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M. Polanyi

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1995 DEXTER AWARD ADDRESS

THE CHEMICAL ORIGINS OF PRACTICAL PHYSICS

William H. Brock, University of Leicester

I should like to thank the Dexter Corporation as well as the Chair and members of the Dexter Award Committee, both present and absent, for this honor. I feel proud to join the roster of a long line of distinguished historians starting with Ralph Oesper in 1956; and it is especially warming to join the list of many UK holders of this honor that began with John Read and has included such illustrious names as Douglas McKie, J. R. Partington, Joseph Needham, and more recently such friends as Trevor Williams, M. P. Crosland, Robert Anderson, and Colin Russell. This lecture is dedicated to the memory of the late Sidney Edelstein.

Apart from art and music, what distinguishes science, medicine, and engineering from all other forms of vocational training is the laboratory/workshop location in which it takes place. In this paper I look at the relation between nineteenth-century physics and chemistry and consider the development of practical physics teaching in the UK and USA.

I have taken as my motto a remark attributed to Bunsen by Sir Henry Roscoe: "Ein Chemiker der kein Physiker ist, ist gar nichts" – a chemist who isn't also a physicist is no chemist (1). Although a modern physicist might well construe this as confirmation that chemistry is merely a part of physics, chemists will accept it in the spirit that Bunsen intended, namely that chemists should be natural philosophers with a broader perspective and agenda than that of mere analysts; chemists explain physical as well as chemical properties, and to do that they must needs grasp and use the principles of mathematics and physics.

In fact, as many scholars have pointed out during the last decade or so, the discipline of physics as we know it today only emerged quite late in the nineteenth century, as reflected by the fact that both the British and



William H. Brock

French Physical Societies were founded in the 1870s (2). Before then, physics (or, strictly speaking, practical physics as opposed to mathematical physics which

did have its own autonomy) was very much part of chemistry, as early nineteenth-century textbooks confirm. Thus as late as 1867, the exciting contents of John Cargill Brough's short-lived *Laboratory* refer solely to chemical spaces, not physical ones.

Put another way, the imponderable bodies of heat, light and electricity remained part of chemistry until subsumed within the concepts of energy and electromagnetism in the 1850s and 1860s. It is not surprising, therefore, that many nineteenth-century chemists who implicitly followed Bunsen's later aphorism in their research activities, when seen from our later disciplinary perspective of physics, seem more like physicists than chemists. Faraday is the most obvious case, and others like André-Marie Ampère, Henri Regnault, Gustav Magnus, and Thomas Andrews easily spring to mind. Less well known are those cases of chemists who exploited their practical laboratory skills to create teaching programs in physics at the very time when the subject was emerging as an autonomous discipline in the 1870s. As George Carey Foster reminisced in 1914, "the transformation ..., from chemist into physicist was a fairly common phenomenon...(3)" This essay is principally about two of these chemists-turned physicists.

Like the 1960s and 1970s, the 1860s and 1870s were a golden age for new laboratories and academic buildings in Great Britain (4). In 1866 Carey Foster began to teach practical physics at University College – to be followed three years later by W. G. Adams at rival King's College. Between 1873 and 1874 the Cavendish physical laboratory was opened at the University of Cambridge, with fittings designed by James Clerk Maxwell based upon the experiences of the Clarendon laboratory at Oxford and of William Thomson's laboratory at Glasgow. In 1874 laboratories were opened at the new Royal Naval College at Greenwich, and science colleges were opened at Bristol and Leeds. In 1878 Alfred Waterhouse's gothic University College opened in Liverpool, with its extraordinary tiered chemical laboratory designed by James Campbell Brown; Sheffield responded with Firth College in 1879; and the decade ended in 1880 with the opening of Mason's College in Birmingham and the beginning of the new City & Guilds of London Institute's ambitious building program for technical education – completed in 1884 as Finsbury Technical College in the city of London and in 1885, at South Kensington, with Waterhouse's elegant Queen Anne-style Central Institution (5).

As implied, although the bulk of this building activity was devoted to opening larger and better facilitated chemistry laboratories, the decade also saw the

emergence of the physics laboratory – for *undergraduates and certificated students* as opposed to a laboratory space like Thomson's in Glasgow and Maxwell's at Cambridge in which advanced (postgraduate) students were encouraged to help a professor with a research problem (6). The pioneers here were undoubtedly two former chemists, George Carey Foster and Frederick Guthrie, the one at University College London, the other at the Royal School of Mines (or Normal School of Science as it became) in South Kensington. How and why did these two men turn aside from promising careers in organic chemistry for uncertain ones in physics teaching? Let's examine each man in turn and look for any common thread.

GEORGE CAREY FOSTER (1835-1919) (7)

A shy, nervous man and son of a Lancashire calico printer, Foster undoubtedly owed a debt for his career to the great theoretical chemist of the 1840s and 1850s, Alexander William Williamson, with whom Foster studied chemistry before briefly acting as his personal assistant from 1855 to 1858. In 1858 Williamson packed Foster off to the continent to study with Kekulé at Ghent, Jules Jamin in Paris (significantly a Professor of experimental physics at the Sorbonne who was much interested in electrical problems), and the young Privatdozent, Georg Quincke, at Heidelberg – a pupil of Bunsen's who was to spend a lifetime devoted to measuring and collecting data on the properties and constants of materials (8).

From these experiences Foster returned to Britain in 1860 not only *au fait* with Kekulé's structural theory, but with a deft hand in French and German experimental physics. Between 1857 and 1867 we find Foster addressing the British Association on organic nomenclature (e.g., he recommended the term isologous to indicate a difference of H_2 in a carbon series, on the analogy of Gerhardt's *homologous* for a difference of CH_2), and on "recent progress in organic chemistry." He also wrote up his Ghent work with Kekulé on hippuric and piperic acids. On his return Williamson had found a position for Foster in the private London laboratory of Augustus Matthiessen (another pupil of Bunsen's who emigrated to Britain in 1857) where Foster produced technically excellent work on the constitution of the alkaloid narcotine.

Meanwhile, in 1862, again due to Williamson and to his Scottish contacts, Foster was appointed to a chair at Anderson's College in Glasgow, not however in chemistry, but in natural philosophy. Perforce, therefore, Foster was obligated to lecture on these aspects of phys-

ics that he best knew from his training with Williamson as a chemist, and Jamin and Quincke as a physicist, namely heat and electricity. These were both subjects that he contributed articles on to Henry Watts's *Dictionary of Chemistry* in 1863. (Incidentally, how many of us have noted the significance of this publication which was hailed by William Crookes in the *Chemical News* on its completion in five volumes in 1868 as "the greatest work which England has ever produced on chemistry, [indeed] one of the greatest she has produced on any subject (9)?"

While Foster was in Scotland, and building on the back of the introduction of the BSc degree within London University, Williamson and other senior professors at University College persuaded the decrepit Professor of Natural Philosophy, Benjamin Potter, to take early retirement. The Natural Philosophy chair was then divided into chairs of mathematical physics (awarded to the geometer, Thomas Archer Hirst) and experimental physics, which went to Foster in October 1865. As Keith Nier has noted in a Harvard thesis (10), at this stage, in 1863, Williamson's chemistry syllabus, which had hitherto contained a good deal of elementary heat, electricity, and optics, now became almost completely chemical because these subjects were now to be taught by Foster. The age of teaching physics separately from chemistry had begun in Britain as a by-product of London chemists' successful campaign to get science degrees awarded by the University of London. Coincidentally, of course, such a change also released valuable time for the rapidly increasing knowledge of organic chemistry that chemists like Williamson wanted to teach (11).

We need not follow Foster's spatial difficulties in teaching a physics of quantitative precision. Suffice to say that initially he had to make do with a room adjacent to the lecture theatre before gaining a couple of workshop/laboratory spaces in the basement of University College. Under these cramped conditions, and working for the British Association Committee on electrical standards, in 1872 he transformed the Wheatstone bridge into a precision instrument usually known in Britain as the Carey Foster Bridge. It is important to note that because apparatus was expensive, Foster and his mechanic (William Grant) often designed and made their own equipment.

In the 1870s Foster campaigned for physics teaching in schools, wrote and edited texts, and in the 1880s argued strongly for the importance of practical physics and the value of accurate measurement as a foundation for research (12). His reward came in 1893 when the

College erected the Carey Foster Physics Laboratory that was destroyed in the 1939-45 war, and knowledge that he had trained England's next generation of physicists such as William Ayrton, Oliver Lodge, and Ambrose Fleming. Foster retired in 1898, only to be made Principal (Provost) of the College, where he played a leading role in the negotiations that led in 1900 to the reconstitution of the University of London as both a teaching and examining body.

One pupil recalled (13):

His nervous manner prevented Carey Foster ever becoming a good lecturer, and his failure in this respect was due, in addition, to a conscientiousness that made it difficult for him to be content with a simple statement that he knew to be only an approximate expression of a truth, and at the same time made him reluctant to adopt the customary method of illustrating physical laws by the use of simple, although entirely imaginary, experimental data. In place of these, his illustrations would often consist of the actual results of laboratory measurements, and the younger students, unless they were of a rather exceptional type, were apt to lose both attention and interest in the details of laborious computation.

His patience in showing students how to conduct their experiments often involved him taking over completely. His character was not unkindly but shrewdly summed up by Oliver Lodge in the phrase: "He was far from fluent, and he was so conscientious about expressing himself correctly that sometimes he failed to express himself at all (14)."

FREDERICK GUTHRIE (1833-1886) (15)

If Guthrie is remembered at all by historians of science and education, it is the terrible portrait of him painted by H. G. Wells in his *Autobiography* (1933) that sticks in the mind. Wells trained to become a secondary school science teacher at the Normal School of Science at South Kensington in 1885. After praising Huxley's biology course for its abiding interest, Wells writes (16):

Now Professor Guthrie, the Professor of Physics, was a man of very different texture from the Dean. He appeared as a dull, slow, distraught, heavily-bearded man with a general effect of never having fully awakened to the universe about him.

Like Watson's unflattering portrait of Rosalind Franklin in *The Double Helix*, Wells was, I think, trying to give an honest impression of his feelings as a science student forty years earlier; he admits that he only learned later that Guthrie was suffering from a throat cancer at



Frederick Guthrie, courtesy Oesper Collection,
University of Cincinnati

the time of these impression in 1885; but unlike Watson, Wells, while admitting that he had been an unruly and unprincipled student, was unforgiving. Guthrie's cancer had only "greatly enhanced the leaden atmosphere of his teaching.....Quite apart from that, he was not an inspiring teacher... to put it plainly, [Guthrie] mandered amidst ill-marshalled facts. He never said anything that was not to be found in a textbook (17)."

Faced with such a brilliant demolition job (but note that Wells failed his Associateship), historians have been reluctant to accept that Guthrie, along with his colleagues at South Kensington T. H. Huxley and Edward Frankland, and later Henry Armstrong, William Ayrton, and John Perry, was one of the great innovators of Victorian science teaching. What are we to make of Guthrie's dedication, as recorded by Lodge (18):

There was a time when Guthrie lived a curious life; he would not leave his laboratory, even at night. He had a hammock rigged up, and used to live in the laboratory.

Guthrie, who was probably of Scottish ancestry, was the son of a London tailor. Two years older than Foster, like him he was educated at University College School and the College before studying chemistry with Graham and Williamson, as well as Henry Watts, who had been his private tutor until the age of twelve. Like Foster, Guthrie had gone to Germany in 1854 to work with

Bunsen at Heidelberg, and then under Kolbe at Marburg, which he described to his friend Henry Roscoe (whom he had met at University College London) as "this dreary valley of desolation (19)!" He seems, however, to have got on with Kolbe very well, the latter describing him as "a well-educated man ... very industrious .. and extremely nice (20)." What Guthrie made of Kolbe's unsuccessful use of him to try to refute Williamson's theory of etherification electrolytically would be interesting to know. The doctorate was earned successfully in 1856 from an experimental study of the salts and esters derived from amyl ether and led on to some eight papers on organic chemistry, including the first preparation of mustard gas in 1860. In view of Foster's work on narcotine, it is intriguing to note that Guthrie was the first chemist to point out the therapeutic action of amyl nitrite (the nitrous acid ester of isoamyl alcohol), though its use as a vaso-dilator in heart disease was not proven until the work of the pharmacologist, Thomas Lauder Brunton, in 1867. Brunton's studies were directly inspired by those of Alexander Crum Brown, the successor to Lyon Playfair at the University of Edinburgh. Guthrie had assisted Playfair in Edinburgh between 1859 and 1861, after serving in a similar capacity with Frankland at Owens College, Manchester from 1856 to 1859. Everything seemed to point Guthrie towards a successful career in chemistry.

However, in 1861 Guthrie made an extraordinary career move, inspired, perhaps, by his brother's growing success as a teacher in South Africa (21). Along with Walter Besant, the future novelist and literary critic, Guthrie became a Professor of Natural Philosophy at the Royal College in Mauritius. The former Ile de France, Mauritius had become an English colony after 1811 as a result of the Napoleonic Wars. When Darwin visited the island in May 1836 he found cultivated fields, sugar cane plantations, bookshops, opera houses, and tarred roads; this was confirmed by Besant who writes of its being "a gay and sociable place" where youth predominated (22). Besant writes of Guthrie as (23):

...a man of infinite good qualities. He was my most intimate friend from our first meeting in 1861 to his death in 1886. It is difficult to speak of him in terms adequate. He was a humorist in an odd, indescribable way; he did strange things gravely; he was a delightful donkey in money matters; when he drew his salary - £50 a month - he prepaid his mess expenses, and then stuffed the rest in his pocket and gave it to whoever asked for it, or they took it. Hence he was popular with the broken down Englishmen of shady antecedents who hung about Port Louis. He never had any money; never saved any; always

muddled it away. Like many such men, he was not satisfied with his scientific reputation; he wanted to be a poet. He published two [pseudonymous] volumes of poetry, both with the same result. He was also clever as a modeller, but he neglected this gift. He did some good work in the colony in connection with the chemistry of sugar cane.

Guthrie's two poetic attempts are not without interest, for their subject matter on both occasions was the outsider: the Jew and the Gypsy. They were both published under the pseudonym of Frederick Cerny; whether the choice of name was significant, we cannot say. *The Jew* (1863), a Miltonesque and Dante-esque meditation on the problem of evil, seen through the eyes of a Jew who offered no solace to Christ on the march to Calvary, is not without fine moments, and may be interpreted as a defense of "seeking knowledge" in order to improve a sinful and intransigent world. A decade later, drawing upon one of the stories in George Borrow's *Gypsies of Spain*, Guthrie published an illustrated two-act metric drama, *Logroño* (1877). This passionate story of a scholar, a gypsy, and a lascivious count, surrounded by a chorus of courtiers, burghers, gypsies, peasants, and flower girls, reads like the libretto of a tragic opera. One cannot help regretting that Verdi or Puccini never came across the script.

Besant's reference to Guthrie's carelessness over money is interesting. Like the Anglo-German chemist, A. W. Hofmann, Guthrie married four times (three of his wives appear to have died in childbirth), and his widow and her three step-children were left in penury in 1886. Huxley launched an appeal in *Nature* and she evidently received a pension from the civil list (24).

It is Besant who also informs us that already in Mauritius, Guthrie was a confirmed agnostic, "who thought it his duty to learn such of the secrets of nature as he could, and not trouble himself about speculations as to the secrets of life, either before the cradle or after the grave (25)." This does much to explain how Guthrie got on so well later with Tyndall, Frankland, and Huxley at South Kensington. Guthrie was one of the new science professionals, convinced that science, not religion, was the key to human progress and happiness (26). Like Tyndall and Huxley, he lectured regularly to working-class men (27).

Examinations for The Royal College in Mauritius were administered by the University of London, but in the absence of a proper chemical laboratory there, Guthrie was thrown upon his own resources, investigating the physics of droplets and bubbles, analyzing local river water and commenting upon sugar cane. As Besant makes clear in his autobiography, the professoriate was

unhappy with the Principal, an ex-Austrian army officer who continually upset the local French population. Eventually Besant complained to the island's Governor, who carried out a Commission of Inquiry. Although the Principal was eventually removed, his reinstatement in 1867 brought about Besant's and Guthrie's resignation in 1867 and their return to England.

Back in England, Guthrie landed on his feet teaching science at Clifton College, Bristol, the proprietary school which was also later to have John Perry, Arthur Worthington, and William Shenstone on its staff, and Eric Holmyard in the twentieth century. Here he polished off a paper on heat which he sent to John Tyndall, who arranged for publication, and who saw to it that Guthrie succeeded him at the Royal School of Mines in Piccadilly, London a year later. In 1872 the School was to move to South Kensington, where Huxley, Frankland, and Guthrie had improved laboratory facilities for teaching practical biology, chemistry, and physics. At this Normal School of Science, Guthrie and his colleagues not only trained would-be science teachers like H. G. Wells, but under the sponsorship of the Department of Science and Art they were able to set up annual summer schools to improve the practical teaching skills of existing teachers.

As Jensen noted some years ago in *Chemistry in Britain*, Guthrie joined the Chemical Society in April, 1868, and promptly described a voltastat to deliver a constant voltage from a battery, and offered an intriguing paper "On graphic formulae." The latter suggested the replacement of Crum Brown's recently introduced graphic formulae by pictorial geometrical symbols which indicated combining power. At the meeting Guthrie's suggestion was treated with derision by William Odling and it led to some correspondence in *Chemical News* and, amusingly, to some buffoonry at the B-Club to which both Foster and Odling belonged (28).

In reply, Guthrie showed his sense of humor in retorting that Odling's own dash valency notation was in reality a system of graphic formulae (29):

Dr. Odling appeared shocked at the idea of an atom of nitrogen supporting three "sticks" one in each hand, and one on its head. Strange objection from one who years ago trained his atom of nitrogen the much more difficult acrobatic feat of balancing simultaneously three sticks on the tip of its nose, - N"

While on the subject of Guthrie's sense of humor and geniality even when under attack, let me mention two other examples that seem to confirm that Wells unfortunately completely misinterpreted his teacher's personality.

First, in the Christmas issue of *Nature* in 1879, writing under the pseudonym A. von Nudeln (i.e., Mr Macaroni), Guthrie humorously ridicules a recent spate of German writings on geometry and mathematical physics with a letter entitled "On the Potential Dimensions of Differentiated Energy"(30):

In his great work, which appears to be but little known in England, *Ueber die stille Bewegung hypotetischer Körper*, Professor Hans points out that the dimensions of 'ideal' matter may not only differ in degree, but also in kind. He deduces by means of implicit reasoning from his three primitive 'stations,' that not only must there be space of 4, 5, 6, etc. dimensions, but also that there must be space of -1, -3, -5, etc. and that there may be space of -2, -4, -6 &c dimensions. Pursuing Hans's train of thought further, Lobwirmiski has quite recently interpreted space of 1.1, 1.2, 1.3 &c dimensions...the same philosopher has also conclusively shown that space of $n \rightarrow -1$ exists [with] all the properties of angular magnitude; like all partly bounded infinities (*theilweise begränzte Unendlichkeiten*), it is unmagnifiable.

This piece of drollery ends with an obscure proof that the moon is, indeed, made of cheese. Guthrie's mixture of simplicity and wisdom, kindness dashed with a pungent, but never caustic, humor, led one anonymous friend (perhaps Besant) to compare him with the Uncle Toby immortalised by Laurence Sterne in *Tristram Shandy* (31).

This spoof probably supports Foster's contention in an obituary that Guthrie, though trained by Augustus De Morgan in mathematics, "was somewhat apt to underrate the scientific importance of the work of mathematical physicists in comparison with that of pure experimentalists (32)." His concentration on the physics of real things like drops and bubbles; thermal conductivity of liquids; salt solutions; the discovery of "cryohydrates;" and the melting points of eutectic mixtures, and his use of a very informal, homespun language to describe nature – all of this seems to have been anathema to James Clerk Maxwell (33). Although Guthrie was elected to the Royal Society in 1873, as a referee Maxwell continually found fault with papers that Guthrie submitted to the Royal Society; and this was undoubtedly the principal reason why Guthrie founded the Physical Society at the end of 1873 (34).

It is again a remarkable example of Guthrie's ability to deflect criticism that in 1878 he was able to reply jokingly to Maxwell's pretty intemperate review of his textbook, *Practical Physics, Molecular Physics and Sound* (35). Maxwell's particular gripe seems to have been Guthrie's language of exposition. For example, he

picked upon the way Guthrie formulated a variation of Hooke's law concerning the elongation of a wire, so that if a length m is extended to become n , the original diameter becomes $d^\circ m/n$. The formula is correct, so presumably Maxwell thought it odd for Guthrie to say it is true if one assumes "the volume of the metal remains approximately unchanged." Guthrie's revenge was a splendid verse *a la Maxwell* and in Scots dialect (35).

"Remonstrance to a Respected Daddie anent his loss of temper"

WORRY, through duties Academic,
It might ha'e been
That made ye write your last polemic
Sae unco keen:
Or intellectual indigestion
O' mental meat,
Striving to solve some question
Fro' "Maxwell's Heat".
Mayhap that mighty brain, in gliding
Fro' space tae space,
Met wi' anither, an' collidin',
Not face tae face.
But rather crookedly, in fallin'
Wi' gentle list,
Gat what there is nae help fo' callin'
An ugly twist.
It 'twas your "demon" led ye blindly,
Ye should na thank him,
But gripe him by the lug and kindly
But soundly spank him.
Sae, stern but patronising daddie!
Don't ta'e't amiss,
If a puir castigated laddie
Observes just this: —
Ye've gat a braw new Lab'ratory
Wi' a' the gears,
Fro' which, the warld is unco sorry,
'Maist naught appears.
A weel-bred dog, yoursel' must feel,
Should seldom bark.
Just put your fore paws tae the wheel,
An' do some Wark. $d^\circ m/n$

Gooday has argued that following the 1867 Paris Exhibition and the success of the electric telegraph, the scientific community was able to promote the teaching of precision measurement in physics laboratories on the assumption that "hands-on" experience was better than teacher demonstration if precision were to be achieved.

In the first place, this would be good for encouraging rational and accurate reasoning within liberal education; and in the second, it would be a scientific alternative to "rule of thumb" methods of industrial apprenticeship, the need for which the electric telegraph had exposed (36). The problem was how to put this into effect. There were three common solutions put into practice in the 1870s (37).

In the first, chemistry model: every student would have had a similar collection of apparatus. While this worked cheaply and well in chemistry, where practical work depended on little more than a set of test tubes, some filter and litmus paper, and a bench stock of standard chemicals, it would have been expensive to achieve the same goal in elementary physics teaching, where relatively expensive optical and electrical apparatus were necessary. Two alternative solutions to the problem of expense were therefore tried during the 1870s: one emanated from the Massachusetts Institute of Technology and spread to Europe; the other was developed by Guthrie at South Kensington.

One of the more remarkable graduates of MIT in 1867 was Edward Charles Pickering (1846-1919), a graduate from the Lawrence Science School at Harvard. William Barton Rogers, MIT's Principal, who thought that the Lawrence School was taking the wrong approach to science teaching, and believing that America desperately needed practical astronomers and physicists rather than engineers, appointed Pickering to MIT with the specific intention of introducing practical physics teaching into the curriculum. Encouraged by Rogers, in the fall of 1868 Pickering fitted up a student laboratory at Boston. With no European model to draw upon, and ignoring any chemical precedent, Pickering devised his own set of physics experiments, apparatus, and instructions for students to follow.

