William B. Jensen
University of Cincinnati

COLLECTED PAPERS

Volume 1

Chemical Thermodynamics, Kinetics and Electrochemistry

Oesper Collections
Cincinnati, OH
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Dedicated to Lawrence Strong

whose small monograph on chemical thermodynamics
first inspired my interest in the subject

Preface

Having reached that point in my career when one starts asking themselves the question of "what does it all add up to?," I find myself compelled to collect my various papers and notes together and to organize them by subject matter in an attempt to assess how my various interests have evolved over time. Though it may seem strange that I would not automatically know the answer to this question without going through such a sorting process, the simple fact is that much in the career of a scientist – even one who has spent most of his time in a classroom rather than a research laboratory – is blatantly opportunistic. Problems and subjects that grab your attention can come your way almost by accident and one of the delights of a fulfilling career in science is the freedom to pursue them when presented with the opportunity. Seldom is there some overarching plan or long-range research goal, unless one has the misfortune, like so many academic drudges, of having their entire career constrained by the fear of not getting the next grant renewal. Luckily I had the good fortune of having held an endowed professorship and so have consequently never been so constrained.

In my capacity as the departmental historian at Cincinnati, I have overseen the collection and binding of the collected papers of any number of retiring chemistry faculty and have often been struck by their indifference to their life's output. For many of them, their papers are just ephemeral vita stuffing – a necessary evil required to gain tenure and assure promotion but of no further interest or significance. I, on the other hand, find that much of what I have written is still of interest to me and hope that it may also prove to be of continuing interest to some of my fellow chemists and teachers, though I can hardly claim that there is anything here of lasting historical or scientific significance.

This volume, the first in a series of at least four, collects together my papers and notes relating – however tangentially – to the subjects of chemical thermodynamics and kinetics. It includes not only conventional technical papers, but also historical and even humorous writings. In order to make it as inclusive as possible, I have also added items, such as those from my "Ask the Historian" column, which have already been collected together in another booklet, as well as about a half dozen that are still in the form of as yet unsubmitted manuscripts.

The reason for this latter inclusion is that publication opportunities are few and far between for the kind of popularized quasi-historical/philosophical articles that I tend to favor, and I have found from experience that such contributions must be doled out sparingly to those few journals willing to accept them, lest they suffer from manuscript glut. Though I obviously hope these manuscripts will all eventually see publication – several are of a rather controversial nature, and at this point in life I may no longer have either the time or the energy to shepherd them successfully through the conventional publication process.

Finally, in closing, I wish to emphasize that papers 16-18 were coauthored by Julia Kuhlmann – at the time a German exchange student in our department – since the format used in this book, which eliminates the repetitious citation of the author on each individual title page, unfortunately tends to obscure this important fact.

William B. Jensen
Cincinnati, OH
October 2015

I

A Short Note on Brønstedian Energetics

I enjoyed the interesting article by Gaggioli and Petit, "Use the Second Law First" (CHEMTECH, August 1977, p 496). It might interest readers to know that the stimulating approach to the second law used by these authors was originally formulated by J. N. Brønsted in the late 1930s and early 1940s. Brønsted called his version of thermodynamics "energetics" (not to be confused with the earlier version of energetics advocated by Mach, Ostwald, and Helm near the turn of the century) in order to emphasize that it dealt with generalized energy transformations and not just with those involving idealized thermal phenomena.

Brønsted's alternative, but equivalent, formulation of thermodynamics is process rather than system oriented and is based on a distinction between idealized reversible processes and naturally-occurring irreversible processes.

In reversible processes, all energy redistributions (i.e., work) can be represented as the transport of some capacity factor between two different intensities or potentials:

$$\delta A_r = (P_1 - P_2)\delta K_r \qquad [1]$$

where P_1 and P_2 represent the two initial potentials and δK_r represents the conjugate capacity factor for the type of work, δA_r, involved. Example capacity factors would be gravitational mass, moles of chemical substance, electrical charge, volume, etc.; the corresponding potentials would be gravitational potential, chemical potential, voltage, and negative pressure.

Brønsted pointed out that reversible thermal interactions are completely analogous to reversible work interactions and can also be represented by means of equation 1, where the absolute temperature functions as the potential and the transferred entropy increment as the capacity factor. In reversible processes, entropy, like most other capacity factors, is conserved.

Reversible changes generally involve the coupling of two or more work processes, and mechanics teaches us that, in an isolated system, the net work change resulting from such couplings among its constituent subsystems is always zero (i.e., work, not just energy, is conserved):

$$\Sigma_r \delta A_r = \Sigma_r (P_1 - P_2)\delta K_r = 0 \qquad [2]$$

Brønsted called this "the work principle."

Irreversible processes, however, represent an entirely different situation. Here equation 2 no longer applies and experience teaches us that, in an isolated system, there is always a net decrease in the available work and a corresponding isothermal generation of entropy:

$$\Sigma_r \delta A_r + T\delta S_{irr} = 0 \qquad [3]$$

This process is unidirectional because entropy at a constant temperature (or indeed, any equipotential energy) cannot be converted back into work. Brønsted called this "the equivalence principle," and it may be combined with equation 2 to give the general relation:

$$-\Sigma_r \delta A_r = T\delta S_{irr} \geq 0 \qquad [4]$$

where the equal sign refers to the reversible case and the inequality to the irreversible case.

In that none of the fundamental work of Brønsted is referenced by Gaggioli and Petit, I take the liberty of attaching a selected bibliography of papers in English which deal with Brønsted's approach. Of particular interest is the 1949 paper by LaMer *et al.* and the 1976 paper by Sørensen, both of which prove the equivalence between equation 4 and the conventional forms of the first and second laws.

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Publication History

Originally published in *Chemtech,* **1977**, *7*, 656.

II

Le Chatelier's Principle, Solubility and Déjà vu

In recent years at least four substantial articles have appeared in this journal dealing with the application of Le Chatelier's principle to the prediction of the temperature dependency of solubility (1-4). The gist of these articles is that naive use of tabulated values of $\Delta H_{sol}°$ at infinite dilution in the van't Hoff relation can lead to errors, the proper value to use being $\Delta H_{sol}°$ for the saturated solution, which may differ in sign from the value at infinite dilution. In addition, when calculating $\Delta H_{sol}°$ for the saturated solution, one must take care to use the solid actually in equilibrium with the solution at that point. This is often a hydrate rather than the anhydrous solid taken from the shelf to make the solution in the first place.

In light of the interest shown in this subject and the space that has been devoted to it in the journal, I was struck by a strong sense of *déjà vu* upon accidentally coming across the following statement in the 1895 English edition of Wilhelm Ostwald's *Outlines of General Chemistry* and thought it would be of interest to the readers of the journal as well (5):

> *Attention should be paid to the fact that it is the sign of the heat of solution in the almost saturated solution which determines the sense of the change of solubility with temperature. Substances which dissolve to a large extent in water usually have their heat of solution smaller the more concentrated the solution becomes, and it is not impossible that such substances, having a small negative heat of solution in dilute solutions, may acquire a positive heat in more concentrated solutions, so that only the sign in the almost saturated solutions is of use in the application of the above principle [i.e., van't Hoff's relation].*

Ostwald's books served as the prototypes for succeeding generations of "P Chem" texts and were, for the most part, based directly on the primary literature. Consequently, it is of interest to note that his caveat on the relationship between $\Delta H_{sol}°$ and the temperature dependency of solubility is already missing from most second generation texts, though many of these were written by his own students (6-8). Indeed, this example illustrates the fate of many discoveries on passing from the primary literature into the textbook literature. First generation texts are usually based on the primary literature and generally comment on difficulties and limitations. Succeeding generations, on the other hand, are based more and more on other textbooks and in the process gradually simplify and idealize things until, in some cases, they are simply incorrect and the difficulties and limitations must be recovered again from the primary literature – a recovery process in which the *Journal of Chemical Education* often plays an important role, as the above articles testify.

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Publication History

Originally published in *J. Chem. Educ,* **1987,** *64,* 287.

III

A Nonsense Book of Thermodynamics

I

There was a young man named Carnot
Who fervently wanted to know
How caloric dispersed
In cycles reversed
Made engines efficiently go.

II

Helmholtz, Mayer, and Joule
All found the very same rule:
The preposterous notion
Of perpetual motion
Is the pipe dream of only a fool.

III

Clausius found law number two:
Die Entropie strebt einem Maximum zu.
Energy dissipate!
Cried Peter G. Tait.
Yes, said Lord Kelvin, *Pray Do.*

IV

Take (said Maxwell) a common foot rule
Like that you had while at school.
By demoniacally sorting
The molecular cavorting
One end is distinctly more cool.

V

Boltzmann (who was one of the best)
Applied a statistically significant test.
To equilibrate
Is everyone's fate
And to "H" with all of the rest.

VI

Gibbs found the famous phase law
Which works with nary a flaw.
f equals c
Plus 2 minus p.
So reads the famous phase law.

VII

Nernst found law number three,
Which he expounded with infinite glee.
As zero you near
Let dS disappear
And dH will equal dG.

Publication History

Published in R. L. Weber, Ed., *Droll Science,* Humana Press: Clifton, NJ, 1988, pp. 145-146.

IV

Whatever Happened to the Nascent State?

In 1884 the British chemist, M. M. Pattison Muir (figure 1), published a textbook on theoretical chemistry entitled *A Treatise on the Principles of Chemistry* in which he attempted to summarize many of the recent results "on the subjects of dissociation, chemical change and equilibrium, and the relations between chemical action and the distribution of the energy of the changing system" – in short, most of the topics which would, within the next ten years, come to be identified with the new and rising field of physical chemistry and the work of Ostwald, Arrhenius and van't Hoff (1). Though Muir himself did not succeed in establishing a British school of physical chemistry and did not make any significant experimental contributions to the new field, he did play a role in disseminating its early results through his review of Ostwald's work on the measurement of affinity coefficients (2), the writing of a monograph on thermochemistry (3), the editing of an influential dictionary of chemistry (4) and, of course, through his textbook.

Muir, who was later to write an important history of chemistry (5), also had an unusual appreciation of the history of his subject and in his textbook attempted to use the new views on chemical equilibrium and kinetics to unravel some long-standing paradoxes of chemical affinity that had been known since the end of the 18th century. Among these were the problems of predisposing affinity, contact actions, and the so-called *status nascens* or nascent state. The first of these topics has long since disappeared from the textbooks, whereas the second, under the rubric of heterogeneous catalysis, has survived. In many ways, however, it is the third topic that is the most fascinating, as not only the explanation of the nascent state, but the very question of whether it really exists, are still unresolved problems. A history of the various attempts to explain this phenomenon provides one with an interesting cross-section of 19th- and 20th-century chemical theory and, though an explicit treatment of this subject has been missing from the textbook literature since the 1940's, it is of interest to note that the term is still to be encountered, albeit in passing and without explanation, in more recent textbooks (6).

Figure 1. Matthew Moncrieff Pattison Muir (1848 -1931).

Origin and Use of the Nascent-State Concept

A knowledge that freshly prepared gases, when generated *in situ* within a reaction system, are frequently more reactive than when added already prepared from an external source seems to date from the late 18th century. This enhanced, but short-lived, reactivity appeared to be associated with the gases only at the moment of their "chemical birth," so to speak, and the resulting metaphor became enshrined within the chemist's lexicon in the phrase "nascent state," though the chemical poet who first coined the term is not known with certainty.

The first explicit use that I have been able to locate occurs in the 1790 edition of Joseph Priestley's work, *Experiments and Observations on Different of Kinds Airs* (7). Having incorrectly postulated that both fixed air (carbon dioxide) and nitrous acid (nitric acid) were compounds of inflammable air (hydrogen) and dephlogisticated air (oxygen), Priestley (figure 2) attempted to rationalize the different products as a function of differences in the reaction conditions, arguing that:

> *... when either inflammable or dephlogisticated air is extracted from any substance in contact with the other kind of air, so that one of them is made to unite with the other in what may be called its nascent state, the result*

will be fixed air; but that if both of them be completely formed before the union, the result will be nitrous acid.

A year earlier, William Higgins, in his book, *A Comparative View of the Phlogistic and Antiphlogistic Theories*, also invoked the unusual reactivity of hydrogen "at the very instant of its liberation" to rationalize the necessity of water for the oxidation of iron (8). Though he did not describe the hydrogen as nascent, he did use the term when paraphrasing his original statement in 1814 (9).

In the examples cited by both Priestley and Higgins, the nascent gases were generated chemically. In 1807 Humphry Davy reported that a similar enhanced reactivity was also present in the case of electrochemically generated gases (10). Upon electrolyzing water, he observed that some nitric acid was invariably formed at the anode and a trace of ammonia at the cathode. These he attributed to the "combination of nascent oxygen and hydrogen respectively with the nitrogen of the common air dissolved in water," since he knew that these reactions did not occur at room temperature when the fully formed gases were allowed to interact. In modern terms, the observed secondary electrode reactions can be represented as:

anode: $5O^* + N_2 + H_2O \rightarrow 2H(NO_3)$ [1]

cathode: $6H^* + N_2 \rightarrow 2NH_3$ [2]

where we have used the starred symbol to represent the nascent state of the element in question in order to avoid the explicit representation of any hypothesis concerning its molecularity or structure.

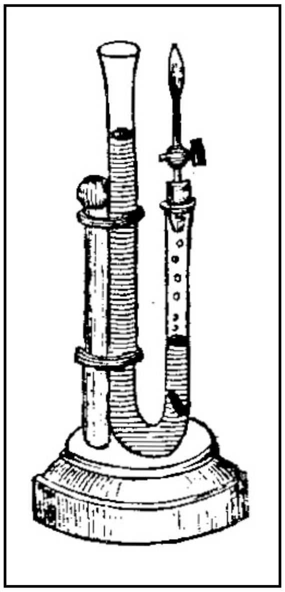

Figure 3. Marsh's apparatus for testing for the presence of arsenic. The unknown is placed in the short arm of the U-tube along with aqueous HCl and a piece of arsenic-free Zn metal. The nascent hydrogen reacts with any arsenic in the sample (usually in the form of the oxide) to generate arsine. The hydrogen/arsine mixture issuing from the end of the tube is lit. The arsine decomposes in the flame and deposits a mirror of elemental arsenic on a cool surface held in the flame.

Figure 2. Joseph Priestley (1733-1804).

An examination of the 19th century chemical literature shows that the nascent state soon became the accepted rationale for a number of otherwise puzzling chemical reactions. Among these were the varying products observed when metals lying above hydrogen on the activity series reacted with either sulfuric (11, 77) or nitric acid (12). At low acid concentrations dihydrogen gas is the major product in both cases, whereas at higher acid concentrations sulfur dioxide, nitrogen oxides and, in some cases, even ammonia are obtained instead. To explain this concentration dependency it was assumed that nascent hydrogen was initially generated in both systems. At low acid concentrations this reverted to normal dihydrogen gas, whereas as at higher acid concentrations it was entirely consumed in reducing the respective acids and dihydrogen gas was no longer observed among the reaction products:

$2H^* + H_2(SO_4) \rightarrow SO_2 + 2H_2O$ [3]

$H^* + H(NO_3) \rightarrow NO_2 + H_2O$ [4]

$3H^* + H(NO_3) \rightarrow NO + 2H_2O$ [5]

$8H^* + H(NO_3) \rightarrow NH_3 + 3H_2O$ [6]

Other classic examples include the use of nascent hydrogen to generate arsine in the famous Marsh test (figure 3) for arsenic (13):

$9H^* + As_2O_3 \rightarrow 2AsH_3 + 3H_2O$ [7]

in the reduction of nitrobenzene to aniline:

$$6H^* + C_6H_5(NO_2) \rightarrow C_6H_5(NH_2) + 2H_2O \qquad [8]$$

in the Clemmensen reduction of carbonyls, and in the Jones reduction column. In each case the hydrogen is generated *in situ* by means of zinc and hydrochloric acid and the reactions are not observed under the same conditions if externally generated dihydrogen gas is used instead.

In all of these examples the actual generation of dihydrogen can be observed as a competing reaction. However, the nascent state concept was soon extended to systems in which the gas corresponding to the nascent intermediate is never observed under the conditions of the experiment and which apparently involve a single overall net reaction rather than two competing reactions. For example, nascent oxygen was used to explain the production of dichlorine oxide in the reaction (14):

$$2Cl_2 + HgO \rightarrow Cl_2O + HgCl_2 \qquad [9]$$

via the mechanism:

$$HgO \rightarrow Hg + O^* \qquad [10]$$

$$O^* + Cl_2 \rightarrow Cl_2O \qquad [11]$$

$$Hg + Cl_2 \rightarrow HgCl_2 \qquad [12]$$

where again it was not possible to produce the highly endoenergetic dichlorine oxide by direct reaction between molecular dioxygen and dichlorine, though in step 11 it is presumed to occur with nascent oxygen.

Likewise, nascent oxygen was frequently invoked to explain the bleaching (or oxidizing) ability of *eau de Javelle* or hypochlorite solutions, via the initial step (15):

$$MClO \rightarrow MCl + O^* \qquad [13]$$

a supposition apparently supported by the fact that their water solutions eventually decompose on standing to give the corresponding metal chloride and dioxygen gas.

Many of the oxidation reactions of nitric acid with the less active metals and with the nonmetals were also rationalized in the same fashion (16):

$$2H(NO_3) \rightarrow 2NO + H_2O + 3O^* \qquad [14]$$

and the ability of *aqua regia*, in contrast to either dichlorine or hydrogen chloride gas, to chlorinate gold was likewise attributed to the initial production of nascent chlorine (16):

Figure 4. Auguste Laurent (1807-1853).

$$3HCl + H(NO_3) \rightarrow NOCl + 2H_2O + 2Cl^* \qquad [15]$$

As will be seen, the use of the nascent state in these cases became the basis of much of the criticism later directed at the concept.

The Free-Atom Hypothesis

The first, and by far the most historically significant, attempt to rationalize the nascent state was made by the French chemist, Auguste Laurent (figure 4), in 1846. Laurent and his collaborator, Charles Gerhardt, were early proponents of the concept that the elements in their standard states were composed of polyatomic molecules rather than isolated atoms. Contrary to the usual accounts found in most histories of chemistry, the supporting evidence for this proposition was based not just on Gay-Lussac's law of combining volumes, but on considerations related to the energetics of chemical reactions as well.

Rephrasing the original arguments of Laurent and Gerhardt in terms of modern bonding terminology, the implied assumption was that chemical bonds could be broken in the course of a spontaneous reaction only if they were replaced by stronger bonds. Given this premise, and the assumption that the elements were monoatomic, it was difficult to understand why some compounds spontaneously dissociated into their elements and, conversely, why it was not possible to synthesize certain compounds directly from the elements themselves, though they could be made indirectly by means of displacement reactions. However, once one accepted the existence of elemental polyatomic molecules, these paradoxes vanished, since in both cases the breaking or making of the bonds in the compounds was competing with the making or breaking of bonds within the elemental molecules or, as Gerhardt put it, with the synthesis or decomposition of a "hydride of hydrogen," a "chloride of chlorine," etc (17).

Applying this concept to the nascent state, Laurent wrote (18):

A binary association of atoms might allow us also to account to a certain extent for the affinity possessed by substances in the nascent state. If two free molecules of bromine and of hydrogen, BB' and HH', are brought together, the affinity of B for B' and of H for H' may suffice to prevent the combination of B and B' with H and H'. But if the substances present are H and B, these two, which have no affinity to overcome, will be able to combine readily. This is what will occur when hydrogen is in the nascent state. That is, whenever it is evolved from hydrochloric acid by the action of a metal, we shall have the equation:

$$HCl + M = ClM + H$$

and there will be a tendency to a reconstruction of a binary molecule either by combination with bromine or with another atom of hydrogen.

Similar arguments were also put forward by the English chemist, Benjamin Brodie, in the early 1850's (19-21).

The value of this interpretation of the nascent state as a minor, but useful, piece of evidence in favor of elemental polyatomic molecules was fully appreciated by the 19th-century chemist, and it is in this context, rather than as a topic in chemical kinetics, that the subject found a place in most chemistry textbooks after 1860. Adolphe Wurtz devoted three pages to the subject in his classic historical study of the development of the atomic theory in 1875 (17) and Pattison Muir was quite explicit about its pedagogical value in his 1884 text (1):

A study of the reactions in which nascent substances play important parts appears to me to keep before the student that all important distinction between the atom and the molecule which is so vital in chemical considerations, and also to draw attention in a marked way to the complexity of all chemical changes.

Though several 19th century chemists (11, 22-23) felt that their experimental investigations of the nascent state were not inconsistent with the free-atom interpretation, there was in fact very little direct experimental evidence for the theory until the second and third decades of the 20th century. This came from studies by Irving Langmuir (24), Karl Bonhoeffer (25-26), Hugh Taylor (27) and others of the gas-phase chemical reactions of atomic hydrogen that had been generated either by thermal dissociation on a heated wire or by means of high voltage electrical discharges. But even here the proof was really indirect and was based on the similarity between the reactions observed in the gaseous phase for atomic hydrogen and those observed in the liquid phase for chemically or electrochemically generated nascent gases. Attempts to bubble gaseous atomic hydrogen into solutions gave negative results due to rapid recombination into dihydrogen gas, whereas attempts to detect the existence of a soluble, diffusible, nascent species in the liquid-phase chemical and electrochemical systems were inconclusive at best (28, 29). Indeed, the results seemed to indicate that in these systems the nascent activity was confined to the surface of either the chemically reacting metal or the active electrode.

The Thermal Excitation Hypothesis

Not all 19th-century chemists were enamored of the free-atom theory of the nascent state and in many ways the opposing experimental evidence was more convincing than the supporting evidence. Much of this was the result of the efforts of the Italian electrochemist, Donato Tommasi (30-33). He pointed out that, if nascent hydrogen was really atomic in nature, its properties should be independent of the metal/acid system used to generate it. But in actual fact, as shown by his own experiments, its reducing ability was highly dependent on the nature of the metal. Thus nascent hydrogen generated by means of zinc and hydrochloric acid was able to reduce chlorates to chlorides, whereas that generated either electrolytically or by means of sodium amalgam produced no reaction. Tommasi further noted that all of the reductions observed for nascent hydrogen at room temperature could also be observed for fully formed dihydrogen gas at higher temperatures. He therefore postulated that nascent hydrogen was nothing more than thermally hot dihydrogen that had not yet had time to thermally equilibrate with the surrounding solvent molecules and that its reducing abilities should directly parallel the enthalpy of the reaction used to generate it. Thus he wrote in 1879 (31):

And if this gas in the nascent state possesses greater affinity than in the natural state, it is solely due to the

> *fact that the hydrogen, the moment it issues from a combination, is found to be accompanied by the whole quantity of the heat produced during the setting free of the hydrogen. Consequently, nascent hydrogen is nothing else than ordinary hydrogen in [different] thermic conditions or, speaking generally, in different physical conditions. To my mind, the expression nascent hydrogen is synonymous with hydrogen + calories. In fact, all the reactions produced by nascent hydrogen can be obtained quite as well with ordinary hydrogen and a high temperature; and the differences observed between the hydrogen resulting from different chemical reactions are simply due to the fact that these reactions do not develop the same quantity of calories.*

Aside from a correction of some of his thermodynamic data by Julius Thomsen (34), Tommasi's theory was generally well received and was often quoted by the authors of advanced textbooks and chemical dictionaries after 1880 (1, 4, 35). Muir expressed a somewhat more sophisticated version of it in his 1884 text, writing (1):

> *In a reaction wherein [a] given compound is produced there must be a moment of time when this compound can only be said to exist potentially, when the atoms which constitute its molecules have not settled down into stable configurations; at this moment the compound may be said to exist in the nascent state. If the atomic vibrations and interactions are allowed to run what might be called their normal course, the compound molecules are certainly produced, but if these interactions are interfered with, a new set of molecules may be formed, which molecules bear a more or less simple genetic relation to those produced in the normal process of chemical change.*

This view of the nascent state has recently been revived among chemists working in the field of molecular reaction dynamics (36), where it is applied to the vibrationally and/or electronically excited species which are the initial products observed in molecular cross-beam studies of gas-phase reactions. Indeed, in 1976, Simon Bauer of Cornell University wrote a short note in which he argued that (37):

> *It is now time to restore the term "nascent" to legitimacy. Much evidence has accumulated, both experimental and theoretical, which demonstrates that in many reactions the partition of nascent products among their characteristic rotational, vibrational, and electronic states differs substantially from that expected were these generated in statistical equilibrium. "Nascent" contrasts with "state relaxed," i.e. a system for which a single temperature and corresponding thermodynamic functions can be defined.*

Though Bauer cited several examples of how the reactivity of these nascent products differed from that of the corresponding state-relaxed products, it is open to question, as in the earlier case of the gas-phase atomic hydrogen experiments, whether this explanation can be extended to the classical liquid-phase chemical and electrochemical systems which gave rise to the concept of the nascent state in the first place.

The Allotrope Hypothesis

Yet a third theory of the nascent state was proposed by the German chemist, Gottfried Wilhelm Osann, in a series of more than a dozen papers published between 1852 and 1864 (38). By electrolysis of a dilute solution of freshly distilled Nordhäusen sulfuric acid (figure 5), Osann obtained a form of activated hydrogen which was capable of reducing solutions of silver salts to metallic silver and mixtures of potassium hexacyanoferrate(III) and iron(III) chloride to Berlin blue. Platinum and porous carbon cathodes were capable of storing the active hydrogen and could be removed from the electrolysis apparatus and placed in other solutions, where they produced reactions not normally observed for dihydrogen gas under similar conditions.

Heavily influenced by Christian Schönbein's discovery of ozone, Osann decided he had discovered an analogous allotrope of hydrogen and since, like ozone, it was much more chemically reactive than the normal form of the element, he gave it the name of *Ozonwasserstoff* (39). In later work he reported that the atomic weight of his new gas was 0.66 or about two thirds that of normal hydrogen (40).

Similar ideas were expressed by T. L. Phipson in 1858 (41):

> *What is called the "nascent state" is, I think, nothing more or less than the allotropic state of bodies entering into combination ... it seems incontestable that every time oxygen enters into or leaves compounds, it is in the state of ozone. When we reflect further on the results already obtained with hydrogen, chlorine, bromine, sulphur, and phosphorus, we are inclined to believe that all simple bodies should behave in the same manner; that is to say, that all bodies may have an allotropic state analogous to ozone, and that they are in this state at the moment of entering into combination, or when they are in the nascent state.*

Osann's results were criticized by J. Löwenthal in 1858, who suggested that the enhanced reducing prop-

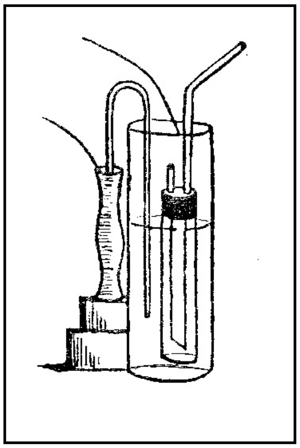

Figure 5. Osann's apparatus for the preparation of *Ozone-Wasserstoff* via the electrolysis of freshly distilled Nordhäusen acid.

erties of the gas were due to the presence of sulfur dioxide from the Nordhäusen acid used in its preparation (42). This criticism was disproved by Osann (43), but more serious problems were uncovered by Gustav Magnus (44), who was unable to duplicate many of Osann's results. He concluded that Osann's materials were contaminated with iron and that this was actually responsible for the observed reductions. Though Hermann Fehling summarized Osann's work in his 1864 *Handbuch* (45), he was critical and, by 1895, Albert Ladenburg felt that Osann's hypothesis had been "aus der Welt geschafft" (35).

Actually Ladenburg's funeral oration proved to be premature as, in a series of papers published between 1920 and 1922, Gerald Wendt and Robert Landauer of the University of Chicago revived a form of Osann's hypothesis (46-47). By means of α-radiation, electrical discharge under reduced pressures, and high potential coronas at atmospheric pressure, they generated an activated form of hydrogen which showed a reactivity different from both normal dihydrogen gas and atomic hydrogen. This they equated with the H_3 molecule originally postulated by Joseph J. Thomson in 1913 (now known to be the H_3^+ ion). Because of both its increased reactivity relative to dihydrogen and the analogy between its formula and that for O_3, they proposed that the new species be called *hyzone*.

As with the work on atomic hydrogen, these results could not be extended to the traditional liquid-phase chemical and electrochemical methods of generating nascent hydrogen (47), though A. C. Grubb, in a short note published in 1923, claimed to have prepared traces of the species by dropping acid on pieces of suspended metal so as to avoid emersion of the metal in liquid (48).

The Polarity Hypothesis

The phenomenon of allotropism was a difficult problem for the 19th century chemist. Rationales based on variations in either the degree of molecular complexity (i.e. polymerization) or variations in molecular structure (i. e., isomerism) had to await the work of Brodie in the 1850's on the concept of elemental polyatomic molecules (49). Indeed, it was because of this very problem that Berzelius had introduced the distinctions between isomerism and polymerism, on the one hand, and allotropism, on the other (50), and he himself favored the idea that allotropes corresponded to different electrical states of an element's atoms.

This concept was widely used to rationalize allotropism in the first half of the 19th century and was applied in great detail by Schönbein in his attempts to explain the behavior of ozone (thought to be negative) and its relationships to normal oxygen (thought to be neutral) and to the antozones (i.e., peroxides, thought to be positive) (51). Not surprisingly, it also made its appearance in discussions of the nascent state via the allotropic theory. Thus Phipson contended that the transient allotropic modification of an element which appeared at the moment of its formation was equivalent to having rendered the element "infinitely more electropositive or electronegative" than its normal state (52).

Like many of the other rationales of the nascent state, this so-called "polar" theory experienced a brief revival in the early 20th century, this time within the context of early electronic theories of the chemical bond. This modernized version was apparently suggested by Harry Shipley Fry (figure 6) of the University of Cincinnati, who was an early proponent of a

Figure 6. Harry Shipley Fry (1875-1948).

polar theory of organic chemistry based on the electron transfer model of chemical bonding first proposed by J. J. Thomson (53).

Consistent with the fact that this theory viewed all bonding as ionic, diatomic molecules of the simple substances were written as H^+H^-, Cl^+Cl^-, etc. This formulation meant that in the generation of dihydrogen gas by reduction of aqueous H^+ solutions, the reduction of the H^+ ion had to proceed all the way to H^-. This then combined with another H^+ ion from the solution to generate the dihydrogen gas. Likewise, generation of dichlorine via oxidation of aqueous chloride solutions required the generation of Cl^+, which then combined with Cl^- to generate the final product. Thus Fry equated the nascent state with the generation of transient free ions having unusual and highly reactive oxidation states. This view was also supported by A. Pinkus (54), but fell out of favor with the eclipse of the polar bonding model by the electron-pair covalent model of G. N. Lewis.

The Occlusion Hypothesis

Even these permutations fail to exhaust the speculations of the 19th-century chemist relative to the nature of the nascent state. Yet a fifth model – the so-called "occlusion" model – was developed by the British chemists, John Gladstone (figure 7) and Alfred Tribe, in the late 1870's as a result of their work on the copper/zinc couple (55- 58). Made by placing a strip of zinc foil in a copper sulfate solution for a few minutes in order to plate out a small quantity of copper on the zinc, Gladstone and Tribe found that in water solutions the resulting couple was able to perform many of the reductions observed for nascent hydrogen, whether generated electrochemically or via metal-acid reactions. Among these were the reduction of chlorate to chloride, nitrate to nitrite and ammonia, hexacyanoferrate(III) to hexacyanoferrate(II), nitrobenzene to aniline, sulfurous acid to sulfur, and diarsenic trioxide to arsine (57).

As a result of their experiments, they became convinced that the zinc portion of the couple reduced the water, that the resulting hydrogen became occluded in the copper, and that this occluded hydrogen was responsible for the observed reductions (56). In support of this model they compared the reducing abilities of the couple with those of hydrogen occluded in platinum, palladium, copper, and porous carbon, concluding that (57):

> *... the increased power of the hydrogen is due to its condensed condition [upon occlusion in the metal], while the observed differences between the action of the different combinations result from variations in this respect, and perhaps also from the more or less firm hold which the metal has upon the gas.*
>
> *The above chemical changes are effected more or less perfectly by nascent hydrogen. But this hydrogen in every case is set free in contact with, or in very close proximity to a metal, which in virtue of the power known to be possessed by such solids very probably condenses and fixes some of this gas. It may therefore be conceived that the activity of the hydrogen under these circumstances is but the consequence of its intimate association with the metals, or, in other words, of its being in the occluded condition.*

This hypothesis is perhaps the most satisfactory when it comes to explaining the known facts about chemically and electrochemically generated nascent hydrogen in the liquid phase. It explains the dependency of the reducing power of the hydrogen on the method of its preparation (variations in the ability of the metals to adsorb or occlude hydrogen), the absence of a soluble, diffusible, active intermediate in the solutions (it is really a surface reaction at the metal or electrode), and the problems with reproducibility and sensitivity to contamination (both highly characteristic of surface reactions). Of course, Gladstone and Tribe were necessarily vague about the exact nature of the chemical species corresponding to the occluded hydrogen, though at one point they did draw an analogy with the reducing ability of copper hydride. Indeed, this question is still a subject of debate among chemists (59).

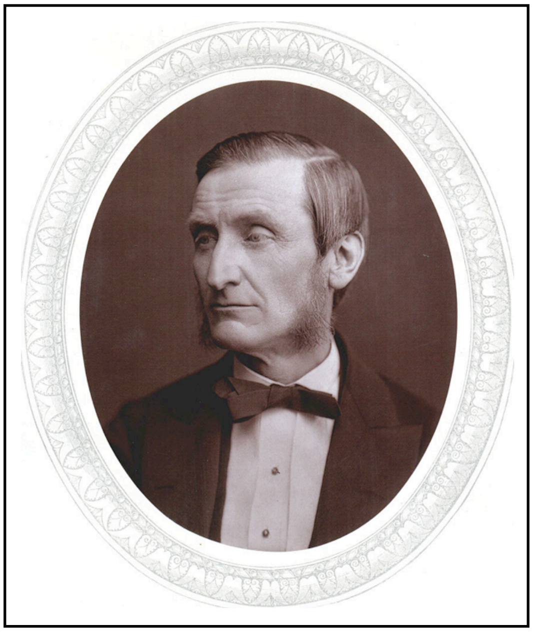

Figure 7. John Hall Gladstone (1827-1902).

In 1927 Joseph Mellor drew attention to the close relationship between this subject and the problem of the hydrogen overpotential in electrochemistry (60). In general, metals with low overpotentials tend to strongly occlude hydrogen, and to act as effective catalysts for the recombination of hydrogen atoms into dihydrogen gas, the hydrogenation of alkenes, etc. (61).

8. The Active Intermediate Hypothesis

A close examination of these five theories – the free-atom, the thermal nonequilibrium, the allotropic, the polar, and the occlusion – shows that, despite of their apparent diversity, they actually have some fundamental points in common. In all five cases, one is postulating that the generation of a gas, X, either chemically, via the reaction of A and B, or electrochemically, proceeds through a short-lived intermediate, I, which, upon further reaction with more B, gives the final product:

$$A + B \rightarrow [I] \qquad [16]$$

$$B + [I] \rightarrow X \qquad [17]$$

If this intermediate is generated in the presence of another chemical species, D, capable of reacting with it to form an alternative product Z

$$D + [I] \rightarrow Z \qquad [18]$$

then one has an example of nascent reactivity. These common features might be characterized as belonging to a generalized "active intermediate" model of the nascent state. Since the intermediate, I, is presumably more endoenergetic than the product gas, X, this means that reaction 18 will be thermodynamically more favorable than the corresponding reaction between X and D:

$$D + X \rightarrow Z \qquad [19]$$

and will necessarily entail a change in its kinetics as well. The only disagreement among the five theories is over the precise nature of the intermediate.

This model further implies that nascent activity can be manipulated by controlling the relative rates of reactions 16-18. Increasing the rate of reaction 17 will increase the rate of evolution of gas X and decrease the amount of product Z, whereas decreasing its rate and/or increasing the rate of reaction 18 will increase amount of product Z. This fact was explicitly recognized by several investigators in the 19th century. Thus, Gladstone and Tribe tested this hypothesis in their study of the reduction of nitric acid during electrolysis, postulating that the failure to observe the production of dihydrogen at the cathode in the case of concentrated acid solutions was due to the fact that reaction 18 consumed all of the intermediate (occluded hydrogen in their theory) in the production of NO and NO_2, leaving none for the generation of dihydrogen gas via reaction 17 (58). By increasing the rate of reaction 16 for a given acid concentration, via an increase in the rate of electrolysis, they were able to provide sufficient intermediate for both reactions 17 and 18 to be observed simultaneously.

Likewise, Thomas E. Thorpe, in his 1882 study of the reduction of ferric salts with nascent hydrogen generated by various acid-metal systems, wrote (23, 62):

> *Any condition which increases the rapidity of the evolution of the hydrogen, without to an equal degree increasing the chance of contact of the hydrogen-atom [i.e., the nascent intermediate, Thorpe accepted the free-atom model] with the ferric sulphate, diminishes the proportion of hydrogen which does work as a reducing agent. By increasing the amount of free acid, we increase the rate at which the hydrogen is evolved, without to an equal degree increasing the molecular movement of the ferric sulphate, and hence an increased amount of hydrogen escapes ... by keeping the amount of acid constant and heating the liquid, we increase the chances of contact between the ferric sulphate and hydrogen-atom, and accordingly obtain an increased reduction ... By diluting the ferric sulfate solution the chances of contact between the hydrogen [atom) and ferric sulphate are of course diminished, and hence more of the hydrogen escapes in the free state.*

Thermodynamics versus Kinetics

Given that the active intermediate model requires an alteration in both the kinetics and thermodynamics of the reactions, the modern chemist cannot resist asking which of these factors is the most important in explaining the enhanced reactivity of the nascent state. There were in fact proponents of both the thermodynamic and kinetic points of view during the 19th century, though both necessarily rejected the active intermediate models, which imply the simultaneous alteration of both.

In a series of papers and books published in the late 1860's and 1870's, the French thermochemist, Pierre Eugene Marcelin Berthelot, argued that the nascent state did not exist and that the phenomena usually attributed to its operation could be explained in terms of thermochemistry alone (14. 63). All of his examples in involved the use of the nascent state to explain the indirect synthesis, by means of displacement reactions, of endoenergetic compounds that could not be directly synthesized from the elements themselves. A case in point is the synthesis of dichlorine oxide outlined earlier in equations 9-12. The difference between the direct synthesis and indirect synthesis, Berthelot argued, had nothing to do with nascent intermediates but was due to the fact that in the latter case the production of the unstable endothernic product (Cl_2O) was accompanied by the simultaneous production of a highly exothermic by-product ($HgCl_2$) and this made the overall process exothermic and hence thermodynamically favorable.

In 1918 Alexander Smith pushed Berthelot's observations on the imaginary role of the nascent state in indirect versus direct syntheses a step further, sarcastically remarking that (74):

> *... since hydrogen and chlorine do not unite in the cold, when sulfuric acid and common salt give hydrogen chloride, to be consistent we must suppose that nascent hydrogen and nascent chlorine were formed and combine. In other words, every union of two elements, other than direct union, must be explained by nascent action, although in double decomposition this logical necessity is uniformly overlooked.*

Nevertheless, not everyone was satisfied by Berthelot's approach. Adolphe Wurtz, for example, characterized Berthelot's arguments as "useless," largely because they were not mechanistic in nature and therefore failed to provide a "natural" explanation (17). More telling were the comments of Tommasi in 1880 (64):

> *M. Berthelot ... not long ago pretended that he was the first to give a rational theory of the nascent state ... But if you open these two volumes, you will not be able to find a single sentence which makes one even suspect why nascent hydrogen is more active than ordinary hydrogen.*

In other words, though Berthelot had given a proper thermodynamic rationale of the indirect synthesis of endothermic compounds, these cases a represented questionable extensions of the nascent state concept in the first place, and he had completely ignored the competitive gas-generating reactions which had originally given rise to the concept.

Indeed, the inappropriateness of Berthelot's rationale in the case of these competitive systems becomes apparent if one evaluates the thermodynamics of most of the classic reduction reactions involving nascent hydrogen, for one quickly discovers that the corresponding reductions with normal dihydrogen gas are all thermodynamically feasible at room temperature. This is true, for example, of the reduction of chlorate to chloride, nitrate to ammonia, diarsenic trioxide to arsine, nitrobenzene to aniline, iron (III) to iron (II), permanganate to manganese(II), etc. Thus our failure to observe these reactions must be kinetic rather than thermodynamic in nature, and a favorable change in the reaction kinetics is both necessary and sufficient to produce an observed reaction at room temperature. Though a change in mechanism may also alter (via coupling) the reaction thermodynamics, this is not a requirement.

The concept of a purely kinetic rationale of the nascent state brings us finally to our last model. This was proposed by Wilhelm Ostwald (figure 8) in 1902, almost as a passing thought, in his famous *Lehrbuch* (65). He pointed out that, when initially formed, small submicroscopic bubbles must be under enormous pressure due to the high surface tension of the surrounding water. At molecular dimensions, a newly formed bubble with a diameter of 10^{-1} cm would contain gas under a pressure of approximately 15,000 atmospheres, and this increased pressure, via the law of mass action, might well account for the enhanced reactivity of so-called nascent hydrogen. Today we would also emphasize the importance of the increased surface area between the smaller bubbles and the surrounding liquid.

This latter aspect was further pursued by the Greek chemist, Constantine Zenghelis, in a series of papers published between 1920 and 1921 (66-68). He created superfine gas bubbles by forcing gases through

Figure 8. Wilhelm Ostwald (1953-1932).

fine filter paper or through dialysis membranes. When this was done in solutions of various reactants, he obtained many of the reactions usually attributed to the nascent state. In the case of dihydrogen, these included the reduction of chlorate to chloride, nitrate to nitrite, and mercury(II) to mercury(I). In the case of mixtures of dihydrogen and dinitrogen, he obtained ammonia, and in the case of carbon dioxide, a variety of reduction products, including formaldehyde. Zenghelis concluded that (68):

> *We believe that on the basis of the preceding results we must reject the generally received hypothesis which attributes the considerable activity of certain gases in the nascent state to the excess energy of free atoms. On the contrary, we believe we have demonstrated that this activity is due to the extreme subdivision of the active masses in contact.*

Using this theory to account for the dependency of the activity of the nascent hydrogen on the nature of the metal-acid system used to generate it, would require that different metals nucleate different size bubbles, a factor that should, in turn, depend as much on the physical roughness of the surface as on the chemical nature of the metal itself.

Some anticipation of the kinetic rationale was already present in the occlusion theory. The enormous decrease in volume accompanying the occlusion of hydrogen in palladium had been noted by Thomas Graham as early as 1868 (69-71). Indeed, he calculated that the density of the hydrogen went from a value of 0.0895 g/mL in the gas phase to a value of 0.733 g/mL in the metal. Chemists had long speculated that hydrogen was an analog of the alkali metals and, under this extreme condensation, Graham felt that it had in fact become a metal, for which he proposed the name *hydrogenium*. He also felt that the proper view of occluded hydrogen in palladium was that it was a metallic alloy of palladium and hydrogenium.

The idea that the increased concentration of occluded hydrogen versus gaseous hydrogen was partly responsible for its increased activity was already hinted at in the statement from Gladstone and Tribe quoted earlier and a similar idea was suggested by Edward Willm in 1873 (72). This is, of course, a purely kinetic effect only if one assumes that the occluded hydrogen is still diatomic and does not chemically interact with the metal lattice – fine points on which the 19th century chemist was understandably vague.

Summary and Conclusions

Having come to the end of our historical survey, what can be said about the fate of the term "nascent state"? Despite its apparent renaissance among chemists in the field of chemical reaction dynamics, it is unlikely that the term will return to the introductory textbook. With the demise of the free-atom model, it no longer has value as a minor piece of evidence for the polyatomic nature of elemental molecules and, though one might argue that historically it represents one of the first sustained attempts to deal with reaction mechanisms, its status as a well-defined concept in chemical kinetics is even more tenuous.

Our survey points to the fact that nascent activity is primarily a kinetic phenomenon and that it basically subsumes any change in reaction conditions that will favorably alter the kinetics of an otherwise thermodynamically allowed reaction. The precise nature of this alteration may vary from one system to the next. Thus the occlusion or gas adsorption model seems best suited to describe nascent activity in the case of gases generated electrochemically or via heterogeneous reactions in the liquid phase; the nonequilibrium model seems best suited to the vibrationally excited products formed in molecular cross-beam studies, and the gas bubble model for activation of absorbed gases in porous carbon. In short, there is no single explanation of nascent activity and hence no well-defined nascent state. Even if one accepts the generalized active intermediate model, the fact remains that similar active gases can be stored in platinum and porous carbon or produced by means of superfine bubbles and that the literal meaning of the term nascent no longer applies under these conditions.

It is of interest to compare these conclusions with those of earlier writers. In a memoir written in 1870, Henri Sainte-Claire Deville objected to the use of the term "state" in conjunction with a transient species which, by its very definition, could not be isolated and assigned definite properties (73). Muir, on the other hand, attempted to weigh both the pros and cons of the concept in his 1884 text (1):

> *The term "nascent action" has probably been at once helpful and harmful to the progress of chemistry. By classing under a common name many phenomena that might otherwise have been lost in the vast mass of fact with which the science has to deal, the expression has, I think, done good service; but in so far as its use has tended to prevent investigation – for it is always easier to say of any unusual reactions, "these are of nascent action" than to examine carefully into their course and conditions ... the use of the expression has, I think, been unfavorable to the best interests of chemical science.*

Indeed, examples of its use as a chemical scapegoat are not hard to find (78-79).

But it was Alexander Smith (figure 9), in the 1918 edition of his popular *Introduction to Inorganic Chemistry*, who came closest to our own conclusion when he wrote (74):

> *The term nascent hydrogen is used in different senses, in a very confusing way. (1) It may mean nascent, literally, that is newly born or liberated. (2) It is also used to mean different-from-ordinary, or, in fact, an allotropic form of hydrogen. (3) It is often used to mean one particular allotrope, namely, atomic hydrogen. (4) It is used ... to mean hydrogen activated by contact with a metal. (5) Finally, its activity is explained as being due to the larger amount of free energy contained in zinc plus acid plus reducing agent, as compared with the free energy contained in free hydrogen plus reducing agent ... The word nascent is, of course, a misnomer, excepting in connection with [usage] 1.*

Finally, in closing, we might briefly note a positive example of the use of the nascent state concept. In 1882 the German chemist, Moritz Traube, successfully used it to unravel the structure of hydrogen peroxide (75-76). Previous to his work chemists had viewed this compound as oxygenated water. In contrast, Traube insisted that it "was not an oxidation product of water ... but rather a compound of an undamaged molecule of oxygen with two added hydrogen atoms." This he proved by comparing the products obtained by passing dihydrogen gas over nascent oxygen generated at the anode, via the electrolysis of water, with those obtained by passing dioxygen gas over nascent hydrogen generated at the cathode. Assuming the free-atom interpretation of the nascent state, Traube reasoned that, if the traditional view of hydrogen peroxide was correct, then it should be produced at the anode via the reaction:

$$H_2 + 2O \rightarrow H_2O_2 \qquad [20]$$

whereas if his interpretation was correct, it should be produced at the cathode via the reaction:

$$O_2 + 2H \rightarrow H_2O_2 \qquad [21]$$

In fact, only water was produced at the anode, whereas a small amount of hydrogen peroxide was formed at the cathode, thus both verifying Traube's hypothesis and providing a sobering reminder of how incorrect assumptions (i.e., the free-atom interpretation of the nascent state) can sometimes lead to correct results.

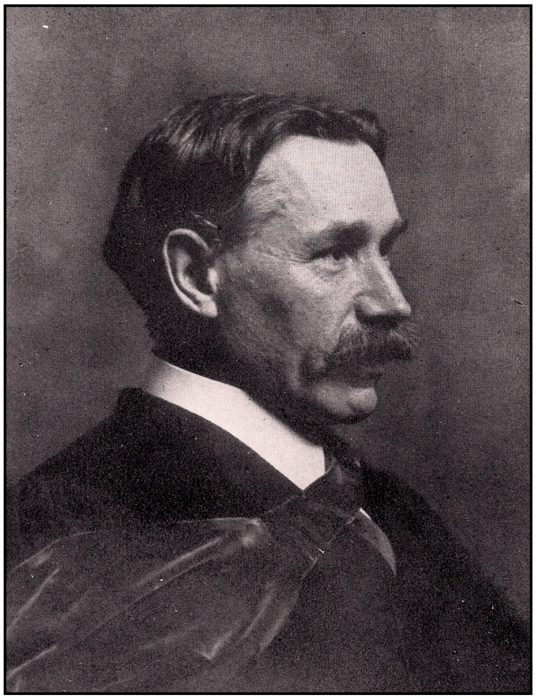

Figure 9. Alexander Smith (1865-1922).

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Publication History

First published in *Bull. Hist. Chem.,* **1990,** *6,* 26-36.

Update

In preparing a new reprint of this paper, I have taken the liberty of adding section headers, as well as several new illustrations taken from the Oesper Collections at the University of Cincinnati. I have also since discovered evidence that most reductions attributed to nascent hydrogen generated in acid-metal systems are due to the metal and that the H_2 generation is merely a competing side-reaction.

V

The Thermodynamics and Kinetics of “Heater Meals”

On a recent speaking trip to Ohio University, my host showed me a clipping from a local newspaper describing a new food product called *Heater Meals,* which was being test-marketed in the Cincinnati area. According to the clipping, these packaged meals came complete with their own “stove” inside:

The stove has a patented food heater made of salt, iron, and magnesium. When salt water is added, it causes the iron and magnesium to produce heat and to thoroughly heat your meal!

Salt, iron and magnesium were just too good a combination for an inorganic chemist to resist and, on returning to Cincinnati, I purchased several of these meals in order to explore the chemistry of their “inorganic stoves.” This chemistry turns out to involve a very clever use of elementary thermodynamics, kinetics, and inorganic electrochemistry.

Since this chemistry is easily understood by the average chemistry major, investigation of this product can serve as a stimulating undergraduate research project. For this reason, rather than simply summarizing what is in the patent literature, I have instead outlined my own course of investigation in order to illustrate what one can reasonably expect a good student to uncover by means of a few simple observations, test tube experiments, and access to a good technical library.

The Product

The product consists of box containing a sealed food pouch which fits into a styrofoam tray (figure 1). Attached to the bottom of this tray is a large porous packet or “tea bag” which contains the heater element. There is also a plastic knife and fork, a napkin, and a packet of salt water. To operate the stove, one pours the salt water into the tray and places the food pouch on top of the tea bag. One then slides the unit back into its box and 14 minutes later removes a fully heated meal.

The Role of the Magnesium

Use of a low-power binocular microscope to examine the heater element contained in the tea bag reveals that it consists of chunks of a silvery metal dispersed in a matrix of partly-fused translucent spheres. Addition of the salt water to about half of a heater element placed in a shallow glass dish results in immediate reaction. There is violent effervescence, followed within seconds by rapid heating and the evolution of steam. The gas bubbles are flammable and can be ignited with a match, provided that this is done before too much steam accumulates. Examination of the heater element after the reaction ceases shows that the matrix of partly-fused translucent spheres has remained intact but that the chunks of silvery metal have either disappeared or have become coated with a white reaction product.

All of these observations are consistent with the hypothesis that the water oxidation of magnesium metal is the source of energy for the heater element:

$$\mathrm{Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)} \qquad [1]$$

The observed white reaction product obviously corresponds to the magnesium dihydroxide and the flammable gas to the dihydrogen, whereas the translucent spheres correspond to some kind of inert material used to disperse the metal reactant and to retain most of the solid reaction products. Reaction 1 has an enthalpy value of -352.96 kJ/ mol rx at STP – more than sufficient to account for the observed heat evolution (1).

Reaction 1 may be profitably compared with the reaction between sodium metal and water, which is often used as a chemical demonstration, and is normally considered to be an archetypical example of an energetically violent chemical reaction:

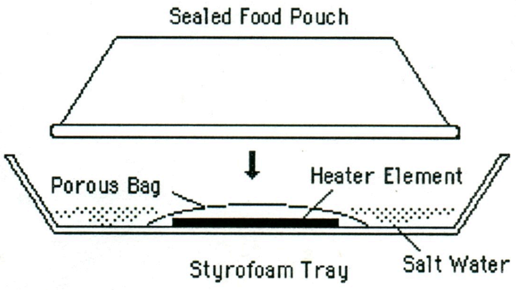

Figure 1. The components of a typical HeaterMeal.

$2Na(s) + 2H_2O(1) \rightarrow 2Na(aq)^+ + 2OH(aq)^- + H_2(g)$ [2]

This reaction has an enthalpy value of -367.52 kJ/mol rx or nearly the same as reaction 1. Indeed, if one calculates enthalpies per mole of metal rather than per mole of reaction, then the water oxidation of magnesium metal is almost twice as exothermic as the corresponding reaction for sodium (-352.96 kJ/mol Mg versus -183.76 kJ/mol Na).

For students taking an inorganic course, this comparison between magnesium and sodium can be taken a step further using the cycle in figure 2 to evaluate both their free energies of oxidation and their oxidation potentials. The free energy of oxidation (ΔG_{ox}), corresponding to the general equation:

$M(s) \rightarrow M(aq)^{z+} + ze^-$ [3]

can be decomposed, in keeping with the cycle in figure 2, into the sum of the free energies of atomization (ΔG_a), ionization (ΔG_i), and solvation (ΔG_{solv}):

$\Delta G_{ox} = \Delta G_a + \Delta G_i + \Delta G_{solv}$ [4]

The values for each of these terms, using the data of Sanderson, are given in Table 1, and result in an overall value of AG_o for magnesium nearly two and a half times that of sodium (2). However, when these values are converted into oxidation potentials by conversion into volts, normalization relative to the moles of electrons involved, and subtraction from the value obtained for dihydrogen gas using the same cycle:

$E_{ox} = \Delta G_{ox}[H_2]/zF - \Delta G_{ox}[M]/zF$ [5]

$E_{ox} = 4.44V - \Delta G_{ox}[M])/zF$ [6]

one again obtains a near equality in the final overall result, as shown in the last column of table 1.

The Role of the Sodium Chloride

If students attempt to confirm the above conclusions, they will be rapidly disappointed. Despite the similarity in both their enthalpy values and oxidation potentials, sodium will give the expected violent reaction on contact with water, whereas magnesium will not. Only by strongly heating magnesium in steam is it possible to observe the reaction in equation 1 (3). Indeed, a detailed study of the reaction between magnesium and water at room temperature, made by Roberts and Brown at the turn of the century, concluded that, even after several weeks (4):

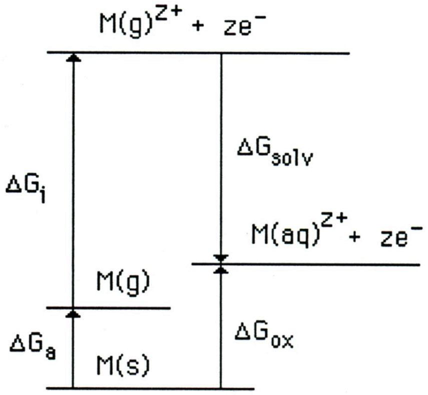

Figure 2. A thermodynamic cycle for the calculation of ΔG_{ox} for a given metal M.

magnesium is without action on distilled water, boiled to free it from gases and carefully cooled out of contact with air.

Since thermodynamic calculations show that reaction 1 is extremely favorable at STP, failure to observe the reaction must be due to kinetic inhibition of some sort, and one does not need to look far for the probable cause. It has long been known that many metals which should react with water or spontaneously oxidize on contact with air do not do so because the resulting hydroxides and oxides formed in the initial stages of the reaction form a coherent film on the remaining metal and thus protect it from further attack. This phenomenon is referred to as “passivity” in the corrosion literature. As Ulick Evans observed in his 1926 volume on *The Corrosion of Metals* (5):

The only metals that react rapidly with pure water are those which have soluble hydroxides.

Inspection of the states in equations 1 and 2 shows that

M	ΔG_a	ΔG_i	ΔG_{solv}	ΔG_{ox}	E_{ox}
Mg	114.22	2191.16	-1903.30	402.8	2.36
Na	77.82	497.48	-410.03	165.27	2.73
H_2	203.34	1313.36	-1088.68	428.02	0.00

Table 1. Thermodynamic data for the evaluation of the values of ΔG_{ox} and E_{ox} for sodium and magnesium. All values of ΔG are kJ mol-1 and all values of E_{ox} are in volts.

they represent a classic example of the situation summarized by Evans. Magnesium dihydroxide is insoluble in water and blocks further reaction with the magnesium metal, whereas sodium hydroxide is soluble and does not inhibit continuous reaction between water and the metal surface.

Not only is insolubility a necessary condition for inducing passivity, the reaction product (p) must also have a unit volume (V/N) equal to or greater than that of the metal (m):

$$(V/N)_p/(V/N)_m \geq 1 \qquad [7]$$

otherwise an insufficient volume of product will be formed to replace the volume of metal that has reacted and thus produce a complete and coherent coating on the remaining metal. From dimensional analysis, it is apparent that the unit volume of a substance, usually measured in units of milliliters per mole, is equal to its unit mass (M/N), measured in units of grams per mole, divided by its mass density (M/V), measured in units of grams per milliliter:

$$(V/N) = (M/N)(V/M) \qquad [8]$$

(where V = volume, N = particle population, M = mass) and thus that the ratio of the molar volume of the product to the molar volume of the metal is the ratio of their respective molar masses multiplied by the inverse ratio of their respective mass densities:

$$(V/N)_p/(V/N)_m = [(M/N)_p/(M/N)_m][(M/V)_m/(M/V)_p] \qquad [9]$$

The necessary data for magnesium metal and magnesium dihydroxide can be found in the *Handbook of Chemistry and Physics* and shows that a sufficient volume of magnesium dihydroxide is formed to provide more than complete coverage of the remaining magnesium metal:

$$(V/N)_{Mg(OH)2}/(V/N)_{Mg} = 1.77 \qquad [10]$$

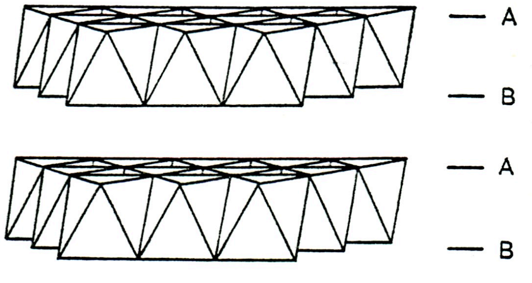

Figure 3. A coordinated polyhedra model of the infinitely extended 6/3 layers found in magnesium dihydroxide (8).

It should be further noted that the condition in equation 7 is necessary but not sufficient for inducing passivity. The resulting solid product, though of sufficient volume, may conduct ions or electrons well enough to allow the reaction to continue or it may be mechanically faulty due to cracking or flaking and so fail to completely protect the underlying metal surface. In the case of magnesium, X-ray diffraction studies of the surface have confirmed that crystalline magnesium dihydroxide or "brucite" is formed during the immersion of pure magnesium in degassed distilled water and that the resulting film is "highly protective" (6).

However, it has also long been known that neutral solutions of the chloride ion cause magnesium metal to react with water at an observable rate at STP. Most of the paper by Roberts and Brown, quoted earlier, was devoted to a study of this phenomenon, and it has been the focus of much of the corrosion literature on magnesium metal because it severely limits the use of magnesium and its alloys in the presence of sea water. As Evans noted in 1926 (5):

> *Magnesium, although scarcely affected by pure water, causes marked evolution of hydrogen when immersed in a solution of potassium chloride ... a film on an anode usually soon ceases to be protective if a small amount of a soluble chloride is added to the solution ... What is quite certain is that the presence of chlorides in solutions tends to prevent the formation of a protective type of film on an anode.*

Just how the chloride ion destroys the passivity of the magnesium dihydroxide film is still open to investigation. What is known is that the infinitely extended 6/3 layer structure of magnesium dihydroxide (figure 3) is highly susceptible to substitution of the hydroxide ions by chloride ions, leading to the formation of a variety of complex chlorohydroxides (Table 2), some of which (e.g., $Mg_3(OH)_5Cl•xH_2O$) have actually been detected on the surface of magnesium metal that has been exposed to chloride solutions (6-8). Whether the structural changes accompanying chloride substitution in the brucite layer result in the layer failing mechanically or whether the resulting chlorohydroxides provide better ionic and/or electronic conductivity and hence lower overpotentials for dihydrogen discharge is still unknown. All that is certain is that the sodium chloride used in the *Heater-Meals*' "stove" functions kinetically to reduce the activation barrier for reaction 1, and that it does this by inhibiting the ability of the magnesium dihydroxide reaction product to form a passive coating on the magnesium metal.

The Role of the Iron

If students place a freshly-cleaned strip of magnesium metal in a neutral sodium chloride solution, they will observe the formation of dihydrogen gas bubbles on its surface, but at a rate far too slow to provide a practical heat source. Indeed, the magnesium soon becomes coated with fine bubbles of dihydrogen gas which block further reaction. This slow rate indicates the presence of a high activation energy or overpotential for hydrogen discharge at magnesium even in the absence of a coherent protective film of magnesium dihydroxide.

This problem can be eliminated by placing the magnesium in contact with a metal having a lower overpotential for hydrogen discharge, such as platinum, palladium, gold, copper, cobalt, nickel, or iron – of which iron is obviously the metal of choice from an economic point of view. The sites for the oxidation and reduction half-reactions are now spatially separated. Magnesium continues to oxidize to Mg^{2+} at the magnesium surface, whereas the water is now reduced to dihydrogen gas at the iron surface. This process is called galvanic corrosion or electrocatalysis. Figure 4, which is taken from the 1957 edition of Pauling's famous textbook, illustrates a simple classroom demonstration of the electrocatalysis of the Zn/H_3O^+ redox reaction using platinum or copper metal, whereas figure 5 graphically summarizes the electrocatalytic effects of various metals on the rate of magnesium corrosion in a 3% salt solution (9-10). Note that iron is so effective, that it drives the corrosion rate vertically off the graph.

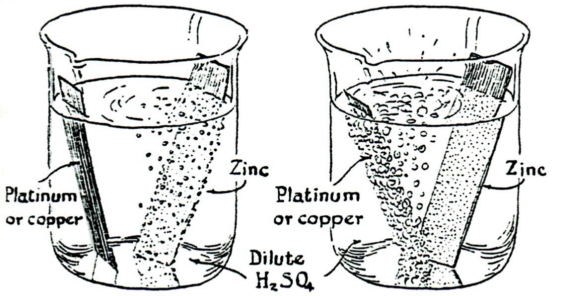

Figure 4. Electrocataysis of the Zn/H_3O^+ redox reaction using platinum or copper metal. (Left) The zinc strip reacts with the H3O+ ion to produce dihydrogen gas, which coats the metal and slows the rate of reaction. (Right) On touching the platinum strip to the zinc strip, the reduction of the H_3O^+ ions is transferred to the platinum surface, which has a lower overpotential, while oxidation of the zinc continues unimpeded at the zinc surface.

There is a vast literature dealing with the question of the electrochemical reduction of hydrogen at metal surfaces. Attempts have been made to correlate the ability of a given metal to lower the overpotential for dihydrogen discharge with the energy of hydrogen adsorption on its surface. A plot of the energy of hydrogen adsorption versus the rate of dihydrogen evolution (measured as the log of the exchange current i_0) is shown in figure 6 for various metals. As can be seen, they fall into two groups, depending on whether the adsorption or desorption step for hydrogen reduction is rate limiting:

Product	%OH replaced	Structure
(Brucite) $Mg(OH)_2$	0%	$^{2}_{\infty}[Mg(OH)_{6/3}]$
$Mg_3(OH)_5Cl \cdot xH_2O$	17%	Unknown
$Mg_2(OH)_3Cl \cdot 4H_2O$	25%	$^{1}_{\infty}[Mg_2(OH)_3(H_2O)_3]Cl \cdot H_2O$
$Mg(OH)Cl$	50%	$^{2}_{\infty}[Mg(OH_{.5},Cl_{.5})_{6/3}]$

Table 2. The composition and structure of magnesium dihydroxide or brucite and of various magnesium chorohydroxides formed by substitution of the hydroxide ion by chloride ion. For background on the crystal coordination formulas used in the last column, see reference 22.

Adsorption:

$$e^- + M(s) + H_3O(aq)^+ \rightarrow MH(s) + H_2O(l) \qquad [11]$$

Desorption:

$$e^- + MH(s) + H_3O(aq)^+ \rightarrow M(s) + H_2(g) + H_2O(l) \qquad [12]$$

For most metals (Pt-Al), including iron, the desorption

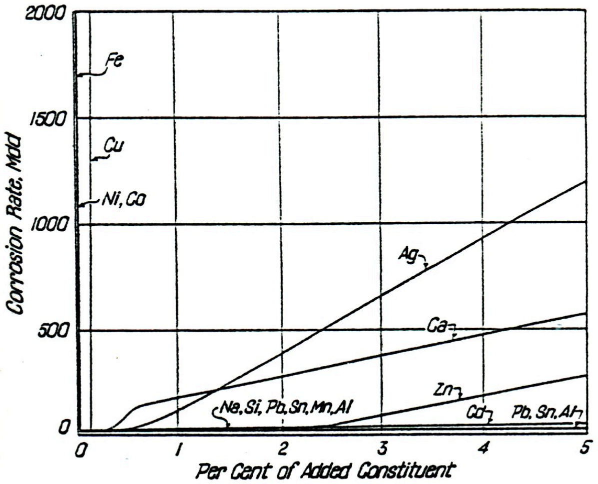

Figure 5. The electrocatalytic effect of various metals on the rate (measured in milligrams per decimeter per day) of magnesium corrosion in a 3% salt solution (10).

step in equation 12 is rate limiting, and the rate of discharge decreases with increasing adsorption energy. For Pb, Hg, Cd, and Tl the adsorption step in equation 11 appears to be rate limiting, and the rate of discharge increases with increasing adsorption energy (11).

If one touches an iron wire to a strip of clean magnesium metal in a neutral salt solution, there is an immediate enhancement of the rate of dihydrogen evolution, though it is still nowhere near what is observed for the heater element. Increasing surface area by using magnesium turnings and iron filings, magnesium powder and iron powder, etc. leads to a further enhancement of the rate, but again does not come close to reproducing the violence of the heater element reaction. Obviously increasing the surface area of the solid reactants is the final key to increasing the rate of reaction 1 to the point where the rate of heat evolution results in a workable heater element.

As noted earlier, examination of the heater element under a low-power binocular microscope shows small chunks of only one kind of metal. Nothing that can identified as separate pieces of iron is visible. This fact, coupled with the observation that the silvery metal has a slight gold- or bronze-like cast to it, suggested the possibility that the iron had been plated unto the magnesium by momentarily dipping the magnesium in a solution of an iron (II) salt, a reaction having a favorable net *E*° value of 1.93 V:

$$Mg(s) + Fe(aq)^{2+} \rightarrow Fe(s) + Mg(aq)^{2+} \qquad [13]$$

This idea was inspired by the classic work of Gladstone and Tribe, who in 1878 had shown that the reducing properties of zinc were greatly enhanced by first dipping it in a copper sulfate solution into order to plate small microregions of copper onto its surface (12-13). Here again the net *E*° value of 1.10V is quite favorable:

$$Zn(s) + Cu(aq)^{2+} \rightarrow Cu(s) + Zn(aq)^{2+} \qquad [14]$$

Gladestone and Tribe explicitly recognized that the resulting "copper-zinc couple," as they called it, was a micro-example of galvanically enhanced dihydrogen generation paralleling the macro-example shown in figure 4, and, indeed, their reduction couple still finds use as a reducing agent in organic chemistry (14). Though the resulting iron-plated magnesium certainly displays enhanced dihydrogen evolution in salt water, the effect is again insufficient to account for the rates observed for the heater element (15).

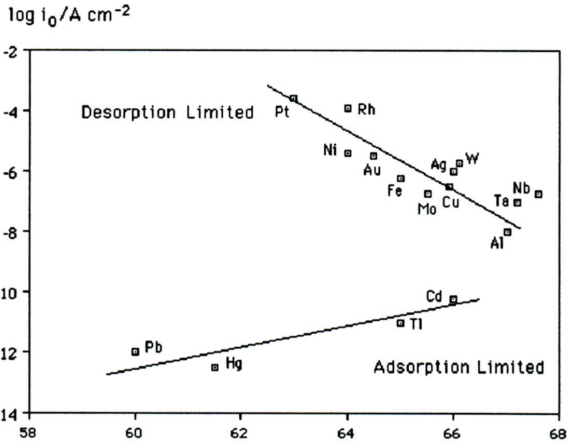

Figure 6. The correlation between the energy of hydrogen surface adsorption and the rate of hydrogen discharge (measured as log i_0) for various metal electrodes (11).

The Patents

It was now time to check our results against the patent literature. The number listed on the "tea bag" containing the heater element was for a 1985 patent entitled "Flexible Electrochemical Heater" (16). This describes a method for making portable heating elements by pressureless sintering of mixtures of a "supercorroding" powdered alloy of magnesium and iron with UHMW polyethylene powders in a mold for 20 minutes at 168°C. The resulting heating elements can be made in any shape or size. The polyethylene matrix determines not only the shape and size of the heater element, it also serves to regulate both the density of alloy dispersal and the rate of salt water uptake, as well as acting as a containment system for the solid waste products.

The sintered polyethylene obviously accounts for the partly-fused translucent spheres that we observed under the microscope. As for the super-corroding alloy, this was described as containing 5 atom % iron and as reacting with the salt water to generate heat and dihydrogen gas. It was also suggested that the thermal output of the heater element could be increased by dispersing chemicals, such as a MnO_2/Pd/C mixture, in the matrix in order to catalyze the air oxidation of the dihydrogen gas generated by the alloy-salt water reaction.

Mention of a 5 atom % iron alloy of magnesium was initially puzzling as examination of the phase diagram for the magnesium-iron system revealed that the two metals are virtually insoluble in one another (17-18). A possible eutectic may exist between 0.0065 and 0.013 atom % iron, but even at 1200°C iron is soluble only to the extent of 0.37 atom %. This puzzlement turned out to be based on an incorrect definition of an alloy. Most chemists I have polled, seem, like myself, to be under the false impression that an alloy must be a solid solution. As it turns out, it may in fact be a heterogeneous micromixture which only appears homogeneous to the unaided eye. As defined by a well-known chemical dictionary (19):

Alloys are to be regarded as mixtures of metals rather than as compounds, although often metallic compounds are present in the mixture and may crystallize out; some alloys are solid solutions of one metal in another, others are mixtures of mutually insoluble metals.

The first patent led, in turn, to a 1981 patent entitled "Supercorroding Galvanic Cell Alloys for Generation of Heat and Gas" (20). This revealed that the magnesium-iron alloy is indeed a micromixture made by blending the proper ratio of the metallic powders in a high-energy steel ball mill by "repeated flattening, fracturing and welding of the metal constituents." According to the patent, during the milling process:

The energy of the impact of the colliding steel balls, with particles trapped between them, creates atomically clean particle surfaces. When these clean surfaces come in contact during collisions, they cold-weld together. An inert atmosphere in the mill prevents reoxidation on the clean surfaces. This also avoids oxide coatings on the particle surfaces which reduce cell reaction.

The resulting alloy particles are between 80 and 100 mesh in size and consist of isolated iron particles of the order of 30 microns embedded in a surrounding magnesium matrix – an elegant solution to the problem of maximizing the area of surface contact between the two metals.

Summary

In summary, the water oxidation of magnesium metal is the thermodynamic source of the heat for the *HeaterMeal* stove, with magnesium dihydroxide and dihydrogen gas as the immediate products. The sodium chloride or salt serves to kinetically enhance the rate of oxidation by preventing the formation of a coherent protective film of magnesium dihydroxide on the magnesium metal. The iron serves to kinetically enhance the rate of reaction by providing an alternative surface of low overpotential for the reduction and discharge of the dihydrogen gas.

