Lessons from the History of Chemistry

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Introduction and Background

When the Editor of *Accounts* invited me to contribute an article on my work on the history of physical chemistry, I at first demurred, as I felt that my contributions in that field did not constitute research. I maintain that there is a fairly sharp distinction between research and scholarship. Research means acquiring knowledge and understanding that has never before been acquired, while scholarship involves careful study of facts and concepts that have already been discovered. At first sight, writing articles and books about the history of science is scholarship and not research. However, one does often discover insights and interpretations that were not previously appreciated. Professional historians often reveal such insights, but scientists should not leave the task of writing the history of science entirely to them. By having a more intimate knowledge of science, a scientist can provide some insights that would be invisible to those who have never themselves carried out scientific research. From this standpoint, then, it seems justifiable to speak of research in the history of science.

Scientists today, and chemists perhaps more than physicists, sometimes despise the history of their subject, but I regret that attitude, for three main reasons. Firstly, many aspects of the history of science are interesting in themselves, and teachers of science can arouse their students' enthusiasm for science by making something of a historical approach. Secondly, and more important, our understanding of certain scientific topics can be much more profound if some historical background is provided.

Thirdly, and perhaps of greatest importance, reading about the history of science teaches us more about scientific method than can be acquired in any other way. This theme is developed later in this Account.

Another reason that caused me to hesitate when invited to write this Account was that I did not think that a shortened version of anything that I had previously written would be appropriate. When I wrote my history of physical chemistry,[1] a number of special themes became apparent, and some of these will be discussed herein. For example, I found that some incorrect ideas about the history of physics and physical chemistry have become entrenched in the scientific literature. In particular, a number of scientists have done work which had a strong impact on the development of chemistry, but which is now almost entirely forgotten. Also, several chemical discoveries now recognized as of great importance to chemistry were at first treated with great contempt. Some 20th century scientists whose work has had a profound influence on the progress of physical chemistry have never received Nobel prizes. Finally, there are a number of cases where great progress was made by methods that would conventionally be regarded as "unscientific".

History and Understanding

The usefulness of a historical approach in the teaching of chemistry will here be touched on only briefly, with reference to the teaching of thermodynamics. The concept of entropy is today often presented to students as a postulate, but this does not lead to a deep understanding of a topic of some subtlety; it must be, if Maxwell, Clausius, Kelvin, and Rayleigh had to struggle with it for so many years. It does not take long to present to students the basic principles of a steam engine of the James Watt type, with its separate cold condenser. It is then easy to explain how Carnot rationalized the theory of the heat engine, and how Clausius built on his ideas. The concept of entropy then emerges clearly as related to the impossibility of obtaining work from an engine without the need for the dissipation of heat from a higher to a lower temperature.

The point is that the way in which concepts were discovered often corresponds to the way in which we now understand them.

Incorrect Attributions

As Lord Macaulay[2] might have said, "every schoolboy knows" that Robert Boyle did not discover Boyle's law,[3] and there are a number of other cases where the wrong person has been credited with an original contribution. One example is what we call the *Le Chatelier principle*. In a paper[4] published late in 1884, the French chemist Henri Louis Le Chatelier (1850–1936) stated this principle, related to shifts in equilibria when the conditions are changed, but explicitly mentioned that the principle had first been deduced by the great Dutch chemist Jacobus Henricus van't

Keith J. Laidler was born in Liverpool, England, in 1916 and did his undergraduate work at Trinity College, Oxford, under C. N. Hinshelwood, with whom he carried out research, publishing his first paper in 1937. His graduate work was done at Princeton under Henry Eyring, and he obtained his Ph.D. degree in 1940; he was later awarded a D.Sc. degree by Oxford. He has carried out experimental and theoretical research on many aspects of chemical kinetics, including gas kinetics and enzyme kinetics. Since 1981, when he became professor emeritus at the University of Ottawa, he has also done much work on the history of physical chemistry, and his book *The World of Physical Chemistry* appeared in 1993. His textbook *Physical Chemistry* with John Meiser (second edition, 1995) not surprisingly develops the subject from a somewhat historical point of view.

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(1) Laidler, K. J. *The World of Physical Chemistry*; Oxford University Press, 1993.

(2) Macaulay, T. B. *Lord Clive*; London, 1804. For the benefit of nonschoolboys, Macaulay's timeless remark was "Every schoolboy knows who imprisoned Montezuma, and who strangled Atahualpa".

