

Furthermore, $2\text{CO} \rightarrow 2\text{C} + \text{O}_2$ (4) is also a dependent reaction. It can be obtained as $2(1) + (2)$ and thus $D_4 = 2D_1 + D_2$. The rates of formation of C and O_2 will be $v_{\text{C}} = K_1D_1 + K_3D_3 + 2K_4D_4 = K_1D_1 + K_3(D_1 + D_2) + 2K_4(2D_1 + D_2) = (K_1 + K_3 + 4K_4)D_1 + (K_3 + 2K_4)D_2$; and $v_{\text{O}_2} = K_2D_2 + K_3D_3 + K_4D_4 = K_2D_2 + K_3(D_1 + D_2) + K_4(2D_1 + D_2) = (K_3 + 2K_4)D_1 + (K_2 + K_3 + K_4)D_2$. Both cross coefficients are thus equal to $K_3 + 2K_4$.

Exercise 4.6.2

Examine if it is possible that the amount of a species decreases although its driving force is positive. To make the discussion more specific, consider the case of L, M and N in the text.

Hint

Consider the formation of N. For a single reaction D and $d\zeta$ must have the same sign (usually '+' by definition) because $Dd\zeta > 0$ for a spontaneous reaction. There is no such restriction on the cross coefficients.

Solution

$v_{\text{N}} = K^{\text{ii}}D^{\text{ii}} + K^{\text{iii}}D^{\text{iii}}$. The second term represents the rate of formation of N by the reaction $\text{M} \rightarrow \text{N}$. Its value and even its sign depends on its driving force. By starting with very little M this reaction would go backwards and consume more N than is produced by $\text{L} \rightarrow \text{N}$ if the amounts of L and N are initially close to their equilibrium.

4.7

Driving force and entropy production in diffusion

The kind of chemical reaction considered in Sections 4.5 and 4.6 occurs in a system that is homogeneous at every instant. It occurs in every point and with the same rate everywhere. It is classified as a homogeneous reaction. The opposite case is a heterogeneous reaction occurring at the interfaces in a system of different regions, usually regarded as phases. A heterogeneous reaction often results in the growth of some phase and the shrinkage of another. Such a reaction is also called phase transformation. If the phase transformation does not result in a change of the local composition, then the driving force is easily obtained as the difference in the value of the appropriate characteristic function, $\Delta\theta$, between the parent phases and the product phases, counted per mole of atoms, for instance. This case and related ones will be further discussed in Section 6.8.

In most cases, a heterogeneous reaction is accompanied by a change in composition and occurs under diffusion. Diffusion itself is yet another type of reaction. It may occur in a system of a single phase which initially has differences in composition. In the general case, it occurs everywhere where there is a composition difference but not with the same rate. The result will be that local differences decrease and eventually disappear. In this case one should discuss the progress of the reaction in each point. At any particular point there may be a flux J of diffusing material and the derivative of the flux results in a change dc of the local composition. Phenomenologically this situation is described with Fick's laws. His first law states that

$$J_1 = - \mathcal{D}_1 \frac{dc_1}{dy}$$

For simplicity we shall introduce the molar content, $x_1 = c_1/V_m$ and assume that the molar volume V_m is constant. Then we obtain

$$J_1 = - \frac{\mathcal{D}_1}{V_m} \frac{dx_1}{dy}$$

We should now like to interpret this equation thermodynamically by starting with our basic expression, $Dd\xi$. In this case it is convenient to consider two large reservoirs, separated by a layer of thickness Δy of the phase in which we are interested. The layer is our system and in this unusual case we have two surroundings and twice as many independent variables as usual. However, if T and P have the same values and are constant in the two reservoirs, then we can formulate the change in a characteristic state function, Θ , related to Gibbs energy,

$$d\Theta = \sum \mu_i' dN_i' + \sum \mu_i'' dN_i'' - Dd\xi$$

where ' and '' identify the two reservoirs. Of course, there is only one $Dd\xi$ term because it represents the effect of the process inside the system. There may be diffusion through the system if μ_i' and μ_i'' are different in the two reservoirs. After a stationary state of diffusion has been established, there will be no further changes inside the system and the value of the characteristic state function will not change with time, $d\Theta = 0$, and $dN_i' + dN_i'' = 0$. If we further assume that there are only two components, 1 and 2, and they diffuse with the same rate but in opposite directions, $J_1 + J_2 = 0$, then we get $dN_1' = -dN_2' = -dN_1'' = dN_2''$ and

$$[(\mu_1 - \mu_2)' - (\mu_1 - \mu_2)''] \cdot dN_1' = Dd\xi$$

The quantity $\mu_1 - \mu_2$ was mentioned in Section 3.5 as the diffusion potential. dN_1' can be expressed as $AJ_1 dt$ where J_1 is the flux of 1 through the layer and A is the area of the cross section.

