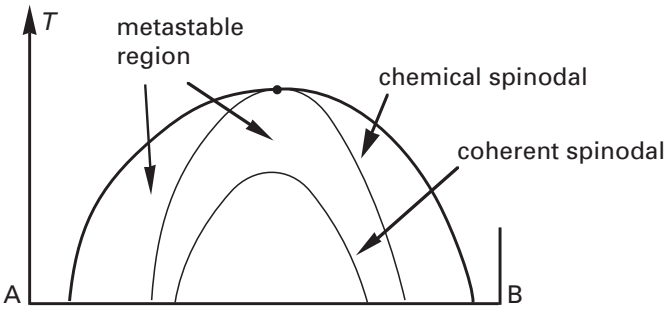

Figure 15.14 A solid-phase miscibility gap showing two spinodals.

Exercise 15.6

Au and Ni both have the simple fcc structure. The Au–Ni system has a miscibility gap in the fcc phase with a consolute point at 1083 K. A homogeneous alloy of the consolute composition, cooled from 1150 to 900 K, will decompose by a microscopically sharp eutectoid-like transformation $\text{fcc}_0 \rightarrow \text{fcc}_1 + \text{fcc}_2$ and not by spinodal decomposition. Suggest an explanation.

Solution

The Au atoms are much larger than the Ni atoms. The molar volumes of pure Au and Ni are 10.2 and 6.59 cm^3/mol, respectively. Fluctuations in composition will thus give rise to high coherency stresses. The coherent spinodal will be depressed to lower temperatures by several hundred kelvin.

15.5 Tri-critical points

In the discussion of order–disorder transitions we only considered a single composition but it is self-evident that one can represent the points for a second-order transition at all compositions in a binary system by a line. For a second-order transition, which is known to occur in one of the components, e.g. a magnetic transition, we would expect a diagram like the one in Fig. 15.15(a). However, now we should also consider the possibility of obtaining a miscibility gap by separation into regions of different compositions. In order to explore this possibility we can use Landau's simple mathematical model, discussed in Section 15.2, where all the parameters may be functions of T and x. In the disordered state $G_\text{m} = g_\text{o}$ and we shall assume that g_o does not contain any factor favouring the formation of a miscibility gap. Then there would be no spinodal inside the region for the disordered state, i.e. above the transition line. In the ordered state we have from before

$$G_\text{m}^\text{ord} = g_\text{o} - \frac{3}{2}(g_{\xi\xi})^2/g_{\xi\xi\xi\xi}, \tag{15.32}$$

and we should consider the possibility of a spinodal reaching the transition line from below. Remembering that $g_{\xi\xi} = 0$ on the transition line, we find there

$$\partial^2 G_\text{m}^\text{ord}/\partial x^2 = \partial^2 g_\text{o}/\partial x^2 - 3(g_{\xi\xi x})^2/g_{\xi\xi\xi\xi}. \tag{15.33}$$

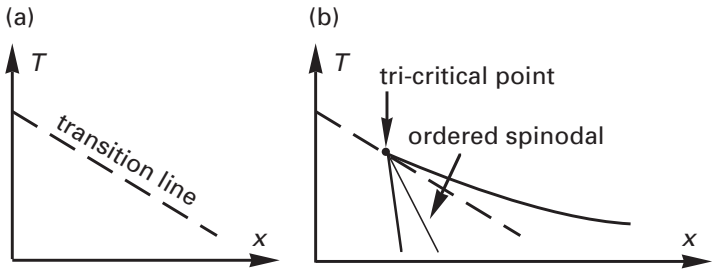

Figure 15.15 The formation of a miscibility gap around the line for a second-order transition.

There would thus be a miscibility gap with its consolute point on the transition line if this expression is zero which could very well happen. The temperature and composition of the consolute point would be found by combination with $g_{\xi\xi} = 0$. The resulting phase diagram would look like the diagram in Fig. 15.15(b). This consolute point is regarded as a **tri-critical point** which is an unfortunate name. It may remind us of a triple point between three phases in a T, μ_B diagram but it has that shape only in a T, x diagram. In the T, μ_B diagram it would just be a point on a line.

It should be emphasized that we here have two internal variables or 'order parameters', one describing the ordering and the other describing the separation into different compositions. We could thus test the stability with respect to variations in one or the other. When testing for variations in ordering we found the transition line. However, the test of the real stability limit must take into account simultaneous variations in both internal variables. That would be the most severe test. We should look for the possibility that a system encounters the real stability limit and transforms *before* reaching the transition line. We could then find one spinodal on each side of the transition line but it would be quite a different case from that illustrated in Fig. 15.2. That case concerned a first-order transition where a system may cross the transition line and reach a limit of stability *on the other side*.

Figure 15.15(b) shows a spinodal below the transition line and it applies to homogeneous, ordered states coming from lower temperatures. We should also look for a spinodal above the transition line, applicable to the disordered state, cooled from a high temperature. It should be given by

$$\partial^2 G_m^{dis} / \partial x^2 = \partial^2 g_o / \partial x^2 = 0, \tag{15.34}$$

because $\xi = 0$. As a consequence, our model which yields this relation cannot predict such a spinodal unless g_o contains a factor promoting a miscibility gap. Otherwise, $\partial^2 g_o / \partial x^2 > 0$. That is why Fig. 15.15 was constructed without a disordered spinodal. The transition line itself acts as the limit of stability for disordered systems coming from higher temperatures. However, it is not the same type of spinodal as the lower one because it does not represent the limit of stability against compositional fluctuations. On the other hand, as soon as the system starts to order, it will find that it is above the spinodal for ordered states and is no longer stable against compositional fluctuations. It may thus be regarded as a **conditional spinodal**.

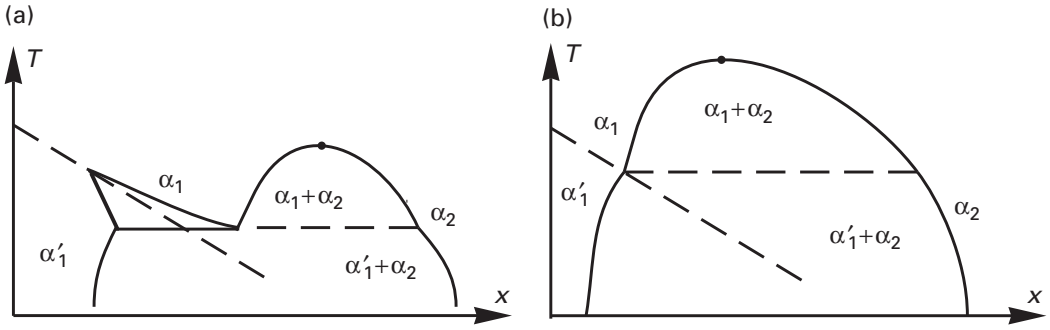

Figure 15.16 Different types of interaction between an ordering transition and a usual miscibility gap.

When looking for spinodals and trying to find the tri-critical point, we have here applied the condition of stability limit to the function $G_m(T, x)$ obtained with the equilibrium value of ξ inserted in $G_m(T, x, \xi)$. We could instead have used $G_m(T, x, \xi)$ directly by applying the stability condition from Section 6.7, reduced to two variables

$$\begin{vmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{vmatrix} = 0; \quad g_{11}g_{22} - (g_{12})^2 = 0. \tag{15.35}$$

Identify Δx with variable 1 and ξ with variable 2. Then G_m from Eq. (15.3) gives

$$\left(\partial^2 g_o/\partial x^2 + \frac{1}{2}g_{\xi\xi xx}\xi^2 + \frac{1}{24}g_{\xi\xi\xi\xi xx}\xi^4\right)\left(g_{\xi\xi} + \frac{1}{2}g_{\xi\xi\xi\xi}\xi^2\right) - \left(g_{\xi\xi x}\xi + \frac{1}{6}g_{\xi\xi\xi\xi x}\xi^3\right)^2 = 0. \tag{15.36}$$

This relation should be applied to the equilibrium value of ξ which is equal to $(-6g_{\xi\xi}/g_{\xi\xi\xi\xi})^{1/2}$ in the ordered region according to Eq. (15.5). Neglecting the ξ^2 and ξ^4 terms in comparison to $\partial^2 g_o/\partial x^2$, and $g_{\xi\xi\xi\xi x}\xi^2$ in comparison to $6g_{\xi\xi x}$ close to the transition line, we get

$$\partial^2 g_o/\partial x^2 = (g_{\xi\xi x})^2 \Big/ \left(g_{\xi\xi}/\xi^2 + \frac{1}{2}g_{\xi\xi\xi\xi}\right) = 3(g_{\xi\xi x})^2/g_{\xi\xi\xi\xi}. \tag{15.37}$$

in full agreement with the previous result.

In the disordered region the equilibrium value is $\xi_e = 0$ and we find

$$\partial^2 g_o/\partial x^2 \cdot g_{\xi\xi} = 0. \tag{15.38}$$

Above the transition line $g_{\xi\xi} > 0$ and we would find a spinodal only if $\partial^2 g_o/\partial x^2$ turns negative before the transition line is approached on cooling. That would yield a usual miscibility gap, which would interact with the one formed due to the tendency of ordering. This is illustrated in Fig. 15.16(a).

If the usual miscibility gap is larger, it may cover the other one, as illustrated in Fig. 15.16(b). At the intersection with the transition line the phase boundary shows an angle. The reason is that g_{22} appears in the denominator of the expression for $(dx_2^\alpha/dT)_{coex}$, given in Section 11.4, and the phase boundary will thus be less steep (smaller dT/dx) below the transition line because g_{22} (i.e. $\partial^2 G_m/\partial x_2^2$) is smaller in the ordered region.

In our first calculation of the tri-critical point we started with a function $G_m(T, x, \xi)$ where ξ is an internal variable. An expression for its equilibrium value was then inserted and a function $G_m(T, x)$ was obtained which had different expressions above and below the transition line. They were then used in the calculation. Of course, one could just as well have used the results of experimental measurements in such a calculation. As a demonstration, let us suppose the contribution G_m^p to the Gibbs energy from an ordering reaction has been measured across the transition line, including the effects of short- as well as long-range order. Suppose further that this effect is found to be approximately the same function of $T - T_{tr}$ for all compositions and the transition temperature, T_{tr}, varies linearly with composition. Then

$$\frac{\partial G_m^p}{\partial x} = \frac{\partial G_m^p}{\partial T_{tr}} \cdot \frac{dT_{tr}}{dx} = -\frac{\partial G_m^p}{\partial T} \cdot \frac{dT_{tr}}{dx} \tag{15.39}$$

and

$$\frac{\partial^2 G_m^p}{\partial x^2} = \frac{\partial^2 G_m^p}{\partial T^2} \cdot \left(\frac{dT_{tr}}{dx}\right)^2 = -\frac{C_P^p}{T} \cdot \left(\frac{\partial T_{tr}}{\partial x}\right)^2, \tag{15.40}$$

where C_P^p is the effect of the ordering reaction on the heat capacity. Suppose the solution is otherwise ideal, $\partial^2 G_m^{ideal}/\partial x^2 = RT_{tr}/x(1-x)$. The intersection of a spinodal with the transition line is found where

$$\frac{\partial^2 G_m}{\partial x^2} = \frac{RT_{tr}}{x(1-x)} - \frac{C_P^p}{T_{tr}} \cdot \left(\frac{\partial T_{tr}}{dx}\right)^2 = 0 \tag{15.41}$$

$$x(1-x) = \left(RT_{tr}^2 / C_P^p\right) \cdot \left(\frac{dx}{dT_{tr}}\right)^2. \tag{15.42}$$

This would be a tri-critical point. It is thus demonstrated that the tri-critical point will be closer to the T axis of the system, the larger the heat effect is. This is an expected result but the direct role played by C_P is very interesting in view of the many measurements indicating that C_P goes to very high values close to T_{tr} and theoretical models of ordering predicting that C_P actually should approach infinity at T_{tr}. The tri-critical point would thus approach the T axis of the binary system but the miscibility gap would there be extremely thin. It is also worth noting that C_P may approach different values on the two sides of T_{tr}. The spinodals on the two sides may thus intersect the transition line at different points. The point of intersection for the upper spinodal could fall much below the other one but would move up along the transition line if there is short-range order in the disordered state above the transition line. However, it could not reach the point of intersection for the lower spinodal because the heat effect of long-range order is larger.

It is also interesting to note the role of the slope of the transition line, dT_{tr}/dx. Its effect is demonstrated in Fig. 15.17(a) which shows an ordering reaction that does not occur in the pure components but has its ideal composition in the middle of the system. Miscibility gaps with tri-critical points may appear on both sides where the transition line is steep enough. It should be emphasized that this case is not related to the case of a first-order transition which forms a complete two-phase field in a binary

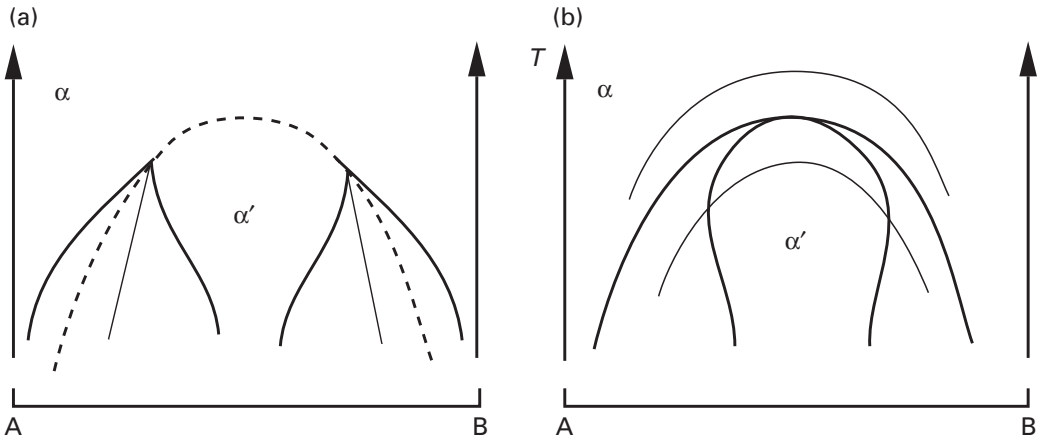

Figure 15.17 Two types of ordering miscibility gaps. (a) The ordering transition is of second order and the dashed line is the transition line. The spinodals are drawn with thin lines. (b) The transition is of first order and the thin lines represent stability limits calculated for a superheated or supercooled homogeneous system and without considering compositional fluctuations.

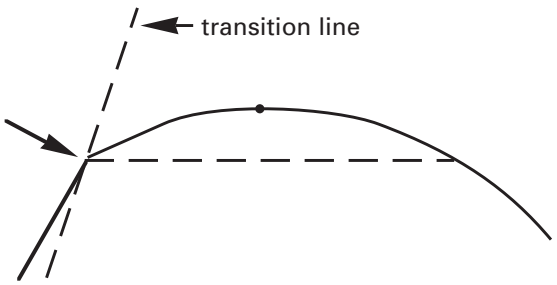

Figure 15.18 See Exercise 15.7.

diagram (see Fig. 15.17(b)). This two-phase field can be regarded as two connected miscibility gaps but there is no ordinary consolute point. Instead, the point of maximum is here a congruent point where the ordered phase can transform into the disordered phase by a first-order transition as it would do if the two phases were not related structurally.

The two points representing the limit of stability for an ordering reaction of first-order, indicated in Fig. 15.4(b), also extend into lines and they also demonstrate that the congruent point is not a critical point. The disordered state is metastable well below and the ordered state is metastable well above the temperature where the ordered and disordered states of the same composition have the same Gibbs energy. However, in order to find the real limits of stability, the spinodals, one should also consider the simultaneous variation in composition. That would make no difference when cooling the disordered state because g_{12}, which is defined as $\partial^2 G_\mathrm{m}/\partial x \partial \xi$, is zero for $\xi = 0$. On the other hand, when heating the ordered state, one may encounter a spinodal before the limit of stability calculated without considering fluctuations in composition. This possibility is not indicated in Fig. 15.17(b).

Exercise 15.7

Figure 15.18 looks like a violation of the 180° rule. Try to find an explanation.

Hint

Compare with Fig. 15.16(b) and apply the same type of argument to the present case.

Solution

In the present case, the lower part of the binodal is situated *above* the transition line. In both diagrams, the binodal is steeper above the transition lines than below and the explanation is the same.

16 Interfaces

16.1 Surface energy and surface stress

By cutting a piece of material in two one can create two fresh surfaces and it is evident that they represent an increase of the energy of the system because bonds between atoms or molecules have been broken. Admittedly, the energy may then decrease somewhat by relaxation in the surface layer. The net effect can be defined as the surface energy or rather surface free energy or surface Gibbs energy under the usual isobarothermal conditions. We shall simply use the term surface energy and apply the same term to real surfaces as well as interfaces. Specific surface energy, i.e. the energy per surface area, will be denoted by σ.

However, the energy of the system may decrease further by minimizing the surface area. Primarily, there would be a tendency of the two new pieces to minimize the surface area by a shape change of the material and for an isotropic material the final shape would be spherical. That could happen quickly if the material is liquid but it could be an extremely slow process for a piece of solid material. The decrease of energy during the shape change is easily calculated for an isotropic material because its specific surface energy, σ, the energy per area, is constant.

Secondarily, the surface could contract further without a shape change by compressing the material in the sphere. It will thus be put under an increased pressure, formally caused by a stress in the surface. For a sphere one would get

$$\Delta P = 2f/r, \tag{16.1}$$

where r is the radius and f is the surface stress. For a liquid phase it seems reasonable to assume that the structure of the surface is reorganized as it contracts and is thus able always to maintain the same structure and the same specific surface energy. The tendency to contract would thus be directly connected to the energy decrease by the decrease of surface area. The surface stress f would then be equal to the specific surface energy σ.

The situation is different for a crystalline material where the surface layer is coherent with the material in the interior. Not only the area of the surface layer but also its structure will contract in order to fit into the structure of the compressed material. It is not even evident that the energy of the surface will decrease at all by such a contraction. In reality one may expect some decrease because there was probably a tendency of relaxation in the surface layer when first formed but it was prevented by the coherency. Some stress

was thus built into the surface layer and probably a compressive stress because the atoms or molecules in the surface layer may tend to attract each other more when losing their neighbours outside the surface. Very little is known about the magnitude of surface stress but it seems evident that it should be lower than the specific surface energy, $f < \sigma$.

What has here been said about surfaces applies as well to interfaces and it is then important to distinguish interfaces between two fluids, for which $f = \sigma$, from those where at least one of the phases is crystalline. For them $f < \sigma$.

Three materials can be in contact with each other along a line. In a section perpendicular to that line one can measure three contact angles and they can be calculated by minimizing the surface energy of the system. They are thus controlled by the three specific surface energies and the result is the same as if they were regarded as three balancing surface tensions. It is thus common to regard the specific surface energy as a surface tension, which is equal to σ. It is important not to confuse surface tension with surface stress, which is the quantity that gives rise to the increased pressure according to Eq. (16.1). The term surface tension should be avoided as much as possible.

The effect of surface energy is particularly pronounced for liquids inside the thin holes of capillaries and this whole field is often referred to as capillarity.

16.2 Phase equilibrium at curved interfaces

We shall start with a general method of finding equilibrium conditions by maximizing the entropy under constant energy, volume and content of matter. It is based on the use of Lagrange's multipliers. We shall apply the method to a system with a spherical β phase in an α matrix. We have $V^\beta = (4\pi/3)r^3$ and the surface energy will be $4\pi r^2\sigma = 4\pi\sigma(3V^\beta/4\pi)^{2/3}$.

For a completely closed (isolated) system with $\mathrm{d}N_i = \mathrm{d}V = \mathrm{d}Q = 0$, and thus $\mathrm{d}U = 0$, the combined law yields, e.g., after rearranging the terms in Eq. (3.1),

$$\mathrm{d}S = (1/T)\mathrm{d}U + (P/T)\mathrm{d}V - \sum(\mu_i/T)\mathrm{d}N_i + (D/T)\mathrm{d}\xi = (D/T)\mathrm{d}\xi. \tag{16.2}$$

The condition of equilibrium is thus obtained from the maximum of S for the total system but we must find that maximum under the constant values of U, V and N_i

$$U^\alpha + U^\beta = U(\text{constant}) \tag{16.3}$$

$$V^\alpha + V^\beta = V(\text{constant}) \tag{16.4}$$

$$N_i^\alpha + N_i^\beta = N_i(\text{constant}). \tag{16.5}$$

According to Lagrange's method we should form a new function which must have its maximum at the same time because the additional terms are always zero.

$$\begin{aligned} L = {} & S^\alpha + S^\beta + \lambda[U - U^\alpha - U^\beta - 4\pi\sigma(3V^\beta/4\pi)^{2/3}] \\ & + \nu(V - V^\alpha - V^\beta) + \Sigma\eta_i\left(N_i - N_i^\alpha - N_i^\beta\right). \end{aligned} \tag{16.6}$$

Here, λ, ν and η_i are Lagrange multipliers and their values will be determined by maximizing L. When searching for the maximum, we get six conditions,

$$\partial L/\partial U^\alpha = \partial S^\alpha/\partial U^\alpha - \lambda = 0 \tag{16.7}$$

$$\partial L/\partial U^\beta = \partial S^\beta/\partial U^\beta - \lambda = 0 \tag{16.8}$$

$$\partial L/\partial V^\beta = \partial S^\beta/\partial V^\beta - \lambda\sigma(32\pi/3V^\beta)^{1/3} - \nu = 0 \tag{16.9}$$

$$\partial L/\partial V^\alpha = \partial S^\alpha/\partial V^\alpha - \nu = 0 \tag{16.10}$$

$$\partial L/\partial N_i^\alpha = \partial S^\alpha/\partial N_i^\alpha - \eta_i = 0 \tag{16.11}$$

$$\partial L/\partial N_i^\beta = \partial S^\beta/\partial N_i^\beta - \eta_i = 0. \tag{16.12}$$

All the derivatives of S are well known from the combined law applied to one phase at a time. We obtain

$$1/T^\alpha = \partial S^\alpha/\partial U^\alpha = \lambda = \partial S^\beta/\partial U^\beta = 1/T^\beta \tag{16.13}$$

$$\mu_i^\alpha/T^\alpha = -\partial S^\alpha/\partial N_i^\alpha = -\eta_i = -\partial S^\beta/\partial N_i^\beta = \mu_i^\beta/T^\beta. \tag{16.14}$$

We have thus derived the well-known conditions of equilibrium, $T^\alpha = T^\beta$, and $\mu_i^\alpha = \mu_i^\beta$. The remaining two equations give

$$\begin{aligned} P^\alpha/T^\alpha = \partial S^\alpha/\partial S^\alpha = \nu &= \partial S^\beta/\partial V^\beta - \lambda\sigma(32\pi/3V^\beta)^{1/3} \\ &= P^\beta/T^\beta - \lambda\sigma(32\pi/3V^\beta)^{1/3} \end{aligned} \tag{16.15}$$

$$P^\beta - P^\alpha = \sigma(32\pi/3V^\beta)^{1/3} = 2\sigma/r \tag{16.16}$$

This is a well-known expression for the pressure difference for fluid/fluid interfaces but we have not been able to take into account the possibility that the pressure difference should instead be given by Eq. (16.1) with f instead of σ if the β phase were a crystalline substance. Furthermore, we found $P^\alpha \neq P^\beta$ and it is evident that the ordinary equilibrium condition, Eq. (16.14) or $\mu_i^\alpha = \mu_i^\beta$ when $T^\alpha = T^\beta$, here applies to two phases under different pressures. For clarity it should thus be written

$$\mu_i^\alpha(P^\alpha) = \mu_i^\beta(P^\beta). \tag{16.17}$$

This is a famous relation derived by Gibbs [3]. It remains to be discussed whether this relation applies to the local situation at any spherical piece of interface where r is the radius of curvature or only when there is a full sphere. In the next section we shall thus examine the problem in more detail.

16.3 Phase equilibrium at fluid/fluid interfaces

The effect of capillarity on the equilibrium between the two phases separated by an interface can be treated with any characteristic state function and we shall now use the Gibbs energy because its natural variables are those that are usually kept constant

experimentally, *P, T* and content of matter. The total Gibbs energy of an $\alpha + \beta$ system with an α/β interface can be given as

$$G = G^{\alpha} + G^{\beta} + G^{\sigma}. \tag{16.18}$$

The α phase will be chosen as the matrix phase and it will be under the same pressure as the surroundings, P. The β phase will be an inclusion under a higher pressure due the surface stress, $P^{\beta} > P$, and it will depend on the size of the β inclusion through Eq. (16.1). The amounts of the various components in the β phase will be regarded as internal variables because they can vary by exchanges with the α phase, which is part of the system. We shall later study the effect on G of a transfer of a small amount of a single component j to β from α, $\mathrm{d}N_j^{\beta}$, but we shall first consider an exchange of balanced amounts of all components, i.e., the composition of the β inclusion will be fixed and given by x_i^{β} and thus $\mathrm{d}N_i^{\beta} = x_i^{\beta}\mathrm{d}N^{\beta}$. The independent variable will thus be N^{β}, and P^{β} is a dependent variable through Eq. (16.1) because the radius r depends on N^{β}.

According to Section 3.4 the Gibbs energy of β must be expressed in the following way using the values of T and P in the surroundings,

$$G^{\beta} = N^{\beta}\left[U_{\mathrm{m}}^{\beta}(P^{\beta}, T^{\beta}) - TS_{\mathrm{m}}^{\beta}(P^{\beta}, T^{\beta}) + PV_{\mathrm{m}}^{\beta}(P^{\beta}, T^{\beta})\right]. \tag{16.19a}$$

The reason is that *U, S* and *V* are additive properties but *G* is not unless *T* and *P* have the same values in all the subsystems. In the present case, which is isothermal we get

$$\begin{aligned} G^{\beta} &= N^{\beta}\left[U_{\mathrm{m}}^{\beta}(P^{\beta}) - TS_{\mathrm{m}}^{\beta}(P^{\beta}) + PV_{\mathrm{m}}^{\beta}(P^{\beta})\right] \\ &= G^{\beta}(P^{\beta}) - (P^{\beta} - P)V^{\beta}(P^{\beta}). \end{aligned} \tag{16.19b}$$

$G^{\beta}(P^{\beta})$ is a Gibbs energy function defined for a β phase in the hypothetical case where the pressure of P^{β} applies to the surroundings as well as the β phase itself. We shall now take the derivative of Eq. (16.18) with respect to the only independent variable, N^{β}, whereas P^{β} is a variable dependent on the size of the β particle through Eq. (16.1), i.e. on N^{β}. However, we would like to use the quantity $G_{\mathrm{m}}^{\beta}(P^{\beta})$, which is defined as $(\partial G^{\beta}/\partial N^{\beta})_{P^{\beta}}$ where P^{β} is treated as an independent variable. Then, we must also take into account the partial derivative with respect to P^{β}.

$$\begin{aligned} \frac{\mathrm{d}G}{\mathrm{d}N^{\beta}} = \frac{\mathrm{d}G^{\alpha}}{\mathrm{d}N^{\beta}} &+ \left(\frac{\partial G^{\beta}}{\partial N^{\beta}}\right)_{P^{\beta}} + \left(\frac{\partial G^{\beta}}{\partial P^{\beta}}\right)_{N^{\beta}} \\ &\times \frac{\mathrm{d}P^{\beta}}{\mathrm{d}N^{\beta}} - \frac{\mathrm{d}P^{\beta}}{\mathrm{d}N^{\beta}} \times V^{\beta}(P^{\beta}) - (P^{\beta} - P) \times \frac{\mathrm{d}V^{\beta}}{\mathrm{d}N^{\beta}} + \frac{\mathrm{d}G^{\sigma}}{\mathrm{d}N^{\beta}}. \end{aligned} \tag{16.20}$$

The third and fourth terms on the right-hand side eliminate each other because $\partial G/\partial P = V$ and it is thus unnecessary to discuss the interpretation of $\mathrm{d}P^{\beta}/\mathrm{d}N^{\beta}$.

$$\mathrm{d}G/\mathrm{d}N^{\beta} = -\sum x_i^{\beta}\mu_i^{\alpha}(P) + G_{\mathrm{m}}^{\beta}(P^{\beta}) - (P^{\beta} - P) \times \mathrm{d}V^{\beta}/\mathrm{d}N^{\beta} + \mathrm{d}G^{\sigma}/\mathrm{d}N^{\beta}. \tag{16.21}$$

Equation (16.21) will now be applied to a spherical β particle in a fluid/fluid system. The surface energy, G^{σ}, is equal to $A^{\beta} \cdot \sigma$ and $\mathrm{d}A^{\beta} = 8\pi r\mathrm{d}r = (2/r)\mathrm{d}V^{\beta}$. The specific

surface energy can be regarded as independent of size except for nano-sized particles, yielding

$$\mathrm{d}G^{\sigma}/\mathrm{d}N^{\beta} = \sigma \times \mathrm{d}A^{\beta}/\mathrm{d}N^{\beta} = (2\sigma/r) \times \mathrm{d}V^{\beta}/\mathrm{d}N^{\beta} \tag{16.22}$$

According to Eq. (16.1) we can express $P^{\beta} - P$ as $2\sigma/r$ since $f = \sigma$ for a fluid/fluid system. The last two terms in Eq. (16.21) thus eliminate each other, leaving

$$\mathrm{d}G/\mathrm{d}N^{\beta} = -\sum x_i^{\beta}\mu_i^{\alpha}(P) + G_{\mathrm{m}}^{\beta}(P^{\beta}). \tag{16.23}$$

At this time it is thus unnecessary to discuss the interpretation of $\mathrm{d}V^{\beta}/\mathrm{d}N^{\beta}$ as well as $\mathrm{d}P^{\beta}/\mathrm{d}N^{\beta}$. At equilibrium with respect to growth of the β inclusion $\mathrm{d}G/\mathrm{d}N^{\beta}$ must be zero and we thus obtain the following equilibrium condition,

$$\sum x_i^{\beta}\mu_i^{\alpha}(P) = G_{\mathrm{m}}^{\beta}\left(P_{\mathrm{e}}^{\beta}\right). \tag{16.24}$$

The subscript 'e' has been added in order to emphasize that this is the increased pressure in β required for equilibrium with the α phase of its given composition. It is important to notice that the properties of each phase must here be evaluated at its own pressure. It is more convenient to compare them at the same pressure. We may thus like to introduce $G_{\mathrm{m}}^{\beta}(P)$. That can be done using the following relations obtained with a constant compressibility κ of the liquid β phase,

$$V_{\mathrm{m}}^{\beta}(P^{\beta}) = V_{\mathrm{m}}^{\beta}(P)(1 - \kappa(P^{\beta} - P)) \tag{16.25}$$

$$\begin{aligned} G_{\mathrm{m}}^{\beta}(P^{\beta}) - G_{\mathrm{m}}^{\beta}(P) &= \int_{P}^{P^{\beta}} V_{\mathrm{m}}^{\beta}(P^{\beta})\mathrm{d}P^{\beta} = V_{\mathrm{m}}^{\beta}(P)\left(P^{\beta} - P - \tfrac{1}{2}\kappa(P^{\beta} - P)^2\right) \\ &= V_{\mathrm{m}}^{\beta}(P)(P^{\beta} - P)(1 - \kappa\sigma/r). \end{aligned} \tag{16.26}$$

We can now introduce the driving force for precipitation of β from the α matrix and using the equilibrium condition Eq. (16.24) we find,

$$\begin{aligned} -\Delta G_{\mathrm{m}} \equiv \sum x_i^{\beta}\mu_i^{\alpha}(P) - G_{\mathrm{m}}^{\beta}(P) &= G_{\mathrm{m}}^{\beta}\left(P_{\mathrm{e}}^{\beta}\right) - G_{\mathrm{m}}^{\beta}(P) \\ &= V_{\mathrm{m}}^{\beta}(P)\left(P_{\mathrm{e}}^{\beta} - P\right)(1 - \kappa\sigma/r_{\mathrm{e}}). \end{aligned} \tag{16.27}$$

$(1 - \kappa\sigma/r_{\mathrm{e}})$ can be regarded as a correction factor to the result for an incompressible β phase. It is close to unity and is thus of minor importance.

