

THE PERMEATION OF THERMODYNAMICS INTO NINETEENTH CENTURY CHEMISTRY*

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Today any serious study of chemistry involves an acquaintance with the principles of thermodynamics. But chemistry as a science has existed for a much longer period of time than our formulations of thermodynamical principles. The impressive nature of this circumstance strikes us when we compare the situation with physics. In this paper the gradual permeation of thermodynamics into chemistry during the nineteenth century is made. Also the possible reasons for this to have taken place then and not earlier are considered.

INTRODUCTION

Today it is impossible to pursue any serious study of chemistry without some acquaintance with the basic principles of thermodynamics. But we must realize that chemistry as a science is much older than our knowledge of the laws of thermodynamics. Chemistry has existed for a much longer period of time than the formulations of the thermodynamical principles in terms of which we understand and interpret chemical phenomena in our own times.

The impressive nature of this circumstance strikes us when we compare the situation with physics. Physics as a modern scientific enterprise began to germinate on the conceptual foundations of mechanics during the seventeenth century. The fruitful notions of velocity, acceleration, momentum and force began to take an exploitable significance during that century, and were further refined and explored in the course of the eighteenth century. And by the close of the nineteenth century classical mechanics had become a crowning achievement of the scientific intellectual adventure. To this day any systematic study of physics is inaugurated with the fundamentals of mechanics. A great deal of physics still rests on the mechanical model, both conceptual and mathematical. Except in situations where the philosophy of the microcosm dominates this model has generally proved to be both useful and consistent. On the other hand the evolution of conceptual chemistry has been quite different. Chemistry graduated from an avid

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search for magic formulas to transmute metals and for immortalizing elixirs into a disinterested field of scientific inquiry at about the same time as physics. Van Helmont (1577–1644) and Glauber (1604–1688) were contemporaries of Galileo (1564–1642) and von Guericke (1602–1686). Boyle's *Sceptical Chymist*¹ appeared in 1661, Newton's *Principia*² in 1687. Yet, a whole century had to pass before chemistry became a mature science³. Still another century rolled by before the thermodynamical foundations of chemistry were laid down. For it was only in the 1870's, just about a century ago, that thermodynamics began to penetrate the conceptual framework of chemistry.

We shall attempt in this paper to discuss some of the major jolts by which thermodynamics gradually became an integral part of chemistry. In our concluding remarks we shall refer to some possible reasons for this to have happened then, and not earlier.

THE ROLE OF HEAT IN CHEMISTRY

If the aim of chemistry is the study of matter and its many transformations, an important agent of such transformations cannot be ignored. From time immemorial fire (or heat) has been known to be that agent. A major step in the evolution of any field of inquiry from commendable curiosity to a scientific discipline consists in efforts at consistent explanations. Not infrequently such explanations are based on abstract and intangible principles. If heat (or fire) is in some way associated with chemical changes one ought to try to explain at least two things: (a) the nature of heat; and (b) how heat accomplishes what it does in a chemical change.

It was as a response to the first problem that the idea of the phlogiston evolved⁴ during the eighteenth century. The concept of the phlogiston—which was in some respects a scientific fantasy—is a fine example of the methodology of hypothesis-framing. It reflects all the strengths, weaknesses, utility, and dangers of that intellectual game. The phlogiston reigned supreme during much of the eighteenth century⁵. The basic tenet of the theory, viz. that combustion results from the presence in the burning substance of a fire-producing principle, accounted reasonably well (with suitable modifications when necessary) for a variety of observed facts. This it did within the narrow framework of scientific explanation that was then in vogue among chemists. This framework was not modified until precise and quantitative methods were introduced into chemistry. The intrinsic feature (and weakness) of phlogiston was that it was more descriptive than explanatory in the modern scientific sense⁶; and as such, it did not differ much from other prescientific theories⁷.

It must be remembered that until the last quarter of the eighteenth century chemistry was essentially a qualitative science. Even the balance was not exploited until Lavoisier came to the scene in the 1770's⁸. In 1780 T. Bergman expressed his displeasure at the fact that "some chemists.....consider thermometers and

such-like measuring instruments to be physical subtleties, superfluous and unnecessary in the chemical laboratories⁹.”

The first significant result of scientific import relating heat and chemical reactions emerged from the work of Lavoisier and Laplace¹⁰. In a classic memoir published in the 1780's¹¹ they stated that chemical compounds are characterized by definite quantities of heat which are absorbed or released when the compounds are formed or decomposed. This principle ushered in what has come to be known as the subject of thermochemistry. In the complex transformations incessantly taking place in the phenomenal world the scientific investigator looks for constant and invariable features. The heat of formation of a compound is one such feature with respect to chemical reactions. Hence its recognition was a major step in the scientific development of chemistry.

But, as in the case of other bold generalizations in science, the Lavoisier-Laplace principle was more the result of insight than of detailed measurements. And although it was an important discovery, neither the then common experimental techniques¹² nor the lingering popularity of phlogiston¹³ spurred many others to explore heats of reaction with great zeal¹⁴. Another half a century had to elapse before thermochemistry took a second major step.

AFFINITY AND THERMOCHEMISTRY

The phenomena of celestial motions could be adequately explained on the basis of a single universal force, viz. gravitation. But chemical combinations are characterized by selective mutual attractions. Chemical forces do not seem to have the universality of gravitation. Consequently one spoke of affinities and hostilities in the description of chemical combinations¹⁵.

From the time of Newton gravitation had become a well-defined mathematical entity¹⁶. Its basic properties were clearly and precisely postulated. Planetary motions could now be exactly described and correctly predicted in terms of these. Hence the further *application* rather than *explanation* of gravitation was what interested physicists and mathematicians. But with affinities the situation was quite different. Like phlogiston, affinity was essentially a descriptive term. Nothing of significance was explained, let alone predicted, on its basis. The most one could do was to compare affinities¹⁷. Hence, a deeper understanding of the nature of affinity was a main concern of chemists during the eighteenth and nineteenth centuries¹⁸.

J. J. Berzelius, whose interest in electricity had been aroused on reading about Volta's epochmaking contrivance in 1800, and stimulated further by his association with Hesinger¹⁹, developed a theory of affinity based on electrical forces²⁰. According to this view all atoms carried positive and negative charges, but in unequal amounts. This rendered some elements naturally electropositive, and others electronegative. Berzelius' theory was put forward in 1819²¹. It was influential for some years.

Germain Hess, born in Switzerland and taken to Russia at the age of three, was a warm admirer of Berzelius, but not of the electrochemical theory of affinity. He realized that "Among the symptoms accompanying each chemical combination there is an essential one which had not been sufficiently studied: I mean the development of heat²²." It occurred to him that a study of this might give a clue to the nature of affinity. Hess began thinking along these lines in the early 1830's²³, and carried out a series of careful experiments on the problem during the closing years of that decade²⁴. In his reports on these experiments²⁵ he gave details of his work from which he drew the important conclusion: "A combination having taken place, the quantity of heat evolved is always constant whether the combination is performed directly, or whether it takes place indirectly and in different steps." Hess noted that this principle should be self-evident to anyone who considered the question.²⁶ Clearly, self-evident truths are not always obvious, and acquire that characteristic only after they are recognized. The importance, let alone the axiomatic nature, of this principle could not be fully realized by chemists until the notion of energy was clarified²⁷.

