# About Correlation between Gibbs' Energy and Mean Orbital Electronegativity for the Interactions between Metal Oxides

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## Abstract

By analogy with thermodynamic notions, implying that the possibility for a reaction to proceed is determined by Gibbs' energy, which is equal to the difference of the energies for the final and initial products, it is proposed to calculate the difference of the sums of mean orbital electronegativities for the final an initial products. A linear correlation has been established between Gibbs' energies of reactions and the mentioned differences, on the basis of vast experimental material for various reaction types. This correlation can be used to estimate the possibility of a reaction between the compounds for which thermodynamic data are unknown, in particular for complicated multicomponent compounds.

## INTRODUCTION

The electronegativity (EN) concept introduced by Pauling is rather widely used in chemistry [1, 2]. He characterized EN as a force with which an atom in a molecule attracts electrons. According to Pauling, the energy of a covalent bond M–X is arithmetic mean of the energies of corresponding uniform bonds:

$$E_{\mathrm{cov}} = 1/2[E(\mathrm{M–M}) + E(\mathrm{X–X})] \quad (1)$$

In the case of polar bond, its energy will be higher than the energy of covalent bond by an ionic additive:

$$\Delta E(\mathrm{MX}) = E(\mathrm{MX}) - 1/2[E(\mathrm{M–M}) + E(\mathrm{X–X})] \quad (2)$$

This value is numerically equal to the thermal effect of the formation of MX molecule from $M_2$ and $X_2$ molecules. The analysis of energies of chemical bonds for a large number of compounds allowed him to define the EN of M and X atoms on the basis of this expression by the following equation:

$$X_{\mathrm{M}} - X_{\mathrm{X}} = Q^{1/2} \quad (3)$$

From this equation it follows that the larger is the difference in EN of atoms, the higher is bond energy between them.

Along with the mentioned thermodynamic EN scale, Mulliken [3] introduced notions about the EN of atoms on the basis of quantum chemical approach. According to them, the EN is defined by the equation:

$$X = (J_v + F_v)/2 \quad (4)$$

where $J_v$ is the ionization potential of atom, $F_v$ is the electron affinity of atom. This scale can be brought in consistence with Pauling's scale and is more convenient because energy stands to the 1 power, not 1/2. It is called absolute EN in reference books [4].

Since Pauling's electronegativity is based on thermodynamic data, it is quite appropriate to solve the inverse problem, *i.e.*, to calculate standard enthalpy of formation (SEF) using the data on EN of atoms. In particular, Aronson [5] proposed to calculate the SEF of complex oxides of the $ABO_3$ type (kcal/mol) using the equation:

$$\Delta H^{\circ}_{298} = -23.06\ \Sigma(X_{\mathrm{A}} - X_{\mathrm{B}})^2 + 26.0 n_{\mathrm{O}} \quad (5)$$

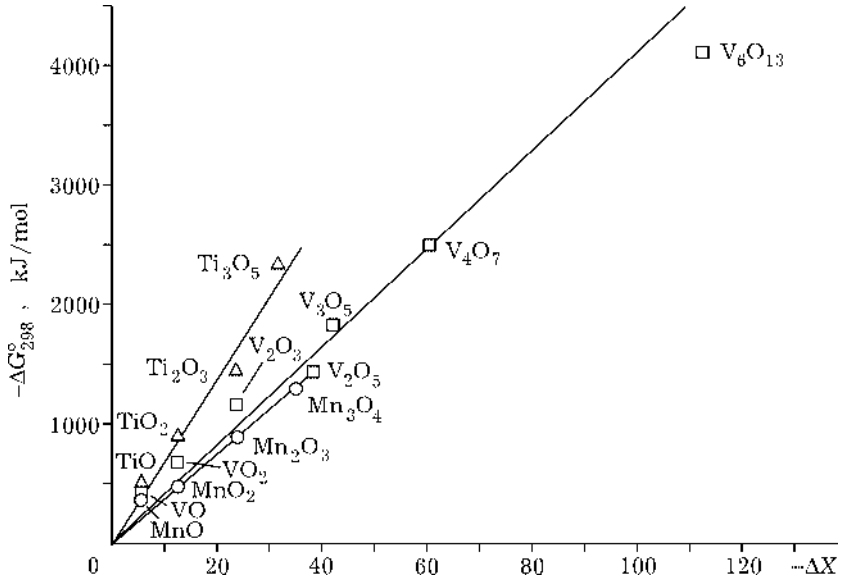


Fig. 1. Correlation between $\Delta G_{298}$ and $\Delta X$ for the formation of titanium, vanadium, and manganese oxides from elements.

where $n_O$ is the number of oxygen atoms in the compound.