(3) Cohen, I. B. Newton, Hooke and "Boyle's law" (discovered by Power and Towneley). *Nature* **1964**, *204*, 618–621.

(4) Le Chatelier, H. L. *C. R. Hebd. Séances Acad. Sci.* **1884**, *99*, 786–789.

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Hoff (1852–1911) earlier in the same year.[5] Van't Hoff, a quiet, dreamy, and romantic man of great modesty, raised no objection when the credit was always given to Le Chatelier. Indeed, in his *Studies in Chemical Dynamics*[6] (1896) van't Hoff wrote, "Le Chatelier obtained this result simultaneously with van't Hoff"!

A similar situation exists with what we always call the *Arrhenius equation*, which is concerned with the effect of temperature on reaction rates. This equation was actually first suggested in 1884 by van't Hoff in his *Études de dynamique chimique*;[5] he pointed out that the equation is a logical consequence of the corresponding equation for equilibrium constant, and he applied it to some of his experimental results. In 1889 the Swedish chemist Svante August Arrhenius (1859–1927) quoted[7] this suggestion of van't Hoff and showed that the equation applied satisfactorily to a number of other reactions. Again, far from objecting to this equation being called the Arrhenius equation, van't Hoff himself gave much of the credit to Arrhenius. In his *Lectures on Theoretical and Physical Chemistry*[8] (1899) van't Hoff said that the equation was "adopted" by Arrhenius, giving a reference without the date. He then said that he himself had obtained favorable results with a more complicated equation, again giving a reference without the date. From the wording the reader would naturally conclude that Arrhenius gave the simple equation first, and that van't Hoff later used the more complicated form. Such charming modesty is too rare in science and is in striking contrast to Isaac Newton's many crafty claims to priority.

There is a similar misunderstanding about the origin of the *steady-state* or *stationary-state hypothesis* in chemical kinetics. This is almost always attributed to the German physical chemist Max Bodenstein (1871–1942), who did indeed do important work related to the hypothesis and ably defended it against its critics. Bodenstein and Dux's paper[9] suggesting the hypothesis appeared in 1913, but six months previously the British chemist David Leonard Chapman (1869–1958) and his student L. K. Underhill[10] had clearly stated the hypothesis and had applied it to the hydrogen–chlorine reaction. Chapman was another man of great modesty, and he never appears to have objected to the incorrect attribution.

Many introductory textbooks of chemistry today include a table giving the *electronic configurations* of the chemical elements, in much the same form as given by Nevil Vincent Sidgwick (1873–1952) in his *The Electronic Theory of Valency* (1927).[11] Ask any expert in the field who first gave such a table, and the answer will almost invariably be Niels Bohr (1885–1962). In 1921 Bohr did write two letters to *Nature* dealing with configurations, but he considered only the noble gases. As recently pointed out by Mansel Davies,[12] the details were actually worked out by Charles Rugeley Bury (1890–1968) in a concise seven-page paper[13] that appeared in 1921. Bury deduced from the chemical evidence that the electrons are arranged in successive layers containing 2, 8, 18, and 32 electrons. He included a clear discussion of the lanthanides and actinides, and even of the transuranic elements. His scheme led directly to the discovery in 1922 of the element hafnium, but he has hardly ever been given the credit for this. It was Bury's scheme that was reported in Sidgwick's book, with due credit given to him, but over the years Bury's important contribution has been forgotten.

Forgotten Geniuses

One of the most obscure but remarkable of the many people who made outstanding contributions to chemistry was Elizabeth Fulhame. Almost all we know of her is derived from reading her book *An Essay on Combustion*,[14] which was published in London in 1794. We do not know her dates of birth and death, but it seems likely that she was married to Dr. Thomas Fulhame, a physician who obtained his M.D. degree at the University of Edinburgh. We know from her book that she began her chemical experiments in 1780 and had been encouraged to continue them by Joseph Priestley (1733–1804). She is on record in 1810 as having been a corresponding member of the Philadelphia Chemical Society, perhaps because of Priestley's influence.