In Pickering's system of instruction, which was ultimately cheap to operate and destined to become universally adopted in schools and universities, students worked singly or in pairs at different experiments, and proceeded in rotation from one experimental table to the next. Only one set of experimental apparatus was therefore needed per student pair. At each bench point students received written instructions on what to do, record, and interpret. These experiments on techniques of measurement, the properties of gases, sound, the mechanics of solids, and the nature of light (including photography), having been tested out at MIT for some three or four years, were published by Pickering in 1873 as *Elements of Physical Manipulation* (38). By then he was able to draw upon the influential German text on university laboratory physics by Friedrich Kohlrausch

(39). A second volume, largely devoted to electricity – "a subject better adapted than any other to the laboratory system" – appeared in 1876 and included an appendix which offered advice on the planning of physical laboratories.

Not surprisingly in view of the fact that Pickering's text was reviewed in Norman Lockyer's *Nature*(40), Lockyer gave publicity to the MIT program in the Sixth Report of the Devonshire Commission on Scientific Instruction, of which he was Secretary (41). Knowledge of Pickering's method of multiple experiments was picked up quite quickly in Britain, probably from both the *Nature* review and from the Devonshire Commission. For example, in an essay on the teaching of physics published by Foster in the *Educational Times*, he referred approvingly to the "American" method of multiple classroom experiments (42).

It seems clear, then, that for anyone planning to develop a new physics teaching laboratory in the 1870s, the proven experience of the MIT laboratory would have been a good model to copy. The fact that William Ayrton, the electrical engineer, left London to teach at the Royal Engineering College in Tokyo in 1873, only a few months after the appearance in Boston of the first volume of Pickering's treatise, is suggestive. For it was in Japan that Ayrton and his mechanical engineering and mathematical colleague, John Perry, put the multiple experiment model of teaching into great effect. On their return to London, they made this method of practical instruction famous at the Finsbury Technical College, from where it was adopted by the Cavendish Laboratory and other physics teaching institutions (43).

Although this method of instruction was destined to become universal and is to this day the preferred method of teaching practical physics, there would have been initially high start-up costs. Indeed, until such times as instrument makers were geared up to making sturdy, cheap but reliable Wheatstone bridges, galvanometers, lens systems, etc., Guthrie's alternative approach must have seemed ingenious.

In Guthrie's system, detested by H. G. Wells, but much admired by writers in *Nature*, students were required to make their own apparatus, before manipulating it experimentally (44). Guthrie gave a long account of the method and the educational philosophy behind it in his Cantor Lectures to the Society of Arts in 1885 (45). A decade earlier, in 1875, either he or William Barrett informed *Nature*'s readers of the method's educational advantages (46).

Students unaccustomed to manipulation find to their astonishment, when they begin, that all their fingers have

turned into thumbs, and they are amazed at their clumsiness and stupidity. Very soon, however, fingers begin to reappear, and the very first successful piece of apparatus that is made gives them a confidence in themselves which they had thought impossible to attain. The pleasure of having made an instrument is increased a hundredfold when it is found that by their own handiwork they may verify some of the more important laws of physics.

Since the final examination depended entirely upon the accuracy and reliability of the apparatus constructed by the student, there was additional incentive to manipulate with care and exactitude (47).

It must not be thought that students were literally expected to make apparatus from scratch. Guthrie's purpose was certainly not to train and produce instrument makers. Apart from needing their own set of tools – a hammer, nails, and other basic tools – in practice they received a kit which Guthrie's workman had already prepared and which they individually assembled by following printed instructions (48):

[The student] receives the wood and metal ... cut in pieces of the right size. He must have to acquire a little skill in bending and blowing glass, and in the use of the soldering iron. But what human being should be without this?

The cost of materials for making the apparatus was some £2, compared with the cost of purchasing a set from a supplier for about £15 – a saving to the Department of Science and Art of £13. Moreover, the student (49): finds himself at the end of the course with a set of apparatus made by himself, and fully tested by himself; and he finds himself in possession of verifications of many of the great generalisations of physics, which generalisations, having been thus acquired by the simultaneous working of brain and hand, he is slow to forget.

Although Guthrie did not mention it, the method also had an advantage over Pickering's system insofar as a newly-certificated science teacher from South Kensington could bring his own set of apparatus with him to his new school teaching post. This would have been important where finances were tight and a new teacher had first to consolidate his position in a school before he could argue for the purchase of apparatus from instrument suppliers.

Finally, we should note the wider influence of Guthrie on physics teaching in his capacity as examiner for Department of Science and Arts examinations in heat, light, sound, electricity, and magnetism. Just as Edward Frankland exploited his examination position to lay down a chemistry syllabus and to demand that all stu-

dents either witnessed or conducted a definite number of experiments (50), so did Guthrie. In 1881 Guthrie's *Outline of experiments and description of apparatus and material suitable for illustrating elementary instruction in sound, light, heat, magnetism, and electricity* was published by the Department of Science and Art for science teachers. These recommendations not only influenced physics teaching in Britain but also in Japan and America. Kanosuke Yoshioka, the Japanese translator of Guthrie's *Practical Physics* (1877), incorporated Guthrie's recommendations and also arranged for a set of apparatus to be displayed at the Tokyo Education Museum from 1895 (51). It appears, then, that Guthrie played a significant posthumous role in rendering Japanese science teaching less didactic and more practical.

In America, there was little "hands-on" experimental work by high school students until the 1890s. Dr Alfred Gage, who opened an English (*sic*) High School in Boston in 1880 and who published a practical text, *Elements of Physics*, in 1882, significantly abandoned teaching in order to make and supply scientific instruments for school use. In the same decade, Frank Wigglesworth Clarke's report on the state of physics and chemistry teaching in American city schools showed that less than ten percent possessed laboratories (52). This situation began to change during the 1880s when Charles William Eliot, President of Harvard University, and himself a trained chemist, deliberately placed physics on the list of matriculation requirements. This led Edwin H. Hall, Professor of Physics at Harvard, to draw up the influential *Harvard Descriptive List of Elementary Physical Experiments* in 1886. By 1902, Hall was able to claim that practical physics teaching in American high schools was in advance of anything to be found in Europe (53).

Initially, in 1886, Harvard allowed two alternatives: either a written examination based upon designated textbooks of astronomy and physics; or a practical demonstration based upon the matriculant's school experience of Hall's "course of experiments in the subject of mechanics, sound, light, heat, and electricity, not less than 40 in number (54)." Although these 40 experiments were chosen from American texts like Pickering's *Physical Manipulation*, they were also considerably influenced by British sources such as Guthrie's *Practical Physics* and A. M. Worthington's *Physical Laboratory Practice* (1886). By the 1890s, Harvard insisted upon practical experience of physics for its entrants to science courses. We may, therefore, conclude that, directly or indirectly, Guthrie also influenced the rise of the elementary physics laboratory in America.

By way of conclusion, I draw attention to the organic chemist Henry Edward Armstrong who, writing in 1933, a year before Wells's cruel portrait of Guthrie appeared in his autobiography, gave a Huxley Memorial Lecture in South Kensington. In this Armstrong suddenly makes an aside (55):

Good as was the top floor [Huxley], it was being beaten, down below in the basement, by the chemist-turned-physicist, Guthrie, who developed a logical, practical course, on self-help lines, of extraordinary value—long since on the scrapheap, I fear, given its final quietus by the all-pervasive electron. It is little short of shameful that South Kensington has let this go by the board – unrecorded. Real earthly physics is a fast-disappearing art. Cannot someone be found to recover the course, if only to put it away in a case in the British Museum, as a monument of a former greatness.

Perhaps this essay goes some way towards satisfying Armstrong's hope. By recalling Bunsen's aphorism and by resurrecting Foster and Guthrie from the scrapheap of history it has been possible to reveal something of their and other chemists' roles in the establishment of practical physics teaching.

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ALMER McDUFFIE McAFEE (1886 – 1972): COMMERCIAL CATALYTIC CRACKING PIONEER

Paul T. Buonora, University of Scranton

Many modern day authors identify the transition from the thermal to catalytic cracking of petroleum as the commercialization of the Houdry process patents (1) in the late 1930s and early years of the World War II. In actuality, commercial catalytic cracking of petroleum began with the anhydrous aluminum chloride-based "McAfee Process" in the years following the World War I. The process was developed and commercialized by the Gulf Refining Co. and is named after its inventor, Almer McDuffie McAfee.

Almer McAfee was a product of his times and the company he kept. No Eugene Houdry, he embodies the image of many industrial chemists of the time when chemical engineering was developing into a separate area of study. It was Almer McAfee and his contemporaries who solved the practical dilemmas of creating national vertically integrated petroleum companies following the dissolution of the Standard Oil Trust.

Early Years

Almer McDuffie McAfee was born near Corsicana, Texas on Sept. 24, 1886, one of eleven children of a local storekeeper. In June of 1894, when he was eight years old, city workers discovered oil while drilling community water wells (2). The Corsicana field became the first oil field of importance in Texas. On Christmas day 1898, the stills were fired on a Standard Oil Company financed 2000 barrel per day refinery at a site one mile from the oil field. It is not surprising that a youngster growing up during those boom days would develop a more than passing interest in petroleum technology.

McAfee attended the University of Texas where he earned the A.B. degree in Chemistry in 1908. In 1907,

while taking a course in organic chemistry, he wrote next to the discussion of the Friedel-Crafts reaction in his textbook the words "Exceedingly useful" (3). This sentiment, expressed by his professor, Dr. J.R. Bailey, would sow a seed for his subsequent career.

Following receipt of his A.B. degree, McAfee spent two years as a graduate student and Tutor in chemistry at the University of Texas. In the Fall of 1910, he became a Goldschmidt Fellow in Chemistry at Columbia University. The next year, McAfee earned the Ph.D. degree in Chemistry, with major work in physical chemistry under the direction of J. Livingston R. Morgan. His 23-page dissertation was entitled "The Drop Weight of the Associated Liquids—Water, Ethyl Alcohol, Methyl Alcohol and Acetic Acid."

While attending Columbia, McAfee would continue a courtship with Marguerite Calfee, whom he had met while at the University of Texas, and who was working toward her Masters degree at Bryn Mawr at that time. In 1914, the two would marry in their home state of Texas where they would raise their three children. Their first child, the late Jerry McAfee, became a chemical engineer and joined Gulf Oil Corp. in 1945. He would rise through the ranks to become Chairman of the Board of Gulf Oil Corp. before retiring in 1981.

The Gasoline Problem

The Corsicana refinery of McAfee's youth was typical of refineries of the day. Petroleum technology was in its straight-run phase, in which the "natural" kerosine, gasoline, fuel oil, etc., fractions of the crude were collected by distillation and refined. The refining process involved treatment, typically with sulfuric acid, to remove color and objectionable odors.

At the turn of the century, gasoline fractions produced at the Corsicana refinery were collected and discarded into the local streams during the spring floods as they were of little value. This situation would not last long. Mass production of the automobile greatly increased gasoline demand throughout the first quarter of the century. In 1907, The Texas Company (now Texaco) became the first refiner to sell more gasoline than kerosine (4). By 1911, nationwide demand for gasoline exceeded the nation's kerosine demand. The gasoline demand was reflected in prices at the pump. During the years 1910 to 1913 gasoline prices increased from approximately 10 cents to 30 cents per gallon (1).

With petroleum technology still in its straight-run phase, the challenge to refiners was to find ways to obtain increasing quantities of gasoline from the crude. Many larger refiners hired industrial chemists specifically to develop methods to wring more gasoline from their crude stocks.

The Texas Company

It was in this climate that McAfee accepted a position at The Texas Company's Bayonne, New Jersey facility after receiving his Ph.D. in 1911. Initially employed in the testing laboratories, McAfee was unhappy with the nature of the work, desiring to become more involved in the challenging gasoline problem research and manufacturing end of the business. McAfee's supervisors agreed to send him to Texas in the fall of 1912 to become one of the first research chemists on staff at the company's Port Arthur facility.

The major part of The Texas Company's refining capacity was in Port Arthur. Located near the mouth of the Sabine River on the Gulf of Mexico, Port Arthur was a two-company town where both The Texas Company and Gulf Refining had built their first refineries in the early part of the century. The two companies were

the offspring of the nearby Spindletop Oil Field discovery of 1901 (4).

As a research chemist at The Texas Company, McAfee was supervised by George William Gray, who already had a long history in the petroleum industry (5). He had followed William Meriam Burton (Burton Process) as superintendent at Standard Oil's Whiting (Indiana) refinery in 1898. Gray, like Burton, was a Ph.D. chemist trained at Johns Hopkins. Gray left Standard Oil shortly after another Hopkins-trained chemist, Robert E. Humphreys, arrived in Whiting in 1900. He then went to the Sunflower Oil Co. and subsequently to The Texas Co. By 1912, he was employed in the Houston headquarters as the Chairman of the Refining Committee. As Chairman, he had direct supervision of the chemical research department and laboratory.

On his way to Port Arthur McAfee stopped in Houston, where he had a lengthy conversation with Gray. Much of their discussion centered on the gasoline problem and both old and new ideas about petroleum refining and cracking. One recent development in the field of industrial chemistry which interested several refiners was the work of David T. Day, who in 1906, had patented a process for the hydrogenation of unsaturated materials with nickel as a catalyst (6). It was known that unsaturates in the gasoline fractions imparted color and

objectionable odors to gasoline, and it was hoped that catalytic hydrogenation processes would yield a "sweet" product. Gray's immediate interest was in refining (sweetening) distilled products by a hydrogenation process.

McAfee went to Port Arthur and initiated the work on hydrogenation research in early November, 1912. Although there was later some contention as to the specifics (7), Gray had instructed McAfee to distill the natural gasoline from the crude with the suggested addition of condensers located in a position to provide careful control of the boiling range of the collected gasoline fraction. This fraction was then to be hydrogenated, with the goal of sweetening the product. Several re-



A. M. McAfee, courtesy Mrs. Jerry McAfee

agents were proposed as hydrogenation catalysts, including aluminum chloride.

After arriving in Port Arthur, in addition to his assigned duties, McAfee looked into other processes which included placing catalysts into the crude during the initial distillation process. One of the catalysts he utilized was anhydrous aluminum chloride. He discovered that, by applying the careful collection of the gasoline fraction via the double condenser system suggested by Gray, and with anhydrous aluminum chloride in the straight run still, he was able to obtain improved gasoline fraction yields which were water-white and odorless.

In December, 1912, he reported his initial success to his superiors in Houston. In January, Gray filed two patent applications based on the process developed by McAfee, without including McAfee's name. McAfee complained to Gray and ultimately to Gray's superior, Robert Holmes (Holmes-Manley Process). Not finding satisfaction, he ultimately sought a position at Port Arthur's other oil company, the Gulf Refining Co., taking his claim of priority in aluminum chloride cracking with him.

Gulf Refining Company

When McAfee presented himself to Gulf Refining, he found a supporter in George H. Taber, the general manager at Gulf's Port Arthur facility. Taber arranged to hire McAfee, promising to support the development of the aluminum chloride process, with McAfee as project leader. Gulf also supported McAfee's application for patents in competition with the Gray patent. This support would initiate a series of patent infringement claims, hearings, litigations, and appeals, beginning in 1913 which would not be resolved until 1928 (9). At that time

the U.S. 5th District Court finally ruled that, although The Texas Company had a shop right (8) to the McAfee Process, the patented work was a creation of McAfee's and not Gray's. Although The Texas Co. funded research into its own aluminum chloride processes, no commercial cracking facilities were ever built.

After the issuance of the first McAfee Process patent in February, 1915, Taber publicly pronounced the

McAfee Process to be a "commercial, scientific, and laboratory success (7)". Taber stated that the process "really is the proposition, more especially as the products it turns out are stable and are what the trade calls 'sweet'".

The first commercial anhydrous aluminum chloride cracking units

were constructed at the Gulf Refining facility in Port Arthur in 1915 and went into operation in 1916. A second cracking still was built in 1918. By the 1920s Gulf had built a total of twenty seven stills at Port Arthur and three at their Fort Worth facility.

Precedent to Aluminum Chloride Catalytic Cracking

In his 1917 review, entitled "The Pyrogenesis of Hydrocarbons," E.L. Lomax expressed some surprise that either the Gray or McAfee aluminum chloride catalytic cracking patents were awarded in view of the precedent in patents and literature reports (9). He noted that aluminum chloride catalysis had a long history in and out of the petroleum industry, citing Elbs' "Synthetische Darstellungsmethoden," Volume 2, published in 1891 which devoted 45 pages to aluminum chloride. Also noted was Mayer and Jacobsen's 1902 edition of their book listing 178 references to various applications of aluminum chloride in synthetic organic chemistry. The

Table I
Precedent in Aluminum Chloride-based Catalytic Cracking and Polymerization.

Patents (Pre 1912)		
1877	Britain	C.D. Abel (for Friedel, C. and Crafts, J.M.)
1903	Britain	Adiassewitch
Literature (Pre 1912)		
1881	G. Gustavson	Kerosine to gaseous hydrocarbons
1888	C. Engler	Distilled fish oil to high boiling oils
1889	C. Engler	Distilled fish oil to high boiling oils
1893	C. Engler	Distilled fish oil to high boiling oils
1896	F. Heusler	Lignite tar distillates to high boiling oils
1902	O. Aschan	Olefin polymerization
1910	C. Engler	Amylene to Lubricating Oil

largely unrealized commercial promise of anhydrous aluminum chloride was summed up by Almer McAfee when he quoted von Baeyer's late 19th-century observation that the myriad uses of aluminum chloride sounded like a fairy tale (10).

The global literature contained several examples of both cracking and polymerization catalyzed by aluminum chloride (Table I). Most importantly, on December 5, 1877, C.D. Abel received a patent in England on behalf of Friedel and Crafts (11). This patent deals with the treatment of low-grade petroleum with 5 to 20 % anhydrous aluminum chloride, or a mixture of aluminum chloride and metallic oxides at 100° to 600° C. The oil was converted to light oils, gas, and heavy paraffin oils. The process was designed to produce lubricating oils, etc., from heavy hydrocarbons.

Given the precedent for aluminum chloride cracking, it is not surprising that other refiners of the day would also investigate this form of catalytic cracking. In his 1918 Willard Gibbs Medal Awardee Address (12), William Burton noted that the first two of the three years of the research that would lead to the development of the Burton Thermal Cracking Process (13) were occupied with attempts to develop an aluminum chloride-based cracking process. The efforts were abandoned because of the unavailability of a low-cost source of aluminum chloride and an inability to develop a method to recycle the catalyst. The development of a low-cost source of aluminum chloride by McAfee was the key feature which allowed Gulf to capitalize effectively on its patents.

Several other refiners also attempted to develop aluminum chloride catalytic cracking methods and/or to solve the catalyst availability and recycle problems (Table II). Of these, published reports indicate that only The Hoover Company ever attempted to commercialize their patents (14). They operated a plant based on their own patent, in Fairmont, Oklahoma in the early 1920s.

The McAfee Process was developed at the same time as Indiana Standard was licensing its Burton Thermal Cracking Process nationally. Gulf Refining chose to go against the industry trend and not license the Burton or other thermal processes in favor of the development of the McAfee Process and, later, its own thermal processes (15).

There were several advantages to the McAfee Process over its thermal counterparts (16). From the engineering standpoint the McAfee Process requires substantially lower temperatures and could be operated at atmospheric pressure. Thermal cracking processes em-

ployed minimum pressures of 60 - 100 psi. Coke deposits reacted with the steel used at that time, causing brittleness in the inner wall of the vessel. Vessels could, and did breach, causing fires and explosions.

Aside from the operational advantages, the quality of the product from aluminum chloride cracking had

Table II
U.S. Corporate Anhydrous Aluminum Chloride
Patent Initiators

Cracking Process Patent Initiators (1913-1925)

- 1913 - The Texas Co.
- 1913 - Gulf Refining Co.
- 1914 - The Chemical Foundation
- 1919 - Standard Oil Co. of New Jersey
- 1922 - Universal Oil Products
- 1922 - The Hoover Co.
- 1924 - The Nitrogen Corp.

Synthesis or Recycle Patents (1914-1925)

- 1914 - Gulf Refining Co.
- 1916 - Alchlor Chemical Co./Standard Oil Co. NJ
- 1919 - The Texas Co.
- 1925 - Sinclair Refining Co.

superior color and odor properties and better anti-knock performance than typical gasoline of the time. The octane scale had not been invented at that time, so Gulf marketed its improved performance product as Gulf No-Nox™ gasoline. Later studies showed that anhydrous aluminum chloride-cracked gasoline had an octane rating of 80 (17).

As ultimately commercialized, McAfee's process utilized a batch operation in which 1000-bbl stills were charged with crude oil, which was heated to remove moisture and then treated with 1 to 5 percent anhydrous aluminum chloride. The stills were heated at 250 - 280° for 24 - 48 hours at atmospheric pressure. Air condensers were used to separate the high-boiling and low-boiling fractions, with the high boilers returned to the vessel. With proper control of the temperature of the vapor leaving the vessel and entering the final condenser, and sufficient time for reaction, McAfee found that high-boiling material could be converted to low-boiling oils. Pot residues were used for the paraffin and lubrication oil markets.

Industrial Synthesis of Aluminum Chloride

As noted previously, the major impediment to the widespread application of aluminum chloride cracking was the high cost of the catalyst. McAfee had paid \$1.50 per pound and waited six weeks for delivery of the anhydrous aluminum chloride used in development of the refining process in 1913 (18). It took approximately one to one and a half pounds of catalyst to produce a gallon of gasoline. With pump prices at 30 cents per gallon the economics were not in Gulf's favor.

McAfee and Gulf realized that they were just embellishing von Baeyer's fairy-tale uses of aluminum chloride unless an economically feasible method of manufacture could be developed. It took three years and an investment of \$1,000,000 by Gulf Refining to develop a practical, large-scale aluminum chloride synthesis (16). Because of McAfee's aluminum chloride synthesis work, Gulf Refining became not only a major producer, but by far the nation's largest producer of anhydrous aluminum chloride (Table III) (19).

The initial attempts by McAfee and Gulf to make aluminum chloride on an industrial scale, begun in 1915,

iron jacket. The largest furnace produced 40,000 lb. per day. The fire brick had to be replaced approximately every 100 days.

The aluminum chloride produced was collected by sublimation. The product was only about 95.1% pure, with traces of iron trichloride, titanium tetrachloride, and other impurities. Nevertheless, the material was usable for petroleum cracking and for the dye or other synthesis industries. In the early days the aluminum chloride was sublimed into condensers of brick, which were cleared by hand. The brick condensers were 30 feet long, 12 feet high, and 6 feet wide. They would frequently become blocked and filled with carbon monoxide causing more than a few explosions and shattering of the condensers. Later, the aluminum chloride was condensed into a 16-inch vertical iron pipe with revolving vertical scrappers. Gulf ultimately found in Suriname a source of cheap high grade bauxite. In 1925, Gulf opened the largest electrolytic chlorine and caustic plant in the US at Port Arthur for the purpose of serving their anhydrous aluminum chloride-based cracking and refining operations (20).

