

## 2008 EDELSTEIN AWARD PAPER

# THE BORDER BETWEEN PHYSICS AND CHEMISTRY\*

---

J.S. Rowlinson, Oxford University

My first and most pleasurable duty is to thank the History of Chemistry Division of the American Chemical Society for the great honor of being chosen to receive the Sidney Edelstein Award for 2008 and for the kind help I have had from its officers in inviting me to this Fall Meeting. The award is particularly gratifying and unexpected to one who came so late to the field of the history of science. My second pleasure is to thank Bill Brock, himself a recipient of the earlier Dexter Award, for arranging this session at the ACS meeting and so giving me the opportunity to open today with the same quotation with which he opened his corresponding paper (1) in 1995, namely the remark of Robert Bunsen that “Ein Chemiker, der kein Physiker ist, ist gar nichts” – a chemist who is no physicist is worthless. It is the often troubled relations of the chemists and the physicists that I should like to explore in this paper.

### Newton and After

It could be argued that chemistry as a field of study, with its practical roots in medicine, agriculture, mining, and brewing, preceded natural philosophy, but that its academic recognition in the universities came later. Thus, to take the two examples that I know best, Oxford had chairs of natural philosophy, geometry, and astronomy from the 1620s but it was not until 60 years later that



*Photo courtesy of Sir John S. Rowlinson.*

it had a chair of chemistry, and this was allowed to lapse early in the 18th century, being firmly established again only in 1803. Cambridge had a chair of mathematics from 1663 which, in Newton's hands, soon also encompassed astronomy and natural philosophy, but chemistry followed only in 1702. It was Newton who first stirred things up with his attempt to reduce chemistry to physics, to use the modern terms. Some of his followers promptly went further and tried to extend such reduction to medicine, geology, botany, and other branches of practical knowledge (2). These extensions foundered for two reasons, the first of which was their obvious lack of success. Their promoters ultimately were to be proved

right in assuming that chemistry, in particular, was to be explained in terms of forces acting apparently instantaneously and at a distance between almost indestructible particles, but they could not carry out the program of interpreting it in those terms in the 18th century; the world was not prepared for quantitative physical chemistry for another 150 years. Their ideas did mesh with some useful thoughts on ‘elective affinities’ throughout the 18th century, but that concept was dying by the time that Goethe used it for the title of a rather difficult novel (3) in 1809; it had been overwhelmed by the advances in chemistry associated with Lavoisier and Dalton.

The second reason for the failure of Newton's program was the resistance of the chemists who insisted that theirs was an autonomous science that could not and should not be derived from what we now call physics. Chemists often envied the respect that was given to the natural philosophers but held that chemistry had its own foundations based on observations and direct deductions from them. These foundations, they argued, should be treated with the same respect as was given to those of natural philosophy. That subject dealt in the general features of the natural world and chemistry in the specific properties of existent substances, and with making new substances, both of which activities were matters of greater complexity. A few areas, such as the study of heat, hovered uncertainly between the two disciplines. Herman Boerhaave of Leiden, perhaps the leading chemist of his generation, admired Newton's defence of the primacy of experiment over the metaphysical speculations of the Cartesians, but he took a down-to-earth view of medicine and chemistry. His principles and those of John Freind, Oxford's Newtonian chemist, were, as an anonymous writer put it, "as different as that of alkali and acid" (4). Leiden was held in high esteem in Scotland, mainly for its standing in medicine, and Boerhaave was abetted by the Scottish chemists, William Cullen and Joseph Black, who also argued for the autonomy of chemistry, again on the ground that it dealt with particular substances and practical matters, and not with the generalities of physics. Cullen defended the teaching of philosophical chemistry to medical students, maintaining that it should be seen as "a considerable part of Natural Philosophy capable of being applied to the very important purposes of Society" (5). Similar arguments for autonomy were put forward also by Georg Stahl, who also stressed the greater complexity of chemistry, and by later generations of German chemists who were rarely tempted to adopt Newton's ideas (6). In Germany, as in Scotland, chemistry was in the medical faculties of the universities and so remote from Newtonian influences.

The heart of 18th century chemistry, however, was inorganic chemistry, and here the discovery of new elements, and new compounds of existing elements, gave the subject a complexion more akin to that of natural history. Description and classification were the dominant themes (7), and this aspect survived the banishment of phlogiston at the end of the century; it is exemplified in the binary notation for salts (as in sodium nitrate, or potassium sulfate) that Lavoisier, Fourcroy and their associates apparently derived from Linnaeus's notation for plants and animals. Physical ideas intruded into chemistry in the experiments on heat and on the newly discovered

'airs' or gases, but they generally played only a minor role. Both Lavoisier and Dalton had had an interest in physical experimentation but their chemistry owed nothing to Newton. There had, however, been throughout the century a small but steady tradition of Newtonian ideas in French chemistry at the hands of men such as Macquer, and this led to a revival of interest in Newton's views in Paris at the opening of the 19th century by Berthollet (a pupil of Macquer), Gay-Lussac and the young Dumas—a move that was encouraged by Laplace's success in interpreting the popular phenomenon of capillarity in terms of Newtonian attractions. The Société d'Arcueil of Laplace and Berthollet became the center of this revival. But even Berthollet, perhaps the most Newtonian of the French chemists, acknowledged that the time was not ripe for a mathematical chemistry resting on forces between atoms, much though he would have liked to have seen one. Laplace was equally pessimistic when questioned by Davy on his visit to Paris in 1813 (8). Such early attempts at what we can see as physical chemistry soon faded away as chemists realised that there was more excitement to be had in exploring the consequences of Dalton's laws, in the chemical effects of electricity at the hands of Davy and Berzelius, and in the realization that organic compounds could be isolated, analyzed and even synthesized. Chemistry became again primarily a science of discovery and classification; numbers appeared mainly in the fascinating arguments about atomic and equivalent weights, and so of organic formulas that marked the first half of the 19th century.