Further Possibilities

A. Students investigating the chemistry of the *HeaterMeal* stove may further wish to determine the average volume of dihydrogen gas produced per heater element, use Graham's law of diffusion to approximate its rate of dispersal compared to an equal volume of natural gas, and discuss the bearing of this result on the use of the stove in open versus closed environments.

B. In June of 1997 the local television news in Cincinnati reported that the fire department had been called out in response to a carbon monoxide detector which had been set off by someone using a *HeaterMeal* stove. The broadcast showed a fireman pointing his electronic carbon monoxide detector at an operating *HeaterMeal* packet and declaring that it was "giving off incredible amounts of carbon monoxide," which was, of course, not true. Students may wish to look into the mechanism behind such detectors and why they are unable to discriminate between dihydrogen gas and carbon monoxide gas. It is also interesting to note that this is not the first time that these two gases have been confused. In the mid-18th century they were referred to as light and heavy inflammable air, respectively. It was Lavoisier who first showed that they were not simply varieties of one substance, but rather that heavy inflammable air was really an oxide of carbon (21).

Acknowledgments

My thanks to Dr. Peter Ramberg, Department of Chemistry, Ohio University, for bringing this product to my attention, and to Rudy Thomas, Department of Chemistry, University of Cincinnati, for his assistance in performing some of the experiments.

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Publication History

Published in *J. Chem. Educ,* **2000**, *77,* 713-717. The section on "Further Possiblities" was deleted from the published version.

VI

Reaction Feasibility and the Planck Function

I welcome the recent article by Rosenberg and Klotz (1) summarizing the advantages of using the Planck function (Y) as an alternative to the Gibbs free-energy function (G) in discussing chemical equilibrium. I have used a slight modification of the Planck function in my classes for the last 20 years. I call this modification the "reaction feasibility" function (F). It is defined as:

$$F = -(\partial G/\partial \xi)/RT = -\Delta H^\circ/RT + \Delta S^\circ/R - \ln Q = F^\circ - \ln Q \qquad [1]$$

where ξ is the well-known extent of reaction parameter of De Donder (2) and Q is the activity quotient for the reaction in question at any given value of ξ:

$$Q = \Sigma_p a^v / \Sigma_r a^v \qquad [2]$$

At equilibrium $F = 0$. Consequently:

$$F^\circ = \ln Q_{eq} \quad or \quad Q_{eq} = e^{F^\circ} \qquad [3]$$

where the equilibrium value of the activity quotient (Q_{eq}) is the same as the equilibrium constant K.

Obviously the reaction feasibility is related to the Planck function by the equation:

$$F = -(\partial Y/\partial \xi)/R \qquad [4]$$

In addition to the merits possessed by the Planck function, the reaction feasibility function has the further advantage of being a dimensionless number whose numerical value is independent of the units used to measure the component standard enthalpy and entropy changes (assuming, of course, that one divides by the appropriate value of the gas constant R).

The name "feasibility" was chosen in order to avoid the kinetic overtones inherent in the use of such terms as "spontaneous" and "spontaneity," which often suggest to the student the incorrect idea of an instantaneous, if not explosive, change. In the applying the function, we are merely assessing whether the reaction in question is possible or feasible. If the answer is no ($F < 0$), we need inquire no further. If the answer is yes ($F > 0$), we then need to ask the further question of how fast the reaction will occur, which is, of course, a problem for chemical kinetics rather than thermodynamics. Describing a feasible, but otherwise kinetically inert, reaction as "spontaneous" obviously does violence to the everyday meaning commonly attached to this word.

One disadvantage of both the Planck function and the reaction feasibility function becomes apparent when one attempts to interface them with our current models of chemical kinetics. While it seems natural to think of a reaction as having to surmount an activation barrier, characterized by a free energy of activation, the alternative picture of the reaction as having to climb out of a "feasibility hole" is much less appealing and far less intuitive.

In passing, it should by noted that the reaction feasibility is also related to the De Donder affinity function (A) by the relation (2, 3):

$$F = A/RT \qquad [5]$$

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Publication History

Published in *J. Chem. Educ,* **2000**, *77,* 1411.

VII

Generalizing the Phase Rule

I would like to make four points supplementing the recent article by Alper on the Gibbs phase rule (1).

First: All of the examples discussed by Alper may be elegantly incorporated within the phase rule by replacing the conventional form of the rule:

$$f = c + 2 - p \qquad [1]$$

with an expanded form:

$$f = (s + 2) - (p + e + r) \qquad [2]$$

in which s stands for the number of chemical species (or constituents, in Alper's terminology), e is the number of independent equilibrated chemical reactions involving these species, and r is the number of additional independent stoichiometric restraints interrelating their concentrations or activities beyond the requirement that the mole fractions in each phase must sum to 1. Most of the examples discussed by Alper involve the temperature and pressure dependency of p, e, and r in the above expression.

Equation 2 has obviously been obtained by replacing the number of components (c) in the conventional form of the phase rule with the expression:

$$c = s - e - r \qquad [3]$$

This expansion was apparently first suggested by Wind in 1899 (2). Since then it has been repeatedly proposed in the literature with minor variations, starting with Richards in 1916 (3), and again with De Donder in 1920 (4), Jouguet in 1921 (5), Van Rysselberghe in 1932 (6), Bowden in 1938 (7), and Franzen in 1986 (8). It has appeared in several books on the phase rule and on thermodynamics in general (9-14), the most thorough discussion being that given by de Heer in his 1986 monograph (15). Since then, an increasing number of physical chemistry textbooks have also contained discussions of the expanded rule, including several of those referenced by Alper.

Second: Setting the value of the number of thermodynamic intensities or field variables (v) at a value of 2 (i.e., for temperature and pressure alone), as is done in the conventional formulation, actually represents a special case of the rule. A truly general statement of the phase rule requires that this parameter be left as a variable whose value is to be assigned according to the nature of the system being described (3, 16, 21, 22). Thus the fully generalized form of equation 2 should be written as:

$$f = (s + v) - (p + e + r) \qquad [4]$$

This is not only necessitated by relatively esoteric systems in which the state of the system is sensitive to magnetic or electric fields, for example, but also occurs in more common situations. Thus introductory textbooks on ceramics (17), metallurgy (18), materials science (19) and geochemistry (20) all make use of the so-called reduced, condensed, or "isobaric" phase rule:

$$f = (s + 1) - (p + e + r) \qquad [5]$$

in which the number of field variables has been reduced from 2 to 1 (temperature only) due to the absence of volatile species in most of the phase diagrams of interest in these fields. Expansion of the number of variables from 2 to 3 occurs in the fields of colloid chemistry and surface chemistry due to the increased importance of surface tension as a variable (21-23):

$$f = (s + 3) - (p + e + r) \qquad [6]$$

and Bikerman has discussed the case of the variation of the vapor pressure of small bubbles of liquids with size from the same standpoint, using the curvature of the bubble as the third variable (24).

Third: There has long been a debate as to whether or not the phase rule needs to be even further modified when dealing with systems involving optical enantiomers (25). Opinion on this issue remains divided. Scott (26) and Wheeler (27) have both proposed modifications, whereas others seem to feel that they are unnecessary (28).

Fourth: There is a pedagogical issue involved in the continued preoccupation with having students do problems in which they are expected assign the number of phases and components ahead of time in order to calculate or predict the degrees of freedom for the system. As pointed out by Ricci almost 50 years ago (28), and more recently by Bent and Bent (29), this is really a case of putting the cart before the horse, since in actual applications of the phase rule one experimentally determines *f* and *p* and then proceeds to calculate *c*, rather than the other way around. Ricci was not particularly impressed with the expanded phase rule, arguing that it merely transferred the problem of determining the number of independent compositional variables from the component term (*c*) to the equilibrated reaction term (*e*). Richards, on the other hand, argued that this was precisely its virtue (3), since it is really the value of *e* rather than *c* that one is attempting to calculate from experiment or, in the words of Bent and Bent, the number of "active tendencies" versus the number of "passive resistances" present in the system.

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Publication History

Published in *J. Chem. Educ*, **2001,** *78*, 1369-1370.

VIII

Entropy and Constraint of Motion

I would like to make several observations supplementing and supporting the recent article by Frank Lambert on entropy as energy dissipation, since this is an approach which I have also used for many years when teaching a qualitative version of the entropy concept to students of general and introductory inorganic chemistry (1).

I begin with the everyday interconversion of potential and kinetic energy as exemplified by either a bouncing ball or an oscillating pendulum:

Potential Energy ⇔ *Kinetic Energy* [1]

According to classical mechanics, this interconversion is totally reversible and the ball should go on bouncing and the pendulum oscillating forever. The reason this does not happen, of course, is because once the potential energy is converted into kinetic energy, the kinetic energy is increasingly dispersed and it is the lower probability of this dispersed kinetic energy reconcentrating into the coordinated motion of the ball or pendulum as a whole that ultimately introduces a directionality into the process:

Potential Energy → *Kinetic Energy* →
Dispersed Kinetic Energy [2]

The point here being that it is not just energy in general that is dissipated, but rather kinetic energy or energy of motion (whether translational, rotational, or vibrational).

This dissipation, dispersion, dilution, or spreading of the kinetic energy need not, however, necessarily correspond to a spreading in space or to a division among a greater number of moving particles, though these are possible mechanisms. A more general concept of dilution is required based on the fact that all kinetic energy is quantized, even in the case of macroscopic bodies in which the quantum spacings are small enough to approximate a continuum. It is the number of available quantum levels, or storage modes, to use Leff's terminology (2), used to store a given amount kinetic energy that determines its degree of dilution or dissipation, and this, in turn, depends on the masses of the moving particles (whether colloids, micelles, molecules, atoms or even, on occasion, electrons and nucelons) and on the number of constraints on their motion. These constraints may correspond to:

1. Constraints on the number of independently moving particles; i.e. on whether the particles must move as an aggregate or can move separately.

2. Constraints on the direction of motion.

3. Constraints on the volume in which the motion is executed.

The relevance of the above factors in determining the spacing and degeneracy of the quantum levels is most easily demonstrated using the simple "particle in a box" model found in most introductory treatments of quantum mechanics. The fewer the number of constraints on a system's motion, the smaller the energy spacing between quantum levels, and the greater the dilution or dissipation of the kinetic energy. In short, the fewer the constraints on how and where the component particles can move, the greater the entropy. The extent to which the mixing or disorder views of entropy, criticized by Lambert in earlier articles (3, 4), are or are not misleading depends on the extent to which they do or do not parallel changes in these constraints (5). This simple correlation between entropy and constraint of motion also allows one to rationalize the qualitative rules for predicting the net sign of die entropy change in simple chemical reactions given by Sanderson for use in introductory chemistry courses (6).

The above approach is based on a fusion of the energy dissipation approach to the second law first pioneered by Lord Kelvin in 1852 (7) and widely used in late 19th-century American and British textbooks (8), with the insights since provided by quantum mechanics and elementary statistical mechanics, as so aptly summarized in the introductory texts by Nash and Bent (9, 10). Indeed, it is interesting to note that the first of these three ingredients formed the basis of the first English-language monograph to deal specifically with chemical thermodynamics, as distinct from the more limited field of thermochemistry. The book in question was published in 1885 by George Downing Liveing (1827-1924) of Cambridge University and bore the title, *Chemical Equilibrium the Result of the*

Dissipation of Energy (10).

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Publication History

Originally published in *J. Chem. Educ,* **2004,** *81,* 639-640.

Update

Since writing this note, I have come across the following relevant quote from the monograph on entropy by K. G. Denbigh and J. S. Denbigh (*Entropy in Relation to Incomplete Knowledge*, Cambridge University Press: Cambridge, 1985, p. 44):

If a verbal interpretation of entropy is required, a far more reliable one is to be found in the notion of "spread," as used by Guggenheim. An increase in entropy may be said to correspond to a "spreading" of the system over a large number (W) of occupied quantum states. Alternatively one might say that entropy is a measure of the extent to which the system in question is unconstrained: the less constrained it is, the greater is the number of accessible quantum states for given values of those constraints.

IX

Ask the Historian

The Universal Gas Constant

Question

Why is the universal gas constant in $PV = nRT$ represented by the letter R?

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Answer

This is best answered by tracing the origins of the ideal gas law itself. One of the first persons to combine Boyle's law (1662) relating volume and pressure and Gay-Lussac's law (1802) relating volume and temperature in a single equation appears to have been the French engineer, Benoit-Paul Emile Clapeyron (1799-1864). In his famous memoir of 1834 on the Carnot cycle, he wrote the combined equation as (1):

$$pv = R(267 + t) \qquad [1]$$

where t is the temperature in degrees centigrade. In 1850, the German physicist, Rudolf Clausius (1822-1888), using the experimental data of the French chemist, Henri Victor Regnault (figure 1), reevaluated the constant inside the parentheses and rewrote the equation as (2):

$$pv = R(273 + t) \qquad [2]$$

and in 1864 he further simplified it by substituting the absolute temperature T in place of the $(273 + t)$ term (3):

$$pv = RT \qquad [3]$$

Being French, Clapeyron had attributed the volume-pressure law to the French scientist, Edmé Mariotte (1620-1684), rather than to Robert Boyle, and Clausius did not question this choice. Indeed, he explicitly proposed that the combined equation be called the Mariotte-Gay-Lussac law or the M-G law for short.

Both Clapeyron and Clausius had used the volume per unit mass of gas ($v = V/M$) rather than the volume per mole of gas ($u = V/N$) in their equations. This meant that their gas constant R was not universal for all gases but was rather a specific constant whose value varied from one gas to another and was, as Clausius noted, roughly inversely proportional to the density (d) of the gas in question (4). The first person to convert the specific constant of Clapeyron and Clausius into a universal gas constant appears to have been Clausius' student, the German chemist, August F. Horstmann (1842-1929), who rewrote the gas law in 1873 as (5):

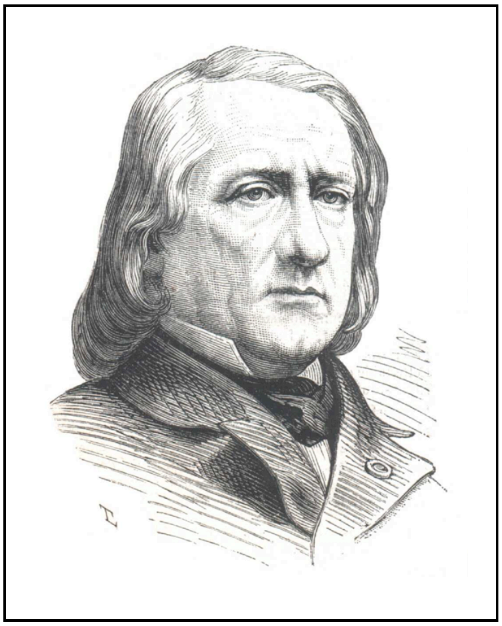

Figure 1. Henri Victor Regnault (1810-1878).

$$up = RT \qquad [6]$$

where p and T have their earlier meaning but u is "the volume of a molecular weight [i.e. mole] of the gas" and "R is the constant for the G-M law with regard to the molecular [i.e. molar] volume."

So why did Clapeyron choose the letter R for the constant in his gas law? The fact is that he doesn't explicitly tell us why and we are left with two speculative answers: (a) it was arbitrary or (b) it stood for *ratio* or one of its French equivalents: *raison* or *rapport*, since Clapeyron noted that the value of R for each gas was obtained by evaluating the constancy of the ratio $pv/(267 + t)$ over a range of pressures and temperatures, a point also emphasized by Clausius using the revised ratio $pv/(273 + t)$.

Given IUPAC's penchant for naming constants after famous scientists, this suggests that it might not be inappropriate to name R in honor of Regnault whose accurate experimental data was used by Clausius not only to correct the conversion factor between the centigrade and absolute temperature scales but also to evaluate the value of R using the above ratio (6). It is also interesting to note that Clausius was aware that Regnault's data clearly showed that (2):

> *... the more distant, as regards pressure and temperature, a gas is from its point of condensation the more correct will be the law [i.e. the more constant R]. Whilst its accuracy, therefore, for permanent gases in their common state is so great, that in most investigations it may be regarded as perfect, for every gas a limit may be imagined, up to which the law is also perfectly true; and in the following pages, where permanent gases are treated as such, we shall assume the existence of this ideal condition.*

In 1864 Clausius further introduced the term "ideal gas" to describe gas behavior under these limiting conditions (7).

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Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu

Publication History

First published in *J. Chem. Educ.*, **2003**, *80*, 731-732.

Update

In creating this new reprint I have deleted the paragraph in the original column which attempted to use dimensional analysis to elucidate the relationship between the universal gas constant and the specific gas constant, since it was both imprecise and unnecessarily complex.

I have also since discovered that Clausius used the term "ideal gas" as early as 1857 in his famous paper on "The Nature of the Motion Which We Call Heat," where he attributes the expression to the earlier work of Regnault. See:

R. Clausius, "Über die Art der Bewegung welche wir Wärme nennen," *Ann. Physik*., **1857**, *100,* 353-380. An English translation appears in *Phil. Mag*., **1857**, *14*, 108-127 and is also reprinted in S. G. Brush, Ed., *Kinetic Theory*, Vol. 1, Pergamon: Oxford, pp. 111-134.

X

Refining Campbell's Rule

In a recent article (1), Norman Craig has proposed the rule-of-thumb that the approximate value of the entropy of reaction ($\Delta_r S°$) is related to the net moles (Δn_g) of gas consumed or generated in the reaction by the relation:

$$\Delta_r S°/J\ (K\ mol\ rxn)^{-1} \approx 140 \Delta n_g/mol \qquad [1]$$

The numerical constant in this approximation was obtained by averaging the values of $\Delta_r S°/\Delta n_g$ calculated for ten of the eleven example reactions (excluding the one for which $\Delta n_g = 0$) given in Table 1 of Craig's paper, and then combining this with the average of the values of $\Delta_r S°/\Delta n_g$ for 18 of the 23 reactions given in Tables 1 and 2 of an earlier paper by Campbell (again excluding the cases where $\Delta n_g = 0$) (2). The average for Craig's data was 148 J (K mol rxn)$^{-1}$(mol)$^{-1}$, whereas that for Campbell's data was 136 J (K mol rxn)$^{-1}$(mol)$^{-1}$, with a combined average of 140 J (K mol rxn)$^{-1}$(mol)$^{-1}$, as given in the approximation in equation 1.

If, instead of following the above procedure, one plots the values of $\Delta_r S°$ versus Δn_g (including those for which $\Delta n_g = 0$) for each data set, and uses a least squares analysis to obtain the best straight line fit, one obtains the results (rounded to the nearest tenth) summarized in the following table, where those for Craig's eleven examples are given in the first row; those for Campbell's 23 examples (3) are given in the second row; and those for the combined Craig-Campbell data sets are given in the third row and in the graph in figure 1.

Correlation of $\Delta_r S°$ and Δn_g

Data Set	*N*	*Correlation Equation*	*R*	*$\Delta n_g = 1$*
Craig	11	$\Delta_r S = 19.2 + 130.6\ \Delta n_g$	0.99	149.8
Campbell	23	$\Delta_r S° = -9.6 + 130.5\ \Delta n_g$	0.96	120.9
Combined	34	$\Delta_r S = -0.8 + 128.8\ \Delta n_g$	0.98	128

If one evaluates the correlation equation for Craig's data (row 1) at $\Delta n_g = 1$, one obtains a value of 149.8 J (K mol rxn)$^{-1}$, which is essentially identical to

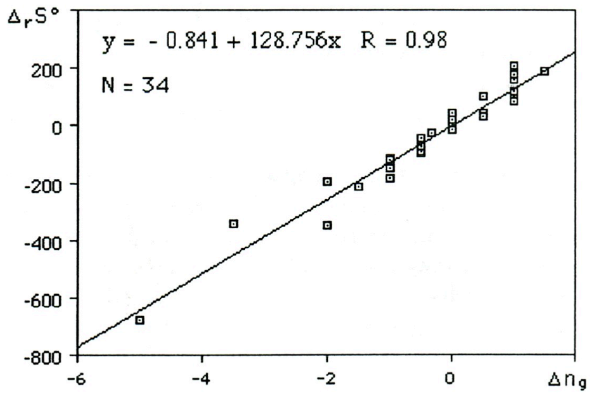

Figure 1. Plot of $\Delta_r S°$ versus Δn_g.

Craig's reported average of 148 J (K mol rxn)$^{-1}$(mol)$^{-1}$. If, however, one does the same for Campbell's data set (row 2), one obtains a value of 120.9 J (K mol rxn)$^{-1}$ at $\Delta n_g = 1$, which is substantially lower than the value of 136 J (K mol rxn)$^{-1}$(mol)$^{-1}$ reported by Craig. This discrepancy is apparently due to the fact that we have included the $\Delta n_g = 0$ cases eliminated by Craig. Because of this discrepancy, a similar divergence is obtained for the case of the combined data sets (row 3), where $\Delta n_g = 1$ now gives an average value of 128 J (K mol rxn)$^{-1}$ rather than the value of 140 J (K mol rxn)$^{-1}$ (mol)$^{-1}$ reported by Craig. Since the intercept of the correlation equation for the combined case is so small (-0.8 J (K mol rxn)$^{-1}$), the full equation may be approximated by the simpler relation:

$$\Delta_r S°/J\ (K\ mol\ rxn)^{-1} \approx 128 \Delta n_g/mol \qquad [2]$$

which gives a more statistically significant result than does the approximation in equation 1.

The question naturally arises as to why the average for Campbell's data set is so much lower than that for Craig's data set. In this regard, it is of interest to note that only 6 out of 23, or about 26%, of Campbell's examples involve solids or liquids as well as gases, whereas 9 out 11, or about 82% of Craig's examples do. In other words, most of Campbell's examples involve only the compensation of Δn_g terms, whereas many of Craig's examples involve the additional compensation of Δn_s and Δn_l, terms as well.

Likewise, 7 out of 23, or about 30% of Campbell's examples involve either $H_2(g)$ or $H(g)$, whereas only 2 out of 11, or about 18% of Craig's examples do. The relevance of this latter observation has to do with the well-known logarithmic dependence of the entropy of translation ($\Delta_{tr}S°$) of gases on their molecular weights (*MW*), as given by the Sackur-Tetrode equation (4):

$$\Delta_{tr}S°/J\ (K\ mol)^{-1} \approx 109 + 28.7 \log MW \text{ (at 298 K)} \quad [3]$$

As Craig emphasizes, Campbell's rule is based on the fact that $\Delta_rS°$ is dominated by the $\Delta_{tr}S°$ values of the gaseous species and this logarithmic dependency means, in turn, that $\Delta_{tr}S°$ varies more rapidly for gases of low molecular weight, such as H_2 and H, than it does for gases of higher molecular weight, as may be seen from figure 4.4 of reference 4 (5).

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3. This correlation incorporates the corrected entropy values given by Craig in footnote 2 of his paper.
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Publication History

Published in *J. Chem. Educ,* **2004,** *81,* 1570. The graph was deleted from the published version.

XI

Introduction to the English Translation of "The Theory of Dissociation"

By August Horstmann

A Forgotten Classic of Chemical Thermodynamics

IT was originally intended that the *Bulletin for the History of Chemistry* should function as a vehicle not only for the publication of scholarly papers dealing with the history of chemistry and alchemy, but also for the publication of translations of key historical documents – a function which has so far been exercised in only a few cases (1, 2). Though the problem of the gradual disappearance of history of chemistry courses and its potential impact on history of chemistry as an academic discipline has been commented on several times in the past (3, 4), the increasing inability of modern-day American chemistry majors to directly access primary documents in the history of chemistry, due either to a lack of modern language skills or the absence of suitable English translations, has so far escaped notice. For most of the 20th century, doctoral programs in chemistry required at least a minimal reading proficiency in either German, French, or Russian. However, beginning in the early 1990s, this requirement was dropped from most of these programs and, as far as most current chemistry majors are concerned, the vast majority of the 18th-, 19th-, and early 20th-century European chemical literature might as well be written in ancient Greek or Latin when it comes to their ability to read it in the original.

Ironically there was a conscious effort to provide suitable English translations of many classic chemical papers during the period when most American chemists still had some reading knowledge of either French or German, though at present, when the need is far more pressing, the majority of publishers are no longer interested in such projects. Thus, beginning in the late 19th century, both Harper Brothers of New York and the British-based Alembic Club, under the leadership of Leonard Dobbin, issued English translations and/or reprints of classic scientific papers of chemical interest (5, 6), and a similar program was initiated by Dover Books in the 1960s (7). In addition, several collections containing translations of selected passages from key papers were also published – most notably the volumes by Leicester (8, 9), Farber (10), and Crosland (11) – as well as several collections of key papers in such specialized fields as colloid chemistry (12) and chemical kinetics (13).

Nevertheless there are still many notable exceptions. Thus it is only recently that an English-language collection of Mendeleev's key papers on the periodic law has been published – nearly 136 years after its initial proposal (14). The classic 1904 and 1916 papers by Abegg (15) and Kossel (16) on the electronic theory of chemical bonding still await translation, as does the famous 1867 paper by Pfaundler on the application of the kinetic theory to chemical reactions (17) and, until now, the foundational 1873 paper by Horstmann on the first application of the second law of thermodynamics to the theory of chemical equilibrium (18).

These latter two examples also illustrate a curious asymmetry in the translation record. More than four decades ago Stephen G. Brush published a three-volume collection of many of the basic papers dealing with the origins of the kinetic theory of gases (19) and several collections of classic papers relating to the establishment of both the first (20) and second laws (21-23) of thermodynamics have also been published, some of which date back to the 19th century. What is missing, however, in all of these collections are translations of the key papers in which these fundamental models and principles were first applied explicitly to chemical processes.

The foundational status of Horstmann's publication of 1873 for the discipline of chemical thermodynamics is justified in the paper which appears elsewhere in this issue and which also serves as a commentary on the following translation (24). Consequently, all that is required here are a few comments on the basic mechanics of the translation process itself. In 1987 I commissioned Heike Ulmer, who was at that time a German exchange student in the chemistry department at the University of Cincinnati, to produce a preliminary translation of Horstmann's paper. This I have since extensively revised. In so doing, I have exercised my preference for a free, rather than a literal, translation in order to avoid what are, from the standpoint of the English reader, awkward sentence structures and word choices. In keeping with this, I have sometimes inverted the order of the various sentence clauses and have modernized some of the chemical nomenclature when I felt this did not introduce a serious historical anachronism.

Perhaps more controversial is my decision to substitute the term "mole" for Horstmann's more awkward phrase *eines Moleculargewichtes* of substance. Though he actually used the abbreviation "Mol." in several places for this concept, this is not quite the linguistic equivalent of the Latin term *mole*, which was first introduced into chemistry by Ostwald sometime around 1900 (25). Likewise, I have taken the liberty of occasionally rendering the term *Zufalligkeiten* or "random accidents," which Horstmann uses when discussing Pfaundler's kinetic approach, as "fluctuations," as this term is more congenial to the modern reader and is certainly in keeping with Horstmann's intended meaning.

The reduction of Horstmann's original equations to a single-line format has also required the introduction of various parentheses and brackets in order to maintain mathematical consistency. Likewise, in keeping with the style of the *Bulletin*, Horstmann's original references have been removed from the bottom of the various pages and have instead been collected together at the end of the translation.

In reprinting Horstmann's paper in 1903 for Ostwald's series, *Klassiker der exakten Wissenschaften*, van't Hoff noted a number of corrections which have been incorporated without comment in the present translation (26). Otherwise any additional editorial clarifications within the body of the translation have been enclosed in square brackets. Interestingly, a more serious problem, which passed unnoticed by van't Hoff, was Horstmann's inconsistent use of the symbol x. In his first four equations he correctly uses it to represent the number of moles of reactant that have decomposed and thus to represent the degree of reaction or dissociation. However, he then immediately turns around and redefines it in his fifth equation as the moles of reactant which have not yet decomposed, thus negating his third equation for total entropy production as a function of x. Luckily this inconsistency does not seriously mar the remainder of his paper and the modern reader is able to make the necessary adjustments.

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Publication History

First published in *Bull. Hist. Chem.,* **2009***, 34(2),* 73-75.

XII

PRIMARY DOCUMENTS

The Theory of Dissociation

A. Horstmann

Annalen der Chemie und Pharmacie, **1873**, *170*, 192-210.
(Received 11 October 1873)

IT is characteristic of dissociation phenomena that a reaction, in which heat overcomes the force of chemical attraction, occurs for only a portion of a substance, even though all of its parts have been equally exposed to the same influences. In the remaining portion, the forces of chemical attraction, which are the only reason for the reaction to proceed in the opposite direction, maintain the upper hand. Hence, for such reactions there is a limiting state which the molecular system in question approaches irrespective of the initial state and, once it is reached, neither heat nor chemical forces can produce further change so long as the external conditions remain constant.

The degree of dissociation, i.e., the size of the portion encompassed by the reaction in the limiting state, depends upon the following external conditions: the temperature, the pressure and volume, the relative quantities of the reacting substances, etc., and indeed the influence of these various factors varies with the state of aggregation and the nature of the substances in question.

A complete theory of dissociation has to explain in general why an equilibrium state, rather than a complete reaction, is possible and, for each individual case, which circumstances are able to influence the degree of dissociation. I believe I can demonstrate the basis for such a theory in the following.

W. Thomson was the first to take note of one of the consequences of the mechanical theory of heat (1) – namely that the entire world is continuously approaching, via the totality of all natural processes, a limiting state in which further change is impossible. Repose and death will then reign over all and the end of the world will have arrived.

Clausius (2) knew how to give this conclusion a mathematical form by constructing a quantity – *the entropy* – which increases during all natural changes but which cannot be decreased by any known force of nature. The limiting state is, therefore, reached when the entropy of the world is as large as possible. Then the only possible processes that can occur are those for which the entropy remains constant, e.g. stationary movements such as those which we attribute to the smallest particles of a body at constant temperature. The cause of the limiting state for dissociation phenomena is, in my opinion, identical; it occurs when the entropy has become as large as possible for the 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.

If we follow the approach of Clausius, we find, first of all, that the more the energy of the world takes the form of heat and the lower the temperature of that heat, the greater the entropy.

If a quantity of heat Q is produced at absolute temperature T, e.g. from mechanical work or chemical potential, then the entropy is increased by Q/T. The reverse process corresponds to an equal decrease in the entropy and, since the total entropy cannot decrease, this will never happen without an increase of equal or greater magnitude occurring at the same time.

From what has been said, it is apparent that the entropy will also increase if a quantity of heat Q is withdrawn from a body at temperature T and is transferred to another at a lower temperature T', since then $Q/T < Q/T'$ if $T > T'$. From this follows the well-known theorem of Carnot that heat cannot be transformed into work without heat being simultaneously transferred from a hotter to a colder body.

However, this theorem is only valid for the production of mechanical work via so-called cyclic processes (i.e., via processes in which all of the participating materials return to their initial states) since, in the transformation of heat into mechanical work or chemical potential, the heat always causes an accompanying (3) alteration in the arrangement of the particles of a body and thereby overcomes the internal and external forces which oppose the change without this being associated with a transport of heat in the sense of Carnot's theorem.

The decrease in the entropy which corresponds to the transformation of heat into potential energy is accompanied in such cases only by a change in the arrangement of the particles of the respective body, and thus it can be seen that the entropy must also be dependent on this arrangement. It is increased by any change in arrangement in which the heat must do work and by at least as much as is required to compensate for the simultaneous decrease. Clausius (4) has described the arrangement of the particles in a body by introducing a new quantity – *the disgregation* – which is dependent on this arrangement and which specifies how large the entropy is for a given arrangement. For the details of how to determine this magnitude, the reader is referred to his original memoir.

Those changes in arrangement which correspond to an increase in disgregation are easily identified because, like those in which the entropy increases, they can occur by themselves without any other accompanying change. In contrast, a decrease in disgregation is only possible if the entropy is also simultaneously increased, e.g. via the conversion of mechanical work or chemical potential into heat.

The disgregation is increased by melting and vaporization, and by the decomposition of chemical compounds. It decreases in all chemical processes which occur with the release of heat. But bodies can also undergo changes in disgregation without a change in their chemical composition or state of aggregation. This is recognizable by means of specific criteria, e.g. the disgregation of a gas increases when it occupies a larger volume. But at constant volume it will be constant and will remain so even if a second gas is introduced into the same space.

Like the density, the disgregation of a liquid is constant at constant temperature. It can only be changed by mixing it with other liquids. The disgregation of each of the two components depends on their ratio in the mixture.

Lastly, the disgregation of a solid body does not change upon mixing with other solids. At constant temperature it can differ only for allotropic modifications of the same solid. Thus one can conclude that the state of aggregation leads to intrinsic differences which also influence the phenomena of dissociation.

In general, save for a few exceptions (5), the disgregation of a body will increase whenever its atoms or molecules are further separated from one another. Hence one is now able to form a picture of the nature of the equilibrium state for dissociation. That is to say, one sees that the process of dissociation may be divided into a series of processes by means of which the entropy is partially increased or partially decreased. If we consider a particular case, e.g., the decomposition of a gaseous compound into gaseous products at constant volume, then the entropy:

1) decreases during the conversion of heat into chemical work;

2) increases as the separation between the atoms of the decomposed molecules increases;

3) increases because the remainder of the undecomposed molecules must expand to fill the same volume;

4) and 5) decreases because the number of molecules for the two decomposition products increases and they are thus forced closer together.

The entropy will therefore will be greatest when as many molecules as possible are decomposed but the least possible amount of heat is consumed, and when the molecules of each of the three gases are separated from one another as much as possible. This is generally not the case for complete decomposition and hence only a portion is decomposed.

A reaction, whatever its type, can only begin and proceed so long as collective sum of the various entropy changes contributed by the individual processes increases, since, as we know, the total entropy cannot decrease. The reaction must therefore stop at the very instance when the decreases become larger than the increases, i.e. at that point when the total increase becomes zero. Thus one arrives at a mathematical expression for the condition for an equilibrium state for dissociation. This requires that $dS = 0$, where S denotes the entropy of the system. This equation contains the entire theory of dissociation. It says that, in general, the degree of dissociation will depend upon all those circumstance which determine the entropy of the system. In order to deduce yet further conclusions we must give this equation another form.

For this purpose let x denote the relative amount, in units of molecular weight [i. e. moles], of a substance that either decomposes or reacts with other substances. Then x can serve as a measure of the degree of dissociation and all other quantities that change during the reaction, such as the entropy, will become functions of x. Thus one can write the condition for the equilibrium state as follows:

$$dS = (dS/dx)dx = 0$$

or

$$(dS/dx) = 0$$

Furthermore, if Q denotes the quantity of heat required to totally decompose one mole of a compound, then for completion of the reaction the quantity of heat Qx is required which must be considered when calculating the entropy of the system. If T is the absolute temperature and Z is the disgregation of the system, then:

$$S = (Qx)/T + Z$$

and, if equilibrium occurs, then:

$$(dS/dx) = [Q + x(dQ/dT)]/T + dZ/dx = 0$$

This equation will be further elaborated only for individual cases, and especially for that case in which a single substance is decomposed into two others. If one mole of this substance is initially present and, at a given moment, x moles remain undecomposed, and if every molecule splits into r and s molecules, respectively, of the decomposition products, and if m moles of one of the products was present initially, then it follows that the relative amounts of the three reacting substances are x, $r(1 - x) + m$, and $s(1 - x)$, respectively, and that:

$$Z = xZ_1 + [r(1 - x) + m]Z_2 + s(1 - x)Z_3$$

where Z_1 , Z_2 and Z_3 represent the disgregation per mole of each substance.

Assume that both the substance being decomposed and one of the decomposition products are solids but that the second decomposition product is a gas which obeys the law of Gay-Lussac and Mariotte [G-M]. Then Z_1 and Z_2 are independent of x and Z_3 depends only on the volume that is available to the gas, i.e., on the density of the gas. If u is the volume per mole, then, according to Clausius, it follows that:

$$Z_3 = Z_3' + ARln(u/u_0)$$

where Z_3' is the disgregation for the same quantity of gas referred to a normal [i.e. standard] volume u_0, R is the constant per mole for the G-M law, and A is the caloric equivalent for work. Thus, if p is the pressure of the gas, one has

$$up = RT$$

In most cases, including that under consideration, Q consists of two parts, one being the actual heat of decomposition, q, which is transformed into chemical potential, and the other being the amount of heat required to generate the mechanical work used in overcoming the pressure p, which is equal to Apu or to ART. Both parts are independent of x. If one uses these data, then for the case under consideration, our basic equation assumes the following form:

$$q/T - ARln(u/u_0) + C = 0$$

where $C = Z_1 - rZ_2 - sZ_3'$ is the change in the disgregation when the newly formed gas occupies the volume u_0 – a quantity which, like q, no longer depends on x but only on the temperature. Hence the equation contains only one variable, u, that can be altered by the reaction and requires that either u or (since $up = RT$) the pressure of the gas must assume a unique value at equilibrium.

This conclusion is confirmed by the well-known dissociation of calcium carbonate, ammonium chloride, and compounds containing water of crystallization. According to the observations of Debray, Lamy and Isambert, the pressure of a gas over solid compounds, like that in the vaporization of a liquid, depends only on the temperature, but not on the ratio of the compound being decomposed and its solid decomposition product (6), as is required in general by our theory

The maximum pressure at constant temperature can only change if, for some reason, q and C assume different values. This is the case, for example, with the above mentioned compounds if only a portion of the water or ammonia is set free because the remaining portion is perhaps bound in a different manner.

C and q may have different values when decomposing *aragonite* versus *calcite* [i.e., two polymorphs of $CaCO_3$], assuming that this difference persists at the high temperature of the experiment, and hence the pressure of the carbon dioxide may be different. (A difference in the vapor pressures for the two modifications of phosphorus, for which precisely the same considerations apply, was demonstrated by Troost and Hautefeuille).

In accord with the experiments of Joulin (7), yet another factor may disturb the process of dissociation for some metal carbonates. Because of the high temperatures, the oxides undergo a modification which makes it impossible for them to rebind the carbon dioxide upon cooling and consequently, bit by bit, a complete decomposition ensues. In keeping with our definition, these cases no longer qualify as dissociation phenomena.

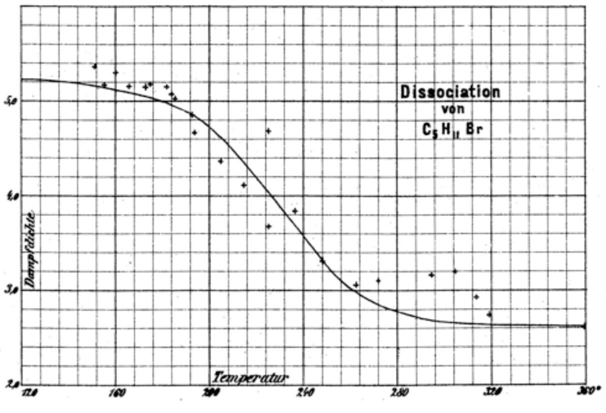
If q and C (which are actually temperature dependent) are treated, to a first approximation, as constant, one obtains the same relation between p and T as was observed earlier for the vaporization of a liquid under similar conditions using a different approach (8).

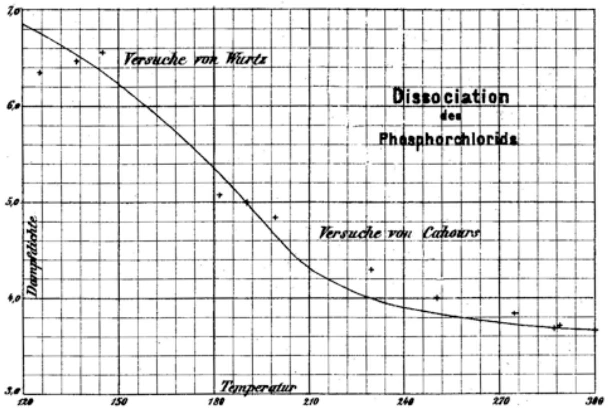
Looking at a second case – the decomposition of a gaseous compound into two gaseous components – Z_1 and Z_2 have the same form as Z_3 had earlier. Like the partial pressures of the three gases, the disgregations in the gas mixture are additive.

In experiments relating to this case, one mole of the initial compound decomposes by forming one mole of each of the decomposition products and during the decomposition the total pressure remains constant. Under these conditions our basic equation assumes the following rather complicated form:

$$q/T + AR\{1 + [2x/(2 - x + m)] - \ln(1/u_0)[x/(1 - x + m)(1-x)]\} + C = 0$$

Here C is the change in disgregation when one mole is decomposed, provided that the gases have the molar volume u_0 before and after the reaction, C is independent of temperature, and the G-M law applies. All other symbols have the same meaning as before. If $m = 0$, then the equation is valid for the well-known experiments of Cahours with PCl_5 and Wurtz with $C_5H_{11}Br$. The degree of dissociation, which is known to depend on the vapor density, must be a function of T alone, as shown by experiment. Again, if one considers, as a first approximation, that C and q are constant, then, by examining the following graphs, it is possible to convince oneself that the form of the function also agrees with experiment (see graphs 1 and 2).





I stress that the absolute pressure at which decomposition takes place does appear in our equation. Hence the curve for phosphorus pentachloride, whose constants are taken from Cahour's experiments at atmospheric pressure, must also be valid for Wurtz's observations at lower pressures (9). For purposes of comparison, the mean values are shown in the graph.

If m is not equal to zero, then a surplus one of the decomposition products has been added and, at a given temperature, the value for x will be larger. The degree of dissociation has been decreased by "mass action," an influence which decreases as the decomposition increases, as shown in the following table:

m	x	d	$t°$
9	0.99	7.13	67
0.5	0.99	7.13	213
0	0.027	3.65	300
0.5	0.027	3.65	322

Since it is impossible to solve the above equation for x, this lists the temperatures at which x (and the vapor density d) have the same value with and without admixture

In the experiments cited above, Wurtz always added more than 0.5 moles of excess PCl_3, the temperature was always lower than 213°, and the average density was 7.2. It must be emphasized that, according to our theory, the addition of chlorine would have the same effect. Each of the gaseous decomposition products can alter the degree of dissociation via "mass action," but solid decomposition products cannot, as we saw in the previous case.

Dissociation phenomena are observed not only during decompositions but also in double displacements. Elsewhere (10) I have pointed out how one can imagine the mechanism by which heat counteracts chemical force in these cases. In my opinion, the effect of heat is always involved whenever an equilibrium is observed whose direction can be arbitrarily changed by external circumstances. In any case, our basic equation is valid for all systems which display an equilibrium since the cause of this equilibrium cannot be anything other than the maximization of entropy.

At this juncture the reactions of steam with iron, of sulfuric acid with sodium chloride in solution, and of potassium carbonate in solution with barium sulfate will be further examined, as all three reactions attain equilibrium before the reaction is complete and have been studied in detail.

Let Z_1, Z_2, Z_3, and Z_4 represent the disgregations for one mole of each reacting substance. In the first example, Z_1 and Z_3 have the form required for gases, whereas Z_2 and Z_4 refer to solids and are hence independent of the degree of dissociation. The external work cancels because for each volume of H_2O an equal volume of H_2 is formed. Hence $Q = q$ and the condition for an equilibrium in a closed space becomes:

$$q/T + ARln(p_1/p_3) + C = 0$$

where C once more stands for the change in the disgregation when the gases are in their normal states [i.e. standard states], and p_1 and p_3 are the partial pressures of the individual gases [in the original Horstmann inconsistently used p_2 instead of p_3]. The ratio of the two is constant at a constant temperature. The amount of one gas cannot be increased without increasing the density of the other in the same ratio. However, the equilibrium state does not depend on the relative amounts of the two solids. If q and C are considered constant, then this equation gives the approximate relationship between p_1/p_3 and T. These conclusions were all tested earlier (10) and were found to correspond to experiment. At that time the equation was deduced using another method, but the present approach provides a stronger justification for its application.

The other two examples cannot be as rigorously subjected to calculation since the relationship between the disgregation of a salt in solution and its concentration is not known. However, it is known, as mentioned earlier, that the disgregation changes with the concentration and this is sufficient to deduce an important conclusion.

When all four substances are in solution, as in the case of the interactions between Na_2SO_4, HNO_3, $NaNO_3$, and H_2SO_4, then the relative amounts of each must influence the degree of dissociation because the disgregation of each changes as the reaction progresses.

The investigations of J. Thomsen (11) confirm this. Each of the four substances can exert a mass action effect and there is an equilibrium only at a certain ratio of the relative amounts of the reacting substances. The relation which must exist at equilibrium may be approximated, according to Thomsen, by the equation:

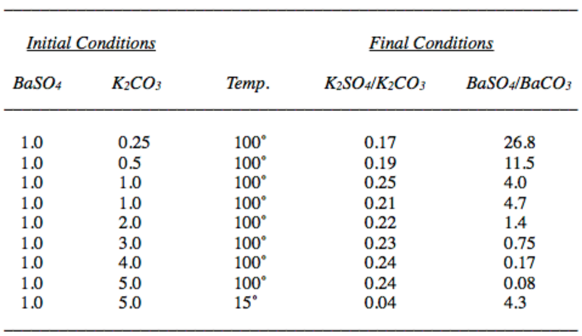
$$apq = p'q'$$

where p, q, p' and q' are the relative amounts and a represents a constant.

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.

In the third example, only two of the reacting substances (K_2SO_4 and K_2CO_3) are in solution, the other two ($BaSO_4$ and $BaCO_3$) being solids, which, according to our theory, should have no influence on the degree of dissociation. This is confirmed by the experiments of Guldberg and Waage (12), who noted themselves that "the action varies only slightly upon increasing the amounts of these solids." I take the following numbers from their work, which show that the relationship between K_2SO_4 and K_2CO_3 in solution is independent of the relative amounts of amounts of the solids:

Interactions Between $BaSO_4$, K_2CO_3, $BaCO_3$ and K_2SO_4 in Solutions Containing 1 Mole of Salt per 500 Moles of Water.



Initial Conditions			Final Conditions	
$BaSO_4$	K_2CO_3	Temp.	K_2SO_4/K_2CO_3	$BaSO_4/BaCO_3$
1.0	0.25	100°	0.17	26.8
1.0	0.5	100°	0.19	11.5
1.0	1.0	100°	0.25	4.0
1.0	1.0	100°	0.21	4.7
1.0	2.0	100°	0.22	1.4
1.0	3.0	100°	0.23	0.75
1.0	4.0	100°	0.24	0.17
1.0	5.0	100°	0.24	0.08
1.0	5.0	15°	0.04	4.3

Compared with the variation in the ratio $BaSO_4/BaCO_3$, the value of the ratio K_2SO_4/K_2CO_3 at the same temperature may be considered constant, which is what would be expected from our theory if the previously mentioned hypothesis concerning the disgregation of dilute salt solutions is correct. According to the table, the ratio K_2SO_4/K_2CO_3 also depends on temperature as is generally required by our theory.

It must be noted here that it is possible that the influence of temperature on the degree of dissociation may become negligible if, for example, Q/T is very small in comparison with the other terms in the basic equation and if the disgregation of the reacting substances varies only slightly with temperature. According the work of Péan de St. Gilles and Berthelot (13) this may be the case for the reaction of organic acids with alcohols.

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. It correctly predicts which circumstances determine the degree of dissociation in general and how in individual cases the degree of dissociation may be altered by changing these circumstance to the extent that we are able to control them. Summarizing the results of the theory, we find that, in addition to the chemical natures of the reacting substance, the most important influences are the temperature (though at times only to a small degree), as well as the volume which is occupied by the reacting substances, and the pressure to which they are subjected, especially when changes in these quantities affect the disgregations of the individual substances in different ways – for example, when some are liquids or solids and some are gaseous. Lastly, there is also the relative amounts of the reacting substances, but only when their disgregation depends on these relative amounts. It is primarily the state of aggregation of the reacting substances which determines whether they can or cannot alter the degree of dissociation by means of "mass action." Such "mass action" effects are always be exerted by gaseous and dissolved reactants but never by solids and liquids that are immiscible, since they may be removed from the reaction without affecting the disgregation of the whole system. It seems to me that these conclusions concerning mass effects are the most important results of the theory and are worthy of further examination.

Until now one has attempted to explain the phenomenon of dissociation (14) on the assumption that the temperature of individual molecules is different from the average temperature which we measure and that, due to random fluctuations, the molecules of a substance capable of undergoing dissociation will, at a given instance, favor reaction in one sense or the other, and thus not all of the molecules will be able to simultaneously react in the same way.

The assumption of random fluctuations, which can cause the molecules to deviate more or less from the average condition, cannot be avoided given a variety of facts and our present views concerning the nature of heat. This is why I believed for a while that I could use it as a basis to develop a theory of dissociation (15). But one soon encounters contradictions with experiment. In particular, one cannot explain in a satisfactory manner the fact, mentioned earlier, that the mass of solids has no influence on the degree of dissociation. I do not wish to further describe the difficulties which discouraged me from pursuing this approach, rather I wish only to discuss how this fact agrees with the present theory. This employs to a certain degree a reversal of the approach used by statistics. The latter assumes a series of identical individual processes and must infer from their resultant in bulk the general laws for the whole, which also prevail for particular cases but which are masked by random fluctuations. In contrast, we know very little of what happens to the individual molecule, but we know the general laws which cannot be infringed upon by any particular process, and we must investigate how much scope remains for the operation of random fluctuations.

We know that there is no reaction between individual molecules which can lead to a lowering of the entropy. This is why, in general, only those changes can occur in which the entropy increases. If this happens, for example, during a decomposition, then in general the decomposition can only proceed if the individual molecules also continuously recombine under randomly favorable conditions.

It is possible to show that, at a certain stage of dissociation, every further change corresponds to a decrease in entropy. In this state as a whole further changes are no longer possible however many fluctuations the individual molecules may undergo in one direction or the other. As mentioned previously, since the assumption of such random fluctuations cannot be avoided, one must imagine, like Pfaundler, that the state of equilibrium for dissociation phenomena is a stationary state in which the forward and reverse reactions are continuously and simultaneously occurring with the same frequency. However, the existence of these fluctuations and the equal number of reactions proceeding in both directions are no longer the reason for the stationary state, as assumed by Pfaundler.

The limits which a molecule can attain via random fluctuations are, in any case, of great importance for the reaction process and are mainly responsible for determining the velocity with which it proceeds. Probably many processes which are slow are only possible because some molecules deviate so far from the average. They would not occur if all of the molecules were in the average state. In contrast, many other reactions cannot occur, even though they would be accompanied by an entropy increase and the atoms would thereby attain a more stable state of equilibrium, because none of the possible molecular fluctuations are able to attain the necessary extremes.

Also with regard to the phenomenon of dissociation, there will be fluctuations that will, bit by bit, make the reaction possible for individual molecules, thereby driving the reaction, faster or slower, towards the stationary limiting state. However, when this limiting state is reached, it is not maintained by randomness, but rather by a general law which governs all individual processes, be they in limited molecular systems or in the world at large. The state remains stationary because the entropy can no longer increase.

References and Notes

1. *Phil. Mag.* [4], **4**, 304.
2. *Abhandlungensammhung II*, 34.
3. See Clausius, *Abhandlungensammlungen I*, 247.
4. *Ibid.*, 248

5. See Clausius, *ibid*., 250.

6. This is contradicted by A. Weinhold, *Pogg. Ann.*, **149**, 217.

7. *Compt. rend.*, **76**, 1588.

8. *Annalen Suppl.*, **8**, 125 ff

9. *Berichte der deutschen chemischen Gesellschaft*, **6**, 450.

10. *Berichte der deutschen chemischen Gesellschaft*, **4**, 636.

11. *Pogg. Annalen*, **238**, 94 ff.

12. *Etudes sur les affinités chimiques*. Programm de l'université Christiana, 1867, 59.

13. *Jahresber. für Chemie*, **1861**, 592.

14. Compare Naumann, *Thermochemie*, 55 ff.

15. *Berichte der deutschen chemischen Gesellschaft*, **1**, 210.

Heidelberg, September 1873

Publication History

First published in *Bull. Hist. Chem.,* ***2009****, 34(2), 76-82*.

XIII

August Horstmann and the Origins of Chemical Thermodynamics

Arguably the single most recognizable equation of modern chemical thermodynamics is that connecting the free energy (ΔG) of a reaction at constant T and P to its standard enthalpy change (ΔH°), standard entropy change (ΔS°), and reaction quotient (Q) (1, 2):

$$\Delta G = \Delta H^\circ - T\Delta S^\circ + RTlnQ \qquad [1]$$

which, in the limiting case of equilibrium ($\Delta G = 0$ and $Q_{eq} = K$), gives us the equally famous equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RTlnK \qquad [2]$$

If asked when these relations were first recognized and by whom, most chemists would probably plead ignorance or perhaps guess, given that ΔG is now known as the Gibbs free-energy function, that they were first derived by the American physicist, Josiah Willard Gibbs.

In fact, as we will see, they were first derived in a different, but equivalent, form in 1873 by an obscure German chemist by name of August Friedrich Horstmann, who has all but disappeared from the modern textbook. But before examining Horstmann's contribution, it is necessary to provide a context for his work by briefly reviewing the early history of both thermochemistry and chemical thermodynamics. This history has been extensively documented by previous historians and is the subject of numerous monographs, several of which which are listed in the accompanying references. It is not our purpose here to repeat this history in detail, but merely to remind the reader of some significant names and dates in order to provide a chronological framework for our more detailed discussion of Horstmann.

The Thermochemical Context

As just suggested, it is necessary to distinguish between the older discipline of thermochemistry, which deals with heat alone, and the discipline of chemical thermodynamics proper, which deals with heat, work, and entropy. Indeed, the history of thermochemistry may, in turn, be further divided into what might be called the "caloric" phase and the "first law" phase (3).

In the caloric phase heat was regarded as a subtle, imponderable (i.e., weightless) fluid which could chemically combine with atoms to form an external atmosphere which rendered them mutually repulsive (4). As such, it worked in opposition to chemical affinity, which caused the atoms to mutually attract. Association reactions were assumed to be inherently exothermic because they decreased the atomic surface area available to bind caloric, thus setting some of it free as sensible heat. In contrast, dissociation reactions were assumed to be inherently endothermic since they increased the atomic surface area available to bind free heat as insensible combined caloric. No necessary relationship was postulated between heat release or absorption and the degree of chemical affinity. If anything, the preoccupation was compositional (i.e., measuring the caloric content or composition of various molecules) rather than dynamic.

The caloric phase began in 1784 with the work of Lavoisier and Laplace on heats of combustion. Its most productive practitioners were the French team of Pierre Favre and Johann Silbermann, who measured many heats of reaction, formation, and transition in the period 1841-1853, and its most important contribution was the law of constant heat summation, first proposed by the Swiss-Russian thermochemist, Germain Hess, in 1840.

As suggested by its name, the first law phase rested on the enunciation, in the period 1842-1847, of the first law of thermodynamics or the law of energy conservation – primarily by James Joule in England and by Robert Mayer and Hermann von Helmholtz in Germany – though there are many other claimants (5). It was first extensively applied to chemical systems a decade later, where it was most closely associated with the work of Julius Thomsen in Denmark in the period 1850-1886 and that of Marcelin Berthelot in France in the period 1864-1897 (6, 7).

Based on the equivalence of heat and work, it postulated, in contrast to the caloric theory, a direct relationship between heat release and the degree of chemical affinity via the so-called "principle of maximum work," which assumed that the greater the heat release, the greater the decrease in the potential energy of the atoms, and the more stable the resulting molecule. Direct application required that a distinction be made between the heat release due to chemical change (ΔH_{chem}) and that due to the physical changes of state (ΔH_{phys}) which necessarily accompanied the reaction:

$$\Delta H_{rx} = \Delta H_{chem} + \Delta H_{phys} \quad [3]$$

a distinction which proved impossible in practice.

The Thermodynamic Context

The passage from thermochemistry to chemical thermodynamics proper is predicated on the enunciation of the second law by William Thomson (Lord Kelvin) in Great Britain (1852) using the concept of energy dissipation and by Rudolph Clausius in Germany (1854, 1865) using the entropy function Q/T (2, 8). However, nearly two decades would pass before the second law was applied to chemical reactions (9). Early contributions of note then came from J. Moutier (1871) and H. Peslin (1871) in France, Lord Raleigh (1875) in Great Britain, J. W. Gibbs (1875-1878) in the United States, and, as we will soon see, from Horstmann in Germany (1869, 1873). The first monograph to deal with chemical thermodynamics proper was published in England by George Liveing in 1885, but was based on the qualitative concept of energy dissipation rather than on Clausius' quantitative entropy function (10).

The Empirical Context

In addition to the above two conceptual threads we also have a final experimental thread based on the empirical concept of chemical equilibrium. First introduced by the French chemist, Claude Berthollet, in the period 1799-1803, the study of equilibrium reactions in solution was pioneered by, among others, L. F. Wilhemy (1850), J. H. Gladstone (1855), M. Berthelot and L. Péan de Saint-Gilles (1862), A. G. V. Harcourt and W. Essen (1864), and, most famously, by the Norwegian team of C. M. Guldberg and P. Waage (1864, 1867) (9, 11).

Empirical equilibrium studies entered a new phase (both literally and figuratively) when they were extended from solution reactions to gaseous dissociation reactions. Typical examples of this type of reaction include:

$$\text{Heat} + CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$$

$$\text{Heat} + NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g)$$

$$\text{Heat} + PCl_5(s) \leftrightarrow PCl_3(g) + Cl_2(g)$$

Though some important early results were obtained by G. Aime (1837) and W. R. Grove (1847), it was the extensive efforts of Henri Sainte-Claire Deville and his colleagues, H. J. Debray, and L. J. Troost, in France in the period 1857-1868 that really brought the experimental study of gaseous dissociation equilibria to the forefront by establishing important analogies between the pressure and temperature dependency of these equilibrium reactions and those observed for the vapor pressures of liquids (12).

Rationalizing Gaseous Dissociation Equilibria

Various attempts to rationalize theoretically these experimental results began to appear in the late 1860s and the 1870s, some of which were based on the newly emerging kinetic-molecular theory of gases and others on the laws of thermodynamics. The most important qualitative kinetic-molecular rationale was given by the Austrian physicist, Leopold Pfaundler, in 1867 based on the temperature and pressure dependence of molecular collision frequencies, the formation of transient collision complexes, and the requirement of threshold reaction energies – ideas which anticipated much of the conceptual basis of modern chemical kinetics (13).

Following the qualitative approach of Pfaundler, Horstmann initially attempted to develop a quantitative theory of dissociation using the kinetic theory of gases, but abandoned these attempts because they appeared unable to explain the absence of a mass action effect in the case of pure solids (14). Adopting an alternative thermodynamic approach instead, Horstmann first applied it to the thermal dissociation of ammonium chloride (the second reaction given in the previous section) in 1869 (15). Using the analogy with vapor pressures, he fit the data for the change in the dissociation pressure of ammonium chloride as a function of absolute temperature to an empirical equation first proposed by Biot for vapor pressures and then applied a rearrangement of the Clausius-Clapeyron equation:

$$(dP/dT) = \Delta H/(T\Delta V) \quad [4]$$

in order to calculate the corresponding heat of dissociation:

$$\Delta H = (T\Delta V)(dP/dT) \quad [5]$$

This was followed by three more papers on dissociation in period 1871-1872, again based on the application of both the differential and integrated forms of the Clausius-Clapeyron equation (16).

In 1873, however, Horstmann returned to the subject once more in a paper entitled *Theorie der Dissociation*, in which he took an entirely new approach based on an explicit application of Clausius' new entropy function (17). Here he formulated the equilibrium condition for dissociation as a direct function of having maximized the change in the total entropy (dS) of the isolated system with respect to the degree of reaction or dissociation (dx):

$$(dS/dx) = 0 \quad [6]$$

in which the total entropy production was given by the equation:

$$S = (Qx)/T + Z \quad [7]$$

where Q/T is the heat of reaction per mole (Q) divided by the absolute temperature (T), and Z is the change in the "disgregation" of chemical reactants and products. This latter quantity was first introduced by Clausius in 1862 and was his rationale for the underlying molecular basis for entropy increase – namely that it corresponded to a decrease in the degree of molecular aggregation and thus to a corresponding increase in the degree of molecular dispersion or disgregation (18). Similarly, Horstmann's requirement that $(dS/dx) = 0$ at equilibrium was nothing less than a direct mathematical expression of Clausius' famous 1865 reformulation of the second law: "Die Entropie der Welt strebt einem Maximum zu."

However, application of these equations to actual chemical reactions required a further elaboration of equation 7, which Horstmann then proceeded to do on a case by case basis. This may be illustrated using his simplest case – the thermal dissociation of a solid reactant to produce a single solid product and an accompanying gaseous product:

$$\text{Heat} + AB(s) \leftrightarrow A(s) + B(g)$$

as exemplified by the thermal dissociation of calcium carbonate shown in the pervious section. Here the final equilibrium condition was given by the specific equation:

$$(dS/dx) = q/T - ARln(u/u_0) + C = 0 \quad [8]$$

where q is the equilibrium value of Qx, A is the mechanical equivalent of heat, R is the universal gas constant, C is the change in the disgregation of the various reactants and products when in their standard states, and u/u_o is the ratio of the equilibrium molar volume (u) of the single gaseous product to that of its standard state (u_o).

In other words, the second term in this equation represents the manner in which the disgregation or entropy of a gaseous species varies as a function of its degree of dilution expressed as volume per mole (V/n). In deriving it, Horstmann made pioneering use of the ideal gas law written for the first time on a per mole, rather than a per gram, basis :

$$up = RT \quad [9]$$

where u is the volume per mole of gas (19). Molar volume (V/n) is, of course, inversely related to both molar concentration (n/V) and partial pressure (p) – the two variables usually employed when writing the reaction quotient.

In his third example, Horstmann derived the specific equilibrium conditions for the reaction of a gas with a solid to generate both a solid and gaseous product, as in the reaction of steam with hot iron to produce dihydrogen gas and iron oxide:

$$H_2O(g) + Fe(s) \leftrightarrow H_2(g) + FeO(s)$$

for which he obtained the specific result:

$$(dS/dx) = q/T + ARln(p_1/p_3) + C = 0 \quad [10]$$

where p_1 and p_3 are the equilibrium pressures of the gaseous reactant and gaseous product respectively (note their inversion relative to u_1 and u_3), and the other symbols have the same meaning as previously.

Lastly, Horstmann applied his approach to the solution-phase double-displacement reaction:

$$K_2SO_4(aq) + BaCO_3(s) \leftrightarrow K_2CO_3(aq) + BaSO_4(s)$$

Using the data and symbolism of Guldberg and Waage, he showed that his approach led to Thomsen's conclusion that, at equilibrium, this reaction obeyed the relationship:

$$apq = p'q' \quad [11]$$

where p and q are the equilibrium concentrations of the reactants, p' and q' are the equilibrium concentrations of the products, not to be confused with Horstmann's earlier use of the same symbols for other quantities (2). The letter a in this equation represents our modern equilibrium constant K, but only if, as Horstmann noted, the concentration dependence of the disgregation for the solute species obeyed a law similar to that for ideal gases and the values of q and q' for the insoluble barium carbonate and sulfate also remained constant. This first condition anticipated by more than a decade the later work of van't Hoff on the theory of dilute solutions and his famous analogy between osmotic pressure and the ideal gas law (20).

In summary, we see that all of Horstmann's specific results at equilibrium can be generalized using the master equation:

$$(dS/dx) = q/T - ARlnK + C = 0 \quad [12]$$

though he himself never took the final step of subsuming all of his specific concentration and/or pressure ratios for the gaseous- and solution-phase species at equilibrium under a single generalized symbol K.

A Comparison with the Modern Free-Energy Equation

To see the equivalence between Horstmann's result and our modern free-energy equation it is necessary to first divide the latter by $-T$:

$$-\Delta G/T = -\Delta H^\circ/T + \Delta S^\circ - R\ln K = 0 \quad [13]$$

and compare both this and equation 12 with a proper accounting of the resulting entropy changes (21):

$$\Delta S_t = \Delta S_e + \Delta S_s \quad [14]$$

where ΔS_s is the entropy change of the closed chemical reaction system, ΔS_e is the entropy change of the surrounding environment, and ΔS_t is the total entropy change for the resulting isolated system corresponding to their sum, whence it is apparent that:

$$\Delta S_t = -\Delta G/T = dS/dx \quad [15]$$

$$\Delta S_e = -\Delta H^\circ/T = q/T \quad [16]$$

$$\Delta S_s = (\Delta S^\circ - R\ln K) = (C - AR\ln K) \quad [17]$$

The absence of a minus sign in front of q in equation 16 reflects a difference in sign conventions for heats of reaction, as formulated by Thomsen in the 19th century, and our modern conventions for enthalpy changes (6), whereas the presence of the minus sign in equation 15 accounts for why maximization of the total entropy corresponds to minimization of the free-energy and vice versa.

Who was Horstmann?

Since the life of Horstmann (figures 1 and 2) has recently become the subject of an excellent biographical monograph by Alexander Kipnis, all that is required here is a brief outline of its bare essentials (22). August Friedrich Horstmann (figures 1 and 2) was born on 20 November 1842 in Mannheim Germany to a family of prosperous merchants. He entered the University of Heidelberg in 1862, where, despite the presence of such luminaries of the future discipline of physical chemistry as Bunsen, Kopp, Kirchhoff and Helmholtz, he chose instead to study organic and theoretical chemistry in the private laboratory of Emil Erlenmeyer. Receiving his D. phil. in 1865, he did postdoctoral work under Rudoph Clausius at Zürich, where he learned thermodynamics, and under Hans Landolt at Bonn, where he learned the techniques for the experimental study of the vapor pressures of volatile liquids. Following a brief visit to Paris, where he met Regnault and Silbermann, he returned once more to Heidelberg in 1867, where he presented a Habilitation thesis dealing with the relationship between the densities and molecular weights of vapors and was appointed as a Privatdozent. There he remained for the rest of his life, eventually becoming Professor of Theoretical Chemistry. He was 26 when he wrote his paper on the dissociation of ammonium chloride in 1869 and 30 when he wrote his definitive paper on the theory of dissociation in 1873. His productivity in later years was increasingly hampered by diminishing eyesight, and he was essentially blind when he died at age 86 on 10 October 1929.

Figure 1. August Friedrich Horstmann (1842-1929)

Why is He Forgotten?

By the end of the 19th century, Horstmann's work was already being regularly mentioned in various histories of chemistry (23). In 1903 his collected papers on the theory of dissociation were reprinted, under the editorship of van't Hoff, as part of Ostwald's series *Klassiker der exakten Wissenschaften* (24), and he was accorded a 25-page obituary notice in the *Berichte* after his death in 1929, as well as numerous shorter notices in other journals (25). Yet unlike Gibbs, for example, his name has all but vanished from the 20th- and 21st-century thermodynamics literature.

One important reason for this neglect is that Horstmann did little to propagate his explicit entropy approach to chemical equilibrium. Thus, in an important dictionary article on "Dissociation," which he wrote for the 1876 edition of Fehling's *Neues Handwörterbuch der Chemie*, he described Pfaundler's kinetic theory in detail, but dismissed the reference to his own work of 1873 with the

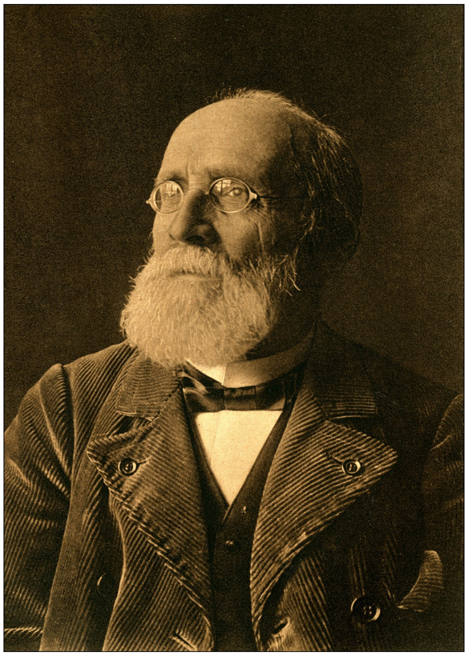


Figure 2. Typical portrait of Horstmann in old age.

comment that it was not possible to describe in detail (26). Though he published at least eight more papers on the theory of dissociation between 1876 and 1884, he made no further mention of his entropy equation, but rather reverted once more to the approach he had originally used in 1869 based on the Clausius-Clapeyron equation (15, 16). Only in his 1885 textbook, *Theoretische Chemie,* did he once again make an explicit, albeit brief, mention of his entropy function (27). However, this book never went beyond the first edition and, to the best of my knowledge, was never translated into other languages.

The reasons for this neglect were simple enough. All of the parameters in the Clausius-Clapeyron equation could be quantitatively evaluated using available experimental data, whereas the same was not true of the standard disgregation term (C) in Horstmann's entropy function. It would not be until the early decades of 20th century and the advent of the thermodynamic quantification program undertaken by G. N. Lewis and his associates at the University of California-Berkeley that both quantified entropy and free-energy data would become widely available (28).

However, a far more important reason for this neglect was the fact that the 19th- and early 20th-century chemical community was extremely uncomfortable with the entropy concept, which is precisely why Horstmann's approach was so unique. Accustomed as we are today to a molecular interpretation of entropy as a measure of kinetic energy dispersion based on the quantum-statistical theory of thermodynamics, it is difficult for us to appreciate how little this physical point of view had permeated chemical and engineering circles by the end of the 19th century and how abstract the purely phenomenological definition found in typical textbooks of the period appeared to the average student of chemistry and engineering. As the engineer, James Swineburne, lamented in 1903 (29, 30):

> *As a young man I tried to read thermodynamics, but I always came up against entropy as a brick wall that stopped my further progress. I found the ordinary mathematical explanation, of course, but no sort of physical idea underlying it. No author seem to try and give any physical idea. Having in those days great respect for textbooks, I concluded that the physical meaning must be so obvious that it needs no explanation and that I was especially stupid in that particular subject ... After a few years I would tackle the subject again, and always I was brought up dead by the idea of entropy. I asked other people, but I never met anyone who could tell me, and I met one – an engineer – who admitted he did not know.*

Initially the free-energy function introduced by Gibbs in 1875, which also contained an explicit entropy term, fared little better (31). French and German translations of Gibbs' epic memoir were made available by Ostwald and Le Chatelier in 1892 and 1899 respectively (32, 33), but the succinctness and rigor of Gibbs' mathematical approach made his work largely inaccessible to the average chemist. Although he would become a virtual icon among physical chemists by the 1920s, this was, as Wilder D. Bancroft observed in 1926, largely a result of their having retrospectively uncovered in his memoir ideas and concepts which they had discovered independently via a much less rigorous and more tortuous path (34):

> *The famous monograph on equilibrium in heterogeneous systems by J. Willard Gibbs is in some respects one of the most remarkable scientific articles that has ever been written. Gibbs was possessed of marvelous and apparently unerring insight, but the gift of expression was denied to him. It is not too much to say that Gibbs wrote in hieroglyphics and that a great part of his manuscript is still undeciphered. We know now that we can find in it the chemical potential, the phase rule, and the theory of osmotic pressure; the theory of electromotive forces, the Donnan equilibrium, and the theory of emulsification. We feel certain that some day we shall find in it theories in regard to all sorts of other things; but we do not know when we shall find them. It used to be popular to ascribe the negligible influence which Gibbs then had on the development of physical chemistry to the fact that his monograph was published in the Transactions of the Connecticut Academy, but this fiction cannot be maintained. Eve-*

ryone knows about Gibbs now; but the only way that one can find anything new in Gibbs is to discover it independently and then look it up in Gibbs.

