

Ask the Historian

Collected Columns on
the History of Chemistry

2003-2012

William B. Jensen



Oesper Collections

Cincinnati OH

2012

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Table of Contents

Preface	vii
1. The Universal Gas Constant	1
2. The <i>KLM</i> Shell Labels	3
3. The Origin of Stoichiometry Problems	5
4. The Symbol for <i>pH</i>	7
5. Did Lavoisier Blink?	9
6. The Origin of “Vinyl”	11
7. The Origin of Alcohol “Proof”	12
8. The Origin of the Mole Concept	14
9. Why Helium Ends in “-ium”	16
10. The Origin of the Name “Nylon”	18
11. The Origin of the Bunsen Burner	19
12. The Origin of the 18-Electron Rule	21
13. The Origins of the Symbols <i>A</i> and <i>Z</i>	23
14. The Symbolism of Chemical Equations	25
15. The Origins of Positive and Negative in Electricity	27
16. The Origins of the Liebig Condenser	29
17. The Origin of Pyrex	31
18. The Origins of the Ortho-, Meta-, Para- Nomenclature	33
19. The Origin of the Term “Allotrope”	35
20. The Hirsch and Büchner Filtration Funnels	38
21. The Origin of the Term “Base”	40
22. The Use of Dots in Chemical Formulas	42

23. The Origin of the Term “Hypervalent”	44
24. Why was Avogadro’s Number Named After Avogadro?	46
25. The Origin of the <i>s</i> , <i>p</i> , <i>d</i> , <i>f</i> Orbital Labels	48
26. Malic, Maleic and Malonic Acid	50
27. The Origin of the Oxidation-State Concept	52
28. The Origin of the Soxhlet Extractor	55
29. Origin of the Polymer Concept	57
30. Why Tungsten Instead of Wolfram?	59
31. Origin of the Rubber Policeman	61
32. The Origin of the Rotavap	63
33. Melting Points and Organic Chemistry	65
34. The Origin of the Metallic Bond	67
35. The Circle Symbol for Aromaticity	70
36. The Origin of the “Delta” Symbol	72
37. Balancing Redox Equations	74
38. The Origin of Bond Lines	77
39. The Origins of the Meker and Tirrill Burners	78
40. The Origins of the Brin Process	80
41. Why is <i>R</i> - Used for Hydrocarbon Substituents?	82
42. The Origin of the Ionic-Radius Ratio Rules	85
43. Onion’s Fusible Alloy	87
44. Why are <i>q</i> and <i>Q</i> Used to Symbolize Heat?	90
45. Why Has the Value of Avogadro’s Constant Changed?	92
46. The Origin of Isotope Symbolism	94
47. When Was Electronegativity First Quantified? I	96

48. When Was Electronegativity First Quantified? II	99
49. Faraday's Law or Faraday's Laws?	102
50. The Origins of Iso-, Neo-, Primary, Secondary, & Tertiary	105
51. The Proper Writing of Ionic Charges	107
52. The Origins of Stereochemical Line & Wedge Symbolism	109
53. The Origin of the Sigma, Pi, Delta Bond Notation	112
54. Reagent, Functional Group, Substituent and Substrate	114
55. The Origin of the Hybrid Orbital Concept	117
56. Origin of the Isoelectronic Principle	121
Index	126

Dedicated to John and Betty Moore
Who provided the opportunity

Preface

In 2003 John Moore, the then editor of *The Journal of Chemical Education*, received a question from a reader concerning the choice of the letter *R* as the symbol for the universal gas constant, which he passed on to me for comment. Based on this interaction, and the fun which I had in tracking down the probable answer, I suggested to John that a permanent question and answer column dealing with the historical origins of the symbols, laws, equations and apparatus which the average chemistry teacher deals with on a daily basis might be of interest to the readers of the journal – a column that would be greatly facilitated by my curatorship of the Oesper Collections in the History of Chemistry at the University of Cincinnati and the ready access to the necessary reference materials which it provided. John enthusiastically agreed and, for the next seven years, a bimonthly column entitled “Ask the Historian” ran in the journal under the watchful editing of Betty Moore.

In November of 2009 John stepped down as editor of the journal and was replaced by Norbert Pienta, who elected to continue the column, albeit now under the rather uninspired title of “History of Chemistry.” However, this transition involved more than just the usual change in editorship, as the journal, after 86 years of being independently published by the Division of Chemical Education, now became absorbed by ACS books and journals. The ACS had computerized the publication process for all of its journals and, in so doing, had rigidly formalized the submission process such that it was difficult to accommodate any exceptions to the standardized format used for full articles. Other

problems soon materialized as well, such as finding an editorial assistant for the column who was knowledgeable about French, German and Latin citations, or a font type in which a dash actually appeared as a dash rather than as an extraneous printer’s mark floating somewhere above the letters of a sentence.

In May of 2011 further change came when the ACS decided to completely reformat the journal and to eliminate all monthly columns. This decision placed all of the columns that were in process in limbo. Though items 47 and 48 were eventually combined and published as a conventional article, as of this writing the fates of items 49-56 are still undetermined with respect to the journal, even though I have chosen to include them in this volume.

In collecting the columns for republication in this book, I have elected to retain the individual monthly column format and the original title for all of the columns, but have reset them and added illustrations, which, because of space limitations, could not be used when they were first published in the journal. I have also added updates to some of the columns based on reader feedback, since I often learned as much from my readers concerning the topic in question as they had hopefully learned from me.

It is my hope that this collection will prove to be a permanent and useful historical resource for teachers of both high school and college chemistry and will alert them to the rich historical legacy of our science, most of which now languishes unnoticed and unused in the storage areas of our libraries and museums.

*William B. Jensen
Cincinnati, OH
December 2011*

I

The Universal Gas Constant

Question

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

Donald R. Paulson
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Answer

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

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

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

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

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

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

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

Both Clapeyron and Clausius had used the volume

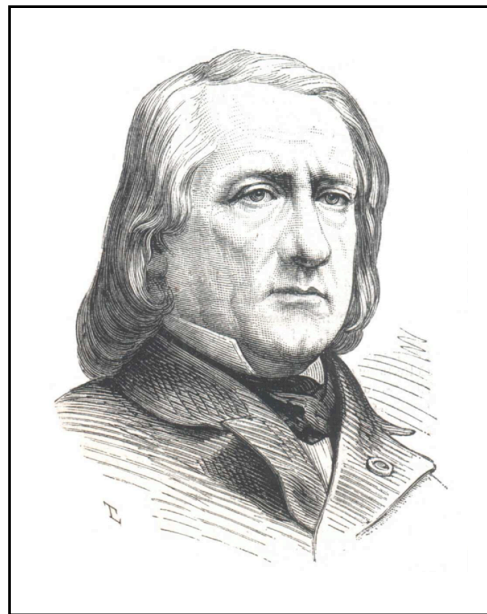


Figure 1. Henri Victor Regnault (1810-1878).

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

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

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

So why did Clapeyron choose the letter R for the constant in his gas law? The fact is that he doesn't explicitly tell us why and we are left with two speculative answers: (a) it was arbitrary or (b) it stood for *ratio* or

one of its French equivalents: *raison* or *rapport*, since Clapeyron noted that the value of R for each gas was obtained by evaluating the constancy of the ratio $pV/(267 + t)$ over a range of pressures and temperatures, a point also emphasized by Clausius using the revised ratio $pV/(273 + t)$.

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

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

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

Literature Cited

1. E. Clapeyron, "Mémoire sur la puissance motrice de la chaleur," *J. l'école polytechnique*, **1834**, *14*, 153-190. An English translation appears in E. Mendoza, Ed., *Reflections on the Motive Power of Fire and Other Papers on the Second Law of Thermodynamics*, Dover: New York, NY, 1960, pp. 71-105.

2. R. Clausius, "Über die bewegende Kraft der Wärme, und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen," *Ann. Phys.*, **1850**, *79*, 368-397, 500-524. This memoir has been translated into English and reprinted many times, including: (a) R. Clausius, "On the Moving Force of Heat and the Laws of Heat which may be Deduced

Therefrom" *Phil. Mag.*, **1851**, *2*, 1-21, 102-119. (b) R. Clausius, *The Mechanical Theory of Heat*, Van Voorst: London, 1867, pp. 14-80. (c) W. F. Magie, Ed., *The Second Law of Thermodynamics*, Harper: New York, NY, 1899, pp. 63-108. (d) E. Mendoza, Ed., *Reflections on the Motive Power of Fire and Other Papers on the Second Law of Thermodynamics*, Dover: New York, NY, 1960, pp. 107-152.

3. Reference 2b, p. 259.

4. The practice of writing R as a specific constant persisted in the physics literature well into the 20th century. See E. H. Kennard, *Kinetic Theory of Gases*, Macmillan: New York, NY, 1938, pp. 23, 26.

5. A. F. Horstmann, "Theorie der Dissociation," *Ann. Chem.*, **1873**, *170*, 192-210.

6. Though explicitly discussing his work, Clausius fails to give specific references for Regnault. However, the papers in question are probably H. V. Regnault, "Recherches sur la dilatation des gaz," *Ann. chem. phys.*, **1842**, *4*, 4-67; *ibid.*, **1842**, *5*, 52-83; and "Sur la loi de compressibilité des fluides élastiques," *Compt. rend.*, **1846**, *23*, 787-798.

7. Reference 2b, footnote, p. 22.

Publication History

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

Update

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

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

* R. Clausius, "Über die Art der Bewegung welche wir Wärme nennen," *Ann. Physik.*, **1857**, *100*, 353-380. An English translation appears in *Phil. Mag.*, **1857**, *14*, 108-127 and is also reprinted in S. G. Brush, Ed., *Kinetic Theory*, Vol. 1, Pergamon: Oxford, 1965, pp. 111-134.

II

The KLM Shell Labels

Question

Why do the labels for the electron orbits in the Bohr model begin with the letter K?

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Answer

The K, L, M-shell labels were not proposed by Bohr as part of his original 1913 quantum model of the atom but were rather the result of experimental studies of the phenomenon of X-ray fluorescence made by the British physicist, Charles Glover Barkla (figure 1), in the period 1906-1911 (1). Barkla characterized the secondary radiations produced when samples of the elements were exposed to an X-ray beam in terms of both their homogeneity and penetrating ability (measured in terms of the number of sheets of aluminum metal required to absorb them). He found that these secondary X-rays fell into two classes, which he labeled K and L, based on the observation that the K radiation was more penetrating than the L radiation. He also observed that the production of K versus L radiation correlated with the atomic weights of the elements, with the elements Ca through Rh producing only K radiation, W through Bi producing only L radiation, and Ag through Ce producing a mixture of both. In 1913 these latter observations were refined by the British physicist, Henry Moseley (1887-1915), in his classic study of the relationship between the frequency of the secondary X-rays and the atomic numbers of the elements (2).

Rationalization of the Barkla-Moseley X-ray fluorescence results in terms of the Bohr model is usually credited to a 1914 paper by the German physicist, Walther Kossel (1888-1956), who argued that the K radiation was due to an excited electron falling back into a vacancy in the first shell of an atom, and the L radiation to an excited electron falling back into a vacancy in the second shell (3, 4). As a consequence, the labels K and L became attached to the first and second shells of the Bohr atom, especially in the literature dealing



Figure 1. Charles Glover Barkla (1877-1944).

with spectroscopy. Already in his 1911 paper, Barkla had speculated on the possible existence of even softer secondary X-rays beginning round Au and Pt and corresponding to possible M and N series, and these labels were soon attached to the third and fourth shells of the Bohr atom as well. Interestingly, Bohr himself seldom made use of these spectroscopic shell labels in his own writings, preferring instead to use numerical quantum numbers (5).

So why did Barkla label his secondary X-ray series K and L? The answer appears in a footnote to his 1911 paper (1):

[These radiations were] previously denoted by the letters B and A ... The letters K and L are, however, preferable, as it is highly probable that series of radiations both more absorbable and more penetrating exist.

In other words, though Barkla assigned arbitrary letters

to his X-ray series, he started in the middle of the alphabet, rather than at the beginning, in order to allow for future expansion of his results in either direction.

Given that M rather than K corresponds to the center of the alphabet, it has been suggested to the author that Barkla began instead at K and L because these two letters are found in his last name. Though a charming idea, I have found no documentary evidence to support this supposition.

Literature Cited

1. C. G. Barkla, "The Spectra of the Fluorescent Röntgen Radiations," *Phil. Mag*, **1911**, 22, 396-412. See especially the footnote, p. 406.
2. H. Moseley, "The High Frequency Spectra of the Elements," *Phil. Mag.*, **1913**, 26, 1025-1034 and *Ibid.*, **1914**, 27, 703-713.
3. W. Kossel, "Bemerkung zur Absorption homogener Röntgenstrahlen," *Verhand. deutschen physik. Gesell.*, **1914**, 16, 898-909.
4. J. L. Heilbron, "The Kossel-Sommerfeld Theory and the Ring Atom," *Isis*, **1967**, 58, 451-485.
5. L. Rosenfeld, Ed., *Niels Bohr: Collected Works*, 9

Vols., North-Holland Publishing: Amsterdam, 1972-1996.

Publication History

First published in *J. Chem. Educ.*, **2003**, 80, 996.

Update

I recently received an e-mail from a reader claiming that Bohr assigned K to the first shell because it is the 11th letter of the alphabet – 11 being shorthand for one shell, one subshell. Likewise L, as the 12th letter of the alphabet, was shorthand for one shell, two subshells, etc. Though this is certainly a clever mnemonic device for students, it has, to the best of my knowledge no basis in the historical record and is essentially a numerical coincidence, which, like the story associating the letters with Barkla's surname, is yet another example of an historical myth. Likewise, I have also encountered the suggestion that K and L were shorthand for the German words, *kurz* (short) and *lange* (long) and were a reference to the respective wavelengths of the two kinds of secondary X-ray radiation, which, given that Barkla was not German, seems improbable.

III

The Origin of Stoichiometry Problems

Question

When did elementary chemistry textbooks begin to include quantitative stoichiometry problems?

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Answer

The simplest way to gauge this is to examine special supplementary booklets designed to specifically teach stoichiometry to beginning students of chemistry. The Oesper Collections at Cincinnati contain roughly 20 of these, spanning the period between 1865 and the present. The two volumes dating from 1865 – one by the German chemist, Albert Frickhinger, and the other by the American chemist, Josiah Parsons Cooke (figure 1), are both later editions of books first published in 1843 and 1857 respectively (1, 2).

Cooke's booklet covered the topics of nomenclature and chemical symbols, formula weights, balancing equations, mass-mass calculations, specific gravity and mass-volume calculations, unit conversions, gas-law calculations, and empirical formulas. Frickhinger's book is similar but also contained an introductory section on mathematical notation, including exponents and logarithms. Despite the work of Cannizzaro in 1858, both of these books continued to use equivalent weights rather than atomic weights. By the first decade of the 20th century, stoichiometry books were also including problems on converting empirical formulas to molecular formulas using experimental molecular weight data, percent composition, normality of solutions, dilution problems, and titration problems (3, 4).

The extent to which the textbooks themselves incorporated student exercises dealing with all of the above topics is more variable, and heavily depended, as it does today, on their intended audience. A survey of introductory American texts from 1820 to 1960 found that none of the textbooks in the survey that were published before 1867 contained numerical prob-



Figure 1. Josiah Parsons Cooke (1827-1894).

lems, whereas all but two published between 1870 and 1900 contained at least simple mass-mass problems (5). Indeed, this inadequate coverage was the main reason why Cooke wrote his small booklet. As indicated by its subtitle, "To Accompany Stockhardt's Elements of Chemistry," it was intended to supplement the textbook used by Cooke at Harvard, whose coverage of the topics in question was, in his opinion, "insufficiently developed for the purposes of college teaching." Once Cooke's own textbook, *First Principles of Chemical Philosophy*, appeared in 1868, this problem was obviated and Cooke allowed his supplementary booklet to go out of print (6).

Literature Cited

1. A. Frickhinger, *Katechismus der Stöchiometrie*, 4th ed., Beck'schen Buchhandlung: Nördlingen, 1865.

2. J. P. Cooke, *Chemical Problems and Reactions*, Butler: Philadelphia, PA, 1865.
3. E. J. Bartlett, *Calculations of the Quantitative Chemical Laboratory*, Dartmouth: Hanover, NH, 1909.
4. G. Bornemann, *Stöchiometrie*, Hirzel: Leipzig, 1909.
5. W. B. Jensen, *The Secondary Chemistry Textbook and the History of Secondary Chemistry Teaching, 1820-1960*, MS Thesis, University of Wisconsin, Madison, WI, 1972.
6. J. P. Cooke, *First Principles of Chemical Philosophy*, Sever, Francis & Co: Boston, 1868.

Publication History

First published in *J. Chem. Educ.*, **2003**, 80, 1248.

Update

Since writing this column the Oesper Collections have considerably expanded their acquisitions in this area. These new acquisitions indicate that the German tradition of speciality monographs on chemical calculations actually goes much further back than indicated in the original column, though the conclusion with regard to the coverage of these topics in the typical introductory textbook remains unchanged. Some of these earlier monographs include:

- * H. Buff, *Versuch eines Lehrbuchs der Stöchiometrie*, Scrag: Nürnberg, 1829.
- * M. Ehrmann, *Die Stöchiometrie*, Ehrmann: Wien, 1829.
- * O. B. Kühn, *Lehrbuch der Stöchiometrie*, Köhler: Leipzig, 1837.

IV

The Symbol for pH

Question

What is the origin of the symbol pH ?

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Answer

The pH concept was introduced by the Danish biochemist, Søren Peter Lauritz Sørensen (figure 1), in 1909 (1). Sørensen was investigating the use of a normal hydrogen electrode, $H^+/Pt/H_2$ to measure the acidity of solutions. If the pressure of the H_2 is fixed at 1 atmosphere, the potential of this electrode is given by the equation:

$$E = 2.3(RT/F)\log(1/[H^+]) = 0.0577\log(1/[H^+]) \quad [1]$$

thus making the potential of the overall cell proportional to $-\log[H^+]$. Consequently Sørensen found that it was convenient to use this term as an indirect measure of acidity in his work, the more so since most of the H^+ concentrations he was working with were much smaller than 1 and could be written (1, 2):

... in the form of a negative power of 10 ... [and] I will employ the name "hydrogen ion exponent" and the symbol p_{H^+} for the numerical value of the exponent of this power.

In other words, Sørensen expressed his hydrogen ion concentrations in the form 10^p in which "p" represented the numerical power (English), *puissance* (French) or *potenz* (German) of the exponent. Variations on Sørensen's symbol soon appeared, including p_{H^+} , P_h and pH , with the latter eventually gaining dominance, largely through its official adoption by the *Journal of Biological Chemistry* in the decade 1910-1919 (3).

Not everyone was pleased with Sørensen's proposal. W. Mansfield Clark, whose monograph, *The Determination of Hydrogen Ions*, was the major American reference for Sørensen's work during the early decades of the 20th century, was certainly convinced of the



Figure 1. Søren Peter Lauritz Sørensen (1868-1939).

importance of the H^+ ion in biochemical phenomena, but was a good deal more ambivalent about the wisdom of using the pH concept to represent variations in its concentration (2):

... both convenience and the nature of the physical facts invite us directly or indirectly to operate with some logarithmic function of $[H^+]$. It is unfortunate that a mode of expression so well adapted to the treatment of various relations should conflict with a mental habit. $[H^+]$ represents the hydrogen ion concentration, the quantity usually thought of in conversation when we speak of increases or decreases in acidity. pH varies inversely as $[H^+]$. This is confusing.

Nevertheless, Clark felt that he had to bow to the trends in the chemical literature, which showed a rapid increase in the use of the concept between 1910 and the appearance of the third the edition of his book in

1928. But even in his acquiescence he could not resist making the somewhat sarcastic observation that (2):

Like the Greeks who personified the virtues, we, having embodied the acidic and basic properties, have lifted to our Olympus the hydrogen and hydroxyl ions ...

Literature Cited

1. S. Sørensen, "Enzymstudien II: Über die Messung und die Bedeutung der Wasserstoffionenkonzentration bei enzymatischen Prozessen," *Biochem. Zeit*, **1909**, 21, 131-200. See especially p. 134.
2. W. M. Clark, *The Determination of Hydrogen Ions*, 3rd ed., Williams and Wilkins: Baltimore, MD, 1928, pp. x, 36, 38. In this source Clark gives a slightly different variation of the above quote, based on a French version of the paper published by Sørensen's Carlsberg laboratory.
3. W. M. Clark, *The Determination of Hydrogen Ions*, Williams and Wilkins: Baltimore, MD, 1920, footnote, p. 26.

Publication History

First published in *J. Chem. Educ.*, **2004**, 81, 21.

Update

Since publishing this column I have been made aware of a debunking literature which rather vociferously claims that Sørensen's choice of the letter *p* in *pH* was totally arbitrary. One of the bizarre arguments used to support this contention is that Sørensen wrote in German and French so *p* could not have stood for power. But of course the corresponding German and French words *potenz* and *puissance*, which Sørensen did use, also begin with *p* and this debunking claim is hard to reconcile with various explicit statements in Sørensen's original papers, such as the following on page 134 of reference 1 above:

The magnitude of the hydrogen ion concentration will accordingly be represented by means of the normality factor with regard to the hydrogen ion, and this factor will be written in the form of a negative potenz (power) of 10. Since I refer to the above in a later section (see page 159), here I will mention only that I employ the name "hydrogen ion exponent" and the symbol pH for the numerical value of this potenz (power).

V

Did Lavoisier Blink?

Question

The story has been circulating on the internet and among various colleagues that Lavoisier made an agreement with Lagrange, shortly before being guillotined, that he would blink his eyes if he retained consciousness after being beheaded, and that he was executed because of his revolutionary scientific views. Is there any truth to these stories?

O. Yavuz Ataman
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Answer

Both stories are false. Though Lavoisier (figure 1) did incur the wrath of the notorious revolutionary, Jean-Paul Marat, through his criticism of Marat's rather amateurish forays into the theory of fire, his trial (figure 2) and death had nothing to do with his science, but were instead based on his involvement, along with his father-in-law, Jacques Paulze, in the notorious *Ferme Générale* or tax farm – a private corporation of financiers commissioned by the French government to collect tolls and taxes. Among other things, the members of the *Ferme* were accused of embezzling government funds and adulterating tobacco in order to increase their profits from the toll duty.

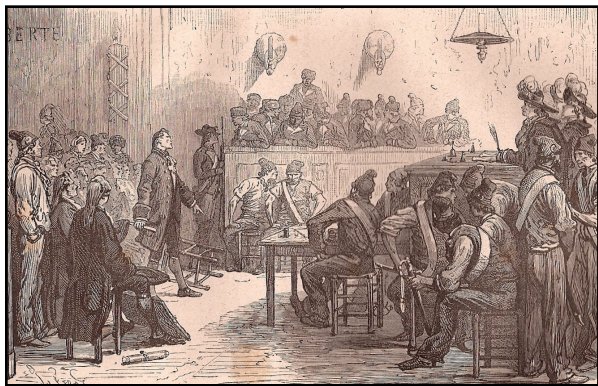


Figure 2. A 19th-century rendition of the trial of Lavoisier and the *Ferme Générale*.



Figure 1. Antoine Laurent Lavoisier (1743-1794). Note the false implication that Lavoisier was beheaded with an axe and chopping block.

As for the story of the postmortem experiment with Lagrange, no mention is made of it in any of the reputable biographies of Lavoisier (1-3). On 8 May 1794 Lavoisier, his father-in-law, and most of the other members of the *Ferme* were taken to the *Place de la Revolution* where they were rapidly guillotined, their heads falling into a common sack and their torsos being tossed into a wagon. After the execution, their remains were carted away and buried in an unmarked mass grave. Lagrange and a small group of other scientists were present at the execution but were standing at a distance in one corner of the square, separated from the guillotine by a line of gendarmes. To have actually performed the experiment, Lagrange would have had

to of been at the base of the guillotine examining each head as it fell into the sack. This “urban myth” apparently started with a special on the guillotine that aired on the *Discovery Channel* several years ago - a source not exactly known for either its reliability or skepticism. Indeed, it even became the subject of a popular syndicated newspaper question-answer column (4).

The circumstances surrounding Lavoisier’s death and burial also cast doubt on the authenticity of the so-called death mask of Lavoisier that the Fisher Scientific Company once claimed to have owned (5).

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1. D. McKie, *Antoine Lavoisier: Scientist, Economist Social Reformer*, Schulman: New York, NY, 1952.
2. F. Szabadváry, *Antoine Laurent Lavoisier*, University of Cincinnati: Cincinnati, OH, 1977.
3. A. Donovan, *Antoine Lavoisier: Science, Administration, and Revolution*, Blackwell: Oxford, 1993.
4. C. Adams, *Triumph of the Straight Dope*, Ballantine Books: New York, NY 1999, pp. 262-264.
5. Undated Fisher brochure describing its historical and art collections.

Publication History

First published in *J. Chem. Educ.*, **2004**, *81*, 629.

VI

The Origin of “Vinyl”

Question

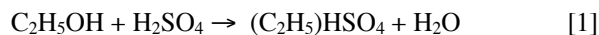
Where does the term “vinyl” come from? Though it permeates polymer chemistry and has even taken on a cultural meaning (i.e., something cheap, plastic, or slick), the organic and polymer texts I have consulted are silent as to its origins.

*Rudi Thomas
Department of Chemistry
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Cincinnati, OH 45221*

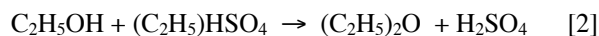
Answer

The term “vinyl” is ultimately derived from the Latin *vinum*, meaning “wine” (*Wein* in German, *vin* in French) and was first applied in chemistry in the early 19th century to describe ethanol or wine alcohol (*Weingeist* in German, *esprit-de-vin* or *alcool vinique* in French).

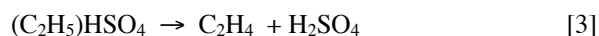
In 1809 von Vogel discovered a compound of ethanol and sulfuric acid, $(\text{C}_2\text{H}_5)\text{HSO}_4$, now known as ethyl hydrogen sulfate, but which was originally called “sulphovinic acid” (*Weinschwefelsäure* in German and *acide sulfovinique* in French) during the 19th century, in honor of its preparation from vinic alcohol (1, 2):



Depending on the conditions, this compound will either decompose into diethyl ether:



or into ethene gas:



Since the ethene produced in reaction 3 was derived from sulphovinic acid and ultimately from vinic alcohol, Gmelin suggested in 1848 that it be called *Vine* or *Vinegas* (3). The final step was taken in 1854 when Kolbe (figure 1) proposed the name “vinyl” for

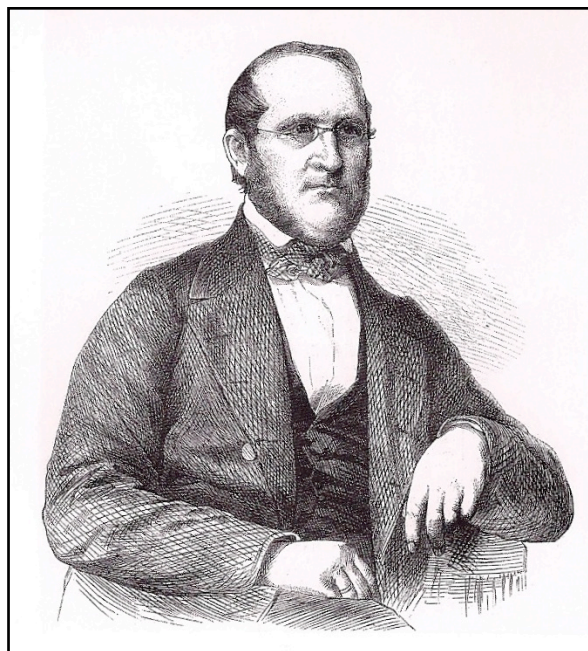


Figure 1. Adolf Wilhelm Hermann Kolbe (1818-1884).

the monovalent radical, $\text{C}_2\text{H}_3\cdot$, of this gas (4), whence the names of its various derivatives: vinyl alcohol ($\text{C}_2\text{H}_3\text{OH}$), vinyl chloride ($\text{C}_2\text{H}_3\text{Cl}$), polyvinyl chloride (PVC), etc.

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2. L. Gmelin, *Handbook of Chemistry*, Vol. 8, Cavendish Society: London, 1853, pp. 415-428.
3. L. Gmelin, *Handbuch der organischen Chemie*, Vol. I, Winter: Heidelberg, 1848, pp. 520-526.
4. H. Kolbe, *Ausführliches Lehrbuch der organischen Chemie*, Vol. 1, Vieweg: Braunschweig, 1854, pp. 345-368.

Publication History

First published in *J. Chem. Educ.*, **2004**, *81*, 464.

VII

The Origin of Alcohol “Proof”

Question

What is the origin of the “proof” system for measuring the ethanol content of alcoholic beverages?

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Answer

The use of the term “proof” in connection with the alcohol content of liquors dates back to 16th-century England. When used in this context, the word refers to “a test, trial or demonstration.” This same usage is found in the well-known maxim “The proof of the pudding is in the eating,” meaning that the test of whether the pudding is a success is in the eating. The proof system is based on the selection of an arbitrary standard (called 100 proof) typical of the alcohol content of distilled liquors and the rating of the alcohol content of other beverages in terms of how much larger or smaller they are relative to this standard (1).

The proof system was originally established for purposes of taxing liquors according to their alcohol content and varies from country to country. In 16th-century England, the original test involved soaking a pellet of gunpowder with the liquor. If it was still possible to ignite the wet gunpowder, the alcohol content of the liquor was rated above proof and it was taxed at a higher rate, and vice versa if the powder failed to ignite. By the end of the 17th century, England had introduced specific gravity as the criterion for measuring proof or alcohol content. Since this was highly sensitive to temperature, it resulted in numerous problems with standardization. Not until 1816 was the primary standard precisely defined as 12/13th the specific gravity of pure distilled water at the same temperature.

The United States was luckier. Its proof system was established around 1848 and was based directly on percent alcohol by volume rather than specific gravity, with 50% alcohol by volume being taken as typical of strong distilled liquors and as the 100 proof standard. The most scientific scale, however, was that used in France, which was established in 1824 by the famous French chemist, Joseph-Louis Gay-Lussac (figure 1),



Figure 1. Joseph-Louis Gay-Lussac (1778-1850).

which took 100% alcohol by volume as 100 proof and 100% water by volume as 0 proof. Thus 100 proof on the American scale is 50 proof on the French scale and about 87.6 proof on the British scale. All in all it is a good example of what happens when standards are set by politicians instead of scientists.

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1. H. A. Klein, *The World of Measurements: Masterpieces, Mysteries and Muddles of Metrology*, Simon and Schuster: New York, NY, 1974, pp. 561-575. This volume has been reprinted as a paperback by Dover Books in 1988 under the title, *The Science of Measurement: A Historical Survey*, and is an absolute must for any chemistry teacher interested in the history of units and measurement.

Publication History

First published in *J. Chem. Educ.*, **2004**, *81*, 1258.

Update

Recently it has come to my attention that many internet sites claim that the gunpowder test dates from the 18th century rather than the 16th century, as suggested by Klein. Regrettably none of these sources, including Klein, provide references that would allow one to double check their claims. However, given the crudity of the gunpowder test and the fact that specific gravity was already suggested as a guide in the 17th century and made official in the 18th century, the claim that the test dates from the 16th century seems the more probably of the two.

Some speculations as to the underlying chemical and physical basis of the gunpowder test have also come to my attention – namely that it ultimately relies on the fact that potassium nitrate is highly soluble in water but only moderately soluble in ethanol. Thus the greater the water content of the alcohol, the more potassium nitrate it leeches out of the gunpowder and the

more likely it becomes that the gunpowder will fail to ignite. By its very nature such a test would lack reproducibility since the size and compactness of the gunpowder grains, the quantity of liquor used to soak the grains, and the time of contact before attempting to ignite the powder would all play a role in determining how much potassium nitrate was dissolved and hence whether or not the gunpowder would ignite.

I have also recently discovered that a separate proof scale was used to rate the strength of vinegar for taxation purposes in early 19th-century England. As with alcohol, specific gravity was used to measure the proof or strength of the vinegar and just as the modified hydrometer used to measure alcohol proof was called an alcoholmeter, so the modified hydrometer used to measure vinegar proof was called an acetometer. For details see:

* C. A. Mitchell, *Vinegar: Its Manufacture and Examination*, 2nd ed., Griffin: London, 1926, Chapter 1.

VIII

The Origin of the Mole Concept

Question

What is the origin of the mole concept?

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Answer

The term “molar” (from the Latin *moles*, meaning “a large mass”) was first introduced into chemistry by the German chemist, August Wilhelm Hofmann (figure 1), around 1865 (1). It was originally intended to indicate any large macroscopic mass, in contrast to a submicroscopic or “molecular” mass (also derived from moles by attaching the Latin suffix *-cula*, meaning “small or diminutive”). In other words, rather than talk about macroscopic versus microscopic, one talks about molar

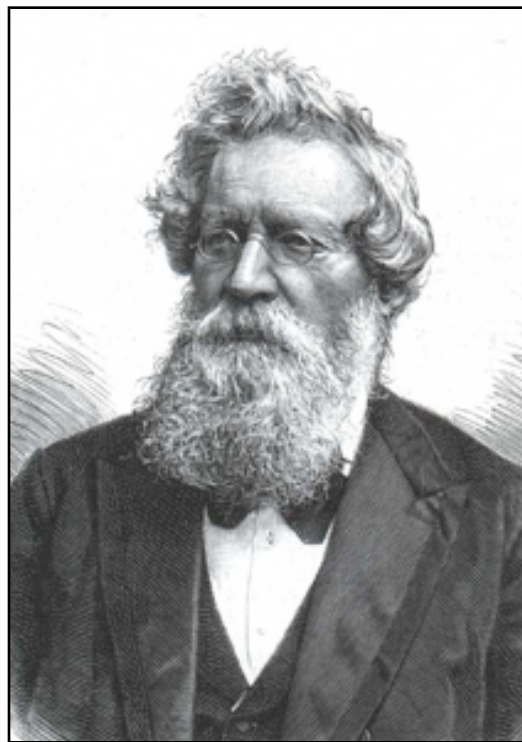


Figure 1. August Wilhelm Hofmann (1818-1892).



Figure 2. Wilhelm Ostwald (1853-1932).

versus molecular. This particular use of the term molar also gained currency in the physics literature, where it was in common use at least through the 1940s.

The more restricted use of the term molar to mean, not just any macroscopic sample, but rather one whose mass in grams directly reflects the mass of its constituent molecules, as well as use of the noun “mole,” is usually attributed (2) to the German physical chemist, Wilhelm Ostwald (figure 2), and appears in several of his textbooks written around the turn of the 20th century (3). Ironically, Ostwald’s use of the term was connected with his attacks on the atomic-molecular theory and his attempt to establish a macroscopic alternative for discussing the laws of stoichiometry (4).

Although use of the volume definition of a mole for gases (22.4 liters at STP) appears relatively early in 20th-century introductory American textbooks, the explicit interconversion of grams and moles as part of standard stoichiometry problems does not appear to have been

THE ORIGIN OF THE MOLE CONCEPT

common before the 1950s (5, 6).

As a linguistic footnote, it is interesting to observe that the term mole or *mola* was also used by the Romans to denote the heavy stones used to construct harbor breakwaters and for millstones. The connection between the latter usage and the act of grinding also accounts for such usages as molar teeth.

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2. M. Trautz, *Lehrbuch der Chemie*, Vol. 1, Vereinigung Wissenschaftlicher Verleger: Berlin, 1922, p. 56.
3. W. Ostwald, *Grundlagen der anorganischen Chemie*, Engelmann: Leipzig, 1900.
4. W. Ostwald, *The Fundamental Principles of Chemistry*, Longmans, Green & Co: London, 1909.
5. S. Benson, *Chemical Calculations*, Wiley: New York, NY, 1952, Chap. IV.
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Publication History

First published in *J. Chem. Educ.*, **2004**, *81*, 1409.

Update

Since writing the original column several related articles on this subject in Japanese have been brought to my attention:

- * H. Onishi, "The Mole: Past and Present," *Kagakushi*, **2002**, *29*, 254-258.
- * H. Onishi, "Early Usage of the Mole, Loschmidt's Number and Avogadro's Constant (or Number)," *Kagakushi*, **2004**, *31*, 35-39.

I have also since encountered the abbreviation "Mol." for a gram-molecular weight of substance in several earlier German publications, though this appears to have been an abbreviation for "molecular weight" rather than for the word "mole." See, for example:

- * A. Horstmann, "Theorie der Dissociation," *Ann. Chem. Pharm.*, **1873**, *170*, 192-210.

IX

Why Helium Ends in “-ium”

Question

Why does helium have the ending “-ium” usually reserved for metals?

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Answer

The story of the element helium begins with the independent discovery by the British astronomer, Norman Lockyer (figure 1), and the French astronomer, Pierre-Jules-Cesar Janssen (1824-1907), of an unidentifiable line in the spectra of the solar prominences observed during the eclipse of 1868. Because the bright yellow line was close to the D1 and D2 lines of sodium, it was designated D3. In order to identify the lines in his spectral data, Lockyer enlisted the help of the prominent British chemist, Edward Frankland (1825-1899). Their laboratory work showed that the majority of the observed solar lines were due to hydrogen, though often modified by changes in temperature and pressure (1). The D3 line, however, could not be reproduced in the laboratory. As a result, Lockyer concluded that it belonged to a unknown element for which the name “helium” (from the Greek, *helios*, meaning “sun”) was contrived.

Most biographies of Lockyer claim that he coined the name (2), whereas other sources attribute it to Frankland (3). However, this latter claim is unlikely, as we know from private correspondence that Frankland did not support the helium hypothesis (4). Well aware of the large number of spurious elements proposed in the chemical literature, he felt that the line would eventually be found to belong to hydrogen under more extreme conditions of temperature and pressure. Further complications arise from the fact that Lockyer never seems to have formally proposed the name “helium” in a published paper nor is it mentioned in his various books (5). However, it appears to have been common knowledge in British scientific circles and was referred to by others in various lectures and books (6).

As is well known, terrestrial helium was finally

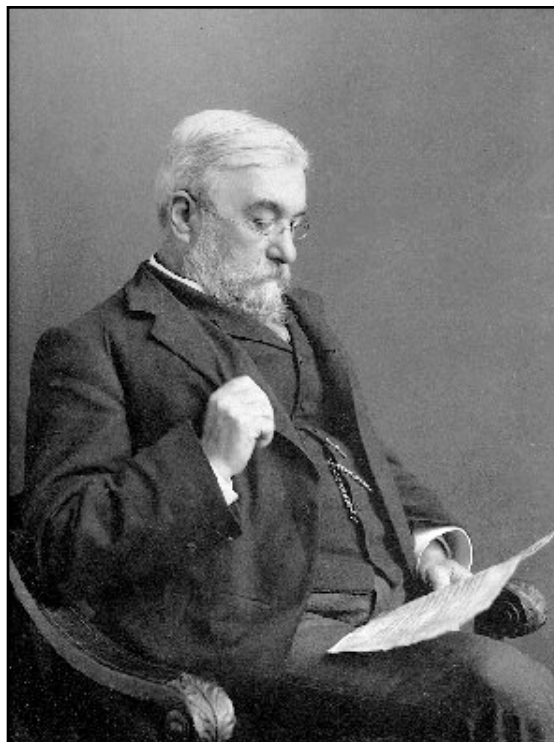


Figure 1. Joseph Norman Lockyer (1836-1920).

isolated by Sir William Ramsay (figure 2) in 1895 from the occluded gases in uranium minerals. Ramsay’s laboratory notebooks reveal that he originally named the new gas “krypton” (7). However, after Sir William Crookes (1853-1925) informed him that the yellow line in the spectrum of the new gas was identical to that of Lockyer’s helium, Ramsay deferred to Lockyer’s name choice, no doubt because of Lockyer’s prominence in the British scientific community, and instead reused krypton for one the heavier noble gases that he later isolated in collaboration with Morris Travers.

The use of a compromise name, such as “helon” or “helion,” does not seem to have occurred to anyone. Since Lockyer apparently never formally proposed the name in print, we do not know why he chose to use a metallic ending. Possibly because of its close association with the lines of sodium, he assumed it would also be a metal, but more likely, as an astronomer, he was unaware of the finer points of chemical nomenclature.