### Chemistry Goes it Alone in the 19th Century

The positivism of Auguste Comte had a strong influence in the early and mid-century, particularly on French and British chemists. A distrust of anything that could not be observed directly led some to have doubts that atoms really existed and were perhaps only convenient book-keeping entities that helped to make sense of the quantitative side of chemical reactions. In Oxford, Benjamin Brodie devised a 'chemical calculus' with which he claimed to re-order chemistry into a form that did not require an assumption of the existence of atoms (9). But this calculus proved sterile and was soon abandoned. Even those who accepted the reality of atoms, however, could doubt whether organic formulas represented real units with a three-dimensional structure. Physics was an irrelevancy to such men.

An interesting example of the claim for the autonomy of chemistry came from William Prout who, in 1834,

put forward some views on the nature of heat, light, and photochemistry that did not conform to the physicists' new advocacy of the wave theory. He accepted that he was out-of-line with them but wrote that he was (10):

...decidedly of the opinion that the *chemical* action of light can be explained only on chemical principles, whatever these may be. Whether these chemical principles will hereafter explain what is now so happily illustrated by undulae, time must determine.

He had a valid point, for the chemical action of light was not to be understood until the advent of Einstein's photon.

There were some chemists who straddled the border between physics and chemistry, such as Faraday with his electrolytic experiments, Bunsen, a powerful figure at Heidelberg with whose epigram I opened this paper, and other perhaps less influential chemists, such as Kopp, Pfandler, Landolt, Graham, Andrews and Crookes, whose interests and useful results kept the connection alive. None of these, however, generated a 'school' or created physical chemistry as a recognised discipline. Their results served to give a quantitative classification of some chemical facts, but they rarely led to much in the way of interpretation. There was even less traffic the other way. Few physicists deigned to interest themselves in what they saw as the messy particularities of chemistry, preferring to concentrate on the wider and apparently more fundamental problems of their own field. Thus Rudolf Clausius was deeply committed to the molecular-kinetic view of matter but he had little contact with the chemists and he irritated them when he thought that his claim that nitrogen was a diatomic molecule would be news to them (11). James Clerk Maxwell was one of the exceptions and it is interesting to speculate what the evolution of physical chemistry might have been had he not died in 1879 at the age of 48. He was, with Clausius, a founder of the kinetic theory of gases and so a firm believer in the real existence of atoms, on which he lectured to the Chemical Society itself in 1875 (12). It was around this time that serious attempts were being made to determine the size of atoms and so attest to their reality. These attempts led to some dialog, if little cooperation, between chemists and physicists. Maxwell wrote perceptively on 'Atom' for the *Encyclopaedia Britannica*, and he never doubted that chemistry was to be counted as one of the physical sciences, as he wrote in 1872 or 1873 (13):

I have not included chemistry in my list [of the physical sciences] because, though Dynamical Science is continually reclaiming large tracts of good ground

from one side of Chemistry, Chemistry is extending with still greater rapidity on the other side, into regions where the dynamics of the present day must put her hand on her mouth. But Chemistry is a Physical Science...

I shall return to this perceptive assessment at the end of this paper.

### Physical Chemistry as a Discipline

As the century advanced it was organic chemistry that first developed into a true discipline, whose practitioners, particularly in Germany, became a recognised community, little interested in other branches of the subject. Even such momentous discoveries as Mendeleev's periodic classification (1869) taught them nothing that they wanted to know about the chemistry of carbon. The 'type' theory of organic compounds in the 1860s again emphasised the degree to which chemistry remained a classificatory science with more in common with natural history than with physics. So physical chemistry as a discipline grew up first in lands where German was the scientific language but outside the German states themselves, with Wilhelm Ostwald from Dorpat (now Tartu) in Estonia, J.H. van 't Hoff from Amsterdam and Svante Arrhenius from Stockholm, as the leading figures. Their foundation of the *Zeitschrift für physikalische Chemie* in 1887 is commonly held to mark the formal launch of the new discipline, but that date disguises the slow rise of different aspects of this new subject from the mid-century onwards. An important landmark for British chemists was Helmholtz's Faraday Lecture to the Chemical Society in 1881 in which he set out clearly the implication of Faraday's work that if matter was atomic, then so was electricity (14).

The classical organic chemists in Germany reacted badly to what they perceived as a challenge to their hegemony from within their own community. Ostwald had moved to Leipzig in 1887 and van 't Hoff to Berlin in 1896, thus taking the fight to the German heartlands. When Ostwald reminded Emil Fischer of the debt that organic chemists owed to physical chemists for the means of determining the molecular weights of his sugars Fischer replied briskly that he had no need of such methods. Hermann Kolbe poured scorn on van 't Hoff's "pencil and paper chemistry". Richard Willstätter complained of Ostwald's pernicious influence on German chemistry, saying that he had created "discord and anger" (15). Early in the 20th century William Perkin Jr, a German-trained organic chemist, imported similar ideas into Oxford. He was said to have remarked that physical chemistry was