While it is true that Planck had used an explicit total entropy function in his 1897 textbook on thermodynamics (35), and both Duhem (36) and van Laar (37) had written early monographs arguing for the use of the Gibbs free-energy function (1886, 1906), most chemists of this period preferred instead to discuss the thermodynamics of chemical equilibrium in terms of the "Arbeit" or "Affinity" (*A*) functions and osmotic pressure analogs advocated in the influential writings of Nernst and van't Hoff. Though mathematically equivalent to the functions of Horstmann, Planck, and Gibbs, these approaches completely disguised the role of the entropy function in chemical reactions by making it implicit rather than explicit.

Thus Nernst preferred to use "the more intelligible" notion of maximum work (*A*) or Helmholtz free energy and always used its temperature coefficient, (dA/dT), rather than $-\Delta S°$ when writing his Arbeit function (38):

$$-RT\ln K = A = U + T(dA/dT) \qquad [18]$$

Even more eclectic was van't Hoff, who preferred an approach formally analogous to the standard equation for the interconversion of heat and work in a steam engine! (39):

$$-RT\ln K = A = Q(T_{eq} - T)/T_{eq} \qquad [19]$$

where Q is the heat of reaction, T_{eq} is the equilibrium temperature for the reaction (i.e., the temperature at which $A = 0$), and T is the actual temperature at which the reaction is being run. At other times he preferred to use the gas law and his famous equation for osmotic pressure to calculate the work required convert the initial system into one at equilibrium via a series of expanding and contracting pistons and selective osmotic membranes assembled in an imaginary device known as an "equilibrium box" (see figure 3) – which calls to mind the famously sarcastic comment by Lewis and Randall concerning so-called "cyclic processes limping about eccentric and not quite completed cycles" (28).

Indeed, an informal survey of introductory physical chemistry textbooks and chemical thermodynamics texts published between 1893 and 1933, showed that 70% preferred the "Arbeit" or work approach of Nernst and van't Hoff, 22% used either Gibbs or Helmholtz free energy with $\Delta S°$ explicitly given, 8% used neither, and 40% contained no index entry for entropy. It is, of course, the famous 1923 textbook of chemical thermodynamics by Lewis and Randall in the United States (28) and its advocacy by Hudleston in Great Britain (40) which are generally credited with having finally made ΔG and $\Delta S°$ an inherent part of every chemist's thinking.

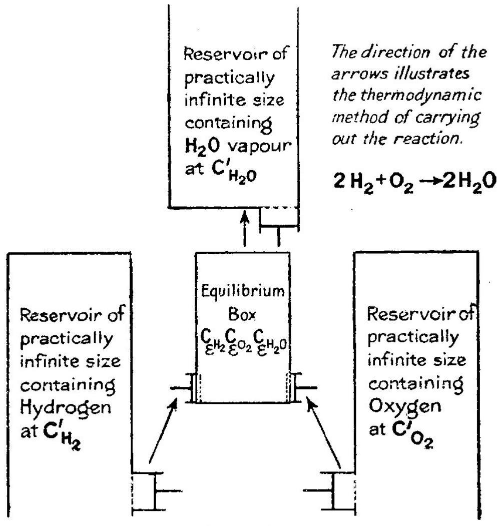


FIG. 18.

Figure 3. Typical example of a van't Hoff equilibrium box. (*Image courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati*).

A third and final reason for this neglect lies in the descriptions of Horstmann's contributions found in the average history of chemistry text, whether written during his lifetime (23) or subsequently (41). Though all of these acknowledged his contributions to the theory of dissociation and often mentioned his use of the Clausius-Clapeyron equation, almost none of them, including the account of his life appearing in the prestigious *Dictionary of Scientific Biography* (42), called explicit attention to his pioneering application of the *(dS/dx)* function to the theory of chemical equilibrium in general. An exception is the 1952 history by Eduard Farber, which was, in fact, responsible for first drawing the present author's attention to this subject (43).

What Goes Around Comes Around

Given Horstmann's almost total disappearance from the 20th-century thermodynamics literature, it is somewhat ironic that several developments in this field during the past century strongly resonate with Horstmann's original approach:

1. The introduction by De Donder in 1920 of the extent of reaction parameter (ξ) and his replacement in certain situations of the ΔG symbol with the differential $dG/d\xi$ – a distinction which greatly clarifies the relationship between the ΔS_t and ΔG terms in equation 15 and

Horstmann's own use of dS/dx (44):

$$\Delta S_t = -\Delta G/T = -(dG/d\xi)/T = dS/d\xi \qquad [20]$$

This unfortunate dual usage of the Δ symbol was characterized by Bent in 1973 as "a weed in the garden of thermodynamics" and has since become a subject of some interest in the chemical education literature (45).

2. The widespread use since the 1960s of a qualitative molecular disorder interpretation of entropy in introductory chemistry courses in order to address, like the original qualitative molecular disgregation interpretation of entropy used by Clausius and Horstmann, Swinburne's "missing physical basis" lament. Of course neither the disorder nor the disgregation interpretations of entropy are absolutely identical to the more sophisticated energy dispersion picture provided by modern statistical mechanics and, as Lambert has repeatedly pointed out, the disorder picture, in particular, can lead to a number of incorrect conclusions if pressed too far (46).

3. The proposal by Rosenberg and Klotz in 1999 that ΔG be replaced by an explicit total entropy function, which they have called the "Planck function" in honor of Planck's use of such an approach in his textbook of 1897, and which they have also since incorporated into the most recent edition of their own popular thermodynamics text (47, 48). They seem unaware that this approach was already used by van Laar in his thermodynamics text of 1893 and that he had already dubbed it the "Planck potential (37). Of course, both terms are, as we have seen, historically inaccurate and a more appropriate name choice would be either the Horstmann function or, perhaps, the Horstmann-Planck potential. As any historian is aware, such historical misattributions are rampant in the textbook literature, where they function as perfect examples of Stigler's famous law of eponymy (49). In addition, there are problems with interfacing this approach with the absolute rate theory of chemical kinetics, as it requires that activation barriers be replaced with entropy sinks (50)..

References and Notes

1. First presented at the 193rd National Meeting of the ACS in Denver, CO, 5-10 April 1987 and in revised form at the 236th National ACS Meeting in Philadelphia PA, 17-21 August 2008 as part of the Edelstein symposium in honor of Sir John Rowlinson.

2. One of the difficulties in reading Horstmann is that his choice of symbols often conflicts with modern thermodynamic conventions. Thus the modern use of Q for reaction quotient will conflict with Horstmann's use of this letter to represent heat of reacton at constant T and P, now symbolized as ΔH. Likewise Horstmann often uses the same symbol to represent more than one quantity. Thus he uses q not only for standard heat of reaction ($\Delta H°$) but also, via Guldberg and Waage, to represent (along with q') the solution concentrations of various reactants and products, as well as p to represent not only partial pressure, but also (again via Guldberg and Waage) solution concentration, etc. Consequently the reader must always be aware of the immediate context in which a particular symbol is being used. It should also be noted that similar examples of context related redundancies also occur in modern thermodynamics, such as the continued use of Q for heat, when discussing Clausius' original formulation of the second law in terms of the quantity Q/T.

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12. The work of the Deville school is summaried in H. Sainte-Claire Deville, "Leçons sur la dissociation (18 Mars et 01 Avril 1864)," in Société chimique de Paris, *Leçons de chimie*, Hachette: Paris, 1866, pp. 255-378 , and H. Sainte-Claire Deville, "Leçons sur l'affinité (28 Févier et 06 Mars 1867);" *Ibid*., 1869, pp. 1-85.

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14. A. Horstmann, "Zur Theorie der Dissociationserscheinungen," *Berichte*, **1868**, *1*, 210-215.

15. A. Horstmann, "Dampfspannung und Verdampfungswärme der Salmiaks," *Berichte*, **1869**, *2*, 137-140.

16. A complete bibliography of Horstmann's publications may be found in reference 22, pp. 185-188.

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Pharm., **1873**, *170*, 192-210. An English translation appears in this issue on pages 76-82.

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Publication History

First published in *Bull. Hist. Chem.*, **2009**, *34(2)*, 83-91.

Update

I have only recently (2015) become aware of the 1977 article by H. A. M. Snelders ("Dissociation, Darwinism and Entropy," *Janus*, **1977**, *64*, 51-75) which also discusses Horstmann's entropy treatment of dissociation reactions. Likewise for the 1996 study by Helge Kragh and Stephen Weininger ("Sooner Silence than Confu sion: The Tortuous Entry of Entropy into Chemistry," *Hist. Stud. Phy. Bio. Sci.*, **1997**, *27*, 91-130) which provides an even more detailed context for the slow entrance of entropy into the chemical literature and independently reaches many of the same conclusions as I have in this and other papers dealing with the history of chemical thermodynamics.

Lastly, in Section 9 I failed to point out the modern nature of Horstmann's molecular rationale for equilibrium based on his application of the disgregation concept to the case of dissociation reactions involving both gaseous reactants and gaseous products – namely that both the reactants and products are simultaneously attempting to increase their degree of disgregation or entropy of dilution, as we would say today. As the reaction proceeds, the reactants become increasingly dilute and thus their entropies of dilution increase, but at the same time the products become increasingly concentrated, so their entropies of dilution decrease. At some point these two entropy changes balance and the system comes to equilibrium before the reaction goes to completion. Though the insight that both the entropy maximum and the equilibrium state are due to the mixing of the various reactant and product gases can be found in a few modern textbooks (see for example, K. Denbigh, *The Principles of Chemical Thermodynamics*, Cambridge University Press: Cambridge, 1956, pp. 134-135), its true significance is often disguised by the misconception – due to the popular disorder interpretation of entropy – that mixing in and of itself always leads to an entropy increase. In fact, mixing will lead to an entropy increase only if the act of mixing also results in the two components undergoing mutual dilution. In other words, the entropy increase is due to the entropy of mutual dilution and not to the supposedly greater disorder of the mixture itself. See, E. F. Meyer, "Thermodynamics of 'Mixing' of Ideal Gases: A Persistent Pitfall," *J. Chem. Educ*, **1987**, *64*, 676.

XIV

Ask the Historian

The Origin of the Brin Process

Question

What is the origin of the Brin Process for the industrial manufacture of oxygen?

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Answer

The Brin process for the industrial manufacture of pure dioxygen gas was based on the thermal reversibility of the reaction between barium oxide (BaO) and dioxygen gas (O_2) to produce barium peroxide (BaO_2):

$2BaO(s) + O_2(g) \leftrightarrow 2BaO_2(s)$ [1]

Since the reaction as written is exothermic ($\Delta H° = -143.1$ kJ/mol rx) combination of the barium oxide with the dioxygen gas of the air is favored at low temperatures, whereas its reverse, the decomposition of the resulting peroxide to give pure O_2 and the original oxide, is favored at high temperatures. The regenerated oxide can then be reused to produce more peroxide and the cycle repeated indefinitely.

Reaction 1 was discovered by the French chemists, Joseph-Louis Gay-Lussac and Louis-Jacques Thenard, in 1811 (1), and was first explored as a method for the industrial separation of dioxygen gas from air by the French chemist, Jean-Baptiste Boussingault, in 1852 (2). However, Boussingault found that the barium oxide became inactive after the process had been repeated about a dozen times and so did not succeed in making it industrially viable.

In 1879 the French team of Quentin and Arthur Brin discovered that this deactivation was primarily due to the barium oxide reacting with the carbon dioxide content of the air to produce barium carbonate:

$BaO(s) + CO_2(g) \leftrightarrow BaCO_3(s)$ [2]

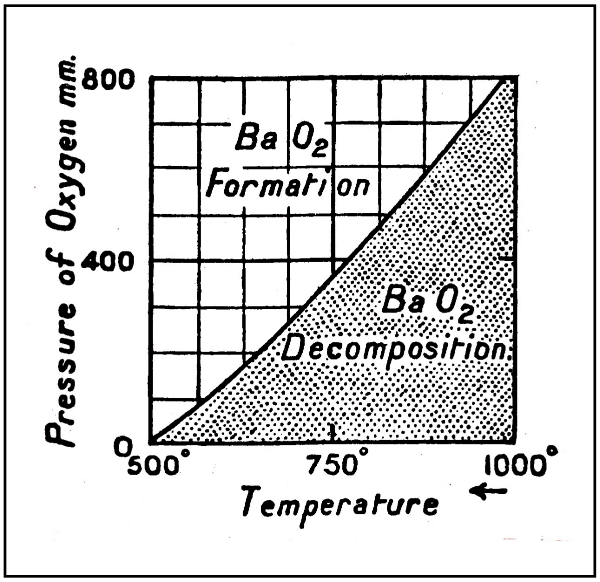

Figure 1. A plot of pressure versus temperature showing the regions corresponding to the favorable production of barium oxide versus barium peroxide (7).

and that if one first removed the carbon dioxide by passing the air over lime ($Ca(OH)_2$) or through a solution of potassium or sodium hydroxide:

$CO_2(g) + 2NaOH(aq) \leftrightarrow Na_2CO_3(aq) + H_2O(l)$ [3]

one could then recycle the barium oxide indefinitely. The next year the Brin brothers were granted a British patent for their process (3) and in 1886 the Brins Oxygen Company was incorporated, which continued to produce industrial quantities of dioxygen gas using the barium peroxide process until 1906, when the name was changed to the British Oxygen Company Ltd. and they began to produce dioxygen gas more economically using the fractionation of liquid air (4, 5).

It should be noted that the industrial use of reaction 1, like the more famous Haber ammonia synthesis, is an excellent textbook example of the practical application of Le Chatelier's principle. Indeed, in 1880, Boussingault, inspired by the earlier work of Henri Sainte-Claire Deville on thermal dissociation reactions, returned to the study of reaction 1 and showed that it could be reversed not only by a change in temperature at constant air pressure, but also by a change in pressure at constant temperature – high pressures favoring the formation of the peroxide and low pressures favoring the formation of the oxide (6). Though, as summarized in figure 1, one can in principle optimize the equilibrium shift by simultaneously manipulating both temperature and pressure, in actual practice it was far easier and more economical to shift the pressure than to shift the temperature. Consequently, when applied industrially, the latter was kept constant at about 700°C while the air pressure was set at 2 atm for peroxide production and then reset at about 0.05 atm for its subsequent decomposition, the gas obtained under these conditions being about 90-96% dioxygen and 4-10% dinitrogen (7).

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Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu

Publication History

Published in *J. Chem. Educ*., **2009**, *86*, 1266-1267.

XV

Ask the Historian

Why Are *q* and *Q* Used to Symbolize Heat?

Question

Why are *q* and *Q* used to symbolized heat and when should one use the lower versus the upper case?

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Answer

An upper-case *Q* was first used to symbolize "the absolute quantity of heat" by the French engineer, Benoit-Paul-Émile Clapeyron (figure 1), in his famous memoir of 1834 in which he first quantified what is now known as the Carnot cycle (1). Carnot himself did not use a symbol for the quantity of heat in his original memoir of 1824, which was largely verbal rather than mathematical in character, and Clapeyron most likely selected the letter *Q* to emphasize that he was dealing with the *quantity* of heat rather than with its *intensity* or temperature, for which he used an upper-case *T*. Building on the work of Clapeyron in the 1850s and 1860s, Clausius not only continued to use *Q* to symbolize heat in his various memoirs on the theory of heat, he also employed an upper-case *W* to represent mechanical work (2).

However, as the theory of thermodynamics continued to evolve, several authors felt the necessity of distinguishing between various sources of heat, while displaying little agreement with regard to the resulting symbolism. Thus, in his famous memoir of 1873 on the application of the entropy concept to the phenomenon of chemical equilibrium, the German chemist, August Horstmann, used an upper-case *Q* to "denote the quantity of heat required to decompose one mole of a compound" but a lower-case *q* to represent "the actual heat of decomposition" or the net heat of reaction (3), whereas Fritz Haber, in his 1901 monograph on the thermodynamics of technical gas-reactions, followed the lead of Helmholtz in using an upper-case *Q* to denote standard heats of reaction and transition, but a lower-case *q* to represent the bound or "latent" heat due to isothermal entropy generation (i.e. $T\Delta S$) (4).

Figure 1. Benoit Paul Émile Clapeyron (1799-1864).

In contrast, Lewis and Randall, in their famous 1923 monograph on thermodynamics, made no use of the upper-case *Q* and instead consistently employed both a lower-case *q* for heat and and a lower-case *w* for work (5), while Samuel Glasstone, in his 1947 textbook, *Thermodynamics for Chemists*, adopted the convention of employing the lower-case letters, *q* and *w*, for arbitrary, path-dependent, infinitesimal quantities of heat and work, but the upper-case letters, *Q* and *W,* for their algebraic sums (6). Apparently this eclecticism is still very much with us as the most recent IUPAC guide to quantities, units, and symbols in physical chemistry lists both *q* and *Q* as equally valid symbols for heat, though it also lists Q as the symbol for electrical charge and for the reaction quotient (7).

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Publication History

Published in *J. Chem. Educ.,* **2010**, *87,* 1142.

XVI

Introduction to the English Translation of "A Contribution to Chemical Statics"

By Leopold Pfaundler

A Forgotten Classic of Chemical Kinetics

The central importance of Leopold Pfaundler's pioneering 1867 paper on the application of the kinetic theory of heat to chemical reactions and the desirability of a long-overdue English translation of the same have already been commented on in the introduction to the recently published English translation of August Horstmann's equally important paper of 1873 dealing with the first application of the second law of thermodynamics to the theory of chemical equilibrium (1). Since this same introduction also reviewed the current status of English-language translations of classic chemical papers in general, and a paper dealing with both Pfaundler's life and the context of his contribution will appear in the next issue of the *Bulletin* (2), all that remains for this introduction is to deal with the technicalities of the translation process itself.

As with the earlier translation of the Horstmann paper, Dr. Kuhlmann, who is a native German speaker, first produced a literal translation, which Dr. Jensen then extensively revised and edited in order to make the phrasing and sentence structures more acceptable to the English reader. As always, he prefers a looser translation which places more emphasis on clarity than on literal accuracy, and any defects in the final translation resulting from this process should be credited to Dr. Jensen alone.

At first we thought that the translation would be simple and straightforward, since Pfaundler's German is quite easy to read in the original. However, this expectation soon proved unfounded, since the simplicity of Pfaundler's German was dependent on conventions unique to the German language which, when literally translated into English, resulted in a nightmare of pronoun ambiguity. In order to avoid the resulting confusion, we have found it necessary to convert many of Pfaundler's pronouns into the corresponding nouns and to make many of his implied meanings explicit. The larger of these interpolations are indicated within the body the translation by enclosing the amplifications in square brackets, though many single word clarifications have been left unmarked as these would have generated too much editorial clutter within the text.

In yet other cases we encountered ambiguities due to Pfaundler's word choices. A frequent example was his use of the phrase "quantity (*Menge*) of molecules," when it is obvious that he meant the "number of molecules," and indeed sometimes even explicitly stated this in a later clause within the same sentence, or his use of the adjective "maximum" when he meant threshold or upper limit. Also, like Clausius, Pfaundler does not use the term "kinetic energy" in his paper, but rather refers to the *lebendig Kraft* of the moving molecules. Since a direct English translation of this term as "living force" seems awkward to the ear of the English reader, we have instead chosen to use the original Latin term for this concept – *vis viva* – which is how it is normally referred to in most histories of mechanics. Similarly, we have modernized Pfaundler's chemical nomenclature and have translated *kohlensauren Kalkes* and *Kohlensäure* as calcium carbonate and carbon dioxide respectively.

In addition to these translation problems, there are also some severe organizational problems with Pfaundler's paper. As originally conceived, the paper was explicitly divided into three parts, in addition to a separate introductory paragraph and an unmarked conclusion. However, after completing the initial draft of his paper, Pfaundler encountered a recently published paper by H. W. Schröder van der Kolk criticizing Henri Sainte-Claire Deville's work on dissociation which Pfaundler felt compelled to comment on, not least because he felt that his own theory of dissociation both clarified and refuted most of Schröder van der Kolk's objections. But rather than attach these comments as an addendum to the end of his paper, Pfaundler chose to insert them as a separate section at the end of Part I, thereby interrupting the flow and organization of his original manuscript. Yet further confusion resulted from Pfaundler's decision to insert a lengthy addendum to the addendum as a footnote, placed not at the end of the original addendum, but at the very end of the entire paper. Other minor problems result from Pfaundler's footnoting and referencing procedures. Most of these are placed at the bottom of the pages in question, but are separately numbered for each page, whereas others are embedded within the body of the text itself. In addition, the citation style for a given journal often varies from page to page.

Since our goal is to make the translation as accessible to the modern reader as possible, we have chosen in the translation to correct these organizational problems by transferring the addendum (which is of only minor interest to the modern reader) to the end of the paper and by also transferring all of the references and notes (both those within the text and at the bottom of the various pages) to the end of the paper, where they have been standardized and renumbered sequentially. Lastly, the various sections resulting from these rearrangements, as well as the original unmarked conclusion, have also been labelled and renumbered sequentially. We have further taken the liberty of merging most of Pfaundler's single-sentence "island" paragraphs with either the preceding or succeeding paragraphs, where they would have normally been placed by most modern writers.

One final problem involves Pfaundler's use of chemical equations. In Parts I and II of his paper, he writes them, as we do today, using linear compositional formulas for the various reactants and products. However, in Part III he suddenly reverts to writing them using type formulas for the reactants and products. Since these involve curly brackets and placement of one symbol above another, they create severe layout problems for the modern computer. Since many of the type formulas in Part III also appear as linear formulas in Parts I and II and it is obvious that Pfaundler clearly understood the equivalency of these two notations, we have chosen, for reasons of both consistency and typographical convenience, to use linear compositional formulas throughout. The only place where this change results in a loss of clarity is in Pfaundler's discussion of his postulated collision complex, ABCD, for a double decomposition reaction, where the type formula more clearly indicates the feasibility of alternative modes of decomposition than does the linear formula. For this reason, a reproduction of Pfaundler's original type formula for this complex will appear in the commentary which will be published in the next issue of the *Bulletin* (2).

References and Notes

1. W. B. Jensen, "Introduction to the English Translation of 'The Theory of Dissociation' by August Horstmann: A Forgotten Classic of Chemical Thermodynamics," *Bull. Hist. Chem.*, **2009**, *34(2)*, 73-75.

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XVII

PRIMARY DOCUMENTS

A Contribution to Chemical Statics

Leopold Pfaundler

Annalen der Physik und Chemie, **1867**, *131*, 55-85

It seems to me that the theory, which I shall develop in this paper, is able to provide an explanation for some chemical facts for which no suitable hypothesis has yet been found. Among these facts are the phenomena of dissociation, the so-called mass-action effect, reciprocal and predisposing affinity, the equilibrium state between opposing reactions, and several other related phenomena.

I. Theory of Dissociation Phenomena

The observation of certain exceptions to the law of vapor densities initially resulted in the hypothesis that those compounds, which showed these exceptions, decompose in the vapor phase. The numerous experiments of Sainte-Claire Deville, Pebal, Würtz, Wanklyn, and of Robinson and Than have confirmed the hypothesis proposed by Hermann Kopp, Cannizzaro and Kekulé. Furthermore, they also prove that this decomposition is often incomplete – in fact, that it is only partial over a wide range of temperatures, such that, within this range, each degree of the temperature [scale] correlates with a different degree of decomposition. The majority of chemists view this partial decomposition as an entirely adequate explanation of the [observed] irregularities in the vapor densities. *However, it does not explain the partial decomposition itself.*

In my opinion, the following two essentially different ideas can be formed concerning the state of a compound, AB, whose vapor has begun to decompose. Either all of the AB molecules experience the same change (a loosening of their bonds [and] an increase in the distance separating their components), and therefore pass into a state which is intermediate between their original state and that of complete decomposition; or this change impacts the individual molecules unequally, such that, for example, only a portion of them are completely decomposed, whereas the remainder remain undecomposed.

At first glance, the former, rather than the latter, assumption seems to have a higher probability, even though it is inconsistent with the results of the experiments of Deville, Pebal and Würtz. Even if it were possible to explain the increase in the volume of the vapor as a consequence of the resulting relaxation of the connection between components A and B, it would still not be possible to understand how something other than a complete regeneration of the original compound could occur after cooling. Nor would cleavage by diffusion be understandable in this case. Eventually, even with this process, the final temperature-induced transition from the state of highest relaxation to the state of complete separation would have to occur in a single bound, whereas experience shows that the change in the vapor densities is continuous.

The second assumption explains the observed facts completely, but involves something which is difficult to imagine. One cannot quite conceive why, at the same temperature, a certain number of evidently identical molecules will decompose, while the remainder remain intact. If it is the temperature which determines their degree of decomposition, and this is the same for all, then all of them must suffer the same change, since identical causes must produce identical effects. I will now try to resolve this difficulty. It will be shown that it is not the correctness of the conclusions that is at fault, but rather that of the premises.

Deville has already emphasized the analogy (1) which exists between the partial decomposition of compounds below the actual decomposition temperature and the evaporation of liquids below the boiling temperature. This very same concept occurred to me while reading Clausius's paper, "On the Form of Motion Which We Call Heat" (2) and led me to investigate whether, as a consequence of the similarity between these phenomena, an hypothesis, like that used by Clausius to explain evaporation, might also be useful in explaining dissociation. I found that his hypothesis was readily applicable to a certain class of dissociation processes. By way of contrast, it was not as directly applicable to the dissociation of vapors, though it is easy enough, using the same fundamental ideas, to construct an alternative hypothesis, which, in my opinion, completely explains this phenomenon as well.

Let us first look at the process of vaporization and its explanation, as given by Clausius. If one heats a liquid in a closed space, a portion of it evaporates –that is, a certain number of molecules on its surface are transferred to the space above until it contains a certain characteristic number. As long as the temperature remains constant, this number remains unchanged. At this point one might ask why all of the molecules at the surface of the liquid do not change into vapor, since their temperature is the same as those that are already in the vapor. This point is crucial for the analogy. Those who are content with the explanation that further evaporation is inhibited by the partial pressure of the vapor, might also be satisfied, when it comes to the dissociation of a compound, with the explanation that the partial pressures of the vapors of the separated components inhibit further decomposition of the compound as long as the temperature remains constant. If this is increased by a certain amount, a further number of molecules will decompose until the increase in the partial pressure of the released components is in equilibrium with the force of decomposition.

I think this explanation is still insufficient, since – apart from the fact that it still remains to be investigated whether one can talk of a partial pressure in this situation similar to that present in evaporation and whether this would have a similar impact with respect to inhibiting the separation of chemically bonded molecules as it has with respect to those bound by cohesion – the difference in the behavior of the individual molecules is still unexplained. One has to look further into this matter and consider the nature *of partial pressure itself*. This has been done by Clausius. According to his theory, the equilibrium which ensues when the vapor pressure has reached its maximum is due to the fact that an equal number of molecules are now leaving the surface of the liquid for the space above it as are simultaneously returning from the vapor to the liquid surface.

As representative of the general dissociation phenomena to which this hypothesis may be immediately applied, I choose the decomposition of [solid] calcium carbonate. When heated in a closed space, this undergoes a dissociation, beginning at a certain fixed temperature, which means that a number of its molecules, whose internal motions have exceeded [the allowed] maximum, decompose. The molecules of liberated carbon dioxide gas are moving in the space [above the solid] in a rectilinear fashion and will increase until the number reabsorbed per unit time is as great as the number expelled per unit time. If the temperature is slightly decreased, then the number of molecules that recombine will exceed the number being expelled and the material will *absorb* carbon dioxide. If the carbon dioxide molecules in the space [above the solid] are now displaced by air (or some other indifferent gas), the expulsion of the molecules of carbon dioxide does not stop, because its cause has not been eliminated, but the absorption of the molecules does, since they are being removed [by the air flow]. Therefore the calcium carbonate *evolves* carbon dioxide in the air stream at the *same* temperature as it absorbs carbon dioxide in its absence. The calcium carbonate and carbon dioxide behave in the air stream in a manner similar to that of a hydrated substance that is being dried (3).

I will now pass to an explanation of the *dissociation of vapors* and, for that purpose, will hypothesize that, in the vapor of a partially decomposed [gaseous] compound at constant temperature, *as many molecules are being cleaved as are being recombined by the [molecular] motions.* This manner of explanation necessarily implies that *not all of the* molecules *simultaneously experience the same state of motion*, just as the explanation of evaporation by Clausius postulates that the states of motion of the molecules on the surface of the liquid are unequal. According to the mechanical theory of heat, such an inequality is highly probable.

The process of decomposition for a compound AB may therefore be thought of in the following fashion: As long as the compound has not yet decomposed, all of the molecules will have the composition AB. They will move in a rectilinear fashion. Furthermore, the components of these molecules will also move relative to each other. However, this movement of the components (as well as the rectilinear motion) is not of equal magnitude for every molecule because, even if they were momentarily equal, they would not remain so as a result of their [mutual] collisions and their collisions with the wall [of the container]. Only the average *vis viva* [i.e. kinetic energy] of these motions remains unchanged at constant temperature and in a certain ratio to the *vis viva* of the rectilinear motion of the molecules. But in the individual molecules it will sometimes be larger and sometimes smaller.

If the temperature is now increased, the *vis viva* of both [kinds of] motion increases. As a result, it may happen that the increase in the internal motion of those molecules, for which, at this instant, the [internal] motion already happens to be quite large, will then become so large that it will result in a complete separation of the components A and B. It is impossible for this separation to happen to all of the molecules at the same time. Rather it must occur first for those whose internal motion happens to be larger than the rest. These separated components, which are now free molecules themselves, now possess rectilinear motion as well. Meanwhile a new selection of previously undecomposed molecules will attain the upper limit for their internal motions, and will, in turn, also decompose. This will happen to equal numbers per unit time and continuously increase the number of dissociated molecules. However, these will, in part, collide with one another. Not all of these collisions will result in the dissociated molecules recombining, but rather only those whose states of motion are such that, when the dissociated compound is reformed, the resulting combined motions of its components are no greater than that required for the original separation. Hence, it necessarily follows that, at a given constant temperature, the free molecular fragments will continue to increase until the number of reuniting molecules per unit time becomes as great as those produced per unit time by cleavage. From this point on an *equilibrium* between decomposition and recombination will dominate, provided that the temperature remains constant. But if this increases, the number of dissociating molecules must also increase, while the number of reuniting molecules will initially decrease. The equilibrium can only be restored when the number of molecules, A and B, in the unbound state is large enough that as many recombine as decompose. If the temperature continues to increase, one will finally reach the point where all of the molecules decompose without being able to recombine. At this juncture the dissociation phase will finally terminate in one of complete decomposition.

If during the dissociation phase, an opening is made in the wall of the container, or the walls are porous, both the undecomposed and decomposed molecules will pass through in a rectilinear fashion, but since their speeds are inversely related to the square root of their masses (4), the dissociation fragments will diffuse faster than the undissociated molecules and, among the former, the lighter faster than the heavier. Based on this, the experiments of Pebal and Deville may be explained and it also leads to the conclusion that it should be possible to use diffusion to gradually increase the [degree of] dissociation of the remaining material in the container without increasing the temperature (5). The same result could be obtained using a chemical medium to absorb both of the components, *or only one* of them (Therefore an analysis of the gas mixture is not feasible without a chemical interaction between the absorbing material and the compound). The fact that decomposition can only occur gradually seems to me to provide the correct explanation for why many reactions require a certain period of time for their completion.

If one cools down a partially or completely decomposed vaporous compound, the process [of decomposition] will generally be reversed. However, it is conceivable, especially with rapid cooling, that the separated components will pass over into a state in which they can no longer recombine before they have had time to reunite. This explanation has already been employed by Deville.

II. Theory of States of Equilibrium Between Reciprocal Reactions, Explanation of Mass Action, etc.

It has been frequently observed that a compound AB is decomposed by material C at the same temperature as compound BC is decomposed by A. Likewise, it is a known fact that reactions of the form AB + CD = AD + BC may become reciprocal at the same temperature, whether one decreases the amounts of the compounds to the left of the equal sign or increases those to the right. As a matter of fact, the affinity of a material is a function of its mass.

At that period when the principle of definite proportions was not as certain as it is today, this and similar facts provided a great deal of support for the theory of Berthollet. They still form a dark chapter in the theory of affinity. The arguments which one can deduce from them in opposition to presently accepted theories are, it seems to me, perhaps silenced by the overwhelming number of supporting arguments, but not altogether eliminated.

The correlation of these facts with those of dissociation and the generality of this phenomenon were first specifically remarked on by Adolf Lieben in his paper: “On the Vapor Densities Known as Abnormal” (6). There he cites the same example of calcium carbonate, which I used earlier; then the facts concerning the decomposition of water, which we owe to Deville; and, finally, the results of the beautiful experiments of Berthelot and Péan de Saint-Gilles concerning the formation and decomposition of compound ethers [i.e., esters], which are, without doubt, of greatest importance for the subject under discussion. Related to this are the recently published and equally interesting discoveries of Berthelot concerning the equilibrium between the opposing reactions for the synthesis and decomposition of hydrocarbons, which Berthelot also compares to dissociation.

All of these facts allow for a single explanation formulated with the help of an hypothesis based upon Clausius’ theory of the [three] states of matter and which consequently replicates his theory of evaporation. Let us assume there are equal numbers of the molecules of three gases, A, B and C, in a closed space. Furthermore, at room temperature, the gases A and B are combined in the form of the gaseous compound AB. Initially two kinds of molecules are moving in this space: AB and C. Now, if the temperature is progressively increased, a number of AB molecules can, as shown earlier, decompose, which means that the compound AB will enter into a state of dissociation. Then the separated molecules, A and B, will, like the others, move in a straight line within the [available] space and will occasionally encounter the molecules of C. Let us assume that substance B has an affinity for C – thus the molecules of B and C can combine on colliding provided that the sum of their motions does not result in a state of motion which makes their attachment impossible.

However, in this case the following process is likely: Even before the temperature has reached a level sufficient to induce the dissociation of AB, the same result can be initiated by the influence of molecule C. Let us examine a molecule of the substance AB, which, because of the high temperature, has already acquired sufficient motion of its components that it is close to decomposition, and which now encounters a molecule C. The external motion of both molecules is now completely or partially converted into internal motion by the impact. The result now depends on whether the affinity is or is not strong enough, given this enhanced internal motion, to keep all three bodies together. If not, then the components are repelled again, which means a part of the internal motion is once again converted to external motion. Apparently the mode of separation now depends on how the internal motion is distributed among the individual parts. If the internal motion of the original AB molecule was already very large prior to impact, and was further increased by the impact, then the cleavage of the transient ABC molecule to form A and BC is more likely than to form AB and C. Therefore, a certain definite portion of the AB molecules which collide with the C molecules will react according to the equation AB + C = A + BC. Here we have a dissociation process which is different from pure dissociation; but also equally different from a complete chemical decomposition in which all of the molecules are decomposed at once. The peculiarity of our process consists in the necessity of only *partial* decomposition.

Besides AB and C molecules, we now have those of A and BC. Provided that even the most favorable combination of motions fails to create a net motion capable of decomposing BC, the reaction will now, in the course of time, proceed to completion without a further increase in temperature (i.e., until all of the molecules of AB have encountered molecules of C under conditions favorable for decomposition) and will terminate in the completion of the equation AB + C = A + BC. If this is not the case, but rather at some other temperature the motion of the components within even a few BC molecules increases to the point that (with the simultaneous assistance of the affinity of A for B) it causes their decomposition, then the process must stop at a certain composition of the mixture, provided that the temperature is held constant. Indeed, decompositions still constantly occur, but they will now be compensated by an equal number of recombinations. Within a certain temperature range, changes in temperature will only affect the reciprocal proportion of the different molecules and a certain [composition of the] mixture will correspond to a certain degree of temperature. It matters which of the combined molecules is most affected by the increase in temperature and approaches the upper limit for its internal motions faster.

Now we want to investigate how the process has to proceed if one adds, without an increase in temperature, more of gas AB to a gaseous mixture of AB, BC, A and C. Thereby the equilibrium between recombination and decomposition must be disturbed, since the number of decomposing AB molecules increases in a manner proportional to the amount present. As a result of this, the number of free molecules of C likewise decreases. More molecules of BC are formed, but more than before are decomposed as well. Equilibrium is only possible at a different composition which contains fewer molecules of C. The larger the amount of gas AB becomes, the smaller that of gas C will be become. This reaction would also be promoted by the removal of the molecules of A, as that would have the result that the accumulated molecules of BC are no longer decomposed by the molecules of A and hence the molecules of C will no longer regenerate. Therefore, if we implement both methods at once – supply of gas AB and removal of gas A – gas C will completely disappear without the need of a higher temperature, as required previously when an equilibrium between decomposition and recombination dominated.

The reverse result will occur when, in the mixture of AB, BC, A and C, we decrease the number of AB molecules, or increase the molecules of A, or both simultaneously. The decrease in AB will result in a decrease in the decompositions of AB and the formation of BC; hence more free molecules of C will remain. An increase in the molecules A will cause an increase in the decompositions of molecule BC, whereby molecules of C are released. Therefore, this reaction can only end with the complete isolation of gas C.

If the three substances, A, B and C, and their compounds are gases, as assumed so far, it is perhaps easy to add arbitrary amounts of each individually, but not to remove each individually, if one cannot use chemical methods. Therefore, one will rarely, if ever, succeed in bringing a reaction to completion solely by changing the proportions. However, one can approach completion to an arbitrary degree through addition of the appropriate gas.

It is different when one of the substances is a liquid or a solid. One example of this case would be the reaction of copper, water vapor and hydrogen (7). If one directs water vapor (AB) over glowing copper (C), hydrogen (A) and copper oxide (BC) are formed. If one directs hydrogen (A) over copper oxide at the same temperature, water vapor (AB) and copper (C) are formed. Here water vapor, in the first case, and hydrogen, in the second case, were added in excess to a limited amount of copper or copper oxide, and the emerging (by)products were simultaneously removed as gases. But if a limited amount of water vapor is heated in a closed tube with a limited amount of copper, only a part of the water is going to be decomposed and a part of the copper is going to be oxidized and, for each degree of temperature, there has to be a certain ratio between the amount of water vapor, hydrogen, copper and copper oxide, at which there is an equilibrium between the oxidations and the reductions. The same occurs if one directs hydrogen over iron oxide and, conversely, water vapor over iron. Zinc, tin, cobalt, nickel, uranium and cadmium behave similarly (8).

If one directs hydrogen chloride gas over glowing silver, silver chloride and hydrogen form – conversely silver chloride is reduced by hydrogen. Zinc, tin and iron behave similarly towards carbon dioxide and carbon monoxide gas. These reciprocal reactions occur at the *same* temperature, as shown by specially designed experiments, (Gay-Lussac, Regnault).

Also related is the observation that many substances, formed by reaction with a gas, can only be distilled or stored in an atmosphere of the same gas (e.g., sulfur chloride in chlorine gas). Conversely, the escape of hydrogen bromide facilitates the action of bromine on organic substances in sealed tubes. Cases of predisposing affinity also belong here and are satisfactorily explained in a similar way. I would be able to multiply my examples indefinitely, but I believe that those given so far are sufficient to illustrate the proposed hypothesis and facilitate its application. It is applicable whenever a partial decomposition occurs. Moreover, the presence of the latter is revealed by a number of characteristics, among which are: the influence of time on the progress of a reaction; the incompleteness of a reaction when occurring in a closed space; reversibility; the necessity of excess reactants; the acceleration of a reaction by removal of products, etc.

III. The Relation of Williamson's Theory of Exchanges to the Proposed Hypothesis and Its Application to the Case of Double Elective Affinity

Already some sixteen years ago Alexander Williamson proposed an hypothesis concerning the nature of decomposition in his paper on the "Theory of Etherification," which is to some extent related to the one just presented. There he developed the view that "in an aggregate of molecules of every compound, there is an exchange constantly going on between the elements which are contained in it." Williamson's hypothesis has little to do with the theory of dissociation phenomena which I have developed in Section I, but is related to my method of explaining mass action and reciprocal affinity. This explanation is based on the assumption of the simultaneous occurrence of opposing reactions in keeping with [the operation of] simple and double elective affinities. These reactions may also be interpreted as *exchanges*, whence the similarity of both hypotheses. However, they also differ substantially on several points:

Firstly I do not assume that *every* compound undergoes a partial decomposition (exchange), but rather only some compounds – though perhaps a great many – and these only above a certain temperature limit (which, of course, in many cases may be so low that we are only aware of the compound when in a state of partial decomposition).

Secondly my hypothesis includes the essential assumption that, within certain temperature limits, *not all* molecules are subject to decomposition (exchange) *at the same time*.

Thirdly I do not base my opinions entirely on the "motion of atoms," but rather on differences in the *momentary states of* motion *of individual molecules* and view this as the basis for the possibility of simultaneously opposing reactions.

Fourthly I would like to assign the merit of greater universality to my hypothesis since all partial decompositions – even those which occur by heat alone without the intervention of another body (dissociation) – may be explained from the very same point of view, whereas I will now demonstrate that Williamson's hypothesis cannot explain this latter mode of decomposition and was never intended to do so.

I will review these points in reverse order and will begin with the fourth one, which, it seems to me, most easily illustrates the relation between both view points.

The following schemes give an overview of three groups of reaction, along with their counter reactions, on whose simultaneous occurrence the phenomena to be explained are based (9):

I. Partial decomposition by means of heat alone (dissociation):

$AB = A + B$ and $A + B = AB$.

II. Partial decomposition by means of so-called simple elective affinity:

AB + C = CB + A and CB + A = AB + C.

III. Partial decomposition by means of so-called double elective affinity (10):

AB + CD = AD + CB and AD + CB = AB + CD.

Williamson's hypothesis is restricted to the explanation of reactions II and III and does so by the simple assumption that atoms (or groups of atoms) A and C constantly change places. The ensuing state of equilibrium is a simple result of the number exchanges of A with B [*sic.* C] being equal to the number of exchanges of B [*sic.* C] with A. If we now try to apply this same manner of explanation to case I, it seems to work there as well. One simply needs to assume that the A within the compound is constantly interchanged with the A found in the free state. The state of equilibrium is thereby explained.

If the hypothesis is supposed to be correct for all three cases, it must not only explain the phenomenon of equilibrium, but also those phenomena which occur when the equilibrium is disturbed. These disturbances occur when:

1) One or more products of the reaction are removed.

2) The temperature is changed.

Experience shows that, when the equilibrium is disturbed by the removal of the products, the partial reaction changes into a complete [reaction] and the reciprocal reaction ceases to function. In the case of schemes II and III, this agrees with Williamson's hypothesis; as may be seen if we consider scheme II:

AB + C = CB + A

If we remove all of the free A or CB that is formed or both, then the reverse exchange of A in place of C is no longer possible, though the exchange of C in place of A in AB can still occur and must lead to completion of the reaction. Conversely, the removal of AB or C or both results in completion of the reciprocal reaction.

As with the above, so Williamson's hypothesis also completely works for the reactions in scheme III. *But it no longer works* as an explanation for the disturbance of the equilibrium in scheme I, for, if this equilibrium also depended only on exchange, it would not be clear how just the removal of A or B or both would give the results that are, in fact, observed. We have the scheme:

AB = A + B, A + B = AB

If, for example, we now remove all of the free A, the exchange with the bound A will stop. The same is true for B. Its removal could only result in a cessation of the reaction and not in its completion, which is, however, what actually occurs, as shown by experience.

This situation clearly occurs in the specific example that I used earlier to illustrate the phenomenon of dissociation. We heat calcium carbonate in a closed tube. Carbon dioxide is formed. If we keep the temperature fixed at a constant value, the amount of carbon dioxide will also stay constant. This state of equilibrium can now be explained by both hypotheses. According to the hypothesis of exchange, free carbon dioxide molecules constantly switch position with bound molecules, which are, in turn, set free. According to the other hypothesis, it is assumed that the number of released carbon dioxide molecules is equal to the number taken up by the quicklime per unit time, *although the absorbed [molecules] do not necessarily substitute for the released [molecules]*. Therefore, according to the first hypothesis, every single release is necessarily coupled to an uptake, whereas, according to the second hypothesis, each release is independent of any given uptake, though the total number of both is constrained by the requirement of equality.

This distinction seems to be negligible, but it immediately becomes crucial when we look at the following process. We direct air (or some other inert gas) through the tube and displace the carbon dioxide. Instantly fresh carbon dioxide is released. Now the first hypothesis is no longer sufficient because, in that case, one would need to assume that the air switches positions with the bound carbon dioxide, which is not the case. In contrast, the second hypothesis corresponds completely [to the facts], since, according to it, the combinations and decompositions are independent of one another [and] the first are easily reduced or eliminated by removal of the carbon dioxide, while the latter continue.

If one had caused the generation of carbon dioxide using [another] gas, capable of chemically combining with the chalk, then the difference between the two hypotheses would have remained undetected. Only the circumstance that the generation [of carbon dioxide] is also possible using an inert gas proves that only the second hypothesis can be correct.

One would reach the same conclusion on trying to explain the disturbance of the equilibrium caused by a change in temperature. According to the exchange hypothesis (11), the exchanges in cases II and III would become more frequent in one direction than in the opposite, until, as a result, the relative numbers of the different molecules had changed to such an extent that, once again, equal numbers of opposing exchanges are produced. From this point on, equilibrium would be established once more. [For these cases] the exchange hypothesis is sufficient. For case I it is not sufficient, as one may be convinced after brief consideration. This may again be demonstrated using the previous example. The fact that calcium carbonate releases more carbon dioxide upon increasing the temperature of a closed space can only be explained by the assumption that the number of detached molecules becomes greater than the number which are simultaneously absorbed. This is not possible using a simple exchange. If one wished to maintain this [mechanism], one would have to consider two processes side by side – the exchange and the decomposition. However, it is simpler to assume that the individual combinations and decompositions are, in general, independent of each other. Thus the concept of an exchange requiring a pairwise coupling of both processes may be abandoned.

One could restrict the exchange hypothesis to cases II and III, for which they were devised by Williamson, and use the second hypothesis to explain case I. However, it seems to me more expedient to extend these hypotheses until they apply equally to all three cases, and this is most easily accomplished if one replaces the narrow conception of exchange with the broader conception of simultaneous individual and independent decompositions and combinations.

More important than the difference discussed above is the one found in *point three*. Williamson assumes an alternating transfer of the molecules [*sic*. atoms] in opposite directions, and hence an opposite movement of the same, without stating a cause for how these opposite effects are brought about. I find this cause, as already stated many times, in the momentary differences in the states of motion of individual molecules, as assumed in the hypothesis of Clausius. I have already explained the reactions found in schemes I and II, now I will attempt to explain the transfer found in scheme III.

We have molecules of AB and CD in a given volume. Depending on whether they are gaseous or liquid, they move throughout this volume in a linear or an irregular, but progressive, direction (external motion). Furthermore, their components move relative to each other, but are bound to a common center of gravity (internal motion). If one does not change the temperature, the sum of the *vis viva* of both motions will remain constant. Even the sum of the *vis viva* of the external motion alone, like that for the internal motion, will remain constant, since Clausius has proven that they must be in a constant ratio to one another. However, the external motion, as well as the internal, must be very unevenly distributed among the individual molecules. Therefore we have the following limiting cases:

1) Molecules possessing the maximum external and internal motion.

2) Molecules possessing the minimum external and internal motion.

3) Molecules possessing the minimum external and maximum internal motion.

4) Molecules possessing the maximum external and minimum internal motion.

Between these limiting cases, there exists, of course, all possible intermediate cases. The maximum for the internal motion is determined by the magnitude of the affinity. We do not know how the magnitude for the external motions is limited – indeed, it seems to me that the existence of such a maximum is not yet proven. However, this does not affect our method of explanation.

Upon the collision of two different molecules, the external motions can be increased at expense of the internal, or the internal at expense of the external, or, as a limiting case, both may remain unchanged. Among the diverse results of such a collision, the following cases should be stressed:

1) Two molecules, whose external and internal motions are very large, meet in such a fashion that, in the next moment, the external motions are completely, or for the most part, converted into internal motions which exceed the upper limits in both molecules. As a consequence, a separation into four parts, A, B, C and D, occurs.

2) Two molecules, whose external and internal motions are very small, collide. Here it is possible that the resulting internal motions are not only too small to split both of the original molecules, but also to prevent their permanent combination. An aggregated ABCD molecule results.

3) Two molecules collide under such conditions that the resulting internal motion is too small to split the molecules, but large enough to prevent a permanent connection. Hence they fly apart like elastic spheres and AB and CD remain as AB and CD.

4) The molecules collide under such conditions that the interplay of the internal motions of the components of the transient double-molecule induce its splitting in a different direction. AB and CD collide and momentarily form ABCD. If the impact was – as we wish to assume in the simplest case, – linear and central, the whole system will continue to initially move in accordance with the redistribution of various quantities of motion, the lost external motion having been transformed into internal motion. Now it depends on the magnitude of the affinity of A, B, C and D for one another and, at the same time, on the previously existing internal motions of the components of AB and CD, as to whether the split due to the increased internal motions occurs in the direction of AB/CD or in direction of AC/BD. The larger the internal motions of the molecules prior to collision, the greater the preparation for the separation of A, B, C and D and the easier it is for a split in the direction AB/CD to occur. One can see that, in general, the best conditions [for a double decomposition] are in those given earlier under limiting case 4.

In this manner it becomes obvious that, in addition to the affinities, the mode of decomposition further depends on the state of motion, and that, consequently, even those reactions that are apparently opposed by affinity may occur (reciprocal reactions).

The first two of the four cases listed earlier require a larger difference in the states of motion of the individual molecules than do cases three and four. Hence it is highly likely that these are not fully achieved in many processes for which the difference is not large enough. This assumption may be made for all those reactions for which there is no basis for assuming the presence of the [product] molecules ABCD, A, B, C or D in addition to the molecules AB, AD, BC and CD. But it is also possible that one will find examples whose explanation makes this assumption necessary (12).

Now I come to the difference between the two hypotheses indicated in point 2. It is self-evident from the above. Although the collision of the molecules is random, they must, according to the principles of probability, result in regularity when the number of impacts becomes extremely large, such that the number of impacts resulting in decomposition always corresponds to the same fraction of the [total] number of impacts under the same circumstances. Therefore, in addition to those molecules that are decomposed (whose parts are exchanged), there will always be those that rebound without decomposition, which means, as I stated in point 3, that *not all of the molecules are being decomposed at the same time*.

Finally, in point 1, I have described as essential to my hypothesis the assumption that a partial decomposition (exchange) does not occur at every temperature. When one considers that, according to the theory of heat, absolutely no motion of the molecules exists at -273° C, it is also apparent that for a considerable number of degrees [above zero] the motion may be so small that it does not exceed the upper limit for internal motion and so induces no decomposition. For this reason there must be an upper temperature limit at which the reactions under consideration first begin. If, for a compound, this is situated higher than the temperature at which we are able to examine it, we will not be able to observe any hint of a decomposition (exchange), and in *this sense* I wish it to be known that Williamson's assumption that "in an aggregate of molecules of every compound, there is an exchange constantly going on between the elements which are contained in it," is restricted in the manner just described.

This also agrees with experience. As evidence, I will cite the same example which led Williamson to the discovery of his hypothesis, namely the formation of ether. This process divides into two reactions, each of which may be reversed. The first is given by the equation:

$C_2H_5OH + H_2SO_4 = (C_2H_5)HSO_4 + H_2O$

Alcohol + sulfuric acid = ethyl sulfuric acid + water

and the second by:

$C_2H_5OH + (C_2H_5)HSO_4 = H_2SO_4 + (C_2H_5)_2O$

Alcohol + ethyl sulfuric acid = sulfuric acid + ether

Both reactions show features that correspond to partial decomposition. In particular, both remain incomplete if one does not remove the products and they may also be reversed. A mixture of sulfuric acid and alcohol never forms so much ethyl sulfuric acid that some portion, not only of the alcohol but also of the sulfuric acid, does not remain unreacted. This is because the products formed – ethyl sulfuric acid and water – continuously give rise to the opposite reaction. These reciprocal reactions can become dominant if the proportions are favorable. It is known that ethyl sulfuric acid changes back to sulfuric acid and alcohol when boiled with water. This last reaction is reduced by removal of water (or ethyl sulfuric acid) (13) – hence, the less water added, the more ethyl sulfuric acid is formed initially.

By continuous removal of water and addition of alcohol the [first] reaction must go to completion in one direction. By addition of water and removal of alcohol it will go [to completion] in the other direction. At a certain ratio of the initial reagents, [the question of] whether the equilibrium between the opposing reactions will correspond to a greater or lesser degree of decomposition will depend on the temperature. Hence there must be a temperature value at which the reaction of the sulfuric acid with the alcohol has not yet begun, at which the internal motions of the molecules – even those in which it is at a maximum – is insufficient, even with support from affinity, to cause a reaction. It is still unknown just how low this temperature value is, but the circumstance that dilute sulfuric acid only forms ethyl sulfuric acid upon heating, suggests that it cannot be very low.

For the second reaction between the alcohol and the ethyl sulfuric acid the same relationship occurs. On reversal, ether and sulfuric acid result in ethyl sulfuric acid and alcohol. Hence even here, if the ether cannot be removed, the degree of conversion must remain fixed at equilibrium, where both opposing reactions occur side by side with the same frequency.

Now, if the water as well as the ether are continuously removed by distillation during production of the latter, both processes will go to completion in one direction, as in both the reaction favoring ether formation outweighs the reverse reaction. If both processes occurred at all temperatures, ether would form at all temperatures sufficient to remove the ether and water by distillation. But this does not happen because only the alcohol distills off below 126° C [at which temperature] the second reaction, at least, cannot have yet begun. This single example will serve for many additional examples that could be quoted in support of the statement that (partial) decomposition (exchange) is correlated with a certain temperature value. I believe that I have now sufficiently discussed the relationship between my proposed hypothesis and the exchange hypothesis of Williamson.

IV. Summary and Conclusions

The assumption that atoms are in a state of rest was first challenged by physicists. However, for quite some time their work attracted little attention and was nearly forgotten. As far as I know, Williamson was the first chemist who – independent of physical arguments and based on chemical facts alone – rejected the assumption of static atoms. His inspired theory of ether formation was accepted, but his simultaneous, and more important, presentation of his theory of the continuous exchange of elements remained almost unnoticed.

The epoch-making papers by Krönig, and especially those of Clausius, abolished the assumption of static atoms forever. Sooner or later the triumphant progress of the mechanical theory of heat had to attract the attention of chemists and invite attempts to apply the highly fruitful assumptions of this new theory to the explication of as yet unexplained chemical phenomena. The present work is such an attempt. Starting with the theory of evaporation proposed by Clausius, I first attempted an explanation of dissociation. Generalization of this approach allowed a transition to reciprocal reactions and the mass action effect. The results of my approach clearly show that the theory of gases as given by Krönig is insufficient and that the more elaborate theory of Clausius is quite indispensable.

It was of great interest to me that volume 101 of this journal contained a paper by Clausius [entitled]: "On the Electrical Conductivity of Electrolytes," in which the fact that very small currents can cause decomposition is explained by postulating that the parts have previously been in partial conversion. Here Clausius refers to Williamson's paper. It now seems to me that my method of explanation agrees even better with the theory of electrolysis. The increase in the conductivity of liquids with temperature may be related to their increasing dissociation. Those that do not conduct are unaffected by dissociation at the temperature in question. However, these are mere assumptions. In the near future, I will amplify this communication with some ideas concerning the constitution of mixtures and solutions, which are related to the above topic.

V. Addendum (14)

Only after completion of this contribution did I discover the critique of Deville's theory of dissociation by Dr. H. W. Schröder van der Kolk (15). Although I now believe that the most important objections which it raised have been refuted by the above arguments, in order to ensure a complete resolution of this interesting and important matter, I will allow myself, even at the risk of repetition, to add the following [remarks].

I completely agree with Schröder van der Kolk that the extensive measurements of flame temperatures by Deville are open to several objections. Likewise, I think his opinion that the temperature of the flame – even without the assumption of dissociation – should be lower than the calculated values is reasonable. Thus one argument in favor of the theory of dissociation is no longer applicable.

However, in spite of this objection, I have to retain the assumption of dissociation and the belief that there is a profound analogy between this and evaporation. I was led to this opinion independently and without knowing that Deville had already mentioned it earlier, for the reasons discussed above.

It appears to me that the disagreements between

Schröder van der Kolk, on the one hand, and Deville and myself, on the other, are focused on the following point: According to the former, it is solely the absorption of heat from the decomposition of the initial molecules which serves to "cool" (16) the neighboring molecules and thus accounts for the *delay in* the decomposition of *all of the* molecules (and which, for lack of time, also prevents it).

According to the opposing view, this retarding influence is certainly present and is sufficient as an explanation for many partial decompositions; but in addition to this retarding influence there is, for compounds undergoing dissociation, yet another cause, which, within certain temperature limits, not only delays the *complete* decomposition but altogether prevents it, however long the temperature is maintained. In opposition to this Schröder van der Kolk then raises a most important argument, which I will directly quote, while retaining only the most important parts:

> *It seems to me that this theory appears to contain an inner contradiction. Water vapor is decomposed at [temperature] T through simple heating. This decomposition gradually progresses and will be complete at constant temperature T provided that a sufficient amount of heat is supplied. This temperature T may change with the pressure, but, in any case, is always the same at the same pressure. At a lower temperature decomposition apparently cannot happen, otherwise it would not be T, but a lower decomposition temperature [that would correspond to the dissociation temperature]. Indeed, the author (Deville) says that in this case the decomposition is only partial; but if it occurs partially, then it must also be possible for it to become total as soon as the decomposition is viewed as a function of only the temperature, as is the case with Deville.*

This is the very same difficulty which I pointed out at the beginning of my contribution and which I think I have eliminated by the necessary assumption of unequal states of motion for the individual molecules.

According to the mechanical theory of heat, the temperature is proportional to the average *vis viva* of the molecules. If one transfers this concept of temperature to individual molecules, one could argue that the temperature of the individual molecules is unequal, although the parts of the body to which they belong have attained a mutual equilibrium of temperature. The temperature of the body is the average temperature of all its molecules.

The decomposition is now a result (function) of temperature, and hence it is now possible that, within certain limits of the average temperature of the body, it extends only to that portion of the molecules which have exceeded a certain temperature limit. The circumstance that the initial decomposition of a molecule depends only on its *internal* motions requires, in turn, that one distinguish between the internal and external temperature of the individual molecules. This has led me to not employ this extension of the term "temperature," not least because the phrase "internal and external motions" expresses the meaning much better than the phrase "internal and external temperature."

In resolving this *internal* contradiction of the theory of dissociation, it seems to us of greater importance to prove by experiment that partial dissociation, even at temperatures produced by sufficient heat input over long periods, does not proceed to complete dissociation (except in the cases presented by me e.g. by diffusion). Likewise, I consider this evidence as already provided by the often mentioned experiment with calcium carbonate, and hence it seems unnecessary for me to explore additional reasons for partial dissociation. Another proof are the so-called abnormal vapor densities[17] measured using the method of Gay-Lussac, which, as I have convinced myself by experiment, result in constant numbers with prolonged heating so long as the temperature of the vapor remains constant.

In the end Schröder van der Kolk expresses the view (page 507) that, based on the molecular theory of chemical compounds, it should be possible to develop a [theory of] partial decomposition related to mass action. I would be delighted if I have succeeded in this paper in making a contribution to the foundations of such a theory.

VI. References and Notes

1. I take this from the abstract of his paper "On Dissociation in Homogeneous Flames" in *Chem. Centralblatt,* **1865**, p. 662, since the original paper is not available to me.
2. This journal, Vol. 100, p. 353.
3. In time I will show that sulfuric acid may be dried with air just as one is accustomed to drying air with sulfuric acid.
4. Krönig already derived the principle of diffusion from his theory of gases (this journal, Vol. 99, p. 320). I briefly mention this because in the widely known monograph of Paul Beis on *The Nature of Heat*, page 150, it is erroneously stated that Krönig did not state this correlation.
5. Two things follow from this: Firstly, that the two methods of vapor density determination by Gay-Lussac and by Dumas should show different results under the same circumstances, since diffusion is impossible with the first, but possible with the second. Secondly, that with the second method, the resulting values would not only be dependent on the temperature, but also on the duration of the experiment. (See note 14).

6. *Bull. soc. chim.*, **1865** p. 90. The remark in question reads: "In fact one frequently finds that it appears to be the general state of affairs that, when a body is decomposed, the presence of the products of the decomposition exercises an influence on the progress of the reaction. There is a tendency to establish a chemical equilibrium between certain proportions of the original products [i.e. reactants] and the products of their decomposition. When in the course of time equilibrium is attained, the decomposition is arrested, etc ... A result which one may express in general terms using the specific case of ammonium chloride, etc..."

7. However, I will later show that, technically speaking, this example belongs to the case of double decomposition discussed later.

8. Gmelin, Vol. I, p. 118.

9. But it should not be said that this scheme includes all reactions requiring a similar explanation. If anything, more complicated ones can exist. The three cases listed are sufficient, since the more complicated ones may be referred back to them.

10. The following reactions could be considered as special instances of case III:

IIIa AB + CC = AC + CB and AC + CB = AB + CC

IIIb AA + BB = AB + AB and AB + AB = AA + BB

Scheme IIIa will be assumed to be the correct one for many reactions, for which scheme II appears to occur. The same goes for scheme IIIb, which can be assumed in place of the often occurring scheme I. For example, the instances cited by me in Part I [of this paper] as special examples of case II would come under IIIa, since, free hydrogen is considered to be HH rather than H.

11. Williamson did not mention the influence of temperature on the rate of exchange. However, it should behave as indicated.

12. For example, the development of so-called condensed compounds at high temperatures. This journal, Vol. 131.

13. Lieben assumed that, in order to remove the disturbing influence of the products of a reaction on its progress, one had to remove *all* of the resulting products. According to the proposed hypothesis, the removal of only one is necessary, as this is sufficient to make the reverse reaction impossible. This is in keeping with experience.

14. Supplement to the addendum. Since the molecules of gaseous bodies under increased pressure are closer together, they will collide more often. As a result of this, reactions based on partial decomposition reach an equilibrium or end faster than under otherwise identical conditions. It seems to me that the dissociation of *vapors* can progress further, before equilibrium is reached, at lower pressures than at higher [pressures], because the number of decompositions, which decreases for compounds in the first case and increases in the second, remain equally great. Hence, when determining the vapor density according to [the method of] Gay-Lussac, one will increase (although less severely) the [degree of] dissociation (and hence the error in the molecular [weight] determination) by a decrease in pressure, as well as by an increase in temperature, if the vapor is already in a state of dissociation, Only by decreasing the pressure at a temperature low enough that dissociation has *not yet occurred*, can one can avoid error when determining the density.

15. This journal, Vol. 129 p. 481.

16. I would substitute "hinders greater heating."

17. In particular, those leading to values that do not exhibit a simple relation to those that are calculated.

XVIII

Leopold Pfaundler and the Origins of the Kinetic Theory of Chemical Reactions

Both the historical development of the kinetic theory of matter and the mechanical theory of heat (1) have been extensively studied by the American historian, Stephen G. Brush, and are the subject of several detailed monographs (2, 3). In addition, Brush has also provided collections and translations of most of the key foundational documents (4-7). However, as with the case of available collections and translations of papers related to the foundations of thermodynamics, these collections are missing the first examples of the application of these fundamental concepts to the phenomena of chemical reactions and equilibrium. In the case of thermodynamics, this missing document was August Horstmann's seminal paper of 1873, "Theorie der Dissociation" (The Theory of Dissociation) (8), which has only recently been made available in English translation (9). In the case of the kinetic theory of matter and heat, this missing document is Leopold Pfaundler's 1867 paper "Beiträge zur chemische Statik" (A Contribution to Chemical Statics) (10), an English translation of which appeared in the previous issue of the *Bulletin* and for which this paper serves as an introductory commentary (11).

The Kinetic Theory of Matter and Heat

Since, as just indicated, both the history of the kinetic theory of matter and of the mechanical theory of heat are the subjects of detailed monographs, all that is required here is to briefly summarize their early historical development in order to provide a proper chronological context for Pfaundler's seminal paper of 1867.

With the revival of the atomic theory in the 17th-century, several writers, such as Francis Bacon and René Descartes, dropped occasional hints that heat might correspond to some kind of "intestine" motion of either the molecules or the underlying ether – a view later supported by both the famous cannon-boring experiment of Count Rumford (1798) (12) and ice rubbing experiment of Humphry Davy (1799) (13). However, the specific association of heat with the translational motions of molecules, rather than with just their vibrational and rotational motions, was due to the development of the kinetic theory of gases. Though its origins date back as far as the 18th century and the work of Daniel Bernoulli (1738) (14), and failed attempts were made to revive it in the first half of the 19th century by both John Herapath (1821, 1847) (15) and John Waterston (1846) (16), this theory did not attract widespread acceptance until the 1850s, when it was revived once more and developed by, among others, August Krönig (1856) (17) and Rudolf Clausius (1857) (18)[1] in Germany, and by James Joule (1851) (19) and James Clerk Maxwell (1860) (20) in England. Clausius referred to the new approach as the "mechanical theory of heat" and the British physicist, John Tyndall, captured its essence in the title which he gave to his popular lectures on the subject in 1862: *Heat Considered as a Mode of Motion* (21).

The reason for the significant time delay separating the work of Bernoulli from that of Krönig and for the failure of Rumford, Davy, Herapath and Waterson to stimulate a widespread acceptance of the kinetic theory of heat and matter in the late 18th and early 19th centuries, was, of course, due to the overriding success of the caloric theory (22) of heat championed by, among others, Joseph Black, Antoine Lavoisier, and Adair Crawford in the last half of the 18th century. This viewed heat as a conserved imponderable fluid, rather than as a form of molecular motion, and, in turn, fostered a static Newtonian model of the three states of matter in which solids, liquids and gases were viewed, not as differing in their degrees of intermolecular organization and freedom of motion, as they are today, but rather as fixed arrays which differed solely in terms of the distance between their statically equilibrated molecules (i.e., in terms of the sizes of their combined caloric envelopes).

In the opinion of Brush, it was the gradual recognition of the principle of the conservation of energy during the 1840s and the accompanying realization that it was not just the heat alone that was conserved in most processes, but rather the sum of the heat and work together, which undermined one of the key assumptions of the caloric model and which is largely responsible for the more favorable reception accorded the kinetic theory in the 1850s, as this approach allowed one to reduce the interconversion of work and heat to a concomitant interconversion of macroscopic motion versus molecular motion.

The realization that the mathematical development of the kinetic model in the cases of gases and liquids required the use of statistical concepts gradually evolved as well, beginning with the work of Clausius and Maxwell and culminating in the formal development of statistical mechanics by the Austrian physicist, Ludwig Boltzmann (23), and the American physicist, Josiah Willard Gibbs (24), near the end of the century.

In his paper of 1856 Krönig had assumed that each molecule possessed only translational motion. It was Clausius, in his elaboration of Krönig's work the following year, who first pointed out that polyatomic molecules could also possess internal rotational and vibrational motions as well and that, as a result, the various molecular collisions should result in a redistribution of the *vis viva* or kinetic energy among these various modes and thus lead to a spread or distribution of the various molecular velocities rather than to a fixed value. In other words, a given temperature would correspond, not to a fixed value of kinetic energy for the individual molecules, but rather to a fixed *average* value.

This statistical view was further elaborated by Clausius in 1858 with his introduction of the concept of mean free path (25) and by Maxwell in 1860 with the introduction of his famous velocity distribution function (20). As we will see, both the concept of the interconversion of translational energy with internal rotational and vibrational energies and the concept that each temperature corresponded to a characteristic energy distribution or average, rather than to a fixed value, would prove central to Pfaundler's application of the kinetic model to chemical reactions.

Figure 1. Rudolf Julius Emanuel Clausius (1822-1888).

Figure 2. Henri Etienne Sainte-Claire Deville (1818-1881).

The Origins of Pfaundler's Paper

It was the work of the German physicist, Rudolf Clausius (figure 1), that served as the inspiration for both Horstmann's paper of 1873 on the application of the second law of thermodynamics to chemical equilibrium and for Pfaundler's paper of 1867 on the application of the kinetic theory of heat and matter. In the case of Horstmann, it was Clausius' 1865 paper on the entropy function (26) which provided the necessary conceptual foundation, whereas in the case of Pfaundler it was Clausius' 1857 paper on the mechanical theory of heat (18). Thus in both cases roughly a decade separated the first enunciation of the underlying concepts in the physics literature and their first explicit application to chemical systems in the chemical literature.

Likewise, both Horstmann and Pfaundler relied primarily on the work of the French chemist, Henri Sainte-Claire Deville (figure 2), and his associates for information on the experimental behavior of equilibrium systems involving either solid or gaseous dissociation, of which the following reactions were typical:

$$\text{Heat} + CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g) \qquad [1]$$

$$\text{Heat} + NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g) \qquad [2]$$

$$\text{Heat} + PCl_5(s) \leftrightarrow PCl_3(g) + Cl_2(g) \qquad [3]$$

In his famous overview summary of his experimental work on dissociation (27), Deville had emphasized the analogy between the behavior of equilibria resulting from the thermal dissociation of solids and those resulting from the evaporation of pure liquids. Just as each temperature for the latter process corresponded to a certain characteristic vapor pressure, so each temperature for the former process corresponded to a fixed degree of dissociation. Just as the vapor pressure increased with increasing temperature and decreased with decreasing temperature, so did the degree of dissociation. And, finally, just as removal of vapor led to further evaporation of the liquid at constant temperature, whereas addition of vapor led to further condensation, so addition of one or more of the gaseous dissociation products at constant temperature led to deposition of the undissociated solid, whereas removal of one or more of the products led to its further dissociation. Indeed, since we know that Pfaundler studied physical chemistry in Paris in the years 1864-1865 and that, while there, attended Deville's lectures, he may well have heard of these analogies directly from Deville himself.

The epiphany came, however, only after Pfaundler had read Clausius' 1857 paper on "The Kind of Motion Which We Call Heat," in which Clausius applied his concepts of internal modes of molecular motion and of characteristic molecular velocity distributions at constant temperature to an explanation of evaporation. Pfaundler quickly put two and two together and was thus inspired (10):

> *... to investigate whether, as a consequence of the similarity between these two phenomena [i.e., dissociation and evaporation], an hypothesis, like that used by Clausius to explain evaporation, might also be useful in explaining dissociation.*

Kinetically Rationalizing Dissociation Reactions

Entitled "A Contribution to Chemical Statics," Pfaundler's paper was divided into three major parts, plus a conclusion and a lengthy addendum. In Part I he dealt with the application of the kinetic model to simple thermal dissociation reactions of the form:

$$\text{heat} + AB \leftrightarrow A + B \qquad [4]$$

beginning with the dissociation of solids and liquids, as originally studied by Deville and his associates, and then generalized the approach to include the dissociation of gases as well.

As already hinted in Section 2, both of these applications rested on two key assumptions:

1. Gaseous polyatomic molecules possess not only translational motion as a whole, but also internal rotational and vibrational motions, and the latter motions are also present in the liquid and solid states as well. Pfaundler referred to the former as "external motions" and to the latter as "internal motions," and further noted that there is a characteristic upper limit to the internal motions, that varies from one chemical species to another, and which, if exceeded, leads to bond cleavage and dissociation.

2. Because of intermolecular collisions not all molecules at a given temperature possess the same magnitude for their external and internal motions or *vis viva* (mv^2 – a quantity closely related to kinetic energy). Rather there is a continuous redistribution of these motions, leading not only to a variation in the magnitudes of each type but to an interchange between the magnitudes of the external and internal motions. In other words, a fixed temperature corresponds to a fixed average for the *vis viva* of the molecules and not to a constant value common to all.

Though both of these assumptions seem commonplace and unexceptional to the modern chemist, they were, prior to Pfaundler's paper, totally missing from the earlier chemical literature.