During the recent years, methods are being developed for calculating group EN for radicals, neutral groups and molecules [2]. In application to oxides, it was proposed to calculate EN of an oxide as a mean value calculated according to the additivity rule:

$$X = (\Sigma n_i X_i)/\Sigma n_i \quad (6)$$

where $X_i$ is the EN of an atom $i$ according to Mulliken, $n$ is the number of atoms of this kind in the molecule (in formula unit) [6]. This value can be considered as an analogue of state functions used in thermodynamics. The notion of a mean orbital EN is based on the

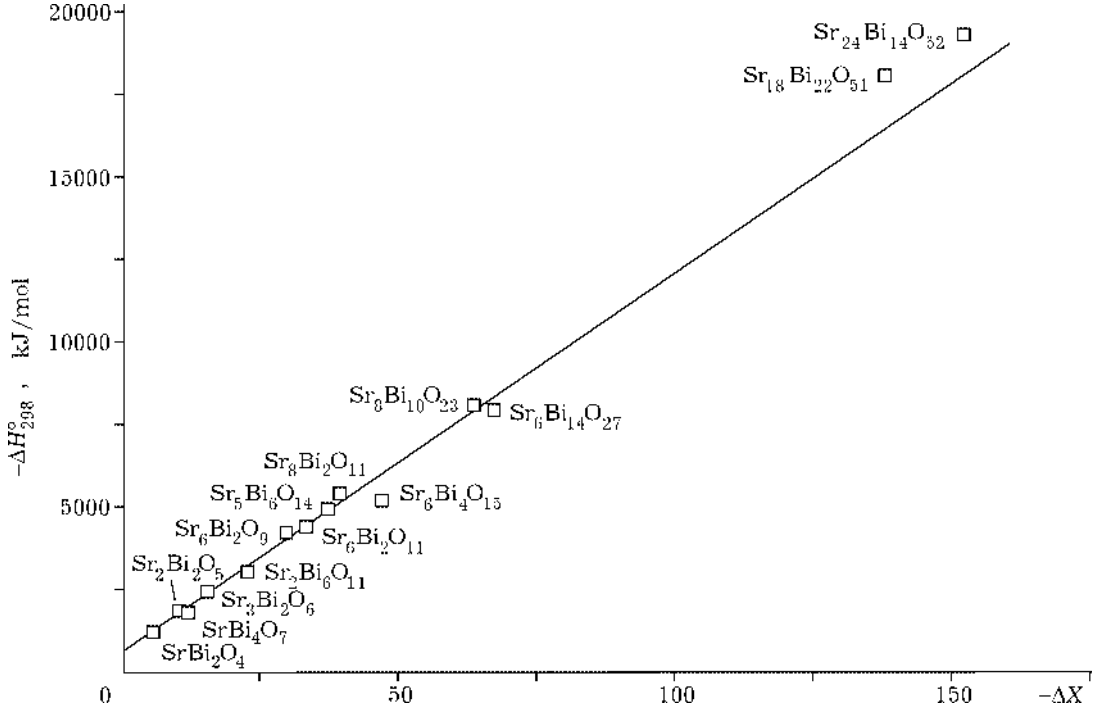


Fig. 2. Reactions of the formation of oxide compounds of strontium with bismuth.

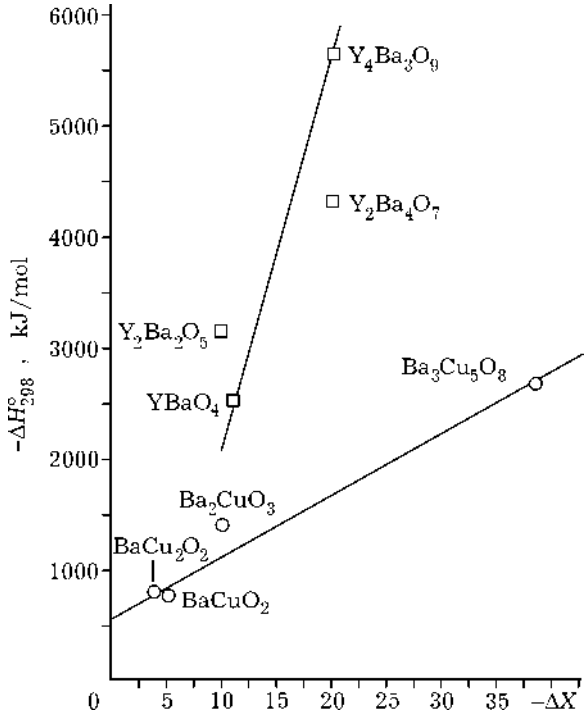


Fig. 3. Reactions of the formation of oxide compounds of yttrium and barium.

known Sanderson's postulate [7] according to which the EN of a molecule is equal to the EN of any atom in it. In other words, the principle of energy leveling or averaging contributions from atoms forming a molecule is postulated. This principle is used in quantum mechanics to describe hybridization of orbitals during the formation of chemical bond [8].