Her book describes many experiments carried out with the main object of deciding between the phlogiston theory and the later theories of Lavoisier. The book contains two pioneering contributions. Mrs. Fulhame was the first to achieve photoimaging, in that she obtained patterns by impregnating pieces of cloth with gold salts and other chemicals and exposing them to light. This work anticipated by nearly half a century the discovery of photography in 1839. Her second great contribution was to demonstrate the participation of water in certain oxidation processes, such as the rusting of iron. This work foreshadowed the recognition of catalysis by Jöns Jacob Berzelius (1779–1848) in 1836. In spite of the great importance of these contributions Mrs. Fulhame is now almost entirely forgotten, but a few publications have revived interest in her.[1,15–17]

Another forgotten genius was John James Waterston (1811–1883), who was born in Edinburgh and educated at the University of Edinburgh. In 1853 he submitted to the *Philosophical Transactions of the Royal Society* an essentially correct paper on the kinetic theory of gases. The time was not ripe for its

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(5) Van't Hoff, J. H. *Études de dynamique chimique*; F. Muller: Amsterdam, 1884.

(6) Van't Hoff, J. H. *Studies in Chemical Dynamics*; F. Muller/Williams & Norgate: Amsterdam/London, 1886. This was an English translation, prepared by Thomas Ewen, of the second edition of ref 5, which had been written jointly by van't Hoff and E. J. Cohen.

(7) Arrhenius, S. *Z. physikal. Chem.* **1889**, *4*, 226–248.

(8) Van't Hoff, J. H. *Lectures on Theoretical and Physical Chemistry*; translated by R. A. Lehrfeld; Edward Arnold: London, 1899–1900; 3 vols.

(9) Bodenstein, M.; Dux, W. *Z. physikal. Chem.* **1913**, *85*, 297–328.

(10) Chapman, D. L.; Underhill, L. K. *J. Chem. Soc.* **1913**, *103*, 496–508.

(11) Sidgwick, N. V. *The Electronic Theory of Valency*; Clarendon Press: Oxford, 1927.

(12) Davies, M. *J. Chem. Educ.* **1986**, *63*, 741–743.

(13) Bury, C. R. *J. Am. Chem. Soc.* **1921**, *43*, 1602–1609.

(14) Fulhame, Mrs. *An Essay on Combustion with a view to a New Art of Dying and Painting, wherein the Phlogistic and Antiphlogistic Hypotheses are Proved Erronious*; published by the author and printed in London, 1794.

(15) Davenport, D. A.; Ireland, K. M. *Bull. Hist. Chem.* **1989**, *5*, 37–42.

(16) Laidler, K. J. *Arch. Hist. Exact Sci.* **1986**, *35*, 345–374.

(17) Wheeler, T. S.; Partington, J. R. *The Life and Work of William Higgins, Chemist (1763–1825)*; Pergamon Press: Oxford, 1960; pp 121–122.

acceptance, however, and it was rejected for publication, one referee describing the attempt to explain pressure as due to molecular bombardment as "nothing but nonsense". In 1892, nine years after Waterston's death, the paper was resurrected from the files of the Royal Society by J. W. Strutt, 3rd Baron Rayleigh (1842–1919), who recognized its importance. Rayleigh then arranged for its publication in the *Transactions*,[18] but by that time the work had been done again, particularly by Rudolph Clausius and James Clerk Maxwell, so that when published Waterston's paper was only of historical interest.

It is impossible to know how many important papers have been permanently rejected for publication, just as one cannot know how many undetected crimes have been committed. One paper that narrowly escaped oblivion was Henry Eyring's classical paper on transition-state theory.[19] Submitted to the *Journal of Chemical Physics* in November 1934, the paper was initially rejected outright by the editor, Harold C. Urey, on the basis of a referee's report. However, H. S. Taylor and Eugene Wigner intervened, and as a result the paper, one of the most important ever written in chemical kinetics, was published in the February 1935 issue of the journal. (This incident throws an interesting light on the speed of publication in those days; in the 18th and 19th centuries the delay between submission and publication was sometimes only a week or two. Modern high-speed electronic communication is not yet reflected in speed of publication in printed form.)

Sir William Robert Grove (1811–1896) is today only remembered by physical chemists for the electrochemical cell he invented, but his scientific accomplishments covered a wider field. His main career was as a lawyer (he became a judge), but for a period, without any training, he was an active scientist. In 1846 he wrote one of the first books to state clearly the principle of conservation of energy, and in 1839 he designed and operated a *fuel cell*,[20] involving the combination of hydrogen and oxygen. Today we think of fuel cells as a 20th century invention.

