Soviet-era science, translated into English

A. N. MEN, N. M. STAFEEVA, V. N. BOGOSLOVSKII, M. G. ZHURAVLEVA,

Corresponding Member of the Academy of Sciences of the USSR G. I. CHUFAROV

1964

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196401.77904

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

PHYSICAL CHEMISTRY

A. N. MEN, N. M. STAFEEVA, V. N. BOGOSLOVSKII, M. G. ZHURAVLEVA,
Corresponding Member of the Academy of Sciences of the USSR G. I. CHUFAROV

ON DETERMINING THE CONCENTRATION DEPENDENCE OF CERTAIN THERMODYNAMIC FUNCTIONS OF SOLID SOLUTIONS OF FERRITES

The statistical calculation of thermodynamic functions of solid solutions is complicated by the presence of a large number of parameters characterizing the interactions of particles in the solid phase. Therefore, one of the tasks is to find reasonable approximations that give the best agreement with experiment.

The change in any thermodynamic function X upon formation of solid solutions is equal to

$$\Delta X_{\text{mix}} = X_{\text{soln}} - (1-c)X_{\Phi_1} - cX_{\Phi_2}, \tag{1}$$

where c and $(1-c)$ are the mole fractions of the components Φ_1 and Φ_2 in the solution.

The configurational entropy of mixing without taking short-range order into account can be calculated most simply by statistical methods.

For solid solutions of copper ferrite (concentration c) with magnetite, ΔS^{conf} is determined as follows:

$$\Delta S^{\text{conf}} = -R\{(c-\lambda)\ln(c-\lambda) + (1-c)\ln(1-c) +$$

$$+(1+\lambda)\ln(1+\lambda) + \lambda\ln\lambda + (1-\lambda)\ln(1-\lambda) -$$

$$-c[2(1-\lambda_0)\ln(1-\lambda_0) + \lambda_0\ln\lambda_0 + (1+\lambda_0)\ln(1+\lambda_0)]\}, \tag{2}$$

where λ is the equilibrium degree of inversion of the solid solution at the given temperature, λ_0 is the equilibrium degree of inversion of copper ferrite at the

SovietRxiv

Fig. 1

Figure 1: Fig. 1

same temperature, and the distribution of cations over the tetrahedral (t) and octahedral (o) sublattices is specified in the form:

$$\begin{array}{c|ccc} & \mathrm{Cu}^{2+} & \mathrm{Fe}^{2+} & \mathrm{Fe}^{3+} \\ \mathrm{t} & \lambda & 0 & 1-\lambda \\ \mathrm{o} & c-\lambda & 1-c & 1+\lambda \end{array} \qquad (3)$$

Formula (2) is valid for all cases in which solid solutions are formed with the same distribution of cations and with the corresponding values of λ for the components.

In order to carry out a quantitative calculation by formula (2), it is necessary to know the explicit form of the dependence $\lambda(c)$, the direct determination of which is often associated with experimental difficulties. For copper ferrite, $\lambda_0(T)$ is known (^{1}), as is the value for the solid solution at $c = 0.5$ (^{2}). These values can be reconciled if one assumes

$$\lambda = \lambda_0 \sqrt{c}. \qquad (4)$$

If the explicit form of the dependence $\lambda(c)$ is unknown, then as a first approximation it may be taken to be linear,

$$\lambda = \lambda_0 c. \qquad (5)$$

or determine from the theoretical equation (3)

$$\lambda = \frac{-[(1+2\alpha) - \alpha(1-c)] + \sqrt{(1+8\alpha) - 6\alpha(1-c) + \alpha^2(1-c)^2}}{2(1-\alpha)}, \qquad (6)$$

where α is a dimensionless parameter.

Figure 1 shows the concentration dependence of the degree of inversion at 900°.

Figure 2 gives the values of ΔS^{conf}, calculated from equation (2) with allowance for (4), (5), and (6) at different concentrations of the solid solution. In this case, the form of the concentration dependence of the degree of inversion has practically no effect on the quantitative or qualitative value of ΔS^{conf}.

Fig. 1. Concentration dependence of the degree of inversion of the solid solutions $\mathrm{CuFe_2O_4}$—$\mathrm{Fe_3O_4}$: 1 –calculated from equation (4); 2 –from equation (6); 3 – from equation (5)

SovietRxiv

Fig. 2

Figure 2: Fig. 2

Fig. 2. Concentration dependence of the entropy of mixing: 1 –experimental; 2 –calculated with allowance for equations (4) and (6); 3 –calculated at $\lambda_0 = \lambda$ with allowance for equation (5)

In the same figure, curve 1 presents the experimental values of ΔS, obtained from data on the oxygen elasticity over the solid solutions (4). Comparison of the theoretically calculated and experimental values of ΔS shows that over the entire composition range of the solid solutions the difference $\Delta S^{\text{conf}} - \Delta S_{\text{expt}}$ is equal to 0.3 cal/mole. Possible reasons for the small discrepancy were discussed in (4), where ΔS^{conf} was determined for the “effective” states of the initial components, in which λ_0 was taken equal to λ (Fig. 2, curve 3). This approximation also gives good agreement with the experimental dependence.