$$D \cdot d\xi/dt = AJ_1 \cdot \Delta(\mu_2 - \mu_1)$$

where Δ means the difference between the two reservoirs. We could now formulate a kinetic equation using the same scheme as before

$$d\xi/dt \equiv AJ_1 = K \cdot \Delta(\mu_2 - \mu_1)$$

However, if we apply this equation to a thin slice of the layer, the result would depend on the thickness. Thus it does not seem very useful to define $d\xi/dt$ as AJ_1 . We would prefer to define it as $AJ_1\Delta y$, yielding the following kinetic equation

$$J_1 = K \cdot \frac{d(\mu_2 - \mu_1)}{dy}$$

It could be brought into the form of Fick's law by writing

$$\frac{d(\mu_2 - \mu_1)}{dy} = \frac{d(\mu_2 - \mu_1)}{dx_1} \frac{dx_1}{dy} = - \frac{d^2G_m}{dx_1^2} \frac{dx_1}{dy}$$

Inserting this and assuming that K is proportional to x_1x_2 , i.e. $K = Lx_1x_2$, where L is a constant, because x_1x_2 gives the probability that 1 and 2 are available for an exchange of positions, we get

$$-J_2 = J_1 = -Lx_1x_2 \cdot \frac{d^2G_m}{dx_1^2} \frac{dx_1}{dy}$$

Comparison with Fick's law gives

$$\frac{\mathcal{D}_1}{V_m} = Lx_1x_2 \cdot \frac{d^2G_m}{dx_1^2}$$

The derivative d^2G_m/dx_1^2 is often regarded as the thermodynamic factor in diffusion.

The interesting question is now to see if we can express the entropy production with the flux and force used in the kinetic equation. For a thin layer we can transform our previous expression, to yield

$$\frac{T \cdot d_{ip}S}{dt} = D \frac{d\xi}{dt} = AJ_1 \cdot \Delta(\mu_2 - \mu_1) = AJ_1 \frac{d(\mu_2 - \mu_1)}{dy} \cdot \Delta y$$

But $A \cdot \Delta y$ is the volume of the system, ΔV . We may thus express the rate of entropy production per volume with the flux and force from the kinetic equation

$$\frac{T \cdot d_{ip}S}{dt \Delta V} = D \cdot \frac{d^2\xi}{dt \Delta V} = J_1 \cdot \frac{d(\mu_2 - \mu_1)}{dy}$$

We may thus identify J_1 with $d^2\xi/dt \Delta V$ and D with $d(\mu_2 - \mu_1)/dy$. Note that K in our equation has different dimensions than in previous kinetic equations.

The present derivation was made under two assumptions that we should now discuss. Firstly, we assumed that $J_1 + J_2 = 0$, which is always satisfied if one uses a so-called 'number-fixed frame of reference' for diffusion. However, one can mathematically transform Fick's law to other frames of reference, e.g. the 'lattice-fixed frame of reference' and one gets different expressions for J_1 and $-J_2$. However, that is just a mathematical operation and the assumption of $J_1 + J_2 = 0$ does not make our derivation less general.

Secondly, we assumed stationary conditions. However, the final equation applies to a thin layer and it is no longer limited to stationary conditions. If the composition profile in a non-stationary case is known, then one could evaluate the entropy production by integration. The equation could then be used in three different forms,

$$\frac{T \cdot d_{ip}^2 S}{dt dV} = D \frac{d^2 \xi}{dt dV} = J_1 \frac{d(\mu_2 - \mu_1)}{dy} = K \cdot \left(\frac{d(\mu_2 - \mu_1)}{dy} \right)^2 = \frac{1}{K} (J_1)^2$$

For stationary states the integration would simply yield the initial equation containing $\Delta(\mu_2 - \mu_1)$, i.e. the difference between the two reservoirs.

Exercise 4.7.1

Derive Fick's law for diffusion of B in an A-B phase assuming that the driving force is $d\mu_B/dy$.

Hint

In this case it would seem reasonable to assume that the rate constant contains a factor x_B , representing the chance that a B atom is in the right place for jumping. Also, remember that $\mu_B = G_m + x_A dG_m/dx_B$.

Solution

$d\mu_B/dx_B = dG_m/dx_B - 1 \cdot dG_m/dx_B + x_A d^2 G_m/dx_B^2 = x_A d^2 G_m/dx_B^2$;
 $J_B = -K_B x_B (x_A d^2 G_m/dx_B^2) dx_B/dy$. In the same way we would find $J_A = K_A x_A (x_B d^2 G_m/dx_B^2) dx_B/dy$. This is in complete agreement with the case $J_A + J_B = 0$ if A and B have the same mobility, i.e. $K_A = K_B = K$.

4.8

Effective driving force

When a phase transformation occurs under diffusion it often happens that the processes occurring at the phase interfaces are rapid compared to the rate of diffusion. The transformation will then be diffusion controlled and the boundary conditions governing the rate of diffusion can be evaluated by assuming that, whenever two phases meet at an interface, their compositions right at the interface are very close to those required by equilibrium. This is called the **local equilibrium** approximation. That approximation will be used in the following, except when other conditions are clearly defined. For such exceptions, see Section 6.8 and Chapter 13.