Cracking Yields to Refining and Lubricating Oil Production

Even as the McAfee Cracking Process was being developed and commercialized, refiners, including Gulf, were taking advantage of new engineering materials and new ideas in thermal cracking. By the late 1920s engineering improvements had overcome much of the difficulty in high-temperature and high-pressure operation. These improvements in thermal cracking processes reduced the cost of gasoline production by the competing thermal process methods of the day (21). Balanced against the cost of the catalyst, the McAfee cracking process was no longer economically competitive. The introduction of tetraethyl lead as an anti-knock agent offset the process other major advantage of superior anti-knock properties. In 1929, approximately one year after prevailing in the patent battle with The Texas Co., Gulf terminated McAfee cracking operations.

The McAfee Process research demonstrated the ability of anhydrous aluminum chloride not only to crack but also to rearrange or polymerize petroleum hydrocarbons (4). Temperature was discovered to be the key factor in selection of the desired properties of the aluminum chloride-petroleum interaction. This knowledge led McAfee's team to develop an anhydrous aluminum chloride refining process requiring much smaller amounts of catalyst to improve octane rating and also

Table III:
U.S. Production of Aluminum Chloride
(Thousand Lb.) (17)

Year	Total	Anhyd.	Gulf	Gulf Percent(anhyd.)
1918-23			6,200	
1924	12,020		10,719	89
1925	26,665		21,387	80
1926	34,500		27,264	79
1927	35,260	29,200	26,550	75 (91)
1928	34,540	28,990	27,017	78 (93)
1929	34,102	28,574	26,840	79 (94)

involved the addition of chlorine to aluminum metal in fire clay retorts (16). The caustic nature of the chlorine gas quickly destroyed the retorts. They changed to fire brick retorts six months later, only to discover that chlorine at 1600° F also attacks brick, as it does porcelain which was subsequently tried, on the advice of ceramics experts. After two years of effort, success came in the form of briquettes of coal and bauxite charged into a chlorinating furnace consisting of two courses of fire brick behind a layer of powdered bauxite encased in an

to produce a premium grade of lubricating oil. Anhydrous aluminum chloride is still utilized in the petroleum refining under the generic name of "Alchlor process refining." In 1927 Gulf began aluminum chloride-based production of high grade oil under the Gulfpride™ name. They continued to produce the oil via the McAfee Process until the late 1960s

With the lower demand for aluminum chloride in the lubricating oil refining process, Gulf was faced with a large investment in catalyst production capacity of 75,000 lb. per day. Gulf met this challenge by having McAfee announce at the 1929 national meeting of the American Institute of Chemical Engineers that Gulf would make aluminum chloride available in carload lots at 5 cents per pound (13). With production costs of 3 cents per pound as early as 1923, Gulf would be able to profit in a market where bulk prices were 12 cents per pound before McAfee's announcement.

The industrial community met McAfee's announcement with revelry. It meant that the fairy-tale uses of aluminum chloride could become reality in the industrial setting. An editorial in *Industrial and Engineering Chemistry* in August, 1929, highlighted the new availability of aluminum chloride(22):

In many a laboratory the long list of Friedel and Crafts syntheses, worked out and described some fifty years ago, will now be reinvestigated from the standpoint of commercial utility, since at last aluminum chloride is available in carload lots.

Of the McAfee team at Gulf it was stated:

Those who make fundamental reagents available to industry at a cost permitting more extensive use perform services the beneficial effects of which will be felt for many a year to come.

Despite calls to move to Gulf's research facilities in Pittsburgh, McAfee remained as Superintendent of the Aluminum Chloride Department in Port Arthur throughout his 38-year career with the company. At the time of his retirement on January, 1, 1952, he held 40 US patents, most on the manufacture and use of aluminum chloride in cracking and refining of petroleum. While the records of this period are missing, several former long-time Gulf employees have indicated that they could not recall any sales of aluminum chloride from the Port Arthur facility. As Gulf developed and brought on-line alternate production processes for high-grade lubricating oils in the late 1940s, the often troublesome production of aluminum chloride was abandoned.

McAfee had a reputation for ingenuity which was not limited to his career. In the early 1920s, he built a

home in the Griffing park suburb of Port Arthur. To provide additional climate control, he installed pipes between the inner and outer walls of the house perimeter. Through these he circulated ground water from a shallow well on the property. This gave him additional cooling in summer and heating in winter.

McAfee was also prominent in civic affairs. He was a member of the Port Arthur Independent School District board of trustees from 1931 to 1941, serving as the board's president from 1934 to 1941. During World War II he was chairman of the Rationing Board of Southern Jefferson County, TX. He also served on the board of the Lamar Junior College (now Lamar University), where he was instrumental in expansion of the institution to a public, four-year college. McAfee became the first Chairman of the school's Board of Regents, serving one term. He was also active in the Port Arthur Chamber of Commerce and served on the national council of the Boy Scouts of America. He was an active layman in the Methodist Church in Port Arthur and was active in the Rotary Club. Following his retirement in 1952, McAfee remained active in civic affairs and operated a small farm in Woodville, TX. He passed away on October 12, 1972, at the age of 86.

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EARLY WOMEN CHEMISTS IN RUSSIA: ANNA VOLKOVA, IULIIA LERMONTOVA, AND NADEZHDA ZIBER-SHUMOVA

Mary R. S. Creese, University of Kansas

About eighty-five percent of the nineteenth-century publications by women in the chemical sciences came from three national groups, Russian, American, and British, other Continental Europeans contributing the remainder (1).

Over the period from 1870 (the year when the earliest chemistry papers by a woman appeared) until the end of the century (2) American output increased steadily, while British women, who started only in the 1880s, were the most productive in the last decade of the century (3). The Russians, a group of about twenty, are especially notable in that they are the most prominent of the early workers, making a strong start in the 1870s and 1880s, although their output declined somewhat in the following decade (see Fig. 1 and 2). Several produced a remarkable amount of very creditable research. Interestingly, a list of their mentors and associates would read like a who's who of turn-of-the-century chemists; among them were Mendeleev, Markovnikov, Favorskii, Menshutkin, Butlerov, and L'vov (4). Sketches of three of the earliest of the Russian women

chemists are offered below: Anna Volkova, the first to publish; Iuliia Lermontova, the first Russian and the second European woman to receive a doctorate in chemistry (5); and Nadezhda Ziber-Shumova, one of the most productive women chemists/biochemists of the late nineteenth-early twentieth century (6)

Anna Fedorovna Volkova (d. 1876) acquired her basic education in chemistry at the systematic public lectures given in the late 1860s by St. Petersburg university faculty members.

Her first research experience was at the St. Petersburg Institute of Agriculture and Forestry, where she worked with chemist and agronomist Aleksandr Engel'gardt, one of the founders of the first Russian-language chemical journal. Engel'gardt and his co-workers were then engaged in investigations on the structure and properties of arylsulfonic acids and their derivatives (7). From 1870, when she moved to the St. Petersburg Technological Insti-

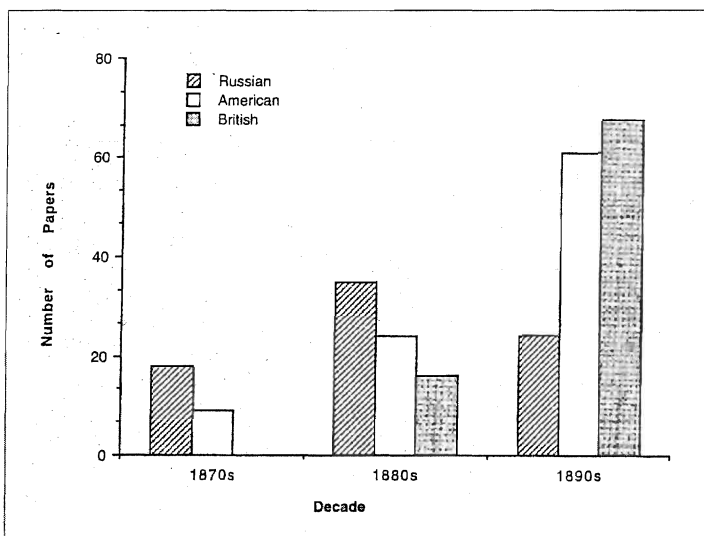


Figure 1. Number of papers authored or co-authored by Russian, American, and British women chemists and biochemists, 1870-1900, by decade. The count includes only full papers; preliminary notes and second-language duplicate papers are excluded. The Russian count does not include 10 papers constituting the combined pre-1901 contribution of Polish women chemists. Data from the London Royal Society *Catalogue of Scientific Papers, 1800-1900*.

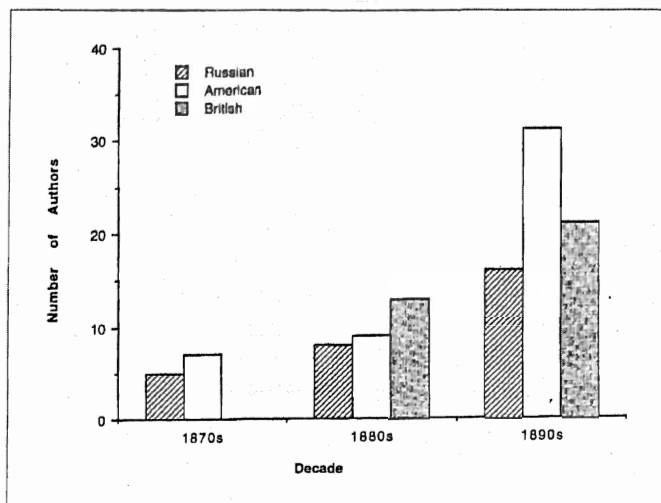


Figure 2. Number of Russian, American, and British women authors or co-authors of chemistry and biochemistry papers, 1870-1900, by decade. Since several women were active throughout the whole period, the 3-decade author total for a given nationality cannot be accurately estimated by adding the counts for the individual decades. Polish women are not included in the Russian count. Data from the London Royal Society *Catalogue of Scientific Papers, 1800-1900*.

tute, Volkova extended studies in this area with encouragement and direction from Dmitrii Mendeleev (8). Her two papers on toluenesulfonic acids and their amides in *Zeitschrift für Chemie* in 1870 were probably the first reporting chemical research by a woman from a modern chemical laboratory (9). Following their publication she was invited to join the recently founded Russian Chemical Society as its first woman member (10); about the same time Nikolai Menshutkin enlisted her help in editing and abstracting work for the society's journal.

Despite a very short career, ended by poverty-related illness and premature death in 1876, Volkova carried out a remarkable amount of synthetic work on aromatic amides, particularly the sulfonic acid amides. The contribution for which she is remembered (9, 11) is her 1870 preparation of the amide of *o*-toluenesulfonic acid, which was to become a key intermediate in the manufacture of saccharine. However, over the period 1870-73, she investigated a number of reactions of both the *o*- and *p*-toluenesulfonic acids or their chlorides, and prepared and studied the properties of several new acid amides (12). She was well regarded by her colleagues and well integrated into the chemical community; not only did she present two papers at the Third Congress of Russian Naturalists at Kiev in 1871, but she was

elected chair of one of the chemistry sessions there. Compounds she synthesized were among the new materials prepared by Russian chemists which were exhibited at the World Industrial Exhibition in London in 1876.

Iuliia Vsevolodovna Lermontova (1846-1919), most likely the first Russian woman to receive a doctoral degree in chemistry (13), is better remembered than Volkova. Born in St. Petersburg, December 21, 1846, she was the daughter of the director of the First Cadet Corps in Moscow, a government-supported military school for future army officers and military specialists. She received a good basic education from private tutors but, even though she had the benefit of an acquaintance with Mendeleev, failed to gain admittance as an auditor (the most she could hope for) at the Institute of Agriculture and Forestry in St. Petersburg.

In 1869, therefore, along with her friend the future mathematician Sof'ia Kovalevskaia, she went to the University of Heidelberg. After persistent effort, mainly on the part of the more confident Kovalevskaia, she was allowed to audit lectures by Robert Bunsen, Gustav Kirchoff, and Herman Kopp. She also obtained a place



Iuliia Lermontova (from D. H. Kennedy, *Little Sparrow: a Portrait of Sophia Kovalevsky*, 1983; the author thanks Christopher Kennedy for permission to reproduce the photo.)

in Bunsen's laboratory; urged by Mendeleev, with whom she kept up a regular correspondence during her years in Germany, she learned Bunsen's methods of ore analysis and joined in his then ongoing research on the separation of metals of the platinum group. Subsequently she was given a place, again as a private student, in August Hofmann's laboratory at the University of Berlin. Although most of his studies concerned coal-tar derivatives, he also worked on several aliphatic series in ongoing efforts to establish structural principles (14). Under his guidance Lermontova carried out her dissertation research, preparing a number of halogen derivatives of short-chain aliphatic hydrocarbons and investigating their properties. Her first paper, however, published in *Berichte* in 1872, described her study of an aromatic compound (4,4'-diamino-azobenzene) (15).

Since neither the University of Berlin nor the University of Heidelberg would consider granting a degree to a woman at the time, an approach was made by Hofmann to the University of Göttingen. A smaller institution of a generally more liberal outlook, it accepted Lermontova as a doctoral candidate, the requirement being that she take an oral examination. On the occasion of her passing, *cum magna laude*, Friedrich Wöhler, one of the two chemists on her examining committee (the other was Hans Hübner), presented her with a memento—a small cut stone of the mineral in which he had first discovered titanium. Her dissertation, "Zur Kenntnis der Methylenverbindungen," was published in Göttingen in 1874.

On her return to Moscow she stopped in St. Petersburg and was given a warm welcome by the chemical community. At a celebration at Mendeleev's home in her honor, speeches were made and toasts drunk. Aleksandr Butlerov, one of the most distinguished of Russia's organic chemists and a strong supporter of higher education for women, suggested she join his research group.

She returned to Moscow, however, and obtained a position there in Vladimir Markovnikov's laboratory where she continued research on aliphatic hydrocarbons. The preparation of 1,3-dibromopropane, reported under her name only in 1876 (16), led to the synthesis, via the corresponding dicyano-compound, of glutaric acid. Moving to St. Petersburg in 1878, she took up Butlerov's earlier invitation and joined him and Mikhail L'vov. One of the leading developers of modern structural theories of organic chemistry, Butlerov carried out extensive experimental work on both saturated and unsaturated series. Lermontova joined in ongoing studies on branched olefins. Much of her work was published

under Butlerov's name (with acknowledgments), although her synthesis of 2,4,4-trimethyl-2-pentene appeared under her own name in 1879 (17).

Going back to Moscow for family reasons and to be near Sof'ia Kovalevskaja, she rejoined Markovnikov, this time assisting with his investigations into the composition of Caucasian petroleum. She was probably the first woman ever to work in petroleum chemistry, a field of applied research in which there was then considerable interest in Russia and elsewhere (18). At Markovnikov's suggestion she investigated high-temperature fractionation processes and metal-catalyzed "cracking," presenting her results at meetings of the Moscow Section of the Russian Technical Society; for a time she was an especially active member of the latter's chemical technology division. She joined the Russian Chemical Society in 1875, elected on Mendeleev's recommendation.

About 1886 she put aside her chemical work and turned her attention to agricultural projects on her estate outside Moscow. Following modern methods for improving soil fertility, she increased yields considerably; she took up cheese-making, also using modern technology, and had moderate success, producing French cheeses for sale in Moscow. She lived through the First World War and the early phases of the social revolution that followed, dying at the age of seventy-three in December, 1919.

Nadezhda Olimpievna Ziber-Shumova (fl. 1870s-1914), from St. Petersburg, the third in this group of early Russian women chemists, probably authored or coauthored more pre-1901 papers in the chemical sciences than any other woman. Both she and her sister Ekaterina studied in Switzerland in the early 1870s. Nadezhda, already married to Nikolai Ziber from Kiev, one of Russia's first Marxist economists, was in Zürich with Ziber in 1872-73, although not formally enrolled at the university. Subsequently, she and Ekaterina, a medical student, continued their studies at Bern University, one of the institutions to which the Russian women students at Zürich scattered after being ordered by their government to leave Zürich in 1873. (With its then large Russian student community, Zürich was considered a hotbed of dangerous revolutionary activity by the tsarist government.)

By 1877 she had joined the research group led by Polish-born Marcell Nencki (1847-1901), head of the biochemical department at Bern and a pioneer in the chemical approach to the study of microorganisms. Their collaboration lasted until Nencki's death twenty-three

years later. Between the late 1870s and the turn of the century, she authored or co-authored more than thirty papers on a variety of biochemical topics, including *in vivo* oxidation, bacterial fermentation and decomposition processes, enzyme studies, and sugar hydrolysis, as well as basic chemical studies, such as the zinc chloride-catalyzed acylation of phenols known as the "Nencki reaction(19)". Her most important early contribution, however, was probably her joint work with Nencki on the constitution of the blood pigment hemin, part of a long series of systematic investigations on the degradation products of hemin, carried out by Nencki and his co-workers over many years. When integrated with the work of Leon Marchlewski on chlorophyll, these studies led Nencki to his hypothesis concerning the chemical relationship between the plant and animal kingdoms (20). The joint Nencki-Ziber papers were among the earliest on hemin (21).

Nencki left Bern in 1891 to assist in organizing the new Imperial Institute of Experimental Medicine in St. Petersburg, where he became head of the department of chemistry and biochemistry. Ziber-Shumova, a widow from 1888, joined the institute staff, along with Szymon Dzierzowski and Martin Hahn, as one of Nencki's three senior co-workers.

During the recurrent and very widespread famines and epidemics which ravaged the country throughout the 1890s, considerable effort was made by Russian professionals in the fields of public health and sanitation to provide assistance and bring about improvement. Measures taken included the organization of clinics and observational units in the countryside. Nencki, Ziber-Shumova, and Dzierzowski joined in this work, their contributions including extensive field observations carried out during a cholera epidemic of 1892. Their search for a source of readily accessible antiseptics led to a detailed investigation of the chemical composition of pine pitch and an examination of its disinfecting properties (22). Later in the decade they published a considerable amount of bacteriological work on the problem of cattle plague, Nencki having been commissioned to carry out immunization field trials in the Caucasus and Siberia (23).

Ziber-Shumova rose to a senior position in the institute's biochemical department and continued to publish at least until the outbreak of World War I. Her later work included investigations of the lipids present in lung tissue and a number of enzyme studies, many of which appeared in *Zeitschrift für Physiologische Chemie*.

Volkova, Lermontova, and Ziber-Shumova form a remarkable group in the history of women chemists,

publishing the first research (Volkova, 1870), taking the second doctoral degree awarded to a European woman (Lermontova, 1874), and creating an early record in publications (Ziber-Shumova, during the 1880s). Indeed among women whose careers in chemical research began before 1900, Ziber-Shumova is perhaps *the* dominant figure; she is also one of the most notable in the half century before World War I (24).

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1. Data from a count of papers by women authors in the nineteen-volume London Royal Society *Catalogue of Scientific Papers, 1800-1900*, University Press, Cambridge, 1867-1925. I have not reclaimed Marie Curie from physics, and so the ten papers she published in the 1890s are not included in the present comparison.
2. One or two pre-1870 publications by nineteenth-century women recording observations on chemical topics are known (see, for instance, D. A. Davenport and K. M. Ireland, "The Ingenius, Lively and Celebrated Mrs Fulhame, and a Dyer's Hand," *Bull. Hist. Chem.*, **1989**, 5, 37-42). The present paper, however, focuses on work carried out in modern chemical laboratories, from which women were virtually excluded until the late 1860s.
3. Accounts of the American and British groups, along with further comparisons and numerical data, will appear in the forthcoming book, M.R.S. Creese, *Ladies in the Laboratory? American and British Women in Science, 1800-1900: A Survey of their Contributions to Research*, Scarecrow Press, Lanham, MD, in press. For an earlier discussion of the British group see M.R.S. Creese, "British Women . . . Research in the Chemical Sciences," *Br. J. Hist. Sci.*, **1991**, 24, 275-305.
4. The long struggle, against powerful government opposition, of Russian women from about 1860 for access to higher education generated much sympathy for their cause in the academic community; further, this sympathy was backed by concrete practical help. For a discussion of the unique alliance between faculty members at Russian universities and women students at this period see, for instance, C. Johanson, *Women's Struggle for Higher Education in Russia, 1855-1900*, McGill-Queen's University Press, Kingston and Montreal, 1987; and R. A. Dudgeon, "The Forgotten Minority: Women Students in Imperial Russia 1872-1917," *Russ. Hist.*, **1982**, 9, 1-26.
5. Lermontova's degree was awarded in the autumn of 1874. Six months previously (April 1874) Lidiia Zesemann from Finland (admittedly then part of imperial Russia) had her inaugural dissertation on dibenzylacetic acid accepted by Zürich University [J. A. Meijer, *Knowledge and Revolution. The Russian Colony in Zürich (1870-1873)*, International Instituut voor Sociale Geschiedenis, Assen, 1955, p. 204, n. 71]. Zesemann worked in the physical chemistry laboratory

- at the University of Leipzig for several years in the 1870s and 1880s, later moving to Firenze (*Ber. Dtsch. Chem. Ges.*, 1877-1914, German Chemical Society membership lists).
6. Information about Volkova and Lermontova came mainly from I. S. Musabekov, *Iuliia Vsevolodovna Lermontova, 1846-1919*, Nauka, Moscow, 1967; the discussion of Volkova appears in Chapter 1, "The First Women Chemists," 7-10. Previously published English-language notes on Lermontova include C. Steinberg's, "Yulia Vsevolodovna Lermontova (1846-1919)," *J. Chem. Educ.*, **1983**, 60, 757, and J. Miller, "Women in Chemistry," in G. Kass-Simon and P. Farnes, Ed., *Women of Science: Righting the Record*, Indiana University Press, Bloomington, IN, 1990, pp. 310-311. Ziber-Shumova is mentioned in a number of scattered sources, including A. Szwejerowa, *Marceli Nencki*, Wydawnictwo Interpress, Warsaw, 1977; V.A. Bazanov and G.A. Vladimirova, "Russkaia koloniia' b Tsiurikhe," ["Russian colony' in Zürich"], *Sovetskoe Zdravookhranenie*, **1969**, 25, 71-76; and Meijer, reference 4. [In Russian sources, dates before the calendar change from Julian to Gregorian (made on February 14, 1918) are traditionally given in the Julian (Old Style) calendar; thereafter they are given in the Gregorian. This article follows that pattern. At the beginning of the twentieth century, the Julian calendar was thirteen days behind the Gregorian.]
 7. See, for example, A. Engelhardt and P. Latschinoff, "Über die Benzoylsulfanilidsäure," *Z. Chem.*, **1868**, 4, 266-270; "Über die Phenoldisulfosäure und die Isäthiosulfosäure," *ibid.*, **1868**, 4, 270-271; "Über isomere Kresole und ihre Derivate," *ibid.*, **1869**, 5, 615-623.
 8. Although remembered especially for his formulation of the Periodic Law of the elements, Mendeleev was a man of exceptionally broad scientific, technological, and general educational interests. His *Organic Chemistry* (1861) was the first systematic textbook in that field written by a Russian, and his three-volume *Principles of Chemistry* (1868-69) was considered a classic. He taught organic chemistry at the St. Petersburg Institute of Agriculture and Forestry from 1861 (A. Vucinich, *Science in Russian Culture 1861-1917*, Stanford University Press, Stanford, CA, 1970, pp. 147-165).
 9. A. Th. Wolkow, "Ueber die isomeren Toluosulfosäuren," *Z. Chem.*, **1870**, 6, 321-327 and *J. Russ. Chem. Soc.*, **1870**, 2, 161-175; "Ueber die Säuren, welche durch Vertretung des Wasserstoffs in den Amididen der Toluosulfosäuren durch saure Radicale entstehen," *Z. Chem.*, **1870**, 6, 577-581 and *J. Russ. Chem. Soc.*, **1870**, 2, 243-252.
 10. The Russian Chemical Society, founded in 1878 with the Russian Physical Society (founded in 1872), becoming the Russian Physical and Chemical Society (Vucinich, Ref. 8, 82, 137).
 11. J. Turkevich, *Chemistry in the Soviet Union*, Van Nostrand, Princeton, NJ, 1965, p. 51.
 12. See A. Th. Wolkow, "Ueber die Einwirkung des β -Toluosulfosäure-chlorides auf Säure-amide," *Z. Chem.*, **1871**, 7, 421-422 and *J. Russ. Chem. Soc.*, **1871**, 3, 239-242; "Ueber neue Amidsäuren," *Z. Chem.*, **1871**, 7, 422-423, *J. Russ. Chem. Soc.*, **1871**, 3, 242-245 and **1872**, 4, 7-15; "Ueber die Einwirkung von Phosphorpentachlorid auf einige Aciamide," *Ber. Dtsch. Chem. Ges.*, **1872**, 5, 137-143. Volkova's last paper ("Iso-Crotylether," *ibid.*, **1873**, 6, 196) suggests that she was then moving to a new area.
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 14. J. R. Partington, *A History of Chemistry*, Macmillan, London, 1964, Vol. 4, pp. 432-444 and many other entries.
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24. The decline in numbers of publications by Russian women chemists in the 1890s from the early peak in the 1880s (Fig. 1) can be correlated in large measure with the diversion of Ziber-Shumova's energies to bacteriology during much of the nineties (her sixteen bacteriological papers published during the nineties are not included in the data in Fig. 1). It is also the case that political events of the time were again influencing Russian women's access to higher education; as part of the counter-reforms instituted after the assassination of Tsar Aleksandr II (1881), most of the university-level Higher Courses for Women, established in several cities in the late 1870s, were discontinued (see both Johanson and Dudgeon, Ref. 4). This made conditions more difficult

for aspiring women chemists, a great many having benefited from these programs. However, as is shown in Fig. 2, the number of Russian women participating in research increased in the 1890s (many of those active then took their training in Switzerland); and so it would not seem to be an exaggeration to say that Ziber-Shumova's activities are the controlling factor in the Russian women's publication profile for the 1880s and 1890s.

