On the Thermochemical and Electrochemical Series of Elements

G. van Hooydonk

Centrale Bibliotheek, Rijksuniversiteit te Gent, Gent, België

(Z. Naturforsch. **29 a**, 969 – 970 [1974] ;
received April 26, 1974)

Standard electrode potentials of elements are compared with the electronegativity values (or electron affinities), proposed earlier. It is concluded that chemical interactions are the result of the oxidising character of elements, in agreement with an ionic approximation to chemical bonding.

The classification of elements only according to their chemical, i. e. interatomic, behaviour is of special interest. Apart from thermochemical methods, there are only very few experimental methods which should enable one to do so directly, such as for instance the determination of electron affinity values $E\,A_X$ [1] and, with certain reservations, of relative electrode potentials E_{0X}. The latter method seems to be more practical, since the determination of $E\,A_X$-values is not a simple matter. The determination of standard electrode potentials E_{0X} is, in general, not difficult, but several effects should be considered in the final evaluation of experimental data, e. g. solvent effects (H_2O), effect of entropy alterations . . . Moreover, the electrochemical series of elements thus obtained cannot be given an absolute zero-point, since only differences in potentials are actually measured. However, all E_{0X} values are found in a range of about 6 V, indicating that the largest "difference in chemical behaviour" of elements, measured in this way, is about 140 kcal. Mole^{-1}.

It has been argued elsewhere [2] that a thermochemical series of (monovalent) elements can be constructed when the covalent bonding powers E_{XX} of elements X is taken as a measure for their electronegativity. In this way, it was shown that these (more absolute) electronegativity values for monovalent atoms can be found in the region 10 – 150 kcal. Mole^{-1}, which is astonishingly close to the range of electrochemical interactions, as given above. In addition, this thermochemical scale has a definite zero-point.

Therefore, it is tempting to correlate both chemical classifications of elements, in spite of the difficulties involved. Fortunately, entropy effects are relatively small [3] and, since the measurements are made on aqueous solutions throughout, solvent effects can be supposed not to alter the final sequence in E_{0X} values. It was even shown by the group of Drago [4] that, under special conditions, ΔH-values for acid-base interactions measured in solutions are linearly correlated with those found in the gaseous phase.

Hence, it is interesting to see that, in spite of these difficulties, the slope for the relation between E_{XX} values and E_{0X} values is very close to the kcal. Mole^{-1} equivalent of eV, as to be seen from Fig. 1 wherein a line with exactly this slope has been drawn. Even a detail of the thermochemical interactions seems to be reproduced in this way, i. e. the case of Li and LiX bonds [2].

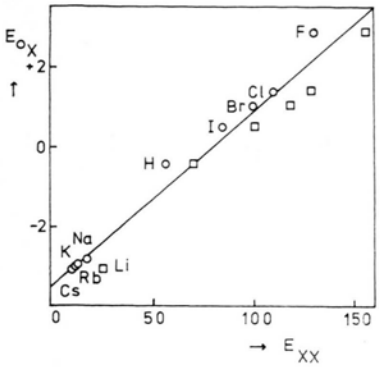

Fig. 1. Plot of E_{0X} (Volt) versus E_{XX} (kcal/mole^{-1}). The line has been drawn with a "theoretical" slope, as indicated in the text, the coordinates for Cs being taken as origin. E_{0X} values taken from Ref. [5] with sign convention given therein, E_{0H} taken from Reference [3]. E_{XX} values are taken from Ref. [2], those marked with □ represent the LiX series.

A first consequence of this relationship between the E_{XX} and E_{0X} values of elements would be that all potentials in the electrochemical series should be given the same (positive) sign. Although this is rather an irrelevant statement, since any potential-difference gives rise to a flow of charge, it turns out to be particularly important when discussed in the light of an ionic approximation to chemical bonding, a question reconsidered recently [1]. Indeed, the fact that all E_{0X} values should be positive, indicates that all elements are oxidising, i. e. they try to take up an extra electron in their valence orbital, instead of the usually suggested distinction between the oxidising or reducing character of elements (or even the amphotere character of several elements).

When it is reminded that redox systems in solution are usually characterised by the following processes

$$(X + e \rightarrow X^-)_{\text{solution}}\,,$$
$$(X - e \rightarrow X^+)_{\text{solution}}$$

it may again [1] be questioned whether or not ionization energies of elements should explicitly be taken

---

Reprint requests to Dr. G. van Hooydonk, Rijksuniversiteit te Gent, Centrale Bibliotheek, Rozier 9, *B-9000 Gent*, Belgien.

into account to describe the net energy alterations accompanying chemical reactions. If indeed the energy alterations in the oxidising and reducing steps in a redox system would be similar to those accompanying chemical interactions in general, one could have an explanation for the fact that the two series of $E_{0\mathrm{X}}$ and E_{XX} values under consideration do coincide. Since electron affinities were shown to be determinating for the net stability of chemical bonds[1], this would be consistent with the now advanced oxidising nature of all elements.

In the supposition that the neglect of solvent effects and of entropy alterations causes no appreciable error in the evaluation of the chemical behaviour of elements by electrochemical measurements, one could extend the previously obtaind relationship[1] to include $E_{0\mathrm{X}}$ values also:

$$e\,\chi_{\mathrm{X}} = E_{\mathrm{XX}} = \alpha_{\mathrm{X}} = 2\,\beta_{\mathrm{XX}} = EA_{\mathrm{X}} = (\partial \varepsilon_{\mathrm{X}}/\partial n_{\mathrm{X}})_{n_{\mathrm{X}}=1} \sim E_{0\mathrm{X}} \tag{1}$$

where all the symbols have their usual meaning.

Finally, the relation

$$E_{\mathrm{BB}} - E_{\mathrm{AA}} \propto E_{0\mathrm{B}} - E_{0\mathrm{A}} \tag{2}$$

suggested by Fig. 1 is in agreement with the previously obtained bond energy expression[1]

$$E_{\mathrm{AB}} = (1/2)\,(E_{\mathrm{AA}} + E_{\mathrm{BB}})\,(1 + I^2) \tag{3}$$

which was deduced with the help of the quantity $(\chi_{\mathrm{B}} - \chi_{\mathrm{A}})$, the difference between the potentials of the two neutral bonding partners A and B when forming the bond AB.

---

[1] G. van Hooydonk, Z. Naturforsch. **28 a**, 933, 1836 [1973].

[2] G. van Hooydonk, Theor. Chim. Acta **22**, 157 [1971].

[3] E. Schwarz-Bergkampf, Allg. Prakt. Chem. **21**, 19 [1970].

[4] R. S. Drago, M. S. Nozari, and G. C. Vogel, J. Amer. Chem. Soc. **94**, 90 [1972].

[5] G. Charlot, D. Bézier, and J. Courtot, Potentiels d'Oxydo-Réduction, Pergamon Press, Paris 1958.