlagsgesellschaft Geest & Portig.

Ehl, R. G., Ihde, A. G. 1954. Faraday's electrochemical laws and the determination of equivalent weights. *JCE* 31: 226-232.

Elkana, Y. 1970. The conservation of energy: A case of simultaneous discoveries? *Archives Internationals d'Histoire des Sciences* XXIII: 31-60.

Elkana, Y. 1974. *The discovery of the conservation of energy*. Cambridge: Harvard University Press.

Fischer, N. W. 1973. Organic classification before Kekulė. *Ambix* 20:106-131; Part II, 209-233.

Fischer, N. W. 1974. Kekulė and organic classification. Ambix 21: 29-52.

Finn, B. S. 1981. Sturgeon William. In: *DSB*, Gillispie, C. C. (Ed.), vol. 13, p. 125. New York: Charles Scribner Sons.

Forrester, J. 1975. Chemistry and the conservation of energy. The work of James Prescott Joule. *SHPS* 6: 275-313.

Fox, R. 1969. James Prescott Joule. In: *Mid-nineteenth century Scientists*. North, J. D.(Ed.). Oxford: Pergamon Press.

Fox, R. 1970. Watt's expansive principle in the work of Sadi Carnot and Nicolas Clément. *Notes and records of the Royal Society of London* 24: 233–253.

Fox, R. 1971. *The caloric theory of gases: From Lavoisier to Regnault*. Oxford: Oxford University Press.

Fox, R. 1986. *Reflexions on the motive power of fire. A critical edition with the surviving scientific manuscripts*. New York Manchester University Press.

Freeman, A. 1878. The analytical theory of heat. London: Cambridge University Press.

Garber, E. W. 1969. James Clerk Maxwell and thermodynamics. AJP 37: 146-155.

Garber, E. 1970. Clausius and Maxwell's Kinetic Theory of Gases. HSPS 2: 299-319.

Gavroglu, K., Patiniotis, M., Papanelopoulou, F., et al. 2008. Science and technology in the European periphery: Some historiographical reflections. HS xlvi: 153-175.

Gavroglu, K., Simoes, A. 2012. From physical chemistry to quantum chemistry: How chemists dealt with mathematics. *International Journal of Philosophy of Chemistry* 18: 45-68.

Gillispie, C. C. 1971. Lazare Carnot, Savant. Princeton NJ, Princeton University Press.

Gillispie, C. C. 1981. *Carnot, Lazare-Nicolas-Margueri*te. In: *DSB*, Gillispie, C. C. (Ed.), vol. 3, pp. 70-79. New York: Charles Scribner Sons.

Gillispie, C. C., Pisano, R. 2013. Lazare and Sadi Carnot. A Scientific and Filial Relationship. Dordrecht, Springer.

Glasstone, S. 1947. *Thermodynamics for Chemists*. New York: Van Nostrand Reinhold Inc.

Golinski, I. (2008). Chemistry. In: *Eighteenth-Century Science*, Porter, R. (Ed.), pp. 375-390, Cambridge: Cambridge University Press.

Gongadze, E., Petersen, 1, S., Beck, U., van Rienen, U. 2009. Classical models of the interface between an electrode and an electrolyte. In: *Proceedings of the COMSOL Conference*. 8-10 October 2009, Milan, Italy.

Guėdon, J.-C. 1980. Conceptual and institutional obstacles to the emergence of unit operations in Europe. In: *History of Chemical Engineering*. Furter W. F. (Ed.), pp. 45, 56. Washington, DC: American Chemical Society.

Guggenheim, E.A. 1933. *Modern-thermodynamics by the methods of Willard Gibbs*. London: Methuen & Co., Ltd.

Hall, V. M. D. 1980. The role of force or power in Liebig's physiological chemistry. *Medical History* 24: 20-59.

Harrow, B. 1920. Eminent chemists of our times. New York: D. Van Nostrand Company.

Heimann, P. M. 1974a. Helmholtz and Kant: The metaphysical foundation of Über die Erhaltung der Kraft. *SHPS ce* 5: 205-238.

Heimann, P. M. 1974b. Mayer's Concept of "Force": The "Axis" of a New Science of Physics. *HSPS* 7: 277-296.

Herivel, J. 1975. Joseph Fourier: The man and the physicist. Oxford: Clarendon Press.