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PAUL D. BARTLETT'S CHEM 17a: A PIONEER COURSE IN PHYSICAL ORGANIC CHEMISTRY

Leon B. Gortler, Brooklyn College of the City University of New York
and Martin D. Saltzman, Providence College

In the decade of the 1930's, *physical organic chemistry* developed to the point where it had become a recognizable and discernable hybrid discipline. The term *physical organic* was first used in print in 1940 by Louis Hammett as the title of his monograph (1). However, several books and monographs covering some of this work by the British chemists Robert Robinson (1933) (2), Christopher K. Ingold (1934) (3), Thomas Martin Lowry and William Alexander Waters (1935, 1937) (4), and Herbert Benn Watson (1937, 1941) (5) had already appeared.

Watson, in the preface to the first edition of his book, summarized the developments that had occurred up to this point (5):

Professor G.N. Lewis's conception of the sharing of one or more electron pairs by two atoms gave a new and illuminating picture of the bonds which link carbon atoms into chains and rings, and set organic chemists the task of interpreting the reactions of carbon compounds of various types in terms of the electronic

structures of the molecules. The problem was attacked ten to fifteen years ago, mainly by Professors Lapworth, Robinson, and Ingold. Considerations of the chemical evidence in the light of the electronic theory of valence led to results of great value, and it now became possible to express many

of the earlier ideas in more definite and elegant language. Then followed the very fruitful alliance of organic chemistry with physics and mathematics, and a much clearer view of the principles underlying the behaviour of organic compounds has been opened up by the aid of modern physical methods of investigation, and of Planck's Quantum Theory and Schrödinger's Wave Mechanics.

A major question is how these new ideas were being disseminated to students in other countries, particularly in the United States. In this article we present a glimpse of this process of transmission of knowledge by examining the content of Chem 17a, "Theoretical Organic Chemistry," given in 1938 at Harvard University by one of the future



P. D. Bartlett, courtesy of G. M. Bartlett

American masters of physical organic chemistry, Paul D. Bartlett (1907-1997). Dr. Ralph Thompson (6) audited the course and his class notes have been deposited in the archives of the Chemical Heritage Foundation in Philadelphia (7). The notes are 177 pages long and cover 27 lectures presented from February 7, 1938 to May 4, 1938.

Chem 17a was the first half of a two-semester course for graduate students. The second half, Chem 17b, dealt with natural products chemistry and both were taught for many years by J.B. Conant (8,9). As Conant successively became department chair and then president of Harvard, his courses were taken over by new faculty members. Given Bartlett's theoretical orientation and the fact that he had been a Conant graduate student, it was only logical that he would teach Chem 17a.

George Miller Bartlett, Paul Bartlett's father, was a mathematically inclined mechanical engineer who had attended Amherst College and taught at Case School of Applied Science and then in the Engineering Department at the University of Michigan. In 1910 the Bartlett family moved to Indianapolis, where Bartlett's father went to work for the Diamond Chain Company. When Paul Bartlett was in college, his father became a professor in the School of Engineering at Purdue.

George Bartlett was a major influence in Paul's life, taking a formal role in his instruction whenever he considered what Paul obtained in school was not satisfactory. In talking about his father, Bartlett said, "He used to read to me quite a lot. We read things like Jules Verne and science fiction and other kinds of things he and I were both more interested in than any [other] people around (10)."

After finishing high school in Indianapolis, Paul Bartlett entered Amherst College, his father's alma mater, to study chemistry. There he was influenced by Ralph Beebe, a young physical chemist familiar with the latest developments in this subject, and Howard W. Doughty, an organic chemist with a Johns Hopkins Ph.D. under Remsen. Bartlett was interested in organic chemistry, but he also took a fair amount of mathematics while at Amherst. Recognizing his physico-mathematical slant, his instructors directed him to Harvard and James B. Conant.

At Harvard Bartlett worked with Conant (9) but was strongly influenced by Elmer Peter Kohler (11). This was a particularly fortunate combination: Conant, the strategist and big thinker, and Kohler, the superb researcher and technician. Bartlett's paper with Conant based on his doctoral dissertation reflects the methodi-

cal analytical approach that was to characterize his later research (12).

After Harvard, Bartlett spent a year with P.A. Levene at Rockefeller Institute working on stereochemical problems. Nights and weekends he did research in a laboratory at Columbia University, finishing up some details from his thesis research (13). From 1932 to 1934 he was an instructor at the University of Minnesota, where he quickly established a research program and published several papers on reaction mechanisms and stereochemistry (14).

After two years at Minnesota, Bartlett was called back to Harvard, where Conant had become president of the university and Kohler was chair of the Chemistry Department. In retrospect, it appears as if they were choosing Conant's successor, his heir apparent, to the deanship of American physical organic chemistry. Within a few years, Bartlett's reputation had spread; soon almost every physical organic chemist to end up in a large research-oriented university had passed through his laboratory as a graduate student or postdoctoral fellow.

The course, Chem 17a, can be summarized as an introduction to the use of physical methods and mathematics to understand organic structure and reactions. The course begins with the structure of organic compounds, later considers the chemical bond, and then takes up the mechanisms of a variety of reactions. Reference to very recent works of leading investigators in the field are made in almost every lecture, thus attesting to the contemporary nature of the course. This reflects Bartlett's familiarity with the current literature and, in a number of instances, his own research interests. It may also reflect the influence of Kohler who, it is said, destroyed his lecture notes for his advanced organic course at the end of each year and began again from the literature the following year.

In an interview with Bartlett conducted by Leon Gortler, Bartlett commented on Kohler's influence on his research and on his teaching (10):

BARTLETT: Certainly the most influential teaching that I encountered in my first year at Harvard was (Elmer P.) Kohler's Chemistry 5.The course that he gave, I think, never left anyone uninfluenced. He centered it around the really important questions and problems, and how these things were solved, and who had done what about them and so on. It was just a great course. Kohler, of course, had been Conant's research professor, and he was one of the people held in highest respect in the university as a whole.

GORTLER: Did you consciously try to pattern your Chem 5 course after his course? [Chem 5, The Car-

bon Compounds, the second course in organic chemistry, had been taught by Kohler until his death in 1938.]

BARTLETT: Not consciously, but actually I was not aware of any other way to teach organic chemistry, except basing it on what are the important problems. If there are lots of people who don't do this, why, it probably means that Kohler was very influential on my teaching. It seemed to me that it was pretty axiomatic that this was the right way to go at it.

Bartlett's choice of topics, then, reveals his views on what were the important problems at the time.

Bartlett's lifelong interest in physical organic chemistry was the result of his interaction with many people: his father, his instructors at Amherst in chemistry and mathematics, Kohler and, of course, Conant. In a letter to William M. Tuttle in 1977, Bartlett gave a retrospective assessment of Conant's research(15):

Conant was an organic chemist interested on the research level in two branches of organic chemistry. The first was so-called physical organic chemistry, which was an uncommon preoccupation in those days in which the mathematical and physical relationships governing reactions or organic compounds were worked out and used as a framework for understanding what was going on at the molecular level. His other field was the chemistry of natural products, notably including chlorophyll. I never knew which of these branches of research he considered more fun, but it was quite clear that he considered natural products the more important. Organic chemistry originally arose in the attempt to understand more about living things, and he felt that chemistry must get back to this objective as fast as it could work through the enormous complexities involved.

During the years of Bartlett's graduate work, 1928 to 1931, Conant became increasingly more interested in biochemistry and natural products. Bartlett, however, throughout his career, never showed an interest in biochemical problems even though he spent a post-doctoral year with P.A. Levene at the Rockefeller Institute.

Bartlett was aware of this intriguing anomaly, and he comments on it on a number of occasions. In the 1978 interview he was asked why he went to work for Levene. He replied (10):

Well, there were two components of that. Conant always felt that you must go on to more important things than you were on and he felt that clearly an end use of organic chemistry on any level was to get into the biochemical side.

Bartlett then comments on the effect of the Rockefeller year on his career:

I don't feel that that was in the direct line of my career at all. If I'd been a different kind of person, I might have picked up all sorts of stuff by osmosis at the Rockefeller Institute, but I didn't. I mean, I just never evolved into an even peripheral biochemist, and I think this was probably a disappointment to Conant, because by his way of analyzing these things, I think it marked me as someone who had reached my high point and wasn't going anywhere from then on.

In 1973, Bartlett wrote to Conant on the occasion of Conant's 80th birthday and expressed somewhat the same concern. After talking about the ways in which he was influenced by Conant he wrote (16):

And yet I realize that I am not a good example of a real Conant disciple, for I never moved into either of those main streams where you correctly predicted that the action be — physics and biochemistry — nor would I, I think, if I had it to do again. I have continued to be fascinated by organic reaction mechanisms, and the field has been anything but static. This fascination, too, I owe in good part to you.

Bartlett was obviously ambivalent about his career. He continued his work in physical organic chemistry because it gave him great pleasure and great satisfaction, and yet he always felt that he was, in some way, a disappointment to his mentor Conant.

Summaries of the Chem 17a lectures can be found in the appendix to this paper. Almost all the lectures included references to the material being discussed, and many included tables of data (meticulously copied by Thompson) and/or mathematical analyses of the problems being discussed. The first several lectures deal with the structure of organic molecules and various physical methods—ultraviolet spectroscopy, electron diffraction, and, especially, X-ray analysis—used for the determination of structure. The data for what appear to be ambiguous bond lengths as well as the unreactivity of vinyl halides are rationalized by the use of resonance theory. At the end of this section he talks briefly about steric factors and their effect on the chemistry of organic molecules. He mentions the failure to synthesize tri-*tert*-butylcarbinol but suggests that it might be synthesized by "some highly refined method." Bartlett was sufficiently intrigued by the problem to attempt the synthesis of this bulky alcohol, and in 1945 he reported the success of this work (17). Inasmuch as the work had been initiated before the war, it is clear that Bartlett had more than an academic interest in the problem when he mentioned it in 1938.

Bartlett then begins a discussion of what Thompson titles "The Nature of the Chemical Bond." He spends several lectures discussing polarizability and dipole moments, bond energies derived from heats of combustion and heats of formation, and then makes a brief shift to a discussion of thermodynamics and its application to organic chemistry. Some of this material has now made its way into many undergraduate textbooks.

Bartlett's interest in physical methods and in thermodynamics reveals something of his approach to research. He was always seeking ways to achieve the quantitative measure of a chemical change. By lecturing on these methods, he was in fact learning by teaching. This approach to research was certainly influenced by Conant. In the 1978 interview Bartlett talked about Conant's approach to research (10):

I remember that fairly early on in the game, Conant said, "Anyone can identify a good research problem. The real work of it is to find something that you can do that works. If you want to measure something, find something that you can measure that works."

In the final fifteen lectures, Bartlett turns his attention to a variety of organic mechanisms. First he takes up free radicals, methods for trapping them and measuring their rates of formation, and the effects of steric bulk and resonance on their formation. Free radicals would eventually be a subject for one of Bartlett's major research programs. He then proceeds to a discussion of acids and bases and the measurement of acid and base strength in aqueous and nonaqueous systems. Acid-base catalysis in ionic reactions was then discussed, followed by a lengthy review of studies of the mechanism of the mutarotation of glucose to illustrate this type of catalysis.

The next several lectures deal with the work of Ingold, Hughes, Hammett, and others on nucleophilic substitution— S_N1 versus S_N2 . In this discussion Bartlett considers kinetics, stereochemistry, and the effects of solvent. At one point he mentions the α -lactone as a possible explanation for the retention of configuration in the reaction of β -chloropropionic acid with dilute base. Thompson writes, "This α -lactone formation looks fishy." It is impossible to tell whether this is the conclusion of Bartlett or Thompson.

Bartlett then takes up molecular rearrangements, where he discusses the work of Whitmore, Meerwein, as well as some of his own results with Pöckel. He completes the course with a discussion of ionic and free radical additions to double bonds. He cites his own recent work with Tarbell as well as the work of Lucas, Conant, Taylor, Ziegler, and Kharasch, but he does not mention

the bromonium ion proposal published by Roberts and Kimball in 1937. To a contemporary observer this course, given in 1938, would still be a very good introduction to physical organic chemistry. This is the best possible tribute to Paul D. Bartlett, one of the outstanding pioneers in American physical organic chemistry.

APPENDIX

CHEM 17a - Theoretical Organic Chemistry, February 7, 1938 - May 4, 1938

Lecture 1 (100)*

Structural considerations; importance of Lewis theory in structure; assignment of number of electrons for stable form of an element. X-ray studies to determine bond lengths; advances in application to less oriented states than crystals.

Lecture 2 (102)

X-ray diffraction discussed in detail. Discussion of normal covalent radii and comparison of bond distances with radius sum.

References to work of Bragg & Bragg, Debye, Compton, DeBroglie, Thomson, Randall, Pauling, Brockway, Sutton.

Lecture 3 (109)

Discussion of C-C bond distances as well as C-X bonds in various aliphatic and aromatic molecules. Other types of bonds discussed based upon X-ray data. Correlation between X-ray data and resonance theory. References to work of Brockway, Sidgwick, Pauling, Lucas.

Lecture 4 (115)

Resonance theory and further explanation of bond lengths discussed with respect to specific examples: vinyl halides; nitro compounds; diazo compounds. Reference made to Robinson's "Outline of an Electrochemical Theory" and Ingold's, 1934 *Chem. Rev.* article.

Lecture 5 ((121)

Further discussion of X-ray results with respect to carbon chains; use of electron diffraction and ultraviolet methods to determine radii. Steric factors governing radii. References to work of Pauling & Brockway, Stuart, Carothers, Heitler, London, Wilson, Dushman, Slater & Frank (*Introduction to Theoretical Physics*).

Lecture 6 (127)

Steric factors in certain molecules, e.g., tri-*tert*-butyl carbinol, biphenyls with restricted rotation. The nature of the chemical bond: derivation of relationships involving dielectric constant and polarization.

Lecture 7 (133)

Discussion of molar refractivity, polarizability, and dipole moments. References to work of Hückel, Debye, Smyth, Sutton.

Lecture 8 (139)

Dipole moments of aliphatic and aromatic compounds, correlation with structure, vector analysis of dipole moments. References to work of Lefevre, Kistiakowsky, Pauling, Kharasch.

Lecture 9 (145)

Calculation of dipole moments and relationship to structure, e.g., conformations in cyclohexane. Bond strengths: Definition of and problem with ionic organic reactions. References to work of Williams, Sutton, Sidgwick, Weissberger.

Lecture 10 (153)

Thermochemical data: Heats of combustion and formation. Bond energies: Methods of measurement and difficulties in interpretation. Resonance energy from heats of formation and combustion. Heats of hydrogenation and their interpretation. References to work of Pauling, Kistiakowsky, Giauque, Pitzer, Kossel, Teller.

Lecture 11 (157)

Thermodynamics: entropy calculations; free energy; equilibrium constants; barriers to rotation.

Lecture 12 (163)

Free energy and solubility; free energy and temperature; introduction to the study of mechanisms; free radical reactions in the gas phase. References to the work of Eyring, Polanyi, London, Gomberg, Walden, Ziegler, Rice & Rice (*The Aliphatic Free Radicals*).

Lecture 13 (169)

Activated complexes; Arrhenius equation; dissociation of bonds to form radicals and methods of measurement; magnetic properties of radicals.

Lecture 14 (175)

Free radicals: Examples involving dissociation of hexaphenylethane and dixanthyls, hydroquinone oxida-

tion. Rates of dissociation and methods of measurement using I_2 , O_2 , and NO. References to Werner, Schlenk & Mark, Marvel, Conant, Ziegler, Michaelis.

Lecture 15 (181)

Effect of aliphatic groups on the dissociation of dixanthyls; resonance effects in dixanthyls and radicals in general; steric effects in radical dissociation. References to the work of Hückel, Pauling & Wheland, Ziegler & Ewald, Bent.

Lecture 16 (187)

Mechanism of the reaction of triphenylmethyl radicals and oxygen. Organic acids and bases; methods of measurement of pK_a and pK_b . References to the work of Conant, Hammett, Hildebrand, Bjerrum, Wheland, Kolthoff.

Lecture 17 (195)

Further discussion of acids and bases; solvent effects; problems of measurement of strength of highly ionized acids in water; experimental methods to determine acidities and basicities in non-aqueous solvents. References to work of Conant, Hammett, Watson's *Modern Theories of Organic Chemistry* (5).

Lecture 18 (201)

Acid and base catalysis in ionic reactions; strength of acids: substituent effects, dipole moments; mutarotation of glucose. References to the work of Brnsted & Guggenheim, Lowry, Dawson, Ingold, Polanyi, Pedersen.

Lecture 19 (207)

Further discussion of the mechanism of the mutarotation of glucose involving acid and/or base catalysis. References to Reaction Kinetics Symposia in *Trans. Faraday Soc.* (1937), *Chem. Rev.* (1932), and work of LeMer.

Lecture 20 (217)

Medium effects in ionic reactions; problems with measurement of parameters that affect reaction — viscosity, dielectric constant, electrolytes. References to the work of Conant, Polanyi, Meisenheimer, Olson.

Lecture 21 (225)

Discussion of rates of reactions: alkyl chlorides with KI in acetone; alkyl bromides with pyridine; enolization versus racemization; kinetics of racemization versus

tautomerization; Discussion of reactions which do not clearly involve ions. References to the work of Olson, Hughes, Ward, Dawson, Cowdrey.

Lecture 22 (231)

Kinetics of decomposition of trialkyl sulfonium compounds; Walden inversion mechanism; various experiments proving inversion of configuration discussed; S_N1 and S_N2 reactions of halides. References to the work of Conant, Hammett, Hughes, Ingold, Polanyi.

Lecture 23 (239)

Problem of the mechanism of the substitution reactions of secondary halides; evidence for the formation of carbocations in organic compounds; structure of carbocations. References to the work of Whitmore, Ingold, Hughes, Ward, Polanyi.

Lecture 24 (245)

Solvolysis reaction mechanisms. Wagner-Meerwein rearrangements; kinetics of rate of rearrangement of camphene hydrochloride.

References to the work of Hammett, Taylor, Whitmore, Meerwein, Bachmann, Bartlett, Young, Winstein, Johnson, Burton, Ingold, Meisenheimer.

Lecture 25 (253)

Carbocations and molecular rearrangements; migration aptitudes; further discussion of the pinacol and the isobornyl chloride rearrangements, including role of catalysts. References to work of Ingold, Bartlett & Pöckel, Meerwein, Whitmore.

Lecture 26 (261)

Mechanism of addition of bromine to double bonds: Role of free radicals; evidence for radical as well as ionic mechanism; Kharasch's mechanism of addition of HBr. References to the work of Price, Pfeuffer, Ingold.

Lecture 27 (269)

Mechanism of ionic addition of bromine to alkenes: Experiments and interpretation. References to the work of Lucas, Francis, Conant, Bartlett & Tarbell, Taylor, Robinson, Ingold.

* Page in notes

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6. Ralph Thompson entered Harvard in 1934 after receiving his B.Ed. from Southern Illinois Normal University. He did his doctoral work principally with E.P. Kohler but also worked with George Kistiakowsky. Dr. Thompson completed his Ph.D. in 1938 and after one year of post-doctoral work with J.B. Conant went to work for Union Oil Products Company in Chicago. In 1961 he moved to Nalco Chemical Company and retired in 1968 to become a self-employed consultant.
7. Archives of the Chemical Heritage Foundation, 315 Chestnut Street, Philadelphia, PA 19106. The archives also contain a collection of the papers of P. D. Bartlett which he donated to the Foundation.
8. We have located Bartlett's own notes for Chem 17a taught by J.B. Conant in 1930 in the Bartlett collection at the Chemical Heritage Foundation. This will be the subject of a separate report.
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NOTE: Professor Bartlett died in Lexington, MA on October 11, 1997; see *Chem. Eng. News*, **1997**, Nov. 10, 45.

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THE pH METER, A PRODUCT OF TECHNOLOGICAL CROSSOVERS

Carl E. Moore and Bruno Jaselskis, Loyola University, Chicago

Aside from the chemical balance, the pH meter (1) is probably the most widely used piece of chemical instrumentation and as such it has contributed much to both the progress and the culture of the hard sciences. This useful device came into being via an almost storybook route of discovery and development which culminated in the practical commercial Model G pH meter devised and marketed by an enterprising young college professor, A. O. Beckman. The flow of ideas, which climaxed in the development of this useful instrument, narrates one of the very interesting adventures in the sciences.