Thus, on the basis of the foregoing it may be said that the entropy of mixing in the formation of solid solutions of components with the spinel structure is determined mainly by the configurational part and depends only weakly on the form of the functional dependence of the degree of inversion on composition.

In addition to the configurational entropy of mixing, for the solid solutions CuFe_2O_4—Fe_3O_4 the configurational internal energy was calculated; in the present case it is identified with the integral enthalpy of mixing ΔH, since the crystal-lattice parameters of copper ferrite and magnetite are equal and no change in the volume of the unit cell occurs upon formation of the solid solutions.

For the calculation we use expression (3) of work (5). The interatomic distances practically do not change with concentration; therefore we equate the corresponding interaction energies in the solution and in the pure components. If the distribution (3) in CuFe_2O_4—Fe_3O_4 is taken into account and one substitutes

$$\begin{gathered}
p_{\text{T}}^{\text{Cu}^{2+}} = \lambda; \qquad p_{\text{T}}^{\text{Fe}^{3+}} = 1 - \lambda; \qquad p_{\text{T}}^{\text{Fe}^{2+}} = 0; \\
p_{\text{O}}^{\text{Cu}^{2+}} = \tfrac{1}{2}(c - \lambda); \qquad p_{\text{O}}^{\text{Fe}^{3+}} = \tfrac{1}{2}(1 + \lambda); \qquad p_{\text{O}}^{\text{Fe}^{2+}} = \tfrac{1}{2}(1 - c); \\
p_{\mu\nu}^{ij} = \left[1 - \delta_{\mu\nu}(1 - \delta_{ij})\right] p_{\mu}^{i} p_{\nu}^{j},
\end{gathered} \tag{7}$$

where i, j are the type of cation ($i, j \equiv \text{Cu}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}$); μ, ν are the type of site ($\mu, \nu \equiv \text{t}; \text{o}$), $p_{\mu\nu}^{ij}$ is the probability of formation of a pair of the corresponding cations, located-

located in the sites of the tetrahedral and octahedral sublattices, we obtain:

SovietRxiv

$$\begin{aligned}\Delta u^{\mathrm{conf}} = -\{&\lambda\Delta_1 + c\lambda_0\Delta_2 + \lambda^2(6\Delta_3 - 2\omega_{\mathrm{TT}}^{\mathrm{Cu^{2+}Fe^{3+}}} + {}^3/_2\omega_{\mathrm{OO}}^{\mathrm{Cu^{2+}Fe^{3+}}})\\ &+ c\lambda_0^2(-6\Delta_3 + 2\omega_{\mathrm{TT}}^{\mathrm{Cu^{2+}Fe^{3+}}} + {}^3/_2\omega_{\mathrm{OO}}^{\mathrm{Cu^{2+}Fe^{3+}}}) + {}^3/_2 c\Delta_4 + c\lambda\Delta_5\\ &- {}^3/_2 c^2\omega_{\mathrm{OO}}^{\mathrm{Cu^{2+}Fe^{2+}}} + {}^3/_2\omega_{\mathrm{OO}}^{\mathrm{Cu^{2+}Fe^{3+}}}\}.\end{aligned} \tag{8}$$

In this expression:

$$\begin{aligned}\Delta_1 = {}&(u_{\mathrm{O}}^{\mathrm{Fe^{3+}}} - u_{\mathrm{T}}^{\mathrm{Fe^{3+}}}) - (u_{\mathrm{O}}^{\mathrm{Cu^{2+}}} - u_{\mathrm{T}}^{\mathrm{Cu^{2+}}}) - 4(u_{\mathrm{TT}}^{\mathrm{Fe^{3+}Fe^{3+}}} - u_{\mathrm{TT}}^{\mathrm{Cu^{2+}Fe^{3+}}})\\ &+ {}^3/_2(2u_{\mathrm{OO}}^{\mathrm{Fe^{2+}Fe^{3+}}} - 2u_{\mathrm{OO}}^{\mathrm{Cu^{2+}Fe^{2+}}} + u_{\mathrm{OO}}^{\mathrm{Fe^{3+}Fe^{3+}}} - u_{\mathrm{OO}}^{\mathrm{Cu^{2+}Cu^{2+}}})\\ &- 6(2u_{\mathrm{TO}}^{\mathrm{Fe^{3+}Fe^{3+}}} - u_{\mathrm{TO}}^{\mathrm{Cu^{2+}Fe^{3+}}} - u_{\mathrm{TO}}^{\mathrm{Cu^{2+}Fe^{2+}}} + u_{\mathrm{TO}}^{\mathrm{Fe^{3+}Fe^{2+}}} + u_{\mathrm{TO}}^{\mathrm{Fe^{3+}Cu^{2+}}});\\ \Delta_2 = {}&(u_{\mathrm{O}}^{\mathrm{Cu^{2+}}} - u_{\mathrm{T}}^{\mathrm{Cu^{2+}}}) - (u_{\mathrm{O}}^{\mathrm{Fe^{3+}}} - u_{\mathrm{T}}^{\mathrm{Fe^{3+}}}) + 4(u_{\mathrm{TT}}^{\mathrm{Fe^{3+}Fe^{3+}}} - u_{\mathrm{TT}}^{\mathrm{Cu^{2+}Fe^{3+}}})\\ &+ 3(u_{\mathrm{OO}}^{\mathrm{Cu^{2+}Cu^{2+}}} - u_{\mathrm{OO}}^{\mathrm{Fe^{3+}Fe^{3+}}}) + 6(2u_{\mathrm{TO}}^{\mathrm{Fe^{3+}Fe^{3+}}} + 2u_{\mathrm{TO}}^{\mathrm{Fe^{3+}Cu^{2+}}} - u_{\mathrm{TO}}^{\mathrm{Cu^{2+}Cu^{2+}}} - u_{\mathrm{TO}}^{\mathrm{Cu^{2+}Fe^{3+}}});\\ \Delta_3 = {}&(u_{\mathrm{TO}}^{\mathrm{Cu^{2+}Fe^{3+}}} + u_{\mathrm{TO}}^{\mathrm{Fe^{3+}Cu^{2+}}} - u_{\mathrm{TO}}^{\mathrm{Cu^{2+}Cu^{2+}}} - u_{\mathrm{TO}}^{\mathrm{Fe^{3+}Fe^{3+}}});\\ \Delta_4 = {}&(2u_{\mathrm{OO}}^{\mathrm{Cu^{2+}Fe^{2+}}} - 2u_{\mathrm{OO}}^{\mathrm{Cu^{2+}Fe^{3+}}} + u_{\mathrm{OO}}^{\mathrm{Fe^{3+}Fe^{3+}}} - u_{\mathrm{OO}}^{\mathrm{Fe^{2+}Fe^{2+}}});\\ \Delta_5 = {}&{}^3/_2(2u_{\mathrm{OO}}^{\mathrm{Cu^{2+}Fe^{2+}}} - 2u_{\mathrm{OO}}^{\mathrm{Fe^{2+}Fe^{3+}}} - u_{\mathrm{OO}}^{\mathrm{Cu^{2+}Cu^{2+}}} + u_{\mathrm{OO}}^{\mathrm{Fe^{3+}Fe^{3+}}})\\ &+ 6(u_{\mathrm{TO}}^{\mathrm{Fe^{3+}Fe^{3+}}} + u_{\mathrm{TO}}^{\mathrm{Cu^{2+}Cu^{2+}}} - u_{\mathrm{TO}}^{\mathrm{Cu^{2+}Fe^{2+}}} - u_{\mathrm{TO}}^{\mathrm{Fe^{3+}Cu^{2+}}});\end{aligned}$$

$$\begin{aligned}\omega_{\mathrm{TT}}^{\mathrm{Cu^{2+}Fe^{3+}}} &= 2u_{\mathrm{TT}}^{\mathrm{Cu^{2+}Fe^{3+}}} - u_{\mathrm{TT}}^{\mathrm{Cu^{2+}Cu^{2+}}} - u_{\mathrm{TT}}^{\mathrm{Fe^{3+}Fe^{3+}}};\\ \omega_{\mathrm{OO}}^{\mathrm{Cu^{2+}Fe^{3+}}} &= 2u_{\mathrm{OO}}^{\mathrm{Cu^{2+}Fe^{3+}}} - u_{\mathrm{OO}}^{\mathrm{Cu^{2+}Cu^{2+}}} - u_{\mathrm{OO}}^{\mathrm{Fe^{3+}Fe^{3+}}};\\ \omega_{\mathrm{OO}}^{\mathrm{Cu^{2+}Fe^{2+}}} &= 2u_{\mathrm{OO}}^{\mathrm{Cu^{2+}Fe^{2+}}} - u_{\mathrm{OO}}^{\mathrm{Cu^{2+}Cu^{2+}}} - u_{\mathrm{OO}}^{\mathrm{Fe^{2+}Fe^{2+}}}.\end{aligned}$$

Expression (8) contains a large number of energy parameters characterizing the interaction energy of cations located in tetra- or octahedra with anions forming the first coordination sphere (u_μ^i or u_ν^j), as well as $u_{\mu\nu}^{ij}$, the energy of interaction of cations with the second coordination sphere, i.e., metal-metal interaction. For a quantitative estimate of Δu^{conf} we shall assume that the change in energy upon formation of the solid solution is determined only by the metal-oxygen interaction. Then expression (8) takes the form

$$\Delta u^{\mathrm{conf}} = -\Delta_0(\lambda - c\lambda_0). \tag{9}$$

However, the values of Δu^{conf} obtained from this equation for different dependences $\lambda(c)$ do not agree with experiment.