We also think of color photography as something that was begun between the two world wars, and it comes as a surprise that excellent color photographs, particularly of spectra, were taken nearly a century before. The main pioneers in that field were Sir John Frederick William Herschel (1792–1871) and Alexandre Edmond Becquerel (1820–1891). Herschel, the son and nephew respectively of the great astronomers Sir William Herschel (1738–1822) and Caroline Herschel (1750–1848), took colored photographs of spectra in 1842,[21] and they are in the possession of the Royal Society. Edmond Becquerel, the father of Antoine Becquerel, who is famous for his work on radioactivity, took colored photographs of the solar spectrum in 1843; examples are at the Conservatoire des Arts et Métiers in Paris and at the Science Museum in London. Hand-tinted engravings of some of Becquerel's colored spectra, made by himself, are reproduced in a recent book by Janet Buerger.[22]

The great American scientist and statesman Benjamin Franklin (1706–1790) is hardly a forgotten genius, but one aspect of his work is often overlooked: his important investigations of surface films of oil on water.[23] An ironic aspect of this neglect has been pointed out by Tanford.[24] When in 1934 Irving Langmuir (1881–1957) was awarded the Franklin Medal by the Franklin Institute in Philadelphia, an institution endowed in honor of Benjamin Franklin, no mention was apparently made of the fact that Franklin had initiated the surface studies for which Langmuir was being honored! Moreover, in none of Langmuir's papers on surface films is there any mention of Franklin!

Controversy or Neglect

In studying the history of science one becomes acutely aware of how often an important discovery is initially either treated with scorn or neglected altogether for a time. Many examples are given in my book,[1] and here I will mention some of the more interesting cases.

The introduction of the concept of *entropy* by Rudolph Clausius (1822–1888) provides one example. Although James Clerk Maxwell (1831–1879) at once appreciated the importance of entropy, many failed to understand it. In particular William Thomson (later Lord Kelvin, 1824–1907), although he had made important contributions to the second law of thermodynamics and was a highly accomplished mathematician, never thought that entropy was a useful concept. Nor did Kelvin appreciate the thermodynamics of Josiah Willard Gibbs (1839–1903), and he wrote in a letter to Rayleigh, "I find no light for chemistry or thermodynamics in Willard Gibbs". The fault here lay partly with the obscurity of Gibbs's writing (although he was concerned with chemical equilibrium, for example, he never mentioned an equilibrium constant). Maxwell was able to understand Gibbs only by working everything out for himself.

The introduction of the *ionic theory* by Arrhenius in 1887 led to much controversy and will be discussed from another point of view later. The fate of the theory of blackbody radiation proposed in 1900 by Max Planck (1858–1947) was rather different, even after 1905 when Albert Einstein pointed out the enormous significance of quantization of energy and of radiation. For several years the *quantum theory* was largely ignored, and chemists paid little attention to it until 1913 when Niels Bohr applied it to the structure of the atom.

A few theories, on the other hand, were accepted by the majority of chemists almost at once. This is true of the *atomic theory*, introduced by John Dalton in 1805. Its influence on mainstream chemistry was considerable, although inevitably there were some dissidents; the great Wilhelm Ostwald (1853–1932) did not accept the reality of atoms until over 100 years later!

The Curious Incident of the Nobel Prizes

"I call your attention to the curious incident of the Nobel prizes awarded to G. N. Lewis and Henry Eyring", as Sherlock Holmes might have said.

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[18] Waterston, J. J. *Philos. Trans. R. Soc. London* **1893**, *A183*, 1–79.

[19] Eyring, H. *J. Chem. Phys.* **1935**, *3*, 107–115.

[20] Grove, W. R. *Philos. Mag.* **1839**, *14*, 127–130.

[21] Herschel, J. F. W. *Philos. Trans. R. Soc. London* **1842**, *132*, 181–204.

[22] Buerger, J. E. *French Daguerreotypes*; University of Chicago Press, 1989.

[23] Franklin, B. *Philos. Trans.* **1774**, *64*, 445–460.

[24] Tanford, C. *Ben Franklin Stilled the Waves: An Informal History of Pouring Oil on Water with Reflections on the Ups and Downs of Scientific Life in General*; Duke University Press: Durham, NC, 1989.

"But they were not awarded Nobel prizes."

"That was the curious incident", remarked Sherlock Holmes.