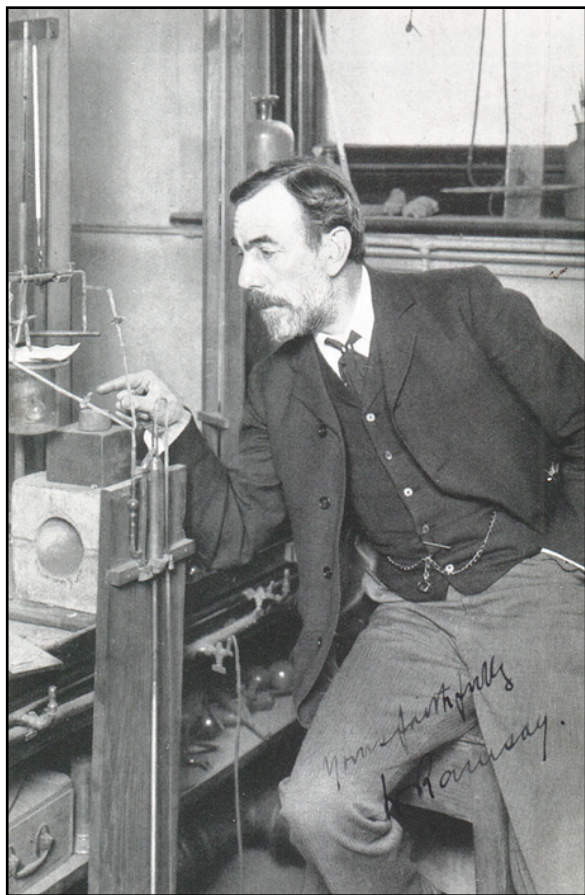


Figure 2. William Ramsay (1852-1916).

This supposition is supported by the fact that, as a result of his own spectroscopic studies of Ramsay's new gas, Lockyer became convinced that it was a mixture of helium and yet another nonmetallic gas which he called “asterium,” thus compounding his initial chemical *faux pas* (8, 9).

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1. E. Frankland, N. Lockyer, “Researches Upon Gaseous Spectra in Relation to the Physical Constitution of the Sun,” *Proc. Roy. Soc.*, **1869**, *17*, 288-291, 453-454; *Ibid.*, **1869**, *18*, 79-80.
2. See T. M. Lockyer, W. L. Lockyer, *Life and Work of Sir Norman Lockyer*, Macmillan: London, 1928, p. 42; and

A. J. Meadows, *Science and Controversy: A Biography of Sir Norman Lockyer*, MIT Press: Cambridge, MA, 1972, p. 60.

3. See C. A. Young, *The Sun*, Appleton: New York, NY, 1881, p. 88; and W. Ramsay, *The Gases of the Atmosphere*, 4th ed., Macmillan: London, 1915, pp. 234-235.

4. Letter from Frankland to Lockyer of 9 September 1872. Quoted in Meadows, reference 2, pp. 59-60.

5. No published source is cited for the proposed name in any of the various histories of the discovery of the chemical elements found on my shelves, nor in any of the biographies of Lockyer, nor in Lockyer's own historical account of the discovery of helium. See N. Lockyer, “The Story of Helium,” *Nature*, **1896**, *53*, 319-322, 342-346. The name helium is also not listed in the indices of Lockyer's books, *The Spectroscope and Its Applications* (1873) and *The Chemistry of the Sun* (1887).

6. The helium hypothesis was first referred to in public by Lord Kelvin in his BAAS address of 1871 and again by W. B. Carpenter in his address of 1872. It is also mentioned in Young, reference 3, p. 88.

7. M. W. Travers, *A Life of Sir William Ramsay*, Arnold: London, 1956, Chap. 8.

8. N. Lockyer, “On the Appearance of the Clevite and other New Gas Lines in the Hottest Stars,” *Proc. Roy. Soc.*, **1897**, *62*, 52-66.

9. The additional lines detected by Lockyer in He are actually those of the He⁺ ion, which are slightly displaced relative to those of the neutral atom.

Publication History

First published in *J. Chem. Educ.*, **2004**, *81*, 944.

Update

Shortly after the publication of this column, James Espenson of Iowa State brought to my attention a footnote on page 108 of the second edition (1953) of Linus Pauling's introductory textbook, *General Chemistry*, which reads:

The ending “ium,” which is otherwise used only for metallic elements, is due to Lockyer's incorrect surmise that the new element was a metal. “Helion” would be a better name.

X

The Origin of the Name “Nylon”

Question

What is the origin of the name “nylon”?

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Answer

The story of the development of nylon and the tragic fate of its discoverer, Wallace Hume Carothers (figure 1), are well known (1, 2). Its importance as a landmark in the evolution of commercial synthetic polymers is uncontested and its preparation is still used as a demonstration in introductory chemistry courses (3). Consequently, it comes as a disappointment that its name is totally devoid of both chemical and historical significance and was selected, not by the chemists involved in its synthesis, but by the managers and executives at Du Pont.

As detailed in Stephen Fenichell’s highly entertaining history of modern plastics and polymers, the more than 350 original contenders for the name of the new polymer included such choices as Amidarn, Amido Silk, Linex, Lastrapon, Moursheen, Poya, Rayamide, Syntex, Tensheer, and Wiralene (4). Among the more imaginative suggestions were Duparoooh (short for “Du Pont pulls a rabbit of the hat”), Dupron (short for “Du Pont pulls a rabbit out of nitrogen, nature, nozzle, or naphtha”), Delawear (Du Pont is located in the state of Delaware), Duponese, and Wacara (short for Wallace Carothers).

Though the final choice of “nylon” has no intrinsic meaning, this has not prevented others from reading unintended interpretations into the name. Thus many of the visitors to the New York World’s Fair of 1939, where its discovery was first publicly announced, came away believing that it was named after the fair’s famous “Trylon” tower, whereas others believed it was a contraction of New York (NY) and London (LON). Reflecting the growing tensions between Japan and the United States shortly before the outbreak of the Second

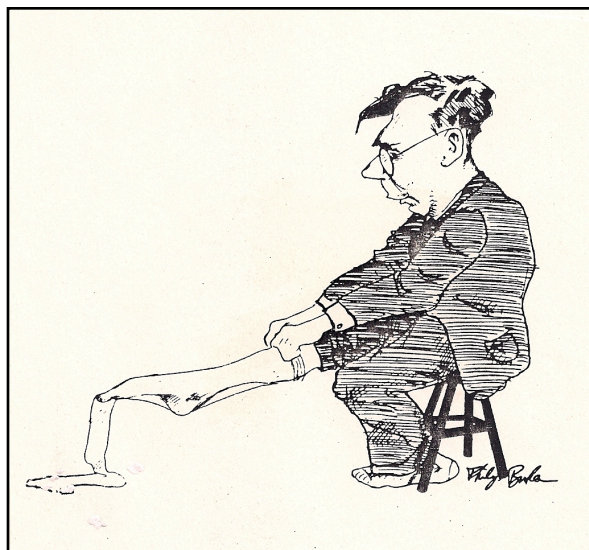


Figure 1. Caricature of Wallace Hume Carothers (1896-1937).

World War, the most bizarre interpretation came from a Japanese newspaper which contended that Du Pont had developed the polymer for the explicit purpose of destroying the Japanese silk industry and that the name was an acronym for an anti-Japanese (Nipponese) slur.

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2. M. E. Hermes, *Enough for One Lifetime: Wallace Carothers, Inventor of Nylon*, Chemical Heritage Foundation: Philadelphia, PA, 1996.
3. B. Z. Shakhshiri, *Chemical Demonstrations*, Vol. 1., University of Wisconsin: Madison, WI, 1983, pp. 213-215.
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Publication History

First published in *J. Chem. Educ.*, **2005**, 82, 676.

XI

The Origin of the Bunsen Burner

Question

When and where did Bunsen propose his famous burner?

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Answer

The famous laboratory gas burner associated with the name of the German chemist, Robert Wilhelm Bunsen (figure 1), was first described in detail in 1857 in the second of a series of papers on photochemistry written by Bunsen in collaboration with the British chemist, Henry Enfield Roscoe (1833-1915) (1), though the burner in question had actually been in use in Bunsen's Heidelberg laboratory since 1855 (2). Proposals for laboratory gas burners date back at least to the 1820s when gas lighting first began to appear in the larger cities and towns of Europe. One such device was described by Michael Faraday (1791-1867) in the 1827 edition of his book, *Chemical Manipulation* (3, 4) and both Dolch (5) and Kohn (6) have also described a



Figure 1. Robert Wilhelm Bunsen (1811-1899).

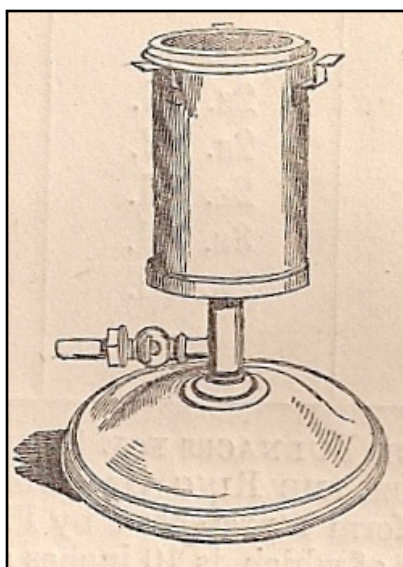


Figure 2. A typical gauze burner (10).

number of pre-Bunsen laboratory gas burners.

In his autobiography, Roscoe claimed that Bunsen's burner was based on a modification of a laboratory gas burner, known as a "gauze burner," that Roscoe had brought to Germany from England and which was in common use the laboratories at University College London (7, 8). As implied by its name, before being lit, the gas and air were mixed in a cylindrical metal chamber (figure 2) having a wire screen or gauze top, in order to prevent (in keeping with the principles of the Davy safety lamp) the danger of a flashback. Unfortunately, the resulting flame was diffuse, relatively cool, and suffered from excessive flickering and coloration, due to contaminants on the metal screen.

An examination of the paper by Bunsen and Roscoe shows that their primary motive in using the new burner (figure 3) was to obtain a virtually colorless, soot-free, flame of constant size which could be used to establish photometric standards. This was accomplished by having the premixed air and gas issue

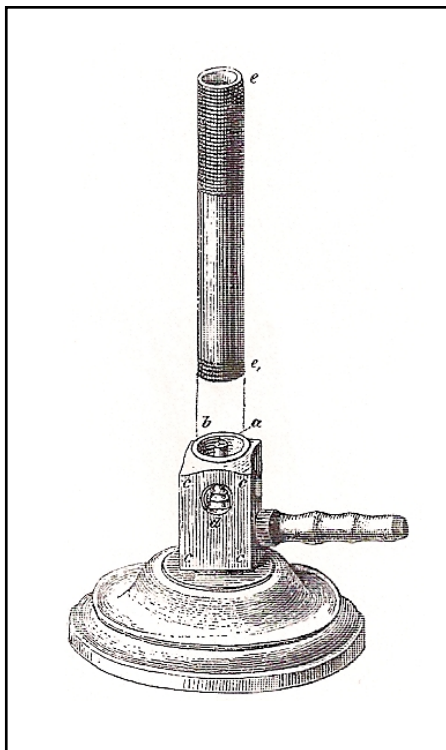


Figure 3. Bunsen's original burner (1).

from a long narrow tube or barrel under positive pressure before being lit (9). If the width and length of the tube are properly selected, the flame will not propagate down the tube and the necessity of using a wire safety screen is eliminated. A side benefit was that the burner also provided a hotter, more concentrated flame for conventional laboratory use. By the end of the 1860s, laboratory gas burners had largely displaced the older charcoal furnaces that had dominated chemistry for most of its recorded history.

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Leipzig, 1904, pp. 19-56, and in W. Ostwald, Ed., *Photochemische Untersuchungen von R. Bunsen und H. E. Roscoe (1855-1859)*, Erste Hälfte, Die Klassiker der exakten Wissenschaften, Nr. 34, Engelmann: Leipzig, 1892. The diagram of the burner appears as figure 6 of this paper.

2. These burners were made by the university's instrument maker, Peter Desaga, based on a simplified version of Bunsen's original design. Priority claims by the Berlin firm of Julius Pintsch (1855) and by the lighting engineer, R. W. Elsner (1856), were successfully contested by Desaga. See P. Desaga, "Ueber den neuen Gasbrenner welchen sich Eisner patentiren liess," *Dinglers poly tech. J.*, **1857**, *143*, 340.

3. M. Faraday, *Chemical Manipulation: Being Instruction to Students in Chemistry on the Methods of Performing Experiments of Demonstration or of Research with Accuracy and Success*, Phillips: London, 1827, p. 107.

4. W. B. Jensen, "Michael Faraday and the Art and Science of Chemical Manipulation," *Bull. Hist. Chem.*, **1991**, *11*, 65-76.

5. P. Dolch, "100 Jahre Bunsenbrenner – einer chemisch-geschichtlich Studie," *Österreich. Chem. Zeit.*, **1955**, *56*, 277-285.

6. M. Kohn, "Remarks on the History of Laboratory Burners," *J. Chem. Educ.*, **1950**, *27*, 514-516.

7. H. E. Roscoe, *The Life and Experiences of Sir Henry Enfield Roscoe*, Macmillan: London, 1906, pp. 51-52.

8. Bunsen biographer, Georg Lockemann, incorrectly suggested that Roscoe had shown Bunsen either an Argand burner or a burner based on Faraday's original design. Though a gauze burner is in fact a modified Argand burner, there is no hint in Roscoe's account that he was even aware of Faraday's earlier burner. This questionable speculation was repeated in G. Lockemann, "The Centenary of the Bunsen Burner," *J. Chem. Educ.*, **1956**, *33*, 20-22.

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10. J. J. Griffin, *Chemical Handicraft: A Classified and Descriptive Catalogue of Chemical Apparatus*, Griffin & Sons: London, 1877, p. 87, item 920.

Publication History

First published in *J. Chem. Educ.*, **2005**, *82*, 518.

XII

The Origin of the 18-Electron Rule

Question

What is the origin of the 18-electron rule?

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Answer

The 18-electron rule, much beloved of the organometallic chemist, was first formulated by the American chemist, Irving Langmuir (figure 1), in 1921 as part of his program to extend the Lewis static-atom model beyond argon in the periodic table (1). Langmuir derived an equation relating the number of shared electrons or the covalence (ν_c) of a given atom in a compound or complex ion to the difference between the number of valence electrons (e) in the isolated atom and the number of electrons (s) required for completion of its valence shell:

$$\nu_c = s - e \quad [1]$$

In the case of organic chemistry, where the component atoms obeyed the octet rule, this reduced to

$$\nu_c = 8 - e \quad [2]$$

whereas in the case of the transition-metal carbonyls, it reduced to:

$$\nu_c = 18 - e \quad [3]$$

Assuming 2c-2e metal-carbon bonds in all cases, Langmuir applied equation 3 to the examples of $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Mo}(\text{CO})_6$. Yet further applications of Langmuir's equation to rationalize speculative metal carbonyl structures were made by the American chemist, Arthur A. Blanchard, in 1926 (2).

An alternative electron-counting procedure, based on the newer electronic configurations of Bohr and Bury, was introduced by the British chemist, Nevil Sidgwick (figure 2), in 1923 (3). Known as the effec-



Figure 1. Irving Langmuir (1881-1957).

tive atomic number (*EAN*) rule, it focused not just on the valence-shell electron count, but on the total atom electron count. Attainment of an octet or an 18-electron outer configuration was equivalent to attaining the total electron count (or atomic number) of the nearest noble gas. Sidgwick's counting procedure was first applied to transition-metal carbonyls and nitrosyls by the German chemist, F. Reiff, in 1931 (4) and in 1934 Sidgwick extended its use to include bridged, as well as mononuclear, complexes (5). By 1940 Blanchard was also using Sidgwick's version of the rule (6) and the same is true of many inorganic texts published in the 1950s (7).

In the late 1960s, however, there was a reversion to the earlier electron-counting procedure of Langmuir (8), no doubt because Sidgwick's procedure, which includes the chemically inactive core electrons, results in a separate numerical stability standard for each row



Figure 2. Nevil Vincent Sidgwick (1873-1952).

of the transition block, whereas Langmuir's procedure, like the octet rule, makes use of a single numerical standard applicable to the entire block. Like the octet rule, the 18-electron rule is subject to many exceptions, but has, nevertheless, proved very useful as a systematizing tool in organometallic chemistry (9).

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2. A. A. Blanchard, W. L. Gulliland, "The Constitution of Nickel Carbonyl and the Nature of Secondary Valence," *J. Am. Chem. Soc.*, **1926**, *48*, 872-882.
3. N. V. Sidgwick, "The Nature of the Non-polar Link," *Trans. Faraday Soc.*, **1923**, *19*, 469-475. Also N. V. Sidgwick, *The Electronic Theory of Valency*, Clarendon Press: Oxford, 1927, Chap. 10.
4. F. Reiff, "Konstitution und Eigenschaften des Tri-carbonylnitrosylkobalt," *Z. anorg. Chem.*, **1931**, *202*, 375-381.
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6. A. A. Blanchard, "Valence Relations Among the Metal Carbonyls," *Chem. Rev.*, **1940**, *26*, 409-422.
7. See, for example, T. Moeller, *Inorganic Chemistry: An Advanced Text*, Wiley: New York, NY, 1952, pp. 233-234, 599-600, 705-706.
8. G. E. Coates, M. L. Green, P. Powell, K. Wade, *Principles of Organometallic Chemistry*, Methuen: London, 1968, Chap. 5.
9. P. R. Mitchell, J. Parish, "The Eighteen-Electron Rule," *J. Chem. Educ.*, **1969**, *46*, 811-814.

Publication History

First published in *J. Chem. Educ.*, **2005**, *82*, 28.

Update

Since writing this column, the nature of the rule has once more been discussed in:

- * P. Pyykkö, "Understanding the Eighteen-Electron Rule," *J. Organomet. Chem.*, **2006**, *691*, 4336-4340.

I have also discovered some early papers dealing with the application of the EAN rule to paramagnetic transition-metal compounds:

- * D. M. Bose, "Valence Theories and the Magnetic Properties of Complex Salts," *Nature*, **1926**, *117*, 84.
- * D. M. Bose, "Über die Magnetonezahl in den Komplexverbindungen einer paramagnetischer Elemente," *Z. Phys.*, **1926**, *35*, 219-223.

XIII

The Origins of the Symbols A and Z for Atomic Weight and Number

Question

What is the origin of the symbols A and Z for atomic weight and number?

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Answer

Though neither symbol seems logical from the standpoint of an English-speaking chemist, they make perfect sense to someone who speaks German, as they are abbreviations for the German words *Atomgewichte* or “atomic weight” and *Zahl* or “number.” Until recently, a lower-case z was also widely used in the electrochemical literature to represent the number of ionic charges and appeared not only in Faraday’s law (1):

$$it = zFN \quad [1]$$

and the Nernst equation:

$$E = E^\circ - (RT/zF)\ln Q \quad [2]$$

but also in such thermodynamic relationships as:

$$\Delta G = -zFE \quad [3]$$

The precise origins of the use of an upper-case Z for the number of nuclear charges are more difficult to trace. Most of Bohr’s early work on the quantized Rutherford atom was published in English and, in keeping with this, he used the letter N rather than Z to represent the number of nuclear charges (2), a practice that was also adopted by Moseley in his seminal papers on the correlation between atomic numbers and X-ray spectra (3). The most likely source for the switch to the German symbol lies in Arnold Sommerfeld’s (figure 1) later refinement of the original Bohr model, as most of Sommerfeld’s work originally appeared in German



Figure 1. A young Arnold Sommerfeld (1868-1951).

rather than English (4). An additional factor which may have played a role in the universal adoption of the German, rather than the English, symbol is that the latter has the disadvantage of possible confusion with the symbols for both nitrogen and Avogadro’s number. In any case, by the late 1920s, the use of Z rather than N for atomic number and nuclear charge was virtually universal (5).

Literature Cited

1. M. L. McGlashan, *Physico-Chemical Quantities and Units*, Royal Institute of Chemistry: London, 1968.
2. This symbolism was introduced in Part II of Bohr’s 1913 trilogy. See, N. Bohr, “On the Constitution of Atoms and Molecules. II. Systems Containing Only a Single

Nucleus," *Phil. Mag.*, **1913**, 26, 476-502. Reprinted in L. Rosenfeld, Ed., *Niels Bohr, Collected Works*, North Holland Publishing: Amsterdam, Vol. 2, 1981, pp. 188-214. The same symbolism is also used in other early papers of Bohr reprinted in this volume.

3. H. G. J. Moseley, "The High-Frequency Spectra of the Elements," *Phil. Mag.*, **1913**, 26, 1024-1034; *Ibid.*, **1914**, 27, 703-713. In Part I Moseley used N not only for atomic number but also for Avogadro's number and for Rydberg's constant, thus providing an excellent example of the potential for confusion associated with the English abbreviation.

4. A. Sommerfeld, *Atombau und Spektrallinien*, Vieweg: Braunschweig, 1919. The 1923 English translation of the 3rd German edition retained Sommerfeld's use of Z for the number of nuclear charges. See A. Sommerfeld, *Atomic Structure and Spectral Lines*, Dutton: New York, NY, 1923, pp. 13, 62-65.

5. See, for example, A. E. Ruark, H. C. Urey, *Atoms, Molecules and Quanta*, McGraw-Hill: New York, NY, 1930.

Publication History

First published in *J. Chem. Educ.*, **2005**, 82, 1764.

XIV

The Symbolism of Chemical Equations

Question

What is the origin of the equal sign and double arrow symbolism used in balanced chemical equations?

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Answer

The earliest precursor of the modern chemical equation is the affinity diagram, first introduced in the late 18th century, and designed to highlight the various competing interparticle forces or affinities at work in a given chemical reaction. A typical example, taken from Antoine Fourcroy's textbook of 1789, is shown in figure 1 for the double decomposition reaction between calcium nitrate and potassium sulfate (1).

By the 1830s the hypothetical numerical affinity values used in these diagrams had been replaced by equivalent or atomic weight values, as shown in the example in figure 2, taken from the 1833 volume on *Chemical Diagrams* by Lee (2). Such diagrams continued to be used well into the 1860s, though the printed names for the various chemicals were gradually replaced by compositional formulas based on the atomic symbolism first introduced by Berzelius in 1814 (3).

The appearance of linear chemical equations and the accompanying use of the equal sign to separate the reactants from the products began in the late 1840s. They were, for example, introduced in the 1847 edition

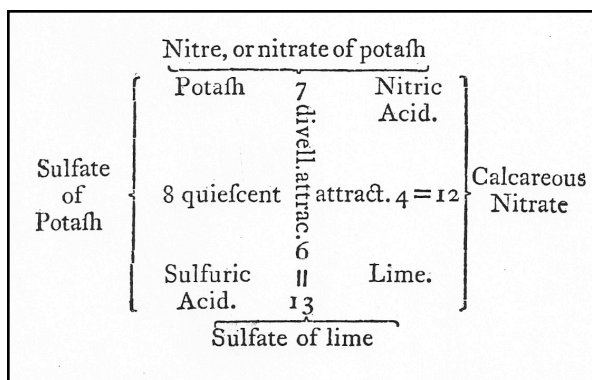


Figure 1. A typical 18th-century affinity diagram (1)

of George Fownes' introductory textbook, where they appear as a supplement to the more common affinity diagrams (4). It has been argued that this switch from diagrams to linear equations reflects a change in emphasis from the inequality of Newtonian forces of affinity to the conservation of Daltonian atomic and/or equivalent weights in chemical reactions (5).

Though the concept of chemical equilibrium was introduced by Berthollet as early as 1801 and was given a kinetic rationale by Guldberg and Waage as early as 1864, it was not until the end of the 19th century that this concept impacted on the symbolism used in the writing of chemical equations. In 1894 Ostwald suggested replacing the equal sign by a flattened "z" to indicate the presence of a reversible equilibrium (6), and in 1898 van't Hoff introduced the use of double arrows for the same purpose (7). A more elaborate symbolism was proposed by Marshall in 1902 which included the use of the currently favored double barb for equilibrium reactions (8).

Literature Cited

1. A. Fourcroy, *Elements of Natural History and Chemistry*, Vol. 1, Elliot and Kay: London, 1790, p. 65. This is a translation of the 3rd French edition of 1789. More elaborate examples of these diagrams may be found in T. Bergman, *A Dissertation on Elective Attractions*, Murray:

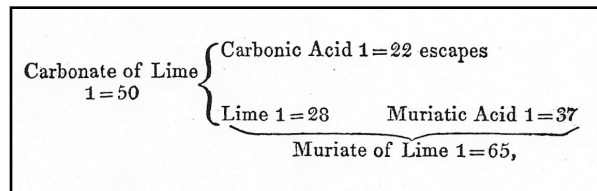


Figure 2. An early 19th-century reaction diagram using equivalent weights (2).

London, 1785. This is an English translation of the original Latin edition of 1775.

2. A. Lee, *Chemical Diagrams, Accompanied by a Concise Description of Each Decomposition*, Cox: London, 1833.

3. J. D. Steele, *A Fourteen Weeks Course in Chemistry*, Barnes: New York, NY, 1868. This was the most popular American high school text of the last quarter of the 19th century and contains more than a dozen reaction diagrams using the symbolism of Berzelius.

4. G. A. Fownes, *Manual of Elementary Chemistry, Theoretical and Practical*, 7th ed. Blanchard and Lee: Philadelphia, 1864. See the preface to the first edition of 1847, p. x. Dual use of both linear equations and affinity diagrams continued at least until the 10th edition of 1868.

5. A. Thackray, *Atoms and Powers. An Essay on Newtonian Matter-Theory and the Development of Chemistry*, Harvard: Cambridge, MA, 1970, p. 276.

6. W. Ostwald, *Die wissenschaftlichen Grundlagen der analytischen Chemie*, Engelmann: Leipzig, 1894, p. 54.

7. J. H. van't Hoff, *Lectures on Theoretical and Physical Chemistry*, Vol. 1, Arnold: London, 1898, p. 13.

8. H. Marshall, "Vorschlag, betreffend den Gebrauch modifizierter Gleichheitszeichen in der chemischen Zeichensprache," *Z. physik. Chem.*, **1902**, *41*, 103-106.

Publication History

First published in *J. Chem. Educ.*, **2005**, *82*, 1461.

Update

Since writing the original column I have discovered that van't Hoff had actually introduced the double-arrow symbolism for equilibrium reactions as early as 1884. See:

* J. H. van't Hoff, *Etudes de dynamique chimique*, Muller: Amsterdam, 1884, p. 5.

XV

The Origins of Positive and Negative in Electricity

Question

What is the origin of the positive and negative sign notation in electricity ?

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Answer

The terms positive and negative were first introduced into electrical theory by Benjamin Franklin (figure 1) in 1747 (1). Franklin is considered to be the originator of the single-fluid theory of electricity, in contrast to the two-fluid (i.e., vitreous and resinous) theory proposed earlier by the Frenchman, Charles Dufay (2). According to Franklin, electrically neutral matter contained a certain equilibrium amount of electrical fluid. However, rubbing an object disturbed that equilibrium and caused certain objects to acquire an excess of electrical fluid and others to acquire a defect of fluid. The terms positive and negative originally had nothing to do with so-called inherent electrical charge, but rather indicated which object had an excess of electrical fluid (positive) and which had a deficiency (negative).

The electrical fluid was attracted to matter but was self-repulsive. Consequently positive-negative interactions were attractive, leading to a flow of fluid from the positive to the negative object and the reestablishment of electrical equilibrium, whereas positive-positive interactions were repulsive. Franklin did not recognize the existence of negative-negative repulsions, and it remained for the German-Russian physicist, Franz Aepinus (1724-1802), to point out that their existence required the additional hypothesis that matter-matter interactions were also inherently repulsive (3). Since this assumption was at odds with the traditional assumption, based on both the theory of gravitation and chemical affinity, that matter-matter interactions were inherently attractive, the two-fluid theory remained dominant throughout most of the 19th century.



Figure 1. Benjamin Franklin (1706-1790).

The most obvious interpretation of the Franklin-Aepinus theory in modern terms is that the electrical fluid corresponds to the electron cloud of an atom and the underlying matter to the atomic nucleus. Unfortunately modern theory also reveals that Franklin's assignments of positive and negative accumulations of electrical fluid are exactly the reverse of those corresponding to an excess or deficiency of electrons, thus necessitating the assignment of a negative sign to electron excesses and a positive sign to electron deficiencies. The result is our current convention of using inherent charge signs and the continued practice of defining current direction as positive charge flow, though in fact it is the negative electrons that are really flowing in the opposite direction.

Franklin's original assignment of positive and negative was an accident of the fact that he began his

electrical experiments as a result of having received a glass “electric tube” as a gift from the Englishman, Peter Collinson, and his assumption that rubbing caused it to accumulate excess electrical fluid (in fact the glass loses electrons to the silk). Had he instead received an amber or resin rod and made the same assumption (amber gains electrons when rubbed with flannel), our current conventions would correspond to Franklin’s original intentions (4).

It should be noted that Franklin did make some attempts to verify his initial assumption and in his early letters to Collinson describes his efforts to determine the “afflux and efflux” of the electrical fluid between objects by means of (5):

... little, light windmill-wheels made of stiff paper vanes, fixed obliquely, and turning freely on fine wire axes; also by little wheels of the same matter, but formed like water-wheels.

Later he thought he could deduce the direction of fluid flow by observing the nature of the electrical discharges around objects (6):

When the brush is long, large, and much diverging, the body to which it joins seems to me to be throwing the fire out; and when the contrary appears, it seems to be drinking in.

Needless to say, both methods were defective and he never detected the fallacy of his initial assumption.

Literature Cited

1. B. Franklin, *Letters and Papers on Electricity*, in J. Sparks, Ed., *The Works of Benjamin Franklin*, Vol. V, Childs & Peterson: Philadelphia, PA, 1840.
2. D. Roller, D. H. D. Roller, *The Development of the Concept of Electrical Charge*, Harvard Case Histories in Experimental Science, No. 8, Harvard: Cambridge, 1964.
3. F. U. T. Aepinus, *Essay on the Theory of Electricity and Magnetism*, Princeton University Press: Princeton, NJ., 1979. English translation of the original Russian edition of 1759.
4. J. Pilley, *Electricity*, Clarendon: Oxford, 1933, p. 33.
5. Letter to Peter Collinson of 11 July 1747, Reference 1, p. 184. An attached note indicates that by 1750 Franklin was aware that the rotation of the paper vanes was due to electrical repulsions and not to the flow of the electrical fluid.
6. Letter to E. Kinnersley of 17 March 1752, Reference 1, p. 282.

Publication History

First published in *J. Chem. Educ.*, **2005**, 82, 988.

XVI

The Origins of the Liebig Condenser

Question

When and where did Liebig propose his famous condenser?

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Answer

The term Liebig condenser, named in honor of the 19th-century German organic chemist, Justus von Liebig (figure 1), is usually applied to laboratory scale, counter-current, water condensers made of two concentric tubes – an inner distillation tube and an outer cooling jacket through which there is a continuous circulation of the cooling water. It has been known for more than a century that Liebig was not the original inventor of this ubiquitous piece of laboratory equipment. As early as 1896, Georg Kahlbaum noted that the counter-current condenser was actually first described in 1771 by the German chemist, Christian Ehrenfried Weigel (1748-1831) (1, 2), and, a few years later, Max Speter

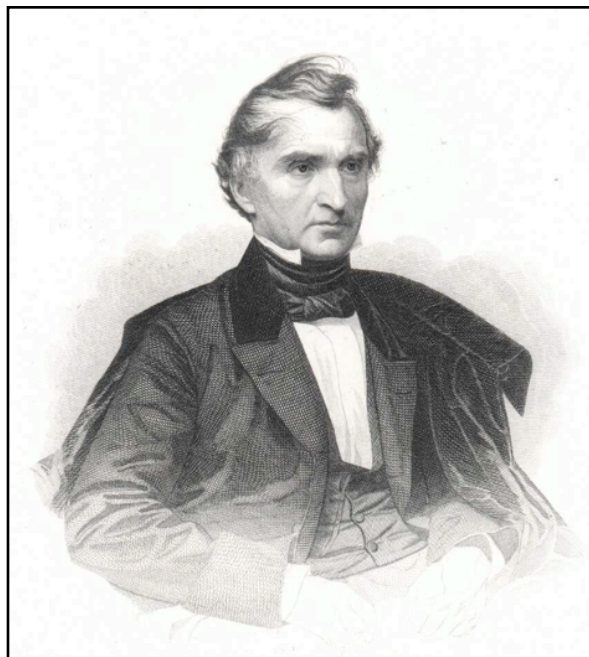


Figure 1. Justus von Liebig (1803-1873).

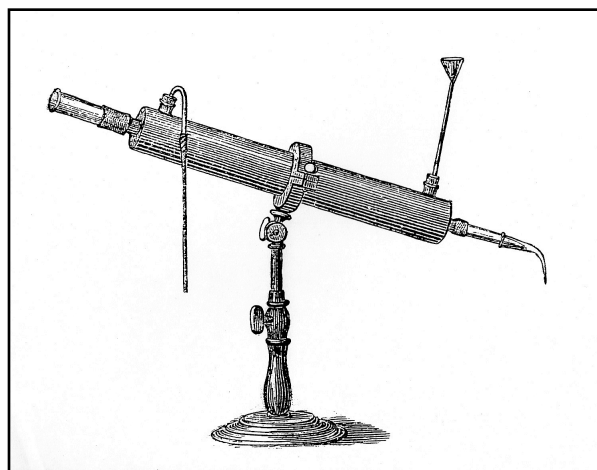


Figure 2. A woodcut of an early 19th-century version of the Liebig condenser (10).

(3) uncovered two additional, but apparently independent, inventors – the Frenchman, P. J. Poissonier, in 1779 (4) and the Finnish chemist, Johan Gadolin (1760-1852) in 1791 (5).

In Weigel's original design, the cooling water was confined between an inner and outer tube made of tin or zinc and the glass distillation tube did not come into direct contact with the cooling water but was rather suspended inside the inner metal tube. Some improvements in Weigel's design were made in 1794 by the German pharmacist, Johann Göttling (1755-1809) (6), and in 1843 Liebig, who incorrectly attributed the condenser to Göttling instead of Weigel, described several further improvements (7). In Liebig's case (figure 2), these apparently consisted of eliminating the inner metal tube and tapering the cooling jacket at each end so that the glass distillation tube could be directly sealed to the outer metal jacket by means of either corks or sections of rubber tubing, thus allowing the

distillation tube to come into direct contact with the cooling water (8).

The large number of chemists and pharmacists trained by Liebig, and who first came into contact with his version of the condenser in his laboratory at Gießen and later at Munich, no doubt accounts for his name eclipsing that of its true inventors, a misidentification that was already in the chemical literature by the 1840s (9) and which has since been reinforced by countless apparatus dealers. Though most specialized histories of distillation give the correct origins of the condenser (10, 11), its identification with Liebig alone persists in most popular articles and histories of chemistry.

Literature Cited

1. G. W. Kahlbaum, "Der sogenannte Liebig'sche Kühapparat," *Berichte*, **1896**, 29, 69-71.
2. C. E. Weigel, *Observationes chemicæ et mineralogicæ*, Goettingæ, 1771.
3. M. Speter, "Geschichte des Liebig'schen Kühapparates," *Chem. Ztg.*, **1908**, 32, 3-5.
4. P. J. Poissonnier, *Appareil distillatoire présenté au Ministre de la Marine*, Paris, 1779.
5. J. Gadolin, "Beskrifning på en forbatrad Afkylnings-Anstalt vid Branvins-Brannerier," *Kongl. Vetenskaps Academiens Nya Handlingar*, **1791**, 12, 283.
6. J. F. Göttling, *Taschenbuch für Scheidekünstler und Apotheker*, 15th ed., Weimar, 1794, p. 129.
7. J. Liebig, *Handbuch der Chemie*, Vol. 1, Winter: Heidelberg, 1843, pp. 173-175.
8. See, for example, C. Ettl, "Destillation," in J. Liebig, J. C. Poggendorff, F. Wöhler, Eds., *Handwörterbuch der reinen und angewandten Chemie*, Vol. 2, Vieweg: Braunschweig, 1842, pp. 531-533.
9. A photograph of two of these Weigel-Göttling-Liebig condensers obtained from Liebig's Munich laboratory can be found in M. Speter, "Die historischen chemischen Originalapparate des 'Deutschen Museums von Meisterwerken der Naturwissenschaft und Technik' zu München," *Zeit. angew. Chem.*, **1908**, 21, 625-632.
10. H. Schelenz, *Zur Geschichte der Pharmazeutisch-Chemischen Destilliergerate*, Schimmel: Leipzig, 1911, pp. 84-87.
11. R. J. Forbes, *A Short History of the Art of Distillation*, Brill: Leiden, 1970, pp. 254-257.

Publication History

First published in *J. Chem. Educ.*, **2006**, 83, 23.

XVII

The Origin of Pyrex

Question

What is the origin of Pyrex?

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Answer

Ideally the glass used to make common laboratory apparatus, such as flasks, beakers, and retorts, should be colorless and transparent; have both a high melting point and resistance to chemical attack by water, alkalis, and acids; and be able to sustain both thermal and mechanical stress. Prior to the 19th century, laboratory glassware did poorly in all of these categories. The glass was often colored brown or green due to iron contamination, had a low melting point, and was extensively corroded by boiling water and alkalis, as witnessed by Lavoisier's famous experiment refuting the supposed transmutation of water into earth during refluxing (1). Because the glass was quite thick, flasks and retorts seldom survived the heating process despite the practice of luting or coating the outside with a mixture of clay and binder prior to heating (2). This was because silica-based glass is a poor conductor of heat. Consequently, when glass objects are rapidly heated or cooled, the temperature of the exterior surface changes much more rapidly than that of the interior. If the specific volume of the glass is highly sensitive to temperature, this imbalance can induce mechanical strains in the glass and result in cracking.

One solution to the heating problem was to make the glass apparatus as thin as possible in order to reduce the temperature gradient between the outer surface and the interior and, starting in the 19th century, thin-walled laboratory glassware made of relatively hard Bohemian glass (also called potash or lime glass because of its high K_2O and CaO content) became common (3). A second solution is to find a glass composition that has a low coefficient of thermal expansion, thus reducing the mechanical stress induced by uneven heating and cooling rates. This was accomplished by the German chemist, Otto Schott (figure 1), through his

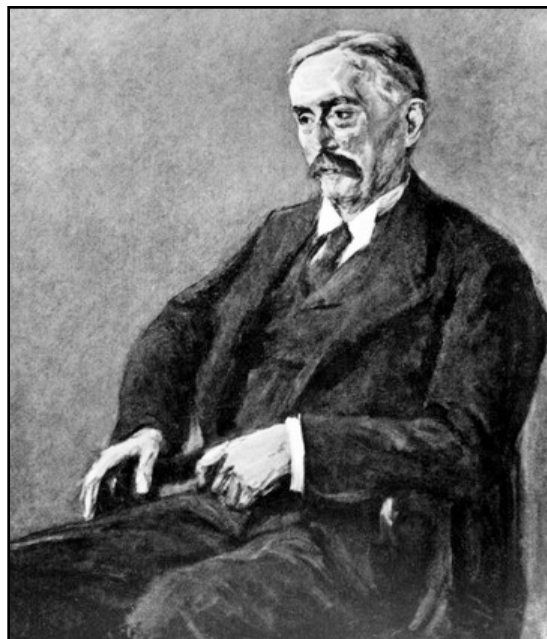


Figure 1. Otto Friedrich Schott (1851-1935).

discovery of borosilicate glass, which has a high B_2O_5 content and a coefficient of thermal expansion that is roughly half that of common lime glass. Originally developed by the Jena Glassworks in the 1880s for use in optical systems, borosilicate glass was soon employed for the glass shades of gas mantles and for thermometer stems and, by the end of the century, so-called "Jena" brand borosilicate laboratory glassware was also available.

By 1902 at least one American firm (Whitall Tatum & Co.) was also making borosilicate laboratory glassware under the trade name of "Nonsol." However, most American glass companies had trouble competing with German-made scientific glassware because it was classified as educational and was hence exempt from import duties. This situation was changed by the First World War, and in 1915 Corning Glass introduced its own brand of borosilicate glass under the trade name of "Pyrex." Initially marketed as glass cookware, the company began offering a modest selection of Pyrex brand beakers, flasks, and glass tubing in 1916 (4). In 1918 the Bureau of Standards published a study of

laboratory glassware comparing the most popular brand of lime glass (Kavalier) with six brands of borosilicate glass (Macbeth-Evans, Pyrex, Jena, Non-sol, Fry, and Libbey) (5). The borosilicate glasses were found to be uniformly superior to lime glass with respect to chemical attack by water and alkalis and with respect to thermal shock, and, of the various borosilicate glasses, Pyrex received the highest rating with respect to its ability to sustain mechanical shock.

As for the origin of the name Pyrex, at least three rationales have been suggested. Reflecting its initial use for cookware, including pie pans, it is either an English-Latin (*py* = pie + *rex* = king) hybrid for “Pie King” or a Greek-Latin hybrid (*pyr* = fire + *rex* = king) for “Fire King,” or it is a contraction for its most important physical property: low thermal (*pyr*) expansion (*ex*) (6). As it turns out, none of these are correct, though the first version is closer to the truth than the others. Reflecting its use for glass pie pans, it was originally called “Pie Rite” or “Py-Right,” but the name was eventually changed to Pyrex in order to rhyme with “Nonex” (for nonexpand) – a earlier brand of borosilicate glass that Corning had marketed for use in railroad signal lamps (7).

