

A.5 Equilibrium constants

In Chapter 8 we introduced the very important relationship between the equilibrium constant, K , and the standard Gibbs energy change, $\Delta_r G^\circ$, for a reaction:

$$\Delta_r G^\circ = -RT \ln K.$$

In this relationship R is the gas constant and T is the absolute temperature. In this section we will look in more detail at how this very important relationship is proved. However, we will not be able to give a complete proof as this would require rather too many results from thermodynamics which we do not have time to develop here.

We will consider the simple equilibrium between two gases, A and B:



You will recall that the position of equilibrium is the mixture of A and B which has the *lowest* Gibbs energy. Figure A.10 (which is identical to Fig. 8.4 on p. 115) illustrates the key idea that the Gibbs energy is a function of the composition of the mixture, i.e. the ratio of A to B, and that there is a particular composition at which the Gibbs energy is a minimum. Our task is to determine this composition.

From Fig. A.10 it is clear that at the position of equilibrium the slope of the graph of Gibbs energy against percentage of B is zero i.e. for a small change in the percentage of B the Gibbs energy of the mixture does not change. We will use this observation as the basis of our method of finding the equilibrium composition.

The Gibbs energy of a mixture of gases

The first thing we have to do is to work out the Gibbs energy of an arbitrary mixture of two gases. To do this we will start by thinking about the Gibbs

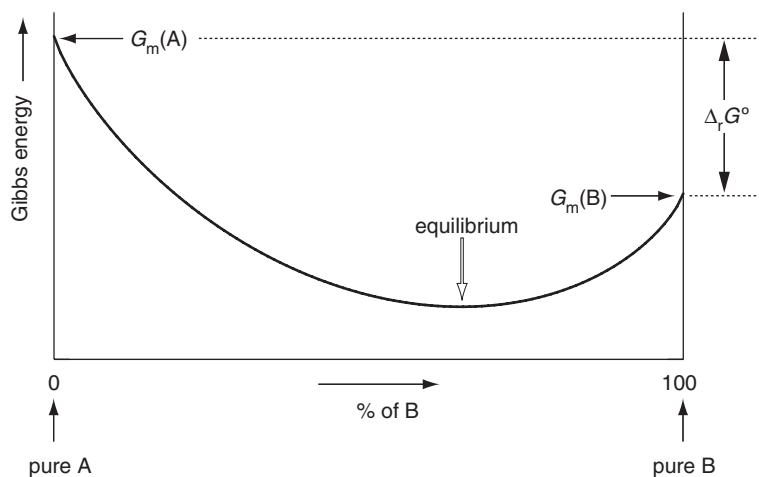


Fig. A.10 Plot showing an example of how the Gibbs energy for the equilibrium between A and B varies with the composition, which in this case can be specified by the percentage of B. Arbitrarily, we have made the molar Gibbs energy of B lower than that of A.

energy of a single pure (ideal) gas. Not surprisingly, the value of the Gibbs energy depends on the identity of the gas, the amount of the gas present (i.e. the number of moles), the temperature and the pressure.

To simplify things, let us imagine that we are working at a constant temperature (e.g. in a thermostat). Under such conditions it turns out (and we will not prove this) that for n moles of gas the Gibbs energy at pressure p_1 , $G(p_1)$, is related to the Gibbs energy at pressure p_2 , $G(p_2)$, according to

$$G(p_2) = G(p_1) + nRT \ln \frac{p_2}{p_1}. \quad (\text{A.7})$$

Rather than working with the Gibbs energy it will be convenient to work with the *molar* Gibbs energy, G_m , which is the Gibbs energy of one mole. In terms of these molar quantities, Eq. A.7 becomes

$$G_m(p_2) = G_m(p_1) + RT \ln \frac{p_2}{p_1}, \quad (\text{A.8})$$

which is simply Eq. A.7 with the Gibbs energies replaced by the corresponding molar quantities and $n = 1$.

