PHYSICAL CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR
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Abstract

Full Text

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THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS

Cu–Ni and Fe–Co

Interest in the thermodynamic properties of alloys of copper with nickel and iron with cobalt is connected with the diverse technical applications of these alloys. By the electromotive-force (e.m.f.) method we determined the free energy, heat, and entropy of formation of Cu–Ni alloys and the activity of iron in Fe–Co alloys.

Measurement of the e.m.f. of Cu–Ni alloys was carried out in the galvanic cell:

$$\mathrm{Cu\,(solid)\,|\,Cu^{+}\,(melt\ CuJ + KJ + NaJ)\,|\,Cu - Ni\,(alloy)}.$$

The alloys were prepared from copper and nickel powders by pressing followed by annealing (up to 100 hr at 1050-1250°C). The current leads were tungsten or molybdenum wires; the experiment was conducted at 620-750° in an argon atmosphere. After the experiment the alloys were analyzed.

Fig. 1. Electromotive forces of copper-nickel alloys as functions of temperature and concentration. Values of N_{Cu}: 1–0.93; 2–0.780; 3–0.663; 4–0.568; 5–0.483; 6–0.282; 7–0.191; 8–0.104.

The results of the experiments are given in Fig. 1. The e.m.f. was quite constant and reproducible within 1.5-2%; from the magnitude of the e.m.f. and its temperature dependence, for each alloy the activity (a_{Cu}), the relative partial heat content $\overline{L}_{\mathrm{Cu}}$, and the partial entropy of mixing of copper ($\Delta\overline{S}_{\mathrm{Cu}}$) were found. Then, by graphical integration of the equation

Fig. 2

Figure 2: Fig. 2

$$g = N_{\mathrm{Ni}} \int_0^{N_{\mathrm{Cu}}} \overline{g}_{\mathrm{Cu}} \, d\frac{N_{\mathrm{Cu}}}{N_{\mathrm{Ni}}} \tag{1}$$

the integral heats and entropies of formation of the alloys of this system were found. The excess entropy of mixing was calculated by the formula:

$$\Delta S^{\mathrm{ex}} = \Delta S + R\left(N_{\mathrm{Ni}} \ln N_{\mathrm{Ni}} + N_{\mathrm{Cu}} \ln N_{\mathrm{Cu}}\right) \tag{2}$$

and the excess free energy at a temperature of 1000°K:

$$\Delta Z^{\mathrm{ex}} = \Delta H - T\Delta S^{\mathrm{ex}}. \tag{3}$$

The course of the change in the activity of both components is shown in Fig. 2, and the integral excess quantities in Fig. 3. Our experimental data for the activity coefficient of copper (γ_{Cu}) and the relative partial heat content of copper ($\overline{L}_{\mathrm{Cu}}$) at 1000°K can be approximately described by the following

···by the following equations, found by the method of least squares:

$$\lg \gamma_{\mathrm{Cu}} = -0.016\, N_{\mathrm{Ni}} + 0.696\, N_{\mathrm{Ni}}^2,$$

$$\overline{L}_{\mathrm{Cu}} = -1824\, N_{\mathrm{Ni}} + 4440\, N_{\mathrm{Ni}}^2.$$

The Cu—Ni system forms a continuous series of solid solutions (1). Wagner (2) believes that the deviations from ideality are small, so that the Cu—Ni system is an exception, since the other systems formed by Cu, Ag, and Au with Fe, Co, and Ni either have no solid solutions at all, or the solid solutions decompose at more or less high temperatures. On the contrary, our data show that the Cu—Ni system gives positive deviations from Raoult' s law, although smaller than in the Au—Fe (3) and Au—Ni (4) systems, yet still significant. However, the excess entropies of mixing of Cu—Ni alloys are negative (see Fig. 2), in contrast to Au—Fe and Au—Ni alloys, which have positive excess entropies of mixing of the order of 1—1.5 entropy units/g-at (3,4).

Fig. 2. Change in the activity of copper (1) and nickel (2) in copper-nickel alloys at 1000° K; points are experimental data.

An ordered distribution of atoms in Cu—Ni alloys is not established by X-ray investigations, since the difference in the diffraction power of copper and nickel atoms is very small. However, measurements of the electrical resistance and

Fig. 3

Figure 3: Fig. 3

Fig. 4. Change in the activity of iron in iron-cobalt alloys at 1000°K

Figure 4: Fig. 4. Change in the activity of iron in iron-cobalt alloys at 1000°K

magnetic properties of copper-nickel alloys ($^{5-7}$) indicate the presence of a certain ordering in them.

Fig. 3. Heat, excess entropy, and excess free energy of formation of Cu—Ni alloys at 1000° K.

Leaving aside the question of the degree of order and the composition of the alloys in which it exists, we note that this ordering is probably connected with the interaction of the free (valence) electrons of copper and nickel. Calculation of the heat of alloy formation associated with this interaction by the Verley method (^{8}) gives a value of -0.6 kcal/g-at for an alloy of equiatomic composition at temperatures of 0—300°K. It follows from this that ordering in Cu—Ni alloys is quite possible. However, according to our data, the heats of formation of Cu—Ni alloys have comparatively small positive values. It is highly probable that the reason for this is the disordering of the alloy at the experimental temperature, deformation of the lattice arising when an alloy is formed from components with different atomic volumes, and the increase in the volume of Cu—Ni alloys upon mixing (^{9}).

Calculation of the entropy constant ($N_{\text{Cu}} = 0.6$) from the heat capacity (^{10}) gives the value $S_{298^{\circ}} = 7.43$ entropy units/g-at, whence the excess entropy of mixing —

the value of order -1.5 e.u./g-atom; thus, the ordering of Cu-Ni alloys strongly affects the magnitude of the excess entropies of mixing. According to our data, $\Delta S^{\text{excess}}_{1000^{\circ}} = -0.5$ e.u./g-atom for an alloy of this composition. Probably, at higher temperatures the alloy becomes disordered, and the excess entropy of mixing decreases in absolute magnitude.

Thus, large negative excess entropies, when subtracted from the relatively small positive heats according to formula (3), give positive excess free energies.

Fig. 4. Change in the activity of iron in iron-cobalt alloys at 1000°K

From Fig. 1 it is seen that the e.m.f. increases with temperature not linearly, as usual, but more rapidly. It follows from this that: 1) with increasing temperature the positive deviations from Raoult' s law rapidly decrease; 2) the heat and entropy of formation of copper-nickel alloys depend on temperature (as was already noted above).

It is obvious that further investigations of the structure of copper-nickel alloys are required.

The e.m.f. of iron-cobalt alloys was measured in the cell:

$$\mathrm{Fe(mb)} \mid \mathrm{Fe}^{\cdot\cdot}\ \text{(in molten chlorides)} \mid \mathrm{Fe-Co}\ \text{(alloy)}$$

at temperatures 650-900°C. In these experiments the reproducibility of the e.m.f. was mediocre (about 10%); the magnitude of the e.m.f. decreased with time, probably because of the reaction:

$$\mathrm{Fe}^{\cdot\cdot}\ \text{(electrolyte)} + \mathrm{Co}^{\cdot\cdot}\ \text{(alloy)} + \mathrm{Co}\ \text{(electrolyte)} \rightleftharpoons \mathrm{Fe}\ \text{(alloy)}.$$

The values found for the activity of iron in Fe-Co alloys are plotted in Fig. 4 and agree rather well with the data of (11), determined by the equilibrium-constant method.

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