Literature Cited

1. A. Lavoisier, “Sur la nature de l'eau et sur les expériences par lesquelles on a prétendu prouver la possibilité de son changement en terre,” *Mem. Acad. Sci.*, **1770**, 73, 90. Reprinted in E. Grimaux, Ed., *Oeuvres de Lavoisier*, Vol. II, Imprimerie Impériale: Paris, 1862, pp. 1-28. Failure to heed this property of glass also led to the polywater scandal of the

1960s. See F. Frank, *Polywater*, MIT: Cambridge, MA, 1981.

2. This is the primary reason why most surviving chemical glassware dates from the 18th century or later. So-called examples of renaissance and medieval laboratory glassware found in many European museums are in fact mostly modern reproductions. However, many broken fragments of older glassware have been recovered by archaeologists. See R. G. W. Anderson, “The Archaeology of Chemistry,” in F. L. Holmes, T. H. Levere, Eds., *Instruments and Experimentation in the History of Chemistry*, MIT: Cambridge, MA., 2000, Chap. 1.

3. E. Child, *The Tools of the Chemist: Their Ancestry and American Evolution*, Reinhold: New York, NY, 1940, pp. 93-111.

4. An early catalog for Pyrex brand laboratory glassware in the Oesper Collections is dated 1916 and is essentially an eight-page pamphlet.

5. P. H. Walker, F. A. Smither, *Comparative Tests of Chemical Glassware*, Technological Papers of the Bureau of Standards, No. 107, Government Printing Office: Washington, DC, 1918.

6. In the 1930s the name Pyrex was also employed for a brand of carbon tetrachloride used in fire extinguishers. In this context, it no doubt stood for a contraction of fire (*pyr*) and extinguish (*ex*). See J. Grant, Ed. *Hackh's Chemical Dictionary*, 3rd ed., Blakiston: Philadelphia, PA, 1944, p. 698.

7. R. L. Blaszczyk, *Imaging Consumers: Design and Innovation from Wedgwood to Corning*, Johns Hopkins: Baltimore, MD, 2000, p. 220.

Publication History

First published in *J. Chem. Educ.*, **2006**, 83, 692-693.

XVIII

The Origins of the Ortho-, Meta-, and Para-Nomenclature

Question

What is the origin of the prefixes ortho-, meta- and para- in both inorganic and organic chemical nomenclature?

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Answer

The prefix ortho- comes from the Greek *ortho-*, meaning “true or correct,” as in the word orthodox. The prefix meta- comes from the Greek *meta-*, meaning “following or after.” Thus the word metaphysics is a result of the coincidence that early editors of the works of Aristotle arranged his writings so that those dealing with speculative topics followed or came after those dealing with physics. Likewise, the prefix para- comes from the Greek *para-*, meaning “akin to or similar,” as in the word paraphrase.

The prefixes meta- and para- were both introduced into chemistry in the 1830s to describe closely related compounds, including various isomers, polymers, and compounds derived from one another via dehydration reactions. Thus in 1830 Berzelius suggested the name paratartaric acid for the racemic form of tartaric acid (1), and in 1833 Graham suggested the term metaphosphoric acid for HPO_3 (2). Within the context of the dualistic theory used at the time, acids were considered to be hydrates of the corresponding acidic oxides, and thus Graham viewed metaphosphoric acid as a monohydrate of P_2O_5 (i.e., $\text{P}_2\text{O}_5 \cdot \text{H}_2\text{O} \approx 2\text{HPO}_3$), derived via dehydration from the parent phosphoric acid, which he viewed as the trihydrate of P_2O_5 (i.e., $\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O} \approx 2\text{H}_3\text{PO}_4$). In 1859 William Odling proposed the use of the prefix ortho- to designate the acid corresponding to the highest degree of hydration and applied the resulting ortho-meta nomenclature to the salts of various inorganic oxoacids, including both the silicates and the phosphates (3). Note that, within this context,



Figure 1. Wilhelm Körner (1839-1925).

the terms ortho- and meta- have a certain logic as the ortho compounds are viewed as the “true or original” compounds and the meta as those which “follow or result” from dehydration.

Application of all three prefixes to the various isomers of disubstituted benzene derivatives was first popularized in the period 1866-1874 by the German-Italian chemist, Wilhelm Körner (figure 1), in connection with his pioneering determination of the structures of these compounds using of the technique of derivative isomer counting (4). Given the rather vague meaning of these terms, it is apparent that, within this context, the specific identification of the term ortho with the 1,2 isomer, meta with the 1,3 isomer, and para with the 1,4 isomer is essentially arbitrary, and indeed, Körner originally used the term ortho to designate the

1,4 isomer, the term meta to designate the 1,2 isomer and the term para to designate the 1,3 isomer. Failure of later chemists to heed Körner's original choices eventually led to our current equally arbitrary usage, which was first officially adopted by the Chemical Society of London in 1879 (5).

However, despite this apparently haphazard path, one can construct a semi-plausible justification for our current usage. One of the lesser meanings of para is "beside or along side of" and this could be construed as reflecting the fact that the para isomer is usually formed along with the ortho isomer as a by-product of an aromatic substitution reaction. Likewise, since meta can mean "beyond," it may be interpreted as meaning that formation of the 1,3 meta isomer involves moving one of the substituents one position beyond that found in the 1,2 ortho isomer. Unhappily, it is not known whether such linguistic considerations actually played a role in the revision of Körner's original choices.

The terms ortho and meta continue to be used in inorganic chemistry to describe oxoacids and oxosalts formally related via dehydration, though it is now known that significant differences in structure and degree of polymerization are also involved in these reactions (6). Likewise, usage of all three prefixes to indicate various isomers is now restricted almost totally to the disubstituted derivatives of benzene, though occasional residues of the older, looser, usage to indicate closely related compounds still persist, such as the terms paraformaldehyde and paraldehyde to indicate various polymers of formaldehyde and acetaldehyde.

Literature Cited

1. M. P. Crosland, *Historical Studies in the Language of Chemistry*, Harvard: Cambridge, 1962, p. 328. Crosland fails to provide an original reference for this assertion.
2. T. Graham, "Researches on the Arsenates, Phosphates and Modifications of Phosphoric Acid," *Phil. Trans. Roy. Soc.*, **1833**, 123, 253-284.
3. W. Odling, "On Ortho and Metasilicates," *Phil. Mag.*, **1859**, 18, 368-374.
4. All of Körner's papers on this subject have been collected together in W. Körner, *Über die Bestimmung des chemischen Ortes bei den aromatischen Substanzen (1866-1874)*, Klassiker der exakten Wissenschaften, No. 174, Engelmann: Leipzig, 1910.
5. Anon. "Instructions to Abstractors," *J. Chem. Soc.*, **1879**, 35, 276-281.
6. IUPAC, *Definitive Rules for Nomenclature of Inorganic Chemistry*, Butterworths: London, 1957, p. 46.

Publication History

First published in *J. Chem. Educ.*, **2006**, 83, 356.

Update

Since writing this column I have discovered an earlier discussion of the history of this question in the privately printed book:

* L. Dobbin, "Ortho, Meta, Para," in *Occasional Fragments of Chemical History*, Privately Printed: Edinburgh, 1942, pp. 45-63.

I have also discovered an earlier example of our current identification of ortho, meta, and para with the 1,2; 1,3, and 1,4 positions, respectively, in disubstituted benzene derivatives:

* A. Ladenburg, *Theorie der aromatischen Verbindungen*, Vieweg: Braunschweig, 1876, p. 30.

XIX

Origin of the Term “Allotrope”

Question

What is the origin of the term “allotrope”?

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Canada

Answer

The term *allotrope* or *allotropic* was introduced by Berzelius in 1841 in the course of a review of the work of the German physicist, Moritz Frankenheim, on the thermal transitions between both the red and yellow forms of HgI_2 and the monoclinic and rhombic forms of sulfur (1). Frankenheim had described these transformations as examples of *isomerism*, a term that had been introduced several years earlier by Berzelius to describe substances having identical compositions but differing properties (2). Soon after, Berzelius had further distinguished between two possible causes of isomerism: *metamerism* or a difference in the arrangement of the component atoms, such as that found in ethyl formate versus methyl acetate; and *polymerism* or a difference in absolute composition, such as that found in ethene versus butene (3). However, he now pointed out that neither of these could be used to explain the difference between two forms of the same element, such as monoclinic and rhombic sulfur or graphite and diamond. This was because Berzelius, in common with most chemists of this period, believed that the pure elements were inherently monoatomic. As a consequence, they had no molecular structures to vary and any differences had to instead reside in an inherent variation in the nature of the atoms themselves. It was in order to call attention to this intrinsic difference that Berzelius proposed the new term *allotrope* as yet a third possible cause of isomerism.

Interestingly, most modern books incorrectly define this word to mean “other form,” a definition that actually corresponds to the word *allomorph* (4). In fact,

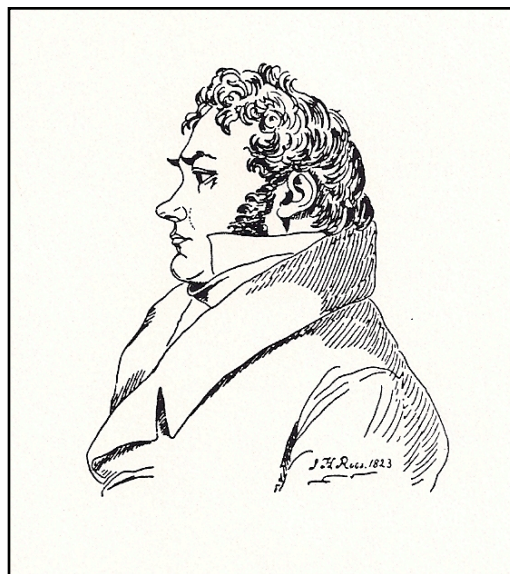


Figure 1. Jöns Jacob Berzelius (1779-1848).

the Greek word *tropos* means “to turn,” as in the biological term *tropism*, and the term *allotrope* literally means “other turn” or, more figuratively, “other behavior.”

As defined by Berzelius, allotropism served not only to rationalize the isomerism of the pure elements, it was also a third potential cause of isomerism among compounds and, in keeping with this, he proposed that the two forms of FeS_2 found in the minerals pyrites and marcasite might be the result of one containing monoclinic sulfur atoms and the other rhombic sulfur atoms. Two years later, based on the discovery of the red and white allotropes of phosphorus, he further suggested that the various forms of phosphoric acid might have a similar cause (5).

With the rise of organic chemistry in the 1840s and 1850s, Berzelius’ original definitions became muddled. Polymerism was given coequal status with isomerism as a separate and distinct phenomenon, isomerism was conflated with metamerism, and allotropy was shunted into inorganic chemistry. Berzelius had offered no opinion as to the cause of allotropy. Later speculations, largely in connection with early attempts to explain the nature of ozone, included the suggestions that it corresponded

to atoms in different states of electrification, to atoms having different energy contents, or to a difference in the arrangement of hypothetical subatomic particles (6). By the 1870s the term had become so vague that it was made the brunt of Stanley Jevons' famous quip concerning those (7):

... curious states, which chemists conveniently dispose of by calling them allotropic, a term freely used when they are puzzled to know what has happened.

But even as Jevons voiced his criticism the term was being imbued with new meaning, this time by the newly emerging field of physical chemistry. In 1877 the German physicist, Otto Lehmann, suggested that the term be used to designate all those variations of a given substance, whether element or compound, that were ultimately traceable to variations in the substance's intermolecular organization, whether these be due to changes in intermolecular structure or to changes in the degree of intermolecular association. This, in essence, subsumed all thermally induced changes in either the degree of aggregation (solid, liquid, gas) or in polymorphism. He further distinguished these underlying intermolecular causes of allotropism by the terms *physical isomerism* and *physical polymerism* in order to differentiate them from the older chemical or intramolecular isomerism and polymerism of the organic chemist, and also introduced the terms *enantiotropic* and *monotropic* to designate reversible and irreversible allotropic transformations (8, 9).

By the end of the 19th century this extended use of the term allotrope as a descriptor for phases of identical composition had become widespread in the literature dealing with the phase rule, where it persisted well into the 1940s (10-12). However, with the advent of X-ray crystal analysis in the early decades of the 20th century it became apparent that Lehmann's distinctions between physical versus chemical isomerism and physical versus chemical polymerism could no longer be maintained (13). Many solid polymorphs were in fact based on differences in the intramolecular structures of infinitely extended species rather than on differences in the intermolecular packing of discrete molecules and many changes of state actually involved concomitant changes in the degree of molecular polymerization or reversible changes in intramolecular structure.

As Lothar Meyer observed in 1888, with the acceptance of Avogadro's hypothesis and the idea that the elements can form polyatomic molecules when in the form of simple substances, it had become apparent that the underlying causes of traditional allotropy in the case of the elements and traditional isomerism and

polymerism in the case of isocompositional compounds were one and the same, and that one must either abandon the traditional restricted usage of the term allotrope (elements only) or accept the extended usage found in the older phase literature (14). The first of these choices was advocated by Wilhelm Ostwald as early as 1912 with regard to the phenomenon of polymorphism, when he noted that there (15):

... is really no reason for making this distinction [between polymorphism and allotropism], and it is preferable to allow the second less common name to die out.

Regrettably, despite this sage advice, which many have since repeated (4), and the passage of more than 90 years, the restricted use of the term allotrope (for elements only) is still endorsed by IUPAC and is still being used in most chemistry textbooks (16).

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Publication History

First published in *J. Chem. Educ.*, **2006**, 83, 838-839.

The Hirsch and Büchner Filtration Funnels

Question

What are the origins of the Hirsch and Büchner vacuum filtration funnels?

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Answer

Vacuum filtration appears to have been introduced into laboratory practice about the middle of the 19th century, probably as an adaptation of its application to industrial filtration. Writing in 1865, the Swiss chemist, Jules Piccard, recommended the apparatus shown in figure 1, consisting of a two-necked Woulfe bottle, a funnel, and a water aspirator or Geissler pump (1), and in 1868 Bunsen described an even more elaborate setup employing a thick-walled flask, a modified Sprengel pump, a pressure gauge, and a safety trap (2). The water aspirator, as Piccard noted, was a great improvement over earlier attempts to produce a vacuum using a hand-operated air pump because it generated a continuous and uniform pressure difference, whereas the intermittent pressures produced by the air pumps tended to tear the bottom out the filter paper during the vacuum stroke.

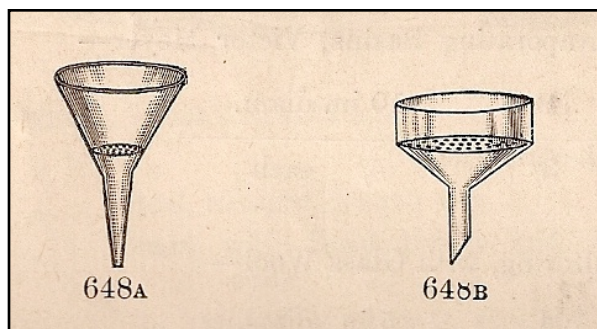


Figure 2. Early depictions of the Hirsch (left) and Büchner funnels (7).

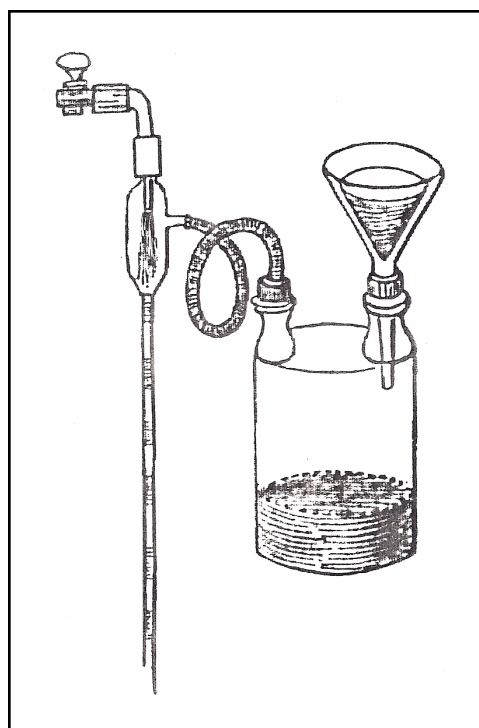


Figure 1. Piccard's original apparatus for vacuum filtration, c. 1865 (1).

Despite this improvement, use of a cone of filter paper placed in a conventional 60-degree funnel meant that the pressure differential was concentrated only at the tip of the filter cone and that, consequently, only a small portion of the available filter area was being effectively used. In 1886 Otto Witt introduced the use of a glass or porcelain plate containing perforated holes which could be wedged into a conventional funnel (3). Large enough to accommodate an unfolded disk of filter paper, it allowed one to apply the pressure differential to the entire surface rather than to just the tip. However, this device had the disadvantage that the plate did not always produce an airtight seal with the funnel and had to be reset after each usage. Hence, in 1888 the industrial chemist, R. Hirsch, patented a funnel (figure 2, left) in which the plate was permanently attached (4), and the same year, the industrial chemist,

THE HIRSCH AND BUCHNER FILTRATION FUNNELS

Ernst Büchner (not to be confused with the famous German biochemist, Eduard Buchner), described a variation of Hirsch's funnel (figure 2, right) in which the section above the perforated plate was expanded and distorted to give vertical rather than slanted sides, which meant that it could accommodate much larger filter disks (5, 6). Both the Hirsch funnel and the Büchner funnel were immediately manufactured by the German firm of Max Kaehler and Martini of Berlin, though early models were often made of enameled iron rather than of porcelain.

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Publication History

First published in *J. Chem. Educ.*, **2006**, 83, 1283.

The Origin of the Term “Base”

Question

What is the origin of the term “base”?

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Answer

The term “base” appears to have been first used in 1717 by the French chemist, Louis Lémery (1672-1743), as a synonym for the older Paracelsian term “matrix” (1). In keeping with 16th-century animism, Paracelsus had postulated that naturally occurring salts grew within the earth as a result of a universal acid or seminal principle having impregnated an earthy matrix or womb (2). By the early 1730s the newer term had largely replaced the older Paracelsian terminology and was being used by such French chemists as Henri-Louis Duhamel du Monceau (1700-1782) (3, 4).

Its modern meaning and general introduction into the chemical vocabulary, however, is usually attributed to the French chemist, Guillaume-François Rouelle (figure 1), who used the term in a memoir on salts written in 1754 (6). In this paper, which was an extension of an earlier memoir on the same subject written in 1744 (5), Rouelle pointed out that the number of known salts had increased significantly during the 17th- and early 18th-centuries, due not only to the preparation of new salts, but also to an increasing ability to distinguish between sodium and potassium compounds, and to a generalization of the concept so as to include many substances, such as the alums and vitriols (i.e., sulfates), that had been previously excluded.

In order to incorporate this newly extended concept of salt formation, Rouelle explicitly defined a neutral salt as the product formed by the union of an acid with any substance, be it a water-soluble alkali, a volatile alkali, an absorbent earth, a metal, or an oil, capable of serving as “a base” for the salt “by giving it a concrete or solid form.” Most acids known in the 18th century were volatile liquids or “spirits” capable of distillation, whereas salts, by their very nature, were

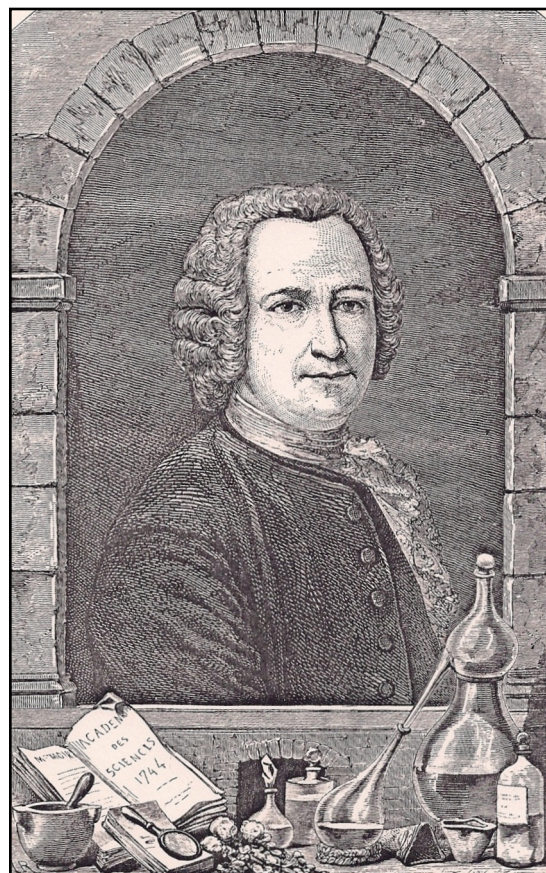


Figure 1. Guillaume-François Rouelle (1703-1770).

crystalline solids. Hence it was the substance that neutralized the acid which supposedly destroyed the volatility or spirit of the acid and which imparted the property of solidity (i.e., gave a concrete base) to the resulting salt (7).

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Publication History

First published in *J. Chem. Educ.*, **2006**, 83, 1130.

XXII

The Use of Dots in Chemical Formulas

Question

What is the origin of the use of dots in chemical formulas?

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Answer

Dots have appeared in chemical formulas in a wide variety of contexts. They were first extensively used by Berzelius (figure 1) in 1814 to abbreviate the oxygen content of various compounds. Thus, rather than write sulfur trioxide as SO_3 , Berzelius wrote just the symbol for sulfur with three dots placed above it (1). With the rise of valence theory in the 1860s, single dots placed to the upper right of a symbol were sometimes used to indicate a free or unsaturated valence, a practice still used today in writing the formulas of free radicals, where the dot is now interpreted as representing an unpaired electron (2). In keeping with this latter usage, dots are, of course, also used to represent valence electrons in modern electronic formulas or Lewis dot diagrams (3).

In the case of inorganic chemistry, the use of dots to separate the various parts of a compositional formula gradually evolved out of the electrochemical dualistic theory of composition and structure first proposed by Berzelius in 1811 (4). Dualism viewed tertiary and higher order compounds as addition adducts of simpler binary compounds. Thus copper sulfate pentahydrate was thought of as an additive adduct of the binary compounds CuO , SO_3 , and H_2O . Originally these parts were separated by means of plus signs, as in $(\text{CuO} + \text{SO}_3 + 5\text{H}_2\text{O})$. Later, in order to prevent confusion with linear chemical equations, a comma was used instead, as in $\text{CuO},\text{SO}_3,5\text{H}_2\text{O}$, and finally, by the end of the 19th century, the ubiquitous dot, as in $\text{CuO}\cdot\text{SO}_3\cdot 5\text{H}_2\text{O}$.

Of course, by the 1860s it was known that CuO and

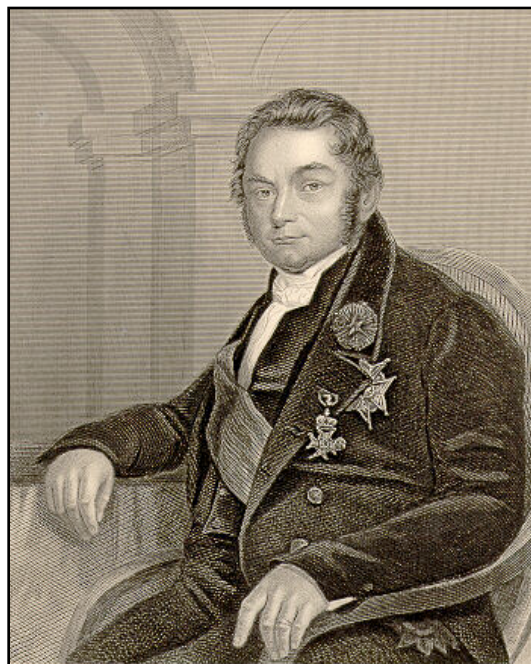


Figure 1. Jöns Jacob Berzelius (1779-1848).

SO_3 did not retain their identities as such inside copper sulfate and that, in fact, these components had undergone a significant structural reorganization on combining with one another, the results of which were better represented as $\text{Cu}(\text{SO}_4)\cdot 5\text{H}_2\text{O}$. A further resolution came with the rise of Alfred Werner's coordination theory at the end of the 19th century, which indicated that four of the five water molecules were actually bonded directly to the Cu in the form of a complex aquo ion, $\text{Cu}(\text{H}_2\text{O})_4^{2+}$, and that the formula was better expressed as $[\text{Cu}(\text{H}_2\text{O})_4][\text{SO}_4]\cdot \text{H}_2\text{O}$ (5). Hence, in the case of inorganic chemistry at least, we find that the dot was and is used essentially as an expression of ignorance to indicate that, though the parts of the molecule separated by the dot are bonded to one another in some fashion, the exact structural details of that interaction are not fully expressed in the resulting formula.

A second use of the dot occurred in the field of

organic chemistry, when, beginning in the late 1860s, it became popular to use dots to separate significant structural subunits inside organic molecules when writing linear structural formulas, as in the case of butanoic acid, $\text{CH}_3\bullet\text{CH}_2\bullet\text{CH}_2\bullet\text{COOH}$ (6). Here the dot does not express an absence of structural knowledge, but rather serves as a convenient short hand for breaking the overall molecule into structurally significant fragments.

Finally, starting in the 1890s, yet a third use of the dot evolved in connection with the construction of phase diagrams to indicate the formulas of various higher order compounds in terms of the compositions of the binary components used to synthesize them. Thus, in the ternary phase diagram for the limiting components, SiO_2 , Na_2O , and Al_2O_3 , the formulas of the various resulting complex sodium aluminosilicates are all expressed in the form $a\text{Na}_2\text{O}\bullet b\text{Al}_2\text{O}_3\bullet c\text{SiO}_2$ in which it is implicitly understood that these initial starting components do not exist as such within the resulting compounds or, in other words, that such formulas are devoid of any structural significance. Formulas of this sort are still widely used in the geochemical, glass and ceramics literature (7).

In summary, when a dot is used to break a formula into subunits, it may signify ignorance of how the subunits are structurally related, as in our inorganic example; or it may correspond to actual significant structural subunits, as in our organic example; or it may represent the combining ratios of the binary starting materials required for the synthesis of the compound, as in our phase diagram example.

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Publication History

First published in *J. Chem. Educ.*, **2006**, 83, 1590-1591.

XXIII

Origin of the Term “Hypervalent”

Question

What is the origin of the term “hypervalent”?

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Answer

The term *hypervalent* was first introduced by Jeremy Musher in 1969 to describe compounds and complex ions of the heavier main-block elements (period 3 and beyond) in which the use of traditional Lewis 2c-2e covalent bonds requires the additional assumption of “octet expansion” for the central atom (e.g. PCl_5 , SiF_6^{2-} etc.) (1). The debate over how to rationalize the bonding in these species goes back to the very origins of the electronic theory of the covalent bond and ultimately revolves around the question of whether the 2c-2e bond or the octet rule is the more rigorous bonding principle. In the 1920s a vigorous debate over this issue was carried on between G. N. Lewis and Irving Langmuir, with the former opting for octet expansion and the dominance of the 2c-2e bond (2) and the latter for the dominance of the octet rule, thus requiring the assumption that the bonding in hypervalent species was ionic rather than covalent (3).

In the late 1920s and early 1930s, Samuel Sugden, on the basis of parachor measurements, argued for the existence of 2c-1e covalent bonds and showed how they could be used, in conjunction with traditional 2c-2e covalent bonds, to rationalize the bonding in hypervalent species without the necessity of either violating the octet rule or invoking ionic bonding, but his suggestions were not widely accepted (4). Ironically, in the 1940s and 1950s essentially the same concept was invoked by Robert Rundle (figure 1) (5) and George Pimentel (6) via MO theory and their introduction of the so-called 3c-4e bond (of which only two of the four electrons are actually bonding and correspond to two collinear 2c-1e bonds in Sugden’s sense, whereas the remaining two electrons correspond to nonbonding or weakly antibonding electrons concentrated on the outer periphery of the molecule).



Figure 1. Robert Eugene Rundle (1915-1963).

In the 1960s and 1970s an extensive literature developed, based on empirical bond-length and bond-angle correlations, which argued for octet expansion, not only in the case of hypervalent species but also for purposes of invoking multiple bond character, via backbonding, in such apparently normal octet species as $\text{N}(\text{SiH}_3)_3$, S_4N_4 and ClO_4^- (7). At about the same time, quantitative MO calculations on hypervalent species began to appear which tended to support the opposite conclusion and to largely confirm the Rundle-Pimentel picture of the bonding in these species (8).

This debate continued throughout the 1980s and 1990s, when it was fueled by both the discovery of an increasing number of hypervalent species for the second row elements, for which outer d-orbital participation seemed even less likely (9), and by increasingly sophisticated calculations, the majority of which again seemed to support the dominance of the octet rule and the validity of the Rundle-Pimentel model (10), with

the provision that it was necessary to carefully distinguish between the use of “d-functions” to improve computational basis sets, on the one hand, and the use of “d-orbitals” to increase the electron population in the bonds, on the other (11).

One additional consequence of this latter phase was that the appropriateness of Musher’s term “hypervalent” also came under attack. Indeed, in the article in which Musher originally introduced the term, he essentially rejected octet expansion and opted instead for the Rundle-Pimental model, thus implying either that hypervalent species were not truly hypervalent or that the term simply denoted a species that required a bonding scheme other than the traditional Lewis 2c-2e model. In 1984 Paul von Rague van Schleyer suggested the use of the term *hypercoordinate*, rather than hypervalent, to describe such species, as this provided an empirical characterization of their experimentally observed molecular structures without the necessity of having to endorse a particular view concerning the theoretical description of their electronic bonding (12).

Despite the cogency of this suggestion, there are still dissenters (13), and despite the nearly unanimous conclusions of theoretical studies that the octet rule is a valid first approximation for the entire main-block and that it is the traditional Lewis 2c-2e model of covalent bonding which requires modification, octet expansion and the 2c-2e bond still reign supreme in introductory chemistry textbooks, in large part because of the widespread belief that they are a necessary component of the highly successful VSEPR model for the prediction of molecular geometries (14).

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Publication History

First published in *J. Chem. Educ.*, **2006**, 83, 1751-1752.

XXIV

Avogadro's Number

How and When Did It Become Associated with Avogadro's Name?

Question

How and when did Avogadro's name become associated with Avogadro's number?

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Answer

Though Avogadro's hypothesis that equal volumes of gases at constant temperature and pressure contain equal numbers of molecules became the established basis of molecular and atomic weight determinations shortly after the publication of Stanislao Cannizzaro's (1826-1910) famous pamphlet of 1858 (1), it did not become a common index entry in American textbooks until the 1880s (2). The reason for this 25-year lag was that the topics of molecular weight determinations and quantitative gas-law problems were considered too advanced for elementary texts prior to this period.

Much the same time lag is found in the case of Avogadro's constant or number. Avogadro, of course, had nothing whatsoever to do with determining this number. Rather, interest in calculating the actual number of molecules in equal volumes of gas at STP was a development of the kinetic theory of gases in the last half of the 19th century (3). The resulting value was usually reported as the number per milliliter of gas, rather than per gram molecular weight or mole of gas, and became known as Loschmidt's number in honor of the Austrian chemist, Joseph Loschmidt (1821-1895), who first suggested a method of estimating it in 1865 (4).

Both the shift to the chemically more relevant magnitude per mole of gas at STP and the association of Avogadro's name with the resulting value occurred in the first decade of the 20th century and are largely associated with the work of French physical chemist, Jean Perrin (figure 1), on the kinetic theory of

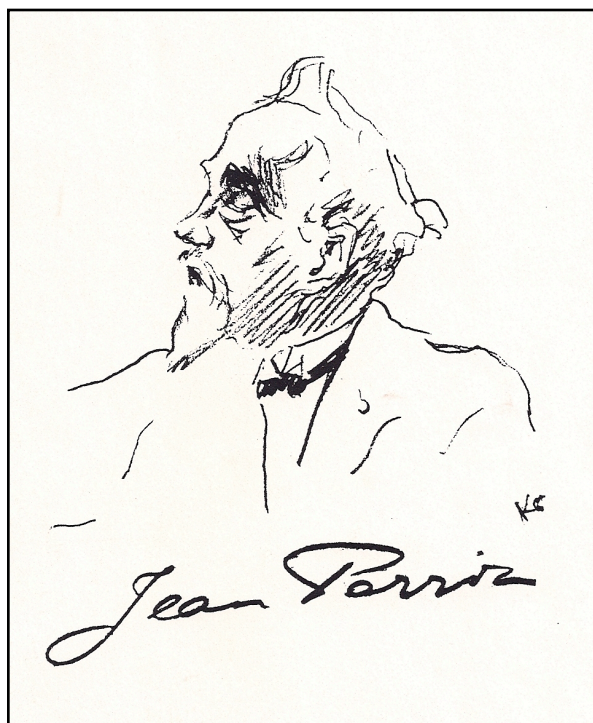


Figure 1. An autographed caricature of Jean Perrin (1870-1942) by Elisabeth Kern, c. 1930.

Brownian motion. In his initial papers of 1908 Perrin simply referred to the constant as the number of particles per "molecule-gramme," but in a massive review published in 1909 he proposed naming the constant in honor of Avogadro (5):

This invariant number N is a universal constant, which may, with justification, be called Avogadro's constant.

a suggestion which he further popularized in his two very successful books: *Brownian Movement and Molecular Reality* (1910) and *Les atomes* (1913) (5, 6).

Though Sir William Ramsay saw fit to mention Perrin's proposal in a popular book on chemistry for the layman as early as 1912 (7), American chemistry

AVOGADRO'S NUMBER

texts were slow to follow his lead, in large part because the topic was considered too advanced for introductory students. As a result, the index entry "Avogadro's Number" does not become common in American college texts until the 1930s (8), and is rare in high school texts prior to the 1950s (9).

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2. This statement is based on a survey of texts in the Oesper Collections. Thus it does not appear as an index entry in the 1869 and 1875 editions of the popular text by Cooley, but it does appear in the 1886 edition. See L. C. Cooley, *A Guide to Elementary Chemistry for Beginners*, Ivion & Blakeman: New York, NY, 1886.
3. See, for example, A. D. Risteen, *Molecules and the Molecular Theory of Matter*, Ginn: Boston, MA, 1895, p. 148.
4. L. Loschmidt, "Zur Grosse der Luftmolecküle," *Sitz. K. Akad. Wiss. Wien: Math-Naturwiss. Kl.*, **1865**, 52, 395-413.
5. J. Perrin, "Mouvement brownien et réalité moléculaire," *Ann. chim. phys.*, **1909**, 18, 1-144. The quote is on p. 16. This review also appeared in English as the book: J. Perrin, *Brownian Movement and Molecular Reality*, Taylor & Francis: London, 1910.
6. See J. Perrin, *Les atomes*, Alcan: Paris, 1913. An

English translation appears as J. Perrin, *Atoms*, Constable: London, 1916.

7. W. Ramsay, *Elements and Electrons*, Harper: New York, NY, 1912, p. 110.

8. Thus the 1921 edition of the popular college text by Harry Holmes has no index entry, and the 1930 edition mentions it only in a problem at the end of a chapter. Only in the 1936 edition is it fully integrated in the text. See H. Holmes, *General Chemistry*, 3rd ed., Macmillan: New York, NY, 1936. Likewise, it is missing from the 1918, 1926, and 1932 editions of Joel Hildebrand's text, appearing only in the 4th edition of 1940. See J. H. Hildebrand, *Principles of Chemistry*, 4th ed., Macmillan: New York, NY, 1940.

9. Thus there is no index entry for the 1931, 1942, and 1954 editions of the popular high school text by Dull, et al. It does not appear until the 1958 edition. See C. E. Dull, H. C. Metcalfe, J. E. Williams, *Modern Chemistry*, Holt, Rinehart & Winston: New York, NY, 1958.

Publication History

First published in *J. Chem. Educ.*, **2007**, 87, 223.

Update

An earlier and more comprehensive survey of the progressive introduction of Avogadro's number into the introductory chemistry textbook may be found in:

* R. M. Hawthorne, "The Mole and Avogadro's Number: A Forced Fusion of Ideas for Teaching Purposes," *J. Chem. Educ.*, **1973**, 50, 282-284.

XXV

The Origin of the s, p, d, f Orbital Labels

Question

Why are the letters s, p, d and f used to label electronic subshells?

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Answer

Writing in 1937, the British physicist, A. C. Candler, divided the history of spectroscopy into four eras, which he called the acoustics period, the series period, the old quantum period, and the newer quantum mechanical period (1, 2). "The first period," Candler observed, "began with the earliest measurements of wave lengths and continued in the work of Boltzmann, Liveing and Dewar until 1881 ... During this period any theories put forward were based on analogies with the harmonic ratios of sound." It is in this period that the story of s, p, d, and f begins and it does so with the work of the last two scientists mentioned by Candler - the British chemists, George Liveing and Sir James Dewar, who published roughly a dozen papers between 1872 and 1880 dealing with the line spectra of the alkali metals (3). In describing these spectra, Liveing and Dewar took to qualitatively characterizing the various lines in terms of both their intensity and definition as being either principle, sharp, or diffuse, and further noted that lines of a given type appeared in groups or series.

Stimulated by Johann Balmer's discovery in 1885 of an empirical formula interrelating the four principle spectral lines of hydrogen, Candler's second or "series" period was, as suggested by its name, characterized by attempts to extend Balmer's approach to other elements. In the case of the alkali metals, this work was done largely by the German team of Heinrich Kayser and Carl Runge (4), and also independently by the Swedish spectroscopist Johannes Rydberg (5).



Figure 1. Friedrich Hermann Hund (1896-1997).

Their work demonstrated that many of the lines in the spectra of the alkali metals could be mathematically modeled as the sum of three independent series, which Rydberg, following the earlier nomenclature of Liveing and Dewar, named the principle, sharp and diffuse series. In 1907 yet a fourth series of lines was discovered in the spectra of the alkali metals by Arno Bergmann and named the fundamental series (6).

As is well known, Chandler's third period was characterized by attempts, starting with Bohr's famous paper of 1913, to provide a physical model of the atom consistent with the empirical series formulas found earlier. Extending this model from hydrogen to other elements led to the introduction of a variety of more complex quantization schemes, none of which proved wholly satisfactory until the work of Stoner, Main Smith, and Pauli and the introduction of the newer

quantum mechanics in the early 1920s (Candler's fourth period). The history of this eventual resolution is far too complex to deal with in the space available. However, one of its most important consequences was the establishment of our modern electronic atomic configurations and an understanding of their relationship to the periodic table.

This breakthrough is usually attributed to a 1922 monograph by Bohr, but close inspection of Bohr's configurations shows that his subshell assignments are incorrect (7). In actual fact, our current configurations first appeared in Max Born's 1925 monograph, *Vorlesungen über Atommechanik*, though in his introduction Born indicated that both the configuration table and the discussion of its relationship to the periodic table were actually the work of "my assistant Dr. Friedrich Hund" (8). Two years later Hund expanded this work into a monograph of his own entitled *Linienspektren und periodisches System der Elemente* (9).

In the version of the configuration table which had appeared in Born's monograph, Hund (figure 1) had followed Bohr's practice of labelling the various shells and subshells in terms of their corresponding numerical quantum numbers as 3_1 , 3_2 , 3_3 etc. In his own monograph, however, he replaced the secondary quantum number with the series notations (s, p, d, and f) used by Sommerfeld and others as abbreviations for the characteristic series constant, μ , which had appeared in Rydberg's original empirical equation for the sharp, principle, diffuse and fundamental line series found the spectra of the alkali metals, and instead wrote 3s, 3p, 3d etc. (10). Beginning in the 1930s both Hund's corrected configurations and his s, p, d, f notation began to slowly leak into the chemical literature, where they have reigned supreme ever since (11).

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1. A. C. Candler, *Atomic Spectra and the Vector Model*, Vol. 1, Cambridge University Press: Cambridge, 1937, pp. 1-2.
2. For a detailed history of Candler's first two periods, see W. McGucken, *Nineteenth-Century Spectroscopy: Development of the Understanding of Spectra 1802-1897*, Johns Hopkins Press: Baltimore, MD, 1969.

3. These mostly appeared in the *Proceedings of the Royal Society* and are conveniently collected together in G. Liveing, J. Dewar, *Collected Papers on Spectroscopy*, Cambridge University Press: Cambridge, 1915.

4. H. Kayser, C. Runge, "Über die Spectren der Alkalien," *Ann Physik*, **1890**, *41*, 302-320.

5. J. R. Rydberg, "Sur la constitution des spectres linéaires des éléments chimiques," *Comptes rendus*, **1890**, *110*, 394-397.

6. A. Bergmann, *Beiträge zur Kenntniss der ultravioletten Emissionsspektren der Alkalien*, Doctoral Dissertation, Jena, 1907.