Beckman described this early venture into pH instrumentation in this manner (2):

.. in 1934, I experienced the type of luck in which preparedness played a role. I was then an assistant professor of Chemistry at California Institute of Technology. One of my University of Illinois classmates, Dr. Glen Joseph,happened to stop by one day for a chat. He told me of a serious problem he was having in making pectin and other by-products from lemon juice He was forced to use a glass electrode, because it was not affected by SO_2 . He used a thin-wall glass bulb about an inch in diameter, very fragile and easily broken. Furthermore, because the electric current used in measurements has to pass through the glass wall of the electrode, the extremely high resistance of the glass bulb (in the multimegohm range) forced him to use the highest sensitivity galvanometer available to serve as a null point in the Wheatstone bridge circuit employed for the voltage measurements.....

Professor Beckman suggested to his friend Dr. Joseph the use of a vacuum tube voltmeter which would allow him to use smaller and more sturdy glass electrodes than



A. O. Beckman, courtesy Beckman Instruments, Inc.

those electrodes that he had employed previously with the various unreliable and difficult to use electrometers. As a result of these discussions Beckman built a two-stage, directly coupled vacuum tube voltmeter for Dr. Joseph. It luckily worked. In a few months his friend asked him to build him another instrument for his personal use. Then Beckman says:

The thought occurred to me — if he needed two of these instruments in his modest laboratory, perhaps other chemists might have a need for such an instrument.

In 1935 Beckman produced a portable rugged pH meter costing \$195 — a princely sum in those days and more than one month's salary for an analytical chemist. In this instrument the amplifier consisted of two vacuum tubes — a tetrode and a triode — and a milli-ammeter placed in the plate circuit of the triode to serve as a balance indicator.

As inconceivable as it may seem, this instrument, when introduced at the 1935 American Chemical Society Meeting in San Francisco, was



The Beckman pH meter

not received with enthusiasm. But some of the leading analytical chemists, though dubious about it, did suggest that he approach the instrument manufacturers and attempt to commercialize it. The instrument makers were generally pessimistic about this new fangled gadget. Beckman instead of letting the matter drop persevered and continued to make pH meters on his own, and in ten years he had made several hundred thousand, and there was no end in sight to the demand. As Beckman later pointed out, he was the right man in the right place at the right time: he had the correct training, foresight and energy to engineer a breakthrough in chemical instrumentation. It was of such mammoth proportions that only historians of a later time will be able to properly evaluate its impact.

But what set the stage for this monumental development? The answer to this question is couched in the romantic science of the electricians (3) which had captured the public imagination in the preceding century. Actually, as with nearly all things electrical, the pH meter can be said to have had its seminal origin in the work of Alessandro Volta, who announced on March 20, 1800 (4) the discovery of what we now call the Voltaic cell, which opened numerous paths of research. Each of these

operated nearly independently of the others, but occasionally these research paths would cross. These crossovers provided the opportunity for sharing vast amounts of an hitherto unknown technology by the investigators on each research path. This crossover phenomenon provided the impetus for many breakthroughs.

There are at least three intersecting courses of ideas — and their research tracks are easily discernible — in the discovery and development of the pH meter. These are

- the communications researchers' path of those researchers principally interested in improving the quality of telegraphic signals,
- the chemical research route of the investigators interested in acid-base chemistry, particularly in biological systems, and
- the physics research track into the study of the electrical properties of glasses.

All three of these lines of investigation were assiduously researched, each with its own specific sets of aims and objectives. However, none of these had goals that included the manufacture of a pH meter.

The Chemical Research Pathway

By 1935 solution chemists — led by Ostwald's Leipzigers and their academic offspring — had elucidated much of the electrochemistry left over from the Faraday era. It was now possible to formulate and utilize Voltaic cells for a wide variety of purposes. Cells of the following general character were common knowledge.

| (Reference Electrode) || (Indicator Electrode) |

One of the applications of the cell was the determination of the concentration of redox substances.

These cells contained three elements:

- a reference electrode
- an indicating electrode and
- a device for measuring the voltage developed by the cell.

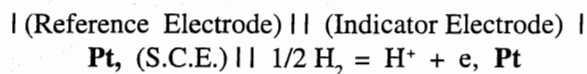
Each of these three cell elements offered many possibilities to experimenters in terms of materials used and devices constructed, and the history of each cell component in itself is a monument to the ingenuity of the early experimenters.

By the time of Beckman, the calomel electrode and its attendant salt bridge, both of which had been developed in Ostwald's laboratory, had been generally accepted as the half cell device most practical for the standard of reference. But there still remained substantial

problems facing workers in the decade of the 1930s in terms of the discovery and fabrication of practical indicating electrodes and in the development of suitable voltage measuring devices.

An indicating electrode for the ubiquitous hydrogen-ion posed some very special and difficult problems in that the hydrogen-ion occurred in all aqueous solutions, and many of these solutions both *in vivo* and *in vitro* contained materials which were deleterious to the usual hydrogen-ion sensing electrodes rendering them useless. However, of the many electrodes studied, two indicating electrodes — the hydrogen electrode and the glass electrode — played the most significant roles in the development of the pH meter. The glass electrode eventually became the electrode of choice for almost all pH measurements.

The pH measuring cell employing the hydrogen electrode may be formulated as follows:



In the case of the hydrogen electrode, which depended on a catalytic platinized-platinum metal surface, there were two major difficulties. First, the electrode became easily "poisoned" in the catalytic sense — its surface was easily contaminated by many things, particularly organic compounds containing sulfur, rendering the electrode erratic or inoperative — and second, the hydrogen electrode was easily polarized if current was drawn from the cell. Thus the use of devices employing bridge circuits required significant amounts of time for each measurement in order to allow the circuit to reestablish equilibrium. This behavior made the hydrogen electrode difficult to use in potentiometric titrations of acids and bases.

The Communications Pathway

There had been intense activity in the communications area following the discovery that telegraphic signals could be sent by wire. It was soon found that telegraphic signals needed power boosts if they were to travel long distances. Thus a research pathway opened up which produced efficient test instrumentation and signal booster devices. Some of this equipment was, with appropriate modification, adaptable to other fields. In the course of this intensive communications research Fleming (1905) discovered the thermionic diode (5). Two years later — still on the communications path — Lee de Forest discovered the triode (6) which was to make Beckman's pH meter possible. The spirit of the

times is captured in de Forest's account of his discovery of the triode to which he gave the name "Audion (6)":

... The "Audion," suggestive of sound, prompts the consideration of an analogy in the realm of sight — the microscope. The Audion, in a measure, is to the sense of sound what the microscope is to that of sight. As the microscope has opened to man new worlds of revelation, studies of structure and life, and manifestations of natural processes and chemical reactions whose knowledge has proven of inestimable value through the past three generations, so history, opened fields of research and wrought lines of useful achievement which may not unfairly be compared with the benefits from that older prototype and magnifier of light waves. But when the first steps were taken in the work which eventually resulted in the Audion of today, I no more foresaw the future possibilities than did the ancient who first observed magnification through a drop of water.

In 1900, while experimenting with an electrolytic detector for wireless signals, it was my luck to be working by the light of a Welsbach burner. That light dimmed and brightened again as my little spark transmitter was operated. The elation over this startling discovery outlasted my disappointment when I proved that the unusual effect observed was merely acoustic and not electromagnetic. The illusion had served its purpose. I had become convinced that in gases enveloping an incandescent electrode resided latent forces which could be utilized in a detector of Hertzian oscillations far more delicate and sensitive than any known form of detecting device. The first "commercial" Audion, as it originally appeared in 1906, was therefore no accident or sudden inspiration.

The advent of the triode opened up a wide area of applications other than in the field of communications. The first application of the triode to hydrogen-ion chemistry (7) appears to be that of Kenneth H. Goode, who carried out a Master of Science degree research project at the University of Chicago. This research involved using the triode in a potentiometric titration setup. The MS degree was granted in August of 1924, but Goode published a paper on the research in 1922. (8) The research was so close to the frontier of the science of the time that this paper contains no references to previous work. He performed the titrations using a hydrogen electrode versus a calomel electrode, with his continuous reading apparatus giving the readout in either volts or Sorensen units, *i.e.*, pH units. Goode gives his reasons for doing the research as follows (7):

...In order to avoid the use of the telescope and scale, which do not lend themselves to convenient use ei-

ther for classroom demonstrations or for routine titration work, it occurred to the writer to make use of the amplifying characteristics of the vacuum tube to magnify the currents to such a value that they could be easily measured with a portable milli-ammeter. ...

Goode in his paper in the *Journal of the American Chemical Society* made the fundamental observation that, because of his use of the triode, his device drew no current. This observation was seminal to its use with the glass electrode which was to follow some seven years later (8):

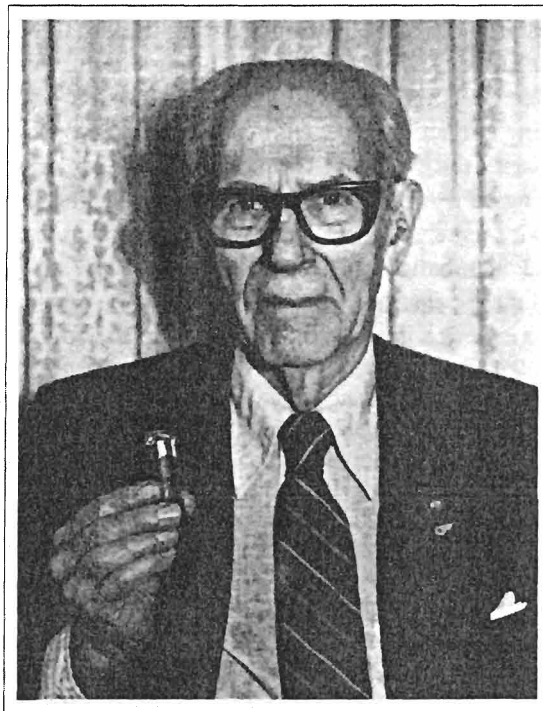
... The simplest possible apparatus for electrometric titration, from a theoretical standpoint, would be a sensitive voltmeter connected between a calomel electrode and a hydrogen electrode. In practice, however, an ordinary voltmeter cannot be used, because the instrument would consume current enough from the cell to discharge the hydrogen electrode, and render it inoperative. For this reason all types of apparatus hitherto in use have depended upon balancing the unknown e.m.f. of the cell being used against a variable known e.m.f. produced by a potentiometer system, the balance being determined by a "null-point" galvanometer. With this type of apparatus a balance of potentials must be made before each reading of the voltage, and there is considerable uncertainty in the readings when the potential of the cell is rapidly changing. The investigation described in this paper has shown that the 3-electrode vacuum valve ("audion") presents almost the ideal case of a "voltmeter" which draws no current from the source to be measured, and can therefore be employed as a continuous-reading instrument for determining the concentration of the hydrogen ion. ...

The Physics Pathway

The electrical properties of glasses which started to attract attention at around the time of the development of the Leyden jar in the 1740s, developed into a major research area. Many famous names are associated with this research pathway. Among these we mention Benjamin Franklin, Lord Charles Cavendish, Lord Kelvin, Helmholtz, Warburg, Cremer, and Haber. Undoubtedly, many frustrating hours, days, perhaps even years were spent in trying to overcome the problems posed by the very high electrical resistance of glass. The glass research pathway intersected both the communications track because of the need for effective insulators and the main stream of solution chemistry because of its possibilities for indicating electrodes for the hydrogen-ion. At these intercepts the fruits of a vast amount of high quality research became available to the pH in-

strument constructors and the communications researchers.

After a surprising lull of around seven years following the publication of Goode's paper, at least three laboratories almost simultaneously developed pH-measuring devices based on the use of the glass electrode. These were Partridge at New York University, Elder and Wright at the University of Illinois, and Stacie and Goodhue at Iowa State College. The first paper to appear in print was that of Elder and Wright (9). We will



Walter H. Wright holding 199 Tube used for glass electrode measurements (1928), (see Ref. 12)

consider the paper of Elder and Wright in some detail, not only because of their established priority, but also because of the fact that, at the time of this literature study, Walter Wright was still alive—albeit in a nursing home—and could provide some very interesting anecdotal information. It was our very good fortune (10) to make contact with Wright (born October 23, 1907), the surviving author of the paper which had appeared in the *Proceeding of the National Academy of Sciences* in 1928. He was kind enough to give us a personal account of his recollections of that research. In this account he indicated that the germ of the idea came from a course entitled Advanced Analytical Instruments which was being taught at the University of Illinois by Dr. Lucius W. Elder, Jr. There was much discussion of pH determination in that class of methods, but Mr. Wright was not

sure who suggested the idea of using a vacuum tube potentiometer with the glass electrode to improve its usefulness as a pH sensing device. Thus, we will probably never know the identity of "the one of us" to whom the paper refers in the quote "...it occurred to one of us that a vacuum tube potentiometer might be preferable."

Under the direction of Elder, Wright did honors undergraduate research and an honors undergraduate thesis (11), which addressed the problem of utilizing a VTVM with the glass electrode. At the time of this summer school class, Mr. Wright, who had a previous interest in radio and electronics dating back to the days of World War I, had built a functioning one-tube radio receiver. Thus, he was well suited for the task of constructing a functioning vacuum tube voltmeter. He was faced with the dual and formidable problems of constructing both a vacuum tube voltmeter and a glass electrode. It is interesting to note from his correspondence that he cannibalized his one-tube radio receiver to get parts for the construction of his VTVM. The essence of these memories is given in the letter on the following page(12):

Three major research pathways — the turbulent torrent of solution chemistry, the difficult trail of the physics of the electrical properties of glass, and the raucous road of communications research — converged. At the convergence point, these combined pathways provided science the information and technology needed to allow skilled hands and creative minds to fabricate the pH meter, an instrument that has impacted on much of succeeding research. The Model G pH Meter of A. O. Beckman was the practical manifestation of these research efforts.

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8. K. H. Goode, "A Continuous Reading Electrotitration Apparatus;" *J. Am. Chem. Soc.*, **1922**, 44, 26.
9. L. W. Elder and W. H. Wright, "pH Measurement with the Glass Electrode and Vacuum Tube Potentiometer," *Proc. Natl. Acad. Sci. USA*, **1928**, 14, 936-939.
10. We owe thanks to the late Prof. John C. Bailar, Jr. of the University of Illinois at Champaign/Urbana, who assisted us in locating Mr. Wright.
11. W. H. Wright, pH Measurement with the Glass Electrode and the Vacuum Tube Potentiometer, B.S. Thesis, University of Illinois, 1929.
12. Letter from W. H. Wright to C. E. Moore, Nov. 7, 1985. It was welcome news to find that the original vacuum tube used in the first VTVM pH meter was still in his possession. The photograph of Wright and his vacuum tube is in the Loyola University Archives in the Moore correspondence. Wright's recollections of the details of this research —nearly 60 years later—are contained in his correspondence with Moore.
13. Some of the early pH sensing electrodes such as quinhydrone contaminated the samples.
14. W. H. Wright died in April, 1990.

ABOUT THE AUTHORS

Professors Moore and Jaselskis are professors of chemistry emeritus at Loyola University Chicago, 6525 N. Sheridan Road, Chicago, IL 60626. Both are considered generalists in the field of analytical chemistry. Jaselskis has worked extensively in the field of solution chemistry and Moore in the domain of organic reagents.

Wilmington, DE 19809

November 7, 1985

Dear Professor Moore:

At the University of Illinois (Urbana) Summer Session in 1928 I was taking a course in Advanced Analytical Instruments under L. W. Elder, Jr. pH instruments were then possible contaminants [(13)] of the sample being examined except for the glass electrode. However, the glass electrode required a quadrant electrometer to avoid polarizing the glass electrode such as when ordinary Wheatstone bridge type instruments were used. Unfortunately, low humidity is essential for accurate readings with quadrant electrometers particularly during a humid summer at U. of Ill.

Goode's proposal (1921) to use a 3 electrode vacuum tube failed to recognize the basic space charge and ion or electron flow factors of the triode. My experience with wireless and radio dating back to World War I gave me electronic training.

For a bachelor degree thesis I proposed a vacuum tube potentiometer with grid voltage set at a value where no current flow in the grid circuit would take place. I dismantled my one tube (UV199) radio set and proceeded to set up the apparatus used in the paper published in the 1928 proceedings N. A. S. pg. 936.

The first attempt at pure soda-lime glass preparation was a disaster! The melt was made in a platinum dish and heated in a 20KW carbon granule furnace equipped with a tap-off transformer and protected by a circuit breaker in the power supply. I had been assured that the furnace would not melt Ferro-Silicon (approx. 1590° C) and was therefore safe for platinum (M.P. 1753° C). I reasoned that furnace power supply maximum could be 20KW so I set the tap-off transformer at the highest voltage to keep under this figure. When the breaker tripped I set the tap-off transformer at the next lower tap, reset the breaker and repeated the process. As the furnace temperature rose, the carbon resistance fell, thus drawing more current and tripping the breaker. I followed the temperature rise by observing a range of segar cones placed alongside the platinum dish. After several cycles of above steps I removed the lid to observe the melt. White light came from the furnace, the segar cones had melted, also the platinum dish and its charge! One explanation was that the platinum dish (\$300 worth) had been purchased during World War I and therefore might not be pure platinum. I then looked up the thesis (CA 1915) covering the original use of the furnace for preparation of Illium type alloys for S. W. Parr. The original user apparently was afraid to trip the breaker and thus never the full 20KW available and hence did not reach the temperature possible. In any event the contents of the furnace bottom was removed and turned over to an inorganic grad student (S.G.Ford) for platinum recovery. The next move was to use a graphite crucible and risk some impurity in the glass being picked up from the binder used in the crucible. The melt from the graphite crucible did have a slight purple cover possibly due to manganese or cobalt(?). Finally, a large Nickel crucible was used resulting in a melt that was drawn into small rods with a slight brown color, probably due to a trace of dissolved nickel oxide.

As Dole pointed out in his book several workers were in this field at the same time. It just so happened that the novelty of the Elder & Wright study led to early publication in the Proceedings of the National Academy of Science 14, 936 - 9 (1928) and thus predated the publications of the other workers.

The first inquiry following publication was from Dr. Ellice McDonald of the Cancer Research Fund, Graduate School of Medicine, University of Pennsylvania Philadelphia, PA.

His interest related to the possibility that Cancer cells differed in pH from normal cells and that the glass electrode could possibly detect the difference

Sincerely yours,

Walter H. Wright (14)

P.S. I still have the 199 tube and some of the soft glass tubing used in this study.

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All inquiries should be directed to:

Dr. Leo B. Slater,
Chemical Heritage Foundation
315 Chestnut Street
Philadelphia, PA 19106/USA
Tel: 215-925-2222
FAX: 215-925-1954

MICHAEL POLÁNYI'S EARLY YEARS IN SCIENCE

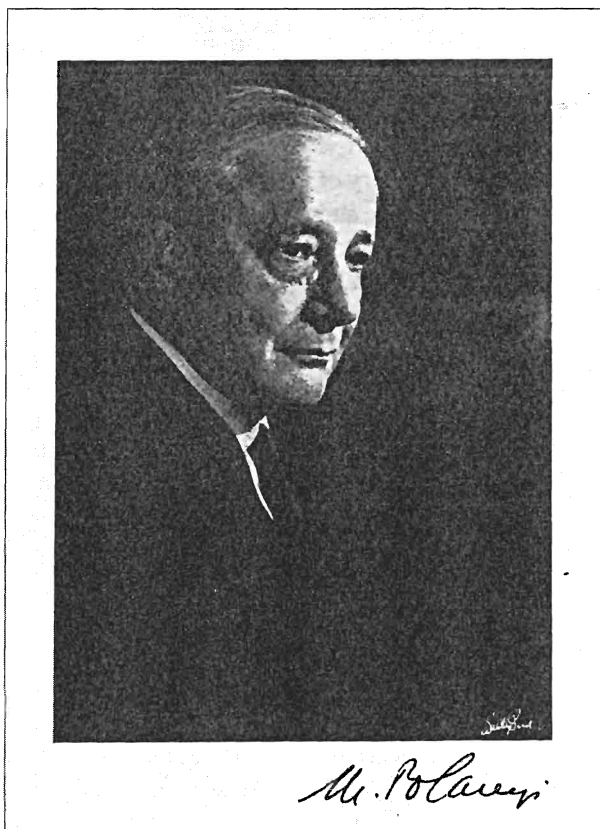
Gábor Palló, *Institute of Philosophy, Hungarian Academy of Sciences*

The literature on Michael Polányi's philosophy is abundant. His philosophical system has become a classic, particularly in the field of philosophy of science(1). His most famous book, *Personal Knowledge*(2), has been analyzed in short papers as well as in substantial books, sometimes in strong agreement sometimes in disagreement but seldom very objectively. Some philosophers are not even aware of Polányi's work in chemistry or else ignore it. On the other hand, historians of science consider him a major figure in 20th century physical chemistry as well as in some fields of physics, and they ignore his philosophy which they regard as unimportant. Both groups seem to feel that the question whether a relationship can be found between Polányi's philosophy and his chemistry is a problem for the future, or else they see the two as totally independent from each other as if they were created by two different persons. In this paper the Hungarian chemical origins of Polányi's scientific thinking will be analyzed. This part of his career has not been investigated. A

detailed Polányi biography does not yet exist, only some sketches having appeared so far(3). Although not analyzed here, his philosophical commitments can also be traced back to his education in Hungary, to his family, to his early schools, and to his early social and political experiences(4).

In 1928, Michael Polányi was living in Berlin where the editor of a popular Hungarian newspaper asked him about the educational scene in Hungary. He contrasted it with Germany where(5):

...the professors grab with great enthusiasm the hands of students who are thought to be gifted. They are like art collectors whose main passion is to discover talent. Here, [in Berlin] this belongs to the duties of a professor. They educated me, they placed me here where I can do my utmost. They provide me with everything and do not ask for anything. They trust that the man who is aware of the joy of science, will not leave it for the rest of his life.



Michael Polányi, *Biogr. Mem. Fellows R. Soc.*, 1977, 23, 413-448

He contrasted this situation with that of Hungary(6):

Looking back, I see many Michael Polányis stuck in the mud halfway, my good friends, unknown poor boys, a dozen of them like me or even better, fired from the university, knocked down by *numerus clausus*.

This sorry description does not explain how he managed to get near the German professors who "grabbed his hands like art collectors"(7). But he says in the same paper(8):

In the second semester of my university years, I got to the laboratory of Ferenc Tangl who took care of me from then on. In 1913, I became a medical doctor. Thanks to the help of Ignác Pfeiffer, by agreeing to serve as a companion to the son of a wealthy family, I was able to go to Karlsruhe [in the summer of 1912 and again in 1913/14] to study chemistry at the Technical University.

