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Abstract

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THE ROLE OF CATION VACANCIES IN OXIDATION-REDUCTION PROCESSES IN IONIC CRYSTALS

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Let us consider an ionic compound $K_m^{+n}A_n^{-m}$, in which part of the cations K is replaced by cations C^{+p} and C^{+q} $(p, q \geqslant n)$. We shall assume that the solid solution formed is stable or decomposes so slowly that, at the given temperature, pressure, and concentration, a quasi-equilibrium distribution between the valence states p and q has time to become established.

A solution in which the concentrations of the cations C^{+p} and C^{+q} are in the ratio $\dfrac{x-y}{y}$ may be obtained by the reaction

$$K^{+n}_{m-\frac{p}{n}x}C^{+p}_{x}\square_{(\frac{p}{n}-1)x}A^{-m}_{n}+A^{-m}_{\frac{y(q-p)}{m}}+\Delta\Phi = K^{+n}_{m-\frac{p}{n}x}C^{+p}_{x-y}C^{+q}_{y}\square_{\frac{x(p-n)+y(q-p)}{n}}A^{-m}_{n+\frac{y(q-p)}{m}}, \tag{1}$$

where $\square$ is a cation vacancy; $\Delta\Phi$ is the change in the free energy of the system

$$\Delta\Phi = \frac{\mu(q-p)}{n}y + \frac{\nu(p-q)}{m}y + \varepsilon(p-q)y + W - T\left[\left(1+\frac{q-p}{mn}y\right)S_2 - S_1\right]; \tag{2}$$

here μ is the vacancy-formation energy; ν is the free energy of a neutral oxidizer atom; $\varepsilon(p-q)$ is the total oxidation work in the transition $C^{+q} \to C^{+p}$; W is the elastic energy associated with the difference in ionic radii of the substituted and substituting cations; S_1 and S_2 are the configurational entropies of the solutions in the left- and right-hand parts of (1), calculated according to Boltzmann.

From $\Delta\Phi'_y = 0$, $\Delta\Phi''_{yy} > 0$, we find the relation between the equilibrium concentration of vacancies c and the concentration of substituted ions ξ

$$\frac{[\xi(p-n)-cp]\,c^{(q-p)/n}}{\xi(n-q)+cp} = \exp\frac{-N_0[\mu(q-p)/n+\nu(p-q)/m+\varepsilon(p-q)+\eta]}{RT}; \tag{3}$$

in (3), N_0 is Avogadro's number; $\eta = \partial W/\partial y \approx 10\chi^{-1} r_K \left(\Delta r_q^2 - \Delta r_p^2 + \frac{q-p}{n}\Delta r_\square^2\right)^{(1)}$, r_K is the radius of the cation K; $\Delta r_i = r_K - r_i$; χ is the coefficient of compressibility.

Apparently, μ, ε, and η vary only weakly with temperature and pressure. The quantity ν, proceeding from molecular-kinetic theory, may be represented in the form

$$\nu = \mathrm{const}(P - P_1), \tag{4}$$

where P is the partial pressure of the oxidizer in the medium; $P_1 \sim \exp(-U/RT)$ is the saturated vapor pressure of the oxidizer above the surface of the solid solution; U has the meaning of the heat of activation of adsorption of neutral oxidizer atoms by the crystal surface.

Let us apply (3) to the analysis of some specific cases. Consider wüstite of composition $\mathrm{Fe}^{2+}_{1-x}\mathrm{Fe}^{3+}_{x}\square_{x/2}\mathrm{O}_{1+x/2}$, obtained by the reaction

$$\mathrm{FeO} + \frac{x}{2}\mathrm{O} + \Delta\Phi = \left(1 + \frac{x}{2}\right)\mathrm{Fe}^{2+}_{\frac{1-x}{1+x/2}}\mathrm{Fe}^{3+}_{\frac{x}{1+x/2}}\square_{\frac{x}{2(1+x/2)}}\mathrm{O}. \tag{5}$$

The equilibrium concentration of vacancies $c = \dfrac{x}{2(1+x/2)}$ is determined, according to (3), from the condition for the minimum of $\Delta\Phi$:

$$\frac{(1-3c)^2}{4c^3} = \exp\frac{N_0(\mu - \nu - 2\varepsilon - 2\eta)}{RT} = B(P,T). \tag{6}$$

The dependence $c = f(\ln B)$ shows (Fig. 1) that the limiting values $c = 0$ and $c = 0.3$ cannot be reached. This is consistent

Fig. 1

Fig. 2

Fig. 1. Dependence of the concentration of cation vacancies in FeO on $\ln B$ according to equation (6)

Fig. 2. Dependence of the concentration of cation vacancies on the concentration of iron ions in MgO. 1 —constructed from the experimental equation $c = 0.2\xi$; 2 —according to equation (8)

with the known data that it is impossible to obtain iron oxide corresponding to the exact stoichiometric composition FeO.*

According to data on the heat of oxidation of FeO to $\mathrm{Fe_2O_3}$ ([2,3]), the value $N_0\varepsilon$ is ~ 35 kcal/mol. Assuming that $N_0\nu_{\max} \sim 10$ kcal/mol (bond energy of molecular crystals), $U \approx 6$ kcal/mol ([4]), and taking into account that in an air atmosphere at $T \sim 1700$°K, $P_1 = P$ $(\nu = 0)$ ([5]), we obtain

Fig. 3 and Fig. 4

Figure 1: Fig. 3 and Fig. 4

$$N_0\nu \approx 10\left[1 - 6\exp\left(-\frac{6000}{RT}\right)\right]\frac{\text{kcal}}{\text{mol}}. \tag{7}$$

On the basis of these estimates it is easy to show that, for $N_0(\mu + 2\eta) < 80$ kcal/mol, $\partial \ln B/\partial T > 0$, i.e., reduction occurs with increasing temperature. For $80 < N_0(\mu + 2\eta) < 90$ kcal/mol, $\partial \ln B/\partial T$ changes sign, which corresponds to a transition from oxidation to reduction as the temperature rises. The situation usually observed corresponds precisely to this case; however, it is most likely caused by the kinetics of the processes occurring during heating of specimens quenched after high-temperature reduction.

