Physical Chemistry

M. G. Zhuravleva, A. N. Men, Corresponding Member of the Academy of Sciences of the USSR G. I. Chufarov

1964

SovietRxiv

Abstract

Full Text

Physical Chemistry

M. G. Zhuravleva, A. N. Men, Corresponding Member of the Academy of Sciences of the USSR G. I. Chufarov

On the Determination of the Concentration Dependence of the Activities of Components for Simple Binary Oxides

The basic thermodynamic functions of solutions can be determined if the activities of the corresponding components are known. The activities can be found if experimental data are available on the dependence of the equilibrium oxygen pressure on the composition of the solid solution.

For the theoretical calculation of the concentration dependence of the activities it is necessary to know the explicit form of the free energy of mixing $\Delta F = \Delta F(c_i)$. For binary oxides, if one restricts oneself to taking into account pair interactions of nearest neighbors metal–oxygen and metal–metal and assumes that the interaction energies of pairs are constant (do not depend on composition and the arrangement of atoms), while the metal atoms are distributed statistically, one obtains for ΔF

$$\Delta F = \Delta U - T\Delta S = Nvc_Ac_B + NkT(c_A \ln c_A + c_B \ln c_B), \tag{1}$$

where

$$v = z\left[v_{AB} - \frac{1}{2}(v_{AA} + v_{AB})\right], \tag{2}$$

v_{ij} are the interaction energies of metals of types i and j, and z is the coordination number.

From this it is easy to obtain for the activities of the components AO(a_A) and BO(a_B):

$$a_A = c_A e^{\alpha c_B^2}; \qquad a_B = c_B e^{\alpha c_A^2}, \tag{3}$$

where

$$\alpha = v/kT. \tag{4}$$

An analogous expression is also obtained for binary metallic alloys in the same approximation (1). From an analysis of (3) it follows that at $\alpha = 0$, $a = c$,

i.e., the solid solution will be ideal; if $\alpha > 0$ ($\alpha < 0$), then $a > c$ ($a < c$), i.e., a positive (negative) deviation from ideality will be observed. A positive (negative) deviation from ideality is characterized in a solid solution by the formation of a smaller (larger) number of bonds of the AB type.

To determine α it is necessary to have one experimental point on the curve $a(c)$.

Table 1

Values of the parameters α ($T = 1373^{\circ}$K)

System	α_{expt}	Lit. source	α_{theor} (8)	α_{theor} (11)	q_{eff}
FeO–MgO	1.2	(3, 4)	0.74	–	2.5
MnO–NiO	0.9	(2)	1.75	2.7	1.4
NiO–MgO	0	(2)	0	–	2
MnO–FeO	0	(5)	0.28	0.47	0

Table 1 gives the values of α_{expt} obtained from experimental data.

With the corresponding α_{expt}, the experimental curves $a(c)$ are well described by equation (3) (Fig. 1).

To determine α it is necessary to know the explicit form of the dependence of V on the equilibrium interatomic distance (R_0). Since for most of the solid solutions of the MeO type known to us Vegard' s rule is fulfilled, R_0

can be expressed through the equilibrium interatomic distances R_A and R_B of the components AO and BO. Treating the oxides MeO as ionic crystals, it is easy to obtain, in the Born approximation, the expression for ΔU:

$$\Delta U = U_p - c_A U_A - c_B U_B = -\beta q^2 e^2 \left(1 - \frac{1}{n}\right)\left[c_A\left(\frac{1}{R_0} - \frac{1}{R_A}\right) + c_B\left(\frac{1}{R_0} - \frac{1}{R_B}\right)\right], \tag{5}$$

where β is the Madelung constant, equal to 1.75; $n = 9$; q is the ion charge, equal to 2;

$$R_0 = \sqrt[n-1]{c_A R_A^{n-1} + c_B R_B^{n-1}} \simeq R_A\left(1 + c_B \frac{R_B - R_A}{R_A}\right) \simeq R_B\left(1 + c_A \frac{R_A - R_B}{R_B}\right). \tag{6}$$

Fig. 1. Dependence $a(c)$ for the solid solution FeO–MgO; $T = 1373^\circ$ K. 1–$\alpha_{\text{exp}} = 1.2$; 2–$\alpha_{\text{theor}} = 0.74$; experimental points: a–according to (3), b–according to (4).

Figure 1: Fig. 1. Dependence $a(c)$ for the solid solution FeO–MgO; $T = 1373^\circ$ K. 1–$\alpha_{\text{exp}} = 1.2$; 2–$\alpha_{\text{theor}} = 0.74$; experimental points: a–according to (3), b–according to (4).

Fig. 2. Lattice energies of MeO oxides.

Figure 2: Fig. 2. Lattice energies of MeO oxides.

Fig. 1. Dependence $a(c)$ for the solid solution FeO–MgO; $T = 1373^\circ$ K. 1 –$\alpha_{\text{exp}} = 1.2$; 2–$\alpha_{\text{theor}} = 0.74$; experimental points: a–according to (3), b–according to (4).

Fig. 2. Lattice energies of MeO oxides.