In the following, I will try to describe these first schools of Michael Polányi which, in spite of his critical remarks, could produce extremely good scientists. Around the turn of the century, a generation of outstanding scientists was born in Hungary. They made their impact in various fields such as philosophy, psychology, sociology, and the natural sciences. Among them were George de Hevesy (1885-1966), the Nobel laureate discoverer of the radioactive tracer method, Albert Szent-Györgyi (1893-1986), who won the Nobel prize for his theory of cellular oxidation and for discovering vitamin C, and physicists who became world-famous for their contributions to the Manhattan Project, among them Leo Szilárd (1898-1964), Eugene Wigner (1902-1995), Edward Teller (1909-), and John von Neumann (1903-1957), who became most famous for building the first giant electronic computer. All went to school in Hungary but at some point in their higher education moved to Germany or Switzerland, where after some years they gained scientific positions. However, they kept their contacts with the Hungarian scientific community and collaborated with their old colleagues in Hungary.

Michael Polányi, one of the most interesting personalities in this remarkable group, was born in Budapest in 1891. He went to high school in Budapest, a "Gymnasium" as it was called, founded by the father of another great emigrant scientist, Theodor von Kármán (1881-1963). Edward Teller, Nicholas Kürti (b. 1908, low temperature physics, Oxford), and the outstanding economists of England, Nicholas Káldor and Thomas Balog, went to the same school(9).

Polányi's career was quite unusual. He not only emigrated from countries like Hungary and Germany, to settle down finally in Manchester, England, but also changed scientific fields. Though as a schoolboy, particularly after reading H. G. Wells' *The World Set Free*, he was deeply interested in science, he became a physician. He decided to do this because his family was in constant financial difficulty after his father's early death, and his relatives felt that a good physician could always earn a fair amount of money. But his attraction to science prevented his staying long in medical practice, and he turned to physical chemistry and some aspects of physics. As a respected, very successful professor, he emigrated once more. In 1948, he resigned his chair of physical chemistry in Manchester and became professor-at-large of social sciences at the same university. He died in England in 1976. As a chemist, he was mostly engaged in the theory of adsorption, mechanical characteristics of solid, and X-ray analysis, but his most successful research was in reaction kinetics and the mechanism of chemical reactions(10). He followed an ambition that originated in his youth, to become a philosopher only after establishing himself as a scientist(11). At the age of 57, he was able to achieve his life-long ambition of becoming a philosopher and was drawn particularly to the philosophy of science, where his views have become classic. They became very influential in sociology, political philosophy, ethics, and even in aesthetics and religious studies.

Polányi's long path from medicine to physical chemistry went through a number of stages. 1. As a student he began to work in the laboratory of Ferenc Tangl. 2. With the help of Ignác Pfeiffer he studied physical chemistry in Karlsruhe, beginning in 1912. 3. He obtained his doctorate in chemistry at Budapest University in 1917 on the basis of his German research publications. 4. He worked as assistant to George de Hevesy in 1919. 5. In the same year, he left for Karlsruhe and then for Berlin to work with Fritz Haber. There are two Nobel laureates on this path, Hevesy and Haber, and two internationally less known persons, Tangl and Pfeiffer.

Ferenc Tangl (1872-1917), professor of physiology had a somewhat unusual career compared to his fellow professors of the time. He did not attain high university or political positions but was a very conscientious, precise researcher. His work in physiology dealt with subjects such as theories of ontogenesis, the development of bird embryos, energetics of the metamorphosis of insects, and problems of metabolism. Perhaps his most important skill was his ability to recognize outstanding intellectual qualities and excellence in research. Because

he could not find a position in the faculty of medicine of Budapest University, he worked for Budapest's Veterinary School and in 1893 was appointed to the chair of physiology and pathology in that school after visiting the most famous laboratories in his field, among them those of Robert Koch and Nathan Zuntz. He became head of the department of physiology at the medical school of Budapest University only in 1914, although he had worked in the university beginning in 1903 but in another department(12). In 1896 he organized a new institute for animal physiology and nutrition, the first in this subject in Hungary. The institute soon became an internationally recognized research center where Russian, English, American, and also Japanese scientists conducted research. This was unique in Hungary at that time. Tangl understood the significance of physical chemistry in physiology. He supported one of his former students, Gyula Groh, to succeed him in his department at the Veterinary School and asked him to help gifted young people as Tangl himself had done. This is how Hevesy carried out some of his earliest experiments with radioactive indicators at this institute, sometimes together with László Zechmeister (1889-1972), later professor at Caltech. Elisabeth Róna (1890-1981), the well-known researcher at Oak Ridge Laboratory after the second World War, also began her career here, continuing it in Vienna at the Institut für Radiumforschung.

This was Michael Polányi's earliest exposure to physical chemistry. His first papers were dated from Tangl's laboratory at Budapest University, where he learned the basic technique of precise experimental work. Polányi's choice was very lucky, as it would have been difficult to find such a serious, fruitful laboratory elsewhere in Hungary. His first paper, published in 1910, dealt with some properties of brain fluid taken from sick people(13). The paper contained accurate measurements of density, surface tension, and conductivity, showing that Polányi had learned to be a scientist. His later papers from the same laboratory contained more and more physical chemistry, especially colloid chemistry(14). This direction became very fruitful to him from two points of view: first, the attention he attracted from Albert Einstein because of his interpretation of the third law of thermodynamics helped him greatly in establishing himself as a scientist(15); second, he found one of his most successful subjects, adsorption, the theme of his doctoral thesis in chemistry(16).

His other mentor, Ignác Pfeiffer (1868-1941), became professor of chemical technology at the Technical University of Budapest in 1912, the year Polanyi made his first trip to Karlsruhe. Pfeiffer's most significant in-

vestigations were related to the hardness of water. He worked out an analytical method to measure hardness and a way to soften water. He published pioneering research on combustibles, firing equipment, fuel technology, particularly coal and gas fuel. Later he was engaged in various problems of lighting devices(17). Although Pfeiffer had not taught Polányi, they had met several times. Their first and, from Polányi's point of view, most important contact occurred in 1912 when Pfeiffer helped him go to Karlsruhe as companion to a wealthy student. There he attended summer courses in elementary physical chemistry, electrochemistry, surface chemistry, and catalysis. This was Polanyi's first schooling in his favorite subject, physical chemistry. He also established some important relationships, particularly with the outstanding Polish scientist, Kasimir Fajans, who later collaborated with Elisabeth Róna, another Tangl and Hevesy student. Moreover, Hevesy had heated discussions with Fajans on the new conception of chemical elements, and Polányi tried to mediate in an unpleasant situation. Both men had been his bosses at some time. It was a small world.

It is difficult to tell how and when Pfeiffer made contact with Polányi. There are various possibilities. First, Pfeiffer knew Tangl well, and the latter may have spoken to him about the extremely gifted medical student who needed first-class training in physical chemistry. The second possibility is more complicated. Pfeiffer suffered seriously from political persecution. After the first World War, two revolutions broke out in Hungary; and Pfeiffer took an active part in the second, the Communist one(18). Though Polányi had never been a revolutionary, a Communist, nor even a leftist, he was a member of a radical intellectual student organization called Galilei Circle. The secretary of this Circle was his brother, the renowned economist, Karl Polányi; and practically all the significant young intellectuals of the time were members, including Leo Szilárd and George Pólya (1887-1985), the famous mathematician who later went to Stanford. Pfeiffer attended the stimulating and nonconformist meetings. The discussions covered the most fashionable intellectual subjects of the time, such as sociology which was a new discipline in Hungary at the time, Ernst Mach's philosophy, and contemporary international and national politics. This professor of the Technical University, a member of the Freemason movement and later of the Zionist movement, was open-minded enough to listen to the younger generation. The two may well have met in this group. Of course, these are only conjectures. Hungarian middle class intellectuals moved in very small circles.

During the first of the two revolutions, the democratic one, Polányi won high rank in the ministry of health. He became state secretary, worked out a way of reorganizing the Hungarian health system, and contemplated giving up his scientific ambitions for a political career. When the Communists came to power, he gave up his position and went to teach in Hevesy's department. Pfeiffer, however, took on an important position during the second, the Communist revolution, becoming head of a section in charge of chemistry.

Both men changed careers after the revolutions. The new rightist regime forced Pfeiffer to retire from his university department. He was offered the position of head of the newly established private research laboratory of the United Lamp factory. He proceeded to organize the laboratory which became highly successful in developing the krypton bulb as well as in some basic research in experimental physics(19).

Polányi was terminated by the university because of his Jewish origin and democratic views, as can be concluded from a letter Hevesy wrote to Niels Bohr. Although he did not mention Polányi by name, he said that his two excellent assistants were ousted for the above mentioned reasons(20). Hevesy lost not only his professorship but also his right to lecture at the university where he had been *Privatdozent* since 1913. He left Hungary for Copenhagen where Bohr gave him a position in his newly established institute, which soon became the famous Copenhagen school of quantum physics. Thus a potentially superb scientific center in Budapest was dissolved because of narrow-minded right wing politics(21).

Pfeiffer, of course, was aware of Polányi's abilities and employed him as a consultant while he was living abroad. It became a long lasting relationship, quite advantageous also for Polányi who earned only a meager salary in Germany. This relationship persisted after Pfeiffer's retirement, during Polányi's Manchester period.

But this is another story; it does not belong to Polányi's early schools in Hungary. It belongs to his period of world success which was a result of his Hungarian schooling. By that time Polányi had become a leading personality in his field and had trained many significant chemists. Two Nobel laureates belong to the wide circle of his students: Eugene Wigner and Melvin Calvin. His Hungarian schooling also contributed to his success. Besides gaining a colorful, rich culture from his family, from high school, and from the lively intellectual life of Budapest [see Paul Ignotus, "The Hungary of Michael Polanyi"](22), he also gained a good

education from his professors. The revolutions, the failures of the extreme right and the extreme left, molded the philosophical convictions and moral commitments that were characteristic of Michael Polányi's thinking throughout his life.

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MAX LE BLANC'S STUDIES ON ELECTROLYTIC POLARIZATION

John T. Stock, University of Connecticut

In 1800, William Nicholson (1753-1815) and Anthony Carlisle (1768-1840) showed that water can be decomposed into its elements by the passage of an electric current (1). This discovery naturally encouraged similar experiments. For example, CuSO_4 solution was found to deposit copper on a platinum cathode; iodine was liberated at the anode when KI solution was electrolyzed. A most striking example was the liberation of elemental potassium or sodium by the electrolysis of the slightly moist hydroxides (2).

The first "battery" was the Volta "pile", described in 1800 (3). This and its immediate successors were based on the cell system copper (or silver)/dilute electrolyte/zinc. Dilute H_2SO_4 was the usual electrolyte. Such batteries became *polarized* when called upon to supply more than a little current. The emf dropped and gas (hydrogen) accumulated on, or rose from, the copper electrodes.

Although these facts of electrolysis are simple, their interpretation raised many questions. On the assumption that the decomposition of water is a *primary* electrolytic process, is the deposition of copper also primary, or does hydrogen, as the primary product, react with CuSO_4 to give copper as a *secondary* product? Although Michael Faraday (1791-1867) had introduced terms such as *electrolyte*, *anion*, and *cation* in 1834 (4), the "ionic theory" of Svante August Arrhenius (1859-1927), postulating that electrolytes are ionized, often extensively, in solution, was not published until 1887 (5). Incidentally, Faraday was convinced that the electrolytic deposition of metals from aqueous solution was a secondary process. He therefore turned to the much

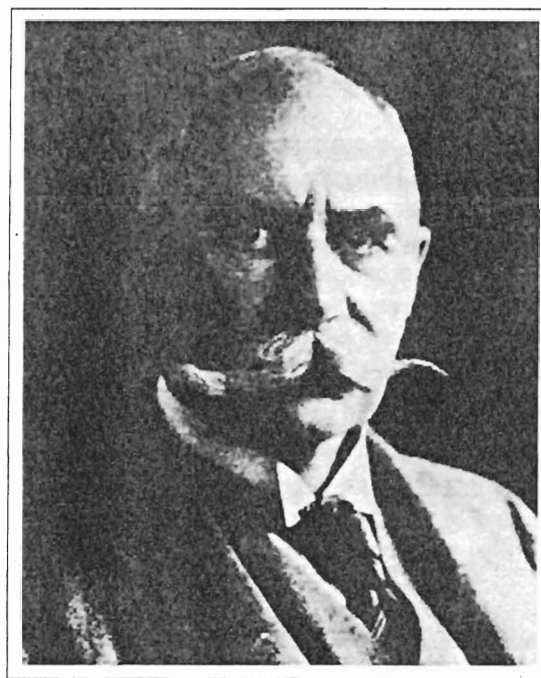


Figure 1. Max Le Blanc (1865-1943)

more difficult area of quantitative fused-salt electrolysis as a basis for the enunciation of the second law of electrolysis.

Commonly, a certain minimum applied emf is needed to produce visible electrolysis. Under comparable conditions, do electrolytes of the same type (*e.g.*, strong acids) require similar minima for electrolysis? In an electrolysis, reactions occur both at the anode and at the cathode. What are the individual contributions of potential that make up this minimum applied emf? Is

there more to the phenomenon of polarization than the mere formation of films of gas on the electrodes? The path to the answers to such questions was by no means simple and direct. It was Max Julius Louis Le Blanc (1865-1943) who surveyed the entire area and placed it on a firm experimental and theoretical foundation.

Le Blanc (Fig. 1) was born on May 26, 1865, in Barten, East Prussia. He studied in Tübingen, Munich, and then Berlin, where he became assistant to August Wilhelm Hofmann (1818-1892). He obtained his doctorate in organic chemistry under Hofmann's direction in 1888 (6). Le Blanc was not impressed by this branch of chemistry. In fact, he even thought of leaving chemistry for geology (7). However, he encountered, and was captivated by, the physical chemical writings of Wilhelm Ostwald (1853-1932). Le Blanc moved to Leipzig in

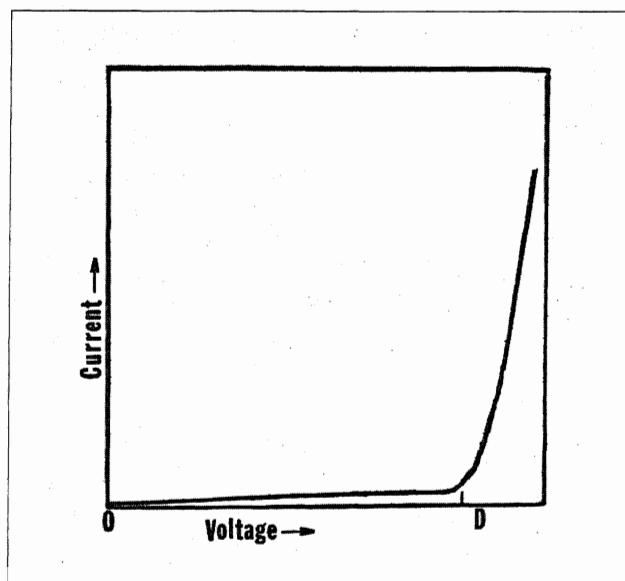


Figure 2. Current-voltage curve showing "decomposition point"

1890 and became assistant to Ostwald. Here Le Blanc began to develop his life work in physical chemistry, especially electrochemistry.

It is interesting to contrast Le Blanc's career with that of Robert Behrend (1856-1926), a colleague at Leipzig (8). After one paper and his dissertation, Le Blanc left organic chemistry. Behrend, after publishing one paper (outstanding, because it described the first potentiometric titrations) on electrochemistry (9), then spent the rest of his career as an organic chemist.

Polarization concerns phenomena occurring at the boundaries between the electrode surfaces and the electrolyte when a current passes through them. Although

Ostwald knew that the term "polarization" had been used since the mid 1830's, he could not trace its origin (10). Nowadays, an electrode is said to be polarized when it adopts a potential impressed upon it with little or no change in the current passing through it. Our understanding of polarization can be traced to the pioneering work of Le Blanc.

Suppose that an increasing emf is applied to a pair of small platinum electrodes immersed in dilute H_2SO_4 and the current that passes through the solution is measured. The resulting current-voltage curve is shown diagrammatically in Fig. 2. In the voltage region $0D$, almost complete polarization of one or both of the electrodes occurs. In this region, only a small *residual current* is observed (11). Beyond D , the *decomposition point*, the current increases rapidly with further increase in applied emf. The "point" is really a narrow voltage region; the observer merely looked for a sudden jump in current.

Early workers attributed polarization to the formation of a poorly conducting layer, such as a film of gas, on the electrodes. By the early 1840's, it was realized that a more general effect was "galvanic polarization", *i.e.*, the generation of an emf that opposed the emf applied to the system. Various investigators examined the effects of applied emf and of the nature of the electrodes and electrolyte. Because of differing methodologies and interpretations, individual reports on similar systems often differed widely (12).

In 1851, William Thomson (1824-1907), later Lord Kelvin, proposed his "mechanical theory of electrolysis" (13). This theory implied that, if the heats of reaction of the substances involved in an electrochemical system were known, then the "intensity" (emf) of the system could be calculated. In fact, Thomson made use of the data of James Prescott Joule (1818-1889) to calculate the "intensity" of the Daniell cell. The conclusions of some later workers tended to support Thomson's theory. However, the investigations of (Karl) Ferdinand Braun (1850-1918) cast doubt on this theory and then refuted it (14). The agreement between the measured "intensity" of the Daniell cell and the value calculated from the heats of reaction was a coincidence, because the emf of this cell has only a very small temperature coefficient (15).

Le Blanc's first paper on polarization began with a discussion of the work of Braun and others, showing that the values of polarization maxima cannot be calculated from the heats of reaction of the chemical processes involved (16). Le Blanc then referred to a paper by Marcellin Berthelot (1827-1907), who retained the

idea of the total convertibility of chemical energy into electrical energy (17). As polarizing source, Berthelot used a battery of cells of differing voltages to find a combination that reached the "decomposition point" (i.e., the polarization maximum), taken as the first appearance of gas bubbles on the electrodes. From a study of the electrolysis of K_2SO_4 solution, Berthelot concluded that water was decomposed and the salt was separated into potash (KOH) and H_2SO_4 . Le Blanc declared that these conclusions were inadmissible. Having the great advantage of working in the Leipzig laboratories, he was exposed to the Arrhenius ionic theory and to the concepts of Hermann Walther Nernst (1864-1941) (18, 19), which are the basis of the familiar "Nernst equation".

The appearance of gas bubbles as an indication of the polarization maximum is open to an obvious objection. Supersaturation may be needed before actual bubble formation begins. The effect is analogous to superheat-

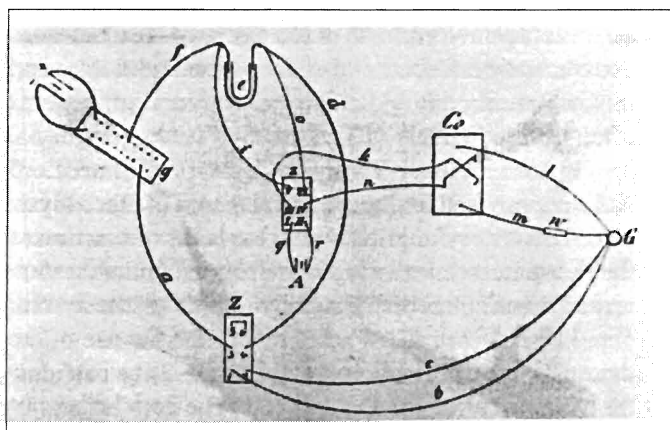


Figure 3. Le Blanc's decomposition value arrangement

ing, which may give rise to "bumping" when a liquid is boiled. Le Blanc therefore decided to locate the "decomposition value" as that at which a small increase in applied emf gave a sharp rise in current.

Figure 3, reproduced from Le Blanc's paper, shows his experimental arrangement. The sketch, not easy to follow, has been redrawn diagrammatically and relettered, as shown in Fig. 4. The following description refers to this latter figure.

The polarizing emf E was selected by potential divider P , supplied by battery B_1 . Le Blanc used as poten-

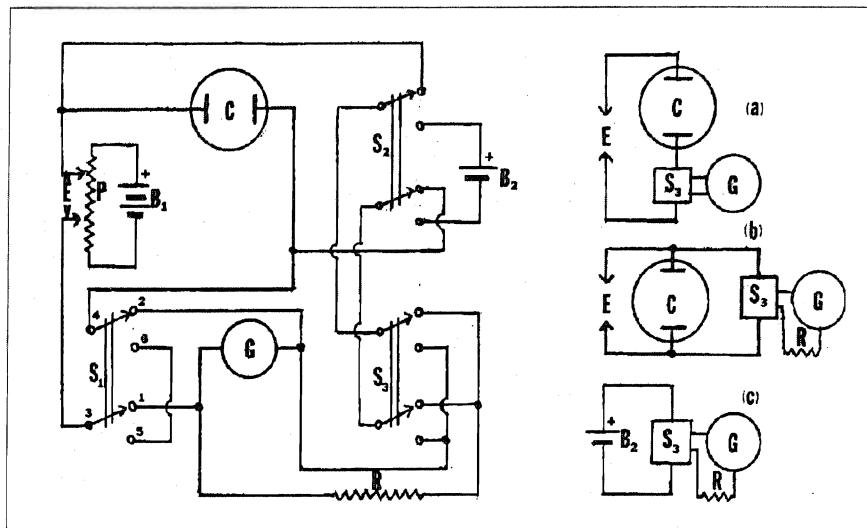


Figure 4. Diagrammatic representation of DV arrangement

tial divider a 1000-W resistance box, into which take-off plugs were suitably inserted. He was thus able to vary E in steps of 0.02 to 0.03 V. With switches S_1 , S_2 , and S_3 in the positions shown, the effective circuit is that of (a). The polarizing emf was then stepped up until the deflection of galvanometer G jumped at the decomposition value (DV). Switch S_3 , which reversed the current direction through G , was not operated at this stage.

Switch S_1 was then shifted, yielding the effective circuit (b), so that G now measured emf E . The 70,000-W resistor R limited the current through G . The deflection of G was noted, and effectively doubled by shifting S_3 . Finally, S_2 was shifted to yield the effective circuit (c) and the deflection of G produced by the standard Clark cell B_2 was observed. Because the deflections were small, their ratio could be taken as the ratio $E:B_2$.

Le Blanc's electrolysis cell was a 7-cc capacity U-tube, mounted in a waterbath held at 20° C. Each 6-mm long, 0.7-mm diameter platinum wire electrode was sealed into the end of a glass tube. Unless otherwise specified, 1*N* solutions were used. Le Blanc found that, with some electrolytes, the DV was not easy to locate; sometimes he made 8 to 10 runs. His first set of experiments showed that, for a given anion, the DVs of sodium and potassium salts were equal.

