

# BULLETIN FOR THE HISTORY OF CHEMISTRY

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## AN ADVANCED TREATISE ON PHYSICAL CHEMISTRY

VOLUME ONE

*Fundamental Principles*

*The Properties of Gases*

by

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**BULLETIN FOR THE HISTORY OF CHEMISTRY**  
**VOLUME 34, CONTENTS**

**NUMBER 1**

<b>2008 EDELSTEIN AWARD PAPER</b> <b>THE BORDER BETWEEN PHYSICS AND CHEMISTRY</b> <i>J.S. Rowlinson, Oxford University</i>	<i>1</i>
<b>J. R. PARTINGTON (1886-1965): PHYSICAL CHEMISTRY IN DEED AND WORD</b> <i>William H. Brock, University of Leicester, UK</i>	<i>11</i>
<b>HARRY S. MOSHER AND ARTHUR C. COPE, EARLY ORGANIC CHEMISTS WHO MENTORED WOMEN</b> <i>Anne M. Wilson, Butler University</i>	<i>21</i>
<b>GMELIN AND HIS <i>HANDBUCH</i></b> <i>Fathi Habashi, Laval University, Quebec City, Canada</i>	<i>30</i>
<b>THE DISCOVERY AND EARLY HISTORY OF CAROTENE</b> <i>Theodore L. Sourkes, McGill University</i>	<i>32</i>
<b>THE HISTORY OF OZONE. VII. THE MYTHICAL SPAWN OF OZONE: ANTOZONE, OXOZONE, AND OZOHYDROGEN</b> <i>Mordecai B. Rubin, Technion, Haifa, Israel</i>	<i>39</i>
<b>WOMEN CHEMISTS IN THE NATIONAL INVENTORS' HALL OF FAME: THEIR REMARKABLE LIVES AND THEIR AWARD-WINNING RESEARCH</b> <i>Mary Virginia Orna, College of New Rochelle</i>	<i>51</i>
<b>BOOK REVIEWS</b>	<b>63</b>

*The Cover... See p 11.*

## 2008 EDELSTEIN AWARD PAPER

# THE BORDER BETWEEN PHYSICS AND CHEMISTRY\*

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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.

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## 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).

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## J. R. PARTINGTON (1886-1965): PHYSICAL CHEMISTRY IN DEED AND WORD

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### Introduction

Today James Riddick Partington (1886-1965) is remembered as an historian of chemistry rather than as the significant British research chemist and textbook writer he was perceived to be in the 1920s and 1930s. Because his textbooks were specifically geared to the British secondary school and university systems, he is probably not well known in the United States as a textbook writer. Nor, in America or in Europe, is he remembered as a practicing physical chemist who made contributions to thermodynamics, the determination of specific heats, and to electrochemical theory. So, for example, he is not mentioned in Keith Laidler's *World of Physical Chemistry* (1993). Nevertheless, as an outstanding example and model of the chemist-historian, it is of interest to examine his career as a chemist. This profile falls into four sections: Partington's early career and his establishment as a London chemist; examples of his research in physical chemistry; the reasons for his failure to gain a Fellowship of the Royal Society; and, a summing up.

### 1. Early Career and Establishment as a London chemist

Partington was born on June 30, 1886, at the tiny coal-mining village of Middle Hulton to the south of Bolton. His father was a book keeper [i.e. in American parlance, an accounting clerk] in Bolton and his mother, from whom he took the middle name of Riddick, was the daughter of a

Scottish tailor. While he was still quite young his parents moved to the seaside town of Southport, to the north of Liverpool, allowing Partington the benefit of education at the Victoria Science and Art School that had opened in 1887 (1). Here his prowess as a mathematician and practical chemist must have been forged. He left school in 1901 when he was 15 because his parents moved back to Bolton. There he began to assist the town's Public Analyst, a post that must have involved the acquirement of the skills in volumetric and gravimetric analysis that were a hallmark of his later work. After a couple of years, and still in local government employment, he became a laboratory assistant in the town's Pupil Teachers Training College before finally becoming a clerk in Bolton's Education offices (2). During these five years between 1901 and 1906, he embarked upon an intensive course of part-time private study, developing his knowledge of foreign languages, and mathematics. In 1906, at the age of 20, he qualified for entry to the University of Manchester to read chemistry and physics. There he would have used the laboratories that Henry Roscoe had erected in Oxford Road in 1872. Among his teachers was Harold Baily Dixon (1852-1930), whose lectures, Partington recalled (3):

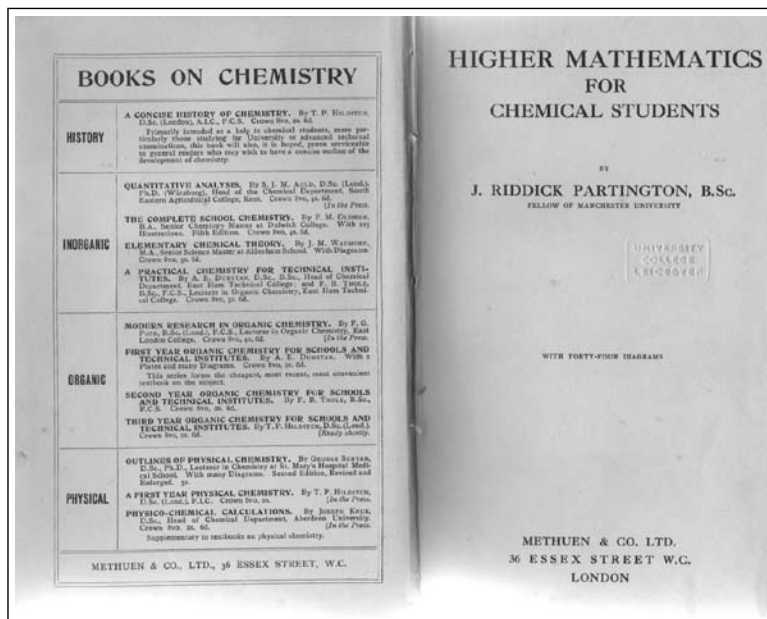
...were illustrated by striking experiments, were brilliant, stimulating, and in close contact with original sources and research. They were sometimes enlivened by touches of his characteristic humour." He was, however, "somewhat hampered by insufficient knowledge of mathematics.

In other words, although it must have been Dixon who taught Partington thermodynamics, the pupil felt he knew more than his teacher. Other instructors included W. H. Perkin Jr., but Partington was never taken with organic chemistry. His interest in the history of chemistry was engendered both by Dixon and Andrew Norman Meldrum (1876-1934), whose Carnegie Research Fellowship overlapped with Partington's undergraduate and postgraduate studies. Meldrum had already published an outstanding study of the atomic theory in 1906 and was planning to write a history of chemistry in his spare time. Although he emigrated to India in 1913, Meldrum and Partington remained in close contact (4).

On graduating in 1909 with first-class honors and being granted a teaching diploma, Partington was awarded a fellowship funded by the Manchester engineering firm of Beyer to begin postgraduate research with the physical organic chemist Arthur Lapworth, whose first research student he was (5). Astonishingly, within a year he had published two papers in the *Transactions* of the Chemical Society and a further four in 1911 before gaining his M.Sc.. The first paper, written with Lapworth, confirmed that the presence of water in the hydrolysis of an ester diminished the catalytic influence of hydrogen chloride. In the second paper he investigated ionic equilibria in electrolytes from a thermodynamic viewpoint. Effectively, this was a study of the literature on Ostwald's dilution law and the reasons strong electrolytes diverged from the law of mass action (6). Both these early papers show Partington's adeptness at thermodynamic reasoning and his commitment to research in the area of electrolysis, as the other four papers confirm. This was, by any measure, an astonishing output from a postgraduate student of 24.

Then, even more astonishingly, in 1911, and while still a graduate student, he published his first textbook, *Higher Mathematics for Chemical Students*. Nernst and Schönflies had published the first "math for chemists" text in 1898, which had appeared in English in 1900. Partington gave no reason for publishing his textbook and this is odd, given that John William Mellor, a previous student of Dixon's (and with his ardent support) had published *Higher Mathematics for Students of Chemistry and Physics* nine years earlier in 1902. Longmans had kept this in continuous print, so why the need for Partington's book? His dense introduction on scientific

method, which shows him already very familiar with the history of chemistry, provides no clue (7). All one can say is that Partington's text was shorter (272 pp) compared with Mellor's (600 pp) and that it was less detailed. Both texts remained rivals and in print until World War



Title page, *Higher Mathematics for Chemical Students*

II, following which Partington re-used much of the material as the introductory chapter of the first volume of his multi-volume treatise on physical chemistry (8). It is little wonder, then, that a reference from Dixon describes Partington as "one of the most brilliant students we have had during the last thirty years" (9).

Armed with his M.Sc. in 1911, Partington went to Berlin to study with Walther Nernst though, for reasons unknown, he did not complete a doctorate (10). When he arrived, he spoke German imperfectly, but was soon asked to give a seminar. He carefully wrote this out to read so as not to stumble, but Nernst kept interrupting, forcing Partington to speak without a script. This was Nernst's way of giving him confidence! Following the deduction of his heat theorem in 1906, Nernst had urged chemists to undertake a program of experimentation on the heats of reaction, specific heats, and temperature coefficients to test whether the theorem was an approximation to truth or a true third law of thermodynamics. In a sense this gave Partington his program of research in physical chemistry for the next thirty years: the testing of theory against very precise physical measurements.

Partington stayed in Berlin until 1913, working on the variations of specific heats of gases with temperature using an adaptation of the adiabatic expansion apparatus first developed at the University of Berlin by Otto Lummer and Ernst Pringsheim (11). He had to persuade Nernst that an improvement of the Berliners' complicated apparatus was needed, since Nernst "had a profound distrust of large, complicated, and expensive apparatus" (Ref. 10, p 2854). Nernst refused to speak to Partington for a couple of days before relenting, and providing him with his own resistance box and string galvanometer for the experiments. Partington used the change in resistance of a Wollaston platinum wire as a thermometer. The wire was placed in a copper balloon of 130-liter capacity, and the gas expanded through a stopcock.

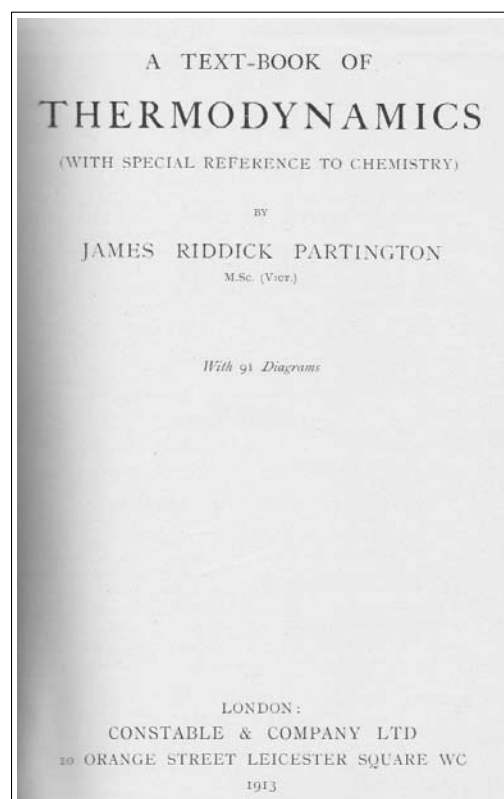
Although there was to be no Berlin D. Phil., Partington did publish five papers in German on his research in the Leipzig journal, *Physikalische Zeitschrift*. These were on the specific heats of air, carbon dioxide and chlorine, and on heats of vaporization and evaporation. While in Berlin he must also have drafted his next book on thermodynamics since it appeared immediately after he returned to England in 1913. The text was indebted to the insights of Nernst's *Theoretische Chemie* (1893), which had been translated into English in 1907. In this detailed account of classical thermodynamics the last two chapters dealt with Nernst's heat theorem and with energy quanta. A reviewer in *Nature* thought it tough reading for chemists unequipped with mathematics (12). Partington later described his thermodynamics as "a pioneer work, [as] nothing of its scope and character was then available in English" (13). This was true since Lewis and Randall's textbook did not appear until 1923, and the only major competitor was Nernst's.

Not surprisingly, he had been welcomed back to the University of Manchester in 1913 as a lecturer. One of his first students was Marian Jones, the daughter of a brickworks manager from Chester, whom he supervised for an M.Sc. degree on supersaturated solutions (14). Partington fell in love with his student and married her after the war on September 6, 1919. She became a chemistry schoolteacher before having two daughters and a son, Roger, who also became a physical chemist (15).

As soon as war broke out in 1914, Partington joined the army, only to be seconded to the Ministry of Munitions to work on water purification with the young physical chemist Eric K. Rideal. Later the two chemists turned to the question of the oxidation of nitrogen to form nitric acid and investigated the Haber-Bosch process that the

Germans were pursuing. This led to a book on the alkali industry in Rideal's series on the chemical industry in 1918 and, later, collaboration with Leslie Henry Parker on a history and analysis of the contemporary post-war nitrogen industry (16). For his war work Captain Partington was awarded the MBE (Military Division) (17). Outside his war work for the government, Partington managed to continue with thermodynamics, joining the Faraday Society in 1915. In 1919 he presented a major review of the literature on the dilution law to the Faraday Society, to whose Council he was elected that same year (18).

In 1919 he was appointed sole Professor of Chemistry at the East London College (renamed Queen Mary College in 1934). This Victorian enterprise had begun life as the People's Palace in 1887 as a place of entertainment and education for the poor living in the insalubrious conditions of London's east end. Its educational functions rapidly became more important than its leisure ones, and it was recognized by the University of London for degree purposes in 1915. Partington's immediate predecessor as professor of chemistry was John Hewitt (1868-1954), an organic chemist whose pupils had included Samuel Glasstone. Hewitt had designed a three-story laboratory in 1914, and Partington subsequently added a fourth story in 1934. The conditions for teaching and research were



Title page, *Text-Book of Thermodynamics*

hardly ideal. Accommodation and discipline were serious problems because of the influx of men from war service, and laboratory stocks of chemicals and equipment were dire (19). However, with the support of the college's administrators, and with small grants from the Chemical Society and the Department of Scientific and Industrial Research, Partington succeeded in establishing a modest research school with colleagues such as W. H. Patterson and D. C. Jones, and on the organic side, F. G. Pope, E. E. Turner, and H. D. K. Drew. College Calendars show that Partington's rate of publication not only outshone that of his chemistry colleagues, but those of colleagues throughout the college. Even so, when Michael Dewar inherited the Department in 1951 he complained at its shabbiness and unsuitability for research. The chemistry building was not demolished and rebuilt, however, until 1967 after Dewar had left (20). Partington chose to lecture exclusively on inorganic and physical chemistry. A compulsory one-term course on the history of chemistry that he introduced in 1919 was soon abandoned, though he revived it as an elective from 1945 onwards.

With the outbreak of World War II in 1939 Partington's department was evacuated to Cambridge, and Partington spent the war years in that city enjoying the facilities of the university's copyright library. Although arrangements had been made for the families of staff to be accommodated at Cambridge, Mrs Partington stayed behind at the family home in Wembley. Tragically, she committed suicide in March 1940, leaving Partington a widower for the remainder of his life (21).

On returning to the badly damaged East End of London in 1945, he more or less abandoned laboratory research and devoted himself instead to historical work and to the completion of his *Advanced Physical Chemistry*. He retired in 1951 to a house in Mill Road, Cambridge, and was looked after by an aged housekeeper. The house was filled with books from cellar to roof. According to Joseph Needham, he became something of a recluse, rarely stirring from his writing desk (22). At the end of 1964, following his housekeeper's retirement, unable to look after himself, he joined relatives in the salt-mining town of Northwich in Cheshire, where he died on October 9, 1965 (23).

## 2. Partington's Research in Physical Chemistry

Throughout the 1920s and 1930s, Partington made many other contributions to Faraday Society discussions. Although never elected President (probably because his

modesty and intense reserve deterred him from seeking such office), he served on Council almost continuously from 1919-38, and particularly on its Publications Committee on which he also served as representative for the American *Journal of Physical Chemistry* (24).

Partington's 1919 Faraday Society paper (Ref. 18) was a critical examination of theories of strong electrolytes. In particular, he examined Jnanendra Chandra Ghosh's theory of strong electrolytes published the previous year and showed that it was not in agreement with experiment (25). Ghosh assumed complete dissociation of strong electrolytes, with the majority of the dissociated ions arranging themselves into a crystal-like space lattice. Partington found the theory "startling" but deduced that it was incompatible with observed data. Ghosh, who was due in England to take up a research post at University College, London, was not present but sent in a reply. Unfortunately, Partington made an arithmetical blunder that enabled Ghosh to rebut the valid criticism Partington had made. Partington's response showed again that Ghosh's theory was based upon "guess-work." According to an appraisal of Ghosh by R. Parthasarathy in *The Hindu* for December 12, 2002, the criticism caused Ghosh to withdraw from being elected FRS! This is obviously based upon a misconception, but may, perhaps, have been an anti-imperialist story told by Ghosh in later years (26).

Partington's other principal research was on the temperature dependence of specific heats. As we have seen, this interest was initiated by Nernst while Partington studied in Berlin. Once settled at Queen Mary College, Partington took up this research again. Whereas Nernst had been interested in the determination of specific heats at low temperatures because of quantum effects, Partington was interested in their behaviour at high temperatures. There were obvious industrial applications in the automobile and refrigeration industries, as well as the need for specific heat data in designing industrial plants involving gases. Instead of measuring specific heats by adiabatic expansion, as he had in Berlin, he determined  $c_p/c_v$  from the velocity of sound by using a modified Kundt tube, as Dixon had recently done at Manchester (27). He initially determined values for air and some simple gases, using a modified electrically-heated Kundt tube to determine the velocity of sound at different temperatures. Later, with W. G. Shilling, the son of the owner of an engineering firm, he developed a modified and improved form of the apparatus to enable measurements up to 1000°C. The joint work was summarized in 1924 as a "coherent and critical account of the state of our knowledge" (28).



Work on specific heats led Partington into an interesting controversy with the young Mrs Ingold. In 1921 Hilda Usherwood, the future wife of Christopher Ingold, working with Martha Whitely at Imperial College, began an investigation of tautomerism by using the variation of specific heats with temperature as a guide to changes of equilibria. Her two papers on “the detection of tautomeric equilibria in hydrocyanic acid” and “specific heats of gases with special reference to hydrogen” (the latter with Ingold) appeared in 1922 (29). In 1925, a year after he and Shilling had published their book, *The Specific Heats of Gases*, Partington challenged Mrs Ingold’s results (30). He claimed her values for hydrogen had been only approximate, that her HCN was impure, and that her values for the hydrogen cyanide-hydrogen isocyanide equilibrium were due not to thermal effects accompanying isomeric change, but polymerization, which Hilda had ignored. She replied, standing her ground; and Partington stood his. But Mrs. Ingold won the day by showing that Partington’s evidence for association was valid only for a very small part of the temperature range studied (31). In his biography of Christopher Ingold, Kenneth Leffek suggests that Partington’s criticisms were weak and that (32):

...in 1925 Partington felt that it was fashionable to attack someone with the name Ingold, in view of all the activity in the Chemical Society and in the pages of *Chemistry and Industry* concerning the theory of chemical reactions.



Partington demonstrating before the Duke and Duchess of York (later King George VI and Queen Elizabeth) May 15, 1928 (courtesy Queen Mary College)

This is unfair. Partington’s 1925 paper, based upon an M.Sc. thesis by his pupil M. F. Carroll, merely noted that measuring the specific heats of HCN by a different procedure from Mrs. Ingold’s gave different results and suggested why this might be so. It is clear, in any case,

that the Ingolds did not hold the controversy against Partington, since Christopher Ingold signed Partington’s Royal Society application in 1926.

### 3. Partington and the Royal Society

Partington had read three papers on specific heats to the Royal Society in the years 1921-1925, and these had been communicated by Dixon and the physicist, J. A. Harker. He was first put up as a candidate for its Fellowship in 1927 during the Presidency of Ernest Rutherford (33). By 1924, when the book on specific heats appeared, Partington had published some eleven papers on specific heats and could be considered the British expert on the subject. Given Partington’s publication record and his prominence in the Faraday Society, why was his candidature a failure?

In the 1920s election to the Fellowship was by recommendation in writing by six or more Fellows, of whom three had to be recommending from personal knowledge. A printed list of candidates was circulated to all the Fellows each January. The Society’s Council then selected twenty of the names by ballot and recirculated its proposals, which were then voted on by those Fellows present at the next ordinary meeting. Proposals were allowed to stand for four further years after initial failure, following which the candidate could be proposed again by new sponsors (34). Election of Partington having failed the first time in the years 1927-31, he was proposed a second time from 1935 to 1939. The first two signatories were conventionally understood to be the proposer and seconder, and in Partington’s case they were the physical chemists Herbert Brereton Baker and Frederick George Donnan in 1927, and Eric K. Rideal and Donnan in 1935. All three sponsors had connections with Partington through his wartime activities and were prominent in the affairs of the Faraday Society.

Baker and Donnan, however, did a poor job of the nomination, merely stating that Partington was “distinguished for his research work in inorganic and physical chemistry,” citing a few papers (but omitting his many contributions to the Faraday Society), and stating that there were 52 other papers as well as books on thermodynamics, inorganic chemistry, mathematics for chemists, and five other books. Despite this lack of specificity, the nomination attracted many additional distinguished chemists, who added the support of their signatures.

*Sir Thomas Henry Holland*, geologist, member of the Munitions Board 1917, Rector Imperial College

*Thomas Martin Lowry*, physical chemist at Cambridge

*Nevil V. Sidgwick*, physical chemist at Oxford

*T. Slater Price*, Director British Photographic Research Association, former physical chemist at Birmingham Municipal Technical School

*Christopher K. Ingold*, physical organic chemist at Leeds

*James C. Philip*, physical chemist at Imperial College

*William Jackson Pope*, organic chemist at Cambridge

*Frank Lee Pyman*, Director Boots Pure Drugs Co, and former physical chemist at Manchester College of Science and Technology

*Alexander Scott*, inorganic chemist, Director of Laboratories at British Museum

*Kennedy Orton*, physical organic chemist at University of Wales (Bangor)

It is curious that Dixon (who died in 1930) was not one of the signatories.

That proposal having failed, Partington was sponsored again in 1936 during the Presidency of William H. Bragg. This time the sponsors, led by Rideal and Donnan, were more elaborate in extolling Partington's virtues as a scientist (35):

The candidate has published numerous scientific papers and several valuable text books since 1910. Of the latter, one on higher mathematics for Chemical Students, the other on Inorganic Chemistry are in their fourth edition, and one on Thermodynamics is in its second edition. His work on the specific heat of gases by classical methods is well known, and several of his determinations are accepted internationally. He has also published two series of papers, one on dielectric polarization and the other on concentration cells which are records of careful and accurate work in physical chemistry. He has investigated analytically a number of unusual inorganic reactions and elucidated their mechanisms. There have been published in the *Journal of the Chemical Society* and the *Transactions of the Faraday Society*. His interests in the history of Chemistry are exemplified by a series of papers and a research monograph of unusual character.

This was signed by:

*Eric K. Rideal*, physical chemist at Cambridge

*F. G. Donnan*

*James C. Philip*

*Alfred C. Egerton*, physical chemist (thermodynamics) at Imperial College

*John Theodore Hewitt*, chemist and inventor; Partington's predecessor at Queen Mary College

*Henry T. Tizard*, physical chemist, Rector of Imperial College

*Arthur John Allmand*, physical chemist at King's College, London. Further support was gained when four physicists added their names in 1938:

*Harold Roper Robinson*, professor of physics and historian of science at Queen Mary College

*William Wilson*, mathematical physicist at Bedford College, London

*Neil Kensington Adam*, physical chemist at University of Southampton

*Edward N. da C. Andrade*, physicist at University College, London

As both proposals show, my initial assumption that being a writer of textbooks and history of science counted against Partington does not seem to have been the case. On the other hand, Partington's research was hardly innovative; rather it relied upon perfecting others' work, or what T. S. Kuhn aptly described as "normal science." Partington was not blazing any new trails in his research such as those being undertaken in the 1920s in quantum chemistry, kinetics, and spectroscopy. A comparison with Mellor, another encyclopedic chemist, is especially apt since he was one of the two chemists elected in 1927 in preference to Partington. Mellor was also largely self-taught before gaining his first degree at the University of Otago in New Zealand by part-time study (36). Like Partington, he had then joined the University of Manchester, where he wrote his previously mentioned mathematics for chemists and his *Chemical Statics and Dynamics* (1904). Unlike Partington, however, he did not become a university teacher; instead he used his deep knowledge of physical chemistry to transform the ceramics industry of Staffordshire. Although, like Partington, he continued to publish excellent textbooks on inorganic chemistry, including the multi-volume *Comprehensive Treatise on Theoretical and Inorganic Chemistry* (1922-1937), it was the originality of his research in ceramics chemistry, where he opened up an economically important industry to scientific scrutiny, that brought him the FRS in 1927. Similar points can be made about originality for all the other chemists who were successfully elected FRS between 1917 and 1939 (See Table).

