ON THE POSSIBILITY OF DISTURBING EQUILIBRIUM IN A HETEROGENEOUS SYSTEM CONTAINING A MICROCOMPONENT, THROUGH RECRYSTALLIZATION OF THE SOLID PHASE

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Abstract

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ON THE POSSIBILITY OF DISTURBING EQUILIBRIUM IN A HETEROGENEOUS SYSTEM CONTAINING A MICROCOMPONENT, THROUGH RECRYSTALLIZATION OF THE SOLID PHASE

Roseboom (^1) showed that, in the state of equilibrium, the distribution of a microcomponent between a crystalline phase and a solution must obey the Berthelot–Nernst law. This was confirmed experimentally by the work of Khlopin (^2) and his students. They demonstrated the possibility of attaining equilibrium between dilute solid and liquid solutions and the applicability to this case of the Berthelot–Nernst distribution law:

$$\frac{X}{Y} = D\frac{a_x}{a_y}, \tag{1}$$

where X and Y are the amounts of the micro- and macrocomponents in the solid phase; a_x and a_y are their amounts in the solution; D is the cocrystallization coefficient.

It is known that, in the presence of a solution, a solid crystalline phase undergoes recrystallization. In the process of recrystallization, imperfect crystals dissolve and well-formed crystals grow. As a result, both macro- and microcomponents pass into solution and then are deposited on the surface of the growing crystals. If the initial solid phase was in equilibrium with the solution, it may turn out that the solid phase formed after recrystallization will be nonequilibrium.

To clarify this question, let us consider a two-phase system consisting of a macrocomponent, a microcomponent, and their saturated solution, in a state of equilibrium. In this system the microcomponent is distributed between the crystalline phase and the solution in accordance with equation (1). Suppose that in the given system the solid phase undergoes a single recrystallization. It is assumed here that the concentration of the macrocomponent does not change during the recrystallization process. At the same time, the concentration of the microcomponent in the solution may change, since it is determined by the balance of transfer of the microcomponent into solution upon dissolution of equilibrium crystals and its deposition from the solution on the surface of growing crystals. Obviously, the distribution between the surface of the growing crystal and the solution will be determined by the differential equation:

$$\frac{dX}{a_x + DY\frac{a_x}{a_y} - X} = \lambda\frac{dY}{a_y}, \tag{2}$$

where X and Y are the amounts of the micro- and macrocomponents in the recrystallized solid phase; a_x and a_y are their amounts in the initial solution; λ is the cocrystallization coefficient, and in the general case $\lambda \neq D$.

Transforming equation (2), we obtain:

$$\frac{dX}{dY} + \frac{\lambda X}{a_y} = \lambda\frac{a_x}{a_y}\left(1 + \frac{DY}{a_y}\right). \tag{3}$$

Integrating equation (3) leads to the following result:

$$X = a_x\left(1 - \frac{D}{\lambda}\right) + \frac{a_x}{a_y}DY + \mathrm{const}\cdot e^{-\frac{\lambda}{a_y}Y}. \tag{4}$$

The integration constant in equation (4) can be found from the initial conditions $X = 0;\ Y = 0$. Then

$$\mathrm{const} = a_x\left(\frac{D}{\lambda} - 1\right).$$

Substituting the value of the integration constant into equation (4) and denoting $X/a_x = n;\ Y/a_y = m$, we obtain

$$n = (1 - D/\lambda)(1 - e^{-\lambda m}) + Dm. \tag{5}$$

Analysis of equation (5) shows that under the condition $D = \lambda$, equation (5) is simplified: $n = Dm$, and coincides with equation (1). It follows from this that under the condition $D = \lambda$, recrystallization of the solid phase does not disturb the equilibrium in the system. Whereas D is a constant, λ depends on the rate of crystallization of the solid phase. With slow crystallization, when equilibrium is attained between the surface of the growing crystal and the solution, $\lambda \to D$ (^{2}). In this case the equilibrium in the system will not change. However, with rapid crystallization $\lambda \neq D$. In some systems, for example $K(Cs)Al(SO_4)_2 \cdot 12H_2O$ –solution (^{3}), a sharp dependence of the value of λ on the crystallization rate of the solid phase is observed, associated with the slow attainment of adsorption equilibrium. Obviously, the deviation from the state of equilibrium due to recrystallization of the solid phase will be the greater, the higher the rate of recrystallization and the more strongly λ depends on the crystallization rate of the solid phase.

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