Pfaundler first applied these assumptions to the thermal dissociation of calcium carbonate or chalk, as shown above in equation 1. As the solid is gradually heated the internal motions of its molecules (in 1867 it was not known that $CaCO_3$ was a nonmolecular solid) gradually increase until a few of them exceed the upper limit required for dissociation and release gaseous CO_2 molecules into the space above the solid. The greater the temperature, the greater the number of chalk molecules that exceed the upper limit for internal motion, and the greater the degree of dissociation. However, the released CO_2 molecules are not only simultaneously colliding with one another, leading to a redistribution of their external and internal motions, but also with the surface of the chalk itself and, at each temperature, a certain fraction will have lost sufficient *vis viva* to recombine with the solid. Eventually the rates of dissociation and readsorption will become equal, leading to an equilibrium and to a characteristic dissociation pressure for the temperature in question.

Not only may this equilibrium be disturbed by altering the temperature, it may also be disturbed by removing CO_2 from the space above the solid by flushing it with a stream of air or some other nonreactive gas. By thus lowering the concentration of the CO_2 gas, the rate of absorption is lowered but not the rate of dissociation, which will continue until it replaces the displaced CO_2 and reestablishes the previous equilibrium (10):

Therefore the calcium carbonate evolves carbon dioxide in the air stream at the same temperature as it absorbs carbon dioxide in its absence. The calcium carbonate and carbon dioxide behave in the air stream in a manner similar to that of a hydrated substance that is being dried.

Extension of these concepts to the dissociation of a gaseous compound is straightforward.

Activated Complex Theory

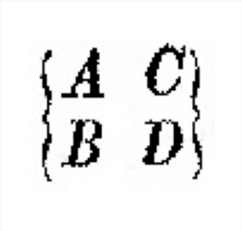
In Part II of his paper Pfaunder extended his theory beyond simple dissociation reactions to include gas-phase single-displacement reactions:

$$AB + C \leftrightarrow CB + A \qquad [5]$$

and, in so doing, also introduced the concept of a collision complex. Depending on how the energy of collision redistributed itself among the internal modes of motion of this complex, it could either decompose back into the original reactant molecules (thus giving rise to a nonreactive collision) or into an new set of product molecules (thus giving rise to a reactive collision). As pointed out by Lund many years ago (28), this concept anticipated in all but name our modern concept of an activated complex or transition state (10):

Let us examine a molecule of the substance AB, which, because of the high temperature, has already acquired sufficient motion of its components that it is close to decomposition, and which now encounters a molecule C. The external motion of both molecules is now completely or partially converted into internal motion by the impact. The result now depends on whether the affinity is or is not strong enough, given this enhanced internal motion, to keep all three bodies together. If not, then the components are repelled again, which means a part of the internal motion is once again converted to external motion. Apparently the mode of separation now depends on how the internal motion is distributed among the individual parts. If the internal motion of the original AB molecule was already very large prior to impact, and was further increased by the impact, then the cleavage of the transient ABC molecule to form A and BC is more likely than to form AB and C. Therefore, a certain definite portion of the AB molecules which collide with the C molecules will react according to the equation AB + C = A + BC. Here we have a dissociation process which is different from pure dissociation; but also equally different from a complete chemical decomposition in which all of the molecules are decomposed at once. The peculiarity of our process consist in the necessity of only partial decomposition.

Figure 3. Pfaunder's structure of the collision complex formed in the double displacement reaction $AB + CD \leftrightarrow AC + BD$.



These comments were then followed by a detailed analysis of the effects of mass action on this equilibrium in terms of changes in relative collision frequencies and the question of whether it was possible to drive the reaction to completion at constant temperature by simultaneously increasing the concentration of AB and removing product A or whether the reaction could be completely reversed by simultaneously removing AB and adding A.

In Part III of his paper, Pfaundler, in addition to addressing the issues discussed below in section 6, further extended his concept of a collision complex to include the case of gas-phase double-displacement reactions as well:

$$AB + CD \leftrightarrow AC + BD \qquad [6]$$

and also provided a drawing of the assumed collision complex itself (figure 3) (10):

The molecules collide under such conditions that the interplay of the internal motions of the components of the transient double-molecule induce its splitting in a different direction. AB and CD collide and momentarily form ABCD. If the impact was – as we wish to assume in the simplest case – linear and central, the whole system will continue to initially move in accordance with the redistribution of various quantities of motion, the lost external motion having been transformed into internal motion. Now it depends on the magnitude of the affinity of A, B, C and D for one another and, at the same time, on the previously existing internal motions of the components of AB and CD, as to whether the split due to the increased internal motions occurs in the direction of AB/CD or in the direction of AC/BD. The larger the internal motions of the molecules prior to collision, the greater the preparation for the separation of A, B, C and D and the easier it is for a split in the direction AB/CD to occur.

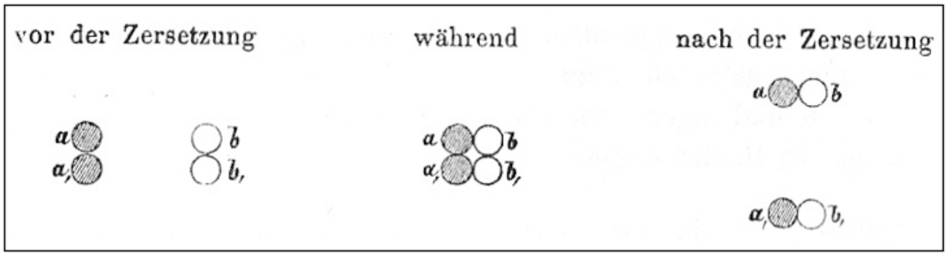


Figure 4. Kekulé's picture of a reaction complex leading to double displacement.

Pfaundler was not the first to suggest that displacement reactions involved the initial formation of some sort of transient complex. A particularly famous example (figure 4), often reproduced in histories of chemistry but not mentioned by Pfaundler himself, was given by the German chemist, August Kekulé (figure 5), in his famous paper (29) of 1858 on "The Constitution and Metamorphoses of Chemical Compounds and the Chemical Nature of Carbon" and later repeated in his equally famous textbook of 1861 (30). However, Kekulé envisioned both the formation and decomposition of this complex to be purely a function of competing forces of affinity in which molecular and atomic motions played no part whatsoever (29):

> *When two molecule react, they first attract each other by virtue of their chemical affinity, and align themselves next to each other. The affinities of the individual atoms then cause atoms which previously belonged to different molecules to come into intimate contact. For that reason, the group that was divided in one direction prior to reaction, now falls apart in another direction. On comparing the product and starting material, the decomposition can be conceived of as a mutual exchange.*

Interestingly, in a footnote, Kekulé further envisioned that this mechanism could also explain mass action and the phenomenon of catalysis, again sans any reference to molecular collisions or various internal molecular motions (29):

> *One may consider that during the approach of the molecules to each other, the connection between the atoms is already loosened, because part of the force of affinity becomes bound by the atoms of the other molecule, until at last the previously united atoms lose their connection together, and the newly formed molecules separate. On this assumption, the conception supplies a certain representation of mass action and catalysis. For in the same manner as a molecule of one substances acts on a molecule of another substance, so also all other molecules in the vicinity will act: they loosen the connection among the atoms. The closest molecule acts most powerfully and suffers double decomposition with the molecule of the other substance. Those further away aid it; while they loosen the connection of the atoms in the other molecule, they suffer the same change. As soon, however, as the decomposition has taken place they regain their earlier state. Mass action and catalysis differ, according to this conception, only in that in the case of the former the catalyzing molecule is of the same kind as one of those decomposing, while in catalysis it is different in substance from both.*

All of this is a far cry from Pfaundler's later kinetic- molecular rationale. Not only is there no mention of molecular motions and collision frequencies, there is also no mention of reversible reactions and equilibrium, all of which, as brilliantly elaborated by Pfaundler, would require an interplay between both affinity

Figure 5. Friedrich August Kekulé (1829-1896).

Figure 6. Alexander William Williamson (1824-1904).

forces and molecular motions for their complete rationalization (10):

In this manner it becomes obvious that, in addition to the affinities, the mode of decomposition further depends on the state of motion, and that, consequently, even those reactions that are apparently opposed by affinity may occur (reciprocal reactions).

Relationship to the Exchange Theory of Williamson

In addition to his explication of the collision complex for a double-displacement reaction, in Part III of his paper, Pfaundler also took great care to explain the relationship between his newer kinetic theory of mass action and an earlier kinetic theory of chemical reactions first proposed by the British chemist, Alexander Williamson (figure 6) in a series of papers and notes published in the years 1850-1851 (31). In these publications Williamson had suggested that the analogous parts (whether atoms or radicals) of neighboring molecules were continuously exchanging places with one another at a rate that varied inversely with their bond strengths. In a pure substance, AB, all of the neighbors were identical and the system looked exactly the same before and after the exchange of A and B among the neighbors. However, in a binary mixture of two different molecules, AB and CD, the fraction of the exchanges producing AD and CB rather than reproducing AB and CD would obviously increase as more and more of the molecules adjacent to a given AB molecule corresponded to CD rather than AB. In other words, the amount of AD and CB formed would increase as the concentration of CD was increased and vice versa as the amount of AB was increased.

From this summary it should be apparent that, while Williamson's mechanism, unlike that later given by Kekulé, did indeed invoke a limited kind of molecular motion (atom or radical exchange between nearest neighbors) and was able to explain mass action without recourse to changes in stoichiometry, it was, in common with Kekulé's later attempt, also totally lacking the concepts of both collision frequency and threshold energies which formed the centerpieces of Pfaundler's approach and thus had little in common with either the mechanical theory of heat or the kinetic theory of gases then coming into vogue.

Pfaundler took great trouble to explain the differences between Williamson's exchange theory of chemical reactions and his own kinetic-molecular collision theory and clearly demonstrated that the former was inconsistent with the experimental facts in a number of instances. Indeed, Williamson had originally presented his theory of chemical reactions in connection with his work on the synthesis of ethers and, to drive home his point, Pfaundler presented a detailed reinterpretation of the acid catalyzed synthesis of ethers from alcohols in terms of his own collision theory of chemical reactions and equilibrium. However, in the end this effort was largely wasted on his fellow chemists. As we will see in Section 9, later writers would often misrepresent Pfaundler's work as a mere elaboration of Williamson's hypothesis, and most histories of chemistry would all but ignore Pfaundler, while continuing to incorrectly credit Williamson as the originator of our current kinetic-molecular theory of chemical reactions.

Conclusion and Addendum

In his brief conclusion (labelled Part IV in the translation), Pfaundler once more credited Clausius with having provided the key ingredients underlying his own kinetic theory of chemical reactions via both Clausius' initial application of the kinetic-molecular hypothesis to the process of evaporation and his elaboration of Krönig's earlier kinetic theory of gases via the added assumption that polyatomic molecules could possess internal as well as external modes of motion. This was followed by mention of an 1857 paper by Clausius (32) in which he foreshadowed Arrhenius's later theory of ionic dissociation via the application of the kinetic-molecular hypothesis to composition of electrolyte solutions, leading to the conclusion that they contained a small equilibrium population of dissociated ions and thus explaining why they conducted electricity even at low values of the applied voltage.

Pfaundler seems to have been under the false impression that Clausius had based his discussion of this subject on Williamson's exchange theory and promised to write a future paper in which he would instead reinterpret Clausius' conclusions in terms of the kinetic-molecular theory, as well as write several future papers applying the theory to various other aspects of solutions and mixtures in general. As it turned out, Clausius' mention of Williamson's theory was only incidental and, as he had already given a proper kinetic-molecular rationale of electrolyte solutions in the paper of 1857, Pfaundler's projected paper on this subject never appeared, although, as also promised, he did later published a paper applying his theory to such miscellaneous, and apparently mysterious, subjects as supersaturated and supercooled solutions, explosions, and the crystallization of amorphous solids (33). In addition, he also published several later accounts of his general theory, the most famous of which applied the Darwinian metaphor of "The Struggle for Existence" to the competition between the various molecular components of an equilibrium mixture (34-35).

The addendum to Pfaundler paper was originally inserted between Parts I and II but in the translation has been transferred to the end of the paper and labelled Part V. It deals with a criticism of the some of the work of Henri Sainte-Claire Deville on dissociation by a physicist by the name of H. W. Schröder van der Kolk, much of which was rendered moot by Pfaundler's kinetic-molecular interpretation of the dissociation process and is now of little or no interest to the modern reader (36).

Who was Pfaundler?

Leopold Pfaundler (figures 7 and 8) was born on 14 February 1839 in Innsbruck, Austria, the son of a local advocate and Professor of Law at the University of Innsbruck (37). After attending the local Volkschule and Gymnasium, Pfaundler entered the University of Innsbruck in 1857, where he studied organic chemistry under Professor Heinrich Hlasiwetz, while also attending lectures in physics and mathematics. In 1859 his university studies were interrupted by military service in the Austro-Sardinian War, also known as the Second War of Italian Independence, followed in 1861 by a semester in Liebig's laboratory at the University of Munich and receipt of a doctorate from the University of Innsbruck.

Following three years as an assistant in Hlasiwetz's laboratory, Pfaundler, as already noted, spent the years 1864-1865 in Paris studying physical chemistry, where he worked in the laboratories of Wurtz and Regnault, and also attended lectures by Deville and Berthelot. In 1866 he became a Privatdozent in physical chemistry at Innsbruck, though once again his academic career was interrupted by military service, this time in the Third War of Italian Independence of 1866. The next year, at age 28, he published his seminal paper on the application of the kinetic theory of matter and heat to chemical reactions and was appointed as Professor of Physics at Innsbruck. Here he remained until 1891, when he succeeded Ludwig Boltzmann as Professor of Physics at the University of Graz. In 1910 he became Professor Emeritus at Graz and was also ennobled by the emperor, receiving the title of Pfaundler von Hadermur.

Figure 7. Leopold Pfaundler (1839-1920).

Like his contemporary – the German physical chemist, Wilhelm Ostwald – Pfaundler was highly eclectic in his scientific interests and often wrote on subjects having broader cultural and social implications. His earliest publications dealt not only with botanical and organic chemistry, as might be anticipated from his association with Hlasiwetz, but also with geodesic measurements – an interest which developed during his military service. His seminal paper of 1867 and several subsequent contributions dealing with the application of the kinetic theory to the phenomena of solutions and crystallization were the obvious result of his study of physical chemistry in Paris during the early 1860s. Because of the poor condition of the physical laboratories at both Innsbruck and Graz, Pfaunder began, starting in the mid 1870s, to increasingly focus on teaching and the writing of popular scientific articles, rather than on laboratory research.

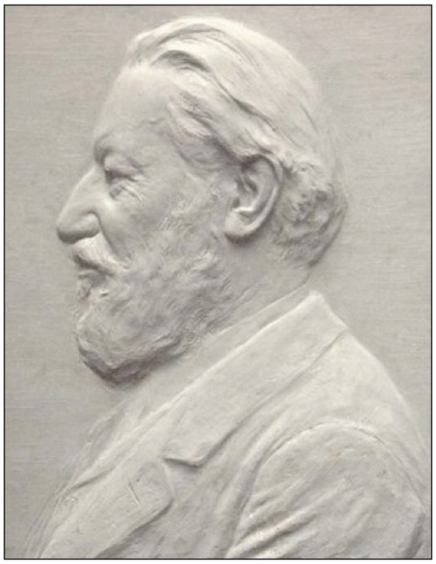


Figure 8. Memorial bas relief of Pfaundler at the University of Innsbruck.

Known for his excellent lecture demonstrations – many of which were of his own design (see figure 9) – and his clear delivery, he was also increasingly in demand as a popular lecturer.

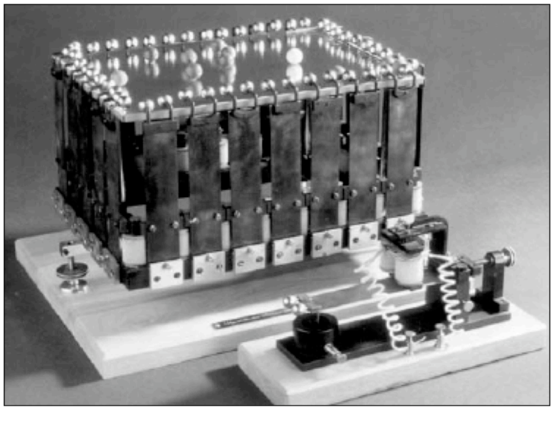
After his move into the field of physics, his work often focused on the development of new instrumentation, much of it connected with the teaching of physics, including the first demonstration of a direct current electrical generator (1870) and of a working telephone (1877). Kipnis estimates that Pfaundler published more than 110 articles and roughly 10 books and pamphlets during his career, including several editions (1877, 1886, 1906) of Müller-Poulett's textbook *Lehrbuch der Physik und Meteorologie* (38), which he used as a text in his physics lectures, and his own popular, *Die Physik des täglichen Leben* (1904) (39).

Pfaundler was active in several scientific societies and also served as Rector of the University of Innsbruck in 1880. He was an avid mountain climber and photographer of mountain landscapes, for which he received a silver medal at the 1901 International Photographic Exhibition, as well as an early enthusiast of the Japanese game of *Go* on which he published a book in 1908. Other interests included ecology and the carrying capacity of the earth and advocacy of an artificial international language for use in the scientific literature. Indeed, in 1914 he published a photographic lexicon in Ido, a simplified version of Esperanto. He died in Graz in May of 1920 at age 81.

The Fate of Pfaundler's Work

Shortly after its publication, Pfaundler's paper came to the attention of the German thermochemist, Alexander Naumann, who quoted it extensively in a review on dissociation phenomena which he wrote for Liebig's *Annalen* later the same year (40). In 1868 August Horstmann attempted to quantify Pfaundler's qualitative arguments by using a probability distribution to calculate the change in the density (and hence the degree of dissociation) of various vapors as a function of temperature (41). By 1873, however, Horstmann had become disillusioned with the kinetic approach – in large part because he felt that it failed to explain why pure solids did not exert a mass action effect (8). This criticism was repeated by Pattison Muir (42) in 1884 and again, in greater detail, by the French chemist, Pierre Duhem (43), in 1898, who triumphantly concluded that failure to resolve this issue meant that a theory of "chemical statics based on the kinetic hypothesis is thus condemned." Instead, both Horstmann and Duhem came to favor a purely thermodynamic approach based on either the maximization of the entropy function or the minimization of the Gibbs free-energy. However, it wasn't until Horstmann repeated his criticism in 1876 (44) that it finally came to Pfaundler's attention and he published a rejoinder (45), though the true reason for the apparent lack of a mass action effect for solids – namely that their kinetic influence depended on the number of collisions per unit area rather than per total area – seems to have eluded him.

In this regard, it is interesting to note that most accounts of the history of the kinetic theory of matter are written from the standpoint of the physicist[2,3] and tend to emphasize the successes of the theory in rationalizing not only the ideal gas law and Graham's law of diffusion, but also in making the nonintutitive prediction that the viscosity of gases should be independent of density and should increase, rather than decrease,



A vibrating bead plate used to illustrate the kinetic theory of the three states of matter designed by Pfaundler for use as a lecture demonstration while at the University of Gratz, circa 1903.

with temperature. The fact that a significant segment of the chemical community rejected the theory because of its mistaken belief that it could not adequately rationalize the absence of a mass action effect for solids is never mentioned. Even more interesting is the fact that this same argument over the relative correctness of kinetic versus purely thermodynamic rationales continues to persist in the current chemical literature, particularly with respect to the rationalization of Raoult's law, and involves the same error of failing to distinguish between collisions per unit area versus per total area (46).

The first references to Pfaundler's work in the monograph literature do not appear until roughly 15 years after the publication of his paper. In 1882 Naumann repeated much of what he had said in his review of 1868 in his book, *Lehr- und Handbuch der Thermochemie* (47), and also added a diagram of a probability distribution similar to that used by Horstmann. This book, in turn, served as the stimulus for the detailed, albeit somewhat confused, account of Pfaundler's views which appeared in the textbook of theoretical chemistry published by the British chemist, M. M. Pattison Muir, in 1884 (42), as well as for the briefer summary in his subsequent, *A Textbook of Thermal Chemistry*, which was published the following year (48). Pfaundler was also mentioned by van't Hoff in the introduction to the first edition of his *Études de dynamique chimique* of 1884 (49), where he is ironically credited with being the first to show that chemical equilibrium was a result of the equalization of the velocities of the forward and reverse reactions – ironic because most historians incorrectly attribute this concept to van't Hoff instead. In fact, it had already been proposed, not only by Pfaundler, but by Williamson (1850), Malaguti (1857) and by Guldberg and Waage (1867) many years earlier.

Interestingly there appears to be no mention of Pfaundler in the 1884 edition of Lothar Meyer's *Die modernen Theorien der Chemie*, though it contains a detailed discussion of thermal dissociation reactions and the mass action effect, nor is there any mention in Meyer's shorter *Grundzüge der theoretischen Chemie* of 1890 (50). Continuing into the 1890s, a single-sentence mention is found in Nernst's 1893 text, *Theoretische Chemie von Standpunkte der Avogadro'schen Regel und der Thermodynamik* (51), where it is implied that Pfaundler had simply amplified Williamson's original exchange theory. Likewise, though several aspects of Pfaunder's various publications are mentioned in Ostwald's massive, multi-volume, *Lehrbuch der allgemeinen Chemie* (52), those sections dealing with his applications of the kinetic theory to chemical reactions are generally highly critical and once again repeat the argument that the kinetic model is unable to account for the absence of a mass action effect for solids. The same is true of Ostwald's more popular textbook, *Grundriss der Allgemeinen Chemie* (53). Though Pfaundler's theory is discussed in the 1890 edition, where it is once again criticized, all references to both Pfaundler and the kinetic molecular theory of equilibrium are missing from the 4th edition of 1908.

Following the trend set by Ostwald, all mention of Pfaundler's various contributions appears to have disappeared from the contemporary chemical literature by the second decade of the 20th century. Thus no mention of him is to be found in the papers by Trautz (1916) (54) and Lewis (1918) (55), which laid the foundations of our current collision model of chemical kinetics, nor in the first detailed book-length treatment of the collision model – C. N. Hinshelwood's 1926 monograph, *The Kinetics of Chemical Change in Gaseous Systems* (56). Nor is he mentioned in the early literature dealing with absolute rate theory (57), though his concept of a critical collision complex is a direct qualitative anticipation of the modern concept of an activated complex, as pointed out earlier by Lund (28).

A somewhat similar scenario played out in the history of chemistry literature. No mention of Pfaundler is to be found in early 20th-century British histories of chemistry, such as those by Thorpe (1909), Pattison Muir (1909), and Hilditch (1911), though he is briefly mentioned in several early German histories, such as those by Ernst Meyer (1889) (58), Albert Ladenburg (1900) (59), and Richard Meyer (1922) (60). However these brief mentions, with the exception of Ladenberg, uniformly failed to properly describe the nature and significance of his contribution. Thus, like Nernst, Ernst Meyer also implied that Pfaundler had simply amplified Williamson's original exchange theory, and, in the case of Richard Meyer, only Pfaundler's early work with Hlasiwetz on the organic chemistry of plant materials is mentioned.

The same is largely true as we move into the 1930s, where the standard histories by Moore (1931, 1939) and Partington (1937) fail to mention him, though he is briefly mentioned in the short history of 19th-century chemistry by Findlay (1938) (68), where, following van't Hoff's earlier error, he is again given credit for being the first to show that chemical equilibrium was dynamic rather than static. This pattern of neglect and misrepresentation continued throughout the 1950s and 1960s, where again there is no mention in the standard histories by Farber (1952, 1964), Leicester (1956) and Ihde (1964), though he is discussed in Partington's massive four-volume reference work (1964) (62). More recent histories, such as those by Brock (1992) and by Fruton (2002), have continued this pattern, the sole exception being the short history by Hudson (1992 (63)), which devotes a single sentence to him.

Thus we see that by the early decades of the 20th century Pfaundler's work was all but forgotten. Most histories of chemistry continue to incorrectly attribute the first application of the kinetic theory to chemical reactions to Williamson rather than Pfaundler and most modern textbooks and monographs on chemical kinetics begin their somewhat perfunctory historical introductions with the Arrhenius equation of 1889 rather than with Pfaundler's paper of 1867 – despite the fact that Pfaundler was the first to rationalize the law of mass action in terms of collision frequencies and anticipated significant aspects of both the collision theory and transition-state theories of chemical kinetics via his concepts of critical threshold energies and collision complexes.

The reasons for this neglect are complex. Certainly the strong bias towards purely phenomenological models based on classical thermodynamics shown by such influential physical chemists as Ostwald and Duhem and by such physicists as Ernst Mach, with their concomitant undervaluation of the kinetic-molecular approach, played an important role in the gradual marginalization of Pfaundler's work as the 19th century drew to a close. Likewise, Pfaundler's progressive career move from chemistry into physics may have also contributed to his equally progressive disappearance, not only from the contemporary chemical community, but from the contemporary chemical literature as well. And, finally, the fact that Pfaundler's approach was essentially qualitative, rather than quantitative, meant that his paper was ultimately equally unsatisfying to both the chemical and physical communities. Its use of statistical arguments, even in a qualitative form, was foreign to most chemists raised to think almost exclusively in terms of static molecular structures and semi-anthropomorphic affinity concepts, whereas its purely qualitative treatment made it largely irrelevant to those physicists concerned with developing ever more sophisticated mathematical formulations of the kinetic theory of gases.

There is some indication that this pattern of neglect is slowly changing. Though the 1968 appreciation by Lund (68) remains, to the best of my knowledge, the only English-language tribute to Pfaundler's work, an analysis, in German, of his contributions has more recently appeared in Berger's (64) 1997 study of the impact of the mechanical theory of heat on the study of chemical reactions. Likewise, though the Canadian kineticist, K. J. Laider, failed to mention Pfaundler in his 1967 collection of readings in the history of kinetics (65), he did include a short summary in the historical appendix to the 3rd edition (1987) of his well-known textbook of chemical kinetics[66] and also repeated that summary, which was based largely on Partington, in his 1993 history of physical chemistry (67). Ironically, however, neither of these accounts mentions Pfaundler's anticipation of the activated complex concept, though this is a subject on which Laidler was an expert, having coauthored the first monographic treatment of absolute rate theory in 1943 (57, 68). On the other hand, there is apparently no mention of Pfaundler in the 1993 history of chemical kinetics by Kritsman *et al* (69).

References and Notes

1. The historical literature generally makes a distinction between the mechanical theory of heat and the kinetic theory of gases, though these two subjects are intimately interconnected, as are the less mathematically developed kinetic theories of liquids and solids. We will use the expression 'the kinetic theory of matter and heat" to subsume all four of these topics, though some authors prefer the expression "the statistical theory of matter" instead.

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Publication History

Published in *Bull. Hist. Chem.,* ***2012****, 37(1), 29-41*.

Update

I have only recently (2015) become aware of the 1977 article by H. A. M. Snelders ("Dissociation, Darwinism and Entropy," *Janus*, **1977**, *64*, 51-75) which also discusses Pfaundler's kinetic treatment of dissociation reactions and the use of Darwinian metaphors in the 19th century chemical literature.

XIX

Ask the Historian

Faraday's Laws or Faraday's Law?

Question

I have noticed that some textbooks refer to Faraday's laws of electrolysis whereas others refer just to Faraday's law. Which is correct and why?

James Bohning
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Answer

In sharp contrast to the approach taken in earlier columns, this question is best answered mathematically, rather than historically, by first providing a rigorous derivation of Faraday's law(s) using the notational system introduced by the Belgian physicist, Théophile De Donder, (1872-1957), in the 1920s (1). Thus, for a generalized chemical reaction:

$$aA + bB \rightarrow cC + dD \qquad [1]$$

the change in the amount or extent of reaction, $d\xi$, measured in units of moles of reaction events, is defined as the change in the moles, dn_s, of any of the various species, s, in the reaction, weighted by its stoichiometric coefficient, ν_s, in the balanced equation:

$$d\xi = dn_s/\nu_s = dn_A/a = dn_B/b = dn_C/c = dn_D/d \qquad [2]$$

where ν_s is assumed to have the units of moles of species s per mole of reaction and to be inherently negative for reactants and inherently positive for products. Using these conventions, De Donder was also able to express the rate of a reaction in terms of the change in its extent of reaction per unit time (2):

$$d\xi/dt = (dn_s/dt)/\nu_s \qquad [3]$$

Applying this notation to the equation for a typical electrochemical reduction:

$$\nu_o\mathrm{Ox} + \nu_e\mathrm{e}^- \rightarrow \nu_r\mathrm{Red} \qquad [4]$$

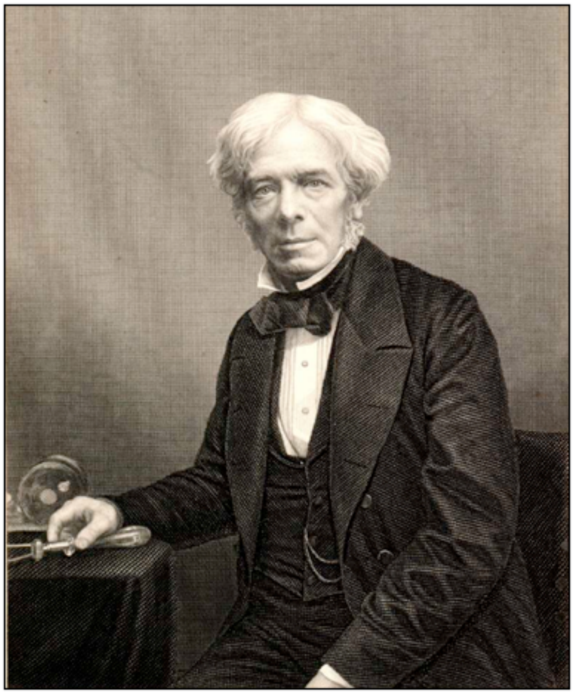

Figure 1. Michael Faraday (1791-1867).

we can express its rate of reaction, $d\xi/dt$, in terms of either the weighted change in the moles of electrons consumed per unit time, $(dn_e/dt)/\nu_e$, or the weighted change in the moles of any one of the various chemical species generated or consumed per unit time $(dn_s/dt)/\nu_s$:

$$(dn_e/dt)/\nu_e = (dn_s/dt)/\nu_s \qquad [5]$$

Multiplying both sides of this equation by Faraday's constant, F, having the units of coulombs per mole electrons, and using the fact that the product, Fdn_e, is equal to the change in the number of coulombs, dQ, and its time derivative, dQ/dt, is, in turn, equal to the electric current, i, gives us:

$$F(dn_e/dt)/\nu_e = (dQ_e/dt)/\nu_e = i/\nu_e = F(dn_s/dt)/\nu_s \qquad [6]$$

Regrouping the terms and defining the ratio (ν_e/ν_s) as z_s, with the units of moles of electrons per mole of species s, we obtain the differential form of Faraday's law:

$$idt = (\nu_e/\nu_s)Fdn_s = z_sFdn_s \qquad [7]$$

In an introductory chemistry course we usually further assume that the current, i, is constant over time, thus allowing us to use a simple integrated form of equation 7 instead:

$$it = z_sFn_s \qquad [8]$$

in which the two most important electrical variables (i and t) are segregated on the left and the two most important chemical variables (z_s and n_s) are segregated the right.

Textbooks have traditionally summarized Faraday's original work on electrolysis, which dates from the 1830s, in the form of two verbal statements known collectively as Faraday's laws of electrolysis (3):

a. The mass of any substance deposited or dissolved is proportional to the absolute quantity of electricity that passes through the cell.

b. The masses of different substances deposited or dissolved by the same quantity of electricity are proportional to their electrochemical equivalent weights.

It should noted that, although these textbook statements accurately summarize his results, Faraday himself never clearly distinguished between these two statements but rather combined them into a single verbal law which he called the "doctrine of definite electrochemical action" (4):

... the chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes ... the results obtained for any one substance do not merely agree among themselves, but also with those obtained from other substances, the whole combining together into one series of definite electrochemical actions.

By the term "definite" Faraday meant that the results were in keeping with the law of definite proportions or equivalents.

In order to recover these two laws from equation 8, we need to make use of the fact that the moles, n_s, of species s is equal to its mass, m_s, divided by its molar weight MW_s, which, upon substitution into equation 8, gives the result:

$$it = z_sF(m_s/MW_s) \qquad [9]$$

Solving this for m_s and recognizing both that the terms in parentheses on the right side of the resulting equation are a constant, k_s, for a given species and that the it term is equal to the total charge Q, we obtain the mathematical equivalent of Faraday's first law of electrolysis:

$$m_s = (MW_s/z_sF)it \quad \text{or} \quad m_s = k_sQ \qquad [10]$$

Regrouping the terms again and recognizing that MW_s/z_s for a given species, s is equal to its electrochemical equivalent weight, EW_s, we obtain, provided that Q is kept constant, the mathematical equivalent of Faraday's second law:

$$m_s = (Q/F)(MW_s/z_s) \quad \text{or} \quad m_s = k'(EW_s)_Q \qquad [11]$$

Based on these derivations, we can draw a number of important conclusions:

1. Since the two traditional verbal laws can be combined into a single mathematical equation (equation 8), it is more appropriate to talk of Faraday's law rather than Faraday's laws (5).

2. As demonstrated by the Italian chemist, Carlo Matteucci (1811-1868), in 1839, the relationship embodied in equation 8 is equally applicable to both an electrolysis cell and to a voltaic cell (in which case it correlates the current generated by the cell with the amount of reaction within the cell, rather than the amount reaction in the cell with the applied current) (6). Hence, it is no longer appropriate to talk of Faraday's law of electrolysis. Rather it should be called, following Faraday's original suggestion, Faraday's law of electrochemical action, in which the concluding qualifier is necessary in order to distinguish it from "Faraday's law of magnetic induction," as used in the field of electromagnetism.

3. Our derivation clearly shows that, in contrast to the Nernst equation, which is thermodynamic in nature, Faraday's law of electrochemical action is kinetic in nature (7).

Though I was taught equation 8 as an undergraduate, I was rather surprised to recently discover that the author of the Freshman textbook used at Cincinnati seems to be unaware of it and that the entire subject is essentially missing from the textbook currently being used in our undergraduate physical chemistry course. A quick review of additional Freshman and physical chemistry textbooks yielded similar results. In many cases only the verbal equivalent of the first law was given or a series of special-case relationships similar to equations 10 and 11, thus suggesting that it is time that we finally update our textbook coverage of this subject.

References and Notes

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Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu

Publication History

First published in *J. Chem. Educ.,* **2012**, *89,* 1208-1209.

XX

Notes from the Oesper Collections

The Parr Calorimeter

The use of either a water or an ice calorimeter to measure the heats of chemical reactions and phase changes is a laboratory technique that dates back to the late 18th century and the work of Joseph Black and Adair Crawford in Scotland and of Antoine Lavoisier and Pierre Laplace in France. Among its most notable practitioners in the 19th century were the Russian chemist, Germain Hess, the French team of Pierre Favre and Johann Silbermann, and the Irish chemist, Thomas Andrews, in the first half of the century, followed by the Danish chemist, Julius Thomsen, and the French chemist, Marcellin Berthelot, in the second half (1).

Inspection of surviving examples of 20th-century American-made calorimeters quickly reveals that the vast majority correspond to so-called "Parr Calorimeters" and were manufactured by The Standard Calorimeter Company of East Moline, Illinois (figure 1), where the "Parr" in question refers to the American chemist, Samuel Wilson Parr (figure 2), who was both the company's founder and its first president.

Parr was born on 21 January 1857 in Granville, Illinois and educated at the University of Illinois, from which he received a B.S. degree in 1884. This was followed by a year of graduate work at Cornell University and an M.S. degree in 1885. That same year Parr was appointed as Professor of General Science at Illinois College in Jacksonville, Illinois, followed six years later by his appointment in 1891 as Professor of Applied Chemistry at the University of Illinois at Urbana-Champaign, where he would remain until his retirement in 1926 (2).

Figure 1. Label from an early Parr calorimeter, c. 1912 (Jensen-Thomas Apparatus Collection).

Figure 2. Samuel Wilson Parr (1857-1931).

As implied by his title, Parr's primary teaching responsibility at Urbana involved the training of industrial chemists and he is widely considered to be the founder of the University of Illinois Chemical Engineering Program, which was first formally listed as such in the university catalog for the 1901-1902 academic year. His research speciality was the evaluation of fuels and especially the scientific development and exploitation of the coal fields of Southern Illinois – a topic on which he published numerous books and monographs (3).

Whereas many of the chemists listed earlier were attracted to calorimetry for its theoretical importance as a possible means for quantifying the concept of

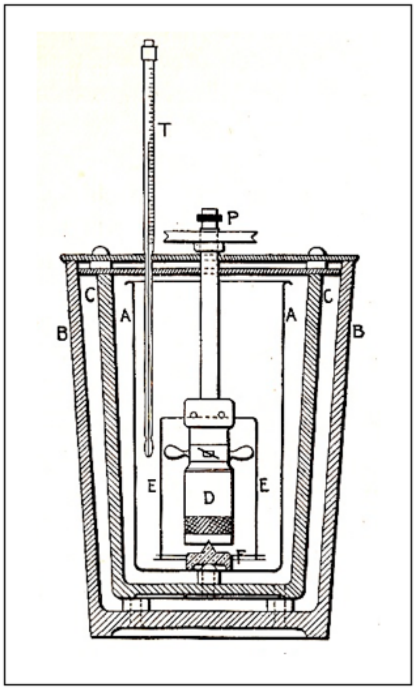

Figure 3. Diagram of the interior of Parr's original peroxide calorimeter, c. 1900.

chemical affinity, Parr's interest in the field was purely practical and centered on its use in quantifying the heating efficiency of coal and other fuels and, more particularly, on his proposal in 1899 of a new method of measuring coal's heat of combustion using a bomb calorimeter in which, rather than directly oxidizing the coal to carbon dioxide in an atmosphere of pure dioxygen gas, it was instead indirectly oxidized by mixing the powdered coal with solid sodium peroxide and initiating the reaction by means of a potassium chlorate accelerant and an electrical ignition source (4, 5). Thus rather than:

$$C(s) + O_2(g) \rightarrow CO_2(g) + \text{heat} \qquad [1]$$

the primary reaction presumably became:

$$C(s) + 2Na_2(O_2)(s) \rightarrow Na_2(CO_3)(s) + Na_2O(s) + \text{heat} \qquad [2]$$

in which the absence of both reactant and product gases made the method both easier to perform in the laboratory and less susceptible to potential explosions.

In order to provide a commercial source of calorimeters especially tailored for use with his new peroxide method, Parr founded the Standard Calorimeter Company in Champaign, Illinois, in 1899, eventually moving it to East Moline, Illinois, in 1911. The outer double insulating walls (BB and CC of figure 3) of his early calorimeters were originally made of molded straw and glue (6). Inside these was a nickel-plated water chamber (AA) to absorb the heat from the combustion reaction and the steel combustion bomb itself with attached stirring paddles (D). This was rotated on pivot F using an external motor and pulley system (P). The Jensen-Thomas Apparatus Collection contains two early Parr calorimeters of the straw-glue variety (figures 1 and 4), both of which probably date from around 1912 and which list only the 1901 and 1902 patent dates on the attached identification plates.

Unfortunately reaction 2 ultimately proved to be more complex and less reproducible than originally thought and in order to improve calorimetric accuracy it became necessary to once again revert to reaction 1. As a consequence, by the 1920s Parr was also manufacturing his version of the traditional Berthelot high-pressure (25-30 atm) oxygen bomb calorimeter, which had been first introduced in 1881. Parr continuously improved the design of his calorimeters by incorporating new materials and conveniences as they became available. As shown in figures 5 and 6, by the 1930s the straw and glue insulating containers had been replaced by black Bakelite and the calorimeter came with the stirring motor permanently attached.

Figure 4. An example of a later variant of the Parr peroxide calorimeter, c. 1912 (Jensen-Thomas Apparatus Collection). The water chamber is to the left and the combustion bomb and pivot support are to the right. The pulley attachment for the top of the combustion bomb and the detachable stirring wings are missing.

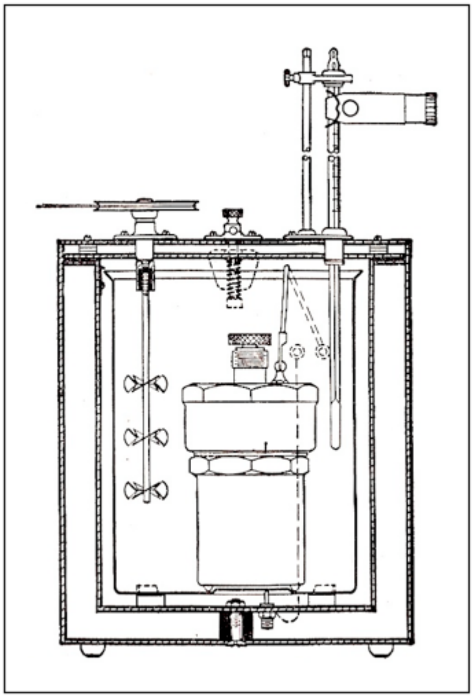

Figure 5. Diagram of the interior of an early Parr oxygen bomb calorimeter, circa 1932.

Figure 6. An example of a Parr oxygen bomb calorimeter, c. 1940 (Jensen-Thomas Apparatus Collection).

Since the combustion bomb required for the solid-gas coal-dioxygen reaction was much larger and heavier than that required for the solid-solid coal-peroxide reaction, the stirring mechanism was separated from the bomb, which now remained stationary. In addition, a small sliding magnifying device was attached to the thermometer to facilitate accurate reading of its scale. A typical example of this design from the Jensen-Thomas Apparatus Collection is shown in figure 6 and probably dates from around 1940.

By the 1930s the company was also offering a larger variant of the oxygen bomb calorimeter known as an adiabatic calorimeter in which the traditional cylindrical design had been replaced by a cubic shape and a permanently attached lid that could be conveniently rotated out of the way when opened (figures 7 and 8). Rather than an insulating air gap between the outer and inner walls, the so-called adiabatic calorimeter used a wall of circulating water. As a result it had two thermometers, one as usual for the nickel-

Figure 7. An example of a Parr adiabatic oxygen bomb calorimeter, c. 1956(Jensen-Thomas Apparatus Collection).

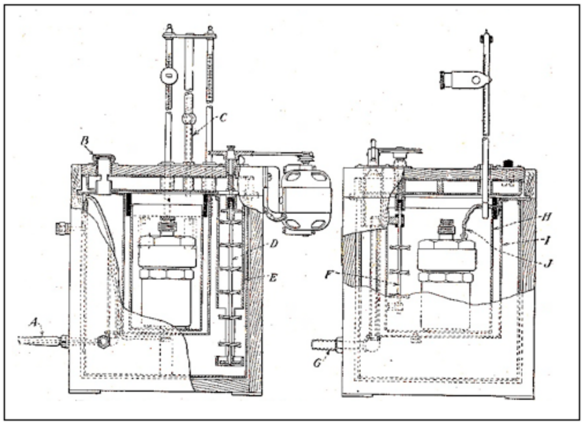

Figure 8. Diagram of the interior of a Parr adiabatic oxygen bomb calorimeter, c. 1932.

plated water chamber surrounding the combustion bomb and one to monitor the insulating jacket of circulating water. Likewise, it also had two stirring systems for the same purpose. When closed, the calorimeter lid could be locked down to produce a water-tight seal, as the stirring system for the water jacket served to pump water through the lid as well. Also required were external inlets and outlets (A and G of figure 8) for the entrance and exit of the water in the circulating jacket.

A typical example of a Parr adiabatic calorimeter from the Jensen-Thomas Apparatus Collection is shown in figure 7 and probably dates from around 1956. It also includes an external push button ignition system (small box to the far left) and an alternative combustion chamber for sulfur determinations (the container in front of the ignition box).

As early as 1915 the corrosion of his steel calorimetric bombs by the acidic oxides of nitrogen and sulfur produced as a necessary by-product in the combustion of coal samples had induced Parr to search for a more corrosion-resistant alloy and had led to his development of *Illium* – a tungsten alloy named after the University of Illinois that contained eight additional components (Cu, Mn, Si, Ni, Al, Fe, Cr, and Mn) and which was not only acid resistant but could be used as a substitute for such noble metals as platinum and palladium in many other laboratory devices (7). This sojourn into the field of metallurgy later led to work on the causes of the embrittlement of boiler plate and to effective remedies for its prevention which eventually produced vast savings for a wide range of industries (8).

In later years Parr was widely acknowledged as a world expert on fuel and coal chemistry and was the recipient of many awards and honors, including the Chandler Medal in 1926 and service as President of the American Chemical Society in 1928 (9). After Parr's death in 1931, his sons continued to run the Standard Calorimeter Company, which by then had branched out into other areas of chemical instrumentation. In recognition of this fact, the company was renamed the Parr Instrument Company in 1933.

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Publication History

Published online in *Museum Notes*, September/November, 2012.

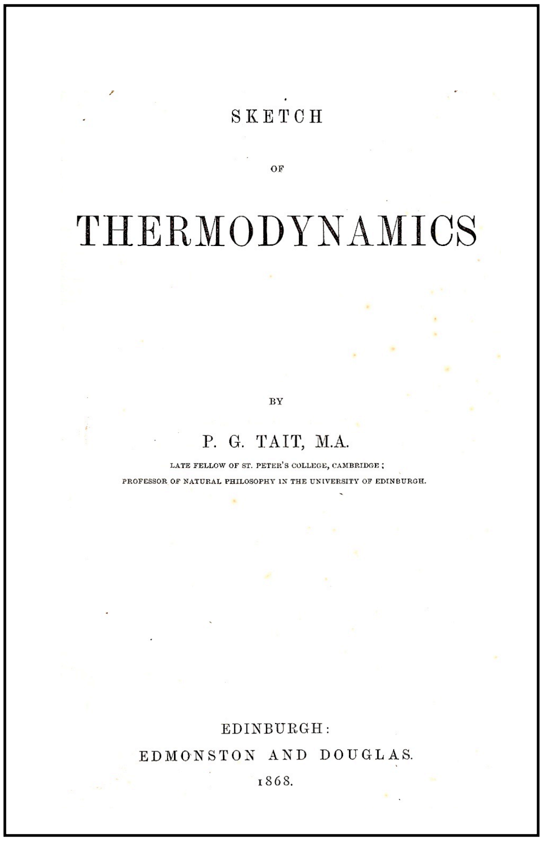
XXI

George Downing Liveing and the Early History of Chemical Thermodynamics

Though the history of thermodynamics, as it relates to both engineering and physics, is well documented in both the journal and monograph literature (1-3), the same is not equally true of the history of its specific applications to the field of chemistry (4). In an attempt to fill this lacuna, the author has recently published English translations and commentaries on the work of both the Austrian chemist and physicist, Leopold Pfaundler, who was the first to apply the newly emerging kinetic theory of gases to chemical rates and equilibria in 1867 (5-6), and the German chemist, August Horstmann, who was the first to apply Clausius' entropy function to the rationalization of chemical equilibria in 1873 (7-8). In keeping with this program, the present paper is concerned with a distinctive British attempt to base the early teaching of chemical thermodynamics on the use of William Thomson's concept of energy dissipation rather than on Rudolf Clausius' more familiar entropy function, as reflected in the pioneering contributions of the British chemist, George Downing Liveing (9-10).

Energy Dissipation versus Entropy Increase

The first English-language textbook on thermodynamics (figure 1) was published by the Scottish physicist, Peter Guthrie Tait (figure 2), in 1868 under the title *Sketch of Thermodynamics* (11). In actual fact, this small volume of only 128 pages consisted primarily of a slightly revised reprint of two popular articles on heat and energy that Tait had published four years earlier in the *North British Review,* plus an additional, far more mathematical, chapter on thermodynamics proper, and was intended for classroom use by his students at the University of Edinburgh.


SKETCH
OF
THERMODYNAMICS

BY
P. G. TAIT, M.A.
LATE FELLOW OF ST. PETER'S COLLEGE, CAMBRIDGE;
PROFESSOR OF NATURAL PHILOSOPHY IN THE UNIVERSITY OF EDINBURGH.

EDINBURGH:
EDMONSTON AND DOUGLAS.
1868.

Figure 1. Title page of Tait's 1868 monograph on thermodynamics.

In his first two chapters Tait had adopted a largely historical approach and, as a result, had managed to ignite two historical debates over issues of priority (12). The first of these involved the law of the conservation of energy and the relative merits of the contributions of the German physician, Robert Mayer, versus those of the Englishman, James Joule, with Tait, not surprisingly, coming down decisively in favor of Joule. This would elicit a defense of the claims of Mayer by both Hermann von Helmholtz and John Tyndall and, if I am to judge from a spirited conversation I had with a visiting British physicist some years ago, this debate is still going strong among determined Anglophiles.

The second debate involved the relative merits of two competing formulations of the second law of thermodynamics. The first of these, by Tait's colleague and frequent collaborator, William Thomson or Lord Kelvin (figure 3), was first formulated in 1852 and was based on the concept that in all spontaneously occurring natural processes a certain portion of the useful energy was necessarily irreversibly dissipated or degraded into isothermal heat, leading to the further conclusion that the universe, once its reserve of available energy was exhausted, would undergo a so-called "heat death" (13):

Figure 2. An etching of Peter Guthrie Tait (1831-1901) lecturing on the subject of electrostatics.

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 subject 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 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.

Though, in his original formulation, Thomson had made reference only to the dissipation of mechanical energy, by 1864 Tait had generalized this to include all forms of useful energy, whether mechanical, chemical, electrical or gravitational, and had enshrined it as one of the three underlying principles of the science of energy (11):

The Theory of Energy, as at present developed, contemplates its Conservation, Transformation, and Dissipation.

The second approach was due to the German physicist, Rudolf Clausius. In his 1850 memoir on heat, Clausius had reconciled Carnot's original theory of heat engines with the newly emerging principle of the conservation of energy and the mutual interconversion of heat and work. In so doing, he had shown that only a portion of the heat passing through the temperature gradient of a heat engine was converted into work, with the remainder being ejected as waste heat at the lower temperature. It was only in 1854 that Clausius reformulated his results using the ratio of heat to absolute temperature or Q/T as a convenient quantitative measure of what he called the system's "equivalence value of transformation," and only in 1865 that he finally gave this ratio the name of *entropy* and assigned it a distinct symbol (S), leading to his often quoted summary of our currently accepted versions of the two laws of thermodynamics, as distinct from Tait's earlier three principles of energy (14):

Die Energie der Welt ist constant.
Die Entropie der Welt strebt einem Maximum zu.

Figure 3. William Thomson (1824-1907) as he appeared in 1852, the year he proposed the principle of energy dissipation.

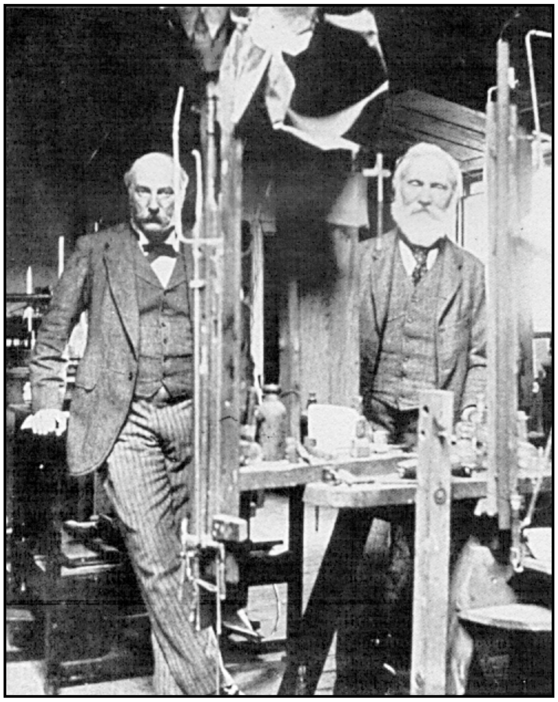


Figure 4. Lord Rayleigh (left) and Lord Kelvin (right) consulting in later life in Rayleigh's private laboratory.

Perhaps the best overall evaluation of the relative merits of these two contributions was given by Horstmann, who had studied under Clausius, in his famous paper of 1873 on the application of the entropy concept to chemical equilibrium, in which he argued that, while Thomson was the first to qualitatively state the underlying physical basis of the second law of thermodynamics, it was Clausius who first gave it a proper mathematical formulation via his entropy function (7):

W. Thomson was the first to take note of one of the consequences of the mechanical theory of heat – namely that the entire world is continuously approaching, via the totality of all natural processes, a limiting state in which further change is impossible. Repose and death will then reign over all and the end of the world will have arrived. Clausius knew how to give this conclusion a mathematical form by constructing a quantity – the entropy – which increases during all natural changes but which cannot be decreased by any known force of nature. The limiting state is, therefore, reached when the entropy of the world is as large as possible.

As might be expected, Tait, with his distinctly British bias, overwhelmingly favored Thomson's dissipation approach over Clausius's entropy approach and would even go so far as to appropriate Clausius's term to describe the opposite of Thomson's concept. Tait, observed a later biographer, "was always ready to put on his armor and place lance in rest for the cause of British science" (15). Believing that the word entropy was Greek for "transformation capacity," Tait argued it should be used to describe the amount of available energy remaining in a system, rather than its loss. Once this energy was dissipated and the system no longer possessed the capacity for further change, its transformation capacity or entropy would be at a minimum rather than at a maximum, as argued by Clausius. Hence Tait proposed reversing both the sign and meaning of Clausius's original entropy function (11):

It is very desirable to have a word to express the "Availability" for work of the heat in a given magazine; a term for that possession, the opposite of which is called "Dissipation." Unfortunately the excellent word "Entropy," which Clausius has introduced in this connexion, is applied by him to the negative of the idea we most naturally wish to express. It would only confuse the student if we were to endeavor to invent another term for our purpose. But the necessity for some such term will be obvious from the beautiful examples which follow. And we have taken the liberty of using the term Entropy in this altered sense ... The entropy of the universe tends continually to zero.

Tait's rationale for this linguistic kidnapping was hardly convincing, since, despite his claim that inventing his own term would prove confusing to students, he had in fact already done so earlier in the paragraph when he chose to highlight the word "Availability." In addition, as we will soon see, his proposed revision of Clausius's terminology would have unfortunate consequences for the early development of chemical thermodynamics in Great Britain

Dissipation and Chemical Equilibrium

Though Tait mentioned chemical reactions in his treatise, most of his passing references had to do with their use in constructing voltaic cells and examples of the application of the conservation of energy. Little or nothing was said on the subject of dissipation and chemical equilibrium. Indeed, it was not until 1875 that this subject was finally raised by Lord Rayleigh (figure 4) in the course of a popular lecture delivered at the Royal Institution (16):

The chemical bearings of the theory of dissipation are very important, but have not hitherto received much attention. A chemical transformation is impossible if its occurrence would involve the opposite of dissipation (for which there is no convenient word); but it is not *true, on the other hand, that a transformation which would involve dissipation must necessarily take place. Otherwise, the existence of explosives like gunpowder would be impossible.*

What is of particular interest in this quote is Rayleigh's explicit recognition of the importance in chemical phenomena of what is now called "kinetic metastability" – the realization that energy dissipation is a necessary, but not a sufficient, condition for a given chemical reaction to occur.

Rayleigh then went on to rather oddly argue that the supposed widespread absence of reversibility in chemical reactions had so far hampered the application of thermodynamics to chemistry – odd because reversible chemical reactions are quite common in gaseous and liquid solution systems, and, in any case, energy dissipation must accompany all spontaneous chemical reactions, reversible or otherwise (16):

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 though unlimited time be allowed. Some progress has, however, recently been made, and the experiments of Debray on the influence of pressure on the evolution of carbonic anhydride [i.e. carbon dioxide] from chalk [i.e. calcium carbonate] throw considerable light on the matter.

He then concluded his lecture with a few remarks on the role of contraction and expansion in altering the degree of energy dissipation for a given chemical reaction.

It was not until 1882 that the relevance of such topics as energy conservation and dissipation, the mechanical theory of heat, and the kinetic theory of gases to the theory of chemical reactions were once again brought to the attention of the British scientific community – this time via an address on "Chemical Dynamics" given in Southampton at the August meeting of the British Association for the Advancement of Science (BAAS) by the Cambridge chemist, George Downing Liveing (figure 5), in his capacity as President of the Chemical Section of the Association (17):

If I were asked in what direction chemical science had of late been making the most important advances, I should reply that it was in the attempt to place the dynamics of chemistry on a satisfactory basis, to render an account of the various phenomena of chemical action on the same mechanical principles as are acknowledged in other branches of physics.

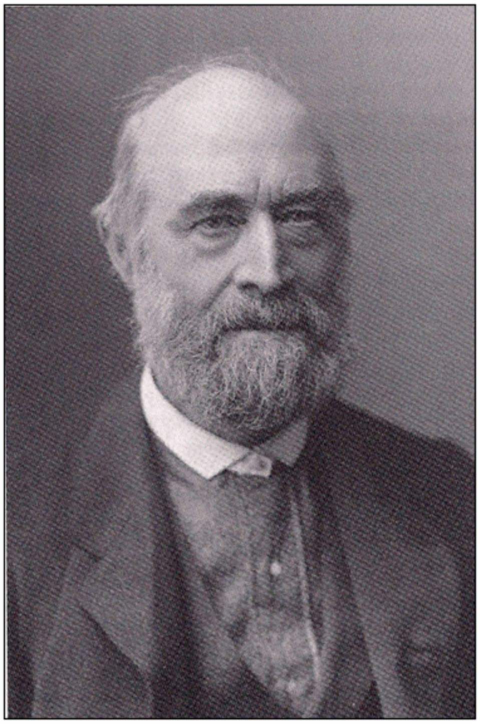


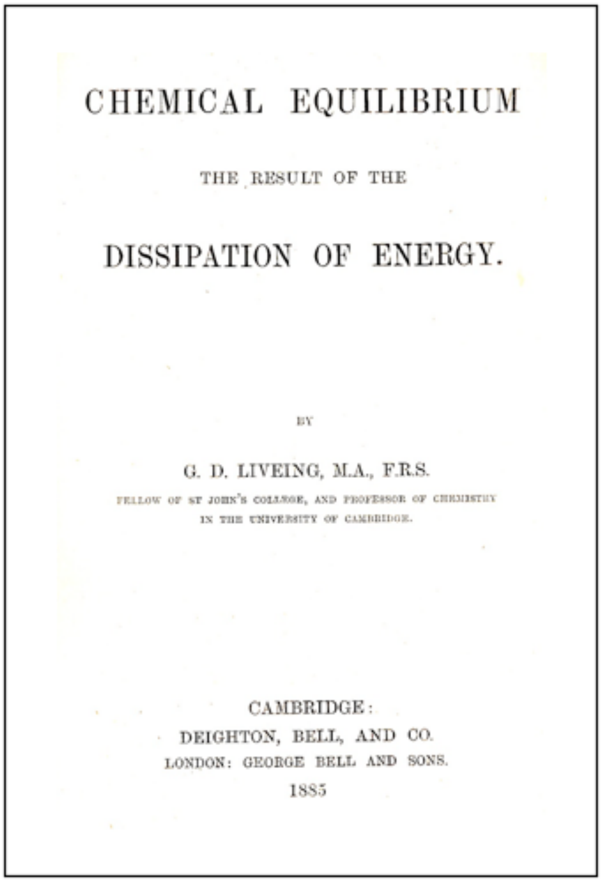
Figure 5. George Downing Liveing (1827-1924).

Liveing then briefly summarized just what these universal mechanical principles were (17):

The kinetic theory of gases has analyzed for us the different motions of the molecules in a mass of matter and has facilitated the conception of the part which heat plays in chemical actions. Hence we have had of late several attempts to reduce to a form susceptible of mathematical calculation the problems of chemistry. Most of these attempts have proceeded on the well-known mechanical principle that the change of vis viva of a system, in passing from an initial to a final configuration, is independent of the intermediate stages through which it may have passed provided the external conditions are unaltered; and on the principle of the dissipation of energy, that is to say, on the condition that the state of the system, if it be a stable one, must be such that the energy run down in reaching it is a maximum.

Citing the recent work of Gibbs, Berthelot, Thomsen, and Deville as examples of this progress, Liveing then called attention to the almost negligible impact that this work had so far had on the average chemistry textbook (17):

But how far can we say that mechanical principles are actually recognized as the true basis of rational chemistry? So far as I know no chemist denies that this is so,



CHEMICAL EQUILIBRIUM

THE RESULT OF THE

DISSIPATION OF ENERGY.

BY

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FELLOW OF ST JOHN'S COLLEGE, AND PROFESSOR OF CHEMISTRY
IN THE UNIVERSITY OF CAMBRIDGE.

CAMBRIDGE:
DEIGHTON, BELL, AND CO.
LONDON: GEORGE BELL AND SONS.
1885

Figure 6. The title page of Liveing's 1885 monograph on chemical thermodynamics.

and yet how little do our textbooks, even the most recent and the most highly reputed, show the predominance of this idea! How very small a portion of such books is taken up with it, how much seems to utterly ignore it or to be couched in language antagonistic to it!

At this point Liveing diverged from his initial theme and spent the remainder of his address (indeed the majority) discussing recent advances in his research speciality of spectroscopy and their bearing on such issues as Prout's hypothesis and the unity of matter and the origins and renewal of the sun's ultimate source of energy.

This address appears to have been a resume of a course on chemical thermodynamics that Liveing had either already given, or was planning to give, to his students at Cambridge – the full contents of which were finally published three years later in the form of a small booklet (figure 6) of only 97 pages entitled, with startling directness, *Chemical Equilibrium the Result of the Dissipation of Energy* (18). This is, to the best of my knowledge, the first English-language monograph to deal specifically with chemical thermodynamics, rather than with either thermochemistry or engineering thermodynamics, and the only such monograph to explicitly adopt an approach based on Thomson's energy dissipation principle rather than on Clausius's entropy function.

Unhappily, it is also very difficult reading for the modern chemist, not because it is crammed with complex mathematics or because it talks of energy dissipation rather than entropy changes, but for precisely the opposite reason. In actuality the book contains virtually no mathematical equations whatsoever and, though it describes a great many chemical reactions, it also contains very few balanced chemical equations. Likewise, though reference is made to various experimental setups, no figures of apparatus appear and, though each chapter addresses multiple topics, there are no section headers or numbered paragraphs to mark the passage from one subject to another. The modern reader, who takes for granted these conventions for summarizing and organizing technical material – conventions already widely used by the 1880s – will quickly discover that their absence, coupled with an almost total reliance on verbal description only, imposes a great burden on both one's memory and attention span.

The book is divided into six brief chapters and also contains a lithograph of typical line spectra and a photographic plate of three complex spectra. The first chapter, entitled "Introduction," verbally defines energy dissipation and discusses various mechanisms for the process, including heat conduction and variations in rarefaction and condensation due to changes of state (taken in the broad sense to also include both mixing and adsorption). It concludes with a summary of the criteria for establishing that energy dissipation has occurred:

1. The system can be returned to its initial state only through addition of available energy from an external source.

2. For small perturbations at least, the system returns to its final state of maximum dissipation when the external energy sources are removed.

The second chapter is entitled "Equilibrium in Dissociation," and attempts to dispel the older belief, based on the caloric theory, that heat is a repulsive force which acts in opposition to chemical affinity. The reason compounds eventually dissociate upon heating is not because the repulsion of the added heat finally overwhelms the attractions of the internal bonds, nor because, in keeping with the newer mechanical theory of heat, the increasing violence of the intramolecular vibrations finally break the internal bonds. Rather it is because the net increase in the number of independently moving species formed upon dissociation is more able to effectively dissipate the system's internal kinetic energy.

The third chapter, entitled "Termination of Reactions," contains the only diagram in the booklet and depicts the gravitational potential of a rolling ball (figure 7). Though admittedly not a direct representation of the actual potential of a chemical reaction system, Liveing nevertheless uses this diagram as an analogy to describe the changes in the potential energy of several example chemical reactions, and thus it is arguably the first known example of the use of a potential energy surface to analyze chemical reactivity. Its primary use by Liveing was to discuss the issue of successive reactions.

As early as 1793 the French chemist, Antoine Fourcroy, had enunciated the principle that, if a set of reactants was able to form more than one alternative set of products, the least stable set was produced first and only subsequently converted into the more stable set (19). This same principle was repeated again by Gay-Lussac in 1842 (20) and again by Ostwald in 1897 under the guise of "the law of successive reactions" (21). In terms of Liveing's potential energy surface of 1885, the initial reactants are represented by position *A* and the successive products by positions *B*, *C,* and *D*. Whether the system stops at one of these local minima (*B* or *C*) or proceeds all the way to the true minimum (*D*) depends on how rapidly it dissipates its kinetic energy. If the dissipation is rapid, the system will stop at either *B* or *C* because it will lack sufficient kinetic energy to surmount the intervening potential energy maxima (*b* and *c*). If, however, it is slow, then the system may retain sufficient kinetic energy to surmount these barriers and will then proceed all the way to the true minimum (*D*).

In our modern terminology, points *a*, *b*, and *c* correspond to activation barriers, and in the first scenario *B* and *C* correspond to kinetically metastable products and *D* to the true thermodynamic product, whereas in the second scenario *B* and *C* correspond to reaction intermediates. However, not only did Liveing lack our modern terminology, he also failed to make a clear distinction between the kinetic and thermodynamic aspects of chemical reactivity, so his analysis is only partially correct by modern standards.

The final issue addressed by Liveing in this chapter was the question of whether a chemical reaction will proceed all the way to completion or will come to equilibrium before completion. In Pfaundler's kinetic approach of 1867 equilibrium was the result of the dynamic equalization of the forward and reverse reaction rates, whereas in Horstmann's entropy approach of 1873 it was a consequence of the competitive demands of the reactants versus the products with respect to maximization of their individual entropies of dilution. Since he did not deal with the question of reaction rates, Liveing's rationale is, not surprisingly, most closely related to that of Horstmann. If gases are generated in a reaction, their accumulation in a closed container creates a pressure which can be used to perform useful work. Likewise, the increase in the concentrations of any dissolved products in a solution can also be used to perform useful work (e.g. in an electrochemical cell). The resulting accumulations of potential energy eventually limit the ability of the system to dissipate its kinetic energy and thus bring the reactions in question to equilibrium before completion. On the other hand, removal of the products from the system via precipitation, or by allowing any product gases to escape into the environment, has the opposite effect and allows the reactions in question to proceed to completion. Unfortunately, this purely verbal rationale via a series of special cases lacks the generality of Horstmann's approach and is further compounded by the absence of any mathematical expressions for equilibrium constants.

The fourth chapter is entitled "The Nascent State." This term was first introduced by Priestley in the 18th century and refers to the observation that gases chemically generated *in situ* within a reaction system are frequently far more reactive than when the same gases are bubbled into the reaction system from an external source. A remarkably large number of rationales have been offered for this phenomenon over the years (22), the most popular of which was the hypothesis that chemically generated gases, such as hydrogen, were initially formed in a monoatomic state, whereas the fully formed gases from the external

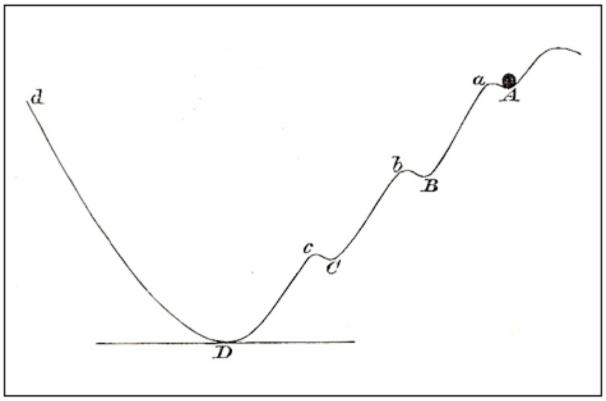

Figure 7. The 2D potential energy surface used by Liveing to illustrate the existence of metastable states (A, B, C) and activation barriers (a, b, c).

source were diatomic. The chapter is essentially an attack on this idea based on the argument that the initial formation of such high potential energy products as free atoms, without any corresponding mechanism for energy dissipation, is impossible.

Liveing's failure to properly distinguish between the kinetic and thermodynamic aspects of chemical reactions and his lack of an adequate vocabulary for this purpose are nowhere more apparent than in chapter five of his booklet entitled "The Passage from One State of Equilibrium to Another." The first part deals largely with the role of external energy sources in stimulating the passage of a reaction system from a high potential metastable state to a lower potential thermodynamically stable state, such as the role of light in initiating the violently explosive reaction between dihydrogen and dichlorine gas:

$$h\nu + H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \qquad [1]$$

In other words, it deals with what we now call activation energy. This would have been an ideal topic for the potential energy diagram introduced in chapter three. But instead of referring this energy requirement back to the energy maxima in his earlier diagram, Liveing instead talks about these stimuli as "opening a new channel for energy dissipation," Also included among his examples are many that would today be classified as catalytic, though he does not employ this term.

The second part discusses the synthesis of metastable compounds or "explosives" from reactants of lower potential energy. Liveing suggests that this happens in one of two ways – either the reactants are first promoted to a higher potential, which lies above rather than below that of the desired products, via addition of external energy, as in the electrical excitation of dioxygen gas in the synthesis of metastable ozone:

$$\Delta E_{el} + 3O_2(g) \rightarrow 2O_3(g) \qquad [2]$$

or the high potential metastable product is formed along with a low potential energy by-product, such that the combined change leads to the required net energy dissipation, as in the synthesis of metastable nitrogen triiodide along with ammonium iodide as the thermodynamically stable by-product.

$$5NH_3(aq) + 3I_2(s) \rightarrow NI_3{\bullet}NH_3(s) + 3(NH_4)I(s) \qquad [3]$$

Again, though these arguments cry out for representation on his earlier potential energy surface, no use is made of it.

Just as the second chapter contained an attack on the outdated concept of heat as a repulsive force, so the sixth and final chapter, entitled "Theoretical View of the Nature of Chemical Combination," contains an attack on the Newtonian concept of chemical affinity as a specific force of interatomic attraction. Here Liveing extends the concept of energy dissipation from a macroscopic reaction system to an individual molecule, arguing that dissipation leads to an equalization of the kinetic energies of all of the atoms within a molecule. This, in turn, leads to a synchronization of their motions and it is this synchronization, rather than specific forces of attraction, which allow the atoms to move together as a single cohesive molecular unit (18):

The consideration of the conditions of chemical equilibrium points to the conclusion that chemical combination is not due to any bonds which have to be untied from one union before they can be tied together again in a new one, nor yet to any special forces of chemical affinity peculiar to each element and "satisfied," whatever that may mean, or disappearing in its combinations; but that it consists rather in a harmony of the motions of the combined atoms in virtue of which they move and vibrate together, and that such harmony is brought about by the general force of nature which compels to an equal distribution of energy throughout the universe.

The resulting complex of harmonized vibrations found in a typical molecule can change on heating, leading, in turn, to changes in atomic valence and spectra (whence the relevance of spectroscopy and the attached plates of spectra) and are probably best envisioned using William Thomson's vortex atom rather than the hard billiard-ball atoms of Dalton and the kinetic theory of gases, though Liveing provides no specific examples.