#### 4. Conclusion

Throughout the 1920s and 1930s Partington regularly published five or six papers a year, either independently or with students, on a variety of topics in inorganic and

**Table 1: Chemists elected FRS 1927-31 and 1936-40**

1927	James P. Kendall (1889-1978), physical chemist Joseph William Mellor (1869-1938), ceramics chemist
1928	Walter Norman Haworth (1883-1950), organic chemist Robert Whytlaw-Gray (1877-1958), inorganic chemist
1929	Cyril N. Hinshelwood (1897-1967), physical chemist
1930	Eric K. Rideal (1890-1974), physical chemist
1931	Ian Morris Heilbron (1886-1959), organic chemist
1936	Joseph Kenyon (1885-1961), organic chemist Ronald G. Norrish, physical chemist
1937	George R. Clemo (1889-1983), organic chemist William Hume-Rothery (1899-1968), metallurgist William Edward Garner (1889-1960), physical chemist
1938	Sir Robert L. Mond (1867-1938), industrial chemist George Ingle Finch (1888-1970), physical chemist
1939	James Irvine Masson (1887-1962), physical chemist Eustace E. Turner (1893-1966), organic chemist
1940	William T. Astbury (1898-1961), crystallographer Charles F. Goodeve (1904-1980), physical chemist Patrick Linstead (1902-1966), organic chemist

physical chemistry. All his work was characterized by meticulous experimentation and the gathering of quantitative information whenever possible. It seems to me that the whole of Partington's research was devoted to the appraisal of deductions made from thermodynamic equations and comparison between theory and experiment with the aim of perfecting theory and the creation of sound and accurate physical constants and measures. For example, he worked prolifically on solubility effects, and devised and developed a new form of electric vacuum furnace in 1925 to investigate high temperature reactions (37).

Partington had well over 70 collaborators between 1914 and 1951, when he retired. Among his pupils were Frederick E. King, later a professor at the University of Nottingham before he entered the chemical industry; Arthur Israel Vogel, the analytical chemist and textbook writer; and Raymond J. W. Le Fèvre, who was not impressed (38). It was said of Harold Dixon that he was singularly reticent and was "difficult to penetrate within his outer ring of electrons" (39). The same was true of

Partington, though one obituarist thought him reserved rather than reticent and that he was "extremely modest" (40). He was a small man with a military bearing, Teutonic, and seemingly testy in manner. Conservative in attire until quite late in life, he still dressed with a wing collar. He spoke very quietly, so that students and fellow academics often found his lectures inaudible, and therefore boring.

His working methods were those of the Victorian and Edwardian scholar. He wrote neatly (or typed) on the backs of proofs, which he then cut up and rearranged as necessary by gluing them together. Patient printers and publishers allowed him to tinker with several proofs until he was satisfied with their accuracy. His encyclopaedic four-volume *Physical Chemistry* (1949) was compiled at Cambridge during the war and kept in a suitcase, which he carried into underground shelters to work on during German air raids.

Partington was a highly competent practical and theoretical chemist and gifted (as Hartley remarked in the

*Dictionary of Scientific Biography*), with an encyclopedic mind; but although the problems he tackled were often intricate, they could be rather dull normal science. He seems to have lacked the ability, or the desire, to tackle frontier problems. Undoubtedly he gave excellent training to several generations of chemists (including several from India) who went into teaching or industry, while his texts offered great value to generations of school and university chemistry students. Nevertheless, just as his four-volume *History* is an indispensable aid to our discipline, his chemistry papers, his *Higher Mathematics for Chemical Students*, his *Thermodynamics*, his *Specific Heats of Gases*, and his huge *Advanced Physical Chemistry* remain monuments to the development of physical chemistry since the 1900s. What Partington wrote of Nernst in 1953 is equally a memorial to his own work as a physical chemist (41):

A physical chemist is at some disadvantage, compared with the organic chemist, since new compounds remain, but new [physical] measurements soon give way to newer, and sometimes better, ones. The pioneering investigations are soon forgotten, and results which in their time were highly important and significant are amplified and revised by later workers, who not infrequently reap the benefit of newer techniques which make their task easier than that of the earlier pioneer experimenters, whose contributions to science tend to be overlooked.

### ACKNOWLEDGMENTS

I am grateful to Lorraine Scheene, archivist at Queen Mary College; and, for information on Partington's relations with the Royal Society, to Nichola Court, archivist at the Royal Society, and Sir John Rowlinson.

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### ABOUT THE AUTHOR

William H. Brock, Professor Emeritus of History of Science at the University of Leicester, resides at 18 Greenway Gardens, Pattingham, Wolverhampton WV6 7DH, UK. He received the Dexter Award for History of Chemistry in 1995. He is the author of *The Norton History of Chemistry* (1993), *Justus von Liebig, the Chemical Gatekeeper* (1997), and *William Crookes (1832-1919) and the Commercialization of Science* (2008).

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## HARRY S. MOSHER AND ARTHUR C. COPE, EARLY ORGANIC CHEMISTS WHO MENTORED WOMEN

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Anne M. Wilson, Butler University

In his 1973 Cope Award address, Robert Burns Woodward jokingly referred to a target molecule as “bigboobsenone” (1). That such humor was acceptable “...reflects the fact that his chemical audiences even into the 1970’s were preponderantly male and such persiflage seemed still at times to be condoned (2).” Woodward, an acknowledged pioneer of American synthetic organic chemistry, had a single woman, Elga Wasserman, complete a Ph.D. in his group, and she subsequently left the field of chemistry (3). That Woodward was able to make such a crass remark in an award address indicates that the attitudes of at least some organic chemists have not been particularly welcoming to women.

The number of female scientists has increased in all of the disciplinary areas of chemistry, including the subdiscipline of organic chemistry (4). However, while female U. S. citizens represent 25% of the doctoral graduates in 2005 (5), none of the organic doctoral graduates from 2005 were women (6). Between 1997-2006, 13.7% of the Ph.D.s in organic chemistry were awarded to women (6). There are and have been organic chemists who support and mentor women. The history of such support has not been fully described or appreciated, even by women in the field.

Many areas of chemistry have prominent women who were early contributors. Female crystallographers can look to Kathleen Lonsdale, Dorothy Hodgkin, and Rosalind Franklin. Female radiochemists have Marie Curie and Irene Joliot-Curie. Biochemists acknowledge Icie Hoobler, Gerty Cori, and Gladys Emerson among

others. Organic chemistry has no acknowledged female “founding mothers,” although there were women making contributions in the field. Many of the accepted “founding fathers” of synthetic organic chemistry had few women in their research groups.

How chemists, male or female, of any subdiscipline are encouraged or supported has not been well documented. Examination of the memoirs of organic chemists can lend some insight into how this encouragement took place, both in terms of how they were encouraged and how they supported others. Hans T. Clarke describes working with women in industry during World War I (7):

In the summer of 1918, Mees charged me with the organization of a laboratory for the preparation of research organic chemicals to meet the urgent needs of universities, whose stocks had become depleted owing to the impossibility of securing supplies from Germany. As at that time almost all the relatively few American-trained organic chemists were actively employed in government service, the laboratory was staffed by young women, all recent college graduates who had majored in chemistry. These girls displayed immense enthusiasm, cooperativeness, and application, but in general were not well adapted to preparative work on a large laboratory scale; accidents were alarmingly frequent, and it proved impossible to assign more than two preparations to each girl for simultaneous operation. After the first year, therefore, replacements and additions to the group were made with men.

Egbert Havinga, an organic chemist at the University of Leiden from 1946-1979, describes working with women differently (8):

At the risk of being considered seriously biased, I would like to report that although only a small number of women choose to study organic chemistry, this in my experience is compensated by the excellent capacities of those few in both experimental research and theoretical exploration..

The male culture of synthetic organic chemistry has not gone unnoticed by all. Carl Djerassi noted in his autobiography (9):

...the American organic chemistry edifice has only two main pillars: physical organic chemistry, with major emphasis on mechanisms of organic reactions; and synthetic organic chemistry, which has become the overriding field in terms of attention and prestige. This includes both 'macho' syntheses of exceedingly complicated natural products and the development of new synthetic methods and reagents.

Female organic chemists may not have enjoyed any less support than in the other subdisciplines of chemistry. Yet, why do percentages of doctoral degrees earned by women in organic chemistry continue to lag behind compared to the overall chemistry Ph.D.s? Is it due to few female role models, overt or concealed sexism, a paucity of research groups where women are encouraged, or a combination of these elements? In 2006 less than one third of the earned doctorates went to female organic chemists, which is still significantly more than in the previous ten years (4, 6). In that same year almost half of the earned doctorates in biochemistry and analytical chemistry were awarded to women (4, 6).

The total percentage of women in the field of chemistry at all education levels was 7.0% in 1947, and in the subfield of organic synthesis in 1956-58, 4.73% of those employed full-time were women (10). While Woodward's research group graduated a single woman, other groups did include a few women. For example, William S. Johnson had a few female students and post-docs (14 of 339 co-workers), and he did acknowledge them as coauthors on his publications (17 of 269) (11). By the last ten years of Djerassi's active research career in the 1980s, about one third (29%) of his publications had female coauthors, although many of Djerassi's later publications could be considered to be biochemistry, an area ostensibly more welcome to women. While there were no women who were faculty members at Ph.D.-granting institutions in the early years of organic chemistry in the United States (10), there were men who supported women to become

top-flight researchers. Some of these men, notably John D. Roberts, describe their professional mentoring relationships with women in their memoirs (12).

The shortage of peer and mentor support for female organic chemists can only partially explain the current relative dearth of women in synthetic organic chemistry. As the role of the research advisor can be crucial (13), some male organic chemists have effectively and consistently mentored women, and high percentages of women were present in their research groups. Arthur C. Cope and Harry S. Mosher are two such organic chemists who valued the contributions of their female research colleagues. The time period of Cope's research was between 1934 and 1966, and Mosher maintained his research group from 1942 to 1980.

### Backgrounds of Cope and Mosher

Arthur C. Cope earned his B.S. in chemistry from Butler University in 1929, and Harry S. Mosher completed a B.S. in chemistry from Willamette University in 1937. These two institutions were founded with remarkably similar missions. Butler was founded in 1855 on the audacious vision to provide interracial coeducation to aspiring students (14), and Willamette, founded in 1842, was one of the early coeducational institutions (15). Butler was the third school in the nation to award a bachelor's degree to a woman, and Willamette's first



Arthur C. Cope, courtesy MIT Museum



graduate was a woman. While it is doubtful that either man encouraged women because of the progressive traditions espoused by their undergraduate institutions, it is remarkable that their undergraduate experiences were at such similar institutions.

Both Cope and Mosher performed their graduate work at state schools, Cope at the University of Wisconsin and Mosher at Pennsylvania State University, with prominent organic chemists. Cope obtained his Ph.D. in organic chemistry under S. M. McElvain in 1932. Two women, Marguerite Kuehn and Mary E. Englert, were coauthors on McElvain's publications. It is possible that Cope may have overlapped with each of these researchers. Mosher earned his Ph.D. in 1942 under the direction of Frank C. Whitmore. Whitmore worked with four different women coauthors, Frances H. Hamilton, Gladys E. Woodward, Harriet A. Southgate, and his wife Marion Gertrude (Mason) Whitmore. There were two other women, Dorothy Quiggle and June Ruth Pfister, who worked in the research groups of collaborators who also appeared on Whitmore's publications. Women did not work in Whitmore's research group beyond 1934, before Mosher began his graduate work. Despite these apparently positive interactions with female co-workers, it appears that McElvain and Whitmore did not have any female researchers in later years. Mosher's brother, William A. Mosher, also earned his Ph.D. in organic chemistry with Whitmore and was chair of the Chemistry Department at the University of Delaware from 1946-1969. William published articles with only two women (Sylvia A. Farnum and Sally McNeill Lemke).

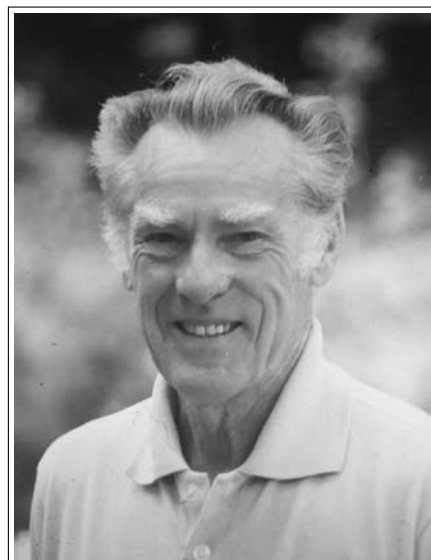
In addition to his training at Wisconsin, Cope was a National Research Council postdoctoral fellow at Harvard, where he worked with E. P. Kohler, who also had a few female colleagues. Kohler published papers with Gertrude L. Heritage and Marie Reimer as coauthors while teaching at Bryn Mawr College, an all women's school. In addition, Kohler published with Alice Graustein in 1922 after he moved to Harvard University (16).

In 1934 Cope took an appointment at Bryn Mawr College. Full-time positions were difficult to find at Ph.D.-granting institutions in the 1930s (17), and this appointment began as a temporary position. Cope's official biographies (18) only acknowledge two female graduate students as coauthors on most of his Bryn Mawr work. In fact, he worked with five female Ph.D. students and one laboratory demonstrator (or lecturer or research assistant, depending on the appointment for that year),

who was misidentified as a graduate student. He also worked extensively with undergraduate students, and eight of them became coauthors on publications. During his brief time at Bryn Mawr, from 1934-1941, Cope was able to amass a significant record of scholarly publication. This positive experience with female students at an all women's school likely made his laboratories welcome to women throughout his career.

As was common for the time, both Cope and Mosher contributed to the World War II effort through organic chemistry research, Cope at Columbia University (1941-1945) and Mosher at Penn. State (1942-1947) as an assistant professor. Each of them moved to their final institutions in the mid-1940s, Cope to the Massachusetts Institute of Technology in 1945, where he spent most of his career as department chair, and Mosher to Stanford University in 1947. At these schools, they were each supportive of all the researchers in their laboratories, undergraduates, graduate students, and postdoctoral fellows, regardless of gender.

Both Cope and Mosher are recognized for reagents or reactions named after them. Cope's research is not-



Harry S. Mosher  
courtesy James D. Morrison

ed for the Cope Rearrangement and the Cope Elimination (19). As a research scientist, he authored or edited over 300 professional articles and patents. Mosher is most widely known for the chiral derivatizing agent that bears his name (20). As a research scientist, Mosher authored over 180 scholarly publications and patents. The American Chemical Society, either nationally or locally, has established awards in each man's name. Cope's life and work have been well documented (18). However, in addition to his named reactions, he is best known to contemporary organic chemists for the two awards that bear his name, administered by the American Chemical Society: the Arthur C. Cope Award and the

Arthur C. Cope Scholar Award (21). A brief biography of Mosher is available (22), and he has been honored with the Carol and Harry Mosher Award through the Santa Clara Valley Section of the American Chemical Society (23). Cope performed research with a total of 27 female researchers, and women were listed as coauthors on 55 of his scholarly articles. Mosher worked with 26 female researchers, and women are listed as coauthors on 57 of his publications.

At MIT, through the late 1960s, only about 2% of the undergraduate population was female (24). By 1963, when other coeducational institutions were awarding doctorates to women in the sciences at levels as high as 28%, MIT did not even make the list of the top 25 institutions for awarding doctorates to women, even though they were ranked fourth overall (10). By comparison, in 1963 Stanford was 19<sup>th</sup> on the list for awarding doctorates to women, while it was ranked 16th for awarding doctorates overall (10).

### The Women

The women who passed through the Cope and Mosher laboratories are listed in Tables 1-3. Women who left these research groups were often able to continue work as chemists or in other areas of science, and many are still active chemists today.

During his years at Bryn Mawr College, Cope was able to establish relationships with pharmaceutical companies to support his research. He was able to secure research associate positions sponsored by Sharp and Dohme, through which he supported several women, the first being Evelyn Margaret Hancock. These sponsored associates continued through much of his career. Hancock earned her Ph.D. at the University of Illinois in 1936, and the demonstrator and research associate positions were her first professional positions. Hancock was supported by Sharp and Dohme in this manner through 1945.

Cope had connections with other pharmaceutical companies as well and was able to persuade these companies to hire his graduates into research positions. Dorothea (Heyl) Hoffman was the first female laboratory research scientist hired by Merck (25). She worked there until 1956, when she was married and was subsequently forced to leave the laboratory—a common practice at the time. After her career at Merck, Hoffman became a chemistry consultant and then a high school chemistry teacher. American Cyanamid, acquired by Wyeth in 1994, employed Corris Maybelle Hofmann (26),

Elizabeth MacGregor Hardy (27), and Mary Elizabeth Wright. Elizabeth Mary Osman worked in a variety of industrial and academic positions after earning her Ph.D. (28). Osman worked as a biochemist at Hercules Powder Co., Corn Products Reference Co., Michigan State University, the University of Illinois, and the University of Iowa. She was the first woman to be elected the chair of the Carbohydrate Division of the American Chemical Society (1966-67) (29).

Of the eight undergraduate women from Bryn Mawr College who worked with Cope, at least four of them continued in the sciences. Ruth Rogan earned a Ph.D. at the University of Chicago in 1949. Norma Finkelstein completed a Ph.D. in physiology at New York University. Kathryn Hoyle started graduate school at the University of Wisconsin, working with Homer Atkins. Esther Hardenbergh earned her Ph.D. in physiology from Harvard University in 1950.

Postdoctoral associates from Cope's years at MIT also went on to a variety of positions. Marion Burg became an instructor in chemistry at Queens College for two years before taking a permanent position at DuPont (30). Patricia Trumbull and Ruta Bly were given the opportunity to do research while their husbands were postdoctoral associates in Cope's laboratory. Bly continued research work with her husband. Elizabeth P. Burrows worked as a research associate at Oakland University and is currently working at the U. S. Army Biomedical Research & Development Laboratories at Ft. Detrick (31).

Cope's Ph.D. students from the MIT years were also successful in fields of education, chemistry, and the corporate environment. Emily Wick, the first woman tenured at MIT in 1963, was selected by the MIT president in 1965 to improve the quality and graduation rate of women in her position as Associate Dean of Student Affairs (24, 32). Phylis Moore was employed at Polaroid Corp. Mary Youngquist was an NIH predoctoral fellow while at MIT, one of few women at the time, and took a position with Eastman Kodak after a postdoctoral stint at the University of Minnesota (33). Beverly Pawson worked her way up to associate director of chemical research at Hoffman-La Roche after a postdoctoral position at the Mellon Institute (34).

In addition to his researchers, other women appeared on Mosher's publications. He coauthored a few publications with his wife, Carol Walker Mosher, a professional chemist (35). This was a temporary situation until she obtained a permanent position at SRI International.

Three women, Geraldine J. Fuhrman, Jane Fail Wakely, and Hanna S. H. Yuan, appear as coauthors on Mosher papers, as they worked in the research laboratories of collaborators (Fuhrman and Wakely in the laboratory of Fuhrman, Yuan in the laboratory of Robert Bau).

In addition to earning her Ph.D. with Mosher in 1959, Lois J. Durham was hired by Stanford in a permanent position as an NMR spectroscopist in 1961 (36). Mosher recognized Durham as a coauthor on numerous publications and in the official history of the department (37):

Although she is not a member of the faculty, Lois Durham merits recognition as the longtime manager of the Nuclear Magnetic Resonance Laboratory. After receiving her Ph.D. in organic chemistry and spending a few years at SRI International, she accepted the position of managing the NMR lab. For 39 years she has trained undergraduate and graduate students in the operation of the instruments, which now number five. She is an invaluable member of the Chemistry Department.

Mosher's postdoctoral students were a very international group. Lotte Fikentscher was a researcher at the Max Plank Institute for Medical Research. Janet Samartino Plummer worked first for Parke-Davis and then Pfizer. Theresa M. Williams earned a position at Merck. Robyn L. Crumbie is a senior lecturer at the University of Western Australia.

The female Ph.D. students from the Mosher laboratory also continued work in chemistry. Elizabeth Parker Burrows also worked with Cope, and she is the one woman whose training was shared by the two men. Dorothy M. Feigl performed postdoctoral research at North Carolina State University and subsequently took a position at St. Mary's College (Notre Dame). Feigl has moved into administration at St. Mary's, serving as Vice President and Dean of the Faculty for fourteen years, before recently returning to chemistry (38). Betty McFarland stayed on at Stanford and work with Harden M. McConnell after her graduate work (39). Joel Schmiegel taught for a while at Marian College in Indianapolis, IN prior to the birth of her second child (40). Betty Ann Winter Stephenson worked in industry and taught at the University of Santa Clara and at Case Western Reserve University (41). Carolyn Lucille Heutter Fisher took a position at McCormick and has published extensively in the area of flavor chemistry (42). Natalie Lewis McClure took a postdoctoral position with Syntex, who then hired her into a permanent position. Alexandra Baran Shortt took a position with Stauffer Chemical Co. and later moved on to Pennzoil Products Co.

Women who took a masters degree from Mosher's group also went on to productive careers in the field. Joan Reinhart worked at the U. S. Naval Test Station in China Lake, CA. Anne Llyod Rieger went on to earn her Ph.D. at Columbia University and then obtain a research position at Brown University (43). Dolores Carlotta Miller found work with IBM. Jane Marie Marshburn took a position at Syntex, then with Gilead Sciences, Inc.

### **Cope and Mosher's Legacies; Awards in Their Names**

In his lifetime Cope amassed a considerable estate from his work with pharmaceutical companies (18). Upon his death, he bequeathed half of this estate to the American Chemical Society to establish an award for outstanding achievement in organic chemistry. Recipients of the Arthur C. Cope Award (21a) have been named since 1973. Awardees are given \$25,000, a medallion, and a \$150,000 research grant. The awardees represent a veritable who's who of organic chemists. Ironically, none of these recipients is female. This is not surprising for the field, but extraordinary considering Cope's impact on the professional training of female scientists.

In 1984 the Arthur C. Cope Scholar Award was established as a consequence of astute investing and subsequent unexpected growth of the Cope Fund (21b). Recipients of this award are given \$5,000 and a \$40,000 research grant. Ten Arthur C. Cope Scholars are named annually; four between the ages of 36 and 49, four age 50 or older, and two 35 and younger. Of the 230 recipients of this award since 1985 (21b), only 14, or 6%, of the awardees are women. By comparison, the National Academy of Sciences chemistry division elected its first woman in 1978 and now lists eight women out of 201 current members (4%) (44). Markedly, three of the 14 female recipients received the award in 2008. While this one-year increase is notable, 11 of the 14 female awardees have received the award in the past 10 years, which is still only 11% of the Cope Scholar Awards given for that time period.

The Harry and Carol Mosher Award was established in 1980 by the Santa Clara Valley Section of the American Chemical Society (23). The award recognizes outstanding work in any subdiscipline of chemistry. Past recipients have included five women (18% of awardees). Although the representation of women for the Harry and Carol Mosher award is greater than that of the Cope Awards, neither award honors the true legacy of either man for mentoring all chemists, regardless of gender.