7. N. Bohr, *The Theory of Spectra and Atomic Constitution*, Cambridge University Press, Cambridge, 1922, p. 133. A more complete, but equally incorrect, table appears opposite page 129 in the second edition of 1924.

8. M. Born, *Vorlesungen über Atommechanik*, Vol. 1, Springer: Berlin, 1925, table opposite page 226.

9. F. Hund, *Linienspektren und periodisches System der Elemente*, Springer: Berlin, 1927, table opposite page 55.

10. A. Sommerfeld, *Atomic Structure and Spectral Lines*, Dutton: New York, NY, 1924, p. 376 (First German edition 1919). Interestingly Sommerfeld used *b* for Bergmann rather than *f* for fundamental as his abbreviation for the fourth series.

11. In the case of introductory textbooks this leakage was often slow. Thus both the fourth (1933) and fifth (1937) editions of James Partington's, *A Textbook of Inorganic Chemistry*, continued to use the labeling scheme found in Born and Bohr. Only in the sixth edition of 1950 did Partington finally adopt the s, p, d, f labels of Hund.

Publication History

First published in *J. Chem. Educ.*, **2007**, *84*, 757-75.

Update

Since writing the column, I have discovered that one of the first advanced monographs to employ Hund's s, p, d, f orbital notation was the 1930 monograph on the periodic table by the German chemists, Eugen Rabinowitsch and Eric Thilo:

* E. Rabinowitsch, E. Thilo, *Periodisches System: Geschichte und Theorie*, Enke: Stuttgart, 1930, pp. 244-245.

XXVI

Malic, Maleic and Malonic Acid

Question

What is the origin of the names malic, maleic and malonic acid?

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Answer

Malic acid [(HOOC)CH₂-CH(OH)(COOH)] was first isolated from apple juice by the Swedish chemist, Carl Wilhelm Scheele (figure 1), in 1785 (1). Scheele simply referred to it as “acid of apples” or as *acide de pommes* in French. Two years later, in 1787, Lavoisier and his collaborators, in their famous memoir on chemical nomenclature, suggested the alternative name *acide malique*, from the Latin *malum* or apple, and this was eventually Anglicized as malic acid (2).

In 1834 the French chemist, Théophile Jules Pelouze (1807-1867), distilled malic acid and identified among the resulting dehydration products two new acids having the same composition [(HOOC)CH=CH(COOH)], but very different properties (3). Following the suggestion of Ampère, Pelouze proposed the names *acide maléique* and *acide para-maléique* for his new compounds – names which were eventually Anglicized as maleic and para-maleic acid. Later the same year, the French chemist, Horace Demarçay, published a short note (4) pointing out that both the composition and the properties of Pelouze’s para-maleic acid were identical to those of an acid isolated two years earlier by the German chemist, F. L. Winckler, from the pharmaceutical preparation *Extractum fumariae*, which was, in turn, prepared from the herb *Fumaria officinalis* (5, 6). In recognition of this fact, Winckler had named his new compound *fumarsäure* or fumaric acid. We now know that the maleic acid of Pelouze and the fumaric acid of Winckler are an example of *cis* and *trans* isomerism and that they would, via the work of van’t Hoff and Wislicenus, play an important role in the development of modern stereochemistry in the last quarter of the 19th-century (7).

In 1858 the French chemist, Victor Dessaignes



Figure 1. Carl Wilhelm Scheele (1742-1786).

(1800-1885), prepared yet a third acid [(HOOC)-CH₂(COOH)] from malic acid via its oxidation with chromic acid, which he identified as a possible isomer of “l’acide nicotique de M. Barral.” In order to emphasize both this relationship and its preparation from malic acid, Dessaignes proposed the name *acide malonique*, which was eventually Anglicized as malonic acid (8). Thus the names of all three acids are ultimately derived from the Latin word for apples.

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2. L. Guyton de Morveau, A. Lavoisier, C. Berthollet, A. Fourcroy, *Méthode de nomenclature chimique*, Cuchet: Paris, 1787, p. 150.
3. T. J. Pelouze, “Mémoire sur les produits de la distillation de l’acide malique,” *Ann. chim. phys.*, **1834**, 56, 72-87.

4. H. Demarçay, "Identité de l'acide fumarique de M. Winckler avec l'acide para-maléique de M. Pelouze," *Ann. chim. phys.*, **1834**, *56*, 429-433.

5. F. L. Winckler, "Ueber eine neue Säure (Fumarsäure) in *Extractum Fumariae*," *Buchners Repertorium*, **1832**, *34*, 48-76.

6. The name *fumaria* or *fumatory* supposedly comes from the Latin words *fume* (smoke) and *terra* (earth) and thus means "smoke of the earth." A variety of contradictory explanations have been offered for this rather imaginative name, none of which are worth repeating here.

7. See the translations in G. M. Richardson, Ed., *The Foundations of Stereo Chemistry; Memoirs by Pasteur, van't Hoff, Le Bel, and Wislicenus*, American Book Co: New York, NY, 1901.

8. V. Dessaignes, "Note sur un acide obtenu par l'oxydation de l'acide malique," *Comptes rendus*, **1858**, *47*, 76-79.

Publication History

First published in *J. Chem. Educ.*, **2007**, *84*, 924.

Update

Since writing the column I have come upon the following rather curious anecdote concerning the Latin word *malum* or apple. It seems that the original manuscripts to the Old Testament do not specify that Eve ate an apple (which in any case is not indigenous to Palestine) while in the Garden, but rather merely that she partook of the "fruit" of the Tree of Knowledge. It is speculated that, when translating the Old Testament into Latin, the Monks translated "fruit" as "apple" because *malum* was a play on the Latin word *malus* for evil – thus providing both a pun and a metaphor for the Fall of Man.

XVII

The Origin of the Oxidation State Concept

Question

What is the origin of the oxidation state concept?

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Answer

The concept of oxidation states ultimately derives from the oxygen-based dualistic system of chemistry introduced by the French chemist, Antoine Lavoisier, in the last quarter of the 18th century (1). It is here that the terms oxidation and reduction first appear in the literal sense of the reaction of an element with oxygen and its converse. The dualistic system further recognized that a given element could exhibit several degrees of oxidation – a fact which was incorporated into Lavoisier’s reform of chemical nomenclature via the introduction of such distinctions as sulfuric versus sulfurous acid (2).

In both Lavoisier’s original system, and in its later electrochemical elaboration by Berzelius, the oxides of nonmetals were thought to function as acids and those of metals as bases. These, on reacting with one another, formed salts, which were, in effect, higher order or ternary oxides. If a particular element gave rise to several oxides, each could generate its own series of salts and these salts were interconvertible through the selective oxidation or reduction of one or both of their component oxides. Thus, using a modernized version of Berzelius’ dualistic formulas, we see that the difference between calcium sulfite [$\text{CaO}\cdot\text{SO}_2 = \text{CaSO}_3$] and calcium sulfate [$\text{CaO}\cdot\text{SO}_3 = \text{CaSO}_4$] was viewed as being literally due to the increased oxidation of the sulfur atom in the acidic oxide component, whereas the difference between ferrous sulfate [$\text{FeO}\cdot\text{SO}_3 = \text{FeSO}_4$] and ferric sulfate [$\text{Fe}_2\text{O}_3\cdot 3\text{SO}_3 = \text{Fe}_2(\text{SO}_4)_3$] was instead due to the further oxidation of the iron atom in the basic oxide component.



Figure 1. Harry Shipley Fry (1878-1949).

Starting with the discovery of Davy and others that the hydracids and halide salts of the halogens contained no oxygen, Lavoisier’s original contention that oxygen formed the common “bond of union” in all salts came under increasing attack in the first half of the 19th century. Yet, despite these discoveries, no attempt was made to discontinue the underlying practice of applying the terms oxidation and reduction to the reactions of salts and other compounds which were now known to contain no oxygen. Thus by 1884, the British chemist, M. M. Pattison Muir, had to confess that the original literal meaning of oxidation had now been considerably widened (3):

... until at present it is applied to all chemical changes

which result in an addition of a negative radicle, simple or compound, to elements or compounds, or to a decrease in the relative quantity of the positive radicle of a compound, whether this is or is not accomplished by substitution of negative radicles.

Writing over 20 years later, the British chemists, Caven and Lander, were still giving essentially the same definition, though they now also attempted to rationalize this extended usage through the concept of “equivalent” processes (4):

Oxidation may therefore be described as the conversion of a compound representing a lower into one representing a higher stage of combination with oxygen, by the addition of either oxygen or an equivalent electro negative atom or radicle, or by the removal of hydrogen or an electropositive atom or radicle. Reduction may be defined as the result of the converse operations.

Meanwhile, in the field of electrochemistry, proponents of the new ionic theory of dissociation began to forge a connection between oxidation and reduction and changes in net ionic charges. Thus, writing in 1893, Wilhelm Ostwald observed that (5):

... fundamentally, oxidation and reduction processes in electrolytes consist in the acquisition or release of ionic charges; oxidants are those substances which acquire negative charges or release positive ones, reductants are those for which the opposite takes place.

– an extension which Talbot and Blanchard tacked on to the more conventional definition in their 1907 student booklet on the ionic theory of dissociation (6):

The oxidation of any body may, then, consist in the addition of the atoms of a negative element to its molecules, atoms, or ions, or the withdrawal of the atoms of a positive element; or it may consist in the addition of positive charges of electricity, or the withdrawal of negative charges. Reduction is the reverse of this...

The fourth and final stage came with the development of the electronic theory of bonding and structure in the first quarter of the 20th century. Already in the last quarter of the previous century chemists had recognized the necessity of having to distinguish between positive and negative valence (7), and in 1907 Caven and Lander had noted in passing that “oxidation usually denotes an increase in the active valency of the central atom” – a view made even more explicit by Hildebrand in 1918 when he wrote that (4, 8):

The term oxidation is applied whenever valence takes on a more positive (or less negative) value. The opposite process ... the decrease in valence, is called by the more obvious general name of reduction.

More radical still was the impact of the ionic bonding model, as it revealed that, not only changes in polar valence, but also the loss and gain of both positive and negative atoms and of positive and negative net charges, were ultimately all reducible to one and the same process – the loss and gain of electrons – thus allowing Fry (figure 1) to conclude in 1914 that (9):

If the substance (ion, atom, or compound) loses negative electrons, it acts as a reducing agent. If it combines with negative electrons, it acts as an oxidizing agent.

As early as 1907 Talbot and Blanchard made reference to the various “oxidation states” of an element, but used the word valence to describe their numerical characterization, whereas Hildebrand preferred the term “valence number.” In 1913 Branch and Bray suggested that the term “polar number” would be less misleading (10), and in 1938 Latimer officially introduced the terms “oxidation number” or “oxidation state,” along with the parallel term “oxidation potential” (11). Though there was little controversy over the final identification of oxidation and reduction with electron loss and gain, the 20th-century chemical education literature would be characterized by considerable debate over the two related questions of how one goes about assigning oxidation numbers and how these numbers are to be used in balancing redox equations. Lack of space precludes further elaboration, but the history of both of these questions, as well as the history of the oxidation potential concept, would make interesting columns of their own.

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3. M. M. Pattison Muir, “Oxidation,” in H. Forster Morley, M. M. Pattison Muir, Eds., *Watts' Dictionary of Chemistry*, Vol. 3, Longmans, Green & Son: London, 1888, pp. 657-658.
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5. W. Ostwald, *Lehrbuch der allgemeinen Chemie*, Vol. 2(1), Engelmann: Leipzig, 1893, p. 891.

6. H. P. Talbot, A. A. Blanchard, *The Electrolytic Dissociation Theory with Some of Its Applications*, Macmillan: New York, NY, 1907, p. 54.

7. W. B. Jensen, "Electronegativity from Avogadro to Pauling. II. Late 19th- and Early 20th-Century Developments," *J. Chem. Educ.*, **2003**, 80, 279-287.

8. J. H. Hildebrand, *Principles of Chemistry*, Macmillan: New York, NY, 1918, p. 94 and Chapter 15.

9. H. S. Fry, "Positive and Negative Hydrogen, The Electronic Formula of Benzene, and the Nascent State," *J. Am. Chem. Soc.* **1914**, 36, 261-272. Definition on page 272.

10. W. C. Bray, G. Branch, "Valence and Tautomerism," *J. Am. Chem. Soc.*, **1913**, 35, 1440-1447.

11. W. M. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solution*, Prentice-Hall: New York, NY, 1938, p. vii.

Publication History

First published in *J. Chem. Educ.*, **2007**, 84, 1418-1419.

Update

Most historians attribute the first explicit identification of oxidation and reduction with electron loss and gain to Harry Shipley Fry, as was done in the original column. However, since writing the column, I have discovered an even earlier source:

* G. Buchner, *Angewandte Ionenlehre*, Lehmann: München, 1912.

where, on page 70, the author writes:

In a wider sense one can now understand the oxidation of metals as any loss of electrons whereby the positive charge increases. Reduction is then the uptake of electrons and/or loss of positive charge.

I have also discovered that Fry's mentor and colleague, Lauder Jones, used the term oxidation state to describe the sum of the polar valences on an atom as early as 1913:

* L. W. Jones, "Applications of the Electronic Conception of Valence," *Am. J. Chem.*, **1913**, 50, 414-443.

XVIII

Origin of the Soxhlet Extractor

Question

What is the origin of the Soxhlet extractor?

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Answer

The well known Soxhlet laboratory extractor was first proposed in 1879 in the course of a paper dealing with the determination of milk fat by the German agricultural chemist, Franz Ritter von Soxhlet (figure 1) (1). Just as there is some ambiguity over the relative contributions of Bunsen versus his machinist, Peter Desaga, with regard to the invention of the Bunsen burner (2), so there is also ambiguity over the invention of the extractor, as in his paper Soxhlet credited its most characteristic feature (figure 2) – the use of constant level siphon to return the extract to the solvent flask after the completion of a given extraction cycle – to one of his staff members, a “Herr Szombathy” (presumably the laboratory glassblower), though he hastened to qualify this attribution by noting that both the optimization of extractor’s dimensions and the proper conditions for its use were the result of his own laboratory studies.

The practice of solid-liquid extraction is as old as recorded history, its most common everyday uses being in the preparation of teas and perfumes. Thus, many years ago, Levey described what is thought to be the remains of a Mesopotamian hot-water extractor for organic matter dating from approximately 3500 BC (3). By the mid-19th-century a variety of terms were being used to describe various versions of this process, including maceration, infusion, decoction, lixiviation and displacement. As summarized by Morfit in 1849, the later two processes involved packing the organic matter to be extracted in either a tall cylinder or cone known as a percolator (4). This was then filled with the hot solvent (usually either alcohol or ether) which was allowed to slowly percolate through the organic matter and to drain out an opening in the bottom, where it



Figure 1. Franz Ritter von Soxhlet (1848-1926).

was collected in a flask or beaker. This process was repeated several times using fresh quantities of solvent and the combined extracts then evaporated to recover the extracted matter.

The idea of automating this process was not original to Soxhlet. Already in the 1830s the French chemist, Anselme Payen (1795-1871), had introduced a continuous extractor in which the vapor from the boiling solvent was conducted by means of a side tube to a condensing bulb (reflux condensers were not introduced until later) mounted on top of the percolation column. After passing through the organic matter in the column, the condensed solvent drained directly into the solvent flask from which it was once more evaporated for another pass through the percolator (5). Indeed, strictly speaking, the Mesopotamian

extractor described by Levey, though very crude and inefficient, was also continuous as it recirculated the hot water for repeated passes through the organic matter. Though the Soxhlet extractor is also often described as being continuous, this is inaccurate and it is better characterized as an automated batch extractor, since the extract does not continuously drain into the solvent flask, as in Payen's apparatus, but rather drains only after it has reached the critical volume determined by the height of the siphon.

Soxhlet's motivation for introducing this innovation was apparently to quantify the extraction process with the intent of using it to quantitatively determine the fat content of organic matter, and his paper contains tables listing the number of extraction cycles for each sample. Even if this feature is not of interest, the Soxhlet extractor still has the advantage of being more efficient than a continuous extractor, since in the latter there is tendency for the condensed solvent to create a channel of least resistance on passing through the organic matter, thus exposing only a fraction of it to the extraction process and then only for a very limited period of contact, whereas in the former not only does each cycle completely surround the organic matter with condensed solvent, it also prolongs the period of contact.

Though chemists would continue to propose new types of extractors long after Soxhlet, his apparatus soon came to dominate laboratory practice. Thus the 1912 catalog of Eimer and Amend, the major American supplier of laboratory apparatus in the late 19th and early 20th centuries, listed 27 different types of extractors of which seven, or nearly a fourth, were variations of Soxhlet's original design and named after him (6). By the end of the 19th century, Soxhlet's apparatus had also inspired an number of attempts to develop similar automated extractors for liquid-liquid extraction (7).

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3. M. Levey, *Chemistry and Technology in Ancient Mesopotamia*, Elsevier: Amsterdam, 1959, pp. 33-34.
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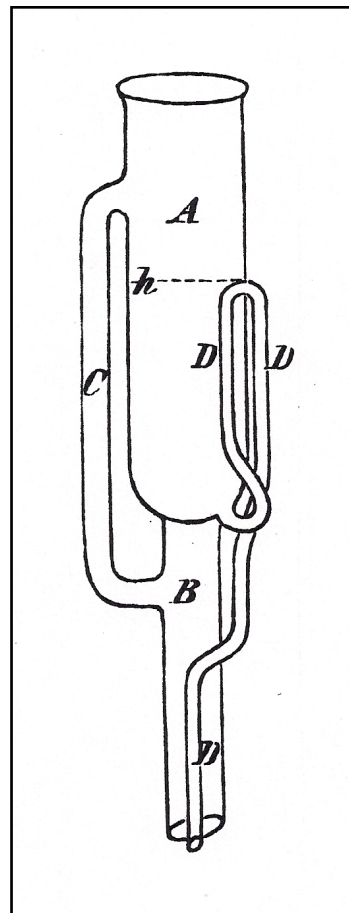


Figure 2. Soxhlet's original illustration of his automated batch extractor with its characteristic constant-level siphon (D) (1).

5. For an illustration of Payen's extractor, as well other contemporary percolators, see J. J. Griffin *Chemical Handicraft: A Classified and Descriptive Catalogue of Chemical Apparatus*, Griffin & Sons: London, 1877, pp. 169-173, item 1659.

6. *Illustrated Catalogue of Chemical Apparatus, Assay Goods, and Laboratory Supplies*, Eimer & Amend: New York, NY, 1912, pp. 157-161.

7. See the descriptions in R. Kemp, "Allgemeine chemische Laboratoriumstechnik," in E. Abderhalden, Ed., *Handbuch der Biochemischen Arbeitsmethoden*, Vol. 1, Urban and Schwarzenberg: Berlin, 1910, pp. 178-185.

Publication History

First published in *J. Chem. Educ.*, **2009**, 84, 1913-1914.

XXIX

Origin of the Polymer Concept

Question

What is the origin of the polymer concept?

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Answer

As noted in an earlier column, the term “polymer” (from the Greek *polys* meaning “many” and *meros* meaning “part”) was first introduced in 1833 by the Swedish chemist, Jöns Jakob Berzelius (1, 2). Though only a year had passed since he had introduced the term “isomer” (from the Greek *isos* meaning “equal” and *meros* meaning “part”) in order to describe substances having identical compositions but differing properties (3), he now felt it was necessary to further distinguish between two possible types of isomerism. The first of these dealt with the isomerism of two substances having identical absolute compositional formulas in which the difference in properties was attributable to *metamerism* or a difference in the arrangement of the component atomic groupings (e.g., ethyl formate versus methyl acetate). The second dealt with the isomerism of two substances having identical relative compositional formulas but different absolute compositional formulas in which the difference in properties was attributable to *polymerism* or a difference in the total number of atoms present (e.g., ethene versus butene).

With the rise of organic chemistry in the 1840s and 1850s, Berzelius’ original distinctions became muddled. Thus, writing in 1888, the British chemist, Henry Armstrong, observed that (4):

Even a superficial reader of the chemical literature will soon become aware that the terms isomeric and the kindred expressions allotropic, metameric, and polymeric are by no means used in consistent senses, and he will have considerable trouble in clearly realizing their exact and relative import.

In the end, polymerism was given coequal status with

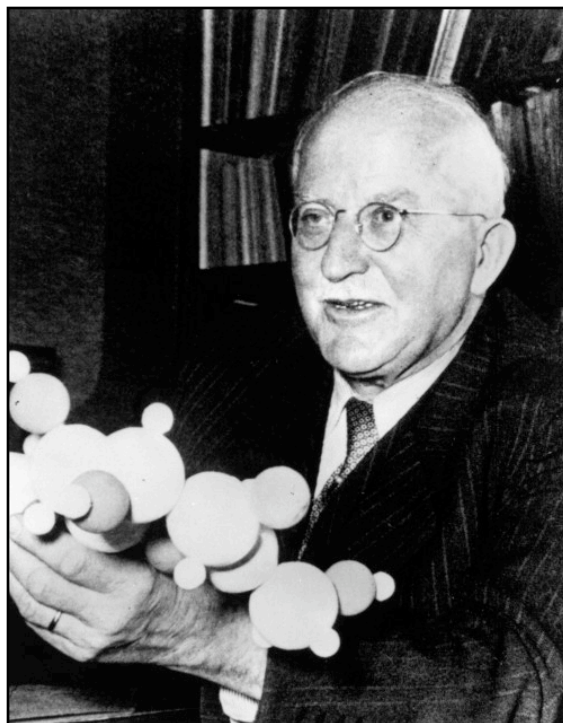


Figure 1. Hermann Staudinger (1881-1965).

isomerism as a separate and distinct phenomenon and metamerism became but one of several varieties of structural isomerism. However, despite this change in status, polymerism, in keeping with Berzelius’s original intent, continued to describe a purely compositional relationship between two substances which carried no requirements concerning the nature of the molecules (e.g. organic versus inorganic), their relative sizes, their structures, or their ability to interconvert (5).

Indeed, it was because the original meaning of the term polymer did not carry any connotation concerning size that the German chemist, Hermann Staudinger (figure 1), felt it necessary to coin the word “macromolecule” in 1922 to describe large covalently bonded organic chain molecules containing more than 10^3 atoms (6). Strictly speaking, the terms macromolecule and polymer stand for logically distinct concepts. There are many polymers which are not macromolecules (e.g. the S_3O_9 ring as a trimer of SO_3) and many

macromolecules which do not compositionally qualify as polymers of the materials from which they are made (e.g. so-called copolymers and condensation polymers). It goes without saying, of course, that the niceties of these logical distinctions have long been ignored by present-day chemists, most of whom now use the term polymer as a trivialized synonym for a covalently bonded organic macromolecular chain molecule (7). Attempts to partially remedy this situation through the coining of additional terms, such as “oligomer”, have not proven helpful (8), in part because the term polymer is still used in its original sense in the literature dealing with glasses, ceramics and inorganic polymers, many of which are noncovalently bonded and may contain not only infinitely polymerized chains but also infinitely polymerized layer and framework structures as well (9).

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6. H. Staudinger, J. Fritsch “Über die Hydrierung des Kautschuks und über seine Konstitution,” *Helv. Chim. Acta*, **1922**, 5, 785-806. Term on p. 788. Staudinger originally used the term *hochmolekulare Verbindungen* (high molecular compounds).
7. The author recalls attending a seminar on the history of polymer chemistry by a noted polymer chemist who was so indoctrinated with this current trivialized usage that he expressed great puzzlement over that fact that 19th-century books listed such species as acetylene (C₂H₂) and benzene (C₆H₆) as examples of polymerism. He ended by making the delightfully ahistorical observation that Berzelius apparently did not understand what a polymer was, never suspecting that it was the modern polymer chemist who had corrupted Berzelius’ original definition rather than vice versa.
8. L. V. Larsen, “Origin of the Term ‘Oligomer,’” *Chem. Eng. News*, **1984**, 62 (Jan. 23), 58.
9. The first comprehensive treatment of nonmolecular inorganic solids from the standpoint of the polymer concept appeared in K. Meyer, *Natural and Synthetic High Polymers*, Interscience: New York, NY, 1942, Chapter BI. Since the 1960s an increasing number of specialist monographs have appeared, including F. Stone, W. Graham, Eds., *Inorganic Polymers*, Academic Press: New York, NY, 1962; D. N. Hunter, *Inorganic Polymers*, Wiley: New York, NY, 1963; and N. H. Ray, *Inorganic Polymers*, Academic Press: New York, NY, 1978.

Publication History

First published in *J. Chem. Educ.*, **2008**, 85, 624-625.

XXX

Why Tungsten Instead of Wolfram?

Question

Why is the name tungsten used for element 74 in the English chemical literature whereas the name wolfram is used in the northern European literature?

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Answer

In 1781 the Swedish chemist, Carl Wilhelm Scheele (figure 1), reported the discovery of a new acidic oxide in a Swedish mineral known locally as “heavy stone” or “tungsten” (from the Swedish *tung* meaning “heavy” and *sten* meaning “stone”), also known as *lapis ponderosus* in Latin, *Schwerstein* in German, and as *tungstène*, *tunstène* or *pierre pesante* in French (1). In honor of this fact, he named the new oxide tungstic acid. Two years later the de Elhuyar brothers isolated the same oxide from the mineral *wolframite* and also reduced it to its component metal (2). They fully recognized that their oxide was the same as that found earlier by Scheele, and it was Scheele who first referred to the new metal as *tungsten regulus* in 1784. Similarly, the traditional French names for the newly discovered metals molybdenum and manganese were *régule de molybdène* and *régule de manganèse* respectively.

However, in their famous proposal of 1787 for the reform of chemical nomenclature, Lavoisier and his collaborators rejected the use of the term *regulus* to describe metals as it conflicted with their nomenclature proposals for binary compounds (3). As a consequence, they shortened these names to *molybdène*, *manganèse* and *tungstène* respectively, thus making the names for the metals identical with the corresponding irregular names for the minerals from which they were extracted. Robert Kerr, the translator of Lavoisier’s famous *Traité* of 1789, rendered these into English as *molybdena*, *manganese* and *tungstein*, respectively (4),



Figure 1. Carl Wilhelm Scheele (1742-1786).

though the first of these was eventually changed to molybdenum and the third to the spelling “tungsten,” as found in Scheele’s original essay (1). Likewise, the original irregular names of the minerals were eventually displaced by the more systematic names of *molybdenite* instead of *molybdena*, *pyrolucite* instead of *manganese*, and *scheelite* instead of *tungsten*.

Though German chemists also eventually adopted the nomenclature reforms of Lavoisier and his colleagues, they often preferred to use German translations of the Greek names favored by the French reformers (thus *Sauerstoff* instead of oxygen and *Wasserstoff* instead of hydrogen). The German and Scandinavian chemical literature of this period was also much more closely allied to the mineralogical literature than was the case with the British and French literature and this quickly produced additional problems with respect to the term *tungsten*, as the mineralogists began to favor the alternative name *wolfram* for the new metal in honor of its original isolation from the mineral *wolframite*. Yet additional confusion was

produced when it was also proposed that the mineral tungsten be renamed *scheelite* and the corresponding element *scheelium* in honor of Scheele. Thus the 1791 German revision of Macquer's famous dictionary of chemistry listed the metal only under the entry "wolfram" (5), whereas the 1793 German dictionary by Remler listed tungsten, wolfram and scheelium as synonyms (6). In sharp contrast, British and French chemical dictionaries of this period, such as those by Nicholson (1795), Cadet (1803) and Ure (1821), make no mention of these alternatives and simply use the name adopted by Lavoisier and his collaborators or its English equivalent (7-9).

Both the names tungsten and scheelium reflect the fact that the element in question was discovered by a Swede and thus there is some irony in the fact that it was a second famous Swedish chemist, Jöns Jacob Berzelius, who ultimately determined that, in the northern European chemical literature at least, the element would come to be known by the name of wolfram instead. This came about via Berzelius' introduction of our current compositional chemical symbolism around the year 1814 in which each element is represented by a one- or two-letter abbreviation (10). In order to more evenly distribute the resulting symbols throughout the alphabet, Berzelius insisted on some unusual name choices, several of which were suggested by his detailed knowledge of the mineralogical literature and by his preference for Latin, such as beryllium instead of *glucinum*, *natrium* instead of sodium, *kalium* instead of potassium, tantalum instead of columbium, and, of course, *wolframium* or wolfram instead of tungsten. Commenting on the latter choice in his famous textbook, Berzelius argued that (11):

Though some chemists have suggested that it should be named scheelium in honor of Scheele, not only does this name fit poorly with the Swedish language, the immortality of our fellow countryman requires no such additional support; thus I have given precedent to the name wolfram instead.

Berzelius' symbolism was rapidly adopted by the German and Scandinavian chemical communities, but was much slower in impacting on the British and French. Indeed, Berzelius' symbols were uncommon in British and American textbooks prior to the 1840s and by that time the discrepancy between the name tung-

sten and the symbol W was dismissed as merely another case of a common name coupled with a symbol based on a Latin alternative (wolframium), not unlike the case of sodium versus Na for natrium. Though also adopting Berzelius' general plan for a chemical symbolism, the French, perhaps in revenge for what the Germans had done earlier with some of Lavoisier's Greek names, altered several of his symbols, thus using G for glucinum, Az for nitrogen or azote, and Tu for tungsten. However, eventually, in the interest of universality, they, like the British and Americans, adopted the symbol W for tungsten, though both communities still retain Lavoisier's original name choice for this element.

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Publication History

First published in *J. Chem. Educ.*, **2008**, 85, 488-489.

Origin of the Rubber Policeman

Question

What is the origin of the rubber policeman and why is it called a policeman?

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Answer

In classical wet gravimetric analysis it is essential, after precipitating the chemical element of interest as a stable, insoluble compound, to successfully transfer all of the precipitate to the filtration funnel for separation from the supernatant liquid. Usually this is done using a stream of distilled water from a wash bottle. However, particularly dense precipitates may become compacted at the bottom of the precipitation beaker and require mechanical loosening or, in the case of light precipitates, may become dispersed on the walls of the beaker. In using a glass rod to pry loose a compact precipitate, one runs the risk of accidentally poking a hole in the bottom of the beaker, whereas use of a glass rod to collect dispersed precipitate is ineffective and may result in scratching of the beaker wall. These problems that were particularly acute prior to the introduction of Pyrex glassware in the early 20th century, before which chemists had to make use of paper-thin glassware made from relatively soft potash or lime glass (1).

To overcome these defects, analytical chemists introduced a variety of devices. Thus the 19th-century German chemist, Carl Remigius Fresenius (figure 1), in his classic manual of quantitative analysis, recommended the removal of any dispersed precipitate from the beaker walls using (2):

.. a feather prepared for the purpose by tearing off nearly the whole of the plumules, leaving only a small piece at the end which should be cut perfectly straight.

An early description of our current method of choice - the rubber policeman - may be found in the 1910 edition of J. C. Olsen's textbook of quantitative analysis (3):



Figure 1. Carl Remigius Fresenius (1818-1897).

... particles adhering to the glass must be removed by means of a so-called policeman, which is made by inserting the end of a rather thick large-sized glass stirring-rod into a short piece of rubber tubing. The rubber tube should be left protruding slightly beyond the end of the glass tube and sealed together with a little bicycle [i.e. rubber] cement.

Olsen, however, does not appear to have been the inventor of this device as the chemical catalogs in the Oesper Collections indicate that prefabricated rubber policemen were being offered for sale by the Henry Heil Company of St. Louis as early as 1904 (4).

Unfortunately, neither Olsen nor the catalog for the Heil Company provided an explanation for why this device was called a policeman, though at least two speculative possibilities suggest themselves:

- a. It policed or protected the beaker from breaking or scratching.
- b. It policed the beaker walls by gathering up any stray or escaped particles of precipitate.

An entry in the 1937 edition of *Hackh's Chemical Dictionary* under "platinum policeman," defined as "a platinum-iridium claw that fits over a glass rod and is used to hold a quantitative filter during ignition," suggests that the second of these speculations is probably the correct one. Just as the purpose of the rubber policeman was to prevent the escape of stray precipitate, so the purpose of this claw device was to prevent the escape of stray filter paper from the crucible during the ignition process due to thermal updrafts from the burner.

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Publication History

First published in *J. Chem. Educ.*, **2008**, 85, 776.

Update

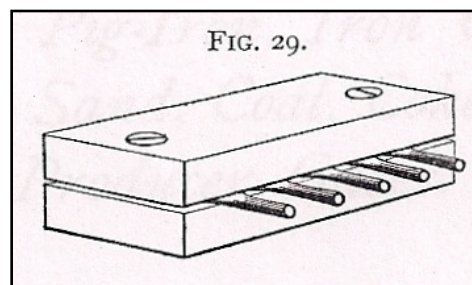
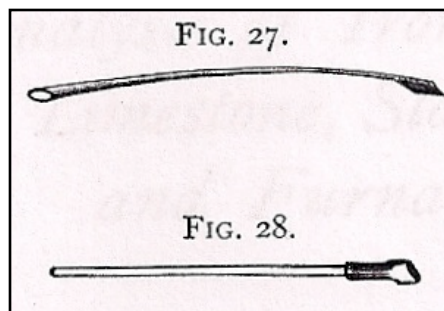
Rather surprisingly this column stimulated more reader response than any before or since. Several correspondents educated in Great Britain and Australia insisted that their Science Masters had told them that the rubber policeman received its name because it resembled the helmets used by British "Bobbies." Of course it looks nothing at all like a policeman's helmet. If anything it resembles the claymation cartoon character "Gumby."

One correspondent pointed out that during his time in the military they would often be ordered to "police an area for trash" – a usage identical to that suggested in the original column. Finally, Keith Sheppard brought an even earlier reference to the rubber policeman to our attention:

* A. A. Blair, *The Chemical Analysis of Iron*, Lippincott: Philadelphia, PA, 1888, p. 3.

which has the following to say on the subject:

A feather trimmed in the way shown in Fig. 27 may be used to remove particles of adhering precipitates from beakers, evaporating-dishes, etc. A piece of soft rubber tubing on the end of a piece of glass rod or sealed glass tube is much more effective and convenient in most cases. It is made by taking a short length of rubber tubing, placing a little pure caoutchouc dissolved in chloroform in one end, squeezing the sides together between two pieces of board (Fig. 29), and allowing it to remain for twenty-four hours. It may then be trimmed down and placed on the end of a piece of glass rod or a piece of glass tubing having the ends fused together (Fig. 28). This little instrument has acquired the name of "policeman."



The Origin of the Rotavap

Question

What is the origin of the laboratory rotary vacuum evaporator or rotavap?

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Answer

The modern laboratory rotary vacuum evaporator (figure 1) was first proposed in 1950 by the American biochemist, Lyman C. Craig, who is perhaps best known for his earlier invention (1949) of the Craig counter-current extractor (1). Variations and improvements were quick to follow, most notably those of Volk (2-5). A commercial version was first manufactured and sold by Walter Büchi of Basel Switzerland in 1957, and by the early 1960s the device had become a standard fixture of the organic and biochemical laboratory (6).

Craig rather unimaginatively referred to his apparatus as a “laboratory condensation device,” whereas both Partridge and Volk used the term “rotary film evaporator.” Büchi named his commercial product the “Rotavapor” and other manufacturers have adopted similar names, such as “Flash Evaporator,” “Power-vap,” “Pilotvap,” etc. Most commonly, however, they are referred to simply as rotary evaporators or “rotavaps” for short, an obvious contraction of Büchi’s original name (though there are some who advocate the alternative spelling “rotovap” instead).

The purpose of the device is to allow for rapid and efficient evaporation of solutions containing thermally sensitive organic and biochemical solutes by combining large surface areas for evaporation, produced by the solution film on the inside of the rotating flask, with low ambient vapor pressures, produced by the vacuum pump, and supplemented, when necessary, by moderate heating provided by a water bath. The rotation also keeps the solution mixed, thereby leading to more uniform crystal growth. Both massive rotating drum evaporators and vacuum evaporators were used by chemical engineers long before Craig proposed his apparatus, but it was his genius to combine both principles into a single, scaled-down, compact, laboratory device (7).

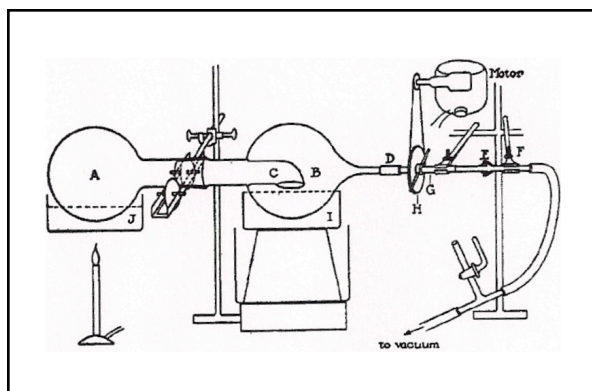


Figure 1. Craig’s original rotary evaporator (1).

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Publication History

First published in *J. Chem. Educ.*, **2008**, 85, 1481

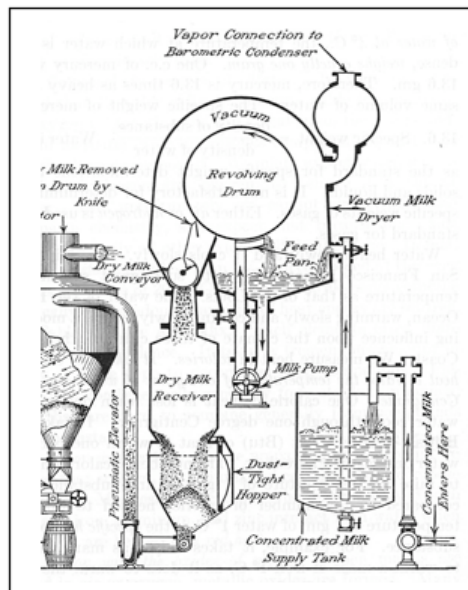
Update

Though the books on chemical engineering which I consulted in writing the original column discussed both rotary drum evaporators and vacuum evaporators, they made no mention of techniques which combined both

ASK THE HISTORIAN

approaches in a single device. However, more recently, on perusing the 1931 edition of Charles Dull's high school chemistry textbook, *Modern Chemistry*, I stumbled upon a diagram for such a machine used in the production of dried milk, parts of which are reproduced in the illustration at the right.

* C. E. Dull, *Modern Chemistry*, Henry Holt: New York, NY, 1931, p. 101.



XXXIII

Melting Points

And the Characterization of Organic Compounds

Question

When was melting point introduced to characterize organic compounds?

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Answer

The Belgian physical chemist, Jean Timmermans, in his classic monograph, *On the Concept of Species in Chemistry*, attributed the first use of melting points as a means of characterizing organic compounds to the famous 1832 paper by the German chemists, Justus von Liebig and Friedrich Wöhler, on the chemistry of the benzoyl radical in which they reported the melting point of benzamide (1, 2). A year later Liebig also reported the boiling point of liquid acetal (3). From this date on, the practice of reporting not only the analytical composition but also the melting and/or boiling points of newly isolated organic compounds seems to have rapidly spread, not only in the pages of Liebig's *Annalen*, but in other chemical journals as well, so by the last decade of the 19th century melting point determinations had become a standard introductory topic in virtually all organic laboratory manuals (4).

Liebig and Wöhler said nothing about their method for determining the melting point of benzamide. However, beginning in 1870s an increasing number of proposals for the rapid and accurate determination of melting points began to appear in the chemical literature (5). By the 1890s the most popular of these (figure 1) involved attaching a melting point capillary to the stem of a thermometer suspended in a long-necked, round-bottom flask filled with concentrated sulfuric acid or some other liquid with a high boiling point and carefully heated using a Bunsen burner – a technique which was still being used when the present writer took introductory organic laboratory in the 1960s (6). By 1900 laboratory supply catalogs were selling several elaborated versions of this flask

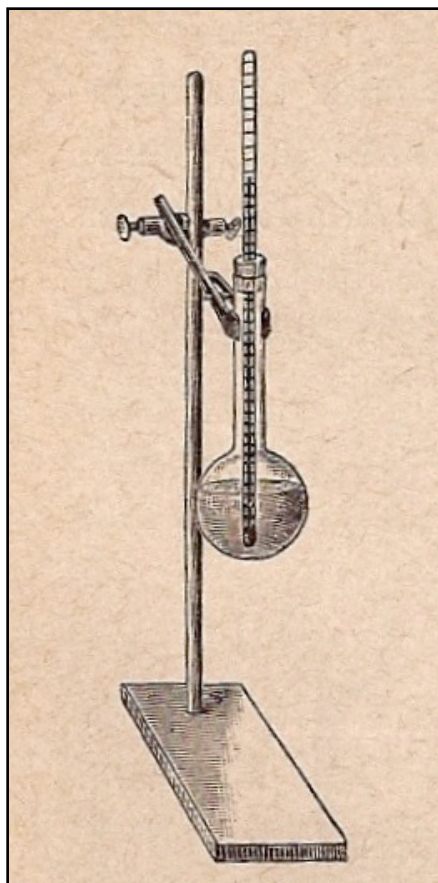


Figure 1. Simple melting-point apparatus as depicted by Gattermann in 1894 (6).