What these conclusions reveal is that Liveing had little sympathy for the entire 19th-century program of synthetic organic chemistry and its accompanying edifice of structural formulas, which he viewed as historical anachronisms based on outdated ideas concerning chemical affinity – a position that was much more explicit in his earlier BAAS address of 1882 (17):

Moreover, we still find in many of our textbooks the old statical notion of chemical combination stereotyped in pictures of molecules. I do not, of course, mean to accuse the distinguished inventors of graphic formulae of meaning to depict molecules, for I believe they would agree with me in thinking that these diagrams do not any more nearly represent actual molecules than they represent the solar system; but unfortunately we cannot prevent beginners from regarding them as pictures, and

> *molding their ideas upon them. They present something easily grasped by the infant mind, and schoolmasters are fond of them; but only those who have each year to combat a fresh crop of misconceptions, and false mechanical notions engendered by them, can be aware of how much they hinder, I won't say the advance, but the spread of real chemical science.*

Nor was Liveing alone in these assumptions. As revealed by the work of McGucken, the Thomson vortex atom was something of a fad among spectroscopists of this period (23) and the idea that valence and chemical combination are really a consequence of synchronized atomic motions forms the climax of Lothar Meyer's 1892 textbook, *Outlines of Theoretical Chemistry* (24):

> *We have gradually receded from the idea of a static state of equilibrium of the atoms brought about by their powers of affinity, and we now consider the atoms, and the molecules which are built up of atoms, as particles in an active state of movement. Their relations to each other are essentially determined by the magnitude and form of their movements. Chemical theories grow more and more kinetic, and although, partly from habit and partly from want of a better expedient, the existence of an attractive force between atoms is frequently assumed in explaining chemical phenomena, this only happens in the conviction that this hypothetical affinity is merely an expression for the real, though imperfectly known, cause of the internal cohesion of chemical compounds.*

Similar ideas concerning a kinetic interpretation of both chemical affinity and valence were still being advocated by the American chemist, Francis Venable, as late as 1904 (25).

Evaluation

By this point it should be apparent to the modern reader that Liveing's unique approach to chemical thermodynamics proved to be a dead end and that his booklet had no intellectual successors. Indeed, an argument can be made that it was already outdated by the time of its appearance. The ground-breaking work of both Horstmann (1873) and Gibbs (1874), which had already laid a proper mathematical foundation for chemical thermodynamics – couched explicitly in terms of Clausius's entropy function in the case of Horstmann and indirectly, via free-energy functions, in the case of Gibbs – were already more than a decade old by the time Liveing's book appeared, and Pfaundler's kinetic molecular rationale of both chemical rates and equilibria (1867) was even older.

Interestingly, in the preface to his booklet, Liveing revealed that he was well aware of the work of both Horstmann and Gibbs, though one suspects that he had mastered neither. His excuse for not employing Gibbs's approach was that it was too mathematical for the average student (an interesting claim given the supposed mathematical prowess of the typical Cambridge undergraduate), though much of the problem was really due to Gibbs's terse prose style and could have easily been compensated for by a good teacher.

Liveing's reason for rejecting the entropy approach of Horstmann is even more interesting (17):

> *I regret that I have been obliged to abandon in this essay the use of the very expressive word "entropy" coined by Clausius. I have done so because it has been used by Clerk Maxwell with a meaning different from that which Clausius intended to express by it, and as Clerk Maxwell's elementary treatises are in the hands of most students of chemistry, I did not wish to run the risk of a misunderstanding of the word.*

What Liveing is referring to in this quote is James Clerk Maxwell's textbook, *Theory of Heat*, which was first published in 1871 and in many subsequent editions (26). In the first edition Maxwell had adopted Tait's earlier suggestion that the term entropy be used to denote the amount of available energy left in a system, rather than in the sense originally intended by Clausius. However, by 1875 Maxwell, as a result of having read Gibbs, had caught his mistake and had corrected it (27):

> *In former editions of this book the meaning of the term Entropy, as introduced by Clausius, was erroneously stated ... the book then proceeded to use the term as equivalent to the available energy; thus introducing great confusion into the language of thermodynamics. In this edition I have endeavored to use the word Entropy according to its original definition by Clausius.*

Thus we find that the excuse cited by Liveing had actually been obviated more than a decade earlier.

There is no doubt that Maxwell's textbook was used at Cambridge. According to Liveing's successor as Professor of Chemistry, William Jackson Pope, Liveing himself had taught the course on heat before Maxwell's arrival at Cambridge as the Cavendish Professor of Physics in 1871 and had even played a role in Maxwell's hiring (28). But by 1885 Maxwell's textbook had passed through at least eight editions and the idea that most Cambridge undergraduates were still using the first edition is either implausible or provides us with an unintended insight into the degree to which used textbooks were recycled by students of the period.

Ironically, the true predecessors of our current textbook tradition in chemical thermodynamics were making an appearance within the same time frame as Liveing's small booklet and include both Jacobus van't Hoff's 1884 monograph, *Études de dynamique chimique* (29) and Pierre Duhem's 1886 monograph, *Le potential thermodynamic et ses applications à la mécanique chimique et à l'étude des phénomènes électrique* (30). As suggested by its title, Duhem's approach was based on the use of Gibbs's chemical potential and was the first of a series of books on chemical thermodynamics that he would write over the next two decades, culminating in his 1902 textbook *Thermodynamique et chimie*, the only one to be translated into English (31).

Justly celebrated as the first modern monograph on chemical kinetics, van't Hoff's book also concluded with a section on chemical thermodynamics based on the concept of equilibrium as an equalization of the forward and reverse phenomenological reaction rates. Although heavily influenced by the work of Horstmann, whose writings on thermodynamics he would later edit (32, 33), van't Hoff unfortunately chose to abandon Horstmann's explicit use of the entropy function and opted instead for an approach based on *Arbeit* or useful work in which the role of entropy was implicit rather than explicit. His work was extremely influential in molding the teaching of chemical thermodynamics for the next 40 years but also condemned it to the use of such artificial devices as reversible cycles, osmotic-pressure membranes, and adiabatic pistons. Only with the publication in 1923 of the famous textbook of Lewis and Randall was this pseudo-engineering approach finally eclipsed and the subject once again returned to the purity of Gibbs (9).

A Modern Reconciliation

In modern terms, the entire hiatus prompted by Tait's ill advised attempt to redefine entropy can be summarized by the fundamental relationship:

$$G = -TS_t \qquad [4]$$

where G is the Gibbs free-energy of the reaction system, S_t is the total entropy of both the reaction system and its surroundings, and T is the absolute temperature. Essentially G is identical to what Tait meant by "Availability" and, like it, tends to a minimum as one approaches equilibrium. This was the term that Tait wished to rename entropy – a proposal that entailed not only a change in the meaning and sign of S_t, as originally defined by Clausius, but also, taking T into account, a change in its fundamental physical dimensions as well (60). TS_t, on the other hand, when taken in Clausius's original sense, is a good measure of the total energy dissipation of the system at the temperature in question and tends to a maximum as one approaches equilibrium.

Unfortunately the term "dissipation," though having uses in modern engineering thermodynamics, seldom appears today in the literature on chemical thermodynamics. However, when used in Thomson's original sense, it has been argued that it is a far better interpretation of the physical meaning of entropy than either disorder or information (10, 34-35). Neither information nor disorder are true causal agents like energy, and entropy is essentially a descriptor for how the energy of a system is distributed. Modern quantum statistics teaches us that movement from a low entropy state to a high entropy state corresponds to a dilution or dissipation of the system's kinetic energy content over an ever greater number of accessible quantum levels. Though increased molecular disorder is frequently, though not invariably, an *indicator* that the system has acquired a greater capacity to disperse its energy, it is not entropy in and of itself. Likewise, the idea that entropy is linked with information is actually based on a formal mathematical isomorphism rather than on a true physical isomorphism, and opens the entire concept to the charge of being subjective (36-37). Had Tait chosen to equate Thomson's dissipation with Clausius's entropy, rather than with available energy, this entire unfortunate episode in the history of chemical thermodynamics might have been avoided.

Having outlined and evaluated Liveing's contributions to the teaching of chemical thermodynamics, it is only fitting that, in conclusion, something should also be said about his life and career in general.

Biographical Background

George Downing Liveing (figure 8) was born on 21 December 1827 in Nayland, a small English village on the Suffolk bank of the River Stour, the eldest son of Edward Liveing and Catherine Downing (28, 38-42). His father was a surgeon by profession and his mother the daughter of a London barrister. In 1845, at age 18, Liveing entered St. John's College of Cambridge University as a pensioner, where he would remain in various capacities until his death 79 years later on 26 December 1924 at age 97.

Matriculating at St. John's in 1846, Liveing was awarded his B.A. in 1850 along with the position of 11th Wrangler in the Mathematical Tripos. Continuing on with postgraduate work at St. John's, he was awarded a first class with distinction in chemistry and mineral-

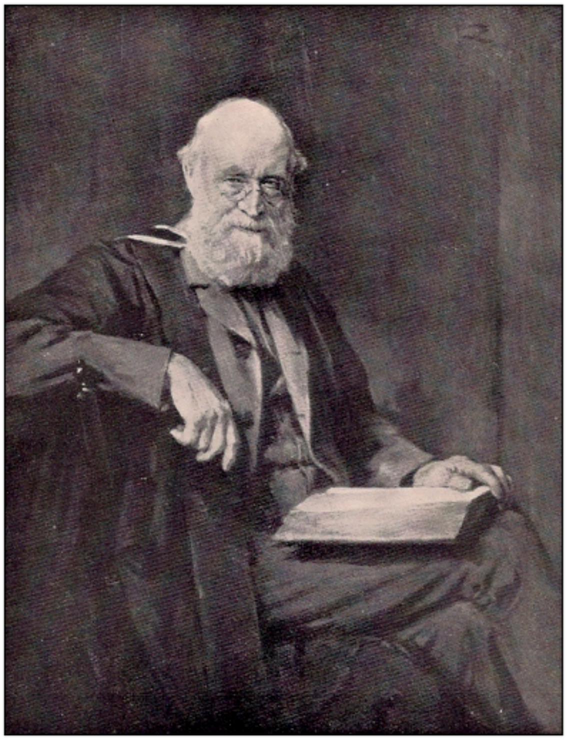

Figure 8. Liveing as he appeared in later life in the full tide of Cambridge honors.

ogy in the Natural Sciences Tripos of 1851, followed by work in the chemical laboratories of August Hofmann at the Royal College of Chemistry in London and Karl Rammelsberg in Berlin.

On his return from Berlin in 1852, he began teaching a practical course in chemistry for medical students in a primitive laboratory which he had outfitted at his own expense in a small cottage on the west side of Corn Exchange Street. However, in 1853 he received not only an M.A. from St. John's, but also appointment as a fellow of the college and an official lectureship in chemistry, along with a teaching laboratory which the College built for him behind New Court – the first of its kind at Cambridge.

By 1860 Liveing was able to supplement his position at St. John's through his appointment as Professor of Chemistry at the Staff College in Camberley and at the Royal Military College in Sanhurst, and in 1861 he was finally appointed as full Professor of Chemistry at Cambridge upon the death of the Reverend James Cummings, who had held the position since 1815. From this point on, he became involved in a continuous campaign to improve and expand the student laboratory facilities at Cambridge.

One of several plans for a chemical laboratory proposed during this period, but subsequently rejected by Liveing, reveals just how leery and unfamiliar the University was with the requirements of experimental chemistry (39):

The laboratory is to be constructed underground and is to be capable of resisting violent explosions and to be as little flammable as possible.

And just how rare the opportunity for actual hands-on laboratory work was in these early years may be gaged from Lord Rayleigh's recollections of his experiences as a student at Cambridge in the 1860s, as later recounted by his son (43):

In 1867 he took a course of qualitative chemical analysis (test-tubing as it is now often called) under Professor Liveing. This was, I think, the only laboratory instruction of any kind which he could get at Cambridge. I have dwelt in detail on the difficulty he found in getting experimental instruction, because it was a subject he often spoke of in telling me of his early years of manhood. "It wasted three or four years of my life."

In 1888 Liveing's efforts finally paid off with the completion of the Pembroke Street University Laboratories, described at the time as "one of the finest facilities in the Kingdom." (41). But even then, as one biographer noted, Liveing's laboratory stipend was only (28):

... 100£ per annum, paid by the government and subject to a deduction of Treasury fees amounting to four guineas. As he has said himself, men in those days had to devote their means as well as their wits to the service of the University.

In keeping with this remark, Liveing was forced, until his retirement two decades later, to finance (28):

... the chemical laboratory as a private venture, and informed me that he declined to submit his accounts, when challenged in later years by the suggestion that he had been drawing a large revenue, because he was ashamed to disclose to his colleagues how large a sum he had thus contributed from his own resources.

The retirement in question finally came in 1908 at age 80, on which occasion Liveing was also awarded an honorary Sc.D. Elected a Fellow of the Royal Society in 1879, he was also a recipient of its Davy Medal in 1901, served as President of St John's College from 1911-1924, and as corresponding secretary to two successive University Chancellors.

Liveing could be terse and abrupt with those who irritated him, either by invading the privacy of his personal work room or by violating the strict working rules of the new University Laboratories – attributes which won him the nickname of "Red Precipitate" among the undergraduates. As recalled by a former colleague (40):

> *Liveing had a great objection to being interrupted when at work in his private room in the Laboratory. One day I was asked by a man whether he could see the Professor and where was his private room. My reply was that the Professor did not see people except by appointment, but there was his room ... I could do no more than point to the door behind which the Professor worked and wait. I heard three taps on the door, a voice "Come in," a louder voice "Get out!," and a shutting of the door. I retreated with discretion. He was indeed extraordinarily terse in his conversation; not exactly abrupt or curt, but sometimes very monosyllabic. Like Captain Cuttle, he did not "waste language as some do."*

On the other hand, Liveing could also be "a very entertaining companion" when he chose to be and especially when one succeeded in tapping his remarkable memory of past events, which remained intact until the end (41):

> *He had a remarkable memory, talked freely of the men and events of the past, but would write no reminiscences. "I never look back," he said, "I always look forward"*

In a similar vein, Pope recalled after Liveing's death in 1924 that (28):

> *In his conversation, always sprightly and vivacious, Liveing seemed often trying to translate our later knowledge into terms of the science of seventy years ago. As befitted one who belonged to the age when the collection of facts was the main objective of science, he was apprehensive as concerned the vast theoretical flights of modern physics and chemistry ... In talking with Liveing and hearing his statement of long obsolete chemical views, one began to realize the difference between the science of seventy years ago and that of today, and to speculate on what our survivors seventy years hence will think of the science of the future. At the same time, and although an authority on older chemical knowledge, Liveing always maintained an excellent appreciation of recent progress.*

After all, as Pope emphasized, here was a man who had completed his chemical training (28):

> *... before Frankland had stated the doctrine of valency and before Kekulé had devised the structural formulae of the chemist. Liveing had been the personal friend of Dr. Whewell, the great Master of Trinity, W. H. Miller, the founder of our present system of crystallographic nomenclature, Adam Sedgwick, Sir Joseph Hooker, Michael Foster, Sir Gabriel Stokes, Sir George Airy, de Morgan and Charles Darwin; he had studied under Rammelsberg, Mitscherlich, Rose and Magnus. He once mentioned to me that he and Hooker, after some preliminary discussion, walked over to see Darwin for the purpose of hastening the publication of the "Origin of the Species," which appeared in 1859.*

Indeed, his life had encompassed so much scientific history, that he occasionally forgot that this was not equally true of his younger colleagues (28):

> *His memory of long-past events was remarkably clear until quite recently, but he sometimes forgot that others could not reach so far back into the past. A few months ago, while still in full mental vigor, he expressed surprise that I had not noticed the splendor of Donati's comet of 1858 [Pope was born in 1870].*

What was true of Liveing's memory was equally true of his physical health, which also remained intact until the end. He seems to have been one of those lucky persons who take their personal good health as an unquestioned given and who remain puzzled as to why others do not display a similar resiliency (28):

> *Like many other men of robust health and great vitality, Liveing found it difficult to understand why his contemporaries dropped out and passed away. Declining health seemed to him as due to a lack of resolution. He was an enthusiastic gardener, and when well past his ninetieth birthday engaged in all the manual toil incidental to the care of a large garden.*

He was also an avid walker in old age and would walk each day from his home in Maid's Causeway to his laboratory in the Goldsmith's metallurgical building, where he was working on a project related to his final publication on "The Recuperation of Energy in the Universe," which he had read to the Cambridge Philosophical Society in May of 1923 (41):

> *In his old age, his tall bent figure as he made his daily journeys between his home and the College, was one of the most familiar in town.*

And it was during one of these daily walks, in early October of 1924, that he was run down by a woman bicyclist – an accident which resulted in his death several months later from the resulting injuries, just five days after his 97th birthday.

Research Activities

During his extraordinarily long career Liveing published over 100 research papers and notes, although this output was not evenly distributed over time (44). For the first 25 years of his active career he published virtually nothing. Indeed, for the years prior to the date of his appointment in 1861 as Professor of Chemistry at Cambridge, the *Royal Society Catalogue of Papers* lists no publications whatsoever and, for the next 16 years, only four are given, all of them dealing with geology and all of them published in the Proceedings of the local Cambridge Philosophical Society. Here we should perhaps heed John Shorter's caution that in the 19th century (42):

> *Cambridge did not seek to produce people who intended to practice chemistry ... At Cambridge, chemistry was a part of a liberal education for those who cared to include it, with the exception of its ancillary role for medicine ... The aim of a Cambridge chemical education through the Tripos was to impart a knowledge of chemistry, not to train chemists.*

As a consequence, there was little incentive to acquire a Professor of Chemistry with an already established research reputation and, in any case, for his first quarter century at Cambridge Liveing's time and energy were largely consumed in establishing the very laboratory facilities necessary for such work in the first place.

A radical change in Liveing's research prospects finally occurred in 1875 with the appointment of Sir James Dewar (figure 9) as the Jacksonian Professor of Physics at Cambridge. Though Liveing was nearly 16 years older then Dewar, the two men soon struck up a friendship that would last for nearly a half century and which would lead to the collaborative publication of more than 78 papers and notes dealing with the subject of spectroscopy. As later noted by Pope (28):

> *The close and intimate friendship which existed between Dewar and Liveing was very striking. Both men were of strong personality, but no two men could have presented a greater contrast in outlook, tastes, and all essential characteristics. Yet each held the other in profound esteem, and neither ever said a word in criticism of his colleague. Without this absolute loyalty, the happy collaboration of Liveing and Dewar could not have persisted for nearly fifty years.*

This collaboration would establish Liveing's reputation as a research chemist and lead to both his election to the Royal Society and his award of the Davy Medal mentioned earlier. After his retirement, he would edit much of it for inclusion in a volume of collected papers published by the Cambridge University Press in 1916 (45).

Most of this work belongs to what A. C. Chandler would later call the "acoustics" period of spectroscopy and consisted of the publication of raw spectral data with some qualitative classification and speculative interpretation of the results, but without the empirical mathematical equations that would characterize the later "series" period of spectroscopy nor the theoretical interpretations that would characterize the later "quantum" period (46, 47). Its most lasting contribution was the division by Liveing and Dewar of the lines in the spectra of the alkali metals into the classes of sharp, principal and diffuse – terms which, via a series of historical twists and turns, would eventually become enshrined in our current atomic orbital abbreviations of *s*, *p* and *d* (48).

Which Tradition?

With the exception of his BAAS address of 1882, five papers published in the late 1880s on the kinetic theory and some aspects of chemical reactions, solution formation and crystallization (49-53), and his final paper of 1923 on cosmology (54), little in Liveing's list of

Figure 9. James Dewar (1842-1923).

research publications would seem to be related to his small monograph on chemical thermodynamics, and it has been our assumption so far that this work evolved primarily out of his teaching duties at Cambridge and is best interpreted in light of two competing approaches to the second law. However, another interpretation is also possible.

Though at least one biographer claimed that Liveing's small booklet "attracted a great deal of attention" when first published (39), I have been able to locate only one book review, and that single review casts a very different light on the subject. Published in the *Chemical News*, it characterized the book as "evidently of a preliminary nature," dismissed its treatment of chemical equilibrium and dissipation of energy as of little interest except to the physicist and "physico-chemist," proceeded to focus solely on the final chapter containing Liveing's speculations on the nature of matter as the only part of interest to the "pure chemist," and concluded with the recommendation that (55):

> *All who are not content to accept the reputed "elements" as the ultimate facts will find this book worthy of careful study.*

The author of the review was not listed, but given its emphasis, it is almost certain that it was the journal's editor, William Crookes, who was well known for his own spectroscopic studies and speculations on the ultimate nature and evolution of the chemical elements – speculations that would attract widespread attention the very next year as a result of his 1886 address as President of the Chemical Section of the BAAS (56). As shown by the pioneering studies of David Knight (57) and William Brock (58) in the 1960s, both Crookes's address of 1886 and Liveing's earlier address of 1882 are part of a long-lived debate among British chemists of the 19th century over the ontological status of both the atomic theory and the ultimate nature of Lavoisier's chemical elements – a debate in which Liveing's research specialty of chemical spectroscopy played a key role in the guise of Norman Lockyer's so-called "dissociation hypothesis" (59).

Nevertheless, while the reviewer's conclusion might have been applicable to Liveing's 1882 address, it is difficult to understand how he could have extracted such a message from Liveing's booklet of 1885, which contains nothing on either Prout's hypothesis or the ultimate nature of the chemical elements. Likewise, though one might surmise that Crookes may have found the principle of energy dissipation relevant to the mechanism for the gradual cooling of the primeval *protyle* that he would postulate as the cause for the gradual evolutionary building-up of our present-day chemical elements – no mention of either Liveing or energy dissipation is to be found in Crookes's famous address of 1886. In short, the implied contention of the reviewer that Liveing's booklet is best viewed as part of a 19th-century tradition of spectroscopic speculation on the ultimate nature of the chemical elements, rather than as part of a tradition of the monographic literature devoted to the theory of chemical thermodynamics, is dubious at best, however consistent it may be with some of Liveing's other writings.

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60. A plot of G versus the extent of reaction parameter ξ would have a U shape with the equilibrium value of G occurring at the base of the U curve, where G has its minimum value. A plot of S_t versus ξ would have an inverted U shape with the equilibrium value of S_t occurring at the top of the inverted U. The S_t curve is transformed into the G curve by multiplying it by $-T$ so as to invert it and to give both curves the units of energy/(mole rx K). ΔG and ΔS_t actually refer to the slopes of these curves or to $dG/d\xi$ and $dS_t/d\xi$ respectively. Thus while G and S_t are at their minimum and maximum respectively at equilibrium, their slopes, ΔG and ΔS_t, are both equal to zero at these points. For a recent discussion of the confusions produced by using ΔX in place of $dX/d\xi$ in chemical thermodynamics, see J. Quílez, "First-Year University Chemistry Textbooks' Misrepresentations of Gibbs Energy," *J. Chem. Educ*., **2012**, *89*, 87-93.

Publication History

Published in *Bull. Hist. Chem*., **2013**, *38(1)*, 37-51.

Update

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XXII

Kinetic versus Thermodynamic Control Some Historical Landmarks

The study of chemical reactivity may be broadly divided into the subject areas of reaction stoichiometry, reaction kinetics, and reaction thermodynamics. The first deals with the classification of chemical reactions, their expression as properly balanced net chemical equations, and the various quantitative calculations that are based upon these balanced equations. The second deals with the determination of rate laws and the deduction of reaction mechanisms, while the third deals with reaction efficiency and chemical equilibrium as a function of the relative stabilities of the various reactants and products, their concentrations, and the ambient temperature and pressure. In more colloquial terms, these three subject areas deal with the theoretical answers to the questions of "What changes in a chemical reaction?," "How fast does it change?," and "How complete is the change?"

Obviously the proper differentiation of these three questions and their resulting areas of specialization only gradually evolved over time. Thus the distinction between questions two and three was probably not complete until the 1880s with the rise of chemical kinetics and chemical thermodynamics as distinct subdisciplines, as personified by the publication of van't Hoff's classic monograph, *Études du dynamique chimique,* in 1884 (1). The key steps in this differentiation are at least implicitly covered in most standard histories of chemistry and it is not our intent to repeat them here. Rather our goal is to trace the subtle manner in which these questions once more became entangled with one another when dealing with the pervasive problem of competing chemical reactions, only to gradually separate once more under the rubrics of kinetic versus thermodynamically controlled chemical reactivity. As we will see, this pertinent distinction was independently discovered at least three times – each time within a different field of chemistry – thereby also providing us with a cautionary tale concerning the importance of the role played by textbooks and university curricula in the preservation and transmission of chemical knowledge, not to mention the perils of overspecialization.

The Laws of Chemical Affinity

Though there are scattered precedents in the 17th century, the first attempts to systematically study and classify chemical reactivity really date from the 18th century and came to constitute what became known as the study of "chemical affinity." This same century also saw the famous chemical revolution of Antoine Lavoisier and his collaborators, which focused instead on the subjects of chemical composition and changes of state. Though Lavoisier fully recognized that the study of chemical affinity was a legitimate and important field of chemical investigation as well, he also felt that it was still too immature and imperfectly developed for coverage in an elementary textbook and, for this reason, purposely chose not to include a discussion of its results in his famous *Traité* of 1789 (2).

So significant was the impact of Lavoisier's revolution for the subsequent development of chemistry that it should come as no surprise to learn that study of its origins and history came to dominate the work of most 19th- and early 20th-century historians of chemistry. It is only in the last few decades that historians have finally begun to examine the origins and history of 18th-century affinity theory in detail, and the fruits of this examination have now become the subject of at least three recent monographs (3-5).

Though excluded from Lavoisier's own textbook, the results of the study of chemical affinity were in fact dutifully summarized in the textbooks of most of his predecessors and contemporaries, where they were presented in at least three different formats: as affinity tables, as affinity diagrams, and as a listing of summary statements known as the laws of chemical affinity. The first of these approaches (figure 1) involved the horizontal listing of a series of important substrates at the heads of each column of a table and the vertical arrangement beneath each of a series of reagents in order of descending affinity for the substrate in question. In other words, the position of the reagent in the column indicated that it would displace all of the reagents below it from combination with the substrate at the column head but would, in turn, be displaced itself by all of the reagents lying above it in the column – the further assumption being that all such displacements were elective or complete. The origin of these tables is usually attributed to the affinity table or "Table of Rapports" first constructed by the French chemist,

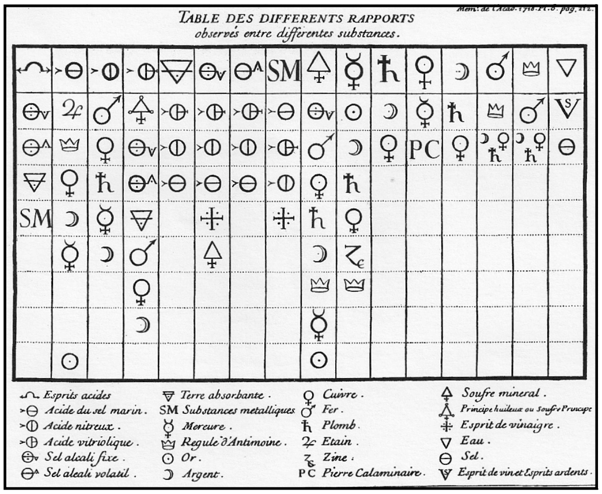

Figure 1. Geoffroy's affinity table of 1718.

Éttienne-François Geoffroy, in 1718 (6).

As suggested by its name, the concept of chemical affinity or rapport was originally an indigenous chemical concept derived from the anthropomorphism of alchemy and implied that chemicals, like humans, exhibited selective likes and dislikes or sympathies towards one another based on similarities in their natures or properties. However, as the 18th century progressed, the concept began to be identified more and more with interparticle Newtonian forces of attraction – a view particularly prominent in Torbern Bergman 1775 work, *A Dissertation on Elective Attractions* (7).

This identification, in turn, found expression in the concept of an affinity diagram (figure 2) which placed the components of a double-displacement reaction at the corners of a square array and indicated their various possible interactions with connecting lines or brackets above or below which were placed numerical estimates of the pairwise interparticle forces in question – both for those holding the components together in the initial reactants and for those holding them together in the final products. If the sum of the latter was greater than that of the former, the displacement reaction was assumed to proceed as written. While the use of diagrams to represent displacement reactions can actually be traced back to the 17th century, the addition of hypothetical numerical affinity values and their interpretation as competitive interparticle attractions was uncommon before the 1780s (8).

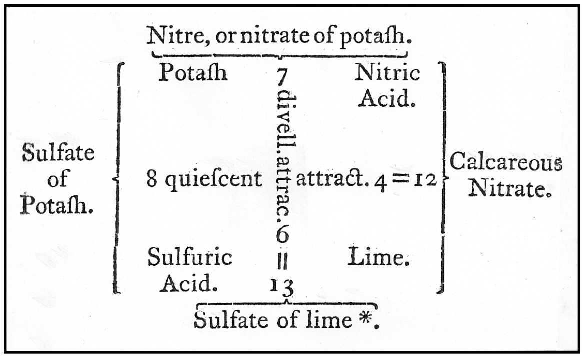

Figure 2. A typical late 18th century affinity diagram.

The third form of presentation – summary laws of chemical affinity – are perhaps the most revealing of the three formats as they were the most explicit when it came to revealing the underlying assumptions of affinity theory. Thus, on examining the seven laws of affinity listed by the French chemist, Pierre Macquer, in his popular textbook of 1749 (9), we quickly discover that he accepted the alchemical concept that affinity was based on a similarity in the properties of the reactants (law 2) and that the properties of the reaction products were an average or blending of those of the starting materials (law 3) – ideas which he had, in turn, probably absorbed from Georg Ernst Stahl's *Fundamente chymiae* of 1723.

Figure 3. Antoine-François de Fourcroy (1755-1809).

Some indication of the progress made in the study of chemical affinity during the century may be gleaned by comparing Macquer's seven laws of 1749 with the eight laws of chemical affinity given by the French chemist, Antoine-François de Fourcroy (figure 3), 33 years later in his own textbook of 1782, where the second and third of Macquer's laws are directly contradicted by the first and sixth of Fourcroy's new laws (10):

1. *The attraction, or affinity of composition, can-*

not act but between bodies of different natures.

6. Two or more bodies united by the attraction of composition, form a substance, the properties of which are different from those which each of the bodies possessed before their union.

– versions which the modern chemist hopefully will recognize as being far closer to our current views on the nature of chemical change than those of Macquer.

But what is far more pertinent to our present inquiry is Fourcroy's seventh law of chemical affinity, which reads (10):

7. The attraction of composition is measurable by the difficulty of destroying the combination formed between two or more bodies.

At first glance this may seem irrelevant to the question of kinetic versus thermodynamic control, but on reading Fourcroy's commentary on this law we quickly discover the following statement (10):

We find it as particularly necessary to insist upon this law because beginners are apt to fall into mistakes when estimating the differences of the attraction which unites the principles of different combinations. From the rapidity with which some substances combine, we are ready to imagine that their mutual attraction must be very considerable. But long experience shows that the eagerness to enter into combination, instead of indicating a perfect composition, is rather proof that the attraction between the bodies is extremely weak, and can produce but a very imperfect compound. In order, therefore, to determine accurately the degree of affinity with which bodies unite and remain in union, we must consider the ease or difficulty with which they are separated.

Both the identical law and a similar commentary appear in the discussion of affinity found in Fourcroy's more elaborate, 11-volume, chemical treatise of 1801, in which his list of affinity laws has been expanded from eight to ten (11):

By attention too immediate to the first appearances, chemists have supposed that those bodies which combine the most speedily or with the greatest quantity of motion, have the strongest affinity for each other; with these chemists the speed of combination became the measure of affinity. It has long been ascertained that this is a source of error and delusion. It often happens, on the contrary, that such substances as are with the most difficulty brought into combination are those which adhere the most strongly to each other. Whence it results that the true and only exact method of determining the force of chemical attraction between bodies is to measure the force we are obliged to employ to separate the constituent parts of a compound.

These two statements are, to the best of my knowledge, the first explicit recognition that there is an important distinction to be made between the speed of a chemical reaction and the stability of the resulting products or, in modern terms, between chemical kinetics, on the one hand, and chemical thermodynamics on the other. And it further implies that there is often, but not always, an inverse relationship between the two.

Though none of the modern historical studies of affinity theory mentioned earlier seem to have called attention to the importance of this observation, several of Fourcroy's contemporaries did and dutifully reproduced versions of it in their own textbooks. Thus the 1819 edition of John Murray's four-volume *System of Chemistry*, which was published nearly a decade after Fourcroy's death, contains the statement (12):

The facility or rapidity of combination depends not on the force of affinity, but on that modified by the cohesion, elasticity, and other qualities of bodies; and we have many examples in which a combination takes place slowly where the attraction from which it arises is strong, or where it is affected with facility, where the attraction is comparatively weak.

Similarly, 23 years later we find a related statement in an 1842 paper by the French chemist, Joseph Louis Gay-Lussac (figure 4), on the complex aqueous solution chemistry of the oxosalts of chlorine (13):

It is a general rule that, if one is able to form, at the same time and with the same elements, various compounds that are unequally stable, but capable of existing under the same circumstances, then it is the least stable that is formed first. If the circumstances change or are impossible to maintain, the compound of intermediate stability succeeds it and so on until one has arrived at the most stable compound or the component elements are separated.

Note that this statement actually goes one step beyond Fourcroy's original law by applying it, not just to the formation of single products, but to a reaction system capable of forming several distinct sets of competing products. Though Gay-Lussac makes no mention of Fourcroy, it is not improbable that he was fully aware of Fourcroy's law from a reading of his treatise of 1801 since Gay-Lussac was only 23 years old at the time and

Figure 4. Joseph Louis Gay-Lussac (1778-1850).

in the midst of his formative student years when it was first published.

The Demise of Affinity Theory

By the late 1850s the original outlines of classical affinity theory had begun to fade. The first facet to go was the affinity table, whose underlying assumptions had been severely undermined by the work of the French chemist, Claude Berthollet, at the turn of the century, on the influences of both changes of state and mass action effects in modifying the outcomes of the displacement reactions which had formed the basis of such tables in the first place (14). By 1819 the value of these tables was already being seriously questioned by the ever-thoughtful Murray in his masterful textbook (12):

From the preceding observations it must be apparent that the common tables of elective attractions do not represent the relative forces of affinity, but only a series of decompositions, which arise as much from the operation of circumstances which influence attraction, as from differences in the strength of the power itself. Nor do they even express the order of these decompositions accurately, since the influence of quantity, which undoubtedly modifies the results to a certain extent, has been neglected in the experiments on which they are founded. They are therefore of less utility than has been believed.

The second facet to disappear was the affinity diagram. Despite the rule set down by Fourcroy in his seventh law, chemists had in fact never agreed on the proper method for measuring chemical affinity, let alone on how to relate such measurements to the hypothetical numerical interparticle force values given in the typical affinity diagram. Thus, for example, the French chemist, Guyton de Morveau, attempted to correlate the affinities of various metals with the force required to separate a disk of the metal in question from a mercury surface; whereas the German chemist, Carl Wenzel, attempted to correlate them with the time required to dissolve a cylinder of the metal in acid; and the Irish chemist, Richard Kirwin, with the weight of an alkali or metal required to saturate a given amount of acid.

With the gift of hindsight, we now know that all of these attempts were fundamentally flawed. Guyton was actually measuring intermolecular forces (called "attractions of aggregation" by 18th-century chemists) rather than the interatomic forces (or "attractions of composition") actually responsible for compound formation; Kirwin was conflating chemical composition with chemical affinity and was actually measuring combining weights; whereas Wenzel was conflating kinetics with questions of stability. Indeed, there is little doubt that Fourcroy's commentary on the inverse relationship between speed of reaction and chemical stability was specifically intended as a criticism of the work of Wenzel, as summarized in his 1777 monograph *Lehre von der Verwandschaft der Körper* (15).

Nevertheless, it should be noted that, while the use of hypothetical force values had largely disappeared from reaction diagrams by the 1820s (only to be replaced in many cases with stoichiometric equivalent weight values instead), chemists continued to use these diagrams, now reinterpreted to show only which components had interchanged places in a reaction, well into the 1860s, when they were finally fully displaced by the use of balanced linear equations (8).

Of the three original affinity formats, it was the so-called laws of chemical affinity that managed to survive the longest in the textbook literature. Thus, in his popular textbook of 1858, the American chemist, David Wells, was still listing nine laws of chemical affinity, several of which echoed the more significant innovations found in Fourcroy's original list, including both Wells' third and fourth laws (16):

3. Generally speaking, the greater the difference in the properties of bodies, the greater is their tendency to enter into chemical combination. Between bodies of similar character, the tendency to union is feeble.

4. Chemical affinity occasions an entire change in the properties of the substances acted upon.

However, no trace can be found of Fourcroy's seventh law or of its concomitant observations on the inverse relationship between speed of reaction and product stability nor of Gay-Lussac's later elaboration. The reasons for this disappearance are not hard to surmise. With the demise of the affinity table and the temporary abandonment of the experimental program to measure affinity values, there was no longer any need for a rule to govern their measurement. As for the still valid observations on the relation between speed of reaction and product stability, the baby was simply thrown out with the bath water and became an artifact of an outdated literature that most chemists no longer read.

The Study of Phase Transitions

One of the defects of Fourcroy's original statements of his rule concerning speed of reaction and product stability was his failure to provide concrete examples of its application to actual reaction systems, and much the same may be said of Murray's later discussion as well, though he did provide a physical example involving the separation of solids from cooled liquids and solutions (12):

When attraction of aggregation is exerted, the particles are sometimes united indiscriminately, so as to form irregular masses: sometimes they pass into arrangements, whence masses of regular figures arise. The former happens generally when attraction is exerted suddenly, and with considerable force. If a liquid be suddenly cooled to a sufficient extent, a mass is formed altogether irregular. Or if a substance be produced by chemical action, the particles of which have a strong mutual attraction, this is exerted at the moment of its production, and it is separated in the form of a powder. This latter case is named in chemical language Precipitation, and the substance is said to be precipitated. The other result occurs when aggregation, previously weakened either by the operation of heat or of chemical attraction, resumes its force more slowly. The particles then assume a particular arrangement so as to form masses of regular figures, or bounded by plane surfaces and determinant angles. The result is named Crystallization, and such regular figured masses are denominated Crystals.

Of course there seems to be only a tenuous relationship at best between the issue of crystal size and the issue of product stability required by a literal reading of the original law, and we must now move forward another 70 years, and switch from the study of chemical affinity to the newly emerging field of phase science, in order to reestablish the necessary connection, as found in a paper published in 1897 by the German physical chemist, Wilhelm Ostwald (figure 5), entitled "Studies on the Formation and Transformation of Solid Bodies" (17).

Figure 5. Wilhelm Ostwald (1853-1932).

As suggested by the paper's subtitle, "Supersaturation and Supercooling," Ostwald was interested in the phenomenon that rapidly cooled gases, liquids, and solutions often persisted long after they had ceased to be thermodynamically stable and, when finally transformed into a more stable solid capable of existing in two or more polymorphic modifications, often initially selected the least stable of these possible alternatives rather than the most stable. Half way through his lengthy 42-page article, Ostwald paused and attempted to generalize – albeit rather awkwardly – these observations in the form of a tentative law:

... I would like to summarize our experiences so far concerning this subject with the general law that, on leaving any state and passing into a more stable one, that which is selected is not the most stable one under existing conditions, but the nearest.

Known sometimes as Ostwald's "law of successive reactions" or "successive transformations" and sometimes as the "Stufenregel" or "rule of stages," it was far more clearly articulated several years later in the 1912 edition of his popular textbook, *Outlines of General Chemistry* (18):

> *If the metastable region has been exceeded, and a new phase appears spontaneously, it is remarkable that the phase which appears is not the most stable phase under the conditions, but is the least stable, i.e., the next in stability to the phase undergoing the transformation.*

A second by-product of Ostwald's work in this area was the establishment of much of our current terminology for dealing with such phenomena. In the 1895 edition of *Outlines of General Chemistry* he had explicitly complained of the absence of a suitable vocabulary (19):

> *Such phenomena have been mostly considered as being to a certain extent unnatural, and the corresponding states have received the names of superheating and overcooling or supersaturation. They are nevertheless very common, and appear whenever, from a substance or mixture of substances in a homogenous state, a part may separate out; thus, for example, gases, solids, or immiscible liquids from liquids, or, on the other hand, liquids or solids from gases. The name "states of instability," which has also been applied in such cases, is equally unsuitable. For the states are not really unstable, since they by no means pass into others on the smallest change. This must rather be compared to the stable equilibrium of a rather tall cylinder standing on one end; the system is certainly stable, but when it suffers a somewhat large displacement it easily assumes another state which is much more stable than the first. It must be admitted, however, that here there is no analogy to the special action exercised by a small quantity of the heterogeneous substance [i.e. a seed crystal] in all the cases above mentioned.*

The term "false equilibria," favored by the French physicist, Pierre Duhem, was not much better (20). However, in his 1897 paper Ostwald finally suggested use of the term kinetically "labile" to describe systems that rapidly underwent the necessary phase change upon reaching their thermodynamically proscribed limits, versus use of the term kinetically "metastable" to describe those that persisted beyond that point and which, in the words of Findlay, exhibited the phenomenon of "suspended transformations" (22).

Though exceptions to Ostwald's rule are known, both it and Ostwald's proposed terminology soon found a place in the first generation of physical chemistry texts (21) – perhaps not surprisingly given that many of them were written by Ostwald's former students – as well as in the advanced monograph literature dealing with both the phase rule (22, 23) and with polymorphism (24-26), though neither of these topics have ever loomed large in the education of the average chemist.

In his later account of 1912 Ostwald also went one step further (no pun intended) and asserted that his rule applied not just to phase transitions but to chemical reactions in general (18):

> *... This phenomenon is quite general in character, and is not limited to equilibrium of the first order, but holds in all changes of state, and especially in chemical reactions in the strict sense.*

This assertion he further illustrated in the 1908 edition of his textbook, *Principles of Inorganic Chemistry*, using the reaction between aqueous sodium hydroxide and dichlorine gas (27). This initially produces the compound known as sodium hypochlorite or Na(OCl):

$$\mathrm{Na(OH)(aq)} + \mathrm{Cl_2(g)} \rightarrow \mathrm{Na(OCl)(aq)} + \mathrm{HCl(aq)} \quad [1]$$

However, if this is allowed sufficient time, it will eventually decompose into the thermodynamically more stable products of sodium chloride and dioxygen gas:

$$\mathrm{2Na(OCl)(aq)} \rightarrow \mathrm{2NaCl(aq)} + \mathrm{O_2(g)} \quad [2]$$

thereby illustrating the rule of stages (27):

> *It might now be asked why hypochlorite is formed at all, and why the whole amount of the substances doesn't straightway pass into the most stable condition, chloride and oxygen ... The answer to this question is again afforded by a general law, which states that in all reactions the most stable state is not straightway reached, but the next less stable or that state which is the least stable of all possible states. Starting from this, the more stable states are reached one after the other, and the process of transformation comes to a stop only when a state is finally attained which cannot further change and is, therefore, the most stable.*

Indeed, Ostwald was quick to point out that the situation was even more complex than this, since in actual fact several additional transient reactions intervened between reaction 1 and reaction 2, leading to the formation of such products as sodium chlorate or Na(ClO_3) and sodium perchlorate or Na(ClO_4) – a situation which he illustrated by means of the free-energy diagram shown in figure 6.

I have been unable to uncover any evidence that Ostwald was aware of Gay-Lussac's earlier statement

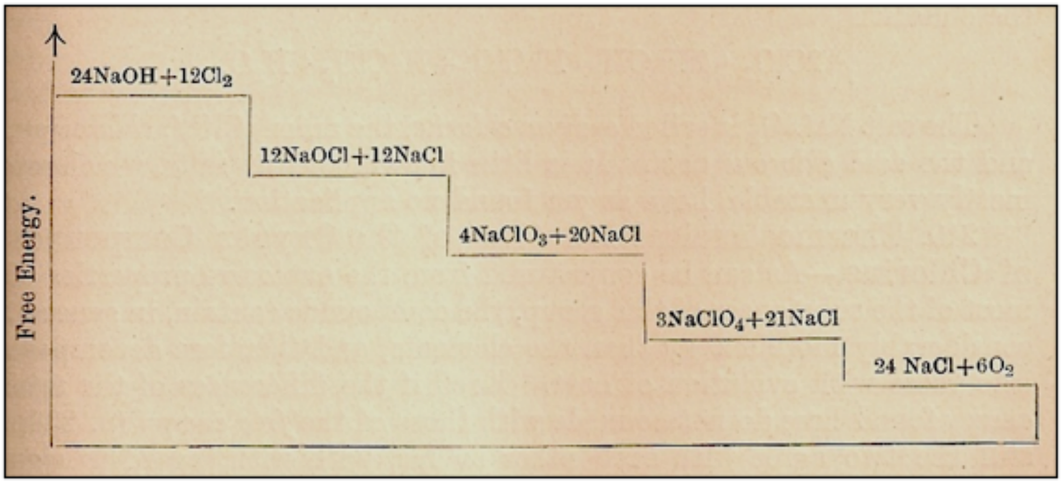

Figure 6. Ostwald 's diagram of 1908 illustrating the successive stages in the reaction between Na(OH)(aq) and Cl_2(aq) as a function of free-energy content.

of 1842. By the 1880s the traditional field of chemical affinity had clearly bifurcated into the newer fields of chemical kinetics versus chemical thermodynamics and there was little motivation for the new generation to consult the outdated paradigms of the older affinity literature. Yet it is certainly curious that Ostwald chose to illustrate the application of his rule to chemical reactions proper using the exact same reaction system as Gay-Lussac had used 66 years earlier!

Transition States and Potential Energy Surfaces

We now fast forward yet another half century and switch from the field of phase science to the field of physical organic chemistry and to a paper published in 1944 by R. B. Woodward (figure 7) and H. Baer on diene-addition reactions (28). In studying the Diels-Alder addition between 6,6-pentamethylenefulvene and maleic anhydride, they found that a mixture of both the *endo-* and *exo-* isomers was obtained for the resulting addition product (figure 8). Initially labelled as the α-*adduct* and β-*adduct*, respectively, these two isomers were found to have quite distinctive physical and chemical properties and to be preferentially favored or disfavored by certain changes in the reaction conditions (28):

... allowed to react in benzene solution, at room temperature, an α*-adduct,* $C_{15}H_{16}O_3$*, m.p. 132°, is obtained. If, however, the mother liquor from the recovery of this product is allowed to stand for several weeks, very large beautiful crystals of a new,* β*-adduct,* $C_{15}H_{16}O_3$*, m.p. 93°, gradually separate. Further, as the initial condensation is carried out at higher temperatures, the formation of the* β*-adduct takes place more rapidly, and less of the* α*-adduct is obtained.*

With the development of absolute rate theory in the 1930s by Eyring in the United States and by Evans and Polanyi in Great Britain (29, 30), Woodward and

Figure 7. Robert Burns Woodward (1917-1979).

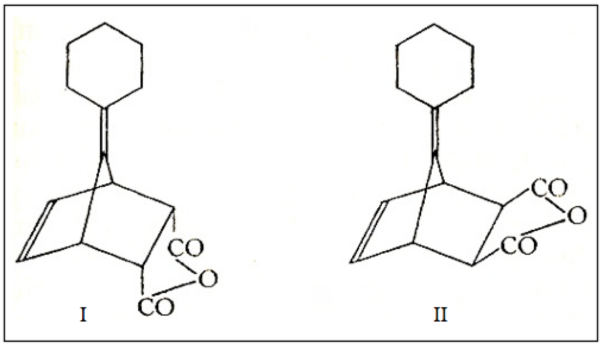

Figure 8. The structures of the *endo-* (I) and *exo-* (II) isomers for the product formed on reacting 6,6-pentamethylene-fulvene with maleic anhydride.

Baer had access to a new set of theoretical concepts for the rationalization of reactivity – such as potential energy surfaces, activation barriers, and transition states – that were largely unavailable to Ostwald in 1897. In order to rationalize their results Woodward and Baer made use of these newer tools by postulating the potential energy surfaces shown in figure 9 in which the rapidly formed *endo*-isomer was assigned a lower activation energy and hence faster kinetics than the *exo*-isomer, but in which the two surfaces crossed before reaching final equilibrium, thereby ultimately making the *exo*-isomer the thermodynamically favored product. Most of the rest of the paper was devoted to experimentally establishing which adduct corresponded to the *exo-* and which to the *endo*-isomer and to electronically and stereochemically rationalizing why the *endo*-isomer might be expected to have a lower activation barrier than the *exo*-isomer.

Though Woodward and Baer did not use the terms kinetic control versus thermodynamic control in their paper, this is still, to the best of my knowledge, the first implicit use of these concepts in the field of organic chemistry, and their experimental observations may be generalized using this terminology by the general rule that:

Low temperatures and/or short reaction times favor kinetically controlled reactivity, whereas high temperatures and/or prolonged reaction times favor thermodynamically controlled reactivity.

As for the terms themselves, they appear to have been first used in the 1956 edition of Jack Hine's textbook, *Physical Organic Chemistry* (31), though it would take another three decades for them to become standard textbook fare. Thus, no mention of them is to be found in an index search of the physical organic texts by Wiberg (1964), Wheeler (1966), Kosower (1968), Hammett (1970), Ritchie (1975) or Jones (1984) and their coverage in the text by Hirsch (1974) is incidental (32). On the other hand, they are employed in the later texts by Lowry and Richardson (1981), Klumpp (1982), Maskill (1985) and Isaacs (1987) (33). Likewise, a computer search of the index for *the Journal of Chemical Education* using the search term "kinetic control" revealed roughly 55 entries, starting very sporadically in 1965 and rapidly increasing only during the last two decades, dealing with laboratory experiments, lecture demonstrations, clever teaching analogies (see figure 10), and popular overview articles related to this topic.

The expected time evolution for the system shown in the potential energy plot in figure 9 is shown in the extent of reaction (ξ) - time (t) plot in figure 11, where, if the reaction is terminated at time $t_1 < t_{eq}$, where t_{eq} is the time required to reach equilibrium, the major product (P') is kinetically controlled, whereas, if it is terminated at $t_2 > t_{eq}$, the major product (P) is thermodynamically controlled. ξ_{max} denotes the stoichiometrically allowed maximum for the extent of reaction parameter as determined by the concentration of the limiting reagent. Of course, the phrase "terminate the reaction" implies that it is possible to alter the reaction conditions such that any further conversion of the kinetic product into the thermodynamic product is completely inhibited, and it becomes possible to isolate the kinetically metastable product and store it in a bottle indefinitely. In the case of the room temperature Diels-Alder addition studied by Woodward and Baer, this was accomplished simply by eliminating contact with the solvent, whereas in high-temperature

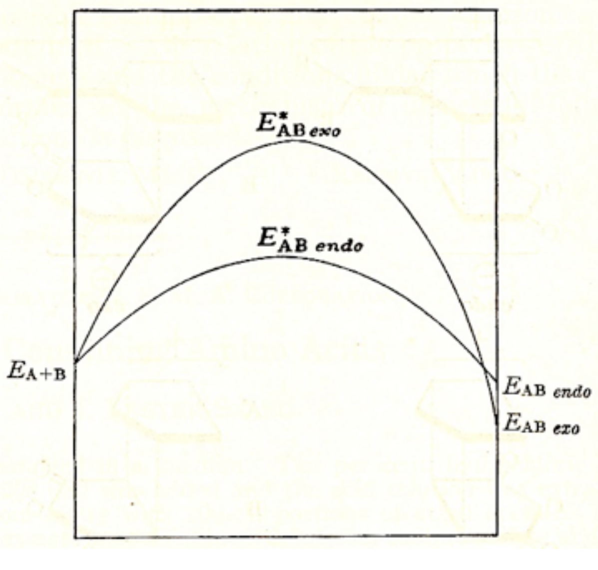

Figure 9. Potential energy diagram used by Woodward and Baer to rationalize kinetic versus thermodynamic control in diene-addition reactions.

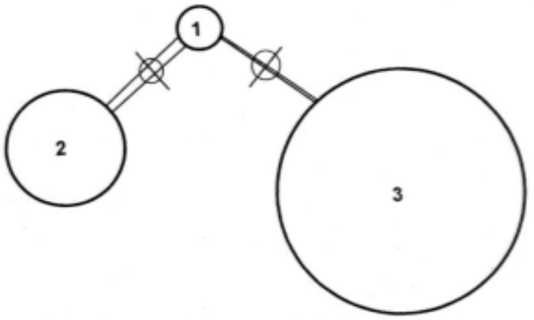

Figure 10. An ideal gas analogy for kinetic versus thermodynamic control proposed by Macomber in 1994 (34). Two evacuated flasks (2 and 3) of unequal volumes are connected to the smaller flask 1 containing an ideal gas, The tube connecting 1 and 2 is 10 times the diameter of that connecting 1 and 3. On quickly opening and closing the two stopcocks the quantity of gas in flask 2 is found to be greater than that in flask 3. This is kinetic control. On reopening the stopcocks permanently, the pressures in all three finally equalize, such that the quantity of gas in 3 is now greater than that in 2. This is thermodynamic control. The volumes of the flasks are analogous to the inverse of their free energy content and hence to their positions on an energy-reaction coordinate plot.

reactions it is usually accomplished by the act of rapidly cooling the kinetic product to room temperature.

From Isomers to Polymorphs

In sharp contrast to the situation in the field of physical organic chemistry, it took a surprisingly long time to arrive at a satisfactory theoretical rationale for Ostwald's law of stages in the field of phase science – a situation not helped by Ostwald's well-known distain for the atomic-molecular theory. One such early attempt was made in 1913 by the Dutch phase scientist, Andreas Smits, using his ill-fated theory of allotropy (35). This postulated that the homogeneous phases of all pure substances, including crystalline solids, were in fact homogenous mixtures of rapidly interconverting molecular clusters of various sizes, known as "pseudo-components." As long as the rate of these interconversions was greater than that for a particular phase change, they had no effect on phase behavior and the substance in question continued to behave thermodynamically as though it had only one component. However, if for some reason, one or more of these cluster interconversions was kinetically inhibited or slowed down in some way, then the substance would begin to display complex phase behavior more typical of multicomponent systems.

In applying his theory to the question of which of several alternative product phases was selected in a polymorphic phase change, Smits assumed that the situation was in fact competitive. Each possible product phase was determined by a particular cluster present in the reactant phase and the question of which product formed first was reduced to the question of which of these competitive alternatives was present in the greatest concentration at the transition point.

By 1925 the German phase scientist, Gustav Tammann, building on work extending back to the 1890s (36), was advocating a related picture based instead upon the formation of centers of nucleation or crystallization in the liquid or gas phases rather than on hypothetical fluctuating molecular clusters. Once again the process was envisioned as being competitive, with the reactant phase at the moment of actual transition containing nuclei for all of the possible solid product phases and the actual solid phase selected being, in turn, determined by their relative concentrations and/or rates of formation (22):

> *Inasmuch as the process of spontaneous transitions is an atomic one it will be subject to the laws of probability. Therefore, only the probability of formation of crystal centers, the forms of which have different stability, may properly be discussed ... Ordinarily grains of the forms with different stability appear simultaneously.*

In 1933 Stranski and Totomanow attempted to test this hypothesis by calculating the relative numbers of different nuclei present in the melts for two example dimorphic systems as a function of temperature and various structural parameters for the product phases using an equation that had been recently proposed by Volmer (37, 38). For the NaBr•2H$_2$O system the more stable polymorph had the greatest nuclei abundance and thus violated Ostwald's rule upon solidification,

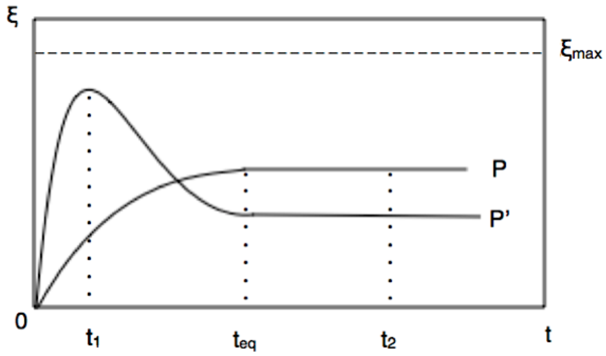

Figure 11. An extent of reaction - time plot for the competitive formation of a kinetically controlled product (P') versus a thermodynamically controlled product (P).

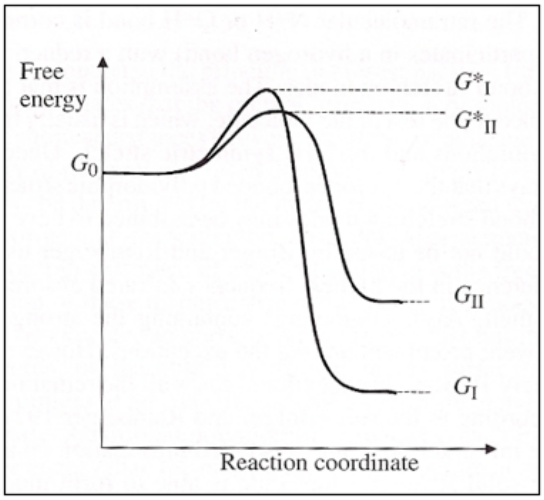

Figure 12. The free-energy surfaces used by Bernstein (26) to rationalize Ostwald's law of stages in terms of kinetic versus thermodynamically controlled reactivity.

whereas for the HgI_2 system the less stable yellow polymorph had the greatest nuclei abundance and thus obeyed Ostwald's rule upon solidification.

It was, however, not until the 1990s that the concepts of kinetic versus thermodynamic control and a potential energy surface (figure 12) similar to that originally proposed by Woodward and Baer in 1944 to rationalize competitive isomers were finally applied to Ostwald's *Stufenregel* and the rationalization of competitive polymorphs, allowing the rule to be reformulated as:

When a solid capable of polymorphic modifications separates from a liquid or gas, the polymorph which is initially deposited is metastable relative to the other potential products and is therefore kinetically rather than thermodynamically controlled.

Furthermore, any apparent exceptions could now be rationalized as cases for which the existence domain for the initial metastable product is so narrow that it is passed through without detection in favor of the more stable product.

It is important to remember that the competitive situation assumed by all of these models applies to the gas or liquid at the point when the first solid phase separates and not necessarily to the subsequent transformation of that solid into more stable modifications. Unlike the competitive formation of isomers dealt with in organic chemistry, in which the various alternative products are simultaneously formed and only their ratios change on moving from the realm of kinetic control to the realm of thermodynamic control, in the case of the competitive formation of polymorphs dealt with in phase science, the winner usually takes all. Indeed, as the names "law of successive reactions" or "rule of stages" strongly imply, the formation of successive solid phases is probably more aptly viewed as a series of consecutive reactions in which each product or stage acts as a metastable reaction intermediate for the production of the next product in the sequence) rather than as the competitive situation envisioned for the initial liquid or gas, and the same may be equally true of the NaOH(aq)-Cl_2(g) reaction system discussed earlier.

It should also be noted that Ostwald's rule probably applies to situations other than just the competitive formation of crystalline polymorphs. Thus Walker suggested as early as 1899 that the initial formation of metastable plastic sulfur rather than crystalline rhombic sulfur upon rapidly cooling molten sulfur or the initial formation of oils and tars in organic chemistry prior to final crystallization of the desired product were all examples of Ostwald's rule in action (21), and the same is probably true of the initial formation of colloidal precipitates and their subsequent aging in the field of traditional wet chemical analysis (39).

Walker also suggested that Ostwald's rule was really a rule of least change – in other words, that the initial product corresponded to whichever phase deviated the least from the reactant phase (21). More recently Isaacs has suggested a molecular version of this idea in the field of organic chemistry based on the "principle of least motion," first suggested by Rice and Teller in 1938 (33, 40):

... those elementary reactions are favored which involve the least change in atomic positions and electronic configurations.

In short, the less structural and electronic rearrangement required, the lower the activation energy for the product in question, and the faster its rate of formation.

Last, but not least, the physical organic textbook by Klumpp has suggested that kinetic control automatically implies that the competitive reactions in question are irreversible, whereas thermodynamic control automatically implies that they are reversible (32). While the second of these statements is true by definition, the first statement is not (41), as demonstrated by the ability of many systems to switch from the domain of kinetic control to the domain of thermodynamic control as a function of reaction time and/or temperature and by our earlier analysis of figures 9, 11 and 12.

Indeed, the situation is even more complex than suggested by the above discussion since yet other possible potential energy surfaces are also conceivable, such as that given in figure 13. For systems of this type both the kinetics and thermodynamics lead to an identical result and the potential energy surfaces are said to obey the so-called "noncrossing rule" (42). This situation is one of the fundamental, albeit often unarticulated, assumptions underlying the application of so-called linear free-energy correlations as well as most of the approximate electronic reactivity indices much beloved of the modern-day organic chemist. This is especially true of those based on the use of perturbation theory, though, as admitted by at least one leading theoretician, its validity appears to have been most often assumed after the fact rather than rigorously proven up front (42):

> *Such a procedure makes use of a rule known as the noncrossing rule, which states that for similar reactants the ratio of the energy necessary to reach any particular (but common) point on the respective reaction path curves is proportional to the ratio of the activation energies ... Although there is neither proof nor reason for such behavior, it has reasonably been verified experimentally and serves as a basis for most attempts to correlate chemical reactivity, particularly aromatic reactivity.*

The Ubiquity of Kinetic Metastability

Though first formulated by Gibbs in 1876, the phase rule did not begin to truly impact on chemistry until the 1890s (43). But once chemists realized that application of the rule held out the promise of definitively characterizing each known reaction system in the form of a summary phase diagram, their enthusiasm knew no bounds. Beginning with the work of the Dutch phase chemist, Bakhuis Roozeboom, in the period 1901-1910 (44), massive collections of experimentally measured phase diagrams began to appear in the literature, especially in those fields dealing with the high-temperature chemistry of metallic alloys and ceramics (45-47) and, with the introduction of the alternative predominance or Pourbaix equilibrium plots in the 1940s, in the field of room-temperature aqueous solution chemistry as well (48-50). Though these latter plots are not identical to phase diagrams, they also deal with equilibrium conditions, albeit with respect to reaction equilibria rather than phase equilibria.

Indeed, so enthusiastic was Ostwald about these developments that in 1907 he wrote a book entitled, in English translation, *The Fundamental Principles of Chemistry: An Introduction to All Textbooks of Chemistry*, in which he attempted to eliminate the atomic-molecular theory from chemistry and to instead operationally derive its most fundamental concepts on the basis of the phase rule and the use of experimentally measured phase diagrams (51). However, about a third of the way through the book, one gets the impression that Ostwald had begun to slowly realize that such an approach failed to capture many essential aspects of chemistry. As we have already seen, he was fully aware of the phenomenon of kinetic metastability in connection with the study of both phase transitions and homogenous reaction systems and dutifully mentioned both, as well as his *Stufenregel*, thus forcing himself to admit, as the book proceeded, the existence of an increasing number of exceptions to his program to base chemistry solely on the study of phase diagrams.

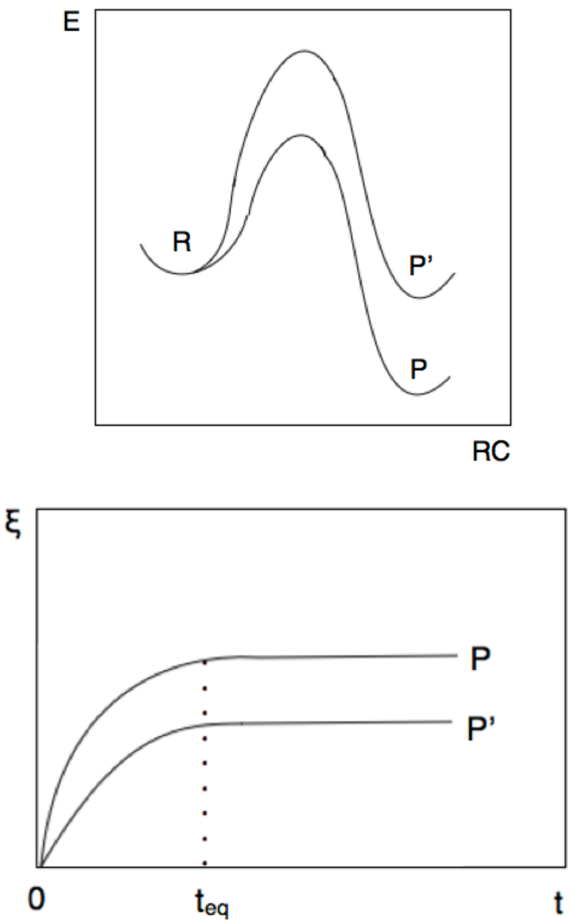

Figure 13. A potential energy plot and the corresponding extent of reaction - time plot for a competitive reaction obeying the noncrossing rule showing that kinetics and thermodynamics both predict the same dominant product (P).

For example, if one goes to the stock room to get a bottle of phosphorus, they will have a choice of either solid white (yellow) or amorphous red phosphorus, both of which are kinetically metastable relative to the thermodynamically stable black form and neither of which appear on the phase diagram for this element (52). Likewise, one may read an extensive literature on the role of ozone in protecting the environment from excessive UV radiation and its significance for the evolution of life on earth, or read of its properties in older descriptive inorganic textbooks, or even demonstrate its preparation for an introductory chemistry class, yet once again no trace of its existence will be found on the phase diagram for the element oxygen (52). Entire classes of chemical compounds, such as the boron hydrides or the nitrogen oxides, also owe their existence to kinetic metastability and are missing from phase diagrams.

As noted by Ostwald near the end of his book, even more significant problems result when one looks at the phenomenon of isomerism and the chemistry of organic carbon compounds (51):

> *Cases of isomerism are found in very great numbers among carbon compounds, and this is because of two reasons: first, carbon compounds are very numerous and varied; second, they almost always exhibit an extremely small reaction velocity. This means that we are able to prepare and observe forms which could not be characterized as individual substances if other conditions held. The result of this condition has been that investigators have studied these individual substances, unstable of themselves, but easy of isolation because of their very small reaction velocities.*

Thus in a few sentences Ostwald managed to dismiss the entire science of organic chemistry as the study of transient metastable reaction intermediates, and it must be admitted that this characterization is not far off the mark, since, with the possible exception of the aqueous phase chemistry of organic species with ionizable functional groups, very few phase studies are known for typical organic systems (53).

The point here is that both phase and Pourbaix diagrams are *equilibrium* diagrams and, as such, display only thermodynamically controlled reactivity. Though they sometimes attempt to incorporate information on kinetically controlled metastability in the form of dotted lines to indicate curves for supercooling or crosshatching to indicate regions of kinetic passivation due to surface precipitation, they, by and large, ignore the rich field of kinetically controlled reactivity with its many metastable compounds and allotropes – a world which gives chemistry much of its variety and fascination. While the information they contain on the equilibrium interactions within a chemical system is extremely valuable, they should never be mistaken for a complete picture of the system's known chemistry as unintentionally implied by the title of at least one such recent compilation (50).

Forgetting Once Again?

I first became interested in the subject of kinetic versus thermodynamic control of competitive chemical reactions when, as a young assistant professor at the Rochester Institute of Technology, I was assigned the task of developing a laboratory course in inorganic synthesis. Among the preparations selected for use were several that involved the synthesis of various coordination isomers and it occurred to me that it would make an interesting exercise for the students to deduce which isomer was the thermodynamic product and which the kinetic product and how manipulation of the reaction conditions favored one over the other. Though this distinction lies at the very foundations of chemical theory and is one of the most fundamental questions that can be asked about a chemical reaction, I quickly discovered that the inorganic synthesis literature was all but silent on this issue. The various preparations given in typical lab manuals were presented as rote recipes to be followed, with little or no rationale as to how they were originally discovered or optimized or how they illustrated the application of the theoretical principles presumably learned in an earlier course on physical chemistry.

I had much the same experience several years later when writing a history of chemistry. In tracing the history of photochemistry, I discovered that much of the early theory in this field was based on supposed analogies with the process of electrolysis (54). In this latter process the applied electrical energy is being used to drive an otherwise thermodynamically unfavorable reaction uphill. Yet in many photochemical processes the applied light energy is obviously acting as a source of activation energy to initiate a thermodynamically favorable but otherwise kinetically inert reaction, such as that between dihydrogen and dichlorine gas. Just what was going on in the newer field of organic photochemistry was not so obvious, so I asked a colleague, who was an expert in the field, whether the majority of the reactions he worked with were thermodynamically allowed, but kinetically inert, and thus being photochemically activated, or whether they were thermodynamically unfavorable and were being photochemically driven uphill. The response was a blank look, as though the question made no sense, and an eventual admission that he had never thought about it one way or another as his focus was totally on the nature of the photochemically excited state and the details of the subsequent reaction mechanism.

Even more disturbing was a more recent incident involving the supposed preparation of $HgF_4(g)$ using matrix isolation (55). I had previously written a paper pointing out that Zn, Cd and Hg were really main-block, rather than transition-block, elements since they never made use of either d-electrons or empty d-orbitals in their bonding (56), and the possible existence of mercury in a IV oxidation state obviously contradicted this conclusion.

This was once again a case of competitive reactions, this time involving the formation of HgF_2 versus HgF_4 rather than alternative isomers or polymorphs, and in my subsequent commentary I pointed out that the latter species, if it actually existed, must be a kinetically metastable reaction intermediate whose detection was made possible only by the fact that the extremely low temperature used (4°K) kinetically inhibited its dissociation (and isomerization when relevant) and the surrounding rare-gas matrix provided a diffusion barrier which kinetically inhibited molecular collisions among the various reactants and products and thus prevented polymerization (and disproportionation when relevant) (57). In this case inhibition of polymerization was key, as the supposed preparation theoretically depended on the favorable competitive formation of a monomeric $HgF_4(g)$ molecule versus that of an isolated monomeric $HgF_2(g)$ molecule and rapidly became unfavorable once the HgF_2 monomer was allowed to polymerize into the far more stable 8/4 infinite framework structure that HgF_2 normally adopts at all temperatures below 919°K.

All of this raised the further fundamental question of whether such transient species represented typical chemical behavior and whether they should be taken into account when classifying elements in the periodic table. However, when discussing the manuscript of the commentary with a colleague who specialized in matrix isolation, and in a subsequent e-mail correspondence with one of the coauthors of the original paper, both expressed great surprise that I had characterized the reported product as a transient kinetically metastable species and had interpreted the rare-gas matrix as a device for kinetically inhibiting polymerization. Though subsequent work failed to reproduce the reported species, the puzzlement that I encountered once again illustrated a widespread failure to explicitly think in terms of kinetic versus thermodynamic factors when dealing with chemical reactivity – a failure all the more disturbing as it involved specialists using a technique explicitly designed to optimize kinetic control.

Although admittedly anecdotal, such incidents would appear to bode ill for the prospect of making the concepts of kinetic versus thermodynamic control an inherent part of every chemist's thinking about competitive chemical reactions, whether they lead to alternative isomers, alternative polymorphs, or alternative oxidation states, and suggests that, once physical organic chemistry ceases to be a cutting-edge field and fades from the curriculum, its textbooks and lessons, like those of both affinity theory and phase science before it, will also fade from the chemical consciousness only to be rediscovered once again in some future context.

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Publication History

Published in *Bull. Hist. Chem.,* **2014**, *39(2)*, 107-121.

XXIII

The Importance of Kinetic Metastability

Some Common Everyday Examples

The chapter on thermodynamics in the typical freshman textbook is likely to leave students with the erroneous impression that the only requirement for a spontaneous chemical reaction to occur is a negative value for the resulting free-energy (ΔG_{rx}) change. While this is certainly a necessary requirement for a favorable reaction, it is not a sufficient requirement, since the reaction in question may also happen to be kinetically metastable or inert – a condition which, unlike thermodynamic stability, cannot be predicted using a simple pen and paper calculation suitable for an introductory chemistry course.

Unfortunately, this misconception is reenforced by the widespread use of the phrase "thermodynamically spontaneous" as a synonym for "thermodynamically favorable." While it is true that the word "spontaneous" does not mean the same thing as "instantaneous," it does imply that the process in question is self-initiating or, in the words of Webster, that it "arises without external constraint or stimulus." This is not the case for thermodynamically favored but kinetically metastable reactions, since they require, by definition, an "external stimulus" in the form of either an external source of activation energy or the addition of a suitable catalyst before proceeding.

