

11.8: The Thermodynamic Equilibrium Constant

11.8.1 Activities and the definition of K

Equation 10.1.9 gives the general relation between the chemical potential μ_i and the activity a_i of species i in a phase of electric potential ϕ :

$$\mu_i = \mu_i^\circ + RT \ln a_i + z_i F \phi \quad (11.8.1)$$

The electric potential affects μ_i only if the charge number z_i is nonzero, i.e., only if species i is an ion.

Consider a reaction in which any reactants and products that are ions are in a single phase of electric potential ϕ' , or in several phases of equal electric potential ϕ' . Under these conditions, substitution of the expression above for μ_i in $\Delta_r G = \sum_i \nu_i \mu_i$ gives

$$\Delta_r G = \sum_i \nu_i \mu_i^\circ + RT \sum_i \nu_i \ln a_i + F \phi' \sum_i \nu_i z_i \quad (11.8.2)$$

(all ions at $\phi = \phi'$)

The first term on the right side of Eq. 11.8.2 is the **standard molar reaction Gibbs energy**, or standard molar Gibbs energy of reaction:

$$\Delta_r G^\circ \stackrel{\text{def}}{=} \sum_i \nu_i \mu_i^\circ \quad (11.8.3)$$

Since the standard chemical potential μ_i° of each species i is a function only of T , the value of $\Delta_r G^\circ$ for a given reaction as defined by the reaction equation depends only on T and on the choice of a standard state for each reactant and product.

The last term on the right side of Eq. 11.8.2 is the sum $\sum_i \nu_i z_i$. Because charge is conserved during the advancement of a reaction in a closed system, this sum is zero.

With these substitutions, Eq. 11.8.2 becomes

$$\Delta_r G = \Delta_r G^\circ + RT \sum_i \nu_i \ln a_i \quad (11.8.4)$$

(all ions at same ϕ)

This relation enables us to say that for a reaction at a given temperature in which any charged reactants or products are all in the same phase, or in phases of equal electric potential, the value of $\Delta_r G$ and $\sum_i \nu_i \mu_i$ depends only on the activities of the reactants and products and is independent of what the electric potentials of any of the phases might happen to be.

Unless a reaction involving ions is carried out in a galvanic cell, the ions are usually present in a single phase, and this will not be shown as a condition of validity in the rest of this chapter. The special case of a reaction in a galvanic cell will be discussed in Sec. 14.3.

We may use properties of logarithms to write the sum on the right side of Eq. 11.8.4 as follows:

$$\sum_i \nu_i \ln a_i = \sum_i \ln(a_i^{\nu_i}) = \ln \prod_i a_i^{\nu_i} \quad (11.8.5)$$

The symbol \prod stands for a continued product. If, for instance, there are three species, $\prod_i a_i^{\nu_i}$ is the product $(a_1^{\nu_1})(a_2^{\nu_2})(a_3^{\nu_3})$.

The product $\prod_i a_i^{\nu_i}$ is called the **reaction quotient** or activity quotient, Q_{rxn} :

$$Q_{\text{rxn}} \stackrel{\text{def}}{=} \prod_i a_i^{\nu_i} \quad (11.8.6)$$

Q_{rxn} consists of a factor for each reactant and product. Each factor is the activity raised to the power of the stoichiometric number ν_i . Since the value of ν_i is positive for a product and negative for a reactant, Q_{rxn} is a quotient in which the activities of the products appear in the numerator and those of the reactants appear in the denominator, with each activity raised to a power equal to the corresponding stoichiometric coefficient in the reaction equation. Such a quotient, with quantities raised to these powers, is called a **proper quotient**. The reaction quotient is a proper quotient of activities.

For instance, for the ammonia synthesis reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$ the reaction quotient is given by

$$Q_{\text{rxn}} = \frac{a_{\text{NH}_3}^2}{a_{\text{N}_2} a_{\text{H}_2}^3} \quad (11.8.7)$$

Q_{rxn} is a dimensionless quantity. It is a function of T , p , and the mixture composition, so its value changes as the reaction advances.

The expression for the molar reaction Gibbs energy given by Eq. 11.8.4 can now be written

$$\Delta_{\text{r}}G = \Delta_{\text{r}}G^{\circ} + RT \ln Q_{\text{rxn}} \quad (11.8.8)$$

The value of Q_{rxn} under equilibrium conditions is the **thermodynamic equilibrium constant**, K . The general definition of K is

$$K \stackrel{\text{def}}{=} \prod_i (a_i)_{\text{eq}}^{\nu_i} \quad (11.8.9)$$

where the subscript eq indicates an equilibrium state. Note that K , like Q_{rxn} , is dimensionless.

The IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, p. 58) gives K° as an alternative symbol for the thermodynamic equilibrium constant, the appended superscript denoting “standard.” An IUPAC Commission on Thermodynamics (M. B. Ewing et al, *Pure Appl. Chem.*, **66**, 533–552, 1994) has furthermore recommended the name “standard equilibrium constant,” apparently because its value depends on the choice of standard states. Using this alternative symbol and name could cause confusion, since the quantity defined by Eq. 11.8.9 does not refer to reactants and products in their standard states but rather to reactants and products in an *equilibrium* state.

Substituting the equilibrium conditions $\Delta_{\text{r}}G = 0$ and $Q_{\text{rxn}} = K$ in Eq. 11.8.8 gives an important relation between the standard molar reaction Gibbs energy and the thermodynamic equilibrium constant:

$$\Delta_{\text{r}}G^{\circ} = -RT \ln K \quad (11.8.10)$$

We can solve this equation for K to obtain the equivalent relation

$$K = \exp\left(-\frac{\Delta_{\text{r}}G^{\circ}}{RT}\right) \quad (11.8.11)$$

We have seen that the value of $\Delta_{\text{r}}G^{\circ}$ depends only on T and the choice of the standard states of the reactants and products. This being so, Eq. 11.8.11 shows that the value of K for a given reaction depends only on T and the choice of standard states. No other condition, neither pressure nor composition, can affect the value of K . We also see from Eq. 11.8.11 that K is less than 1 if $\Delta_{\text{r}}G^{\circ}$ is positive and greater than 1 if $\Delta_{\text{r}}G^{\circ}$ is negative. At a fixed temperature, reaction equilibrium is attained only if and only if the value of Q_{rxn} becomes equal to the value of K at that temperature.

The thermodynamic equilibrium constant K is the proper quotient of the activities of species in reaction equilibrium. At typical temperatures and pressures, an activity cannot be many orders of magnitude greater than 1. For instance, a partial pressure cannot be greater than the total pressure, so at a pressure of 10 bar the activity of a gaseous constituent cannot be greater than about 10. The molarity of a solute is rarely much greater than 10 mol dm^{−3}, corresponding to an activity (on a concentration basis) of about 10. Activities can, however, be extremely small.

These considerations lead us to the conclusion that in an equilibrium state of a reaction with a very *large* value of K , the activity of at least one of the *reactants* must be very small. That is, if K is very large then the reaction goes practically to completion and at equilibrium a limiting reactant is essentially entirely exhausted. The opposite case, a reaction with a very *small* value of K , must have at equilibrium one or more *products* with very small activities. These two cases are the two extremes of the trends shown in Fig. 11.16.

Equation 11.8.10 correctly relates $\Delta_{\text{r}}G^{\circ}$ and K only if they are both calculated with the same standard states. For instance, if we base the standard state of a particular solute species on molality in calculating $\Delta_{\text{r}}G^{\circ}$, the activity of that species appearing in the expression for K (Eq. 11.8.9) must also be based on molality.

11.8.2 Reaction in a gas phase

If a reaction takes place in a gaseous mixture, the standard state of each reactant and product is the pure gas behaving ideally at the standard pressure p° (Sec. 9.3.3). In this case, each activity is given by $a_i(\text{g}) = f_i/p^{\circ} = \phi_i p_i/p^{\circ}$ where ϕ_i is a fugacity coefficient

(Table 9.5). When we substitute this expression into Eq. 11.8.9, we find we can express the thermodynamic equilibrium constant as the product of three factors:

$$K = \left[\prod_i (\phi_i)_{\text{eq}}^{\nu_i} \right] \left[\prod_i (p_i)_{\text{eq}}^{\nu_i} \right] \left[(p^\circ)^{-\sum_i \nu_i} \right] \quad (11.8.12)$$

(gas mixture)

On the right side of this equation, the first factor is the proper quotient of fugacity coefficients in the mixture at reaction equilibrium, the second factor is the proper quotient of partial pressures in this mixture, and the third factor is the power of p° needed to make K dimensionless.

The proper quotient of equilibrium partial pressures is an **equilibrium constant on a pressure basis**, K_p :

$$K_p = \prod_i (p_i)_{\text{eq}}^{\nu_i} \quad (11.8.13)$$

(gas mixture)

Note that K_p is dimensionless only if $\sum_i \nu_i$ is equal to zero.

The value of K_p can vary at constant temperature, so K_p is not a thermodynamic equilibrium constant. For instance, consider what happens when we take an ideal gas mixture at reaction equilibrium and compress it isothermally. As the gas pressure increases, the fugacity coefficient of each constituent changes from its low pressure value of 1 and the gas mixture becomes nonideal. In order for the mixture to remain in reaction equilibrium, and the product of factors on the right side of Eq. 11.8.12 to remain constant, there must be a change in the value of K_p . In other words, the reaction equilibrium *shifts* as we increase p at constant T , an effect that will be considered in more detail in Sec. 11.9.