(known as Roth and Anschutz-Schulze flasks respectively). Though first proposed in 1907, it was not until the 1920s that supply catalogs began to offer specialized “Thiele melting-point tubes,” whose characteristic “b” shape (figure 2) allowed one to position the burner to one side rather than directly beneath the thermometer bulb (7). Early versions of electrically heated melting point devices first appear in laboratory supply catalogs in the 1930s, but dependable, inexpensive models suitable for student use are uncommon before the late 1950s.

Liebig and Wöhler also failed to indicate their motivation in reporting the melting point of benzamide. One may, however, speculate that it had its origins in their first encounter with one another eight years earlier in 1824. That year Liebig, working in Gay-Lussac's laboratory in Paris, had reported his analysis of the compound silver fulminate, only to discover that it was identical to the analysis reported by Wöhler for silver cyanate while working in the laboratory of Berzelius in Stockholm, though the two compounds had radically different properties (most notably that silver fulminate was explosive whereas silver cyanate was not) (8). Since these results violated the then accepted postulate that all differences in properties were traceable to differences in composition, Liebig initially claimed that Wöhler's analysis was faulty, though this was soon shown to be incorrect. This encounter not only led to a life-long friendship between Liebig and Wöhler but to the formulation of the concept of isomerism by Berzelius in 1831 (9). It is probably not a coincidence that the practice of supplementing compositional analytical data for organic compounds with melting and/or boiling point data began shortly after the explicit recognition of the concept of isomerism, since this data served as a convenient way of unambiguously detecting yet further examples of this new phenomenon.

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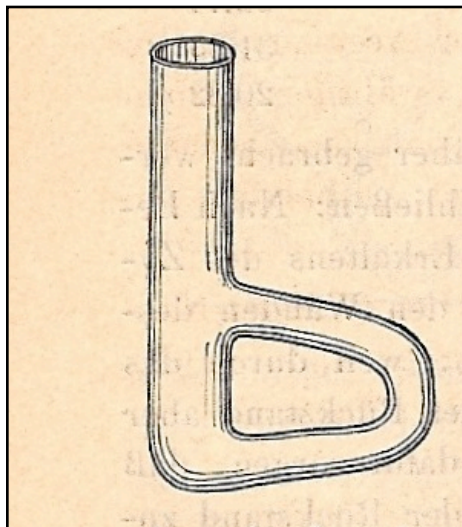


Figure 2. Thiele's original melting point tube, circa 1907 (7).

4. See, for example, the organic laboratory manuals by Lassar-Cohen (1890), Orndorff (1893), Gattermann (1894), Hewitt (1897), Cohen (1900), and Holleman (1904).
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Publication History

First published in *J. Chem. Educ.*, **2009**, 86, 23-24.

Origin of the Metallic Bond

Question

What is the Origin of the Metallic Bond?

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Brazil*

Answer

The basis of our modern electronic interpretation of metals was laid by the German physicist, Paul Drude (figure 1), and the Dutch theorist, Hendrik Lorentz, in the first decade of the 20th century (1, 2). Both assumed that the weakly bound conduction electrons could be modeled using the classical kinetic theory of gases. Though this “electron-gas” model gave an adequate qualitative rationale of metallic properties, it incorrectly predicted both the heat capacity of metals and the temperature dependence of their electrical conductivity. In addition, it could not explain their magnetic properties (3). In 1928 the German physicist, Arnold Sommerfeld, partially resolved these problems by imposing quantum restrictions on the electron distributions – a lead followed by the Swiss physicist, Felix Block, whose classic paper, published the same year, laid the foundations for modern band theory (4, 5).

The possible relevance of Drude’s original model to the theory of the chemical bond was first pointed out by G. N. Lewis in a paper published in 1913 (6). Though the main thrust of this paper was to argue for the separate existence of a nonpolar (covalent) bond, as distinct from the then generally accepted polar or ionic bond, in its final section, entitled “A Third Type of Chemical Bond,” Lewis further argued that (6):

To the polar and nonpolar types of chemical compound we may add a third, the metallic. In the first type the electrons occupy fixed positions within the atom. In the second type the electrons move freely from atom to atom within the molecule. In the third or metallic type the electron is free to move even outside the molecule ... All known chemical compounds may be grouped in the three classes: nonpolar, polar and metallic; except



Figure 1. Paul Karl Ludwig Drude (1863-1906).

in so far as the same compound may in part or at times fall under two of these groups.

Two years later, the German physicist, Johannes Stark, independently expressed the same idea and also made the first attempt to visualize all three bonding situations (figure 2), though he pictured metals as a rigid lattice of positive ions and electrons rather than as a free-electron gas (7) – a metallic model also advocated by the British physicist, F. A. Lindemann (8). In 1928 the German chemist, Hans Georg Grimm, published his “Dreieckschema” in which he plotted the elements of one row of the periodic table versus another and listed their binary compounds in the resulting triangular matrix, indicating that the three corners corresponded to salt-like compounds, covalent com-

pounds, and metallic compounds respectively (9). Though usually attributed to the Dutch chemist, Anton van Arkel, the first generalized equilateral bond-type triangle in which the corners corresponded to the ionic, covalent, and metallic bonding extremes, and intermediate bond types were explicitly indicated along the edges, was actually published in the *Journal of Chemical Education* by the American chemists, Conard Fernelius and Richard Robey, in 1935 (10, 11).

The metallic bond has had a very spotty history in the chemical literature. Whereas the thrust of band theory has been the prediction and rationalization of the thermal, electrical, and magnetic properties of metals, chemists are far more interested in bonding models which offer simple correlations between valence-electron counts and both the compositions and structures of possible compounds. Though they have been very successful in developing such correlations in the cases of both the covalent and ionic bonding extremes, similar success in the case of intermetallic compounds and alloys has been almost totally lacking. While one can cite the pioneering attempts of such metallurgists as Hume-Rothery, Laves, and Engels, as well as the brilliant work of the German chemist, Eduard Zintl, on the transition between ionic and metallic bonding, the situation today remains much the same as when it was summarized by Fernelius and Robey in 1935 (9):

The classification of intermetallic compounds is very difficult. Not only are the experimental difficulties great, but as yet no single theoretical or empirical method of treatment has been sufficiently powerful to elucidate more than a portion of the entire field.

More recently there has also been a debate on the very question of whether there is such a thing as a distinct metallic bond, though in the present writer's opinion this was predicated on a misunderstanding of both the nature of idealized bonding extremes and the proper interpretation of bond-type triangles (11). Given these problems, it is perhaps not surprising that 85 years after Lewis first proposed the metallic bond, the vast majority of introductory chemistry texts continue to ignore it and to incorrectly inform their readers that all bonding is either ionic or covalent.

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2. H. A. Lorentz, *The Theory of Electrons and Its Application to the Phenomena of Light and Radiant Heat*, Teubner: Leipzig, 1906.

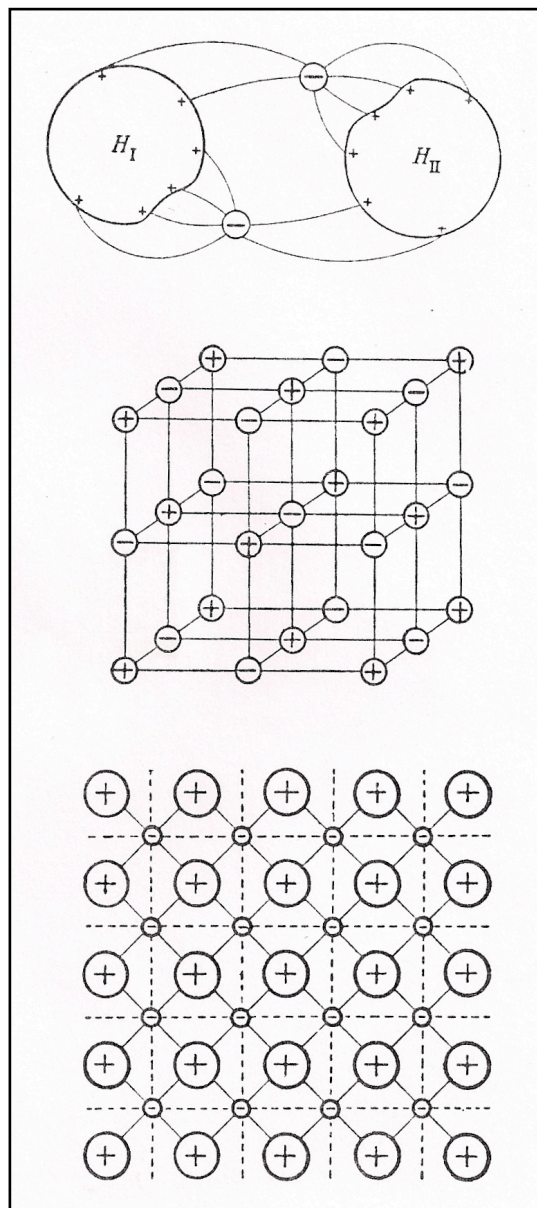


Figure 2. From top to bottom: Stark's 1915 rendition of the shared electron-pair bond in H_2 ; the ionic bond in $NaCl$; and a typical metal viewed as a rigid lattice of positive ions and free electrons (7).

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Publication History

First published in *J. Chem. Educ.*, **2009**, 86, 278-279.

The Circle Symbol for Aromaticity

Question

What is the origin of the circle symbol for aromaticity?

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Answer

The use of a circle enclosed within a hexagon to represent the “aromatic sextet” of benzene was first introduced by the British chemists, James Wilkins Ait and Sir Robert Robinson (figure 1), in a paper published in 1925 (1). Just as the fundamental role played by the electron pair or duplet in the electronic formulation of molecular structures merited its own distinct symbol in the form of a straight line connecting two atoms, so these authors felt that a planar ring or sextet of electrons imparted sufficiently distinctive properties to certain organic molecules so as to also merit a unique symbol of its own (1):

The circle in the ring symbolizes the view that six electrons in the benzene molecule produce a stable association which is responsible for the aromatic character of the substance.

Though this proposal predates the rise of the delocalized molecular orbital approach to aromaticity and our current σ/π distinctions (2, 3), these authors further hinted that their theory of the aromatic sextet and its accompanying symbol did not “require any particular assumption in regard to the position of the electrons or their orbits in space.”

While occasionally mentioned in passing in advanced monographs the period 1925-1959 (4), the circle symbol appears to have had no impact on introductory organic textbooks (5). Indeed even Robinson himself seems to have abandoned it, as it does not appear in his famous 1932 resume of his version of the electronic theory of organic chemistry (6) nor in Michael Dewar’s 1949 update of Robinson’s system, though the latter does show the delocalized π -orbitals on benzene and makes occasional use of dotted lines to indicate



Figure 1. Robert Robinson (1886-1975).

electron delocalization in various transition states and intermediates (7).

Only in the late 1950s and early 1960s did the circle symbol finally make an appearance in the introductory organic textbook and most notably in the 1959 edition of the highly popular text by Morrison and Boyd, where it was used not only for benzene but also for naphthalene, anthracene, phenanthrene and other polycyclic aromatics (8). By this point all connection with Robinson’s original proposal seems to have been lost and the symbol’s reemergence as a textbook icon appears instead to have been a by-product of the increasing popularity of the delocalized MO approach to the description of π -electron systems. Even then, its textbook usage has been variable, with some books, such as the 1965 text by Roberts and Caserio, rejecting it as “quite uninformative and even misleading” when it comes to electron counting, while yet others have

followed the lead of Morrison and Boyd and have applied it to cyclic π -systems in general, as well as consistently employing it in equations representing their chemistry (9).

Finally, it should be noted that there continues to be debate over the exact meaning of the symbol. While several of the above textbooks have used it to denote cyclic π -electron delocalization irrespective of electron counts, some advanced monographs restrict its use only to those monocyclic π -systems which obey the Hückel $4n+2$ rule for aromaticity, thus allowing for 2, 6, 10, etc. π -electron systems (10), whereas yet others restrict it, in keeping with Robinson's original intent, to monocyclic systems containing only six π -electrons (11).

This latter usage is perhaps the most precise and the most defensible. Just as the line always represents a 2c-2e bond, and the "Y" symbol used in boron hydride structures always represents a 3c-2e bond, so the circle may be thought of as representing a special kind of 6c-6e bond. Just as the 3c-2e symbol eliminates (by definition) the need for resonance using only 2c-2e bonds in certain species and reduces the number of required resonance structures in others, so the 6c-6e circle symbol eliminates (by definition) the need for resonance in certain monocyclic species, such as benzene, pyridine, the cyclopentadienyl anion, etc, and reduces the number of required structures in yet others. Thus naphthalene has three major resonance structures using only 2c-2e bonds, but just two using the circle symbol, each of which consists of one hexagon with a circle and one with two localized (albeit conjugated) double bonds.

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10. G. M. Bader, *Aromatic Character and Aromaticity*, Cambridge University Press: Cambridge, 1969 and P. J. Garrett, *Aromaticity*, McGraw-Hill: London, 1971.
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Publication History

First published in *J. Chem. Educ.*, **2009**, 86, 423-424.

Update

In 1967 Robinson retrospectively, albeit briefly, commented on his original concept of the aromatic sextet and essentially concurred with the views of Clair in reference 11 as to when and how the symbol should be used. See:

- * R. Robinson, "The Concept of the Aromatic Sextet," in *Aromaticity: An International Symposium*, The Chemical Society, Burlington House: London, 1967, pp. 47-53.

XXXVI

Origin of the “Delta” Symbol

Question

What is the origin of the “delta” symbol for fractional charges?

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Answer

One of the important consequences of G. N. Lewis' proposal in 1916 of the shared electron-pair or covalent bond was the possibility, in addition to the conventional integral ionic charges resulting from complete electron transfer, of developing intramolecular partial or fractional charges due to unequal sharing of the electron pair - a possibility succinctly summarized by Lewis in his 1923 monograph on *Valence and the Structure of Atoms and Molecules* (1):

The pair of electrons which constitutes the bond may lie between two atomic centers in such a position that there is no electric polarization, or it may be shifted toward one or the other atom in order to give to that atom a negative, and consequently to the other atom a positive charge. But we can no longer speak of any atom as having an integral number of units of charge, except in the case where one atom takes exclusive possession of the bonding pair, and forms an ion.

Application in the 1920s of Lewis' shared electron-pair bond to the electronic theory of organic reactivity by such British chemists as Christopher Ingold, Robert Robinson, Arthur Lapworth, and Thomas Lowry soon revealed the necessity of introducing a new symbolism in order to differentiate between the use of the + and - signs to indicate net ionic charges, on the one hand, and their use to indicate relative polarity due to fractional charges, on the other. It was with this in mind that the “delta” symbolism for fractional charges was first introduced by Ingold (figure 1) and his wife Hilda in a footnote to a 1926 paper on the electronic theory of aromatic substitution (2):



Figure 1. Christopher Kelk Ingold (1893-1970).

In this formula, and those which follow, δ^+ and δ^- are used to signify small fractions of a unit charge; n represents neutrality, and the signs + and - connote unit charges.

Despite the intense rivalry between Ingold and Robinson, Robinson was, rather surprisingly, one of the first to adopt Ingold's suggestion and employed it in his famous 1932 summary of his own version of the electronic theory of organic reactivity (3, 4). Nevertheless, the symbol was used only sparingly during the 1930s in the monograph literature dealing with the electronic theory of organic chemistry (5, 6), with a

ORIGIN OF THE “DELTA” SYMBOL

substantial increase in usage not occurring until the 1940s and 1950s (7, 8).

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6. H. B. Watson, *Modern Theories of Organic Chemistry*, Clarendon: Oxford, 1937, pp. 23, 68.
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Publication History

First published in *J. Chem. Educ.*, **2009**, 86, 545.

XXXVII

Balancing Redox Equations

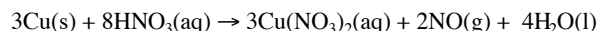
Question

What is the origin of our current techniques for balancing redox equations?

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Answer

Most students of chemistry are currently taught to balance simple chemical equations by “inspection,” which is a polite way of saying that each student develops his or her own personal, albeit often subconscious, method based on practice (1). This haphazard approach also works with simple oxidation-reduction or redox equations, but usually proves insufficient when it comes to relatively complex redox reactions, such as the oxidation of copper with nitric acid:



The most common approach in these cases is to explicitly identify which species is being oxidized and which is being reduced. By applying the general rule that the change in oxidation must be equal to the change in reduction, one then obtains the coefficients for these two species, after which those of the remaining reactants and products are easily determined by inspection. What has evolved over time is, of course, the definition of what changes during oxidation and reduction, and, not unexpectedly, the historical evolution of the various techniques for balancing redox equations is a direct reflection of this changing definition as outlined in a previous installment of this column (2).

In keeping with the original literal meaning of oxidation and reduction as the addition and removal of oxygen, respectively, the earliest conserved quantity for redox reactions was nascent or atomic oxygen (O). Rewriting the oxidizing ($2\text{HNO}_3 = \text{H}_2\text{O}\cdot\text{N}_2\text{O}_5$) and reducing ($\text{Cu(NO}_3)_2 = \text{CuO}\cdot\text{N}_2\text{O}_5$) agents in modernized dualist notation and focusing on only those por-



Figure 1. Victor Kuhn La Mer (1895-1966).

tions actually undergoing oxidation and reduction, one obtains the result that the coefficients for $\text{Cu(NO}_3)_2$ and NO must be 3 and 2, respectively, after which the remaining coefficients are easily determined (3):

oxidation:



reduction:

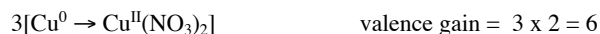


With the advent of the concept of polar valence in the 1870s and the generalization of oxidation to subsume valence increase in general and reduction to subsume valence decrease in general, the conserved quan-

BALANCING REDOX EQUATIONS

tity now became the change in valence:

oxidation:



reduction:



from which it once again follows that the coefficients for $\text{Cu}(\text{NO}_3)_2$ and NO must be 3 and 2, respectively. This approach was first explicitly articulated by the American chemist, O. C. Johnson, in 1880, though he unfortunately equated valence with the number of bonds an atom could form and was thus forced to awkwardly talk of balancing changes in positive and negative bonds (4). Reformulated in terms of changes in valence number, it was still being used by some authors as late as the 1920s (5).

With the explicit identification of oxidation and reduction with electron loss and gain, respectively, in the first decade of the 20th century, the polar valence method was modified to reflect conservation of electrons:

oxidation:



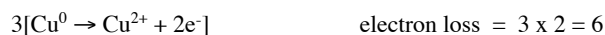
reduction:



In this form it was made the subject of a small monograph by Keach in 1926 (6) and is still taught in our textbooks under the guise of the oxidation number or oxidation state method.

The advent of the electron loss and gain approach was also closely allied to the ionic theory of dissociation and the electrochemical theory of electrolysis and voltaic cells, and in 1927 Eric Jette and Victor K. La Mer (figure 1) published an article in the *Journal of Chemical Education* arguing that, since all aqueous redox reactions could in principle be made the basis of various voltaic cells, they should be written as the sum of the resulting balanced cathode and anode cell reactions using net ionic rather than molecular equations (7):

oxidation:

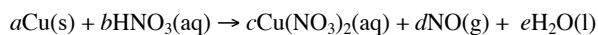


reduction:



Furthermore, they argued that both electron loss and gain and the subsequent weighting of the two half-cell equations should be based on the balancing of net ionic charges rather than on hypothetical polar valence or oxidation numbers. Dubbed the ion-electron method, the approach was made the basis of a small book published by Jette the same year and was also the subject of a subsequent debate in the pages of the journal (1, 8). Like the valence or oxidation number approach, it is still widely used in modern textbooks.

Finally, mention should be made of a far more general method of balancing all chemical equations, whether redox or nonredox, molecular or net ionic. Introduced by the British chemist, James Bottomley, in 1878, it is variously known as the algebraic method or the method of material balance and is based on the fundamental principle of the conservation of chemical elements in chemical reactions first explicitly articulated by Lavoisier in 1789 (9, 10). In this approach one represents the various coefficients in the unbalanced equation as variables:



and writes down explicit equations of balance for each element (and for charge in the case of net ionic equations):

$$\begin{array}{ll} \text{Cu:} & a = c \\ \text{H:} & b = 2e \\ \text{N:} & b = 2c + d \\ \text{O:} & 3b = 6c + d + e \end{array}$$

These are then solved using any of the various methods available for the solution of simultaneous equations. Since such algebraic prowess is beyond the abilities of most introductory students, this approach is seldom taught in chemistry departments, though it is widely employed by chemical engineers. As a result, the chemical education literature continues to be plagued with arguments over the best approximate method for balancing equations – so much so that some years ago the editor of this journal felt compelled to call a moratorium on papers dealing with this subject (11).

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Publication History

First published in *J. Chem. Educ.*, **2009**, *87*, 681-682.

XXXVIII

The Origin of Bond Lines

Question

What is the origin of bond lines?

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Answer

The first use of lines in chemical formulas to indicate pairwise bonding interactions between atoms within molecules is usually attributed to the Irish chemist, William Higgins, in 1789 (1). However, Higgins's notation never caught on, in part because his molecular structures were purely speculative. Though the Scottish chemist, Archibald Scott Couper, used dotted lines for the same purpose in his famous paper of 1858 on the formation of chains and rings in carbon compounds (2), the use of solid bond lines in conjunction with the rise of modern structure theory is usually credited to the Scottish chemist, Alexander Crum Brown, in 1864 and to the German chemist, Lothar Meyer, who also used them in some of the formulas appearing in the first edition of his famous monograph, *Die modernen Theorien der Chemie*, published the same year (3, 4).

Unlike Meyer, Crum Brown enclosed the atomic symbols in his formulas in circles, a practice which gave them appearance of two-dimensional projections of ball and stick models (figure 1). This practice was repeated in Edward Frankland's popular 1866 textbook, *Lecture Notes for Chemical Students*, which played an important role in popularizing Crum Brown's symbolism (5). By end of the decade, however, the circle had largely been eliminated as an unnecessary embellishment and structural formulas began to appear much as they are today. Frankland is also generally credited with being the first to popularize the term "chemical bond" (6).

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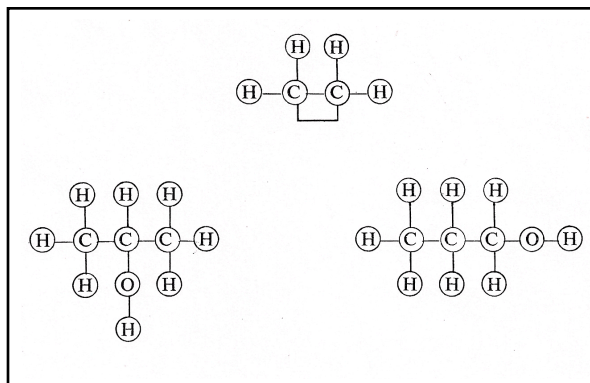


Figure 1. Examples of Crum Brown's "ball and stick" structural symbolism of 1864 (3).

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Publication History

First published in *J. Chem. Educ.*, **2009**, 86, 791.

The Origins of the Meker and Tirrill Burners

Question

What are the origins of the Meker and Tirrill laboratory burners?

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Answer

Aside from the original Bunsen burner itself, whose origins were traced in an earlier installment of this column, the Meker and Tirrill burners are perhaps the best known varieties of laboratory gas burners still found in the modern American chemical laboratory (1). The Meker burner (figure 1) was first proposed by the French chemist, M. G. Meker, in 1905 (2). It was based on the observation that the region of maximum temperature in the standard Bunsen burner flame is restricted to a small area centered above the outer tip of the flame. In the Meker burner the grid breaks the flame into an array of smaller flames, each with its own maximum temperature zone. These act collectively to produce a much larger area of maximum temperature, as well as a net overall increase in temperature – features which Meker demonstrated using comparative heating curves which showed that his design could reach temperatures of 1180 °C as compared to an average of about 935 °C for the more traditional Bunsen burner. A further modification of the burner, employing compressed air, was able to reach a temperature of 1500 °C. By 1912 the various forms of Meker's burner had become a standard feature of laboratory supply catalogs, whether American, British or European (3).

The most characteristic feature of the Tirrill burner – a needle valve for gas regulation located in the base of the burner – was first proposed by the American chemist, Francis Preston Venable, in 1887 (4). In Venable's original design (figure 2) the thumb nut controlling this valve was located in a hollow in the bottom of the cast-iron base of the burner and the air sup-

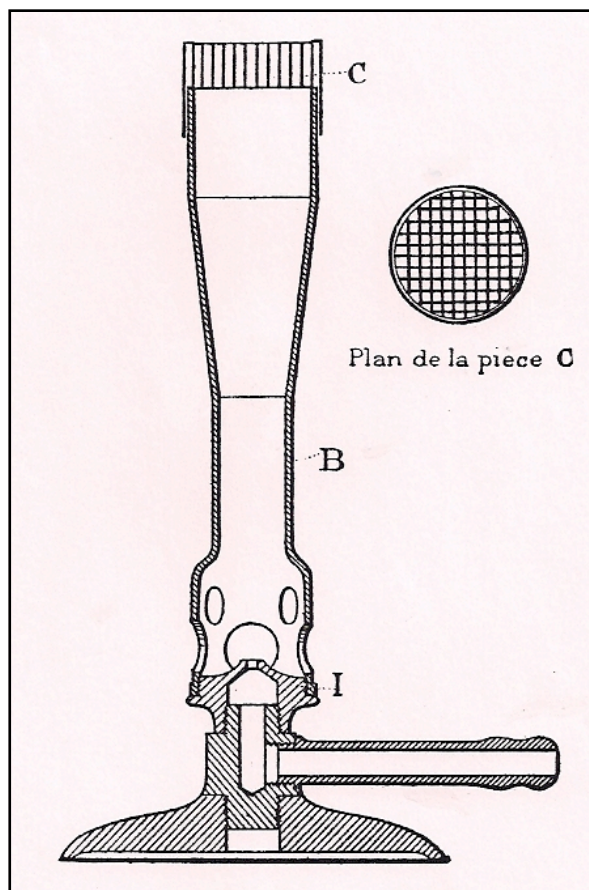


Figure 1. A cross-section of Meker's original burner (2).

ply was regulated by a metal collar turned by means of a small knob. In the Tirrill modification of Venable's burner the thumb nut was made more accessible by stripping away most of the solid base so as to leave only an open vertical half circle fused to a horizontal hexagonal or circular frame, and the air was regulated by screwing the burner barrel up and down on a threaded mount so as to partially unblock or block a series of circular air holes located in its base. The 1904 catalog of the Henry Heil Co. continued to attribute this modification to Venable, but starting around 1910 laboratory supply catalogs began to uniformly identify

THE ORIGINS OF THE MEKER AND TIRRILL BURNERS

this variation as either a Tyrell, Tirill or Tirrill burner (5).

Unfortunately we have been unable to identify either Tirrill (let alone the correct spelling of the name) or the exact date of this modification, though we did find several patents relating to the design of gas lighting fixtures and commercial heating devices issued under this name or variants thereof, strongly suggesting that Tirrill was the name of the company which manufactured the burner. This is further supported by the fact that a second variation of Venable's burner employing essentially the same open base and threaded air control, but manufactured by the Boyce Company, also appears in supply catalogs starting around 1904 and that both the Boyce and Tirrill burners are found only in American supply catalogs (6). This is because in the late 19th and early 20th century laboratory burners appear to have been manufactured as a side line by the same companies that manufactured gas lighting fixtures and heaters and many of the burners found in American versus British versus German laboratory supply catalogs are in fact quite unique to the country in question.

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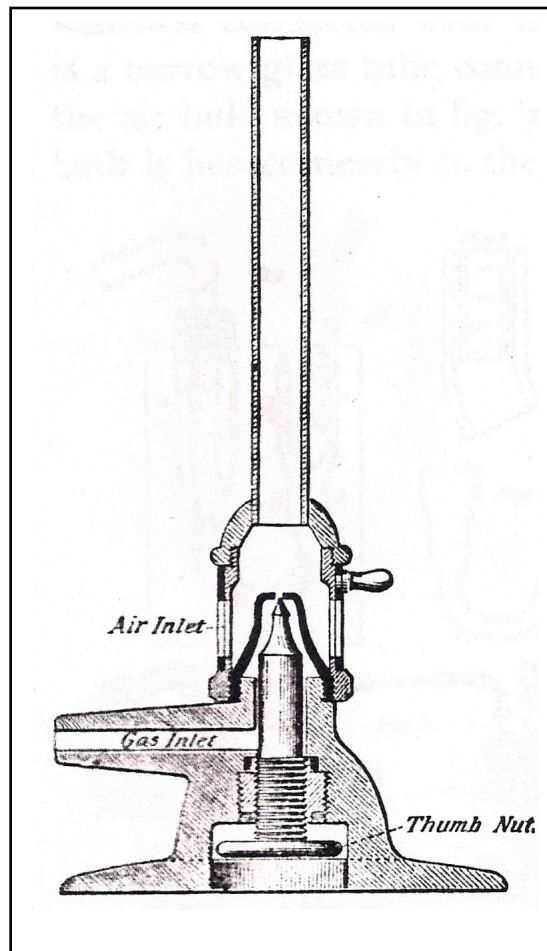


Figure 2. A cross-section of Venable's original burner (4).

6. An example of yet a third variation of the Venable burner involving an open tripod base is on display in the Oesper Museum and is identified by the 1920 catalog for Eimer and Amend as a "Detroit Burner."

Publication History

First published in *J. Chem. Educ.*, **2009**, 86, 1362-136.

XL

Origin of the Brin Process

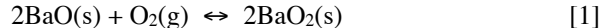
Question

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

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Answer

The Brin process for the industrial manufacture of pure dioxygen gas was based on the thermal reversibility of the reaction between barium oxide (BaO) and dioxygen gas (O₂) to produce barium peroxide (BaO₂):



Since the reaction as written is exothermic ($\Delta H^\circ = -143.1 \text{ kJ/mol rx}$) combination of the barium oxide with the dioxygen gas of the air is favored at low temperatures, whereas its reverse, the decomposition of the resulting peroxide to give pure O₂ and the original oxide, is favored at high temperatures. The regenerated oxide can then be reused to produce more peroxide and the cycle repeated indefinitely.

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

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



and that if one first removed the carbon dioxide by

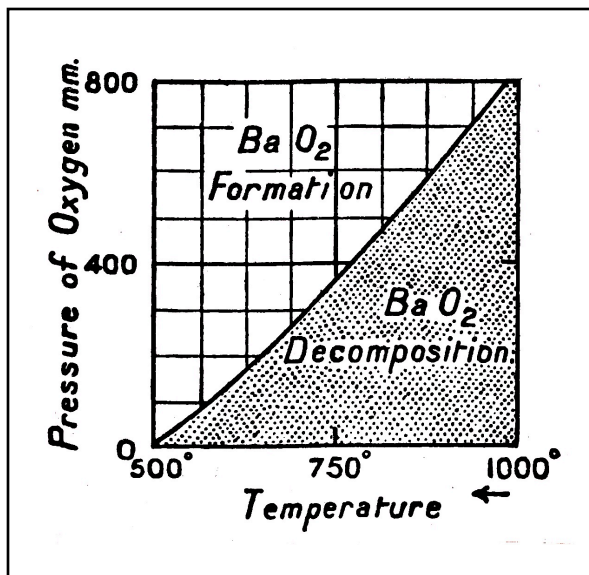


Figure 1. A plot of pressure versus temperature showing the regions corresponding to the favorable production of barium oxide versus barium peroxide (7).

passing the air over lime (Ca(OH)₂) or through a solution of potassium or sodium hydroxide:



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

It should be noted that the industrial use of reaction 1, like the more famous Haber ammonia synthesis, is an excellent textbook example of the practical application of Le Chatelier's principle. Indeed, in 1880, Boussingault, inspired by the earlier work of Henri Sainte-Claire Deville on thermal dissociation reactions, returned to the study of reaction 1 and showed that it could be reversed not only by a change in temperature at constant air pressure, but also by a change in pres-

THE ORIGIN OF THE BRIN PROCESS

sure at constant temperature – high pressures favoring the formation of the peroxide and low pressures favoring the formation of the oxide (6). Though, as summarized in figure 1, one can in principle optimize the equilibrium shift by simultaneously manipulating both temperature and pressure, in actual practice it was far easier and more economical to shift the pressure than to shift the temperature. Consequently, when applied industrially, the latter was kept constant at about 700°C while the air pressure was set at 2 atm for peroxide production and then reset at about 0.05 atm for its subsequent decomposition, the gas obtained under these conditions being about 90-96% dioxygen and 4-10% dinitrogen (7).

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Publication History

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

XLI

Why is R Used to Symbolize Hydrocarbon Substituents?

Question

Why is R used to symbolize hydrocarbon substituents?

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Answer

The symbol R was first extensively used in the writing of generalized organic formulas by the French chemist, Charles Gerhardt (figure 1), in his famous *Précis de chimie organique* of 1844, a work which pioneered the use of generalized functional groups and homologous series to organize the known organic compounds of carbon (1). Gerhardt's choice of the letter R remains something of a mystery. The most obvious explanation is that was an abbreviation for the word "radical" – a term introduced by the French chemist, Guyton de Morveau, in 1786 to designate the element or combination of elements which formed acids upon reacting with oxygen (2). By the early 19th century, however, the term had come to stand for any reactive monoatomic (simple radical) or polyatomic (compound radical) fragment of a larger molecule that maintained its identity throughout a series of chemical reactions (3).

A second, less likely, candidate for R is the word "residue" and its German equivalent "Rest." These terms had been introduced by Gerhardt in 1839 as part of his famous residue theory of organic reactions. This postulated that such reactions were driven by the elimination of small, stable, inorganic molecules, such as H₂O, HCl, NH₃, etc., the accompanying organic by-products being merely the result of the haphazard combination of the left-over organic fragments or residues found in the starting molecules after extraction of the necessary components for the primary inorganic product (4).

Gerhardt's use of the letter R in his *Précis* is not completely consistent with either of these explanations, as he used it to symbolize both hydrocarbon molecules

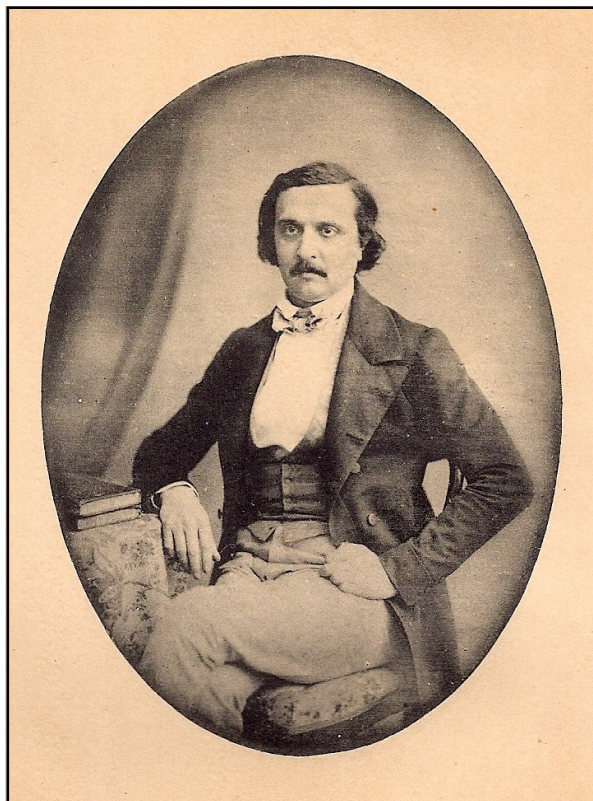


Figure 1. Charles Frédéric Gerhardt (1816-1856).

and the hydrocarbon portion of more complex molecules or, as he phrased it, to represent "les éléments combustibles." Indeed, he later restricted its use to hydrocarbons and hydrocarbon fragments containing a 2/1 ratio of hydrogen to carbon (i.e. C_nH_{2n}) and employed more elaborate symbols to indicate other ratios, such as R+2 for C_nH_{2n+2} and R-4 for C_nH_{2n-4}, etc.

In his *Méthode de chimie*, of 1854, Gerhardt's friend and sometime collaborator, the French chemist, August Laurent, used R in Guyton de Morveau's original sense to generalize the formulas of various binary oxides (i.e., RO, RO₂, R₂O₃, etc.), as well as to symbolize the hydrocarbon nucleus or "noyau" of various organic molecules (5). This dual usage was carried

over in Cannizzaro's famous pamphlet of 1858 on the determination of atomic weights, which contains the first explicit identification of R with the word radical that I am aware of (6):

I indicate by the symbol R^I_m any monoatomic metallic radical, whether simple or compound, and with the symbol R^{II}_m any biatomic metallic radical.

By monatomic and biatomic, Cannizzaro meant monovalent and bivalent. In general, his simple radicals corresponded to electropositive atoms or elements and his compound radicals to hydrocarbon fragments. He also introduced the symbol X to represent electronegative substituents, such as O, OH, and the halides.

Following Cannizzaro, Mendeleev, in his famous review of 1871, made extensive use of R to represent generalized classes of atoms or elements when writing type formulas for both the oxides (R_2O , RO, RO_2 , etc.) and hydrides (RH, RH_2 , RH_3 , etc) – formulas which were enthroned at the top of the short form of the periodic table for more than 70 years (7). In contrast, the early organic textbooks by Löwig (1846), Gregory (1852), Kolbe (1854), and Limpricht (1855) made no use of the symbol, though it does briefly appear in the 1867 text by Erlenmeyer, after which its use in the organic literature slowly increases throughout the rest of the 19th and early 20th centuries (8).

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Publication History

First published in *J. Chem. Educ.*, **2010**, 87, 360-361.

Update

Pierre de Menten has supplied the author with some additional early references on the use of R in chemical formulas which nicely fill in the gap separating Guyton de Morveau from Gerhardt. The most important of these occur in the writings of Berzelius, who introduced the letter R into his new alphabetic chemical symbolism as an abbreviation for any "radical combustible" (in the original sense of Guyton) in the new preface which he added to the 1819 French translation of his work "Försök till en theoretisk åsift af läran om de kemiska proportionerna, samt af elektricitetens inflytelse såsom kemiskt agens" (Essay on the Theory of Chemical Proportions and on the Chemical Influences of Electricity) and which had first appeared the previous year in volume 3 of his famous *Lärbok i Kemien*. Berzelius used this abbreviation in the 1819 translation and later editions to write generalized formulas for various oxides, such as $R + O$, $R + 2O$, $R + 3O$, etc., in which R usually stood for a simple radical or chemical element. It is this particular usage, albeit slightly modernized, which is found in the later writings of Laurent and Mendeleev cited in the original column.

De Menten also notes that, prior to the publication of the *Précis* of 1844, Gerhardt sporadically used R to represent compound hydrocarbon radicals in his 1840-1842 translation of Liebig's *Traité de chimie organique*. All of this, in combination with Gerhardt's definition of R as representing "les éléments combustibles," strongly suggests that Gerhardt was still using the term and symbol in the Guyton-Berzelius sense as a symbol for any atom or collection of atoms capable of forming an oxide and not in the modern sense of exclusively representing a reactive fragment of a neutral hydrocarbon molecule.

Indeed, it would appear that this latter usage did not become exclusive until the early 20th century and the disappearance of the generalized oxide and hydride formulas at the top of most periodic tables. Its transitional nature in the late 19th century is well illustrated by van't Hoff, who used R extensively in his famous pamphlet of 1874 on the stereochemistry of the tetrahedral carbon atom and also in his far less successful 1884 monograph *Ansichten über die organische Che-*

mie in the same sense as Cannizzaro to represent not just alkyl groups, but any “generalized univalent group” whether it was monoatomic or polyatomic, including halides, the hydroxyl group, the amine group, etc.

* J. J. Berzelius, *Essai sur la théorie des proportions chimiques et sur l'influence chimique de l'électricité*,

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XLII

The Origin of the Ionic-Radius Ratio Rules

Question

What is the origin of the ionic radius ratio rules?

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Answer

Generally speaking, the ionic-radius ratio rules are either incorrectly attributed to Linus Pauling in the chemical literature (1) or to Victor Goldschmidt in the geochemical literature (2). In actual fact they were first proposed within the context of the coordination chemistry literature by the Austrian chemist, Gustav F. Hüttig (figure 1), in a brief note published in 1920 in which he reported the R/R_+ ratio for possible geometries corresponding to coordination numbers of 2, 3, 4, 5, 6, 8, 12 and 20 (3). Two years later the German chemist, Alfred Magnus, gave a more detailed treatment explicitly linked to Walther Kossel's recently proposed electrostatic screening theory of complex ion formation and also included values for various alternative coordination geometries, such as square-planar versus tetrahedral and hexagonal-planar versus octahedral (4, 5). In 1923 Hüttig's original results were cited by Max Lambert in a discussion of the structures of complex hydrates (6) and the following year they were incorporated into the second edition of Rudolf Weiland's textbook *Einführung in die Chemie der Komplexverbindungen* (7). In a series of papers published in 1925 by Rudolf Straubel and Hüttig, the rules were further linked to the concept of packing efficiency (8, 9).

