Ask the Historian

The Origin of the 18-Electron Rule

William B. Jensen

Department of Chemistry, University of Cincinnati
Cincinnati, OH 45221-0172

Question

What is the origin of the 18-electron rule?

Allan Pinhas
Department of Chemistry
University of Cincinnati
Cincinnati, OH 45221-0172

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:

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

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

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

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

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

Assuming 2c-2e metal-carbon bonds in all cases, Langmuir applied equation 3 to the examples of $Ni(CO)_4$, $Fe(CO)_5$, and $Mo(CO)_6$. 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 effective 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).

Figure 1. Irving Langmuir (1881-1957).

In the late 1960s, however, there was a reversion to

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

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 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).

Literature Cited

1. I. Langmuir, "Types of Valence," *Science*, **1921**, *54*, 59-67. Reprinted in C. G. Suits, Ed., *The Collected Works of Irving Langmuir*, Vol. 6. Pergamon: New York, NY, 1961, pp. 128-139.

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 Tricarbonylnitrosylkobalt," *Z. anorg. Chem.*, **1931**, *202*, 375-381.

5. N. V. Sidgwick, R. M. Bailey, "Structures of the Metallic Carbonyls and Nitrosyls," *Proc. Roy. Soc.*, **1934**, *A144*, 521-537.

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.

Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu

2009 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 Magnetonenzahl in den Komplexverbindungen einer paramagnetischer Elemente," *Z. Phys.*, **1926**, *35*, 219-223.