**Table 1:** Women At Bryn Mawr College who worked with Cope\*

<b>Undergraduates</b>	<b>Ph.D. Students</b>	<b>Research Assistant</b>
Ruth Rogan	Corris Mabelle Hofmann (1941)	Evelyn Margaret Hancock
Norma Finkelstein	Elizabeth Mary Osman (1942)	
Dorothea Peck	Elizabeth MacGregor Hardy (1942)	
Catherine Eide	Dorothea R. (Heyl) Hoffman (1942)	
Arsenia Arroyo	Mary Elizabeth Wright (1943)	
Kathryn Hoyle		
Cornelia Wyckoff		
Esther Hardenbergh		

\*Women who were included as coauthors on papers or patents or women for whom a master's or doctoral thesis is found in the appropriate school library catalog are listed. It is possible that female undergraduates who worked with Cope or Mosher are not listed as Bryn Mawr, MIT, and Stanford do not catalog undergraduate theses.

**Table 2:** Women at MIT who worked with Cope

<b>Undergraduates</b>	<b>Masters Students</b>	<b>Ph.D. Students</b>	<b>Post-doctoral Fellows</b>
Aubrey Knowles	Anne Ames Gillis (1951)	Phyllis Louise Magat (1947)	Marion Burg
Hannelore Keller	Patricia A. Starke (1954)	Emily Lippincott Wick (1951)	Patricia A. Trumbull
	Phylis Tocco Moore (1959)		Ruta K. Bly
	Mary J. (Hazard) Youngquist (1961)		Elizabeth Parker Burrows
	Beverly Ann Pawson (1966)		

**Table 3:** Women from Stanford who worked with Mosher\*\*

<b>Undergraduates</b>	<b>Masters Students</b>	<b>Ph.D. Students</b>	<b>Post-doctoral Fellows</b>
Leslie Dean Turner	Mary Holbrook (1947)	Nydia B. Goetz-Luthy (1948)	Paula Kaufmann Loeffler
	Joan Reinhart (1950)	Elizabeth Parker Burrows (1956)	Erna Kaufmann
	Marilyn S. Gregory (1951)	Lois Jean Durham (1959)	Lotte Fikentscher
	Martha Helen Fronk (1957)	Dorothy Feigl (1965)	Janet Samartino Plummer
	Anne Lloyd Rieger (1959)	Betty Jean Gaffney McFarland (1965)	Robyn L. Crumbie
	Maravene Edelstein (1963)	Joel Marie Larkin Schmiegel (1967)	Theresa M. Williams
	Beverly Ann Braman (1967)	Betty Ann Winter Stephenson (1971)	
	Delores C. Miller (1975)	Carolyn Lucille Heutter Fisher (1978)	
	Jane M. Marshburn (1977)	Natalie Lewis McClure (1979)	
		Alexandra Baran Shortt (1982)	

\*\*In the cases where an M.S. and Ph.D. were earned by the woman at Stanford, the final degree is indicated.

## Conclusions

Women who worked with Cope and Mosher have gone on to become scientists of considerable talent. They have become noteworthy industrial scientists (Merck, American Cyanamid, Hoffman LaRoche, Kodak, Dupont, Syntex, IBM, Pfizer), leaders in the academic world (University of Iowa, MIT, Case Western, St. Mary's of Notre Dame, Brown University), government researchers (U. S. Naval Test Station, U. S. Army Biomedical Research & Development Laboratory) and respected by their professional peers (American Chemical Society). It would seem that Cope's most recognizable legacy—his fortune, in the forms of the Arthur C. Cope Award and Arthur C. Cope Scholar Award—is not reflective of his personal legacy of gender diversity in his research group. The recipients of the Carol and Harry Mosher Award come closer to representing the diversity of chemists mentored by Mosher.

As individuals, Cope and Mosher supported women scientists when many of their peers did not. Their motivation for mentoring, supporting, and collaborating with female chemists may never be fully appreciated. It is not clear why the subdiscipline has not recovered from its slow start with regard to women. Cope and Mosher demonstrated that women were able to perform top-notch science. Clearly, the women who were mentored by these two men have gone on to be successful scientists. These women became many of the first women to travel down their career paths, paths that were traveled as early as the 1940s. The continued relative shortfall of female Ph.D.s in organic chemistry could be improved by studying the examples of Cope and Mosher and learning from their leadership.

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## FUTURE ACS MEETINGS

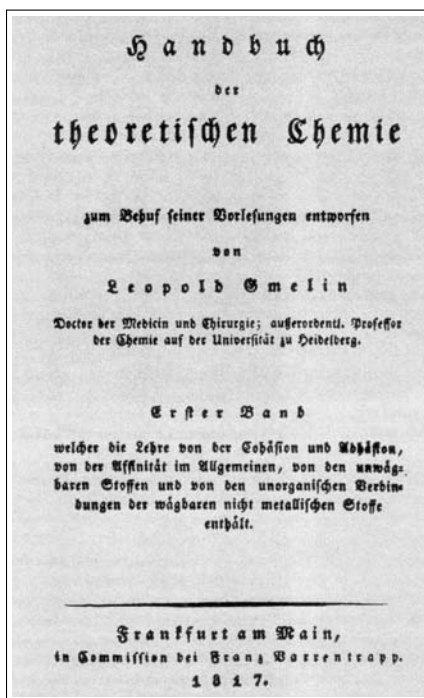
March 22-26, **2009**—Salt Lake City, UT  
August 16-20, **2009**—Washington, DC  
March 21-25, **2010**—San Francisco, CA  
August 22-26, **2010**—Boston, MA  
March 27-31, **2011**—Anaheim, CA  
August 28-September 1, **2011**—Chicago, IL  
March 25-29, **2012**—San Diego, CA  
August 19-23, **2012**—New York, NY  
April 7-11, **2013**—New Orleans, LA  
September 8-12, **2013**—Indianapolis, IN  
March 16-20, **2014**—Washington, DC  
September 7-11, **2014**—San Francisco, CA  
March 22-26, **2015**—Denver, CO  
August 16-10, **2015**—Boston, MA  
March 13-17, **2016**—San Diego, CA  
August 21-25, **2016**—Philadelphia, PA  
April 2-6, **2017**, San Francisco  
September 10-14, **2017**, St. Louis

## GMELIN AND HIS *HANDBUCH*

Fathi Habashi, Laval University, Quebec City, Canada

The first edition of Leopold Gmelin's three-volume work, *Handbuch der theoretischen Chemie*, published by Verlag Chemie in Heidelberg in 1817, was reprinted in 1988 on the occasion of the 100th anniversary of the author's birth (Fig. 1). The book contains a portrait of Gmelin (Fig. 2). A postage stamp was also issued in Germany to mark this event (Fig. 3). The importance of this work lies in the fact that Gmelin was the author who attempted for the first time in the history of chemistry to cite the original literature; i.e., he not only acknowledged his contemporary chemists and their work as other authors before him had done, but he systematically indicated where their work was published. As he prepared new editions of the book, the lists of references increased. This was the motive behind which the German Chemical Society decided to continue preparing new editions and creating the Gmelin Institute for that purpose.

Leopold Gmelin (1788-1853) was born in Göttingen into a distinguished family of chemists, traveled to Tübingen, Vienna, and Italy, and then settled down at the University of Heidelberg in 1813. In 1817, at the age of 29, he held the first chair of medicine and chemistry at the University of Heidelberg, the same year in which he published his *Handbuch*. His book was expanded in successive editions into a multi-volume reference work. He systematically arranged all facts concerning every



Front page of the first volume of Gmelin's *Handbuch der theoretischen Chemie* of 1817

element and compound, giving references to the pertinent literature. In 1922 the German Chemical Society assumed the continuation of this monumental work with the eighth edition. Later the Gmelin Institute was founded in Frankfurt to keep the *Handbuch* up to date (Table 1). The full collection is now a multivolume work of great importance as a research tool (Fig. 5). It was ultimately translated into English.

The Table of Contents of Vol. One is shown in Fig. 4. Printed in the old German Gothic script, the book opens with an introduction of four pages, in which the author defines chemistry as a part of natural science and then goes on to explain the plan of the book. The contents are presented in four parts: Cohesion (7 pages), Adhesion (6 pages), General Chemistry (37 pages), and Special Chemistry (1499 pages), the last comprising the bulk of the book.

Under General Chemistry the topics discussed are: Chemical Affinity, Saturation, Neutralization, Decomposition, and related topics. The Special Chemistry is composed of two parts: Chemistry of Unweighable Matter (light, heat, electricity), and Chemistry of Weighable Matter, which is further divided into two large sections: Inorganic Compounds and Organic Compounds (Tables 2 and 3). The inorganic compounds are subdivided into



10 nonmetals, 11 light metals, and 25 heavy metals. It should be noted that sodium was known as natronium, magnesium as magnium, beryllium as glycium, aluminum as aluminium, and tungsten as scheel. Volume One covers all the material up to and including the nonmetals, Volume Two the metals, and Volume Three the organic compounds. No equations and no drawings are to be found in the text. A few tables showing analysis of material are followed by an index of 29 pages. Lacking drawing, formulas, and equations, the text could easily be mistaken for a novel.

The fifth edition was prepared in 1852-53 but without inclusion of organic compounds. Later Friedrich Konrad Beilstein (1838-1906) in Saint Petersburg under-

took updating this part, which eventually developed into the widely valued *Beilsteins Handbuch der organischen Chemie*, first published in 1880-1882.

Gmelin was succeeded at Heidelberg in 1852 by Robert Bunsen (1811-1899), but his legacy, in the form of his *Handbuch*, was sustained.

## ABOUT THE AUTHOR

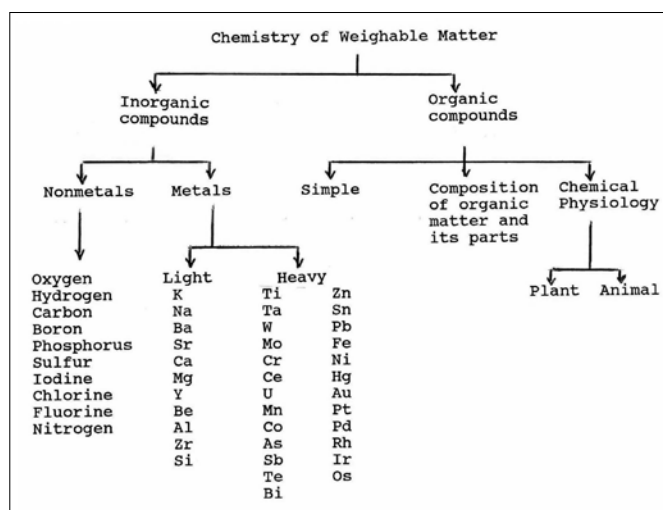
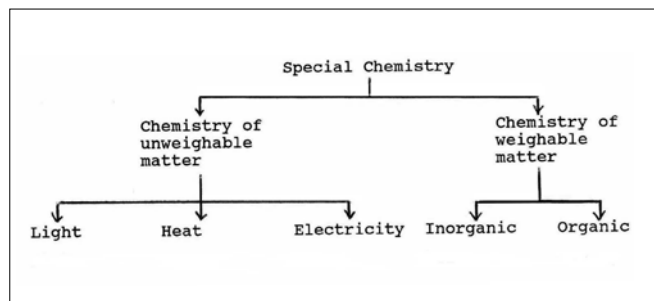
Fathi Habashi, Professor Emeritus, Laval University in Quebec City, Canada, has published widely in the field of metals. His most recent book is *Researches on Rare Earths: History and Technology*, 2008.

Inhalt des ersten Bandes.	
	Seite.
Einleitung.	1 — 4
Cohäsion.	5 — 11
Adhäsion.	12 — 17
Erster Theil. Allgemeine Chemie.	19 — 56
Zweiter Theil. Specielle Chemie.	57
Erster Abschnitt. Chemie der unauflösbaren Stoffe.	57 — 131
Kapitel 1. Licht.	59 — 90
— 2. Wärme.	91 — 117
— 3. Electricität.	118 — 131
Zweiter Abschnitt. Chemie der auflösbaren Stoffe.	132
Erste Abtheilung. Chemie der unorganischen Verbindungen.	134 — 934

Table of Contents of volume one of Gmelin's *Handbuch*



Leopold Gmelin (1788-1853)



## THE DISCOVERY AND EARLY HISTORY OF CAROTENE

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Theodore L. Sourkes, McGill University

*“Wild carrot, Daucus carota, a member of the natural order Umbelliferae, grows wild in fields and on roadsides and sea-shores...It is the origin of the cultivated carrot, which can be developed from it in a few generations...As usual in members of the order Umbelliferae, the wall of the fruit is penetrated lengthwise by canals containing a characteristic oil.”* Encyclopedia Britannica, Eleventh ed. 1910.

Carotenoid pigments are today counted in the many hundreds. The best known member of this group is carotene, which plays a remarkable role in health and medicine as the progenitor of Vitamin A. When one examines the record, it becomes evident that carotene was discovered as a byproduct of the search for a medicinal agent of a quite different kind, namely, an anthelmintic for use in ridding the body of parasitic worms, especially from the intestine. Credit for that discovery goes to the German pharmacist, Heinrich Wilhelm Ferdinand Wackenroder.

### Heinrich Wilhelm Ferdinand Wackenroder (1798-1854)

In June, 1826 Wackenroder (Fig. 1) published his doctoral dissertation, “On Anthelmintics in the Vegetable Kingdom,” as presented to Göttingen University. The thesis earned him very high praise, as well as the Royal Prize (1). A few years later he published the results of his examination of carrots, one of the purposes of that research being the search for the presence in the juice

of that vegetable of an effective anthelmintic (2). According to a statement in that paper, “The carrot-juice provided good service in helminthiasis.” This prompted Wackenroder to undertake chemical analysis of the juice in the attempt to identify the constituent that was medically active. The results of this work were published in 1831 (3). In that paper, he described how he pressed out carrots, obtaining a significant amount of a reddish juice.” In fact, the juice was brick-red in color, turbid, with an aromatic taste, which was at the same time somewhat sweet and tart. Wackenroder described how he diluted the juice with water, and then extracted the liquid with ether. Upon evaporation of the ether extract, there resulted “a yellow fatty oil and carotin” (4). His first attempts to separate these two components failed. Furthermore, the oil underwent rancidization, which consequently affected the carotin; but eventually he obtained the pigment as small ruby-red flakes. These were odorless and tasteless, and showed no reaction with litmus paper or turmeric paper. The crystals were soluble in ether, less so in absolute alcohol, and not at all in water. Dissolved in fats like butter, they imparted “a beautiful yellow color.”

Wackenroder, the discoverer of what was to become known as “carotene,” was born in Burgdorf, near Hannover, Germany, in 1798. His father, qualified as a physician and as an apothecary, practiced both professions. Young Wackenroder had his first professional training as an apothecary and worked in that capacity for his father for two years. In 1819 he began the study of pharmacy, medicine, and science at Göttingen University.

After graduation in 1825 he became assistant to Friedrich Stromeyer in the Göttingen Pharmacy Institute. Having obtained the D. Phil. degree, in short order he was promoted to Privatdozent, but was then attracted to the University of Jena as Professor extraordinarius.



Figure 1: H. W. F. Wackenroder

In 1836 he was appointed Professor ordinarius and Director of the Pharmacy Institute, later known as the “Chemical-Pharmaceutical Institute.” He became especially known for his discovery of carotene and his correspondence with Goethe. In subsequent years he became co-editor of *Archiv der Pharmazie*, and was elected to the Leopoldina and to many foreign societies, a clear reflection of the eminent position to which he had risen in science (1, 5).

His research was mainly concentrated in plant chemistry, his discovery of carotene in the ether extract of carrot juice being a prime example. He is still remembered for his discovery of the solution of polythionic acids that result from the reaction of dilute sulfurous acid with hydrogen sulfide.

Wackenroder’s accomplishment in characterising “carotin” stands in contrast to the efforts of two earlier outstanding French chemists, Edmé Jean Baptiste Bouillon-Lagrange (1764-1840) and Nicolas Louis Vauquelin (1763-1829). Lagrange held a senior position at the Paris School of Pharmacy and at the same time was a Health Officer of the Army of the French Republic. He later was appointed Professor of physics and chemistry at the Central School of the Pantheon and at the Polytechnical School (6). He was the author of many papers in the field of pharmaceutics. His attempts to analyze the pigment of carrot-root failed; he could describe it only as “yellow oily material.”

Nicolas Louis Vauquelin, born in the north of France at St. André d’Hébertot (Calvados) in 1763, died in his native town in 1829. He came from a poor peasant family but was recognized for his brilliance and was helped to obtain a good education. When he was fourteen years old he left home, eventually arriving in Paris where, by chance, he came into contact with Fourcroy, who gave him the freedom of his laboratory. In 1792 he received his pharmacy degree. Two years later he won a post at the new School of Mines, and soon after an additional post at the École Polytechnique. In 1801 he was named Professor of Chemistry at the Collège de France and, in succession, assayer at the Mint (1802), Director of the School of Pharmacy (1803), and Professor of Chemistry at the *Jardin des Plantes* (1804) and at the Faculty of Medicine (1811) (7). Vauquelin was regarded as a leading analytical chemist in Europe (8). His examination of carrots led him to conclude that the material he was after was simply “a resinous pigment” (9).

### Hydrocarbon Nature of the Carrot Pigment

Some sixteen years after Wackenroder’s identification of the carrot pigment, William Christopher Zeise (1789-1847) attempted to purify it. Zeise was born in Slagelse, Denmark, a town south of Copenhagen, in 1789. His father was a pharmacist, a profession which the young Zeise eventually entered. His studies of chemistry convinced him of Lavoisier’s novel teachings, which he took up enthusiastically. For a few years beginning in 1806 he served in Copenhagen as assistant to H. C. Oersted (1777-1851), but in 1809 he began studies that led to his receiving a degree in pharmacy in 1815. Two years later he was awarded the doctorate. Specializing in analytical and organic chemistry, he discovered mercaptans and thioethers (10).

It was during his appointment at the Copenhagen Polytechnic Institute that Zeise undertook his work on carotene, perhaps the last of his studies, for he died in 1847, the year that his articles on that subject were published. In the two nearly identical papers (11), Zeise described his procedure, starting with the press-juice of the root vegetable. On its acidification with dilute sulfuric acid, a colored precipitate developed, which was freed from oily matter (and some protein) by treatment with alkali. In a novel contribution to this work, Zeise found that carotene is soluble in carbon disulfide, yielding a red color. From this extract he was able to obtain small, dark red, lustrous crystals, with melting point 168°. Zeise recognized that he was dealing with a hydrocarbon,

but his analyses gave him  $C_5H_8$  as reported in one of his papers, and a ratio of the two elements of 5:10 in the other. As  $\beta$ -carotene has the molecular formula  $C_{40}H_{56}$ , it is evident that he had not succeeded in obtaining a pure product.

Some years later August Husemann (1833-1877) took up the study of carotene. Husemann had studied pharmacy at Göttingen, receiving his D. phil. in 1860. After graduation he remained at that university as assistant in the laboratory of physiological chemistry. In 1865 he took up a position as Professor of chemistry and physics in the Cantonal School in Chur, Switzerland. His publications include texts in plant chemistry and toxicology (12). Husemann, recognizing that carotene is an unsaturated compound, prepared halogenated derivatives of it (13). He also described the gradual bleaching of the pigment upon exposure to air. The product, unlike carotene itself, was now practically insoluble in carbon disulfide and benzene but was readily soluble in alcohol and ether.

Zeise's recognition of carotene as a hydrocarbon was confirmed many years later by Albert Léon Arnaud (1853-1915), at one time a pupil of Michel Chevreul (1786-1889), and later professor of organic chemistry at the Museum of Natural History in Paris. Arnaud dealt mainly with plant chemistry, including the study of toxic substances of plant origin, such as strophanthine, digitalis, and ouabaine. His analysis of the sample of carotene he had prepared from carrot juice demonstrated the presence only of carbon and hydrogen. His calculations led him to propose the formula  $C_{26}H_{38}$ , which is close to the theoretical proportions (14). He noted that his purified carotene crystallized in thin rhombic plates, exhibiting dichroism, and that it was easily oxidized and halogenated.

Among his achievements, Arnaud developed a colorimetric method for the determination of carotene (against a standard he prepared from carrot juice), which he applied to the determination of that pigment in some 30 different plants (15). In that paper Arnaud suggested that carotene plays a role in oxygen transfer reactions, somewhat analogous to the action of hemoglobin in blood. This concept was subsequently taken up by a few experimenters, including Richard Willstätter and Heinrich Escher (16), but without concrete results.

### Carotenoids in Animal Tissues

The identification of carotene in animal tissues came about through the initiative of Adolf Lieben (1836-1914)

(Fig. 2), a young Austrian chemist, when he took up a position at the University of Palermo in 1863. Lieben came from a very well-to-do family, whose members were occupied with various business interests, but with concern for the progress of science and the recognition of scientific achievement (17). Adolf, unlike other members of his family, chose to follow an academic career. After being home-schooled as a youth, he developed an interest in chemistry while studying at the Vienna Polytechnikum and the University of Vienna. He spent some time in the laboratory of Robert Wilhelm Bunsen (1811-1899) at the University of Heidelberg in 1855, where he met Henry

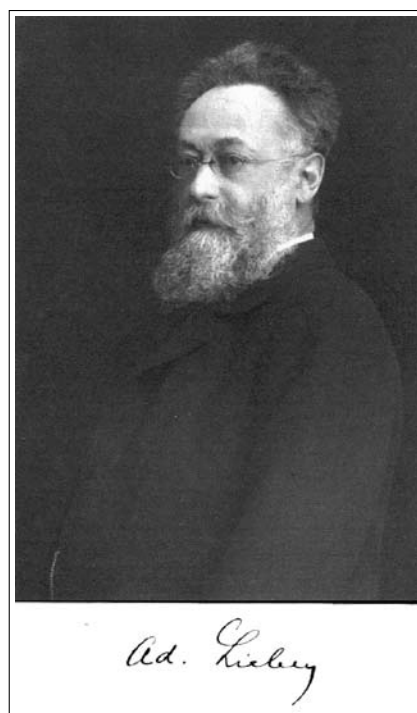


Figure 2. Adolf Lieben

Roscoe (1833-1915), Julius Lothar Meyer (1830-1895), and Friedrich Konrad Beilstein (1838-1906). Upon receiving his D. phil. from Heidelberg, he moved to Paris to work with Charles Adolphe Wurtz (1817-1884). Here he became acquainted with Charles Friedel (1832-1899), Alexander Butlerow (1828-1886), and Stanislao Cannizzaro (1826-1910). After a brief period as industrial chemist in Lille, he accepted an invitation tendered by Cannizzaro to join the faculty of the University of Palermo. Cannizzaro, a native of Palermo, and now professor of chemistry at its university, was seeking to build up his department. Lieben taught there for a few years (1863-1867) and then moved to the University of Turin. In 1871 he accepted a professorship in Prague. In 1875 he

was appointed professor of general and pharmacological chemistry at the University of Vienna. He died in Vienna in June, 1914 (18).

During his career, Lieben published extensively in organic chemistry. The work relevant to carotenes is his study of the pigment occurring in the corpus luteum (*yellow body*), an organ that arises in the ovary of mammals immediately following ovulation. It is highly developed in some species. For example, in the cow it may occupy much of the ovary, so that its prominence must have long been recognized by butchers and those who observed their work. But the nature of the colored matter was unknown. This was one of the problems Lieben undertook during his period in Palermo.

He and his collaborator G. Piccolo began their investigation by accumulating a large number of bovine corpora lutea (19) which, after undergoing air-drying, were cut into small pieces and then extracted with ether. This yielded a yellowish solution. After evaporation of the solvent, the residue was boiled with concentrated potassium hydroxide for many hours. The nonsaponifiable (water-insoluble) fraction was found to contain two compounds: cholesterol and a red crystalline substance. Piccolo and Lieben, assuming the latter was a product of animal metabolism, sought to identify it with one of the limited number of colored substances known in animals. Hemoglobin, or rather its heme prosthetic group, seemed an obvious source. Piccolo and Lieben were able to eliminate bilirubin as a candidate and also 'hematoidin,' a presumed, but never identified, iron-free porphyrin metabolite or mixture of compounds. Concluding that the red crystalline substance they had extracted from the corpus luteum of the cow was a new derivative of hemoglobin, Piccolo and Lieben chose the alternative names 'luteo-hematoidin' or 'hemolutein.'

Another chemist, F. Holm, based in St. Petersburg, but working temporarily in Städeler's laboratory in Zürich, had begun the search for hematoidin in pathological brains of persons dying of stroke, but soon turned to the more readily available corpora lutea of cows. He mistakenly concluded that the pigment therein was hematoidin (20).