The thrust of all of the above papers was the problem of how to predict the maximum coordination numbers for discrete complex ions and of explaining why there were few, if any, known examples of species having coordination numbers of five or seven. While not the first person to propose the radius ratio rules, the Swiss-Norwegian geochemist, Victor Goldschmidt, does



Figure 1. Gustav Franz Hüttig (1890-1957).

appear to have been the first to apply them to infinitely extended ionic lattices rather than to discrete complex ions – an application first described in German in 1926 and 1927 in Parts VII and VIII of his famous series of short monographs dealing with the laws governing the geochemical distribution of the elements in nature and again in English in 1929 (10-12). Even this cannot be said of Pauling, however, who was quite late in coming to the rules and who first invoked them in his 1927 paper on ionic radii and once again in his 1929 summary of the various principles governing the structures of complex ionic crystals (13, 14).

In his various monographs Goldschmidt acknowledged the earlier work of both Hüttig and Magnus, whereas in his own publications Pauling failed to note either – an oversight which he partially corrected in the case of Magnus a decade later in the first edition of *The Nature of the Chemical Bond* (15). This neglect, coupled with the unfamiliarity of most American chemists with both the early German literature on coordination chemistry and the geochemical literature probably accounts for the incorrect association of the rules with Pauling's name. Luckily this association has never been strong enough to become a full-fledged example of "Stigler's Law of Eponymy" (16):

No scientific discovery is ever named after its original discoverer.

though it is certainly an example of Robert Merton's more famous "Matthew Effect" (17) whereby the famous are often credited, not only with their own discoveries, but occasionally with some they never made:

For unto every one that hath shall be given, and he shall have abundance: but from him that hath not shall be taken away even that which he hath. (The Gospel of Saint Matthew)

While the ionic-radius ratio rules are known to have many exceptions, they have remained a standard feature of most inorganic textbooks since the 1950s and have also been the subject of numerous articles in this journal (18).

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phy of Hüttig, with a portrait, may be found in R. E. Oesper, "Gustav F. Hüttig," *J. Chem. Educ.* **1952**, 29, 622-623.

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Publication History

First published in *J. Chem. Educ.*, **2010**, 87, 587-588

XLIII

Onion's Fusible Alloy

Question

What is the origin of the name "Onion's Fusible Alloy"?

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Answer

"Onion's Fusible Alloy" is the name given to a low melting (92°C) ternary alloy composed of 50% Bi, 30% Pb, and 20% Sn by weight, and which is currently being marketed to high school chemistry teachers as a novelty item for use in demonstrations and laboratory experiments. It is actually one of an entire family of fusible ternary Bi/Pb/Sn alloy systems which melt at or just below the boiling point of water and which have been used since the 18th century for such purposes as temperature standards, solders, safety plugs for steam boilers, and valves for automatic sprinkler systems. On a more frivolous note, these alloys have also occasionally been used to make such joke items as trick spoons designed to melt when used to stir a cup of hot coffee or tea (1).

The first set of these alloys was reported by Sir Isaac Newton (1642-1727) in 1701 for use as temperature standards (2). In fact Newton recorded two compositional variations, the lowest melting of which is listed in the attached table and is now commonly referred to in the literature as "Newton's Metal." A similar set of low melting Bi/Pb/Sn alloys of varying composition were reported posthumously in 1772 by the German pharmacist, Valentin Rose the Elder (1736-1771), and are commonly referred to as "Rose's Metal," though the particular composition and melting point reported under this name varies considerably from one source to another (3). A final set of more than ten compositional variations for this system was reported by the French chemist, Jean D'Arcet (1725-1801), in 1775 and are known collectively as "D'Arcet's Alloys" (4). As with the case of Rose's Metal, the particular composition and melting point reported under this name varies considerably from source to source, though the French engineer, A. Guettier, in his 1871 treatise on alloys, felt that the terms Rose and D'Arcet Alloy were essentially synonymous and were best characterized by the idealized composition 50% Bi, 20% Pb, and 30% Sn by weight – a composition which happens to be identical to one of the variations first

Example Fusible Alloy Systems

Year	Discoverer	Composition by Weight	mp/°C
1701	Newton	50% Bi, 20% Pb, 30% Sn	98
1772	Rose	50% Bi, 27.1% Pb, 22.1% Sn	95
1775	D'Arcet	49.2% Bi, 21.2% Sn, 27.6% Pb	95
Before 1888	Onion	50% Bi, 30% Pb, 20% Sn	92
1860	Wood	50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd	70
1860	Lipowitz	50% Bi, 27% Pb, 13% Sn, 10% Cd	74
1935	French	41% Bi, 22.1% Pb, 10.6% Sn, 8.2% Cd, 18.1% In	46.9

reported by Newton in 1701 (5).

A search of the literature dealing with fusible alloys from 1872 to the present revealed numerous references to the alloys of Newton, Rose and D'Arcet but only one to Onion's alloy (5-9). This occurs in an 1889 guide to alloys systems by Krupp and Wildberger, but provides no clue as to who Onion was or where he originally proposed his particular variation of the Bi/Pb/Sn system (6). Indeed the book in question has been scanned by Google and is currently available on the internet, which is where I suspect the laboratory supplier of this product got both the name and the recipe.

The particular compositions reported by Newton, Rose, D'Arcet and Onion were all the result of haphazard empirical investigation and it was not until 1898 that Charpy reported a complete ternary phase diagram for the Bi/Pb/Sn system which revealed (figure 1) the existence of a single ternary eutectic point at 96°C corresponding to the composition 52% Bi, 32% Pb, and 16% Sn by weight (10). This implies that many of the melting points given in the attached table and reported in references 5-9 – and especially the melting point reported for Onion's alloy – must either be inaccurate or the metals used in their preparation must be contaminated with other ingredients.

There are, of course, fusible alloys systems with melting points much lower than those reported for the Bi/Pb/Sn system, the most famous of which are those found in the quaternary Bi/Pb/Sn/Cd system (see table), as first reported by the American physician, Barnabas Wood, of Nashville, Tennessee, in 1860 and subsequently by Lipowitz the same year (11, 12). Wood's discovery attracted considerable attention and was subsequently reported in both the German and French literature as well (13). It was the editor of *The American Journal of Science* – the Harvard mineralogist, James Dwight Dana – who first suggested that these alloys be called "Wood's Fusible Metal" in honor of their discoverer (14). Unfortunately, because of problems with cadmium toxicity, these alloys are no longer recommended for student use. Work in the 20th century has since revealed more complex alloys systems having even lower melting points, such as those reported by French in 1935 (see table), some of which are liquid at room temperature and are currently being explored as possible substitutes for liquid mercury (15).

We would obviously like to hear from any readers having further information on either Onion or his alloy (16).

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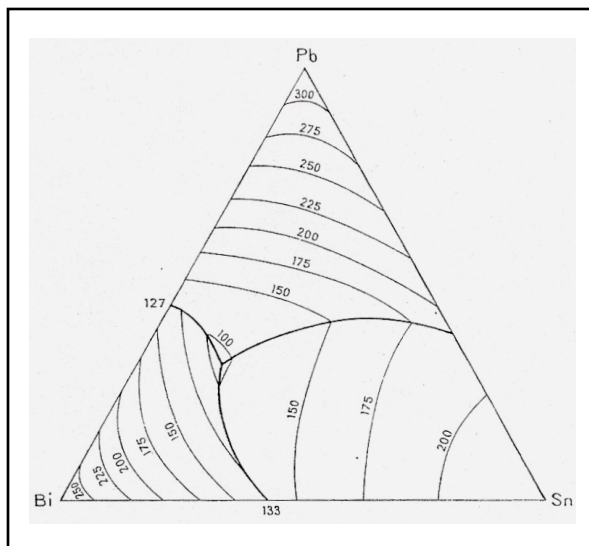


Figure 1. Phase diagram for the Bi/Pb/Sn system showing a ternary eutectic at 96° C (10). Compositions are in weight percentages.

1701, 270, 824-829. An English translation appears as I. Newton, "A Scale of the Degrees of Heat," *Phil. Trans., Abridged*, **1809**, 4, 572-575. Both are reproduced in I. B. Cohen, Ed., *Isaac Newton's Papers & Letters on Natural Philosophy*, Harvard University Press: Cambridge, MA, 1958, pp. 259-268.

3. V. Rose, "Vermischung einiger Metalle, welche in kochende Wasser die laufende Gestalt des Quecksilbers annehmen," *Stralsund. Magaz.* **1772**, 2.

4. J. D'Arcet, "Expériences sur l'alliage fusible de plomb, de bismuth, et d'étain," *Journal de médecine*, **1775**.

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6. A. Krupp, A. Wildberger, *The Metallic Alloys: A Practical Guide*, Baird: Philadelphia, 1889, p. 305.

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8. Anon., *Bismuth*, United States Bureau of Standards, Circular 382, Government Printing Office: Washington, DC, 1930.

9. P. Pascal, "Alliages ternaires ou plus complexes," in P. Pascal, Ed., *Nouveau traité de chimie minéral*, Vol. 20, Masson et Cie: Paris, 1963, pp 1911-1924.

10. G. Charpy, "Sur les états d'équilibre du système ternaire: plomb-étain-bismuth," *Compt. rend.*, **1898**, 126, 1569-1573.

11. B. Wood, "Improved Alloy or Metallic Composition Suitable for a Metallic Cement in the Manufacture of Tin, Pewter, and Other Metals; Also Useful for Casting and Other Purposes," *J. Franklin Inst.*, **1860**, 40 (Third Series), 125-128.

12. A. Lipowitz, "Ueber Wood's leichtflüssiges Metall," *Dingler's Polytech. J.*, **1860**, 158, 376-377.

13. Anon. "Sur une nouvelle alliage très-fusible," *Répertoire chim. appl.*, **1860**, 2, 313-314; Anon., "Wood's leichtflüssiges Metall," *Dingler's Polytech. J.*, **1860**, 158, 271-272.

14. Anon., "A New Fusible Metal," *Am. J. Sci.*, **1860**, 30 (Second Series), 271-272.

15. S. J. French, "A New Low-Melting Alloy," *Ind. Eng. Chem.*, **1935**, 27, 1464-1465.

16. Onion may be the name of a 19th-century company that specialized in the manufacture of this alloy.

Publication History

First published in *J. Chem. Educ.*, **2010**, 87, 1050-1051.

Update

George Rizzi tells the author that he was recently surprised, on breaking a thermometer, to discover that the silver liquid inside was not mercury but rather a ternary Ga/In/Sn alloy called Galinstan, which melts at -19°C and boils above 1300°C . Likewise, Dr. H. J. Wagner of the University of Paderborn has provided the missing information on Onions' alloy. This alloy was introduced as a packing material for a rotary steam engine first patented by the British engineer, William Onions,

in 1812. This would explain why I was unable to find anything on it in the chemical and metallurgical literature and, of course, it never occurred to me to look in the literature dealing with the history of the steam engine. This also means that it should be called "Onions' alloy" rather than "Onion's alloy," as it is universally, but incorrectly listed on the web and also referred to by its current manufacturer. Dr. Wagner has also kindly provided a number of relevant references:

* H. W. Dickinson, A. Lee, *Transactions of the Newcomen Society*, **1925**, 4 (1925), 48-63 (especially pp. 53-55).

* J. Millington, *An Epitome of the Elementary Principles of Natural and Experimental Philosophy*, Part I, Sherwood, Jones & Co: London, 1823, p. 336.

* E. Galloway, *History of the Steam Engine From Its Earliest Invention to the Present Time*, 2nd ed., Steill: London, 1828, p.156.

* R. Stuart, *Historical and Descriptive Anecdotes of Steam-Engines and of Their Inventors and Improvers*, Vol. II, Wightman & Cramp: London, 1829, p. 511.

* Anon., "On the Preparation of Various Fusible Metals and on Using Them to the Most Advantage," *Gill's Technical Repository*, **1822**, 1, 348-348.

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* A. A. Hopkins, *The Standard American Encyclopedia of Formulas*, Grosset & Dunlap: New York, 1953.

XLIV

Why Are q and Q Used to Symbolize Heat?

Question

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

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Answer

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

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



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

lower-case q to represent the bound or “latent” heat due to isothermal entropy generation (i.e. $T\Delta S$) (4).

In contrast, Lewis and Randall, in their famous 1923 monograph on thermodynamics, made no use of the upper-case Q and instead consistently employed both a lower-case q for heat and a lower-case w for work (5), while Samuel Glasstone, in his 1947 textbook, *Thermodynamics for Chemists*, adopted the convention of employing the lower-case letters, q and w , for arbitrary, path-dependent, infinitesimal quantities of

WHY ARE q and Q USED TO SYMBOLIZE HEAT?

heat and work, but the upper-case letters, Q and W , for their algebraic sums (6). Apparently this eclecticism is still very much with us as the most recent IUPAC guide to quantities, units, and symbols in physical chemistry lists both q and Q as equally valid symbols for heat, though it also lists Q as the symbol for electrical charge and for the reaction quotient (7).

Literature Cited

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2. The most important of these papers are collected together in English translation in R. Clausius, *The Mechanical Theory of Heat*, Van Voorst: London, 1867.

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Publication History

First published in *J. Chem. Educ.*, **2010**, *87*, 1142.

XLV

Avogadro's Constant

Why Has Its Value Changed Over Time?

Question

Why has the value of Avogadro's constant changed over time?

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Answer

As noted in an earlier column, the concept of Avogadro's constant or number (N_A) was not introduced by Avogadro in 1811, but rather by the French physical chemist, Jean Perrin (figure 1), in 1908 (1). It may be formally thought of as being numerically determined the value of the conversion factor between the gram (g) and the unified atomic mass unit (u), as may be seen from the requirement that the molecular mass of a given atom, molecule, or ion, as expressed in atomic mass units per entity, must be numerically equal to the molar mass of the same substance as expressed in grams per mole. Thus for example:

$$207.2 \text{ g/mol Pb} = (207.2 \text{ u/Pb atom})(1 \text{ g}/N_A \text{ u})(N_A \text{ Pb atoms}/1 \text{ mol Pb})$$

There are two reasons why the value of N_A has changed over time. The first, and most obvious, is that any change in the standards used to define either the atomic mass unit or the gram will cause a shift in the value of their conversion factor and hence in the value of N_A . Such a change occurred in 1960 when the standard for the atomic mass unit was changed from the O = 16 scale to the $^{12}\text{C} = 12$ scale. A similar shift would have occurred around 1900 with the shift from the H = 1 to the O = 16 scale, but, of course, the concept of N_A was not a part of chemistry at that time (2). The second reason for a shift in the value of N_A has to do with an ever increasing ability to accurately measure the value of this constant, as illustrated by the selected examples given in the accompanying table (3).

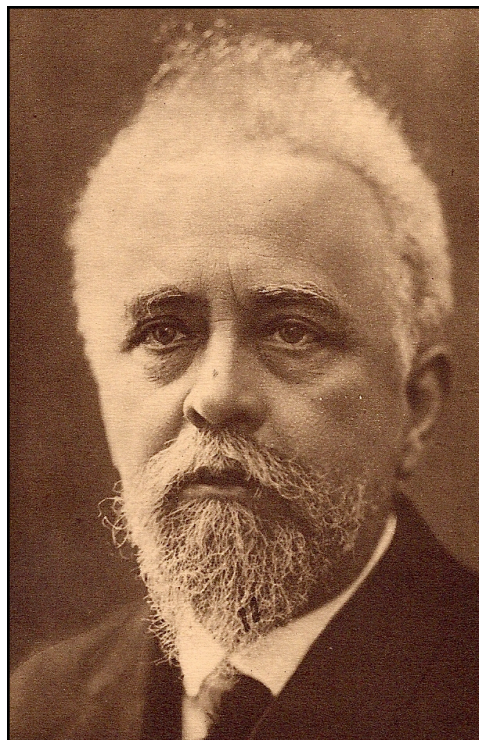


Figure 1. Jean Perrin (1870-1942).

The standard definition of N_A is that it is the same number of entities as there are carbon atoms in exactly 12 grams of carbon-12. Consequently students are often surprised when they are told that its numerical value is actually fixed by the conversion factor between the gram and the atomic mass unit. If chemists had failed to adopt the metric system and had instead continued to use some older conventional mass unit, such as the ounce, drachm or grain, to weigh chemicals in the laboratory, it would still have been expedient to maintain a numerical identity between atomic and molecular masses, as measured in atomic mass units, and the molar masses of the various substances as measured in the lab. Under such conditions, Avogadro's constant would have had a very different value, and it makes an interesting teaching exercise to assign

AVOGADRO'S CONSTANT: WHY HAS ITS VALUE CHANGED OVER TIME?

Year	Author	$N_A/10^{23}$
1908	Perrin	6.7
1917	Mullikan	6.064
1929	Birge	6.0644
1931	Bearden	6.019
1945	Birge	6.02338
1951	DuMond	6.02544
1965	Bearden	6.022088
1973	Cohen	6.022045
1987	Deslattes	6.022134
1994	Basile	6.0221379
2001	De Bièvre	6.0221339

Table 1. Selected values reported for the value of N_A over time. A more complete listing may be found in reference 3.

students the task of calculating the corresponding values of N_A for each of these alternative macroscopic mass units. Likewise, students are often puzzled as to why Avogadro's constant has such an odd numerical value and it is also of interest to challenge them to invent a new macroscopic mass unit for laboratory use that would yield a more aesthetic number, such as 1.0×10^{24} for the value of N_A .

Literature Cited

1. W. B. Jensen, "How and When Did Avogadro's Name Become Associated with Avogadro's Number?," *J. Chem. Educ.*, **2007**, *84*, 223.
2. Estimates of the number of molecules per given volume (though not the number per mole) were made by

various 19th-century physicists and can be retrospectively used to calculate estimates of N_A . See, for example, R. W. Hawthorne, "Avogadro's Number: Early Values by Loschmidt and Others," *J. Chem. Educ.*, **1970**, *47*, 751-755.

3. Based on the values reported in P. Becker, "History and Progress in the Accurate Determination of the Avogadro Constant," *Rep. Prog. Phys.*, **2001**, *64*, 1945-2008. The author would like to thank Juris Meija of the Institute for National Measurement Standards of Canada for bringing this report to his attention. Readers should be warned, however, that the author of this report makes numerous incorrect historical statements about the origins of Avogadro's work and related concepts, such as the false implication that Avogadro derived his hypothesis from the kinetic theory of gases.

Publication History

First published in *J. Chem. Educ.*, **2010**, *87*, 1302.

Update

The fact that the numerical value of N_A is ultimately fixed by the conversion factor between the gram and the atomic mass unit was first pointed out in the *Journal of Chemical Education* by F. E. Brown in 1933:

* F. E. Brown, "Molecular and Atomic Weights," *J. Chem. Educ.*, **1933**, *10*, 308-309.

yet 40 years later Hawthorne was describing this view as "remarkable" by which he obviously meant "eccentric:"

* R. M. Hawthorne Jr., "The Mole and Avogadro's Number: A Forced Fusion of Ideas for Teaching Purposes," *J. Chem. Educ.*, **1973**, *50*, 282-284.

That an experienced teacher like Hawthorne had difficulty grasping this point says much about how this concept is or is not taught in the average chemistry textbook.

XLVI

Origin of Isotope Symbolism

Question

What is the origin of our current nomenclature and symbolism for isotopes?

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Answer

Prior to the introduction of the isotope concept by the British radiochemist, Frederick Soddy, in 1913, radioelements were given names based on the nature of their parent element within a given radioactive decay series (1). Under this system, radioelements having widely divergent chemical properties were often assigned chemically similar names (2):

<i>Original Name</i>	<i>Current Name</i>	<i>Current Symbol</i>
thorium	thorium-232	(²³² Th)
mesothorium I	radium-228	(²²⁸ Ra)
mesothorium II	actinium-228	(²²⁸ Ac)
thorium emanation	radon-220	(²²⁰ Rn)
thorium A	polonium-216	(²¹⁶ Po)
thorium C	bismuth-212	(²¹² Bi)

whereas those which we now recognize as chemically identical isotopes were often assigned widely divergent names (3):

<i>Original Name</i>	<i>Current Name</i>	<i>Current Symbol</i>
uranium X ₁	thorium-234	(²³⁴ Th)
ionium	thorium-230	(²³⁰ Th)
radiothorium	thorium-228	(²²⁸ Th)
uranium Y	thorium-231	(²³¹ Th)
radioactinium	thorium-227	(²²⁷ Th)

Our current symbolism and naming system for isotopes were first introduced by the British physicist, Francis Aston (figure 1), in his 1922 monograph, *Isotopes* – at first sparingly and then with increasing fre-

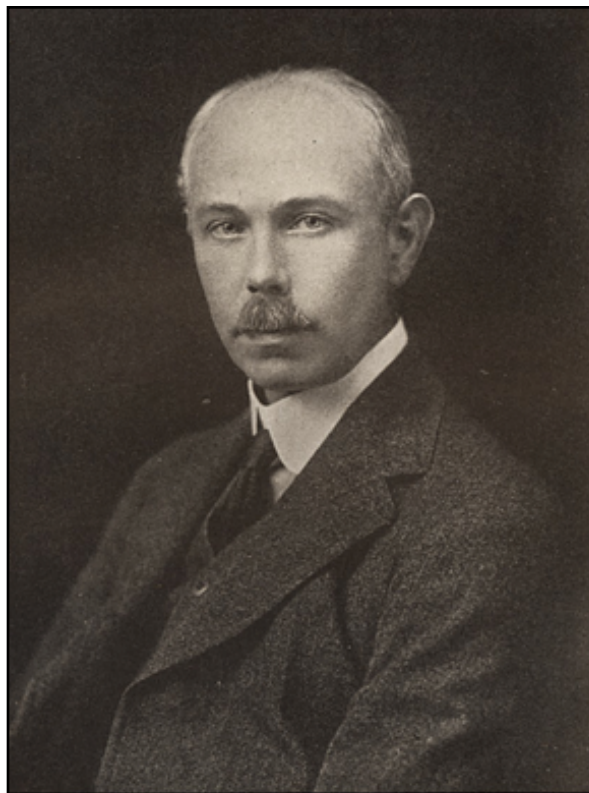


Figure 1. Francis William Aston (1877-1945).

quency throughout subsequent editions (3):

The problem of nomenclature of the isotopes became serious when the very complex nature of the heavy elements was apparent. It has been decided for the present to adopt the rather clumsy but definite and elastic one of using the chemical symbol of the complex element with an index corresponding to its mass; e.g Ne²², Rb⁸⁷. This system is made reasonable by the fact that the constituents of complex elements have all so far proved to have masses expressible as whole numbers.

Why Aston thought this method was “clumsy” compared to the older method based on decay series is something of a mystery.

As is well known, Aston was largely responsible

for having developed, in the years immediately following the First World War, J. J. Thomson's positive-ray method into the present technique of mass spectroscopy and for having applied it to the detection and cataloging of the isotopes of the nonradioactive elements, which, unlike their radioactive counterparts, could not be detected and categorized by means of characteristic radioactive decay constants. Despite the clarity of his nomenclature proposals, traditional radiochemists were slow to adopt them and many textbooks on radiochemistry written before the Second World War continued to employ the older decay-series nomenclature or an uncomfortable mixture of the two (4). All of this was changed by the war and the advent of the atomic bomb, so by the late 1940s Aston's nomenclature and symbolism were widely accepted.

In his original symbolism, Aston placed the superscripted mass number of the nucleus to the right of its symbol. However in 1940 the Committee for the Reform of Inorganic Nomenclature of the International Union of Pure and Applied Chemistry (IUPAC) recommended moving it instead to the left of the element symbol so that it did not interfere with the older tradition of placing superscripted ionic charge numbers to the right of the symbol (5). This change was adopted by Aston in the fourth edition (1942) of his book, and was also anticipated in the second edition (1938) of the well-known textbook, *A Manual of Radioactivity*, by the radiochemists George Hevesy and Fritz Paneth (4, 6), though the older convention persisted in

most American publications well into the 1960s.

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2. Assembled from the tables given in S. Glasstone, *Sourcebook on Atomic Energy*, Van Nostrand: New York, NY, 1950, pp. 125-128.
3. F. Aston, *Isotopes*, Arnold: London, 1922, p. 61.
4. Thus, for example, O. Hahn, *Applied Radiochemistry*, Cornell University Press, 1936. does not use Aston's symbolism, whereas G. Hevesy, F. Paneth, *A Manual of Radioactivity*, 2nd ed., Oxford University Press: Oxford, 1938 uses it to describe induced nuclear reactions in Chapters 7 and 10 but ignores it in the later chapters dealing with isotopes and the placement of the radioelements in the periodic table.
5. W. P. Jorissen et al, "Report of the Committee for the Reform of Inorganic Nomenclature, 1940," *J. Chem. Soc.*, **1940**, 1404-1417. Isotope symbolism, p. 1407.
6. F. Aston, *Mass Spectra and Isotopes*, 2nd ed., Arnold: London, 1942, p. 54. This is actually the fourth edition of reference 3.

Publication History

First published in *J. Chem. Educ.*, **2011**, 88, 22-23.

XLVII

When Was Electronegativity First Quantified? I

Question

When was electronegativity first quantified?

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Answer

Most chemists are under the false impression that the electronegativity concept was first introduced by the American chemist, Linus Pauling, in 1932 (1). However, in a series of historical papers published in this *Journal* it was shown that both the term and the concept predate Pauling by more than a century (2). These earlier 19th-century electronegativity scales were essentially qualitative in nature and consequently a weaker claim can still be made that Pauling – if not the originator of the electronegativity concept – was at least the first to provide a fully quantified scale for its measurement. Unfortunately even this weaker claim requires substantial qualification since recent work has uncovered two earlier pre-Pauling attempts to quantify this important chemical concept – attempts whose subsequent fates illustrate some important lessons about how one goes about successfully developing and marketing a scientific concept. Since much of this material has not been published elsewhere, we will take the unusual step of devoting two separate columns to this subject – one for each of these earlier anticipations.

The first and earliest of these precursors was due to the American physical chemist, Worth H. Rodebush (figure 1), who is perhaps best known as the coauthor, along with Wendell Latimer, of the first paper to deal with the concept of the hydrogen bond (3). In 1925, seven years before the publication of Pauling's paper, Rodebush published an article in *The Journal of Chemical Education* dealing with the Bohr atom and the periodic table in which he made the following passing comment (4):

If it might be permissible to introduce a qualitative formula into science which is rapidly becoming exact,



Figure 1. Worth Huff Rodebush (1887-1959).

we might represent the electronegativity as a function of V/S where V is the number of valence electrons and S the number of shells. The basis of this formula is Coulomb's law and I believe that in a few years we shall calculate the energy changes in chemical reactions by means of it.

Ignoring Rodebush's inappropriate description of his equation as "qualitative," which may have been a typo for "quantitative" (as an equation must necessarily be), there is little doubt that this interesting suggestion was the result of an explicit attempt on the part of Rodebush to make the electronegativity concept more rigor-

Rodebush V/S Electronegativity Values

	1	2	3	4	5	6	7	8
2	Li (0.50)	Be (1.00)	B (1.50)	C (2.00)	N (2.50)	O (3.00)	F (3.50)	Ne (4.00)
3	Na (0.33)	Mg (0.67)	Al (1.00)	Si (1.33)	P (1.67)	S (2.00)	Cl (2.33)	Ar (2.67)
4	K (0.25)	Ca (0.50)	Ga (0.75)	Ge (1.00)	As (1.25)	Se (1.50)	Br (1.75)	Kr (2.00)
5	Rb (0.20)	Sr (0.40)	In (0.60)	Sn (0.80)	Sb (1.00)	Te (1.20)	I (1.40)	Xe (1.60)
6	Cs (0.17)	Ba (0.33)	Tl (0.50)	Pb (0.67)	Bi (0.83)	Po (1.00)	At (1.17)	Rn (1.33)
7	Fr (0.14)	Ra (0.29)						

ous, as shown by his comments in an article written for *Science Magazine* the previous year (5):

I had hoped that we might be able to substitute electron affinity or ionizing potential for the wretched term electronegativity, but these quantities are measured for the gaseous state and our ordinary chemical properties are concerned with the condensed phases. For instance the electron affinity of the chlorine atom is less than the ionization energy of sodium, so that a chlorine atom should never rob a sodium atom of its electrons, and yet nothing is more certain than that it does so in a solution of sodium chloride.

The historical ambiguity is, of course, that, having suggested this explicit formula for calculating electronegativity values, Rodebush apparently did nothing further with it, though it requires only about five minutes to calculate the resulting electronegativity values for the main-block elements using valence-electron and Bohr-atom shell counts readily available in 1925, as summarized in the attached table. The resulting values show a 0.92 linear correlation coefficient with the corresponding Pauling electronegativity scale for these elements and a 0.97 correlation coefficient with the corresponding Allred-Rochow scale, results which are essentially identical with the correlation coefficients interrelating the 25 or so modern electronegativity scales.

There are, of course, problems with extending this definition to the transition metals, since the valence electrons for these atoms reside in two different shells, though use of an averaged shell number would probably give consistent results. A second problem is that the Rodebush definition gives values for the post-transition elements (Zn, Cd, Hg, Ga, In, Tl) which are too low since it does not take into account the effects of the d-block and f-block insertions on the screening constants for these elements. Likewise it gives values for H and He which are far too small, though it shares this problem with the majority of modern definitions, most of which have to instead make use of the corresponding Pauling value.

Despite these problems, the history of the electronegativity concept would have been quite different if Rodebush had properly developed his suggestion. Having a complete scale in 1925 for even just the main-block elements would have been a considerable advance over what in fact actually happened. Few chemists are aware that in his original paper of 1932 Pauling provided quantitative electronegativity values for only ten nonmetallic elements. In the 1939 edition of his famous monograph, *The Nature of the Chemical Bond*, he extended his scale to 33 elements, though he never published the data or calculations on which this extension was based (6). Not until 1960, and the publication of the third edition of his book, did a complete scale finally appear (7).

In addition, while the Rodebush electronegativity definition is an example of what Ferreira calls a primary definition, meaning one based on fundamental atomic properties and having a clear theoretical justification, the Pauling thermochemical definition is actually an example of a secondary definition, meaning one that is based on an empirical correlation between a macroscopic property of some sort (in this case thermochemical bond energies) and electronegativity and which is, consequently, lacking a clear theoretical justification (8).

Lastly, it is of interest to note that the Rodebush scale provides, as shown on the attached table, an unambiguous criterion ($EN > 1.00$) for the zig-zag line separating the metals and nonmetals commonly found in introductory textbooks, though it still begs the question of whether this line accurately represents the separation of these two classes of simple substances in the first place.

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2. W. B. Jensen, "Electronegativity from Avogadro to Pauling: Part I. Origins of the Electronegativity Concept," *J. Chem. Educ.*, **1996**, *73*, 11-20; "Electronegativity from Avogadro to Pauling: Part II. Late Nineteenth and Early Twentieth-Century Developments," *J. Chem. Educ.*, **2003**, *80*, 279-287.

3. W. M. Latimer, W. H. Rodebush, "Polarity and Ionization from the Standpoint of the Lewis Theory of Valence," *J. Am. Chem. Soc.*, **1920**, *42*, 1419-1433.

4. W. H. Rodebush, "Compact Arrangement of the Periodic Table," *J. Chem. Educ.*, **1925**, *2*, 381-383.

5. W. H. Rodebush, "The Subject Matter of a Course in Physical Chemistry," *Science*, **1924**, *59*, 430-433.

6. L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press: Ithaca, NY, 1939, p. 58. The same table appears in the second edition of 1948, p. 64.

7. L. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press: Ithaca NY, 1960, p. 93.

8. R. Ferreira, "Electronegativity and Chemical Bonding," *Adv. Chem. Phys.*, **1967**, *13*, 55-84. There have been several attempts to theoretically justify the Pauling scale, but I agree with Ferreira's assessment that they are all lacking in theoretical rigor.

Publication History

First published in *J. Chem. Educ.*, **2012**, *89*, 94-96.

XLVIII

When Was Electronegativity First Quantified? II

Question

When was electronegativity first quantified?

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Answer

In the first installment of the answer to this question we dealt with the quantitative definition of electronegativity first proposed by the American physical chemist, Worth H. Rodebush, in 1925, which predated the work of Pauling by seven years (1). In this installment we will deal with the quantitative definition given by the American chemist, Groves H. Cartledge (1891-1980), in 1928, which predated the work of Pauling by four years, though a proper understanding of Cartledge's work requires some background context.

Younger chemists are often unaware that the early decades of the 20th century saw the development of two alternative approaches to the description of bond polarity. The first of these, due largely to the American chemist, G. N. Lewis, began with an idealized covalent bond and discussed bond polarity as a deviation from this ideal which could be expressed in terms of the relative electronegativity difference between the two bonded atoms (2). The second approach, due largely to the Polish chemist, Kasimir Fajans, began with an idealized ionic bond and discussed bond polarity (figure 1) as a deviation from this ideal which could be expressed in terms of the polarizing ability of the cationic bonding component, on the one hand, and the polarizability of the anionic bonding component, on the other (3). The Lewis "covalent/electronegativity" model was subsequently developed by Pauling in the 1930s and became the prevailing paradigm in the United States and Great Britain, whereas, prior to the Second World War at least, the Fajans "ionic/polarization" model was the prevailing paradigm in Continental Europe and Russia.

The resulting bifurcation of the literature on bond

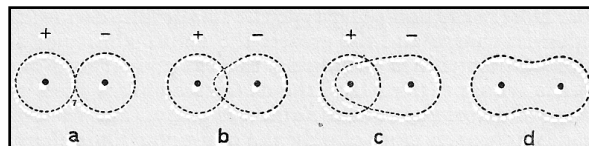


Figure 1. Fajans' concept of the formation of various polar covalent (b and c) and covalent (d) bonds via the progressive polarization of an idealized ionic bond (a) (3).

polarity has resulted in most chemists failing to recognize that the various numerical scales of cationic polarizing ability, which have been proposed over time within the context of the Fajans approach, are essentially identical to the various electronegativity scales which have been proposed over time within the context of the Lewis-Pauling approach. Most cations correspond to atomic cores and since scales of cationic polarizing ability are intended to measure the ability of the cation to attract additional electron density, they can also serve as a crude measure of the ability of an atom's core to retain its valence electrons, as well as to attract additional electrons – in short, they can serve as a measure of an atom's electronegativity.

In 1928 Cartledge proposed a quantitative measure of cation polarizing ability which he called the "ionic potential" (ϕ) and which he defined as the ratio of a cation's net charge to its radius (4):

$$\phi = (Z/r)_{\text{cation}}$$

In subsequent papers in which he attempted to correlate various properties with the ionic potential, Cartledge came to the conclusion that the square root of the ionic potential ($\phi^{0.5}$) was a more effective parameter (5-7). A plot of the numerical values for $\phi^{0.5}$ provided by Cartledge in 1928 for the main-block elements (see table) versus the corresponding Pauling electronegativity values gives a linear correlation coefficient of 0.91, whereas that for the Allred-Rochow scale is 0.96. Once again these are both comparable to the correlation coefficients interrelating various modern definitions and indicate that the $\phi^{0.5}$ scale could

Cartledge $\phi^{0.5}$ Values (NG = Not Given)

	1	2	3	4	5	6	7	8
2	Li (1.29)	Be (2.54)	B (3.87)	C (5.16)	N (6.71)	O (8.19)	F (10.0)	Ne (NG)
3	Na (1.02)	Mg (1.76)	Al (2.45)	Si (3.13)	P (3.83)	S (4.55)	Cl (5.20)	Ar (NG)
4	K (0.87)	Ca (1.42)	Ga (2.20)	Ge (2.74)	As (3.26)	Se (3.78)	Br (4.24)	Kr (NG)
5	Rb (0.82)	Sr (1.33)	In (1.92)	Sn (2.36)	Sb (2.84)	Te (3.27)	I (3.74)	Xe (NG)
6	Cs (0.77)	Ba (1.21)	Tl (1.78)	Pb (2.18)	Bi (2.60)	Po (3.02)	At (NG)	Rn (NG)
7	Fr (NG)	Ra (1.24)						

also have functioned as a quantitative electronegativity scale had Cartledge chosen to present it as such. Note that, like the Rodebush scale, the Cartledge scale also provides a criterion ($\phi^{0.5} > 3.02$) for the so-called zig-zag line separating the metals from the nonmetals.

Of course neither Rodebush's electronegativity equation nor Cartledge's ionic potential had an impact comparable to Pauling's thermochemical electronegativity scale, though both had the ability to generate a complete set of quantitative electronegativity values several decades before this was finally achieved for the Pauling definition. In the case of Rodebush this negligible impact was due to the simple fact that Rodebush failed to properly develop and publicize his definition, whereas in the case of Cartledge, it illustrates the importance of selecting proper terminology and aligning oneself with the prevailing theoretical paradigm.

A similar fate befell the measure of cation polarizing ability proposed by the Hungarian chemist, Bela Lakatos, almost 30 years after Cartledge (8). Termed the "effective field strength" by Lakatos, it made use of effective core charges and the Slater screening constants to define the electrostatic force field around the cation:

$$F^* = Z^*e/r^2 = (Z - S)e/r^2$$

The next year the American chemists Eugene Rochow and A. Louis Allred proposed the same definition as a measure of the electronegativities of neutral atoms (9).

While the Allred-Rochow electronegativity definition is now discussed in virtually every inorganic textbook, the Lakatos field strength, like the Cartledge ionic potential, has passed into virtual oblivion.

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Publication History

First published in *J. Chem. Educ.*, **2011**, 89, 94-96.

XLIX

Faraday's Laws or Faraday's Law?

Question

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

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Answer

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



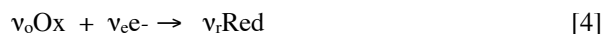
the change in the amount or extent of reaction, $d\xi$, measured in units of moles of reaction events, is defined as the change in the moles, dn_s , of any of the various species, s , in the reaction, weighted by its stoichiometric coefficient, ν_s , in the balanced equation:

$$d\xi = dn_s/\nu_s = dn_A/\nu_A = dn_B/\nu_B = dn_C/\nu_C = dn_D/\nu_D \quad [2]$$

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

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

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



we can express its rate of reaction, $d\xi/dt$, in terms of

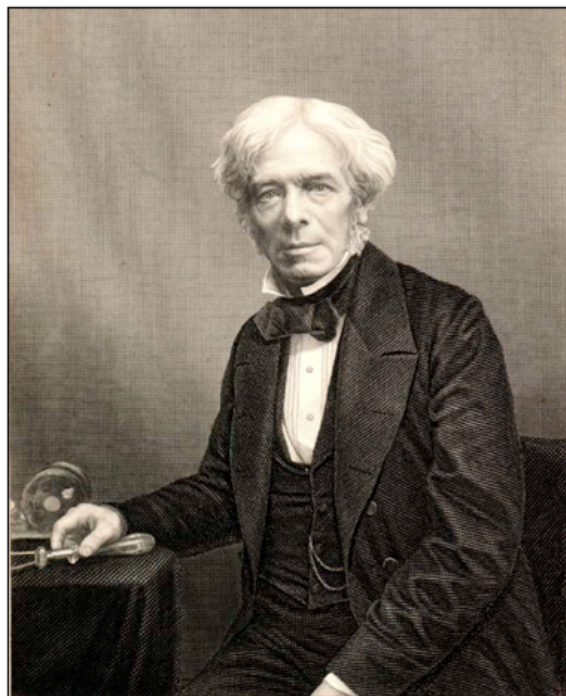


Figure 1. Michael Faraday (1791-1867).

either the weighted change in the moles of electrons consumed per unit time, $(dn_e/dt)/\nu_e$, or the weighted change in the moles of any one of the various chemical species generated or consumed per unit time $(dn_s/dt)/\nu_s$:

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

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

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

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

$$idt = (\nu_e/\nu_s)Fdn_s = z_s Fdn_s \quad [7]$$

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

$$it = z_s F n_s \quad [8]$$

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

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

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

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

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

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

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

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

$$it = z_s F (m_s / MW_s) \quad [9]$$

Solving this for m_s and recognizing both that the terms in parentheses on the right side of the resulting equation are a constant, k_s , for a given species and that the it term is equal to the total charge Q , we obtain the

mathematical equivalent of Faraday's first law of electrolysis:

$$m_s = (MW_s / z_s F) it \quad \text{or} \quad m_s = k_s Q \quad [10]$$

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

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

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

1. Since the two traditional verbal laws can be combined into a single mathematical equation (equation 8), it is more appropriate to talk of Faraday's law rather than Faraday's laws (5).
2. As demonstrated by the Italian chemist, Carlo Matteucci (1811-1868), in 1839, the relationship embodied in equation 8 is equally applicable to both an electrolysis cell and to a voltaic cell (in which case it correlates the current generated by the cell with the amount of reaction within the cell, rather than the amount reaction in the cell with the applied current) (6). Hence, it is no longer appropriate to talk of Faraday's law of electrolysis. Rather it should be called, following Faraday's original suggestion, Faraday's law of electrochemical action, in which the concluding qualifier is necessary in order to distinguish it from "Faraday's law of magnetic induction," as used in the field of electromagnetism.
3. Our derivation clearly shows that, in contrast to the Nernst equation, which is thermodynamic in nature, Faraday's law of electrochemical action is kinetic in nature (7).