So far, we have chosen to regard $T \cdot d_{ip} S/d\xi$ as the driving force for the process,

the progress of which is measured by ξ , and it thus seemed natural to assume that the rate of the process is proportional to $D = T \cdot d_p S / d\xi$, at least as a first approximation, yielding $d\xi/dt = KD$. However, one should be aware of the possibility that a process may be accompanied by an entropy production that does not contribute to the rate of the process. This possibility may be best explained by an example from a very simple type of transformation.

Let us first consider particles of pure A immersed in liquid B. The component A may dissolve in the liquid to a small but measurable extent, but B does not dissolve in the solid. It is well known that smaller particles will dissolve and larger ones will grow, so-called coarsening or 'Ostwald ripening'. The driving force comes from the increased pressure inside the smaller particles. Next, suppose that B can dissolve in solid A but the temperature is so low that diffusion can be neglected. We would still expect that the pressure difference makes the smaller particles go into solution and the larger ones grow. However, the growing layer of a large particle should now be a solid solution of B in A and the process could be written as: solid A + liquid B \rightarrow solid A-B alloy. The chemical driving force for such a reaction can be evaluated from $-\Delta G_m$ assuming that all the phases are under the same pressure but then we should add the effect of the pressure difference. It would seem that the chemical driving force should give a drastic increase of the driving force for the process and make it possible even without the pressure effect, at least after the process has started. Such a process has actually been observed in sintering in the presence of a liquid.

However, in this description of the process we did not consider the local equilibrium conditions at the solid A/liquid interface. Even though the rate of diffusion inside solid A is negligible, the rate of transfer of atoms between the solid and liquid may be appreciable. Under ordinary conditions the net rate of dissolution of A is obtained as the difference between opposite fluxes that are much larger. We should thus recognize that there is a very localized reaction at the interface by which a monolayer of an A + B solid solution forms. The chemical driving force will drive that reaction but it will soon slow down if B does not diffuse into the interior of the A particle. Only the pressure difference may remain and cause material from the monolayer to go into solution and diffuse to a larger, growing particle. B from the liquid will then again react with the fresh A surface and the monolayer will be healed.

This example has demonstrated that the Gibbs energy may decrease as a result of the progress of a process without actually driving the process. One might say that the decrease of Gibbs energy depends on the progress of the process but the process does not depend on the decrease of Gibbs energy. The effective driving force, from which one may estimate the rate of reaction, has to come from another source, in our example from a pressure difference.

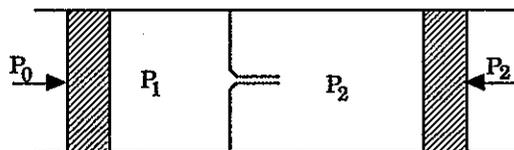
In the above example, it was fairly easy to identify the various steps in the whole process and thus to identify what part of the total driving force actually contributes to the rate. The example gets more complicated if we replace the liquid by a grain boundary which has contact with a B-rich reservoir outside the A material. Even in that case it has been observed experimentally that an A-B solid solution can grow at the

expense of pure A, a phenomenon called DIGM (diffusion-induced grain boundary migration). This is actually the case for which Cahn, Pan and Balluffi (1979) first emphasized that the whole driving force does not necessarily contribute to driving a process. For DIGM they argued that the chemical driving force does not contribute at all and they proposed that the effective driving force comes from the process of diffusion of B down the grain boundary. Later, it was proposed that a part of the chemical driving force is not dissipated, as described above, thanks to the action of coherency stresses, and that this undissipated part thus is able to drive the main process. There may also be a deviation from the local-equilibrium approximation by the sluggishness of processes occurring at or in the interface. Contrary to the natural expectation that this would cause further dissipation of the driving force, it may, in fact, result in less dissipation and thus again leave some of the driving force to drive the main process.

This kind of complication has not attracted much attention and it will not be further considered in this book. Thus, we shall regard chemical driving forces as forces actually contributing to the rate of processes and the local-equilibrium approximation will be applied in most cases.

Exercise 4.8.1

Consider the mechanical device shown here. The left hand piston is supposed to have a friction against the cylinder, but not the right-hand piston. Between the two chambers there is a thin tube and the rate of transfer of gas from left to right is governed by the flow of gas through that tube. Examine how close an analogue this device would be to the example discussed in the text?



Exercise 4.8.1

Hint

Suppose the friction force is constant, i.e. independent of the rate of movement.

Solution

If we compare $P_0 - P_1$ with the chemical driving force and $P_1 - P_2$ with the effect of the pressure difference between small and large particles, then the analogue is very close. The friction between piston and cylinder corresponds to the dissipation of chemical driving force by the interface reaction.