Lieben was thus the first chemist to study in animal tissue what came to be known as carotenoids. These pigments occur not only in the corpora lutea, but also in nervous tissue, retina, adipose tissue, and various viscera. It has long been known that plant foods are the source of the pigment in animal organs (21). This is demonstrated clearly by investigations showing that carotene accumu-

lates in tissues in proportion to its availability in the diet (22).  $\beta$ -Carotene has long been recognized as the precursor of vitamin A, an important dietary requirement for animals. Whether these pigments play additional roles in the animal organism is being investigated in some laboratories and clinics. For example, recent studies suggest some role for  $\beta$ -carotene in luteal function, at least in the cow (23).

### The 'Luteines' of J. L. W. Thudichum (1829-1901)

At about the same time that the Palermo workers were isolating the luteal pigment, Johann Ludwig Wilhelm Thudichum (Fig. 3) was conducting research on the "yellow organic substances contained in animals and plants." Thudichum was a physician who, after graduating from the University of Giessen, received training in chemis-

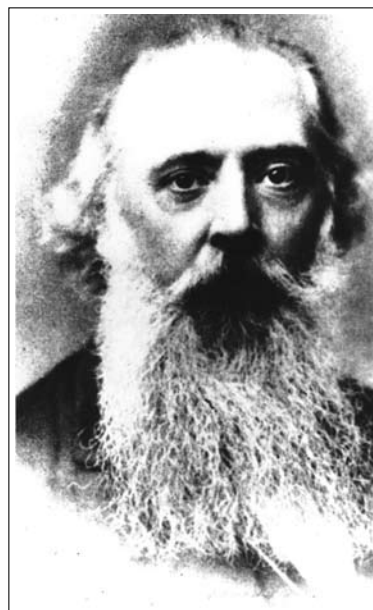


Figure 3. J. L. W. Thudichum

try under Justus Liebig (1803-1873). On emigrating to London, Thudichum established his medical practice, but for a time he also taught at a now defunct medical school. His enthusiasm for the application of chemistry to medicine caught the attention of John (later, Sir John) Simon, the Medical Officer of Health for England and Wales. Holding similar views himself, Simon was quick to employ Thudichum as a part-time research consultant (24).

One of the techniques Thudichum used in his work was spectroscopic analysis, which he had learned in

Heidelberg from Bunsen in 1855 during an interlude in his medical studies. In 1868 he published a classic paper in the *Proceedings of the Royal Society* (25), in which he provided spectroscopic details for a multitude of colored substances, among them Wackenroder's carotene. Although Thudichum was aware of Holm's paper, but apparently not of the work of the Palermo chemists, the spectrum for carotene proved to be virtually identical to that of Piccolo and Lieben's luteal pigment (25). Thudichum assigned the name "luteine" to this yellow crystallizable substance. He pointed out that (25):

[I]n the vegetable world it is observed in seeds, such as maize; in the husks and pulps of fruits, such as annatto; in roots, such as carrots; in leaves, such as those of the coleus; and in the stamina and petals of a great variety of flowers.

He examined 42 different plants in this study. Thudichum's luteine, insoluble in water, was easily soluble in alcohol, ether, and chloroform, forming yellow solutions. The chloroform solution when concentrated had an orange-red color. Thudichum is widely acknowledged as the first to define these yellow organic pigments as belonging to a new class of organic compounds (26).

### Richard Martin Willstätter (1872-1942)

In the course of his extensive investigations into the chemistry of chlorophyll, Richard Willstätter (Fig. 4), working at the Swiss Polytechnikum in Zürich (27), also paid attention to these yellow pigments. The results of these studies appeared between 1907 and 1913. He and his assistant Walter Mieg first of all distinguished between the hydrocarbon carotene, to which they assigned the formula  $C_{40}H_{56}$  (28), and the similar, but oxygen-containing, xanthophyll, having the molecular formula  $C_{40}H_{56}O_2$ . The two compounds were distinguished by their contrasting solubilities: carotene being easily soluble in petroleum ether, but not alcohol; and xanthophyll exhibiting opposite solubility properties. With Heinrich Escher, Willstätter identified the pigment lycopene in tomatoes. By comparing this with purified carotene as to crystal structure and other physical properties, they demonstrated that lycopene is an isomer of carotene (29).

These authors then carried out an examination of the pigment occurring in egg yolk (30). The question was whether it was carotene or some other compound. Previously Chevreul, Théodore-Nicolas Gobley (1811-1876), and Georg Städeler (1821-1871) had attempted to identify the pigment, but without success. Now, from

6,000 hen's eggs Willstätter and Mieg isolated a pigment belonging to the xanthophyll group, and to which they gave the name 'lutein.' Considering that they recognized Thudichum's work, their choice of the same name for a different product was unfortunate. However, this class of pigments soon became known as "luteines," a name that was eventually superseded by the rubric "carotenoids." The next publication from Willstätter's Zürich laboratory dealing with this subject was by Escher, who studied the pigment of the cow's corpus luteum (31). Escher found that the addition of carbon disulfide to the yolk extract did not yield a distinct red color, given by carotene, as in the extract of corpus luteum. Moreover, the compound extracted from hen's eggs yielded crystals of a different color from those obtained from the corpus luteum. Escher's work thus distinguished between the egg yolk and luteal pigments and established carotene as characteristic of the corpus luteum of the cow.

It is interesting that when Willstätter came to write his memoirs (32), he devoted little space to the work on the carotenoids. His main concern was clearly his studies of the chemistry of chlorophyll. This work was prominent in his being awarded the Nobel Prize in Chemistry in 1915 (33).

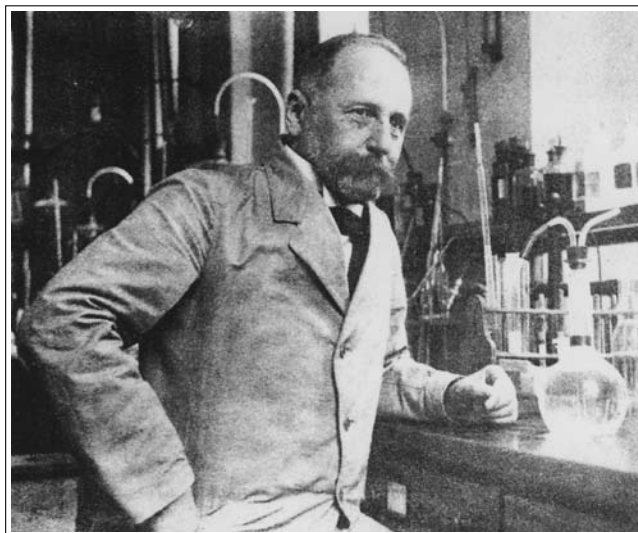


Figure 4. Richard M. Willstätter in the laboratory

### ACKNOWLEDGMENT

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## THE HISTORY OF OZONE. VII. THE MYTHICAL SPAWN OF OZONE: ANTOZONE, OXOZONE, AND OZOHYDROGEN (1)

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### Introduction

It is a truth generally acknowledged that, a single chemist in possession of a good laboratory must be in want of a theory (2). Thus C. F. Schönbein (Fig. 1), the discoverer of ozone, wrote in an 1857 letter entitled "On the Various Conditions of Oxygen" which was read before the Philosophical Society in 1858 by his friend, Michael Faraday (3):

Be this, however, as it may, as we philosophers cannot do any notable work without having some hypothetical view in our heads. I shall place myself for some time under the guidance of the conjecture alluded to, and see what can be made out of it. If it leads to the discovery of some interesting facts I shall not feel ashamed of it, though it may turn out to be fallacious. We are but short-sighted men, and must be content with finding out a little bit of truth in wading through a sea of errors.

The modesty of the last sentence proved to be well justified.

Noyes and Kassel pointed out the danger involved (4):



*Figure 1.* Christian Friedrich Schönbein, Basel, 1799-1868 from Bull Hist Arch. Orig. photo from Univ of Basel Library

...the human mind is so constituted that it must have a picture as a working basis. .... Far too frequently, however, authors have been lead to form pictures and then to seek an interpretation of all data obtained subsequently in terms of these pictures, thereby overlooking many important points. It must be borne in mind that several different pictures will usually interpret a given set of data with equal exactness.

Schönbein's original proposal of ozone (5) had been based simply on odor. It had been a great success, winning from Berzelius (6) the comment that it was one of the most important discoveries in chemistry. Perhaps the ephemeral basis of its discovery prompted, in Schönbein and others, the notion that additional world shaking discoveries could be made on the

basis of minimal evidence. In the case of ozone, however, it should be pointed out that, within a year after its initial proposal, a large number of its properties had been established, unlike the substances described herein, which consistently eluded their pursuers.

This paper describes three examples from ozone chemistry of substances—antozone, oxozone, and

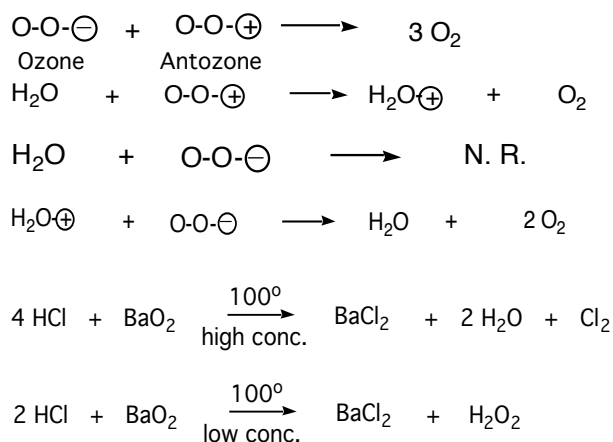
ozohydrogen—which were proposed by eminent chemists of their time in order to explain certain experimental phenomena. They consumed considerable research effort before disappearing from the literature.

### Antozone

Schönbein was one of the outstanding chemists of the 19th century. In addition to the discovery and study of ozone, he developed commercial nitroglycerin explosives and studied a variety of physiological processes. He was particularly interested in an understanding of oxidation in chemical and biological systems. In this connection he came to the conclusion that some activated form(s) of ordinary oxygen was required for oxidation to occur. In a sense he was anticipating the idea of activation energy in chemical reactions. This consideration and the fact that ozone was formed by electrolysis led him to the idea that there were two species involved, negatively charged ozone  $\text{O}-\text{O}-\ominus$  and a positively charged counterpart, antozone  $\text{O}-\text{O}-\oplus$ . Furthermore, the low yield of ozone obtained in electrolysis could be rationalized by assuming that two simultaneously formed but oppositely charged species neutralized one another to give ordinary oxygen; it was never clear why a small amount of ozone survived.

These ideas were first presented by Schönbein in an 1857 lecture before the Bavarian Academy of Science published in three parts in 1859 (7) and in the 1858 paper cited in the Introduction. The name antozone first appeared in a second 1858 paper (8). A succession of publications involving antozone appeared during the next five years (9).

Scheme 1



The great difficulty with antozone was that it was never possible to obtain a defined gas that could be recognized as a new substance with specific properties of its own, as had been the case with ozone 20 years earlier. There was no positive evidence for the existence of antozone. The best that Schönbein could do was to claim that antozone reacted with water to form hydrogen peroxide while ozone did not, so that the formation of  $\text{H}_2\text{O}_2$  became a major criterion for the prior presence of antozone. Ozone on the other hand, did not react with water to form the peroxide but destroyed hydrogen peroxide, as shown in Scheme 1. This was explained by assuming an atom of antozone in  $\text{H}_2\text{O}_2$ ; this reacted with ozone to give oxygen. He even developed (10) an improved analytical procedure for  $\text{H}_2\text{O}_2$ . Another criterion was the reaction of metal peroxides containing antozone with HCl to liberate  $\text{Cl}_2$ ; peroxides containing ozone did not undergo this reaction. According to this view, barium peroxide contained antozone ( $\text{BaO}-\oplus$ ), lead dioxide did not ( $\text{PbO}\ominus$ ). The weakness of this approach was the fact that it was only as valid as the choice of reaction conditions (see Scheme 1). Schönbein devoted much work to categorizing various substances as ozonides (containing negative oxygen) and antozonides (containing positive oxygen).

Thus Schönbein, an avowed doubter of the existence of atoms, was led to consider molecules in which one of the atoms bore a charge. This was actually not a new idea. Brodie (11) had proposed alternating charge polarization to explain certain kinds of reactivity ten years earlier; Schönbein, to Brodie's annoyance, did not cite this earlier work. In 1862 Brodie published a paper (12) in which, without ever mentioning the word antozone, he showed that reactions of metal peroxides could vary depending on the reaction conditions (Scheme 1). Among a number of examples was the reaction of barium peroxide with hydrochloric acid, which was shown to depend on HCl concentration: in dilute solution  $\text{H}_2\text{O}_2$  was formed, in concentrated solution  $\text{Cl}_2$ . Similar behavior was found for lead dioxide. According to Schönbein's criteria, the barium peroxide results indicated that this peroxide contains antozone when allowed to react with concentrated HCl but not with dilute HCl. Brodie wrote (12):

It is thus seen that those differences in the behavior of the different classes of peroxides, from which an imaginary distinction has been drawn between the oxygen respectively contained in them as positive or negative, are not fundamental and characteristic differences...nor are the peculiarities in the reactions of the oxygen of the alkaline peroxides of such a nature as to need any special hypothesis to account for them.

So much for antozone. Nothing further was heard from Schönbein on the subject of antozone, and he never referred in print to Brodie's paper.

An amusing side issue which has perpetuated the name of antozone came from geology. A fluorite mineral (German, *Flussspath*) studied in 1859 by the geologist (and musicologist) Schafhaeutl (13) in Germany gave off a bad odor and formed  $\text{H}_2\text{O}_2$  when crushed. Schönbein obtained samples and leaped to the conclusion, because of the  $\text{H}_2\text{O}_2$  formation, that the odor was due to antozone. The difficulties involved in the study of antozone are illustrated by Schrötter's attempt (14) to establish that the volatile substance was ozone. Schrötter passed the volatiles over a heated surface which would destroy ozone and then into KI solution. Unheated volatiles gave a strong positive test for iodine, whereas heated volatiles did not. He concluded the material was ozone, which was known to be thermally unstable (5). However, since the behavior of antozone on heating was not known, the result is consistent with ozone but not conclusive. After a long series of investigations, Becquerel and Moissan (15) showed in 1890 that free fluorine was present in such minerals and that the reaction of fluorine with water to form ozone (16) was responsible for the odor. Schönbein thought he had antozone in hand. In fact, his sense of smell had let him down. There is a family of fluorite minerals found all over the world that exhibit this behavior when crushed with water. They have been named antozonites and are the only survivors of the antozone theory.

The chemical community in general ignored antozone and wisely so. The major supporter of antozone after Schönbein was the physiologist, G. Meissner (Fig. 2), who had made important discoveries in physiology at an early stage of his career. Certain sensors in the body bear his name, and he advanced rapidly at an early age. Meissner spent the years 1855-1857 (age 26-28) as professor in Basel, where he apparently came under Schönbein's influence, although there is no evidence for any collaboration between the two, nor does Schönbein

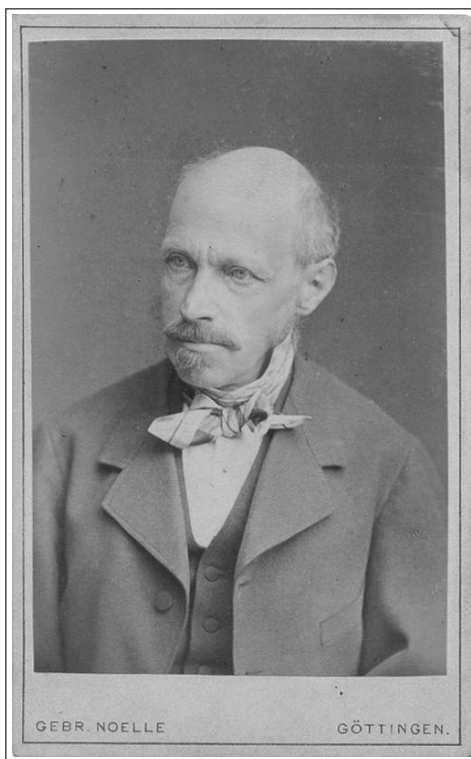


Figure 2. Georg C. F. Meissner, Göttingen, 1829-1905

refer to Meissner in any of his publications. After his move from Freiburg back to Göttingen in 1860 Meissner strayed in part far from physiology by carrying out intensive investigations on antozone even after Schönbein abandoned it. Instead of publishing in the journals of the time, his papers appeared in three bound volumes (17). Meissner observed that when ozone was passed into a solution of potassium iodide, which destroyed the ozone, a white fog was formed which passed through water wash bottles. He called this fog "atmizone" and later decided that it was identical to Schönbein's antozone. Upon standing for about an hour, the fog disappeared and droplets were formed in the vessel. Unfortunately, their composition was not studied in detail until the work of Engler and Nasse (see below). Meissner's analytical method for

establishing the presence of antozone was the appearance of this fog. Rothmund (18) investigated fog formation in some detail about 50 years later and showed that it was a general phenomenon in ozone systems and had nothing to do with antozone. Meissner's work was received in America with considerable interest, in the form of summaries by two distinguished American chemists (19).

The possibility that the fog contained hydrogen peroxide was ruled out since it passed through water. Both Babo (20) and Weltzien (21) suggested that it was nonetheless  $\text{H}_2\text{O}_2$ . The matter was settled by Engler and Nasse in 1870 (22) who identified the fog unequivocally as dilute aqueous  $\text{H}_2\text{O}_2$  by condensing it in cold traps followed by characteristic tests for  $\text{H}_2\text{O}_2$ . They also showed that similar fog could be obtained by applying reduced pressure to aqueous  $\text{H}_2\text{O}_2$ . So much for atmizone and antozone. Meissner continued his other academic activities but retired from research, apparently because of flawed results in some of his physiology research; but this may also have been related to the antozone fiasco. In Fox's 1873 book on ozone and antozone (23), one of the chapter headings is "Does the atmosphere contain antozone, alias the peroxide of hydrogen?" Leeds, summarizing the history of antozone in a very critical 1879 article, wrote (24):

By far the most important fact in the long and perplexing history of Antozone, is the recent discovery that there is no Antozone

All that remains is the designation of certain minerals and a valiant, if misguided, attempt to understand oxidation.

### Oxozone

C. D. Harries (Fig. 3) was responsible for introducing the use of ozone into organic chemistry during the first two decades of the 20th century (25). In four summary articles of his ozone work (26, 27, 28, 29), as well as a collected volume of his ozone publications (30), he established the utility of ozone in organic synthesis and in structure determination of organic compounds. Harries established that the reaction of ozone with the double bond of an alkene gave a labile addition product ( $R + O_3 \rightarrow RO_3$ ), to which he assigned the trioxolane structure **1** (Scheme 2) and gave the name ozonide (31).

Harries' procedure was to pass ozonized oxygen into cooled solutions of alkene in a volatile solvent (27) and then remove the solvent. In some cases the residue could be purified by distillation or crystallization (explosion hazard) and the product submitted to combustion analysis and cryoscopic molecular weight determination. In many cases, the addition of ozone to the double bond to form the ozonide was established by molecular formula; other methods for structure determination were not available; in fact, his trioxolane structure for the ozonide is not correct. If purification was not feasible, the crude reaction product was evacuated exhaustively and tested directly or separated into fractions on the basis of solubility or boiling point. Subsequent reaction of the ozonides, with water in the earlier years and later with zinc, afforded the familiar cleavage products, aldehydes and/or ketones and/or carboxylic acids.

However, at a fairly early stage in his investigations, products having the formulae  $RO_4$  were also obtained (26, p 319; 27, p 289). This was observed to be a general phenomenon with carbonyl containing compounds and

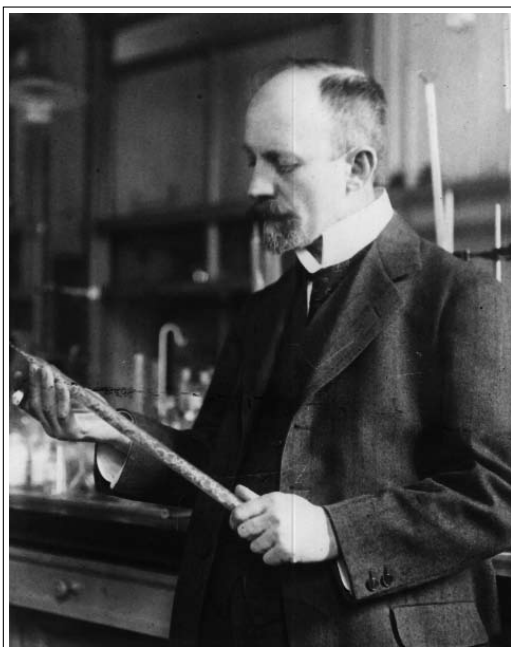


Figure 3. Carl Dietrich Harries, Kiel, 1866-1923  
Photo from Siemens Archives

was attributed to the formation of peroxides which reverted back to the original carbonyl compounds on work-up with water. No such simple explanation was available for a number of alkenes possessing only the multiple bond but which formed, in addition to normal ozonides, products in which four oxygen atoms were incorporated (27). These included 2-butene, amylene, cyclohexene, pinene, and others (28).

Harries proposed that the products containing four oxygen atoms were formed from a new allotrope of oxygen, with molecular formula  $O_4$ , which he named oxozone; its reaction with alkenes produced the addition products, oxozonides

( $R + O_4 \rightarrow RO_4$ ). Interestingly, the output of Harries' ozone generator increased from about 5% ozone in oxygen in 1905 to as high as 14% by 1910 and close to 20% during the last years of his ozone work at Kiel, values much higher than reported by other laboratories where the silent discharge apparatus was used. These higher concentrations resulted in higher yields of oxozonides, suggesting to Harries that the production of oxozone was greater in these years. Further, base treatment of the initially formed gas mixture produced an effluent gas with reduced oxidizing power (reaction with KI solution) and produced only the "normal" ozonides. His conclusion was that oxozone is destroyed by alkali. The amount of oxozone in the original gas mixture corresponded to the reduction in oxidizing power on treatment with alkali and was on the order of one third or higher in a number of cases involving high ozone concentrations. Substances corresponding to dimeric ozonides ( $R_2O_6$ ) and dimeric oxozonides ( $R_2O_8$ ) were also obtained in some reactions, Harries suggested—but with no supporting evidence—that both  $O_3$  and  $O_4$  were in equilibrium with their dimers  $O_6$  and  $O_8$  and that the dimeric species were favored at lower temperatures.

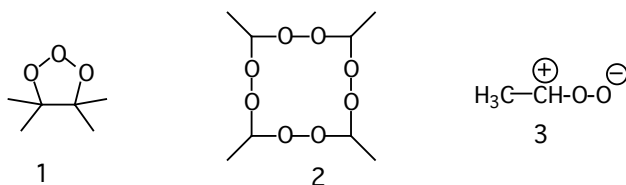
One might have thought that the proposed discovery of new allotropes of oxygen would have occasioned much interest in the chemical world. This was not the case, and rightly so as it turned out. Except for an occasional reference to an ozonolysis-induced product with an extra

oxygen atom, there seemed to be little or no interest in ozonone. As with antozone, there was no direct evidence for the existence of  $O_4$ , nor are there any published reports of attempts to isolate it or obtain it in enriched form. In fact, within a short time (1922), Riesenfeld and Schwab (32) isolated pure ozone and reported that there was no evidence at all for a higher molecular weight component such as  $O_4$ . Lainé (33), searching for an  $O_4$  species in his studies of the magnetic susceptibility of ozone, also concluded that the product of silent discharge on oxygen was the single substance,  $O_3$ . Except for one 1967 paper (34), it has not been mentioned in the literature for decades.

Less than ten years after Harries abandoned Kiel for Siemens and Halske,  $O_4$  reappeared in a new guise. In 1924 Lewis (35) proposed it as a metastable dimer of molecular oxygen in order to explain the concentration dependence of the magnetic susceptibility of oxygen. Since then  $O_4$  has flourished (36 and references therein) as well as higher allotropes ( $O_6$ ,  $O_8$ ) of oxygen, none of them having any connection with the oxidative cleavage of alkenes.