Gilbert Newton Lewis (1875–1946) made two contributions, each one of which was worthy of a Nobel prize. Between 1900 and 1907 he revolutionized the new science of thermodynamics, in particular introducing the concepts of fugacity and activity; his 1923 book on thermodynamics[25] with Merle Randall is a classic which remained in print and was much used for many decades. In 1916 he published a pioneering paper on valence theory,[26] in which he introduced the idea of groups of eight electrons ("octets"), and suggested that bonding would involve the sharing of a pair of electrons. Over the years he greatly developed these ideas, and he expounded them in an important book[27] which also appeared in 1923. Like this work on thermodynamics, these ideas about the valence bond form the basis of our present understanding of these topics.

Lewis's failure to receive a Nobel prize is probably due to misunderstanding that arose regarding his valence theory. Some of Lewis's American colleagues were partly to blame, in that they at first ignored his ideas, which were better appreciated in Europe. Lewis had begun his work on valence theory as early as 1902, when we was at Harvard, and he so resented the indifference of his colleagues there that in 1929 he refused an honorary degree from Harvard. Also, unfortunate consequences arose from the fact that his valence theories were in 1919 taken up with great enthusiasm by Irving Langmuir (1881–1957), who already had a wide reputation for his important work on solid and liquid surfaces, work that was later to bring him the 1932 Nobel prize. Langmuir extended Lewis's ideas and also suggested a number of the terms that are used today, such as *covalence* and *electrovalence*. Although Langmuir always gave due credit to Lewis, the theory began to be known as the Lewis–Langmuir theory, which did not entirely please Lewis. In Britain, in fact, the theory was sometimes known as the Langmuir theory, which Lewis not surprisingly regarded as "inexcusable".

Many physicists regarded Lewis's theory as naive, in that he seemed to be regarding the electrons as fixed in certain positions. This opinion of the physicists may have been the determining factor with regard to the Nobel prize. The fact that in his 1923 book[27] Lewis had developed his ideas into a form acceptable to the physicists seems to have been forgotten; the harm had already been done.

In the 1920s and 1930s the nominations of Niels Bohr were given much consideration by the Nobel prize committee, and many of his nominees received the award. He nominated a number of physicists whose work was of special interest to chemists, and Langmuir specifically for his work on surfaces, but he never nominated Lewis.

A few physicists have, however, appreciated what Lewis did, as illustrated by the following passage from *Wave Mechanics* (1945) by Walter Heitler:

> Long before wave mechanics was known Lewis put forward a semi-empirical theory according to which the covalent bond between atoms was effected by the formation of pairs of electrons shared by each pair of atoms. We see now that wave mechanics affords a full justification of this picture, and, moreover, gives a precise meaning to these electron pairs: they are pairs of electrons with antiparallel spin.

Henry Eyring (1901–1981) made many outstanding contributions that relate not only to chemistry but to fields outside it, such as metallurgy. His most important work involved the use of potential-energy surfaces in the treatment of the rates of chemical and physical processes. In 1935 he formulated transition-state theory,[19] and he subsequently developed the theory greatly and applied it to a wide range of systems. He received several strong nominations for a Nobel prize, but was never awarded one, much to the surprise of most physical chemists.

The explanation is probably somewhat similar to that for the failure of Lewis to obtain the prize. To many physicists, and to some more mathematically inclined chemists, transition-state theory seemed crude, having too many assumptions that could not be fully justified. With the development of computers since World War II it seemed for many years that it would soon be possible to make exact quantum-mechanical calculations of the rates of reactions, and that then Eyring's theory would be obsolete. Eventually, however, it turned out that such calculations would inevitably be very time consuming. In any case, such computer calculations, although of undoubted importance, do not provide the practical chemist with insight as to how chemical reactions proceed.

Transition-state theory does provide such an insight and is now becoming appreciated more and more. Its value is not so much in providing a way of calculating rates, but rather in leading to useful qualitative predictions on matters such as solvent effects, kinetic-isotope ratios, and influence of pressure. The theory thus has something of the same status as Lewis's theory of the covalent bond, in providing a conceptual basis, valuable to chemists, to the more advanced quantum-mechanical treatments. An appreciation of this apparently came too late for Eyring to win a Nobel prize.