Hiebert, E. N. 1981a. Ostwald, Wilhelm Friedrich In: *DSB*, Gillispie, C. C. (Ed.), vol. 15, Supplement I, pp. 455-469. New York: Charles Scribner Sons.

Hiebert, E.N. 1981b. Nernst, Hermann walther. In *DSB*, Gillispie, C. C. (Ed.), vol. 15, pp.432–453. New York: Charles Scribner Sons.

Hiebert, E. N. 1981c. Development in physical chemistry at the turn of the century. In *Science technology and society in the time of Alfred Nobel*. Bernard, C. G., Crawford, E.,

Sorbom, P. (Eds.). Oxford: Pergamon Press.

Hildebrand, J. H. 1958. Gilbert Newton Lewis 1975-1946. A Biographical Memoir.Washington D.C. National Academy of Sciences.

Holleman, A. F. 1952. My reminiscences of van 't Hoff. JCE 29: 379-382.

Holmes, F. L. 1962. From Elective Affinities to Chemical Equilibria- Berthollet's Law of Mass Action. *Chymia* 8: 105-145.

Holmes, F. L. 1963. Elementary Analysis and the Origins of Physiological Chemistry. *Isis* 54: 50-81.

Holmes, F. L. 1964. Introduction to the latest English reprint of Justus Liebig, Animal chemistry, or organic chemistry in its application to physiology and pathology. New York, Johnson Reprint Corporation.

Holmes, F. L. 1975. The transformation of the science of nutrition. *Journal of the History of Biology* 8: 135-144.

Homburg, E. 1992. The emergence of research laboratories in the dyestuffs industry, 1870-1900. *BJHS* 25: 91-111.

Homburg, E., Travis, A. S., Schröter, H. G. 1998. The Chemical Industry in Europe, 1850–1914. In: *Industrial Growth, Pollution, and Professionalization*. pp. 9-120. Dordrect: Kluwer Academic Publishers.

Hougen, O. A. 1977. Seven decades of chemical engineering. *Chemical Engineering Progress* 57: 89-93.

Hunt, L. B. 1958. The Ammonia Oxidation Process for Nitric Acid Manufacture. Early developments with platinum catalysis. *Platinum Metals Review* 2: 129-134.

Jaki, S. L. 1984. Uneasy Genius: The Life and Work of Pierre Duhem. The Hague: Martinus Nijhoff Publishers.

Jaselskis, B., Moore, C. E., von Smolinsk, A. 2007. Theodor von Grotthuss (1785-1822)—A trail blazer. *BHC ry* 32: 119-128.

Jensen, W. B. 1984. Abegg, Lewis, Langmuir, and the Octet Rule. JCE 61: 191-200

Jensen, W. B. 2009. August Hortsmann and the origin of chemical thermodynamics. *BHC* 34: 83-91.

Jensen, W. B. 2005. *G. N. Lewis and the quantification of 20thcentury chemical thermodynamics. A tribute to the text "Thermodynamics and the Free Energy of Chemical Substances" by G. N. Lewis and M. Randall.* American Chemical Society Division of the History of Chemistry, Copy available online.

Jensen, W. B., Kuhlmann, J. 2012. Leopold Pfaundler and the origin of the kinetic theory of chemical reactions. *BHC* 37: 29-41.

Jensen, W. B. 2017. The mystery of G. N. Lewis's missing Nobel Prize. In: *The Posthumous Nobel Prize in Chemistry. Volume 1. Correcting the Errors and Oversights of the Nobel Prize Committee*, Strom, E. T., Mainz, V. V. (Eds). ACS Series, vol. 1262, pp. 197-120. Washington, DC: Oxford University Press.

Johnson, J. A. 1985. Academic chemistry in imperial Germany, Isis 76: 500-524.

Jolls, K. R. 1989a. Gibbs and the Art of Thermodynamics, In *Proceedings of the Gibbs Symposium*, eds. Caldi, D. G., and G. D. Mostow, pp. 293-321. Providence, RI: American Mathematical Society.

Jolls, K. R. 1989b. Understanding Thermodynamics through Interactive Computer Graphics. *Chemical Engineering Progress* 85: 64-69.