Kinetic metastability is neither rare nor unusual. In fact, an incredible number of chemical compounds and allotropic modifications of simple substances owe their continued existence to this phenomenon. Of course, it is meaningless to talk of a species as being either inherently thermodynamically stable or kinetically metastable. These terms must always be used with reference to a specific chemical reaction and set of reaction conditions. When evaluating whether a given species can be prepared and stored in bulk under normal laboratory conditions, at least five such reactions must be evaluated with respect to their thermodynamic feasibility at room temperature and pressure (RTP): oxidation, hydrolysis, internal decomposition, polymerization, and isomerization (1). If the species in question is found to be thermodynamically unstable with respect to one or more of these, but can still be prepared and stored in bulk, then it may be safely inferred that it is kinetically metastable with respect to the process or processes in question.

In what follows, we will first provide a brief discussion, with examples, of the relevance of kinetic metastability to each of the above five processes, followed by a more detailed discussion of three common household chemicals that owe both their existence and/or commercial use to this often neglected phenomenon. We will conclude with a brief discussion of the status of the metastability concept in the typical chemistry textbook. In all cases, whether dealing with pure substances or solutions, we will assume that we can evaluate the sign of ΔG using the sign of the corresponding standard-state free energy change ($\Delta G°$), since we are only interested its sign and not necessarily in its precise numerical value (2, 3).

Oxidation

Essentially all organic compounds that can be stored and/or manipulated in the presence of air are thermodynamically unstable, but kinetically metastable, with respect to oxidation at RTP – the simplest example being the combustion of methane or natural gas (2):

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta G° = -817.95 \text{ kJ/mol rx} \quad [1]$$

Though such materials are said to be to be flammable, they usually require an external source of activation energy in the form of either a flame or spark before oxidation can commence.

The same is also true of virtually all of the metals from which we fabricate so many everyday items – the most obvious example being the rusting of iron:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) \qquad \Delta G° = -1487.22 \text{ kJ/mol rx} \quad [2]$$

Though this reaction does occur at RTP, it does so quite slowly and then only in the presence of moisture. For most metals this kinetic metastability is a function of the low surface to volume ratio found in everyday metal objects but rapidly disappears when the metals are finely powdered, in which case they frequently become pyrophoric.

Less often appreciated is the fact that many halide and chalcide salts are also thermodynamically unstable, but kinetically metastable, with respect to oxidation at RTP, though chemists manipulate them with impunity in the air – typical examples being the oxidation of either copper iodide or zinc sulfide:

$$2CuI(s) + O_2(g) \rightarrow 2CuO(s) + I_2(s) \qquad \Delta G° = -128.8 \text{ kJ/mol rx} \quad [3]$$

$$2ZnS(s) + O_2(g) \rightarrow 2ZnO(s) + 2S(s) \qquad \Delta G° = -274.64 \text{ kJ/mol rx} \quad [4]$$

Hydrolysis

Exposure to the air means contact not only with dioxygen gas but also with water vapor. Indeed, water, as both a vapor and liquid, is ubiquitous in both nature and most laboratory settings. Yet, once again, we encounter many substances which, though thermodynamically unstable at RTP with respect to hydrolysis or reaction with water, may be handled with impunity in its presence due to kinetic metastability. A typical example is the liquid, carbon tetrachloride, which can be used to extract organic materials from aqueous solutions in a separatory funnel and which was once sold as a common household spot remover:

$$CCl_4(l) + 2H_2O(l) \rightarrow CO_2(g) + 4HCl(g) \qquad \Delta G° = -236.48 \text{ kJ/mol rx} \quad [5]$$

A more spectacular example is metallic aluminum, which is even more thermodynamically unstable with respect to reaction with water at RTP than are the alkali metals:

$$2Al(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 3H_2(g) \qquad \Delta G° = -870.77 \text{ kJ/mol rx} \quad [6]$$

Here kinetic metastability is the result of the formation of a coherent microfilm of $Al_2O_3(s)$ on the surface of the metal that protects it from further reaction with water and air, thus allowing us to use it for the manufacture of everything from beer cans to airplanes.

Internal Decomposition

Substance that are both thermodynamically allowed and kinetically reactive with respect to oxidation and/or hydrolysis at RTP can, of course, alway be prepared on a vacuum line or in a glove box and stored in evacuated and hermetically sealed glass containers. But even then, these materials may still be thermodynamically unstable with respect to internal decomposition of some sort and can thus exist only if they also happened to be kinetically metastable with respect to these processes.

A good example is the compound, diborane, which must be protected from contact with both dioxygen gas and water, but which is also thermodynamically unstable, but kinetically metastable, with respect to dissociation into its component simple substances at RTP:

$$B_2H_6(g) \rightarrow 2B(s) + 3H_2(g) \qquad \Delta G° = -173.2 \text{ kJ/mol rx} \quad [7]$$

Even more common than decomposition via dissociation is decomposition via disproportionation, a process in which a compound having an intermediate oxidation state decomposes into two products – one having a lower oxidation state and the other a higher oxidation state – as illustrated by the kinetically metastable compound titanium triiodide:

$$2TiI_3(s) \rightarrow TiI_2(s) + TiI_4(s) \qquad \Delta G° = -44.3 \text{ kJ/mol rx} \quad [8]$$

in which half of the Ti(III) is reduced to Ti(II) and half is oxidized to Ti(IV).

Polymerization

Even when a substance is kinetically and/or thermodynamically protected from internal decomposition, yet other processes may still be capable of compromising its existence. Thus white tetraphosphorus is thermodynamic unstable, but kinetically metastable, with respect to polymerization to red phosphorus at RTP:

$$xP_4(s) \rightarrow (P_4)_x(s) \qquad \Delta G° = -12.12 \text{ kJ/mol rx} \quad [9]$$

Though red phosphorus is amorphous, and hence lacking a crystal structure, it has long been assumed to be composed of infinite chains of some sort produced by linking the discrete tetrahedral molecules of white phosphorus together via the opening of one or more of their edge bonds.

Both white and red phosphorus are also thermodynamically unstable with respect to oxidation at RTP, but whereas white phosphorus is kinetically labile and must be stored under water to protect it from contact with air, red phosphorus is kinetically metastable and may be handled and stored in its presence. Ironically, the use of water to protect white phosphorus from air oxidation is yet another instance of kinetic metastability, since white phosphorus is also thermodynamically unstable with respect to hydrolysis:

$$P_4(s) + 16H_2O(l) \rightarrow 4H_3(PO_4)(aq) + 10H_2(g) \qquad \Delta G° = -677.55 \text{ kJ/mol rx} \quad [10]$$

Isomerization

The fifth and last method of compromising the existence of a species is the possibility of internal rearrangement or isomerization. A particularly striking example is the kinetic metastability of diamond, which is thermodynamically unstable at RTP with respect to rearrangement to graphite:

$$\text{C (diamond)} \rightarrow \text{C (graphite)} \qquad \Delta G° = -2.83 \text{ kJ/mol rx} \quad [11]$$

a situation that has caused more than one chemical wag to comment on the irony of using diamond engagement and wedding rings as symbols of eternal love. Even more numerous examples are found among the thousands of isomers that have been prepared by the organic chemist since, within any given set of isomers, one of them must be thermodynamically more stable than the others (3).

Hydrogen Peroxide Solution

Moving on to our everyday household examples, we begin with a product found in most bathroom medicine cabinets – a bottle of a 3% aqueous solution of hydrogen peroxide, $H_2(O_2)$ (figure 1), commonly used for cleaning cuts and scraps (4). This compound is already oxidized, is thermodynamically stable with respect to reaction with water, and neither polymerizes nor isomerizes. Since it has a negative free-energy of formation, it is also thermodynamically stable with respect to dissociation into its component simple substances:

$$H_2(O_2)(l) \rightarrow H_2(g) + O_2(g) \qquad \Delta G° = +120.41 \text{ kJ/mol rx} \quad [12]$$

Nevertheless, it turns out that it is thermodynamically unstable with respect to disproportionation into water and dioxygen gas :

$$2H_2(O_2)(l) \rightarrow 2H_2O(l) + O_2(g) \qquad \Delta G° = -233.54 \text{ kJ/mol rx} \quad [13]$$

a process in which half of the oxygen in the peroxide anion is oxidized from O(-I) to O(0) and half is reduced from O(-I) to O(-II).

Since it is possible to purchase a bottle of a 3% aqueous solution of hydrogen peroxide at your local drug store and keep it for some time in your medicine cabinet, reaction 13, though thermodynamically allowed, must be kinetically inhibited. In other words, hydrogen peroxide must be kinetically metastable with respect to disproportionation into water and dioxygen gas at RTP. Here, as mentioned earlier, we are assuming that, though the value of ΔG for the decomposition of a dilute solution of hydrogen peroxide will differ numerically from the value of $\Delta G°$ in equation 13, which applies to the pure substance in its standard state, the sign of the free energy change will still be negative (3).

Figure 1. A typical bottle of 3% hydrogen peroxide.

As already noted, when talking about metastability one must specify not only the nature of the reaction under consideration, but the reaction conditions as well. If the latter are altered so as to enhance the rate of reaction, the species in question may well disappear in accord with the dictates of its thermodynamics. In general, at least four factors must be considered when attempting to preserve a kinetically metastable chemical, all of which are relevant when it comes to working with hydrogen peroxide (6):

1. Sensitivity to concentration
2. Increases in temperature
3. Contact with catalysts
4. Exposure to light

The first of these factors is only relevant when dealing with gases and solutions, rather than pure substances (7), but this is precisely the case with hydrogen peroxide which is almost always in the form of an aqueous solution of some sort, ranging from the 3% solution found in drug stores, to the 30% solution normally used in chemical laboratories, to various industrial grades approaching concentrations of 90% and greater. As might be anticipated from the basic principles of chemical kinetics, the more dilute the solution, the slower the rate of reaction 13, thus making the dilute solution in your medicine cabinet less susceptible to disproportionation than the more concentrated laboratory and industrial grades.

An increase in temperature almost always increases the rate of a chemical reaction and reaction 13 is no exception. Indeed, it almost perfectly follows the traditional rule of thumb that the rate of a reaction will double with each 10° C increase in temperature (6). For the dilute solution in your medicine cabinet, storage at room temperature is generally sufficient, but for the preservation of more concentrated solutions refrigeration is recommended.

Many substances are able catalyze reaction 13, including hemoglobin, transition metal ions, halide ions, many enzymes, and even rough surfaces that can provide nucleation sites for the formation of dioxygen gas bubbles. Protection of hydrogen peroxide solutions from contamination with trace amounts of these catalytic agents is perhaps the greatest challenge when it comes to prolonging its existence. With this in mind, most hydrogen peroxide solutions contain small amounts of other chemicals called "stabilizers" that have been added on purpose. These may range from organic additives, such 8-hydroxyquinoline and acetanilide, to inorganic additives, such as sodium stannate and sodium pyrophosphate. The assumption seems to be that these materials are somehow able to deactivate potential trace catalysts, through there seems to be little consensus concerning their mode of operation or even over the question of whether they are truly effective (6). Both laboratory experiments and classroom demonstrations illustrating the catalytic decomposition of hydrogen peroxide by such materials as $MnO_2(s)$, activated charcoal, or saturated KI solutions are relatively easy to locate on the internet.

Figure 2. A typical bottle of household bleach.

The fourth and final factor listed above is seldom discussed in freshman chemistry treatments of chemical kinetics, since not all reactions are photochemically sensitive. However, reaction 13 is, and especially to UV light. For this reason the hydrogen peroxide in your medicine cabinet traditionally came in a dark brown glass bottle, though this has now been largely replaced with opaque plastic containers instead.

If all of the above precautions are followed, at least one commercial manufacturer of hydrogen peroxide was willing to claim on its website that "the losses of hydrogen peroxide will be very slight even during extended periods (years) of storage."

Household Bleach

For our second everyday household example, we move to the laundry room and examine the bottle of so-called chlorine bleach (figure 2). Its label indicates that it actually contains a 8.25% solution of sodium hypochlorite, Na(OCl), as the active ingredient (8). In addition, it also contains some sodium chloride and sodium hydroxide. These are in fact the remnants of its mode of manufacture, since it is not made by directly dissolving pure solid sodium hypochlorite in water but rather by bubbling dichlorine gas through an aqueous solution of sodium hydroxide (9):

$$2Na(OH)(aq) + Cl_2(g) \rightarrow Na(ClO)(aq) + NaCl(aq) + H_2O(l) \quad \Delta G° = -90.45 \text{ kJ/mol rx} \quad [14]$$

Though pure Na(OCl)(s) can also be prepared, it is presumably completely ionized in aqueous solution, so that our concern here is rather with the stability of the $ClO^-(aq)$ anion instead. This is thermodynamically stable with respect to direct reaction with the dioxygen gas in air:

$$ClO^-(aq) + O_2(g) \rightarrow ClO_3^-(aq)$$

$$\Delta G^\circ = +33.5 \text{ kJ/mol rx} \quad [15]$$

as well as with respect to hydrolysis:

$$ClO^-(aq) + H_2O(l) \rightarrow H(ClO)(aq) + OH^-(aq)$$
$$\Delta G^\circ = +36.79 \text{ kJ/mol rx} \quad [16]$$

and, in any case, the high pH of the commercial solution, due to the slight excess of Na(OH)(aq) present, further guarantees that this equilibrium will be displaced far to the left, though the reverse will happen if the bleach is diluted with large amounts of water.

Nor are there issues with polymerization and isomerization. Rather it is two thermodynamically favorable modes of decomposition at RTP that are of most concern. The first of these involves disproportionation to the chloride and chlorate anions:

$$3ClO^-(aq) \rightarrow 2Cl^-(aq) + ClO_3^-(aq)$$
$$\Delta G^\circ = -155.01 \text{ kJ/mol rx} \quad [17]$$

in which two-thirds of the Cl(I) is reduced to Cl(-I) and one third is oxidized to Cl(V). The second reaction involves decomposition into chloride ion and dioxygen gas:

$$2ClO^-(aq) \rightarrow 2Cl^-(aq) + O_2(g)$$
$$\Delta G^\circ = -184.51 \text{ kJ/mol rx} \quad [18]$$

in which Cl(I) is reduced to Cl(-I) and O(-II) is oxidized to O(0). Though reaction 18 is thermodynamically more favorable than reaction 17, the latter reaction is less kinetically metastable at RTP and accounts for over 90% of the decomposition observed over time in commercial bleach solutions at RTP (10). As with the earlier hydrogen peroxide solution, in the above analysis we are assuming that the sign of the actual ΔG values for corresponding reactions of the dilute bleach solution are the same as the sign of the ΔG° values for a standard state solution (3).

The same four factors that affected the metastability of hydrogen peroxide with respect to reaction 13 also affect the metastability of our hypochlorite solution with respect to reactions 17 and 18. Thus the more concentrated the solution and the higher the temperature, the greater the rate of decomposition. Likewise, these reactions are sensitive to UV light and for this reason bleach was originally sold in dark brown glass bottles, though it now comes in opaque plastic containers. In keeping with these factors, the label on the bleach bottle instructs the user to "store this product in a cool, dry area, away from direct sunlight and heat to avoid deterioration." Reaction 18 in particular is also catalyzed by various transition metal ions and several laboratory experiments illustrating this phenomenon are available on line, though this problem doesn't seem to be as serious a concern as was the case with hydrogen peroxide (11).

Carbonated Water

For our third and final everyday example we move to the kitchen refrigerator and examine a bottle of soda. In order to avoid any complications due to coloring, flavoring, or sweetening agents, we will select a bottle of seltzer water (figure 3), which is a simple solution of carbon dioxide in water (12). Though there are also small amounts of carbonic acid, bicarbonate anion, and $H^+(aq)$ present due to hydrolysis:

$$CO_2(aq) + H_2O(l) \rightarrow H_2(CO_3)(aq) \rightarrow H^+(aq) + HCO_3^-(aq) \quad [19]$$

$CO_2(aq)$ is by far the dominant species in solution and is the only one of interest to us as it is primarily responsible for the fizz that we associate with carbonated beverages. In other words, when considering the level of carbonation, we are primarily concerned with the simple equilibrium:

$$CO_2(aq) \rightarrow CO_2(g) \qquad \Delta G^\circ = -8.18 \text{ kJ/mol rx} \quad [20]$$

where once again we are assuming that the sign of the actual ΔG value for corresponding reaction of the

Figure 3. Typical bottles of carbonated water or seltzer.

commercial carbon dioxide solution is the same as the sign of the $\Delta G°$ value for a standard state solution (3).

At room temperature the dissolved carbon dioxide in a sealed can or bottle of carbonated water is in equilibrium with the small volume of gaseous carbon dioxide above the liquid, which is usually set at an average pressure of roughly 2.5 atm, and is thus thermodynamically stable. When the can or bottle is opened, however, this is no longer true as the ambient carbon dioxide pressure rapidly falls to the value of the partial pressure of carbon dioxide in the surrounding air. This is approximately 3.9×10^{-4} atm or roughly 10,000 times less than that in the sealed container (13). Thus, on opening the container, the equilibrium in equation 20 is subjected to a massive Le Chatelier perturbation, which shifts it far to the right, with the result that, when it finally reequilibrates, it has lost most of its detectable fizz.

Indeed, carbonated water approximately obeys Henry's law for the solubility of gases in liquids, which states that, at constant temperature, the concentration of the dissolved gas (C_g) is directly proportional to the partial pressure (P_g) of the gas above the liquid:

$$P_g = kC_g \qquad [21]$$

This means, of course, that once the carbonated water equilibrates with the atmosphere, the concentration of the dissolved carbon dioxide will also be roughly 10^{-4} or 10,000 times less than that in the unopened can or bottle.

Luckily the rate at which reaction 20 re-equilibrates is relatively slow so that, despite the initial release of dissolved carbon dioxide on opening the container, it takes roughly a half hour or so for the level of carbonation, on exposure to the atmosphere, to fall to a level where the liquid has lost sufficient fizz so as to be declared "flat" and several hours more before it finally comes to equilibrium with the ambient carbon dioxide pressure. Thus, strongly carbonated beverages in an open container or glass are in effect metastable and, if not for the intervention of sluggish kinetics, we would not have the pleasure of drinkable carbonated beverages.

In keeping with this, anything that increases the rate of re-equilibration will also increase the rate at which the carbonation is lost and thus diminish the period of metastability – whence the well-known fact that the warmer the beverage the quicker it losses its fizz. Likewise, rough surfaces that can act as nucleation sites for the formation of carbon dioxide gas bubbles are able to catalyze the rate of decarbonation, as may be demonstrated by dropping some activated charcoal or, better still, a "Mentos" candy mint into a bottle of seltzer water. As may be inferred from the fact that carbonated beverages often come in clear glass or plastic bottles, reaction 20 is fortunately not particularly sensitive to either visible or UV light.

There are, however, some significant differences between this example and our earlier examples, not the least of which is the much shorter time frame. Nevertheless it serves to further underscore the necessity of tempering purely thermodynamic considerations with a knowledge of the relevant kinetic factors, as well as calling attention to the fact that the metastability concept is both time dependent and the subject of a ongoing debate over how to best define it.

The definition problem was already discussed by Lewin many years ago (14). After first noting that use of the term had become broader and broader with the passage of time, this author advocated limiting it to its original usage in the phase literature to describe phases no longer in equilibrium with their environment but which could be induced to transform into the proper equilibrium phase only by addition of an appropriate seed crystal. To deal with yet other kinds of what he called "nonstability," Lewin proposed a five-category classification, which, besides metastable states in this very limited sense, also included unstable states, pseudo-stable states, quasi-stable states and meso-stable states. According to this classification – which to the best of my knowledge has never gained widespread acceptance – the re-equilibrating carbonated water is actually an example of an unstable system and the hydrogen peroxide and bleach solutions are examples of a pseudo-stable system. However, in keeping with the above comment on the role of time, the sole difference between these two classes, according to Lewin, was their rate of transformation, with unstable states "undergoing continuous transformation into states possessing lower free energy content," and pseudo-stable states only appearing to be in equilibrium, but "nevertheless slowly, or very slowly, changing continuously into lower free energy states."

In contrast, Luisi, in a study of the formation of micelles and vesicles, concluded that "metastable states are kinetic traps" which, once surmounted, need not necessarily lead to a true equilibrium state (15). This definition is much broader than that of Lewin and is much closer to the concept of metastability used in this paper, where we have used the term to denote any thermodynamically unstable substance that persists, for kinetic reasons, for a sufficiently long time period so as to have practical commercial applications. Nevertheless, because of the difference in the time frame and lack of external stimulus, some readers may feel that the example of the re-equilibrating carbonated water is better thought of as a case of simple thermodynamic instability coupled with relatively sluggish kinetics.

Metastability in the Textbook Literature

The concept of kinetic metastability was first introduced by Wilhelm Ostwald in 1897 in connection with his studies of kinetically inhibited phase changes and by 1909 he had extended it to the case of conventional chemical reactions as well (16). Both the topic and term were mentioned in most monographs on the phase rule and in most chemical dictionaries written prior to the 1960s, but references to these traditional applications have since become increasingly rare. To the extent that the terms "metastable and/or metastability" appear in current physical chemistry textbooks, they are used instead to describe either excited spectroscopic states or reaction intermediates with prolonged lifetimes. In no case could I find the terms listed in the indices of introductory chemistry textbooks or in more recent chemical dictionaries.

In their chapters on chemical thermodynamics, some of the more detailed freshman textbooks, after first defining spontaneous as a process that proceeds without external assistance, do admit that many so-called spontaneous reactions actually require an external source of activation energy before proceeding, and at least one gave an example of a thermodynamically allowed process (the dissociation of benzene into its component simple substances) for which the activation barrier was so high that it essentially never occurred. But these few explicit examples are isolated and never generalized under the rubric of kinetic metastability, thus leaving the student with the false impression that they are relatively uncommon.

However, as has hopefully been demonstrated in this paper, such examples are anything but rare and every introductory textbook discussion of chemical thermodynamics should include a cautionary section dealing with the phenomenon of kinetic metastability and its role in creating chemical diversity in both the laboratory and the world at large. Though we have limited ourselves to examples of metastable molecules and ions, the phenomenon is actually more widespread. Thus Everett has emphasized the importance of metastability in preparing colloidal dispersions that are thermodynamically unstable with respect to coalescence into their component bulk phases (17), and Cahn has singled out its importance in the field of materials science with respect to the preparation of unusual alloy phases with unique properties (18). The same is equally true of various glasses, all of which are metastable relative to the corresponding crystalline solids (19).

In keeping with this, use of the misleading descriptors "thermodynamically spontaneous and non-spontaneous" should be eliminated and replaced by a less suggestive terminology, such as "thermodynamically allowed and disallowed" or "thermodynamically feasible and unfeasible" (20). I am hardly the first to object to the restricted thermodynamic use of the word spontaneous. Ochs, for example, has presented a detailed list of reasons for why the term should be eliminated, not only from thermodynamics, but from chemical discourse in general (21). In contrast, Luisi has argued for retaining it in chemical discourse but decoupling it from its restricted thermodynamic sense by adding a kinetic component as well so as to describe a reaction that is both thermodynamically and kinetically favored – a usage that would more closely match its everyday meaning (15). Lastly, Earl has argued for retaining the word in its restricted thermodynamic sense but always coupling it with the qualifier "thermodynamic" in order to explicitly indicate that it is being used in a special way (22).

Personally, I have come to prefer the descriptors "thermodynamically favored and disfavored" and have used them throughout this paper. This is because the condition $\Delta G > 0$ does not mean – at least in the case of reversible reactions – that absolutely no reaction will occur in the direction indicated but only that the reaction as written is not favored by the thermodynamics of the situation and therefore will not be as extensive as the reverse reaction. For example, the phase change:

$$\mathrm{Hg(l)} \rightarrow \mathrm{Hg(g)} \qquad \Delta G^\circ = +31.9 \text{ kJ/mol rx} \qquad [21]$$

is thermodynamically disfavored at RTP, yet sufficient Hg evaporates so as to constitute a potential health hazard in the case of laboratory mercury spills. In short, a terminology based on the word "favored" is less rigid in its unintended implications than is one based on such words as "spontaneous," "allowed" or "feasible."

As for the term "kinetically metastable," I have chosen to use it because of historical precedent. The only alternative I am aware of are the descriptors "kinetically labile and kinetically inert," first introduced in 1952 by Henry Taube in connection with the study of substitution reactions in transition-metal complexes (23). While I find the term "labile" useful, the term "inert" seems a bit extreme save for the most intractable cases of kinetic metastability, and the more neutral term "kinetically inhibited" may be a better alternative.

References and Notes

1. Standard-state thermodynamic data is usually listed at 25°C and 1 atm. I have chosen to abbreviate this as room

temperature and pressure or RTP to differentiate from it from standard temperature and pressure or STP (0°C and 1 atm) normally used when working gas law problems.

2. Unless otherwise stated, all thermodynamic data is from A. J. Bard, R. Parsons, J. Jordan, Eds., *Standard Potentials in Aqueous Solutions*, Deker: New York, NY, 1984.

3. The only circumstance under which the signs of ΔG and $\Delta G°$ would differ would be if the $RTlnQ$ term in the equation $\Delta G = \Delta G° + RTlnQ$ is positive and sufficiently large to off set a negative value for $\Delta G°$ or vice versa. Since each ten fold increase in Q corresponds to only +5.7 kJ/mol at RTP, a many fold increase in Q, and thus a many fold decrease in the activities of the reactants, would be required to affect a reversal in the sign of ΔG versus that of $\Delta G°$. Given the observed behavior of the solutions discussed in this paper, this is obviously not the case. In addition, $\Delta G°$ values have the advantage that they can be unambiguously calculated from free energies of formation, whereas proper ΔG calculations for solution-gas reactions would rapidly mire one in issues of activities and fugacities versus concentrations and pressures, let alone experimental proof that the reactions in question are truly reversible – topics which are glossed over in the typical freshman text. Finally, since at equilibrium $\Delta G°$ equals $-RTlnK$, it also has the advantage of being a direct measure of the equilibrium constant, which tells us, in turn, how complete the reaction in question will be at equilibrium irrespective of its initial state.

4. M. L. Frenkel, G. Y. Kabo, G. N. Roganov, *Thermodynamic Properties of Isomerization Reactions*, Hemisphere Publishing: Washington, DC, 1993.

5. A more systematic name for this compound would be dihydrogen peroxide or, better still, dihydrogen polydioxide, which makes explicit the fact that the oxygen atoms are dimerized or bonded to one another. In keeping with this, the peroxide anion in the compound's molecular formula has also been enclosed in parentheses in order to emphasize that it is a distinct entity within the molecule and not two separate oxide anions.

6. An excellent summary of the older literature on this compound may be found in W. C. Scumb, C. N. Satterfield, R. L. Wentworth, *Hydrogen Peroxide*, Reinhold: New York, NY, 1955.

7. The concentration of gases and solutions may be varied at constant temperature and pressure whereas that of a pure solid or liquid substance at RTP cannot. However, application of high pressures can alter the mole to volume ratio of pure substances as well and raises the question of its potential effects on metastability, though this factor is not discussed here.

8. A more systematic name for this compound would be sodium oxochlorate. As with the peroxide anion, the discrete hypochlorite anion in the compound's formula has been enclosed in parentheses to emphasize that it is a distinct entity in which the chlorine and oxygen are bound to one another, thus differentiating it from a formula like that for gallium oxide chloride, GaOCl, in which they are not.

9. An excellent summary of the older industrial literature on this compound may be found in J. S. Sconce, Ed., *Chlorine: Its Manufacture, Properties and Uses*, Reinhold: New York, NY, 1962, Chapter 17.

10. *Sodium Hypochlorite – Stability*, PCH-1400-0007, Solvay Chemicals International: Brussels, 2005. Document available on line.

11. *Sodium Hypochlorite: General Information Handbook*, Powell Fabrication and Manufacturing: St. Louis, MI, 2002. Document available on line.

12. For background on carbonated beverages see M. B. Morris, *Manufacture and Analysis of Carbonated Beverages*, Chemical Publishing Co: New York, NY, 1959; and D. P. Steen, P. R. Ashurst, Eds., *Carbonated Soft Drinks: Formulation and Manufacture*, Blackwell: Oxford, 2006.

13. The atmosphere is roughly 3.9 x 10^{-2} percent carbon dioxide by volume. For gas mixtures at constant temperature and total pressure the volume fraction of a component is equal to its mole fraction, and this, in turn, is equal to its partial pressure when the total pressure is fixed at 1 atm.

14. S. Lewin, "Nonstable States," *J. Chem. Educ*., **1953**, *30*, 136-138.

15. P. L. Luisi, "Are Micelles and Vesicles Chemical Equilibrium Systems?," *J. Chem. Educ*., **2001**, *78*, 380-384.

16. For historical background, see W. B. Jensen, "Kinetic versus Thermodynamic Control," *Bull. Hist. Chem*., **2014**, *39(2)*, 107-121.

17. D. H. Everett, *Basic Principles of Colloid Science*, RSC: London, 1988, Chapters 2-3.

18. R. W. Cahn, *The Coming of Material Science*, Pergamon: Amsterdam, 2000, pp. 82-83.

19. See, for example, the popular account F. J. T. Maloney, *Glass in the Modern World: A Study in Materials Development*, Doubleday: Garden City, NY, 1968, pp. 13-18.

20. W. B. Jensen, "Reaction Feasibility and the Planck Function," *J. Chem. Educ*., **2000**, *77*, 1411.

21. R. S. Ochs, "Thermodynamics and Spontaneity," *J. Chem. Educ*., **1996**, *73*, 952-954.

22. B. L. Earl, "Thermodynamics and Spontaneity," *J. Chem. Educ*., **1998**, *75*, 658-659.

23. H. Taube, "Rates and Mechanisms of Substitution in Inorganic Complexes in Solution," *Chem. Rev*., **1952**, *50*, 69-126. Ostwald also used the term labile as early as 1897.

Publication History

First published in *J. Chem. Educ*., **2015**, *92*, 649-654.

XXIV

Reply to the Letter “Textbooks and Kinetic Metastability”

My thanks to Dr. Moore for bringing this oversight to my attention (1). His use of the terms “thermodynamic stability versus kinetic stability,” introduced by Roald Hoffmann in his essay of 1987 (2), rather than the standard terms “stable versus metastable,” calls attention to yet an additional problem of terminology beyond those associated with use of the terms “spontaneous versus nonspontaneous” that were discussed in my paper. There is no doubt that Dr. Hoffmann’s terminology is very attractive. It unambiguously describes what is going on and why, as well as nicely paralleling the terms “thermodynamic control versus kinetic control” now used by all physical organic chemists. In addition, it is becoming increasingly common, as may be verified by consulting the Internet.

Nevertheless, it is not currently accepted by IUPAC (3) and disregards the massive literature in physical chemistry, materials science, and physics based on use of the older unmodified terms “stable versus metastable.” Nor is it true, as implied in Hoffmann’s essay, that this older terminology is now used mostly by physicists rather than chemists. As indicated in a previous historical study, this older terminology was first introduced by the chemist Wilhelm Ostwald in 1897 (4) and all of the literature that I consulted on this subject not only used this older terminology but was written by chemists rather than by physicists. Perhaps the best compromise is to explicitly apply Hoffmann’s modifiers to the older terminology and to talk of “thermodynamic stability versus kinetic metastability,” as was partially anticipated in my paper.

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Publication History

Originally published in *J. Chem. Educ.*, **2015**, *92*, 1599.

XXV

The Quantification of 20th-Century Chemical Thermodynamics

A Tribute to "Thermodynamics and the Free Energy of Chemical Substances"

Most chemists would count themselves as lucky to have written a book now considered to be a chemical classic, but to have written two such books in widely different areas of chemistry and to have published both in the same year is, I believe, almost unprecedented (1). Indeed, it is an accomplishment which, to the best of my knowledge, has been achieved by only one person – the American chemist, Gilbert Newton Lewis (figure 1) – who in 1923 not only published *Valence and the Structure of Atoms and Molecules*, describing his seminal contributions to the electronic theory of bonding, but also his classic monograph *Thermodynamics and the Free Energy of Chemical Substances* (figure 2), which he coauthored with Merle Randall and which laid the foundations for the quantification of modern thermodynamics (2). I have already described the first of these books in the morning session of this symposium, and it is the second of these books which forms the subject of this afternoon's presentation.

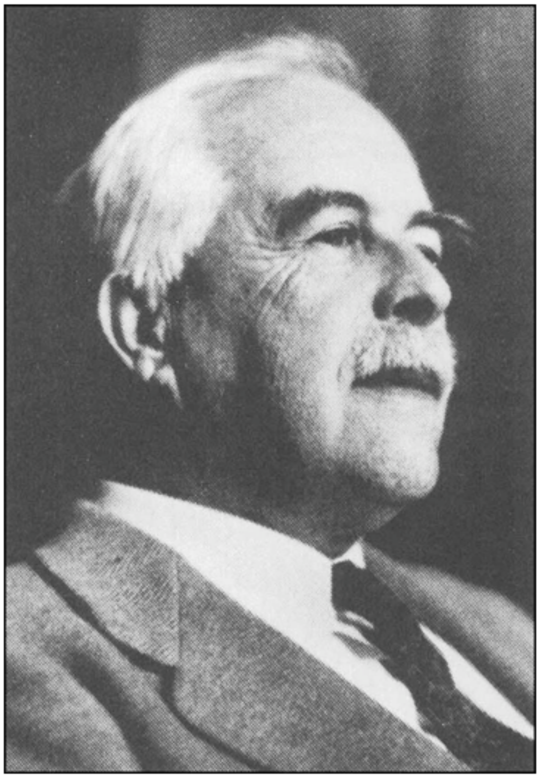
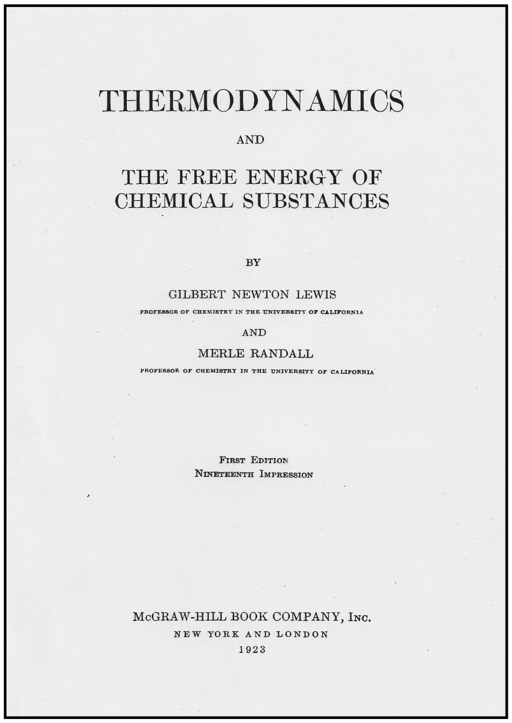


Figure 1. Gilbert Newton Lewis (1875-1946) in later life.



THERMODYNAMICS

AND

THE FREE ENERGY OF
CHEMICAL SUBSTANCES

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FIRST EDITION
NINETEENTH IMPRESSION

McGRAW-HILL BOOK COMPANY, INC.
NEW YORK AND LONDON
1923

Figure 2. The title page to the first edition of *Thermodynamics and the Free Energy of Chemical Substances*.

The Authors

Since I have already summarized the life of Lewis when discussing *Valence* in this morning's session, I will not bore you with a repetition of the facts, but will instead say a little about his coauthor, Merle Randall. Born in 1888, Randall received both his B.S. (1907) and M.S. (1909) degrees in chemistry from the University of Missouri, followed by a Ph.D. from MIT in 1912 for the thesis, *Studies in Free Energy*, based on work done under the supervision of Lewis.

When Lewis departed for Berkeley later that year, Randall went with him, initially serving as his private assistant. In 1917 he 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. Until his death in 1950, he was involved with J. M. Ritchie in the production of the notorious battery additive AD-X2 which eventually led to a major scandal at the National Bureau of Standards. In addition to his collaboration with Lewis, he also published a textbook of physical chemistry in 1942 (3).

The Book

Thermodynamics was published by McGraw-Hill of New York in 1923 using the same characteristic brown cover and black and gold spine label that would later become the hallmark of its "International Chemical Series." The book, in sharp contrast to Lewis's much shorter monograph on *Valence*, was 653 pages in length and consisted of 42 chapters and four appendices. It was the culmination of a research program undertaken by Lewis in 1899 which was directed at the clarification and quantification of chemical thermodynamics as summarized in a 55-item bibliography of the publications of Lewis and his students appended to the book.

The Context

In chapter 1 Lewis noted that the development of chemical thermodynamics was characterized by three distinct periods:

1. The establishment of the basic laws of thermodynamics (1842-1865).

2. The application of these laws to the theory of chemical affinity and equilibrium (1873-1905).

3. The quantification of chemical thermodynamics via a fusion of theory with experimental data (1905-1923).

The first of these periods began with the enunciation of the first law of thermodynamics by Mayer (1842), Joule (1843), and Helmholtz (1847) in the 1840s and the equally important enunciation of the second law by Clausius (1850) and Kelvin (1852) in the 1850s. It was completed in 1865 when Clausius explicitly reformulated the second law in terms of his famous entropy function.

The second period began with the first application of the entropy function to the phenomenon of chemical equilibrium by Horstmann in 1873, followed by its application to heterogeneous phase equilibria, the introduction of the phase rule, and the introduction of both the chemical potential and free-energy functions by Gibbs in the period 1874-1878. Of equal importance was the further elaboration of the *Arbeit* and free energy concepts by Helmholtz (1882) in the 1880s and the translation of Gibbs' work into both German (Ostwald 1892) and French (Le Chatelier 1899) in the 1890s.

This stage was also characterized by the publication of several monographs explicitly devoted to the theory of chemical thermodynamics, the most important of which are summarized in the following table:

Table 1. Early monographs dealing with the theory of chemical thermodynamics.

Date	Author	Title	Approach
1884	van't Hoff	*Etudes de dynamique chimique*	Arbeit or affinity
1885	Liveing	*Chemical Equilibrium the Result of Dissipation of Energy*	energy dissipation
1886	Duhem	*Le potential thermodynamique*	chemical potential
1893	Nernst	*Theoretische Chemie*	Arbeit or affinity
1893	van Laar	*Die Thermodynamik in der Chemie*	total entropy
1897	Planck	*Vorlesung über Thermodynamik*	total entropy
1906	van Laar	*Sechs Vorträge über das thermodynamische Potential*	chemical potential

The foundations of the third period were actually laid nearly a half century before the formal development of thermodynamics itself with the first measurements of heats of combustion by Lavoisier and Laplace (1783) and with the extensive measurements of heats of reaction and specific heats within context of the caloric theory during the period 1840-1854 by such thermochemists as Hess, Andrews, and the French team of Favre & Silbermann, leading to the enunciation of the law of constant heat summation by Hess in 1840. These results were translated into the context of the first law of thermodynamics and greatly augmented by the work of Thomsen (1882-1884), and Berthelot (1879, 1897) during the last half of the 19th century.

Thus, by the turn of the 20th century there already existed an extensive data bank of quantitative enthalpy values. However, this remained largely localized in a separate literature dealing with thermochemistry rather than with chemical thermodynamics proper, and the books listed in Table 1 remained primarily theoretical, rather than practical, in their orientation, in large part because that theory showed that what was important in determining the chemical affinity of a reaction was not just the enthalpy of the reaction, but its ability to perform useful work, whether measured in terms of *Arbeit,* energy dissipation, total entropy change, chemical potential or free energy. What was needed before this enthalpy data could be fully exploited by the newer field of chemical thermodynamics was an equally comprehensive collection of either free-energy or entropy values.

As a consequence the true quantification of chemical thermodynamics, as distinct from the more traditional field of thermochemistry, did not really begin until the enunciation of the third law of thermodynamics by Walther Nernst (figure 3) in 1906, though important anticipations of this approach were made by Richards and especially by Haber (1905). Starting around 1905-1906, one sees the appearance of an increasing number of German monographs (Table 2) devoted to this subject, though not formulated in terms of ΔS and ΔG, as we might think today, but rather in terms of evaluating the reaction isochor directly in terms of thermochemical data alone and within the context of the *Arbeit* or Helmholtz free-energy function (A).

Table 2. Early monographs dealing with the quantification of chemical thermodynamics.

Date	Author	Title	Approach
1905	Haber	*Thermodynamik technischer Gasreaktionen*	A isochor
1906	Nernst	*Experimental and Theoretical Applications of Thermodynamics to Chemistry*	A isochor
1908	Sachur	*Die chemische Affinität und ihre Messung*	A isochor
1912	Pollitzer	*Die Berechnung chemischer Affinitäten nach dem Nernstschen Wärmstatzes*	A isochor
1918	Nernst	*Die theoretischen und experimentellen Grundlagen des neuen Wärmstatzs*	A isochor

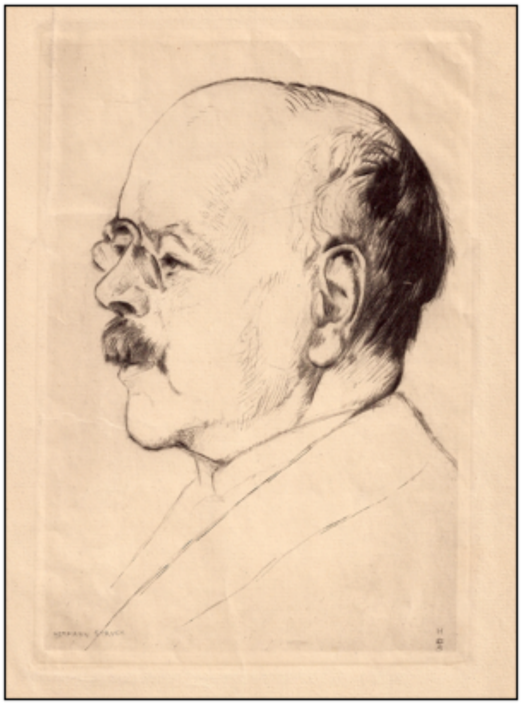


Figure 3. Walther Nernst (1864-1941).

Lewis clearly conceived of his book as belonging to this third phase and, in particular, as an extension of the work of the German chemist, Fritz Haber (figure 4), whom he singled out for special praise (4):

The first systematic study of all the thermodynamic data necessary for the calculation of the free energy changes in a group of important reactions was published in Germany by Haber. This book, "Thermodynamik der technischen Gas Reaktionen," is a model of accuracy and of critical insight.

In keeping with this self-evaluation, Lewis originally intended that his book should merely be a summary of the free-energy data that he and his associates had collected over the previous quarter of a century:

We [originally] proposed merely to collect, for the practical use of the chemist and the chemical engineer, the data which we have obtained, or which we have assembled from the work of other investigators, pertaining to the great problem of chemical affinity.

However, it was soon realized that it was also necessary to include a description of the methods used to obtain the data:

But then we were convinced that mere reference tables would hardly render full service without some description of the methods by which they were obtained ... we

Figure 4. Fritz Haber (1868-1934).

> *have been forced to develop a variety of special methods chemical, algebraic, arithmetical and graphical – and it is our hope that a full presentation of these methods may spare other workers in this field much of the arduous labor which we ourselves have spent.*

And lastly, it became apparent that these purely technical aspects were best appreciated if they were first prefaced by an introductory overview of the underlying principles of thermodynamics:

> *Finally, these methods themselves require a fuller understanding of the underlying principles of thermodynamics than most elementary treatises afford... Partly for this reason, and partly perhaps because of a temptation to present in a somewhat novel manner the basic principles of thermodynamics, we devote the first part of our book to a presentation of the elements of thermodynamic theory.*

In keeping with this plan, Chapters 1-26 of the final book dealt with theory and chapters 27-42 with methods and data.

Innovations

The best way of appreciating the unique features of the Lewis-Randall text is through a comparison with the earlier textbook and monograph literature listed in Tables 1 and 2, and especially with the American text, *Thermodynamics and Chemistry*, by F. H. MacDougall of the University of Minnesota, which was published in 1921, only two years before the Lewis-Randall text.

Though the early works by Duhem (1886) and van Laar (1906) made explicit use of the Gibbs chemical potential, it is apparent from Tables 1 and 2, that they were the exception rather than the rule and that most previous writers on chemical thermodynamics preferred instead to use the so-called *Arbeit* or affinity functions derived from the work of Helmholtz in which the role of entropy was implicit rather than explicit. This may come as something of a surprise to the modern chemist, but, in fact, in the period 1876-1923, Gibbs was far better known for his enunciation of the phase rule than for his free-energy function.

The manner in which the role of entropy was made implicit rather than explicit may be seen in the approaches favored by van't Hoff and Nernst, which dominated the chemical literature in the period between 1884 and 1922. Thus van't Hoff preferred to write the *Arbeit* equation in a form that was analogous to the classical Carnot equation for calculating the efficiency of a steam engine:

$$A = Q[(T_{eq} - T)/T_{eq}]$$

in which ΔS appeared only as Q/T_{eq}, whereas Nernst always used the temperature dependency of the *Arbeit*, (dA/dT), in place of $-\Delta S$ when writing the equation for Helmholtz free energy:

$$A = U + T(dA/dT) \;=\; Q + T(dA/dT)$$

In keeping with these preferences, an informal survey of 17 physical chemistry texts published during this period showed that 11 or 65% did not list entropy as a index entry, whereas 5 of the remaining 6, though listing it once, devoted little more than a paragraph to the subject. Likewise, the 1921 text by MacDougall has only three index entries for free energy, two of which refer to Helmholtz free energy and only one to Gibbs free energy.

In sharp contrast, the Lewis-Randall text is firmly and unambiguously based on the Gibbs free-energy function (symbolized as ΔF rather than as ΔG) and formulated in terms of explicit enthalpy and entropy terms:

$$\Delta F = \Delta H° - T\Delta S° + RT\ln Q$$

Other important innovations may be briefly enumerated as follows:

1. The Lewis-Randall text makes extensive use of partial molal properties in discussing the thermodynamics of solutions, whereas this topic is missing from the MacDougall text.

2. The Lewis-Randall text extends the concept of standard states ($\varDelta X°$ vs $\varDelta X$) beyond the Nernst equation ($E°$ vs E) so as to also include the free energy, enthalpy and entropy functions. The MacDougall text does not.

3. Building on the thermochemical tradition of Berthelot (1879, 1897) and Nauman (1882), the Lewis-Randall text essentially perfects our current suffix conventions for indicating physical states (e.g. $CO_2(g)$, $H_2O(l)$ $Fe(s)$). The MacDougall text does not.

4. The Lewis-Randall text deals with the issue of nonideality through the introduction of such concepts as fugacity (1901), activity (1907), and ionic strength (1921). The MacDougall text mentions activity but neither fugacity nor ionic strength.

5. In sharp contrast to the Lewis-Randall text, the Haber-Nernst tradition deals with the quantification of affinity in terms of a power expansion of the temperature dependency of either the *Arbeit* function or the integrated van't Hoff isochore:

$$InK = Q_0/RT + (\Sigma\nu\alpha/R)lnT + (\Sigma\nu\beta/R)T + \ldots I/R$$

rather than in terms of explicit tabulations of $\varDelta F°$, $\varDelta H°$ and $S°$ values.

6. The Lewis-Randall text contains a table of $S°$ values at 298 K for 75 elements and a table of $\varDelta F°$ values at 298 K for 140 ions and compounds. The MacDougall text contains no entropy or free energy data, only tables of heats of formation and various phase diagrams – a topic that is completely missing from the Lewis-Randall text.

Points 5 and 6 represent the most defining feature of the Lewis-Randall text and are what distinguish it from all of its predecessors. Whereas the primary contact with experimental data, if any, for most thermodynamic texts written in the period 1884-1922 was via the phase rule and various phase diagrams, for the Lewis-Randall text this contact was made for the first time via the use of tabulated free energy and entropy values.

Prose Style

As with many of his papers and reviews, Lewis dictated *Thermodynamics* to his coauthor and, not unexpectedly, like his monograph on *Valence*, it contains many superb examples of the "Lewis style" in technical writing, of which I have time to quote only a few representative examples:

1. On the quality of the thermodynamic literature:

We have seen "cyclical processes" limping about eccentric and not quite completed cycles, we have seen the exact laws of thermodynamics uncritically joined to assumptions comprising half truths or no truth at all, and worst of all we have seen ill-begotten equations supported by bad data.

2. On the question of thermodynamic nomenclature:

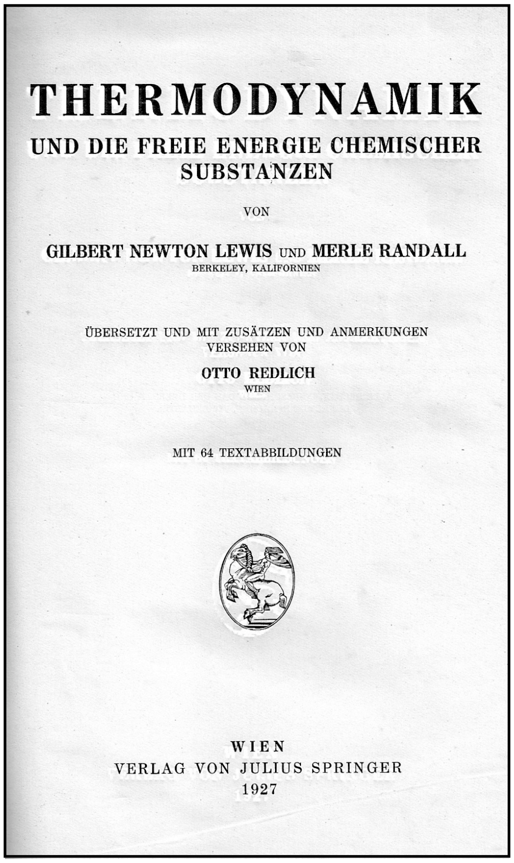
We presume that every author regards his own as the best of all possible notations. While we may privately be victims of some such hallucination, all that we care to claim publicly is that our system of nomenclature and notation is one which has gradually developed through many years of practical work and the teaching of many types of students, and that it has proved satisfactory.

3. On the intended uses of the book:

Our work is not a textbook in the ordinary sense of the term. A textbook is a sort of table d'hote to which anyone may sit down and satisfy his hunger for information with no thought of the complex agricultural processes which gave rise to the raw materials, nor of the mills which converted these raw materials into foodstuffs, nor of the arts of cookery responsible for the well-prepared meal which has been set before him. It has not been our desire to offer such a repast to the reader.

4. And, most famous of all, the opening paragraphs of the book's preface:

There are ancient cathedrals which, apart from their consecrated purpose, inspire solemnity and awe. Even the curious visitor speaks of serious things, with hushed voice, and as each whisper reverberates through the vaulted nave, the returning echo seems to bear a message of mystery. The labor of generations of architects and artisans has been forgotten, the scaffolding erected for their toil has been removed, their mistakes have been erased or have become hidden by



THERMODYNAMIK
UND DIE FREIE ENERGIE CHEMISCHER SUBSTANZEN
VON
GILBERT NEWTON LEWIS UND MERLE RANDALL
BERKELEY, KALIFORNIEN

ÜBERSETZT UND MIT ZUSÄTZEN UND ANMERKUNGEN VERSEHEN VON
OTTO REDLICH
WIEN

MIT 64 TEXTABBILDUNGEN

WIEN
VERLAG VON JULIUS SPRINGER
1927

Figure 5. The title page to the 1927 German translation.

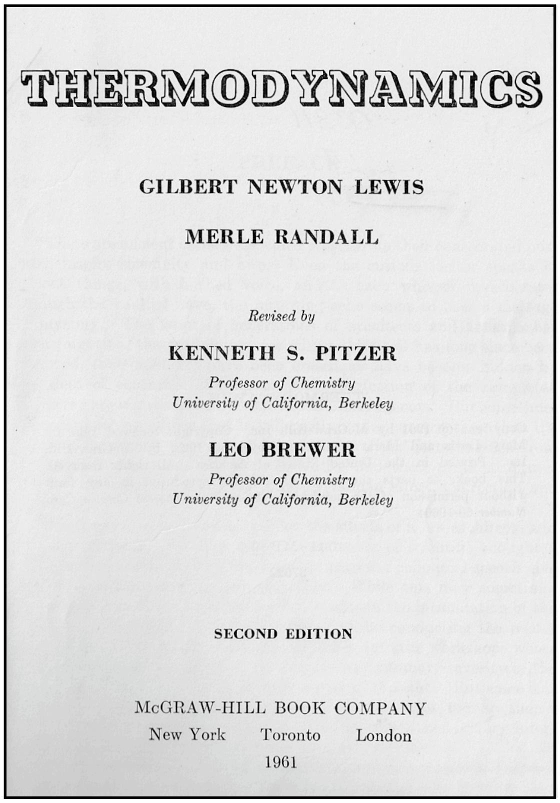
the dust of centuries. Seeing only the perfection of the completed whole, we are impressed as if by some supernatural agency. But sometimes we enter such an edifice that is still partly under construction; then the sound of hammers, the reck of tobacco, the trivial jests bandied from workman to workman, enable us to realize that these great structures are but the result of giving to ordinary human effort a direction and a purpose.

Science has its cathedrals, built by the efforts of a few architects and of many workers. In these loftier monuments of scientific thought a tradition has arisen whereby the friendly usages of colloquial speech give way to a certain severity and formality. While this may sometimes promote precise thinking, it more often results in the intimidation of the neophyte. Therefore we have attempted, when conducting the reader through the classic edifice of thermodynamics, into the workshops where construction is now in progress, to temper the customary severity of the science in so far as is compatible with clarity of thought.

The Legacy

In 1927 Springer Verlag published a German translation by Otto Redlich of the Lewis-Randall text (figure 5), and Lachman has also hinted at an unauthorized Russian translation, though I have been unable to confirm this (5, 6). In addition, in 1961, after remaining in print and active use for almost four decades, the original book was finally updated and revised by Kenneth Pitzer and Leo Brewer (both Berkeley doctorates and faculty members) and published as a second edition (figure 6) as part of the "McGraw-Hill Series in Advanced Chemistry" (7). But the legacy of the Lewis-Randall text is reflected in more than just translations and new editions. It is also reflected in the many additional contributions made by the faculty and students at Berkeley to the quantification program first envisioned by Lewis in 1899 and of which the Lewis-Randall text was merely the fountainhead.

Thus by 1930 Randall was able to contribute 81 pages of enthalpy, entropy, and free-energy data to the seventh volume of the *International Critical Tables* (8) – a significant increase over the tables given in 1923 – and by 1938 Wendell Latimer (figure 7), who was also a Berkeley doctorate and faculty member, was able to list free-energy values for 531 species in the first edition of his monograph, *The Oxidation States of the*



THERMODYNAMICS
GILBERT NEWTON LEWIS
MERLE RANDALL

Revised by
KENNETH S. PITZER
Professor of Chemistry
University of California, Berkeley
LEO BREWER
Professor of Chemistry
University of California, Berkeley

SECOND EDITION

McGRAW-HILL BOOK COMPANY
New York Toronto London
1961

Figure 6. The second edition of the Lewis and Randall text as revised by Kenneth Pitzer and Leo Brewer and published by McGraw-Hill in 1961.

Figure 6. A young Wendall Latimer (1893-1955).

Elements and their Potentials in Aqueous Solutions (9).

Building on the 1936 monograph, *The Thermochemistry of the Chemical Substances* by Francis Bichowsky and Frederick Rossini (a Berkeley graduate and student of Randall) (10), the National Bureau of Standards undertook a program in 1940 to collect and collate thermodynamic data, the results of which were distributed after the Second World War in the form of loose-leaf tables (later known as the JANAF tables). In 1952 Rossini (figure 7) and associates published a revised, single volume, edition of these tables under the title, *Selected Values of Chemical Thermodynamic Properties,* which contained more than 1160 pages of enthalpy, free-energy, entropy and heat capacity data (11).

Today vast stores of thermodynamic data are available at the touch of a computer key board and we give little thought to the many workers who contributed to their measurement, compilation, and critical assessment. Indeed, in many ways we have reached the state predicted by Lewis almost 80 years ago:

> *... we realize that the time may arrive when handbooks of thermodynamic data will be placed in the hands of the craftsman, that he may follow a recipe, or substitute numerical values in a formula of origin unknown to him.*

Substitute "student" for "craftsman," and we have a perfect description of our current state of affairs.

In a 1928 letter to James Partington relative to his possible nomination for a Nobel Prize, Lewis summarized his own achievements as follows (3):

> *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 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.*

Indeed, the data collection and formatting program undertaken by Lewis and his associates over a century ago so permeates our current thermodynamic thinking that we may, with considerable justification, characterize our present approach as the Gibbs-Lewis formulation of chemical thermodynamics.

References and Notes

1. An invited lecture given at a symposium organized

Figure 7. Frederick Dominic Rossini (1899-1990).

by the Bolton Society on classic 20th-century chemistry textbooks held at the 230th National Meeting of the ACS in Washington, DC, on 29 August 2005.

2. G. N. Lewis, M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill: New York, NY, 1923.

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5. G. N. Lewis, M. Randall, *Thermodynamik und die freie Energie chemischer Substanzen,* Springer: Wein, 1927.

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10. F. R. Bichowsky, F. D. Rossini, *The Thermochemistry of Chemical Substances*, Reinhold: New York, NY, 1936.

11. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, NBS Circular 500, U. S. Government Printing Office: Washington, DC., 1952.

Publication History

Published in *Bull. Hist. Chem.*, **2015**, xx, in press.

Update

I have only recently (2015) become aware of the 1996 study by Helge Kragh and Stephen Weininger ("Sooner Silence than Confusion: The Tortuous Entry of Entropy into Chemistry," *Hist. Stud. Phy. Bio. Sci.*, **1997**, *27*, 91-130) which provides an even more detailed context for the emergence of Lewis' textbook and independently reaches many of the same conclusions as I have in this and other papers dealing with the history of chemical thermodynamics.

XXVI

Did Vonnegut Read Bridgman?

Some Speculations on the Origins of Ice-Nine

The 1963 novel, *Cat's Cradle*, by the American author, Kurt Vonnegut Jr. (figure 1), has always been a favorite of scientists interested in clever applications of scientific concepts in fiction (1) and has even been employed by some to generate student interest when teaching the basic thermodynamics of phase changes (2).

The novel (figure 2) centers around the discovery of a hitherto unknown polymorph of ice known as "ice-nine," which melts at 114.4 °F (i.e., 45.78 °C) – in other words, a new form of ice which is a solid at ambient temperatures and pressures. This means that liquid water, under normal conditions, is actually kinetically metastable and exists only because of the absence of a suitable seed crystal needed to catalyze its conversion into the far more stable form of ice-nine. As it turns out, such a crystal has in fact been synthesized by a highly eccentric, and socially oblivious, scientist and Nobel Prize winner named Felix Hoenikker while in the employ of the industrial giant General Forge and Foundry Company of Ilium, New York, as part of a request from the Marine Corp for a technical solution as to how to deal with the ubiquitous problem of mud in hampering military transport and other operations. Unknown to both his employer and fellow scientists, Hoenikker succeeds in making a seed crystal of "blue-white" ice-nine which will instantly freeze mud, and which he takes home for Xmas to show to his three highly disfunctional adult children. However, he suddenly dies before explaining its nature and purpose and the children, finding the bottle containing the crystal in his pocket, divide it among themselves. They, in turn, through a series of bad life choices and flawed judgment calls – involving many a pithy comment on religion, the unintended consequences of science, politics, sex, and fate – eventually, albeit accidently, allow its release into the environment, where it instantly causes all water to freeze solid and results in the destruction of all life on earth.

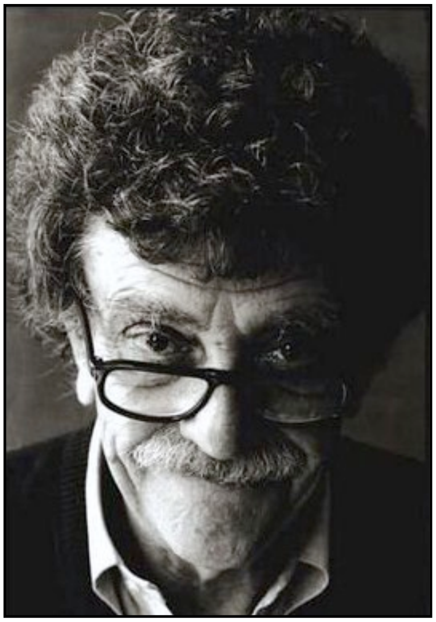


Figure 1. Kurt Vonnegut Jr. (1922-2007).

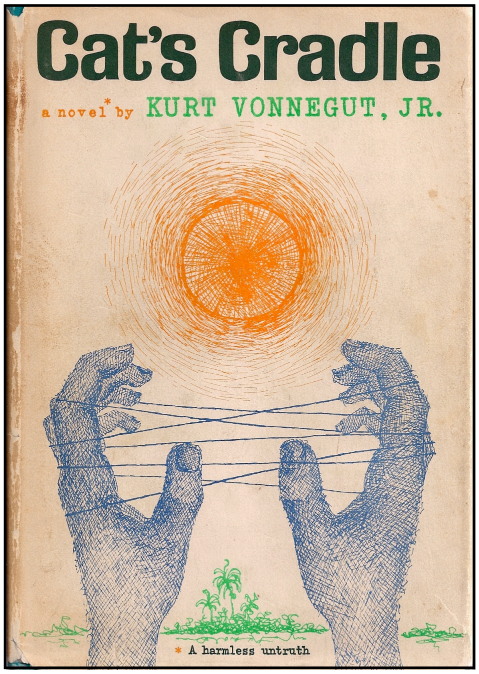


Figure 2. Dust jacket for the first edition (1963) of Vonnegut's novel *Cat's Cradle*.

In 1969 Vonnegut was invited to address the American Physical Society in New York City and in his talk, which was finally published in 1974 (3), he gave an account of the origins of the concept of ice-nine. From 1947-1950 Vonnegut worked in the Public Relations Department of the General Electric Company

Figure 3. Irving Langmuir (1881-1957), Vonnegut's prototype for Dr. Felix Hoenekker.

of Schenectady, New York, where his older brother, Bernard Vonnegut (1914-1997) – a trained physicist – worked in the research laboratory with Irving Langmuir (figure 3) and Vincent Schaefer on the seeding of clouds with either dry ice or silver iodide in order to induce rain or snow formation (4). As Vonnegut related (3):

I got this lovely idea while I was working as a public-relations man at General Electric. I used to write Publicity releases about the research laboratory, where my brother worked. While there, I heard a story about a visit that H. G. Wells had made to the laboratory in the early Thirties.

General Electric was alarmed by the news of his coming, because they did not know how to entertain him. The company told Irving Langmuir, who was the most important man in Schenectady, the only Nobel Prize winner in private industry, that he was going to have to entertain Wells. Langmuir didn't want to do it, but he dutifully tried to imagine diversions that would delight Mr. Wells. He made up a science fiction story he hoped Mr. Wells would want to write. It was about a form of ice which was stable at room temperature. Mr. Wells was not stimulated by the story. He later died, and so did Langmuir. After Langmuir died, I thought to myself, well I think maybe I'll write a story.

This account strongly implies that the General Forge and Foundry Company of Ilium, New York, was a thinly disguised version of the General Electric Company of Schenectady, New York, and that Dr. Felix Hoenekker, industrial chemist and Nobel Prize winner, was a thinly disguised version of Irving Langmuir, industrial chemist and Nobel Prize Winner. Indeed this latter identification seems highly probable, since a reading of Albert Rosenfeld's 1961 biography, *The Quintessence of Irving Langmuir*, reveals that Langmuir had the same apparent child-like self-absorption in his work that Vonnegut would later attribute to Hoenekker (5).

This biography also reveals several other parallels. Thus, in the novel, the Vice-President of Research at General Forge and Foundry – one Dr. Asa Breed – under the false impression that Hoenekker had died before successfully synthesizing his magic seed crystal, expresses his relief that Hoenekker had failed because he is now fully aware that it would have had horrific environmental consequences beyond the mere freezing of mud for military convenience and thus dire legal repercussions for his company. Indeed, he becomes upset when he suspects that the narrator might be a yellow journalist intent on publicly exposing the entire project and so generating potentially negative publicity for the company.

A somewhat similar situation occurred in real life when the legal department at General Electric got wind of Langmuir's successful cloud-seeding experiments and realized that the possible side-effects could not be successfully controlled (5):

As a possible force for good, rainmaking and snow-making had tremendous potential, and the owner of those patents ought to have a large, steady income from the royalties. Yes – but suppose you made rain for a rancher, and the rain soaked a crop of hay drying in a nearby field; couldn't the farmer sue you for the loss of his hay? Or suppose you made rain in order to fill New York City's reservoirs during a dry summer; couldn't the owners of mountain and seaside resorts whose weather and business you ruined hold you accountable? ... GE decided to divorce itself from cloud-seeding in every possible legal manner. The company threw the patents open for public use and waived all royalty rights, and there was much relief when the government took over the work of Langmuir, Schaefer, and Vonnegut under project Cirrus, in March of 1947.

One of the more impressive scenes in *Cat's Cradle* is the description of what happened once a sliver of ice-nine is released into the environment and it initiates a chain-reaction as the ice-nine which it nucleates, nucleates, in turn, yet more ice-nine, and so *ad infinitum* (1):

There was a sound like that of the gentle closing of a *portal as big as the sky, the great door of heaven being closed softly. It was a grand AH-WHOOM. I opened my eyes – and all the sea was ice-nine. The moist green earth was blue-white pearl. The sky darkened. Borasisi, the sun, became a sickly yellow ball, tiny and cruel. The sky was filled with worms. The worms were tornadoes.*

Once more we find a suggestive parallel with Langmuir's work on cloud-seeding. Impressed by the ability of a single silver iodide crystal to stimulate the formation of billions of small ice crystals, Langmuir, according to Rosenfeld, also began worrying that his seeding experiments might accidently generate a runaway effect (5):

"If the particles [i.e. seed crystals] retain the activity they had in laboratory tests, a wide distribution of them in the atmosphere might perhaps have a profound effect upon the climate"... Langmuir had become fascinated with the idea of causing a chain-reaction in the atmosphere. Just as a chain-reaction of atom-splitting can be caused by the impingement of a single slow neutron on a critical mass of uranium, so, Langmuir thought, could a single ice crystal or water droplet impinging on a critical cloud mass, under the right conditions, set off the entire cloud. "The chain reaction," he explained, "is one where you start out with one snow flake and by some mechanism it becomes two. Then those two become four, and those four, eight, and so on, and the thing propagates rapidly, in exactly the same way as a haystack when you light it with a match. It starts burning. It does not make a difference where it is ignited, in three places or one, it spreads through the whole haystack. The heat produced by burning one particle of hay has to be enough to heat the next particle.

On the other hand, though Rosenfeld explicitly describes Langmuir's tastes in music, art, fiction, religion, and politics, no mention is made of his ever having read any science fiction or of having ever met H. G. Wells. Likewise, official biographies of Wells fail to mention both the visit to General Electric and the meeting with Langmuir, though this most likely took place in May of 1934 when Wells visited the United States for the explicit purpose of evaluating the progress of Roosevelt's "New Deal" which he hoped to compare with Joseph Stalin's various economic reforms in the Soviet Union (6). That Wells had no interest in Langmuir's story proposal is hardly surprising. All of Wells' science fiction had been written prior to the First World War and by the 1930s he had become obsessed with the subject of futuristic social and economic planning instead.

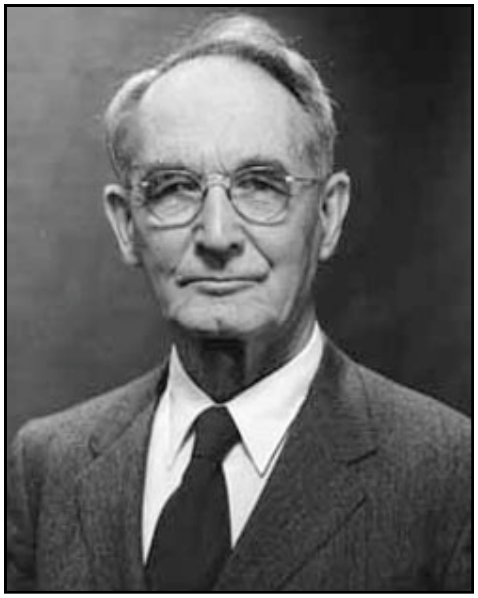


Figure 4. Percy W. Bridgman (1882-1961).

As suggestive as Vonnegut's account is, it still leaves some unanswered questions? As he admitted in his talk to the American Physical Society, neither Langmuir nor Wells had left an account of the plot to Langmuir's proposed story, and though, as we have just seen, there are some very suggestive parallels with the work of Langmuir and Bernard Vonnegut on cloud seeding, the heterogenous nucleation of saturated water vapor to form the normal liquid and/or solid and the homogeneous nucleation of a liquid to induce crystallization of a hitherto unknown solid polymorph differ sufficiently so as to require some further knowledge of the scientific literature on polymorphism.

The most probable scenario is that Vonnegut's older brother provided him with appropriate literature references and that Vonnegut was able to read and understand them because of his background in chemistry and mechanical engineering, both of which he had studied (albeit, by his own account, not very successfully) prior to the Second World War. But what was the nature of the scientific literature that he would have consulted?

Prior to World War II, the single most important authority on polymorphism and polymorphic transitions was, without a doubt, the Harvard physicist, Percy W. Bridgman (figure 4), who would receive the Nobel Prize in physics in 1946 "for his invention of an apparatus to produce extremely high pressures, and for the discoveries he made therewith in the field of high pressure physics." Much of Bridgman's work on high pressure polymorphs, including those of ice, was

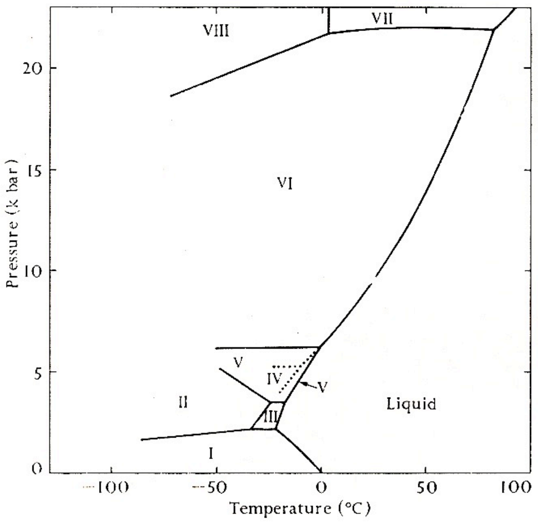


Figure 5. A phase diagram for the eight known polymorphs of ice as envisioned by Eisenberg and Kauzmann in 1969. Note that the type of transition envisioned by Vonnegut would be potentially possible for ice VI and liquid water around 50° C but only at pressures of 15 kbar rather than at room pressure.

summarized in his 1931 monograph, *The Physics of High Pressures* (7). At the time six polymorphic varieties of ice were known to Bridgman, which he labeled as ice I - ice VI, where ice I refers to the common form. Ice II and ice III had been discovered by the German phase scientist, Gustav Tammann in 1900, and ice IV, ice V, and ice VI by Bridgman himself in 1912. In 1937 Bridgman discovered a seventh polymorph – ice VII – and an eighth form – ice VIII – was found by Kamb and Davis in 1965 (figure 5), two years after the publication of *Cat's Cradle* (8). Thus Vonnegut's numbering of his fictitious ice polymorph was in the right ball park, and certainly suggests that he was well aware of the existing state of research in this area. Currently more than 15 polymorphs of ice have been reported.