THE ENERGY CONSERVATION PRINCIPLE AND CHEMISTRY

The 1840's saw the emergence of a new and powerful idea in scientific thought: the principle of energy conservation²⁸. In retrospect it may not seem to have been an entirely new idea, as it is implicit in the writings of many earlier investigators: Stevin, Galileo, Descartes and Huygens, for example²⁹. And yet the most spectacular achievements of eighteenth century celestial mechanics were made without using the energy concept explicitly. Also, the recognition of heat as yet another form of energy, measurably equivalent to mechanical energy, was essential before the energy principle could be formulated in its most general form³⁰.

The energy principle expressed the invariability of the totality of energy in the universe: its relevance lay in the contexts of energy transformations. Of all such transformations those in which heat was involved were the ones that interested chemists primarily³¹. Consequently interest in the precise determination of heats of reaction began to develop once again.

One of the first chemists to apply the energy conservation principle specifically to chemical problems was Julius Thomsen of Copenhagen³². Thomsen, who is credited with well over three thousand calorimetric measurements, began his studies on the thermal aspects of chemistry in the early 1850's. His findings led him to the conclusion that "every simple or complex action of a purely chemical character is accompanied by the production of heat³³."

In 1864 M. Berthelot began his extensive experiments in thermochemistry, quite unaware and independently of Thomsen's work³⁴. He was led to very similar numerical results, and to a similar general principle also. Berthelot expressed his conclusion as the principle of maximum work³⁵ according to which "every chemical

change, accomplished without the intervention of an extraneous energy tends to the production of the substance or system of substances which evolves the greatest amount of heat³⁶."

Both Thomsen and Berthelot suggested that the heat evolved in the decomposition of a compound may be taken as a measure of chemical affinity³⁷.

THE SECOND LAW OF THERMODYNAMICS

Even as the energy principle was being gradually clarified during the 1840's some confusion developed regarding the ultimate nature of heat. This was because the experimentally established mechanical equivalence of heat seemed to be in apparent contradiction with Carnot's principle³⁸. If the caloric view of heat is taken literally, Joule's result cannot be reconciled with Carnot's principle³⁹.

A great deal of light was thrown on the puzzling situation by the work of R. Clausius who recognized that the energy principle and the Carnot principle are, in fact, two different aspects of nature. Clausius stated that these were two basic laws pertaining to transformations between heat and work, and he referred to them as the two laws of thermodynamics⁴⁰. His investigations, along with those of R. Rankine⁴¹ and W. Thomson⁴², brought into focus the importance of irreversible processes, and the related notions of degradation, dissipation, and entropy.

DIFFICULTIES WITH THE THOMSEN-BERTHELOT PRINCIPLE

Two important implications of the Thomsen-Berthelot principle are the following. (i) If one considers a chemical reaction and its inverse, only the one which results in the production of heat, i.e. the exothermic reaction⁴³ alone will occur; and (ii) if two substances combine exothermically, then when mixed together the resulting chemical combination would be complete; the same should hold for the (exothermic) chemical decomposition of a substance also.

These consequences of the so-called third law of thermochemistry—as the Thomsen-Berthelot principle was sometimes called—did not stand the test of observation in some instances. To begin with, spontaneous endothermic processes were also observed. The melting of ice is a simple case in point. Berthelot explained this by suggesting that this is a physical change and is to be distinguished from a chemical change. But this view was not very convincing at a time when the universality of energy and its transformations were becoming more and more apparent. How could the direction of flow of the same energy be determined by nature in two different ways, according as a process is described (by us) as being physical or chemical? Then again, how can we account for the apparent stability of some endothermic compounds? Acetylene and cyanogen, for example, are formed by the absorption of heat⁴⁴, and hence must, according to the Thomsen-Berthelot principle, be unstable.

Certain investigations at fairly high temperatures seemed to suggest that there was in fact no intrinsic difference between physical and chemical changes in energetic terms. These investigations were initiated by St. Clair Deville in 1857⁴⁵. His researches with substances at high temperatures led him to the discovery of the phenomenon which he called "the dissociation of compound substances"⁴⁶. It was soon recognized that the incomplete dissociation of compounds was in fact a kind of chemical reaction in which the Thomsen-Berthelot principle did not hold. For, if the reaction in question is exothermic at the temperature of dissociation why should only some of the molecules dissociate, and not all⁴⁷?

Finally, Berthelot's own discovery of the esterification of alcohol⁴⁸ posed even further difficulties. It was found that as long as the temperature is maintained constant not all the alcohol and acid in a given container react. Once again, we have a situation somewhat similar to dissociation in which an equilibrium is maintained between the reactants and the products.

By the closing years of the 1860's it became quite clear that in order to understand reversibility and equilibrium, which implied the direction and amount of chemical reactions, criteria other than just the heat involved in the reactions must be introduced. The mere evolution or absorption of heat certainly did not appear to be the sole determining factor in the initiation and maintenance of a chemical reaction, let alone its direction.

THE SECOND LAW IN CHEMISTRY

Energy conservation implies something invariant in the universe. The total amount of energy remains the same for all time. Thus that which is unaffected by the passage of time is a quantity which is conserved. On the other hand, if we consider irreversible phenomena, that is to say, phenomena which are determined by the passage of time we are dealing with some aspect of nature which does not remain the same at all times. Like energy, then, there must be some quantity which is not conserved in the universe; in fact, whose change in the universe would be intimately tied to the flow of time itself. This indeed is the underlying idea in the development of the concept of entropy⁴⁹. Considering the fact that many chemical reactions are irreversible it might be expected that the second law of thermodynamics (which involves the notion of entropy) must be intimately related to chemical reactions.

However, although by the mid-1850's the two laws of thermodynamics had been formally stated, for over fifteen years they did not attract the attention of the majority of chemists. The first law was at least occasionally referred to, but the second law was practically ignored by the chemists of the period.

Indeed when the 1870's began there was no well defined theoretical basis for chemistry, and many leading chemists were fairly despondent on account of this. Thus F. A. Kekulé noted in one of his lectures in 1870 at the University of Bonn

that chemistry had reached a dead point and that there was "no visible prospect of new advance⁵⁰." H. Kopp wrote in 1873: "No theory has as yet been formed in chemistry which, starting from a definite principle, attempts to deduce the results of experience as necessary consequences. The doctrines which have been termed in chemistry theoretical are still only such as permit us to bring connection into the results which practical chemistry has gained in special directions; or to form a picture how we might think of them as mutually related⁵¹."

One reason for all this was that chemists had not exploited the second law. That the majority of chemists were indifferent to the second law of thermodynamics at that time is reflected in Lord Rayleigh's remark in an address to the Royal Institution that "the chemical bearings of the theory of dissipation are very important, but have not hitherto received much attention⁵²." It must be recalled, however, that the seeds for this had already been sown in a short mathematical note which appeared in 1869. Also, before Rayleigh's appeal to chemists to make use of the second law, at least two other major investigators had done this.

The Massieu Functions

In 1869 F. Massieu published a short note on what he called the characteristic functions of various fluids⁵³. The aim of this essentially mathematical paper was to show that entropy and internal energy, as also pressure and volume, may all be derived from a single function. Massieu further showed that the various physical and mathematical coefficients of a substance, such as specific heat, coefficient of expansion, etc. may be got from this single function which he termed *characteristic function*. The fundamental equations of thermodynamics could now be recast in terms of the characteristic function and its derivatives. The actual form of the function would depend on whether volume and temperature, or pressure and temperature were taken as the state variables⁵⁴.