Jones, P. J. 2012. Contrasting mentors for English-speaking chemistry students in Germany in the nineteenth century: Liebig, Whöler, and Bunsen. *BHC* 37: 14-23.

Jungnickel C., McCormmach R. 1986. *Intellectual Mastery of Nature. Theoretical Physics from Ohm to Einstein*, vol.1. Chicago: The University of Chicago Press.

Kasha M. 1984. The triplet state. An example of G. N. Lewis' research style. *JCE* 61: 204-215.

Kauffman, G. B. 1966. Reflections on Chemistry and its Teaching. On the occasion of the Alfred Werner Centennial. *JCE* 43: 677-679.

Kerker, M. 1960. Sadi Carnot and the steam engine engineers. Isis, 51: 257-270.

Kim, M. G. 2003. *Affinity, That Elusive Dream_A Genealogy of the Chemical Revolution*. Cambridge: MIT Press.

Kipnis, A, Ya. 1991. Early chemical thermodynamics: Its duality embodied in Van 't Hoff and Gibbs. In *Thermodynamics, history, and philosophy, facts, trends, and debates,* K. Martinas, K., Ropolyi, L., P. Szegedi, P. (Eds), pp. 492–507. London: World Scientific Publishing Co.

Kipnis, A. 1997. August Friedrich Horstmann und die physikalische Chemie. Berlin: ERS Verlag.

Kipnis, N. 2000. Debating the Nature of Voltaic Electricity 1800. In: *Nuova Voltiana: Studies on Volta and his Times*. Bevilaqua, F., Pregonese, L. (Eds.), pp. 121-151. Milano: Editore Ulrico Hoepli.

Kipnis, N. 2014. Thermodynamics and Mechanical Equivalent of Heat. *Science* &*Education* 23: 2007-2044.

Klein, M. J. 1966. Thermodynamics and quanta in Planck's work. *Physics Today* 19: 23-32.

Klein, M. J. 1969. Gibbs on Clausius. HSPS 1: 127-149.

Klein, M. J. 1974. Carnot's contribution to thermodynamics, *Physics Today* 27: 23-28.

Klein, M. J. 1984. The scientific style of Josiah Willard Gibbs. In: *Essays of founders of modern science*, Aris. A., Davis, H. T., Stewers, R. H. (Eds.), pp. 142-162, Minneapolis: University of Minnesota Press

Klein, M. J. 1989. The physics of J. Willard Gibbs in his time. In: *Proceedings of the Gibbs Symposium*. Caldi, D. G., and Mostow, G. D. (Eds.), pp. 5-8, Providence, RI: American Mathematical Society.

Klein, M. J. 1990. Duhem on Gibbs. In: *Essays in honor of Robert Schofield*. Garber E (Ed.), pp. 52-67. London: Associated University Press Inc.

Koenig, F. 1959. On the history of science and the second law of thermodynamics. In: *Men and moments in the history of science*. Evans H. M. (Ed), pp. 57–111. Seattle: The Washington University Press, Seattle.

Koenigsberger, L. 1906. Herman von Helmholtz. Oxford: Clarendon Press.

Kohler, R. E. 1974. Irving Langmuir and the Octet Theory of Valence, HSPS 4: 39-87.

Kragh, H. 1993. Between Physics and Chemistry: Helmholtz's Route to a Theory of Chemical Thermodynamics. In: *Hermann von Helmholtz and the foundations of nineteenth-century science*. Cahan, D. (Ed.), pp. 403-431. Berkeley, University of California Press,

Kragh, H., Weininger, S. J. 1996. Sooner Silence than Confusion: The Tortuous Entry of Entropy into Chemistry. *HSPBS* 27: 91-130.

Kragh, H. 2000. Confusion and Controversy: Nineteenth-Century Theories of the Voltaic Pile. In: *Nuova Voltiana: Studies on Volta and his Times*. Bevilaqua, F. L. Pregonese, L. (Eds.), pp. 133-157. Milano, Milano: Editore Ulrico Hoepli.

Kragh H., Bak M. M. 2000. Christoph H. Pfaff and the controversy over voltaic electricity. *BHS* 25: 83-90.

Kragh, H. 2009. *Conservation and controversy: Ludvig Colding and the imperishability of forces*. RePoSS: Research Publications on Science Studies 4. Aarhus: Centre for Science Studies, University of Aarhus.