Not to win a Nobel prize puts one in excellent company. Neither Dmitri Mendeleev (1934–1907) nor Ludwig Boltzmann (1844–1906) won a Prize, but their failure is easily explained by the fact that both had done their great work a good many years before the awards were first made in 1901. Less easy to understand is that Prizes were never awarded to Lise Meitner (1878–1968), Christopher Kelk Ingold (1893–1970), and Friedrich Hund (born 1896). When Robert Sanderson Mulliken (1895–1986) was awarded his Prize for chemistry in 1966, he expressed regret that he had not shared it with Hund, and this would indeed have been appropriate. Although the two never published a joint paper, they worked closely together on molecular orbital theory in its early years, and Hund made many contributions of great importance.

On the whole, however, the passage of time has confirmed that the Prizes for chemistry have for the most part been awarded wisely. It has been suggested that to minimize mistakes the Prizes should only be

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(25) Lewis, G. N.; Randall, M. *Thermodynamics and the Free Energy of Chemical Substances*; McGraw-Hill: New York, 1923. There was a revised second edition in 1961.

(26) Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762–785.

(27) Lewis, G. N. *Valence and the Structure of Atoms and Molecules*; Chemical Catalog Co.: New York, 1923.

awarded posthumously, like inclusion in the *Dictionary of Scientific Biography*! That idea, however, has obvious disadvantages.

"Unscientific" Method

Research scientists who delve into what has been written about the "scientific method" often have the feeling that what they read does not relate to the way they go about their own research. A view that is sometimes presented is that, to apply the scientific method, one assembles data and then formulates an explanation or theory that best fits the data. This may well be the way in which a detective solves a crime, or a lawyer prepares a case. It may be the way in which some routine science is carried out. Historians and philosophers of science, however, have long recognized that this is not the way in which important advances in science are made.

The truth is that there is no one scientific method. As one struggles through the jungle of experimental data, there is no well-marked path to a satisfactory theory, and there are no rules of the road but only a few general guidelines. To be successful a scientist should feel free to use any methods (short of dishonesty!) and should not be afraid of using imagination and intuition, or of breaking any so-called rules. "Imagination in Science" was the title of the inaugural address delivered by van't Hoff in 1878 at the University of Amsterdam; he said that he had made a special study of the way in which scientific advances had been made, and he stressed that observation and imagination were both of great importance.

The work of Isaac Newton provides a good example. One is struck by the fact that by conventional standards his methods were most unscientific: he was much guided by religious and metaphysical arguments and did not hesitate to keep quiet about facts that did not fit his theories. In spite of this, because of his imaginative insights, he is generally regarded as one of the greatest scientists who ever lived.

It is not difficult to find examples in physical chemistry where progress was made by accepting a theory that did not best fit the available data, in other words, by using methods that would conventionally be called "unscientific"! My first of three examples involves a purely mathematical point. The *Arrhenius equation* involves a linear relationship between the logarithm of a rate constant k and the reciprocal of the absolute temperature T. For nearly half a century there was controversy about the equation, and in particular a rival relationship was advocated by Augustus George Vernon Harcourt (1834–1919) and William Esson (1839–1916). In papers published in 1895 and 1912 they claimed,[28,29] from analysis of numerous data, that there is a better linear relationship between $\ln k$ and $\ln T$ than between $\ln k$ and $1/T$. There is no doubt that they were correct in this claim.

Why, then, did the Arrhenius equation, and the theory that lay behind it, prevail over the Harcourt–Esson equation? The answer is twofold. In the first place, taking a logarithm narrows the range of data, so that one is intrinsically more likely to find a linear relationship with $\ln T$ than with T or $1/T$. The better fit obtained by Harcourt and Esson is therefore of no significance. Secondly, the Arrhenius relationship can be given a theoretical interpretation in terms of energy barriers to reaction. The Harcourt–Esson relationship, on the other hand, was theoretically barren.

The second example relates to the Arrhenius theory of *ionic dissociation*, first presented[30] in 1887. Arrhenius envisioned a shifting equilibrium between undissociated molecules and ions, and in the following year Wilhelm Ostwald formulated his dilution law[31] which related molar conductivity to concentration. What appeared to be a crucial test of the theory was to see if the equilibrium constants calculated from the data were true constants. However, even before Ostwald's paper appeared in print it was pointed out to Arrhenius that the experimental "constants" for strong electrolytes sometimes varied by several powers of ten!