This significance of Massieu's paper lies in the fact that he realized the importance of other purely mathematical functions than simply the energy or the entropy in the effective description of physical phenomena. Whether these functions admitted of direct physical meanings did not matter; they were convenient in the theoretical analysis of the problem⁵⁵. Unfortunately Massieu did not explore the importance of these functions with reference to chemistry.

Horstmann's Use of the Second Law

In 1870 A. Horstmann published a paper in which he applied the second law of thermodynamics to the phenomenon of chemical decomposition⁵⁶. In this paper he derived a very fundamental equation, using the equations corresponding to the two thermodynamical laws⁵⁷. Three years later, in yet another paper on the application of the second law of dissociation⁵⁸ Horstmann suggested that one ought to consider entropy rather than energy as the influencing factor in dissociation. Although energy may be released in a process of dissociation the process itself would

stop once the entropy of the system attained its maximum possible value for the particular concentrations of the substances involved and at that particular temperature. This would be in accordance with the second law, and would explain the non-completion of an exothermic reaction as observed in the phenomena of dissociation. The problem would thus be solved, Horstmann argued, if we knew under what circumstances and by what manner the entropy of the process in question changes.

These contributions and endeavours of Horstmann's were not fully recognized for many years; and in 1883 Helmholtz claimed priority over Rayleigh in the application of the entropy principle to chemistry⁵⁹.

Chemical Equilibrium and the Work of Gibbs

Closely associated with the phenomenon of chemical reaction is that of chemical equilibrium⁶⁰. Already in 1799 C. L. Berthollet had suggested that the amounts of reacting substances played an important role in determining the equilibrium condition⁶¹. As noted earlier, the experiments of St. Clair Deville on dissociation, and those of Berthollet on alcohol gave further instances of chemical equilibrium. Finally the classic paper by C. M. Guldberg and P. Waage propounded the famous law of mass action in 1864.⁶² For a thermodynamical interpretation of chemical equilibrium one had to wait for the highly original and truly revolutionary work of Willard Gibbs.

In 1871 and 1872 Gibbs, Professor of Mathematical Physics at Yale University, taught classical mechanics and optics to the two students who had enrolled in this course. For the year 1872-73 he decided to give a course on potential theory, and used for this purpose a small text authored by Clausius. In April and May of 1873 Gibbs submitted to the Connecticut Academy two papers on thermodynamics⁶³.

Gibbs' considerably mathematical memoirs dealt primarily with the possibilities of representing graphically various thermodynamical processes, using different pairs of variables. These were ingenious extensions of the idea of the pressure-volume diagram⁶⁴. In his second memoir Gibbs studied methods for representing three dimensional variations. These results were interesting not only from a purely mathematical point of view, but from engineering considerations also⁶⁵.

But it was in his third fundamental paper on thermodynamics⁶⁶ that Gibbs introduced his famous and fruitful phase rule. This paper, which begins with Clausius' statements in German of the two laws of thermodynamics, was to inaugurate a new era in the application of thermodynamics to chemistry⁶⁷.

After a preliminary discussion of the various aspects of equilibrium in terms of energy, entropy, volume, etc.⁶⁸ Gibbs took up the question of arriving at a fundamental equation from which the various chemical, thermal, and mechanical properties of a substance may be deduced. Modifying in this quest the functions introduced previously by Massieu⁶⁹, Gibbs brought in three functions which he

represented by the Greek letters ψ , χ , ζ .⁷⁰ He interpreted these as force functions for constant energy, for constant entropy, and for constant temperature respectively. Gibbs applied these to the problem of dissociation of gaseous compounds. His theoretically derived results were in remarkable agreement with experimentally amassed data. In chemistry, as in physics, theory could predict and confirm numbers got from observations.

Unfortunately, the mathematical sophistication in the thinking and writings of Gibbs was not within easy grasp of all chemists⁷¹. Nevertheless a few enterprising chemists, but only a few, took notice, and attempted extensions of Gibbs' work⁷². In the 1880's W. Ostwald brought out a German translation of Gibbs' paper⁷³, so that "this long-overlooked treasure would finally be uncovered and converted into the current coin of progress⁷⁴."

Helmholtz' Free Energy

In 1882 Helmholtz published a significant paper on the thermodynamics of chemical phenomena⁷⁵. Here he suggested that for a proper understanding of chemical phenomena one should distinguish between two aspects of energy: energy which can be transformed into work, and energy which can be manifest only as heat. He called these *free* and *bound energies* respectively⁷⁶. Helmholtz pointed out that the Thomsen-Berthelot principle would be valid only if one referred to the free energy, not to the total energy. It is the variation of free energy, not of total heat release, whose sign determines the direction of chemical reactions. Helmholtz stated that "in a system whose temperature is maintained constant, reactions which begin spontaneously without external aid can take place only in the direction of diminishing free energy⁷⁷." Helmholtz's free energy is simply Gibbs' ψ .⁷⁸

Helmholtz applied his ideas to the chemical reaction of the voltaic pile⁷⁹; and derived a formula connecting the e.m.f. of the battery to the free energy of the chemical reaction taking place in the cell⁸⁰. The equation which Helmholtz deduced in this context⁸¹ has come to be known as the Gibbs-Helmholtz equation in textbooks on physical chemistry. However, it must be pointed out⁸² that Gibbs did not explicitly establish or use this equation. Also, it had been brought in, albeit in a different framework, by Horstmann and by Kelvin even before Helmholtz.

Although the idea of free energy—though not the term—had indeed been introduced in the investigations of other workers before Helmholtz⁸³, the latter's paper did much to make the concept relevant and fruitful among chemists in general, and was largely responsible for the elucidation of the confusion surrounding the Thomsen-Berthelot principle. The very title of Helmholtz's paper brought home to theoretical chemists that there was an aspect of chemical processes which may properly be called thermodynamical.

Ostwald and Thermodynamics in Chemistry

While Gibbs was working on his papers on thermodynamics W. Ostwald was still a student in Dorpat in Estonia. Ostwald was soon to become an ardent

sponsor and propagandist for physical chemistry. Fascinated to the point of obsession with the laws of thermodynamics Ostwald lost his head and heart to the energy concept. He pleaded its cause unrelentingly, and would accept nought as reality but the energy principle. The whole universe was for him merely a stage for energy-transformations, subject to the eternal laws of thermodynamics. In his all-embracing view the realm of the second law extended way beyond mere physico-chemical phenomena, and well into matters of less universal implications: in society and in economics, in culture, philosophy and human happiness itself⁸⁴.

Ostwald was a man of enormous learning, a prolific writer and an ample thinker. He was always eager to encourage the cause of science, but he was also intellectually opposed to the materialism which he thought classical science was leading to.

In 1887 Ostwald founded with the collaboration of Van't Hoff, the first journal devoted entirely to physical chemistry⁸⁵. Two years later he began publication of a series of scientific classics⁸⁶. In 1901 he initiated another journal whose purpose was to serve as a medium for synthesizing scientific and philosophical thought⁸⁷. His famous textbooks on chemistry were noted for their clarity and extensive references, and they helped spread the knowledge and study of systematic chemistry⁸⁸. In particular they also propagated the principles of thermodynamics among chemists.