Expressing $P_{\mathrm{e}}^{\beta} - P$ as $2\sigma/r_{\mathrm{e}}$ we can write the equilibrium condition, Eq. (16.24), as

$$\sum x_i^{\beta}\mu_i^{\alpha}(P) - G_{\mathrm{m}}^{\beta}(P) = -\Delta G_{\mathrm{m}} = (2\sigma/r_{\mathrm{e}})V_{\mathrm{m}}^{\beta}(P)(1 - \kappa\sigma/r_{\mathrm{e}}). \tag{16.28}$$

The equilibrium size of a spherical droplet is thus

$$r_{\mathrm{e}} = 2\sigma(1 - \kappa\sigma/r_{\mathrm{e}})\Big/\left(-\Delta G_{\mathrm{m}}/V_{\mathrm{m}}^{\beta}(P)\right). \tag{16.29}$$

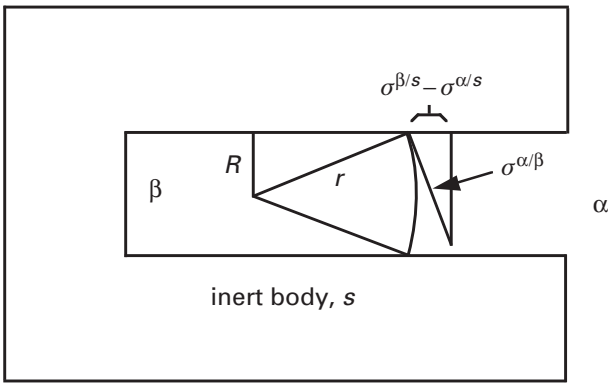

Figure 16.1 The use of a cylindrical hole in an inert body to achieve a constant pressure P^{β} in an included phase.

Of course, $-\Delta G_{\mathrm{m}}$ is a positive quantity if there is a tendency to form β from the α phase.

For a gas bubble one has $PV_{\mathrm{m}} = RT$ and obtains

$$\int V_{\mathrm{m}}^{\beta} \mathrm{d}P = RT \ln\left(P_{\mathrm{e}}^{\beta}/P\right) \tag{16.30}$$

$$-\Delta G_{\mathrm{m}} = \sum x_i^{\beta} \mu_i^{\alpha}(P) - G_{\mathrm{m}}^{\beta}(P) = RT \ln\left(P_{\mathrm{e}}^{\beta}/P\right) \tag{16.31}$$

$$P_{\mathrm{e}}^{\beta} = P \exp(-\Delta G_{\mathrm{m}}/RT) \tag{16.32}$$

$$r_{\mathrm{e}} = 2\sigma \Big/ \left(P_{\mathrm{e}}^{\beta} - P\right) = 2\sigma/P \left[\exp(-\Delta G_{\mathrm{m}}/RT) - 1\right]. \tag{16.33}$$

When the β particle grows, its internal pressure decreases and one may wonder if that fact should not affect the equilibrium condition. It should thus be interesting also to consider a case where P^{β} does not vary with the size of the β phase. That could be realized with the arrangement in Fig. 16.1. When β is growing, the spherical α/β interface moves a distance dl without any change of shape. The change of surface energy will depend on the changes of the interfaces to the wall of the container, $(\sigma^{\beta/\mathrm{s}} - \sigma^{\alpha/\mathrm{s}}) \times 2\pi R \mathrm{d}l$. However, that difference controls the contact angle of the α/β interface to the surface of the container through an energy balance and thus its curvature. Figure 16.1 yields

$$\mathrm{d}G^{\sigma} = 2\pi R(\sigma^{\beta/\mathrm{s}} - \sigma^{\alpha/\mathrm{s}})\mathrm{d}l = \pi R^2 (2\sigma^{\alpha/\beta}/r)\mathrm{d}l. \tag{16.34}$$

In the following we shall drop the superscript in $\sigma^{\alpha/\beta}$. Introduction of the change of volume, $\mathrm{d}V^{\beta} = \pi R^2 \mathrm{d}l$, yields

$$\mathrm{d}G^{\sigma} = (2\sigma/r)\mathrm{d}V^{\beta}. \tag{16.35}$$

This is the same result as for the spherical particle. We may conclude that the effect of surface energy can be applied locally to any piece of a fluid/fluid interface. An explanation why a possible change of P^{β} during growth has no effect on the equilibrium conditions is provided by the fact that the two terms containing the derivative $\mathrm{d}P^{\beta}/\mathrm{d}N^{\beta}$ in Eq. (16.20) eliminated each other. Furthermore, according to Eq. (16.22) there are two terms in Eq. (16.21) with the derivative $\mathrm{d}V^{\beta}/\mathrm{d}N^{\beta}$, which actually contains $\mathrm{d}P^{\beta}/\mathrm{d}N^{\beta}$, in the same way as the full derivative $\mathrm{d}G^{\beta}/\mathrm{d}N^{\beta}$ was represented by two terms in Eq. (16.20)

containing dP^β/dN^β. They also eliminated each other. Finally, it may here be mentioned without giving the proof that for a non-spherical interface one should replace $2/r$ by an expression using the principal radii of curvature, $1/\rho_1 + 1/\rho_2$.

Exercise 16.1

Evaluate the equilibrium size of a bubble if the supersaturation of the matrix, expressed as $-\Delta G_m$, is very low.

Hint

$\ln(1+\varepsilon) \cong \varepsilon$

Solution

Equation (16.32) gives for small $(P^\beta - P)/P$:$-\Delta G_m = RT \ln(P^\beta/P) = RT \ln(1 + (P^\beta - P)/P) \cong RT((P^\beta - P)/P) = (2\sigma/r)V_m^\beta(P)$. In this limit there is full agreement with an incompressible liquid according to Eq. (16.29).

16.4 Size stability for spherical inclusions

We have derived an equilibrium condition for a spherical particle in a fluid/fluid system but should now examine if it is a stable or unstable equilibrium. According to Chapter 6 we could examine the stability through the second derivative of G. We shall thus evaluate the derivative of Eq. (16.23). The α phase gives no contribution since its chemical potentials are not affected by the size and the stability is obtained as

$$\frac{d^2G}{d(N^\beta)^2} = \frac{dG_m^\beta}{dP^\beta} \cdot \frac{dP^\beta}{dN^\beta} = V_m^\beta \cdot \frac{dP^\beta}{dN^\beta}. \tag{16.36}$$

This will be zero when P^β is kept constant, as in Fig. 16.1. That can be compared to the case in the left-hand part of Fig. 6.1 for a circular cross-section. All positions are equivalent.

If the hole in Fig. 16.1 is slightly conical, r could either increase or decrease during growth. If the hole is narrowing to the right, r will decrease and the pressure will increase as the β phase grows. The stability will be positive and there is a stable situation at the position where the equilibrium condition, Eq. (16.29), is satisfied. If it is widening to the right, the stability will be negative and the situation will be unstable. The β phase would either grow out of the hole or shrink.

It is evident that for a spherical particle the instability will be even larger. The pressure will decrease during growth. There would be a critical size satisfying the equilibrium condition, Eq. (16.29). If the β particle were just a little smaller, it would shrink and disappear. If it were just a little larger, it would grow even larger. If the reservoir of α phase were not infinite, the supersaturation would decrease gradually during growth and

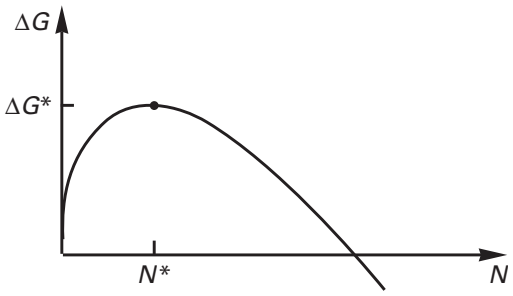

Figure 16.2 The Gibbs energy increase as a function of the size of a spherical particle of a liquid phase. N^* is the size of a critical nucleus and ΔG^* is its activation energy.

the growth would eventually stop. If there were a large number of β particles, they would be smaller when growth stops. On the other hand, not even such an ensemble would be stable. A small fluctuation in size would make the slightly larger particles grow at the expense of the smaller ones because the composition of the α matrix in local equilibrium with a particle would differ depending on the size, according to the equilibrium condition Eq. (16.28). There would thus be diffusion of material through the α matrix from the smaller particles to the larger ones. This phenomenon is called Ostwald ripening.

16.5 Nucleation

For a system with a spherical β particle included in an α matrix we can formulate the total Gibbs energy from Eq. (16.18), e.g. by inserting Eq. (16.19). The result will depend on the size N^β.

$$G(N^\beta) = \sum \left(N_i^\circ - N_i^\beta\right)\mu_i^\alpha(P)\big) + G^\beta(P^\beta) - (P^\beta - P)V^\beta(P^\beta) + A\sigma, \qquad (16.37)$$

where N_i° is the initial i content in the α matrix. For a spherical β particle the last term can be expressed as $3\sigma V/r$ and we can express $P^\beta - P$ as $2f/r$ according to Eq. (16.1). The change of Gibbs energy from the initial homogeneous α matrix will be

$$\begin{aligned}\Delta G(N^\beta) &= G(N^\beta) - G(0)\\ &= -\sum N_i^\beta \mu_i^\alpha(P) + G^\beta(P^\beta) - (2f/r)V^\beta(P^\beta) + (3\sigma/r)V^\beta(P^\beta).\end{aligned} \qquad (16.38)$$

For a liquid β phase $f = \sigma$ and Eq. (16.37) simplifies to

$$\Delta G(N^\beta) = N^\beta\left[-\sum x_i^\beta \mu_i^\alpha(P) + G_{\mathrm{m}}^\beta(P^\beta) + (\sigma/r)V_{\mathrm{m}}^\beta(P^\beta)\right]. \qquad (16.39)$$

Since r is proportional to $(N^\beta)^{1/3}$, the function will look as illustrated in Fig. 16.2. It is evident that the formation of β cannot start spontaneously from a zero size. There is a barrier of height ΔG^*, which must be overcome by some kind of activated process. A β particle of a critical size N^* is in an unstable equilibrium. However, at both types

of equilibrium the first two terms in Eq. (16.39) eliminate each other according to the equilibrium condition in Eq. (16.24). Using $P_e^\beta - P = 2\sigma/r_e$ we obtain

$$\Delta G^* = N^* \cdot (\sigma/r_e)V_m^\beta\left(P_e^\beta\right) = \frac{1}{2}N^* \times \left(P_e^\beta - P\right)V_m^\beta\left(P_e^\beta\right) = \frac{4}{3}\pi\sigma(r_e)^2$$
$$= \frac{16\pi\sigma^3}{3\left(P_e^\beta - P\right)^2}. \tag{16.40}$$

This is the energy, which must be supplied by some kind of activated process in order for the β phase to form. It is regarded as the **activation energy**. A particle of this size can either grow or shrink by a small fluctuation in size. It is regarded as a **critical nucleus**. Equation (16.40) expresses the activation energy in the most general way but in order to apply it to a particular case one must relate it to the driving force, $-\Delta G_m$. It is then necessary to define the compressibility of the β phase. For a compressible liquid one can use Eq. (16.27), obtaining

$$\Delta G^* = \frac{16\pi\sigma^3}{3\left(-\Delta G_m/V_m^\beta(P)\right)^2}(1 - \kappa\sigma/r_e)^2$$
$$\cong \frac{16\pi\sigma^3}{3\left(-\Delta G_m/V_m^\beta(P)\right)^2}(1 - 2\kappa\sigma/r_e). \tag{16.41}$$

Equation (16.40) is still valid for a bubble of an ideal gas but one should insert Eq. (16.32) instead of Eq. (16.27),

$$\Delta G^* = \frac{16\pi\sigma^3}{3P^2[\exp(-\Delta G_m/RT) - 1]^2}. \tag{16.42}$$

Finally, we should discuss the fact that a supersaturated solution can be unstable with respect to two quite different kinds of fluctuations. Here we have considered a critical nucleus being a fluctuation small in extent but large in composition (and structure). In Chapter 15 we discussed spinodal decomposition, which can start spontaneously without any activation barrier, i.e. without any critical nucleus. However, that treatment also describes critical nuclei when the composition is moved outside the spinodal. Right on the spinodal the critical nucleus is represented by a point at $1/\lambda = 0$ and of composition x^o. In principle, it is thus an infinitely extended fluctuation with an infinitely small change of composition. With an initial composition further outside the spinodal, the change in composition grows and an arrow in Fig. 15.13 illustrates such a case. A detailed calculation would show that the critical fluctuation, i.e. nucleus, becomes more localized and starts to resemble the kind of critical nucleus described in the present chapter. The explanation why the two treatments give different results is that a constant σ was used here whereas it decreases with decreasing difference in composition between fluctuation and matrix in the spinodal treatment. The use of a constant σ in the present case can be justified by assuming that it mainly depends on the difference in structure between the two phases. In the spinodal treatment there is only a difference in composition.

Exercise 16.2

In textbooks one often finds the following simple treatment of nucleation. The increase of the Gibbs energy of a system due to a nucleus is given as $\Delta G = (4\pi/3)r^3(\Delta G_m/V_m) + 4\pi r^2\sigma$ which yields: $\partial\Delta G/\partial r = 4\pi r^2(\Delta G_m/V_m) + 8\pi r\sigma = 0$; $r^* = 2\sigma/(-\Delta G_m/V_m)$; $\Delta G^* = (4\pi/3)r^3(\Delta G_m/V_m) + 2\pi r^3(-\Delta G_m/V_m) = (2\pi/3)r^3(-\Delta G_m/V_m) = (16\pi/3)\sigma^3/(-\Delta G_m/V_m)^2$. Compare this result with the correct result given by Eq. (16.42) when applied to the nucleation of a gas bubble at a temperature above the boiling point of a liquid composed of only one species.

Hint

Approximate the gas as ideal. The vapour pressure of the liquid matrix, corresponding to P^β in our treatment, must be larger than the pressure on the liquid from the surroundings, P.

Solution

Equation (16.32) reduces to the textbook result for small $-\Delta G_m/RT$: $\Delta G^* \cong (16\pi/3)\sigma^3/[-\Delta G_m P/RT]^2 = (16\pi/3)\sigma^3/(-\Delta G_m/V_m)^2$. However, small $-\Delta G_m/RT$ means small $\ln(P^\beta/P)$. Large values of P^β/P can easily be obtained by superheating of a liquid or when the gas is dissolved in a liquid or solid. The textbook treatment holds strictly for incompressible phases, only.

16.6 Phase equilibrium at crystal/fluid interface

If one of the phases is crystalline, the derivations will be more complicated because $f \neq \sigma$. There will be even more complications if the crystalline phase is the matrix phase because it may build up internal stresses in the matrix during a growth process. We shall thus limit the discussion to cases with a crystalline phase included in a fluid matrix.

Equation (16.21) was derived without any particular requirement about the nature of the interface but was then applied to a fluid/fluid interface. It will now be applied to a crystalline/fluid interface. When expressing the pressure difference, we shall thus retain the surface stress, f from Eq. (16.1). On the other hand, the specific surface energy, σ, should still appear when expressing the surface energy term, G^σ. However, there one must notice an important difference. It has already been mentioned that a fluid/fluid interface will reorganize its structure if expanded or contracted and the surface energy is always proportional to the actual area, i.e., σ is constant in the expression $G^\sigma = A\sigma$. With full coherency to the interior, the surface of a crystalline phase will not change its structure if the bulk is expanded or compressed. It may thus seem reasonable to approximate the surface energy as $A_P\sigma_P$, evaluated at the pressure in the surroundings,

P. Furthermore, in the case where the matrix is a condensed fluid, i.e. a liquid, one may argue that the structure on that side of the interface should relax to some degree. However, that possibility will be neglected whereas the consequences of the above approximation will be examined.

The surface energy will be described with $G^\sigma = A_P\sigma_P$ where σ_P is measured at a planar interface and will be treated as independent of P^β. Eq. (16.22) will give

$$\frac{\mathrm{d}G^\sigma}{\mathrm{d}N^\beta} = \frac{\mathrm{d}A_P}{\mathrm{d}N^\beta}\cdot\sigma_P = \frac{2\sigma_P}{r_P}\cdot\frac{\mathrm{d}V^\beta(P)}{\mathrm{d}N^\beta} = \frac{2\sigma_P}{r_P}\cdot V_\mathrm{m}^\beta(P). \tag{16.43}$$

The radius r_P is also measured at the pressure P.

In analogy to the description of G^σ we may introduce f_P/r_P in Eq. (16.1) obtaining

$$\begin{aligned}\mathrm{d}P^\beta &= (-2f_P/r_P^2)\mathrm{d}r_P = (-2f_P/r_P^2)\cdot r_P\mathrm{d}V^\beta(P)/3V^\beta(P)\\ &= \left(-2f_P/3r_PV^\beta(P)\right)\cdot V_\mathrm{m}^\beta(P)\mathrm{d}N^\beta,\end{aligned} \tag{16.44}$$

since $3\mathrm{d}r/r = \mathrm{d}V/V$. This time we must study how to interpret $\mathrm{d}V^\beta/\mathrm{d}N^\beta$ in Eq. (16.21), considering the dependent variable P^β. Inserting $(\partial V^\beta/\partial P^\beta)_{N^\beta}$ from Eq. (16.25) and $\mathrm{d}P^\beta/\mathrm{d}N^\beta$ from Eq. (16.44) we obtain

$$\begin{aligned}\mathrm{d}V^\beta/\mathrm{d}N^\beta &= (\partial V^\beta/\partial N^\beta)_{P^\beta} + (\partial V^\beta/\partial P^\beta)_{N^\beta}\cdot\mathrm{d}P^\beta/\mathrm{d}N^\beta\\ &= V_\mathrm{m}^\beta(P^\beta) - \kappa V^\beta(P)\cdot\left(-2f_PV_\mathrm{m}^\beta(P)/3r_PV^\beta(P)\right)\\ &= V_\mathrm{m}^\beta(P)(1 - 2\kappa f_P/r_P + 2\kappa f_P/3r_P)\\ &= V_\mathrm{m}^\beta(P)(1 - 4\kappa f_P/3r_P).\end{aligned} \tag{16.45}$$

From Eq. (16.26) we find

$$G_\mathrm{m}^\beta(P^\beta) = G_\mathrm{m}^\beta(P) + (P^\beta - P)V_\mathrm{m}^\beta(P)(1 - \kappa f_P/r_\mathrm{e}). \tag{16.46}$$

Inserting Eqs (16.45) and (16.46) and the definition of ΔG_m from Eq. (16.27) in Eq. (16.21) we obtain

$$\begin{aligned}\mathrm{d}G/\mathrm{d}N^\beta &= -\sum x_i^\beta\mu_i^\alpha(P) + G_\mathrm{m}^\beta(P)\\ &\quad -(P^\beta - P)\mathrm{d}V_\mathrm{m}^\beta(1 - \kappa f_P/r_P - 1 + 4\kappa f_P/3r_P)\\ &= \Delta G_\mathrm{m} + [(2f_P/r_P)(\kappa f_P/3r_P) + (2\sigma_P/r_P)]\,V_\mathrm{m}^\beta(P).\end{aligned} \tag{16.47}$$

In Eq. (16.21) the third and fourth terms eliminated each other because $f = \sigma$. That is not the case here and it was thus necessary this time to interpret $\mathrm{d}V^\beta/\mathrm{d}N^\beta$ and the result depended on the compressibility, κ. It is interesting to note that for an incompressible β phase the third term in Eq. (16.21) would be eliminated by a term appearing in Eq. (16.46) when $G_\mathrm{m}^\beta(P)$ was introduced. Only a correction term proportional to κ remained when the compressibility was considered. In practice, P^β would probably be unknown because of lack of information on the surface stress, f_P, and one would be dealing with $G_\mathrm{m}^\beta(P)$. It is evident that the surface stress is not of much practical importance and the compressibility will cause only a small correction term.

Putting $\mathrm{d}G/\mathrm{d}N^{\beta}$ to zero in Eq. (16.47) we obtain the equilibrium condition for crystalline/fluid interfaces.

$$-\Delta G_{\mathrm{m}} = \left[(2\sigma_P/r_{P\mathrm{e}}) + (2\kappa/3)(f_P/r_{P\mathrm{e}})^2\right] V_{\mathrm{m}}^{\beta}(P) \tag{16.48}$$

$$r_{P\mathrm{e}} = 2\sigma_P/\left[-\Delta G_{\mathrm{m}}/V_{\mathrm{m}}^{\beta}(P) - (2\kappa/3)(f_P/r_{P\mathrm{e}})^2\right]. \tag{16.49}$$

It may be added that the actual radius at equilibrium is obtained as

$$r_{\mathrm{e}} = r_{P\mathrm{e}}\left(1-\kappa(P^{\beta}-P)\right)^{1/3} \cong r_{P\mathrm{e}}\left(1-\tfrac{2}{3}\kappa f_P/r_{P\mathrm{e}}\right). \tag{16.50}$$

The important conclusion to be drawn from Eq. (16.48) is that the effect of surface energy is the same for solid and liquid inclusions. The Gibbs energy of both kinds of phases is increased by $2\sigma V_{\mathrm{m}}/r$ which is equal to $V_{\mathrm{m}}\Delta P$ only for liquids. It is common to neglect this fact and to express $2\sigma/r$ as ΔP also for solids, a procedure that does not cause any erroneous results. There are several equations in the present textbook where $V_{\mathrm{m}}\Delta P$ is used without explicit mention that it should be interpreted as $2\sigma V_{\mathrm{m}}/r$ for solids.

By modifying Eq. (16.38) for the present case we obtain for the increase of Gibbs energy due to the precipitation of a β inclusion,

$$\begin{aligned}\Delta G(N^{\beta}) &= N^{\beta}\left[-\sum x_i^{\beta}\mu_i^{\alpha} + G_{\mathrm{m}}^{\beta}(P^{\beta}) - (P^{\beta}-P)V_{\mathrm{m}}^{\beta}(P^{\beta}) + (3\sigma_P/r_P)V_{\mathrm{m}}^{\beta}(P)\right]\\ &= N^{\beta}\Big[\Delta G_{\mathrm{m}} + (P^{\beta}-P)V_{\mathrm{m}}^{\beta}(P)(1-\kappa f_P/r_P) - (P^{\beta}-P)V_{\mathrm{m}}^{\beta}(P)(1-2\kappa f_P/r_P)\\ &\quad + (3\sigma_P/r_P)V_{\mathrm{m}}^{\beta}(P)\Big] = N^{\beta}\left[\Delta G_{\mathrm{m}} + (2f_P/r_P)V_{\mathrm{m}}^{\beta}(P)(\kappa f_P/r_P) + (3\sigma_P/r_P)V_{\mathrm{m}}^{\beta}(P)\right].\end{aligned} \tag{16.51}$$

Inserting ΔG_{m} from Eq. (16.48) we obtain for equilibrium of a spherical crystalline inclusion

$$\begin{aligned}\Delta G^{*} &= N^{*}V_{\mathrm{m}}^{\beta}(P)\left[-2\sigma_P/r_{P\mathrm{e}} - (2\kappa/3)(f_P/r_{P\mathrm{e}})^2 + 2\kappa(f_P/r_{P\mathrm{e}})^2 + 3\sigma_P/r_{P\mathrm{e}}\right]\\ &= \tfrac{4}{3}\pi r_{P\mathrm{e}}^3\cdot(\sigma_P/r_{P\mathrm{e}})\left(1+4\kappa f_{P\mathrm{e}}^2/3\sigma_P r_{P\mathrm{e}}\right) = \frac{16\pi\sigma_P^3\left(1+4\kappa f_P^2/3\sigma_P r_{P\mathrm{e}}\right)}{3\left[-\Delta G_{\mathrm{m}}/V_{\mathrm{m}}^{\beta}(P) - (2\kappa/3)(f_P/r_{P\mathrm{e}})^2\right]}.\end{aligned} \tag{16.52}$$

Again we find that the surface stress is of minor importance and enters only in corrections, depending on the compressibility. For incompressible crystalline solids the result is identical to the result for incompressible liquids obtained from Eq. (16.41).

Exercise 16.3

Consider two solid (β) spherical particles of a pure element, floating in a melt of the same element. Derive an equation for the difference in temperature between them if they have different radii, r_1 and r_2. Which one will grow as a result of the heat flow between them?

Hint

Simplify the problem by assuming incompressibility. Two phases at an interface might have the same T, yielding $\Delta G_{\mathrm{m}} = \Delta H_{\mathrm{m}} - T\Delta S_{\mathrm{m}}$. At the melting point T_{o}, $\Delta G_{\mathrm{m}} = 0$

and we get $\Delta G_m = (T_o - T)\Delta S_m$. For solidification we define ΔG_m and ΔS_m as negative.

Solution

Equation (16.48) yields $\left(2\sigma V_m^\beta / r\right) = -\Delta G_m = (T_o - T)(-\Delta S_m)$. Compare two particles: $2\sigma V_m^\beta (1/r_1 - 1/r_2) = (T_2 - T_1)(-\Delta S_m)$. Suppose $r_2 > r_1$. Then $T_2 > T_1$. Heat will flow from the larger one and the heat of solidification can thus leave that region. The larger particle will thus grow at the expense of the smaller one if the system is thermally insulated. This is an example of Ostwald ripening.

16.7 Equilibrium at curved interfaces with regard to composition

So far we have only considered the equilibrium with respect to the transfer of balanced amounts of the various components. Now we shall study the transfer of a single component, dN_j^β, by again regarding only two variables, the independent variable N_j^β and the dependent variable P^β. Instead of Eqs (16.20) and (16.21) we now obtain

$$\frac{dG}{dN_j^\beta} = -\mu_j^\alpha(P) + \mu_j^\beta(P^\beta) + \left(\frac{\partial G^\beta}{\partial P^\beta}\right)_{N^\beta} \frac{dP^\beta}{dN_j^\beta} - \frac{dP^\beta}{dN_j^\beta} \cdot V^\beta(P^\beta)$$

$$-(P^\beta - P) \cdot \frac{dV^\beta}{dN_j^\beta} + \frac{dG^\sigma}{dN_j^\beta} = -\mu_j^\alpha(P) + \mu_j^\beta(P^\beta) - (2f/r)dV^\beta/dN_j^\beta$$

$$+(2\sigma/r)dV^\beta/dN_j^\beta. \tag{16.53}$$

For a fluid/fluid interface we have $f = \sigma$ and the last two terms eliminate each other. At equilibrium $dG/dN_j^\beta = 0$ and the equilibrium condition would then be

$$\mu_j^\alpha(P) = \mu_j^\beta(P_e^\beta). \tag{16.54}$$

We have again derived Gibbs' famous relation. However, he did not have to introduce the limitation that σ is independent of composition because he considered a β phase with only one component. His result is a special case of Eq. (16.24).

When replacing P^β by P we must know how the partial molar volume, V_j^β varies with P^β. For simplicity we shall assume that the same compressibility applies to the partial volumes as to the integral volume. By integration we obtain similar to Eq. (16.26),

$$\int V_j^\beta dP = V_j^\beta(P)(P^\beta - P)(1 - \kappa\sigma/r). \tag{16.55}$$

We can thus write the equilibrium condition, Eq. (16.54), as

$$\mu_j^\alpha(P) = \mu_j^\beta(P) + (2\sigma/r_e)V_j^\beta(P)(1 - \kappa\sigma/r_e). \tag{16.56}$$

By summing this over all the components, we can recreate Eq. (16.28). Equation (16.56) describes the equilibrium for all the components whereas Eq. (16.28) is a necessary but

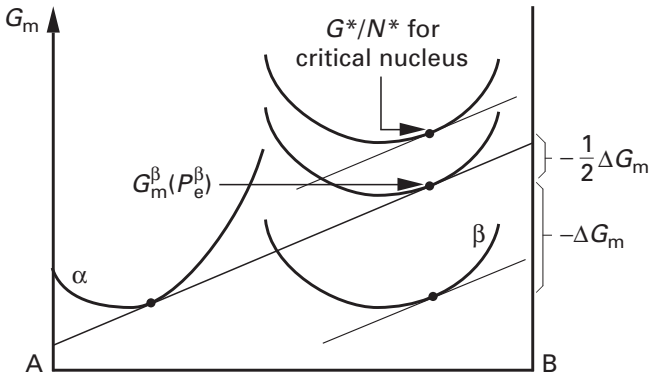

Figure 16.3 Molar Gibbs energy diagram for nucleation of β from a supersaturated α solution.

not sufficient condition. The equilibrium size, r_e, was then expressed in terms of ΔG_m in Eq. (16.29). It can now be inserted into Eq. (16.56) yielding for the equilibrium condition

$$\mu_j^\alpha(P) = \mu_j^\beta(P) - \Delta G_m \cdot V_j^\beta / V_m^\beta. \tag{16.57}$$

From its definition in Eq. (16.27) one can evaluate the driving force, $-\Delta G_m$, provided that one knows the critical composition of the β phase. However, the driving force and the composition can both be determined graphically for any given supersaturated α matrix. One should draw the tangent to the α curve for the composition of the matrix and then lower it until it becomes a tangent to the G_m^β curve. That should be done by a parallel displacement if all $V_j = V_m$ and the magnitude of the displacement gives the driving force, $-\Delta G_m$. This means that one has made a parallel tangent construction. If $V_j \neq V_m$ then Eq. (16.57) requires that one rotates the tangent slightly to make sure that the displacements on the component axes are proportional to the V_j values. If all $V_j = V_m$ then one could instead lift the G_m^β curve until it touches the α tangent. That would be a common tangent construction. See Fig. 16.3.