Kranzberg, M. 1982. The interchange of technology and society: 1860-1914. In: *Science and technology and society in the time of Alfred Nobel. Proceedings of Nobel symposium.* Bernhard, C.G., Crawford, E., Sorbom Per, (Eds.) pp.209-230. New York: Pergamon Press. **Kremer, R. L. 1984**. The Thermodynamics of Life and Experimental Physiology, 1770-1880. Doctoral dissertation, Harvard University.

Kremer, R. L. 1986. Defending Lavoisier: The French Academy's Prize Competition of 1821. *History and Philosophy of the Life Sciences* 8: 41-65.

Kuhn, T. S. 1955. Carnot's version of "Carnot's cycle". AJP 23: 91-95.

Kuhn, T. S. 1958. The caloric theory of adiabatic compression. *Isis* 49: 132-140.

Kuhn, T. S. 1977. Energy conservation as an example of simultaneous discoveries. In:

The Essential Tension, pp. 66-104. New York: The University of Chicago Press.

Lachman, A. 1955. Borderlands of the unknown: The life story of Gilbert Newton Lewis.

Ph.D. dissertation. The Johns Hopkins University. New York: Pageant Press.

Laidler, K. J. 1984. The Development of the Arrhenius Equation. JCE 61: 493-498.

Laidler, K. J. 1985. Chemical kinetics and the origins of physical chemistry. *AHES* 32: 43-75.

Laidler, K. J. 1993. The World of Physical Chemistry. Oxford: Oxford University Press.

La Mer, V. K. 1954. Some Current Misinterpretations of N. L. Sadi Carnot's Memoir and Cycle. *AJP* 22: 20-27; ibid. 1955. 23: 95-102.

Lawrence, S. 2011. Developable surfaces: Their history and application. *Nexus Network Journal* 13: 701–714.

Lenoir, T. 1982. The strategy of life. Teleology and mechanics m nineteenth-century German biology. In *Studies in the history of modern sciences*. Cohen, R. S., Hiebert, E., Mendelsohn, E. (Eds.), Vol. 13. Dordrecht: D. Reidel Publishing Company.

Lervig, P. 1972. On the structure of Carnot's theory. AHES 9: 222–239.

Levere, T. H. 2001. *Transforming matter: History of chemistry from Alchemy to the Buckyball*. Baltimore: The John Hopkins University Press.

Lewis, E. S. 1998. A Biography of distinguished scientist Gilbert Newton Lewis. Lewiston, NY: The Edward Mellen Press.

Lindauer, M. W. 1962. The evolution of the concept of chemical equilibrium from 1775-1923. *JCE* 39: 384-390.

Logan, S. R. 1982. The origin and status of the Arrhenius equation. JCE 59: 279-281.

Lund, E. W. 1965. Guldberg and Waage, and the law of mass action. JCE 42: 548-550.

Lund, E. W. 1968. Activated Complex—A Centenarian? A Tribute to Leopold Pfaundler. *JCE* 45: 125-128.

Marsch, U. 1995. Strategies for success: Research organization in German chemical companies and I.G. Farben until 1936. *History and Technology* 12: 23-77.

Martins, R. 2003. Resistance to the discovery of electromagnetism: Ørsted and the symmetry of the magnetic field. In: *Volta and the History of Electricity*, Bevilacqua, F., and Giannetto, E. (Eds.), pp. 245-265. Pavia: Editore Ulrico Hoepli.

Mathias, P.M. 2016. The Gibbs–Helmholtz equation for chemical process and technology. *Industrial and Engineering Chemistry Research* 55: 1076–1087.

Maugin, G. 2014. Continuum mechanics through the eighteenth and nineteenth centuries. Historical perspectives from John Bernoulli (1727) to Ernst Hellinger. Heidelberg: Springer.

McClelland, C. E. 1980. *State, Society, and University in Germany, 1700-1914.* New York: Cambridge University Press.

Meheus, J. 1999. Clausius's discovery of the first two laws of thermodynamics a paradigm of reasoning from inconsistencies. *Philosophica* 63: 89-117.

Mendoza, E. 1959. Contributions to the Study of Carnot. *Archives Internationals d'Histoire des Sciences* 12: 377-396.