Aside from his own scientific contributions to chemistry⁸⁹ Ostwald will also be remembered in the history of scientific thought as the founder and staunch upholder of the energetic school. The aim of this school, as Ostwald conceived it, was as much to explore a new worldview as to combat the mechanistic picture of the universe and its most recent expression, viz. the molecular-kinetic theory of matter and its statistical offshoots⁹⁰. Statistical analysis of random molecular motions was beginning now to invade thermodynamics⁹¹. Ostwald viewed this trend with great alarm. The controversies between the upholders of the purely energetic view and those who attempted interpretations at a deeper atomic level, i.e. between those who refused and considered it unscientific to go beyond the experimentally observed and measured quantities of energy, expansion, gross matter, etc. and those who took the atomic hypothesis more seriously and attached objective existence to atomic entities, form a subject of great interest in the intellectual history of science. But what is interesting for our present discussion is the fact that when the opposing philosophies came to a head-on collision in the famous Lubeck Conference of 1895⁹², physicists pleaded the cause of matter and atoms, and chemists argued for energy⁹³. When it is realized that generally speaking physics is described as the study of the various forms of energy, and chemistry as that of matter and its transformations, it is surprising that the protagonists were not the other way round.

Van't Hoff's Study of Chemical Dynamics

One of Ostwald's close friends and collaborators was the Dutch chemist J. H. Van't Hoff⁹⁴. Van't Hoff, who was once refused a school teacher's position because

of "sloppy appearance and brooding", revealed scientific creativity at an early age, and became the recipient of the first Nobel Prize for chemistry⁹⁵.

Van't Hoff's attention turned to thermodynamics not long after he propounded his picture of the tetrahedral carbon atom for which he has justly become famous⁹⁶. He applied the principles of thermodynamics to problems of chemical kinetics and osmotic pressure. In 1884 Van't Hoff published a lucid study of chemical dynamics⁹⁷ which became a classic in science. His study presented systematically several applications of thermodynamics to chemical problems, and quite a few of these were his own results. Van't Hoff's presentations of these problems have permeated in form and content many textbooks on physical chemistry to this day. His independent re-derivation of the law of mass action⁹⁸, his famous formula revealing the influence of temperature on the rate of chemical reactions⁹⁹, his principle of mobile equilibrium¹⁰⁰, his introduction of the double-arrow symbol for reversible reactions, all these are to be found in this work¹⁰¹. This book played a major role in the dissemination of chemical thermodynamics.

Soon after the publication of this work Van't Hoff turned his attention to the theory of osmotic pressure¹⁰². He used the concept of the semi-permeable membrane in his application of thermodynamic principles to the theory of solutions¹⁰³. It may be noted in passing that the successes of the thermodynamic relations occurring in the theory of solutions do not throw any light on the ultimate constitution of solutions.

DUHEM'S THERMODYNAMIC POTENTIAL

Along with Gibbs, Ostwald, and Van't Hoff, the honour of being one of the first to perceive the significance of thermo-dynamics in chemistry goes to P. Duhem¹⁰⁴. Like Ostwald, Duhem was also a man of extraordinary breadth of learning and interest¹⁰⁵. In his doctoral thesis, submitted in 1884, Duhem questioned Berthelot's principle of maximum work. By now Berthelot had become, and deservedly so, one of the most eminent and powerful of French chemists. Having spent over two decades establishing, expounding, and defending that principle Berthelot was not very inclined to accept the objections of a 23 year old doctoral candidate. Duhem's thesis was summarily rejected¹⁰⁶.

Instead of modifying his thesis to overcome the discrepancies resulting from Berthelot's principle, Duhem went ahead and published his thesis as a book in 1886¹⁰⁷. This was also the year when Berthelot became the Minister of Public Instruction. As a consequence Duhem could not get a teaching position in Paris¹⁰⁸.

Gibbs had already introduced the concept of a potential in thermodynamics in relation to chemical equilibrium¹⁰⁹. Duhem, by his clear analysis of the accomplishments of the Massieu-Gibbs functions, brought out the powers of the thermodynamic potential¹¹⁰. He also clarified the principal differences, in spirit as well as in methods, between thermochemistry and its daughter, chemical thermodynamics¹¹¹. His own investigations established the important relationship—

present also in Gibbs' work¹¹²—which has come to be known as the Gibbs-Duhem equation¹¹³. Duhem made a significant contribution to the growing number of influential texts on physical chemistry during the closing years of the 19th century through his four-volumed treatise on chemical mechanics¹¹⁴. Duhem also wrote on the thermodynamics of viscosity and friction¹¹⁵, and developed the idea of false equilibrium¹¹⁶.

NERNST AND THE THIRD LAW

A discussion of the interplay of thermodynamics and chemistry would be incomplete if one did not refer to the work of W. Nernst¹¹⁷. Nernst's interest in chemistry was aroused by Ostwald¹¹⁸ soon after he received his doctorate, prior to which his leanings had been towards physics. His application of thermodynamics in 1889 to the theory of voltaic pile is one of the beautiful results of chemical thermodynamics¹¹⁹. In an influential text on theoretical chemistry Nernst discussed the subject from the points of view of Avogadro's law, as well as of thermodynamics which was considered from a purely phenomenological point of view in the spirit of the energetics school¹²⁰.

Nernst classified natural phenomena on the basis of the so-called Gibbs-Helmholtz equation which he described as containing "in a general manener all that the laws of thermodynamics can teach concerning chemical processes¹²¹." He then examined the cases in which (a) the free energy change is equal to the change in total energy; (b) there is no change in the total energy; (c) the free energy change is zero; and (d) there is no change either in free energy or in total energy¹²².

His analysis of the equation led him to a very fundamental result. He recognized that the Thomsen-Berthelot principle, which identified total energy with free energy, would be valid at absolute zero¹²³. He further showed that the principle is valid even at temperatures close to the absolute zero¹²⁴. The discovery of this theorem is a remarkable example of how a profound law of nature may lie hidden in a simple looking equation for many years until a penetrating mind disentangles it from the cryptic symbols. Nernst's heat theorem was discovered in 1906. It was named the third law of thermodynamics by Sommerfeld who called it "the most ingenious development of classical thermodynamics in our century¹²⁵."

OTHER CONTRIBUTORS TO CHEMICAL THERMODYNAMICS

We have mentioned in our survey only some of the more important names associated with the introduction of thermodynamics into chemistry. Needless to say, as no war is won by generals alone, no scientific advance is possible by the genius of only a few individuals. Scores of other workers, spanning a wide spectrum of talents and significance, also contribute to the march of science in each one of its branches. This has been just as true in the case of chemical thermodynamics also. Thus, F. M. Raoult's significant experimental work on solutions¹²⁶ inspired

theoretical explorations by others¹²⁷. S. Arrhenius' extensions of Van't Hoff's theories led him to the concept of the activation energy¹²⁸. Le Chatelier's investigations in chemical thermodynamics resulted in the discovery of the famous principle that bears his name¹²⁹. H. B. Roozeboom's efforts led to the application of the phase rule in the classification of chemical equilibria, and to the question of the formation and decomposition of double salts¹³⁰. Van Laar gave a number of rigorous proofs for the important theorems of chemical thermodynamics¹³¹.