For the critical nucleus, including the contribution from the surface energy, one can give a point representing its Gibbs energy divided byN^*. It is obtained by adding the activation energy, ΔG^*, divided by N^* to the G_m value of β on the common tangent. $\Delta G^*/N^*$ is obtained from the first part of Eq. (16.40) by inserting σ/r_e from Eq. (16.28). We find $\Delta G^*/N^* = -\Delta G_m/2$, a value that applies even for a compressible β phase. In Fig. 16.3 the whole G_m^β curve has been lifted by $-\Delta G_m/2$. However, tangents to that curve do not have the usual properties because the curve is defined for a certain pressure, which is given by the size. When adding some A or B atoms, one should move to a curve for a slightly larger particle, i.e., for a slightly lower pressure. It is illustrated with a thin curve in Fig. 16.4. The chemical potentials of A and B are thus obtained from the intersection of the thin straight lines with the component axes and they will actually coincide with the intersections of the common tangent.

The effect of a pressure difference on the composition of the two phases was examined already in Section 7.6. We shall now base a derivation on Eq. (16.54) by first applying the Gibbs–Duhem relation to each one of the phases. Starting from the equilibrium at a

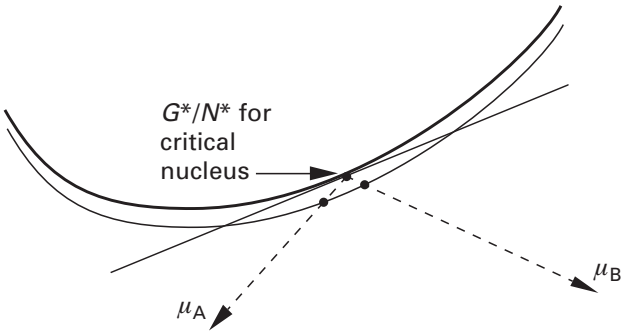

Figure 16.4 Enlarged detail of Fig. 16.3, illustrating that the critical nucleus has the correct values of the chemical potentials.

planar interface and introducing a small curvature that will give rise to a small difference in pressure, $\mathrm{d}P^{\beta}$, we obtain

$$\sum x_i^{\beta} \mathrm{d}\mu_i^{\beta} = V_{\mathrm{m}}^{\beta} \mathrm{d}P^{\beta}. \tag{16.58}$$

For the α phase there is no change of pressure and, whatever changes there will be in composition, they also must obey the Gibbs–Duhem relation which now gives

$$\sum x_i^{\alpha} \mathrm{d}\mu_i^{\alpha} = 0. \tag{16.59}$$

From Eq. (16.54) we can see that maintained equilibrium requires that $\mathrm{d}\mu_i^{\beta} = \mathrm{d}\mu_i^{\alpha}$ even though the pressure inside β is increasing. We can thus reformulate Eq. (16.58),

$$\sum x_i^{\beta} \mathrm{d}\mu_i^{\alpha} = V_{\mathrm{m}}^{\beta} \mathrm{d}P^{\beta}. \tag{16.60}$$

Combination of Eqs (16.59) and (16.60) will yield a unique answer only for a binary system, which yields, after eliminating $\mathrm{d}\mu_{\mathrm{A}}^{\alpha}$,

$$\left(x_{\mathrm{A}}^{\alpha} x_{\mathrm{B}}^{\beta} - x_{\mathrm{A}}^{\beta} x_{\mathrm{B}}^{\alpha}\right) \mathrm{d}\mu_{\mathrm{B}}^{\alpha} = x_{\mathrm{A}}^{\alpha} V_{\mathrm{m}}^{\beta} \mathrm{d}P^{\beta} \tag{16.61}$$

$$\mathrm{d}\mu_{\mathrm{B}}^{\alpha} = \frac{x_{\mathrm{A}}^{\alpha} V_{\mathrm{m}}^{\beta}}{x_{\mathrm{B}}^{\beta} - x_{\mathrm{B}}^{\alpha}} \cdot \mathrm{d}P^{\beta} \tag{16.62}$$

$$\mu_{\mathrm{B}}^{\alpha}(r) - \mu_{\mathrm{B}}^{\alpha}(\infty) \cong \frac{x_{\mathrm{A}}^{\alpha} V_{\mathrm{m}}^{\beta}}{x_{\mathrm{B}}^{\beta} - x_{\mathrm{B}}^{\alpha}} \cdot \frac{2\sigma}{r}. \tag{16.63}$$

Any solution model can be applied to the α phase to evaluate its change in composition. Using Eq. (16.54) we get for the β phase,

$$\begin{aligned} \mu_{\mathrm{B}}^{\alpha}(r) - \mu_{\mathrm{B}}^{\alpha}(\infty) = \mu_{\mathrm{B}}^{\beta}(r, P^{\beta}) - \mu_{\mathrm{B}}^{\beta}(\infty, P^{\beta}) = \mu_{\mathrm{B}}^{\beta}(r) + \int V_{\mathrm{B}}^{\beta}(r) \mathrm{d}P^{\beta} \\ -\mu_{\mathrm{B}}^{\beta}(\infty) - \int V_{\mathrm{B}}^{\beta}(\infty) \mathrm{d}P^{\beta} \cong \mu_{\mathrm{B}}^{\beta}(r) - \mu_{\mathrm{B}}^{\beta}(\infty) \cong \frac{x_{\mathrm{A}}^{\alpha} V_{\mathrm{m}}^{\beta}}{x_{\mathrm{B}}^{\beta} - x_{\mathrm{B}}^{\alpha}} \cdot \frac{2\sigma}{r}. \end{aligned} \tag{16.64}$$

The result is thus the same for both phases when expressed as the change in chemical potential. It is interesting to note that this final result is independent of the partial molar volume for the component although it appears in Eq. (16.57). It may be concluded that

the partial molar volumes have a negligible effect on the composition as well as on the activation energy of a critical nucleus.

Exercise 16.4

A liquid substance A in an inert atmosphere of 1 bar has an equilibrium vapour pressure of P_A^o. What would be the vapour pressure of a droplet of the same substance if its radius is (a) 1 μm or (b) 1 nm and the surface energy is 1 J/m^2? Suppose the molar volume is 5×10^{-6} m^3 and the temperature is 25°C and use the ideal gas law. First, assume that the substance is incompressible. Would the pressure in case (b) be higher or lower if A is compressible?

Solution

Equation (16.56) yields (a): $\mu_j^\alpha(P) = \mu_j^\beta(P) + (2\sigma/r)V_j^\beta = \mu_j^\beta(P) + (2 \times 1/10^{-6}) \times 5 \times 10^{-6} = \mu_j^\beta(P) + 10$; $P_A(1\ \mu m) = P_A^o \exp(10/8.3145 \times 298) = 1.004 P_A^o$ and (b): $P_A(1\ nm) = P_A^o \exp[(2 \times 1/10^{-9}) \times 5 \times 10^{-6}/8.3145 \times 298] = 57 P_A^o$. For a compressible liquid the effect would be lower.

16.8 Equilibrium for crystalline inclusions with regard to composition

For a crystalline inclusion in a fluid matrix we shall start with Eq. (16.43), giving the effect of the surface energy, and with a similar equation for the effect of surface stress. When applying Eq. (16.53) we obtain

$$\frac{\partial G}{\partial N_j^\beta} = -\mu_j^\alpha(P) + \mu_j^\beta(P^\beta) - (2f_P/r_P)\mathrm{d}V^\beta/\mathrm{d}N_j^\beta + (2\sigma_P/r_P)\mathrm{d}V^\beta/\mathrm{d}N_j^\beta. \tag{16.65}$$

We shall again assume that the same compressibility applies to the partial volumes as the integral volume. We shall thus modify Eqs (16.45) and (16.46) to partial quantities.

$$\mathrm{d}V^\beta/\mathrm{d}N_j^\beta = V_j^\beta(P)(1 - 4\kappa f_P/3r_P) \tag{16.66}$$

$$\mu_j^\beta(P^\beta) = \mu_j^\beta(P) + (P^\beta - P)V_m^\beta(P)(1 - \kappa f_P/r_e) \tag{16.67}$$

Introducing these results into Eq. (16.65) we obtain, similar to Eq. (16.48),

$$\mu_j^\alpha(P) = \mu_j^\beta(P) + \left[(2\sigma_P/r_P) + (2\kappa/3)(f_P/r_P)^2\right] V_j^\beta(P). \tag{16.68}$$

When applying Eq. (16.53) to an interstitial component, k, we shall accept that it does not affect the surface energy even if it increases the volume somewhat. On the other hand, the effect of surface stress will be given by the same expression as for substitutional components because it depends primarily on the effect on the volume. Instead of Eq. (16.68) we thus obtain

$$\mu_k^\alpha(P) = \mu_k^\beta(P) + (2\kappa/3)(f_P/r_P)^2 V_k^\beta(P). \tag{16.69}$$

It is interesting to note that $\mu_k^{\beta}(P)$ could be approximated by $\mu_k^{\alpha}(P)$ for an interstitial component if its partial molar volume were negligible.

When now summing this over all the components we do not recreate Eq. (16.48). It seems that, when accepting Eq. (16.69) for an interstitial component, we should introduce a correction to the second term in Eq. (16.68) for the substitutional components.

$$\mu_j^{\alpha}(P) = \mu_j^{\beta}(P) + (2\sigma_P/r_P)\left[V_j^{\beta}(P) + x_k V_k^{\beta}\Big/\left(1 - x_k^{\beta}\right)\right] + (2\kappa/3)(f_P/r_P)^2 V_j^{\beta}(P). \tag{16.70}$$

The equilibrium conditions are obtained by inserting r_{Pe} instead of r_P in Eqs (16.69) and (16.70).

Finally, we shall evaluate the effect on the compositions from the Gibbs–Duhem relation. Then we need a relation between $\mathrm{d}\mu_i^{\alpha}$ and $\mathrm{d}\mu_i^{\beta}$. For simplicity we shall limit this discussion to incompressible β phases. Equations (16.67) and (16.70) yield

$$\mathrm{d}\mu_k^{\alpha}(P) = \mathrm{d}\mu_k^{\beta}(P^{\beta}) - V_k^{\beta}(P^{\beta})\mathrm{d}P^{\beta} \tag{16.71}$$

$$\mathrm{d}\mu_j^{\alpha}(P) = \mathrm{d}\mu_j^{\beta}(P^{\beta}) - V_j^{\beta}(P^{\beta})\mathrm{d}P^{\beta} + \left[V_j^{\beta}(P) + x_k^{\beta} V_k^{\beta}/\left(1 - x_k^{\beta}\right)\right]\mathrm{d}(2\sigma_P/r_P). \tag{16.72}$$

Inserting this in Eq. (16.58) we obtain

$$V_{\mathrm{m}}^{\beta}\mathrm{d}P^{\beta} = \sum x_i^{\beta}\mathrm{d}\mu_i^{\beta} = \sum x_i^{\beta}\mathrm{d}\mu_i^{\alpha} + \sum x_i^{\beta} V_i^{\beta}\mathrm{d}P^{\beta} - \sum x_j^{\beta}\left[V_j^{\beta}(P) + x_k^{\beta} V_k^{\beta}/\left(1 - x_k^{\beta}\right)\right]\mathrm{d}(2\sigma_P/r_P) = \sum x_i^{\beta}\mathrm{d}\mu_i^{\alpha} + \sum V_{\mathrm{m}}^{\beta}\mathrm{d}P^{\beta} - \mathrm{d}(2\sigma_P/r_P) \tag{16.73}$$

$$\sum x_i^{\beta}\mathrm{d}\mu_j^{\alpha} = V_{\mathrm{m}}^{\beta}\mathrm{d}(2\sigma_P/r_P). \tag{16.74}$$

For a binary system we get instead of Eq. (16.62)

$$\mathrm{d}\mu_{\mathrm{B}}^{\alpha} = \frac{x_{\mathrm{A}}^{\alpha} V_{\mathrm{m}}^{\beta}}{x_{\mathrm{B}}^{\beta} - x_{\mathrm{B}}^{\alpha}} \cdot \mathrm{d}(2\sigma_P/r_P). \tag{16.75}$$

The final result will be identical to Eq. (16.63) except for the slightly different interpretation of σ and r. Equation (16.63) can thus be applied to all kinds of interfaces.

Exercise 16.5

Somebody has derived the following equilibrium condition for the case where the partial molar volume of an interstitial component is small but not negligible, $\mu_i^{\alpha}(P) = \mu_i^{\beta}(P) + (2f/r)V_j^{\beta}$. Give a physical argument for or against this relation.

Hint

Even if we do not consider compressibility, Eq. (16.68) shows that it is wrong. It may thus be easier to find an argument against it.

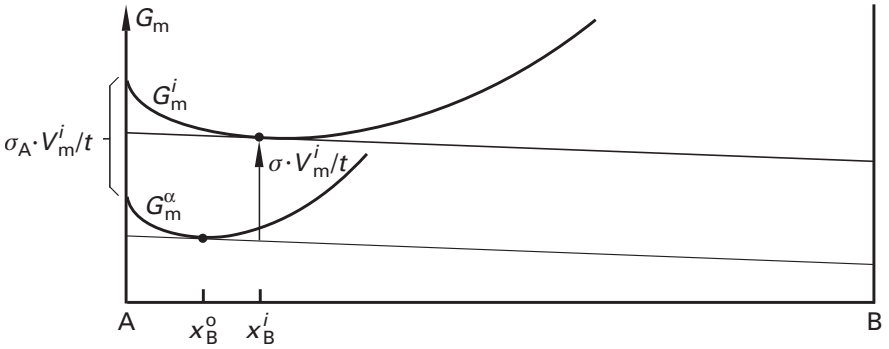

Figure 16.5 The parallel tangent construction to find the interface composition.

Solution

For an incompressible phase it is not reasonable that the surface stress has any effect because the phase is not affected. The last term should thus contain the compressibility as a factor.

Exercise 16.6

The partial molar volume for an interstitial component is small and is sometimes approximated as zero. Accepting that approximation, how should one formulate the equilibrium for the interstitial component in a compressible β phase?

Solution

For $V_k^\beta = 0$, Eq. (16.67) gives directly $\mu_k^\alpha(P) = \mu_k^\beta(P)$. The internal pressure has no effect in this case.

16.9 Surface segregation

Another important aspect is segregation of the components to or from the surface or interface. In order to describe this phenomenon we shall use a very crude model. It applies to surfaces as well as interfaces and in the formulation of the model it will be sufficient to consider the properties of one of the phases at an interface because it is assumed that the whole system is in equilibrium. Suppose the interface can be approximated as a thin layer of a homogeneous phase of constant thickness and with its own Gibbs energy function. We shall also assume that the partial molar volumes of all the phases, including the interfacial phase, are independent of composition. It is then easy to see that the composition of the material in the interface can be found by a parallel tangent construction when the volume of the interface is constant. Then we cannot consider the addition of N_A to the interface but the exchange of N_A for N_B. Thus, it is the slopes of the tangents that must be equal, not their intersections with the component axes. Figure 16.5 shows a reasonable molar Gibbs energy diagram for a one-phase material with an interface between two crystals, a so-called grain boundary. The distance between the two

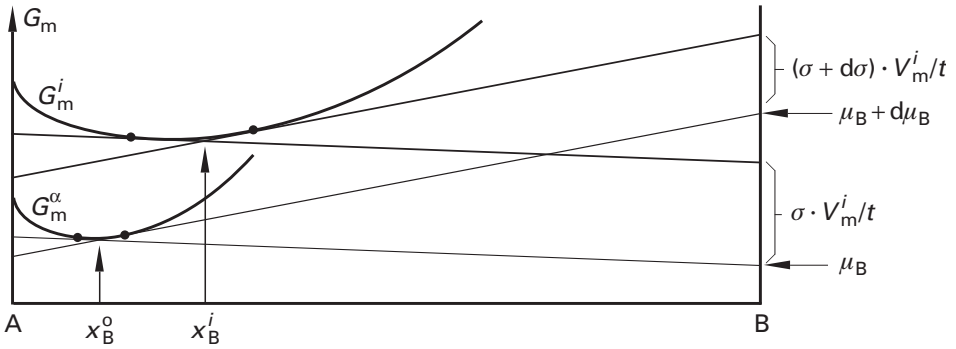

Figure 16.6 Derivation of Gibbs' adsorption equation.

curves on the left-hand side is equal to $\sigma_A \cdot V_m^i/t$ where σ_A is the specific interfacial energy of pure A, V_m^i is the molar volume of the interfacial phase and t is its thickness. Now, suppose the material has the composition x_B^o. The composition of the interface material, x_B^i, is obtained from the parallel tangent construction and the length of the vertical arrow is equal to $\sigma_A \cdot V_m^i/t$ because it is the energy required for the formation of an interface of composition x_B^i from an α reservoir of composition x_B^o.

Let us now vary the composition of the material and, thus, its chemical potential for B from μ_B to $\mu_B + d\mu_B$. By comparing triangles in Fig. 16.6 one can derive an equation, called Gibbs' adsorption equation,

$$-d\sigma = \frac{x_B^i - x_B^o}{1 - x_B^o} \cdot \frac{t}{V_m^i} \cdot d\mu_B. \tag{16.76}$$

Exercise 16.7

Apply the regular solution model and use the parallel tangent construction to calculate the composition of a grain boundary. Examine what factor can give strong segregation.

Hint

The regular solution model gives $G_m^\alpha = x_A^{\alpha o} G_A^\alpha + x_B^{\alpha o} G_B^\alpha + RT(x_A^\alpha \ln x_A^\alpha + x_B^\alpha \ln x_B^\alpha) + L^\alpha x_A^\alpha x_B^\alpha$. We should apply the same type of model to the interface. Remember that ${}^oG_A^i - {}^oG_A^\alpha = \sigma_A V_m^i/t$ and ${}^oG_B^i - {}^oG_B^\alpha = \sigma_B V_m^i/t$. The tangent construction gives $G_A^\alpha - G_B^\alpha = G_A^i - G_B^i$.

Solution

$dG_m/x_A^\alpha = {}^oG_B^\alpha - {}^oG_A^\alpha + RT\ln(x_B^\alpha/x_A^\alpha) + L^\alpha(x_A^\alpha - x_B^\alpha) = {}^oG_B^i - {}^oG_A^i + RT\ln(x_B^i/x_A^i) + L^i(x_A^i - x_B^i)$; $RT\ln(x_A^\alpha x_B^i/x_B^\alpha x_A^i) = (\sigma_A - \sigma_B)V_m^i/t + L^\alpha(x_B^\alpha - x_A^\alpha) - L^i(x_B^i - x_A^i)$.

For ordinary metals $\sigma \cong 1\text{J/m}^2$, $V_m \cong 7\ \text{cm}^3/\text{mol}$, $t \cong 10^{-7}$ cm.

At $T = 1000$ K the first term on the right-hand side will be less than RT even if $\sigma_B = 0$. Strong segregation must be due to the L terms and, in particular, to a large negative value of L^i, i.e. to the tendency of A and B to mix in the interface. However, the L^i term will go to zero at $x_B^i = 0$. Thus, the regular solution model predicts that

$x_B^i < 0$ even for the strongest segregation. The strongest segregation is thus predicted to give not much more than what corresponds to a monolayer.

Exercise 16.8

Gibbs' adsorption equation is usually written as $-d\sigma = \Gamma_{B(A)} \cdot d\mu_B$ where $\Gamma_{B(A)}$ is a notation for $\Gamma_B - \Gamma_A x_B^o/(1 - x_B^o)$ and Γ_B and Γ_A are the excess amounts of B and A per unit area, due to segregation. Show that it gives the same result as the equation derived graphically.

Hint

Remember that we assumed that the volume of the interfacial phase is constant. Thus, $-\Gamma_A = \Gamma_B$.

Solution

$-\Gamma_A = \Gamma_B = (x_B^i - x_B^o) \cdot t/V_m^i$; $\Gamma_{B(A)} = (x_B^i - x_B^o)/(1 - x_B^o) \cdot t/V_m^i$ in full agreement with our result.

16.10 Coherency within a phase

The lattice parameter of a phase usually varies with the composition. The composition differences in a surface layer obtained by diffusion through the surface may thus result in internal stresses that could be partially relieved by the formation of dislocations. However, if the composition gradient is very strong, the affected surface layer could be so thin that it is difficult for dislocations to form. We shall now assume that no dislocations form and the surface layer will then be stressed to the same lattice parameter as the bulk in the planes parallel to the surface. Suppose the lattice parameter is a_1 in a binary phase of composition x_1. In the unstressed condition the lattice parameter in a thin surface layer of a slightly different composition would be $a = a_1 + (x - x_1)da/dx$. The stresses in the plane parallel to the surface in an isotropic material would have to be

$$\sigma_1 = \sigma_2 = \frac{E}{1-\nu}\frac{d\ln a}{dx}(x_1 - x). \tag{16.77}$$

They will allow the surface layer to be coherent with the bulk. E is the elastic modulus and ν is Poisson's ratio. The elastic energy per mole of the material in the thin layer would be

$$W = \frac{E V_m}{1-\nu}\left(\frac{d\ln a}{dx}\right)^2 (x_1 - x)^2 = M(x_1 - x)^2. \tag{16.78}$$

The coefficient M is introduced for convenience. The composition may vary gradually with the distance from the surface but we shall apply Eq. (16.78) to the outermost layer and x will thus be the composition of the surface. We shall now examine how the equilibrium composition in a surrounding liquid solution will be affected by the coherency stresses.

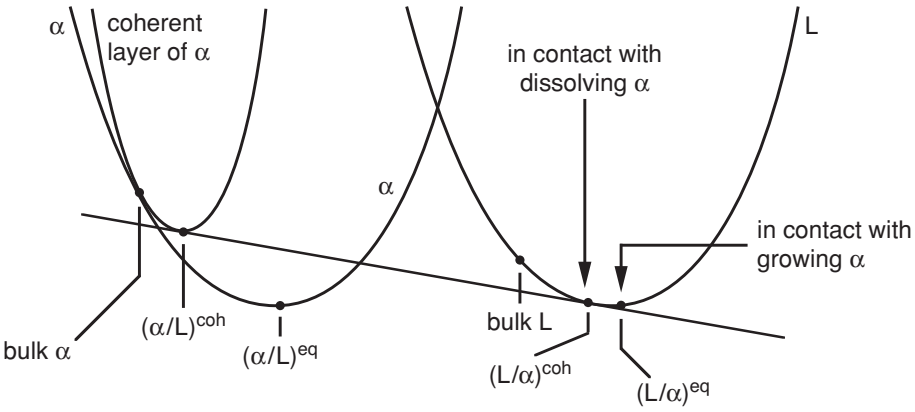

Figure 16.7 Equilibrium between a supersaturated liquid, initially x_1^{L}, and a crystalline α phase, initially x_1^{α}. The composition of the surface layer, x^{coh}, will not reach the equilibrium composition because it is coherent with a bulk of a different composition.

Introducing the elastic energy in the Gibbs energy of a surface layer coherent with an α layer of composition x_1, we obtain

$$G_{\mathrm{m}}^{\mathrm{coh}}(x) = G_{\mathrm{m}}^{\alpha}(x) + M(x_1 - x)^2. \tag{16.79}$$

Fig. 16.7 illustrates the situation where the bulk of the α phase is within the α phase field but the liquid has a composition within the $\alpha + \mathrm{L}$ two-phase field and should thus have a tendency to precipitate α. The diagram demonstrates that the coherent surface layer will not reach the solubility limit, $x_{\mathrm{eq}}^{\alpha/\mathrm{L}}$, and the composition of the liquid in contact with α will still be within the $\alpha + \mathrm{L}$ two-phase field.

When a supersaturated solid solution precipitates a new phase, it happens that the new phase grows together with a new grain of the parent phase and both phases are in contact with the supersaturated solution. Such observations are made at fairly low temperatures where volume diffusion is slow. The precipitated phase has received its alloy content by boundary diffusion along the grain boundary between the new, growing grain of the parent phase and the adjoining supersaturated parent grain. It was long a mystery what force made the new grain grow into the supersaturated grain of the same phase. Evidently, there is a force because the growing grain has been observed to be bowing out and is thus growing against the action of surface energy. The explanation is given by Fig. 16.8. In contact with the grain boundary the supersaturated α grain will be less supersaturated because of loss by grain boundary diffusion. However, due to coherency stresses the outermost surface layer will have a higher Gibbs energy than normal. See the point marked on the curve for $G_{\mathrm{m}}^{\alpha} + W$. It can thus be in local equilibrium with a growing grain but subject to an effect we shall represent by $\Delta P = 2\sigma/r$. The common tangent shows that there can still be a driving force for the precipitation of the new phase.

This phenomenon is usually called discontinuous precipitation because the supersaturation drops discontinuously to a lower level represented by the new growing α grain. It usually develops into a lamellar aggregate of the new phase mixed with a depleted grain of the parent phase. Sometimes, the new phase develops as more massive particles and the depleted grain of the parent phase bows out from the initial grain boundary to pick up the alloying element and feed it to the particles. That is the normal case when the

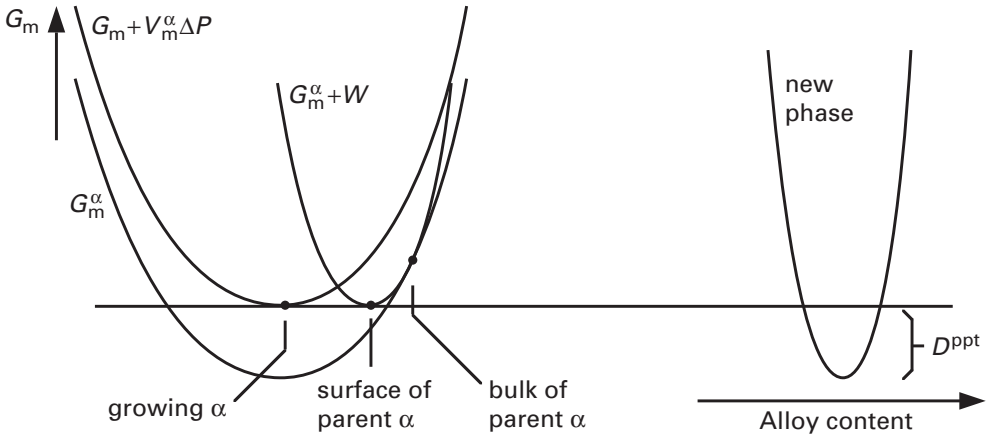

Figure 16.8 Illustration of grain boundary migration induced by grain boundary diffusion. In discontinuous precipitation the new phase is usually a solid phase but could also be liquid. In DIGM it is the atmosphere.

new phase is liquid. A related phenomenon has been observed where the alloy content diffuses through the grain boundary and is disposed of into the atmosphere instead of a new phase. It has been called DIGM for Diffusion Induced Grain boundary Migration. Both phenomena should be described as 'grain boundary migration induced by grain boundary diffusion'. It should be mentioned that DIGM occurs also when the alloying element diffuses into the grain boundary and could thus be a mechanism of alloying a surface layer at a temperature where volume diffusion is too slow.

Exercise 16.9

When a liquid film of Cu has penetrated a grain boundary in pure Ni due to wetting, there will be a tendency of Cu to dissolve in Ni. One has observed that this has resulted in one of the Ni grains growing into the other one while the liquid film is migrating between them. The new parts of the growing grain will be alloyed with Cu that comes from the liquid reservoir but its Ni must come from the other grain. This is why that grain shrinks. This phenomenon looks very similar to discontinuous precipitation and DIGM and is called LFM for Liquid Film Migration. Explain why Ni should diffuse across the liquid film.

Hint

Once a grain has started to grow, the alloyed layer is thick enough to be less affected by the bulk. The shrinking grain will not have time to build up a thick surface layer alloyed with Cu because it will constantly be dissolved. Its alloyed surface layer will thus be more affected by coherency.

Solution

Figure 16.7 can be used to illustrate this case as well but the new phase, which may be an atmosphere in the case of DIGM, must here be replaced by the liquid reservoir. The

new Cu is provided by fresh liquid being sucked in between the Ni grains instead of by grain boundary diffusion but that difference does not affect the diagram. The L phase in the diagram is rich in Cu. It will thus have a higher Ni content in contact to the coherent layer than to the growing grain. Ni will thus diffuse to that grain.

16.11 Coherency between two phases

When a new phase precipitates from a supersaturated solid solution, it is common that many small particles form with such an orientation that they fit well into the parent phase acting as a matrix. The two crystalline lattices are then coherent with each other and structurally the phase interface is regarded as a coherent interface. This is favourable, particularly during the nucleation stage, because the coherent interface has a lower surface energy than an incoherent interface. As the new particles grow larger they may gradually lose coherency by the formation of interface dislocations. However, we shall neglect that possibility and examine the effect of coherency from the overall volume fractions of the phases. To simplify the discussion we shall also neglect the ordinary surface energy.