As an example of the difference between K and K_p , consider again the ammonia synthesis $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ in which the sum $\sum_i \nu_i$ equals -2 . For this reaction, the expression for the thermodynamic equilibrium constant is

$$K = \left(\frac{\phi_{\text{NH}_3}^2}{\phi_{\text{N}_2} \phi_{\text{H}_2}^3} \right)_{\text{eq}} K_p (p^\circ)^2 \quad (11.8.14)$$

where K_p is given by

$$K_p = \left(\frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}^3} \right)_{\text{eq}} \quad (11.8.15)$$

11.8.3 Reaction in solution

If any of the reactants or products are solutes in a solution, the value of K depends on the choice of the solute standard state.

For a given reaction at a given temperature, we can derive relations between values of K that are based on different solute standard states. In the limit of infinite dilution, each solute activity coefficient is unity, and at the standard pressure each pressure factor is unity. Under these conditions of infinite dilution and standard pressure, the activities of solute B on a mole fraction, concentration, and molality basis are therefore

$$a_{x,\text{B}} = x_{\text{B}} \quad a_{c,\text{B}} = c_{\text{B}}/c^\circ \quad a_{m,\text{B}} = m_{\text{B}}/m^\circ \quad (11.8.16)$$

In the limit of infinite dilution, the solute composition variables approach values given by the relations in Eq. 9.1.14: $x_{\text{B}} = V_{\text{A}}^* c_{\text{B}} = M_{\text{A}} m_{\text{B}}$. Combining these with $a_{x,\text{B}} = x_{\text{B}}$ from Eq. 11.8.16, we write

$$a_{x,\text{B}} = V_{\text{A}}^* c_{\text{B}} = M_{\text{A}} m_{\text{B}} \quad (11.8.17)$$

Then, using the relations for $a_{c,\text{B}}$ and $a_{m,\text{B}}$ in Eq. 11.8.16, we find that the activities of solute B at infinite dilution and pressure p° are related by

$$a_{x,\text{B}} = V_{\text{A}}^* c^\circ a_{c,\text{B}} = M_{\text{A}} m^\circ a_{m,\text{B}} \quad (11.8.18)$$

The expression $K = \prod_i (a_i)_{\text{eq}}^{\nu_i}$ has a factor $(a_{\text{B}})_{\text{eq}}^{\nu_{\text{B}}}$ for each solute B that is a reactant or product. From Eq. 11.8.18, we see that for solutes at infinite dilution at pressure p° , the relations between the values of K based on different solute standard states are

$$K(x \text{ basis}) = \prod_{\text{B}} (V_{\text{A}}^* c^\circ)^{\nu_{\text{B}}} K(c \text{ basis}) = \prod_{\text{B}} (M_{\text{A}} m^\circ)^{\nu_{\text{B}}} K(m \text{ basis}) \quad (11.8.19)$$

For a given reaction at a given temperature, and with a given choice of solute standard state, the value of K is not affected by pressure or dilution. The relations of Eq. 11.8.19 are therefore valid under all conditions.

11.8.4 Evaluation of K

The relation $K = \exp(-\Delta_r G^\circ / RT)$ (Eq. 11.8.11) gives us a way to evaluate the thermodynamic equilibrium constant K of a reaction at a given temperature from the value of the standard molar reaction Gibbs energy $\Delta_r G^\circ$ at that temperature. If we know the value of $\Delta_r G^\circ$, we can calculate the value of K .

One method is to calculate $\Delta_r G^\circ$ from values of the **standard molar Gibbs energy of formation** $\Delta_f G^\circ$ of each reactant and product. These values are the standard molar reaction Gibbs energies for the formation reactions of the substances. To relate $\Delta_f G^\circ$ to measurable quantities, we make the substitution $\mu_i = H_i - TS_i$ (Eq. 9.2.46) in $\Delta_r G = \sum_i \nu_i \mu_i$ to give $\Delta_r G = \sum_i \nu_i H_i - T \sum_i \nu_i S_i$, or

$$\Delta_r G = \Delta_r H - T \Delta_r S \quad (11.8.20)$$

When we apply this equation to a reaction with each reactant and product in its standard state, it becomes

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \quad (11.8.21)$$

where the standard molar reaction entropy is given by

$$\Delta_r S^\circ = \sum_i \nu_i S_i^\circ \quad (11.8.22)$$

If the reaction is the *formation* reaction of a substance, we have

$$\Delta_f G^\circ = \Delta_f H^\circ - T \sum_i \nu_i S_i^\circ \quad (11.8.23)$$

where the sum over i is for the reactants and product of the formation reaction. We can evaluate the standard molar Gibbs energy of formation of a substance, then, from its standard molar enthalpy of formation and the standard molar entropies of the reactants and product.