Nonetheless, one must seek an explanation for why Harries went wrong. This was provided in 1942, 30 years after Harries' work, in an extensive paper on ozonolysis by Rieche, Meister, and Sauthoff (37). They repeated his ozonolysis of 2-butene and, following his manipulations, obtained a material with properties very similar to those described earlier and with a molecular formula  $C_8H_{16}O_8$ . This is the correct formula for the dioxozonide of 2-butene ( $2 C_4H_8 + 2 O_4$ ) as proposed by Harries. However, Rieche identified it as the cyclic peroxide 2, (Scheme 2), the tetramer of the Criegee zwitterion 3 (carbonyl oxide) which is an intermediate in the ozonolytic cleavage of double bonds. The empirical formulae of the zwitterion, its oligomers, the addition product of putative  $O_4$  to butene, and the dioxozonide are all identical –  $(CH_2O)_n$ !

Scheme 2



Harries' problem was his fertile imagination and the limited knowledge he had available to him on the structures of the intermediates in ozonolysis. Aside from empirical or molecular formula, he had no other evidence;

nor had work progressed to an understanding of the detailed mechanism of alkene–ozone chemistry. Part of the problem was his use of acetic acid in the determination of molecular weights, which leads to decomposition reactions; Rieche et al. used benzene as solvent in their cryoscopic measurements.

A second explanation was the possible occurrence of additional reactions of ozone, particularly with the high ozone concentrations of the later Kiel years. The reaction of ozone with C-H bonds to produce alcohols is well documented, albeit slower than the reaction with double bonds; its rate would be enhanced by the high ozone concentrations. This was briefly considered by Harries and discarded because he claimed, interestingly, to have interrupted the reactions as soon as the alkene was consumed.

## Ozohydrogen

In 1853 Osann (G. not H.) (Fig. 4) reported that acid solutions of metal salts, particularly silver salts, deposited the metal at the cathode upon electrolysis (38). He went on to record this same observation in a number of additional papers (39). A further observation was that these reductions were not achieved by chemically generated hydrogen gas but only upon electrolysis. Based on the analogy that oxygen is converted in part to ozone upon electrolysis, Osann proposed from the beginning of his work that the reductions were effected by a new, active form of hydrogen which he called ozohydrogen. The name implied it had the molecular formula  $H_3$ ; another name was hyzon. Considerations of bonding did not come into play in 1853. Ozohydrogen could, according to Osann, be stored for long periods of time without losing its special reducing power (39). Osann's papers were summarized uncritically by Jensen (40) in 1990 in a very interesting article on the nascent state.

Apparently Osann was completely unaware of the fact that Hisinger and Berzelius (41), 49 years before his work, had proposed that electrochemical reactions could be effected by direct interaction between the electrode and species in the solution being electrolyzed, or indirectly by formation of an intermediate that reacted further. He also apparently had no knowledge that electrodeposition of metals was well-known; a patent had been granted in 1840 for electroplating with gold or silver, and commercial application had followed. The generally accepted point of view had been that the reaction was a direct one, involving the electrode and the metal in solution and thereby completely independent of any species of

hydrogen. It should be noted that Faraday, who initially supported this view (42) later favored an indirect reaction involving nascent hydrogen formed at the electrode. Five years after Osann's first report, Magnus (43) did address the question of the mechanism of the silver precipitation. He reported that a new American student, "Dr. Dean," had arrived in his laboratory and been given this as a research problem. When Dean failed to reproduce Osann's results on the activity of electrolytically generated hydrogen, Magnus himself made two attempts, and, luckily for Dean, also failed to reproduce Osann's results. Silver was only deposited during the time when current passed through the solution. Magnus came out unequivocally on the side of a direct electrochemical reaction, which is clearly, in modern perspective, correct. None of this had any influence on Osann, who continued to publish his work with ozohydrogen, his last paper on the subject appearing in 1864, two years before his death.



Figure 4. Gottfried Wilhelm Osann, Würzburg 1797- 1866.

This is a very curious story involving a complete neglect of the chemical literature; the only citations in all of these papers are a few references to Osann's own work, mainly to lectures he presented in Würzburg. Osann was not an amateur chemist as can be seen in the biographical section of Ref. 37; he was also rector of his university for some years.

$H_3$ , however, has been a subject of interest for many decades. It first reappeared about 50 years after Osann's work in Thomson's studies on cathode rays (44) with the detection of a species having  $m/e = 3$ , which he designated  $X_3$  and considered most probably to be the cation of

triatomic hydrogen. Three years later Dempster obtained the same species in relatively high concentration (45).

A number of reports of  $H_3$  appeared later in the literature but were shown by Smallwood and Urey to be due to insufficient attention to blank experiments (46 and references cited therein). Herzberg has provided an interesting account of his accidental discovery of the spectrum of  $H_3$  (47). Triatomic hydrogen continues to be a subject of interest to the present day but bears no resemblance to Osann's reducing agent for metal ions in solution.

### Sin in Chemistry

In the years preceding his retirement and immediately after (1985-1995), the author of this paper presented a lecture entitled, "Sin in Chemistry—Mistakes and Fraud in the Chemical Literature," at institutions in Europe, North America, Australia, and New Zealand. The essential point was that the chemical literature is the repository of our knowledge of chemistry, and we chemists have a moral commitment to publish material that is as close to the truth as we can possibly get. Fraud is, of course, the ultimate sin and should be punished with excommunication (for a prime example of fraud see Ref. 48). Mistakes cover a wide range, from trivial issues like typographical errors to premature publication before serious examination of results, or fundamental mistakes in interpretation. Among the lesser, but real, sins is the proposal of new substances without any real evidence for their existence. Speculation, even wild speculation, is entirely appropriate in private but should not take up space in the chemical literature until it has a reasonable degree of real support.

Sin is rampant in all three of the supposed substances discussed in this paper. Interesting new compounds were proposed without serious attempts to establish their existence. The result in all three cases was the expenditure of considerable useless effort, which encumbered the chemical literature without contributing anything of value.

Schönbein wrote in his first paper on antozone that (3):

If it (his conjecture) leads to the discovery of some interesting facts I shall not feel ashamed of it, though it may turn out to be fallacious.

It did not lead to any interesting facts, and he should have been ashamed of it. In his case, at least he was attacking a fundamental problem, the nature of combustion.

When Brodie demolished his scheme, he abandoned antozone.

His partner in sin, Meissner, is subject to more serious criticism. He considered antozone to be the fog formed with ozone under certain conditions. Upon standing, this fog condensed to leave droplets in its container. No attempt was reported by Meissner to determine the constitution of those droplets. Had this been done, as it was years later by Engler and Nasse, it would not have been difficult to establish that one was dealing with dilute aqueous hydrogen peroxide, and that would have been the end of it.

Harries' oxozone is another case where a substance was proposed without any real evidence for its existence, nor was any ever obtained. At least it can be said in his defense that his experimental procedures were sound. Rieche successfully repeated his work in order to obtain the tetramer **2** and establish its structure. If one skips over the oxozone and  $O_4$  parts in Harries' papers, there is no problem. Unfortunately, there are many such discussions in his papers. He also proposed new allotropes of oxygen,  $O_6$  and  $O_8$ , which had no basis in fact.

Osann's ozohydrogen work can only be described as an aberration. He overlooked a considerable body of earlier work; some of his key results could not be reproduced, and he ignored criticism. Inquiries at the University of Würzburg established that he was rector of the university in the late 1840s (and apparently a progressive rector at that) but provided no insights that might have explained his behavior with ozohydrogen.

As already noted, all three of the imaginary substances discussed here disappeared quickly from the chemical literature after their initial proponents ceased to support them. The chemical community of their time showed very little interest, in contrast to the considerable activity in ozone chemistry as soon as ozone's existence was proposed by Schönbein. The common wisdom operated well.

### Summary

Three substances, antozone, oxozone ( $O_4$ ), and ozohydrogen ( $H_3$ ), were invented, the first and third in the mid-19th and the second in the early 20th century, in order to explain certain experimental facts. None of these substances could be isolated or characterized, each serving as a rationale for certain experimental results and consuming considerable experimental effort while contributing a minimum to chemical knowledge.

Antozone was proposed by C. F. Schönbein to explain various observations in ozone chemistry and oxidation reactions in general. It was, at least, a valiant attempt at the understanding of oxidation reactions and can be said to be an early expression of the idea of activation energy in chemical reactions. Oxozone was proposed by Harries to account for the presence of one too many oxygen atoms in some products of ozonolysis of olefins but turned out to be the result of formation of ozonolysis products which were not known at the time of his work. Ozohydrogen, a special form of hydrogen with unique reducing power, was an invention of Osann which lacked any merit whatsoever. All three of these "substances" died with their inventors.

In his first paper on antozone, Schönbein wrote (3):

We philosophers cannot do any notable work without having some hypothetical view in our heads.

While this is a valid point of view, it is usually best to keep such hypothetical views unpublished until they can be supported.

### ACKNOWLEDGMENT

It is always a pleasure to acknowledge the manifold help of science librarians. They are so helpful and so competent, both at the computer and in the library itself; they include Ms. H. Ilovich and Ms. E. Raskin of the Chemistry and Biology Library in Haifa and Ms. V. Mitchell, Ms. A. Zeidman-Karpinski, and Mr. D. Walton at the University of Oregon Science Library. Special thanks go to Prof. M. Christl (Würzburg) for the photo and for information concerning G. Osann and to Prof. A. de Meijere for the photo of G. Meissner. The photo of C. F. Schönbein was provided by the library of the University of Basel and that of C. D. Harries by the Siemens Corp. The continuing summer hospitality of the Chemistry Department at the University of Oregon is enormously appreciated.

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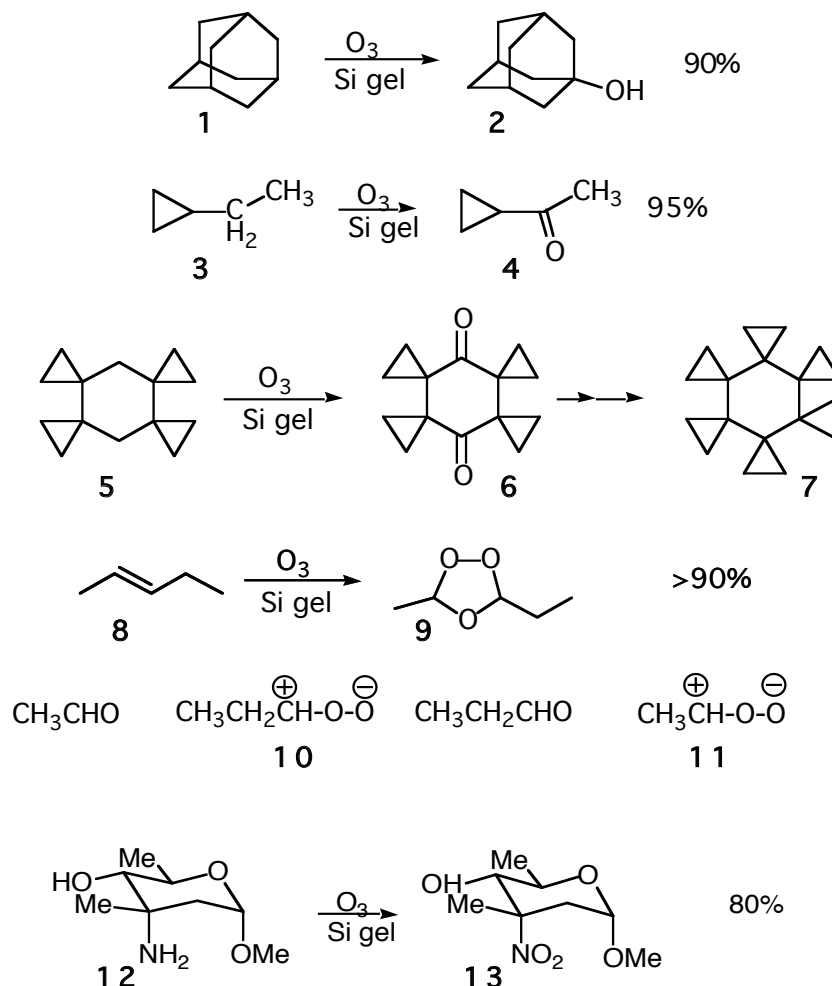
Saskatchewan 1936-45. Prof. Spectroscopy, Yerkes Observatory, Un. of Chicago, 1945-48. Director Div. of Pure Physics, Natl. Res. Council of Canada 1948-1969; Distinguished Research Scientist, Natl. Res. Council of Canada, 1969. Nobel Prize Chem. for contributions to electronic structure and geometry, 1971. Chancellor Carleton Un., Ottawa 1973-80.

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## ABOUT THE AUTHOR

Mordecai B. Rubin has been emeritus professor of chemistry at the Schulich Faculty of Chemistry, Technion, Haifa since 1994. He can be contacted at [chrubin@tx.technion.ac.il](mailto:chrubin@tx.technion.ac.il). Retirement is like a permanent sabbatical if one can remain healthy. He did some work with ozone in his postdoctoral incarnation and ozone has been the companion of his later years. Three atoms can combine into a plethora of chemistry.

**Editor's Note:** The Scheme below was inadvertently omitted from the previous paper on ozone, ["Ozone VI.,"] which appeared in the *Bulletin*, **2008**, 33, 68-75. My sincere apologies to the author, M. Rubin.



## WOMEN CHEMISTS IN THE NATIONAL INVENTORS' HALL OF FAME: THEIR REMARKABLE LIVES AND THEIR AWARD-WINNING RESEARCH

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Mary Virginia Orna, College of New Rochelle

The National Inventors' Hall of Fame (NIHF) celebrates the creative and entrepreneurial spirit of great inventors by showcasing exhibits and presentations that allow visitors to experience the excitement of discovery, creativity, and imagination. Founded in 1972 and located in Akron, Ohio, USA, the Hall of Fame is dedicated to the individuals who conceived the great technological advances which the USA fosters through its patent system. Each year a Selection Committee composed of representatives from national scientific and technical organizations votes to select the most qualified inventors from those nominated for the current year. To date, only 13 women of the more than 375 inventors thus honored are members of the Hall of Fame, and of these 13, six are chemists (1): Rachel Fuller, Brown, Gertrude Belle Elion, Edith Flanigen, Stephanie Louise Kwolek, Helen Murray Free, and Patsy O'Connell Sherman.

One may ask what circumstances gave rise to the induction of each of these women. Their successes spanned the entire 20<sup>th</sup> century; some were inducted at the height of their careers, and others were admitted to the NIHF posthumously. In examining their very diverse careers, each of them was characterized by several or all of the following qualities: drive to better the human condition, hard work and perseverance, systematic and consistent experimentation, collaborative efforts with one

other individual or with a team, taking advantage of a serendipitous event, curiosity, creativity, innovation, and a passion for chemistry. The qualities most applicable to each individual will be stressed in each section.

### **Collaborative Efforts, Financial Straits: Rachel Fuller Brown and Gertrude Elion**

The lives and careers of two of the earliest inductees parallel one another in a remarkable way. Both Rachel Fuller Brown (1898-1980), inducted posthumously in 1994 (2), and Gertrude Belle Elion (1918-1999), inducted in 1991 (3), carried on their research in close collaboration with one other scientist.

Brown carried on a long-distance joint effort with Elizabeth Lee Hazen (1885-1975), a mycologist and bacteriologist who single-mindedly pursued a search for an antifungal antibiotic. Brown brought the chemical skills needed to identify, characterize, and purify the various substances produced by culturing bacteria found in the hundreds of soil samples they examined.

Prior to their work, there was no antifungal agent that matched the efficacy of penicillin and streptomycin against bacterial infections. Hazen felt that such an agent might be found by examining a wide variety of soil samples, since streptomycin had been found in the same

way. The samples she studied came from many sources worldwide. If a preliminary test showed antifungal activity, she sent the sample to Brown in order to extract the active component—by a painstaking series of solvent extractions since methods like HPLC were not available at that time. Fig. 1, taken from the original patent application (2), illustrates the multistep method needed prior to the advent of chromatographic methods.

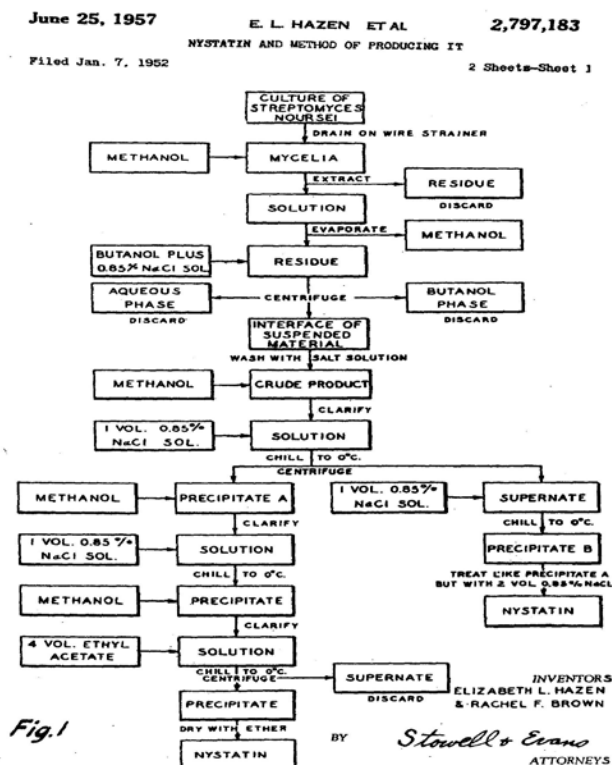


Figure 1. Brown's Scheme for Extraction of Nystatin  $A_1$  from *Streptomyces noursei* Culture

Virtually all were found unsuitable for human use because the microorganism activity was too toxic. Hazen herself serendipitously discovered the winning candidate in a soil sample taken from a farm in Virginia where she was visiting her friends, the Nourses. She grew large quantities of this previously unknown organism (later named *Streptomyces noursei* in honor of its source), so that Brown could extract usable amounts of the active component. The antibiotic they developed, named 'Nystatin' for the New York State Department of Health, was first introduced in practical form in 1954 following Food and Drug Administration approval (4, 5). Further work revealed the presence of three biologically active components in the extract called, respectively, Nystatin

$A_1$ , Nystatin  $A_2$ , and Nystatin  $A_3$ . The structure (Fig. 2) of Nystatin  $A_1$  was determined more than twenty years after its discovery (6).

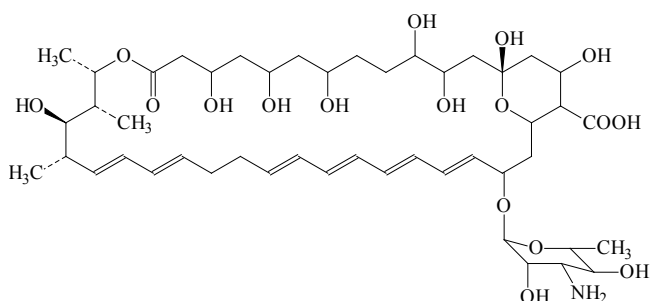


Figure 2. Nystatin  $A_1$

Not only did Nystatin cure many disfiguring and disabling fungal infections of the skin, mouth, throat, and intestinal tract, but it could be combined with antibacterial drugs to balance their effects. Uses for Nystatin have been as varied as treating Dutch elm disease to rescuing water-damaged works of art from molds and mildew.

Gertrude Belle Elion's cooperation in drug development with a very unusual biochemist, George Hitchings (1905-1998), mirrored Rachel Fuller Brown's experience in many ways but diverged in others. Hitchings invited Elion into his Wellcome research laboratory (later Burroughs Wellcome) at a time when women found it difficult to secure scientific positions, and he continued to encourage her in her career development long after the hiring spurt for women during World War II was over (7). His was, at first, a helping role, whereas Brown and Hazen were equal copartners from the beginning. There were also differences and similarities in their scientific approach. Historically, drug developments frequently resulted from a trial-and-error process. As a consequence, the element of chance has been essential in developing new pharmaceuticals, as we have seen in the example of the suitable soil sample Elizabeth Lee Hazen found by chance. Gertrude Elion and George Hitchings, diverged from this traditional path in their research, using what is termed today "rational drug design." They methodically investigated areas in which they could see cellular and molecular targets for the development of useful drugs. During their long collaboration, Hitchings and Elion produced a number of effective drugs to treat a variety of illnesses, including leukemia, malaria, herpes, and gout.

The development of sulfa drugs by Gerhard Domagk (1895-1964) in the 1930s led the team to think that other substances that interfered with the metabolism of microbes—such as the sulfa drugs had been shown to

do—could also be developed as drugs. As a result, they began examining the nucleic acids, DNA and RNA, and their building blocks, the purines adenine and guanine. They soon discovered that bacterial cells cannot produce nucleic acids without the presence of certain purines. They then set to work on antimetabolite compounds, which locked up enzymes necessary for incorporating these purines into nucleic acids.

By 1950 this line of research had paid off. Using references from the old German literature, Elion and Hitchings synthesized two substances: diaminopurine and thioguanine, which the enzymes apparently latched onto instead of adenine and guanine. These new substances proved to be effective treatments for leukemia. Elion later substituted a sulfhydryl group (–SH) on a purine molecule, thereby creating 6-mercaptapurine (also known as 6-MP and trade named Purinethol); and subsequent substitution of a 2-amino group gave rise to the molecule which they patented and for which Elion was inducted into the Hall of Fame (8).

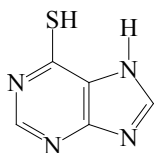


Figure 3. 6-Mercaptopurine

After this success they developed a number of additional drugs by using the same principle that had led them to 6-MP. Later these related drugs were found not only to interfere with the multiplication of white blood cells but also to suppress the immune system. This latter discovery led to a new drug, Imuran (azathioprine), and a new application, organ transplants. Imuran suppressed the immune system, which would otherwise reject newly transplanted organs (9).

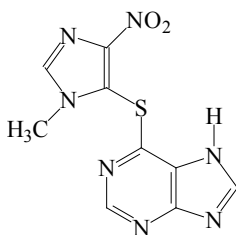


Figure 4. Imuran

### Financial Difficulties and Altruism

Both Brown and Elion experienced great difficulty in financing their educations, and for both of them, their career trajectories were greatly impacted by these cir-

cumstances. For example, both financed their higher education by teaching high school, at least for a time. Brown's father deserted her family when she was just starting high school. A wealthy family friend financed her education at Mount Holyoke College where, as a history major, she took her first chemistry course to fulfill her science requirement. Hooked on chemistry from that moment, she continued as a double major, receiving her A.B. degree in 1920. She then went to the University of Chicago where she completed her Master's degree in organic chemistry, but then had to take time off to teach high school because of lack of funds. She was finally able to submit her Ph.D. thesis in 1926; but again, because of financial difficulties, she was forced to take a position with the New York State Department of Health in Albany, New York, and her thesis defense was thus delayed for another seven years. Brown, and Hazen, too, were especially fortunate to find a welcome in one of the few laboratories noted for hiring women, and also in receiving the help and encouragement from their laboratories administrator, Gilbert Dalldorf. It was he who promoted an announcement of the discovery of Nystatin in order to establish the Brown/Hazen priority.

Elion, born in New York City, attended the city's public schools, including Hunter College, where she received an excellent education although the crash of 1929, in which her father lost all his money, continued to shadow her for much of her early life. Elion lost her beloved grandfather to cancer while she was quite young, but this event was a major factor in her decision to study science so as to better the human condition. With her degree in chemistry (1937), she tried to enter graduate school but was rejected by 15 institutions. Instead she was offered a job washing dishes in a laboratory. She turned to teaching chemistry and physics in high school and meanwhile attended New York University on a part-time basis. Because of her financial hardship, she never completed her Ph.D. Nevertheless, she was hired by the Wellcome Research Laboratories, where she broadened her interests from chemistry to include biochemistry, pharmacology, immunology, and virology. She pursued her ground-breaking research at a time when there was virtually no scientific instrumentation, no carbon-14-labeled compounds to trace metabolites, and no theoretical basis since the Watson-Crick model of DNA structure had not yet been developed. Elion's work was recognized by the American Chemical Society in 1968 when she received the Garvan Medal, the Society's only award designated for women. Elion and George Hitchings shared the 1988 Nobel Prize in physiology or

medicine (10), along with Sir James W. Black (b. 1924). At the time of her retirement from Burroughs Wellcome, which had moved by this time to Chapel Hill, North Carolina, Elion became associated with Duke University as a research professor who mentored student research and taught pharmacology courses. Her academic life had come full circle.