Consequently, it is necessary to take into account not only the energy of the metal-oxygen interaction, but also the energy of the metal-metal interaction.

SovietRxiv

Since the energy of pair interactions depends strongly on distance, one should first of all consider the interactions of cations located in octahedral sites (^{6}). The strongest may be considered the pair interaction between equivalent cations of one kind (in our case Fe^{2+} and Fe^{3+}). Such an approximation, without changing the qualitative character of the concentration dependence, makes it possible to carry out numerical calculation. Then expression (8) takes the form

Fig. 3. Concentration dependence of the heat of mixing: 1 –experimental; 2 –calculated from equation (9) with allowance for (4); 3 –from equation (10) with allowance for (4); 4 –from equation (12) with allowance for (5) at $\Delta_0 = -26.5$ kcal/mole; 5 –from equation (12) with allowance for (5) at $\Delta_0 = -15.6$ kcal/mole.

$$\Delta u^{\mathrm{conf}} = -\Delta_0(\lambda - c\lambda_0) - 3\Delta\lambda(1-c), \tag{10}$$

where Δ_0 is an energy term characterizing the Me–O interaction

$$\Delta_0 = \left(u_o^{\mathrm{Fe}^{3+}} - u_T^{\mathrm{Fe}^{3+}}\right) - \left(u_o^{\mathrm{Cu}^{2+}} - u_T^{\mathrm{Cu}^{2+}}\right), \tag{11}$$

$$\Delta = u_{oo}^{\mathrm{Fe}^{2+}\mathrm{Fe}^{2+}}.$$

The values of Δu^{conf}, calculated from equation (10) with allowance for (4), agree well with the experimental ones (curve 3, Fig. 3) for $-\Delta_0 \simeq 3\Delta \simeq 90$ kcal/mole. It follows from this that, in the formation of solid solutions with the spinel structure, the change in the energy of the system is determined mainly by the metal–metal interaction energy, which is of the same order of magnitude as that obtained for simple nonstoichiometric oxides (^{7}).

To determine Δu^{conf}, one can introduce "effective" states of the components of the solution, analogously to what was done for ΔS^{conf}, and, discarding all terms characterizing the metal–metal interaction in expression (8), obtain

$$\Delta u'^{\mathrm{conf}} = \Delta'\lambda(1-c). \tag{12}$$

Generally speaking, equation (12) can be obtained formally from equation (10), if one adopts the concentration dependence for the degree of inversion (5) and $\Delta' = -3\Delta = -\Delta_0$. The introduction of the effective state makes it possible to regard Δ' as the Me–O interaction energy, which, according to (11), characterizes the preference energy and can be taken from works (^{8},^{9}). Using these data in equation (12), we obtain a concentration dependence of Δu^{conf} that agrees well with the experimental one if $\Delta_0 = -26.5$ kcal/mole (^{8}) is adopted (curve 4, Fig. 3), and considerably worse if $\Delta_0 = -15.6$ kcal/mole (^{9}) is adopted (curve 5, Fig. 3). This is explained by the fact that in work (^{8}), in determining the

SovietRxiv

preference energy, the metal—metal interaction was taken into account more consistently.

Calculations of an analogous type can also be carried out for other solid solutions of ferrites.

Institute of Metallurgy
Sverdlovsk

Received
20 IV 1964

REFERENCES

1. F. Bertaut, J. Phys. Rad., **12**, 252 (1952).
2. E. W. Gorter, Adv. in Phys., **6**, 336 (1957).
3. A. N. Men' , G. I. Chufarov, Ukr. fiz. zhurn., **8**, 1—3, 344 (1963).
4. A. N. Men' , N. M. Stafeeva, V. N. Bogoslovskii, M. G. Zhuravleva, G. I. Chufarov, DAN, **156**, No. 4 (1964).
5. A. N. Men' , Fiz. tverd. tela, **4**, 889 (1962).
6. E. W. Gorter, UFN, issue 2, 279 (1955).
7. S. M. Ariya, Author' s abstract of doctoral dissertation, L., 1964.
8. A. Miller, J. Appl. Phys. Suppl., **30**, No. 4, 24 (1959).
9. D. S. McClure, J. Phys. Chem. Solids, **3**, 311 (1957).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.