THERMODYNAMICS AND PHYSICAL CHEMISTRY

Berthollet's studies on the decomposition of salts by acids already revealed the importance of physical conditions (aside from chemical affinities) in the phenomenon of chemical reactions¹³². However, during the first part of the nineteenth century interest in the physical aspects of chemistry did not grow¹³³. And when the Berthelot-Thomsen principle obviously failed in processes like melting and vaporisation, one tended to make distinctions between physical and chemical processes.

But the permeation of thermodynamics, both at the theoretical and experimental level, caused a merger of the two facets of natural phenomena, and led to the development of the new and fruitful discipline of physical chemistry. Indeed, the major names we have had to refer in our discussion of the impact of thermodynamics on nineteenth century chemistry are also among the founders of the science of physical chemistry¹³⁴.

From the 1880's on several centres for the specialized study of physical chemistry were established, first in Germany¹³⁵, then in Holland, France, the United States, and elsewhere. Similarly the Ostwald-Van't Hoff venture of the journal for physical chemistry was followed and complemented by other journals of the kind in other countries¹³⁶. So that by the beginning of the twentieth century physical chemistry had become an independent line of search, an integral branch of science in its own right. The role of thermodynamics in the conceptual framework of this science is well known.

CONCLUDING REMARKS

Considering the fact, now recognized, that a great deal of theoretical chemistry rests on thermodynamical foundations, i.e. many facets of chemical phenomena admit of coherent and simple explanations on the basis of thermodynamical principles, one may ask: Why did not chemists develop and explore the laws of thermodynamics before physicists did? Our survey of the development of chemical thermodynamics throws some light on the question.

As we have seen, although heat has long been recognized as an important factor in chemical changes, one had to gain a clear understanding of the phenomenon of combustion before a meaningful scientific theory could be developed. This

meant the abandonment of the phlogiston idea which, again, could not be accomplished until careful and systematic quantitative methods were introduced into chemistry.

Even after the heat aspects of chemical reactions became a matter of general and well defined principles, other conceptual problems engaged the attention of chemists. The laws of fixed proportions according to which chemical reactions take place, and of matter conservation, led to the development of Dalton's atomic theory. This, as we have seen, spurred researches in the direction of precise measurements of weights.

By the time the basic laws of thermodynamics were formally stated, i.e. by the middle of the nineteenth century, two major themes interested most theoretical and experimental chemists. These were : organic chemistry, and the elucidation of atomic and molecular concepts. These preoccupations turned the attention of chemists away from any developments in thermodynamics¹³⁷.

For a fruitful exploitation of thermodynamics, abstract and mathematical formulations are necessary. Consequently, for any systematic application of thermodynamics to chemistry the investigator needs a reasonable mathematical interest and background. Generally speaking, mathematically inclined men of science tended towards physics. Therefore, for the permeation of thermodynamics into chemistry, either a physicist had to take interest in chemical questions, or some one with a mathematical bent of mind had to go into chemistry. We find such happy combinations in men like Helmholtz, Gibbs, Ostwald, Duhem, Van't Hoff, and Nernst.

In addition to these general observations, one might say that there was yet another reason why chemists did not develop thermodynamics before physicists did. This is the triumph of Newtonian physics. For, as a result of that triumph chemists tried to build up a conceptual structure of their discipline that would either adopt entirely, or at least resemble closely, elements of the Newtonian physical system.

The predominant concepts of eighteenth century physics were those of mechanics : at the base of mechanics were the notions of force and velocity. Consequently chemists began to introduce the idea of velocity in chemistry also. C. F. Wenzel used this concept as early as 1777. Berthollet spoke of the propagation of chemical reaction, and stated that the velocity of the reaction is greater than the force acting on it. The idea of affinity was thus explored in terms of force. Unfortunately the notion of energy was introduced by physicists only during the mid-nineteenth century. Hence chemists did not think in terms of energy before that.

Here it is important to distinguish between fields like thermochemistry, photochemistry, or electrochemistry on the one hand, and a field like chemical dynamics on the other. In the first instances one is concerned with specific chemical pheno-

mena in which heat, light, or electricity may be involved. In the second case, however, one tries to study chemical phenomena in the framework of concepts developed in dynamics. It is in this spirit that Berthollet wrote on chemical statics, Berthelot wrote on chemical mechanics, Van't Hoff on chemical dynamics, Duhem on chemical potential. One spoke of reaction kinetics and chemical equilibrium. And after physicists had inaugurated thermodynamics we find works on chemical thermodynamics.

All this is very understandable. In view of the enormous successes of physics there was little reason to suspect that its concepts and images would not be adequate in the description of chemical phenomena also. Van't Hoff's assistant van Deventer expressed it this way: "Whoever knows the Amsterdam laboratory knows that things do not take place there in any ordinary way. There is something mystical, something uncanny in the air. And this demonic something is the belief—one might call it the superstition if success had not so often followed it—the belief of Van't Hoff that his fundamental idea, the analogy between chemical and physical phenomena, is profoundly true¹³⁸."

On the other hand, if chemists had already thought during the eighteenth century that chemical phenomena could perhaps be described in terms not necessarily already in vogue in physics, they would perhaps independently have introduced an idea such as the chemical potential. In this manner they could have forged insights into the nature of the physical world, and enriched thereby the physicist's worldview also. That this is not entirely inconceivable is shown by many modern texts on physical chemistry which introduce the notions of energy and entropy without bringing in first the idea of force or velocity.

The significance of such an imaginary possibility lies in the following: Just as chemistry has been earnestly trying to incorporate the paradigms of physics in its explorations, so biology has been following faithfully the concepts and framework of both physics and chemistry. And one cannot deny the great successes of the physico-chemical view of matter, life, and their transformations. However, it is entirely possible that some of the mysteries of biology could yet be solved only by adopting totally new concepts or points of view. These, in turn, might serve to clear some of the clouds hanging over the physics of fundamental particles. Such a possibility has indeed been considered by some physicists. Thus G. F. Chew, for example, has suggested that a breaking away of current ideas along completely new directions "would be immensely more profound than anything comprising the hadron bootstrap (approach); we would be obliged to confront the elusive concept of observation and, possibly, even that of consciousness. Our current struggle... may thus be only a foretaste of a completely new form of human intellectual endeavour, one that will not only lie outside physics but will not even be described as 'scientific'¹³⁹."

On the other hand the history of the permeation of thermodynamics into chemistry also exemplifies the manner in which the paradigms of a more successful

science are imitated and taken over by another science, Whether this is due to the uniqueness of the paradigms that are adopted or due to the appeal associated with their successes is a different question.