According to thermodynamics, the possibility for a reaction to occur is determined by Gibbs' energy. A reaction between substances proceeds to the formation of a product if

$$\Delta G_{reac} = (\Sigma\Delta G_{fin.\ prod} - \Sigma\Delta G_{init.\ prod}) < 0 \qquad (7)$$

and it proceeds in the opposite direction if $\Delta G_{reac} > 0$. Calculations with this equation are performed on the basis of the known Gibbs' energy, enthalpy and entropy values given in reference books.

By analogy with thermodynamic insight, the authors of [10] proposed to calculate the difference between mean orbital EN values similarly to Gibbs' energy of a reaction

$$\Delta X_{reac} = \Sigma X_{fin.\ prod} - \Sigma X_{init..\ prod} \qquad (8)$$

Calculations were performed for the formation of silicates of alkaline earths (common anion) from simple oxides, for the formation of various compounds containing calcium (common cation), and for the formation of complex silicates (like $CaMgSi_2O_7$, $CaTiSiO_5$, *etc.*). A correlation between D*G* and D*X* was observed for all the indicated reactions. In the present paper, similar calculations are performed for the reactions of other types.

## RESULTS AND DISCUSSION

The results of calculations according to eqs. (7) and (8) for the formation of titanium, vanadium, and manganese oxides from a metal and oxygen are shown in Fig. 1. One can see that a linear correlation between Gibbs' energy and the difference between the sums of mean EN of final and initial products is observed for all the oxides. A linear correlation between enthalpy of reaction and difference of the sums of mean EN is observed for oxide compounds of strontium with bismuth (Fig. 2), as well as for the oxide compounds of yttrium and barium with copper (Fig. 3). Standard enthalpies of the formation of the indicated compounds have been taken from [11].

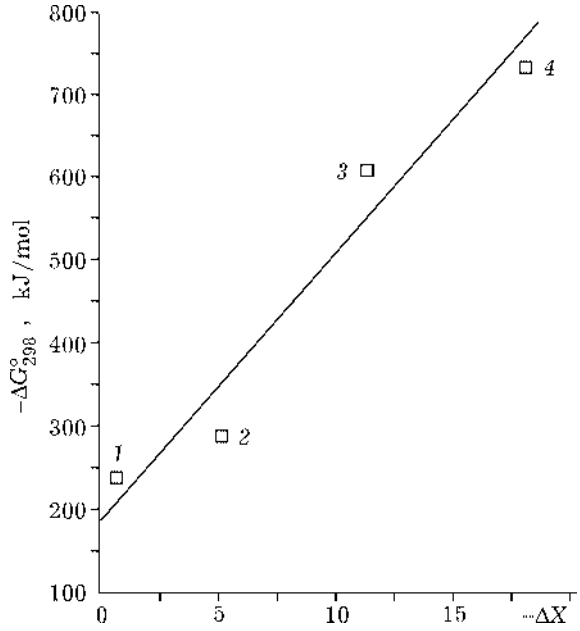


Fig. 4. Correlation between $\Delta G^\circ_{298}$ and $\Delta X$ for the reactions of ferrites with oxides: *1* – $Fe_2SiO_4 + TiO_2 + 1/2\ O_2 = Fe_3O_4 + FeTiO_3 + 2SiO_2$; *2* – $Fe_2SiO_4 + CaO + 1/2\ O_2 = CaFe_2O_4 + SiO_2$; *3* – $Fe_2SiO_4 + 2Na_2O + 1/2\ O_2 = Na_2Fe_2O_4 + Na_2SiO_3$; *4* – $3Fe_2SiO_4 + 3CaO + 1/2\ O_2 = 2Fe_3O_4 + 3CaSiO_3$.

Thus, the indicated data suggest that the correlation can be followed at a sufficient accuracy for many reactions of the formation of simple and complex oxides. However, it is not universal in the sense that a definite D*X* value should correspond to each Gibbs' energy value. One can see in Figs. 1–3 that several Gibbs' energy values can correspond to one D*X* value (for different compounds differing by a cation or by an anion).

The data shown in Figs. 1–3 are obtained for reactions in which a single product is formed. The major part of reactions leads to the formation of several compounds. These reactions include, for example, interaction of ferrites with oxides. Calculations for these reactions have been performed using the eqs. (7) and (8) involving the data from [12]; the results are shown in Fig. 4. The correlation in this case is satisfactory, too.

## CONCLUSION

It is demonstrated that the correlation between Gibbs' energy and the difference of the sums of mean orbital EN for final and initial products, stated previously in [10], is observed for reactions in which not only one but also several products are formed.

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