Another remarkable parallel distinguishes these two women in the area of altruism. Brown (and Hazen) received no financial benefit from their work. They donated all Nystatin royalties—more than \$13 million by the time the patent expired—to academic science through the nonprofit Research Corporation. Furthermore, by the time of her death, Brown had repaid every grant-in-aid she had ever received in support of her education. Elion, in like manner, donated the fund she received from Burroughs Wellcome to match her Nobel Prize money to her Alma Mater, Hunter College, to further women's education in the sciences.

### **A Passion for Chemistry; Systematic and Consistent Experimentation; Effective Teamwork: Edith Flanigen and Stephanie Kwolek**

Edith Flanigen (b. 1929) is one of the most inventive chemists of all time. Her creative and outstanding work in materials science and engineering has greatly affected modern life. Her discoveries have resulted in more than 100 patents and have revolutionized the world of molecular sieve materials. How did all this come about? In her own words, in an interview with the author, she said that you must love what you do because if there is any other reason for doing what you do, it just won't work. Edith's early inspiration came in high school where she and her two sisters were first introduced to chemistry. All of the Flanigen sisters were taught by Sister St. Mary, who emphasized hands-on activities and exciting demonstrations of chemical processes in her classes. After high school, first Joan, then Edith, and four years later Jane, as well, majored in chemistry at D'Youville College. There they took courses with Dorothea Fitzgerald, who was responsible for all chemistry courses. Both Joan and Edith earned master's degrees in chemistry from Syracuse University. All three Flanigen sisters eventually came to work at Union Carbide.

That early inspiration plus Flanigen's conviction that effective teamwork (within the same laboratory environment, as opposed to collaborative efforts separated by distance) and self-knowledge of one's own unique

characteristics and talents led to her playing a major role in the development of molecular sieve zeolites, a billion dollar industry that has impacted almost every area of life.

When Flanigen joined the Linde Division at Union Carbide in 1952, she was first assigned to silicone chemistry, and in 1956 she joined the molecular sieve group. Molecular sieves (or zeolites) are made of microporous materials that trap only molecules small enough to fit into their cavities while excluding larger molecules. This characteristic makes zeolites ideal for use as catalysts in various industrial processes.

It was primarily for this work that in 1992 she earned the first Perkin Medal ever awarded to a woman; the Perkin Medal is the highest honor for outstanding work in applied chemistry in the United States. She has received many other honors and awards during her 42-year career in industry, including the prestigious Lemelson-MIT Award in 2004 (11, 12).

While Edith Flanigen drew her early love of chemistry from her teachers, Stephanie Kwolek (b. 1923) attributes her love of science to her father. Kwolek's parents were immigrants from a town near Krakow, Poland. Both had the equivalent of a high school education and were voracious readers. Her father was an amateur naturalist, and Stephanie spent many hours with him exploring the woods and fields near home, looking at animals and bugs, as well as filling scrapbooks with leaves, wildflowers, seeds, grasses, and detailed descriptions. Her mother was primarily a homemaker (great cook, excellent seamstress, and terrific storyteller) who became a working parent after her husband's early death when her daughter was ten. In Stephanie's childhood she "played school" (of course, she was the teacher), drew hundreds of dresses and outfits (she considered becoming a fashion designer), wrote poetry and short stories (an early practice for her later chemical papers perhaps), but always returned to science.

Her elementary and high school education was a "mishmash" of public and parochial schools. She had no chemistry or physics courses in high school, only mathematics, biology and general science. When Kwolek graduated from high school, she entered Margaret Morrison Carnegie College of Carnegie-Mellon University and did a year of science courses (biology, chemistry, physics and mathematics, only 10-12 students per class) in addition to working 20 hours a week and making the honor roll (to her surprise). Kwolek was interested in medicine at the time. She majored in chemistry, minored

in biology and earned a B.S. degree in four years, working summer jobs and using various scholarships. As a high school sophomore, Kwolek was encouraged by a social science teacher and later two college chemistry professors were very supportive. After her college graduation, she was still interested in medicine but realized that expenses would be great. She decided to get a temporary job, save money, and enter medical school later. After interviewing at a number of companies, Kwolek decided that the work at DuPont was the most interesting and the starting salaries there were the same for women and men (not the case at other places).

Her interviewer at DuPont was Hale Charch, a research director at the company and the inventor of waterproof cellophane tape. Charch told Stephanie that he would let her know of his decision in a few weeks. Kwolek replied that she had other offers to consider and needed an answer sooner. Charch called in his secretary, dictated a letter making the job offer and gave it to Kwolek. She took the letter home, thought about it and accepted the offer. Reflecting on this bold request for a woman to make in 1946, Kwolek suspects that her assertiveness got her the job offer from DuPont. The polymer research she worked on was so interesting and challenging that she gave up the idea of medical school and made chemistry her lifelong career (13).

The chemistry accomplished by these two women is highly innovative and creative, born of team effort, and systematic, consistent experimentation.

### Breakthroughs with Zeolites

Edith Flanigen's "claim" to the Hall of Fame in 1994 is for her contributions to the product development of Zeolite Y, an aluminosilicate "molecular sieve" used to make oil refining more efficient, cleaner, and safer (14). Flanigen began working on the emerging technology of molecular sieves, crystalline microporous structures with large internal void volumes and molecular sized pores, in 1956. These compounds can be used to purify and separate complex mixtures and catalyze or speed the rate of hydrocarbon reactions, and they have widespread application in the petroleum refining and petrochemical industries.

Natural zeolites occur in sedimentary and volcanic rocks, altered basalts, ores, and clay deposits. The 18<sup>th</sup> century Swedish mineralogist Axel Cronstedt coined the word "zeolite" from the Greek words "zein" (to

boil) and "lithos" (stone). He had observed that when a natural mineral was heated rapidly, the stones began to dance about as the water evaporated—they were literally "stones that boil." Chemically, natural zeolites are crystalline, hydrated alkali-aluminum silicates with mobile cations capable of undergoing ion exchange (15).

Since natural zeolite minerals are rare and difficult to obtain in large quantities, scientists developed methods of synthesizing zeolites in the laboratory as early as 1949. In the late 1970s, a team led by Flanigen was called upon by Union Carbide management to develop a new class of synthetic molecular sieves. By 1985 Flanigen and her team had filed more than 30 patents and had succeeded in developing a whole new generation of synthetic zeolites. Prior to Flanigen's work, it was thought that the electrovalent balance within the framework of silica and alumina tetrahedra during synthesis would be only attainable by having present in the reactant mixture a substantial quantity of metal cations, such as sodium. Once the metal cation had been included in the reactant mixture and the synthesis reaction completed, the metal ions that occupy the cationic sites of the crystal could then be replaced by a wide variety of other metallic cations using ion exchange techniques. Flanigen and her team succeeded in preparing for the first time crystalline zeolites containing a substantial weight percent of a cation other than sodium or other metal cation. This novel process afforded the incorporation of nonmetallic, nitrogenous cations, ammonium, tetramethylammonium ion, or lower derivatives such as  $\text{NH}_2(\text{CH}_3)_2^+$ .

These new zeolites were found to have a wide variety of applications such as separation of one fluid species from a stream containing many species by adsorption either preferentially or on the basis of the molecular dimensions of a particular fluid species. Unlike common adsorbents such as charcoal or silica gel which show selectivity based primarily on the boiling point or critical temperature of the adsorbate, the activated zeolites of Flanigen's invention exhibited a selectivity based on the size, shape, degree of unsaturation, polarity, or polarizability of the adsorbate molecule. Her patent application also noted that the rejection characteristics of the new zeolites were as important as the adsorption characteristics. The interstitial channels of these zeolites were such that at their narrowest points molecules with critical dimensions exceeding the pore diameter of the zeolite structure would not readily enter into the channels (Fig. 5).



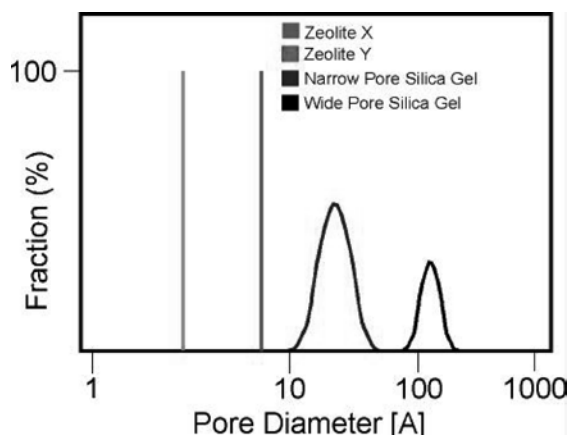


Figure 5. Distribution of pore sizes of zeolites and of silica gels

In addition, these zeolites were able to adsorb relatively large quantities of adsorbate at either very low adsorbate pressure or concentrations (Fig. 6), thus allowing these zeolites to be used to remove adsorbable impurities from gas and liquid mixtures, and also to recover minor components of such mixtures (14).

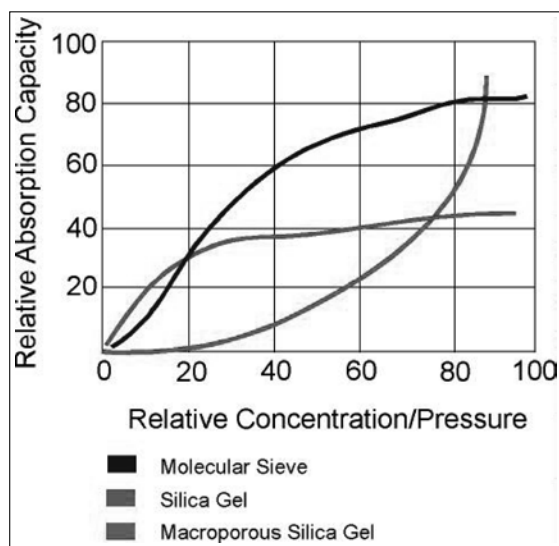


Figure 6. Relative adsorption capacities of molecular sieves compared with silica gels

When Jeffrey Seeman, in an interview with Edith Flanigen on April 6, 2008, asked her to what she attributed her breakthrough successes in novel zeolite development, she unhesitatingly replied that it was due to the unswerving dedication of a team of scientists whom she had personally selected for the work. She said that this teamwork made all the difference both in the quality and quantity of work achieved.

## The First Synthetic Ultrahigh-Strength Fiber

All three of the characteristics highlighted in this section—effective teamwork, a passion for chemistry, and systematic creativity—enabled Stephanie Kwolek to make the breakthrough in the search for high-strength fibers. This search is very old, ever since sailors sought better cordage for their lines and sails, but right down to the 20<sup>th</sup> century, their choices were limited to natural fibers: hemp, manila, and cotton. Advances in this technology were only possible with the advent of synthetic polymers. Strong fibers depend upon the degree of alignment of the polymer chains, usually achieved by drawing out spun chains to fourfold their original length, a process that orients the polymer chains and markedly increases their strength. However, synthetic polymers, such as nylon, contain large portions of amorphous chain which are in random molecular order and contribute little to the fiber's strength (16).

In 1995 Stephanie Kwolek was inducted into the Hall of Fame for her discovery of an amazing group of super-strong polymers (17). Her earliest work pioneered low-temperature processes for the preparation of condensation polymers and resulted in hundreds of new polymers, including Kapton polyimide film and Nomex aramid polymer and fiber. As she carried out experiments to make stronger and stiffer fibers, she discovered an amazing branch of polymer science: liquid crystalline polymers of such great strength that the fruits of her inventiveness can be found in mooring ropes, fiber-optic cables, aircraft parts, canoes, and—most important to police—in lightweight bullet-resistant vests.

Kwolek, working at the DuPont Experimental Station in Wilmington, DE, made her breakthrough when she prepared a liquid-crystalline solution of poly (*p*-aminobenzamide) polymer that was spun to fibers with an extremely high tensile strength. These fibers could not be drawn because they were already fully aligned during the spinning operation. It was the liquid-crystalline nature of the spin solution that allowed for spontaneous alignment of the chains, thus overcoming the problem of amorphous chain parts that were strength-limiting. She selected as a monomer a *p*-aminobenzoyl halide salt represented in Fig. 7.

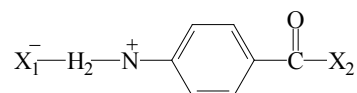
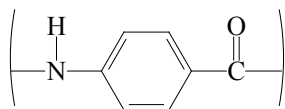


Figure 7. *p*-Aminobenzoyl Halide Salt Monomer

where  $\text{X}_1^-$  represents an arylsulfonate or similar group,

and  $X_2$  represents a halide, preferably bromide or chloride. The resulting polymer had the formula shown in Fig. 8,



**Figure 8.** Homopolymeric Poly(*p*-Benzamide)

but it was insoluble in all solvents that had been tried up to this point (17). Kwolek needed to have the polymer in solution in order to spin it into fibers. She finally succeeded in dissolving it in tetramethylurea, producing an opalescent, turbid liquid crystal solution—a state of matter intermediate between truly liquid and truly crystalline. This was the first crystalline solution of an aromatic polyamide. Later it was shown that liquid-crystalline solutions are composed of small domains where polymer chains are perfectly aligned with respect to each other. Spinning these solutions causes enough shear to rotate the liquid-crystalline domains so that they align in unison, reaching a high state of orientation that is retained as the fibers coagulate (16). DuPont's development of this and other fibers that are up to five times stronger than steel led to such products as lightweight building materials, inflatable boats, airplane parts, ropes and cables, and bullet-proof vests (18).

And so, someone who did not have enough money to realize her dream of attending medical school went on to accomplish a larger dream evoked from centuries past: ultra-high strength synthetic fibers. She became so interested in this work that she remained at DuPont for her entire career, retiring in 1986. By her own admission, she was driven onward by her love of basic science and the fact that she was fascinated with the process of discovery. She has received many honors, including the Perkin Medal in 1997, the Kilby Award, the National Medal of Technology (1996), and the American Chemical Society Award for Creative Invention. Her name appears on 17 patents issued between 1961 and 1986 (19).

### **Innovation, Hard Work, and Perseverance: Helen Murray Free and Patsy Sherman**

In 2000 Helen Murray Free (b. 1923) was inducted into the Hall of Fame for her contributions to the development of dry reagents that have become the standard in laboratory urinalysis and the more consumer-oriented “dip-and-read” tests, which first enabled diabetics to easily and accurately monitor and help control inde-

pendently their disease (20). Free's research in clinical chemistry not only revolutionized diagnostic testing in the laboratory but also in the home, where diabetics could test themselves. Free and her husband Alfred coauthored *Urodynamics: Concepts Relating to Urinalysis* in 1972 (21) and *Urinalysis in Clinical Laboratory Practice* in 1975 (22), which still remain standards in the field.

Helen Murray was born on February 20, 1923 to Daisy Piper and James Summerville Murray in Pittsburgh, Pennsylvania. In 1941 she graduated from Poland (Ohio) Seminary High School as valedictorian and then went on to the College of Wooster, where she graduated with a B.S. in chemistry in 1944. That same year she accepted a position as a control chemist at Miles, Inc. (which later became Bayer). She worked her way up the corporate ladder while developing and teaching both management and technical courses. She retired in 2007 as Professional Relations Consultant in the Diabetes Care Division. Free has also been awarded seven patents for her clinical diagnostic test inventions.

Early on at Miles, Helen collaborated with biochemist Alfred Free. Helen married Alfred Free in 1947 and they had six children. He died in 2000 (23, 24).

The Free invention had as one of its primary objects the provision of a simple, rapid, and convenient means for performing a test for the detection of glucose with a high degree of simplicity and without the need for extensive equipment or trained personnel. There have been available over the years a number of methods to measure the amount of glucose in urine. The more widely used of the conventional methods are based on the use of alkaline copper solutions which are heated with the materials being tested to precipitate copper (I) oxide (Fehling's Test; Benedict's Test). The disadvantage of these methods is that their use has required a certain amount of skill and familiarity with the use of measuring equipment such as pipets and graduated cylinders, and the use of liquid reagents some of which were dangerous to handle and inconvenient to transport. Furthermore, these tests all required heat supplied by an extraneous source, such as a Bunsen burner. On the contrary, the Free invention was a highly effective means for detecting glucose in various materials that is specific, economical, rapid, convenient, reliable, does not require use of any heat source, and lends itself to mass screening of people for diabetes detection.

The invention consists of two enzymes, glucose oxidase and peroxidase, an indicator whose color is affected by hydrogen peroxide in the presence of one of

these enzymes, and a buffer to maintain the pH within a predetermined range, a stabilizer such as gelatin, and in some cases a dye to make color reading easier. The reactions are as follows (20).

Glucose oxidase + Glucose + O<sub>2</sub> (atmospheric) → Gluconic acid + H<sub>2</sub>O<sub>2</sub>

H<sub>2</sub>O<sub>2</sub> + Peroxidase + Dye (Reduced form) → Dye (Oxidized form) [Color change]

Free likes to tell the story about another of her inventions, a urine protein test using the dipstick method, which she helped popularize while working in the Technical Services Department, where she fielded questions from customers. Many of these customers were medical technicians who did not take kindly to her trying to make testing for them more convenient. They felt that if anybody could do dipsticks, the technicians would lose their jobs to, as they put it, to “kids off the street.” The protein test was based on the protein error of certain pH indicators, and the color change was from yellow to blue (beginning with pH 4). When one medical technician complained that she never got a negative answer with these new-fangled reagents, Helen asked if she followed directions and dipped the strip quickly into the urine specimen. She replied, “Oh, no, of course not. I stir it around to get the last little bit of protein out” And so she was actually washing the pH 2 buffer off the strip—and every urine specimen has a pH of more than 4!!

Because of the tremendous impact of her work, Free has been awarded many honors, including the American Chemical Society Garvan Medal (1970), The Honor Scroll Award of the Chicago chapter of the American Institute of Chemists (1967), and the Kilby Foundation Award (1996).

Throughout her career Helen Murray Free has been an active advocate of science education. From 1987 to 1992 she chaired the ACS National Chemistry Week Task Force. In 1993 she was elected president of the ACS. Because of her extraordinary work in public science education, the ACS instituted the Helen M. Free Award in Public Outreach in 1995. She was the first recipient.

In a recent conversation with the author, Helen Free expressed some characteristics that she felt helped her enormously in her career both at home and at work. She said that innovation, hard work, and perseverance could only be sustained by flexibility, openness to opportunity, and a large dose of joy.

### Serendipity, Creativity, Curiosity,

In 2001 Patsy Sherman (1930 – 2008) was inducted into the Hall of Fame for her creation of Scotchgard™ while working at the 3M Company. In the late 1960s her research culminated in the development of a product that both repelled stains and also permitted the removal of oily soils from synthetic fabrics, including the newly popular permanent press fabrics (25).

In 1952 fluoro-chemicals were not well understood. Chemist Sherman and colleague Sam Smith, working at 3M Company, were eager to find applications for them. Their most famous application, Scotchgard™, is one of the most widely used and valuable products, eventually bringing in over \$300 million annually for 3M. Their discovery of Scotchgard was serendipitous. After an accidental spill of a fluorochemical-latex emulsion rubber intended for jet fuel hoses showed resistance to water and oily liquids, they suddenly understood the potential of this mixture for the protection of fabrics. After much experimentation and testing, they patented Scotchgard and over a dozen other inventions.

Patsy Sherman was born in Minneapolis, Minnesota in 1930. She majored in chemistry and mathematics at Gustavus Adolphus College, receiving her baccalaureate degree in 1952. She then joined 3M as a research chemist and was assigned to work on fluorochemical polymers. Sherman was one of very few women chemists to work for a major corporation in 1952. Her work was an essential part of the introduction of 3M's first stain repellent and soil release textile treatments which have grown into an entire family of products known as Scotchgard® protectors.

Patsy Sherman regards the discovery of Scotchgard as one of her most significant accomplishments because many experts had written that such a product was “thermodynamically impossible.” She said, “We were trying to develop a new kind of rubber for jet aircraft fuel lines, when one of the lab assistants accidentally dropped a glass bottle that contained a batch of synthetic latex I had made. Some of the latex mixture splashed on the assistant's canvas tennis shoes and the result was remarkable.”

That day in the lab is legendary. Sherman and her colleague, Sam Smith, were working on another project when they observed that the accidental spill on a white tennis shoe would not wash off nor would solvent remove it. The area resisted soiling. They recognized the

commercial potential of its application to fabrics during manufacture and by the consumer at home.

As described in their initial patent application, their invention involves the synthesis of hybrid polymers that provide sufficient oleophobicity and hydrophilicity in water so that fabrics treated with the polymer have increased ability to release oily stains on laundering. They combined oleophobic and hydrophilic moieties in coatable copolymers, so that the relative mobility of the moieties was assured at normal conditions of temperature and environment. The surfaces treated with these copolymers responded reversibly to changes of environment, thus making them repeatedly launderable to remove oily stains.

An important characteristic of the hydrophilic segments of the polymer was that they be solvatable, and thus must contain structural units containing characteristic polar groups. One particular type of hydrophilic segment they used consisted of the product between hydrogen sulfide reacted and polyethylene glycol dimethacrylates to give sulfhydryl terminated prepolymers of the type called "H" to indicate hydrophilic:

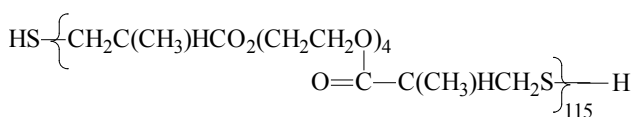


Figure 9. A Type "H" Prepolymer

A block copolymer is formed when an ethylenically unsaturated fluorinated monomer, called a Type "F" (to indicate "perfluorinated/oleophobic") monomer (Fig. 10) is polymerized by free radical initiation in the presence of the sulfhydryl terminated prepolymer. The segmentation of the polymer arises as a result of free radical chain transfer of the growing fluorinated polymeric unit to the sulfhydryl end groups.

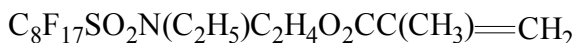


Figure 10. A Type "F" Monomer

Coating a surface with this polymer works in the following way. Fig. 12a shows diagrammatically an exposed surface treated with an oil and water repellent finish. The circles 10 designate the fluorochemical terminating groups which are seen when the surface is sufficiently enlarged. The terminating groups tend to be in some degree organized and will cover most of the

surface to form domains of oleophobicity. The ultimate end of each terminating group may be considered to be a trifluoromethyl group; the last three carbon atoms of a terminating group should be completely fluorinated to assure suitable oleophobicity.

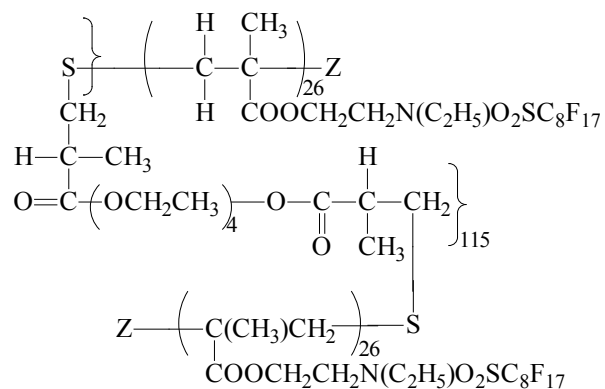


Figure 11. A Block Copolymer of the Type "F-H-F"

Fig. 12b shows an exposed hydrophilic surface comprised of hydrophilic constituent groups such as  $-\text{COOH}$  and  $-\text{OH}$ . A fabric provided with such a surface is water-wettable and is cleanable by laundering. Prior to the Sherman invention it had been inconceivable that a given fabric could be treated so as to possess characteristics of both Fig. 12a and 12b depending on the environment and that change of environment would effect repeated reversal of the characteristics.