Extensive tables are available of values of $\Delta_f G^\circ$ for substances and ions. An abbreviated version at the single temperature 298.15 K is given in Appendix H. For a reaction of interest, the tabulated values enable us to evaluate $\Delta_r G^\circ$, and then K , from the expression (analogous to Hess's law)

$$\Delta_r G^\circ = \sum_i \nu_i \Delta_f G^\circ(i) \quad (11.8.24)$$

The sum over i is for the reactants and products of the reaction of interest.

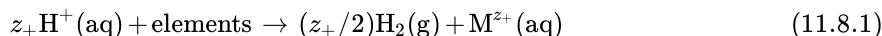
Recall that the standard molar enthalpies of formation needed in Eq. 11.8.23 can be evaluated by calorimetric methods (Sec. 11.3.2). The absolute molar entropy values S_i° come from heat capacity data or statistical mechanical theory by methods discussed in Sec. 6.2. Thus, it is entirely feasible to use nothing but calorimetry to evaluate an equilibrium constant, a goal sought by thermodynamicists during the first half of the 20th century. (Another method, for a reaction that can be carried out reversibly in a galvanic cell, is described in Sec. 14.3.3.)

For *ions in aqueous solution*, the values of S_m° and $\Delta_f G^\circ$ found in Appendix H are based on the reference values $S_m^\circ = 0$ and $\Delta_f G^\circ = 0$ for $H^+(aq)$ at all temperatures, similar to the convention for $\Delta_f H^\circ$ values discussed in Sec. 11.3.2. For a reaction with aqueous ions as reactants or products, these values correctly give $\Delta_r S^\circ$ using Eq. 11.8.22, or $\Delta_r G^\circ$ using Eq. 11.8.24.

Note that the values of S_m° in Appendix H for some ions, unlike the values for substances, are *negative*; this simply means that the standard molar entropies of these ions are less than that of $H^+(aq)$.

The relation of Eq. 11.8.23 does not apply to an ion, because we cannot write a formation reaction for a single ion. Instead, the relation between $\Delta_f G^\circ$, $\Delta_f H^\circ$ and S_m° is more complicated.

Consider first a hypothetical reaction in which hydrogen ions and one or more elements form H_2 and a cation M^{z+} with charge number z_+ :



For this reaction, using the convention that $\Delta_f H^\circ$, S_m° , and $\Delta_f G^\circ$ are zero for the aqueous H^+ ion and the fact that $\Delta_f H^\circ$ and $\Delta_f G^\circ$ are zero for the elements, we can write the following expressions for standard molar reaction quantities:

$$\Delta_r H^\circ = \Delta_f H^\circ(M^{z+}) \quad (11.8.25)$$

$$\Delta_r S^\circ = (z_+/2)S_m^\circ(H_2) + S_m^\circ(M^{z+}) - \sum_{\text{elements}} S_i^\circ \quad (11.8.26)$$

$$\Delta_r G^\circ = \Delta_f G^\circ(M^{z+}) \quad (11.8.27)$$

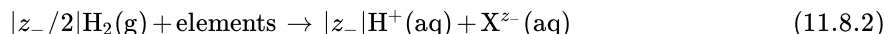
Then, from $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, we find

$$\Delta_f G^\circ(M^{z+}) = \Delta_f H^\circ(M^{z+}) - T \left[S_m^\circ(M^{z+}) - \sum_{\text{elements}} S_i^\circ + (z_+/2)S_m^\circ(H_2) \right] \quad (11.8.28)$$

For example, the standard molar Gibbs energy of the aqueous mercury(I) ion is found from

$$\Delta_f G^\circ(Hg_2^{2+}) = \Delta_f H^\circ(Hg_2^{2+}) - T S_m^\circ(Hg_2^{2+}) + 2T S_m^\circ(Hg) - \frac{2}{2} T S_m^\circ(H_2) \quad (11.8.29)$$

For an anion X^{z-} with negative charge number z_- , using the hypothetical reaction



we find by the same method

$$\Delta_f G^\circ(X^{z-}) = \Delta_f H^\circ(X^{z-}) - T \left[S_m^\circ(X^{z-}) - \sum_{\text{elements}} S_i^\circ - |z_-|/2 S_m^\circ(H_2) \right] \quad (11.8.30)$$

For example, the calculation for the nitrate ion is

$$\Delta_f G^\circ(NO_3^-) = \Delta_f H^\circ(NO_3^-) - T S_m^\circ(NO_3^-) + \frac{1}{2} T S_m^\circ(N_2) + \frac{3}{2} T S_m^\circ(O_2) + \frac{1}{2} T S_m^\circ(H_2) \quad (11.8.31)$$

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