Did this cause Arrhenius and his fellow "Ionists" to reject the ionic theory? By no means; the inconvenient facts were simply brushed under the carpet. Arrhenius suggested to his colleagues that it was best to ignore the strong electrolytes, as the data did not cover a sufficiently wide range of conductivities! In the first edition of his *Theoretische Chemie* (1891) Walther Nernst (1864–1941), an enthusiastic Ionist, went so far as to write that "the Ostwald formula does not exactly fit the observed facts in the case of highly dissociated acids and bases". "Does not exactly fit" seems a remarkable understatement for variations over several powers of ten! Arrhenius and his fellow Ionists were convinced—and they proved to be correct—that dissociation into ions occurs, and they were not going to be put off even by large discrepancies between the theory and the data. As is well-known, there was much controversy about the ionic theory for many years; for details see my book[1] and the excellent accounts by Ihde[32] and Brock.[33,34]

The third and last example relates to the idea of *chain reactions*, which arose from the extensive experimental work on the thermal and photochemical reactions between hydrogen and chlorine, carried out from the 1890s and for many decades by Max Bodenstein and D. L. Chapman. There were many experimental difficulties, including an exasperating lack of reproducibility in the results. This was traced to the fact that the reaction rate is extremely sensitive to the surface of the vessel and to the presence of minute traces of impurities. Oxygen had a particularly marked effect; its removal increased the rate, and in its absence the reaction became too fast for the rate to be measured.

Chapman and Bodenstein made many attempts to explain the results, but with limited success. As already mentioned, Chapman in 1913 introduced the steady-state hypothesis to interpret composite mech-

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(28) Harcourt, A. V.; Esson, W. *Philos. Trans. R. Soc. London* **1895**, *A186*, 817–895.

(29) Harcourt, A. V. *Philos. Trans. R. Soc. London* **1912**, *A212*, 193–204. This paper has an extensive mathematical appendix written by Esson.

(30) Arrhenius, S. A. *Z. physikal. Chem.* **1887**, *1*, 631–648. Translation in *The Foundations of the Theory of Dilute Solutions*, Alembic Club Reprint No. 19, 1929.

(31) Ostwald, W. *Z. physikal. Chem.* **1888**, *2*, 270–283.

(32) Ihde, A. J. *Chemistry as Viewed from Bascom's Hill*; Department of Chemistry, University of Wisconsin: Madison, 1990. The quotation from Lewis at the end of the present Account is on p 322.

(33) Brock, W. H. *The Norton History of Chemistry* (in the U.K. *The Fontana History of Chemistry*); Norton/Fontana: New York/London, 1992.

(34) Nernst, W. *Z. Elektrochem.* **1918**, *24*, 335–336.

anisms, and in the same year Bodenstein and his student Walter Dux (1889–1987) specifically suggested the idea of a chain reaction. Dux later recalled that Bodenstein demonstrated the transmission of an impulse along his gold watch chain. Bodenstein and Chapman's attempts to explain the results in terms of a specific chain of reactions were, however, unsuccessful.

Walther Nernst had done much important work in thermodynamics and electrochemistry, but until 1918 had paid little attention to kinetics, and was not aware of the experimental complications of the hydrogen–chlorine reaction. In spite of this, however, he did not hesitate to suggest a specific chain mechanism for the reaction, involving the processes $Cl + H_2 \rightarrow HCl + H$ and $H + Cl_2 \rightarrow HCl + Cl$ as chain-propagating steps. This was undoubtedly along the right lines, but the mechanism was far from being able to explain the experimental facts; the influence of surface and of oxygen was not explained at all. Bodenstein and Chapman would hardly have proposed such a scheme, since they knew too much about the facts!

Again we have an example of an idea of great scientific importance that in its original form was inconsistent with experiment, but that became suitably modified over the years in order to accommodate the data.

Concluding Remarks

The way in which science develops has been discussed in detail by Sir Karl Popper,[35] Thomas Kuhn,[36] Gerald Holton,[37] and many others. But it seems appropriate to allow G. N. Lewis the last word on the subject of scientific method, with a comment[32] that he made in 1906. It related specifically to the ionic theory, controversial at the time, but it is true for any chemical theory, and perhaps for any theory in any branch of science:

> Perfection is rare in the science of chemistry. Our scientific theories do not spring full-armed from the brow of the creator. They are subject to slow and gradual growth....

He then added, specifically of the ionic theory but applying to other theories,

> Instead, however, of judging it according to the standard of perfection, let us simply ask what it has accomplished, and what it may accomplish in scientific service.

Perhaps this is the most important lesson we can learn from a study of the history of chemistry.

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