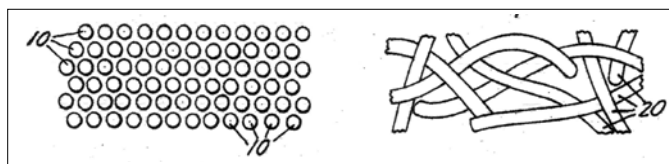
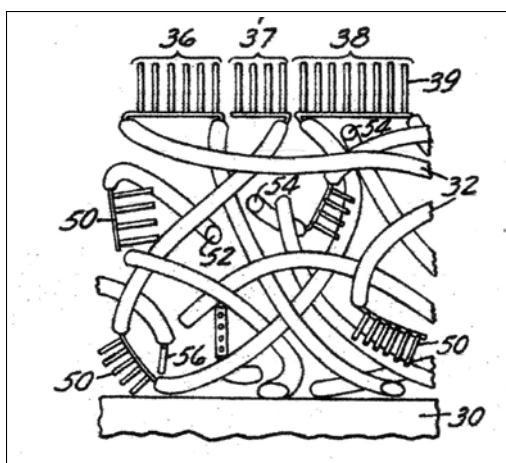


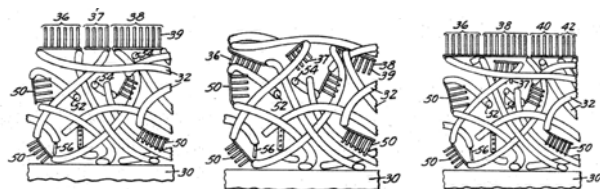
Figure 12a. Exposed Treated Surface Figure 12b. Exposed Hydrophilic Surface

Fig. 13 shows in highly diagrammatic fashion and in section, the outer layer of fiber 30 in a nonpolar, i.e., nonaqueous, medium such as air. Deposited on this surface is an autoadaptable segmented polymer having hydrophilic "H" segments designated by the strands 32 and hydrophobic and oleophobic "F" segments 36, 37, and 38, comprising a multiplicity of fluoroaliphatic or pendent groups, represented by slender rectangles 39, having fluorochemical terminating groups.



**Figure 13.** Fiber surface upon which is deposited an “F-H-F” segmented polymer

Fibers treated with an “F-H-F” segmented polymer can be cleansed in a mode that is quite different from normal cleansing action by emulsification. Soaps and detergents emulsify soil, which is normally hydrophobic and therefore can be dissolved in the hydrophobic portion of the soap or detergent, and then be dissolved in aqueous medium by means of the hydrophilic portion of the emulsion. On the contrary, cleansing action for an “F-H-F” treated fiber follows the sequence illustrated in Fig. 14:



**Figure 14a**      **Figure 14b**      **Figure 14c**  
**Figure 14.** Surface transformations of a type “F-H-F” polymer with changing environment.

In Fig. 14a the top of the fiber coating has an organized layer of oleophobic polymer which, when immersed in water (Fig. 14b) becomes submerged in the body of the polymer while the hydrophilic strands rise to the top. When the aqueous medium is removed, by drying, for example, a new surface of oleophobic polymer rises to the surface (Fig. 14c). Such movement repels oily stains and at the same time allows them to be washed away since they cannot adhere in any way to the fiber. The coating is self-renewing, thus allowing for multiple washings of the coated fiber.

After the introduction in 1956 of a stain repellent treatment for wool, Sherman and Smith later developed products designed for clothing, household linens, uphol-

stery, and carpeting. They jointly hold 13 patents in fluorochemical polymers and polymerization processes.

So an initial serendipitous event turned into a blockbuster invention through the follow-up curiosity and creativity necessary for the perfection of any invention. An interview with Sherman’s daughter, Shari Loushin (also a 3M chemist), revealed some of the qualities that helped her to follow the path of invention: high energy, competitive, active, feisty in the face of prejudice, and loyal to her profession and to the professionals with whom she worked. These characteristics enabled Sherman to continue to develop a whole new line of products based upon her initial discovery and eventually to move into a top managerial position at 3M.

## Conclusion

In 1777, Restif de la Bretonne could write to his contemporaries: “All women should be prohibited from learning to write and even read. This would preserve them from loose thoughts, confining them to useful tasks about the house, instilling in them respect for the first sex.” (26). We have seen in this paper that “loose thoughts” arising from literacy, and not only from literacy, but scientific literacy, have given rise to useful inventions that have improved the quality of life of entire generations. Usefulness “about the house” has been transformed into universal usefulness, instilling in us all a respect for the female gender, not as a first, but as an equal participant in the field of human endeavor.

There are so many different characteristics that come into play in the field of scientific discovery. Many of these were touched on in the various sections of this essay. Each of the inventors highlighted here has attributed her success to several of these qualities, and while they might be necessary, one could never say that they are sufficient. The congeries of “success recipes” would never have worked unless each of these dedicated women, in her own way, were on a single-minded but multi-faceted trajectory that included as much emotional power as intellectual achievement, driven overall by a supreme sense of purpose. But in the end, is all analysis fruitless? Can outstanding success be diagrammed like a sentence or chromatographed for an ingredient profile? That barriers to success exist is evident. That these barriers can be overcome in a variety of ways that span every aspect of human endeavor is also clear, perhaps rendered even more so by the stories presented in this paper. But in the end, it all seems to depend on the indomitability of the human spirit, “free at last!”

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## ABOUT THE AUTHOR

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## LOST ARTIFACTS?

### The F. J. Moore Portrait Collection

In 1949 Henry Monmouth Smith of MIT published a collection, titled *Torchbearers of Chemistry*, of 250 portraits and prints of famous chemists, with short biographical captions by Ralph Oesper of the University of Cincinnati (1). In the forward to the book it was indicated that these portraits were part of a collection which hung in the halls of the Chemistry Department at MIT and that many of them had been purchased with a fund established by the widow of the late Forris Jewett Moore, who had been Professor of Organic Chemistry at MIT and the author of a highly successful history of chemistry (2). The question is what has happened to the Moore Portrait Collection since the publication of Smith's book 60 years ago? Does it still hang in the halls of MIT? Is it in the archives of MIT? Or has it been dispersed and lost to future historians?

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*Readers having information relating to the above artifacts or questions of their own, which they would like to see addressed in future columns, should send their comments and questions to Dr. William B. Jensen, Oesper Collections, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to [jensenwb@email.uc.edu](mailto:jensenwb@email.uc.edu).*

## RESPONSE TO LAST ISSUE'S COLUMN

Numerous responses were received to last issue's question concerning the The Squibb Ancient Pharmacy Museum, which established the following facts. After being purchased in Europe by Squibb in 1932, the artifacts were put on display at the 1933 Chicago Century of Progress Exhibition. From 1934 to 1945 the collection was on display at the New York offices of the Squibb Company, as described in the small booklet mentioned in the previous column. In 1945 the collection was loaned to the Smithsonian. In 1989 Squibb was purchased by Bristol-Meyers, and in 1991 the collection was permanently donated to the Smithsonian. It was previously on display in the Hall of Pharmacy of the National Museum of American History but is currently in storage. Persons interested in further information should contact Judy M. Chelnick, Associate Curator, Division of Medicine and Science, National Museum of American History, 14th Street and Constitutional Avenue NW, MRC 637, PO Box 37012, Smithsonian Institution, Washington, DC, 20013-7012. Thanks to Lydia Hines, Ron Brashear, Richard Ulrych, Arnold Thackray, and Judy Chelnick for their helpful responses.

## BOOK REVIEWS

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*William Crookes (1832-1919) and the Commercialization of Science.* William H. Brock, Ashgate Publishing Company, Burlington, VT, 2008, 586 pp, ISBN 978-0-7546-6322-5, £65, \$124.95.

This hefty biography is a contribution to the publisher's 'Science, Technology and Culture, 1700-1945' series. Even that broad rubric scarcely encompasses the multifarious activities of William Crookes, whose proud and ambiguous motto for his escutcheon was *Ubi Crux Ibi Lux*.

The son of a prosperous tailor, Crookes received a somewhat sporadic education, the most important part of which was an apprenticeship at Prince Albert's Royal College of Chemistry under the tutelage of August Wilhelm Hofmann. Subsequently, a rather aimless year spent in Oxford completed his formal education. He is a supreme example of the autodidact. In spite of the fact that he had no formal degree and never held an academic position, he was to make major contributions to photography, chemistry, physics, agricultural science, public health, scientific journalism, and, astonishingly, spiritualism. An ambitious, flamboyant and at times ruthless man, he rose to be knighted by Queen Victoria and elected President of both The Chemical Society and The Royal Society.

To write the biography of such a varied man is a challenge, but Brock has met that challenge in superb fashion. He summarizes Crookes' principal achievements in the following words:

He is remembered chiefly for five things: the discovery of thallium in 1861; the invention of the eye-catching and puzzling radiometer in 1875; his brilliant experimental work on cathode rays using the eponymous Crookes tube in the 1870s; his dire prediction that mankind would starve unless chemists learned how to 'fix' nitrogen; and for his seemingly unorthodox spiritualism in the 1870s.

Brock goes into all this (and much else) in meticulous detail. Indeed, for the general reader the detail at times is a trifle overwhelming, but one of Crookes' talents was to recognize significance in seemingly trifling experimental observations.

To a modern reader Crookes' deep interest in spiritualism from the 1870s on is most strange. It was an interest shared by many eminent Victorians. Not all were believers—Faraday and Tyndall, for instance, were skeptical—but many scientists (Lord Rayleigh and Dewar) and other intellectuals (such as Arthur Conan Doyle) shared Crookes' passion, if not his intensity. A later wag even modified Crookes' proud motto to *Ubi Crookes Ibi Spookes*.

The last major biography of Crookes was written by Fournier d'Albe in 1923. Brock's achievement is such that there should be no need to write another for at least 86 more years. *Derek A Davenport, Purdue University, West Lafayette, IN 47906.*



*A Strange and Formidable Weapon: British Responses to World War I Poison Gas.* Marion Girard, University of Nebraska Press, Lincoln, NE, 2008, xii + 284 pp, ISBN 978-0-8032-2223-6, \$45.

I always feel a bit apprehensive when I start to read a book that began its life as a dissertation. Perhaps it's from thinking about my own eminently unpublishable dissertation, or perhaps it's the graduate-school memory of seemingly endless rows of dissertations in the library. They seemed to collect dust and be mostly unread, except by each candidate's committee members (and sometimes not even by them). It is true that turning a dissertation into a published book is more common in the humanities than in the hard sciences, and there are many successful and interesting books that have come into being via that route. Whether Marion Girard's *A Strange and Formidable Weapon*, which is based on her 2002 dissertation at Yale, is such a book may well depend on your point of view and reason for reading it. The blurb on the inside front jacket claims that it "uncovers the history of this weapon of total war and illustrates the widening involvement of society in warfare." I found much more of the latter than the former, and in that respect the subtitle, *British Responses to World War I Poison Gas*, is more indicative of the real intent of the book.

This is not a history of chemical weapons; Girard had a different goal in mind. Chemical weapons are her vehicle for investigating larger issues surrounding the war. Two ideas central to the book are that gas is "a tool of total war and [also] of post-Great War military policy" (p 6). The term "total war" refers to the dedication of all the people and resources of a nation to a particular war effort, but Girard suggests that viewing poison gas as a "total weapon"—i.e., one that affected everyone, on the home front, as well as on the battlefield—is both a novel way of looking at Great Britain as a participant in WWI and a means of examining the effect of the war on its citizens. Since different segments of society viewed and reacted to chemical weapons differently, "[c]omparing and contrasting these views offer a wider window into total war, First World War Britain, and the mixed reputation of gas" (p 7).

Girard sets up two pairs of opposites in connection with the use of chemical weapons in WWI: (1) the Western view of the superiority of its own civilization versus the barbarity of deploying poison gases on the battlefield; and (2) the terror that such weapons could evoke, not only among soldiers at the front (at least before adequate antigas protection became available), but also

among civilians at home, versus desensitization toward the horrors of poison gas by some people as they became more familiar with these weapons. Somewhat mechanically, Girard then devotes one chapter each to examining the views of politicians, the military, chemists and army physicians, industrialists, and general civilians along the spectra of these two pairs of opposites.

Chapter 3, "The Scientific Divide: Chemists versus Physicians," might be one of the more interesting chapters to many readers of the *Bulletin*. In a sense, these two groups fit together as opposite sides of the same coin. Physicians treated victims of the poison gases developed by research chemists. Girard portrays chemists as having "enjoyed a positive experience with gas" (p 76) as they played a crucial role in developing both new chemical weapons and effective antigas measures and, in doing so, enhanced the prestige of their profession. This picture of chemists working on chemical weapons in WWI bears more than a superficial resemblance to that of physicists working on atomic weapons in WWII. The author also does a good job, in just a few pages (pp 80-88), of succinctly describing the state of British chemistry at the start of the 20th century and the participation of individual chemists and scientific organizations in the war effort. Besides their research in the laboratory, looking for poison gases that might be suitable for the battlefield, chemists served on government committees that worked directly with the military. Among the list of names are such well-known British chemists as F. G. Donnan of University College, London, P. F. Frankland of Birmingham University, and W. J. Pope of Cambridge University.

I found that Chapter 5 covers a somewhat different topic from what Girard indicated. She states that "Chapter 5 analyzes general civilians" (p 12), but its title, "Gas as a Symbol: Visual Images of Chemical Weapons in the Popular Press," is a better description of its actual topic. While I accept the author's claim that people generally read newspapers and magazines offering points of view they agree with, I don't think this leads to her conclusions that "[t]he tone of the pictures also illustrates attitudes held by the British public about gas and war" (p 127) and that the "[v]isual images in journals therefore offer rich insights into perceptions of poison gas by the British public" (pp 127-8). While these images—mostly drawings and cartoons, along with a few photographs—may offer insights into what editors thought their reading public wanted, there is no discussion of the response of the British public to these images. Despite her description of a number of images that seem clearly intended

as propaganda (at least it seems that way to me) and even her own admission that some of them might be propagandistic, Girard never discusses the role of these images in shaping popular opinion, maintaining instead that they captured “public sentiment about poison gas” (p 154) and “helped the British to comprehend the horrors of World War I” (p 156). These latter claims may be true, but published illustrations that reflect (and may help shape) public sentiment are not public sentiment themselves.

Chapter 6, “The Reestablishment of the Gas Taboo and the Public Debate,” focuses on the postwar debate about chemical weapons both within and between different groups in Great Britain. Girard sets up the debate broadly between those who were “gas-tolerant” (including the biologist J. B. S. Haldane) and those who were antigas (including the writer H. G. Wells), though each side included individuals with a broad range of views and attitudes. The debate was carried out within the context of certain beliefs by both sides: (1) another war was inevitable; and (2) the coming war would include the use of chemical weapons, possibly against civilians, as well as against soldiers. Nevertheless, the antigas arguments eventually prevailed as public opinion came to embrace the taboo against such weapons and the hope that international treaties would prevent their use in the future.

The “Epilogue” is intended to extend the lessons about chemical weapons from WWI down to the present, but I did not find that, even in conjunction with the

previous chapter, it tied together the five chapters about different segments of British society. Much of this final chapter focuses on the taboo against such weapons, which was strengthened through the public debate between the two world wars. Girard poses the question whether it is the taboo or the idea of deterrence that accounts for the fact that chemical weapons have not generally been used in wars since WWI. She does not explicitly consider the possibility that as more effective and deadly weapons were developed, the need for chemical weapons by conventional military forces diminished. While the vagaries of wind and weather would always influence the use and effectiveness of chemical weapons, there are no such problems with atomic and nuclear weapons.

As a final note, the book’s origins as a dissertation are obvious in its documentation. Although it is listed at 284 pages, the text ends on page 199, and notes take up the next fifty pages, along with an 11-page bibliography. The documentation is obviously important to a scholar interested in this topic, especially since many of the notes are references to material in British archives. However, as a general reader, I became annoyed with so many references, few of which added directly to the text.

The book is a well-researched and documented scholarly work, which can obviously provide important material and references for the specialist. The general reader, however, may find it too narrowly focused on a very specific slice of the overall story of chemical weapons. *Richard E. Rice, P.O. Box 1210, Florence, MT 59833; charrice@juno.com.*

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*Perspectives on Risk and Regulation: The FDA at 100.* Arthur Daemmrich and Joanna Radin, Ed., Chemical Heritage Foundation, Philadelphia, PA, 2007, 163 pp, ISBN 978-0-941901-42-0, \$12.

This volume contains the proceedings from a one-day conference held in 2006 in Philadelphia, at the Chemical Heritage Foundation, to celebrate 100 years of the Food and Drug Administration. Attendees at the conference, one of several events held throughout the country, included people from industry, trade organizations, and the FDA. Although each person’s perspective differed, there was common ground: science is the basis for decisions made by the FDA; adequate funding is necessary to continue the work of the administration; the policies and regulations set forth by the FDA allow

the United States to have the “gold standard” in terms of consumer safety as it related to food, drugs, cosmetics and medical devices; and historical perspective illumines the present and points the way to the future. The book’s structure reflects that of the conference itself, with an introduction, division into three sections—historical perspective, drug and medical devices, and food and dietary supplements—and a conclusion from FDA Commissioner Andrew Eschenbach. In addition, a streamlined Q&A appears after the second and third sections. A time line of the FDA at the beginning of the book is very helpful. In organization, in brevity and in content, this book provides a comprehensive survey of the many ways in which the FDA ensures the public’s safety on a daily basis.

The historical section, by Peter Barton Hutt, is framed around ten events that Hutt sees as turning points in FDA history. Hutt suggests that science is the basis for the FDA and allows it to move forward. He also notes that he could have chosen many other examples for his ten “critical” events. A mix of public outcry following accidents, legal cases, and Congressional maneuvering comprise his list.

The second section focuses on drug and device regulation from industry and administration perspectives. Steve Galson explains how the Center for Drug Evaluation and Research works to ensure drug safety. With new processes initiated, he sees communication with the public, with health care professionals, with industry, and with other governmental agencies as critical to the success and continued safety of the American drug market. Ronald Krall envisions the future of pharmaceuticals as individualized, genetic-based medicine and the concomitant regulation of said pharmaceuticals as one of continual and active surveillance in this personalized medicine world. Krall offers suggestions to help keep the United States at the forefront of worldwide regulation. Daniel Schultz explores the world of device safety as this becomes increasingly complex with the creation of items that are both device and drug, such as coated stents. As the medical marketplace moves forward, Schultz notes that the personnel at the FDA who evaluate such items will need increasing resources to stay atop the latest developments in two different regulatory fields. Robert O’Holla offers a mini-retrospective of how the changes in device regulation have affected industry as he ponders thirty years of device manufacture and design and regulatory approval.

The third section considers those items we ingest through food, including dietary supplements, the latter not regulated until 1994. Robert Brackett posits that the FDA’s challenge to keep our food supply safe has grown commensurate to our changing food habits: we consume items grown or produced across the world; we demand raw or organic foodstuffs; we travel globally; and all of

this affects what we eat and how our bodies react. The FDA does keep our food safe, but with expedited air travel and new fruits and vegetables entering the market all the time, scientists are continually creating new tests for new items. Idamarie Laquatra advances an industry’s appreciation for regulation. The extant guidelines help companies as they look to current research and the FDA’s interpretation of the latest scientific studies to craft regulations relating to labeling and nutrition information. Barbara Schneeman proffers the FDA view on dietary supplement regulations, and Steven Mister counters with an industry perspective. In both cases, the authors emphasize the relationship between science and public health. Not surprisingly, they differ in what they think the FDA should do with the relevant labeling and education laws.

In the final section, FDA Commissioner Andrew von Eschenbach looks at the past and glimpses the future of all that the FDA did, does, and should do. His vision is one of solidity: to keep our food and drug supply as safe as it can be, within the financial constraints imposed by Congress and limitations of staff. As do all the other chapters, this final one emphasizes how much we have gained from the FDA’s vigilance on our behalf over the last 100 years.

The editors compiled the chapters fairly quickly after the conference. The Chemical Heritage Foundation is to be commended both for sponsoring the conference and printing this book. Each chapter is a crisper version of the conference paper, and the incorporated discussion sections offer an opportunity for readers to know how the authors responded “off the cuff” to questions that arose after each of the two major sessions. In some cases, the chapter offered one version and the answers revealed current and future plans for industry or enforcement. This book is one that can be read either cover to cover or selectively, depending on one’s background and interest. Given that we all depend on the FDA for ensuring the safety of our food and drug supplies, cosmetic items and medical devices, this should be a topic of interest to all. *Gwen Kay, State University of New York, Oswego.*

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*Collected Papers on Philosophy of Chemistry.* Eric R. Scerri, World Scientific Publishing Co., Pte Ltd, Singapore, 2008, 235 pp, ISBN-13 978-1-84816-137-5, \$95.

The author, Malta-born (1953) and UK-educated, received his Ph. D. in history and philosophy of science

from King’s College, London, in 1992. After postdoctoral appointments at the London School of Economics and at Caltech, he taught at Bradley University and at Purdue. He joined UCLA in 2000 as a lecturer in the Department of Chemistry. This book gathers a selection of his papers. It is organized in three parts, dealing with the reducibility

of chemistry to quantum mechanics, with the periodic table, and with the issues of realism/anti-realism in relation to chemical education. An introduction states the general goals and traces the intellectual itinerary of the author during the period 1992-2007.

Scerri's core intuition is shared by many of us: chemistry is an autonomous science. This is a point I will return to. Before doing so, I will examine Scerri's approach and the topics he chose to study, its originality, the relevance of his ideas to chemical education, and I will note strengths and weaknesses. I will conclude with stating my views on philosophy of chemistry, its purpose and usefulness.

Scerri's approach is to bring up statements made by various historians and philosophers of science and to demolish them as mistaken. His main evidence is the periodic table of the elements. Scerri argues that the periodic table, and chemistry accordingly, were established from empirical data rather than being derived deductively from first principles stated in quantum mechanics. In terms of a general philosophy of chemistry, this is a rather narrow viewpoint. The book is underlined by a teaching of general chemistry at the high school-college level, 1950s-vintage, emphasizing electronic configurations for the elements and valency—rather than, say, coordination numbers—that has become somewhat dated. Likewise with the near-exclusive focus on the periodic table. Instead of attacking the claim by some physicists of the periodic table deriving directly and exclusively from quantum mechanics, Scerri might have performed a more useful task by analyzing, historically and philosophically, the *chemical* evidence on which the periodic table relies.

Yes, Mendeleev discovered what one might term, metaphorically, the Rosetta Stone for chemistry. As such, the periodic table is a monument of science. Its iconic status is sufficiently obvious to need no reiteration. But a distinction is essential. While reverence is amply justified, to treat the periodic system of the elements in like manner to the Ten Commandments is uncritical and, ultimately, unscientific. I am referring here to the naïve illusion, harbored by many a student—of course not by Dr. Scerri—of the periodic table as providing the answer to any exam question. While this may be axiomatically true, it is far from being pragmatically useful. One ought to keep this key distinction in mind: to endow the periodic table with talismanic value amounts to treating it as an object of magic.

Which makes it all the more difficult to examine it as a topic for historical and philosophical appraisal and discussion. Art historians, for a similar reason, steer clear of the Mona Lisa. The way to go about, with such idolized artifacts, is to treat them with levity and wit, seriously of course, but not solemnly, with a measure of disrespect. In a word, one has to first remove the veneer. At least, this is my intuitive understanding of how to treat such monuments to fit them into intellectual history. Scerri's attitude of reverential respect, while warranted may be self-defeating: the periodic table is not central to an understanding of chemistry, a point I shall now examine.

Three axioms undergird Scerri's enterprise: A. the periodic table is the concept, the organizing principle most important to chemistry; B. the main goal for a philosophy of chemistry is to critically examine the concepts at the core of the science; C. hence, if Eric R. Scerri devotes himself to studying the periodic table, he fulfills a most essential task.

While C is a winsome belief, it remains an act of faith. As such, it can be followed or it can be ignored. The other two axioms deserve closer scrutiny.

There is a host of other candidates for A. One might argue for the primacy of any of the following: A<sub>2</sub>, chemistry is a molecular science; A<sub>3</sub>, chemistry is subsumed by the Pauli Principle; A<sub>4</sub>, chemistry deals with the organization of matter at the microscopic level, the way in which atoms cluster, form bonds and molecules and supramolecular assemblies, enter coordination complexes, ...; A<sub>5</sub>, formation and breaking of bonds between atoms is at the heart of chemistry; A<sub>6</sub>, catalysis cements the synergy between chemistry as a science and as an industry; etc.