REFERENCES AND NOTES

- ¹ The importance of this work lay in its merciless criticism of the obscurantism and verbal chicanery that went by the name of chemistry, and in its exposition of what ought to be a meaningful scientific methodology. In this work Boyle also revealed his insight into the nature of a chemical element.
- ² The *Principia*, as everybody knows, inaugurated a new and fruitful chapter in the development of physics.
- ³ Most historians of chemistry grant that Lavoisier was the founder of modern chemistry. Lavoisier's great systematizing masterpiece, *Traite Elementaire de Chimie*, was published in 1789, the year of the French Revolution.
- ⁴ Johann Joachim Becher (1635-1682) introduced three types of elementary earths which he called: *terra vitrescibile* (for substances), *terra pinguis* (for combustion), and *terra fluida* (for form, smell, and weight). He also referred to the second of these as *sulfur phlogistos* (burnt sulphur).
- ⁵ The phlogiston theory in its eighteenth century form was put forward by G. E. Stahl in his *Eymotechnia fundamentalis sive fermentationis theoria generalis*, which was published in 1697. For details on the phlogiston theory and its eventual overthrow, see, Conant, J. B., *The Overthrow of the Phlogiston Theory, Case 2, Harvard Case Histories in Experimental Science*, Harvard U. Press, Cambridge (1957).
- ⁶ A descriptive theory introduces terms and concepts which are useful in describing and relating facts of observation. An explanatory theory introduces principles from which observed phenomena follow as natural consequences.
- ⁷ A great deal of pre-scientific speculation consisted of purely descriptive theories. These often served quite well in the absence of quantitative components to observations.
- ⁸ Lavoisier's fascination for accurate measurements was reflected in his very first work (1764) on the composition of gypsum.
- ⁹ Quoted in Mellor, J. W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, London (1927), p. 189 of volume I.
- ¹⁰ For a historical background to Lavoisier's first experiments on combustion, see, Guerlac, H. *Lavoisier—The Crucial Year*, Cornell U. Press, Ithaca (1961).
- ¹¹ These memoirs were inspired by studies on the nature of animal heat. The memoir in which Lavoisier and Laplace expressed as self-evident the equality between the heat required to form a compound and that given out when it is decomposed, was published in the *Mem. de l'Acad. des Sc. de l'Inst. de France*, (1784), p. 359. For a background to and details on these memoirs, see, Mendelsohn, E., *Heat and Life*, Harvard Univ. Press, Cambridge (1964), Ch. VI.
- ¹² Effective calorimeters for this purpose were not invented until the nineteenth century.
- ¹³ Even after the beginning of the nineteenth century there were controversies relating to the phlogiston.
- ¹⁴ Also, one impact of the law of conservation of matter was to encourage researches on precise measurements of weights in chemical reactions.
- ¹⁵ The notion of affinities goes back to medieval times.
- ¹⁶ For a look into pre-Newtonian gravitation, see, Raman, V. V., *A Background to Gravitation, The Physics Teacher*, 10.8 (1972), pp. 439-442.
- ¹⁷ As was done by Bergmann, for example, in 1775.

- ¹⁸ During the first decades of the nineteenth century, however, this preoccupation was pushed a little to the background.
- ¹⁹ Wilhelm Hisinger (1766–1852) was a mineralogist. He and Berzelius collaborated in the discovery of the element cerium (1803). Hisinger also studied the effect of electric currents in salt solutions. Here again, he and Berzelius worked together.
- ²⁰ Berzelius' first book was a treatise on galvanism (1802).
- ²¹ *Essai sur la théorie des proportions chimiques*, Paris. H. Davy had thought along similar lines in 1807 in his *On Some Chemical Agencies in Electricity*.
- ²² Hess, G. H. *Thermochemische Untersuchungen*, *Pogg. Ann.* 50 (1840), p. 384.
- ²³ See H. M. Leicester's article on Hess in the *Dictionary of Scientific Biography*, Vol. VI, Charles Scribner's Sons, N.Y. (1972), p. 354.
- ²⁴ Hess's first publication on this subject appeared in French in the *Bulletin scientifique de l'Académie impériale des Sciences de St. Petersburg*.
- ²⁵ Ostwald's *Klassiker*, Vol. IX, Leipzig (1890). A Russian translation of the major thermochemical papers of Hess were published in Moscow in 1958.
- ²⁶ T. Andrews also expressed the view in 1840 that the law of Hess is, "almost self-evident and scarcely required so elaborate a proof."
- ²⁷ It must be remembered that in 1840 the equivalence between the different forms of energy had not yet been perceived.
- ²⁸ Even the term *energy* had not yet come into current use.
- ²⁹ See, in this connection, Theobald, D. W., *The Concept of Energy*, E. and F. N. Spon Ltd., London (1956).
- ³⁰ For a historical perspective of the development of the energy conservation principle, see, Kuhn, T., Energy Conservation Principle as an Example of Simultaneous Discovery, in Clagett, M. C. (ed.), *Critical Problems in the History of Science*, Univ. of Wisconsin Press, Madison (1959), pp. 321–356.
- ³¹ Although some were also concerned with electrochemical reactions.
- ³² Thomsen's many papers on this subject began to appear in the *Ann. de Phys.* of 1853 and 1854.
- ³³ A view which he was to correct in his *Thermochemische Untersuchungen* which he published in four volumes between 1882 and 1886.
- ³⁴ As Berthelot expressed it, "par une coïncidence aussi heureuse que rare dans l'histoire des sciences, un savant professeur danois, M. Thomsen, exécutait de son côté, dans des vues différentes, une série de déterminations numériques, parallèles aux miennes sur bien des points." *Essai de Mécanique chimique fondée sur la Thermochimie*, Paris (1878), p. x.
- ³⁵ The term derives from an analogy with a similar principle in classical mechanics.
- ³⁶ *loc. cit.* Ref. 34, p. xxiv.
- ³⁷ For the first time the concept of affinity was now related to that of energy rather than to the force concept.
- ³⁸ It was this dilemma which led W. Thomson to his thermodynamical investigations.
- ³⁹ In Carnot's hydrodynamical analogy (related to the caloric concept) the heat from the source, after doing the work in an engine, falls (like water) completely into the sink.
- ⁴⁰ For details on this, see, Raman, V. V., Evolution of the Second Law of Thermodynamics, *Jour. Chem. Ed.*, 47 (1970), pp. 331–337.
- ⁴¹ For Rankine's contributions to thermodynamics, see, Raman V. V., William John Macquorn Rankine: 1820–1872, *Jour. Chem. Ed.*, 50 (1973), pp. 274–276.
- ⁴² Who later became Lord Kelvin.
- ⁴³ The terms 'exothermic' and 'endothermic' were introduced by Berthelot.
- ⁴⁴ Interestingly enough, acetylene was re-discovered by Berthelot after it had been ignored for nearly 25 years.

- ⁴⁵ Henri Etienne Sainte Claire Deville (1818–1881) also worked on the purification of aluminium and sodium ores, and thus brought down the price of these metals. This had a great impact on technology.
- ⁴⁶ Deville's first results on dissociation were published in the *Comptes Rend. Acad. Sc. Paris*, 45 (1857), pp. 857–861.
- ⁴⁷ Many other workers, notably Débray, Troost, and Hautefeuille, also contributed significantly to experimental work on dissociation.
- ⁴⁸ In this work he collaborated with L. Pean de St. Gilles. See, *Ann. de chimie et de physique*, ser. 4, 37 (1865), pp. 290–291.
- ⁴⁹ A recognition of this aspect of entropy came only much later.
- ⁵⁰ Quoted by Van't Hoff in his *Physical Chemistry in the Service of the Sciences*, The Univ. of Chicago Press (1903), p. 3–4. Van't Hoff referred to this as an unfortunate utterance, "a sort of remark, we may say in passing, such as a teacher ought perhaps never to make before his pupils." However, from the science historian's point of view, it was very fortunate that Kekulé did make such a remark, for it gives us an insight into what some of the leading chemists of the time were feeling with regard to the situation in their field. Also, Kekulé was not entirely mistaken when he stated that there was no *visible prospect* of new advance. After all thermodynamics was as yet invisible to most chemists.
- ⁵¹ Kopp, H., *Entwicklung der Chemie* Munich (1873), p. 844. Quoted in Mertz, J. T., *A History of European Scientific Thought in the Nineteenth Century*, (1904), Vol. I of the Dover Ed. (1965), p. 421.
- ⁵² *Nature* XI (1875), pp. 454–455. Rayleigh added: "The difficulty in applying thermodynamical principles to chemistry arises from the fact that chemical transformations cannot generally be supposed to take place in a reversible manner, even although unlimited time be allowed."
- ⁵³ Massieu, M. F., Sur les fonctions caractéristiques des divers fluides, *C.R. Acad. Sc. LXIX* (1869), p. 858 and p. 1057.
- ⁵⁴ In this memoir Massieu introduced the functions

$$\psi = S - \frac{U}{T}, \text{ and } \psi' = S - \frac{U'}{T}, \text{ where } U' = U + A p v,$$