all very well but it didn't apply to organic molecules. The physical chemists to whom he reluctantly gave laboratory space used to leave a bottle of pyridine open on the bench so that the 'old man' passing by would get a whiff and think that some real organic chemistry was underway (16). His successor in Oxford, Robert Robinson, trained by Perkin, also saw little need to go beyond the classical organic methods of degradation and synthesis, and so was beaten by Dorothy Hodgkin, an X-ray crystallographer and his Oxford colleague, in the race to determine the structure of penicillin in 1945 (17). But by then such attitudes were becoming eccentric and organic chemists were usually willing to embrace any physical technique that would accelerate their work. This acceptance did, however, carry with it in the eyes of some organic and inorganic chemists the view that physical chemistry was essentially a service industry, useful only for methods of analysis that allowed 'proper' chemists to do their job more easily or more quickly. This attitude is still not entirely banished, and there is some truth in it, for that is one of the functions of physical chemistry, but it is far from being the whole truth.

The physical chemistry that Ostwald, van 't Hoff and Arrhenius set out was based on careful studies of the properties of liquid solutions, both ionic and non-ionic, studies that were given theoretical backbone by the newly-developed subject of chemical thermodynamics. Here August Horstmann had been the pioneer but the master was Willard Gibbs, with a group of long and difficult papers in the 1870s. At first few chemists could follow him and so used many of his results in the later, clumsier, but more transparent formulations of Helmholtz and van 't Hoff. But with the increasing appreciation of the value of thermodynamics, chemists had finally lost their lingering fondness for forces and replaced it by a trust in energy, and later, in combination with entropy, in free energy or Gibbs's chemical potential. This change was an important one for a clear discussion of the mechanical foundations of both physics and chemistry. It was Maxwell, van der Waals, van 't Hoff and Ostwald who introduced Gibbs's work to the European physico-chemical community (18). The founding books of the new subject of physical chemistry were van 't Hoff's *Études de dynamique chimique* of 1884 and Ostwald's *Lehrbuch der allgemeinen Chemie* which began to appear the next year, but it is interesting to see that neither book had the words 'physical chemistry' in its title (19). This absence reflects an uncertainty of the aims and position of the subject that was to shape its development for the next 40 years.

## What is Physical Chemistry?

Few answers have been given to this difficult question. After some reflection, G.N. Lewis is said to have come up with the witty but unhelpful reply that "it is what physical chemists do". It might be thought that consulting one of the many excellent text-books now available would produce a more informative answer, but it does not. Neither Glasstone, nor Moore, nor Atkins, nor Berry, Rice and Ross (to take just four of the text-books most used throughout the English-speaking world for the last 50 years) gives a cogent definition of the field (20). Cyril Hinshelwood, in his, *The Structure of Physical Chemistry* (1951), which was aimed at describing the essence of the subject, saw it as part of a humanistic or liberal education, but he missed the opportunity to define it further (21). Surely then a man of Partington's historical interests would have attempted a full answer in his five-volume treatise. But even he only goes as far as to quote with approval a late definition of van 't Hoff (1905) that it is the "science devoted to the introduction of physical knowledge into chemistry with the aim of being useful to the latter"—a definition that comes too close to the defining of physical chemistry as merely a service industry to be acceptable to most physical chemists (22). A simple definition as the subject on the boundary of physics and chemistry, an obvious reply that many practitioners might now give if asked for a quick answer, fails to do justice to the size and complexity of the subject. A boundary is of a lower dimension than that of the bulk fields it separates and this definition does not describe adequately the bulky and sprawling field that is modern physical chemistry. It should be emphasised strongly that its practitioners create new chemistry as well as providing physical interpretations of existing chemistry and tools for use by their organic and inorganic colleagues. This innovative aspect has been particularly evident in the last fifty years with, for example, the growth of reaction dynamics, surface and polymer chemistry, and, most recently, nanochemistry. Let us therefore first see how the pioneers saw the new subject that they were creating.

Ostwald accepted Comte's hierarchical ordering of the sciences; chemistry had reached both the first stage of determining the facts, and the second of classifying them in an orderly way, but only physics had reached the third of determining the general laws that described the phenomena. He saw his new field as the way of bringing chemistry into the third stage. He called it "die allgemeine Chemie;" it was to constitute the general foundation for

the whole of chemistry. Vernon Harcourt, a leading British physical chemist and a pioneer of the study of reaction kinetics, had earlier called for the need for more attention in the universities to the teaching of the principles of chemistry and less concern with the accumulation of facts and the making of new organic compounds. He had written in 1875 (23):

we are occupied in amassing a vast collection of receipts for the preparation of different substances... which may be of no more service to the generalizations of the science [of chemistry], whenever our Newton arises, than, I conceive, the bulk of the stars were to the conception of gravitation.

It was a view of physical chemistry that is implicit also in Hinshelwood's book.