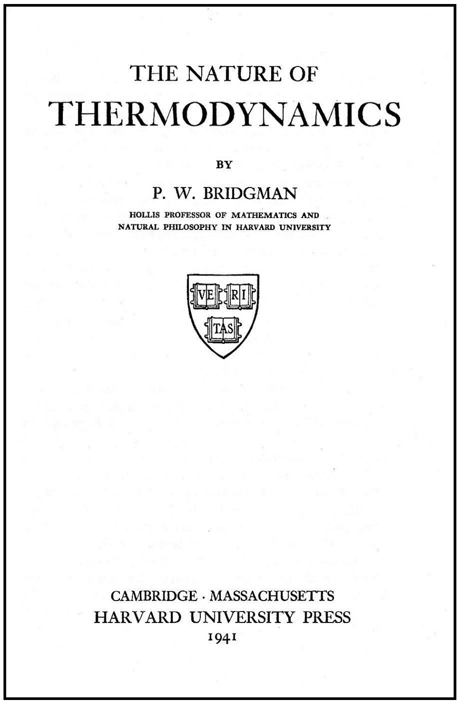
But the ice-nine concept requires more than an understanding of how many polymorphs of ice were known in the 1960s. It also requires a knowledge of the difference between true thermodynamic stability, on the one hand, and kinetic metastability, on the other, and the possibility of not only high-pressure polymorphs, but hitherto unknown polymorphs stable at ambient temperatures and pressures. As it turns out, these missing prerequisites may also be found in the writings of Bridgman, and most particularly in what is perhaps his best known book – the 1941 monograph, *The Nature of Thermodynamics* (figure 6), in which, during a discussion of the role of kinetic hinderances to thermodynamically spontaneous phase transformations, we find the following remarkable quote (9):

> *In many cases it is easy enough to see when these hinderances to a complete and final smoothing out are operative, but in other cases it is impossible to be sure that the lowest potentialities have been realized, as in that of a test tube of supercooled water that suddenly changes to ice after ten day's quiescence, or the glycerin in the chemical laboratory at Berkeley that froze solid after the importation of a nucleus of the solid from Oregon. There is no way whatever of being sure that any of the ordinary objects of daily life do not have other polymorphic forms into which they may sometime change spontaneously before our eyes [emphasis added].*

All of the necessary ingredients for the physics of ice-nine are present in this quote – the metastability of a liquid finally overcome by an imported seed crystal, the possibility that everyday materials might be only metastable rather than thermodynamically stable, etc.

Yet other suggestive hints are to be found in Bridgman's books. Thus with respect to the explosive transformation of normal water into ice-nine already mentioned above, we read the following comment by Bridgman on the rate of conversion of ice I onto ice III in his high pressure apparatus (7):

> *A particular striking example is that of ice I-III. Near the upper limit of this transition line, which is termi-*



THE NATURE OF
THERMODYNAMICS
BY
P. W. BRIDGMAN
HOLLIS PROFESSOR OF MATHEMATICS AND
NATURAL PHILOSOPHY IN HARVARD UNIVERSITY

CAMBRIDGE · MASSACHUSETTS
HARVARD UNIVERSITY PRESS
1941

Figure 6. The title page of Bridgman's classic monograph, *The Nature of Thermodynamics* (1941).

nated by the triple point with the liquid, the transition runs with almost explosive rapidity; in fact pressure so rapidly follows the change of volume produced by the moving piston that the pressure gauge will show no change of pressure.

Of course, we will probably never know for certain whether Vonnegut – either at his brother's prompting or on his own – ever read Bridgman, but the parallels found in Bridgman's books with the underlying imaginative scientific speculations found in *Cat's Cradle* are far too suggestive to simply ignore.

In closing, it should be pointed out that Vonnegut left us with one more hint concerning his knowledge of the scientific literature dealing with crystallization and polymorphism. In attempting to explain the theory behind ice-nine to the novel's narrator, the Vice-President of Research at General Forge and Foundry, Asa Breed, makes reference to the compound ethylenediamine tartrate, $[C_2H_4(NH_3)_2][C_4H_4O_6]$, also known as EDT or 1,2-ethylenediammonium tartrate (1):

He told me about a factory that had been growing big crystals of ethylenediamine tartrate. The crystals were useful in certain manufacturing operations, he said. But one day the factory discovered that the crystals it was growing no longer had the properties desired. The atoms had begun to stack and lock – to freeze – in a different fashion. The liquid that was crystallizing hadn't changed, but the crystals it was forming were, as far as industrial application went, pure junk.

How this had come about was a mystery. The theoretical villain, however, was what Dr. Breed called "a seed." He meant by that a tiny grain of the undesired crystal pattern. The seed, which had come from God-only-knows-where, taught the atoms the novel way in which to stack and lock, to crystallize, to freeze.

In the late 1940s and 1950s, when Vonnegut was working for the Public Relations Department of GE, large crystals of this compound were attracting considerable attention for their potential use as a replacement for quartz in piezoelectric devices and Western Electric had constructed a large plant in Allentown, Pennsylvania, for their manufacture (10). However, the subsequent development of techniques for growing synthetic quartz crystals eventually caused the plant to close.

The phenomenon referred to by Breed involves the initial synthesis of a useful, but metastable, polymorph which eventually becomes impossible to replicate once seed crystals of a less useful, but thermodynamically more stable, polymorph become prevalent in the environment. Dubbed "disappearing polymorphs" by Dunitz and Bernstein in 1995, numerous examples of this phenomena have been documented in the literature, most of them referring to compounds of pharmacological importance (11). The commercially useful crystals of EDT, referred to by Breed, were anhydrous and, after four years of operation, the chemical plant became infected with seed crystals of the more stable, and commercially worthless, monohydrate. Since this has a different composition than the anhydrous form, Breed's example was, strictly speaking, not a true case of competing polymorphs. In any case, the problem was soon identified and rectified by altering the temperature so as favor the formation of the anhydrous product rather than the monohydrate (12-13).

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Published in W. B. Jensen, *Captain Nemo's Battery:*

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XXVII

A Simplified Phase Rule for Two-Dimensional Phase Diagrams

The Gibbs phase rule is normally written as:

$$f = c - p + 2 \qquad [1]$$

where f is the degrees of freedom, c is the number of components, and p is the number of phases (1). When applied to the phase behavior of a pure substance ($c = 1$) this reduces to:

$$f = 3 - p \qquad [2]$$

and gives the results: $f = 2$ when $p = 1$, $f = 1$ when $p = 2$, and $f = 0$ when $p = 3$. In other words, on a conventional 2D-phase diagram, such as the *P-T* phase plot for water shown in figure 1, single phases correspond to areas ($f = 2$), equilibria between two phases correspond to lines ($f = 1$), and triple points or equilibria between three phases correspond to points ($f = 0$). This agrees nicely with the purely mathematical meaning of degrees of freedom as applied to a generalized 2D *x-y* plot in which areas have two degrees of freedom (*x* and *y* are each independently variable), lines have only one degree of freedom (*x* and *y* are constrained by a function such that either *x* or *y* may be independently varied but not both), and points have zero degrees of freedom (both *x* and *y* are uniquely determined).

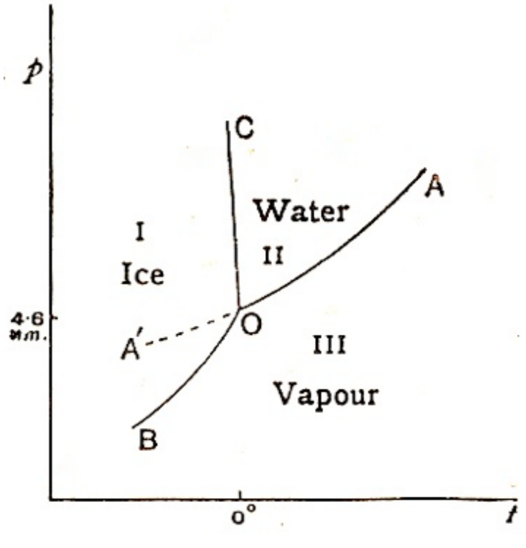

Figure 1 A 2D-phase diagram for water obeying the $f = 3 - p$ rule.

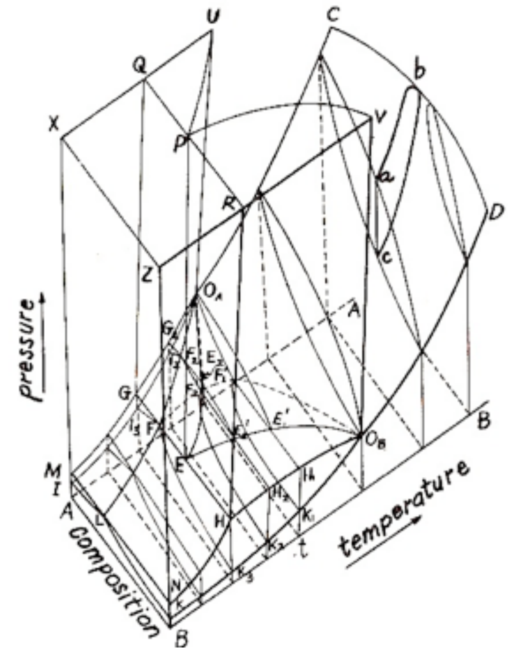

Figure 2. A full 3D binary phase diagram obeying equation 1.

When applied to the phase behavior of a binary system ($c = 2$) equation 1 reduces to:

$$f = 4 - p \qquad [2]$$

and gives the results: $f = 3$ when $p = 1$, $f = 2$ when $p = 2$, $f = 1$ when $p = 3$, and $f = 0$ when $p = 4$. This result can no longer be fully represented using a 2D diagram, but rather requires use of a 3D solid, like that shown in figure 2, where single phases now correspond to volumes ($f = 3$), binary equilibria to surfaces ($f = 2$), ternary equilibria to lines ($f = 1$), and quaternary equilibria to points ($f = 0$) (2).

Though perspective drawings of 3D phase diagrams, like that in figure 2, are often shown in textbooks, they are not practical when it comes to quantitative applications and 2D isobaric cross-sections (normally corresponding to P = 1 atm) are given instead, like that shown in figure 3. Since the pressure variable

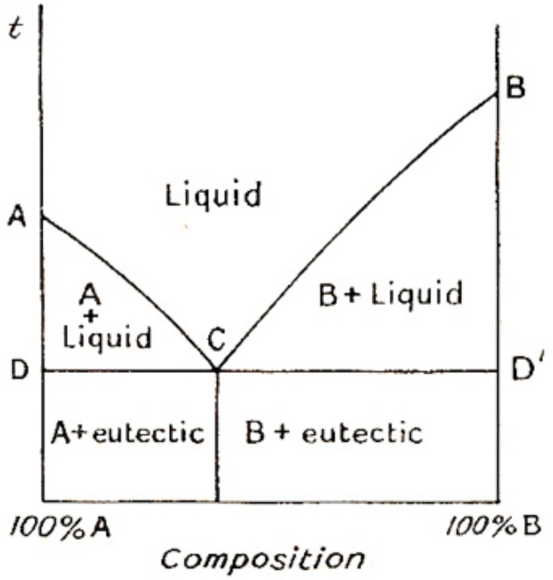

Figure 3. A 2D isobaric cross-section of a binary phase diagram for a simple eutectic obeying the $f = 3 - p$ rule.

incorporated into the full phase rule in equation 1 is now being held constant, equation 1 no longer applies to these cross-sections and should be replaced instead by the so-called "reduced" phase rule in which the number of variables, and hence the degrees of freedom, has also been reduced by one:

$$f_P = c - p + 1 \qquad [3]$$

Upon substitution of $c = 2$, this gives us the same result for a 2D cross-section of a binary system as equation 2 does for a pure substance:

$$f_P = 3 - p \qquad [4]$$

Unfortunately, the interpretation of areas, lines and points is less straight forward in these diagrams than in those for pure substances. In the latter, as we have seen, each phase occupies its own exclusive area. In contrast, in binary and higher order 2D diagrams the areas for the various phases often overlap. These overlap regions correspond to heterogeneous mixtures of variable composition for the phases in question (3). Likewise not all lines in these diagrams represent binary equilibria. Thus, in figure 3, the vertical line extending from point C down to the compositional axis has been added to draw attention to a stoichiometric aspect of the diagram related to eutectic formation rather than to a binary equilibrium. In reality the entire region below the solidus line (DD') is a mechanical mixture of only two phases – A(s) and B(s) – and point C, as required by equation 4, is a eutectic point for an equilibrium involving just the three phases: A(s), B(s) and liquid.

When applied to the phase behavior of a ternary system ($c = 3$) equation 1 reduces to:

$$f = 5 - p \qquad [5]$$

and gives the results: $f = 4$ when $p = 1$, $f = 3$ when $p = 2$, $f = 2$ when $p = 3$, $f = 1$ when $p = 4$, and $f = 0$ when $p = 5$. Complete display of these results would require use of a 4D phase diagram and cannot be represented using conventional graphing techniques. Instead what is usually employed are 2D cross-sections, like that in figure 4, in which both the temperature and pressure are kept constant. This means that the degrees of freedom in equation 1 should be reduced by two to give:

$$f_{T,P} = c - p \qquad [6]$$

which, upon substitution of $c = 3$, once more gives us the same result for a 2D cross-section of a ternary system as equation 2 does for a pure substance:

$$f_{T,P} = 3 - p \qquad [7]$$

As with the binary cross-sections, the reading of these ternary cross-sections is also made difficult by the practice of using lines to represent features other than binary equilibria. As a result, many have an appearance that – in the words of one contemporary author – borders on the "absurdly complicated" (4).

In short, whenever one employs a 2D x-y plot to

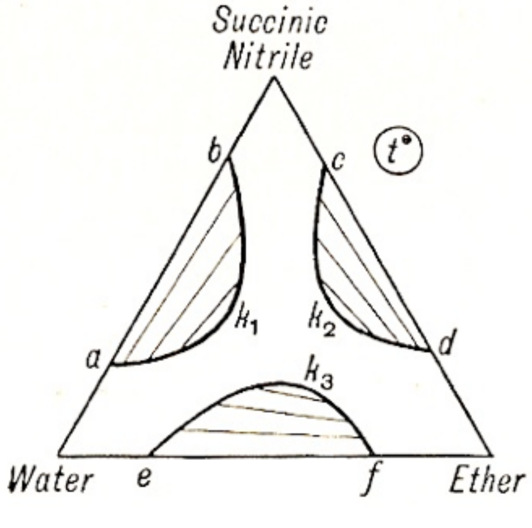

Figure 4. A 2D isobaric-isothermal cross-section of a ternary phase diagram obeying the $f = 3 - p$ rule.

represent a phase diagram, whether for a pure substance, an isobaric cross-section of a binary system, or an isothermal-isobaric cross-section of a ternary system – as is done in most textbooks and reference compilations – the conventional form of the phase law in equation 1 reduces to the simplified form in equations 2, 4 and 7:

$$f = 3 - p \qquad [8]$$

Though this simplified result is implicit in many books dealing with the phase rule (4), and most particularly in the 1938 volume by Bowden (5), it has never, to the best of my knowledge, been explicitly called to the attention of chemical educators.

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Publication History

Unsubmitted manuscript

XXVIII

Some Novel Voltaic Cells

An explicit discussion of the thermodynamics of chemical reactions and equilibria in terms of Gibbs free-energy changes is now a standard feature of most introductory chemistry textbooks:

$$\Delta G_{rx} = \Delta G_{rx}^\circ + RTlnQ \qquad [1]$$

where ΔG_{rx} is the change in the net free-energy for the reaction; ΔG_{rx}° is the corresponding change in the standard-state free energy; R is the universal gas constant; T is the absolute temperature; and Q is the corresponding activity quotient for the reaction. In contrast, discussion of the thermodynamics of the electrochemical reactions responsible for the operation of typical voltaic cells is normally done in terms of the well-known Nernst equation:

$$E_{cell} = E_{cell}^\circ - (RT/zF)lnQ \qquad [2]$$

where E_{cell} is the net electrical potential of the cell; E_{cell}° is the corresponding standard-state potential of the cell; z is the moles of electrons transferred per mole of reaction, F is Faraday's constant, and R, T and Q have the same meaning as in equation 1.

The similarity in form between equations 1 and 2 is, of course, not accidental but is rather a direct result of having derived equation 2 from equation 1 using the fundamental electrochemical identity:

$$\Delta G_{rx} = -zFE_{cell} \qquad [3]$$

where E_{cell} has the units of volts or joules/coulomb: F the units of coulombs/mole electrons: z the units of moles electrons/mole reaction; and ΔG the units of joules/mole reaction. This conversion results in the feasibility of electrochemical reactions being expressed in terms of an intensive potential rather than in terms of an extensive energy change, and the presence of the negative sign in the identity means that the criterion for reaction feasibility has also changed sign, such that:

Feasible reactions: $\Delta G_{rx} < 0$ or $E_{cell} > 0$

Nonfeasible reactions: $\Delta G_{rx} > 0$ or $E_{cell} < 0$

The average introductory text generally discusses three limiting cases of the Nernst equation (1). The first case corresponds to what might be called a "standard-state cell." Here the half reactions for the cathode and anode are chemically different but the activities of all of the soluble electrolytes and gases are set at their standard-state values. As a consequence $Q = 1$ and the $(RT/zF)lnQ$ activity term in equation 2 becomes equal to zero, thus making the net cell potential equal to the standard-state potential alone:

$$E_{cell} = E_{cell}^\circ = E_c^\circ - E_a^\circ \qquad [4]$$

where E_c° and E_a° are the standard-state half-cell reduction potentials for the cathode and anode respectively.

The second case corresponds to what might be called an "equilibrium cell." Here the various activities are set at their equilibrium values such that $Q = K_{eq}$. As a consequence the E_{cell} term in equation 2 becomes equal to zero and the standard-state potential and the activity term become equal to one another:

$$E_{cell}^\circ = (RT/zF)lnK_{eq} \qquad [5]$$

thus allowing one to use standard-state cell potentials to measure and/or calculate equilibrium constants.

The third and final case is what is called a "concentration cell," though the term "activity cell" would be more appropriate. Here the cathode and anode reactions are equal but opposite such that the E_{cell}° term in equation 2 becomes equal to zero but the various activities in the $(RT/zF)lnQ$ term are set at neither their standard state values nor their equilibrium values. As a consequence the net cell potential is determined solely by the value of the activity term:

$$E_{cell} = -(RT/zF)lnQ \qquad [6]$$

The coverage of voltaic cells in the typical physical chemistry text is very similar, though it frequently includes further discussion of the application of concentrations cells to such topics as the measurement of pH values, solubility constants for various precipitates, and stability constants for various complex ions (2).

However, these three cases and their accompanying applications hardly exhaust the uses of the Nernst equation. Perusal of older textbooks and monographs often reveals discussions of other kinds of voltaic cells, many of which are of possible interest to present-day teachers, though they have all but disappeared from current textbook literature. These cells can be used to illustrate such topics as polymorphism, the relationship between mechanical strain and corrosion, and the interconversion of various energy forms. It is the purpose of this paper to once more call attention to some of the more novel of these cells, as well as to provide a simple, albeit often naive, Freshman-level analysis of their underlying thermodynamics in terms of the Nernst equation.

Allotrope Cells

One of the most interesting of these novel voltaic cells was first described in 1899 by the Dutch phase chemist, Ernst Cohen, in connection with his studies of the allotropes of tin (3), and was later summarized in his delightful Baker Lectures of 1925, *Physico-Chemical Metamorphosis and Some Problems in Piezochemistry* (4). Tin has two common allotropes: white or metallic tin, which has a distorted 6/6 infinite framework structure and is quite malleable, and grey or nonmetallic tin, which has an infinite 4/4 framework structure like that of diamond and is brittle. These two forms are in equilibrium at 13.2°C (5):

$$\text{white Sn} \leftrightarrow \text{grey Sn} \qquad [7]$$

with the grey form being favored at lower temperatures and the white form at higher temperatures.

Since temperatures less than 13.2°C (55.8°F) are not uncommon in temperate climates, this means that objects made of metallic tin are thermodynamically unstable much of the time. Luckily the rate of interconversion is normally negligible, though cases have been observed for very old tin objects stored in unheated museums for long periods. The transformation begins with a blistering of the metal surface and ends with the gradual crumbling of the object into a shapeless grey mass. For this reason it is colloquially known as "tin disease" or "tin pest." Under extreme winter conditions, it has given rise to several historical myths, including the supposed disintegration of the tin buttons on the coats of Napoleon's army during its disastrous winter retreat from Moscow, and the crumbling of the tin solder on the seams of Scott's fuel cans, leading to contamination of his food supplies and ultimately to the demise of his exploration party during its unsuccessful track back from the south pole (5).

Cohen realized that, being chemically distinct species, the two forms of tin should display a difference in their electrode potentials and that this difference could be exploited to construct a simple voltaic cell of the form:

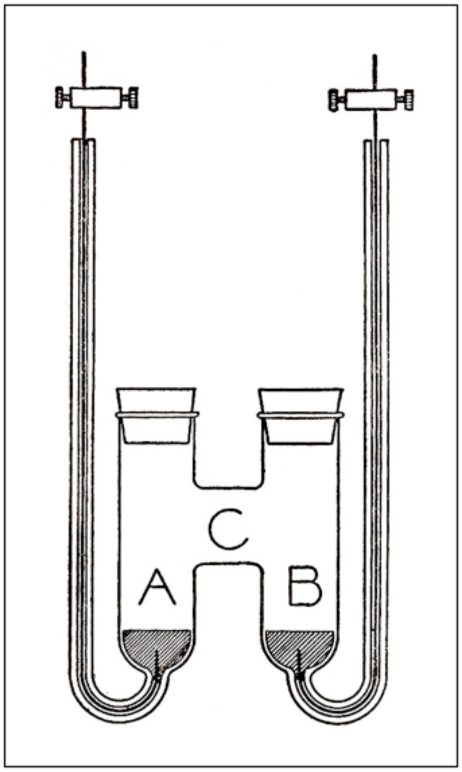

Figure 1. Cohen's voltaic cell based on the allotropes of tin. Electrode *A* corresponds to white tin, electrode *B* corresponds to grey tin, and electrolyte *C* to a dilute solution of tin dichloride with a few drops of HCl added to suppress hydrolysis.

$$\textit{white Sn / } SnCl_2(aq) \textit{ / grey tin} \qquad [8]$$

as shown in figure 1. Since both electrodes share the same electrolyte, the activity term in the Nernst equation is zero by virtue of all of the activities being equal. As a result, the net cell potential becomes equal to the standard-state potential, and the half-cell reduction potential of the anode must be altered to incorporate the free-energy difference between the two allotropes, otherwise known as the free-energy of transition (ΔG_{tr}°):

$$E_{cell} = E_c^\circ - [E_a^\circ + \Delta G_{tr}^\circ/(zF)] \qquad [9]$$

Since, for the cell in question, $E_c^\circ = E_a^\circ$, this reduces to:

$$E_{cell} = -\Delta G_{tr}^\circ/(zF) \qquad [10]$$

Indeed, in recognition of this fact Cohen named voltaic cells of this type "transition cells" and employed them to study many types of phase transitions other than those involving allotropes (6). However, since it is the specific application of these cells to the allotropic forms of tin that is of most interest to teachers of introductory chemistry, we have taken the liberty of adopt-

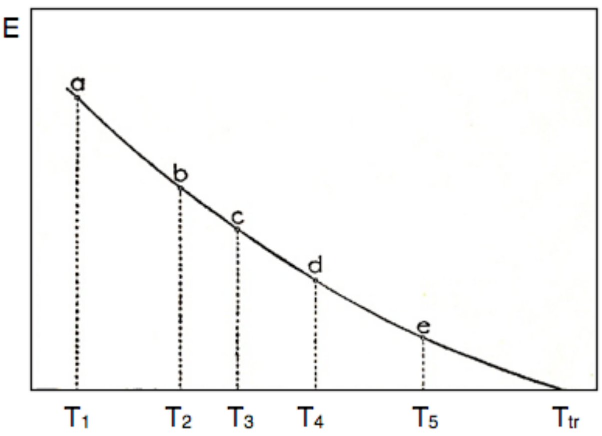

Figure 2. Cohen's plot of cell potential versus temperature for the tin allotrope cell in figure 1. The potential (a-e) decreased as the temperature (T_1-T_5) increased and was assumed to be equal to zero at the transition temperature.

ing the alternative name of "allotrope cell" (7).

Cohen's primary interest in this cell was not as a source of electrical energy but rather its use in determining the transition temperature for the two tin allotropes. Realizing that the free energy for the transition, as written in equation 7, decreases with increasing temperature and becomes zero at the transition point where the two forms are in equilibrium, Cohen measured the cell potential at progressively increasing temperatures and extrapolated the result to zero to approximate the temperature for the phase transition, as shown in figure 2. At temperatures above the transition point the anode and cathode should reverse with the grey allotrope now being oxidized and the white allotrope being reduced.

Strain Cells

The 1909 edition of J. W. Mellor's monograph, *Chemical Statics and Dynamics*, contains the following intriguing footnote (8):

> *If two springs, one wound and the other unwound, were both dissolved in acid, it is supposed that the dissolution of the wound spring would be attended with the production of the greater amount of heat. The energy stored up in the wound spring would then be converted into thermal, not [macro] kinetic energy. This supposition has never been verified experimentally. But let two pieces of soft steel wire be cut from the same piece, and let one piece be hardened by hammering or burnishing. Dip the two pieces in dilute acid and connect up with a suitable galvanometer. The swing of the needle corresponds to the extra state of energy in the hardened wire. The extra energy stored in the hardened wire will be transformed into electrical energy.*

The extra energy content of metal samples subjected to compressional hammering is known as strain energy and Mellor's suggestion had already been tested by the Belgian chemist, Walter Spring, as early as 1904 for the metals Sn, Pb, Cd, Ag, and Bi using simple cells of the form (figure 3):

strained metal / salt solution / unstrained metal [11]

In each case he was able to detect a net cell potential, though it was only of the order of 10^{-4} volts (9).

As explained in greater detail by Findlay in the 1927 edition of his classic monograph on the phase rule (10):

> *That a metal, which has been subjected to considerable mechanical stress, passes into a less stable form is shown by the fact that the metal, after being strained, possesses a higher solution pressure than the normal metal. That is to say, it acts as an anode to a piece of the normal metal when the two are placed in a solution of a salt of the metal ... The change which occurs in the nature of the metal when mechanically worked has been studied by a number of investigators, and it has been found that, in the process of working, the metal crystals become more or less completely destroyed and*

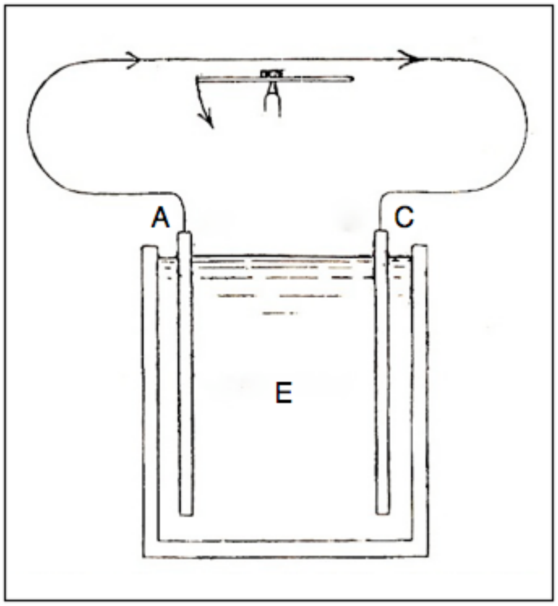

Figure 3. A simple strain cell. *A* is the strained metal electrode or anode, *C* is the unstrained electrode or cathode, *E* is the electrolyte, and the arrows indicate the direction of electron flow.

pass into an amorphous or quasi-amorphous state. A metal in such a state will therefore be related to the normal crystalline metal in much the same way as superfused solid or glass is related to the stable crystalline form.

This implies that the stressed metal is not in a well-defined thermodynamic state to which one can assign a reproducible free-energy value or half-cell potential. Rather the potential of each sample will vary with the nature of its mechanical history and the resulting strain energy (W_{stain}) added to the system.

As in the case of the allotrope cell, the activity term in the Nernst equation is once more equal to zero due to the sharing of a common electrolyte and it is the half-cell reduction potential of the anode or strained sample that must be altered to incorporate the added strain energy:

$$E_{cell} = E_c^\circ - [E_a^\circ - W_{stain}/(zF)] \quad [12]$$

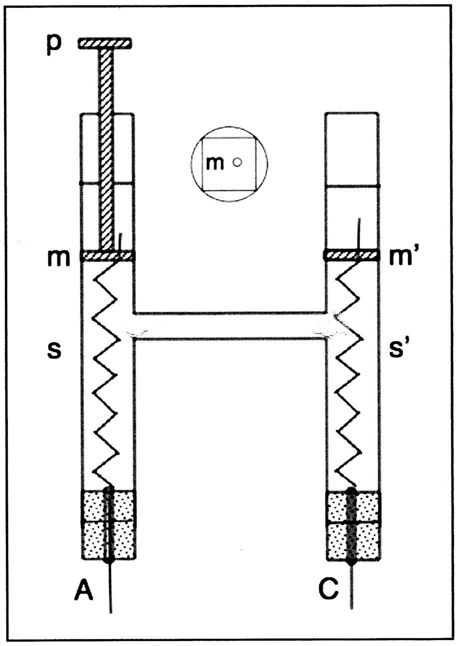

Figure 4. Proposed design for a simple compression cell. An H shaped glass cell is filled with a dilute solution of $FeCl_2$ with a little HCl added to suppress hydrolysis. Each arm of the cell contains a steel spring (*s* and *s'*) as the electrode. At the bottom of each arm the springs pass through rubber stoppers via short sections of glass tubing sealed with wax and at the top through off-center holes in the lucite mounting squares *m* and *m'*. Square *m* is free to move whereas square *m'* is attached to the wall of the tube. Square *m* is also permanently attached to the lucite piston *p* allowing one to compress spring *s* by pressing down with one's thumb or by placing weights on platform *p*.

Since, once again, $E_c^\circ = E_a^\circ$, this reduces to

$$E_{cell} = W_{stain}/(zF) \quad [13]$$

Starting in the early 1900s this result attracted a good deal of interest in the literature dealing with corrosion since it directly implied that stressed metal objects, due to bending, hammering, drawing, or previous thermal treatments, should exhibit enhanced levels of corrosion (11). Though this has generally proven to be the case, the phenomenon is often more complex and erratic than might be supposed from equation 13, since such treatments can simultaneously alter a number of other factors relevant to the corrosion process such as the integrity of protective oxide coatings (12).

When I first read Mellor's footnote many years ago as a graduate student at the University of Wisconsin, I was particularly intrigued by his example of the wound or compressed watch spring and thought about how one might electrochemically test that specific claim in a manner more direct than hammering on a piece of metal. My resulting cell design is shown in figure 4. Whether the magnitude of W_{stain} resulting from simple compression of spring *s* relative to spring *s'* is sufficient to produce a detectable cell potential is not known, since I have never found the time to build or test the cell in question, but invite readers of the journal to try it for themselves.

Gravity Cells

A third type of novel voltaic cell encountered in the older chemical literature is the so-called gravity cell. Not to be confused with the well-known Daniell gravity cell, where the term gravity actually refers to the specific gravities of the anode and cathode electrolytes, a true gravity cell is based on the interconversion of gravitational potential energy and electrical energy. Cells of this type were first experimentally described by the Russian physicist, R. Colley, in 1876 (13), and subsequently studied by the German physicist, Theodore Des Coudres (14), and the British chemist, George Gore (15). They were also discussed in some detail in such popular early 20th-century textbooks as those by LeBlanc (16) and Lewis (17), as well as being the subject of several extensive review articles (18-19).

A gravity cell is simply a very long glass tube (of the order of between 9 and 12 feet), with identical metal electrodes at each end, that is filled with an electrolyte composed of an aqueous solution of an appropriate metal salt (figure 5). Half way down the tube is a short side tube at right angles which is used to fill and empty the cell and which acts as a pivot, allowing one to rotate the cell from a horizontal to a vertical posi-

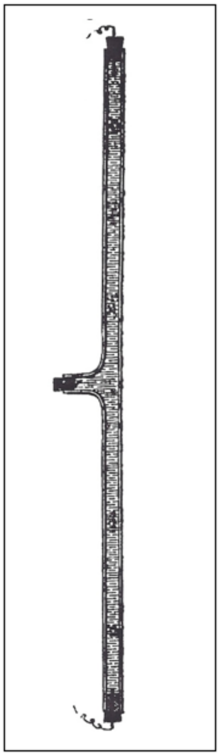

Figure 5. An etching of one of George Gore's gravity cells as first described in his paper of 1893.

tion. When placed in a horizontal position and filled, no net cell potential is detected. However, when stoppered and rotated to a vertical position, a net cell potential slowly develops – albeit an extremely weak one of the order of only 10^{-4} volts:

elevated electrode / metal salt (aq) / lowered electrode [14]

In order to amplify the effect, some workers, such as Gore, for example, constructed arrays or batteries of as many as five of these cells mounted on boards and connected in series.

Because, in simple cells of this type, the cation moves from the anode to the cathode and vice versa for the counter anion, the question of whether the elevated or the lowered electrode will function as the anode will depend upon the relative masses of the cation and anion in the electrolyte. This is because the ion which passes from the elevated to the lowered electrode is falling in the gravitational field and is therefore capable of performing work, whereas the counter ion, which moves in the opposite direction, is being raised in the gravitational field and is therefore consuming a portion of the work generated by the falling ion. The resulting difference between these two processes expresses itself in the form of a net cell potential. Thus, in the case of a $BaCl_2(aq)$ electrolyte, where the cation (Ba^{2+} = 137.3 amu) is heavier than the anion (Cl^- = 35.45 amu), it is experimentally observed that the elevated electrode acts as the anode, whereas in the case of a LiCl (aq) electrolyte, where the cation (Li^+ = 6.94 amu) is lighter than the anion, it is the lowered electrode that acts as the anode.

Since both electrodes once again share a common electrolyte, the activity term in the Nernst equation is zero and the only difference between the reduction potentials for the two electrodes will be due to the difference in the gravitational potentials of the ions which are being transferred during the cell's operation:

$$E_{cell} = \Delta mgh/(zF) \qquad [15]$$

where g is the acceleration of gravity, h is the height of the vertical cell and Δm is the difference in the masses of the transferred cations and anions. In reality, this equation is an oversimplification and must be corrected for such factors as ionic transport numbers, the degree of ionic hydration, possible buoyancy effects, etc. – topics which are not generally covered in introductory chemistry textbooks.

The expression for gravitational potential energy (*mgh*) contains three terms. In the cell just described it was the mass term that was varied in order to generate a cell potential. In yet a second type of gravity cell, also described by Des Coudres (14) and discussed in LeBlanc's textbook (16), it is the *h* term which is varied instead. This is shown in figure 6 and is based on the arrangement:

tall Hg anode / $Hg(NO_3)_2(aq)$ / short Hg cathode [16]

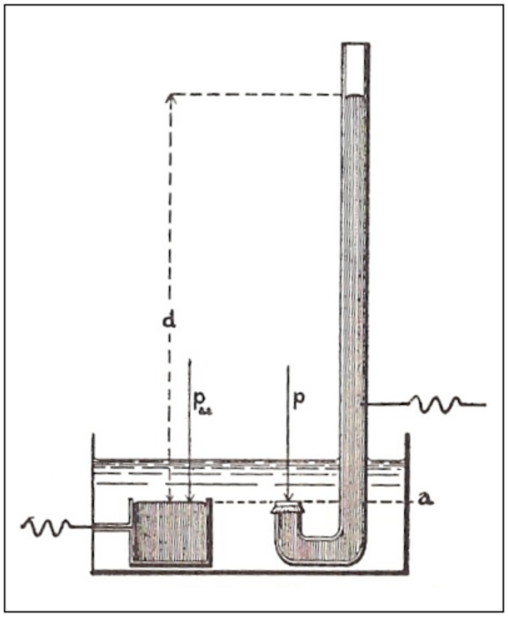

Figure 6. LeBlanc's drawing of Des Coudres' original gravity cell of 1892. The cathode is on the left and the anode on the right.

The surface of the short Hg cathode is in direct contact with the electrolyte, whereas that for the short arm of the tall Hg anode is covered with an ion-permeable membrane in order to mechanically support the connecting column of Hg in the tall side arm. The cell potential is determined by the conditions at these two contact surfaces and, taking these surfaces as our zero point, since both are at the same height, we find that they differ solely in the fact that the surface of the anode is subjected to the compression generated by the Hg column in the tall side arm. To a first approximation, we can equate the resulting compression strain with the excess gravitational potential energy of this column:

$$W_{stain} = mg\Delta h \qquad [17]$$

where Δh is the height of the column relative to the electrode surface and is labelled as d in LeBlanc's original figure. Following the derivation given earlier for strain cells, we then obtain the approximate result that:

$$E_{cell} = (mg\Delta h)/(zF) \qquad [18]$$

A third type of gravity cell is based on varying the value of the *g* term by subjecting the cell to centrifugal acceleration in a specially designed centrifuge. Also known, for obvious reasons, as a centrifugal cell, this variation, though mentioned by Gore and studied by Des Coudres, was actually perfected by the American chemist, Richard Tolman (19), in the first decade of the 20th century and is also described in the textbook by Lewis (17).

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Publication History

Unsubmitted manuscript

XXIX

Reformatting the Ideal Gas Law

Every teacher of chemistry, whether at the college or high-school level, now teaches the ideal gas law using the equation:

$$PV = nRT \qquad [1]$$

and most are by now so familiar with it that they give it little thought. Yet, when looked at objectively, this particular formulation of the law contains several unusual features. Thus, for example, in most equations containing a simple proportionality constant, the constant is placed in front of the variables rather than inserted among them, in which case we might expect the law to be written instead as:

$$PV = RnT \qquad [2]$$

There are several historical reasons for why our current formulation of the law violates this expectation, the most important of which is the fact that for much of the time since the law was first formulated by Horstmann in 1873 on a per mole basis rather than on a per mass basis, it has been written in the form (1-2):

$$Pv = RT \qquad [3]$$

where v represented the volume per mole (V/n) rather than the total volume V – a practice that was continued in physics textbooks well into the 1960s (3). Hence when the mole was finally made explicit, as in equation 1, rather than implicit, as in equation 3, its symbol was simply tacked onto the front of the RT term in equation 3.

However, correction of this placement problem, as was done in equation 2, gives a result which looks typographically odd to the modern eye, in large part because of the lower case n inserted among the upper case letters for the other variables and constants, and this issue brings us to the most controversial aspect of reformatting equation 1 – the ontological status of n.

Variables, Units, and Constants

It is universally understood that the symbols P, V. and T stand for the general physical variables or quantities that we call pressure, volume, and temperature and that, not only may these variables be measured using a wide variety of alternative units, the value of the so-called constant R will also vary depending on these choices. Thus when P is measured in units of atmospheres and V in units of liters, R has the value $8.21\text{x}10^{-2}$ atm L/(mol K), whereas when P is measured in units of Pascals and V in units of cubic meters, it has the value of 8.31 J/(mol K).

Indeed, even T could be measured in alternative units, such as degrees Celsius or degrees Fahrenheit, though this would require modification of equation 2 to incorporate a second constant, θ, whose value would also vary with the choice of temperature scale:

$$PV = Rn(T + \theta) \qquad [4]$$

The usual choice of degrees Kelvin as the preferred unit may be viewed simply as the option for which θ happens to have a value of zero, and in fact an equation of this form was used by both Clapeyron and Clausius to express the ideal gas law prior to the latter's adoption of the absolute temperature scale in 1864 (1).

In actual practice, equation 4 is never used today and, if the experimental temperature is given in units other than degrees Kelvin, the necessary temperature conversion is first performed as a separate preliminary calculation using equations of the form (4):

$$K = a(T + b) \qquad [5]$$

before substitution into equation 2. One reason for this asymmetry in the treatment of T vs P and V is that alternative units for the latter two variables differ in size but agree upon a common zero, whereas those for T also differ in the choice of zero.

But if it is agreed that P, V, and T are generalized variables, which may be measured using a variety of units, and R is a constant whose numerical value depends on the choice of these units, what exactly is n? Since it is not a constant, logic would dictate that it is also a general physical variable or quantity like P, V and T, and that, like them, it may also be measured using a variety of units. Yet consultation of various IUPAC guides declares otherwise and insists that n is a property variously defined as the "amount of substance," "chemical amount," or "enplethy" and that, as such, it is uniquely and exclusively measured in units of moles (5).

Counting Units

This seems strangely at variance with what the kinetic theory of gases tells us about the origins of the ideal gas law at the molecular level, where the pressure of a gas is found to depend on the number of molecules present in a given volume of gas at a given temperature (interpreted as a measure of the average kinetic energy of the molecules) (6). And just as IUPAC has endorsed the symbols P, V, and T for pressure, volume and temperature, so it has also endorsed the symbol N to represent the number of entities (in this case, molecules). In short, the kinetic theory of gases tells us that:

$$P = f(N, T, V) \qquad [6]$$

which leads, in turn, to the explicit function:

$$P = RNT/V \qquad [7]$$

and thus to:

$$PV = RNT \qquad [8]$$

as the proper generalized form for the ideal gas law (7).

The only way to reconcile equation 8 with equation 2 is to interpret the mole as but one of several alternative units for counting the number of molecules present. The idea that the number of objects in a population can be measured or counted using a variety of alternative counting units has long been an established concept in commerce, if not in science. The simplest counting unit is individuals – a direct enumeration of each object in the collection:

$$n \text{ in units of individuals} = N/1 \qquad [9]$$

But in everyday life it is common to use larger counting units as well, such as dozens to count eggs:

$$n \text{ in units of dozens} = N/12 \qquad [10]$$

or reams to count sheets of paper:

$$n \text{ in units of reams} = N/500 \qquad [11]$$

So in chemistry we count in units of moles:

$$n \text{ in units of moles} = N/N_A \qquad [12]$$

where N_A is Avogadro's number.

Many chemistry teachers have long advocated this interpretation of the mole and its apparent rejection by IUPAC appears to be based on the fact we do not literally determine the number of moles present by counting but rather calculate the value from mass measurements using molar or molecular weights. This is, of course, a result of the fact that, since molecules are so small and there are such huge numbers present in the gram-sized samples used in most laboratory work, direct counting would be impractical in the extreme. If we knew the average mass per dozen eggs or the average mass per ream of paper, we could also calculate dozens and reams from mass measurements, but here the practical situation is precisely the opposite of that for molecules and it is far easier to directly count. The point of this comparison is that, even if we calculated dozens and reams indirectly from mass measurements, this would not lead anyone to deny that these units were in fact measures of the number of objects present, and, for the same reason, this difference in procedure is not a proper objection to the view that the mole is ultimately a counting unit.

The same is true of the objection that the numerical value for the molar counting unit, N_A, is ultimately determined by the conversion factor between two mass units – the gram and the atomic mass unit (8, 9). The reason for this is purely one of convenience since it means that molar masses measured in units of grams are automatically numerically identical to molecular masses measured in units of atomic mass units and that, as a result, we require only a table of atomic mass values in order to perform mole calculations. The size of most units are determined for reasons of convenience and that convenience may be determined as much by how we perform the measurement as by what is being measured. Thus, for example, the choice of 12 as the size for a counting unit in commerce, rather than 10, as used in the metric system, probably had to do with the convenience that, unlike 10, 12 gives integral values for 1/4, 1/3, 1/2, 2/3 and 3/4 of the resulting unit, whereas 10 gives an integral value only for 1/2 of its unit (10).

What is Amount?

A more serious objection to the IUPAC definition of the mole as the "amount of substance" is that it assigns a restricted meaning to the word "amount" which is at variance with both its everyday meaning and with its historical use in chemistry – something which was recently brought to the senior author's attention when he was told by a journal editor that he could not use the word amount when referring to mass in discussing Faraday's laws of electrolysis and that it was now the journal's official policy that the word referred exclusively to moles.

Both historically and in everyday practice the word amount is used as a synonym for quantity and may be measured in any one of three different ways, corresponding to the common questions of how heavy?, how big? or how many? In other words, it may be measured in units of mass, units of volume or in counting units. Thus, when we go to a grocery store, the amount of cheese which we purchase is measured by mass or weight (ounces, pounds, etc.), the amount of milk by volume (pints, quarts, gallons, etc.), and the amount of eggs by counting (half dozen, dozen, etc.).

Likewise in chemistry we have historically measured the quantities or amounts of each element present in a given chemical compound using either mass, volume, or atom counts, corresponding to percent composition by weight, percent composition by volume, and atomic composition respectively. Thus water is a compound containing 11.11% H and 88.89% O by weight, 66.67% H and 33.33% O by volume, or a ratio of 2 atoms of H to one atom of O by number To declare that only the last of these characterizations measures the amounts present is eccentric in the extreme.

Indeed, a large percentage of the introductory chapters of freshman textbooks deals with interconverting between these alternative measures of amount. This is accomplished (figure 1) using a set of derived properties constructed by taking various ratios of the three fundamental measures of amount – mass *(M)*, volume *(V)*, and number or population *(N)*. Thus mass density *(M/V)* and specific volume *(V/M)* are used to convert between mass and volume, unit mass *(M/N)* and specific population *(N/M)* to convert between mass and population, and population density *(N/V)* and unit volume *(V/N)* to convert between volume and population (11).

The names of these derived properties should be general and not tied to any specific choice of the units used to measure them. This is widely recognized for both mass density and specific volume in which the former is commonly measured in units of either g/mL or kg/m^3 (and their inverse for specific volume). In the case of the derived properties involving *N*, however, this has not been the case, due to the pervasive use of the mole to measure *N*. Thus instead of talking of population density and unit volume, we commonly talk instead of molarity and molar volume. In the case of unit mass, we commonly employ units of either grams/mole or amu/molecule. However, rather than recognizing these as alternative unit choices for the general property of unit mass, we have instead given each of them their own individual names (i.e. molar mass and molecular mass respectively).

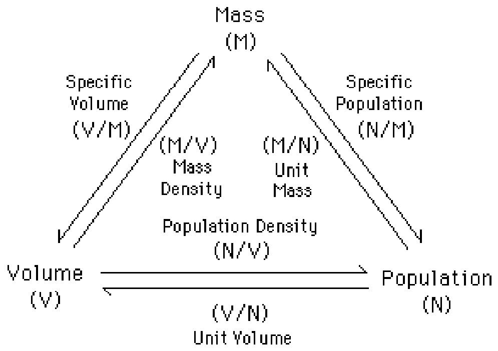

Figure 1. Generalized diagram for the interconversion of alternative measures of amount.

A final objection to the IUPAC definition is its implication, intensional or otherwise, that the mole is to be used only to measure the amounts of various chemicals or substances. In fact, like all counting units, we may use it to measure the amounts of anything we please and we are free to talk of the moles of chairs in an auditorium or the moles of stars in the heavens, however improbable such applications. Furthermore, there are concrete examples in chemistry in which the mole is actually used to measure amounts or numbers of events rather than various chemical species (12, 13). These include the various applications of the de Donder extent of reaction parameter (ξ), which is best measured in units of moles of reaction events (mol rx), and its application to both chemical kinetics, in which rates, $d\xi/(Vdt)$, are now measured in units of moles of reaction events per unit volume and time, mol rx/(L sec), and to thermodynamics, in which such parameters as the enthalpies and free energies of reactions are now measured in unit of kilojoules per mole of reaction events, kJ/(mol rx).

An Important Consequence

We have already seen that a change in the units used to measure *P* and *V* changes the numerical value of the constant *R,* and once it is accepted that the mole is merely a counting unit and that equation 8 is a more general expression of the ideal gas law than equation 2, the question naturally arises as to how a similar change in the units used to measure *N* will affect the value of *R*. It is doubtful that we would ever have an occasion to measure *N* in units of dozens or reams, but there are many situations in which it is convenient to measure it in units of individuals, in which case *R* takes on the value of 1.38 x 10^{-23} J/(molecule K). However, instead of recognizing this as merely another unit change for *R*, the resulting value has, for both historical reasons and because of the continued use of *n* instead of N in the gas law, been traditionally given both its own unique symbol (k) and name (the Boltzmann constant) (5). Use of equation 8 would eliminate this practice and result in a more consistent application of the distinction between variables, units, and constants in chemistry.

Conclusions

In summary, we have argued that the mole is a unit rather than a general property and that, as such, it is a counting unit used to measure the number of entities or events (N) in a given population rather than some uniquely defined measure of chemical amount. It is further argued that adoption of these conclusions not only leads to an improved formulation of the ideal gas law, but to a significant clarification of the concept of amount as it is used in both commerce and science.

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Publication History

Unsubmitted manuscript.

XXX

Entropy Balls

Entropy and Constraint of Motion
A Mechanical Analogy

Sometime ago the author called attention to the correlation that exists between the entropy of a material and the various constraints on the motion of its constituent particles (whether colloids, micelles, molecules or atoms) (1). This correlation predicts that the fewer the constraints on these motions, the greater the entropy of the system and vice versa.

It was also pointed out that changes in any of the following factors can lead to a change in entropy, where the motions in question may be translational, rotational or vibrational in nature:

1. Constraints on the number of independently moving particles, i.e., on whether the particles must move as an aggregate or can move independently.

2. Constraints on the direction of motion.

3. Constraints on the volume in which the motion is executed.

It is important to emphasize that, like the popular metaphor which correlates entropy with molecular disorder, constraint of motion is not the same thing as entropy itself (2). Entropy is an energy based concept with the units of energy per degree Kelvin, rather than a structurally based concept, and is ultimately a measure of the ability of a system to dilute or disperse its kinetic energy over as many accessible quantum levels as possible (3, 4). Rather molecular disorder and changes in constraint of motion are both useful structural indicators that the system in question has gained access to additional quantum levels, either through an increase in the number of independent levels (via factor 1) or by decreasing the energy spacing between previously inaccessible levels (via factors 2 and 3). Indeed, the relevance of factors 2 and 3 may be easily rationalized using a simple quantum mechanical "particle in a box" model.

This view of entropy was singled out by Denbigh and Denbigh in their 1985 monograph on the nature of entropy as being perhaps the single best way of qualitatively defining the concept (5):

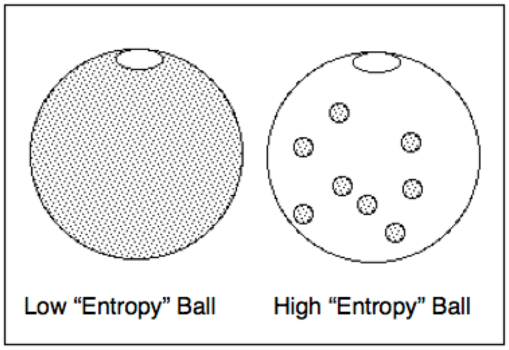

Figure 1. Cross-sections of the two "entropy" balls.

> *If a verbal interpretation of entropy is required, a far more reliable one is to be found in the notion of "spread," as used by Guggenheim. An increase in entropy may be said to correspond to a "spreading" of the system over a large number (W) of occupied quantum states. Alternatively one might say that entropy is a measure of the extent to which the system in question is unconstrained: the less constrained it is, the greater is the number of accessible quantum states for given values of those constraints.*

A Mechanical Analogy

In class I illustrate the first of the above three cases using two specially prepared pingpong balls (figure 1). A hole of sufficient size to introduce small glass beads is burned in each of the pingpong balls using a cork borer of suitable diameter that has been heated in the flame of a Bunsen burner. The first or low entropy ball is filled, via its hole, with polyurethane foam sealant from a spray can (6). After drying, the excess protruding from the hole is trimmed level with the ball's outer surface and the ball is weighed. A number of small glass beads sufficient to approximate the weight of the first ball after filling (about 20 in our experience) are then dropped through the hole of the second or high entropy ball and the hole resealed using a small piece of scotch tape.

As may be seen from the figure, we now have

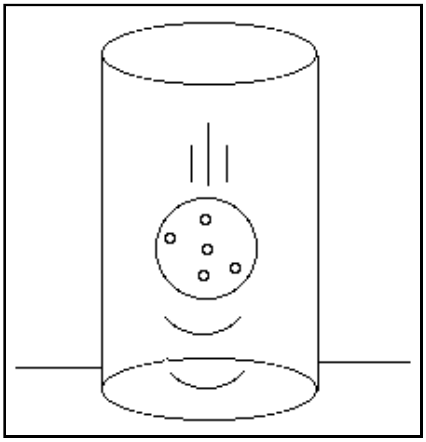

Figure 2. Bouncing the ball inside the plexiglass cylinder.

two balls of approximately equal mass, but with the important difference that the internal components (beads) of the high entropy ball are free to move independently of one another and of the ball as a whole, whereas the components (the polyurethane foam) of the low entropy ball are constrained to move as a single unit which includes the ball itself.

To demonstrate how this difference impacts on the ability of the two balls to dissipate kinetic energy, they are each dropped (plug side up) down the interior of a clear 3" x 12" plexiglass cylinder, as shown in figure 2. Whereas the low entropy ball will bounce nine or ten times before coming to rest, the high entropy ball will bounce only once, thus illustrating the ability of the freely moving beads in its interior to dissipate or randomize the kinetic energy acquired by the ball during its initial descent.

Limitations

Like all mechanical analogies, this one has several limitations. Thus, despite the macro damping provided by the freely moving glass beads, both balls are also simultaneously undergoing a true molecular dissipation of their kinetic energy and this is, of course, what ultimately brings them both to rest. In addition, we must remind ourselves that the balls illustrate only one of the three possible ways in which a change in the constraints of motion can alter the ability of a system to disperse or dissipate its kinetic energy. Given these limitations, are there any real systems for which the pingpong balls can serve as a crude mechanical analogy?

Happy and Sad Balls

The most likely candidate to come to mind is probably the popular demonstration of the difference in the mechanical behavior of the so-called "happy" and "sad" rubber balls that have been the subject of several articles and notes in this journal and on the internet (7-12). The so-called happy ball is made of polychloroprene (known commercially as Neoprene®) and, like the low entropy pingpong ball, it will, on being dropped, bounce repeatedly before coming to rest, whereas the so-called sad ball is made of polynorbornene (known commercially as Norsorex®) and, like the high entropy pingpong ball, it will, on being dropped, come to rest almost instantly.

Polychloroprene is frequently crosslinked in order to improve its mechanical resiliency. This makes it stiffer and constrains the motion of its individual polymer chains relative to that of the freely moving chains in polynorbornene. The importance of crosslinking in determining the behavior of the two balls is underscored by an alternative set of commercially available balls known as "smart" and "stupid" balls (13). Here the highly resilient smart ball is made of crosslinked polybutadiene, whereas the energy-absorbing stupid ball is made of a copolymer of either poly(vinyl-butadiene) or poly(styrene-butadiene) with substantially less crosslinking. Indeed, these balls have been recommended as a way of explicitly demonstrating the role of crosslinking in determining polymer properties.

Unfortunately, in the case of the happy/sad ball combination, this simple molecular rationale is complicated by the fact that the polynorbornene ball is actually a two-phase system (9). Because of its polar chloro substituent (figure 3), polychloroprene is oil resistant, whereas the pure hydrocarbon chain in poly-

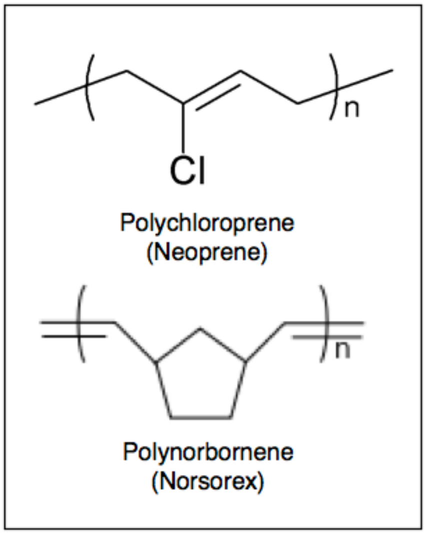

Figure 3. The repeat units for polychloroprene versus polynorbornene.

norbornene is oil compatible and indeed the sad ball actually contains a fair quantity of high viscosity oil that has been added as a plasticizer (7). As noted by Nicholson, it is highly probable that this oil, like the independently moving beads in the high entropy pingpong ball, plays a significant role in creating the internal molecular "friction" that accounts for rapid dissipation of the kinetic energy of the bouncing polynorbornene ball (8).

The Atomic Trampoline

At first glance, a second possible candidate is the so-called "atomic trampoline" demo, which superficially seems to behave in a manner similar to the happy and sad balls. This demo may be purchased from the Institute for Chemical Education (ICE) at the University of Wisconsin and consists of two 2" x 14" clear plastic cylinders, two small steel ball bearings, and two cylindrical metal bases which fit inside the plastic cylinders (14). A metal ball bearing is dropped down each of the plastic cylinders onto a metal base. In one case the ball rapidly comes to rest after a few bounces, whereas in the second it bounces many times before finally coming to a halt.

However, in this demo the difference in behavior lies not in the ball bearings, which are identical in both cases, but rather in the nature of the metal surfaces on which they are bouncing. In the case of the rapidly equilibrating ball, the surface corresponds to stainless steel, whereas in the case of the slowly equilibrating ball, it is composed of a special amorphous, five-component, metallic glass known commercially as Liquidmetal® ($Zr_{41.2}Be_{22.5}Ti_{13.8}Cu_{12.5}Ni_{10.0}$).

In addition, the underlying mechanism for energy dissipation in this demo turns out to be very different from that for either the pingpong balls or the happy and sad rubber balls. Examination of the surface of the stainless steel base shows that the bouncing ball bearing leaves small pits, whereas the surface of the metallic glass remains dent free. In other words, unlike the elastic rebound of the pingpong and rubber balls, the main mechanism for energy dissipation in the case of the rapidly equilibrating ball bearing is permanent plastic deformation of the stainless steel surface, whereas this mechanism is lacking in the case of the metallic glass surface.

These differences reveal that the behavior of a bouncing ball depends not only the nature of the ball itself but on the nature of the surface on which it is bouncing. This may be illustrated by comparing the behavior the polyurethane-filled pingpong ball when dropped on the surface of the demo bench, as in the earlier demonstration, with its behavior on being dropped onto the lid of a closed, but empty, plastic CD case.

Acknowledgement

I would like to thank Rudy Thomas, our departmental demonstrator, for his assistance in preparing this demonstration.

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Publication History

Unsubmitted manuscript

XXVI

Ask the Historian

The Origins of the Gibbs-Helmholtz Equation

Question

When and where did Gibbs first derive the Gibbs-Helmholtz equation?

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Answer

The first problem in attempting to answer this question is the ambiguous way in which the term "Gibbs-Helmholtz Equation" is used in the thermodynamic literature to describe at least a dozen different equations, albeit all of them derivable from one another (1). Thus, in their simplest form, equations bearing this name may involve either the Helmholtz free-energy function (A):

$$(\partial A/\partial T)_V = -S \qquad [1]$$

the Gibbs free-energy function (G):

$$(\partial G/\partial T)_P = -S \qquad [2]$$

or the electrochemical cell potential (E):

$$(\partial E/\partial T)_P = \Delta S/\nu_e F \qquad [3]$$

where F is Faraday's constant and ν_e is the stoichiometric coefficient for the number of electrons transfered in the balanced half-cell reactions.

The above name may also be applied to a variety of more complex equations derived from these, as illustrated below for the specific case of the Gibbs free-energy function:

$$\Delta H = \Delta G - T(\partial \Delta G/\partial T)_P \qquad [4]$$

$$\Delta G = \Delta H + T(\partial \Delta G/\partial T)_P \qquad [5]$$

$$\partial(\Delta G/T)/\partial T)_P = -\Delta H/T^2 \qquad [6]$$

$$\partial(\Delta G/T)/\partial(1/T)_P = \Delta H \qquad [7]$$

Figure 1. Hermann von Helmholtz (1821-1894).

Historically, versions of equations 1 and 3 were first derived by the German physicist, Hermann von Helmholtz (figure 1), in 1882, as well as the Helmholtz free-energy and electrochemical cell potential equivalents of equation 4 (2, 3):

$$\Delta U = \Delta A - T(\partial \Delta A/\partial T)_V \qquad [8]$$

$$\Delta U = -\nu_e F[E - T(\partial E/\partial T)_V] \qquad [9]$$

Trying to determine when and where the American physicist, Josiah Willard Gibbs (figure 2), first derived an equivalent equation or equations has, however, proved to be much more difficult and involves several false leads. Thus, for example, Partington, in his 1913 treatise on chemical thermodynamics, states (4):

There is a very important equation relating to the electromotive forces of reversible cells which was deduced independently by J. Willard Gibbs (1875) and H. von

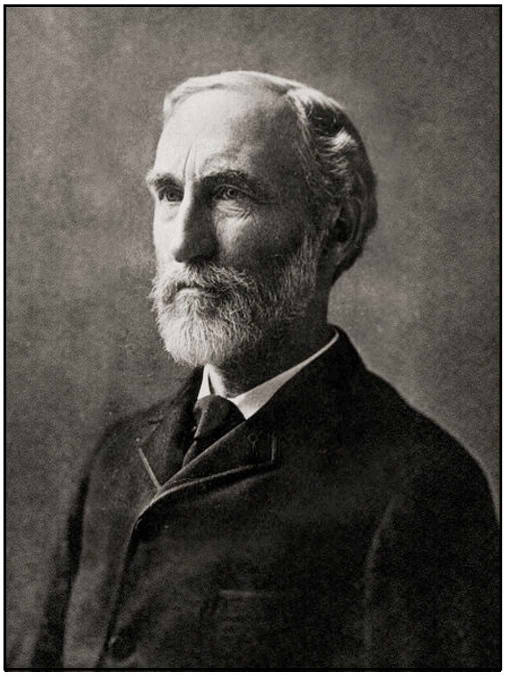

Figure 2. Josiah Willard Gibbs (1839-1903).

Helmholtz (1882), and is usually called the Gibbs-Helmholtz Equation.

However, an examination of Gibbs' epic 1875 paper, "On the Equilibrium of Heterogeneous Substances" (5), fails to reveal any such equations, and 31 years later Partington would correct his earlier statement in Volume 4 of his massive *History of Chemistry*, where he admitted that the Gibbs-Helmholtz equation "was never given or used by Gibbs" (6).

But if this is the case, how was Partington misled in 1913? The answer seems to lie in a passing comment in L. P. Wheeler's 1951 biography of Gibbs, where we read (7):

> *Another physicist who, according to the testimony of Professor Michael Pupin, must have become acquainted with Gibbs' work in the mid-eighties was Hermann von Helmholtz. In 1882 the latter had published a derivation of an equation giving the rate of change of the electromotive force with temperature for a reversible electrolytic cell which generally became known as the Gibbs-Helmholtz equation after it was pointed out that it was implicit and more readily derivable from Gibbs' work of some four or five years previous.*

There are three things to note in this quote: first the unsubstantiated suggestion that Helmholtz had gotten the idea for his equation from the earlier work of Gibbs; second, the admission that the equation in question was only "implicit" in that work; and third, Wheeler's failure to tell us who it was that first called attention to this fact.

As it turns out, that someone was probably none other than Gibbs himself in a letter to Sir Oliver Lodge published in the 1888 volume of the *Report of the Meetings of the British Association for the Advancement of Science*. Here, after reviewing the equations he had given in 1875 for the potential of an electrochemical cell at constant temperature, he notes that (8):

> *It is very easy to show that these results are in complete accordance with Helmholtz's differential equation. We have only to differentiate [with respect to the temperature] the value which we have found for the electromotive force.*

After six subsequent substitutions and rearrangements, Gibbs finally arrives at his version of equation 3 (9), albeit six years after Helmholtz rather than seven years before him, as originally implied by Partington and Wheeler (10).

Thus we find that Partington's conclusion in 1964 was no more correct than his statement of 1913. But does the derivation of an already known equation six years after the fact really entitled one to equal billing? This question is even further complicated by Partington's claim in his history that relationships equivalent to equation 4 had already been derived by both Horstmann in 1872 and by Lord Kelvin in 1857, though I have been unable to verify this claim (6, 11).

All of these difficulties are a reflection of the pitfalls that underlie the widespread practice of eponymy or the naming of equations, laws, elements, compounds, apparatus, etc. after famous scientists. For a variety of reasons, these names are almost invariably historically misleading and it would save much gnashing of teeth on the part of historians if this practice was discontinued (12). This, of course, is unlikely to happen since canonization in this fashion is probably the unspoken fantasy of every practicing scientist.

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9. As in the case of Helmholtz, there are differences in both Gibbs' choice of symbols and sign conventions versus our modern usages. In addition, Gibbs, unlike Helmholtz, completely ignores the issue of units and unit conversions.

10. The discrepancy between the timing in Partington versus Wheeler is due to the fact that the difference is seven years if one uses the date 1875, which is when the first installment of Gibbs' memoir was published, but only four years if one takes into account that the section dealing with electrochemistry did not appear until 1878.

11. I could find nothing in the six-volume set of Kelvin's collected papers nor in Horstmann's publications on thermodynamics. For more on Horstmann and his lesser known contributions, see W. B. Jensen "August Horstmann and the Origins of Chemical Thermodynamics," *Bull. Hist. Chem.,* **2009**, *34(2)*, 83-91.

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Publication History

Published in *ChemTexts*, **2016**, *2*, 1.

XXXII

A More Precise Mathematical Formulation of the Second Law of Thermodynamics

In 1865 Clausius first gave his famous verbal summary of the second law of thermodynamics in terms of his newly formulated entropy function (1):

The entropy of the universe tends to a maximum.

Most freshman chemistry and introductory thermodynamics textbooks mathematically formulate this law as:

$$\Delta S \geq 0 \qquad [1]$$

where the equal sign applies to reversible processes and the inequality to irreversible processes.

Yet others are careful to stipulate that the entropy in question is the total entropy of both the system and its environment:

$$\Delta S_{total} = \Delta S_s + \Delta S_e \geq 0 \qquad [2]$$

whereas yet others stipulate, in keeping with Clausius's original statement, that the entropy in question is the entropy of the universe as a whole:

$$\Delta S_{univ} \geq 0 \qquad [3]$$

Though, in principle, the environment of a finite system is by definition the rest of the universe, and thus formulations 2 and 3 are equivalent, some purists are uncomfortable about making blanket claims for the universe as a whole.

Yet a third alternative is to make use of the thermodynamic distinction between open, closed, and isolated systems, where the boundary of an open system allows passage of both energy (U) and matter or mass (m) between the system and its environment, that of a closed system allows passage of only energy, and that of an isolated system allows passage of neither. Formulation 1 actually applies only to an isolated system which can often be approximated locally without reference to the universe as a whole. Thus a more workable and precise mathematical statement of relation 1 would be:

$$(\Delta S)_{U,m} \geq 0 \qquad [4]$$

which has the advantage of explicitly indicating that both energy and mass are kept constant (2, 3). For the closed systems of most interest to chemical thermodynamics (see below), the system, together with its immediate environment, constitute, in keeping with formulation 2, just such an isolated, albeit approximately localized, system.

A Mathematical Weed

To a beginning student, Clausius's verbal statement and relations 1-4 often appear contradictory, since Clausius states that entropy tends to a maximum and not to zero. Such a confusion is, of course, based on a failure to distinguish between the total entropy (S) in Clausius' statement and the change in entropy (ΔS) found in relations 1-4. Yet this confusion still has some justification, since what is actually being referred to in these relations is not a true finite delta or difference, but rather the first derivative (dS/dx) or slope of a plot of total entropy with respect to a progress variable (x) of some sort (figure 1). Some authors, such as Planck, attempt to at least partially correct this problem by writing these relations using dS instead of ΔS (4):

$$(dS)_{U,m} \geq 0 \qquad [5]$$

but this still leaves the progress variable implicit. This widespread practice in the thermodynamics literature

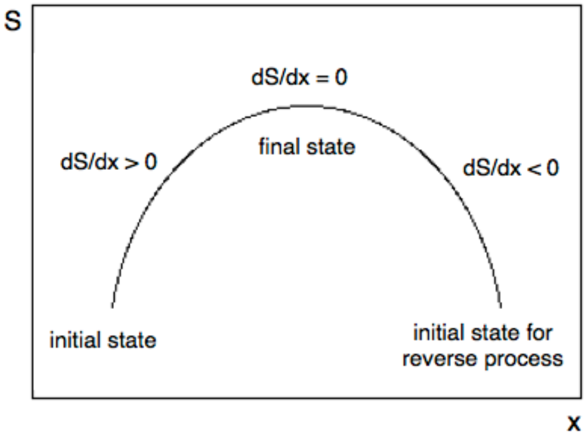

Figure 1. An idealized S-x plot showing variations in the sign of dS/dx.

of writing Δy when one actually means (dy/dx) has been aptly characterized by Bent as "a mathematical weed in the garden of thermodynamics" (5).

But what shall we select as our progress variable when attempting to mathematically formulate a properly generalized statement of the second law? As suggested by Denbigh some years ago, the most general choice for such a variable is nothing other than time (t) itself, thus giving as our final, and most precise, mathematical statement of the second law (6):

$$(dS/dt)_{U,m} \geq 0 \qquad [6]$$

This formulation ties in nicely with the widespread identification of entropy as "time's arrow," that is, as a single unique physical measure of the direction of time in the universe (7, 8).

An Alternative Progress Variable for Chemistry

But, in proposing formulation 6, have we not violated yet another premise of conventional thermodynamics – namely that it deals only with initial and final states and neither with issues of mechanism or time? This apparent paradox can be resolved by factoring relation 6 into two parts, using an alternative progress variable, such that one part contains the purely thermodynamic factors and the other contains the time dependency. In the case of chemical reactions this is best done by using as our alternative progress variable de Donder's well-known extent of reaction parameter (ξ), and a similar procedure may be employed for other thermodynamic applications by using yet other alternative progress variables specific to the type of system under consideration (9).

Thus, on multiplying relation 6 by $d\xi/d\xi$ or unity and factoring, we obtain:

$$(d\xi/dt)(dS/d\xi)_{U,m} \geq 0 \qquad [7]$$

in which the second factor $(dS/d\xi)$ now contains our purely thermodynamic terms and the first factor $(d\xi/dt)$ our kinetic or time-dependent terms. Indeed this latter factor corresponds to de Donder's formal definition of the absolute velocity (v') of a chemical reaction:

$$v' = (d\xi/dt) \qquad [8]$$

which allows us to rewrite the inequality in relation 7 in a more concise manner (10):

$$v'(dS/d\xi)_{U,m} \geq 0 \qquad [9]$$

An idealized plot of S versus ξ is given in figure 2 in order to illustrate the behavior of the purely thermodynamic term $(dS/d\xi)$ in relation 9 and, though we have factored out the time dependency, it nevertheless illustrates the quip of at least one pair of thermodynamic wags when they observed that "if entropy is time's arrow, then equilibrium is its target" (11). But far more important is the fact that this inequality also makes explicit the fundamental principle that the kinetic and thermodynamic or stability aspects of chemical reactions are largely independent of one another, as first observed by Fourcroy near the end of the 18th century (12).

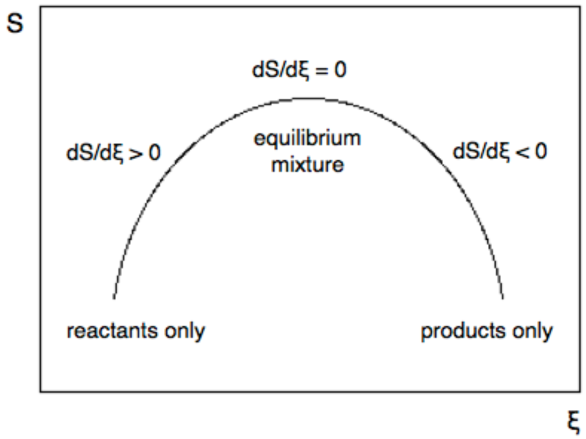

Figure 2. An idealized S-ξ plot for a chemical reaction showing variations in the sign of $dS/d\xi$. For real equilibrium reactions neither the endpoints nor the maximum are symmetrical. Rather the later would be displaced either to the left or right depending on the magnitude of the equilibrium constant. For reactions that proceed to completion, rather than equilibrium, the descending branch of the curve would be missing and the curve would continue to rise until it intersects the right side of the graph at the value for ξ_{max}.

It also reminds us that, though a consideration of the thermodynamic aspects of a chemical reaction is necessary whenever we attempt to predict whether it will or will not be spontaneous, it is not sufficient. A reaction may well be thermodynamically allowed, but if it is also kinetically metastable or inert, it will not be observed.