It is usual to rewrite Eq. A.8 by supposing that pressure p_1 is the *standard pressure*, p° , of 1 bar:

$$G_m(p_2) = G_m(p^\circ) + RT \ln \frac{p_2}{p^\circ} \quad (\text{A.9})$$

We then write $G_m(p^\circ)$, the molar Gibbs energy at standard pressure, as G_m° ; Eq. A.9 then becomes

$$G_m(p) = G_m^\circ + RT \ln \frac{p}{p^\circ} \quad (\text{A.10})$$

where instead of p_2 we have written a general pressure, p . Equation A.10 tells us how the molar Gibbs energy of a pure gas varies with pressure (at a fixed temperature).

The next concept we need to introduce is that of the *partial pressure*. In a mixture of A and B the partial pressure of A is the pressure that A would exert if it occupied the volume *on its own*, i.e. with B taken away. Similarly, the partial pressure of B is the pressure that B would exert if it occupied the volume on its own. The idea is illustrated in Fig. A.11

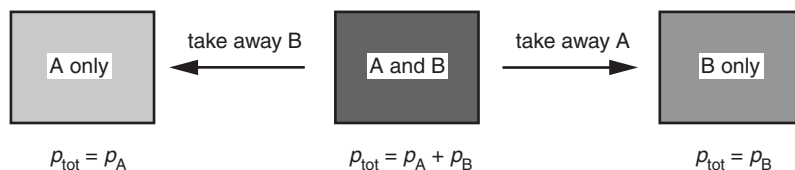


Fig. A.11 The partial pressure of a gas is the pressure it would exert if it occupied the volume on its own; the sum of the partial pressures is equal to the total pressure.

Dalton's Law of partial pressures tells us that the total pressure, p_{tot} , exerted by the mixture is the sum of the partial pressures of A and B (p_A and p_B , respectively):

$$p_{\text{tot}} = p_A + p_B.$$

The partial pressure of A depends on its *mole fraction*, x_A , which is defined as the ratio of the number of moles of A, n_A , to the total number of moles, n_{tot} . The mole fraction of B, x_B is defined similarly in terms of the number of moles of B, n_B :

$$x_A = \frac{n_A}{n_{\text{tot}}} \quad x_B = \frac{n_B}{n_{\text{tot}}}.$$

Clearly if only A and B are present, $n_{\text{tot}} = n_A + n_B$.

For ideal gases (which is the only case we will consider), the partial pressure of A is given by

$$\begin{aligned} p_A &= x_A p_{\text{tot}} \\ &= \frac{n_A}{n_A + n_B} p_{\text{tot}} \end{aligned}$$

and similarly for B

$$p_B = \frac{n_B}{n_A + n_B} p_{\text{tot}}.$$

The reason for introducing partial pressures is that, in a mixture, the molar Gibbs energy of A depends on its *partial pressure* in the same way that for a pure gas G_m depends on the pressure. So, by analogy to Eq. A.10 we can write

$$G_{m,A}(p_A) = G_{m,A}^\circ + RT \ln \frac{p_A}{p^\circ} \quad (\text{A.11})$$

where $G_{m,A}(p_A)$ is the molar Gibbs energy of A in the mixture and $G_{m,A}^\circ$ is the molar Gibbs energy of *pure* A at the standard pressure. The reason that we can write Eq. A.11 in this way is that we are considering ideal gases which do not interact with one another.

Suppose that we have a mixture of n_A moles of A and n_B moles of B, and that the partial pressures of A and B are p_A and p_B , respectively. We can now write down the Gibbs energy of the mixture as

$$G = n_A G_{m,A}(p_A) + n_B G_{m,B}(p_B). \quad (\text{A.12})$$

All we are doing here is multiplying the molar Gibbs energy of each species by the number of moles present; importantly, though, we are recognizing that the molar Gibbs energies depend on the partial pressures. We have now achieved our first goal of finding an expression for the Gibbs energy of a mixture of A and B.