Ostwald, however, was to bring to the task of reform an authority and enthusiasm that Harcourt could never have mustered. His influence spread widely not only throughout Europe but also in the United States where research in the universities was beginning to be taken seriously. Servos lists 43 American academic chemists who studied at Leipzig between 1889 and 1904 (24). Among these was Wilder Bancroft who was in Leipzig from 1890-1892 and who was to spend his career at Cornell University. He had subscribed to Ostwald's vision of the proper position of physical chemistry as the foundation of chemistry, had probably also been infected by Ostwald's increasingly anti-atomic attitude, but was ultimately to try to lead the field into a backwater of his own making. He had little skill or enthusiasm for mathematics and specialized in branches of physical chemistry that could be handled qualitatively such as Gibbs's phase rule, Le Chatelier's principle for predicting the direction of displacement of chemical equilibria, and the study of colloids. All these, he maintained, were relevant to the practical and technological sides of chemistry. Lawrence Bigelow, at the University of Michigan (Leipzig, 1895-1898) later shared Bancroft's belief that physical and theoretical chemistry could be studied without mastering mathematics (25). But Bancroft's specialities were only minor parts of the field and not those of interest to most of its practitioners by the end of the century. Ostwald, in Europe, and Bancroft in America had noble aims for what physical chemistry might achieve but in the end neither succeeded in realizing them. In Ostwald's case his advocacy was undermined by his increasingly anti-atomic position, and in Bancroft's by his narrow view of what should be included in the field, which was expanding rapidly in the early years of the 20th century. The heart of the subject remained in the study of solutions and in

chemical kinetics, sustained by an increasing understanding of thermodynamics, but new interests were coming to the fore in the early years of the 20th century. Walther Nernst's attempts to determine equilibrium constants from purely thermal measurements led to what came to be called the third law of thermodynamics, the work of Jean Perrin and others led to the determination of Avogadro's constant and so attested to the real existence of atoms, the electric properties of molecules were yielding dipole moments and, it was hoped, would reveal something of the origin of the intermolecular forces. The new physics of X-rays and radioactivity had wide implications for the chemists as, for example, in Moseley's revelation of the importance of atomic number, and in the determination of the atomic structure of crystals by von Laue and the Braggs.

It seemed as if the physicists were taking over the subject and a second group of Leipzig graduates had different aims from those of Ostwald, and, even more obviously, from those of Bancroft. The leader here was Nernst, who had trained as a physicist and had been recruited by Ostwald, on the recommendation of Arrhenius, as an assistant in physical chemistry when Ostwald took the chair at Leipzig in 1887. Unlike the first American arrivals, he was a competent mathematician and physicist and saw in the new field a chance of interpreting chemistry in physical terms. His preferred name for the field was "die theoretische Chemie" since he saw it as parallel with "die theoretische Physik". Nernst's book on the new subject made clear that his aim differed from that of his mentor. He "laid particular emphasis" on the fact that his aim was "not so much the shaping of a new science, but rather the co-operation of two sciences which have been, on the whole, quite independent of each other"(26). It soon became clear that if either discipline were to surrender any of its independence it was to be chemistry. His book was followed a few years later by J.J. Thomson's identification of the electron, an event that led to an increased interest in physics throughout the chemical community. The tide had turned; Newton's programme of reducing chemistry to physics had been revived in a way that has continued to this day, although Nernst's preferred adjective of 'theoretical' was soon subsumed into 'physical,' with the former name becoming reserved for the mathematical and paper-and-ink aspects of the subject.

In America Nernst's physical approach was taken up by others trained by Ostwald, such as A. A. Noyes, first at MIT and then at Cal. Tech., and G. N. Lewis at Berkeley. Inevitably they ran into opposition from Bancroft whose

aims were so different from theirs and who had at his disposal the *Journal of Physical Chemistry*, which he had founded in 1896 and which often became a vehicle for his views. American and British chemists were usually ill-equipped mathematically to cope with this increasing dependence of their new subject on the physics of the early 20th century. In 1914 Farrington Daniels took his Ph.D. at Harvard in physical chemistry, knowing nothing of the differential calculus, and Noyes had to work hard to remedy his deficiency in mathematics. Those who followed them, such as Lewis (to a degree), and later Linus Pauling, were better prepared and unashamedly turned much of the field into a dependency of theoretical physics. The discovery of the electron, Rutherford's nuclear atom and the 'old' quantum theory of Bohr and Sommerfeld provided material for a start on the great problem of chemical bonding. Lewis, a chemist, and W.L. Kossel, a German physicist, introduced the idea of shared or transferred electrons as the key to the understanding of chemical bonds. Nevil Sidgwick, an Oxford chemist, who extended their ideas into other parts of organic and inorganic chemistry, was clear that a chemist must not borrow timidly from physics: "He must not use the terminology of physics unless he is prepared to recognise its laws" (27).

The understanding of valency and molecular structure came to fruition with the new quantum theory of 1925-1930. Within those few years the whole of the microstructure of chemistry was revealed, at least in principle, and Paul Dirac could famously declare in 1929 that (28):

The underlying physical laws necessary for a mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

It was no wonder that Einstein was said to have exclaimed that chemistry was too difficult to be left to the chemists.

The new quantum mechanics of Heisenberg and of Schrödinger in 1925-1926 led Heitler and London in 1927 to the first successful attack on the problem of atomic bonding in the hydrogen molecule but the adaptation of the new theory to chemistry owed more to the efforts of the chemists from 1931 onwards: Linus Pauling, Robert Mulliken, and physicists and mathematicians who had moved into quantum chemistry, such as John Slater, John Lennard-Jones and Charles Coulson. (In Germany the organic tradition was still strong and the

chemists contributed little to the new field.) Moreover when quantum mechanics allowed the measurements of the spectroscopists to be used to elucidate the details of molecular structure, a whole range of new experimental methods was added to the armory of the physical chemistry. All these developments came to be summarized under the name of 'chemical physics.' In America it was realized that Bancroft's journal was not the place to publish such material and the *Journal of Chemical Physics* was created in 1933, nominally by the physicists because of conservative opposition from some chemists; but from the outset the journal was used more by chemists than by physicists (29). At the same time Bancroft ceded the control of the *Journal of Physical Chemistry* to the American Chemical Society.