Indeed, kinetically metastable reactions are ubiquitous. We need only remind ourselves of how many everyday materials are kinetically metastable with respect to oxidation, from the paper we write on, to the wood we build our homes with, to our own bodies. Indeed, the widespread practice of referring to thermodynamically allowed reactions as "spontaneous" may, with justification, be characterized as a "verbal weed in the garden of thermodynamics." Though, as several authors have pointed out, the word spontaneous does not imply instantaneous, it does imply self-acting or self-initiating, which kinetically inert reactions are not,

		$(dS/d\xi)_{U,m}$		
		> 0	**0**	**< 0**
v'	**> 0**	forward reaction both kinetically and thermodynamically allowed	ideally reversible	forward reaction kinetically allowed but thermodynamically disallowed
	0	forward reaction thermodynamically allowed but kinetically inert	equilibrium	reverse reaction thermodynamically allowed but kinetically inert
	< 0	reverse reaction kinetically allowed but thermodynamically disallowed	ideally reversible	reverse reaction both kinetically and thermodynamically allowed

Table 1. Behavior corresponding to the various realizable combinations of v' and $(dS/d\xi)_{U,m}$ corresponding to the fundamental inequality in relation 9.

since they require either an external source of activation energy or the addition of a catalyst before proceeding. In short, true spontaneous behavior, as relation 9 reminds us, is a function of both kinetic and thermodynamic factors:

spontaneity = f(kinetic factors, thermodynamic factors)

Table 1 summarizes the various physical situations that are compatible with relation 9 and thus with the second law of thermodynamics, as summarized in relation 6. Though most of these are self-evident, the two boxes in the center column labelled "ideally reversible" require further explanation. Unlike the case of true equilibrium, for which both the net velocity and the change in entropy are zero, these two cases correspond to a finite velocity in either the forward or reverse direction without any accompanying entropy generation. While I am unaware of any chemical processes corresponding to these cases, they do correspond to the situation assumed by classical mechanics in which objects move reversibly in an imaginary friction-free environment.

A Few Chemical Transformations

The average chemistry student is, of course, accustomed to discussing the thermodynamics of chemical reactions in terms of the Gibbs free-energy function (G) rather than the total entropy (S). These two functions are interrelated by the equation:

$$(dG)_{T,P} = -T(dS)_{U,m} \qquad [10]$$

Likewise, most students are accustomed to measuring the rates of homogeneous chemical reactions using the reaction velocity per unit volume or reaction density (v) rather than the absolute velocity (v'), where once again the functions in question are related by the equation:

$$v = v'/V = (d\xi/Vdt) \qquad [11]$$

Thus multiplication of the fundamental inequality in equation 9 by $-T/V$ converts it into an equivalent inequality involving v and $(dG/d\xi)$ rather than v' and $(dS/d\xi)$:

$$(d\xi/Vdt)(-TdS/d\xi)_{E,m} = v(dG/d\xi)_{T,P} \leq 0 \qquad [12]$$

where the reversal of the inequality is due to the negative sign that appears on the right side of equation 10.

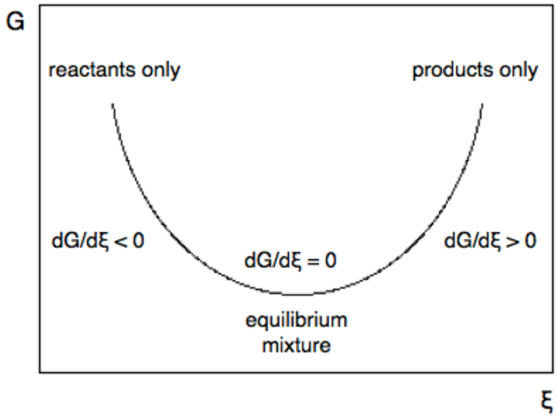

Figure 3. The G-ξ equivalent of figure 2.

		$(dG/d\xi)_{T,P}$		
		< 0	0	> 0
v	> 0	forward reaction both kinetically and thermodynamically allowed	ideally reversible	forward reaction kinetically allowed but thermodynamically disallowed
	0	forward reaction thermodynamically allowed but kinetically inert	equilibrium	reverse reaction thermodynamically allowed but kinetically inert
	< 0	reverse reaction kinetically allowed but thermodynamically disallowed	ideally reversible	reverse reaction both kinetically and thermodynamically allowed

Table 2. The v and $(dG/d\xi)_{T,P}$ equivalent of Table 1.

Thus, while the total entropy is maximized at equilibrium, the free energy is minimized. In keeping with this, one can also construct both a G-ξ plot (figure 3) and a G-v matrix (Table 2), equivalent, save with respect to the sign inversions, to those given for the total entropy in figure 2 and Table 1.

One More Mathematical Weed

A further connection with the thermodynamics of freshman chemistry may be established by making use of the fact that $(dG)_{T,P}$ for a chemical reaction is the sum of the chemical potentials (μ_s) of each species in the reaction weighted by the corresponding change in the number of moles (dn_s) for the species in question:

$$(dG)_{T,P} = \Sigma\mu_s dn_s = \Sigma(\mu_s{}^\circ + RTlna_s)dn_s \qquad [13]$$

Solving de Donder's definition of the extent of reaction parameter (where ν_s is the stoichiometric coefficient of the species in question in the balanced chemical equation and is inherently negative for reactants and inherently positive for products):

$$d\xi = dn_s/\nu_s \qquad [14]$$

for dn_s and substituting into equation 13, gives:

$$(dG)_{TP} = \Sigma(\mu_s{}^\circ + RTlna_s)\nu_s d\xi \qquad [15]$$

which, upon division by $d\xi$, gives the final result for the value of $(dG/d\xi)_{T,P}$:

$$(dG/d\xi)_{T,P} = \Sigma\nu_s\mu_s{}^\circ + \Sigma\nu_s RTlna_s \qquad [16]$$

The standard-state chemical potential of each species ($\mu_s{}^\circ$) is equal to its standard-state free-energy of formation per mole ($\Delta G_f{}^\circ$):

$$\mu_s{}^\circ = \Delta G_f{}^\circ \qquad [17]$$

and the sum of these, in turn, each weighted by the proper stoichiometric coefficient in the balanced reaction equation, is equal to the net standard-state free-energy change per mole of reaction ($\Delta G_{rx}{}^\circ$):

$$\Sigma\nu_s\Delta G_f{}^\circ = \Delta G_{rx}{}^\circ \qquad [18]$$

Likewise, the sum of the stoichiometrically weighted logarithms of the activity terms is equal to the well-known reaction quotient (Q):

$$\Sigma\nu_s RTlna_s = RTlnQ \qquad [19]$$

Further substitution of equations 18 and 19 into equation 16, then gives us:

$$(dG/d\xi)_{T,P} = \Delta G_{rx}{}^\circ + RTlnQ \qquad [20]$$

a result usually expressed in freshman textbook as:

$$\Delta G_{rx} = \Delta G_{rx}{}^\circ + RTlnQ \qquad [21]$$

Hence we discover that, while $\Delta G_{rx}{}^\circ$ is a true delta or finite difference (recall the sign conventions for the stoichiometric coefficients), ΔG_{rx} is actually a derivative and we have yet another example of Bent's mathematical weed. Though numerous authors have previously called attention to this problem, most freshman textbooks have continued to ignore it (13-15).

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3. It might be thought that the well-known relativistic relation $\Delta U = c^2\Delta m$ would complicate the requirement that both U and m be kept separately constant. This would be true for a closed system, where the loss or gain of large amounts of energy by the system would result in a corresponding loss or gain of mass. However, since for an isolated system $\Delta U = 0$ by definition, it automatically follows from the relativistic relation and that Δm must also be equal to zero and that U and m are each separately conserved.

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Publication History

Unsubmitted manuscript

XXXIII

Ask the Historian

The Chemistry of the Gold Penny Trick

Question

What is the chemistry behind the gold penny trick?

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Answer

The common instructions for this trick may be broken into three steps (1):

1. Preparation of a sodium zincate solution
2. Use of this solution to plate zinc onto a copper penny
3. Formation of a golden brass on the penny's surface.

and it is convenient to discuss the chemistry of each of these steps separately.

Preparation of the Sodium Zincate Solution

Step 1 involves placing zinc metal, whether granulated, mossy, or sheet, in a 3M $Na(OH)(aq)$ solution and heating it to boiling. In most accounts it is assumed that this leads to the formation of an aqueous solution of the dioxozincate or ZnO_2^{2-} anion, commonly referred to simply as just the "zincate" anion. Though some evidence for the presence of this anion as a discrete species in solution has been reported (2), zinc's well-known preference for a coordination number of four rather than two, makes it far more probable that the predominant zinc species in this solution is actually the tetrahydroxozincate anion or $Zn(OH)_4^{2-}$ (3).

Assuming this to be the case, the net reaction for the dissolution process would be:

$$Zn(s) + 2OH^-(aq) + 2H_2O(aq) \rightarrow Zn(OH)_4^{2-}(aq) + H_2(g) \quad [1]$$

in which Zn(0) is oxidized to Zn(II):

$$Zn(s) + 4OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2e^- \quad [2]$$

and half of the hydrogen in the water molecule is reduced from H(I) to H(0):

$$2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g) \quad [3]$$

Since reaction 1 is thermodynamically quite favorable ($\Delta G° = -88.46$ kJ/mol rx) (4), the reason for boiling the solution must be primarily to kinetically facilitate the reaction, though disruption of any passivation of the Zn surface by occluded $H_2(g)$ bubbles may also play a role.

If the solution formed by reaction 1 is slowly evaporated, it is possible to isolate the salt disodium tetrahydroxozincate or $Na_2[Zn(OH)_4](s)$ and, when this is strongly heated, it dehydrates to form disodium dioxozincate or $Na_2[ZnO_2](s)$:

$$Na_2[Zn(OH)_4] + \text{heat} \rightarrow Na_2[ZnO_2](s) + 2H_2O(g) \quad [4]$$

in which, however, the formula ZnO_2^{2-} does not represent a discrete anion in which Zn displays 2/1 coordination but is rather the relative or stoichiometric formula of an infinitely extended chain anion in which Zn exhibits 4/2 coordination (5).

The above chemistry is much too complex for grade school students and this is probably equally true for the average high-school student as well. Luckily this problem can be avoided through the discovery by several internet sites that the tetrahydroxozincate solution can be replaced by a simple solution of either zinc sulfate or zinc dichloride made by dissolving the salt in question directly in water (6). We have confirmed this in our laboratories at Cincinnati and use of this simple $Zn^{2+}(aq)$ solution greatly simplifies our discussion of the next – and least understood step – the plating of the zinc onto a copper penny.

Plating of the Zinc onto a Copper Penny

Step 2 is done by placing a freshly cleaned copper penny in either the boiling tetrahydroxozincate solution described above or in our alternative zinc sulfate solution (also heated to boiling). In both systems unreacted zinc metal must also be present at the bottom of the beakers containing the solutions and in both systems the copper penny must make physical contact with the zinc metal. After a certain amount of time (about 1 minute for the tetrahydroxoxzincate solution and about 10 minutes for the zinc sulfate solution) both pennies are observed to acquire a silver colored coating of zinc metal, at which point they are removed from the beakers, dipped in distilled water to cool and wash them, and allowed to dry.

As already noted, the question of how the zinc metal comes to be plated on the penny is the least understood aspect of this trick, though there is little doubt that the process involved is electrochemical in nature. Thus the definitive reference book for chemical demonstrations by Shakhashiri freely admits that "the exact nature of the electrochemical process is not known" (1). However, this source also calls attention to the electrochemical cell shown in figure 1. When the zinc and copper electrodes in this cell are connected by means of a wire, zinc is deposited on the copper electrode. This is obviously a concentration cell driven by the difference in the concentration of the $Zn(OH)_4^{2-}$ anion on the left versus the right side of the glass frit. However, the further suggestion that "perhaps a similar driving force produces the zinc coating in this demonstration" is unlikely since the agitation produced by boiling the solution would quickly eliminate any significant concentration gradients.

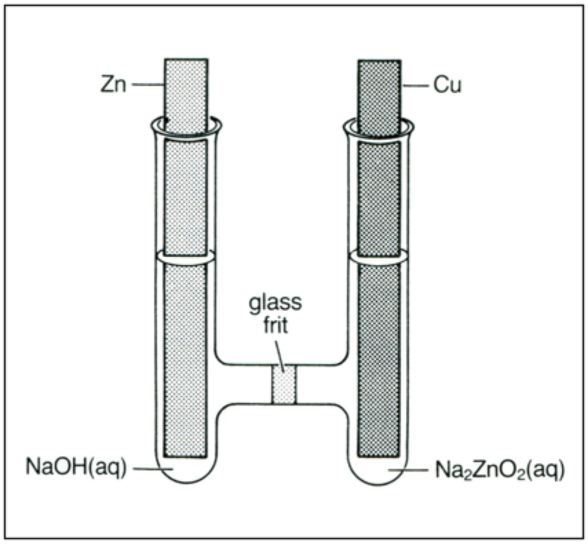

Figure 1. A concentration cell for plating Zn on Cu.

Rather the driving force appears to be the Volta or contact potential ($\mathcal{V}$) produced when the zinc and copper metals come into physical contact (7-9). This is due to an equalization of the Fermi levels in the two metals (figure 2) and is ideally proportional to the difference in their respective work functions ($\Delta\phi$), which measure the energy required to eject an electron from their surfaces, though a consideration of the relative electronegativity values (ΔEN) of the two metals is probably qualitatively sufficient for a typical chemistry course. Though Volta established the qualitative concept of contact potentials in the 18th century (9), it was not until the last quarter of the 19th century that actual quantitative measurements were made which gave a value of 0.738V for the Cu/Zn couple (10).

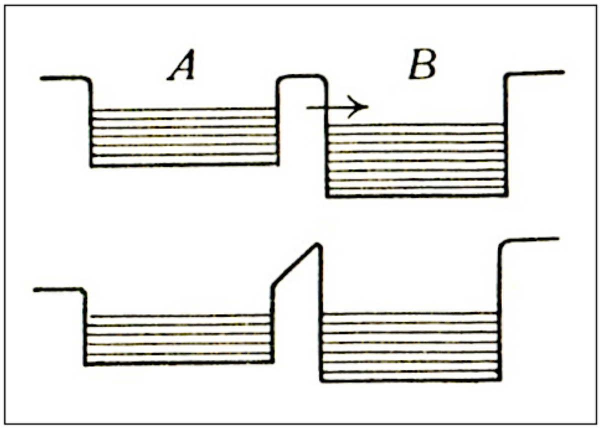

Figure 2. The Fermi levels of two metals (A and B) before (top) and after (bottom) contact. Here A has a small work function and corresponds to Zn whereas B has a large work function and corresponds to Cu. The arrow indicates the direction of net electron flow required for equalization.

This equalization of the Fermi levels is due to a net electron flow from Zn to Cu, leading, in turn, to the development of a positive charge at the Zn surface and a negative charge at the Cu surface. In other words, the Zn becomes anodic and the Cu cathodic (figure 3). In a dry metal couple both the net electron flow and the

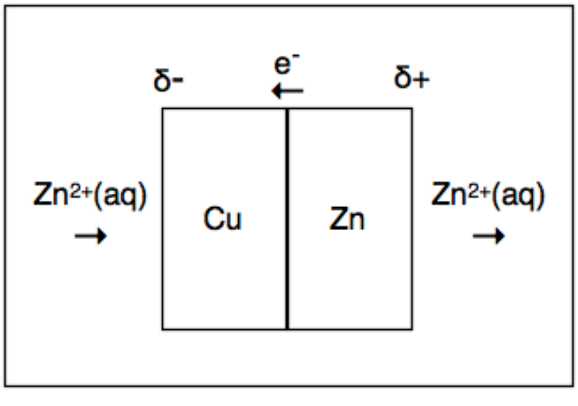

Figure 3. The Cu/Zn couple showing the directions of electron and cation flow and the surface charges due to the contact potential.

charging stop once the Fermi levels are equalized. However, if this couple is immersed in our Zn^{2+}(aq) solution, reduction of Zn^{2+}(aq) at the Cu surface will consume electrons, thereby upsetting this balance, and a net electron flow from Zn to Cu will once more be initiated. The concomitant loss of electrons by the Zn leads, in turn, to its oxidation and the generation of additional Zn^{2+}(aq) at the Zn surface. Thus the net flow of negative electrons from Zn to Cu is counterbalanced by a net flow of positive Zn^{2+}(aq) cations from the Zn anode to the Cu cathode. Though, chemically speaking, the oxidation Zn and the reduction of Zn^{2+}(aq) are the opposite of one another, the net free energy change is not zero since the oxidation and reduction processes are occurring at two different locations and potentials.

Once the Cu surface is completely covered with Zn, the system once more returns to equilibrium and net transfer of both electrons and Zn^{2+}(aq) ceases. This is because both exterior metal surfaces are now composed of Zn and are thus at the same, rather than different, potentials (figure 4). Contact potentials do not depend on the size, shape, or area of contact between the two metals. Hence, as long as some free copper surface remains, the contact potential persists. The fact that the potential disappears once the plating is complete reflects the rule originally established by Volta that the contact potential between two metals is independent of any metal inserted between them. Thus the potential between the original piece of zinc metal and the plated zinc surface, though mediated by Cu, is the same as if the two pieces of Zn were in direct contact.

Formation of Brass on the Penny's Surface

This step is the least complicated of the three and involves heating (whether on a hot plate or in a burner flame) the zinc coated penny produced in step 2. This allows the Zn atoms in the coating to diffuse into the copper of the penny and results in a copper-rich brass alloy having a golden-yellow color – whence the so-called gold penny.

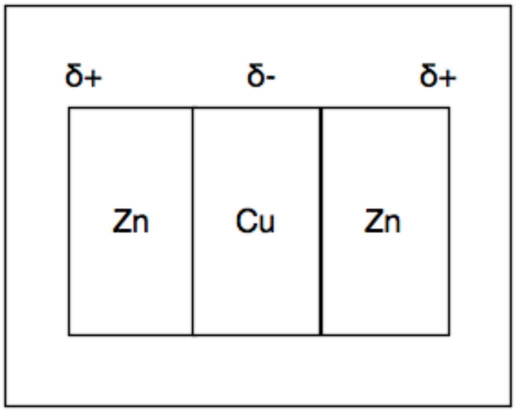

Figure 4. The final equilibrium state of the Cu/Zn couple in which both net electron and net cation flow have ceased due to equalization of the exterior surface potentials.

Assessment and Further Variations

Though many college-level textbooks, in their brief discussion of metallic corrosion, take note of the enhanced oxidation of certain metals when placed in contact with more noble metals, none, to the best of my knowledge, makes mention of Volta or contact potentials (11). This means that the theoretical rationale of the plating step given above involves use of concepts not normally considered to be part of the introductory college chemistry curriculum. When coupled with the complex chemistry of the tetrahydroxozincate solution in step 1, these problems largely account for why the gold penny is always presented as a chemical "trick" rather than as a legitimate demonstration of established chemical principles – a status that it is likely to retain in the future as well.

In closing, it should be noted that a further variation of this experiment may be found in reference 1 which shows that a similar three-step procedure, using tin rather than zinc, will ultimately produce a bronze rather than a brass penny (1).

Acknowledgements

The author would like to thank the departmental demonstrator, Rudy Thomas, for performing the necessary experiments.

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4. A. J. Bard, R. Parsons, J. Jordan, Eds., *Standard Potentials in Aqueous Solution*, IUPAC and Dekker: New York, NY, 1985.
5. A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon Press: Oxford, 1984, p. 1152. Wells actually reports the structure of the potassium salt, though there is no reason for not assuming that the same anionic substructure

exists in the sodium salt.

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9. S. Ross, "The Story of the Volta Potential," in G. Dubpernell, J. H. Westbrook, Eds., *Selected Topics in the History of Electrochemistry*, Electrochemical Society: Princeton, NJ, 1978, pp. 257-278.

10. S. P. Thompson, *Elementary Lessons in Electricity and Magnetism*, Macmillan: London, 1891, p. 69.

11. See, for example, M. S. Silverberg, *Principles of General Chemistry*, 2nd ed., McGraw-Hill: New York, NY, 2010, pp. 737-738.

Publication History

Unsubmitted manuscript

XXXIV

An Electrochemical Ambiguity

Recently, in revising a paper on the Gibbs-Helmholtz equation, an ambiguity in electrochemical notation came to my attention with respect to the z term appearing in such well-known electrochemical relationships as the equivalence between the Gibbs free energy of reaction ($\Delta_r G$) and the electrochemical cell potential (E_{cell}):

$$\Delta_r G = -zFE_{cell} \qquad [1]$$

the Nernst equation:

$$E_{cell} = E^{\circ}_{cell} - (RT/zF)lnQ \qquad [2]$$

and Faraday's law of electrolysis (2):

$$idt = zFdn_s \qquad [3]$$

I was originally been taught to use z in all three of the above equations to represent the number of electrons transferred in the corresponding balanced half-cell reactions. However, the IUPAC "Green Book" on *Quantities, Units and Symbols Used in Physical Chemistry* is inconsistent with respect to its use of this symbol, and sometimes uses n rather than z for this purpose (3). Likewise, consultation of a representative sample of textbooks for both general and physical chemistry revealed a similar division between those authors using z and those preferring n (4).

The Definition of *z*

Each of these choices has a certain logical justification. The symbol *z,* from the German word *zahl* for number, was originally used to denote the "charge number" of an ion, i.e. a unitless number indicating the number of ionic charges, but not their sign (5-6). In the case of either the oxidation of a neutral atom to a positive ion A^{z+} or its reduction to a negative ion B^{z-}:

$$A \rightarrow A^{z+} + ze^- \qquad [4]$$

$$ze^- + B \rightarrow B^{z-} \qquad [5]$$

there is indeed a simple correlation between the magnitude of the ionic charges and the number of electrons transferred. However, in the case of redox reactions in which both the reactants and products have net ionic charges – for example, Fe^{2+} and Fe^{3+} – this simple correlation is no longer straightforward. To avoid this problem, IUPAC has invented a second definition of z, which it rather awkwardly calls "the electron number of an electrochemical reaction" even though in generalized half-cell reactions, like the above, it may lead not only to z simultaneously appearing in two different contexts but also representing two different numerical values (7).

The Definition of *n*

The symbol n, on the other hand, is used by IUPAC to denote "the amount of substance" uniquely measured in units of moles and so can be defined, in the above context, as representing the moles of electrons transferred in the redox reaction. However, use of n alone for this purpose violates IUPAC's rule concerning labeling which requires that one always specify what entities are being measured in units of moles (8):

The definition [of n] applies to entities B which should always be indicated by a subscript or in parentheses, e.g. n_B *or* $n(B)$.

Thus one should use always the symbol n_e rather than n alone when referring to moles of electrons. Though this mole definition works perfectly well, when defined in this fashion, n is obviously not a unitless number like z and, in order to equate the two, IUPAC has instead invented a second definition of n, also called "the electron number of an electrochemical reaction" but now considered to be without units (7).

A More Fundamental Definition

Since the 1980s IUPAC has accorded official recognition to the extent of reaction parameter (ξ) first introduced by DeDonder in the 1920s and its accompanying symbolism (9). This parameter (in units, as we shall see, of moles of reaction events) is defined for a balanced chemical reaction as:

$$d\xi = dn_s/\nu_s \qquad [6]$$

where dn_s is the change in the moles of any species (s) in the balanced equation for the reaction and is defined as inherently negative for reactant species (which are being consumed and are thus decreasing) and as inherently positive for product species (which are being generated and are thus increasing). Likewise ν_s represents the corresponding stoichiometric coefficient for species s in the balanced equation and follows the same sign conventions as dn_s.

Applying this notation to a balanced half-cell reaction leads to the symbol ν_e for the stoichiometric coefficient for the number of electrons transferred and to IUPAC's further recognition that this can function as a more fundamental definition for both z and n as redefined above (7):

$$z = n = |\nu_e| \qquad [7]$$

where $|\nu_e|$ is the absolute value of the electron's stoichiometric coefficient in a balanced half-cell reaction. This, of course, implies that ν_e is also a unitless number.

Since DeDonder's extent of reaction concept and accompanying notation have many fundamental applications to such areas as stoichiometry, thermodynamics and kinetics, an increasing number of authors are now favoring its use, rather than either z or n, in their electrochemical equations (10-13). Thus Atkins, in his well known textbooks, now writes equations 1 and 2 as (10):

$$\Delta_r G = -\nu_e F E_{cell} \qquad [8]$$

$$E_{cell} = E^{\circ}_{cell} - (RT/\nu_e F) \ln Q \qquad [9]$$

and Castellan (11), in his physical chemistry text, writes Faraday's law in a form equivalent to:

$$idt = \nu_e F d\xi \qquad [10]$$

which may be converted into equation 3 using the definition of $d\xi$ in equation 6.

$$idt = (\nu_e/\nu_s) F dn_s \qquad [11]$$

This reveals that z in equation 3 is really not the same as that in equations 1 and 2 but is rather the ratio of ν_e to ν_s instead of ν_e alone (2):

A Source of Confusion

Unfortunately there are some fundamental problems with these results – aside from the rather obvious fact that the redefinitions of both z and n are after-the fact, *ad hoc* attempts to make the two symbolisms agree. These problems are ultimately traceable to the failure of IUPAC to explicitly recognize that the mole is a counting unit, like individuals, dozens or reams, and as such can be used not only to measure the amounts of various substances in terms of their constituent particle populations, but also anything else that can be counted, such as the number of elementary reaction events (14). This in turn brings us back to IUPAC's rule that when something measured (i.e., counted) in units of moles, this something must be explicitly indicated. You cannot measure moles of nothing. This rule, as it applies to the resulting symbolism for amount of substance, has already been quoted and is repeated in a more extended form later in the "Green Book" (8):

> *When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles or specific groups of such particles.*

though, in light of what has just been said, this should now be amended to read:

> *When the mole is used, the elementary entities being counted must be specified and may be atoms, molecules, ions, electrons, other particles, specific groups of such particles, or elementary reaction events.*

The relevance of this modification has to do with the definition of De Donder's extent of reaction parameter given in equation 6. Though IUPAC recognizes that this quantity should be measured in units of moles, it never tells us what it is that is being counted, even though one of the editors of "Green Book" suggested many years ago that the answer was "moles of reaction events" or "moles of reaction" (abbreviated as $\mathrm{mol_{rx}}$) for short (15). Once this is accepted, then the further supposition in equation 7 that ν_e (and by implication all stoichiometric coefficients) have no units is also called into question, since equation 6 will not pass a unit cancellation test unless ν_s is assigned the units of $\mathrm{mol_s/mol_{rx}}$:

$$(\mathrm{mol_{rx}}) = (\mathrm{mol_s})/(\mathrm{mol_s/mol_{rx}})$$

since it is rule in unit cancellation that moles of A do not cancel moles of B even though their ratio is dimensionless (16).

A Check on Units

These conclusions may be further verified by subjecting equations 8, 9 and 11 to the test of unit cancellation. If we apply the assumption in equation 7 that ν_e has no units, we obtain in the case of equation 8:

$$(\mathrm{J/mol_{rx}}) = (\mathrm{C/mol_e})(\mathrm{J/C}) = (\mathrm{J/mol_e})$$

where J is joules, mol_{rx} is moles of reaction events, mol_e is moles of electrons transferred, and C is coulombs of electrical charge. In the case of equation 9 we obtain:

$$V = (J/C) = (J/C) + (J/[mol_{rx}\ K])(K)/(C/mol_e)$$

or $$(J/C) = (J/C) + (J/C)(mol_e/mol_{rx})$$

where K is degrees Kelvin and V is volts. Finally, for equation 11 we obtain:

$$(C/sec)(sec) = (C_s/mol_e))(mol_s)$$

or $$C = C(mol_s/mol_e)$$

where sec is the time in seconds and mol_s is moles of species *s*. In short, all three equations fail the unit cancellation test.

On the other hand, if we apply the conclusion that v_s actually has the units of mol_s/mol_{rx}, we obtain for equation 8:

$$(J/mol_{rx}) = (mol_e/mol_{rx})(C/mol_e)(J/C)$$

or $$(J/mol_{rx}) = (J/mol_{rx})$$

For equation 9:

$$(J/C) = (J/C) + [J/(mol_{rx}\ K)](K)/[(mol_e/mol_{rx})(C/mol_e)]$$

or $$(J/C) = (J/C) = V$$

and for equation 11:

$$(C/sec)(sec) = [(mol_e/mol_{rx})/(mol_s/mol_{rx})](C/mol_e)(mol_s)$$

or $$C = C$$

In short, all three equations now pass the unit cancellation test.

Conclusions

In summary, ν_e is a more fundamental and unambiguous choice of symbol than either *z* or *n* for use in basic electrochemical equations, but leads to equations that pass the unit cancellation test only when it is assigned the units of mol_e/mol_{rx}.

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2. W. B. Jensen. "Faraday's Laws or Faraday's Law?," *J. Chem. Educ*., **2012**, *89*, 1208-1209.

3. E. R. Cohen et al, Eds., *Quantities, Units and Symbols in Physical Chemistry,* 3rd ed., IUPAC and RCS: Cambridge, 2007, pp. 71-72, 74.

4. Thus a survey of physical chemistry texts on the shelves in my office gave a 50/50 division (7 to 7) for those texts favoring *z* versus those favoring *n*. In contrast, a similar survey of general chemistry texts overwhelmingly came down in favor of *n* (23 to 1).

5. Reference 3, pp. 49, 70.

6. W. B. Jensen, "The Proper Writing of Ionic Charges," *J. Chem. Educ,*, **2012**, *89*, 1084-1085.

7. Reference 3, p. 71.

8. *Ibid*., pp. 47, 88.

9. *Ibid*., pp. 48, 53.

10. P. W. Atkins, *Physical Chemistry*, 4th ed., Freeman: New York, NY, pp. 260-261. Note, however, that, like those authors who violate IUPAC's rule about always indicating the entities measured in moles by using *n* instead of n_e, Atkins fails to identify the nature of the stoichiometric coefficient by using ν instead of ν_e.

11. G. W. Castellan, *Physical Chemistry*, 3rd ed., Addison-Wesley: Reading, MA, 1983, pp. 874-875.

12. G. M. Barrow, *Physical Chemistry*, 6th ed., McGraw-Hill: New York, NY, 1996, pp. 397-398.

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14. IUPAC already uses *N* (reference 3, pp. 45, 47) to signify the number of particles (N_s) or reaction events (N_{rx}) but fails to recognize that such populations can be counted in units of moles as well as individuals. Just as temperature (*T*) and pressure (*P*) can be measured, sans a change in symbol, using a variety of units, so can *N* (i.e., as individuals, dozens, reams, moles, etc.). Once this is accepted, it is unclear why both N_s or N_{rx} require special symbols (*n* and ξ) only when measured in units of moles. For more on this subject, see W. B. Jensen, "Reformatting the Ideal Gas Law," Paper No. 29, this volume

15. T. Cvitas, N. Kallay, "A Mole of Chemical Transformations," *Educ. Chem*., **1980**, *17*, 166-168.

16. The term "dimensional analysis" denotes a consistency test based upon reducing each term in an equation to a a set of agreed-upon fundamental quantities, such as mass, length, time, etc., without reference to the units used to measure them, whereas unit cancellation makes the units explicit. Though equations which pass the unit cancellation test are automatically dimensionally homogeneous, the reverse is not necessarily true. See H. E. Huntley, *Dimensional Analysis*, Dover: New York, NY, 1967.

Publication History

Unsubmitted

XXXV

Six Chemists on Energy, Population, and the Environment

I first became interested in the questions of available energy supply, population growth, and environmental pollution in the 1970s while still a graduate student at the University of Wisconsin. These three topics (figure 1) are, of course, intimately interconnected via what I call "the master equation," which postulates that the average potential economic well-being (*EWB*) of an individual in a given society is measured by the available energy flow or power (*P*) available to that society, minus the energy costs of pollution (*P'*) abatement, divided by the population (*P"*) of the society among whom the available energy must be divided (1):

$$\text{Economic Well Being} = \frac{(\text{available power} - \text{pollution costs})}{\text{population}}$$

or more symbolically:

$$EWB = (P - P'')/P'$$

To use a simplified industrial metaphor, these three topics roughly correspond to the concepts of production (available energy generation), demand (population), and the tax on doing business (pollution abatement).

The 1960s and 1970s also saw the publication of a large number of books dealing with these three questions. These included not only advanced monographs and popular accounts for the general public, but also college-level textbooks in such fields as engineering (2), ecology (3), physics (4) and even chemistry (5), which attempted to cash in on the public's sudden interest in these questions. Unhappily, the latter textbooks (figure 2), in particular, often – though one hopes unintentionally – left students with the impression that chemists and chemistry were the villains responsible for most of our collective woes, a view which persists to this day, especially among more extreme ecological fanatics.

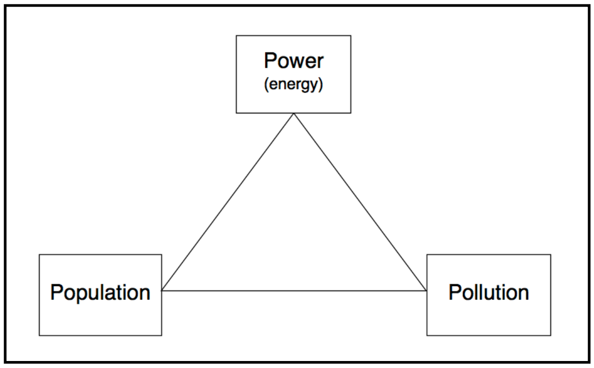
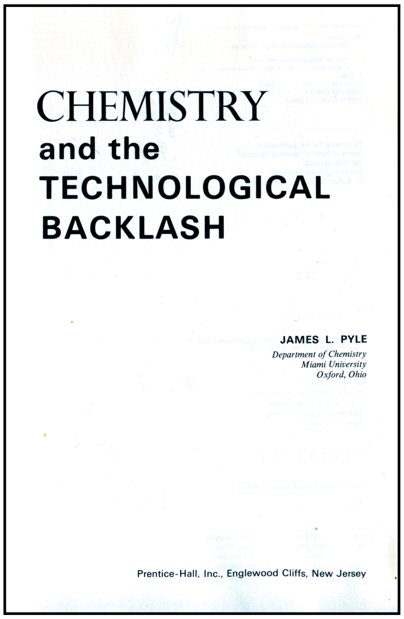


Figure 1. The triad of available energy production or power generation, population growth, and environmental pollution.



CHEMISTRY
and the
TECHNOLOGICAL
BACKLASH

JAMES L. PYLE
Department of Chemistry
Miami University
Oxford, Ohio

Prentice-Hall, Inc., Englewood Cliffs, New Jersey

Figure 2. Title page of a typical chemistry textbook from the 1970s that attempted to cash in on the sudden surge of interest in the questions of energy production, overpopulation, and environmental pollution.

This is, of course, a vast oversimplification of a complex situation, and over the years I gradually discovered that chemists, far from being the universal purveyors of ecological evil they had been made out to be, had in fact made some significant contributions to our understanding of these questions. In what follows I will briefly outline some of these contributions using the examples of six chemists from the past, three of whom were winners of the Nobel Prize in Chemistry, and two of whom would eventually leave the field of

Figure 3. William Stanley Jevons
(1835-1882)

chemistry in order to pursue other interests. All six illustrate that knowledgeable chemists have always been aware of the challenges of dwindling energy resources, the dangers of overpopulation, and the ongoing tragedy of environmental degradation.

No. 1. William Stanley Jevons on the Coal Question

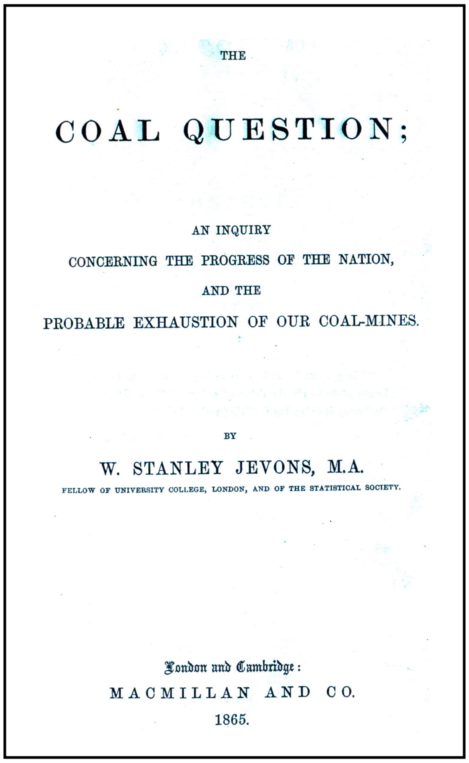
William Stanley Jevons (figure 3) was born on 01 September 1835 in Liverpool, England, the ninth of eleven children of Thomas Jevons, an iron merchant, and Mary Anne Roscoe (6). He obtained his chemical training at University College London under Thomas Graham. During this period he also roomed with his older cousin, Henry Enfield Roscoe, who would go on to become an eminent British chemist, Principal of Owens College in Manchester, and later Vice-Chancellor of the University of London.

Toward the end of Jevons' second year at University College, Graham received a request from the newly established Mint in Sydney, Australia, asking him to recommend a chemist for the post of assayer. Graham first recommended Henry Roscoe, but Roscoe was planning to leave for Germany to complete his doctoral degree under Robert Bunsen, and so he, with the further urging of Jevons' father, convinced his younger cousin to take the job instead.

Jevons arrived in Sydney in 1855 at age 20. However, not only did his work as an assayer prove to be repetitious and boring, it also left him with a great deal of spare time, which he filled by reading books on philosophy and economics. Having finally decided that a career as a chemist was not for him, Jevons resigned his position in 1859 and returned to England, where he pursued his new interests by completing B.A. and M.A. degrees at University College, followed by his appointment in 1866 as Professor of Logic and Political Economy at Owens College in Manchester, where his cousin Henry was then serving as Professor of Chemistry. This was followed by his appointment as Professor of Political Economy at University College London in 1876, from which he resigned in 1881, and his untimely death on 13 August 1882 at age 46 as the result of a swimming accident.

Jevons was a prolific writer and, despite an active career of only two decades, would author at least 15 books on the subjects of logic and economics, including a well known volume on the philosophy of science (7). At present he is widely considered to be the founding father of the subject of mathematical economics (6). Of greatest interest to us, however, is his fourth book (figure 4), first published in 1865 under the title of *The Coal Question,* and whose focus was well described by its subtitle, *An Inquiry Concerning the Progress of the Nation, and the Probable Exhaustion of our Coal Mines* (8).

As indicated in his Introduction, Jevons was fully aware that it was energy, of which coal was the major source, that was the true driving force of modern civilization (8):



THE

COAL QUESTION;

AN INQUIRY
CONCERNING THE PROGRESS OF THE NATION,
AND THE
PROBABLE EXHAUSTION OF OUR COAL-MINES.

BY
W. STANLEY JEVONS, M.A.
FELLOW OF UNIVERSITY COLLEGE, LONDON, AND OF THE STATISTICAL SOCIETY.

London and Cambridge:
MACMILLAN AND CO.
1865.

Figure 4. Title page of the first edition (1865) of Jevons' book on the coal question.

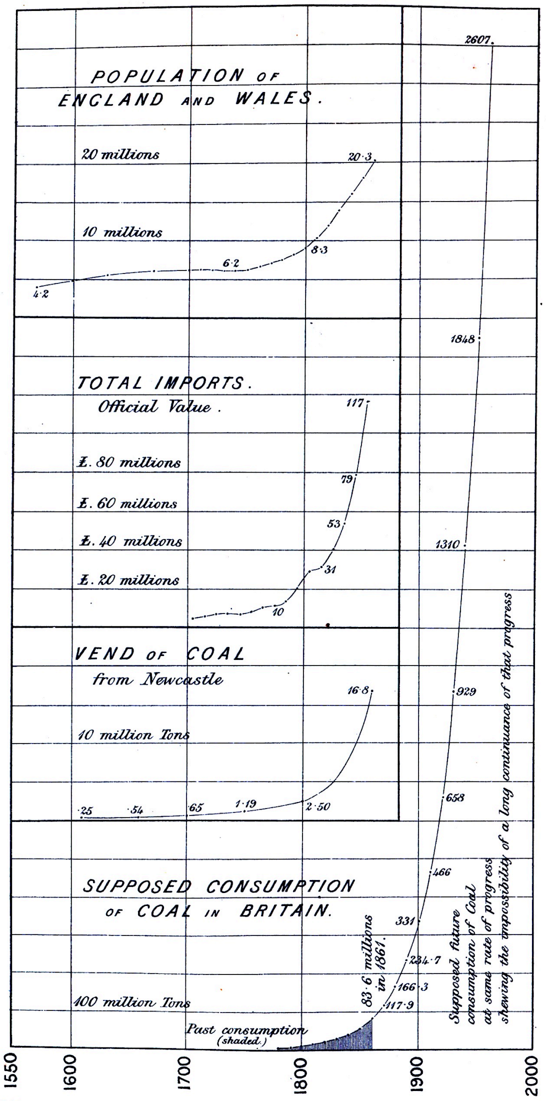


Figure 5. Frontispiece to Jevons' book showing graphs of population growth, imports, the sale of coal, and projected coal consumption extrapolated to 1970.

Coal in truth stands not beside, but entirely above, all other commodities. It is the material source of the energy of the country — the universal aid — the factor in everything we do. With coal almost any feat is possible or easy; without it we are thrown back into the laborious poverty of earlier times.

Here we need to remind ourselves that, when Jevons was writing, coal was the only major fossil fuel in use, since the widespread use of oil and natural gas still lay in the future. And, of course, the same is equally true of other major energy sources such as hydroelectric and nuclear energy. Thus to write about an impending future coal crisis in 1865 was equivalent to writing about an impending future energy crisis and, to the best of my knowledge, Jevons' book was the first to deal with this question. In pursuit of this goal he would discuss, using numerical data whenever possible, the geology of coal, its geographical distribution, its mining, its most important industrial uses, possible energy alternatives, and its consequences for technological innovation, population growth, and Great Britain's balance of trade.

By 1865 geologists were estimating that Great Britain had roughly 90 billion tons of coal reserves. Given that Jevons' data showed that coal consumption was accelerating at an annual rate of 3.5% and that the cost of mining coal must necessarily increase as one was forced to mine deeper and deeper deposits, he estimated that this reserve would become insufficient in just under a century, at which point production would peak, followed by a decline and by dire economic and social consequences (8):

Suppose our progress to be checked within a half a century ... how shortened and darkened will the prospects of the country appear, with mines already deep, fuel dear, and yet a high rate of consumption to keep up if we are not to retrograde.

One of the unique features of Jevons' analysis was his recognition of the importance of population growth, the second major factor in our master equation. Once again his data showed that the increased availability of energy per capita supplied by coal consumption had stimulated a corresponding rapid growth in population, as more and more children were able to survive to the age of reproduction. However, he went on to warn that, when the coal begins to run out, the country would no longer be able to support such a population, at least in the manner to which it will have become accustom (8):

But long-continued [population growth] in such a manner is altogether impossible – it must outstrip all physical conditions and bounds; and the longer it continues, the more severely must the ultimate check be felt.

Jevons summarized many of these trends in a series of graphs that appeared as the frontispiece to his book (figure 5). All of them show a period of rapid exponential growth starting slowly in the 18th century and anticipate the "hockey stick" graph made famous by Al Gore in his 2006 movie on carbon dioxide and global warming.

One of the chapters of greatest interest to the modern reader deals with Jevons' treatment of possible energy alternatives. Here he discussed the possible use of wind, water, tidal, biomass, geothermal, solar, and electrical energy sources, and though he felt that some of these would be useful on a small scale, none, in his opinion, would be able to supply the quantities of energy currently produced from coal. Even more astounding was his discussion of the possibility of using electrolytically generated hydrogen as an alternative fuel, though in the end he felt that its low energy density as a gas made this impractical.

He also discussed the question of whether Britain could postpone its ultimate energy fate by banning the export of coal, by heavily taxing its use, and by increasing the efficiency of its steam engines. With respect to the latter tactic, however, Jevons' analysis showed that increased efficiency tended to stimulate increased demand and to further accelerate the rate of consumption, rather than the reverse – a result known as "Jevons' Paradox" (8):

It is wholly a confusion to suppose that the economical use of fuel is equivalent to a diminished consumption. The very contrary is true ... Whatever conduces to increase the efficiency of coal, and to diminish the cost of its use, tends to augment the value of the steam-engine, and to enlarge the field of its operations.

In the end Jevons did not have a very optimistic future prognosis for Great Britain, feeling that it had to choose between purposely slowing its rate of growth so as to enjoy a more prolonged, but less spectacular, period of prosperity, or allowing things to progress unrestrained, leading to a shorter, but more glorious, burst of progress (8):

We have to make the momentous choice between brief greatness and longer continued mediocrity.

No. 2. Svante Arrhenius on Global Warming

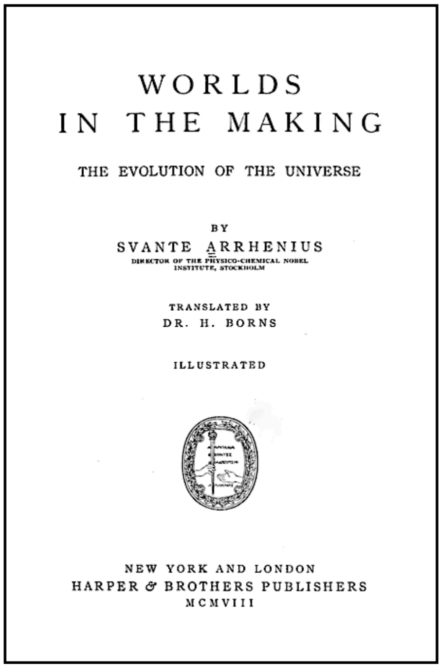
Svante Arrhenius (figure 6) was born on 19 February 1859 in Vik, Sweden, the second of two sons of Svante Gustaf Arrhenius, a land surveyor, and Carolina Thunberg (9). His chemical training was obtained at the University of Uppsala and at the Physical Institute of the Swedish Academy of Sciences in Stockholm. His best known contribution to chemistry – the theory of ionic dissociation – was the subject of his 1884 doctoral thesis. Considered controversial by his professors, the thesis was given only a third-level pass. However Arrhenius mailed copies to several renowned chemists and physicists, who took a far more favorable view of the work, which would eventually form the basis of his 1903 Nobel Prize in Chemistry.

Following his graduation, Arrhenius obtained a travel grant from the Swedish Academy of Sciences that allowed him to study abroad in the laboratories of Ostwald, Kohlrausch, Boltzmann and van't Hoff. In 1891 he was appointed as Lecturer in Physics at the *Stockholms Högskola*, followed by promotion to full professor in 1896. In 1905 he was appointed head of the newly founded Nobel Institute for Physical Chemistry, where he remained until his death on 02 October 1927 at age 68.

Figure 6. Svante Arrhenius
(1859-1927)

Arrhenius' principal biographer, Elisabeth Crawford, has noted that his scientific work falls into three distinct periods (9). The first period, from 1884-1890, dealt with physical chemistry and included not only his theory of ionic dissociation and his well-known ionic acid-base definitions, but his equally famous equation relating the temperature dependence of reaction rates to the concept of activation energy. The second period, from 1895-1900, dealt with cosmic physics, and the third and last period, from 1901-1907, with immunochemistry. It was during the second period, when he was serving as a Lecturer in Physics, that he first developed a correlation between the carbon dioxide content of the atmosphere and the surface temperature of the earth.

Inspired by the work of the Swedish geologist Arvid Högsbom, Arrhenius published a lengthy paper in 1896 attempting to show that past ice ages were due to decreases in the carbon dioxide content of the atmosphere. This culminated in a large table showing the relationship at various latitudes between the



WORLDS
IN THE MAKING

THE EVOLUTION OF THE UNIVERSE

BY
SVANTE ARRHENIUS
DIRECTOR OF THE PHYSICO-CHEMICAL NOBEL
INSTITUTE, STOCKHOLM

TRANSLATED BY
DR. H. BORNS

ILLUSTRATED

NEW YORK AND LONDON
HARPER & BROTHERS PUBLISHERS
MCMVIII

Figure 7. The 1908 English translation of Arrhenius' popular book on cosmic physics.

change in temperature and the change in carbon dioxide content (10). No mention was made of possible future changes in temperature due to the impact of carbon dioxide generation from the burning of coal for purposes of industrial manufacturing and domestic heating.

This latter subject, however, had been briefly mentioned by Arrhenius earlier that year in a popular lecture (11), and repeated once again in a popular book on cosmic physics that was translated into English in 1908 (figure 7). But, far from viewing the gradual future warming of the earth, due to the burning of fossil fuels, as a tragedy, and ignorant of its possible consequences for changes in sea level and the ecological survival of many plants and animals, Arrhenius actually thought that such warming might have positive benefits (12):

> *We often hear lamentations that the coal stored up in the earth is wasted by the present generation without any thought of the future, and we are terrified by the awful destruction of life and property which has followed the volcanic eruptions of our days. We may find a kind of consolation in the consideration that here, as in every other case, there is good mixed with the evil. By the influence of the increasing percentage of carbonic acid in the atmosphere, we may hope to enjoy ages with more equable and better climates, especially as regards the colder regions of the earth, ages when the earth will bring forth much more abundant crops than at present, for the benefit of rapidly propagating mankind.*

Thus Arrhenius himself did little to publicize the link between his theory and its possible future ecological consequences, and it would remain for others, more than a half century later, to begin the process of forging these connections, as detailed in the popular history of global warming by the American historian Gale Christianson (13).

As a final irony, it should be pointed out that Arrhenius's theory of the origin of the ice ages is no longer accepted and the current consensus attributes them instead to changes in the earth's orbit. Similarly, Arrhenius' own predictions about future warming were off by a factor of 10. In his popular lecture of 1896 he predicted that it would take roughly 3000 years for human activity to double the carbon dioxide content of the atmosphere, leading to a mean temperature increase of 6 C°. Current estimates are closer to 250 years.

No. 3. Leopold Pfaundler on Carrying Capacity

Leopold Pfaundler (figure 8) was born on 14 February 1839 in Innsbruck, Austria, the son of a local advocate and Professor of Law at the University of Innsbruck (14). After attending the local Volkschule and Gymnasium, Pfaundler entered the University of Innsbruck in

Figure 8. Leopold Pfaundler
(1839-1920)

1857, where he studied organic chemistry under Professor Heinrich Hlasiwetz, while also attending lectures in physics and mathematics. In 1859 his university studies were interrupted by military service in the Austro-Sardinian War, also known as the Second War of Italian Independence, followed in 1861 by a semester in Liebig's laboratory at the University of Munich and receipt of a doctorate from the University of Innsbruck.

Following three years as an assistant in Hlasiwetz's laboratory, Pfaundler, spent the years 1864-1865 in Paris studying physical chemistry, where he worked in the laboratories of Wurtz and Regnault, and also attended lectures by Deville and Berthelot. In 1866 he became a Privatdozent in physical chemistry at Innsbruck, though once again his academic career was interrupted by military service, this time in the Third War of Italian Independence of 1866. The following year he was appointed as Professor of Physics at Innsbruck. Here he remained until 1891, when he succeeded Ludwig Boltzmann as Professor of Physics at the University of Graz. In 1910 he became Professor Emeritus at Graz and was also ennobled by the Emperor, receiving the title of Pfaundler von Hadermur. He died in Graz on 16 May 1920 at age 81.

Pfaundler's fame as a chemist rests on a paper he published in 1867 in which he was the first to apply the newly emerging kinetic theory of gases to chemical equilibrium and reaction kinetics. In the course of this paper he also postulated the formation of a transient but critical collision complex between the various reactants which anticipated our modern concept of an activated complex.

Pfaunder had many interests besides chemistry. He had a significant reputation as a photographer of alpine scenery, was an early enthusiast of the Japanese game of *Go*, and an advocate of a simplified universal language called *Ido*. In 1902 he published a lengthy article in the *Deutsche Revue* entitled, in translation, "The World Economy in the Light of Physics," in which he made the first reasonable estimates of the carrying capacity of the earth (15).

Carrying capacity refers to the maximum population that a given geographical area can support and must take into account the nutritional energy requirements per human, and the total free energy flow available to the region in question, whether for agricultural or industrial purposes. Attempting to apply these criteria to the planet as a whole also requires estimating what percentage of the land area is suitable for food production, and the average agricultural output per capita with and without extraneous energy supplements, such as tractors, fertilizers, etc.

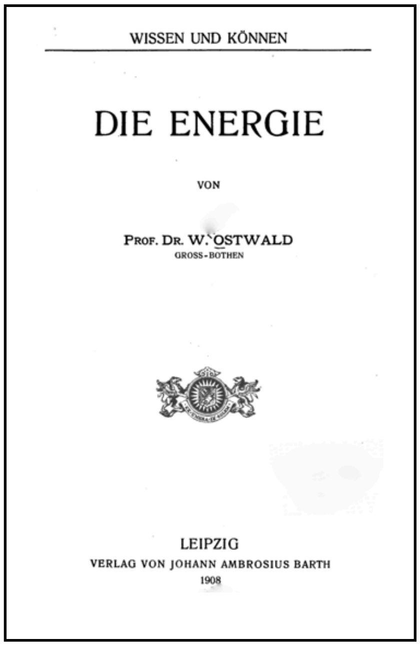
Pfaundler was not the first to estimate the earth's carrying capacity, but he was among the first to base his estimate on an energy analysis. He concluded that land suitable for food production could support an average of five people per hectare, thus establishing a lower limit of 11 billion people for the sustainable carrying capacity of the entire planet. Estimates made since Pfaundler have varied widely, some being lower and others higher than his estimate (16). As of 2016 the current world population stands at 7.5 billion.

Figure 9. Wilhelm Ostwald
(1853-1932)

No. 4. Wilhelm Ostwald on Energy and Culture

Friedrich Wilhelm Ostwald (figure 9) was born on 02 September 1853 in Riga, Latvia, the second of three sons of Gottfried Ostwald, a master-cooper, and Elisabeth Leuckel (17). Both parents were native Germans. His chemical training was obtained at the University of Dorpat (now Tartu) in Estonia, from which he received his doctorate degree in 1878 for work done under the supervision of Carl Schmidt.

Ostwald served as Professor of Chemistry at the Riga Polytechnicum until 1887, when he was appointed Professor of Physical Chemistry at the University of Leipzig, where he remained until his early retirement in 1906 at age 53. This move to Germany was due not only to recognition of his published research record but also to his monumental multivolume treatise, *Lehrbuch der allgemeine Chemie*, published between 1885 and 1887, and his founding, with van't Hoff as coeditor, of the *Zeitschrift für physikalische Chemie* in 1887. For these reasons Ostwald is widely regarded by historians of chemistry as the founding



WISSEN UND KÖNNEN

DIE ENERGIE

VON

PROF. DR. W. OSTWALD
GROSS-BOTHEN

LEIPZIG
VERLAG VON JOHANN AMBROSIUS BARTH
1908

Figure 10. The title page of Ostwald's 1908 popular account of energy and its uses.

father of the modern discipline of physical chemistry.

In 1909 Ostwald was awarded the Nobel Prize in Chemistry for his work on the theory of catalysis in which he clearly differentiated between the kinetic and thermodynamic aspects of chemical reactions. His name is also associated with the "Ostwald Process" for the catalytic oxidation of ammonia to nitric acid, which would later play a key role in the development of the Haber-Bosch process for nitrogen fixation. In retirement he became involved in several movements dedicated to the scientific reorganization of science and society, as well as doing fundamental work on the classification of colors.

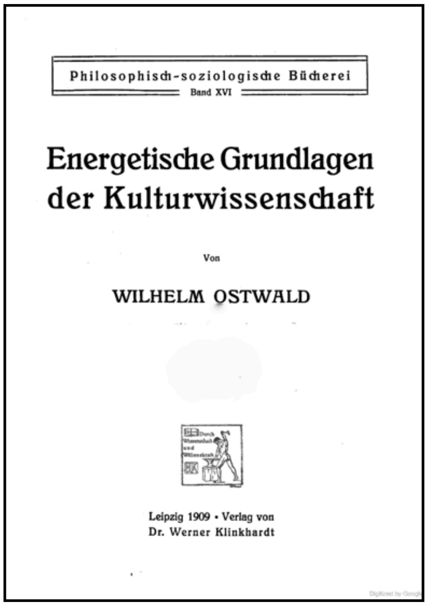
A prolific writer, it has been estimated that, during the course of his life, Ostwald authored 45 books, 500 articles, 5000 book reviews, and 10,000 letters. Though his early textbooks on chemistry were quite popular and were widely translated, his later writings on philosophical and social issues are available only in German. He died on 04 April 1932 in Leipzig at age 78.

Early in his career Ostwald became aware of the importance of thermodynamics, which he eventually generalized into what he called the science of "energetics." Initially this was applied to purely chemical questions and an attempt to displace the atomic theory, which Ostwald considered as unsubstantiated speculation, with a purely phenomenological chemistry based on the phase rule. After his retirement, however, he began broadening the scope of its application to include the subjects of psychology and sociology.

In 1908 he published a popular book on energy (figure 10) and its various applications for the general public in which he included brief chapters on energy and psychology and energy and sociology (18). The next year he expanded upon the latter subject in a booklet (figure 11) entitled, in translation, *The Energetic Foundations of the Science of Culture* (19). Ostwald used the word "culture" to denote the sum of all activities, however mundane, that occurred within a given society and not just *haute culture,* such as the creation of famous oil paintings or great operas. The majority of these activities were, in his opinion, shaped by the available energy flows accessible to society and were, in many cases, designed, either consciously or unconsciously, to help maintain that flow.

He also illustrated his argument by briefly sketching the historical evolution of various societies as they gained access to ever greater amounts of available energy flow and learned how to both control and modify those flows. Thus, beginning with the primitive club, and proceeding through such devices as the spear, knife, and bow and arrow, primitive mankind learned how to redirect and concentrate muscle power. This was followed by the discovery of how to control fire, the use of draft animals, human slaves, wind and water power and, finally in the 18th century, by the invention of the steam engine which allowed mankind to tap the earth's reserves of fossil fuels.

Every increase in available energy flow stimulated a corresponding increase in human population and led, in turn, to ever larger and more complex so-



Philosophisch-soziologische Bücherei
Band XVI

Energetische Grundlagen
der Kulturwissenschaft

Von

WILHELM OSTWALD

Leipzig 1909 • Verlag von
Dr. Werner Klinkhardt

Figure 11. The title page of Ostwald's 1909 booklet on energetic foundations of sociology.

cieties. Referring to the unidirectional flow of energy, postulated by the second law of thermodynamics, from high potential available energy into isothermal waste energy, the American science writer, Edwin Slossen, rather aptly summarized Ostwald's major premise with the catchy phrase:

The rise of civilization is coupled to the fall of energy.

Ostwald was rather appalled at the low efficiency of most known means for capturing and interconverting various forms of energy. Thus green plants utilize between only 0.1% and 2% of the incoming solar energy and steam engines between only 5% and 25% of the thermal energy generated in their boilers. The rest was allowed to degrade into unused isothermal waste heat. Rather he hoped that the future would bring the development of highly efficient photovoltaic cells that would allow mankind to tap the incoming light of the sun at high efficiencies and thereby free civilization from its dependency on finite fossil fuels and inefficient heat engines.

In keeping with this, Ostwald soon came to believe that the superiority of any given society was a function of the efficiency of its energy conversion devices, an idea that he extended not just to a society's existing energy technology but also to many other realms of social activity (18):

The economic coefficient [i.e. efficiency] of energy transformation is thus, finally, the general yardstick against which all human affairs should be measured.

Thus, for example, he was an advocate, like Pfaundler, of an auxiliary universal language, since he believed that the necessity of translating books and papers from one language to another was an unnecessary waste of energy, and, for the same reason, he advocated the elimination of Latin and Greek from the school curriculum.

Indeed, in later writings, this obsession with the efficient use of energy led Ostwald to formulate – in imitation of Kant's "categorical imperative" in the field of ethics – what he referred to as the "energetic imperative." This read (20):

Vergeude kein energie, verwerte sie.

which translates as "waste no energy, utilize it." Later writers have renamed this the "thermodynamic imperative."

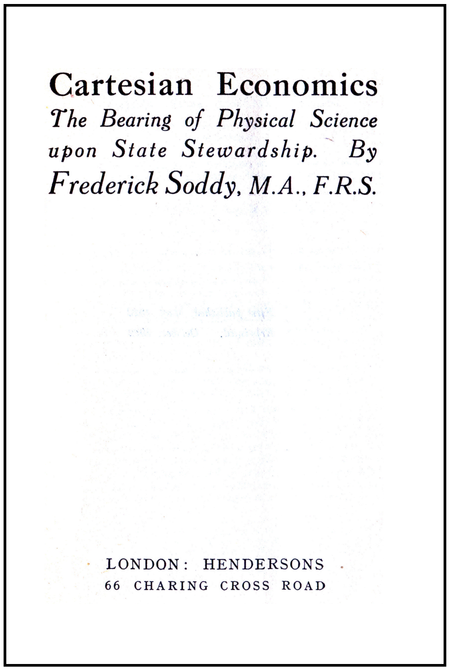
As some of Oswald's critics were quick to point out, many of his ideas on energy and culture were sketched out in very general terms and often failed to provide supporting details and data. In the case of sociology, in particular, it was not until 1955 that this detail was finally provided in the form of the classic textbook, *Energy and Society*, by the American sociologist Fred Cottrell (21).

Figure 12. Frederick Soddy
(1877-1956)

No. 5. Frederick Soddy on Energy and Economics

Frederick Soddy was born on 02 September 1877 in Eastbourne, England, the youngest of four sons of Benjamin Soddy, a corn merchant, and Hannah Green (22). His chemical training was obtained at University College of Wales in Aberystwyth and at Oxford University. In 1900, after two years of postgraduate research at Oxford, Soddy was appointed as a Demonstrator in Chemistry at McGill University in Canada, where he collaborated with the newly appointed Professor of Physics, Ernest Rutherford, in establishing that radioactivity was the result of the transmutation of one element into another – work that would lead to a Nobel Prize for Rutherford in 1908.

On returning to England in 1902, Soddy entered into a collaboration with Sir William Ramsay that demonstrated that helium was a by-product of certain kinds of radioactive decay. In 1904 he was appointed Lecturer in Physical Chemistry and Radioactivity at the University of Glasgow, where he and his students mapped the radioactive decay series for alpha particle emission, discovered the element protactinium, and formulated the concept of isotopes, for which Soddy was given the 1921 Nobel Prize in Chemistry. In 1914 he was appointed Professor of Chemistry at the University of Aberdeen, and in 1919 as Lee's Professor of



Cartesian Economics
The Bearing of Physical Science
upon State Stewardship. By
Frederick Soddy, M.A., F.R.S.

LONDON: HENDERSONS
66 CHARING CROSS ROAD

Figure 13. The title page of Soddy's 1922 booklet on energy and economics.

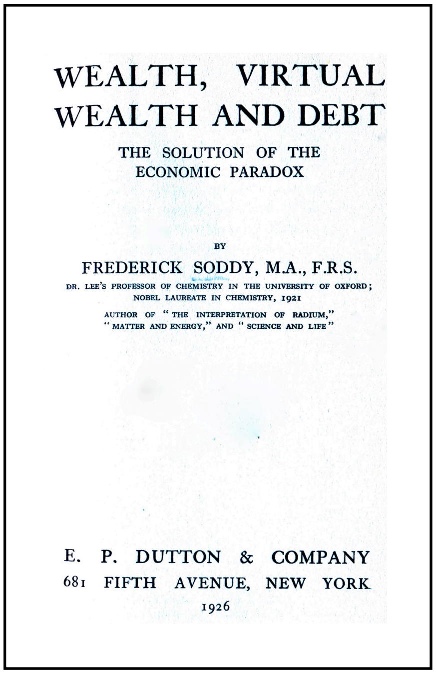
Chemistry at Oxford, where he remained until his early retirement in 1937 at age 60. He died on 22 September 1956 in Brighton, England, at age 79.

In 1912 Soddy published a small popular book entitled *Matter and Energy* in which he outlined the importance of energy for society, warned of the prospect of a future energy crisis if we continued to be dependent on fossil fuels, and broadly hinted at the future possibility of the practical application of nuclear energy (23). A decade later, heavily influenced by World War I and the subsequent economic depression in Great Britain, Soddy began to turn his thoughts to the relationship between energy and economics, and especially to the relationship between energy and money. The result was a small booklet published in 1922, entitled *Cartesian Economics* (figure 13) (24), followed by a major book four years later, entitled *Wealth, Virtual Wealth, and Debt* (figure 14) (25). Yet a third book was published in 1933 (26), as well as several more pamphlets on the same subject.

In these writings Soddy argued that science had shown that the basis of economic prosperity was available energy flow, whether renewable energy from the sun or nonrenewable energy from fossil fuel deposits. When we purchased food or various goods and services, we were exchanging money for something that required the consumption of a certain quantity of available energy to produce, and this suggested, in the most abstract terms, that money was simply a symbolic token exchanged for a certain quantity of available energy. In short, available energy flowed through the economy unidirectionally as it was degraded from its initial high potential input sources into useless isothermal waste heat, while money circulated continuously as a counterflow in the opposite direction.

This suggested to Soddy that the amount of money in the economy should be regulated so as to vary with the available energy flow, thereby keeping its purchasing power as constant as possible and thus avoiding alike both potential inflation (too much money per unit of available energy flow) and potential depression (too little money per unit of available energy flow). This would require some type of national or international organization to monitor energy use and adjust the currency accordingly.

However, instead of this, Soddy found that bankers, governments, and economists had artificially tied the value of money, not to energy flow, but to meaningless material standards, such as the gold standard, and were constantly manipulating the money flow without regard to energy flow in an attempt to create wealth where none existed through such paper creations as loans, the issuing of interest bearing bonds, etc. This they referred to as the creation of wealth, when in fact it was the creation of debt, since it did nothing to stimulate increased energy flow, which was the only true source of wealth. Soddy was particularly opposed to the concept of compound interest which he



WEALTH, VIRTUAL
WEALTH AND DEBT
THE SOLUTION OF THE
ECONOMIC PARADOX

BY
FREDERICK SODDY, M.A., F.R.S.
DR. LEE'S PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF OXFORD;
NOBEL LAUREATE IN CHEMISTRY, 1921
AUTHOR OF "THE INTERPRETATION OF RADIUM,"
"MATTER AND ENERGY," AND "SCIENCE AND LIFE"

E. P. DUTTON & COMPANY
681 FIFTH AVENUE, NEW YORK
1926

Figure 14. The title page of Soddy's 1926 book on energy and economics.

Figure 15. Alfred J. Lotka
(1880-1949)

viewed as a perpetual and undeserved drain upon society's future energy resources.

During his lifetime Soddy's views on economics were met with derision and he was dismissed as a crank by most economists. At present many of his views have been accepted, often without acknowledgement, and they have now been incorporated into a school of economic thought known by its followers as "ecological economics" (27).

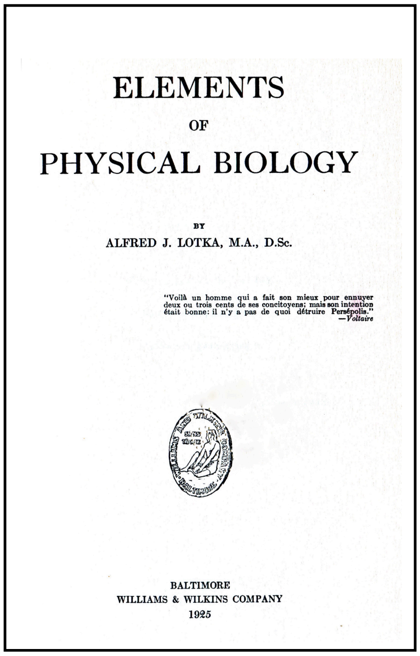
No. 6. Alfred Lotka on the World Engine

Alfred J. Lotka (figure 15) was born on 02 March 1880 in Lemburg, Austria (now Lvov, Ukraine), the son of Jacques Lotka and Marie Dobeley (28). Both parents were American citizens. Educated in Europe, he received his chemical training at the University of Birmingham, followed by a year of postgraduate study in Leipzig, where he was heavily influenced by Ostwald's program in energetics.

Returning to the United States in 1903, Lotka would hold a bewildering variety of jobs over the next two decades, including work as an industrial chemist, a patent examiner, a physicist with the US Bureau of Standards, an assistant editor at *Scientific American*, and a research fellow at Johns Hopkins. During this period he published numerous articles on the application of energetics and statistics to problems in physical chemistry, biology, evolution, and demographics, as well as picking up both a MS degree from Cornell University and an external doctoral degree from the University of Birmingham based on his published papers. Finally, in 1924, he obtained a position as a statistician for the Metropolitan Life Insurance Company, where he would remain until his retirement in 1947. He would die on 05 December 1949 in New York City at age 69.

In 1925 Lotka published his magnum opus, *Elements of Physical Biology* (figure 16) (29). In many ways this was a poor choice of title and something along the lines of *Ecological and Evolutionary Energetics* would have been closer to the mark. In this book Lotka attempted to trace the unidirectional flow of energy through the ecosystem and the various material cycles that it drove, such as the recirculation of water, carbon dioxide, nitrogen and phosphorus. But his central focus was the role of energy as a driving force in evolution. Adopting Boltzmann's observation that the struggle for existence was the struggle for free energy, Lotka arrived at what he called the "Law of Maximum Energy Flux," which stated that any species able to tap those portions of the available energy flux in nature that were currently wasted would not only have a reproductive and evolutionary advantage but would also accelerate the rate of available energy flow (29):

> *The general effect will be to increase the rate of energy flux through the system of organic nature, with a parallel increase in the total mass of the great world transformer, of its rate of circulation, or both ... one is tempted to see in this one of those maximum laws*



ELEMENTS
OF
PHYSICAL BIOLOGY

BY
ALFRED J. LOTKA, M.A., D.Sc.

"Voilà un homme qui a fait son mieux pour ennuyer deux ou trois cents de ses concitoyens; mais son intention était bonne: il n'y a pas de quoi détruire Persépolis."
—*Voltaire*

BALTIMORE
WILLIAMS & WILKINS COMPANY
1925

Figure 16. The title page of Lotka's 1925 book on energy flow in biology and ecology.

which are so commonly found to be apt expressions of the course of nature.

The most obvious example of such as species was mankind itself, which, via its many technological advances, had tapped virtually all of Nature's available energy sources and whose ever-increasing population and demand for land was gradually pushing many other species to the edge of extinction.

Lotka's book would greatly influence the American ecologist, Howard T. Odum, who would write numerous books on energy and ecology in the 1970s based on the energy flow or flux concepts of Soddy and Lotka and heavily illustrated with explicit flow diagrams and a complex symbolism inspired by that used for electronic circuits (3, 30).

Summary

In summary, we see that significant contributions to the questions of energy use, population growth, and the energetics of ecology were made by chemists in the late 19th and early 20th century. Jevons was the first to detail the future consequences of fossil fuel depletion and to link it with the problem of unchecked population growth. Arrhenius was the first to establish a link between the carbon dioxide content of the atmosphere and the surface temperature of the earth. Pfaundler was among the first to apply an energy analysis to the problem of estimating the carrying capacity of the earth. Ostwald was the first to suggest that available energy was a determining factor in both the historical development and structure of human societies. Soddy was the the first to suggest that the realities of energy use required a significant reform of our economic system, and Lotka the first to attempt to comprehensively map its role in both biological evolution and the ecosystem.

Missing from these early contributions is any consideration of the problems of pollution, which seem to have first surfaced as a major public issue in the 1960s and 1970s. However, if one extends their historical survey forward to cover this period, it is once again easy enough to find significant contributions by chemists to this question, such as those of Mario Molina and F. Sherwood Rowland in uncovering the role of chlorofluorocarbons in ozone depletion (31).

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Publication History

Written for this volume.