B is also questionable. One may want to replace the emphasis on *concepts* by one on *actions*, i.e., what chemists do: B<sub>1</sub>, purifying substances; B<sub>2</sub>, synthesizing molecules; B<sub>3</sub>, putting together nanometric structures; B<sub>4</sub>, interconverting chemical entities on hypersurfaces; B<sub>5</sub>, determining reaction mechanisms; B<sub>6</sub>, pursuing the artificial, in its infinite variety of costumes; B<sub>7</sub>, mastering a combinatorial artistry; etc.

I have put together these, admittedly short, lists to stress that Scerri's endeavor may not belong, as he so clearly trusts and would have us believe, at the apex of any philosophy of chemistry.

To return to the periodic table, its iconic status is undeniable. Does that justify treating it as the only worthwhile topic for philosophy of chemistry? To use a

comparison, Marilyn Monroe also enjoyed iconic status. Does it make her in any way an important object of study in terms of, say, American womanhood in the Sixties? The recently departed Studs Terkel made a lasting contribution to American sociology from focusing, not on individuals with iconic status but, conversely, on ordinary men and women. Would not an analogous attitude make a lot more sense for building a genuine philosophy of chemistry?

Despite the present times being the age of hype, the author's smugness, his constant one-upmanship make a bad impression. He presents himself as a founder, if not the founder of the whole field of philosophy of chemistry. In so doing, he ignores the earlier, much earlier contributions by the likes of Emile Meyerson, Hélène Metzger, or Gaston Bachelard (except, in this last case, for the flimsiest of mentions), not to mention Hegel, who wrote an entire book on the philosophy of chemistry. Moreover, did not our ancestors, the alchemists, term themselves "philosophers," admittedly in a different sense?

Take this for instance. Scerri writes: "I am not aware of anybody other than myself who has written about the nature of the most recent density functional approaches in the philosophical literature." Assuming that the assertion is true, and turning to what Scerri has written about the density functional approach (pp 160-162), one is bound to ask "where is the beef? What philosophical questions or issues has he raised? In what way is Scerri's description of the density functional approach enlightening?"

An important point is absent from Scerri's book: how does philosophy of chemistry fit into philosophy of science? Is it exceptional and, if so, in what way? It would have been most useful had Scerri distinguished between synchronic and diachronic approaches to epistemology. The former describes deductive logic, the strategy which Paul Dirac asserted—which incidentally may be irrefutable in principle—would ultimately make chemistry a daughter science to quantum physics. The latter is illustrated, among others, by Sir Karl Popper's notion of conjectures and refutations: scientific epistemology, in that tradition, is procedure-driven.

Scerri's constant self-reference and self-assurance grate all the more that the book is marred by quite a few mistakes. Examples? Stating nitric oxide to be an unstable molecule (p 74) is a patently untrue assertion: unstable relative to *what*? Clearly, NO is stable, not unstable, with respect to its dissociation. Scerri blames the purported instability on the presence of an odd number of electrons. OClO is a highly persistent entity, yet it is a free radical, too. Dioxygen is a diradical in the ground state; does it

make it unstable? It explains its reactivity, which is not the same thing. As for NO, its falsely asserted instability runs in the face of its multitudinous physiological functions.

Another questionable assertion concerns isotopes. Scerri repeats the old chestnut of isotopes having identical chemical properties (p 16), whereas primary or secondary isotope effects, from protium-deuterium substitution for instance, are ample evidence to the contrary. Each atom of carbon in a natural product has a distinct and measurable (at the 1% difference level)  $^{12}\text{C}/^{13}\text{C}$  ratio, because of such isotope effects.

But let us examine the main emphasis of the book: the effect of the irreducibility of chemistry in general, and of the periodic table in particular, to quantum mechanics. As already stated, Scerri is to be commended for taking issue with Paul Dirac's statement (1929 -1930). The very course of chemistry since Dirac's famous dictum, especially during the second half of the twentieth century, has made it moot and has abundantly displayed the autonomy of chemistry from physics.

Scerri thus puts the question (p 60): "Has Chemistry Been At Least Approximately Reduced to Quantum Mechanics?" One is reminded, let me note in passing, of the theological discussions on whether the sacred wafer is consubstantial with the body of Christ.

Scerri's question is of the logical type "Does A cause B?" where A stands for quantum mechanics and B stands for chemistry. But is it a well-posed question? Chemistry is a field of science. Quantum mechanics does not enjoy an equivalent status. Quantum mechanics is a toolbox, drawing on various mathematical equations. Granted, it is an extremely powerful toolbox. It allows calculation of many observables to impressive accuracy. If I am allowed the comparison, would one even think of raising the formally identical question: "Has Astronomy Been Redefined by the Hubble Telescope?"

But let us turn from the unfortunate wording of the title of that chapter to its content. It has considerable merit. Scerri presents in clear, succinct and rather objective manner the gist of the main quantum chemical calculations. The interesting question is, I submit, not that of the reducibility of chemistry to quantum mechanics. Instead, it is that of the chemical *insights* gained through quantum chemical calculations: one judges a tool by how efficient it is, not by metaphysical considerations as to its generative prowess. This is again, as with the (iconic status/talismanic value) a fine distinction. But—and this is a crucial point—the role of philosophy is to

make such fine distinctions, not to use language and concepts loosely.

Philosophy of chemistry calls for scrutiny of what chemists actually do. This is all the more challenging that the science does not stand still. It has evolved more since 1950 than between 1789 and 1950. Textbooks lag behind by necessity and because of the conservatism of teachers. They simply fail as sourcebooks for philosophical issues and discussions.

Philosophy of chemistry deals with questions both old and new. An example of the former, reinvigorated by recent developments, is the heap of sand. Greek philosophy of Antiquity raised that paradox. It concerns meaning and naming both. When is it legitimate to name an aggregate of grains of sand a heap? If we remove a single grain, clearly it remains a heap of sand. But let us continue likewise to reduce the heap indefinitely, grain by grain. Is it still a heap when only six grains of sand, say, are left? Clearly not. Then, at what stage does the collection of grains switch from being a heap to being something else? This question, as old as philosophy itself, assumes renewed urgency nowadays with quantum dots. Those are aggregates, not of grains of sand, but of atoms.

There is a critical number, of the order of magnitude of 30-50, when such a cluster, instead of displaying the usual macroscopic properties of a condensed phase, switches into an entirely different set of properties, describable by quantum theory. Even more interesting, the critical number is observable-dependent: whether one looks at the cohesive energy, conductivity, spectrum, ... the crossover occurs at different aggregate sizes.

An altogether different question is that of the epistemic status of molecular *models*: what are they? They obviously differ from their homonyms, those intellectual constructs in-between working hypotheses and fully-fledged theories. They resemble more the dummies architects rely upon. A careful delineation of the two kinds of models is in order.

Any philosophy of chemistry has to address a central cognitive issue, that of the iconic language of chemistry (formulas), in relationship to division of labor between the two hemispheres of the brain, pictograms and other visual languages.

One could go on and on! Scerri has merely scratched the surface of the bounty, too often in the same spot. *Pierre Laszlo, Prades, F-12320, Senergues, France.*

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*Fermentation: Vital or Chemical Process?* Joseph S. Fruton, History of Science and Medicine Library, Vol. 1, Koninklijke Brill NV, Leiden, Boston, MA, 2006, xv + 116 pp, ISBN 978 90 04 15268 7, € 75, \$98.

*Fermentation* is the last book written by Joseph Fruton, who died at the age of 95 on July 29, 2007, two days after the death of his wife and long time collaborator, Sophia Simmonds. Fruton had distinguished careers as a biochemist and as an historian. It is quite apparent that he had given a great deal of thought to fermentation and its importance to science and to human activity. It is also apparent that he did not intend the book to be the last word in the history of fermentation, but rather a cruise through the thoughts and actions of philosophers and scientists with respect to fermentation from the early Greeks to the mid-twentieth century.

A careful reading of the introduction is necessary to understand where the book is going and what the author is attempting to accomplish. Perhaps one sentence in the introduction (pp xiii-xiv) best describes Fruton's

intentions, and perhaps excuses many of the shortcomings of the book:

In this book, I offer a *sketch* of the usage in the Mediterranean world and western Europe of the terms fermentation and ferment (or their Greek, Latin, Arabic, or German equivalent) in alchemical efforts and in subsequent controversies about the nature of alcoholic fermentation.

The word "sketch," which I have italicized and underlined, is the operative word. Fruton is covering the mention of fermentation over time, and hitting the highlights in the nineteenth and twentieth centuries; but he apparently had no intention of presenting a coherent picture of the development of the modern theory of fermentation.

After the short introduction the book has four chapters, each covering a period in the history of mankind, and a brief conclusion. Fermentation, the action of yeast in the making of wine, beer, and bread and in the processes of digestion and putrefaction has been important as both

a useful process and a subject for speculation and study from the early Greeks to the present. The first chapter, only 15 pages long, covers Aristotle to Paracelsus, a period of almost 2,000 years (400 BC to 1600 AD). Essentially it covers the mention of fermentation or ferments over this period of time. Fruton quickly takes us through some of the thought of Aristotle on fermentation, the influence of Aristotle on the alchemists, the translation of the Greek scientific literature into Arabic and eventually into Latin, the use of the terms fermentation and ferment in describing the transmutation of metals, and a little of the history of Paracelsus and the Paracelsians. The second chapter, titled van Helmont to Black, covers the 17<sup>th</sup> and much of the 18<sup>th</sup> centuries. It begins with Joan Baptista van Helmont, a Flemish physician and the most important of the Paracelsians, who had a strong influence on the thinking of a number of English physicians and on Robert Boyle. Fruton covers the speculations regarding fermentation of many of the premier thinkers, scientists and physicians of this period, including Francis Bacon, René Descartes, Robert Boyle, Isaac Newton, Herman Boerhaave, and Johann Bernoulli. With the invention of the pneumatic trough by Stephen Hales, it became possible to trap gases evolved in chemical reactions. This led to Joseph Black's discovery of "fixed air," carbon dioxide, which was later identified as the gas evolved during vinous fermentation. Henry Cavendish did some crude quantitative work on the fermentation of brown sugar. During these two centuries the picture of fermentation had evolved from a mystical view to a more mechanistic view.

In the third chapter Fruton covers the period from the late 18<sup>th</sup> century and the classic work of Antoine Lavoisier on fermentation to the late 19<sup>th</sup>-century work

of Emil Fischer on the chemical structure of the sugars and the action of enzymes. In the century between the efforts of these two chemical giants, there was the work of many in discovering that yeast was a living organism and finding a host of soluble "ferments" that eventually came to be known as enzymes. Some of the best known contributors were Justus Liebig, Friedrich Wöhler, Jons Jacob Berzelius, Theodor Schwann, and, of course, Louis Pasteur. These discoveries raised the issue of vitalism versus chemical processes, although Fruton says very little of this debate.

Chapter Four, *The Buchners to the Warburg Group*, covers much of the work of the early 20<sup>th</sup> century leading to the Embden-Meyerhoff-Parnas (EMP) pathway for the yeast fermentation of glucose to ethanol and CO<sub>2</sub>. Although this chapter contains an enormous amount of information regarding the work of the Buchner brothers, Arthur Harden, Otto Warburg, Otto Myerhoff, Gustav Embden, and Jacob Parnas, and it deals with the importance of the isolation and purification of the enzymes, it does not present a logical development of the theory. This should have been a chapter in which the evidence built inexorably to a grand conclusion, and that just does not happen. We are left wondering how the biochemical community ever arrived at the final pathway.

The brief conclusion does not offer any relief. If anything, it leaves us wondering once more what Fruton had in mind for this book.

There is an extensive bibliography, a very complete index of personal names, and an almost nonexistent subject index. If nothing else, this book should prompt some enterprising young historian to write the really exciting story that the scientific work demands. *Leon Gortler, Brooklyn College.*

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*Max Perutz and the Secret of Life.* Georgina Ferry, Cold Spring Harbor Laboratory Press, Woodbury, NY, 2008, 352 pp, ISBN 978-0-87969-785-3, \$39.

One might quibble with the title as a bit melodramatic, but, in every other respect, Georgina Ferry got it right. Even the title is based on Perutz's 1936 question to British crystallographer Desmond Bernal, "How can I solve the secret of life?" Bernal replied, "The secret of life lies in the structure of proteins, and X-ray crystallography is the only way to solve it."

Perutz summoned Georgina Ferry to his bedside shortly before his death from cancer in 2002. He wanted her to write his biography, probably because she had written a biography of Dorothy Hodgkin, another Nobel crystallographer, and he knew she understood the discipline and could relate it to nonspecialists. Ferry responded with an engaging read. While the book is largely chronological in presentation, Ferry freely steps back in time with almost every chapter to develop a particular theme. The result is an insightful look at Perutz's life and work and the role he played in what was

arguably the most productive collaboration of scientists in twentieth-century molecular biology. Max Perutz was born into a Jewish family of the moneyed, educated Viennese society. He was a sickly child. In fact health issues dominated his life, leading, especially in his later years, to renowned eccentricities. He did manage good health during his early adulthood, becoming an excellent skier and mountaineer.

After studying chemistry at the University of Vienna, he left for Cambridge in 1936, only two years before Hitler's *Anschluss*, the reunification of Austria and Germany. Perutz had money, so an offer for a graduate position was easily obtained. While Bernal attracted Perutz to X-ray crystallography, his cousin's husband, Felix Haurowitz, professor of biochemistry at the German University of Prague, enticed Perutz into his life-long pursuit of hemoglobin. Perutz shared the 1962 Nobel Prize in Chemistry with his former student and colleague John Kendrew—Perutz for the structure of hemoglobin, Kendrew for the structure of myoglobin. Perutz did not stop there. Perhaps his best work was developing a mechanism for how hemoglobin functions, in his words, as a molecular lung.

Ferry guides the reader through this pursuit. Much of the book follows the painstaking process of elucidating the hemoglobin structure. Perutz was criticized for selecting such a complex molecule for study. Gradually, improved methods and techniques gave better and better glimpses of the structure. Ideas came from many other sources: Linus Pauling, Francis Crick, Lawrence Bragg, John Kendrew, and Michael Rossman. In each case Perutz incorporated those ideas into the next set of experiments. One of Perutz's strengths was to take ideas, even when delivered as criticism, and put them into play. For example, when Cal Tech's Linus Pauling postulated an  $\alpha$ -helix structure for proteins, Perutz immediately recognized support for the idea from his X-ray patterns. That led Perutz to postulate a model for the hemoglobin structure. In a seminar setting, Francis Crick completely demolished Perutz's model. Perutz was not offended and set about to devise new experiments. That reaction typified Perutz in the early years. He knew he lacked the mathematical abilities of the physicists. Crick later suggested isomorphous replacement, whereby a marker atom is incorporated into a structure without altering its three-dimensional folding pattern. Perutz used mercury atoms for a critical breakthrough in protein imaging.

John Kendrew began studying the smaller myoglobin molecule. Michael Rossman joined the group as a programming expert, which led to even better results. In fact, it was Rossman who saw that hemoglobin looked like four myoglobins. Perutz immediately began to build a model.

The Nobel Prize gave Perutz new confidence. His own best thinking appears to have been in obtaining images of oxygenated and deoxygenated hemoglobin and subsequently postulating the oxygen binding mechanism. Whereas during the structure years, Perutz lacked a certain amount of self-esteem, he now defended his binding mechanism like a bull dog.

Ferry does not limit the story to hemoglobin. During Perutz's graduate student years, Bernal left Cambridge for London, but Perutz stayed behind. To Perutz, science and Cambridge were inseparable. Sir Lawrence Bragg came to the Cavendish Laboratory and became Perutz's new champion. The *Anschluss* changed Perutz from a visiting foreign national to a refugee. His source of income evaporated as his family fled Austria. Bragg, however, succeeded in securing support for Perutz from the Rockefeller Foundation. Perutz's parents managed to get to Cambridge. He was now supporting his family too, a matter complicated because his parents were not willing to live at the level he could now afford. Financial pressures led to new health issues. To supplement his income, Perutz engaged in periodic studies of glaciers, an opportunity that arose from his crystal expertise and his mountaineering abilities.

In 1940 Perutz received his Ph. D. for X-ray studies on hemoglobin. Less than two months later, British authorities took him into custody and sent him to internment camps in England and Canada. It took nine months for family and colleagues to gain his release.

All British scientists had war work in addition to their normal scientific pursuits. Perutz's glacial experience led to an involvement with the Habbakuk project, Lord Louis Mountbatten's attempt to build aircraft carriers from hybrids of wood and ice. It was eventually abandoned.

Bragg convinced the Medical Research Council to found the MRC Unit on Molecular Structures of Biological Systems, with Perutz as head. Hugh Huxley and Francis Crick were recruited to the Unit. Bragg himself joined Perutz in madly pursuing the hemoglobin structure.



James Watson joined the Unit. Watson and Crick were interested in DNA, but Bragg forbade it. Wilkins' group in London was working on that project, and a gentlemen's agreement did not allow competition with another MRC unit. Watson had already seen data during a visit to Wilkins' laboratory that suggested a helix pattern. Things changed, however, when Richard Pauling, a graduate student with Kendrew, indicated that his father, Linus Pauling, was also working on the DNA structure. To Bragg, losing to the Americans was not acceptable, so he relaxed his edict. As fate would have it, unpublished data from Wilkins' group came to Perutz as a member of the MRC Biophysics Committee. When Watson asked to see it, Perutz showed it to him. After all, it was not marked confidential. Crick immediately saw the anti-parallel helix pattern, and the rest is history. Fifteen years later, when that story came out, Perutz was criticized for the ethical lapse. At the time, however, he was very pleased that the unit got the structure for DNA ... and the secret of life.

Perutz considered 1953 the *annus mirabilis*. Edmund Hillary conquered Mount Everest, Elizabeth II was crowned, Watson and Crick solved DNA, Huxley described muscle fiber contraction, and he got definitive hemoglobin patterns. The unit was on top of the world.

That same year Bragg moved to London to become Director of the Royal Institution. The new physics chair at the Cavendish did not share Bragg's devotion to the unit. It was moved from Cavendish into a hut and placed on borrowed time. Across campus, a similar fate befell biochemist Fred Sanger, who was supported by MRC grants but lacked regular faculty status. Sanger had published the structure of insulin, which was to lead to his first Nobel Prize in 1958. Discussions between Perutz and Sanger led to requesting the MRC to build a new laboratory for molecular biology. Perutz took the lead

that resulted in the MRC Laboratory of Molecular Biology and a new facility in 1962, which he headed. That fall the number of Nobel Laureates rose from one to five as the chemistry prize went to Perutz and Kendrew and the medicine prize went to Watson and Crick.

Even at the unit, Perutz had followed the "Cambridge tradition of recruiting excellent people and letting them do what they wanted." At the LMB, a canteen was built on the top floor to facilitate discussions over tea or lunch. Perutz's greatest strength was in fostering those interactions. He said, "Creativity in science, as in the arts, cannot be organized. It arises spontaneously from individual talent. Well-run laboratories can foster it, but hierarchical organization, inflexible, bureaucratic rules, and mountains of paperwork can kill it." As of 2002, the year of Perutz's death, the LMB had produced twelve Nobel Laureates.

Ferry had access to volumes of Perutz's letters. She richly used them to accent the narrative. She paints a sympathetic picture of Perutz, but in no way glosses over his shortcomings. In most respects, she leaves it to the reader to interpret Perutz.

Max Perutz is probably not among the names most people associate with the champions of twentieth-century molecular biology. However, Georgina Ferry captures the essence of Max Perutz. He was not the intellect of the Cambridge revolution in molecular biology; he was the glue that held it together. Francis Crick said, "Max wasn't a particularly quick thinker. He was a plodder, but a persistent plodder, and he had considerable insight as a result of his plodding." Perutz was not threatened by the genius of people like Francis Crick, James Watson, or Sydney Brenner; rather he reveled in them and helped develop a system that allowed science to reap their collective benefits. He was the master at understated direction. *Joe Jeffers, Ouachita Baptist University, Arkadelphia, AR 71998-0001.*

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*Cathedrals of Science: The Personalities and Rivalries That Made Modern Chemistry.* Patrick Coffey, Oxford University Press, New York, 2008, xix + 325 pp, ISBN 9780195321340. \$29.95.

This book is an enjoyable presentation of the evolution of physical chemistry during approximately the first half of the twentieth century. The focus is upon the

personalities and rivalries of six dominant figures, S. Arrhenius, W. Nernst, G. N. Lewis, I. Langmuir, F. Haber, and L. Pauling, who made much of modern physical chemistry. There are as well as a number of others who interacted strongly with these principals in producing much of modern physical and theoretical chemistry. The geographic playing fields are primarily the United States, Germany, and Sweden. Winning is clearly defined by the

Nobel Prize in chemistry. The rules of the game were relatively straightforward: develop an important area experimentally and present a theoretical explanation for the observations. It should be noted that of the selected six only G. N. Lewis did *not* receive the Nobel Prize. An extremely readable review of this book, which properly stresses personalities and rivalries, has been given by Sam Kean [*Chem. Eng. News*, October 6, 2008].

The competition and rivalry characterized by the personalities of the players are certainly the theme of this work. It is more difficult to place this competition into the scientific mindsets of physical chemistry that existed during the periods of development in the approximately half century 1890-1950. Understanding and determining *chemical affinity* play a fundamental role in the evolution of useful chemical thermodynamics. As noted by Lewis and Randall "...numerous applications of thermodynamics to physics and especially to chemistry. Here the methods of thermodynamics have brought quantitative precision in place of the old vague ideas of chemical affinity and thus chemistry has made the greatest advance toward the status of an exact science..." [G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill, New York, 1923, 1st ed., 1923, 2.]

This history of leaders of physical chemistry presents discussions essentially in terms of concepts and language of their period rather than through the hindsight of contemporary vision. I have found that having Lewis and Randall, which was published midway through the period, at hand is extremely useful in strengthening the science basis of the development, as well as the language changes that have occurred.

The educational consequences of being at the forefront of evolving knowledge are clearly developed by Coffey. The American leaders Richards, Lewis, and Langmuir all studied in Germany with Nernst. Lewis, who is the central figure of this book, is the leader in the development of physical chemistry in the United States. He moved from MIT in 1912 to become chairman of the department of chemistry as well as dean of The College of Chemistry at the University of California at Berkeley, positions he held for thirty years. In this period Berkeley became the leading institution for the education of physi-

cal chemists. The faculty grew from within at Berkeley and developed under the unique personality of Lewis. This imprint remained at Berkeley long after Lewis' death in 1946.

The first Nobel Prize was awarded in 1901 to J. H. van 't Hoff for the laws of chemical dynamics and osmotic pressure. The personality conflicts among the protagonists are probably most glaring by the role of Svante Arrhenius (who won the 1903 Chemistry Nobel Prize for his electrolytic theory of dissociation). His personality and actions in blocking the award of the Nobel Prize to Nernst for fifteen years are spelled out in detail. G. N. Lewis never received the Nobel Prize, a point which occupies a considerable part of this book. Whether this is entirely a consequence of his personality and verbal communication skills is not clear to me. The contrast between Langmuir and Lewis in this respect is quite dramatic. Langmuir is a self-taught alpine skier, while Lewis is a chain smoker of cheap Philippine cigars. Of considerable importance to Langmuir was the General Electric Research Laboratory, led by Willis Whitney, where basic research was valued. The description of the invention (discovery?) of the inert gas-filled incandescent light bulb by Langmuir is delightful and important, showing that skillfully planned basic research before full-scale industrial production is a very cost effective step.

The history of physical chemistry is a large project, with many facets. This work of Patrick Coffey will remain an essential component in this project. The emphasis is on the people who were responsible for its development. The final chapters bring nuclear chemistry and isotopes, especially deuterium to the science of physical chemistry. The presentation of the very altruistic personality of Harold Urey, the discoverer of deuterium, is especially enriching. In summary, this book by Patrick Coffey is an enjoyable read. It furthermore stimulates the desire of the reader for further professional history of physical and theoretical chemistry providing clear delineation of the science development associated with the developers. Chemistry is a rich science, frequently called the central science (by chemists) by its place between biology and physics. This book is thoroughly documented. It sets a professional standard for the further historical analysis of the evolution of physical and theoretical chemistry. It is difficult in a short review to fully expose the richness of this text. *William Klemperer, Harvard University.*

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