Mendoza, E. 1960. *Reflections on the Motive Power of Fire. Sadi Carnot and other Papers on the second law of thermodynamics by Clapeyron, É. and Clausius, R.* New York: Dover Publications Inc.

Mendoza, E. 1961. A sketch for a history of early thermodynamics. *Physics Today* 14: 32-42.

Mendoza, E. 1981. The life and work of Sadi Carnot. BJHS 14:75-78,

Mendoza E., Cardwell, D. S. L 1981. On a Suggestion concerning the work of J. P. Joule. *BJHS* 14: 177 180.

Merton, R. K. 1957. Priorities in scientific discovery: A chapter in the sociology of science. *American Sociological Review* 22: 635-659.

Meyer-Thurow, G. 1982. The industrialization of Invention- A case study from the German chemical industry. *Isis* 73: 363-381.

Mi Gyung, K. 2006. *Wilhelm Ostwald (1853-1932)*. HYLE Biography, http://www. hyle.org/journal/issues/12-1/.bio_kim.htm.

Miller, D. G. 1963. Duhem and the Gibbs-Duhem Equation. JCE 40: 648.

Miller, D. G. 1966. Ignored intellect: Pierre Duhem. *Physics Today* 47-53.

Miller, D. G. 1981. Duhem, Pierre-Maurice-Marie. In: DSB, Gillispie, C. C. (Ed.), vol 4,

pp. 225-233. New York: Charles Scribner's Sons.

Moore, C.E., von Smolinski, A., Jaselskis, H. 2002. The Ostwald–Gibbs correspondence: An interesting component in the history of the energy concept. *BHS* 2: 114–127.

Morus, I. R. 1991. Correlation and control- William Robert Grove and the construction of a new philosophy of scientific reform, *SHPS* 22: 589-621.

Müller, F. 2011. Johann Wilhelm Hittorf and the material culture of nineteenth-century gas discharge research. *BJHS* 44: 211-244.

Müller, I. 2006. A history of thermodynamics. The doctrine of energy and entropy. pp. 127-164. Berlin: Springer.

Needham, P. 2011. *Commentary of the principles of thermodynamics by Pierre Duhem* Dordrecht, Heidelberg: Springer.

Ostwald, C. 1953. Wilhelm Ostwald. Mein Vater. Stuttgart: Berliner Union.

Owen D. 2001. The Constant Battery and the Daniell-Becquerel-Grove Controversy. *Ambix* 48: 25-40.

Partington, J. R. 1972. *History of Chemistry*. vol. 4. London: The MacMillan Press.

Partington, J. R. 1913. A textbook of thermodynamics (with special reference to chemistry). London: Constable & Company Ltd.

Paul, E. R. 1978. Alexander W. Williamson on the atomic theory: A Study of nineteenth-century British atomism. *Annals of Science* 35: 17–31.

Pauling. L.1984. G. N. Lewis and the chemical bond. JCE 61: 201-203.

Petit, A. 2013. *Histoire du concept d' ion au dix-neuvième siècle*. Thèse Doctoral, Université de Nantes, Faculté des Sciences et des Techniques.

Petit, A. 2016. Associating physics and chemistry to dissociate molecules: The history of the Clausius-Williamson hypothesis. *Historical Studies in the Natural Sciences* 46: 360-391.

Pitzer, K. S. 1984. Gilbert N. Lewis and the thermodynamics of strong electrolytes. *JCE* 61: 104-107.

Poncet, S., Dahlberg, L. 2011. The legacy of Henri Victor Regnault in the arts and sciences. *International Journal of Arts and Sciences* 4: 377-400.

Potter, H. 1963. A Note on the Carnot function. *Journal of the Franklin Institute* 276: 507-518.

Psillos, S. 1994. A philosophical study of the transition from the caloric theory of heat to thermodynamics: Resisting the pessimistic meta-induction. *SHPS Part A* 25: 159-190.

Reinhardt, C. 1998. An Instrument of corporate strategy: The central research laboratory at BASF 1868-1890. In: The Chemical Industry in Europe, 1850–1914: Industrial growth, pollution, and professionalization. Homburg, E., Travis, A. S., Schröter H. G. (Eds), pp. 239-260. Dordrect, the Nethelands: Kluwer Academic publisher.

