1. According to the generalization of the Brönsted–Lewis theory, there is a profound relationship between the acid–base and oxidation–reduction properties of substances; moreover, they can be considered as a single process, in which there is a partial or complete transfer of an electron pair from one atom to another. Since a quantitative characterization of acidity in this sense can be given from the standpoint of the charges of atoms (positive charge – acid, negative – base), it is natural to establish an analogous correlation between the oxidative properties and charges of the atoms.

A general consideration of the reaction of oxidation as a process of stripping of electrons from an atom leads to a trivial conclusion – the atom will be oxidized more readily the lower its positive charge or the greater its negative charge. However, the difficulty lies in determining the charge of the atom itself in a complex molecule or crystal, which is subjected to oxidation. Therefore, before presenting the theoretical and experimental material on the interdependence of the charges of atoms and their oxidative properties, we should define the concept of the "charge of the atom." This concept evidently is meaningful only in the case when the space within which a given charge acts is determined. From this it is clear that various methods can give different values for the charges of the atoms for the same substance, depending upon the portions of the atoms and molecules that they affect.

Since the outer electron layers are important for the chemical properties of atoms, let us consider only the type of charge that represents the result of interaction of the given atom with all the atoms of the first coordination sphere. We have called this charge the "effective coordination charge" ([1], p. 105); it is numerically equal to the algebraic sum of the formal valence of the central atom and the number of electrons that is received from bonds with atoms of the first coordination sphere. Naturally the coordination charge will be localized in the interatomic space, analogously to the σ- and π-electronic charges of the bonds in organic compounds [2]. The coordination charges can be determined directly from the x-ray absorption spectra [3–5], calculated from data on quadrupole resonance [6, 7] or calculated theoretically by the electronegativity method ([1], p. 106). From the standpoint of chemistry, these charges would be the most substantial for reactions of oxidation and in general for processes of deformation of the electron clouds of the chemical bonds.

In the case of crystalline compounds of metals in a lower oxidation state, possessing rather high values of the electronegativities, it may happen that the metal atom receives more electrons from its partner than it donates to the formation of chemical bonds. Then the effective coordination charge of the metal will possess a negative sign. This circumstance has been indicated for a number of years [8–11], but such a possibility was confirmed experimentally comparatively recently [7, 12, 13].

The presence of negative charges on the metal atoms physically means that in a crystalline coordination compound there are chemical bonds, which are formed on account of the unpaired electrons of the anions and vacant orbitals of the cations. It is easy to ascertain that such conditions are realized in crystalline compounds of metals of the B-subgroups and certain cations of the A-subgroups in the lower oxidation states.

In 1959 we proposed that the sign of the coordination charge on metal atoms is correlated with their oxidative properties. It is precisely in the presence of a negative charge on metal atoms possessing variable valence that the action of oxidizing agents is reduced not to a displacement of anions, but to an increase in the valence of the metal, as a result of which an oxidized salt with mixed anions will be obtained, for example, PtX₂ + Y₂ → PtX₂Y₂.
We have used this hypothesis as a working hypothesis for a number of years, and it has led to the synthesis of dozens of new compounds of the type MX\textsubscript{n}Y\textsubscript{m}, where M is Cu, Hg, Tl, Sn, Cr, Mn, or Pt and X, Y are halogens, chalcogens, and various acid residues [14-26].

2. Now let us attempt to give a thermodynamic substantiation of the hypothesis of the relationship of the coordination charge and the relative energetic profitability of the oxidation reaction. This premise may be considered proven if a reaction of the type

\[ 2\text{MY} + \text{X}_2 \rightarrow 2\text{MYX} \]  

is energetically more profitable than the process

\[ 2\text{MY} + \text{X}_2 \rightarrow 2\text{MX} + \text{Y}_2 \]  

with a definite nature of the M-Y bond. The energy balance of reaction (1) will consist of the energy expenditures

\[ \Delta E = (Q_3 - Q_1 - Q_2) - (Q_5 + Q_6 - Q_3 - Q_4) = (Q_3 - Q_5 - Q_6) + (Q_4 - Q_5 - Q_6) \]  

For reaction (2), analogously we will have

\[ \Delta E = (Q_2 - Q_1) - (Q_5 + Q_6 - Q_2 - Q_3) = (Q_2 - Q_5 - Q_6) + (Q_4 - Q_6 - Q_3) \]

Now let us compare the energy balances of the two reactions

\[ \Delta Q = (Q_3 - Q_1 - Q_2) - (Q_5 + Q_6 - Q_3 - Q_4) = (Q_3 - Q_5 - Q_6) + (Q_4 - Q_5 - Q_6) \]  

Q\textsubscript{3} is always somewhat greater than Q\textsubscript{3}, since as the valence of the metal increases, the strength of its bonds, for example, with halogens, drops. To determine the order of magnitude of the excess of Q\textsubscript{5} over Q\textsubscript{3}, let us cite the values of the average M-Hal bond energies according to the data of the Handbook [27].

The influence of valence on the bond energy is cited in Table 1. From the table it is evident that the average value of \( \Delta Q_{5-3} \) is 12 kcal/mole. The generality of this conclusion is indicated by all the thermodynamic material generalized in the concept of electronegativities.

It is known that when the valence is increased by a unit, the electronegativity (X) increases, as a rule, by 0.2. If now we consider the A-B bond, where A is a metal with variable valence (let X\textsubscript{A\textsuperscript{II}}=1.6 and X\textsubscript{A\textsuperscript{III}}=1.8) and B is a halogen (let X\textsubscript{B}=3.1, just as for chlorine). Then we can write

\[ (X_{A\textsuperscript{II}} - X_{B})^2 = 0.0433\{E(A\textsuperscript{II} - B) - 1/2[E(A - A) + E(B - B)] \]  

and analogously

\[ (X_{A\textsuperscript{III}} - X_{B})^2 = 0.0433\{E(A\textsuperscript{III} - B) - 1/2[E(A - A) + E(B - B)] \]

The combination of (4) and (5) gives

\[ \Delta X_{A\textsuperscript{II} - B}^2 - \Delta X_{A\textsuperscript{III} - B}^2 = 0.0433\{E(A\textsuperscript{II} - B) - E(A\textsuperscript{III} - B) \]

Substituting the average values of X\textsubscript{A} and X\textsubscript{B} cited above, we find that the energy difference \( \Delta Q_{5-3} = \Delta E_{(A\textsuperscript{II} - B) - (A\textsuperscript{III} - B)} = 13 \) kcal/mole.

Returning to Eq. (3) and taking as an assurance \( \Delta Q_{5-3} = 15 \) kcal/mole, we can state that the condition \( \Delta Q > 0 \) reduces to the requirement

\[ Q_4 - Q_2 = Q_5 - 15 > 0 \]  

Limiting ourselves to the case of halogens, we obtain as averaged values Q\textsubscript{5}=45 kcal/mole and Q\textsubscript{4}=90 kcal/mole for metals with variable valence in a lower oxidation state.