Table 1 lists the DVs of some of the acids and bases examined by Le Blanc. Except for the halide acids, the values clustered around 1.7 V. This suggested a common electrolytic process, the decomposition of water. In acid solutions, hydrogen obviously came from the discharge of the sole cation. Analogously, discharge and breakdown of OH^- , the sole anion in the basic solutions, was the source of oxygen. Hydrogen from these solu-

Table 1
Decomposition Values (DV) of Acids and Bases

Acids	DV, V	Bases	DV, V
H ₂ SO ₄	1.67	NaOH	1.69
HNO ₃	1.69	KOH	1.67
H ₃ PO ₄	1.70	NH ₃	1.74
HClO ₄	1.65	*MeNH ₂	1.75
Tartaric	1.62	**Et ₂ NH	1.68
HCl	1.31	***Me ₄ NHOH	1.74
HBr	0.94		
HI	0.52		

tions *might* have arisen from cation discharge, followed by immediate reaction with water. Similarly, oxygen from acid solutions *might* have resulted from anion discharge, followed by immediate reaction with water. The obvious liberation of halogen from the halide acids, together with their lower DVs, indicated that processes other than the decomposition of water were involved. An alternative explanation for the similarity of results for both acid and alkaline solutions (excepting the halides) involved the assumption that the primary electrolytic process was the decomposition of water. Although the OH⁻ concentration in the acid is only about 10⁻¹⁴, the discharge of this ion must occur at a potential lower than that needed to discharge the acid anion. Simi-

Table 2
Decomposition Values of Inorganic Salts and Sodium Salts of Organic Acids (1.0N)

Inorganic Salts	DV, V	Sodium Salts	DV, V
Na ₂ SO ₄	2.21	Acetate	2.10
K ₂ SO ₄	2.20	Butyrate	2.05
NaNO ₃	2.15	Malonate	2.05
KNO ₃	2.17	Tartrate	1.98
LiNO ₃	2.11	Succinate	2.06
Ca(NO ₃) ₂	2.11	Benzoate	2.00
Sr(NO ₃) ₂	2.28	Monochloracetate	2.17
*Ba(NO ₃) ₂	2.25	Dichloracetate	2.23
NH ₄ NO ₃	2.08	**Oxalate	1.13

*0.5N

**Potassium Salt

larly, in alkaline solutions, hydrogen ion must discharge more readily than the base cation. Le Blanc found that the DVs of H₂SO₄, NaOH, etc., were essentially constant over a 60-fold concentration change. However, the DVs of HCl and HBr rose as the concentration was decreased.

The electrolysis of K₂SO₄ solution, like that of the parent acid and base, yields hydrogen and oxygen. If the fundamental process is the decomposition of water, the salt, acid, and base might be expected to have the same DVs; yet Le Blanc found that DVs for salts were significantly greater. Some typical values that he found are listed in Table 2. He recognized that the radicals of oxalic and some other organic acids might undergo anodic oxidation and thus give anomalous results. Le Blanc found that the DVs for the salts of sodium and potassium were not sharp. He recognized that, in these electrolyses, formation of alkali at the cathode and of acid at the anode introduced new unknowns. These salt solutions have negligible buffer capacity, so that even slight electrolysis could produce a hydrogen-ion concentration cell. The back emf of this would raise the DV above that of the constituent acid or base. To demonstrate his recognition of the localized formation of acid and base, Le Blanc measured the DVs of the system 1N NaOH/1N acid (the slash represents a paper or clay diaphragm). For H₂SO₄, HClO₄, H₃PO₄, and HNO₃, the values ranged from 2.41 to 2.46 V.

Having examined solutions of various salts that gave metal deposits on the cathode, Le Blanc concluded that metal deposition is a primary process. He noted that salts of lead, cobalt, and nickel gave dull-red "superoxide" deposits on the anode. In experiments with electrodes of zinc, cadmium, or silver in solutions of the corresponding salts, he observed that the slightest applied emf caused dissolution from one electrode and deposition of metal on the other.

When the electrolysis of a potassium salt is carried out at a mercury cathode, hydrogen does not appear immediately. Le Blanc attributed this well-known fact to amalgam formation, i.e., dissolution of potassium in the mercury, so that K⁺ is discharged more readily than the hydrogen ion. The interpretation of the fact gave rise to considerable controversy. [It was not until 1899 that it was definitely shown that discharge of hydrogen ion at a mercury cathode required a potential much more negative than at a platinum cathode (20)]. A mercury cathode thus exhibits a high *hydrogen overpotential*. Polarography, introduced much later by Jaroslav Heyrovsky (1890-1967), makes use of the high hydrogen overpotential of a dropping mercury cathode (21).

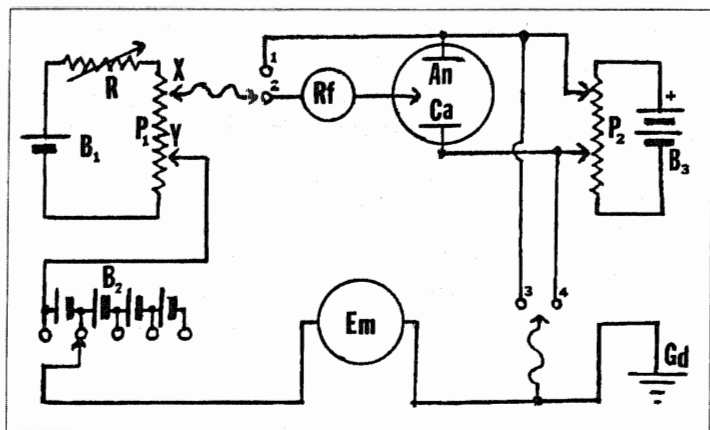


Figure 5. Diagram of arrangement for the measurement of individual electrode potentials.

Following the appearance of Le Blanc's paper (16), Arrhenius critically examined the electrolysis of solutions of alkali metal salts between a large platinum anode and a small mercury cathode (22). He measured the time between closure of the circuit and the first appearance of hydrogen bubbles. He noted that if the circuit was opened *before* this time had elapsed, pronounced hydrogen evolution occurred. He attributed this to the attack on water by the metal amalgam that had formed.

Arrhenius concluded that hydrogen was produced by the same mechanism when the circuit remained closed. This implied that the deposition of the alkali metal is a *primary* process, giving hydrogen as a secondary step. Arrhenius felt that the same mechanism held for a platinum cathode; here hydrogen evolution began rapidly because deposited alkali metal could not penetrate the solid electrode. Analogously, oxygen liberation was attributed to attack on water by the primarily-discharged acid anion.

Responding to a claim to have demonstrated the constancy of the minimum emf required to bring about the electrolysis of alkali salt solutions (23), Le Blanc summarized his results, pointing out his priority (24). This elicited comments from Berthelot (25), who accused Le Blanc of forgetting that his work agreed with that described by Berthelot in 1882 (17). Le Blanc replied vigorously (26), pointing out that his 1891 paper (16) acknowledged Berthelot's memoir. Subsequently, Berthelot had stated that, for the electrolysis of an alkali salt, the minimum emf was effectively governed by the sum of the heat absorbed in the separation of acid and base, and the heat of decomposition of water into hydrogen and oxygen. Berthelot described this as an *experimental law, independent of all theory* (25). Le Blanc proceeded to demonstrate that this "law" did not exist

(26)! Nevertheless, Berthelot persisted, stating that his own experimental results were "independent of theory, fundamental or illusory, to which a clever physicist, such as Le Blanc, perhaps would attribute an immoderate importance" (27).

Le Blanc's second paper on polarization appeared in 1893 (28). Now convinced that the electrolytic decomposition of water was a primary process, he stated his intention to deal with this and with the opposing view of Arrhenius. This was covered in a separate paper (29). Fully aware that the DVs reported in his first paper (16) were the joint contributions of the anodic and the cathodic potentials, Le Blanc planned the separate determination of these potentials.

Le Blanc's experimental arrangement is diagrammed in Figure 5. Adjustable resistor R enabled Leclanché cell B_1 to produce 1.00 V across the measuring potential divider P_1 . When needed, the Helmholtz cells (30) in battery B_2 provided additional 1-V steps. The polarity of the B_1 — B_2 combination was set as required. The two Leclanché cells in battery B_3 and potential divider P_2 provided the adjustable polarizing emf.

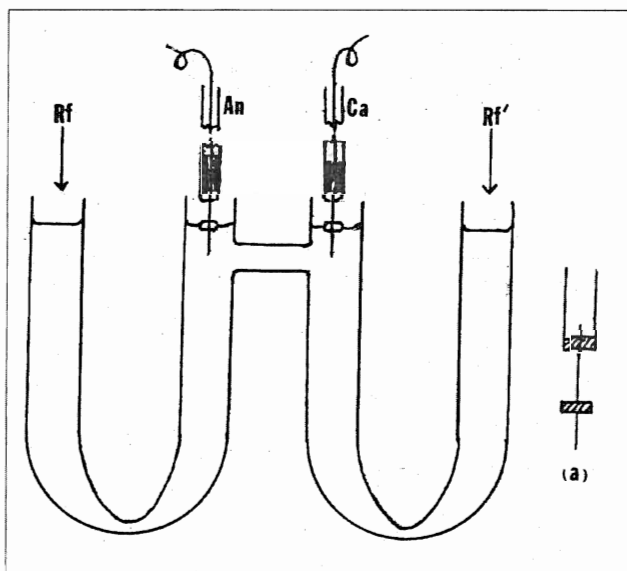


Figure 6. Le Blanc's electrolysis cell

Capillary electrometer Em (30) was used for balance detection. Arrangements were such that contact X of P_1 could be connected to the anode, An, of the cell, to its cathode, Ca, or to the normal calomel electrode, Rf. Also, either An or Ca could be grounded.

The 9-cm long limbs of the electrolysis cell were narrowed at the bottom, as shown in Fig. 6. The aim was to prevent KCl in the reference electrode from reach-

ing the platinum electrodes. One of these is shown at (a); the glass bead on the wire is a guide for depth of immersion. The reference electrode was inserted at Rf for anode potential measurement, or at Rf' for cathode

Table 3
Cathode Potentials at the Decomposition Point*

Cation	1N Salt	Cathode potl., V	Electrode potl., V**
Cadmium	CdSO ₄	0.16)	0.19
"	CdCl ₂	0.18	
Zinc	ZnSO ₄	0.515	0.51
Cobalt	CoSO ₄	0.17	-
Copper	CuSO ₄	-0.56	-0.60
Silver	AgNO ₃	-1.055	-1.01

*See text

**Metal in 1M metal salt solution; Ostwald (30a)

potential measurement. To measure a DV, contact X (Fig. 5) was connected to point 1, while point 4 was grounded. The DV set up by adjustment of P₂ was measured as the sum E at balance, of the voltage across XY and any supplied by B₂. X was then shifted to point 2, when the new value of E required to restore balance gave the cathode potential. To measure the anode potential, grounding was shifted from point 4 to point 3.

Le Blanc concentrated on the determination of cathode potentials, regarding these as the more important. Some of his findings are summarized in Table 3. Because of accompanying liberation of hydrogen, Le Blanc's results for zinc were at first unsatisfactory. By preliminary electrolysis at an applied emf of about 4.5 V, however, zinc was deposited on the cathode, satisfactory results then being obtained.

Le Blanc conducted experiments with other than platinum cathodes, e.g., CdCl₂ solution and a copper cathode, or AgNO₃ solution and a gold cathode. This led to the conclusion, "*The polarization value of the cathode at the decomposition point is equal to the potential that the metal concerned shows with respect to the liquid; it is independent of the electrode material*".

The strange appearance of the data in the tables is partly due to the use of Ostwald's sign convention, which is opposite to that of present-day reduction potential. For example, Le Blanc's value for zinc is +0.515 V; the modern value is -0.763 V. The numerical discrepancy

arises largely from Le Blanc's acceptance of -0.560 V as the potential of his reference electrode (31b). The modern value of this electrode would be +0.280 V.

Le Blanc measured the potentials of both of the polarized platinum electrodes used in his study of the electrolysis of 1N H₂SO₄. He saturated the system with hydrogen and oxygen by a preliminary electrolysis to set up a "Gaskette" (gas chain, i.e., a hydrogen-oxygen cell). He reasoned that the combined electrode potentials of the "Gaskette" should be equal to the applied emf at the balance point, so that the current through the system should be zero. He increased the applied emf in steps, measuring the electrode potentials after each increment. He found that the anode potential increased with increasing applied emf, but that the cathode potential remained essentially constant. In fact, he stated that, with a given pressure of hydrogen, the cathode behaved in acid solution like a metal electrode immersed in a solution containing the metal ions. He is thus regarded as the originator of the *hydrogen electrode*, later to become important in the establishment of standard potentials and in the measurement of pH.

Le Blanc repeated experiments with solutions of CdSO₄ and of ZnSO₄, now measuring the potentials of both electrodes above and below the "gas chain" value. He found that essentially constant cathode potentials could be obtained after the metal deposit had coated the cathode. Without such coating, discharge of hydrogen must occur, because both metals are electronegative to hydrogen. However, the lack of buffer capacity causes rapid depletion of hydrogen ion in the immediate vicinity of the cathode, with development of alkaline conditions in this vicinity. Deposition of zinc, favored by higher current density, can then accompany the liberation of hydrogen, as both ions migrate or diffuse from the bulk of the solution. Local alkaline conditions could convert Zn²⁺ into the zincate anion; Le Blanc actually considered that "insoluble zinc hydroxide" might influence the cathode process, but regarded this as improbable.

Le Blanc remained in Leipzig until 1896 and then joined the firm of Höchster Farbwerke as director of electrochemistry. In 1901, already known for his researches, as well as for his text on electrochemistry (32), he was appointed Professor of Physical Chemistry in the Technische Hochschule, Karlsruhe. Le Blanc's strong liking for electrochemistry did not prevent the spread of his activities to other branches of chemistry. His numerous publications cover topics as diverse as problems concerning rubber, the preparation of chromium and its

compounds, and the X-ray study of mixed crystals. An excellent experimenter, Le Blanc insisted that his students should become well versed in practical work. He retired in 1933 and died in Leipzig on July 31, 1943.

ACKNOWLEDGMENT

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MYER E. JAFFA: PIONEERING CHEMIST IN THE FOOD AND NUTRITION SCIENCES

Patricia B. Swan, Iowa State University, and Kenneth J. Carpenter, University of California, Berkeley

Introduction

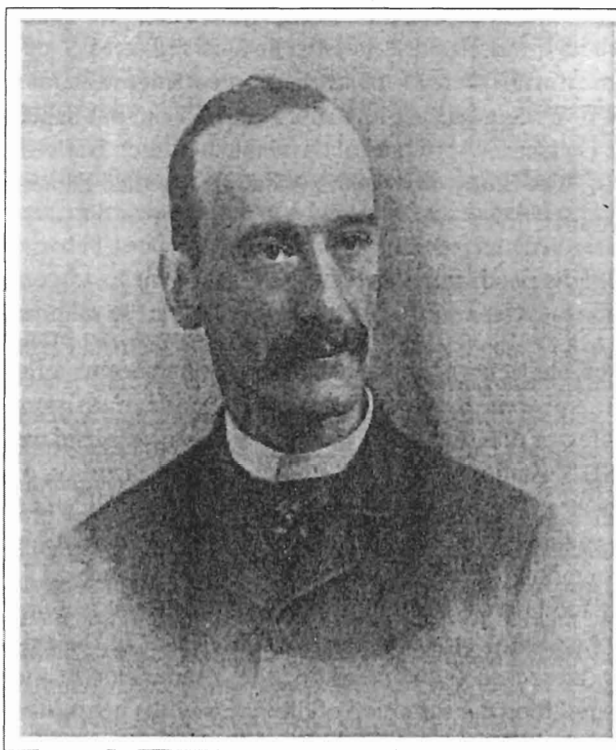
During the 19th century, many Americans whose professional training had been in chemistry pioneered the development of new disciplines, including those related to agriculture and health such as nutrition and food science. Notable examples were Wilbur O. Atwater, Professor of Chemistry at Wesleyan University and the first director of the Office of Experiment Stations in the U.S. Department of Agriculture, and Harvey Wiley, Professor at Purdue University and later head of chemistry at the U.S. Department of Agriculture (USDA). Under the organizational guidance of Atwater, chemists employed in state agricultural experiment stations undertook analyses of foods and studies of food intake and digestion in the first nationally coordinated program of human nutritional studies. Under the leadership and encouragement of Wiley and the guidance of the Association of Official Agricultural Chemists, the state experiment station chemists also undertook analyses of adulterants in foods. Collectively, the work of these chemists led to the first systematic tables of food composition data as well as to the guidelines that were used in the enforcement of the first federal pure food and drug legislation passed in 1906.

The career of a California chemist, Myer Edward Jaffa (1857-1931), illustrates some ways in which chemists contributed to the development of food and nutrition sciences. Jaffa, a long-time member of the University of California faculty and the agricultural experiment station staff, was the first in the United States to hold the title "Professor of Nutrition(1)." He was also the

first director of the State of California's Food and Drug Laboratory.

Early History

In 1866, at the age of 9, Jaffa was brought by his parents to San Francisco from Sydney, Australia. The family, including a brother and two sisters, arrived at a time



Myer E. Jaffa, courtesy Bancroft Library

when San Francisco was a bustling seaport that had grown rapidly during the gold rush days of the previous two decades. The University of California, however, was not formed until two years after the Jaffa family arrived. By the time Jaffa was 16, he was able to enter the university as a member of the first class to take instruction at the present Berkeley location. He majored in the Mining Department, which had a curriculum rich in chemistry, and in 1877 was granted the Ph.B. degree, writing his senior paper on "The Analysis of Auriferous Pyrites in the Grass Valley Region."

In 1879 Jaffa obtained employment on the Berkeley campus as an analytical chemist in the agricultural experiment station. For two years he worked on the study of soils in California, as a part of the 1880 Census and Transcontinental Survey, and then was given responsibilities in the Viticulture Laboratory, a legislatively funded and important program in the early years of the California station. Under the direction of the well-known soil scientist, E. W. Hilgard (1833-1916), the station took on increased responsibilities for providing technical information to the state's farmers, and Jaffa was put in charge of the agricultural chemistry laboratory. There he analyzed crops as well as the soils on which they were grown, publishing a well-received bulletin on cattle foods (2). His first analysis of human foods was to settle a dispute among producers as to whether brown-shelled eggs were more nutritious than white ones. He could find no difference (3). In 1896 he received an M.S. degree from Berkeley for a thesis entitled "Investigations of Food Materials, Animal and Human," and published the California Agricultural Experiment Station Bulletin 110, "The Study of Human Foods and Practical Dietetics" (4).

Nutrition Investigations

In 1895 Jaffa married Adele R. Solomons, a San Francisco physician. In the following year he became a father and at the university was given the title of assistant professor of agriculture. In that year, also, he joined the USDA's national nutrition study under the direction of Atwater. Not surprisingly, one of his first studies was a 10-month record and analysis of the food intake of his own infant son begun in July 1896. He also made a 17-day food intake study of the university football team as they undertook training for the 1896 season. In December, he recorded and measured the composition of the overall food consumption of the seven adults in his own household for three weeks. The following year he conducted a second study with his son as a subject and a

digestion study and two food intake studies with his second-born, a daughter. The nutrition investigations conducted from 1896-98 were published along with the extensive food composition analyses as a single bulletin from the USDA (5). Jaffa's son, at age 4-7 months, averaged an intake of 643 Calories, and by the end of the study his intake was 785 Calories and 23 g protein per day. These values are below the current norms, but during the 10-month study, his food intake was said to have been adversely affected by the family's relocation from San Francisco to Berkeley, which entailed a change in the source of milk, and by his teething.

From his records, Jaffa calculated a 4,185 per man (or 3,700 per head) Calorie intake for the adult individuals in his household. This was larger than expected and was equivalent to the standard of Atwater and others for "men at hard muscular work." Even though the chemist's household members were classed as sedentary workers, the amount of physical activity they had during a normal day, including walking to and from work and manual household chores, was considerably more than is typical of a sedentary worker today. However, this still does not seem to explain fully the high values recorded. His own explanation was that the family "having recently moved to Berkeley they were all stimulated by the change, and craved and ate larger quantities of meat than they had done before, or have done since. The large quantity of fat in the dietary (195 g/head/day) was supplied in part by the meat, and in part by the unusual quantity of pancakes and fritters used, these being fried in butter or fat (6)." At that time there was, of course, no knowledge of a relation between heart disease, cholesterol, and dietary fat.

The intake of the California football team as estimated by the disappearance of food from their training table was over 7700 Calories per head per day. Jaffa suggested that this very large value was due to their being in the early and active part of their training period and still "building up" their muscles, and indulging in the novelty of unlimited free eating. It may also have been that more people than just the football team were taking food from the training table. In any case, all the intakes that Jaffa estimated for adult subjects in his early studies were excessive by today's standards.

The Bay Area was unique in having a considerable Chinese community. Its members were regarded as being capable of hard work under adverse conditions, even though they were, it was thought, living on little but rice. This was an apparent paradox since at that time it was the orthodox view that people who did physical work needed a great deal of protein (and that generally meant

large amounts of meat), if they were to maintain their strength. Jaffa was the first to make a quantitative investigation of their diets (7). His most extensive study was carried out for 18 days with a group of 12 Chinese men working on a truck farm (or "vegetable garden") in Berkeley. They performed severe outdoor work from 6 AM to 7 PM, with a one-hour break for dinner. They lived in a bunk house on the farm and their meals were supplied by the manager. People familiar with life in China told Jaffa that these men's diet was very close to that of their home country. It was true that rice formed a very large part of the diet with the men using 1 lb 13 ounces of rice (weighed before cooking) per head per day, and this alone provided nearly 3,000 Calories. However, they also obtained another 1,100 Calories from animal products (mostly pork and fish) and ate a variety of vegetables, especially cabbage and radishes. Their total protein intake was 145 g per day. They therefore just met the high protein standard of the day for men at active work, which is almost double the present standard. Their diet included no milk, butter, eggs or sugar. It was a low-fat diet, with 21% of the energy coming from fat, as contrasted to the current national average intake of about 40%.

Another unusual group in California, this time of Caucasians, were fruitarians - that is to say vegetarians who also did not believe in eating any kind of cooked food and restricted themselves to fruits, nuts, and a small amount of cereals. Such diets were of double interest to Jaffa; first because they went against the orthodox belief in the special value of meat; second because of the special importance of fruits and nuts in California farm production, any indications of their nutritional value might help to upgrade these products in consumers' minds from being just afterthoughts to a real meal. The vitamins and their contribution from fruit were, of course, still to be discovered. Among fruitarians Jaffa studied the diets of two men in their 60's, two women in their 30's, and three children aged 6, 9, and 13 (8). They all had surprisingly low calculated protein and energy intakes about one half the standards of the day. A large proportion of their Calories came from the fat in the almonds and other nuts in their diet. Jaffa was clearly most surprised by the results but wrote of one group, "We hesitate to pronounce judgment. The adults have lived like this for 7 years, and the children, though below average in height and weight, have the appearance of health and strength, and run and jump and play all day... and were said to be unusually free from colds and other complaints common to childhood (9)."

Jaffa must have wondered whether one needed time to adapt to a fruitarian diet, because he asked an athletic

student volunteer to try its effect. For a week the student ate his usual diet, in which 40% of the Calories came from animal products. For a second week he made a partial change, and then for a final 8 days went all the way, eating mostly nuts (particularly walnuts), oranges, bananas, and dried fruits. In this period he consumed nearly 3,000 Calories per day, and felt fully able to continue all his usual term-time activities (10).