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

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Publication History

Submitted to *J. Chem. Educ.*, **2011**,

L

Origins of the Qualifiers Iso-, Neo-, Primary, Secondary and Tertiary

Question

What are the origins of the qualifiers *iso-*, *neo-*, *primary*, *secondary*, and *tertiary* in organic nomenclature?

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Answer

The qualifiers *primary*, *secondary*, and *tertiary* were first applied to the classification of the organic amines in 1856 by the French chemist, Charles Gerhardt, in volume four of his famous *Traité de chimie organique* in order to distinguish between amines resulting from the first (*primary*), second (*secondary*), and third (*tertiary*) stages in the progressive substitution of the three hydrogen atoms of the ammonia molecule (NH_3) by various alkyl radicals (1):

One might call the nitrogen compounds primary, secondary or tertiary according as they represent the ammonia type with substitution of one, of two, or of three atoms of hydrogen.

This terminology was extended to the description of alcohols in 1864 by the Russian chemist, Aleksandr Butlerov, who first prepared what is now known as 2-methyl-2-propanol, but which he viewed as “trimethylated methyl alcohol” or “tertiary pseudo butyl alcohol” (2). In other words, his new alcohol corresponded to the third or tertiary stage in the progressive substitution of the three hydrogen atoms on the methyl group of methanol (CH_3OH) just as the tertiary amines did with respect to the three hydrogens of ammonia. From this point of view, what is now known as 2-propanol represented the second stage of this substitution process and thus corresponded to a secondary alcohol, whereas ethanol resulted from the first stage of substitution and thus corresponded to a primary alcohol.

By the 1920s this terminology had also been trans-



Figure 1. Aleksandr Butlerov (1828-1886).

ferred from the naming of specific classes of compounds to the naming of the carbon atoms within a given carbon chain or ring, thus giving rise to our current concept of primary (one C-C link), secondary (two C-C links), tertiary (three C-C links) and, by extension, quaternary (four C-C links) carbon centers (4).

The alternative name of isopropyl alcohol for what is now called 2-propanol is derived from a paper on its structure written by the German organic chemist, Hermann Kolbe, in 1862, where he referred to it as “isomeric propyl alcohol” (i.e., as an isomer of normal or 1-propanol) or “isopropyl alcohol” for short (3). According to Crosland (5), the use of the prefix *iso-* to name isomers of known compounds was established before Kolbe applied it to the alcohols, but obviously resulted in ambiguity if more than one isomer was known for the compound in question.

The prefix *neo-*, from the Greek *neos*, meaning “new,” was first applied in sciences other than chemistry (e.g., neolithic). Beginning in the 1880s it became fashionable in mineralogy as a way of distinguishing newly discovered varieties of previously known minerals (e.g., neocyanite, neotestite, etc.). It appears to have been first applied in chemistry proper by Auer von Welsbach in 1885 when he succeeded in separating the rare earth didymia into two new fractions, one of which he named neodymia (6). According to both Beilstein and the *Chemischen Central-Blatt*, the qualifier was first applied in organic chemistry in 1898 by the British chemist, Martin Onslow Forster, who used it to name the derivatives of a newly discovered isomer of bornylamine (7). However, as with the prefix *iso-*, use of the prefix *neo-* to distinguish isomers also proved to be a nomenclature dead-end once more than two isomers of the compound in question became known.

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3. H. Kolbe, “Ueber die chemische Constitution des aus dem Aceton durch nascirenden Wasserstoff erzeugten Alkohols,” *Zeit. Chem. Pharm.*, **1862**, 5, 687-690.
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6. C. Auer von Welsbach, “Die Zerlegung des Didyms in seine Elemente,” *Monatsh. Chem.*, **1885**, 6, 477-491. The other fraction was called praseodymia because of the greenish color of its salts. These two fractions contained the elements now known as neodymium and praseodymium.
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Publication History

Published in *J. Chem. Educ.*, **2012**, 89, 953-954.

Update

Dr. Heinz-Jürgen Wagner of the Universität Paderborn

has informed me that he has traced the use of the qualifier *quaternary* to describe a carbon atom bonded to four other carbon atoms to an 1866 paper by Adolf von Baeyer, where one reads:

With respect to the bonding of the carbon atoms with one another, these compounds [i.e., the condensed products of acetone] are noteworthy because they contain a carbon atom bound to four other carbon atoms, and if one maintains that it is characteristic of the aliphatic group that an atom will always be bound to another carbon atom using only a single affinity, then one obtains four classes of bonding interactions for carbon in the same:

*Primary, 1 atom of carbon bound to 1 other
Secondary, 1 atom of carbon bound to 2 others
Tertiary, 1 atom of carbon bound to 3 others
Quaternary, 1 atom of carbon bound to 4 others*

A similar suggestion was made the same year by Charles Friedel and Albert Ladenburg, though they applied the term quaternary to the overall hydrocarbon rather than to the individual carbon centers as was done by von Baeyer.

Dr. Wagner has also traced the prefix *iso-* to an 1833 paper by Gustav Magnus in which he claimed to have made two new organic acids of identical composition. Magnus explicitly used the term isomeric to describe his new compounds, though it had only recently been introduced by Berzelius, and, among several alternative name choices for his products, suggested “Aetherschwefelsäure” or “Aethionsäure” and “Isoätherschwefelsäure” or “Isaethionsäure.” Unlike Kolbe, Magnus did not explicitly state that the prefix *iso-* was an abbreviation for isomeric, though there is little doubt that this was his intention, and in any case, it was his second, rather than his first, name choice for the latter compound – isethionic acid – which ultimately entered the chemical literature. Further complications arise from the fact that his two acids were later shown to have different compositions and thus this example seldom appears in historical accounts of isomerism.

* A. Baeyer, “Ueber die Condensationsproducte des Acetone,” *Ann. Chem. Pharm.*, **1866**, 140, 297-306.

* C. Friedel, A. Ladenburg, “Sur une hydrocarbure nouveau,” *Comptes rendus*, **1866**, 63, 1083-1090.

* G. Magnus, “Ueber die Weinschwefelsäure, ihren Einfluss auf die Aetherbildung, und über zwei Säuren ähnlicher Zusammensetzung,” *Pogg. Ann. Phys.*, **1833**, 27, 367-388.

LI

Proper Writing of Ionic Charges

Question

Why in writing ionic charges do the charge signs follow rather than precede the numbers?

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Answer

Though the term “ion” was first introduced by Michael Faraday in 1834 (1), the concept of free ions in solution, and the corresponding need for a modification of conventional chemical symbolism in order to distinguish them from free atoms, did not come about until the introduction of Svante Arrhenius’ theory of ionic dissociation in the 1880s (2). The impact of Arrhenius’ theory on the introductory textbook was largely driven by the concomitant rise of modern physical chemistry in the 1890s under the leadership of the German chemist, Wilhelm Ostwald.

In his own textbooks Ostwald chose to represent the charge on positive ions by a series of superscripted dots placed to the right of the atomic symbol, and the charge on negative ions by a series of superscripted primes (3). Thus the barium cation was symbolized as $Ba^{..}$ and the phosphate anion as PO_4''' . In contrast, the German chemist, Walther Nernst, in his equally influential 1893 textbook of theoretical chemistry, chose to place an appropriate number of superscripted + or - signs directly above the ion’s atomic symbol (4), a practice which was soon modified by placing them instead to the immediate right of the symbol, as in Ba^{++} and PO_4^{--} (5).

The IUPAC guide to *Quantities, Units and Symbols* claims that yet a third “algebraic” method of indicating ionic charges was also used in the past in which the charge preceded the numerical value, as in Ba^{+2} and PO_4^{-3} , even though this particular sequence of symbols was originally intended to represent the inherent sign of a number or exponent and not the number of signs (6). However, inspection of nearly three dozen general, inorganic, and analytical textbooks, spanning the period 1909-1975, revealed that the vast majority employed



Figure 1. Svante Arrhenius (1859-1927).

the modified Nernst notation, with a smaller number – mostly of European or Russian origin – using the Ostwald notation instead. Rather surprisingly, very few examples of texts using the algebraic notation could be found, all of them post-1970 (7).

Since at least the 1950s IUPAC has ruled that ionic charges or “charge numbers,” as they are now officially called, should be written instead with the number preceding the charge sign, as in Ba^{2+} and PO_4^{3-} (6, 8, 9). There are several reasons for this decision. It is more concise than the typographically inelegant Nernst approach and more physically meaningful than the Ostwald notation. Unlike the algebraic notation, it avoids confusion with the conventional symbolism for inherently positive and negative numbers and maintains consistency in how we count physical entities. Thus, in counting apples, we say two apples, three apples, etc., not apples two, apples three – that is, the number always precedes the name of the entity being counted. Likewise, when counting charges, we should say two positive charges or three negative

charges, not positive charges two or negative charges three. The IUPAC ruling was intended to make the charge number symbolism consistent with this verbal convention.

Most introductory chemistry textbooks now employ the IUPAC notation for ionic charges. However, while our survey of older textbooks uncovered only a few examples in which algebraic notation was used to symbolize ionic charges, it did disclose that this notation was used from a fairly early date to indicate so-called polar valence values or oxidation numbers (10) – a practice that is still widely found in general chemistry texts despite the fact that it is at variance with IUPAC recommendations, which unambiguously state that oxidation numbers are always to be symbolized using Roman numerals rather than Arabic numerals (6, 9).

Further confusion results from the fact that these same textbooks employ the algebraic notation to symbolize oxidation numbers when balancing redox equations, but the IUPAC Roman numeral notation when naming compounds using the Stock oxidation-number system. This eclecticism is further compounded by the fact that virtually all introductory texts also incorrectly state that the Stock system is to be used only when naming so-called ionic metal-nonmetal compounds (e.g. iron(II) chloride for FeCl_2), whereas the stoichiometric prefix system is to be used only when naming so-called covalent nonmetal-nonmetal compounds (e.g. dinitrogen trioxide for N_2O_3). As even a superficial glance at the IUPAC rules shows, this is incorrect (9). Rather the Stock and prefix systems represent two alternative, but equally valid, naming systems applicable to all binary inorganic compounds irrespective of any imagined differences in their ionicity or covalency (11).

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Publication History

Published in *J. Chem. Educ.*, **2012**, *89*, 1084-1085.

LII

Origin of Stereochemical Line and Wedge Symbolism

Question

What is the origin of the line and wedge symbolism used in modern stereochemistry?

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Answer

This is a topic which, despite its pervasive impact on how we presently write chemical structures, probably has no clear cut origin but rather only gradually “seeped” into the chemical literature, while simultaneously undergoing numerous modifications. Standard histories of stereochemistry are silent on this subject (1, 2) and attempting to determine its first appearance in the research literature would be a momentous undertaking. However determining the approximate date at which it became sufficiently established to appear in the monograph and textbook literature is a more manageable task.

No trace of the line and wedge symbolism is to be found in the early monographs on stereochemistry by Bischoff (1894), Hantzsch (1904), Werner (1904) and Stewart (1919) (3-6). The three-dimensional orientation of bonds was instead initially represented by enclosing the topological formula of the molecule or complex ion within an appropriate polyhedron, such as a tetrahedron or an octahedron, and showing how these polyhedra interacted with one another via the sharing of their vertices, edges or faces in order to build up more complex chains or rings.

The first indications of our modern line and wedge symbolism are found in the 1930 monograph on stereochemistry by the German chemist, Georg Wittig (7), and involve the representation of ring systems in which the projecting edges of rings perpendicular to the plane of the paper were printed using thick lines in order to differentiate them from rings within the plane



Figure 1. Richard Kuhn (1900-1967).

of the paper – a practice which may have first evolved in the literature dealing with carbohydrate chemistry.

Two years later, in a contribution to the 1932 collection on stereochemistry edited by Karl Freudenberg, the German biochemist, Richard Kuhn, used thick black lines to represent terminal bonds which projected from the plane of the paper and dotted lines to represent those receding from the plane of the paper (figure 2a) (8). The next year, the monograph by Stefan Goldschmidt on stereochemistry did the same, but replaced Kuhn’s dotted lines for the receding bonds with thickened, but unblackened lines (figure 2b) (9).

Consistent use of wedges rather than thickened lines to represent bonds not lying within the plane of the paper seems to have first appeared in the literature

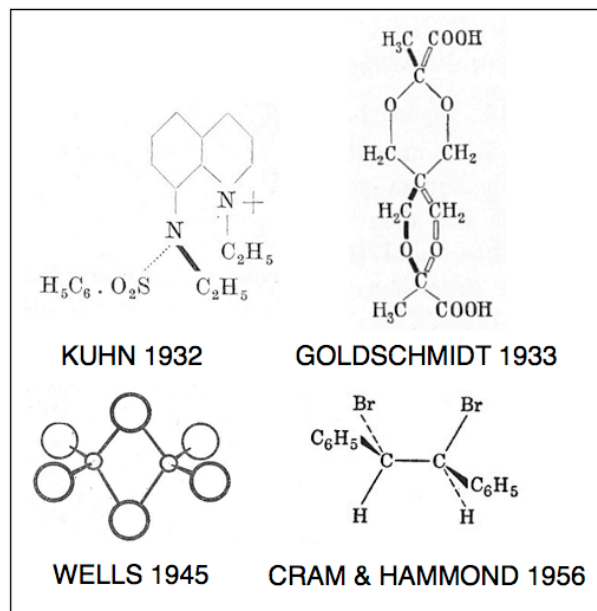


Figure 2. The development of stereochemical line and wedge symbolism.

dealing with inorganic crystal chemistry rather than with organic stereochemistry (7). Thus, A. F. Wells, in the 1945 edition of his classic monograph, *Structural Inorganic Chemistry*, used both projecting and receding wedges to represent the orientation of the bonds in many of his drawings of inorganic crystal structures (figure 2c) (10). The combination of thickened wedges for projecting bonds and dashed lines for receding bonds (figure 2d) finally makes an appearance in the papers contributed by Donald Cram and George Hammond to the 1956 collection on stereochemistry edited by Melvin Newman of Ohio State University(11).

Despite the appearance in stereochemical monographs dating from the 1930s of earlier precursors of the symbolism, it seems to have had no impact on the introductory organic textbook until the publication of the 1959 text by Cram and Hammond, which used the form employed earlier in their contributions to the monograph edited by Newman (12, 13). This important textbook was quite influential in molding a new approach to introductory organic chemistry in the 1960s and undoubtedly acted as a major vector for the spread of the line and wedge symbolism throughout the textbook literature during this decade.

Of course, minor modifications continue to appear, the most common being the use of either horizontally hatched wedges or thickened horizontally hatched lines to represent receding bonds. Of these, the use of the hatched wedge is the most objectionable and has apparently led to considerable confusion. Since both the

use of hatching and the wedge direction were intended to indicate the presence of receding bonds, this symbol contains an unnecessary redundancy, which is further compounded by the fact that the wedge aspect of the symbol is often incorrectly applied by pointing – in direct opposition to the laws of perspective – the thick end at the atom furthest from the viewer rather than at the atom closest to the viewer (14). It is geometrically impossible to correctly represent a tetrahedral arrangement of bonds using only wedges if the narrow ends of all four wedges are connected to the central atom, an arrangement which actually corresponds to a square-based pyramid.

In the examples shown in figure 2 the line and wedge symbolism has been used in formulas in which the atomic centers are explicitly indicated using either their letter symbols or spheres. However, the line and wedge may also be used in conjunction with the highly abbreviated framework formulas increasingly popular among biochemists and organic chemists (15). In these formulas the symbols for C and H are suppressed unless they are part of a functional group, as are all C–H bonds. This latter practice, however, creates a problem when it comes to representing the absolute configuration around a chiral center in which one of the four attached atoms is a terminal H. Though this is really an issue related to the conventions for drawing minimalist framework formulas and should be independent of the issue of which particular symbolism is used to represent projecting versus receding bonds, the two seem to have become entangled in recent debates over the problem of how to unambiguously represent absolute configurations in connection with the development of self-consistent computerized data banks for molecular structure.

Speaking as an inorganic chemist, and solely to the issue of a self-consistent stereo symbolism, rather than to the issue of suppressed bonds in framework formulas, I would conclude that a symbolism based on either thickened bold and hatched straight lines or one based on bold wedges applied using the laws of perspective, as per Wells' original suggestion and as used in the representation of simple crystal structures and VSEPR geometries, is infinitely preferable to one using hatched wedges with reversed perspective.

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LINE AND WEDGE SYMBOLISM

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Publication History

Submitted to *J. Chem. Educ.*, **2012**

LIII

The Origin of the Sigma, Pi, Delta Bond Notation

Question

What is the origin of the sigma, pi, delta notation for chemical bonds?

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Answer

Having successfully used the new quantum mechanics to rationalize the line spectra of discrete atoms and monoatomic ions, physicists began, starting in the 1920s and early 1930s, to apply these ideas to the study and systemization of the band spectra of diatomic molecules and molecular ions in the hope of achieving similar success. Among these pioneers was Robert Sanderson Mulliken (figure 1), who, along with the German physicist, Friedrich Hund, and the British physicist, John Lennard-Jones, is widely regarded as one of the founding fathers of modern molecular orbital theory.

Not unexpectedly, in attempting to extend the study of atomic line spectra to the study of molecular band spectra, these early workers also attempted to apply those concepts which had proved so successful in the study of the former to the study of the latter, including the concepts of orbits or orbitals and the assignment of both term symbols for electronic states and quantum numbers for individual electrons. Also, not unexpectedly for a newly developing field, there was initially a great diversity in the symbolism and terminology used by these pioneers.

Mulliken exploited the atom-molecule analogy more rigorously than many others active in the field via his so-called "united atom" approach, which postulated that the molecular orbitals of the diatomic molecule smoothly transformed into a set of corresponding atomic orbitals for a hypothetical atom created by uniting or fusing together the two atoms of the diatomic.



Figure 1. Robert S. Mulliken (1896-1986).

By 1926, he was assigning atomic term symbols, such as 2S , 1P or 3D , and individual electron quantum numbers, such as s , p and d , to diatomics based on those of the corresponding hypothetical united atom (1). By 1928, he had further refined his symbolism for the molecular quantum numbers of individual electrons and was talking instead of $(1s^s)^2$, $(2s^p)^1$ electrons, etc., where $(2s^p)^1$, for example, referred to an electron in the diatomic corresponding to an electron in the united atom with the quantum numbers $n = 2$, $l = 1$ or p and $m_l = 0$ or s (2).

Shortly after this Mulliken seems to have hit on the simple expedient of using the corresponding Greek letters for molecular states and quantum numbers while retaining the original Latin letters for the atomic states and quantum numbers. Thus the 2S , 1P and 3D term symbols of the united atom became instead the $^2\Sigma$, $^1\Pi$

$^3\Delta$ term symbols of the diatomic and the $(1s^s)^2$ and $(2p^p)^1$ configurations of the united atom became the $1s\sigma^2$ and $2p\pi^1$ configurations of the diatomic, etc. where $1s$ and $2p$ now referred to the atomic orbitals of the isolated atoms used to create the σ and π MO's rather than to the atomic orbitals formed by collapsing the MOs into the corresponding atomic orbitals of the united atom. If the nature of the component atomic orbitals was well known, it was further suggested that the molecular electron quantum numbers could simply be written as σ^2 , π^1 , etc.

Feeling that the time had come to finally standardize the symbolism used in molecular spectroscopy, Mulliken circulated these ideas for discussion and modification among his fellow spectroscopists in the form of a printed flyer. Though it is unclear from his published accounts how much of the final consensus was based on Mulliken's original suggestions and how much on the suggestions of others, the final result was, in any case, submitted for presentation at a meeting of the Faraday Society on "Molecular Spectra and Molecular Structure" held at the University of Bristol in September of 1929 (3, 4). Since Mulliken was unable to attend in person, his nomenclature proposals were presented instead by O. W. Richardson (5) of the University of London, along with some written comments from Mulliken himself (6), and Mulliken also summarized them early the next year for American physicists in a report written for the *Physical Review* (7). Still later the order of writing the atomic components versus the resulting MO would be inverted from $1s\sigma^2$ to $(\sigma 1s)^2$ and then eventually subscripted as $(\sigma_{1s})^2$.

It was, however, not until 1931 that these purely spectroscopic considerations were further connected with the theory of valence and chemical bonding, leading, in turn, to the introduction of the asterisk notation for distinguishing between antibonding and bonding electrons and to the eventual transference of the symbols σ , π , and δ from the electrons to the resulting bonds (8). This was followed, in turn, by the practice of applying these labels to single and multiple bonds in molecules other than the diatomics, thereby dissociating them from their original connection with the net symmetry of the overall molecule. The

first experimental ground-state δ -bond was reported by F. A. Cotton in 1965 for the $[\text{Re}_2\text{Cl}_8]^{2-}$ anion (9).

The best way of seeing the analogy between the s , p , and d atomic orbitals, which are the ultimate origin of this nomenclature system (10), and the σ , π , and δ molecular orbitals is to take a cross-section of the bond MO perpendicular to the bond axis. That for a σ -bond will resemble the cross-section of an s -orbital, that for a π -bond will resemble the cross-section of a p -orbital, and that for a δ -bond will resemble the cross-section of a d -orbital.

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Publication History

Submitted to *J. Chem. Educ.*, **2012**,

Reagent, Functional Group, Substituent, and Substrate

Question

What is the origin of our present-day generalized terminology for the systematic description of organic reactivity, such as the terms reagent, functional group, substituent, and substrate?

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Answer

Some technical terms, and especially those having either Greek or Latin roots, are explicitly coined for a definite purpose, and it is usually possible to trace their introduction to a specific date and a specific scientist. Many others, however, are merely unconscious adaptations of everyday language which gradually seep into the scientific literature and only eventually acquire an official technical significance of their own. In these instances it is usually impossible to assign a specific date and originator and one must instead remain content with merely characterizing the general time period corresponding to their introduction. All four of the above terms, which form the core of our present-day vocabulary for the description of organic reactivity, appear to be examples of this more indirect process.

The earliest of these adaptations is the word “reagent,” which was first introduced into the analytical chemical literature in the late 18th-century along with the systematic use of color and precipitation reactions to test for the presence of various substances in aqueous solution. Solutions of the chemicals used to perform these tests became known as “test solutions” or as “tests” for short. Because they were responding or reacting to the presence of various agents in the water, such as acids, iron, free ammonia, etc., they also eventually became known as reagents. In other words, reaction is to action as reagent is to agent, where agent and action describe the causative factors and reagent and



Figure 1. Torbern Bergman (1735-1784).

reaction describe the responding factors. Obviously both the terms chemical reaction and chemical reactant also evolved from this same usage.

Though scattered examples of the use of color and precipitation reactions for analytical purposes date back to the 17th century, the first attempts to collect and systemize them appear in the writings of the 18th-century Swedish chemist, Torbern Bergman (figure 1). Bergman preferred to refer to his test solutions as “precipitants,” and it was actually his translator, Edmund Cullen, who provided one of the earliest chemical uses of the term reagent in one of his editorial footnotes to his 1784 English translation of Bergman’s *Physical and Chemical Essays* (1).

The second of these adaptations is the term “functional group,” which first makes an appearance in the writings of various French organic chemists in the 1840s in connection with the recognition that organic compounds could be classified into such groups as the acids, the alcohols, the amines, etc. based on their

chemical behavior or *fonctions chimique*. Thus Gerhardt, in his famous *Précis de chimie organique* of 1841 wrote (2):

In this section we will examine the principle groups of organic compounds classified according to their "chemical functions" ... We will review in succession: 1. the salts (acids); 2. the anhydrides; 3. the amides, 4. the alkaloids, 5. the alcohols; 6. the ethers; 7. the acetones; 8. the hydrocarbons; and 9. the glycerides.

Thus one began to talk of a given compound as behaving or functioning as an acid or as an alcohol, etc. Once it was realized that this common class behavior was associated with the presence of certain common atomic groupings within the molecules themselves, it was only natural to begin referring to these common groupings as functional groups.

The third of these adaptations is the word "substituent," which first begins to appear in the organic chemical literature in the late 19th century. Derived from the Latin word *substituere*, meaning "to substitute," it was used to describe an atom or group of atoms that had been introduced into a parent hydrocarbon via substitution of its terminal hydrogen atoms. The term is not used in the classic 1874 paper by Körner on isomer counting and the structure of benzene (3), nor in the classic 1892 paper by Crum Brown and Gibson on ortho-para and meta directing substituents in benzene (4), with the former preferring to use the term "Gruppe" or group and the latter the term "radicle" instead. However, it does appear in an 1896 article by Meldola and Streatfeild in which the phrase "influence of ortho-substituents" is used once in passing (5).

The fourth and final adaptation is the term "substrate," from the Latin *substratum*, meaning foundation. This was first introduced into the biochemical literature in connection with the study of enzymes sometime in the first decade of the 20th century. Standard histories of enzymology are silent as to who first used it or when (6, 7). However, in his 1958 monograph on enzymes, Dixon observes that (8):

The substance on which an enzyme acts, and which is activated by the enzyme is termed the "substrate" of the enzyme. This term, originally introduced by German workers, has been in common use for over fifty years and is to be preferred to the more general word "reactant" when enzymic reactions are concerned.

This historical conjecture is confirmed by the comments of Bayliss in his 1908 monograph on enzymes in which he implies that the term is of recent coinage and is still provisional (9):

A name is frequently needed for the substances on which enzymes exert their activity ... On the whole, "substrate," already in use by many writers, seems to answer the purpose best.

Generalization of this term from "enzyme substrate" to "reaction substrate" appears to be due to C. K. Ingold. Having already appropriated the term reagent in his famous *Chemical Review* article of 1934 to describe the displacing agent in a typical organic reaction (10), he almost nonchalantly appropriated the term substrate in his famous Baker lectures of 1953 to describe the object of the reagent's attack (11):

It is, of course, a pure convention which of the two interacting substances is regarded as "the reagent" and which "the substrate," that is the substance on which the reagent acts. However, in many of the reactions of organic chemistry a definite convention concerning this is established.

That same year the term was also used in the classic 1953 paper by Swain and Scott on linear free-energy relationships for nucleophilic displacement reactions (12). Starting in the 1960s the term occasionally appears in textbooks on physical organic chemistry, though often only in the context of a discussion of the Swain-Scott equation (13), and is finally used in Ingold's fully generalized sense in the 1976 text by Lowry and Richardson (14). As indicated by the most recent edition of IUPAC's *Compendium of Chemical Terminology*, it is now, along with the terms reagent, functional group, and substituent, an official part of the chemist's lexicon (15).

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Publication History

Submitted to *J. Chem. Educ.*, **2012**

The Origin of the Hybrid Orbital Concept

Question

What is the origin of the hybrid orbital concept?

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Answer

The realization that the arrangement of the valence electrons in an isolated atom may be considerably altered by the act of chemical combination goes back to the work of G. N. Lewis and his postulate of the static cubic atom. In his classic paper of 1916 on the shared electron-pair bond, Lewis recognized that the cubic arrangement of an octet of valence electrons which he had postulated for the isolated atom was incompatible with the known facts of stereochemistry and unable to rationalize an electronic interpretation of a triple bond in terms of three-mutually shared electron pairs (1). Consequently, he further postulated that, upon bond

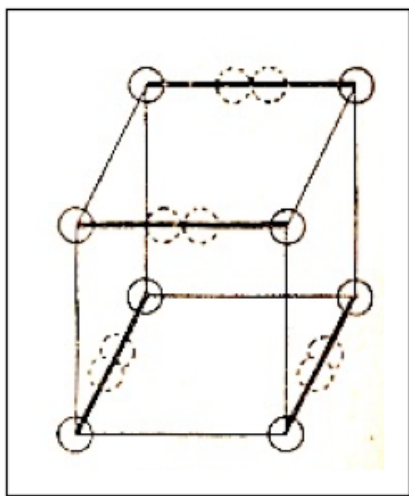


Figure 1. Lewis's diagram of 1916 illustrating the tetrahedral rearrangement of the cubic octet upon bond formation.

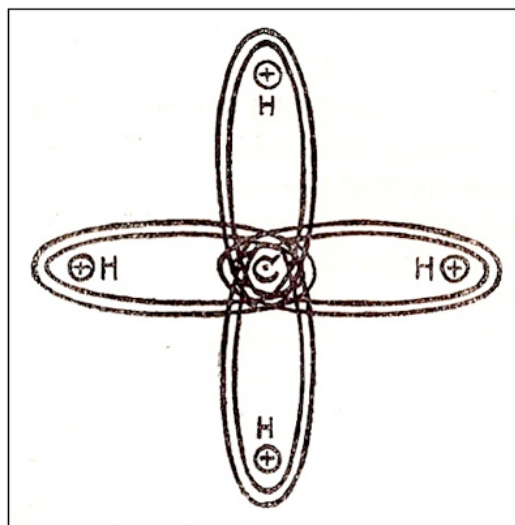


Figure 2. Ludwig Knorr's 1923 diagram of the requantized Bohr orbits about carbon in methane. The double line is intended represent the separate orbit required for each electron of a given bonding pair. Though drawn in a plane, Knorr was careful to state that they were actually arranged tetrahedrally.

formation, the electrons of the isolated cubic atom were forced into a tetrahedral arrangement of four close-paired electrons – a process which he illustrated by means of the diagram shown in figure 1.

Even graver problems were apparent with the Bohr-Sommerfeld atom with its rapidly moving electrons and monocentered elliptical orbits. As the British chemist, Alfred Steward noted in 1922 (2):

Bohr's atom appears to be considerably overrated, especially by those who seem to have accepted it blindly without applying any critical examination. It appears to have failed when attempts were made to utilize it in the case of helium, and heavier elements. As far as chemical and radiochemical problems are concerned it is quite worthless. In fact it makes no pretense to offer an explanation of any of the commoner problems of chemistry.

Lewis was likewise highly critical of the Bohr atom



Figure 3. Linus Pauling (1901-1994).

(3). Whatever its virtues with respect to spectroscopy, its rapidly moving electrons and centrosymmetric atomic orbits appeared to be totally incompatible with the facts of stereochemistry and, in particular, with the known tetrahedral arrangement of the bonds about carbon in thousands of organic compounds and with the known stabilities of hundreds of molecular isomers.

Here again it was obvious that there must be some major rearrangement of the initial atomic orbits upon bond formation, the most obvious solution being the formation of eight tetrahedrally arranged two-center orbits like those postulated by the German chemist, Ludwig Knorr, in 1923 and shown in figure 2 (4). Somewhat similar, albeit less explicit, resolutions were also advocated by Fowler (5) and by Lewis himself, who ultimately concluded that all that was needed in order to reconcile the dynamic atom of the physicist with the static atom of the chemist was (6):

... to postulate that it is the orbit as a whole, and not the electron in some one position within the orbit, which is the building stone of atomic and molecular structure ...

By the late 1920s and early 1930s the original Bohr atom was becoming rapidly eclipsed by the newer wave-mechanical atom of Schrödinger and the shapes and orientations of its postulated atomic orbitals presented much the same problem with respect to the

facts of stereochemistry as had the earlier elliptical orbits of the Bohr-Sommerfeld atom. In their initial application in 1927 of the Schrödinger atom to chemical bonding, the German physicists, Heitler and London, appeared all but oblivious to these problems and Heitler, as late as 1945, was quite content to represent water and ammonia with 90° bond angles formed through interaction of the s-orbital of H with the pure p-orbitals of O and N, and to dismiss the experimental bond angles (104° and 107° respectively) as being only “slightly larger” than the theoretical bond angles of 90° (7).

In contrast, the American chemist, Linus Pauling (figure 3), who was a close student of Lewis’ work on the shared electron-pair bond and who was also attempting to provide it with an underlying wave-mechanical justification, was fully aware of this stereochemical problem and tentatively outlined a solution in 1928 based on a possible “requantization” of the pure atomic orbitals upon bond formation (8):

In the case of some elements of the first row the interchange energy from the formation of shared electron bonds is large enough to change the quantization, destroying the two subshells with $l = 0$ and $l = 1$ of the L-shell. Whether this will or will not occur depends largely on the separation of the s-level ($l = 0$) and the p-level ($l = 1$) of the atom under consideration; this separation is very much smaller for boron, carbon, and nitrogen than for oxygen and fluorine or their ions, and as a result the quantization can be changed for the first three elements but not for the other two. The changed quantization makes possible the very stable shared electron bonds of saturated carbon compounds and the relatively stable double bonds of carbon, which are very rare in other atoms, and in particular are not formed by oxygen. This rupture of the l-quantization also stabilizes structures in which only three electron pairs are attached to one atom, as in molecules containing a triple bond, the carbonate, nitrate, and borate anions, the carboxyl group and similar compounds. It has further been found that as a result of the resonance phenomena a tetrahedral arrangement of the four bonds of the quadrivalent carbon atom is the stable one.

No further details were provided, though Pauling promised that a followup was in the works.

It was, however, not until 1931 that Pauling was finally spurred into action again by the publication of a major article on “Directed Valence in Polyatomic Molecules” by a 30-year old physicist at MIT by the name of John Slater (figure 4). Slater’s paper was remarkably “chemically friendly” for a physicist. It contained no high powered mathematics and was lavishly illustrated with photographs of models of typical mole-

THE ORIGIN OF THE HYBRID ORBITAL CONCEPT

cules and crystals made from cork balls and wire (9). Whereas Pauling had invoked the energy separation between the various atomic orbitals in his brief 1928 summary as the critical criterion for whether they could or could not hybridize, Slater used maximization of the overlap between the ligand orbitals and those of the central atom as his criterion. For compounds of the elements of groups 7 through 5 Slater assumed that all of the bond angles were 90° and were formed using unhybridized p-orbitals on the central atom. Only for the compounds of the elements of group 4, where the tetrahedral stereochemistry could no longer be ignored, did he invoke the necessity of maximizing orbital overlap by creating a new set of tetrahedrally arranged orbitals via an appropriate linear combination of the vectors for the unhybridized atomic orbitals.

Though Slater's paper was published in the March 1931 issue of the *Physical Review*, Pauling had probably been aware of his work as early as April of 1930 when Slater had presented a talk on the same subject at the Washington Meeting of the Physical Society. This would explain why Pauling was able to submit a lengthy and detailed paper on the same subject to the *Journal of the American Chemical Society* in February of 1931, which appeared one month (April) after Slater's article (10) and which was followed by a letter to the *Physical Review* the next month (May) calling attention to his publication (11). Pauling later confessed that the reason for the delay in following up his note of 1928 was that he was unable to find a way of simplifying the wavefunctions so as to make the hybridization scheme mathematically tractable. Slater's brief comments provided the missing key by suggesting that one could ignore the radial part of the function and concentrate solely on the angular part (12).

Pauling's paper, which became the first in his famous series on "The Nature of the Chemical Bond," was far more detailed than Slater's and, unlike the latter, contained drawings of the resulting hybrid orbitals, including those for geometries other than tetrahedral and for the d-block elements as well as for the main-block elements. As such, it, rather than Slater's more qualitative paper, became the true source of our current views on orbital hybridization and stereochemistry.

Though we have used the terms "hybridization" and "hybrid orbital" when describing the work of Slater and Pauling, these terms were not used by either author in their initial papers. Instead Pauling talked of trigonal or tetrahedral quantization. Rather it would appear that the first use of the term "hybridization" to describe the orbital mixing process was due instead to a 1933 paper by the American physicist, John Van Vleck (13). Pauling apparently found Van Vleck's term more congenial than requantization and so went on to



Figure 4. John Slater (1900-1976).

employ it in the various editions of his famous monograph on *The Nature of the Chemical Bond*. Only near the end of his 1931 paper did Pauling begin to use such symbols as sp^3 and dsp^2 and to talk of either sp^3 bonds or d^2sp^3 bond eigenfunctions. Similarly, in his 1933 paper Van Vleck referred to either sp^3 valencies or sp^3 wavefunctions but not to sp^3 hybrid orbitals.

Currently we interpret the superscripts in such symbols as sp^3 and sp^2 as numerical measures of the weighting factors for the contribution of each atomic orbital to the final hybrid orbital. However, as originally used by Pauling, these symbols were apparently a simple extension of the symbols for atomic electron configurations in which the superscripts represented electron occupancies and were meant to imply that the tetrahedral hybrids were formed from the unhybridized hypothetical atomic configuration s^1p^3 , the trigonal hybrids from the unhybridized hypothetical atomic configuration s^1p^2 etc.

In closing, I cannot resist pointing out a curious historical irony. Neither Pauling nor Slater were willing to initially consider the possibility that hybridization was also possible for the compounds of oxygen and were content, like Heitler, with the prediction of a 90° bond angle for water. Yet a decade earlier, Eustace Cuy, a colleague of Lewis at Berkeley, had published a short note in which he used Lewis' earlier tetrahedral static atom (recall figure 1) to correctly predict that water had a structure "identical to a methane molecule which was lacking two hydrogen atoms" – in short that

water had a bond angle close to 109° – a far more accurate prediction than the 90° value based on the unhybridized Schrödinger atom (14). Likewise, through out the 1920s another Berkeley educated chemist by the name of Maurice Huggins would publish a series of articles rationalizing the structures of crystals based on the Lewis tetrahedral atom which gave predictions far closer to the truth than did the 90° structures assumed by Slater in 1931 (15-16). The transition between Lewis' isolated cubic atom and his chemically bonded tetrahedral atom would become the basis in the 1960s of an elaboration of Lewis' original ideas by the British chemist, John Linnett, known as double-quartet theory (17-18), which would, in turn, serve as a rationale for the current approach to the prediction of molecular geometries now known as Valence-Shell Electron-Pair Repulsion or VSEPR theory.

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Publication History

Submitted to *J. Chem. Educ.*, **2012**

LVI

Origins of the Isoelectronic Principle

Question

What are the origins of the isoelectronic principle?

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Answer

The isoelectronic principle was first proposed in 1919 by the American chemist, Irving Langmuir (figure 1), though in formulating his principle he employed the term “isosteric” rather than the term “isoelectronic”(1):

The octet theory of valence indicates that if compounds having the same number of atoms also have the same total number of electrons, the electrons may arrange themselves in the same manner. In this case the compounds or groups of atoms are said to be isosteric. Such compounds should show remarkable similarity in their physical properties, that is, in those properties that do not involve a separation of the atoms in the molecules.

The first two sentences of this quote deal with the definition of isosterism and reveal that two species are isosteric if, and only if, they have three things in common:

1. The same total number (but not kind) of atoms
2. The same total number of electrons
3. The same structural arrangement of those electrons

Though Langmuir used the ambiguous term “compound” in his formal definition, we have substituted the term “species” in our commentary, since it is apparent from reading his paper that he intended his definition and principle to apply equally to neutral molecules, ions, and unsaturated atomic groups, whether homoatomic or heteroatomic in composition.

The third sentence of the quote deals with what the



Figure 1. Irving Langmuir (1881-1957).

principle is intended to predict, namely the proposition that two isosteric species will have similar physical properties. Again, a reading of the paper reveals that implicit in this proposition is the further assumption that isosteric polyatomic species not only have identical electronic structures, but will, as a result, also have identical molecular geometries. Even then, the conclusion that the two species will have similar physical properties will follow only if they also have identical net charges (or are, in Langmuir’s terminology, “isoelectric” with one another). To illustrate this principle, Langmuir made a detailed comparison of the physical properties of the two isosteric neutral molecules, CO₂ and N₂O, and of the ability of various isosteric ion combinations to form isomorphous crystal structures.

The first independent paper to further test the isosteric principle was published in 1923 by the American chemist, Wallace Carothers, who would later



Figure 2. Walter Hückel (1895-1973).

gain fame for his work on the synthesis of nylon (2). One of the predictions made by Langmuir in his original paper was that the azide anion (N_3^-) should have a linear, double-bonded, structure similar to that of the isosteric isocyanate anion (NCO^-) rather than the cyclic structure assumed at the time. Carothers proposed to test this prediction by preparing the compounds phenyl isocyanate ($\phi\text{-NCO}$) and diazobenzene imide ($\phi\text{-N}_3$) and measuring their physical properties. He found that their densities, vapor pressures, and viscosities were quite similar, thus confirming both the linear structure for the azide grouping and Langmuir's isosteric principle.