A being the heat equivalent of mechanical work. However, in E. Bouty's report on Massieu's papers, published in the *Journal de Physique*, VI (1877), pp. 212–22, the following functions were given:

$$H = TS - U, \text{ and } H' = TS - U - A p v.$$

This report appeared after Gibbs' memoirs.

- ⁵⁵ The Lagrangian, the Hamiltonian, and the vector potential are other examples of such functions.
- ⁵⁶ Ueber den II Hauptsatz der mechanischen Warmetheorie und dessen Anwendung auf einige Zertzung's Erscheinungen, *Ann. Chem.* (1870), pp. 112–132.
- ⁵⁷ In Horstmann's symbols, this equation was written in the form:

$$W = E + J = T \frac{\delta E}{\delta T}.$$

This equation embodies the essence of the so-called Gibbs-Helmholtz equation.

- ⁵⁸ Theorie der Dissociation, *Ann. Chem.* A170 (1873), pp. 192–210.
- ⁵⁹ *Berl. Mitteil.* (1883), p. 373.
- ⁶⁰ For a historical account of this, see, Lindauer, M. W., The evolution of the Concept of Chemical Equilibrium from 1775 to 1923, *Jour. Chem. Ed.* 39.8 (1962), pp. 284–390.
- ⁶¹ He discussed this in detail in his *Recherches sur les Lois de l'Affinité*, Paris (1801).

- ⁶² Guldberg and Waage published their theory first in Norwegian in 1864. The French version, 'Etudes sur les Affinités chimiques' appeared in *Christiana* in 1867. See, Ostwald's *Klassiker*, No. 104, Leipzig (1899).
- ⁶³ Graphical Methods in the Thermodynamics of Fluids, *Trans. Connecticut Acad.* 2 (1873), pp. 309-342; and A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces, *ibid.*, 2 (1873), pp. 382-404.
- ⁶⁴ The p - v diagram had been introduced by J. Watts in the 18th century.
- ⁶⁵ The recognition of the usefulness of these diagrams in engineering problems came only later.
- ⁶⁶ On the Equilibrium of Heterogeneous Substances, *loc. cit.* Ref. 63, 3 (1876), pp. 108-248, and (1878), pp. 343-524.
- ⁶⁷ Donnan, F. G., described this work as "one of the mightiest works of genius the human mind has ever produced." (*The Influence of J. Willard Gibbs on the Science of Physical Chemistry*, The Franklin Institute, Philadelphia (1924), p. 4.).
- ⁶⁸ Gibbs summarized the criterion of equilibrium (already stated by Clausius in what he called "two entirely equivalent forms." Representing the total energy by ϵ , and the entropy by η , for any system, he put : I. $(\delta\eta)_{\epsilon} \leq 0$, and II. $(\delta\epsilon)_{\eta} \geq 0$. The deltas indicate here variations, and the subscript indicates the quantity which is held constant.
- ⁶⁹ Gibbs did refer to Massieu's work, but later writers have generally tended to ignore this.
- ⁷⁰ In Gibbs' notation and according to this definitions,

$$\psi = \epsilon - t\eta, \quad \chi = \epsilon + pv, \quad \zeta = \epsilon - t\eta + pv.$$

Here t stands for temperature, ϵ for energy, and η for entropy. Note the resemblance to the Massieu functions under Ref. 54.

- ⁷¹ It was feared that Maxwell was about the only human being who could decipher Gibbs.
- ⁷² For details on this, see, Wheeler, L. P., *Josiah Willard Gibbs*, Yale Univ. Press, New Haven (1951), Ch. VI.
- ⁷³ *Thermodynamische Studien*, Leipzig (1892).
- ⁷⁴ Quoted in Ref. 72, p. 100.
- ⁷⁵ Zur Thermodynamik chemischer Vorgänge, *Sitz. Akad. Wiss. Berlin*, I (1882), p. 23.
- ⁷⁶ Helmholtz defined $F = U - JTS$ (U : total internal energy, J : mechanical equivalent of heat, S : entropy, T : absolute temperature) as *freie Energie*, and $U - F = JTS$ as *gebundene Energie*.
- ⁷⁷ Ref. 75, p. 28.
- ⁷⁸ See Ref. 70.
- ⁷⁹ Helmholtz had examined the problem of chemical energy and the e.m.f. of a battery in the 1850's. It is while attempting to modify those results that he developed the idea of the free energy.
- ⁸⁰ Previously it had been imagined that the electrical energy was simply equal to the heat evolved in the chemical reaction.
- ⁸¹ Helmholtz wrote this equation in the form :

$$U = F - \theta \frac{\partial F}{\partial \theta}$$

p. 31 of *loc. cit.* Ref. 75.

- ⁸² As W. D. Bancroft noted several years ago in a book review. "... this is an equation (the Gibbs-Helmholtz equation) which Helmholtz did deduce and which Gibbs could have and perhaps should have, deduced but did not." *Jour. Phys. Chem.* 31 (1927), p. 638.
- ⁸³ Motivity (Thomson) and available energy (Maxwell) were other names for Helmholtz's free energy.
- ⁸⁴ Ostwald gave the formula, $G = E^2 - W^2$, for happiness (Glück), where E is the energy (Energie) spent agreeably, and W (widerwillig) is the energy spent in disagreeable ways.