Reynolds, O. 1892. Memoirs of James Prescott Joule. In: *Memoirs and Proceedings of Manchester Literary & Philosophical Society, fourth series*, vol. VI. Manchester: T. Sowler and Co.

Reynolds, T., Forman, J. C., Resen, L. 1983. 75 Years of Progress: A history of the American Institute of Chemical Engineers 1908-1983. New York: The Institute.

Rittman, W. F. 1914. The application of physical chemistry to industrial processes. *The Journal of Industrial and Engineering Chemistry* 6: 684–687.

Roberts, G. K. 1997. Physical chemistry for industry: The making of chemist at University College London, 1914-1939. *Centaurus* 39: 291-319.

Rocke, A. J. 1993. *The quiet revolution. Hermann Kolbe and the science of Organic chemistry*. Berkeley: University of California Press.

Rocha-Homem, T. 2015. Robert Mayer Conservation of Energy and venous blood. *Advances in Historical Studies* 4: 309-313.

Root-Bernstein, R. S. 1980. *The ionists: Founding physical chemistry 1872-1890*. Ph.D. dissertation. Ann Arbor: Princeton University.

Rosenberg, N. 1982. The growing role of science in the innovation process. In: *Science* and technology and society in the time of Alfred Nobel. Proceedings of Nobel symposium.

Bernhard, C.G., Crawford, E., Sorbom Per, (Eds.), pp. 231-250. New York: Pergamon Press.

Rosenfeld, L. 2003. Justus Liebig and the animal chemistry. *Clinical Chemistry* 49: 1696–1707

Ross, S. 1961. Faraday consults the scholars: The origins of the terms of electrochemistry. *Notes and Records of the Royal Society of London* 16:187-220.

Sarton, G. 1929. The discovery of the law of conservation of energy. *Isis* 13: 18-44.

Schirra, N. 1991. Die Entwicklung des Energibe griffs und seines Erhaltung konzepts. Thun, Frankfurt am Main: H. Deutch.

Scott, E. L. 1981. Grove William, Robert. In: *DSB*, vol. 15, Supplement I, pp. 455-469. New York: Charles Scribner Sons.

Seaborg, G. T. 1984. The research style of Gilbert N. Lewis: Acids and Bases. *JCE* 61: 93-100.

Servos, J. W. 1980. The industrial relations of science: Chemical engineering at MIT, 1900-1939. *Isis* 71: 530-549.

Servos, J. W. 1982. A disciplinary program that failed: Wilder D. Bancroft and the journal of Physical Chemistry, 1896-1933 *Isis* 73: 207-232.

Servos, J. W. 1984. G. N. Lewis: The disciplinary setting. JCE 61: 5-10.

Servos, J. W. 1990. *Physical chemistry from Oswald to Pauling. The making of a science in America*. Princeton, NJ: Princeton University Press.

Sherwood Taylor, F. 1957. *A History of Industrial Chemistry*. London: Heinemann, pp. 228-230.

Sheysnin, O. B. 1979. C. F. Gauss and the theory of errors. A historical essay. *AHES* 20: 21-72.

Shinn, T. 1980. From 'corps' to 'profession': the emergence and definition of industrial engineering in modern France. In: *The organization of science and technology in France 1808-1914*. Fox, R., Weisz G. (Eds.), pp. 183-208. Cambridge, Cambridge University Press.

Shinn, T. 2001. The industry, research, and education nexus. In: *The Cambridge history of science. The modern physical and mathematical science*, Nye M. (Ed.), vol. 5, pp. 133-153. Cambridge: Cambridge University Press.

Smith, C. 1976. Natural philosophy and thermodynamics: William Thomson and the dynamical theory of heat. *BJHS* 9: 293-319.

Smith, C. 1977. William Thomson and the creation of thermodynamics: 1840-1855. *AHES*16: 231-288.

Smith, C., Wise, M. N. 1989. Energy and Empire: A biographical study of Lord Kelvin. New York, Cambridge University Press.

Snelders, H. A. M. 1981a. Arrhenius, Svante August. In: *DSB*, Gillispie, C. C. (Ed.), vol 1, pp. 296-302. New York: Charles Scribner's Sons.

Snelders, H. A. M. 1981b. Van 't Hoff, Jacobus Hernicus. In: *DSB*, Gillispie, C. C. (Ed.), vol 13, pp. 575-581. New York: Charles Scribner's Sons.