In statistical mechanics, the other main branch of theoretical physics, a similar but later fusion took place. R.H. Fowler's great book on *Statistical Mechanics* of 1929 was a physicist's book, founded on a prize essay on the atomic structure of stars, but in what, in effect, became its last edition in 1939 it acquired a chemist as co-author and was intended "for students of physics and chemistry" (30). The leading American books on statistical mechanics of this era were written by R.C. Tolman, whose title was Professor of Physical Chemistry and Mathematical Physics, and by the husband-and-wife team of J. E. and M. G. Mayer, an Associate Professor of Chemistry and a Lecturer in Chemistry, respectively (31). It seemed that the reduction of physical chemistry to physics was now a *fait accompli*, and, as the theoretical understanding of organic molecules advanced, that it would not be long before much of organic chemistry followed.

After World War II the trend continued. The armory of physical chemistry was strengthened by the invention of the laser, and its adaption to their ends by the experimental chemists, by the introduction of new techniques such as NMR, and by the invention of the computer, which was to change profoundly much of what the theoreticians had been able to do 'in principle' to what they could now do in practice. Many of Dirac's insoluble equations had become soluble. Moreover, both physicists and chemists discovered that their tools could now help with some of the problems of their biological colleagues and of the material scientists. Branches of these fields were added to the more traditional ones in laboratories of physical chemistry. Whatever coherence the subject might have had in the time of Ostwald has by now been totally lost, and, if we judge by the range of subjects offered today by seminar speakers in physi-

cal chemistry in Oxford, the physicists, biologists and material scientists are mixed with traditional physical chemists in research collaborations that would seem to defy any rational analysis.

### Reduction or Autonomy?

It is interesting to consider how far this increasing power of physical methods has encroached on the traditional belief of most chemists that theirs is an autonomous science. The basis of this belief is that chemists devised methods of analyzing and representing their science which preceded any of the physical understanding that followed from quantum and statistical mechanics (32). Moreover it was believed that such methods were, and still are, needed for the everyday practice of the chemists. Both statements are true. Chemists knew, for example, some years before the quantum mechanics of the 1920s, that an alkyl carbon atom had four bonds that were arranged tetrahedrally and that each of these bonds involved a pair of electrons. The use of such notions was necessary for chemists to be able to discuss their problems intelligibly. But did such representations imply any fundamental autonomy? Several arguments suggest otherwise. Thus the different modes of 'physical' and 'chemical' thinking are only one example of a hierarchy of representations. Let us take air as an example. To an aeronautical engineer air is a single substance,  $MW = 29.0$ , and the question of the entropy of mixing oxygen and nitrogen is, rightly, outside his (or her) conception. If, however, we want to separate oxygen and nitrogen by the fractional distillation of liquid air, we can talk to a chemical engineer who will tell us how to calculate the size of the distillation column from the number of theoretical plates we need. A chemist (and indeed many chemical engineers) might not be satisfied by such a crude representation and would turn for the design to calculations based on chemical potentials and partial molar enthalpies. A theoretical physicist could base his calculations on solutions of Schrödinger's equation to tell him the strength of the various intermolecular forces involved, cross-check these against the second virial coefficients of the gases, and then turn to statistical theories of liquids to tell him what these forces meant for the partial vapor pressures of oxygen and nitrogen. Where in this hierarchy one decides to work is a matter of choice, but it is hard to see anything here that enables the engineers to claim autonomy with respect to the chemist or the chemist with respect to the physicist since we now know how the theoretical plates of the engineer can be based on the thermodynamic representations of

the chemist and how these in turn can be based on the molecular calculations of the physicist.

Moreover, the boundaries are always changing. What one generation of chemists interprets as well as it can in terms of its own concepts, the next is able to reduce to a deeper physical understanding. Thus, to my knowledge, there has been no measurement of the heat capacities of gaseous oxygen and nitrogen for the last eighty years since everyone now has complete confidence in the greater accuracy of values calculated from molecular physics. In the 1920s chemists used a parameter called the 'parachor,' essentially a normalized molar volume, to attempt to decide between alternative possible molecular structures; its use was a more sophisticated version of Kopp's program sixty years earlier (33). But in the 1930s, when quantum mechanics allowed the interpretation of spectroscopic measurements, chemists had more effective means of determining molecular structures, and the parachor has vanished from their vocabulary. Similarly, in the 1930s, 1940s and 1950s there was no acceptable theory of the liquid state or of liquid solutions and attempts to create these led chemists, and some physicists, to introduce what were named lattice theories and the concept of a 'free volume,' and also to calculate the thermodynamic properties of liquid mixtures from 'solubility parameters'. Now that we understand more clearly the theory of liquids (that is, we can go from a knowledge of the intermolecular forces to a knowledge of the boiling point etc. of a liquid) no one hears anything more of lattices or of 'free volumes' or of 'solubility parameters' (34). Finally, Prout's photochemical dilemma of 1834 was resolved eighty years later, not by a new 'chemical principle' as he expected, but by a deeper understanding of the physics of quanta. Reduction is a one-way process; once it has been achieved it is never reversed. Within the physical sciences at least, there seems to be no limit in sight. But if we recall Maxwell's shrewd remark of 1872, such reduction of chemistry to physics does not mark the end of chemistry, for as soon as a successful reduction of one branch of chemistry has been achieved several new branches are created where, as he put it, modern physics must still "put her hand on her mouth." No one is suggesting that the chemist will ever be able to do without his own concepts, but he cannot expect that any one of these will survive indefinitely without a deeper microscopic interpretation, although many of the concepts will still be retained for day-to-day convenience. But as each chemical concept falls to the physicist another will be needed to make as much sense as possible of some new branch of chemistry, as Maxwell foresaw in 1872.