In general, the dimensions of the two lattices are not perfect for an exact fit to each other. There will thus be coherency stresses. In the previous section we discussed coherency stresses present in a thin surface layer when coherent with the bulk. In the present case we shall assume that they will apply to the whole phase. We shall assume that each phase is homogeneous with respect to composition as well as stresses. The coherency stresses in a thin precipitated plate will deform it to fit into the matrix, which is deformed very little. The elastic energy per mole of the new phase can depend on several factors. The present discussion will be limited to cases where the misfit between the two lattices is independent of composition and depends solely on the two crystal structures. M in Eq. (16.78) will thus be constant. It is defined per mole of the deformed phase and the energy increase, ΔG_m, will thus be $f^\beta W$ per mole of the material as a whole. f^β is the mole fraction of the new phase. However, a correction must be introduced to make the elastic energy go to zero as f^β goes to unity. The following equation seems reasonable if the phases have the same mechanical properties.

$$\Delta G_m = f^\alpha f^\beta W. \tag{16.80}$$

The Gibbs energy for a binary alloy can be written as

$$G_m = f^\alpha G_m^\alpha + f^\beta G_m^\beta + \Delta G_m(f^\beta). \tag{16.81}$$

The state of equilibrium for a material of average composition x_B^o is found by minimizing G_m with respect to the independent variables, which should be x^α, x^β and x^o. The phase fractions are dependent variables through the mass balance

$$x^o - f^\alpha x^\alpha - f^\beta x^\beta = 0. \tag{16.82}$$

We could thus eliminate the phase fractions but Liu and Ågren [32] have demonstrated that the calculations can be simplified by keeping the phase fractions and use Eq. (16.82)

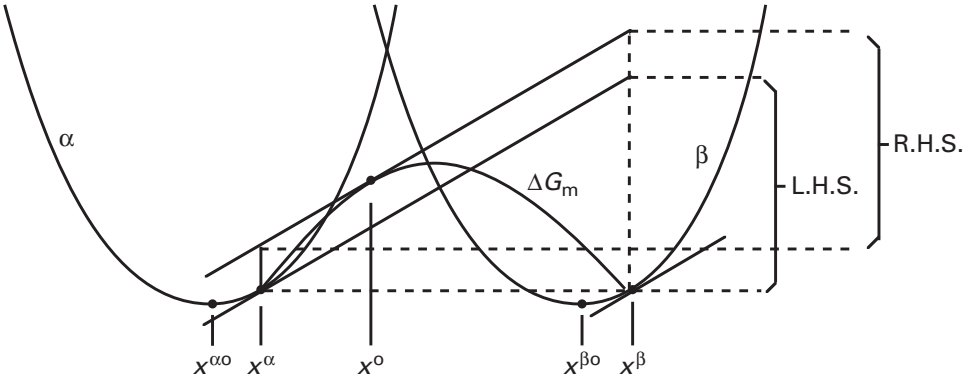

Figure 16.9 Conditions for coherent $\alpha + \beta$ equilibrium. $x^{\alpha o}$ and $x^{\beta o}$ are the ordinary equilibrium compositions. x^{α} and x^{β} represent a possible coherent equilibrium. The lever rule can be applied to the $x^{\alpha} - x^{\beta}$ tie-line using the average composition x^{o}. The parabola between x^{α} and x^{β} represent the elastic energy caused by coherency. The tangents through x^{α} and x^{β} are parallel. The tangent through x^{o} is at least approximately parallel to the other two.

as an auxiliary condition. Applying a Lagrange multiplier, λ, we shall thus minimize the function

$$L = G_m + \lambda(x^o - f^{\alpha}x^{\alpha} - f^{\beta}x^{\beta}) \tag{16.83}$$

$$\frac{\partial L}{\partial x^{\alpha}} = f^{\alpha}\frac{dG_m^{\alpha}}{dx^{\alpha}} + \lambda(-f^{\alpha}) = 0 \tag{16.84}$$

$$\frac{\partial L}{\partial x^{\beta}} = f^{\beta}\frac{dG_m^{\beta}}{dx^{\beta}} + \lambda(-f^{\beta}) = 0 \tag{16.85}$$

$$\frac{\partial L}{\partial f^{\beta}} = -G_m^{\alpha}(x^{\alpha}) + G_m^{\beta}(x^{\beta}) + \frac{\partial \Delta G_m}{\partial f^{\beta}} + \lambda(x^{\alpha} - x^{\beta}) = 0. \tag{16.86}$$

Equations (16.84) and (16.85) yield

$$\frac{dG_m^{\alpha}}{dx^{\alpha}} = \lambda = \frac{dG_m^{\beta}}{dx^{\beta}}. \tag{16.87}$$

Graphically the compositions of the two phases are thus related by a parallel tangent construction (see Fig. 16.9). $\partial \Delta G_m/\partial f^{\beta}$ in Eq. (16.86) can be expressed as $\partial \Delta G_m/\partial x^o \cdot \partial x^o/\partial f^{\beta}$ and Eq. (16.82) yields $\partial x^o/\partial f^{\beta} = -x^{\alpha} + x^o$. We can thus write $\partial \Delta G_m/\partial f^{\beta}$ as $(x^{\beta} - x^{\alpha})\partial \Delta G_m/\partial x^o$ where $\partial \Delta G_m/\partial x^o$ is the slope of the ΔG_m curve at the composition x^o. By further inserting the expression for λ from Eq. (16.87) into Eq. (16.86) we obtain

$$G_m^{\alpha}(x^{\alpha}) + (x^{\beta} - x^{\alpha})\frac{dG_m^{\alpha}}{dx^{\alpha}} - G_m^{\beta}(x^{\beta}) = (x^{\beta} - x^{\alpha})\frac{d\Delta G_m}{dx^o}. \tag{16.88}$$

The left-hand side represents the driving force for further formation of β from the α reservoir. Equation (16.88) requires that it is equal to the right-hand side, which represents the rate of increase of the elastic energy. Figure 16.9 demonstrates this relation. That diagram is based on $G_m^{\alpha}(x^{\alpha})$ and $G_m^{\beta}(x^{\beta})$ having the same shape and the frame of reference was chosen to make the common tangent horizontal. Both phases will thus have the same G_m value when x^{α} and x^{β} yield the same slope, which is required by Eq. (16.88).

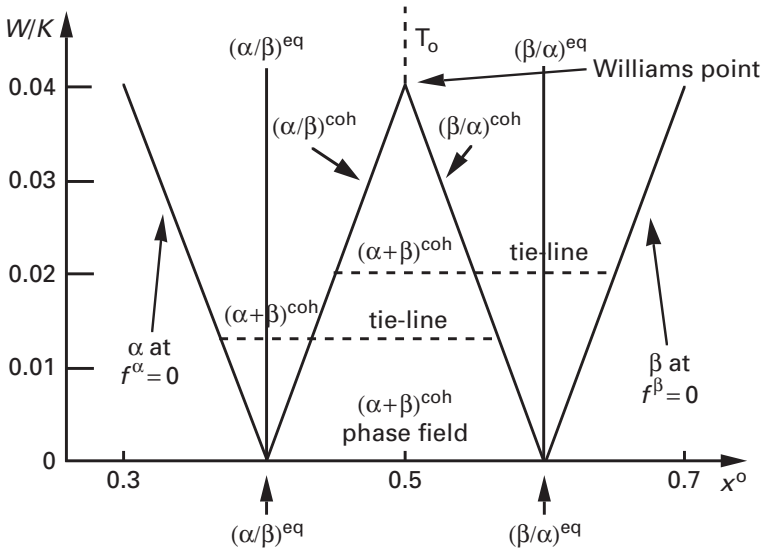

Figure 16.10 Binary phase diagram with coherent phase boundaries. The point where two coherent phase boundaries and the T_o –line meet is a Williams point. The boundaries of the coherent $\alpha + \beta$ two-phase field fall inside the ordinary $\alpha + \beta$ two-phase field. The lines representing compositions of a new phase forming at a coherent phase boundary or the last portion of the initial phase to disappear fall within the respective one-phase field.

In that case the tangent to the ΔG_m curve must also have the same slope. For any phase fraction f^β one knows the point on the ΔG_m curve. The slope of the three parallel tangents is thus known and one can easily find x^α, x^β and x^o. When the G_m curves have different shapes, the parallel tangent construction may still be used as an approximation.

For an analytical calculation one must give the exact shapes and for simplicity we shall assume parabolic shapes, which is always good enough in a small range of composition except for close to a pure component. Equation (16.81) will thus become

$$G_m = f^\alpha K^\alpha (x^\alpha - x^{\alpha o})^2 + f^\beta K^\beta (x^\beta - x^{\beta o})^2 + f^\alpha f^\beta W, \tag{16.89}$$

where $x^{\alpha o}$ and $x^{\beta o}$ are the equilibrium compositions of the two phases and G_m is given relative to the state of equilibrium and the common tangent is used as a line of reference. It was thus drawn horizontally in Fig. 16.9. Equations (16.86) and (16.87) yield

$$2K^\alpha (x^\alpha - x^{\alpha o}) = 2K^\beta (x^\beta - x^{\beta o}) \tag{16.90}$$

$$K^\alpha (x^\alpha - x^{\alpha o})^2 + (x^\beta - x^\alpha) \cdot 2K^\beta (x^\beta - x^{\beta o}) - K^\beta (x^\beta - x^{\beta o})^2 = (1 - 2f^\beta) W. \tag{16.91}$$

Equations (16.82), (16.90) and (16.91) can be used for calculating x^β, x^o and f^β for a series of x^α values at a given set of $x^{\alpha o}$, $x^{\beta o}$, K^α, K^β and W. These calculations will apply to the coherent $\alpha + \beta$ equilibrium and intuitively one could expect it to extend between the compositions where $x^o = x^\alpha$ and $x^o = x^\beta$, i.e., between $f^\beta = 0$ and $f^\alpha = 0$. This is indeed so for the symmetric case where $K^\alpha = K^\beta = K$ and it is interesting to note that the boundaries of the coherent $\alpha + \beta$ phase field fall within the ordinary $\alpha + \beta$ phase field. The result varies with the W value as illustrated in Fig. 16.10, which would be a classical T–x phase diagram if W/K varies linearly with T.

The coherent $\alpha + \beta$ two-phase field coincides with the ordinary $\alpha + \beta$ field if $W = 0$ because there are no stresses although the phases are coherent with each other. They fit together perfectly. As W/K is increased, the coherent $\alpha + \beta$ two-phase field will shrink and the two phase boundaries will finally meet in a point. A coherent $\alpha + \beta$ mixture cannot be stable above that point. The dashed line starting from that point is the well-known equal Gibbs energy curve (T_o) where, in principle, α and β could transform into each other without diffusion. Usually, such a transformation is difficult to study because the system could easily start to transform by diffusion. It may now be concluded that diffusional formation of coherent particles can be prevented if the coherency effect is strong enough. The point where the T_o line meets the two coherent phase boundaries is called Williams point after the person who first predicted such points [33]. The Williams point may be an important feature of coherent phase diagrams. The physical factor behind the Williams point is easy to understand. If the coherency effect is increased by magnifying the ΔG_m curve in Fig. 16.9 until it finally intersects the point where the two Gibbs energy curves cross. A coherent $\alpha + \beta$ mixture can be stable only when part of the ΔG_m curve falls below both Gibbs energy curves.

It should be emphasized that the lever rule cannot be applied to the two boundaries of a coherent $\alpha + \beta$ phase field because they do not represent the compositions of coexisting phases. It is evident from Fig. 16.9 that the coexisting phases must be represented by the two end-points of the parabolic ΔG_m curve because the elastic energy is evaluated from them. Due to the parallel tangent construction x^β must fall inside the ordinary β phase field if x^α falls inside the ordinary $\alpha + \beta$ phase field. The compositions of minute amounts of coherent α or β are represented by lines extending into the respective one-phase field in Fig. 16.10. The lever rule can be applied to the tie-lines between the two kinds of coherent boundaries. This is better demonstrated in Fig. 16.11 showing what should happen if one could gradually increase the average alloy content of the system. Starting from the lower left corner the system is in the α one-phase field and $x^\alpha = x^o$. At $x^o = 0.4$ the ordinary solubility limit is reached and β should start to form if there were no coherency effect. See the horizontal line at $x^\alpha = 0.4$ which is marked with 0. If there is an effect of the strength 100 $W/K = 1.2$ then coherent precipitation of β could not start until $x^o = 0.43$. A minute amount of β with composition $x^\beta = 0.63$ could form. As the average alloy content is rising further, the amount of β will grow and the alloy content of both phases will decrease gradually. The composition of the α phase will cross the ordinary phase boundary, $x^\alpha = 0.4$, when the β phase takes over the role of majority phase above $x^o = 0.5$ and most of the elastic energy will then be stored in the α phase.

If the coherency effect has the strength $100W/K = 4$, the α one-phase state will remain until the Williams point is reached at $x^o = 0.5$. On passing that point α will be fully transformed into β by a sharp transformation. However, it will occur gradually in time because the first portion of β is stable only with the composition $x^\beta = 0.7$ and the transformation will thus be rate controlled by diffusion. The alloy content of β can decrease only as the α matrix decreases its alloy content.

The result will be different for an asymmetric system, $K^\alpha \neq K^\beta$. Figure 16.12 is part of a diagram like Fig. 16.11 but calculated for $K^\alpha = 2K^\beta$. The result is shown only for 100 $W = 3K^\alpha$. As the average composition x^o is increased, minute amounts of β could start forming at $x^o = 0.465$. Due to precipitation of the solute-rich β phase, the solute

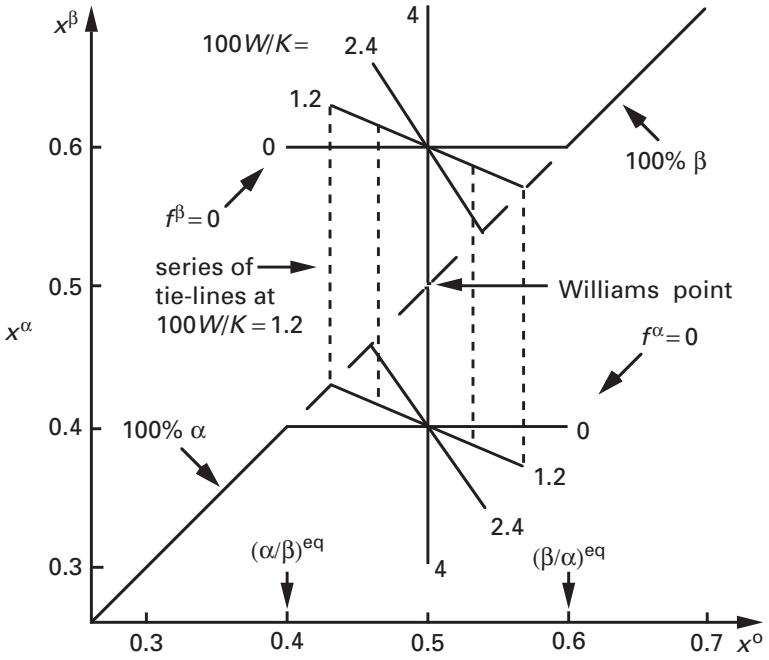

Figure 16.11 The change in composition of two coherent phases as the average composition is varied. The effect of different strengths of the coherency effect is examined.

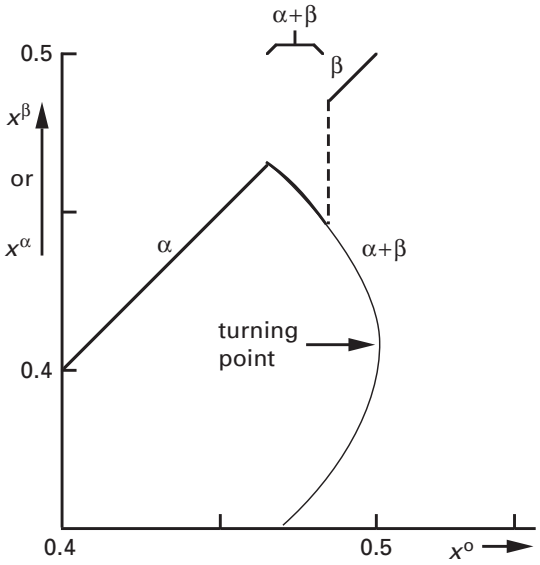

Figure 16.12 Part of a diagram like Fig. 16.11 but for an asymmetric system. According to this equilibrium diagram, the disappearance of the α phase should here be discontinuous and occur along the dashed line. In reality it may be more probable that it will happen at the point where the α + β curve turns back.

content of α will decrease as in Fig. 16.11. However, due to the asymmetry of the system, the coherent α + β mixture will soon be less stable than pure β. Thermodynamically one could expect a discontinuous change into pure β as indicated by the vertical dashed line. The phase boundary in a coherent phase diagram should thus fall on the composition of that line. Kinetically, one should expect the process to be impossible because it is difficult

to imagine a continuous path between the two states without involving intermediate states of higher energy. In practice, the system should rather follow the curve for coherent $\alpha + \beta$, which is getting steeper and finally even turns back. At higher alloy contents there is no stable $\alpha + \beta$ mixture and it has been proposed that the discontinuous change into pure β will occur spontaneously at the turning point of the $\alpha + \beta$ curve. Fig. 16.12 could as well be used to illustrate the process when one starts from pure β at the upper right corner.

It has been emphasized that the present discussion of coherent phase equilibria is based on a very simple model. Complications of large practical importance could be that the mechanical properties are anisotropic and different in the two phases and the elastic energy could depend on the composition difference. However, the existence of Williams points and discontinuous changes of the phase fractions are probably typical of coherent phase diagrams.

As another simple case one could assume that the elastic energy only depends on the difference in composition as described by Eq. (16.78) and not on a structural difference. However, then it would be logical to allow the interface to lower the elastic energy by spreading out into a diffuse transition zone between the two phases. That is actually how the theory of spinodal decomposition is constructed. As mentioned in Section 15.4 it also results in the prediction that the coherent miscibility gap is more limited than the ordinary one and the coherent spinodal thus falls inside the ordinary one.

Exercise 16.10

Sketch a diagram like Fig. 16.9 but showing the situation exactly when the coherent phase boundary is reached.

Hint

The compositions x^{α} and x^{o} should then coincide.

Solution

Accepting the parallel tangent construction, the two tangents should coincide. Figure 16.13 illustrates the only possibility for that.

16.12 Solute drag

In Section 16.9 we discussed the segregation of solute atoms to a stationary grain boundary. If the boundary starts moving, there would be a tendency of the segregated atoms to stay inside the boundary. They would thus have to diffuse with the migrating boundary and that process would dissipate Gibbs energy and consume some of the driving force for the grain boundary migration. The rate of migration would be lower than in a pure material. An alternative approach would be to consider the force that makes the segregated

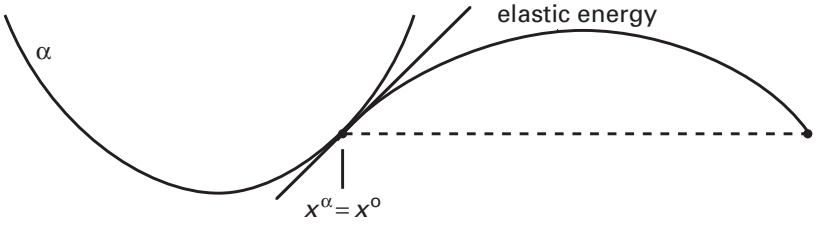

Figure 16.13 Solution to Exercise 16.10.

atoms diffuse with the boundary. It could be concluded that those atoms exert an opposite mechanical force on the grain boundary, a force that should be subtracted from the force driving the boundary migration. That approach gave rise to the term 'solute drag' for this phenomenon.

The driving force for grain boundary migration in so-called grain growth, by which the average grain size increases, derives from the surface energy of the curved grain boundary. It will thus be denoted P^σ and for a spherical boundary we have $P^\sigma = 2\sigma/r$. In a pure material this driving force will be balanced by friction connected to the grain boundary migration and also in an alloy, where the solute drag will be added.

$$P^\sigma = P^{\text{fric}} + P^{\text{s.d.}}. \tag{16.92}$$

In the thermodynamic approach to a $\beta \rightarrow \alpha$ phase transformation one first evaluates the chemical driving force acting over the interface under steady state conditions, which means that the new phase grows with a constant composition, inherited from the initial composition of the parent phase, x_i^o. When the interface is passing by, material of that composition will move to lower chemical potentials and the net effect on the interface will be

$$D^{\text{chem}} = \sum x_i^o \left(\mu_i^{\beta/\text{int}} - \mu_i^{\alpha/\text{int}}\right), \tag{16.93}$$

where $\mu_i^{\beta/\text{int}}$ and $\mu_i^{\alpha/\text{int}}$ are the chemical potentials of component i in the two phases on the sides of the interface. Together with the effect of surface energy of a curved interface, the chemical driving force will pay for the dissipation of Gibbs energy caused by friction and by diffusion of the segregated atoms. The balance of Gibbs energy will yield

$$D^{\text{chem}} + P^\sigma V_{\text{m}} = P^{\text{fric}} V_{\text{m}} + \Delta G^{\text{diff}}. \tag{16.94}$$

Two of the pressures in Eq. (16.92) appear here but multiplied by V_{m} in order to express the change of Gibbs energy per mole of material passed by the migrating interface. Comparison of Eqs (16.91) and (16.93) shows that the two approaches would yield the same result if

$$D^{\text{chem}} = \Delta G^{\text{diff}} - P^{\text{s.d.}} V_{\text{m}}. \tag{16.95}$$

There is no reason why both models should not apply to migration of grain boundaries as well as phase interfaces. When modelling ΔG^{diff} and $P^{\text{s.d.}}$ one should thus make sure that Eq. (16.95) is satisfied.

When evaluating the dissipation by diffusion inside the interface we should integrate over the width of the interface, say from $z = 0$ to δ. At each position, the segregated amount of component i is defined as $x_i - x_i^{\circ}$ and the driving force on them will be $-\mathrm{d}\mu_i/\mathrm{d}z$ under isobarothermal conditions. The flux relative to the migrating interface will be $x_i - x_i^{\circ}$ per mole of material the interface is passing through. Equation (5.94) will thus yield

$$\Delta G^{\mathrm{diff}} = -\int_0^{\delta} \sum \left(x_i - x_i^{\circ}\right) \frac{\mathrm{d}\mu_i}{\mathrm{d}z} \mathrm{d}z. \tag{16.96}$$

When evaluating the solute drag we shall also integrate over the width of the interface but we shall now consider the forces acting on all the atoms. The force on the atoms is the same as before and the opposite force on the interface will have the same magnitude but opposite direction. The solute drag will thus be

$$P^{\mathrm{s.d.}} = \frac{-1}{V_{\mathrm{m}}} \int_0^{\delta} \sum x_i \frac{\mathrm{d}\mu_i}{\mathrm{d}z} \mathrm{d}z. \tag{16.97}$$

Inserting Eqs (16.96) and (16.97) into (16.95) we find

$$\begin{aligned} D^{\mathrm{chem}} &= \Delta G^{\mathrm{diff}} - P^{\mathrm{s.d.}} V_{\mathrm{m}} = \int_0^{\delta} \sum x_i^{\circ} \frac{\mathrm{d}\mu_i}{\mathrm{d}z} \mathrm{d}z \\ &= \sum x_i^{\circ} \int_0^{\delta} \mathrm{d}\mu_i = \sum x_i^{\circ} \left(\mu_i^{\beta/\mathrm{int}} - \mu_i^{\alpha/\mathrm{int}}\right) = D^{\mathrm{chem}}. \end{aligned} \tag{16.98}$$

We may conclude that the two approaches are indeed equivalent. It may be argued that the force on the interface should only include the part of μ_i which originates from how the structure varies through the interface because that is what attracts atoms to remain inside the interface. One should thus exclude from μ_i all parts that originate from the variation of the composition. However, for those parts the Gibbs–Duhem relation yields $\sum x_i \mathrm{d}\mu_i = 0$. The only contribution to the summation in Eq. (16.97) comes from factors that depend on position and not composition. It is thus permitted and indeed convenient to evaluate the solute drag by interpreting $\mathrm{d}\mu_i/\mathrm{d}z$ as the derivative of the energy of atoms with respect to position without counting interactions from other atoms. In practice, one must first calculate how the composition varies through the interface taking all contributions to μ_i into account. It will not be very important how the solute drag is then evaluated.

It may be informative to represent the equations with molar Gibbs energy diagrams. For the mechanical approach that is done by simply dividing G_{m} with V_{m}. See Fig. 16.14(a), where the arrow representing P^{σ} points upwards because it is the force driving the process. The Gibbs energy for the parent grain has been lifted a distance $P^{\sigma} V_{\mathrm{m}}$ because it is under the influence of the surface energy as compared to the new grain. The corresponding diagram for the thermodynamic approach is more complicated (see Fig. 16.14(b)). The curves for the two grains are the same as before and their distance

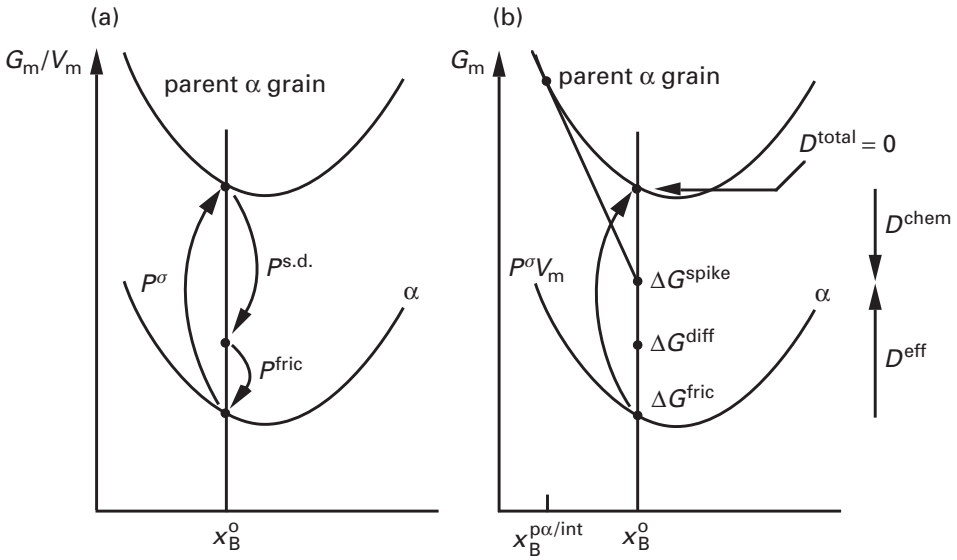

Figure 16.14 Illustration of the effect of diffusion inside a migrating grain boundary. (a) This is based on the solute drag approach and considers mechanical forces. (b) This is based on dissipation of Gibbs energy. It illustrates that a negative chemical driving force, D^{chem}, is acting on the boundary. As the boundary migrates, the material of composition x_B^o moves down the vertical line, starting from the interior of the parent grain. It first moves through the spike and then crosses the boundary.

is given by $P^\sigma V_m$. The dissipation by friction is also directly related to the corresponding force, $\Delta G^{fric} = P^{fric} V_m$, but the solute drag in Fig. 16.14(a) now corresponds to two dissipations. According to Eq. (16.95), $P^{s.d.} V_m$ should correspond to $\Delta G^{diff} - D^{chem}$, where D^{chem} is a driving force, not a dissipation. However, for grain growth there is no chemical driving force for the process because the new grain has the same structure as the parent grain and inherits its initial composition (see Fig. 16.14(b)). On the other hand, if the solute atoms are attracted to the grain boundary during its migration, then there must be a deficit of solute atoms just in front of the boundary, a negative spike. Diffusion in that spike will dissipate Gibbs energy, ΔG^{spike}. The chemical potentials on the forward side of the boundary, $\mu_i^{\beta/int}$ in Eq. (16.93), will have to be evaluated from the local composition of the parent grain, i.e., from the bottom of the negative spike. That will result in a negative driving force, D^{chem}. It can be shown that under steady state conditions it will be equal to the dissipation in the spike. The driving force for the migration, which is given by the left-hand side of Eq. (16.94), is thus lower than $P^\sigma V_m$ because D^{chem} is negative. We could write

$$D^{chem} + P^\sigma V_m = D^{eff} = \Delta G^{fric} + \Delta G^{diff}. \tag{16.99}$$

The two diagrams give equivalent results but the thermodynamic one gives a more complete picture of the process. The mechanical diagram neglects the existence of the negative spike.

Figure 16.15(a) and (b) illustrate the two approaches applied to a $\beta \rightarrow \alpha$ phase transformation. Again the thermodynamic diagram gives the more complete picture. As for grain growth in Figs 16.14(a) and (b), the new diagrams are constructed for a partitionless

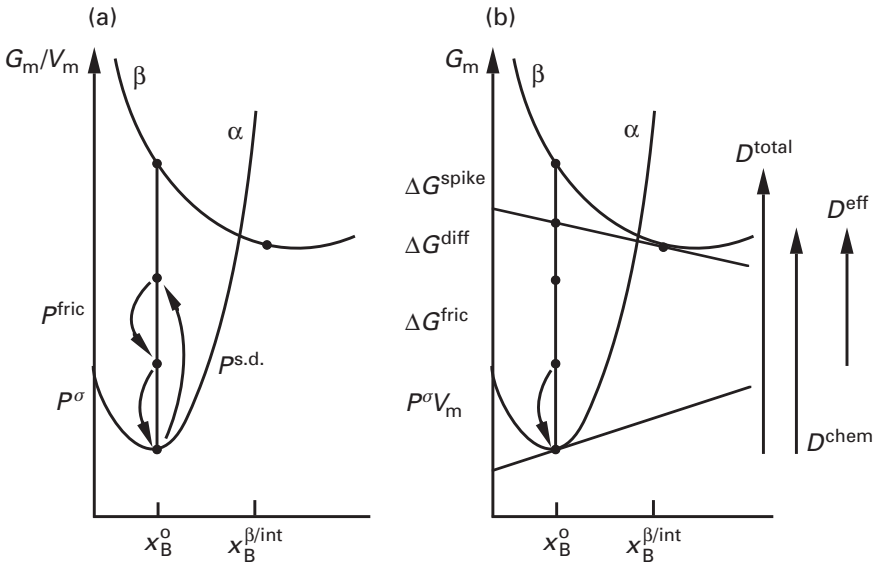

Figure 16.15 Illustration of the effect of diffusion inside a migrating phase interface. (a) This is based on the solute drag approach and considers mechanical forces. It illustrates that the so-called solute drag can act as a driving force because $P^{s.d.}$ points upwards here but downwards in Fig. 16.14(a). (b) This is based on dissipation of Gibbs energy and shows that the chemical driving force is here positive, pointing upwards. For grain growth in Fig. 16.14(b) it was negative, pointing downwards.

reaction, i.e., the new phase inherits the initial composition of the parent phase. Again there is dissipation in a spike but now there is a positive chemical driving force for the whole reaction, $D^{total} > 0$, and it is more than sufficient to balance the dissipation in the spike. There will thus be a positive chemical driving force on the interface, represented by the arrow for D^{chem} pointing upwards in Fig. 16.15(b), in contrast to grain growth where it was pointing downwards in Fig. 16.14(b). Now it is thus possible for the interface to migrate against the action of a negative curvature. The growing α phase may thus bow out into the parent β phase. To illustrate this possibility, the arrow representing $P^{\sigma} V_m$ is pointing downwards in Fig. 16.15(b).

When applying Eq. (16.99) to grain growth we found that D^{chem} was negative and the effective driving force was thus less than $P^{\sigma} V_m$. For a phase transformation $P^{\sigma} V_m$ may be positive or negative depending on how the interface is curved. In any case, the effective driving force must be equal to $\Delta G^{fric} + \Delta G^{diff}$ but how it is divided between the two depends on the detailed model of the interface, which will not be discussed here.

When applying Eq. (16.92) to a partitionless phase transformation we could rearrange the terms to make them all positive,

$$-P^{s.d.} = P^{fric} - P^{\sigma}. \tag{16.100}$$

This is illustrated in Fig. 16.15(a) and it is particularly interesting that the definition of the solute drag through Eq. (16.97) can make it negative. It has then become *a driving force instead of a drag*. Of course, the tendency of segregated atoms to stay inside the migrating interface will still act against the migration but how that is accomplished can only be explained by the thermodynamic diagram in Fig. 16.15(b).

The fact that the solute drag can turn negative and become a driving force for the migration suggests a new possibility of providing a driving force for DIGM, which is a kind of grain growth. DIGM was discussed in Section 16.10 and it was there explained that it may be driven by coherency stresses.

For low rates of migration, the segregated solute atoms can diffuse with the interface under a low dissipation of Gibbs energy. At very high rates of migration they may not be able to keep pace with the interface and the amount of segregated atoms will decrease and approach zero. After having reached a maximum at some intermediate rate, the dissipation will thus decrease and almost vanish if the remaining resistance to migration, mainly friction at high rates, is not too large. With increasing driving force, whether by a decreasing initial grain size or an increasing supersaturation, there may be a discontinuous jump from a region of low rates to a region of high rates on the other side of the maximum.

All the derivations in this section have concerned interfaces migrating under steady state conditions. The new grain or phase is thus assumed to inherit the initial composition of the parent. However, since the interfaces are extremely thin, compared to ordinary diffusion distances, the equations can also be applied to cases where there is long-range diffusion in the grains or phases. Only one modification must be made. The composition of the material passing through the interface may not be given by x_i^{o}. In Section 17.5 it will be shown that it depends on the long-range diffusion. For such cases one should substitute x_i^{tr} from Eq. (17.56) for x_i^{o} in Eqs (16.93), (16.96) and (16.98).