As a second example, permitting more definite numerical estimates, solid solutions of $MgFe_2O_4$ in MgO were considered. In this case, from (3) it follows that

$$\xi = 3c\left[1 + \sqrt{B(P,T)c}\right]. \tag{8}$$

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* This result is also valid for other analogous oxides: MnO, TiO, CoO, etc.

To find $B(T)$ at $P = \text{const} = 152$ mm Hg, we require that (8) agree with the experimental dependence $\xi = f(c)$. The measurements performed show that, for samples of solid solutions quenched from a temperature of 1500°K, the empirical relation $a_0 - a(\xi) = \Delta a \approx 10^{-2}\xi$ Å is valid, where a is the lattice parameter. Since (^{6,9})

$$\Delta a = 2\sum c_i \Delta r_i \tag{9}$$

(c_i are the atomic concentrations of cations of the i-th kind, including vacancies), $c \approx 0.2\xi$, which practically coincides with (8) at $B(1500^\circ) \simeq 15$ (Fig. 2).

Fig. 3. Dependence of the degree of reduction of the solid solution $MgFe_2O_4$ in MgO on $\sqrt{Bc}$. Solid line—theory; points—experiment

Fig. 4. Change in the degree of reduction of the solid solution $MgFe_2O_4$ in MgO with temperature. Solid lines—theory; points—experiment. The numbers associated with the lines and points indicate the concentration z of iron ions

Assuming that ν varies with temperature in the same way as for pure iron oxide (7), we obtain $N_0(\mu - 2\varepsilon - 2\eta) \approx 10$ kcal/mol and, consequently,

$$B(T) = \exp\frac{60\exp(-6000/RT)}{RT}. \tag{10}$$

Using data on the displacement of ions located in the two nearest coordination spheres of a cation vacancy (^{6}), we obtain $N_0\eta \approx -1$ kcal/mol. The value $N_0\mu$, calculated from the change in bond energy between ions in the vicinity of a vacancy with allowance for the degree of ionicity of the MgO lattice bond (^{7,8}), is $70 \div 80$ kcal/mol, so that $N_0(\mu - 2\varepsilon - 2\eta) \approx 2 \div 12$ kcal/mol, which agrees well with the estimate given above.

Let us denote the total concentration of iron ions in the solid solution by $z = \xi - c$ and the degree of reduction by $Q = (z - 2c)/z$.

We had at our disposal data on the change in the phase composition as a function of the quenching temperature of a sample of a solid solution of magnesium ferrite in magnesium oxide with initial $z = c_{\mathrm{Fe}^{2+}} + c_{\mathrm{Fe}^{3+}} = 8$ at. %, obtained as a result of quenching from 1800°K.* The concentrations $c_{\mathrm{Fe}^{2+}}$ and $c_{\mathrm{Fe}^{3+}}$ were determined from X-ray and magnetic measurements (Table 1). Comparison of the experimental dependence $Q = f(\sqrt{Bc})$ (B was calculated from (10)) with the theoretical formula $Q_t = 3\sqrt{Bc}/(2 + 3\sqrt{Bc})$, which follows from (8), shows exceptionally good agreement (Fig. 3).

It follows from Table 1 that, as a result of the thermal treatment carried out, along with a change in the degree of reduction, the concentration changes solid solution. In this case, the decay observed at first is due to the kinetics of the process—the annealing of quenched solutions. If, in the sample, the quasi-equilibrium concentration of vacancies has time to become established at each temperature, then the experimental values $Q(T)$ must lie on curves $z =$ const, constructed on the basis of the theory presented. As can be seen from Fig. 4, the experimental points fit well on the curves corresponding to the respective concentrations of solid solutions.

Table 1

Dependence of the degree of reduction of samples of solid solutions MgO—$\mathrm{MgFe_2O_4}$ on the quenching temperature

T_{quench}, °K	$c_{\mathrm{Fe}^{2+}}$, at. %	$c_{\mathrm{Fe}^{3+}}$, at. %	B	Q	T_{quench}, °K	$c_{\mathrm{Fe}^{2+}}$, at. %	$c_{\mathrm{Fe}^{3+}}$, at. %	B	Q
800	2.0	5.5	2.45	0.267	1200	0.9	2.0	7.80	0.310
900	1.0	3.0	3.30	0.250	1400	3.0	4.0	12.50	0.420
1000	0.1	0.6	4.20	0.143	1800	4.0	4.0	24.0	0.500

As was to be expected, at an approximately constant concentration, increasing the temperature brings about reduction of the solid solution. Oxidation of the solutions upon heating to ~ 1000°K is due to a decrease in their concentrations

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* A. I. Kaplienko participated in the measurements.

as a result of decomposition. This circumstance is well illustrated by the arrangement of the points in Fig. 4 relative to the isoconcentration theoretical curves.

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