## Is There a Chemical Philosophy?

The defenders of chemical autonomy have argued recently that the need for chemists to retain their own language of interpretation justifies the creation of a distinctive chemical philosophy, separate from that of physics. This concern has led, for example, to a new journal devoted mainly to this enterprise (35). I have argued here that the continual movement of the boundary between what can now be reduced and what cannot yet be reduced shows that the distinction between physics and chemistry is not absolute, but a matter of contemporary convenience.

There is now a substantial literature on the difficulties facing reductionists of which only a small selection can be cited here (36). I believe, however, that there are four kinds of error that have been committed by some of the would-be chemical philosophers. The first and simplest is the citing of the views of past distinguished chemists and physicists that have now been overtaken by events, or the claim that some chemical concept is physically inexplicable when in fact a good explanation is now known. The ever-increasing power of the computer has often been underestimated. But beyond such simple cases of error is a second failure in not distinguishing history from philosophy, for no one would deny that chemistry has developed in the past its own criteria for judging explanations of chemical phenomena nor that it will continue to develop new ones in response to new developments in chemistry. But such purely 'chemical' explanations, as we have seen, have usually resulted eventually in a real physical understanding which goes a long way beyond merely setting out the relevant laws of physics that bind all chemical phenomena. A third confusion is the implication that a failure of present-day quantum mechanics or statistical mechanics to explain some experimental facts is a failure of the essential correctness of the theories. The history of the last eighty years tells us that such setbacks are temporary and not faults of principle. There is, I believe, still no reason to doubt the correctness of Dirac's analysis of the position. A fourth confusion arises from an excessively legalistic approach to the points under discussion, as, for example, in asking if water and  $H_2O$  mean the same thing. The biggest consulting fee that I ever received arose from a patent case that centered on the question: is carbon dioxide an organic or an inorganic molecule? Legally-minded scientists can make endless difficulties with such questions, but a competent chemist can usually see the problem and so deal with the question on sight. Perhaps the most notorious of such problems is 'Gibbs's paradox;' the mixing of two samples of the same gas leads to no

change of entropy, but the mixing of two different gases leads to a change of entropy whose size is quite independent of the degree of difference of the gases. Thus if we have two samples of hydrogen the answer can depend on whether one sample is ortho- $H_2$  and one para- $H_2$ , and whether we choose to recognize this difference. If we do, the answer is that there is a change of entropy, and if we do not or cannot, the answer is that there is not. The resolution of the paradox is subtle, within both classical thermodynamics and statistical mechanics (37); it does not, however, raise any questions that require a new philosophy. I would not dispute that both quantum mechanics and statistical mechanics do raise philosophical or metaphysical problems (one recalls Bohr's saying that anyone who is not shocked by quantum mechanics has not understood it), but it is hard to see anything specifically chemical in the questions they raise.

Where does this leave physical chemistry? It is today an untidy but vigorous subject, now so meshed with physics (and increasingly with biological problems that I am not competent to discuss) that formal distinctions are impossible. Chemists still use chemical explanations when these are convenient; the organic chemist will still decorate his formulas with curly arrows to signify electron displacements since this is the easiest way to convey the information that he seeks to impart. However other chemical concepts, such as the 'parachor,' the 'free volume,' and the 'solubility parameter,' vanish as the theoretical and physical chemists advance further into organic and inorganic territory and enlarge the domain of what, if challenged, they can reduce to recognized physical principles. But as they do this they find, as Maxwell foresaw, that new branches of chemistry are continually being created some of which, for the time being, are only in Comte's second stage of understanding. There is little danger of future unemployment for the well-trained physical or theoretical chemist.

## REFERENCES AND NOTES

- \* Award address presented at the Edelstein Symposium at the 236<sup>th</sup> American Chemical Society Meeting, Philadelphia, PA, August, 19, 2008, HIST 29.
1. W. H. Brock, "The Chemical Origins of Practical Physics," *Bull. Hist. Chem.*, **1998**, *21*, 1-11.
  2. The extension to chemistry came first through his manuscript of 1692, *De natura acidorum*, then more publicly in the queries attached first to the Latin edition of his *Opticks* of 1706, and more fully in the 3000-word essay that we commonly refer to as 'Query 31' of the last English edition. For attempted extensions of Newtonian



