LETTERS

The Origin and Nature of the Electronegativity Scale

To the Editor:

In a recent article (1) Sanderson mentions textbooks containing discussions of the electronegativity scale, and then begins a sentence with the words "Their leaders will learn the erroneous Pauling derivation of electronegativity...." This incorrect characterization of my work in introducing the concept of electronegativity and formulating the electronegativity scale about 50 years ago has prompted me to write an account of the origin and nature of the electronegativity scale.

Shortly after the introduction of quantum mechanics 60 years ago it was recognized that the value of the energy of the normal state of a molecule lies below the value corresponding to any hypothetical structure different from the actual structure. As a result of this theorem, it can be stated confidently that the energy of a molecule containing a single bond with partial ionic character, such as HCl, would be less than the energy calculated for a normal covalent structure, without ionic character. In 1932 Don M. Yost and I (2) published evidence supporting the postulate that the energy of a normal covalent single bond between two unlike atoms is very closely equal to the arithmetic mean of the energies of the corresponding bonds between like atoms. With this postulate, the amount of energy liberated when elements involving single bonds react to form compounds involving single bonds should always be positive. In fact, the experimental values of the decrease in enthalpy when gas molecules of hydrogen and the halogens react to form gaseous hydrogen halide and halogen halide molecules are all positive, supporting the postulate.

The values of $-\Delta H$ vary from 0.04 kcal/mol for BrCl to 64 kcal/mol for HF. This fact suggested to me that these values might be expressed as a function of the difference in electronegativity of the two elements, and that an electronegativity scale might be formulated. If $-\Delta H$ were expanded in a Taylor series of $x_A - x_B$ for the bond A–B, the linear term would be 0 and the first significant term would be $(x_A - x_B)^2$. This quadratic relationship was found to be reasonably satisfactory, and electronegativity values for 10 elements were assigned in 1933 (3). In 1939 the electronegativity scale was extended to include 33 elements, with use of the values of $-\Delta H$ for reactions involving the elements and compounds in their stable forms at standards conditions (4), and in 1960 approximate values for 50 more elements were added (5).

An important contribution to the theory of the electronegativity scale was made by Mulliken (6), who pointed out that the average of the ionization energy and electron affinity might well be a measure of the electronegativity of an atom in a molecule. In fact, this average (in kcal/mol) multiplied by 0.016 gives values for halogen and alkali metal atoms within 0.01 of the values in my scale, but for hydrogen there is a difference of 0.56, probably indicating that the hydrogen atom in compounds has a significantly different structure from that of the free atom.

Refinements and improvements of the electronegativity scale have been proposed by many authors, including Sanderson. The purpose of the present note is to point out that my derivation of the scale was not erroneous. The arguments used were all compatible with the basic principles of quantum mechanics, and the relative values of the electronegativity, as originally derived, are still to be considered as essentially correct.

Literature Cited

1. Sanderson, R. T. *J. Chem. Educ.* **1986,** *63,* 845.
2. Pauling, L. and Yost, D. M. *Proc. Acad. Sci. USA,* **1932,** *18,* 414.
3. Pauling, L. *J. Am. Chem. Soc.* **1932,** *54,* 3574.
4. Pauling, L. *The Nature of the Chemical Bond,* 1st ed; Cornell University Press: Ithaca, NY, 1939.
5. Pauling, L. *The Nature of the Chemical Bond,* 3rd ed; Cornell University Press: Ithaca, NY, 1960.
6. Mulliken, R. S. *J. Chem. Phys.* **1934,** *2,* 782; **1935,** *3,* 573.

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Silver Recovery from Lab Wastes

To the Editor:

Although the procedure recommended by J. P. Rawat and S. Iqbal Kamoonpuri (1) for the recovery of silver from laboratory wastes is simple and elegant, it makes no mention of the possible formation of dangerously explosive fulminatins silver if ammoniacal solutions of silver salts are allowed to stand for more than an hour or so. The operations described in steps 1 and 2 should therefore be carried out without undue delay. Also, in paragraphs 2 and 4 the word "amine" should be replaced by the word "ammine", which is the proper nomenclature for coordinated NH_3. "Amine" should be used only for the $-NH_2$ group (2).

Literature Cited

1. Rawat, J. P.; Kamoonpuri, S. I. *J. Chem. Educ.* **1986,** *63,* 537.
2. International Union of Pure and Applied Chemistry. *Nomenclature of Inorganic Chemistry,* 2nd ed.; Pergamon: Oxford, 1971; Rule 7.322(p 45).

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Life After Graduation: Cartoons in the Hall

To the Editor:

A perpetual problem in chemical education is that of trying to give students a better idea of what chemists do after graduation. In addition to the seminars previously described (1), we have found it useful to post the cartoons from the calendars published annually by I^2R (2) in the hall just outside our chemistry laboratories. These cartoons reflect the humor, dreams, and frustrations of many working chemists. Students can often be seen musing over them, and a number of students have made a point of telling me that they enjoy them.

Literature Cited

1. Hill, J. W., *J. Chem. Educ.* **1978,** *55,* 101.
2. Instruments for Research and Industry, 108 Franklin Ave., Cheltenham, PA 19012.

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