If one restricts oneself to the linear terms of the expansion in the small parameter $|R_A - R_B|$, then formula (5) takes the form

$$\Delta U = \beta q^2 e^2 \left(1 - \frac{1}{n}\right) c_A c_B \frac{(R_A - R_B)^2 (R_A + R_B)}{R_A^2 R_B^2}, \tag{7}$$

whence we obtain an expression for α

$$\alpha_{\text{theor}} = \beta q^2 e^2 \left(1 - \frac{1}{n}\right) \frac{(R_A - R_B)^2 (R_A + R_B)}{kT R_A^2 R_B^2} = 10^6 \frac{(R_A - R_B)^2 (R_A + R_B)}{T R_A^2 R_B^2} \tag{8}$$

(R_i in angstroms).

The calculated values of α_{theor} are given in Table 1. The difference of α_{theor} from α_{exp} (for $\alpha > 0$) may be connected with the fact that, in the expression for U_p, a statistical distribution of metal atoms in the solution was assumed, whereas for $\alpha > 0$ one may expect some aggregation of like atoms, which may be taken into account by introducing an effective charge

$$q_{\text{eff}} = 2\sqrt{\frac{\alpha_{\text{exp}}}{\alpha_{\text{theor}}}}. \tag{9}$$

The corresponding values of q_{eff} are given in Table 1. For the solid solution CoO–MnO ([6]) a slight negative deviation from ideality is observed. Such a dependence of activity on composition cannot be described by equation (8). This is apparently due to the fact that a purely ionic approximation is not applicable

to the indicated solid solutions. Therefore, the study of such solutions is of great interest from the standpoint of determining the nature of the bonding forces.

Let us find an expression for α, starting from the approximation of crystal-field theory. We shall represent the energy of an oxide as the sum of two terms, the first of which characterizes the energy of the oxide in which the ion has a filled shell (U_0), while the second is an addition associated with the stabilization energy (U_{stab}) ([7,8]). Such a representation describes well the lattice energies of oxides for ions of the iron group ([9]). The data are given in Table 2.

Table 2

Values of crystal-lattice energies

Oxide	R_A, Å	U_{exp}, kcal/mol	U_0, kcal/mol	U_{stab}, kcal/mol
MnO	2.21	890	890	0
FeO	2.16	920	908	12
CoO	2.12	942	922	17
NiO	2.10	963	930	29

In this approximation (using Vegard' s rule)

$$\Delta U = -5c_{Ac}B(R_A - R_B)\left[\frac{U_A^{\text{stab}}}{R_A} - \frac{U_B^{\text{stab}}}{R_B}\right], \tag{10}$$

whence

$$\alpha = \frac{5(R_A - R_B)}{kT}\left[\frac{U_A^{\text{stab}}}{R_A} - \frac{U_B^{\text{stab}}}{R_B}\right] = -2500\frac{R_A - R_B}{T}\left[\frac{U_A^{\text{stab}}}{R_A} - \frac{U_B^{\text{stab}}}{R_B}\right]. \tag{11}$$

The values of α calculated from formulas (8) and (11) are given in Table 1. In both cases α has a positive sign and is close in order of magnitude to α_{exp}. The deviation from α_{exp} in this case may be connected with the fact that the contribution from U_0 was not taken into account in ΔU, since there is no explicit form of the dependence of U_0 on R_0.

The results obtained make it possible to carry out a theoretical calculation of the activities of the components of a solid solution without any additional parameters. On the basis of knowledge of the activities, one can obtain the explicit form of the dependence of the equilibrium elasticity and the thermodynamic functions of mixing on the composition and properties of the initial components.

In conclusion, we shall make some remarks concerning the definition of the concept of stabilization energy in oxides. The stabilization energy of an impurity

ion in a crystal is taken to be the difference between the energy of the free ion and the lower energy level of the ion in the crystal. It is evidently expedient to introduce the concept of the stabilization energy of an oxide. By this quantity, for oxides of the MeO type of the iron group, one should understand the difference between the energy of formation of the given oxide from the elements and this energy for CaO (Fig. 2). When two oxides are compared, the stabilization energy will be equal to the absolute difference of their total energies.

Institute of Metallurgy
Sverdlovsk

Received
20 VII 1964

CITED LITERATURE

1. B. N. Finkelshtein, *Problemy metalloved. i fiz. met.*, No. 3, 275 (1952).
2. W. G. Hahn, A. Muan, *Phys. Chem. Solids*, **19**, 3/4, 338 (1961).
3. W. G. Hahn, A. Muan, *Trans. Met. Soc. AIME*, **224**, No. 3, 416 (1962).
4. A. V. Shashkina, Ya. I. Gerasimov, *ZhFKh*, **27**, issue 3, 399 (1953).
5. P. K. Foster, A. Y. E. Welch, *Trans. Farad. Soc.*, **52**, 12, 1636 (1956).
6. E. Aukrust, A. Muan, *Trans. Met. Soc. AIME*, **230**, 3, 378 (1964).
7. K. B. Yatsimirskii, *ZhKhKh*, **3**, No. 10, 2244 (1958).
8. L. E. Orgel, *J. Chem. Phys.*, **23**, 10, 1819 (1955).
9. L. Žagar, *Sprechsaal Keramik, Glas, Email*, **93**, 6, 153 (1960).

Note: Figure translations are in progress. See original paper for figures.