Locating the minimum in the Gibbs energy of the mixture

Now let us imagine that, starting from a mixture with n_A moles of A and n_B moles of B, the reaction proceeds by a small amount δ so that the number of moles of A decreases by δ to $(n_A - \delta)$ and B increases by δ to $(n_B + \delta)$. After these changes the Gibbs energy of the mixture becomes

$$G_{\text{new}} = (n_A - \delta) G_{m,A}(p_A) + (n_B + \delta) G_{m,B}(p_B) \quad (\text{A.13})$$

where we have assumed that the change is so small that molar Gibbs energies are not affected.¹

The change in Gibbs energy, ΔG , resulting from this small amount of A becoming B is found by subtracting Eq. A.12 from Eq. A.13

$$\begin{aligned}\Delta G &= G_{\text{new}} - G \\ &= (n_A - \delta)G_{\text{m,A}}(p_A) + (n_B + \delta)G_{\text{m,B}}(p_B) \\ &\quad - [n_A G_{\text{m,A}}(p_A) + n_B G_{\text{m,B}}(p_B)] \\ &= \delta (G_{\text{m,B}}(p_B) - G_{\text{m,A}}(p_A)).\end{aligned}\tag{A.14}$$

Now, when we are at the equilibrium position, changing the composition by a small amount leads to *no* change in the Gibbs energy (see Fig. A.10 on p. A-16), so ΔG given by Eq. A.14 will be zero *at equilibrium*:

$$\text{at equilibrium } \delta (G_{\text{m,B}}(p_{\text{B,eq}}) - G_{\text{m,A}}(p_{\text{A,eq}})) = 0.$$

$p_{\text{A,eq}}$ is the equilibrium pressure of A and likewise for B. It follows that at equilibrium

$$G_{\text{m,B}}(p_{\text{B,eq}}) - G_{\text{m,A}}(p_{\text{A,eq}}) = 0.\tag{A.15}$$

Each of the molar Gibbs energies in Eq. A.15 can be substituted using the relationship of Eq. A.11 to give

$$\left[G_{\text{m,B}}^0 + RT \ln \frac{p_{\text{B,eq}}}{p^0} \right] - \left[G_{\text{m,A}}^0 + RT \ln \frac{p_{\text{A,eq}}}{p^0} \right] = 0.\tag{A.16}$$

Equation A.16 can be rewritten

$$\begin{aligned}G_{\text{m,B}}^0 - G_{\text{m,A}}^0 &= RT \ln \frac{p_{\text{A,eq}}}{p^0} - RT \ln \frac{p_{\text{B,eq}}}{p^0} \\ &= RT \ln \frac{p_{\text{A,eq}}}{p^0} \frac{p^0}{p_{\text{B,eq}}} \\ &= RT \ln \frac{p_{\text{A,eq}}}{p_{\text{B,eq}}} \\ &= -RT \ln \frac{p_{\text{B,eq}}}{p_{\text{A,eq}}}.\end{aligned}\tag{A.17}$$

The quantity on the left-hand side of Eq. A.17 is the standard molar Gibbs energy of the product B, minus that of the reactant A; this is the standard Gibbs energy change for the reaction, $\Delta_r G^\circ$:

$$\Delta_r G^\circ = G_{\text{m,B}}^0 - G_{\text{m,A}}^0.$$

For gases, partial pressures are simply another way of expressing concentrations. Therefore, the ratio $p_{\text{B,eq}}/p_{\text{A,eq}}$ which appears on the right-hand side

¹This may seem rather contradictory as changing the number of moles of A and B will change the mole fractions and hence the partial pressures and the molar Gibbs energies. However the point to grasp here is that δ is very small so, although the amounts of A and B change, the change is insignificant compared to the total number of moles of A and B present. Thus, the partial pressures of A and B are unaltered, so that the molar Gibbs energies are also unaffected.

of Eq. A.17 is the equilibrium constant, K , expressed, not in the usual units of concentration, but in terms of partial pressures. Thus we can write Eq. A.17 as:

$$\Delta_r G^\circ = -RT \ln K \quad (\text{A.18})$$

which is what we set out to prove. This derivation can easily be generalized for any reaction.

It is important not to forget that $\Delta_r G^\circ$ is itself a function of temperature, so Eq. A.18 does not, on its own, predict how the equilibrium constant varies with temperature.