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Abstract

Full Text

Chemistry

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On the Separation of Alloy Components in the Presence of a Temperature Difference

(Presented by Academician G. V. Kurdyumov, 12 X 1960)

At present a number of methods are known for separating the components of a mixture: distillation, recrystallization, zone melting, zone purification in the solid state, and thermodiffusion. All these methods, with the exception of diffusion, are based on the different solubility of the second component in coexisting phases (gas—liquid, liquid—crystal, two modifications of a solid). Thermodiffusion also occurs in a single-phase substance (a mixture of gases, a solution).

Thermodiffusion is usually regarded as a consequence of the difference in the velocities of motion of the components. In the present work we approach the question from the standpoint of the energetic favorability of thermodiffusion. Such a consideration can answer the question of within what limits and in what direction, without taking into account the velocities of motion of the atoms of the components, the process can proceed.

Fig. 1. Phase diagram of the eutectic type

Fig. 2. Curves of the dependence of free energy on concentration for two temperatures T_1 and T_2 (see Fig. 1)

First of all, let us determine whether the process of redistribution of an impurity in an initially homogeneous solid body can be energetically favorable under the condition that a heated zone is present. We shall assume that one part of the body (a rod) has a low temperature (T_1), while the other part is heated to a higher temperature (T_2). As an example, let us consider the case of limited solubility of the components in the solid state. Let us denote the initial concentration of the impurity in the rod by C_0, the solubility of the impurity in the solid being purified at temperature T_1 by C_1, and at temperature T_2 by C_2 (Fig. 1); in this case the condition $C_1 < C_0 < C_2$ must be satisfied (the solubility increases with increasing temperature). Another case may also be considered: $C_1 < C_0 < C_2'$. Let us estimate the change in the free energy of the body if, when part of it is heated,

of the body to the temperature T_2, a redistribution of the impurity will occur in such a way that in the cold part of the rod the impurity content will decrease (C_1) and approach the solubility limit at temperature T_1, while in the hot part of the rod the impurity content will increase (C_2) and approach the solubility limit at temperature T_2.

In the case of limited solubility, the dependence of the free energy of the alloy on concentration has the form shown in Fig. 2. At temperature T_1 the equilibrium solubilities are C_1 and C_1', at temperature T_2 they are C_2 and C_2'. The change in free energy upon redistribution of the impurity is equal to:

$$\Delta F = \frac{1}{2}\left(F_{T_1,C_1} + F_{T_2,C_2} - F_{T_1,C_0} - F_{T_2,C_0}\right). \tag{1}$$

(The indices indicate the values of the free energy at the given temperatures and concentrations.)

According to the lever rule we find:

$$F_{T_1,C_0} = \frac{C_1' - C_0}{C_1' - C_1} F_{T_1,C_1} + \frac{C_0 - C_1}{C_1' - C_1} F_{T_1,C_2'}. \tag{2}$$

Substituting this expression into (1) and simplifying, we obtain:

$$2\Delta F = -\frac{C_0 - C_1}{C_1' - C_1}\left(F_{T_1,C_1'} - F_{T_1,C_1}\right) - \left(F_{T_2,C_0} - F_{T_2,C_2}\right). \tag{3}$$

It follows from relation (3) that, for certain ratios of the quantities entering into (3), the free energy of the system under the specified conditions may decrease ($\Delta F < 0$), and the process of impurity redistribution will be energetically favorable. This will occur, in particular, when $F_{T_1,C_1'} > F_{T_1,C_1}$ and $F_{T_2,C_0} > F_{T_2,C_2}$ (conditions sufficient, but not necessary).

Effective purification of the cold end of the rod will proceed up to the solubility limit of the impurity at the temperature of this part of the rod. Further redistribution is possible up to such values C_1 and C_2 at which ΔF becomes equal to zero.

It follows, in particular, from the discussion above that, when calculating the process of zone melting, in addition to the usually considered redistribution of impurities associated with their different solubility in the liquid and solid phases, it is also necessary to take into account the possible redistribution associated with the temperature difference along the specimen being purified.

The above consideration is applicable also to liquid mixtures.

Condition (3) can be made more specific if, for the free energy $F_{T,C}$, one uses a function expressing its dependence on concentration and temperature.

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