In summary, it may be concluded that, from a practical point of view, it is just a matter of personal taste whether to prefer the mechanical, solute drag approach or the thermodynamic, dissipative approach. On the other hand, from a physical point of view the latter alternative is preferable. In Section 16.8 it was shown that the mechanical driving force for grain growth, $P^{\sigma} = 2\sigma/r$, is not the pressure difference between the two grains. It cannot be interpreted physically until it is multiplied with a partial molar volume which is done in the dissipation approach.

Exercise 16.11

Apply Eq. (16.96) to a binary system and simplify the expression. Interpret the result physically.

Hint

Use $x_{\mathrm{A}} = 1 - x_{\mathrm{B}}$

Solution

$(x_{\mathrm{A}} - x_{\mathrm{A}}^{\mathrm{o}})\mathrm{d}\mu_{\mathrm{A}} + (x_{\mathrm{B}} - x_{\mathrm{B}}^{\mathrm{o}})\mathrm{d}\mu_{\mathrm{B}} = (x_{\mathrm{B}} - x_{\mathrm{B}}^{\mathrm{o}})\mathrm{d}(\mu_{\mathrm{B}} - \mu_{\mathrm{A}})$. Even though Eq. (16.96) concerns individual diffusion, the net result for the dissipation is the same as for interdiffusion.

17 Kinetics of transport processes

17.1 Thermal activation

Arrhenius noticed that the velocity of many reactions increases with temperature according to a simple law

$$J = K \exp(-Q/RT). \tag{17.1}$$

He proposed that the reactant molecules must be thermally activated in order to react and Q represents the activation energy. According to Boltzmann statistics, the probability of such an activation is proportional to $\exp(-Q/RT)$. Eyring *et al*. [34] introduced a frequency factor in order to predict an absolute reaction rate, kT/h, where k is Boltzmann's constant and h is Planck's constant. The kinetic coefficient in Eq. (17.1) may thus contain T as a factor. We shall accept this but shall trust experimental information for the estimate of the absolute reaction rate by adding the factor RT to the K coefficient. In general we shall consider a reaction between two states with the driving force D but with a barrier of height Q in the middle between the two states. The driving force will affect the need of activation energy and it will be $Q - D/2$ in the forward direction and $Q + D/2$ in the reverse direction. The net rate of reaction will be the difference between two opposite reactions, each one of which is described with Eq. (17.1). For low driving forces relative to RT we get

$$\begin{aligned} J &= KRT\left[\exp -\frac{Q - D/2}{RT} - \exp -\frac{Q + D/2}{RT}\right] \\ &= KRT \exp(-Q/RT) \cdot 2\sinh(D/2RT) \cong K \exp(-Q/RT) \cdot D. \end{aligned} \tag{17.2}$$

$K \exp(-Q/RT)$ is a kinetic coefficient and it is common to define it as the mobility M in a linear kinetic equation,

$$J = M \cdot D. \tag{17.3}$$

The first line of Eq. (17.2) shows that without any driving force, the two reactions would balance and the net flux would be zero. This is an example of the **principle of detailed balance**, which is supposed to hold at equilibrium for each mechanism even if there is more than one mechanism for a given reaction.

It should be emphasized that Eq. (17.2) became a linear kinetic law through the approximation of $\sinh(D/2RT)$ as $D/2RT$, which is allowed for low driving forces compared to RT. Without that approximation the model can be applied outside the linear

range. Since the driving force is expressed as D J/mol, the flux J must have the dimension mol/s because the product $J \cdot D$ would then have the dimensions J/s, which is correct for dissipation of Gibbs energy. The mobility, M, would have the dimensions mol^2/J s.

Diffusionless migration of a grain boundary. As a first application we shall examine the migration of a grain boundary in a one-component system, i.e. the interface between two crystals of the same material but different orientations. Some kind of unit of the material on one side of the grain boundary may be transferred to the other side by some deformation and rotation or individual atoms may simply jump across the interface. Those two mechanisms will be discussed further in Section 17.6. In any case, there may be an energy barrier, Q, and a driving force, D, e.g. caused by the boundary being curved. We can directly apply Eq. (17.3) with $M = M_o \exp(-Q/RT)$ but in this case it may be more convenient to express the driving force in Eq. (17.3) as D/V_m which has the dimension J/m^3, i.e. N/m^2. If the flux J is expressed as the velocity υ in m/s, then the rate of dissipation of Gibbs energy, obtained from the product of flux and driving force, will have the dimensions J/s m^2 and the rate of dissipation of Gibbs energy in J/s is obtained by multiplying with the cross-section of the grain boundary, a m^2. The mobility M would then have the dimensions m^4/J s.

$$J \equiv \upsilon = M \cdot (D/V_m). \tag{17.4}$$

For the dissipation of Gibbs energy we get from Eq. (5.133), considering the cross-section,

$$-\dot{G} = T\sigma = a\upsilon(D/V_m) = a(1/M)\upsilon^2. \tag{17.5}$$

Evidently, these equations can also be applied to the migration of a phase interface in a pure element and in an alloy if the atoms do not move individually with respect to each other, i.e. for so-called diffusionless transformations. However, it must be modified if the new grain or phase has a different composition. See Section 17.5.

Interstitial diffusion. The next application will be diffusion of an interstitial solute C, which can jump between the interstitial sites in a host lattice. During each jump a C atom has to squeeze between the neighbouring host atoms and that gives rise to an energy barrier. The kinetic equation will be very similar to the previous case but this time the rate of the process must depend on how many C atoms take part in the process. Presumably, they all take part but per mole of host atoms there is only a fraction y_C of C atoms. Furthermore, according to Section 5.7 the force for diffusion is $-\nabla(\mu_C/T)$. As T is now constant, we could consider the negative of the chemical potential gradient, $-\nabla\mu_C$, as the driving force. However, we now use a detailed model according to which the atoms exchange positions with vacancies. Their chemical potential should also be considered and also their fraction. We should thus write the kinetic equation for the exchange of positions of an interstitial atom with a vacancy as

$$J_C = -M_C y_C y_{Va} \cdot \nabla(\mu_C - \mu_{Va}). \tag{17.6}$$

In this case J_C is a real flux expressed in the lattice-fixed frame and has the dimensions mol/s m^2. If $-\nabla(\mu_C - \mu_{Va})$ is accepted as the driving force with its dimensions J/mol m, then the entropy production given by the product would have the dimensions J/s m^3,

which is correct for the dissipation of Gibbs energy per volume. The mobility would then have the dimensions $\mathrm{mol}^2/\mathrm{J\,s\,m}$.

Substitutional diffusion. Let us consider substitutional diffusion in a binary A–B solution and as a background to a more realistic case we shall now accept the less probable mechanism where atoms diffuse by exchanging positions with each other. In that special case there would be no difference between the lattice- and number-fixed frames. It seems reasonable that the diffusion of A in exchange of B across a certain plane in the system is proportional to the probability that an A and a B atom are in the correct positions on opposite sides of the plane, i.e. proportional to $x_\mathrm{A}x_\mathrm{B}$. We shall now treat the problem of activation and consider two opposite fluxes. By comparing with Eq. (17.2) it may seem reasonable to write the net flux as

$$\begin{aligned} J &= KRT\left[x'_\mathrm{A}x''_\mathrm{B}\exp-\frac{Q-D/2}{RT}-x''_\mathrm{A}x'_\mathrm{B}\exp-\frac{Q+D/2}{RT}\right] \\ &= KRT\exp\frac{-Q}{RT}\left[x'_\mathrm{A}x''_\mathrm{B}\exp\frac{D}{2RT}-x''_\mathrm{A}x'_\mathrm{B}\exp-\frac{D}{2RT}\right]. \end{aligned} \tag{17.7}$$

The two sides are identified by ($'$) and ($''$) and the driving force for the exchange of A and B is $D=-\Delta(\mu_\mathrm{A}-\mu_\mathrm{B})$. It looks as if the effects of the two opposite fluxes cannot be combined into a sinh function due to the different pre-exponential factors. However, it should be realized that the chemical potentials depend on the mole fractions of A and B, which are also present in the pre-exponential factors. In order to avoid counting their effects twice, one should not let the driving forces include the ideal entropy of mixing, which is $R\ln(x''_\mathrm{A}x'_\mathrm{B}/x'_\mathrm{A}x''_\mathrm{B})$ and $R\ln(x'_\mathrm{A}x''_\mathrm{B}/x''_\mathrm{A}x'_\mathrm{B})$, respectively. We shall thus modify Eq. (17.7),

$$\begin{aligned} J &= KRT\exp\frac{-Q}{RT}\left[x'_\mathrm{A}x''_\mathrm{B}\exp\frac{D+RT\ln(x''_\mathrm{A}x'_\mathrm{B}/x'_\mathrm{A}x''_\mathrm{B})}{2RT}\right. \\ &\qquad\left.-x''_\mathrm{A}x'_\mathrm{B}\exp-\frac{D+RT\ln(x'_\mathrm{A}x''_\mathrm{B}/x''_\mathrm{A}x'_\mathrm{B})}{2RT}\right] \\ &= KRT\exp(-Q/RT)\sqrt{x'_\mathrm{A}x''_\mathrm{B}x''_\mathrm{A}x'_\mathrm{B}}\cdot 2\sinh(D/2RT) \\ &\cong -KRT\exp(-Q/RT)x_\mathrm{A}x_\mathrm{B}\cdot\Delta(\mu_\mathrm{A}-\mu_\mathrm{B}). \end{aligned} \tag{17.8}$$

It is more convenient to express the difference $\Delta(\mu_\mathrm{A}-\mu_\mathrm{B})$ between two neighbouring sites by the gradient $\nabla(\mu_\mathrm{A}-\mu_\mathrm{B})$ multiplied with the jump distance. Including the latter in the mobility we write

$$J=-M_\mathrm{AB}x_\mathrm{A}x_\mathrm{B}\nabla(\mu_\mathrm{A}-\mu_\mathrm{B}). \tag{17.9}$$

We have here assumed that the difference in composition is very small. The flux and driving force again have the dimensions $\mathrm{mol/s\,m^2}$ and J/mol m, respectively, and their product has the dimensions $\mathrm{J/s\,m^3}$, which is correct for dissipation of Gibbs energy per volume. $M_\mathrm{AB}x_\mathrm{A}x_\mathrm{B}$ is the phenomenological coefficient and has the dimensions $\mathrm{mol^2/J\,s\,m}$.

Vacancy mechanism for diffusion. Finally, let us consider the more realistic vacancy mechanism for diffusion in a substitutional solution. The diffusion of an element by exchanging positions with vacancies or with atoms of a second element will be very

similar. We can adopt Eq. (17.6) or (17.9) with very slight modifications. The driving force will now be $-\Delta(\mu_A - \mu_{Va})$ and the crucial question is what happens to the vacancies. Contrary to vacancies in the interstitial sublattice and to atoms, vacancies in the host lattice can be generated or absorbed at crystalline defects, mainly dislocations. The frame of reference based on the lattice or on the number of atoms will thus make a difference. We shall only discuss the simplest case and assume that the mechanisms of regulating the local number of vacancies are so efficient that equilibrium is maintained everywhere. The possible gradients of μ_{Va} may thus be neglected and the driving force will simply be $-\Delta\mu_A$. The fraction of vacancies should be retained in Eq. (17.6) but expressed by the ordinary mole fraction x_{Va} instead of y_{Va}, which was a site fraction in the interstitial sublattice. In Eq. (17.9) it would replace x_B. However, for practical reasons the equilibrium fraction of vacancies may be incorporated in the M coefficient. For small composition gradients the flux of element A can thus be approximated by

$$J_A = -M_A\sqrt{x'_A x''_A}\cdot\nabla\mu_A \cong -M_A x_A\cdot\nabla\mu_A. \tag{17.10}$$

This flux is given in the lattice-fixed frame and M_A is regarded as the individual mobility of A. Its activation energy, Q, would be the sum of activation for creating vacancies and for atoms jumping into vacant sites. $M_A x_A$ corresponds to the first diagonal coefficient in the phenomenological equation for a lattice-fixed frame, L_{AA}, and again has the dimensions $\text{mol}^2/\text{J s m}$. It is evident that no coupling effects were considered in the present modelling of diffusion of A and B and it should be emphasized that correlation effects were also neglected, i.e., the fact that a reverse jump is always more probable directly after a jump because the atom and the vacancy are in the correct positions for an exchange in the reverse direction.

Diffusion in number-fixed frame. If the net effect of diffusion by the vacancy mechanism is expressed in the number-fixed frame, the net effect will be the same as if atoms exchange positions with each other. It should thus be interesting to change the description of individual diffusion by the vacancy mechanism to the number-fixed frame and compare with predictions based on interdiffusion, i.e. Eq. (17.9).

Equations (5.115) to (5.118) yield the kinetic coefficients after transformation to the number-fixed frame by inserting the value 1 for all the a parameters. By again neglecting cross coefficients in the lattice-fixed frame we obtain for the number-fixed frame in a binary system,

$$\begin{aligned} L^*_{11} = L_{11}(1-x_1)^2 + L_{22}x_1^2 &= \left(M_A x_A x_B^2 + M_B x_B x_A^2\right)/V_m \\ &= x_A x_B(x_B M_A + x_A M_B)/V_m. \end{aligned} \tag{17.11}$$

L_{11} and L_{22} were identified as $M_A x_A$ and $M_B x_B$ using Eq. (17.10). Comparison with Eq. (17.9) shows that the results may indeed be formally identical and the requirement is

$$M_{AB} = x_B M_A + x_A M_B. \tag{17.12}$$

For a formal description of interdiffusion one may thus use the number-fixed frame and from experiments one may evaluate the M_{AB} mobility without specifying or even

knowing the particular diffusion mechanism. If the individual mobilities in the lattice-fixed frame are known experimentally, then M_{AB} can be calculated from Eq. (17.12).

Exercise 17.1

Estimate at what temperature the deviation from the linear law is 100% for solidification of a pure metal.

Hint

This exercise concerns the approximation of sinh in Eq. (17.2). The entropy of *melting* for ordinary metals can be approximated to $\Delta S_m = R$. The enthalpy of *melting* can be estimated from $\Delta G_m = \Delta H_m - \Delta(TS_m) = \Delta H_m - T_0 \Delta S_m = 0$ at the melting temperature T_0.

Solution

Assuming that ΔS_m and ΔH_m are independent of temperature, the driving force for *solidification* at T will be $-\Delta G = \Delta H_m - T\Delta S_m = RT_0 - TR = R(T_0 - T)$.

When is $2\sinh[(T_0 - T)/2T] = 2(T_0 - T)/T$? A table gives $\sinh 2.18 = 4.36$. We find $T = 0.19T_0$.

Exercise 17.2

Evaluate the Kirkendall velocity in the number-fixed frame from Eq. (5.109) for a binary system in terms of the individual mobilities.

Hint

The Gibbs–Duhem relation yields $x_A d\mu_A + x_B d\mu_B = 0$ under isobarothermal conditions.

Solution

$$J_K^* = -J_A - J_B = (M_A x_A / V_m) \cdot d\mu_A/dz + (M_B x_B / V_m) \cdot d\mu_B/dz$$
$$= (M_A / V_m) \cdot x_A d\mu_A/dz + (M_B / V_m) \cdot x_B d\mu_B/dz = (1/V_m)(M_A - M_B) \cdot x_A d\mu_A/dz.$$

17.2 Diffusion coefficients

In lattice-fixed frame. In experiments on diffusion one usually studies how the composition profiles change with time and from the composition one can in principle evaluate the chemical potentials of the components and their gradients that drive the diffusion. However, it is then necessary to know the thermodynamic properties of the system,

which may not be available. It is thus more practical to regard the composition gradient as the driving force for diffusion. In a binary system there will be only one independent composition variable and only one such driving force, say $\mathrm{d}x_\mathrm{A}/\mathrm{d}z$, which is equal to $-\mathrm{d}x_\mathrm{B}/\mathrm{d}z$. By not neglecting the cross terms in the basic phenomenological equations in the lattice-fixed frame, we find by using the Gibbs–Duhem relation

$$J_\mathrm{A} = L_{\mathrm{AA}}X_\mathrm{A} + L_{\mathrm{AB}}X_\mathrm{B} = -L_{\mathrm{AA}}\nabla\mu_\mathrm{A} - L_{\mathrm{AB}}\nabla\mu_\mathrm{B} = -\left(L_{\mathrm{AA}} - L_{\mathrm{AB}}x_\mathrm{A}/x_\mathrm{B}\right)\nabla\mu_\mathrm{A}$$
$$= -\left(L_{\mathrm{AA}} - L_{\mathrm{AB}}x_\mathrm{A}/x_\mathrm{B}\right)\frac{\mathrm{d}\mu_\mathrm{A}}{\mathrm{d}x_\mathrm{A}}\frac{\mathrm{d}x_\mathrm{A}}{\mathrm{d}z} = -\frac{\mathcal{D}_\mathrm{A}}{V_\mathrm{m}}\frac{\mathrm{d}x_\mathrm{A}}{\mathrm{d}z}. \tag{17.13}$$

This defines $\mathcal{D}_\mathrm{A}$, the individual or intrinsic diffusion coefficient of component A. The molar volume, V_m, was introduced in the equation in order to give $\mathcal{D}_\mathrm{A}$ the dimensions m^2/s, the same as in an equation based on the gradient of the concentration instead of mole fraction. There is no cross coefficient in Eq. (17.13) in spite of the fact that there are two diffusion coefficients, one each for A and B, the reason being that there is only one driving force. Neglecting the cross coefficient L_{AB} we can identify L_{AA} with $M_\mathrm{A}x_\mathrm{A}$ in Eq. (17.10) and express the diffusion coefficient as

$$\frac{\mathcal{D}_\mathrm{A}}{V_\mathrm{m}} = M_\mathrm{A}x_\mathrm{A}\frac{\mathrm{d}\mu_\mathrm{A}}{\mathrm{d}x_\mathrm{A}} = M_\mathrm{A}\frac{\mathrm{d}\mu_\mathrm{A}}{\mathrm{d}\ln x_\mathrm{A}}, \tag{17.14}$$

where $\mathrm{d}\mu_\mathrm{A}/\mathrm{d}\ln x_\mathrm{A}$ is called thermodynamic factor. For dilute and ideal solutions it is equal to RT, yielding

$$\mathcal{D}_\mathrm{A} = M_\mathrm{A}V_\mathrm{m}RT. \tag{17.15}$$

It should be noticed that mobility has the dimensions $\mathrm{mol}^2/\mathrm{J\,s\,m}$ but it is more common to include V_m in the mobility, which would then have the dimensions $\mathrm{mol\,m}^2/\mathrm{J\,s}$.

Many diffusion experiments are made with radioactive isotopes. They may be used as a method of following the diffusion of an element, usually at a very low content and Eq. (17.15) then applies. It is more common to study how the radioactive atoms mix with stable atoms of the same element that are distributed homogeneously in the system. That phenomenon is regarded as self-diffusion and can also be described with Eq. (17.15) because the mixture of isotopes of the same element is extremely close to ideal. This is called a tracer diffusion experiment and the diffusion coefficient is usually denoted by $\mathcal{D}_\mathrm{A}^*$.

Of course, the thermodynamic factor cannot be evaluated without information about the thermodynamic properties and, if one likes to use such information in the analysis of experimental data, it makes no difference in practice if one uses the diffusion coefficient or the mobility. It should be emphasized that most diffusion studies only concern interdiffusion that will be discussed next. They are not sufficient for evaluating individual diffusivities like $\mathcal{D}_\mathrm{A}$.

In number- or volume-fixed frame. Considering the fact that there will be one independent force less than the number of components due to the Gibbs–Duhem relation, it may be interesting to define diffusion coefficients in the number- or volume-fixed frame where the number of independent diffusional fluxes is also one less. In order to have two independent diffusional fluxes in those frames we shall consider a ternary system with

two independent composition variables, x_A and x_B with $x_C = 1 - x_A - x_B$. The driving force is given by Eq. (5.121) and for a ternary case we obtain

$$\begin{aligned} J_A^* &= L_{AA}^* \nabla X_A^* + L_{AB}^* \nabla X_B^* = -L_{AA}^* \nabla(\mu_A - (a_A/a_C)\mu_C) - L_{AB}^* \nabla(\mu_B - (a_B/a_C)\mu_C) \\ &= -\left[L_{AA}^* \frac{d(\mu_A - (a_A/a_C)\mu_C)}{dx_A} + L_{AB}^* \frac{d(\mu_B - (a_B/a_C)\mu_C)}{dx_A} \right] \frac{dx_A}{dz} \\ &\quad -\left[L_{AA}^* \frac{d(\mu_A - (a_A/a_C)\mu_C)}{dx_B} + L_{AB}^* \frac{d(\mu_B - (a_B/a_C)\mu_C)}{dx_B} \right] \frac{dx_B}{dz}. \end{aligned} \tag{17.16}$$

The L_{ij}^* coefficients are those given by Eq. (5.115) and the asterisk is used to indicate a new set of processes. It should not be mistaken for the asterisk often used for tracer diffusion. We would like to write Eq. (17.16) as

$$J_A^* = -\frac{\mathcal{D}_{AA}}{V_m}\frac{dx_A}{dz} - \frac{\mathcal{D}_{AB}}{V_m}\frac{dx_B}{dz} \tag{17.17}$$

and similarly for J_B^*. $\mathcal{D}_{AA}$ is regarded as the chemical, mutual or interdiffusion coefficient. The value of $\mathcal{D}_{AB}$ is given by the second expression in brackets in Eq. (17.16). A similar expression is obtained for the cross coefficient $\mathcal{D}_{BA}$ but they are not equal. This is another demonstration that Onsager's reciprocal relation applies only to a set of conjugate pairs of flux and force.

For a system with n components we obtain

$$J_i^* = -\sum_{j=1}^{n-1}\sum_{k=1}^{n-1} L_{ik}^* \frac{\partial(\mu_k - (a_k/a_n)\mu_n)}{\partial x_j}\frac{dx_j}{dz} \tag{17.18}$$

$$\frac{\mathcal{D}_{ij}}{V_m} = \sum_{k=1}^{n-1} L_{ik}^* \frac{\partial(\mu_k - (a_k/a_n)\mu_n)}{\partial x_j}. \tag{17.19}$$

It should be noticed that individual diffusion coefficients, $\mathcal{D}_A$, etc., always refer to the lattice-fixed frame and interdiffusion coefficients, $\mathcal{D}_{AA}$, etc., always refer to the volume- or number-fixed frame. Furthermore, in order to avoid confusion one could give the dependent component as a superscript, e.g. $\mathcal{D}_{AA}^C$. For clarity it could also be given in the subscript for the flux, e.g. J_{A-C} because it gives the interdiffusion between A and C.

Exercise 17.3

For a binary A–B system, derive a relation between the interdiffusion coefficient in a number-fixed frame, $\mathcal{D}_{AA}$, and the individual diffusion coefficients, $\mathcal{D}_A$ and $\mathcal{D}_B$.

Hint

In the number-fixed frame all $a_i = 1$. Use the Gibbs–Duhem relation to relate $d\mu_B$ and $d(\mu_A - \mu_B)$ to $d\mu_A$.

Solution

$x_B d\mu_B = -x_A d\mu_A$; $d(\mu_A - \mu_B) = (1 + x_A/x_B)d\mu_A = (1/x_B)d\mu_A$. Equations (17.16) and (17.17) yield for a binary system $\mathcal{D}_{AA} = V_m L^*_{AA} d(\mu_A - \mu_B)/dx_A = (V_m L^*_{AA}/x_B)$ $d\mu_A/dx_A$. Insert L^*_{ii} from Eq. (17.8) as L^*_{AA}, take $\mathcal{D}_A$ from Eq. (17.14) and a similar expression for $\mathcal{D}_B$: $\mathcal{D}_{AA} = (x_B M_A + x_A M_B) \cdot x_A d\mu_A/dx_A = x_B M_A x_A d\mu_A/dx_A + x_A M_B x_B d\mu_B/dx_B = x_B \mathcal{D}_A + x_A \mathcal{D}_B$.

Exercise 17.4

Express the result for the Kirkendall velocity in a binary system, given in Exercise 17.2, in terms of the individual diffusion coefficients.

Solution

$J^*_K = (M_A/V_m)x_A d\mu_A/dz + (M_B/V_m)x_B d\mu_B/dz = (1/V_m)\mathcal{D}_A dx_A/dz + (1/V_m)$ $\mathcal{D}_B dx_B/dz = (1/V_m)(\mathcal{D}_A - \mathcal{D}_B)dx_A/dz$.

17.3 Stationary states for transport processes

A state of stationary flow through a system can be established if the system is subjected to different but constant conditions at different parts of its contact with the surroundings. We shall consider the simple case of a cylindrical system of length l where heat and some substance or substances can enter and leave the system through the two flat ends. We shall also assume that other substances cannot leave the system but can diffuse inside it. The phenomenological equations for them must give zero flux in the stationary state and for the other substances the fluxes must become constant but non-zero due to constant actions from the outside. For the case of one substance of each kind we get,

$$J_1 = (L_{11}\Delta X_1 + L_{12}\Delta X_2)/l = C_1 \tag{17.20}$$

$$J_2 = (L_{21}\Delta X_1 + L_{22}\Delta X_2)/l = 0. \tag{17.21}$$

The two ΔX are the potential differences between the ends. ΔX_1 is controlled from the outside and is assumed to be kept constant. ΔX_2 varies with time but approaches a certain value when the stationary state is being established and the J_2 flux stops. ΔX_2 is given by Eq. (17.21).

$$\Delta X_2 = -\Delta X_1 L_{21}/L_{22}. \tag{17.22}$$

Combination with Eq. (17.20) yields

$$J_1 = (L_{11}/l)(1 - L_{12}L_{21}/L_{11}L_{22})\Delta X_1 \tag{17.23}$$

Since $L_{12} = L_{21}$ and L_{11} and L_{22} must be positive, we find that the internal process, that is not directly affected by the external conditions, will decrease the flux of the other process if there is a coupling between them.

Prigogine [7] has proposed that in the stationary state of flow the diffusing substances will distribute themselves in such a way that the flow produces least entropy. This principle of minimum entropy production should apply to all transport processes, e.g. heat conduction and diffusion and can be demonstrated as follows.

Consider the transport of several substances through a cylindrical system of length l. For each substance there is a phenomenological equation

$$J_j = \sum_k L_{jk} \nabla X_k. \tag{17.24}$$

The total entropy production will be obtained by multiplying with the force and integration over the length of the system,

$$\sigma = \int \sum_j J_j \nabla X_j \mathrm{d}z = \int \sum_j \sum_k L_{jk} \nabla X_j \nabla X_k \mathrm{d}z. \tag{17.25}$$

The integration is carried out between the two sides of the system. According to Euler's equation, which is based on variation analysis, we can evaluate the distributions of all the X_i potentials through the system for which σ has an extremum. The integrand will be denoted by I and it contains the variables X_i, which are functions of z. However, in our case they enter into the integrand only as their derivatives with respect to z. For that case the Euler equation is simply

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(\frac{\mathrm{d}I}{\mathrm{d}\nabla X_j}\right) = 0. \tag{17.26}$$

From Eq. (17.25) we find if all the L_{ij} coefficients are constant,

$$\frac{\mathrm{d}I}{\mathrm{d}\nabla X_j} = 2L_{jj}\nabla X_j + \sum_k (L_{jk} + L_{kj})\nabla X_k \tag{17.27}$$

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(\frac{\mathrm{d}I}{\mathrm{d}\nabla X_j}\right) = 2L_{jj}\frac{\mathrm{d}^2 X_j}{\mathrm{d}z^2} + \sum_k (L_{jk} + L_{kj})\frac{\mathrm{d}^2 X_k}{\mathrm{d}z^2} = 0. \tag{17.28}$$

There is such an equation for each process and the solution to that system of equations is

$$\frac{\mathrm{d}^2 X_i}{\mathrm{d}z^2} = 0 \tag{17.29}$$

$$\frac{\mathrm{d}X_i}{\mathrm{d}z} = K_i, \tag{17.30}$$

where K_i is a constant for each process and it can be found by integrating over the whole length of the system. Since K_i is constant we obtain

$$K_i = \frac{\mathrm{d}X_i}{\mathrm{d}z} = \frac{\Delta X_i}{l}. \tag{17.31}$$

It is evident that this result is identical to the stationary state of flow through the system. Prigogine thus concluded that the stationary state is a state of extremum in the entropy production and, in fact, a minimum because the entropy production can never be negative. It should thus be possible to find the stationary state distribution of the potentials in the system by minimizing the entropy production if one has an analytical expression for the

dissipation of Gibbs energy, which is equal to $T\sigma$. However, it should be noted that the derivation was based on the assumption that all L_{ij} are constant.

It should be emphasized that Prigogine's extremum principle has no similarity with Onsager's, which was discussed in Section 5.9, except for the fact that they both involve a search for an extremum. Onsager's principle can be used to find how a system in a given state will change, Prigogine's principle concerns a final stationary state where there will be no more changes. It is less interesting that they also differ by Onsager's principle dealing with a maximum and Prigogine's with a minimum. The purpose of the principles is not to give information on the entropy production itself but to predict the behaviour of the system.

It has often been emphasized that Prigogine's principle is limited to cases where the phenomenological coefficients are constant. This condition is rarely fulfilled but it has been proposed that his principle could nevertheless be applied if the difference in potential over the system is small enough. This will now be tested with a simple case, that of interstitial diffusion.