- ⁸⁵ *Zeitschrift für physikalische Chemie*. The frontispiece in the first issue is a picture of Bunsen.
- ⁸⁶ The *Klassiker der exacten Wissenschaften* did much to propagate current and past science through the medium of original papers.
- ⁸⁷ *Annalen der Naturphilosophie*.
- ⁸⁸ He began this with his two volumed *Lehrbuch der allgemeinen Chemie* (1883–1887).
- ⁸⁹ Which won him the Nobel Prize for chemistry.
- ⁹⁰ This was especially due to the efforts of Maxwell and Boltzmann.
- ⁹¹ The energeticists insisted that thermodynamics can and should be developed from purely phenomenological considerations, and without any reference to atoms and molecules.
- ⁹² For a recent study of the background and implications of that conference, see, Hiebert, E. N., *The Energetics Controversies and the New Thermodynamics*, in Roller, D. H. D. (ed.), *Perspectives in the History of Science and Technology*, Univ. of Oklahoma Press (1931), pp. 67–86.
- ⁹³ The two major opponents in the intellectual encounter were Ostwald and Boltzmann.
- ⁹⁴ As noted earlier, Van't Hoff was one of the founding editors of the first Journal of Physical Chemistry.
- ⁹⁵ Van't Hoff received the Nobel Prize in 1901 for his work on solutions.
- ⁹⁶ For a background to the tetrahedral carbon atom, see, Larder, D. F., Historical Aspects of the Tetrahedral Chemistry, *Jour. Chem. Ed.*, 44, 11 (1967), pp. 661–666.
- ⁹⁷ *Etudes de Dynamique chimique*, Amsterdam (1884).
- ⁹⁸ Van't Hoff was not aware of the fact that Guildberg and Waage had stated the result almost 20 years before.
- ⁹⁹ This result led to the so-called reaction isochore equation.
- ¹⁰⁰ According to this principle, "every equilibrium involving two different conditions of matter is displaced by a drop in temperature (at constant volume) towards that system which evolves heat when it is formed."
- ¹⁰¹ An English translation of the work, by T. Ewan, entitled *Studies in Chemical Dynamics*, appeared in 1896.
- ¹⁰² The phenomenon of osmotic pressure had been studied extensively experimentally by the German botanist W. Pfeffer (1845–1920), before Van't Hoff.
- ¹⁰³ This was one of the great achievements of chemical thermodynamics.
- ¹⁰⁴ For biographical and scientific details on Duhem, see, Picard, E., *La Vie et l'Oeuvre de Pierre Duhem*, Paris (1921),
- ¹⁰⁵ Helene Pierre Duhem, *Un Savant français: Pierre Duhem*, Paris (1936).
- ¹⁰⁶ For details on this, see, Miller, D., Ignored Intellect: Pierre Duhem, *Physics Today*, 19.12 (1966), pp. 27–53.
- ¹⁰⁷ *Le Potentiel Thermodynamique et ses Applications à la Mécanique chimique et à l'Etude des Phenomenes électriques*, Paris (1886).
- ¹⁰⁸ It must be noted that there were other reasons, relating to his political and religious views, for this.
- ¹⁰⁹ Gibbs was the first to introduce the notion of the potential into chemistry.
- ¹¹⁰ Different authors give slightly different meanings to this term now.
- ¹¹¹ See the concluding chapter of his book in Ref. 107.
- ¹¹² In his paper in the *Trans. Conn. Acad.* 3 (1875), p. 143.
- ¹¹³ Duhem deduced the equation by using Euler's theorem of homogeneous functions. See, in this connection, Miller, D. G., Duhem and the Gibbs-Duhem Equations, *Jour. Chem. Ed.* 41 (1964), p. 648.
- ¹¹⁴ *Traité de Mécanique chimique*, Paris (1897–1899).
- ¹¹⁵ *Théorie thermodynamique de la viscosité, du frottement, et des frux équilibres chimiques*, Paris (1896)

- ¹¹⁶ This referred essentially to a kind of metastable state of certain substances which are unstable from a thermodynamic point of view with respect to other substances, but which have been unaffected for many long centuries. Examples would be petroleum and diamond. They can, however, be transformed into stable products when subjected to large perturbations.
- ¹¹⁷ For details of Nernst, see the recent biography by Mendelsohn, K., *The World of Walther Nernst: The Rise and Fall of German Science, 1864-1941*, MacMillan, London (1973).
- ¹¹⁸ After receiving his Ph.D. in 1887 under F. Kohlrausch, Nernst became Ostwald's assistant in Leipzig exactly at a time when physical chemistry was beginning to assert itself as an independent discipline.
- ¹¹⁹ Nernst worked both on the experimental and the theoretical aspects of the problem. This work established Nernst's reputation as a physical chemist.
- ¹²⁰ The title of the work suggested the two points of view: *Theoretische Chemie von Standpunkte der Avogadroschen Regel und der Thermodynamik*, Stuttgart (1893).
- ¹²¹ Nernst, W., *Experimental and Theoretical Applications of Thermodynamics to Chemistry*, Yale Univ. Press, New Haven (1903), p. 3-4.
- ¹²² Starting from the so-called Gibbs-Helmholtz equation,

$$A - Q = T \frac{dA}{dT},$$

where A is the change in free energy, and Q is the change in total energy, and T is absolute temperature, Nernst considered the cases: (a) $A = Q$; (b) $Q = 0$; (c) $A = 0$; (d) $A = 0 = Q$.

- ¹²³ Note that from the equation above, for $T = 0$, $A = Q$. This indeed is the Berthelot-Thomsen principle. This fact had been recognized by Van't Hoff also.
- ¹²⁴ This result is of enormous importance in the theoretical calculation of free energies. It also raises fundamental questions in the concepts of thermodynamics. It also led to various investigations in low temperature phenomena.
- ¹²⁵ Quoted in Hermann, A., *The Genesis of Quantum Theory (1899-1913)*. English trans. by C. W. Nash, The M.I.T. Press, Cambridge (1971), p. 129.
- ¹²⁶ Raoult's famous law of partial pressures of a solvent vapour was propounded in 1886.
- ¹²⁷ Arrhenius' theory of electrolytic dissociation resulted from the anomalous behaviour of electrolytes as found in experiments related to Raoult's law.
- ¹²⁸ The activation energy idea was suggested in 1889, and it proved to be very useful in the theory of catalysis.
- ¹²⁹ Le Chatelier also translated Gibbs' fundamental paper on thermodynamics into French.
- ¹³⁰ For details on this, see, Van Klooster, H. D., *Jour. Chem. Ed.* 31, (1954), p. 594.
- ¹³¹ For more on van Laar, see, van Kloster, H. S., J. J. van Laar, Pioneer in Chemical Thermodynamics, *Jour. Chem. Ed.*, 39 (1962), p. 74.
- ¹³² This is why some authors trace the origins of physical chemistry of Berthollet. See, for example, Lemoine, G. L'Évolution de la Chimie Physique', *Revue Scientifique*, 22-2 (1912) p. 673: "Nous n'hésiterons pas à faire remonter à Berthollet la première origine de la chimie physique."
- ¹³³ Thus Duhem noted: "Tandis que les chimistes, repudiant toute alliance avec les physiciens, multipliaient les analyses et les synthèses, les physiciens reprenaient avec une nouvelle ardeur l'étude des conditions dans lesquelles les composés chimiques sont engendés ou détruits, des effets qui accompagnent cette formation ou cette décomposition." *Une Science Nouvelle, La chimie Physique*, *Révue Philomathique de Bordeaux et de Sud-Ouest*, (1902), p. 261.

- ¹³⁴ Ostwald, Gibbs, Nernst and Van't Hoff, for example.
- ¹³⁵ The first chair in physical chemistry was established in Göttingen, and occupied by Nernst.
- ¹³⁶ Thus the *Journal of Physical Chemistry* was started in 1896, from the Cornell University by W. D. Bancroft and J. E. Trevor.
- ¹³⁷ Indeed very few of the major chemists were even aware of developments in thermodynamics in the early periods. And men like Ostwald and Arrhenius were not looked upon favourably by many leading chemists for many years.
- ¹³⁸ Quoted in Walker, J., 'Van't Hoff Memorial Lecture', *Jour. Chemical Society (London)*, **103** (1913), p. 1136.
- ¹³⁹ Quoted in Holton, G., *Thematic Origins of Scientific Thought : Kepler to Einstein*, Harvard Univ. Press (1973), p. 25-26.