

Tutorial problems and questions

1. Derive an expression for the solubility of a phase β (assuming it to be almost pure B) in a solid solution of α (assuming it to be a regular solution). Derive the expressions both for planar and curved α - β - interfaces.

Answer

Given is pure β and B is a solid solution (assumed to be regular), the phase diagram and the free energy versus composition diagrams at the temperature T_1 are as shown in Fig. 6. As we notice, since A has almost no solubility in β , the free energy curve for β raises sharply with concentration and the maximum concentration of B soluble in A is given by the common tangent condition,

$$\mu_B^\alpha = \mu_B^\beta \approx G_B^\beta \quad (1)$$

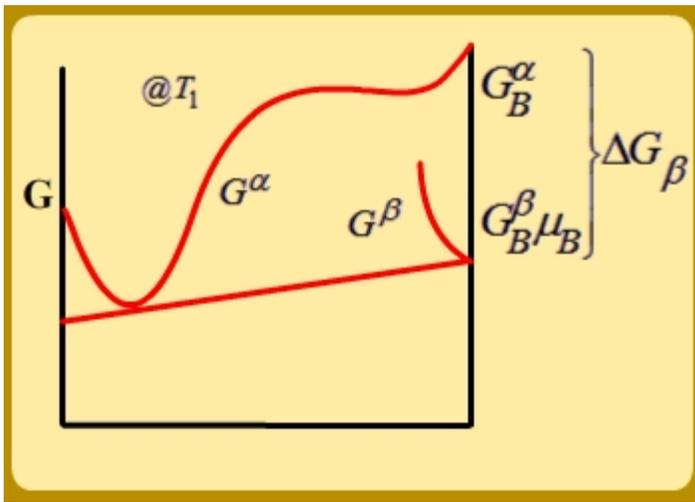


Figure 6: Free energy versus composition diagram.

For regular solution,

$$\mu_B^\alpha = G_B^\alpha + \Omega(1 - X_B)^2 + RT \ln X_B = \mu_B^\beta \approx G_B^\beta \quad (2)$$

Also, from Fig. 6, since $\Delta G_B = G_B^\alpha - \mu_B^\alpha$, we get

$$\Delta G_B = -RT \ln X_B^e - \Omega(1 - X_B^e)^2 \quad (3)$$

For low solubility, $X_B^e \ll 1$

$$X_B^e = \exp \left[-\frac{\Delta G_B + \Omega}{RT} \right] \quad (4)$$

As shown in Fig. 7, due to the Gibbs-Thomson effect, the free energy of the β phase raises by $\frac{2\gamma V_m}{r}$; hence,

$$X_r = \exp \left[-\frac{\Delta G_B + \Omega - 2\gamma V_m/r}{RT} \right] \quad (5)$$

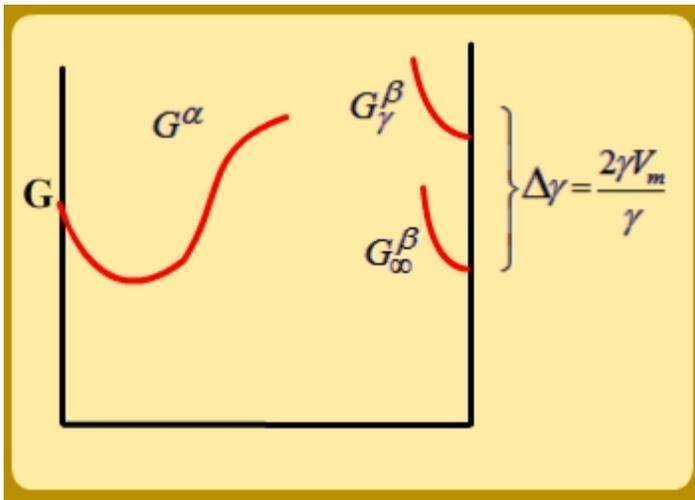


Figure 7: Capillary (Gibbs-Thomson) effect induced increase in free energy shown on a free energy versus composition plot.

That is, if X_{∞} is the equilibrium concentration for a planar interface between the α and β phases,

$$X_r = X_{\infty} \exp \left[\frac{2\gamma V_m}{RT_r} \right] \quad (6)$$

For small values of the exponent, this can further be simplified as

$$X_r = X_{\infty} \left(1 + \frac{2\gamma V_m}{RT_r} \right) \quad (7)$$

2. Consider a β the growth of a precipitate of almost pure B growing behind a planar interface into A-rich α ; the initial composition of is X_0 . The composition profile across the interface, the driving forces in terms of chemical potentials and the schematic free energy versus composition diagrams are shown in Fig. 8. At the α - β interface, the net flux of B atoms from α to β makes the interface grow with a velocity v which is given by

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$$v = \frac{M \Delta \mu_B^i}{V_m} \quad (8)$$

where M is the interface mobility, V_m is the molar volume of the β phase, and $\Delta \mu_B^i$ is the driving force for B atoms to move from the α to β phase. Hence, the flux of B atoms (moles per m^2 per s) is given by

$$J_B^i = - \frac{M \Delta \mu_B^i}{V_m^2} \quad (9)$$

In phase the diffusional flux of B atoms due to the concentration gradients is given by

$$J_B^{\alpha} = -D \left(\frac{\partial C_B}{\partial x} \right)_{interface} \quad (10)$$

At steady state, the fluxes balance: $J_B^i = J_B^{\alpha}$

From these expressions, it is clear that the value of M has a say on $\Delta \mu_B^i$ and hence on X_i . If M is large, then $\Delta \mu_B^i$ can be very small; in other words, in such circumstances $X_i \approx X_{\infty}$. Such cases are

known as diffusion controlled growth; in these cases the diffusional flux of atoms from the phase to the interface is what controls the rate of the growth of the β phase. On the other hand, if M is very small, larger $\Delta\mu_B^i$ are required to drive the reaction; this means, the interface composition X_i is not the equilibrium composition X_e but is different; it could even be X_0 . Such cases are said to be interface controlled growth; in these cases, it is not the diffusion in the α phase but the reaction at the interface that controls the rate of growth of the β phase.