For a dilute interstitial solution one may disregard the variations in y_{Va} and μ_{Va} and simplify Eq. (17.6),

$$J_{\mathrm{C}} = -M_{\mathrm{C}} y_{\mathrm{C}} \nabla \mu_{\mathrm{C}}, \tag{17.32}$$

where $M_{\mathrm{C}} y_{\mathrm{C}}$ is the phenomenological coefficient and it may vary linearly with composition. However, it is common to introduce the composition gradient using the dilute solution approximation,

$$\nabla \mu_{\mathrm{C}} \equiv \frac{\mathrm{d}\mu_{\mathrm{C}}}{\mathrm{d}z} = \frac{RT\,\mathrm{d}\ln a_{\mathrm{C}}}{\mathrm{d}z} = \frac{RT}{a_{\mathrm{C}}}\frac{\mathrm{d}a_{\mathrm{C}}}{\mathrm{d}z} \cong \frac{RT}{y_{\mathrm{C}}}\frac{\mathrm{d}y_{\mathrm{C}}}{\mathrm{d}z}. \tag{17.33}$$

We thus obtain

$$J_{\mathrm{C}} = -\mathcal{D}_{\mathrm{C}}\frac{\mathrm{d}y_{\mathrm{C}}}{\mathrm{d}z}, \tag{17.34}$$

where the diffusion coefficient is equal to RTM_{C} and may be treated as constant. However, the rate of entropy production is based on the basic phenomenological equation, Eq. (17.32) with its variable coefficient. We obtain for the dissipation

$$T\sigma = \int M_{\mathrm{C}} y_{\mathrm{C}} (\nabla \mu_{\mathrm{C}})^2 \mathrm{d}z = \int M_{\mathrm{C}} y_{\mathrm{C}} \left(\frac{RT}{y_{\mathrm{C}}}\right)^2 \left(\frac{\mathrm{d}y_{\mathrm{C}}}{\mathrm{d}z}\right)^2 \mathrm{d}z = \int \frac{\mathcal{D}RT}{y_{\mathrm{C}}} \left(\frac{\mathrm{d}y_{\mathrm{C}}}{\mathrm{d}z}\right)^2 \mathrm{d}z, \tag{17.35}$$

where $\mathcal{D} = M_{\mathrm{C}} RT$. The integral will be transformed in order to apply Euler's equation

$$\sigma = \int 4\mathcal{D}R \left(\frac{\mathrm{d}\sqrt{y_{\mathrm{C}}}}{\mathrm{d}z}\right)^2 \mathrm{d}z = \int 4\mathcal{D}R \left(\nabla\sqrt{y_{\mathrm{C}}}\right)^2 \mathrm{d}z \tag{17.36}$$

$$\frac{\mathrm{d}I}{\mathrm{d}(\nabla\sqrt{y_{\mathrm{C}}})} = 8\mathcal{D}R\nabla\sqrt{y_{\mathrm{C}}} \tag{17.37}$$

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(\frac{\mathrm{d}I}{\mathrm{d}(\nabla\sqrt{y_{\mathrm{C}}})}\right) = 8\mathcal{D}R\frac{\mathrm{d}^2\sqrt{y_{\mathrm{C}}}}{\mathrm{d}z^2} = 0 \tag{17.38}$$

$$\frac{\mathrm{d}\sqrt{y_{\mathrm{C}}}}{\mathrm{d}z} = K = \frac{\Delta\sqrt{y_{\mathrm{C}}}}{l}. \tag{17.39}$$

From Eq. (17.36) we now obtain

$$\sigma^{\min} = 4\mathcal{D}R\int K^2 \mathrm{d}z = 4\mathcal{D}RK^2 l = (4\mathcal{D}R/l)\left(\sqrt{y'_{\mathrm{C}}} - \sqrt{y''_{\mathrm{C}}}\right)^2. \quad (17.40)$$

Since it has been proposed that the minimum principle can be applied if the difference across the system is small enough, we shall start by representing the difference with

$$\varepsilon \equiv \sqrt{y''_{\mathrm{C}}/y'_{\mathrm{C}}} - 1 \quad (17.41)$$

$$\sigma^{\min} = \frac{4\mathcal{D}Ry'_{\mathrm{C}}}{l}\left(\sqrt{y''_{\mathrm{C}}/y'_{\mathrm{C}}} - 1\right)^2 = \frac{4\mathcal{D}Ry'_{\mathrm{C}}}{l}\varepsilon^2. \quad (17.42)$$

The stationary state solution yields from Eqs. (17.33) and (17.34)

$$T\sigma^{\mathrm{ss}} = -\int J_{\mathrm{C}}\nabla\mu_{\mathrm{C}}\mathrm{d}z = -J_{\mathrm{C}}\int \frac{RT}{y_{\mathrm{C}}}\frac{\mathrm{d}y_{\mathrm{C}}}{\mathrm{d}z} = \mathcal{D}_{\mathrm{C}}\frac{\Delta y_{\mathrm{C}}}{l}\cdot RT\ln\frac{y''_{\mathrm{C}}}{y'_{\mathrm{C}}} \quad (17.43)$$

$$\sigma^{\mathrm{ss}} = \frac{R\mathcal{D}_{\mathrm{C}}y'_{\mathrm{C}}}{l}\left(\frac{y''_{\mathrm{C}}}{y'_{\mathrm{C}}} - 1\right)\cdot 2\ln(1+\varepsilon) = \frac{2R\mathcal{D}_{\mathrm{C}}y'_{\mathrm{C}}}{l}((1+\varepsilon)^2 - 1)(\varepsilon - \varepsilon^2/2 + \varepsilon^3/3)$$

$$= \frac{2R\mathcal{D}_{\mathrm{C}}y'_{\mathrm{C}}}{l}(2\varepsilon^2 + \varepsilon^4/6) \quad (17.44)$$

$$(\sigma^{\min} - \sigma^{\mathrm{ss}})/\sigma^{\mathrm{ss}} = -\varepsilon^2/12 \quad (17.45)$$

The error in the entropy production will indeed be small if ε is small. However, to keep ε small is a very severe restriction for diffusion. The error may be very large if a low content is used at one end of the system.

As already stated, the minimum in entropy production itself is seldom of much interest. It should be more interesting to examine how well the principle of minimum entropy production can predict the stationary state of the system. Equation (17.34) shows that y_{C} should vary linearly through the system if $\mathcal{D}_{\mathrm{C}} = RTM_{\mathrm{C}}$ is constant but Eq. (17.39) shows that the principle predicts that $\sqrt{y_{\mathrm{C}}}$ should vary linearly. Furthermore, when evaluating the flux one must use the gradient of y_{C} and the principle would give different results from the two ends of the system. If one could accept an average one could just as well have made an estimate without studying the stationary state but using the two constant boundary conditions directly. It thus seems difficult to use this simple example for justifying the principle when the thermodynamic coefficients are not constant. On the other hand, it may not be sufficient ground for ruling out the principle in more complicated cases. Anyway, there is no justification for using it in cases that do not concern stationary states, i.e., without constant boundary conditions.

Exercise 17.5

Carry out the variation analysis for heat conduction, accepting that the phenomenological coefficient can be given as λT^2.

Hint

Remember that the force for heat conduction is $\mathrm{d}(1/T)/\mathrm{d}z$. Introduce $\mathrm{d}\ln T = (1/T)\mathrm{d}T$.

Solution

$\sigma = \int L\,(\mathrm{d}(1/T)/\mathrm{d}z)^2\,\mathrm{d}z = \int \lambda T^2(1/T^4)(\mathrm{d}T/\mathrm{d}z)^2\mathrm{d}z = \int \lambda(\mathrm{d}\ln T/\mathrm{d}z)^2\mathrm{d}z;$
$\dfrac{\mathrm{d}I}{\mathrm{d}(\mathrm{d}\ln T/\mathrm{d}z)} = 2\lambda\dfrac{\mathrm{d}\ln T}{\mathrm{d}z};\quad 2\lambda\mathrm{d}^2\ln T/\mathrm{d}z^2 = 0;\quad \mathrm{d}\ln T/\mathrm{d}z = K = \ln(T_2/T_1)/l;$
$\sigma^{\min} = \lambda(\mathrm{d}\ln T/\mathrm{d}z)^2\cdot l = (\lambda/l)\cdot(\ln T_2/T_1)^2$ and the heat flux would then be $J_Q = -\lambda\mathrm{d}T/\mathrm{d}z = -\lambda T\,\mathrm{d}\ln T/\mathrm{d}z = -(\lambda T/l)\ln(T_2/T_1)$.

17.4 Local volume change

In the following sections we shall examine what happens at the interface during a diffusional phase transformation. The material leaving one phase at the interface must be received by the other phase. The flux of component j transferred across the interface, J_j^{tr}, can thus be given in two ways:

$$J_j^{\alpha} - \frac{x_j^{\alpha}\upsilon^{\alpha/\beta}}{V_{\mathrm{m}}^{\alpha}} = J_j^{\mathrm{tr}} = J_j^{\beta} - \frac{x_j^{\beta}\upsilon^{\beta/\alpha}}{V_{\mathrm{m}}^{\beta}}, \tag{17.46}$$

where $\upsilon^{\alpha/\beta}$ and $\upsilon^{\beta/\alpha}$ are the velocities of the lattices of the two phases relative to the interface. They will generally be different because the phases may move relative to each other. All υ and J are defined as positive in the same direction, the direction from α to β. It should be emphasized that this equation is quite different from Eq. (5.110). Both are material balances but in Eq. (5.110) υ is the velocity of Kirkendall markers (or of any plane in the lattice) relative to the volume-fixed frame. J_j in Eq. (5.110) was given in the lattice-fixed frame and so are J_j^{α} and J_j^{β} in Eq. (17.46) but it should be emphasized that they are given relative to the lattice of each phase.

The difference between the two velocities will have little practical consequences in a planar case where the phases are free to move and maintain a stress free contact with each other at the interface. The situation is quite different in a two- or three-dimensional system where a maintained contact will cause stresses, which in turn will deform the material and thus create the required local change of volume. Several deformation mechanisms may be involved and result in very complex situations. They will not be further discussed here but an early treatment of the growth of spherical particles may be mentioned where elastic and plastic deformation was considered, including pressure-induced diffusion as a possible creep mechanism [35]. Here we shall only examine how the processes of ordinary diffusion will give rise to a requirement of local volume changes. Summation of Eq. (17.46) over all the components yields

$$\upsilon^{\beta/\alpha}/V_{\mathrm{m}}^{\beta} - \upsilon^{\alpha/\beta}/V_{\mathrm{m}}^{\alpha} = \Sigma J_i^{\beta} - \Sigma J_i^{\alpha}. \tag{17.47}$$

By inserting this in Eq. (17.46) we find

$$J_j^\alpha - J_j^\beta = x_j^\alpha \upsilon^{\alpha/\beta} / V_\mathrm{m}^\alpha - x_j^\beta \upsilon^{\beta/\alpha} / V_\mathrm{m}^\beta = \left(x_j^\alpha - x_j^\beta\right)\upsilon^{\alpha/\beta} / V_\mathrm{m}^\alpha - x_j^\beta \left(\Sigma J_i^\beta - \Sigma J_i^\alpha\right) \tag{17.48}$$

$$\upsilon^{\alpha/\beta} / V_\mathrm{m}^\alpha = \left[J_j^\alpha - J_j^\beta - x_j^\beta \left(\Sigma J_i^\alpha - \Sigma J_i^\beta\right)\right] / \left(x_j^\alpha - x_j^\beta\right) \tag{17.49}$$

$$\upsilon^{\beta/\alpha} / V_\mathrm{m}^\beta = \left[J_j^\alpha - J_j^\beta - x_j^\alpha \left(\Sigma J_i^\alpha - \Sigma J_i^\beta\right)\right] / \left(x_j^\alpha - x_j^\beta\right) \tag{17.50}$$

$$\begin{aligned}\Delta\upsilon &= \upsilon^{\alpha/\beta} - \upsilon^{\beta/\alpha} = V_\mathrm{m}^\alpha \cdot \upsilon^{\alpha/\beta} / V_\mathrm{m}^\alpha - V_\mathrm{m}^\beta \cdot \upsilon^{\beta/\alpha} / V_\mathrm{m}^\beta \\ &= \left[\left(V_\mathrm{m}^\alpha - V_\mathrm{m}^\beta\right)\left(J_j^\alpha - J_j^\beta\right) - \left(V_\mathrm{m}^\alpha x_j^\beta - V_\mathrm{m}^\beta x_j^\alpha\right)\left(\Sigma J_i^\alpha - \Sigma J_i^\beta\right)\right] / \left(x_j^\alpha - x_j^\beta\right).\end{aligned} \tag{17.51}$$

For a binary system the result will be

$$\Delta\upsilon = \left[\left(V_\mathrm{m}^\alpha x_\mathrm{B}^\beta - V_\mathrm{m}^\beta x_\mathrm{B}^\alpha\right)\left(J_\mathrm{A}^\alpha - J_\mathrm{A}^\beta\right) - \left(V_\mathrm{m}^\alpha x_\mathrm{A}^\beta - V_\mathrm{m}^\beta x_\mathrm{A}^\alpha\right)\left(J_\mathrm{B}^\alpha - J_\mathrm{B}^\beta\right)\right] / \left(x_\mathrm{A}^\alpha - x_\mathrm{A}^\beta\right). \tag{17.52}$$

$\Delta\upsilon$ has the dimensions of a velocity (m/s) and should here be interpreted as the requirement of volume (m^3/s) per area of the interface (m^2) in order to provide room for the concentration of material to the interface.

Exercise 17.6

Pure C as graphite may precipitate on small spherical inclusions in a solution of C in bcc–Fe. Consider the thickening of the layer of graphite. You may approximate the mole fractions of C in graphite and of Fe in bcc as 1.

Hint

Graphite will grow by a supersaturation of C in bcc diffusing to the growing particle. Diffusion in graphite and of Fe in bcc may be neglected.

Solution

Equation (17.52) yields $\Delta\upsilon = \left[\left(V_\mathrm{m}^\mathrm{graphite} \cdot 1 - 0\right)\left(0 - J_\mathrm{C}^\mathrm{bcc}\right) - \left(0 - 0\right)\left(0 - 1\right)\right] / \left(1 - 0\right) = -J_\mathrm{C}^\mathrm{bcc} V_\mathrm{m}^\mathrm{graphite}$ which is positive because the flux of C towards the particle, identified as α, is counted as negative. All the volume of the graphite has to come from deformation of the bcc matrix. When the graphite layer is still very thin, it is almost as a one-dimensional case and growth is easy. When it is much larger than the inclusion, then the graphite is situated in a spherical hole in the bcc matrix that must have been created by severe deformation of the matrix. A corresponding amount of material must have moved far away from the hole either by plastic deformation or elastic compression.

17.5 Composition of material crossing an interface

In order to evaluate the driving force for the migration of an interface through a material, it is necessary to know the composition of the material crossing the interface as a result of the migration. It can be evaluated from Eq. (17.46) as follows. Insert Eq. (17.49) in the first part of Eq. (17.46),

$$\begin{aligned} J_j^{\mathrm{tr}} &= J_j^{\alpha} - x_j^{\alpha} \upsilon^{\alpha/\beta} / V_{\mathrm{m}}^{\alpha} \\ &= \left[\left(x_j^{\alpha} - x_j^{\beta} \right) J_j^{\alpha} - x_j^{\alpha} \left(J_j^{\alpha} - J_j^{\beta} \right) + x_j^{\alpha} x_j^{\beta} \left(\Sigma J_i^{\alpha} - \Sigma J_j^{\beta} \right) \right] / \left(x_j^{\alpha} - x_j^{\beta} \right) \\ &= \left[x_j^{\alpha} \left(J_j^{\beta} - x_j^{\beta} \Sigma J_i^{\beta} \right) - x_j^{\beta} \left(J_j^{\alpha} - x_j^{\alpha} \Sigma J_i^{\alpha} \right) \right] / \left(x_j^{\alpha} - x_j^{\beta} \right) \\ &= \left(x_j^{\alpha} J_j^{\beta *} - x_j^{\beta} J_j^{\alpha *} \right) / \left(x_j^{\alpha} - x_j^{\beta} \right) \end{aligned} \tag{17.53}$$

We have here introduced the fluxes in the number-fixed frame from Eq. (5.111) with $a_i = 1$,

$$J_j^{*} = J_j - x_j \Sigma J_i \tag{17.54}$$

By instead inserting Eq. (17.49) in Eq. (17.46) after first summing over all the components, we obtain,

$$\begin{aligned} \Sigma J_j^{\mathrm{tr}} &= \Sigma J_j^{\alpha} - \upsilon^{\alpha/\beta} / V_{\mathrm{m}}^{\alpha} \\ &= \left[\left(x_j^{\alpha} - x_j^{\beta} \right) \Sigma J_j^{\alpha} - \left(J_j^{\alpha} - J_j^{\beta} \right) + x_j^{\beta} \left(\Sigma J_i^{\alpha} - \Sigma J_j^{\beta} \right) \right] / \left(x_j^{\alpha} - x_j^{\beta} \right) \\ &= \left[\left(J_j^{\beta} - x_j^{\beta} \Sigma J_i^{\beta} \right) - \left(J_j^{\alpha} - x_j^{\alpha} \Sigma J_i^{\alpha} \right) \right] / \left(x_j^{\alpha} - x_j^{\beta} \right) \\ &= \left(J_j^{\beta *} - J_j^{\alpha *} \right) / \left(x_j^{\alpha} - x_j^{\beta} \right). \end{aligned} \tag{17.55}$$

The mole fraction of component j in the transferred material is thus obtained as

$$x_j^{\mathrm{tr}} = J_j^{\mathrm{tr}} / \Sigma J_i^{\mathrm{tr}} = \left(x_j^{\alpha} J_j^{\beta *} - x_j^{\beta} J_j^{\alpha *} \right) / \left(J_j^{\beta *} - J_j^{\alpha *} \right). \tag{17.56}$$

Alternatively, we should express the result in terms of the fluxes in the lattice-fixed frame, J_j. For each phase in a binary system we should then insert a relation obtained from Eq. (17.54),

$$J_j^{*} = J_j - x_j \Sigma J_i = x_{\mathrm{B}} J_{\mathrm{A}} - x_{\mathrm{A}} J_{\mathrm{B}}. \tag{17.57}$$

It is interesting to note that it was here possible to simplify the expressions by introducing the fluxes in the number-fixed frame, not those in the volume-fixed frame (unless all $V_i = V_{\mathrm{m}}$) although Eq. (17.46) was formulated to account for changes in volume. The reason is that we have considered the flow of material across an interface with only one composition for each phase being involved.

Exercise 17.7

Examine the composition of the material crossing the liquid(α)/solid(β) interface in the following two cases of melting. (1) The dissolution of a solid stoichiometric phase into an undersaturated liquid. (2) The formation of a liquid from a solid, supersaturated with respect to the liquid phase, i.e. superheated.

Solution

In case (1) there is no diffusion in the solid phase. Equation (17.56) yields $x_j^{\mathrm{tr}} = -x_j^{\mathrm{sol}} J_j^{\mathrm{liq}*}/(-J_j^{\mathrm{liq}*}) = x_j^{\mathrm{sol}}$.

In case (2) there is no diffusion in the liquid phase, $x_j^{\mathrm{tr}} = x_j^{\mathrm{liq}} J_j^{\mathrm{sol}*}/J_j^{\mathrm{sol}*} = x_j^{\mathrm{liq}}$.

Comment: These results are self-evident. Equation (17.56) is mainly useful for intermediate cases with diffusion in both phases.

17.6 Mechanisms of interface migration

We shall now examine the role of various mechanisms of migration of a phase interface in an $\alpha \rightarrow \beta$ transformation under isothermal conditions. Fluxes in the direction α to β will be regarded as positive. The deviation from equilibrium at the interface, which provides the driving force for the interface migration, i.e., $\Delta\mu_i$ over the interface, will be defined as $\mu_i^{\beta/\alpha} - \mu_i^{\alpha/\beta}$ and α will be the A rich phase. The basic idea is that the flux of i atoms leaving one phase must enter the other one and is related to the fluxes in the two phases. In that respect it is independent of the mechanism of transfer across the interface. On the other hand, the fluxes across the interface must keep pace with the fluxes in the phases, which can only be accomplished by an effect on $\Delta\mu_i$. That will also have an effect on the fluxes in the two phases. There is thus strong coupling between the fluxes. In order to understand this complex situation we have to consider the role of the mechanisms of material transfer across the interface. In doing so, we shall first assume that there are no cross terms in the phenomenological equations.

In principle, there are two limiting cases, individual diffusion of atoms and a cooperative mechanism, which may be regarded as diffusionless. In reality there may be intermediate cases but we shall instead discuss a combination of the two if occurring simultaneously. It should be noted that the net effect of the two mechanisms of transfer must give the correct composition of the transferred material according to Eq. (17.56).

Let us start by considering individual diffusion of atoms across the interface. We can apply Eq. (17.10) but not use the approximation of almost same composition, which would be a natural approximation for diffusion inside a phase. For a phase interface it would apply only to diffusionless transformations. Furthermore, we shall apply the discontinuity in the chemical potentials, $\Delta\mu_i$. Including the thickness of the interface in its mobility, we write Eq. (17.10) as

$$J_j = M_j \sqrt{x_j^{\alpha/\beta} x_j^{\beta/\alpha}} \cdot (-\Delta\mu_j). \tag{17.58}$$

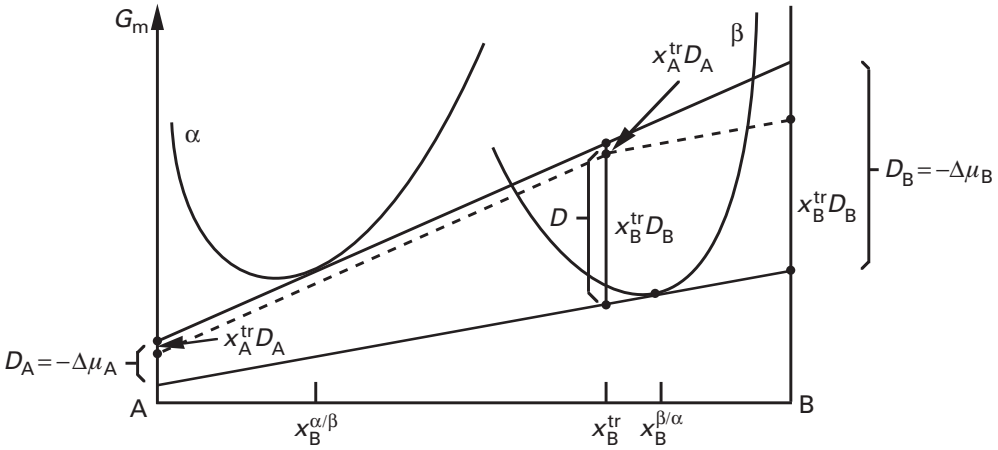

Figure 17.1 Molar Gibbs energy diagram for precipitation of β from α assuming that x_B^{tr} is the composition of the material transferred across the interface. The dissipation by diffusion of each component, counted per mole of precipitated β, is obtained by multiplying its driving force with the ratio of the fluxes, which must be equal to the mole fractions $f_j = J_j/\Sigma J_i = x_j^{tr}$. The sum of the dissipations is equal to the total driving force, D.

For a binary system this diffusion-controlled process can be illustrated with a molar Gibbs energy diagram. Figure 17.1 shows how α of composition $x_B^{\alpha/\beta}$ precipitates β of composition $x_B^{\beta/\alpha}$ and the driving forces for diffusion of A and B, $D_A = -\Delta\mu_A$ and $D_B = -\Delta\mu_B$, are given on the two sides of the diagram. The net composition of the material transferred across the interface, x_B^{tr}, depends on diffusion inside the phases as given by Eq. (17.56). The fluxes per mole of transferred material are thus x_A^{tr} and x_B^{tr} and the dissipation for each flux is obtained by multiplying with its driving force, $x_i^{tr}D_i$. The total driving force per mole, evaluated for the actual fractions of A and B, is

$$D = x_A^{tr}D_A + x_B^{tr}D_B. \tag{17.59}$$

It is evident that individual diffusion across an interface cannot describe a transfer of atoms across an interface against their own driving force, a phenomenon that has been observed and is called trapping. One way to describe that phenomenon would be to introduce a cooperative mechanism by which atoms of different components are transformed as a group. A negative driving force for some component could then be compensated by a strong driving force for another component.

As an introduction to the cooperative mechanism it is instructive again to consider the effects of individual diffusion but now expressed through a new set of processes obtained after transforming the primary set of processes. One of the new processes should be the transfer of atoms in the correct amount to equal the total transfer of atoms, $J_2^* = J_A^{tr} + J_B^{tr}$. One may regard this process as diffusionless and the diffusion, necessary for giving the correct composition to the transferred material, is achieved by the other process, interdiffusion by the exchange of A and B atoms across the interface. Its driving force could be defined as $D_1^* = D_B - D_A = -\Delta\mu_B + \Delta\mu_A$ or one could use the opposite sign.

This particular way of introducing two new processes was discussed by Eqs (5.35) to (5.40), which contained an arbitrary parameter α_{11}. Those equations were described for thermodynamic forces and can be applied to driving forces under isothermal conditions. From the definitions of forces and fluxes we now have $-\beta_{11} = 1 = \beta_{12}$ and $\alpha_{21} = 1 = \alpha_{22}$ and Eqs (5.38) to (5.40) yield $\beta_{22} = -\alpha_{11}$ and $\alpha_{12} = 1 + \alpha_{11} = \beta_{21}$. We may choose to represent $-\alpha_{11}$ with a composition x_B^*. Comparison with Eqs (5.16) and (5.26), which define the α and β coefficients, gives

$$J_1^* = \alpha_{11} J_A^{tr} + \alpha_{12} J_B^{tr} = -x_B^* J_A^{tr} + (1 - x_B^*) J_B^{tr} \tag{17.60}$$

$$D_2^* = \beta_{21} D_A + \beta_{22} D_B = (1 - x_B^*) D_A + x_B^* D_B = \Sigma x_i^* D_i. \tag{17.61}$$

For the dissipation by the interdiffusion process we thus get by using the definition of x_B^{tr} in Eq. (17.56)

$$J_1^* D_1^* = \left(- x_B^* J_A^{tr} + x_A^* J_B^{tr} \right) \left(D_B - D_A \right) = \left(- x_B^* x_A^{tr} + x_A^* x_B^{tr} \right) \left(J_A^{tr} + J_B^{tr} \right) \left(D_B - D_A \right). \tag{17.62}$$

Per mole of transferred atoms, $J_A^{tr} + J_B^{tr} = 1$, this reduces to

$$J_1^* D_1^* = \left(x_B^{tr} - x_B^* \right) \left(D_B - D_A \right). \tag{17.63}$$

The dissipation by the diffusionless process will be

$$J_2^* D_2^* = \left(J_A^{tr} + J_B^{tr} \right) \left(x_A^* D_A + x_B^* D_B \right). \tag{17.64}$$

Per mole of transferred atoms we thus get

$$J_2^* D_2^* = x_A^* D_A + x_B^* D_B. \tag{17.65}$$

This is illustrated in Fig. 17.2 where the composition of the diffusionless process, x_B^*, has been chosen arbitrarily. With that choice D_2^* is the driving force for the diffusionless process and it is also its dissipation per mole of transferred material. The dissipation by the interdiffusion process is the fraction f_1 of its driving force D_1^* where $f_1 = x_B^{tr} - x_B^*$. As in Fig. 17.1 the dissipations of the two processes will together balance the total driving force, D, but in a different way. It should again be emphasized that we are free to choose any convenient value of x_B^* because α_{11} is an arbitrary parameter.

We may now examine the cooperative mechanism. It should be recognized that on a microscale the transfer of atoms across the interface goes in both directions and the net result is given by the difference. The problem is that it should seem natural to expect from a cooperative mechanism that each phase should transfer material of its own composition to the other phase. However, the consequence for a stationary interface with no net transfer of atoms would be a net transfer of A atoms in one direction and B atoms in the other. That would not be an acceptable model. It seems necessary to accept that the two opposite fluxes carry material of the same composition. It will be denoted by x_A^{co}, x_B^{co} and it will soon be discussed by what physical factors it may be determined. The driving force for the cooperative mechanism should be given by the same expression as

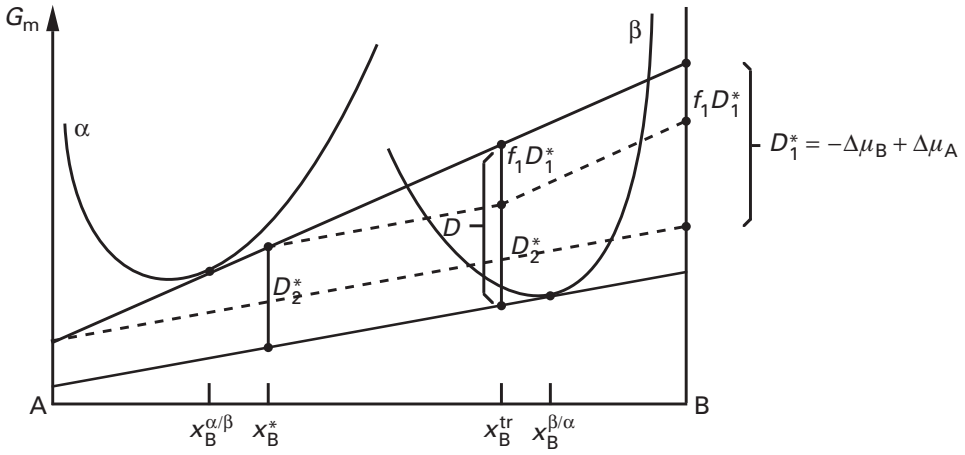

Figure 17.2 The same reaction as in Fig. 17.1 but described with a different set of processes, based on the number-fixed frame. $f_1 = x_B^{tr} - x_B^*$.

for the diffusionless process introduced by transforming the set of individual diffusion processes, Eq. (17.61). The flux would thus be

$$J^{co} = (M^{\alpha/\beta}/V_m)\sum x_i^{co} D_i. \tag{17.66}$$

The cooperative mechanism cannot be the only one unless the two phases have the same composition. In general, it will thus be necessary also to consider interdiffusion. However, it is difficult to imagine a true interdiffusion mechanism by direct exchange of A and B atoms, especially over an interface. It seems more natural to consider interdiffusion occurring by individual diffusion of atoms and those fluxes would hardly be of the same magnitude. It seems that one should combine the cooperative mechanism with individual diffusion mechanisms for A and B. For a binary system that would make three independent mechanisms. That situation is illustrated in Fig. 17.3 and it is demonstrated how the three dissipations add up and balance the total driving force.

In contrast to the diffusionless mechanism in Fig. 17.2, the dissipation by the cooperative mechanism will now be less than its driving force because only a fraction of the atoms are transferred by that mechanism,

$$f^{co} = J^{co}/(J^{co} + \Sigma J_i). \tag{17.67}$$

The overall process now has a mixed character and f^{co} represents the importance of the cooperative mechanism. It is evident that $f^{co} = 1$ can only be achieved when x_B^{co} coincides with x_B^{tr}.

One may replace the new set of two individual diffusion processes by interdiffusion and diffusionless transformation as demonstrated in Fig. 17.2. The two mechanisms would coincide in the diagram by choosing x_B^* for the new diffusionless mechanism, which is an arbitrary parameter, as x_B^{co}. It would then look much like Fig. 17.2 and, formally, one could represent the interface migration as if there were only two processes but the flux equation for the combined diffusionless and cooperative process would be more complicated than Eq. (17.66).

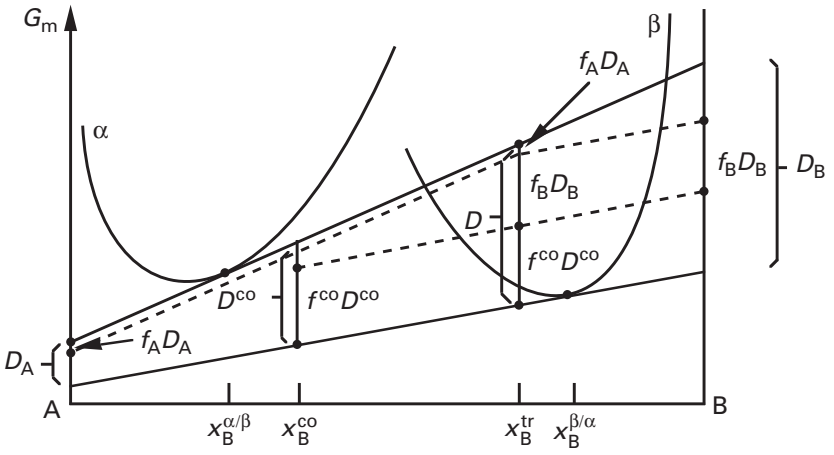

Figure 17.3 Precipitation of β from α by three processes, individual diffusion of A and B and a cooperative mechanism. The dissipations per mole of transferred atoms are obtained from each driving force multiplied by the fraction of its flux, $f_j = J_j/(J^{co} + \Sigma J_i)$.