After Atwater's disabling stroke in 1904, federal support of dietary studies lapsed. In the 1904 report of the California Agricultural Experiment Station we read that (11):

Professor Jaffa's nutrition investigations have received high commendations both at home and abroad.... His continued participation in this work will greatly redound to the credit of the University; but it is much regretted that the means and appliances for this purpose are very inadequate.... lack of room has compelled Professor Jaffa to locate his operations. . . apart from the main laboratory, in the old boiler-house, . . . and in a corner of the attic provisionally partitioned off and lighted by a small skylight. [where] he is at least enabled to work undisturbed.

In July 1906, Jaffa was named Assistant Professor of Nutrition, and in 1907 Professor of Nutrition.

Pure Food and Drug Laboratory

In 1907 Jaffa was made founding director of the State Food and Drug Laboratory, which was housed on campus, and his \$4,000 salary was divided equally between the State Board of Health and the University. State law charged the laboratory with preventing the manufacture, sale, or transportation of adulterated, mislabeled or misbranded foods, liquors, and drugs. In the first seven months of the laboratory's operation, it received 1400 samples of foods and food materials for analyses; laboratory chemists actually analyzed 989 of these. For most foods, the major problems were in misbranding (misleading as to product origin) or mislabeling (failure to note additives on the label). Some products labeled as olive oil contained a portion of cotton seed oil. For meat products, preservatives such as boric acid were frequently found and, under the law, were considered adulterants. In the case of confectioneries and spices, analyses revealed a variety of adulterants, such as charcoal added to black pepper or talc to candy. Only 57 % of all samples met the requirements of the law (12).

In the second and third years the analytical activity remained high. While there was some decrease in the amount of adulteration, mislabeling increased and the percentage of samples meeting the state requirements

did not change. By the year ending in 1912, however, more than two-thirds of the samples fully complied with the law, and less than 5% were adulterated, a situation that Jaffa described as "certainly very encouraging and indicates that beneficial results are being obtained (13)."

During this period of time, Jaffa concluded each of his reports with a plea for more funds, more personnel, and better quarters for the work. He also emphasized the need for additional work on nutrition. In his report for 1910-12 he commented: "It does not appear that a laboratory operated under the auspices of the State Board of Health, and located in the Department of Nutrition of the University, is doing its best work if original investigations in nutrition are not being conducted (14)."

In July 1915 one of Jaffa's colleagues, E. J. Lea, took over the directorship of the laboratory and Jaffa became a "consulting nutrition expert" to the laboratory, now renamed the Bureau of Foods and Drugs. In this role he provided education and information and investigated food problems in state-owned hospitals and asylums. He made two or more trips to each institution to study dietary and food conditions and make recommendations for change. He was encouraged by the cooperative attitude of those who were responsible for feeding individuals in these institutions and urged that this advisory role be maintained to provide an incentive to the institutions to continue to make progress toward routinely providing high quality diets.

Jaffa resumed the directorship of the Bureau of Foods and Drugs in 1924 and in the first biennial report during this period the secretary of the State Board of Health noted that the bureau had turned its attention from food as sold in the marketplace to "the improvement of food supplies at their sources." The bureau also had additional responsibilities for monitoring feeds under the California Feeding Stuffs Act (15). In the report for 1928, Jaffa placed emphasis on the condition of the hamburger samples tested. Ninety-four percent "were found to be in violation of the law, in that there was added to the meats a forbidden preservative—some compound of sulphurous acid" (16). In the two years ending in July 1930, the bureau's inspectors "destroyed or condemned as undesirable for human consumption" over 1.6 million pounds of food, most of which was walnut meats. They also destroyed "181,500 assorted labels and 8,000 booklets which contained misleading or false statements concerning the respective food product." In that period they analyzed over 5,000 samples and found 17% in violation of the law (17).

In June, 1931, upon Jaffa's death, the chief of the Bacteriological Laboratory took over the Bureau of Food

and Drugs and, later, these two laboratories were merged. The value of chemistry in improving the quality of the food supply was noted by the new director in his 1932 report (18):

These methods are founded on the development within the last thirty years of laboratory technique which is competent to disclose the fitness for human consumption of many finished products, also their quality and pertinent information concerning the circumstances of their production. Knowledge of the existence of such laboratory facilities in the hands of the enforcement organization furnishes an incentive for production and distribution within the requirements of the law which is quite as effective in most instances as a complete system of personal inspection

Jaffa as Educator

As an assistant professor, Jaffa taught courses in human and animal nutrition, adulteration of human and animal foods, and the detection of adulterants, and was responsible for supervision of graduate research in agricultural chemistry. In 1908, as professor of nutrition, he also lectured specifically on dairy chemistry, poultry husbandry, and the marketing of poultry products.

The surviving outline of a lecture that Jaffa gave to an undergraduate general science class provides evidence of the way in which he was able to gain the interests of the audience, convey some basic scientific principles, and draw practical conclusions that could be used by the listeners in their everyday lives (19). He focused his lecture on the respiration calorimeter, the leading-edge technology in nutrition science of the time. The students must have been intrigued by the idea of a human subject living in an enclosed chamber and carrying out various activities so that the caloric output of that subject could be measured with amazing accuracy. An important question of the time was whether the Law of the Conservation of Energy held for the human body, and experiments in the calorimeter showed that it did. Jaffa discussed the composition of food and the evidence that protein, fat, carbohydrate, and minerals, the known nutrients, each played a special role in the body. Finally, he described how results obtained with the respiration calorimeter would allow nutrition scientists to describe more precisely how much of each of the nutrients was required for various activities and physicians to prescribe for the dietary needs of their patients.

By 1910 the University of California was responding to local and national demands for domestic science

or home economics curricula for women students. At the same time the USDA was helping to promulgate national guidelines that would ensure a satisfactory science basis for these curricula. Jaffa took responsibility for communication between the university curriculum committee, of which he was a member, and the Department of Agriculture to assure that the university curriculum met the highest standards. For this curriculum he taught courses in pure food laws, food and household chemistry, human and animal nutrition, composition of human foods, and dietary standards.

In 1915, Agnes Faye Morgan (1884-1968) joined the faculty and began her outstanding career as the developer of home economics and nutritional sciences at Berkeley. Applied dietetics and infant nutrition courses were added to the curriculum. Within a year, however, the household science program was moved from agriculture to another college; but Jaffa continued to be heavily involved in instruction until 1924, when he took leave to direct once again the state's food and drug laboratory on a full-time basis. The following year he retired from the university, holding the record for the longest period of service among the faculty at that time.

Nutrition Education for the Public

In addition to university teaching, Jaffa was interested in the education of the lay public or consumers so that they would make healthful food choices. In the first human nutrition bulletin written by Jaffa for the agricultural experiment station, he provided extensive information about the composition of human foods, especially California foods, and gave advice about the application of scientific principles to diet (20). He lectured widely to a variety of lay audiences about the application of science, especially chemistry, to the practical problems of choosing an economical, nutritious and safe diet. His topics ranged from the value of basic foods such as milk, to the value of foods important to California's agriculture such as fruits, and the nature of the newly discovered vitamins.

Jaffa's views of the importance of education for consumers were stated in his report for the work of the state laboratory from 1910-1912 (21):

The Director of the laboratory has delivered a large number of lectures during the past two years before women's clubs, schools, farmers' institutes, etc. The purpose of these talks is to indicate to the consumers the fact that there are certain responsibilities which they must assume if they expect to receive the greatest benefit from the [pure food] law. The State is doing a great deal toward safeguarding the food of

the people, but it can not accomplish all, and in order that the best results be obtained it is necessary that there should be earnest activity and intelligent cooperation between those who purchase food and those engaged in the enforcement of the law.

Personal Characteristics

In carrying out his work, Jaffa encountered adversities that sometimes resulted in major set-backs. In 1897, when he was in the midst of the work for the national nutrition study, a fire destroyed most of the station's building and a large portion of their records was burned. In 1906, as he was beginning work with a bomb calorimeter to improve his measurements of the energy value of foods, the San Francisco earthquake and subsequent fire eliminated his source of compressed oxygen for the calorimeter and the studies had to be postponed. The final, and perhaps most distressful, event was the complete destruction of his home by the devastating Berkeley fire in September, 1923.

Upon Jaffa's retirement a former student wrote (22):

(Jaffa) has a remarkable way of seeing the bright side of life. During the fire in the fall of 1923, which wiped out in a few hours many blocks of Berkeley's fine homes, Professor Jaffa lost his home and all but a few of his personal effects. His home was the last of eleven hundred to burn. I came upon him in his office in the evening after the fire and found him nervously playing with a pencil. He looked more tired than usual, but otherwise appeared just the same as ever. He said "It feels mighty queer not to have any place to go home to tonight—well, anyway Mrs. Jaffa won't have to climb the hill anymore."

Jaffa and his wife were Jewish, so that he was part of a small minority in the university at that time. It is not evident that this affected his career, however, as he played leadership roles in at least two organizations. One was the faculty club at UC-Berkeley, where he was a founder and a director for many years. The other was the Association of Official Agricultural Chemists. Jaffa hosted this group for a national meeting in San Francisco and a tour of parts of California in 1899. In 1904 he served as national president of the Association, but was prevented from attending the annual meeting that year by "severe family illness (23)."

As a physician, Jaffa's wife must have been understanding and helpful with the studies of their infants' food intake. She also lectured in the university for a period on infant nutrition, worked in the university's Institute for Child Welfare and, after her husband's death,

reissued some of his recommendations for healthy, economical diets (24).

In Retrospect

Jaffa's career was characterized by several "firsts" as the first US faculty member to hold the title "Professor of Nutrition," and the first director of California's Food and Drug Laboratory. Trained at the university as a mining chemist, Jaffa successfully applied his knowledge of analytical techniques to problems of soil composition, as well as food and feeds composition and adulteration. Moreover, he applied chemistry to studies of energy and protein intake by animals and human and to food composition and safety.

August Glaive, one of Jaffa's proteges and later director of the California Food and Drug Laboratory, wrote of his mentor (25):

Dr. Jaffa was one of the pioneers in the field, a patient researcher, ...also a teacher par excellence, a great chemist, a humanitarian with an exceptional understanding of human nature as well as a keen sense of responsibility for the well-being of his community.

As early as 1911, there was a published tribute headed: "The Man Behind the Food Law." In part it said (26):

While many men play some part in the enforcement of the pure food laws, it is practically certain, wherever these laws are being operated actively and to the satisfaction of both consumer and producer, that one will find a good chemist behind the law. Food and drug analysis ranks among the most difficult and technical of the divisions of chemistry...It is a tribute to the accuracy of work done by Professor M. E. Jaffa, director of the Food and Drug Laboratory, and his competent staff, that in none of these cases [found in violation of the law] have the chemical findings been questioned in court.

Upon Jaffa's death, after a very brief illness in 1931, A. F. Morgan, his successor at the university wrote (27):

He was appreciated by state officials, food manufacturers and distributors as honest, courageous and just, qualities indispensable in the important position which he occupied. The state of California has benefited in many ways from this man's services.

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BOOK NOTES

Enough for One Lifetime: Wallace Carothers, Inventor of Nylon. M. W. Hermes, American Chemical Society and Chemical Heritage Foundation, Washington, DC, 1996. xvii + 345 pp. Cloth (typeset), \$38.95.

Wallace H. Carothers was a brilliant chemistry, whose research at DuPont on polymerization resulted in an intellectual clarification of this field. On the practical side, his work produced neoprene, a useful type of synthetic rubber, and the nylon polyamide fibers and plastics. He was thus the founder of a new chemical industry, and his career deserves a full-length biography. The book by Matthew Hermes fills this gap. Hermes is a Ph.D. chemist and professional research worker.

Carothers (1896-1937) received his bachelors degree at tiny Tarkio College in Missouri. His father Ira was connected with Capital Cities Commercial College in Des Moines, Iowa, and Wallace had a year of study there. He transferred because Ira was a devout member of the United Presbyterian Church, which ran Tarkio College; Tarkio wished to recruit more students. Wallace had become interested in chemistry from reading books on popular science, and his interest was solidified by Arthur Pardee, a Johns Hopkins Ph.D., who taught at Tarkio during Wallace's second and third year. Wallace taught Tarkio's science courses for two years after Pardee's departure. Graduating at the age of 24, Carothers took graduate work in chemistry at Illinois, where he earned his Ph.D. in 1924 with Roger Adams, working on the development of platinum oxide for catalytic reduction. He became the accepted leader of the graduate students at Illinois; Marvel called him the best organic chemist he had ever seen. Although occasionally moody, he published independent work as instructor at Illinois which showed his ability and originality.

In 1926 he became instructor at Harvard, where the senior organic chemistry, E. P. Kohler and J. B. Conant, were both old friends of Roger Adams.

He does not seem to have been very happy at Harvard; he was not a particularly good lecturer, and he was not a natural experimentalist, preferring to read and think about organic chemistry.

At DuPont, C. M. A. Stine had proposed that an outstanding chemist be hired, to work on problems of his own, with several Ph.D. collaborators. Stine felt that such a program would be valuable to DuPont, in ways which could not be specified in advance. Adams, Marvel, and Conant recommended Carothers, and he started work at DuPont in 1928. He had evidently been thinking about polymerization and high-molecular-weight compounds for some time, and his work at DuPont involved fundamental studies in polymer chemistry. After three years of experimental work and study, Carothers published in *Chemical Reviews* a comprehensive discussion of polymerization, which distinguished addition polymerization from condensation polymerization. This paper showed remarkable insight and a very broad knowledge of organic chemistry. Kohler assigned it as required reading to his class in advanced organic chemistry at Harvard, and he appeared to take satisfaction in Carothers' accomplishments.

In about seven years of work at DuPont, Carothers not only clarified the conceptual bases for polymer formation and structure but also did the research from which neoprene rubber and nylon eventually developed. In 1935, the nylon project was removed from Carothers' control, partly because of his increasing absences and disabilities.

Nylon required extensive development work before it was brought to market, and the indispensable effort of E. K. Bolton at DuPont in this respect is de-

scribed in the book. Bolton realized that if polyamides were to be commercially successful, they must be made from readily available starting material. He thus insisted on 6-6 nylon (from adipic acid and hexamethylenetetramine) and worked out practical methods for obtaining these starting materials from benzene. Carothers' polyamide was a 5-10 polymer, with a diacid from castor oil as one component; Bolton saw that this starting material could not support any appreciable commercial development.

Carothers' problems with alcoholism and depression increased during the early 1930s; and, although he got what medical care was available, there was no effective treatment for either condition at that time. Hermes gives the harrowing details of his path to suicide, which occurred on April 29, 1937, before the practical results of his nylon research became known. Adams was telling graduate students in 1937 that outstanding results would come from Carothers' work.

Hermes, a former employee at DuPont, has done a thorough piece of research, interviewing surviving con-

temporaries of Carothers and utilizing the available documentation. The book, although not always felicitous in style, provides as complete a picture of Carothers as we are likely to get. In addition to his scientific talents, Carothers had lively and broad cultural interests, particularly in classical music; and these are described in detail. He appears to have been a man worth knowing for many reasons.

We may think that Carothers was fortunate to have moved to DuPont. Even if he had attained tenure at Harvard, he would not have had the skilled assistants and facilities which he enjoyed at DuPont, and his production of significant work was undoubtedly greater there than it would have been at Harvard. Stine's project at DuPont was important for the company and also for Carothers personally.

Hermes' book gives us a good picture of a great chemist and his times. It can be recommended to students and general readers, as well as to chemists. *D. S. Tarbell, Distinguished Professor of Chemistry Emeritus, Vanderbilt University, Nashville, TN 37235.*

Arrhenius. From Ionic Theory to the Greenhouse Effect. Elisabeth Crawford, Science History Publication/USA, Canton, MA 02021, 1996, xiv + 320 pp. Cloth, \$49.95.

This is a research-oriented book dealing with the scientific career of Svante August Arrhenius, pioneer physical chemist and Nobel laureate in 1903. It is a well-documented account of his accomplishments, the ups and downs of his professional life, and his interactions with other scientists. As such, it should be of value to anyone doing research in the history of chemistry, particularly a person contemplating a biographical study of one of Arrhenius's colleagues, perhaps Wilhelm Ostwald or Jacobus Van't Hoff.

This book is not likely to appeal to a chemist who simply wants to learn more about Svante Arrhenius, the man and the scientist. There are three problems.

The book contains almost nothing about the personal life of Arrhenius. His second marriage, in 1905 to Maria Johannsen, is covered in one sentence. Of his four children, only one is even mentioned and then only in infancy. More critically, reading this book, I got no

impression as to what kind of a person Arrhenius was outside the laboratory.

Neither the author nor the publisher seems to have made any effort to make the book interesting. It is bound in black and set in small type; page after page after page consists of unbroken prose. I was never able to get through more than one chapter in a single sitting.

The author consistently uses the scientific language of a century ago in describing Arrhenius's research. Crawford, like Arrhenius, uses the terms "active molecules" and "inactive molecules." It would have helped to point out that today we refer to these simply as ions and molecules. The phrase "activity coefficient" was used by Arrhenius (and Crawford) to mean something completely different from what it connotes today. This makes it difficult, indeed nearly impossible, for the modern-day reader to follow Crawford's description of the development of Arrhenius's model of ionic dissociation.

This is the first book-length biography of Arrhenius to appear in the English language. There are, however, several well-done biographical sketches written in English. The best of these, in my opinion, is that written

by H. A. M. Selders in (surprise!) the *Dictionary of Scientific Biography*, Vol. 1, pp. 296-302. Another sketch of interest to the nonspecialist is that written by George Fleck in *Nobel Laureates in Chemistry 1901-1922*, pp. 115-22.

Finally, there are two splendid articles relating to Arrhenius and the ionic theory in the scientific literature of long ago. One of these, entitled "Electrolytic

Dissociation," was produced by Arrhenius himself when he received the J. Willard Gibbs Medal at Yale [*J. Am. Chem. Soc.*, 1912, 34, 353-364.] Then there is the "Arrhenius Memorial Lecture" delivered by a friend and colleague, Sir James Walker [*J. Chem. Soc.*, 1928, 1380-1401.] Both are anecdotal, informative, and well worth reading today. *William L. Masterton, Department of Chemistry, U. Connecticut, Storrs, CT 06269.*

Edward Frankland. Chemistry, Controversy and Conspiracy in Victorian England. Colin A. Russell, Cambridge University Press, Cambridge, 1996. xx + 520 pp. Cloth (Typeset), \$100.

The source material for this first-ever, full biography of Edward Frankland (1824-1899) is largely private: five sets of papers, those still extant numbering in the several thousands, all in the possession of descendants of Frankland. Author Russell was fortunate enough to gain access to this material and arrange for its photocopying on microfilm, which is permanently housed at the Open University [C. Russell and S. Russell, "The Archives of Sir Edward Frankland: Resources, Problems, and Methods," *Brit. J. Hist. Sci.*, 1990, 23, 175-185.] An autobiography (*Sketches from the Life of Sir Edward Frankland*) printed privately in 1901, 2nd expurgated edition 1902, served as an additional resource but in a very limited way.

This biography is a realization of Professor Russell's long-held goal of presenting a well-rounded picture of a fellow Lancastrian whom he describes as "probably the most important figure in British chemistry in the last century." It includes the material on Frankland's early life in Russell's publication: *Lancastrian Chemist: The Early Years of Sir Edward Frankland*, Open University Press, Milton Keynes, 1986. The book consists of 17 chapters, in which Frankland's life is traced from his illegitimate birth to his "last journey," with copious details in between about his education both in England and under Kolbe in Germany, his early research which contributed so significantly to the understanding of valency, his professional career as academician in Queenwood, Manchester, and finally London, his role as a public servant, consultant, and entre-

preneur, the evolution of his own family, and his retirement. Throughout the book the author paints vivid images of Frankland the man: his fragile self-confidence, enormous experimental skills, strong personal ambitions, lack of effectiveness as a lecturer, solitary personality, ambivalence toward religion. The style of writing convinces readers that Professor Russell is taking us on a personal voyage with Frankland, reliving his 75 years, much as the Ghost of Christmas Past accompanied Ebenezer Scrooge on such a journey. We are often invited to consider what Frankland was 'thinking' at critical junctures in his life and made to sense his devotion or antipathy toward family, friends, and professional colleagues.

The book is handsomely presented in sharp print on glossy paper with a generous offering of choice photographs, figures, and drawings. It is full of quotations all carefully annotated as befits a scholarly work; yet the style makes it eminently readable. This reviewer noted very few typographical errors. It was a surprise that there is no mention of Edward's chemist grandson, Edward Percy Frankland (b. 1908), the son of Percy Faraday Frankland (b. 1880); for these constitute one of the few known trios of chemists spanning three successive generations.

Author Russell has made an immeasurably significant contribution to chemical historians by facilitating access to the archival material from Edward Frankland's private papers. The Open University deserves credit for its financial support of this project over an extended period. Furthermore, he has used the material to provide insight into the scientific and social historical setting in which Frankland exerted considerable influence on the way in which chemists thought, practiced their skills, and communicated their ideas. *Paul R. Jones, University of Michigan*

A Life as Lived. Leonore Hollander, Raspberry Press, Sebastopol, CA, 1996. (Paper).

Dr. Hollander's book is a delightful autobiography, with all the joys and hardships, the terror and sympathy, the hope and realism, the light and darkness one could imagine. She is the American daughter of a Jewish father and German mother, and much of the book relates to her life in Germany during World War II. She wrote the book in bits and pieces, with some repetition at times which makes the book that much more interesting. It is enjoyed best by reading whichever chapter strikes one's fancy as a vignette which stands alone. Then one can read the whole book in stricter chronological order.

Those of us who are "golden-aged" will chuckle and reminisce as we read about Leonore's childhood; perhaps members of the Division of the History of Chemistry will best note the historical events in chemistry which are described from time to time; women will read with awe about the trials the young mother of three experienced after her divorce as she cared for her children during World War II and will marvel at the attempt she

made to keep her marriage together over those trying times and will relate to the problems she had finding a suitable position when she returned to America (in contrast to her fulfilling work in Europe); and all chemists will be fascinated, as I was, as Dr. Hollander describes her interaction with several Nobel laureates in chemistry (three of whom were her colleagues in the laboratory; her Ph.D. mentor at Illinois was Vincent duVigneaud). This wonderful woman chemist is a compassionate, caring person who has lived a full life as a scientist, mother, grandmother, and benefactor. Her Quaker persuasion has kept her strong through her troubles and happy in better times. Her travels have given her the opportunity to meet people in all walks of life, in many countries. Her advice is a summation of her "life as lived:

The way to learn about our world is to travel as much as possible, do as much as you can, and open your heart and your eyes—rather than your mouth—to the people who come your way. *Helen M. Free, Bayer Diagnostics, Elkhart, IN 46515-0070*

Eilhard Mitscherlich. Prince of Prussian Chemistry. Hans-Werner Schütt, American Chemical Society and Chemical Heritage Foundation, Washington, DC, 1997. xvi + 220 pp. Cloth (Typeset).

This is a translation into English by Professor William Russey, Juniata College, of the original German

edition, *Eilhard Mitscherlich: Baumeister am Fundament der Chemie*, Deutsches Museum, München, 1992. The original was reviewed in this journal by A. J. Rocke (*Bull. Hist. Chem.*, 1992-93, 13-14, 70).

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