Steffens, H. J. 1979. James Prescott Joule and the concept of energy. New York: Dawson:
Science History Publications.

Stewart, G. W. 1995. (Gauss) Theory of the combination of observations least subject to errors. Philadelphia: Society for Industrial and Applied Mathematics.

Thackray, A. 1981. Daniell John, Frederic. In: *DSB*, Gillispie, C. C. (Ed.), vol. 3, pp. 556-558. New York: Charles Scribner Sons.

Thomas, T. A. 2017. Theodor Schwann: A founding father of biology and medicine. *History of Medicine* 15: 299-301.

Thompson, S. P. 1910. *The Life of William Thomson, Baron Kelvin of Largs*. Vol. 1. London: Macmillan.

Thurston, R. H. 1897. *Reflexions on the motive power of fire*. 2nd edition. New York: John Wiley & Sons.

Truesdell, C. 1952. The mechanical foundations of elasticity and fluid dynamics. *Journal of Rational Mechanics and Analysis* 1: 125–300.

Truesdell, C. 1980. *The tragicomical history of thermodynamics 1822-1854*. New York: Springer-Verlag.

Truesdell, C. 1984. Rational thermodynamics. (2nd Ed.). New York, Springer-Verlag.

Truesdell, C. 1986. What did Gibbs and Caratheodotory leave us about thermodynamics? In *New perspectives in thermodynamics*, Serrin, J, (Ed.), pp. 101-113. Berlin: Springer-Verlag.

Truesdell, C., Bharatha, S. 1977. *The Concepts and Logic of Classical Thermodynamics as a Theory of Heat Engines. Rigorously Constructed upon the Foundation Laid by S. Carnot and F. Reech.* New York: Springer-Verlag.

Turner, R. S. 1981. Helmholtz, Hermann von, In: *DSB*, Gillispie C. C. (Ed.), vol. 6. pp. 241-253. *New York*: Charles Scribner Sons.

Turner, R. S. 1981. Mayer, Julius Robert, In: DSB, Gillispie C. C. (Ed.), vol. 9, pp. 233-

240. New York: Charles Scribner Sons.

Turner, R. S. 1982. Justus Liebig versus Prussian chemistry: Reflections on early institutebuilding in Germany. *HSPS* 13: 129-162.

Tyndall, J. 1853. On the conservation of force, a physical treatise. In: *l*. pp. 114-162. London: Taylor and Francis.

Tyndall, J. 1864. Notes on scientific history. PM 28: 25-51.

Walker, J. 1913. Van 't Hoff memorial lecture. JCS Transactions 103: 1127-1143.

Walker, J. 1928. Arrhenius memorial lecture. JCS 1380-1401.

Walker, W. H. 1905. Some present problems in technical chemistry. *Popular Science Monthly* 66: 435-448.

Weyrauch, J. J. 1893a. Die Mechanik der Warme in gesammelte Schriften von Robert Mayer. Stuttgart: Verlag der J. G. Cotta'schen Buchhandlung.

Weyrauch, J. J. 1893b. *Kleinere Schriften und Briefe von Robert Mayer*. Stuttgart: Verlag der J. G. Cotta'schen Buchhandlung.

Wheeler, I. P. 1962. *Josiah Willard Gibbs the history of a great mind*. New York: Yale University Press.

Wilson. E. B. 1936. Papers I and II as Illustrated by Gibbs' lectures on thermodynamic, In *Commentary on the Scientific Writings of J. Willard Gibbs*, Donnan, F. G., and A. Haas (Eds), 2 Vols, 19-59 pp. New Haven, Connecticut: Yale University Press.

Wise, G. 1983. Ionists in industry: Physical chemistry at General Electric, 1900-1915. *Isis* 74: 7-21.

Wisniak, J. 2000. Jöns Jacob Berzelius A Guide to the perplexed chemist. *The Chemical Educator* 5: 343–350.

Wisniak, J. 2003. Hendrik-Willem Bakhuis Roozeboom: Equilibrium and Phase Topology. *JCE* 24: 422-430.

Wisniak, J. 2003. Max Margules—A Cocktail of Meteorology and Thermodynamics. *Journal of Phase Equilibri*a 24: 103-109.