An alternative way of reducing the net effect of the three processes to an effect of two may be preferable. One would then divide the cooperative flux on the individual components obtaining $J_j^{co} = x_j^{co} J_j$. For the total flux of component j one would then obtain

$$J_j^{total} = J_j + x_j^{co} J^{co} = \sqrt{x_j^{\alpha/\beta} x_j^{\beta/\alpha}} M_j(-\Delta\mu_j) + x_j^{co}(M^{\alpha:\beta}/V_m)\sum x_i^{co}(-\Delta\mu_i) \tag{17.68}$$

Then one could determine the composition of the cooperative mechanism by inserting Eq. (17.68) into Eq. (17.56), whose right-hand side is given by the fluxes inside the α and β phases.

We can now see from Eq. (17.68) that by adding the cooperative mechanism to the individual diffusion of the components we have actually entered cross terms into the individual phenomenological equations. It may thus seem that one could have obtained the same effect by taking cross terms into account directly without modelling any mechanism. However, there is a major difference. Through the presence of x_j^{co} and x_i^{co} Eq. (17.68), which are related to the fluxes inside the phases through Eq. (17.56), it is possible to make the cross coefficients change automatically as the growth conditions vary during a process. Furthermore, through Eq. (17.68) the cross coefficients of various components are related and the summation in Eq. (17.68) also contains a term for the component under consideration, i.e. for $i = j$, and it will also change with the growth conditions. Finally, it will also be easy to introduce a non-linear kinetic law for the cooperative part of the phase transformation by making the mobility $M^{\alpha:\beta}$ depend on the velocity.

Exercise 17.8

Prove that the introduction of the processes defined by Eqs (17.60) to (17.63) actually kept the rate of entropy production invariant.

Hint

One can add $\left(J_n - x_n \sum_k^n J_k\right)(D_n - D_n)$ which is equal to zero.

Solution

$$\begin{aligned}\sum_{i=1}^{n} J_i^* D_i^* &= \sum_{i=1}^{n-1}\left(J_i - x_i \sum_k^n J_k\right)(D_i - D_n) + \sum_{i=1}^{n} J_i \sum_k^n x_k D_k \\ &= \sum_{i=1}^{n}\left[J_i D_i - J_i D_n - x_i D_i \sum_{k=1}^{n} J_k + x_i D_n \sum_{k=1}^{n} J_k\right] + \sum_{k=1}^{n} J_k \sum_{i=1}^{n} x_i D_i \\ &= \sum_{i=1}^{n} J_i D_i - D_n \sum_{i=1}^{n} J_i - \sum_{k=1}^{n} J_k \sum_{i=1}^{n} x_i D_i \\ &\quad + D_n \sum_{k=1}^{n} J_k \sum_{i=1}^{n} x_i + \sum_{k=1}^{n} J_k \sum_{i=1}^{n} x_i D_i = \sum_{i=1}^{n} J_i D_i .\end{aligned}$$

17.7 Balance of forces and dissipation

We shall now examine how the driving forces and dissipations of Gibbs energy are balanced in a simple case of diffusional phase transformation. The equation for diffusion by the vacancy mechanism will be applied. A limited mobility of the interfaces will also be considered. Svoboda *et al*. [36] has emphasized that this is a case where it may be an advantage to apply Onsager's extremum principle from Section 5.9 because one cannot make any *a priori* assumption about the conditions at the migrating interfaces if there is friction in them and those conditions are usually required as boundary conditions for solving the diffusion equations inside the phases. We shall follow that procedure.

We shall consider a binary case where all phases have almost constant compositions and a β phase is being formed from an initial interface between an A-rich α phase and a B-rich γ phase. In α and γ there will be no diffusion. The system is shaped as a rod with a constant cross-section of a and with the α:γ interface perpendicular to the length coordinate. Because the β phase has an almost constant composition, the fluxes of A or B can at each moment be approximated as constant through the whole length of β.

First we must find the rate of change of Gibbs energy of the whole system. Gibbs energy per area a of the rod is

$$G/a = \Sigma l^{\varphi} G_{\mathrm{m}}^{\varphi} \,/\, V_{\mathrm{m}}^{\varphi} \,, \tag{17.69}$$

where l^{φ} is the length of the respective phase. The velocities of the interfaces are obtained from the time derivatives of l^{φ} and the rate of change of Gibbs energy will be

$$\frac{\dot{G}}{a} = \sum G_{\mathrm{m}}^{\varphi} \frac{\upsilon^{\varphi}}{V_{\mathrm{m}}^{\varphi}} = G_{\mathrm{m}}^{\alpha} \frac{\upsilon^{\alpha/\beta}}{V_{\mathrm{m}}^{\alpha}} - G_{\mathrm{m}}^{\beta} \frac{\upsilon^{\beta/\alpha}}{V_{\mathrm{m}}^{\beta}} + G_{\mathrm{m}}^{\beta} \frac{\upsilon^{\beta/\gamma}}{V_{\mathrm{m}}^{\beta}} - G_{\mathrm{m}}^{\gamma} \frac{\upsilon^{\gamma/\beta}}{V_{\mathrm{m}}^{\gamma}}. \tag{17.70}$$

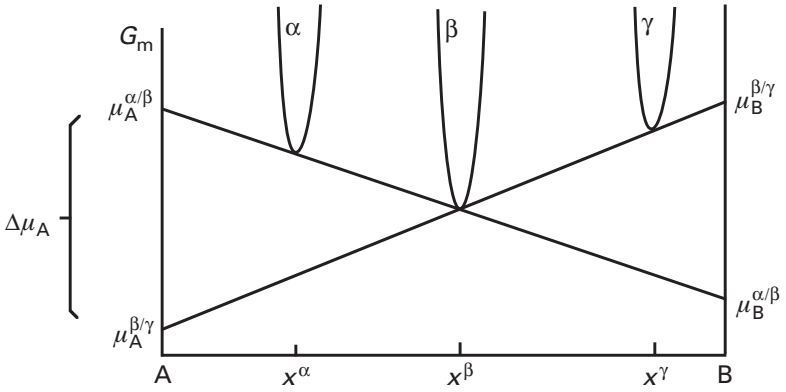

Figure 17.4 Molar Gibbs energy diagram for a system with three phases. A will diffuse from the α/β interface to the β/γ interface and B in the other direction. β will grow into both α and γ.

By inserting the velocities from Eqs (17.49) and (17.50) we can evaluate two driving forces for diffusion through the β phase, $\partial\dot{G}/\partial J_A^\beta$ and $\partial\dot{G}/\partial J_B^\beta$.

$$\frac{1}{a}\frac{\partial\dot{G}}{\partial J_A^\beta} = \frac{-G_m^\alpha x_B^\beta + G_m^\beta x_B^\alpha}{x_A^\alpha - x_A^\beta} + \frac{G_m^\beta x_B^\gamma - G_m^\gamma x_B^\beta}{x_A^\beta - x_A^\gamma}. \tag{17.71}$$

Figure 17.4 illustrates that this result can be expressed as $\Delta\mu_A = \mu_A^{\beta/\gamma} - \mu_A^{\alpha/\beta}$, where the chemical potentials are evaluated for full equilibrium between the phases across the interface, as if there were no losses in the interface. The diagram shows that $\Delta\mu_A$ is negative and we have thus a positive driving force for diffusion of A in the direction from α to γ. On the other hand, $\Delta\mu_B$ will be positive and the driving force for B would thus drive B in the opposite direction.

The rate of dissipation of Gibbs energy for a process is given by Eq. (5.133) if the cross coefficients can be neglected,

$$\phi_i = X_i J_i = (1/L_{ii})J_i^2. \tag{17.72}$$

We shall first apply this to the two individual diffusion processes. As explained below Eq. (17.6), for diffusion this is the dissipation per volume of the phase. We can easily integrate over the whole length of the β phase because the fluxes can be treated as constant, as already explained. The volume of the β phase is $a \cdot l^\beta$ and the diffusion equation, Eq. (17.10), yields for diffusion of A,

$$\phi_A = al^\beta J_A^2 / L_{AA} = al^\beta J_A^2 / M_A^\beta x_A^\beta. \tag{17.73}$$

We shall soon need the derivative with respect to the diffusion fluxes, e.g.,

$$\frac{1}{a}\frac{\partial\phi_A}{\partial J_A^\beta} = \frac{2l^\beta J_A}{M_A^\beta x_A^\beta}. \tag{17.74}$$

The present problem would have been trivial if the two diffusion processes were the only ones to consider. However, we shall also consider friction of the migrating interface caused by a cooperative mechanism. For that process one would perhaps like to apply Eq. (17.4) but there is a problem because, according to Section 17.5, there are two

different velocities depending on what lattice is used as reference. The difference is caused by the two elements having different diffusivities in the β phase. The velocity relative to the lattice of the β phase is affected by the difference resulting in a net transportation of vacancies to or from the interface. However, there is no diffusion in the α phase and the velocity relative to that lattice is caused only by the atoms crossing the interface. We shall thus use $\upsilon^{\alpha/\beta}$ from Eq. (17.49). Furthermore, there is a factor V_{m} on the right-hand side of Eq. (17.4) which may also be different for the two phases. However, it was eliminated in Eq. (17.5) although the choice of V_{m} in Eq. (17.4) has affected the value of the mobility M. The rate of dissipation of Gibbs energy due to the friction in the interface is thus obtained as

$$T\sigma_{\alpha/\beta} = \phi_{\alpha/\beta} = a\upsilon^{\alpha/\beta}\left(-\Delta G_{\mathrm{m}} \,/\, V_{\mathrm{m}}^{\alpha}\right) = a\frac{1}{M^{\alpha/\beta}}(\upsilon^{\alpha/\beta})^2 = a\frac{\left(V_{\mathrm{m}}^{\alpha}\right)^2}{M^{\alpha/\beta}}\left(\frac{\upsilon^{\alpha/\beta}}{V_{\mathrm{m}}^{\alpha}}\right)^2. \tag{17.75}$$

Comparison with Eq. (17.73) shows that the thickness of the interface has been included in the mobility. Using Eq. (17.49) we can evaluate the derivatives with respect to the fluxes,

$$\frac{1}{a}\frac{\partial\phi_{\alpha/\beta}}{\partial J_{\mathrm{A}}^{\beta}} = \frac{2\left(V_{\mathrm{m}}^{\alpha}\right)^2}{M^{\alpha/\beta}}\frac{\upsilon^{\alpha/\beta}}{V_{\mathrm{m}}^{\alpha}}\frac{-x_{\mathrm{B}}^{\beta}}{x_{\mathrm{A}}^{\alpha}-x_{\mathrm{A}}^{\beta}}. \tag{17.76}$$

We get similar equations for the β/γ interface. The complete dissipation function will be

$$\Phi = \phi_{\mathrm{A}} + \phi_{\mathrm{B}} + \phi_{\alpha/\beta} + \phi_{\beta/\gamma}. \tag{17.77}$$

We can evaluate $\partial\Phi/\partial J_{\mathrm{A}}^{\beta}$ and $\partial\Phi/\partial J_{\mathrm{B}}^{\beta}$ and Onsager's extremum principle, Eq. (5.141), yields two kinetic equations,

$$-\frac{\partial\dot{G}}{\partial J_i^{\beta}} = \frac{1}{2}\frac{\partial\Phi}{\partial J_i^{\beta}}, \tag{17.78}$$

where i is either A or B. In principle we can thus solve for J_{A}^{β} and J_{B}^{β}. We can insert the right-hand side of Eq. (17.71), which is equal to $\Delta\mu_{\mathrm{A}}$ according to Fig. 17.4, and of Eq. (17.74). By first omitting the effects of the friction in the interfaces we find

$$-\Delta\mu_{\mathrm{A}} = \frac{l^{\beta}J_{\mathrm{A}}}{M_{\mathrm{A}}^{\beta}x_{\mathrm{A}}^{\beta}}; \quad -\Delta\mu_{\mathrm{B}} = \frac{l^{\beta}J_{\mathrm{B}}}{M_{\mathrm{B}}^{\beta}x_{\mathrm{B}}^{\beta}} \tag{17.79}$$

$$J_{\mathrm{A}} = \frac{M_{\mathrm{A}}^{\beta}x_{\mathrm{A}}^{\beta}}{l^{\beta}}(-\Delta\mu_{\mathrm{A}}); \quad J_{\mathrm{B}} = -\frac{M_{\mathrm{B}}^{\beta}x_{\mathrm{B}}^{\beta}}{l^{\beta}}\Delta\mu_{\mathrm{B}}. \tag{17.80}$$

These are well-known equations obtainable by classical methods. However, the result will be more complicated by including the effects from the interfaces given by Eq. (17.76).

$$-\Delta\mu_{\mathrm{A}} = \frac{l^{\beta}J_{\mathrm{A}}^{\beta}}{M_{\mathrm{A}}^{\beta}x_{\mathrm{A}}^{\beta}} + \frac{\left(V_{\mathrm{m}}^{\alpha}\right)^2}{M^{\alpha/\beta}}\frac{\upsilon^{\alpha/\beta}}{V_{\mathrm{m}}^{\alpha}}\frac{-x_{\mathrm{B}}^{\beta}}{x_{\mathrm{A}}^{\alpha}-x_{\mathrm{A}}^{\beta}} + \frac{\left(V_{\mathrm{m}}^{\gamma}\right)^2}{M^{\beta/\gamma}}\frac{\upsilon^{\gamma/\beta}}{V_{\mathrm{m}}^{\gamma}}\frac{x_{\mathrm{B}}^{\beta}}{x_{\mathrm{A}}^{\beta}-x_{\mathrm{A}}^{\gamma}}. \tag{17.81}$$

$$J_{\mathrm{A}} = \frac{M_{\mathrm{A}}^{\beta}x_{\mathrm{A}}^{\beta}}{l^{\beta}}\left(-\Delta\mu_{\mathrm{A}} + \frac{\left(V_{\mathrm{m}}^{\alpha}\right)^2}{M^{\alpha/\beta}}\frac{\upsilon^{\alpha/\beta}}{V_{\mathrm{m}}^{\alpha}}\frac{x_{\mathrm{B}}^{\beta}}{x_{\mathrm{A}}^{\alpha}-x_{\mathrm{A}}^{\beta}} - \frac{\left(V_{\mathrm{m}}^{\gamma}\right)^2}{M^{\beta/\gamma}}\frac{\upsilon^{\gamma/\beta}}{V_{\mathrm{m}}^{\gamma}}\frac{x_{\mathrm{B}}^{\beta}}{x_{\mathrm{A}}^{\beta}-x_{\mathrm{A}}^{\gamma}}\right). \tag{17.82}$$

In the present case where β grows into both α and γ, $\upsilon^{\alpha/\beta}$ is negative and $\upsilon^{\gamma/\beta}$ is positive. Equation (17.82) demonstrates that for weak effects of friction they may both be regarded as negative corrections to the driving force, $-\Delta\mu_{\mathrm{A}}$, caused by deviations from local equilibrium at the interfaces. For stronger effects it may be more natural to regard them as dissipations of Gibbs energy as in Eq. (17.81). There may be a numerical problem because the contributions from the interfaces contain the velocities and they are functions of the fluxes. However, with computerized methods there should be no great problem.

With this example we have demonstrated that even in a case with several processes that dissipate Gibbs energy it may be possible to formulate the kinetic equations directly.

18 Methods of modelling

18.1 General principles

By 'modelling' we shall understand the selection of some assumptions from which it is possible to calculate the properties of a system. Sometimes it is possible to obtain a close mathematical expression giving a property as a function of interesting variables. In this chapter and the following ones we shall mainly concern ourselves with such models. However, in many cases the model cannot be expressed in a closed mathematical form but results can also be obtained by numerical calculations using some iterative method. When the iteration in some way resembles the behaviour of a real physical system one talks about 'simulation'. Such methods are becoming increasingly more powerful thanks to access to more and more powerful computers.

The purpose of modelling is two-fold. From a scientific point of view one likes to learn how nature functions. One way of gaining knowledge is to define some hypothesis resulting in a model and test it by comparing the predictions from the model with experimental information. Then, it does not matter much if the predictions are made by an analytical calculation or by some numerical method. From a more technological point of view one likes to predict the properties of a particular system in order to put it to efficient use in some practical construction or operation. Then it is often most convenient to have a model which yields an analytical expression.

In the simplest case, modelling is just the selection of a mathematical form which has proved useful, whether it is based on some physical model or not. However, experience shows that a model is usually more powerful if it is based upon physically sound principles. With such a model one can hope to make predictions outside the tested range with some confidence.

The first question to discuss is what thermodynamic function to model. That question will be addressed in the next section.

Exercise 18.1

Figure 18.1 shows a P, V diagram for a pure substance at a high temperature where only gas and liquid exist. Above the critical point c there is no sharp difference between the two phases. It is thus tempting to try to apply a single mathematical model for both phases but it would then give values also for one-phase states inside the two-phase field, i.e., below the thick line. Such states would be metastable or unstable. The thermodynamic

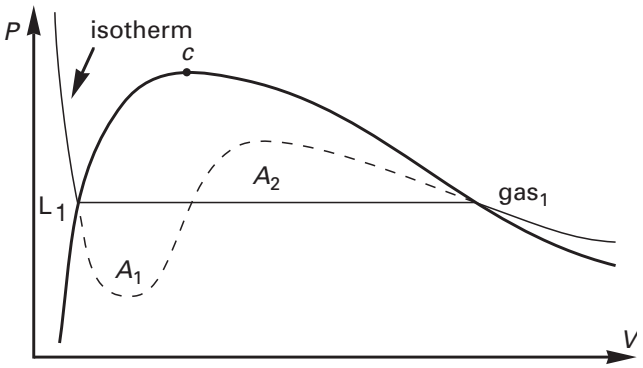

Figure 18.1 See Exercise 18.1.

properties of unstable states may be questioned but it seems reasonable at least to obey basic thermodynamic principles when constructing the model.

The thin line represents an isotherm. Show that the model must be constructed in such a way that the two areas A_1 and A_2 are equal. Actually, this is a way of identifying the equilibrium points, L_1 and gas_1, on the curve from a model that extends over the whole range (sometimes called Maxwell's construction).

Hint

Evaluate the change in Gibbs energy along the dashed line. It is an isothermal change and thus $dG = V\,dP - S\,dT = V\,dP$. Then remember that the Gibbs energy of L_1 and gas_1 must be equal because they represent two states of the same substance in equilibrium with each other at given values of P and T.

Solution

$G(gas_1) - G(L_1) = \int V\,dP = A_1 - A_2$. But $G(gas_1) = G(L_1)$. Thus, $A_1 = A_2$. This result demonstrates that satisfactory modelling is more than just choosing a mathematical expression.

18.2 Choice of characteristic state function

From a practical point of view we are most interested in models giving the Gibbs energy which has temperature and pressure as its natural variables. They are usually the most convenient experimental variables. On the other hand, the physical model itself may make a different choice more natural. An example is the effect of thermal vibrations of the atoms. The frequencies depend upon the forces between atoms which in turn, depend upon the atomic distances. In that case it is most straightforward to consider the effect under a constant volume in spite of the fact that the vibrations themselves tend to expand the system. It is thus natural to consider the Helmholtz energy. The formation of thermal vacancies is a very different case. There the physical picture is that an atom is removed

from the interior of a crystal and placed on the surface. The volume is thus increased by one lattice site. If the atomic distances are to be kept constant, it is now necessary to let the volume increase. It will thus be more straightforward to consider this process under a constant pressure and to work with the Gibbs energy. It may be emphasized that one should choose to model the internal energy only for a case where it is natural to consider entropy and volume as constant and that may be very rare. On the other hand, there may be cases where the internal energy and the volume are kept constant and one could then model the entropy.

A different question is how to model the simultaneous effects of two different phenomena. It is true that the law of additivity applies to all the extensive state functions as far as contributions from different parts of the system are concerned. However, it must be remembered that the internal energy, volume or entropy of the whole system is then the sum of the values for the parts, whereas the variables T and P are often the same in all the parts and in the whole system. If there are curved interfaces between different parts then the parts may be under different pressures and it must be remembered that the variable P in the Gibbs energy for the whole system refers to the externally applied pressure. It may then be more straightforward to consider the Helmholtz energy but, even so, one must take into account the effect of the actual pressure inside each part because it affects the molar volume.

The situation is quite different if each one of two phenomena applies to the whole system. Each phenomenon may contribute to the total pressure which may be regarded as the sum of two partial pressures but only if the two phenomena do not interact with each other. On the other hand, the two phenomena in this case refer to the same volume.

In the present chapter the discussion of modelling will simply be limited to the use of Gibbs energy.

Exercise 18.2

What would be the most natural quantity to use in a model of evaporation of a solid?

Hint

Consider which state variables should be kept constant in order to leave the bulk of the solid unaffected by the process of evaporation.

Solution

It is not convenient to require that the volume should stay constant because then one must compress the solid to make room for the vapour. The bulk will be unaffected if the pressure is kept constant. One should thus model the Gibbs energy.

18.3 Reference states

As an introduction to our discussion of the modelling of the Gibbs energy it is instructive to examine some real cases. The Gibbs energy is always given relative to some reference.

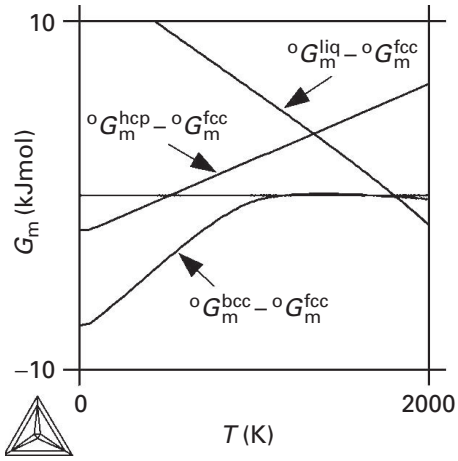

Figure 18.2 The Gibbs energy of various forms of iron, given relative to the fcc form at the same temperature and a pressure of 1 bar.

As an example, if one inquires about the Gibbs energy for the various forms of pure solid iron one may find information on all the other forms relative to the fcc form. Figure 18.2 shows how these Gibbs energy differences vary with temperature at 1 bar. It is a striking feature that such curves are often rather straight but in some regions the curvature is strong.

Since the negative slope of these curves is identical to the entropy difference between the two phases, we may conclude that the entropy difference is often rather constant. In regions of strong curvature there is a strong variation of the entropy difference and this should in turn be due to some special physical effect. The strong curvature in ${}^{o}G_{Fe}^{bcc} - {}^{o}G_{Fe}^{fcc}$ above 1000 K is due to the magnetic transition in bcc–Fe with a Curie temperature at 1043 K. It is evident that in order to model this curve one must include a description of the magnetic contribution to the Gibbs energy. Furthermore, all the curves start out parallel to the T axis at absolute zero in accordance with the third law which states that all ordered forms of a substance should approach the same entropy at absolute zero. On heating from absolute zero, a difference in entropy between the various forms develops at fairly low temperatures resulting in strong curvatures. This is due to differences in the vibration frequencies, a factor which evidently must be taken into account in modelling these curves at low temperatures. These two physical factors (magnetic and vibrational) will be discussed in some detail in Chapter 19. Except for such specific physical phenomena the Gibbs energy difference is often described with fairly simple mathematical expressions. The use of a power series in T will be described in the next section.

Before discussing the use of a power series it is useful to examine a different way of choosing the reference for the Gibbs energy. When representing the Gibbs energy for a substance as a function of T, one can use as reference the same substance at some constant T and P. As an example, Fig. 18.3 shows the Gibbs energy of graphite as a function of T at 1 bar, and three different curves are presented because three different references have been used.

It is evident that changing the choice of reference does not always displace the curve vertically; the slope may also be affected. This is due to the fact that Gibbs energy may

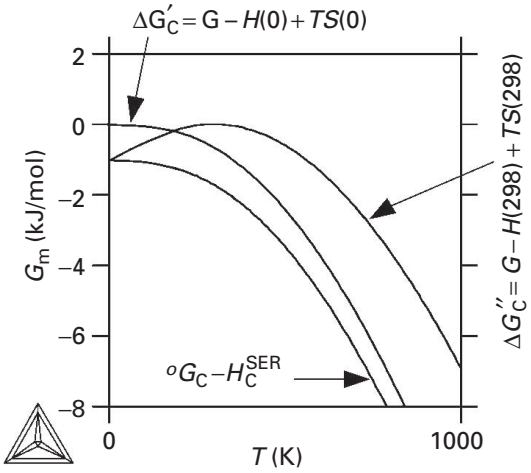

Figure 18.3 The Gibbs energy of graphite, given relative to various references. The pressure is 1 bar.

be regarded as composed of an enthalpy part and an entropy part and neither of these quantities has a natural zero point. In reality, one must define references for both. This can be done by choosing graphite of some temperature, e.g. 0 or 298.15 K. The quantities plotted with these choices are

$$\Delta^{\circ}G'_{\mathrm{C}} = {}^{\circ}G_{\mathrm{C}}(T) - {}^{\circ}H_{\mathrm{C}}(0) + T\,{}^{\circ}S_{\mathrm{C}}(0) \tag{18.1}$$

$$\Delta^{\circ}G''_{\mathrm{C}} = {}^{\circ}G_{\mathrm{C}}(T) - {}^{\circ}H_{\mathrm{C}}(298) + T\,{}^{\circ}S_{\mathrm{C}}(298), \tag{18.2}$$

where 298.15 K has been abbreviated as 298. The slope of the curves is obtained as

$$\mathrm{d}\Delta^{\circ}G'_{\mathrm{C}}/\mathrm{d}T = -{}^{\circ}S_{\mathrm{C}}(T) + {}^{\circ}S_{\mathrm{C}}(0) \tag{18.3}$$

$$\mathrm{d}\Delta^{\circ}G''_{\mathrm{C}}/\mathrm{d}T = -{}^{\circ}S_{\mathrm{C}}(T) + {}^{\circ}S_{\mathrm{C}}(298). \tag{18.4}$$

These are both satisfactory results.

It is also possible to define the references for H and S using different states. A rather popular choice is the following

$$\Delta^{\circ}G_{\mathrm{C}} = {}^{\circ}G_{\mathrm{C}}(T) - {}^{\circ}H_{\mathrm{C}}(298) + T^{\circ}S_{\mathrm{C}}(0). \tag{18.5}$$

It is usually combined with the convention to set ${}^{\circ}S_{\mathrm{C}}(0)$ to zero. The last term is thus omitted. Furthermore, ${}^{\circ}H_{\mathrm{C}}(298)$ is often chosen as the value for the element in its most stable form at 298 K and 1 bar, a quantity which is sometimes denoted by H^{SER} for stable element reference. This is why the third curve in Fig. 18.3 is identified as ${}^{\circ}G_{\mathrm{C}} - H_{\mathrm{C}}^{\mathrm{SER}}$. When no reference entropy is given, it means that one has in fact chosen ${}^{\circ}S_i(0)$ and set this quantity to zero. In any case, it is not necessary to decide on the choice of reference until one wants to put in numerical values. In the present text we shall use the notation H_i^{REF} and it mainly serves the purpose of reminding us that for each element one should normally decide on a particular choice and then stick to it. However, it is only after one has started to put in numbers that one must not change the reference.

Before leaving the discussion of reference states we should mention one more alternative. One sometimes uses $G(298)$ as reference for $G(T)$. However, $G(298)$ is just a number and could be interpreted as a reference for enthalpy chosen in such a way that $\Delta^{\circ}G_{\mathrm{C}} = 0$ at 298 K when ${}^{\circ}S_{\mathrm{C}}(0) = 0$ is the reference for entropy. This alternative may lead to misunderstandings.

For compounds we shall use the weighted average of H^{REF} for the components,

$$H^{\mathrm{REF}} = \Sigma \nu_i H_i^{\mathrm{REF}}, \tag{18.6}$$

and thus plot a quantity ΔG_{m} which is defined as $G_{\mathrm{m}} - H^{\mathrm{REF}}$. The ν_i parameters are the stoichiometric coefficients for the substance, i.e. the number of moles of each component i in one mole of the substance.

Exercise 18.3

Show how one can calculate the change of Gibbs energy on heating a substance from 273 to 373 K under a constant pressure of 1 bar. Assume C_P has a constant value.

Hint

Start by evaluating the changes in H and S separately.

Solution

$H'' - H' = \int C_P \mathrm{d}T = 100C_P$; $\quad S'' - S' = \int (C_P/T)\mathrm{d}T = C_P \ln(373.15/273.15) = 0.312C_P$; $\quad G'' - G' = H'' - 373.15S'' - H' + 273.15S' = H'' - H' - 373.15(S'' - S') - 100S' = 100C_P - 373.15 \cdot 0.312C_P - 100S' = -16.4C_P - 100S'$.

We thus find that it is necessary to have a numerical value of S at some temperature. It is not sufficient to be able to calculate the changes in H and S. The change in G also depends upon the choice of reference for S.

18.4 Representation of Gibbs energy of formation

The molar Gibbs energy of formation of a stoichiometric compound θ from the pure elements at any temperature and pressure is obtained by combining expressions for the compound and the component elements, respectively, if they are available,

$$\Delta_{\mathrm{f}}^{\circ}G_{\mathrm{m}}^{\theta} = {}^{\circ}G_{\mathrm{m}}^{\theta} - \Sigma \nu_i {}^{\circ}G_i^{\alpha}. \tag{18.7}$$

This quantity is usually regarded as the standard Gibbs energy of formation of θ and was illustrated in Fig. 7.3. The pressure is chosen as 1 bar but any one temperature can be chosen. Often one evaluates this quantity at the actual temperature of interest. ${}^{\circ}G_{\mathrm{m}}^{\theta}$ for the compound can be given for any type of formula unit. ν_i denotes the stoichiometric coefficients of the compound according to the formula unit chosen and ${}^{\circ}G_i^{\alpha}$ usually represents G_{m} for pure element i in the stable state at 1 bar and the temperature chosen.