Three years after the publication of Carother's paper, Pauling and Hendricks made use of the isosteric principle to predict the relative stabilities of various isomeric isosteres, such as the cyanate (NCO^-), the fulminate (CNO^-), and the unknown CON^- anions (3). Since, by definition, these species had both similar electronic structures and overall geometries (in this case linear), these authors argued that the primary energy difference between one isomer and another lay, not in the differences in their electron-electron repulsions and electron-core attractions, but rather in the differences in their core-core repulsions, and that these could be calculated using a classical ionic model. On this basis they correctly predicted that the cyanate anion was more stable than the explosive fulminate anion, and that this was, in turn, more stable than the unknown

and unnamed CON^- anion.

In 1926 Latimer successfully applied the core-core repulsion principle of Pauling and Hendricks to the prediction of the relative stabilities of non-isosteric isomers, as revealed by the thermochemistry of their isomerization or so-called molecular rearrangement reactions (4). Though making no reference to Langmuir's principle, this paper was important in calling attention to factor three in the above definition of isosterism, since all isomers meet requirements 1 and 2, but only the special subclass of isosteric isomers studied by Pauling and Hendricks also meets requirement 3. In other words, not all species having identical atom and electron counts will automatically be isosteric, let alone isostructural.

Meanwhile, in Germany a second, independent, series of events was occurring which would eventually impact on the further development of Langmuir's principle. In 1921 Walter Hückel (figure 2), the older brother of Erich Hückel of MO fame, published a paper calling attention to the bonding analogies implicit in the concept of protonated anions (5). Commenting on Kossel's formulation of hydrogen compounds using the ionic model, Hückel pointed out that, unlike other positive ions, H^+ had no inner electronic core and thus would not remain adjacent to its counter anion as a contact pair, but rather would penetrate into its electron shell to form a "pseudoatom" having bonding properties similar to those of a simple atom with the same electron count. Applying this concept to hypothetical anions having electron-counts less than those of an inert gas produced neutral, chemically unsaturated pseudoatoms, such as $-\text{CH}_3$, $-\text{NH}_2$, and $-\text{OH}$, all of which had an electron count of seven like a neutral $-\text{F}$ atom, and all of which, like the F atom, displayed a nonpolar valence of one, as illustrated by their self-dimerization to form $\text{H}_3\text{C}-\text{CH}_3$, $\text{H}_2\text{N}-\text{NH}_2$, and $\text{HO}-\text{OH}$, and $\text{F}-\text{F}$, respectively, as well as such mixed species as $\text{H}_3\text{C}-\text{F}$, $\text{H}_3\text{C}-\text{NH}_2$, $\text{H}_3\text{C}-\text{OH}$, etc.

The resulting concept of protonated pseudoatoms was further generalized and systematized in tabular form (Table 1) by the German chemist, Hans Georg Grimm (figure 3) in 1925:

Table 1: Grimm's Hydride Displacement Law

C	N	O	F	Ne	Na
	CH	NH	OH	FH	-
		CH_2	NH_2	OH_2	FH_2^+
			CH_3	NH_3	OH_3^+
				CH_4	NH_4^+

and soon became known in the literature as Grimm's

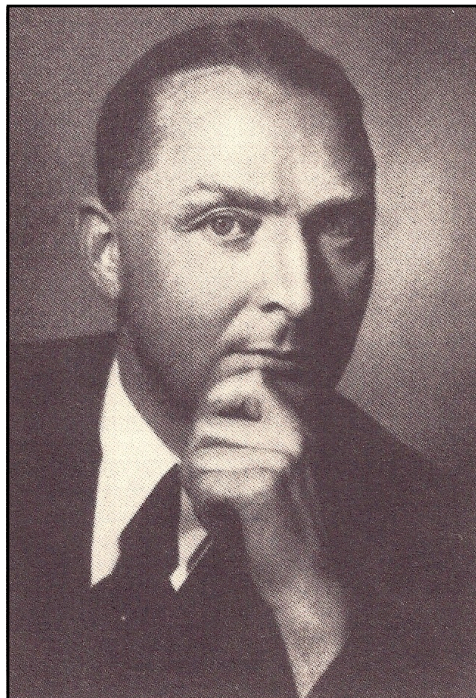


Figure 3. Hans Georg Grimm (1887-1958).

hydride displacement law (6):

Through the uptake of 1, 2, 3, or 4 hydrogen atoms, those atoms lying up to four places in front of a noble gas can form "pseudoatoms" whose properties resemble those of atoms which lie 1, 2, 3, or 4 places to their right in the periodic system.

Beginning in 1932, the Swiss chemist, Hans Erlenmeyer, began publishing a series of articles in which he applied the results of both Langmuir's isosteric principle and Grimm's hydride displacement law to molecules of biochemical and medicinal interest (7). The resulting fusion led to a modification of condition 1 for isosteres by requiring that they contain not the same number of atoms, but rather the same number of heavy (i.e. nonprotonic) atoms – in other words, hydrogen did not contribute to the atom count.

In addition, Erlenmeyer gradually extended the pseudoatom concept to include any polyatomic group having the same valence or substitution value, irrespective of its total atom or electron count. Thus he came to view the $-\text{CH}=\text{CH}-$ group as isosteric with the $-\text{S}-$ atom, the $-\text{CF}_3$ and $-\text{CN}$ groups as isosteric with the $-\text{Cl}$ atom, etc. Indeed, to this day, cyanides and thiocyanates are still referred to in the chemical literature as pseudohalides. Even though these larger pseudoatoms, unlike the protonated pseudoatoms of

Grimm, were no longer isosteric in the original sense of the word, the literature on medicinal chemistry and drug design has continued to this day to use this expanded (or degraded, depending on one's point of view) version of the word, where it is now often further qualified by the term "bioisosterism" (8).

As the term isostere was gradually absorbed into the medicinal and pharmacological literature, it was being simultaneously replaced within the purely chemical literature by the term "isoelectronic." This term appears to have been introduced into the field of molecular spectroscopy sometime in the 1930s to describe diatomic molecules and ions having identical electron counts and analogous MO configurations, such as CO^+ , CN , and BO . I have not been able to locate who first coined the term, but it does appear in a 1935 monograph by Kronig, where it is explicitly defined as a synonym for the term isosteric (9, 10).

By the late 1950s and early 1960s, the replacement of the term isosteric with the term isoelectronic within the chemical literature appears to have been complete, as revealed in a major review on "isoelectronic systems" published by the American chemist, Henry A. Bent (figure 4), in 1966 (11). In this citation classic, Bent not only incorporated the protonic pseudoatoms of Hückel and Grimm (albeit unacknowledged as such), as Erlenmeyer had before him, he also called attention to numerous special applications of the isoelectronic principle in the chemical literature, often by chemists either unaware that they were using the

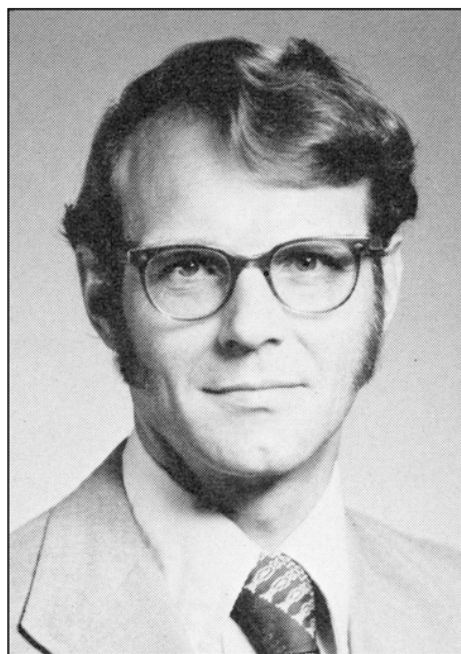


Figure 4. Henry A. Bent (b. 1927).

principle or who did so under the guise of alternative names, such as “Grimm-Sommerfeld compounds”, “molecular homologs”, “Zintl phases”, “Hume-Rothery phases”, and “periodic compounds.”

However, unlike Erlenmeyer and the medicinal chemistry literature, Bent did not conflate the isoelectronic principle with the concept of nonprotonic pseudoatoms. This extended pseudoatom concept is in fact an entirely independent principle for generating chemical analogs with a history of its own. It has been extensively developed by Haas (12, 13) and also has its own subvariants with various alternative names, such as “the electronic equivalency principle,” and the isobal principle.”

Bent also provided an updated definition of the isoelectronic principle which entailed some important modifications of Langmuir’s original concept (11):

As a general rule or principle, molecules are isoelectronic with each other when they have the same number of electrons and the same number of heavy-atoms. Usually, then, they have the same heavy atom geometries – and, by inference, similar electronic structures.

The first of these is the explicit modification of criterion 1 to indicate equal numbers of nonprotonic heavy-atoms rather than total atoms. The second involves abandoning criterion 3 as part of the definition of isoelectronic and making it instead a part of what the principle purports to predict. In other words, isoelectronic is now a purely compositional concept which allows one to make probable inferences about both electronic structure and molecular structure.

But even then, Bent’s definition is still incomplete. As pointed out by Gillis as early as 1958 (14), and as implied by Bent in his discussion of the relationship between the periodic table and the isoelectronic principle, what is important in criterion 2 is not the total number of electrons, but rather the total number of *valence* electrons. Likewise, as noted earlier with respect to Langmuir’s original definition, the more general term “species” is preferable to “molecule,” since the principle applies equally to discrete molecules, nonmolecular solids, ions and molecular fragments. This also requires that we specify that the electron counts refer to the species’ compositional formula, since in the case of discrete species we are making absolute counts, whereas in the case of nonmolecular species we are making relative counts. Lastly, as shown by several examples in Bent’s review, the isoelectronic principle not only predicts that isoelectronic species will have similar electronic and molecular structures, it also implies that they will

exhibit analogous reactivity patterns. All of this leads us then to the following modified definition:

Species having formulas with identical valence-electron counts and identical nonprotonic or heavy atom counts are isoelectronic. Such species often have similar electronic structures, heavy atom geometries, and reactivity patterns.

Far less important is the prediction of analogous physical properties, as originally emphasized by Langmuir and Carothers.

Examination of the literature on the isoelectronic principle reveals five fundamental methods for generating isoelectronic analogs, where Z represents the atomic number of the atom being modified within the initial species along with its normal valence-electron count (17):

$$Z \approx Z' \quad [1]$$

$$ZZ \approx (Z-1)(Z+1) \quad [2]$$

$$ZH \approx Z+1 \quad [3]$$

$$Z \approx (Z\pm 1)^{\pm 1} \quad [4]$$

$$ZH \approx Z^- \quad [5]$$

The first method represents the replacement of an atom by an isovalent analog from the same group of the periodic table, such as replacing O with S or its reverse. The second method represents the simultaneous replacement of two atoms with one atom of lower atomic number and one of higher atomic number, as in the Grimm-Sommerfeld sequence: CC, BN, BeO, LiF or in Brown’s so-called molecular homologs in which C-C bonds are replaced by B-N bonds. The third method is an expression of the Hückel-Grimm concept of protonated pseudoatoms, as in the replacement of OH by F or its reverse. The fourth method involves the replacement of a neutral atom by the cation of an element of higher Z or by an anion of lower Z, as in the replacement of O by F⁺ or by N⁻. Finally, the fifth method represents the protonation or deprotonation of an anion, as in the isoelectronic equivalence of NH₃ with NH₂⁻ or of H₂O with OH⁻.

Bent, on the other hand, formalized processes 2-5 as proton transfers of various sorts: the second as an internuclear transfer, the third as a protonated electron-pair/nuclear transfer, the fourth as an environment/nuclear transfer, and the fifth as a protonated electron-pair/environment transfer. This formalism ignores concomitant adjustments in neutron counts and cannot be

applied in a straight-forward manner to method 1.

Again, the question of whether the isoelectronic analogs generated by these substitutions will actually be stable enough to exist or, if they do exist, whether they will prefer to adopt an isomeric structure other than that initially predicted for the analog, are questions which must be answered by other means.

The creative function of the isoelectronic principle is merely to suggest possibilities, not to guarantee realities.

If the proposed species do not exist, despite the fact that they “do not offend the simpler rules of valence,” then one may resort to the kinds of rationales employed by Dasent in his classic monograph on *Nonexistent Compounds* (15). If they do exist, but only as isomers of the predicted analog, then one may resort, as a first approximation, either to use of the Pauling-Hendricks-Latimer core-core repulsion principle (16), or to constraints imposed by the use of resonance structures (17), or extreme variations in relative electro-negativity (18).

This latter point also brings up a final lingering semantic problem. By definition the isomers of a given species automatically have identical valence-electron and heavy atom counts and so are, by our current compositional definition, also isoelectronic with one another. Yet, with the exception of the special class originally studied by Pauling and Hendricks, such isomers usually have both different electronic and molecular structures. A great deal of clarity would result if one used separate terms to distinguish between the premise of the isoelectronic principle (equal valence-electron and heavy-atom counts) and its conclusions (analogous electronic and molecular structures). It seems to me that, just as “isoelectronic” is a perfect description of the compositional premise, so Langmuir’s original term “isosteric” – which literally means “equal shape” – is a perfect description of its structural conclusions, in which case the isoelectronic principle may be succinctly summarized as:

Isoelectronic species are frequently isosteric.

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Publication History

Submitted to *J. Chem. Educ.*, **2012**

Index

A

absolute temperature 1
acetal 65
acetaldehyde 34
acetometer 13
acetylene 58
ACS journals vii
Adams, C. 10
Addison, W. E. 36
Aepinus, F. U. T. 27, 28
affinity diagram 25
alcoholmeter 13
alcohol proof 12-13
alkali metals 48
Allen, L. C. 69
Allen, P. B. 68
allomorph 35
allotropes 35-37
alloy
 d'Arcet's 87, 88
 French 87, 88
 Lipowitz 87, 88
 Newton's 87, 88
 Onions' 87-89
 Rose's 87, 88
 Wood's 87, 88
Allred, A. L. 100
Amit, J. W. 70, 71
Ampère, A. M. 50
Anderson, H. V. 15
Anderson, R. G. W. 32
Anderson, W. P. 69
Andraos, J. 19, 29, 38, 55, 74
Annalen 65
Anschutz-Schulze flask 65
anthracene 70
Argand burner 20
Aristotle 33
Armstrong, H. 57, 58
aromatic sextet 70
aromaticity 70-71
Arrhenius, S. 107, 108
Aston, F. W. 94-95
Ataman, O. Y. 9
atomic mass unit 92
atomic mass scales 92
atomic number 23-24
atomic weight 23-24
Auer von Welsbach, C. 106

Ault, B. 7
Avogadro, A. 46
Avogadro's number 46-47, 92-93
azide anion 121-122
azote 60

B

Bader, G. M. 71
Bailey, R. M. 22
balancing redox equations
 electron method 75
 ion-electron method 75
 material balance method 75
 nascent oxygen method 74
 polar valence method 74
Balmer, J. 48
band theory 67
barium carbonate 80
barium oxide 80
barium peroxide 80
Barkla, C. G. 3-4
Barnett, B. 111
Bartlett, E. J. 5
base 40-41
Bayliss, W. M. 115, 116
Becker, P. 93
Bennett, G. W. 76
Benson, S. 15
Bent, H. A. 16, 44, 123-125
benzamide 65
benzene 58, 70-71
benzene derivatives 33-34
benzoyl radical 65, 66
Bergman, T. 25, 114, 115
Bergmann, A. 48, 49
Berthollet, C. 25, 50, 53, 60
Berzelius, J. J. 25, 26, 33, 35-36, 42, 52, 57-58, 60, 66, 83-84
bioisosterism 123
Bischoff, C. A. 109, 110
Blair, A. A. 62
Blanchard, A. A. 21, 22, 52, 108
Blaszczyk, R. L. 32
Block, F. 67, 69
Bodenstein, M. 20
Bohemian glass 31
Bohning, J. 102
Bohr atom 3-4, 117-118
Bohr, N. 3-4, 21, 23, 48, 49

Boltzman, L. 48
bonds
 2c-1e 44
 2c-2e 44
 3c-2e 71
 3c-4e 44
 6c-6e 71
 classical 77
 covalent 67
 delocalized 70-71
 delta 112, 113
 ionic 67, 85-86
 metallic 67-69
 pi 70-71, 112-113
 polar 72-73
 sigma 70, 112-113
Born, M. 49
bornylamine 106
borosilicate glass 31
Bornemann, G. 6
Bose, D. M. 22
Bottomley, J. 75, 76
Bouchardat, A. 11
Boussingault, J. B. 80, 81
Bowden, S. T. 36
Boyce burner 79
Boyd, R. N. 70, 71
Boyle, R. 1
Boyle's law 1
Branch, G. 53, 54
Bray, W. C. 53, 54
Brill, T. B. 45
Brin, A. 80, 81
Brin, Q. 80, 81
Brin Oxygen Company 81
Brin process 80-81
British Oxygen Company 81
Brown, A. C. 77, 115
Büchi, W. 63
Büchner, E. 39
Büchner funnel 38-39
Buchner, G. 54
Buff, H. 6
Bunsen burner 19-20, 79
Bunsen, R. W. 19-20, 38, 39, 55
Burdett, J. K. 69
burners
 Boyce 79
 Bunsen 19-20, 79
 Detroit 79
 Meker 78, 79
 Tirrill 78, 79
Bury 21
butene 35, 57

Butler, W. H. 68
Butlerov, A. 105, 106

C

Cadet, C. L. 60
calcium sulfite 52
calcium sulfate 52
Candler, A. C. 48, 49
Cannizzaro, S. 46-47, 82-83
Capitani, J. F. 69
carbon dioxide 80, 121
Carnot cycle 1
Carnot, S. 90
Carothers, W. H. 18, 121-122, 125
Cartledge, G. H. 99-100
Caserio, M. C. 70, 71
Castellan, G. W. 104
Caven, R. M. 43, 52-53
Charpy, G. 88
chemical affinity 27
chemical equations 25-26
Chemischen Central-Blatt 106
Child, E. 32
Clapeyron, B. P. E. 1-2, 90, 91
Clar, E. 71
Clark, W. M. 7-8
Castellan, G. W. 86
Clausius, R. 1-2, 90, 91
Coates, G. E. 24
Cohen, E. J. 66
Cohen, E. R. 91, 108
Cohen, I. B. 88
Collison, P. 38
Conant, J. B. 71
Connelly, N. G. 108
Conover, W. 23
Cooke, J. P. 5, 6
Cooley, L. C. 47
copolymer 58
Corning Glass 31-32
Cosandey, M. 77
Cotton, F. A. 113
Coulson, C. A. 47, 125
Couper, A. S. 77
Craig, L. C. 63
Cram, D. J. 71, 110, 111
Cranston, J. A. 43
Crookes, W. 16
Crosland, M. P. 43, 60, 105, 106
Culp, B. 3
Cuy, E. 119, 120
cyanate anion 122
cyanide anion 123

cyclopentadienyl anion 71
Czech, P. T. 69

D

Dalton, J. 25
Dana, J. D. 88
d'Arcet, J. 87, 88
d'Arcet's alloys 87, 88
Dasent, W. E. 125
da Silva, R. R. 67
Davenport, D. A. 85
Davy, H. 52
Davy safety lamp 19
decoction 55
de Donder, T. 102, 104
Deer, W. A. 43
de Elhuyar, F. 59, 60
de Elhuyar, J. J. 59, 60
de Gyrs, H. 87
delta polarity symbol 72-73
Demarçay, H. 50, 51
de Menten, P. 83-84
Desaga, P. 20, 55
Dessaignes, V. 50, 51
Detroit burner 79
Dewar, J. 48-49
Dewar, M. 70, 71
diamond 35
diazobenzene imide 122
Dickinson, H. W. 89
diethyl ether 11
dinitrogen 81
dinitrogen oxide 121
dinitrogen trioxide 108
dioxygen gas 80-81
distillation 29-30
Dixon, M. 115, 116
Dobbin, L. 34, 50
Dolch, P. 19, 20
Donovan, A. 10
d-orbitals 44-45, 48-49
dots in formulas 42-43
Douglas, S. H. 76
Drude, P. 67, 68
dualism 42, 52
Dufay, C. 27
Duhamel du Monceau, H. L. 40, 41
Dull, C. E. 47, 64
Dumas, J. B. 83
Du Pont 18
didymia 106

E

EAN rule 21, 22
Ehl, R. E. 104
Ehrmann, M. 6
eighteen-electron rule 21-22
Eimer & Amend 55, 79
Eisner, W. 20
electrical sign conventions 27-28
electron duplet 70
electron-gas model 67
electron-lattice model 67
electrolysis 103
electron sextet 70
electronegativity
 Allred-Rochow scale 97, 99, 100
 Cartledge scale 99-101
 Lakotos scale 100
 Pauling scale 96-97, 99, 100
 Rodebush scale 96-198, 99-100
enantiotropic 36
Engels, N. 68
enzymes 115
Epenson, P. 17
equivalent weights 25
Erlenmeyer, E. 43, 83
Erlenmeyer, H. 123-125
ethanol 11, 12-13
ethene 11, 35, 57
ethyl formate 35, 57
ethyl hydrogen sulfate 11
Ettling, C. 30
eutectics 88
evaporated milk 64
extent of reaction 102
extraction 55

F

Faigl, P. 50
Fajans, K. 99, 100
Faraday, M. 19, 20, 102-104, 107, 108
Faraday's law 23, 102-104
fat determination 56
Fenichell, S. 18
Ferme Générale 9
Fernelius, C. 68, 69
Ferreira, R. 97, 98
ferric sulfate 52
ferrous chloride 108
ferrous sulfate 52
Fieser, L. 71
Fieser, M. 71
Fisher, H. L. 39

Fisher Scientific 10
Flash Evaporator 63
formaldehyde 34
formulas
 dualistic 42, 52
 framework 110
 Lewis dot 42
 organic 43
 stereochemical 1091-111
Forbes, R. J. 30
f-orbitals 48-49
Foster, M. O. 106
Fourcroy, A. 25, 50, 60
Fowler, R. H. 118, 120
Fownes, G. A. 25, 26
Frank, F. 32
Frankenheim, M. 35
Frankland, E. 16, 17, 77
Franklin, B. 27-28
free radicals 42
Fremy, E. 88
French, S. J. 88, 89
French's alloy 87, 88
Fresenius, C. R. 61, 62
Freundenberg, K. 109, 111
Frickhinger, A. 5
Fruton, J. S. 116
Fry Glass 32
Fry, H. S. 52-54
Fryhle, C. B. 111
fulminate anion 122
fumaric acid 50, 51
functional group 114-115
fusible alloys 87-89

G

Gadolin, J. 29, 30
Galloway, E. 89
Gardner, W. E. 113
Garrett, P. J. 71
Garrigós i Oltra, L. 75
gas constant vii, 1-2
Gattermann, L. 65, 66
gauze burner 19
Gay-Lussac, J. L. 1, 12, 66, 80, 81
Gay-Lussac's law 1
Gee, N. 46
Geisler pump 38
Gerhardt, C. F. 82-83, 105, 106, 114, 115
Gibson, J. 115
Gillespie, R. J. 45
Gillis, R. G. 124, 125
glass composition 43

Glasstone, S. 90, 91, 95, 104
glassware 31-32
glucinium 60
Gmelin, L. 11
Godefroy, L. 88
Goldschmidt, S. 109, 100, 111
Goldschmidt, V. 85, 86
Google 88
Göttling, J. 39, 30
Graham, T. 33, 34
Graham, W. 58
gram 92
Grant, J. 32
graphite 35
Green, M. L. 22
Gregory, J. D. 63
Griffin, J. J. 20, 56
Gregory, W. 83
Grimaux, E. 32
Grimm, H. G. 67, 69, 122-125
Grimm hydride displacement law 122-123
Grimm-Sommerfeld compounds 122, 123
Guettier, A. 87, 88
Guilliland, W. L. 22
guillotine 9-10
Guldberg, C. M. 25
gunpowder test 12, 13
Guyton de Morveau, L. 50, 53, 60, 82, 83

H

Haas, A. 124, 125
Haber ammonia synthesis 80
Haber, F. 90, 91
Hackh, I. W. J. 62, 76
Hahn, O. 95
Hammond, G. S. 71, 110, 111
Hantzsch, A. 109, 111
Hardie, D. W. F. 81
Harvard 5
Hausmann, W. 63
Hawthorne, R. W. 93
heat 90-91
Heidelberg 19
Heilbron, J. L. 4
Heitler, W. 118, 119, 120
helium 16-17, 117
helion 16, 17
Helmholtz, H. von 90
helon 16
Hendricks, S. 122, 125
Henry Heil Chemical Co. 61, 62, 78, 79
Hermes, M. E. 18
Herndon, W. C. 76

Hevesy, G. 95
Hewitt 66
Higgins, W. 77
Hildebrand, J. 47, 53, 54
Hine, J. 116
Hiorns, A. H. 89
Hirsch funnel 38-39
Hirsch, R. 38, 39
hochmolekulare Verbindungen 58
Hofmann, A. W. 14-15
Holleman, A. F. 66
Holmes, F. L. 32
Holmes, H. 47
Hopkins, A. A. 89
Horsey, D. 90
Horstmann, A. F. 1-2, 15, 90, 91
Houndshell, D. A. 19
Howie, R. A. 43
Hückel, E. 71, 122
Hückel, W. 122, 125
Hückel $4n + 2$ rule 71
Huggins, M. L. 120
Hume-Rothery phases 123
Hume-Rothery, W. 68
Hund, F. H. 48-49, 112
Hunter, D. N. 58
Hüttig, G. F. 85-86
hybridization 117-120
hydrogen electrode 7
hydrometer 13
hypercoordinate 45
hypervalent 44-45

I

ideal gas 2
Ihde, A. 104
infusion 55
Ingold, C. K. 72-73, 115, 116
Ingold, E. H. 72, 73
ionic bonding model 85-86, 99
ionic charges 107-108
ionic polarization 99, 100
ionic potential 99-101
isocyanate anion 122
isoelectric 122
isoelectronic principle 121-125
isomers 33-34, 35-36, 57, 66, 105-106, 122-125
isomorphism 121
isopropanol 105
isosteric 121-125
isotope symbolism 94-95
IUPAC 2, 34, 36, 90, 91, 95, 107-108, 115

J

Janssen, P. J. C. 16
Jena glassware 31, 32
Jena Glassworks 32
Jensen, W. B. 6, 20, 41, 54, 56, 58, 62, 69, 76, 79, 83, 93, 98, 100, 108, 125
Jette, E. 75, 76
Jevons, S. 36
Johnson, O. C. 75, 76
Jones, H. C. 98
Jones, P. R. 63
Jorrisen, W. P. 95
Joseph, M. S. 109
Journal of Biological Chemistry 7
Journal of Chemical Education vii
Jurkevica, A. 52

K

Kaehler & Martini of Berlin 39
Kahlbaum, G. 29, 30
kalium 60
Kavalier glass 32
Kayser, H. 48, 49
Keach, D. T. 75, 76
Kekulé, A. 43
Keller, A. 95
Kelvin, Lord 17
Kemp, R. 56
Kennard, E. H. 2
Kern, E. 46
Kerr, R. 59
kinetic theory 46, 93
Kinnersley, E. 28
Klein, H. A. 13-14
Knorr, L. 117, 118, 120
Kohn, M. 19, 20
Kolbe, A. W. H. 11, 83, 105, 106
Körner, W. 33-34, 115
Kosower, E. M. 116
Kossel, W. 3, 4, 85, 86
Kronig, R. 123, 125
Krupp, A. 88
krypton 16
K shell 3-4
Kuhn, O. B. 6
Kuhn, R. 109, 110, 111
Kutzelnigg, W. 45

L

Ladenburg, A. 34
Lagrange 9-10

Lakatos, B. 100
 La Mer, V. K. 74, 75, 76
 Lander, G. D. 52-53
 Landis, C. 45
 Langmuir, I. 21-22, 44, 121-125
 Lapworth, A. 72
 Larsen, L. V. 58
 Lasser-Cohen, E. 66
 Latimer, W. 53, 54, 96, 98, 122, 125
 Laurent, A. 82, 83
 Laves, F. 68
 Lavoisier, A. L. 9-10, 31, 32, 50, 52, 53, 59-60, 75, 76
 Le Chatelier's principle 80
 Lee, A. 25, 26
 Leffek, K. T. 73
 Lehmann, O. 36
 Leicester, H. 41
 Leigh, G. J. 37
 Lambert, M. 85, 86
 Lémery, N. 40
 Lennard-Jones, J. 112, 113
 Lenson, I. A. 27
 Leo, M. 125
 Levere, T. H. 32
 Levey, M. 55, 56
 Lewis cubic atom 21
 Lewis dot diagram 42
 Lewis, G. N. 44, 45, 67, 68, 69, 72, 73, 90, 91, 99,
 100, 117, 119, 120
 Libbey Glass 32
 Liebig condenser 29-30
 Liebig, J. 29-32, 65, 66, 83
 Liebman, J. 121, 125
 lime 80
 lime glass 31
 Limpricht, H. 83
 Lindemann, F. A. 67, 69
 Linnett, J. W. 120
 Lipowitz, A. 88, 89
 Lopwitz's metal 87, 88
 Liveing, G. 48-49
 lixiviation 55
 Lockemann, G. 20
 Lockyer, J. N. 16-17
 London, F. 118
 Lorentz, H. 67, 68
 Loschmidt, J. 46, 47
 Löwig, C. J. 83
 Lowry, T. 72
 Lowry, T. H. 115, 116
 L-shell 3-4
 Lukens, R. 31
 Lyon, J. M. 125

M

Macbeth-Evans Glass 32
 Macquer, J. 60
 macromolecule 57-58
 Magie, W. F. 2
 Magnus, A. 85, 86
 Magnusson, E. 45
 Main-Smith, J. D. 48
 maleic acid 50-51
 malic acid 50-51
 malonic acid 50-51
 marcasite 35
 Marat, J. P. 9
 Mariotte, E. 1
 Mariotte's law 1
 Marsh, B. B. 63
 Marshall, H. 25, 26
 Martin, J. C. 45
 Mason, B. 86
 mass spectroscopy 95
 Mathewson, C. L. 76
 matrix 40
 Matteucci, C. 103, 104
 Matthew effect 86
 McKie, D. 10
 McGlasham, M. I. 23
 McGucken, W. 49
 McMurry, J. 71
 McNaught, A. D. 116
 Meadows, A. J. 17
 Meija, J. 35, 93
 Meker burner 78-79
 Meker, M. G. 78, 79
 Meldola, R. 115, 116
 Mellor, J. W. 81
 melting points 65-66
 Mendeleev, D. I. 83
 Mendoza, E. 2, 91
 mercury diiodide 35
 Merton, R. 86
 Mesopotamia 55
 Mester, Z. 94
 meta- 33-34
 metallic bond 67-69
 metamerism 35, 57
 metal carbonyls 21
 metal nitrosyls 21
 metal-nonmetal division 99, 100
 Metcalfe, H. C. 47
 methyl acetate 35, 57
 Meyer, K. 58
 Meyer, L. 36, 37, 77
 Millington, J. 89

Mitchell, C. A. 13
Mitchell, K. A. R. 45
Mitchell, P. R. 22
Moeller, T. 22
mole 1-2, 14-15
molecular homologs 123, 124
molecular orbitals 112-113
molybdenite 59
monotropic 36
Moore, B. vii
Moore, J. vii, 76
Morfit, C. 55, 56
Morley-Foster, H. F. 36, 58
Morrison, R. T. 70, 71
Moseley, H. 3, 4, 23, 24
M-shell 3-4
Muir, M. M. P. 37, 52, 53, 58
Mulligan, W. O. 45
Mulliken, R. S. 112-113
Musher, J. 44, 45

N

Nagarajam, K. 33
naphthalene 70, 71
Naquet, A. 36
Nathan, L. C. 86
natrium 60
neocyanite 106
neodymia 106
neotestite 106
Nernst equation 23, 106
Nernst, W. 107, 108
Neuberger, M. C. 36
Newman, M. 110, 111
Newton, I. 27, 87, 88
Newton's metal 87, 88
Nicholson, W. 60
Noller, C. R. 71
Nonsol glass 31-32
Nottingham, P. M. 63
N-shell 3
Numerof, P. 63
nylon 19

O

octachlorodirhenium(VI) anion 113
octet rule 21, 22, 44-45, 121
Odling, W. 33, 34
Oesper Collections vii, 6, 32
Oesper, R. E. 86
Ojala, W. 18
oligomer 58

Olsen, J. C. 61, 62
Onions, W. 89
Onions' alloy 87-89
Onishi, H. 15
orbitals
 antibonding 113
 atomic 48-49, 112-113
 bonding 113
 delocalized 70-71
 hybrid 117-120
 molecular 112-113
Orchin, M. 70
Orndorf 66
ortho- 33-34
Ostwald, W. 14-15, 20, 25, 26, 36, 37, 52, 53, 107, 108
Ouerdane, L. 96, 99
oxidation 52-54, 74-76
oxidation number 53
oxidation potential 53
oxidation state 52-54
Oyler, J. 61
ozone 36

P-Q

Paneth, F. 95
para- 33-34
parachor 44
paraldehyde 33
paraformaldehyde 33
Parish, J. 22
Parnicke, A. 63
Partington, J. 49, 77
Partridge, S. M. 63
Pascal, P. 88
Pauli, W. 48
Pauling, L. 17, 85, 86, 96-98, 99, 118-120, 122, 125
Paulson, D. L. 1
Paulze, J. 9
Payen, A. 55, 56
Pelouze, T. J. 50
Pepper, J. H. 88
percolator 55
perfume 55
periodic compounds 124
periodic table 49, 83
Perrin, J. 46-47, 92, 93
Petit, L. D. 45
pH 7-8
phase diagrams 43
phenanthrene 70
phenyl isocyanate 122
phosphoric acids 33, 35
phosphorus allotropes 35

pi-bond 70, 112-113
Piccard, J. 38, 39
Pienta, N. vii
Pilley, J. 28
Pilotvap 63
Pimentel, G. 43, 44, 108
Pinhas, A. 21
Pintsch, J. 20
Poggendorff, J. C. 30
Poissonnier, P. J. 29
polarity 72-73
polycyclics 70
polymers 33, 35-36, 57-58
polyvinyl chloride 11
polywater 32
p-orbitals 48-49, 112-113
positive ray method 95
potash glass 31
potassium hydroxide 80
potassium nitrate 13
Powell, P. 22
praseodymia 106
Pratt, J. D. 81
prefixes
 iso- 105-106
 neo- 106
 primary 105
 secondary 105
 tertiary 105
Prescott, A. B. 76
proton transfers 124
pseudoatoms 122-125
pseudohalides 123
Puckett, J. 107
Pyrex glass 31-32, 61
pyridine 71
pyrites 35
pyrolucite 59
Pyykkö, P. 20

R

Rabinowitsch, E. 49
radicals 82-84
radius ratio rules 85-86
Rae, I. D. 48
Ramberg, P. J. 65, 110
Ramsay, O. B. 5, 110
Ramsay, W. 16-17, 46, 47
Randall, M. 90, 91
Ray, N. H. 58
reactant 114
reaction 114
reagent 114

redox equations 53, 74-76
reduction 52-54, 74-76
Regnault, H. V. 1-2
regulas 59
Reiff, F. 21, 22
Reinhardt, K. 63
Remick, A. E. 73
Remler, J. 60
residue theory 82
resonance 71
Richardson, G. M. 51
Richardson, K. S. 115, 116
Richardson, O. W. 113
Riegel, E. R. 63
Risteen, A. D. 47
Rizzi, G. 89
Robey, R. 68, 69
Roberts, J. D. 70, 71
Robinson, E. A. 45
Robinson, R. 70, 71, 72, 73
Rodebush, W. H. 96-98, 99, 100
Rochow, E. 100
Roller, D. 28
Roller, D. H. D. 28
Romer, A. 95
Roscoe, H. E. 19, 20
Rose, V. 87, 88
Rose's metal 87, 88
Rosenfeld, L. 4, 24
rotary vacuum evaporator 63-64
rotavap 64
Rotavapor 64
Roth flask 65
Rouelle, G. F. 40-41
Ruark, A. E. 24
rubber policeman 61-62
Rueckberg, F. 92
Rundle, R. E. 44, 45
Runge, C. 48, 49
Russell, C. A. 43, 77
Rutherford, E. 23
Rydberg, J. 48, 49

S

Sainte-Claire Deville, H. 80
sauerstoff 59
Scheele, C. W. 50, 59-60
scheelite 59
scheelium 60
Schelenz, H. 30
Schleyer, P. R. van 45
Schmidt, J. 106
Schön, J. C. 69

Scott, C. B. 115, 116
Schrödinger, E. 118
Schwanert, H. 76
Senning, A. 59, 80
Shakhashiri, B. 19
Sheppard, K. 62
Sidgwick, N. 21-22
Siegfried, R. 41
sigma bond 70, 112-113
silver cyanate 66
silver fulminate 66
Slater, J. 118-120
Smith, D. W. 45
Smither, F. A. 32
Smits, A. 36
Soddy, F. 94, 95
sodium hydroxide 80
s-orbitals 48-49, 112-113
solar eclipse 16
solar spectrum 16
solder 87
Solomons, T. W. G. 71, 111
Sommerfeld, A. 23-24, 49, 67, 68, 117
Sørensen, S. P. L. 7-8
Soxhlet extractor 55-56
Soxhlet, F. R. von 55-56
Sparks, J. 30
Spratley R. D. 108
specific gravity 12-13
spectra
 band 112-113
 line 48-49, 112
spectroscopy 3
Speter, M. 29, 30
Stark, J. 67, 68, 69
Staudinger, H. 57-58
Steele, J. D. 26
stereochemical symbols 109-111
Steward, A. 109, 111, 117, 120
Stigler's law of eponymy 86
Stigler, S. M. 86
Stock nomenclature 108
stoichiometry 5-6
Stone, F. 58
Stoner, E. C. 48
Strom, T. 117
Strong, F. C. 104
Stuart, R. 89
Straubel, R. 85, 86
Streatfeild, F. W. 115, 116
substituent 114, 115
substrate 114, 115
Sugden, S. 44, 45
Suits, C. G. 22

sulfur allotropes 35
sulfur trioxide 58
sulfuric acid 52
sulfurous acid 52
Swain, C. G. 115, 116
symbols
 alkyl substituents 82-84
 framework 110
 gas constant 1-2
 heat 90-91
 polarity 72-73
 stereochemical 109-111
 work 90-91
Szabadváry, F. 10
Szombathy, H. 55

T

Talbot, H. P. 53-54, 108
tartaric acids 33
tea 55
term symbols 112-113
tertiary butanol 105
Thackray, A. 26
Theile, J. 66
Theile melting point tube 65-66
Thenard, L. J. 80, 81
Thilo, E. 49
thiocyanate anion 123
Thomas, R. 11
Thomson, J. J. 95
Thorpe, T. E. 20, 81
Timmermans, J. 65, 66
Tirrill burner 78-79
Townson & Mercer of London 39
Trautz, M. 15
Travers, M. 16, 17
Trujillo, C. A. 14
Tubert-Brohman, I. 82
tungsten 59-60

U

University College-London 19
Ure, A. 60
Urey, H. C. 24

V

vacuum filtration 38-39
van Arkel, A. 68
van Rysselbergh, P. 104
van't Hoff, J. 25, 26, 50, 76, 83-84
Van Vleck, J. 119, 120

Venable, F. P. 78, 79
vinegar 13
vinegas 11
vinic alcohol 11
vinyl 11
vinyl alcohol 11
Vogel, von 11
Vogel, W. 43
Vogelezang, M. 40
Voltaic cell 103
Volk, M. E. 63
VSEPR theory 110, 120

W

Waage, P. 25
Wade, K. 22
Wagner, H. J. 89
Wahab, M. F. 42, 72, 112
Walker, P. H. 32
wasserstoff 59
water aspirator 38
Waters, W. A. 71, 73
Watson, H. B. 73
Webb, E. C. 116
Weigel, C. E. 29, 30
Weinhold, F. 45
Weinland, R. 85, 86
Wells, A. F. 110, 111
Wermuth, C. G. 125
Werner, A. 42, 43, 109, 111
Wheeler, T. S. 77
Wheland, G. W. 71
Whitall Tatum Co. 31
Whitmore, F. C. 71

Wiberg, K. B. 65, 116
Wiechmann, F. G. 76
Wiest, K. 12
Wildberger, A. 88
Wilkinson, A. 116
Williams, J. E. 47
Williams, T. I. 73
Winckler, F. L. 50, 51
Wislicenus, J. 50
Witt, O. N. 38, 39
Wittig, G. 109, 111
Wöhler, F. 30, 65, 66
wolfram 59-60
wolframite 59
Wood, B. 88, 89
Wood's metal 87, 88
Woods, G. 25
work 90-91
Woulfe bottle 38

X

X-rays 3-4

Y

Young, C. A. 17

Z

Zintl, E. 68
Zintl phases 123
Zudans, I. 57
Zussman, J. 43