- ideas to chemistry and other fields, see [G. Cheyne], *An Essay Concerning the Improvements in the Theory of Medicine*, London, 1702; J. Freind, *Emmenlogia*, London, 1703 (physiology); James Keill, *An Account of Animal Secretion*, London, 1708; J. Freind, *Praelectiones chymicae*, London, 1709; S. Hales, *Vegetable Staticks*, London, 1727; S. Switzer, *An Introduction to a General System of Hydrostaticks and Hydraulicks*, London, 1729 (geology). Only the last was to prove seriously amiss; capillarity did not explain the presence of water high up in mountains.
3. J. W. Goethe, *Die Wahlverwandschaften*, Tübingen, 1809.
  4. *Gentleman's Magazine*, **1732**, 2, 1099-100.
  5. Ms. of W. Cullen, cited by A. Duncan, *Laws and Order in Eighteenth-century Chemistry*, Oxford University Press, Oxford, 1995, 5.
  6. H. Metzger, *Newton, Stahl, Boerhaave et la doctrine chimique*, Blanchard, Paris, 1930; A. Thackray, *Atoms and Powers: An Essay on Newtonian Matter Theory and the Development of Chemistry*, Harvard University Press, Cambridge, MA, 1970; A. L. Donovan, *Philosophical Chemistry in the Scottish Enlightenment*, Edinburgh University Press, Edinburgh, 1975; J. S. Rowlinson, *Cohesion: A Scientific History of Intermolecular Forces*, Cambridge University Press, Cambridge, 2002.
  7. U. Klein and W. Lefèvre, *Materials in Eighteenth-century Science*, MIT Press, Cambridge, MA, 2007.
  8. J. Davy, *Memoirs of the Life of Sir Humphry Davy, Bart.*, Longman, London, 1836, Vol. 1, 470; the passage is quoted by T. H. Levere, *Affinity and Matter: Elements of Chemical Philosophy, 1800-1865*, Oxford University Press, Oxford, 1971, 54.
  9. W. H. Brock, *The Atomic Debates: Brodie and the Rejection of the Atomic Theory*, Leicester University Press, Leicester, 1967.
  10. W. Prout, *Chemistry Meteorology and the Function of Digestion Considered with Reference to Natural Theology*, William Pickering, London, 1834, 49.
  11. M. J. Nye, *From Chemical Philosophy to Theoretical Chemistry: Dynamics of Matter and Dynamical Disciplines*, University of California Press, Berkeley, CA, 1993, 55.
  12. J. C. Maxwell, "On the Dynamical Evidence of the Molecular Constitution of Bodies," *Nature*, **1875**, *11*, 357-9, 374-7.
  13. J. C. Maxwell, "Manuscript on the Classification of the Physical Sciences," in P.M. Harman, *Scientific Letters and Papers of James Clerk Maxwell*, Cambridge University Press, Cambridge, 1995, Vol. 2, 776-82. The same comment appears in his posthumous article on 'Physical Sciences' in the 9th edition of *Encyclopaedia Britannica* in 1885.
  14. H. Helmholtz, "On the Modern Development of Faraday's Conception of Electricity," *J. Chem. Soc.*, **1881**, 39, 277-304. George Stoney had drawn attention to this point at the meeting of the British Association in Belfast in 1874 but his paper did not appear until 1881; G.J. Stoney, "On the Physical Units of Nature," *Philos. Mag.*, **1881**, *11*, 381-90.
  15. J.W. Servos, *Physical Chemistry from Ostwald to Pauling*, Princeton University Press, Princeton, NJ, 1990, 331-32.
  16. J. B. Morrell, "Research as the Thing: Oxford chemistry 1912-1939," in R. J. P. Williams, J. S. Rowlinson, and A. Chapman, Ed., *Chemistry at Oxford: a History from 1600 to 2005*, Royal Society of Chemistry, Cambridge, 2009, Ch. 5.
  17. D. Crowfoot [Hodgkin], C.W. Bunn, B. Rogers-Low, and A. Turner-Jones, "The X-ray Crystallographic Investigation of the Structure of Penicillin," in H.T. Clarke, J.R. Johnson, and R. Robinson, Ed., *The Chemistry of Penicillin*, Princeton University Press, Princeton, NJ, 1949, Ch. 5.
  18. J. C. Maxwell, *The Theory of Heat*, Longmans, Green, London, 1871, and nine further editions up to 1891; A. Ya. Kipnis, B. E. Yavelov, and J. S. Rowlinson, *Van der Waals and Molecular Science*, Oxford University Press, Oxford, 1996, 108-16; C. E. Moore, A. von Smolinski, and B. Jaselskis, "The Ostwald-Gibbs Correspondence: An Interesting Component in the History of the Energy Concept," *Bull. Hist. Chem.*, **2002**, *27*, 114-127.
  19. J. H. van 't Hoff, *Études de dynamique chimique*, Amsterdam, 1884; W. Ostwald, *Lehrbuch der allgemeinen Chemie*, Leipzig, 1885-1887.
  20. S. Glasstone, *Text-book of Physical Chemistry*, Macmillan, New York, 1940; W. J. Moore, *Physical Chemistry*, Longmans, London, 1972; P. W. Atkins, *Physical Chemistry*, Oxford University Press, Oxford, 1978; R. S. Berry, S. A. Rice and J. Ross, *Physical Chemistry*, Wiley, New York, 1980.
  21. C. N. Hinshelwood, *The Structure of Physical Chemistry*, Oxford University Press, Oxford, 1951.
  22. J. R. Partington, *An Advanced Treatise on Physical Chemistry*, Longmans, London, 1949-54, Vol. 1, preface, vii.
  23. A. G. V. Harcourt, Presidential Address to the Chemistry Section, *Rep. Brit. Assoc. Adv. Sci.*, **1875**, *45*, *Trans. Sect.*, 32-36. (24) Ref. 15, pp 54-55.
  24. Ref. 15, pp 54-55.
  25. S. L. Bigelow, *Theoretical and Physical Chemistry*, Duckworth, London, 1912.
  26. W. H. Nernst, *Theoretische Chemie vom Standpunkte der Avogadro'schen Regel und der Thermodynamik*, Enke, Stuttgart, 1893. The quotation is from the English translation of the first German edition, published by Macmillan, London, 1895, preface, xii. This was made by C. S. Palmer, then of the University of Colorado, who had worked with Ostwald from 1892-1893.
  27. N. V. Sidgwick, *The Electronic Theory of Valency*, Oxford University Press, Oxford, 1927, preface, 5. The state of understanding of valency under the old quantum theory is set out in this book, in an earlier one by G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, Chemical Catalog Co., New York, 1923, and in a General