The quantity H^{REF} which refers to a particular temperature and pressure does not enter into the equation and one could thus describe experimental information on $\Delta_{\mathrm{f}}^{\mathrm{o}}G_{\mathrm{m}}^{\theta}$ without involving H^{REF}. However, in order to evaluate ${}^{\mathrm{o}}G_{\mathrm{m}}^{\theta}$ from a tabulated value of $\Delta_{\mathrm{f}}^{\mathrm{o}}G_{\mathrm{m}}^{\theta}$ we must introduce H^{REF} through the following modification of Eq. (18.7) by the use of Eq. (18.6),

$$ {}^{\mathrm{o}}G_{\mathrm{m}}^{\theta} - H^{\mathrm{REF}} = \Delta_{\mathrm{f}}^{\mathrm{o}}G_{\mathrm{m}}^{\theta} + \Sigma \nu_i \left({}^{\mathrm{o}}G_i^{\alpha} - H_i^{\mathrm{REF}} \right). \tag{18.8} $$

The temperature dependence of ${}^{\mathrm{o}}G_i^{\alpha} - H_i^{\mathrm{REF}}$ may be known for all the components through mathematical expressions, e.g. power series in T, and stored in that way in a data bank. For the θ compound one may thus store $\Delta_{\mathrm{f}}^{\mathrm{o}}G_{\mathrm{m}}^{\theta}$ and the set of ν_{i} values, or one may store an expression for the temperature dependence of the whole right-hand side of the equation, i.e. of ${}^{\mathrm{o}}G_{\mathrm{m}}^{\theta} - H^{\mathrm{REF}}$. A drawback with the first method is that one must also store information on the particular state α for each element that $\Delta_{\mathrm{f}}^{\mathrm{o}}G_{\mathrm{m}}^{\theta}$ refers to. Furthermore, $\Delta_{\mathrm{f}}^{\mathrm{o}}G_{\mathrm{m}}^{\theta}$ will contain all the peculiarities of the states of the component elements and may thus require a complicated mathematical representation. The second method may thus be more convenient. It may be argued that for many compounds the properties are only known in a narrow range of temperatures and could thus be adequately represented by $\Delta_{\mathrm{f}}^{\mathrm{o}}G_{\mathrm{m}}^{\theta}$ using a few parameters. On the other hand, the representation of ${}^{\mathrm{o}}G_{\mathrm{m}}^{\theta} - H^{\mathrm{REF}}$ provides a better means of extrapolation because it only involves the temperature dependence of the compound itself. It thus seems that this second method should be recommended for general use although the first method may occasionally be used, especially if the experimental information is meagre. One may then use the Neumann–Kopp rule stating that the heat capacity of a substance can be estimated as an average of the values of the components. This leads to the simple expression

$$ \Delta_{\mathrm{f}}^{\mathrm{o}}G_{\mathrm{m}}^{\theta} = A + BT. \tag{18.9} $$

In the field of oxides it is common to talk about the Gibbs energy of formation of a complex oxide from its component oxides and apply the same type of expression

$$ \Delta_{\mathrm{f}}^{\mathrm{o}}G_{\mathrm{m}}^{\mathrm{complexoxide}} = {}^{\mathrm{o}}G_{\mathrm{m}}^{\mathrm{complexoxide}} - \Sigma \nu_i {}^{\mathrm{o}}G_i^{\mathrm{componentoxide}}. \tag{18.10} $$

What has here been said about compounds also applies to various states of a pure element. Using a different notation for this case we can write the equation as,

$$ {}^{\mathrm{o}}G_i^{\beta} - H_i^{\mathrm{REF}} = \Delta_{\mathrm{f}}^{\mathrm{o}}G_i^{\beta/\alpha} + {}^{\mathrm{o}}G_i^{\alpha} - H_i^{\mathrm{REF}}. \tag{18.11} $$

The quantity $\Delta_{\mathrm{f}}^{\mathrm{o}}G_i^{\beta/\alpha}$ is the Gibbs energy of formation of β from α and is often called **lattice stability** because it represents the stability of the element in a kind of lattice compared to a reference. In view of the discussion above it is recommended that ${}^{\mathrm{o}}G_i^{\beta} - H_i^{\mathrm{REF}}$ be stored rather than $\Delta_{\mathrm{f}}^{\mathrm{o}}G_i^{\beta/\alpha} = {}^{\mathrm{o}}G_i^{\beta}(T) - {}^{\mathrm{o}}G_i^{\alpha}(T)$.

Solution phases differ from stoichiometric phases by having variable composition instead of the constant stoichiometric coefficients ν_i. As a consequence, it is not practical to store the properties of solution phases as $G_{\mathrm{m}} - H^{\mathrm{REF}}$. It is more convenient first to compare with the reference states chosen for the components at the same T and P.

Usually one chooses the pure components in the same structure as the solution, the so-called end-members, and the quantity thus defined for the solution is the Gibbs energy of mixing

$$^{\mathrm{M}}G^{\alpha}_{\mathrm{m}}(x_i) = G^{\alpha}_{\mathrm{m}}(x_i) - \Sigma x_i\, {}^{\mathrm{o}}G^{\alpha}_{\mathrm{m}} \tag{18.12}$$

$$G^{\alpha}_{\mathrm{m}}(x_i) - H^{\mathrm{REF}} = {}^{\mathrm{M}}G^{\alpha}_{\mathrm{m}}(x_i) + \Sigma x_i \left({}^{\mathrm{o}}G^{\alpha}_{\mathrm{m}} - H^{\mathrm{REF}}_i\right). \tag{18.13}$$

Exercise 18.4

From a database using H^{SER} as reference, we get the following Gibbs energy values in J/mole of atoms at 1000 K: For bcc–Cr – 36 694, for C as graphite – 12 659, for Cr_7C_3 – 47 633. Calculate the standard Gibbs energy of formation of Cr_7C_3 at 1000 K.

Hint

We must trust that a database is self-consistent and always uses the same references, whether H^{SER} or another kind. We can thus forget what references this particular database uses.

Solution

$\Delta^{\mathrm{o}}_{\mathrm{f}}G^{\mathrm{Cr_7C_3}}_{\mathrm{m}} = {}^{\mathrm{o}}G^{\mathrm{Cr_7C_3}}_{\mathrm{m}} - 0.7H^{\mathrm{SER}}_{\mathrm{Cr}} - 0.3H^{\mathrm{SER}}_{\mathrm{C}} - 0.7{}^{\mathrm{o}}G^{\mathrm{bcc}}_{\mathrm{m}} + 0.7H^{\mathrm{SER}}_{\mathrm{Cr}} - 0.3{}^{\mathrm{o}}G^{\mathrm{graphite}}_{\mathrm{C}} + 0.3H^{\mathrm{SER}}_{\mathrm{C}} = {}^{\mathrm{o}}G^{\mathrm{Cr_7C_3}}_{\mathrm{m}} - 0.7{}^{\mathrm{o}}G^{\mathrm{bcc}}_{\mathrm{m}} - 0.3{}^{\mathrm{o}}G^{\mathrm{graphite}}_{\mathrm{C}} = -18150$ J/mol.

18.5 Use of power series in T

Before discussing more sophisticated models for various types of substances, it may be useful to consider the use of a power series in T and P. Let us start with terms in T. Using an ordinary power series we get

$$G_{\mathrm{m}} - H^{\mathrm{REF}} = a + bT + dT^2 + \cdots \tag{18.14}$$

$$C_P = -T\partial^2 G_{\mathrm{m}}/\partial T^2 = -2dT + \cdots. \tag{18.15}$$

Comparison with experimental data shows that this expression for C_P is not very satisfactory and the addition of higher-power terms like T^3 to G_{m} does not improve the situation much. There are strong experimental indications that one should first of all add a constant term in C_P in order to describe information from well above room temperature. That can be done by adding a term in $T \ln T$ to G_{m}:

$$G_{\mathrm{m}} - H^{\mathrm{REF}} = a + bT + cT\ln T + dT^2 \tag{18.16}$$

$$S_{\mathrm{m}} = b - c - c\ln T - 2dT \tag{18.17}$$

$$H_{\mathrm{m}} - H^{\mathrm{REF}} = a - cT - dT^2 \tag{18.18}$$

$$C_P = -c - 2dT. \tag{18.19}$$

It could be suggested that we should have written the new term as $cT\ln(T/T_0)$ in order to make the argument dimensionless. However, it is generally agreed to express T and T_0 in kelvin and to include $-cT\ln T_0$ in the bT term.

We may conclude that in the expression for a quantity, representing a contribution to the Gibbs energy, one should normally use $cT\ln T$ as the first term after a and bT. This may simply be regarded as a mathematical model for Gibbs energy which has proved itself useful. It may also be possible to justify the $T\ln T$ term by a physical model predicting that the leading term in the heat capacity should be a constant under some conditions.

When higher-power terms are needed it may seem natural to continue with a T^2 term, possibly followed by even higher powers. However, the coefficients are usually fitted to information from room temperature and up and sometimes one likes to extrapolate to temperatures above the experimental range. Terms in T^2 and T^3 may then give difficulties because they increase rapidly with temperature. For this reason, it is often preferred to use T^{-2} instead of T^2. Of course, T^{-2} will give the same kind of difficulty in extrapolations below room temperature. However, the power series is already quite inadequate at low temperatures because of the $T\ln T$ term. It is thus necessary to use at least two different mathematical descriptions, one for low temperatures and one for high. The description for low temperatures will be discussed in Chapter 19. For practical reasons, it would often be advantageous to choose 298 K as the break point. It must be noticed that special care must be taken to make H_m, S_m and C_P continuous at the break point.

18.6 Representation of pressure dependence

Let us now define a mathematical model for the pressure dependence by adding terms in P to the power series representation of the Gibbs energy of a substance

$$G_\mathrm{m} - H^\mathrm{REF} = a + bT + cT\ln T + dT^2 + \ldots + eP + fTP + gP^2 + \ldots . \tag{18.20}$$

It yields the following expressions for other quantities, if the power series is truncated.

$$C_P = -c - 2dT \tag{18.21}$$

$$V_\mathrm{m} = e + fT + 2gP \tag{18.22}$$

$$S_\mathrm{m} = -b - c - c\ln T - 2dT - fP \tag{18.23}$$

$$H_\mathrm{m} - H^\mathrm{REF} = a - cT - dT^2 + eP + gP^2 \tag{18.24}$$

$$F_\mathrm{m} - H^\mathrm{REF} = a + bT + cT\ln T + dT^2 - gP^2 \tag{18.25}$$

$$U_\mathrm{m} - H^\mathrm{REF} = a - cT - dT^2 - fTP - gP^2 \tag{18.26}$$

$$\alpha = f/V_\mathrm{m} = \frac{f}{e + fT + 2gP} \tag{18.27}$$

$$\kappa_T = -2g/V_\mathrm{m} = \frac{-2g}{e + fT + 2gP}. \tag{18.28}$$

If we only use G_m terms up to P^2, we can invert $V_\mathrm{m}(P)$ to $P(V_\mathrm{m})$ and thus replace the variable P and express the Helmholtz energy, F_m, as a function of its natural

variables:

$$F_m - H^{REF} = a + bT + cT \ln T + dT^2 - (e + fT - V_m)^2/4g. \quad (18.29)$$

On the other hand, we cannot replace T by an expression in terms of S_m if we use terms higher than bT. In general, it is thus impossible to get a closed mathematical expression for H_m or U_m as functions of their natural variables, which are (S_m, P) and (S_m, V_m), respectively.

From F_m we get

$$C_V = -T(\partial^2 F/\partial T^2)_V = -c - 2dT + f^2 T/2g. \quad (18.30)$$

The term gP^2 in G_m causes severe difficulties at high P. From the expression for V_m it is evident that g must be negative and V_m will go through zero at some high P, a result which is non-physical. Like the power series in T, a power series in P can thus be used only in a limited range.

As an example of the many alternative models suggested for the representation of the P dependence up to very high P, the following expression may be mentioned for a special reason

$$G_m - H^{REF} = a + bT + cT \ln T + dT^2 + A[(1 + nPK)^{1-1/n} - 1] \times \exp(\alpha_0 T + 0.5\alpha_1 T^2)/K(n-1). \quad (18.31)$$

It yields the following expression for the molar volume, which is a form of an equation named after Murnaghan [37].

$$V_m(T, P) = A(1 + nPK)^{-1/n} \exp(\alpha_0 T + 0.5\alpha_1 T^2). \quad (18.32)$$

It is evident that the parameter A is formally equal to the molar volume at zero T and P. Furthermore, it can be shown that K is equal to the isothermal compressibility at zero pressure and $\alpha_0 + \alpha_1 T$ can be used to represent the thermal expansivity. This model correctly predicts that the volume should decrease monotonously with increasing pressure but the volume is predicted to approach zero at infinitely high P, which is not realistic. To compensate for this one may add a constant V_0 to the expression for $V_m(T, P)$, which means that one should add a term $V_0 P$ to the G_m expression:

$$G_m - H^{REF} = a + bT + cT \ln T + dT^2 + V_0 P + [(1 + nPK)^{1-1/n} - 1] \times \exp(\alpha_0 T + 0.5\alpha_1 T^2)/K(n-1). \quad (18.33)$$

The interesting property of Murnaghan's expression for $V_m(T, P)$ is that it can be analytically solved for $P(T, V_m)$,

$$P(T, V_m) = \{A^n (V_m - V_0)^{-n} \exp[n(\alpha_0 T + 0.5\alpha_1 T^2)] - 1\}/nK. \quad (18.34)$$

This is thus a rare case where $F_m(T, V_m)$ can be derived analytically from $G_m(T, P)$,

$$F_m(T, V_m) = G_m - PV_m = H^{SER} + a + bT + cT \ln T + dT^2 + \frac{A^n (V_m - V_0)^{1-n}}{Kn(n-1)} \cdot \exp[n(\alpha_0 T + 0.5\alpha_1 T^2)] - \frac{A}{K(n-1)} \cdot \exp(\alpha_0 T + 0.5\alpha_1 T^2) + \frac{V_m - V_0}{Kn}. \quad (18.35)$$

Many models for the effect of P are formulated as an equation for P as a function of V_m. Integration yields an expression for the Helmholtz energy. If the equation can give the same P value for two different values of V_m, then it is, in principle, impossible to invert the equation to get $V_m(T, P)$ and to get the Gibbs energy by integration. There are substances which can thus be modelled by the use of the Helmholtz energy but not by using the Gibbs energy which will always give a unique V_m for each P. The critical phenomenon at the gas–liquid transition is a case which cannot be modelled by the use of a Gibbs energy expression.

Exercise 18.5

Show that K in Murnaghan's equation is equal to the isothermal compressibility at zero P.

Hint

Equation (2.37) gives $\kappa_T = -(\partial V/\partial P)_T/V$ which is equal to $-(\partial V_m/\partial P)_T/V_m$ or $-(\partial \ln V_m/\partial P)_T$.

Solution

In $V_m = \ln A - (1/n)\ln(1 + nPK) + \alpha_0 T + 0.5\alpha_1 T^2$; $\kappa_T = (1/n) \cdot 1/(1 + nPK) \cdot nK = K/(1 + nPK)$; $\kappa_T \to K$ when $P \to 0$. However, this is no longer true if we add a constant V_0 to V_m.

18.7 Application of physical models

When a particular physical effect can be identified, it could be better described with some special mathematical expression than with a power series. The power series could still be retained for the purpose of describing other effects occurring simultaneously. We may thus divide the molar Gibbs energy into two parts, one due to the special physical effect, G_m^p, and one describing a hypothetical state without that effect, G_m^h,

$$G_m = G_m^p + G_m^h \tag{18.36}$$

$$G_m - H^{REF} = G_m^h - H^{REF} + G_m^p. \tag{18.37}$$

We may apply some special expression for G_m^p and a power series for $G_m^h - H^{REF}$ and adjust the values of *a, b, c,* etc., to give a satisfactory representation of the experimental information on $G_m - H^{REF}$.

In the following chapters we shall examine a large number of different substances or phases and discuss mathematical models based upon some information on their physical or structural properties. The superscript 'p' in G_m^p will sometimes be replaced by letters referring to the particular effect under consideration.

18.8 Ideal gas

In order to demonstrate the principles of modelling, we shall now consider gases. The simplest model of a gaseous element A is defined by the following expression,

$$G_m = {}^oG_A(T, P_0) + RT \ln(P/P_0). \tag{18.38}$$

This expression is defined for one mole of gas molecules. ${}^oG_A(T, P_0)$ is the value of G_m at any temperature but at a reference pressure usually chosen as $P_0 = 1$ bar $= 100\,000$ Pa. ${}^oG_A(T, 1$ bar$)$ is usually expressed as a power series $K(T)$, including the term $-RT \ln P_0$ which is equal to $-RT \ln 10^5$ if one uses the SI unit, pascal (Pa).

$$G_m - H^{REF} = K(T) + RT \ln P. \tag{18.39}$$

It should be remembered that one must express P in the term $RT \ln P$ in the same unit that was used in evaluating $K(T)$.

Using the standard procedures we find that this mathematical model yields

$$V_m = RT/P \tag{18.40}$$

$$S_m = -K'(T) - R \ln P \tag{18.41}$$

$$F_m - H^{REF} = K(T) + RT \ln P - PV_m = K(T) - RT + RT \ln P \tag{18.42}$$

$$U_m - H^{REF} = K(T) - RT + RT \ln P + TS_m = K(T) - RT$$
$$+ RT \ln P - TK'(T) - TR \ln P = K(T) - RT - TK'(T), \tag{18.43}$$

where $K' = \mathrm{d}K/\mathrm{d}T$. This is a very useful model because it has been found that many gases have an internal energy which is a function of T but varies very little with P or V under constant T, and they also satisfy the expression for V_m very well. In fact it seems that all gases approach this model at low enough pressures.

This model is regarded as the model for an **ideal gas** and $PV_m = RT$ is called the ideal gas law. It is usually written for N moles of gas molecules (not N moles of atoms),

$$PV = NRT, \tag{18.44}$$

We can easily express the Helmholtz energy as a function of its natural variables

$$F_m - H^{SER} = K(T) - RT + RT \ln(RT/V_m). \tag{18.45}$$

It is sometimes convenient to express $K(T)$ as a power series in T and from Section 18.5 we remember that it should include a $T \ln T$ term. We may thus write the model for an ideal gas as

$$G_m - H^{REF} = a + bT + cT \ln T + dT^2 + eT^3 + \cdots + RT \ln P. \tag{18.46}$$

and by standard procedures we obtain

$$S_m = -b - c - c \ln T - 2dT - \cdots - R \ln P \tag{18.47}$$

$$V_m = RT/P \tag{18.48}$$

$$F_{\mathrm{m}} - H^{\mathrm{REF}} = a + (b - R)T + cT \ln T + dT^2 + eT^3 + \cdots + RT \ln P \tag{18.49}$$

$$H_{\mathrm{m}} - H^{\mathrm{REF}} = a - cT - dT^2 - 2eT^3 - \cdots \tag{18.50}$$

$$C_P = -c - 2dT - 6eT^2 - \cdots \tag{18.51}$$

$$U_{\mathrm{m}} - H^{\mathrm{REF}} = a - (c + R)T - dT^2 - 2eT^3 - \cdots \tag{18.52}$$

$$C_V = -c - R - 2dT - 6eT^2 - \cdots = C_P - R. \tag{18.53}$$

Sometimes one defines an **ideal classical gas** by further requiring that C_V should be independent of T, which means that *d, e* and all higher coefficients must be zero.

For monatomic gases the 'ideal classical value' of C_V is $1.5R$ and for diatomic gases it is $2.5R$. Values found experimentally for diatomic gases confirm that they can often be approximated as ideal but not as ideal classical.

Exercise 18.6

A thermally insulated container has two compartments of volumes V_1 and V_2. A gas is contained in V_1 but V_2 is empty. Suddenly, the wall between the two compartments is removed. Calculate the change in T of the gas when it has come to rest in the whole volume. Assume that the gas is ideal.

Hint

There is no exchange of heat or work with the surroundings.

Solution

The internal energy has not changed because there was no interaction with the surroundings. Since the internal energy is only a function of T and not of P, we realize that T has not changed.

18.9 Real gases

The properties of a real gas can sometimes be approximated by a model obtained by adding a power series in P to the ideal gas model in Eq. (18.39),

$$G_{\mathrm{m}} - H^{\mathrm{REF}} = K(T) + RT \ln P + LP + MP^2 + NP^3 + \cdots \tag{18.54}$$

where *L, M, N* etc., may depend on T. By standard procedures we obtain

$$V_{\mathrm{m}} = RT/P + L + 2MP + 3NP^2 \cdots \tag{18.55}$$

$$F_{\mathrm{m}} - H^{\mathrm{REF}} = G_{\mathrm{m}} - H^{\mathrm{REF}} - PV_{\mathrm{m}} = K(T) + RT \ln P - RT - MP^2 - 2NP^3 - \cdots. \tag{18.56}$$

It is evident that the V_m expression cannot be inverted to $P(V_m)$ and it is thus impossible to derive an analytical expression for $F_m(T, V_m)$. However, by using only the LP term from the power series one obtains an expression for V_m which can be inverted

$$P = RT/(V_m - L). \tag{18.57}$$

We could then express F_m in its natural variables,

$$F_m - H^{REF} = K(T) - RT + RT \ln \frac{RT}{V_m - L}. \tag{18.58}$$

A gas obeying this model is sometimes called a **slightly imperfect gas**.

It is sometimes convenient to treat real gases by introducing a new quantity f, called **fugacity**, through the expression

$$G_m - H^{SER} = K^f(T) + RT \ln f, \tag{18.59}$$

where $K^f(T)$ has been chosen in such a way that f approaches P for low P. Using this concept one can temporarily treat any gas as if it were ideal and postpone the introduction of its real properties until later. Sometimes one introduces the **fugacity coefficient**, f/P, and it is evident that it approaches the value 1 at low P. However, if this approach is applied to a gas with molecules, e.g. O_2, it should be realized that there may be some dissociation into atoms $O_2 \rightarrow 2O$ which would increase the pressure. This effect would be more pronounced at low pressures. The concept of fugacity should thus be applied to each gas species separately but it must then be combined with a calculation of the equilibrium contents of the species.

So far we have based the modelling of gases on the Gibbs energy, using T and P as the variables. However, it is sometimes more convenient to use T and V_m as the variables and thus to define the model using the Helmholtz energy. One may for instance define a model with the following expression where $K(T)$ is not the same as before,

$$F_m - H^{REF} = K(T) + RT\left[- \ln V_m + B_2/V_m + B_3/2V_m^2 + \cdots \right], \tag{18.60}$$

which gives

$$P = RT[1/V_m + B_2/V_m^2 + B_3/V_m^3 + \cdots], \tag{18.61}$$

where B_2, B_3, etc., are called virial coefficients. There is no exact relation between these coefficients and those introduced through the G_m expression, but in order to compare them we can write the expressions in the following forms

$$PV_m = RT + LP + 2MP^2 + 3NP^3 + \cdots. \tag{18.62}$$

$$PV_m = RT + RTB_2/V_m + RTB_3/V_m^2 + \cdots. \tag{18.63}$$

For small values of the coefficients, we may first approximate $1/V_m$ by P/RT. By introducing this in the second term in Eq. (18.63) and dropping the last term we get

$$PV_m = RT + RTB_2P/RT = RT + B_2P. \tag{18.64}$$

We can use

$$1/V_m = 1/(RT/P + B_2) = (P/RT)/(1 + B_2P/RT) \cong P/RT - B_2(P/RT)^2. \tag{18.65}$$

as a better approximation. By introducing this we get

$$PV_m = RT + B_2P + (B_3 - B_2^2)P^2/RT, \tag{18.66}$$

when omitting higher-order terms. Comparing with Eq. (18.62) we may thus approximate L as B_2 and M as $(B_3 - B_2^2)/2RT$.

Another model based on $F_m(T, V_m)$ is the following

$$F_m - H^{REF} = K(T) - a/V_m - RT\ln(V_m - b). \tag{18.67}$$

It gives

$$P = -a/V_m^2 + RT/(V_m - b), \tag{18.68}$$

which can be rearranged into

$$\left(P + a/V_m^2\right)(V_m - b) = RT. \tag{18.69}$$

This expression was proposed by van der Waals. The terms a/V_m^2 and $-b$ may be regarded as corrections to the ideal gas law. This expression correctly predicts that there is a critical point below which a system decomposes into a liquid and a gas. However, it does not describe real systems with any accuracy. Many improvements of the van der Waals equation have been suggested but they will not be discussed here.

Exercise 18.7

Derive an expression for the fugacity of a gas obeying the van der Waals equation of state. Then calculate the fugacity coefficient, f/P.

Hint

$G_m - H^{REF} = F_m - H^{REF} + PV_m = K(T) - a/V_m - RT\ln(V_m - b) - a/V_m + RTV_m/(V_m - b)$ should be compared with $G_m - H^{REF} = K^f(T) + RT\ln f$.

At small P, and thus large V_m, the two expressions should be equal if f is replaced by P.

For large V_m we find that $G_m - H^{REF}$ goes towards $K(T) - RT\ln RT + RT\ln P + RT$. We should thus identify $K^f(T)$ with $K(T) - RT\ln RT + RT$.

Solution

For any P we can write $K(T) - RT\ln RT + RT + RT\ln f = K(T)2a/V_m - RT\ln(V_m - b) + RTV_m/(V_m - b)$ and get $RT\ln f = -RT\ln[(V_m - b)/RT] + RTb/(V_m - b) - 2a/V_m$.

This yields $f = RT/(V_m - b)\cdot\exp[b/(V_m - b) - 2a/RTV_m]$. By dividing with $P = -a/V_m^2 + RT/(V_m - b)$ we finally find $f/P = [1 - a(V_m - b)/RTV_m^2]^{-1}\cdot\exp[b/(V_m - b) - 2a/RTV_m]$.

18.10 Mixtures of gas species

Gases dissolve in each other so readily and with so little interaction that the resulting phase is regarded as a mixture of the component species (free atoms, molecules and ions). In principle, it may also be regarded as a solution. We shall first discuss a mixture of several species, each one of which forms an ideal gas when pure. Let y_k be the fraction of species k and thus $\sum y_k = 1$. Let us consider a mixture of one mole of species. Each gas will fill the complete volume V, but in line with the ideal gas concept we shall assume that there is no interaction between them. We shall thus assume that the ideal gas law applies to the mixture, $PV_m = RT$, and that the chemical potential of a component k, μ_k, has the same value it would have, had it been alone in the same volume V. The pressure of that component would then be $P_k = y_k RT/V = y_k P$ where P is the pressure of the mixture

$$\begin{aligned}\mu_k &= G_m(k) = {}^{o}G_k(T, P_0) + RT \ln P_k \\ &= H_k^{REF} + K_k(T) + RT \ln P_k = H^{REF} + K_k(T) + RT \ln y_k + RT \ln P,\end{aligned} \tag{18.70}$$

and we get for the mixture

$$\begin{aligned}G_m &= \Sigma y_i \mu_i = \Sigma y_i^{o} G_i(T, P_0) + RT \Sigma y_i \ln P_i \\ &= H^{REF} + \Sigma y_i K_i(T) + RT \Sigma y_i \ln y_i + RT \ln P \qquad (18.71)\\ G_m - H^{REF} &= \Sigma y_i K_i(T) + RT \ln P + RT \Sigma y_i \ln y_i. \qquad (18.72)\end{aligned}$$

The last term may be regarded as the contribution from the mixing of different molecules. It is proportional to T and is thus of pure entropy character. $-R\Sigma y_i \ln y_i$ may be regarded as the ideal entropy of mixing.

For a mixture of ideal gases it can be imagined that gas k actually has the pressure P_k in the gas mixture and that the total pressure of the mixture is the sum of the pressures of the individual gases. We have thus used

$$\Sigma P_i = \Sigma y_i P = P. \tag{18.73}$$

P_k is regarded as the **partial pressure** of gas k in the mixture. It is interesting to note that the expression for ideal entropy of mixing appears in Eq. (18.72) as a direct result of the model. For real gases it is no longer possible to define the partial pressure in a strict sense but it is common to use this concept and the relation $P_i = y_i P$ even in such cases. As a first attempt to model G_m for a mixture of real gases, one could add the terms for slightly imperfect gases in the form $\Sigma y_i L_i P_i$ which can be written as $\Sigma y_i^2 L_i P$ The second power of y_i indicates that these terms describe the interaction of molecules with other molecules of the same kind. It would be natural also to add terms representing interactions between different kinds of molecules, $\Sigma\Sigma y_i y_j L_{ij} P$. We thus get

$$G_m - H^{REF} = \Sigma y_i K_i(T) + RT \ln P + RT \Sigma y_i \ln y_i + P\Sigma\Sigma y_i y_j L_{ij} \tag{18.74}$$

It is interesting to calculate what pressure, P', the same amount of gas k would have if it were alone in the same volume. For pure k we get

$$^{\circ}G_k - H_k^{\mathrm{REF}} = K_k(T) + RT \ln P' + P' L_{kk}. \tag{18.75}$$

The molar volume would be $RT/P' + L_{kk}$ and the volume of the actual amount y_k would be

$$V = y_k(RT/P' + L_{kk}). \tag{18.76}$$

However, this is supposed to be equal to the molar volume of the mixture,

$$y_k(RT/P' + L_{kk}) = RT/P + \Sigma\Sigma y_i y_j L_{ij}. \tag{18.77}$$

We thus find

$$\begin{aligned} 1/P' &= 1/y_k P + \left(\Sigma\Sigma y_i y_j L_{ij} - y_k L_{kk}\right)/RTy_k \\ &= 1/P_k + \left(\Sigma\Sigma y_i y_j L_{ij} - y_k L_{kk}\right)/RTy_k. \end{aligned} \tag{18.78}$$

We have here expressed $y_k P$ through the partial pressure and it is evident that it is no longer equal to the pressure of the same amount of pure k, unless all the interactions are zero. The concept of partial pressure is thus less useful for real gas mixtures than for ideal ones. The concept of fugacity is more useful. For a component k in a mixture it is defined from

$$\mu_k - H^{\mathrm{REF}} = K_k(T) + RT \ln f_k, \tag{18.79}$$

where K_k(T) is formulated in such a way that f_k approaches $y_k P$ for low P. In order to evaluate the fugacity from a particular model one must first derive an expression for μ_k from the model. From Eq. (18.74) we get

$$\mu_k - H^{\mathrm{REF}} = K_k(T) + RT \ln(y_k P) + P\left(2y_k \Sigma L_{kj} - \Sigma\Sigma y_i y_j L_{ij}\right), \tag{18.80}$$

and for the fugacity coefficient we obtain

$$f_k/P_k = f_k/y_k P = \exp[P(2y_k \Sigma L_{kj} - \Sigma\Sigma y_i y_j L_{ij})/RT]. \tag{18.81}$$

For an ideal gas mixture we get

$$f_k/P_k = f_k/y_k P = 1. \tag{18.82}$$

A similar model based upon the Helmholtz energy is generally written as

$$\begin{aligned} P &= RT\left[1/V_{\mathrm{m}} + \left(\Sigma y_i^2 B_{ii} + \Sigma\Sigma y_i y_j B_{ij}\right)/V_{\mathrm{m}}^2\right] \\ &= RT\left[1/V_{\mathrm{m}} + \left(\Sigma y_i B_{ii} + \Sigma\Sigma y_i y_j \left(B_{ij} - \left(B_{ii} + B_{jj}\right)/2\right)\right)/V_{\mathrm{m}}^2\right] \end{aligned} \tag{18.83}$$

and it is often found that $B_{ij} - (B_{ii} + B_{jj})/2$ is small.

Exercise 18.8

Examine a slightly imperfect gas with two kinds of molecules, A and B. Is there any relation between the L coefficients which would make the fugacity coefficients independent of the composition?