- Discussion of the Faraday Society, at which Lewis, R. H. Fowler and Sidgwick gave the opening papers; *Trans. Faraday Soc.*, **1923**, *19*, 450-543.
28. P. A. M. Dirac, "Quantum Mechanics of Many-electron Systems," *Proc. R. Soc. A*, **1929**, *123*, 714-33.
  29. Of the first 100 papers in this journal, 74 came from chemistry departments, 16 from physics departments, and 10 from other laboratories or from ones not easily identified.
  30. R. H. Fowler, *Statistical Mechanics*, Cambridge University Press, Cambridge, 1929; R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics, A Version of Statistical Mechanics for Students of Physics and Chemistry*, Cambridge University Press, Cambridge, 1939.
  31. R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, Oxford, 1938; J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Wiley, New York, 1940. This book is dedicated to Gilbert N. Lewis, a chemist, and Max Born, a physicist.
  32. A. Shimony, "The Methodology of Synthesis: Parts and Wholes in Low-energy Physics," 399-423 in R. Kargon and P. Achenstein, Ed., *Kelvin's Baltimore Lectures and Modern Theoretical Physics: Historical and Philosophical Perspectives*, MIT Press, Cambridge, MA, 1987; E. N. Hiebert, "Discipline Identification in Chemistry and Physics," *Science in Context*, **1996**, *9*, 93-119.
  33. S. Sugden, *The Parachor and Valency*, Routledge, London, 1930.
  34. For lattice theories and free volumes, see "Liquids and solutions of Non-electrolytes," Fowler and Guggenheim, Ref. 30, Ch. 8; and "The Equation of State of Dense Gases and Liquids" in J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954, Ch. 4; and for solubility parameters, "The Heat of Mixing" in J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, Reinhold, New York, 1950, Ch.7.
  35. *Foundations of Chemistry*, Kluwer, Netherlands. Vol. 1 appeared in 1999.
  36. L. Sklar, "Historical Sketch" (Ch. 2) and "The Reduction of Thermodynamics to Statistical Mechanics" (Ch. 9), in *Physics and Chance: Philosophical Issues in the Foundations of Statistical Mechanics*, Cambridge University Press, Cambridge, 1993; G. K. Vemulapalli and H. Byerly, "Remnants of Reductionism," *Found. Chem.*, **1999**, *1*, 1-25; J. van Brakel, "Alleged Reduction of Chemistry to Physics," in *Philosophy of Chemistry*, Leuven University Press, Leuven, 2000, Ch. 5; A. Simões and K. Gavroglu, "Issues in the History of Theoretical and Quantum Chemistry, 1927-1960" in C. Reinhardt, Ed., *Chemical Sciences in the 20th Century*, Wiley-VCH, Weinheim, 2001, Ch. 3; D. Baird, E. Scerri, and L. M. McIntyre, Ed., *Philosophy of Chemistry: Synthesis of a New Discipline*, Springer, Dordrecht, 2006; E. Scerri, in "Quantum Mechanics and the Periodic Table," in *The Periodic Table*, Oxford University Press, Oxford, 2007, Ch. 9; M. L. Harris, "Chemical Reductionism Revisited: Lewis, Pauling, and the Physico-chemical Nature of the Chemical Bond," *Stud. Hist. Philos. Sci.*, **2008**, *39*, 78-90.
  37. J. W. Gibbs, *The Collected Works*, Longmans, Green, New York, 1928, Vol. 1, 166-68, from a paper of 1878. A detailed modern discussion is given by K. G. Denbigh and J. S. Denbigh, "Identity and Indistinguishability" in *Entropy in Relation to Incomplete Knowledge*, Cambridge University Press, Cambridge, 1985, Ch. 4.

### ABOUT THE AUTHOR

Address: Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, Great Britain. John Rowlinson was educated at Oxford University where he completed his D. Phil. in 1950. After a post-doctoral year at the University of Wisconsin, he taught chemistry at Manchester University from 1950 to 1960, when he was appointed to the chair of Chemical Technology in the Chemical Engineering Department at Imperial College, London. He moved to the chair of Physical Chemistry at Oxford in 1974 and retired in 1993. He was elected to the Royal Society in 1970 and served as its Physical Secretary from 1994 to 1999. He was a founding Fellow of the Royal Academy of Engineering in 1976, was elected an Honorary Foreign Member of the American Academy of Arts and Sciences in 1994, and knighted in 2000. His books include *Liquids and Liquid Mixtures* (1959), *Molecular Theory of Capillarity* (1982, with B. Widom), *Van der Waals and Molecular Science* (1996, with A. Ya. Kipnis and B. E. Yavelov), and *Cohesion: A Scientific History of Intermolecular Forces* (2002).

### WEBSITES, EMAILS

HIST: <http://www.scs.uiuc.edu/~mainzv/HIST>  
 HISTORY OF CHEMISTRY LISTSERVE: [chem-hist@listserv.uni-regensburg.de](mailto:chem-hist@listserv.uni-regensburg.de)  
 CHEMICAL HERITAGE: <http://www.chemheritage.org>  
 HISTORY OF SCIENCE SOCIETY: <http://www.hssonline.org>  
 HISTORY OF CHEMISTRY EuCheMs: <http://www.euchems.org>