Chapter 8
Equilibria of Chemical Reactions

In this chapter, we remove the nonreactivity constraint imposed on simple systems and allow for chemical reactions to occur. Obviously, this is the most interesting application for chemists. Although the expression "chemical interaction" has been mentioned several times in previous chapters, it has always referred to the spatial displacement of chemical species; they could leave or enter the system (open systems), or pass from one phase to another (phase equilibria). This chapter deals with the possibility of "real" chemical reactions, when the amount of chemical species can change without spatial displacement. Nevertheless, reacting species can be not only within the same homogeneous phase, but also in different phases.

Chemical reactions are usually described by *stoichiometric equations*.[1] In thermodynamics, stoichiometric equations are written in a special form, so that the equation is set equal to zero. The advantage of this form is that reactants and products (species on the left-hand side and on the right-hand side in the more common equation) can be treated the same way, thus simplifying the mathematical treatment. The general stoichiometric equation of this form can be written as:

$$\sum_{i=1}^{R} v_i A_i = 0. \tag{8.1}$$

The symbol A_i denotes the stoichiometric formula of the species i and v_i is the *stoichiometric number* of this species. The index i runs over all the *reacting species* whose number is R. (Components that do not react – like an inert solvent – would have a zero stoichiometric number, thus it is superfluous to include them in the sum.) As an example, let us write one of the possible equations of the formation of ammonia:

$$1\mathrm{NH_3} - 1½\ \mathrm{H_2} - ½\ \mathrm{N_2} = 0. \tag{8.2}$$

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[1] The word is coined from the Greek nouns $\sigma\tau o\iota\chi\varepsilon\iota o\nu$ = element and $\mu\varepsilon\tau\rho o\nu$ = measure, meaning the quantity of elements in a compound or in a reaction.

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In this equation $A_1 = NH_3$, $A_2 = H_2$, $A_3 = N_2$, $\nu_1 = 1$, $\nu_2 = -1½$ and $\nu_3 = -½$. As explicitly written chemical equations are normally not written in this form, we frequently keep the familiar form

$$1½\ H_2 + ½\ N_2 = NH_3, \tag{8.3}$$

but still consider the stoichiometric number ν_i of the reactants as *negative* and that of the products *positive*, in accordance with the form of (8.1). We shall use this convention in the rest of this book.

8.1 Condition of a Chemical Equilibrium at Constant Temperature and Pressure

Let us consider a reacting thermodynamic system at constant pressure and temperature. The condition of equilibrium in this case is the minimum of the Gibbs potential function $G(T, P, \boldsymbol{n})$ – as listed in Table 4.1. At the minimum of the function, its first differential is zero:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_{i=1}^{K} \mu_i \mathrm{d}n_i = 0. \tag{8.4}$$

As the temperature T and the pressure P, as well as the amounts n_i of the $K - R$ nonreacting species are constant, the condition of chemical equilibrium simplifies to:

$$\sum_{i=1}^{R} \mu_i \mathrm{d}n_i = 0. \tag{8.5}$$

Let us examine this condition in case of a general chemical reaction:

$$\sum_{i=1}^{R} \nu_i A_i = 0. \tag{8.6}$$

The chemical potential of each component A_i can be written as:

$$\mu_i = \mu_i^{\ominus} + RT \ln a_i. \tag{8.7}$$

Substituting this formula into (8.5), we get:

$$\sum_{i=1}^{R} \left(\mu_{\,i} + RT \ln a_i\right) \mathrm{d}n_i = 0. \tag{8.8}$$

As we can see, there are R different increments $\mathrm{d}n_i$ in this formula. However, we know that they cannot be independent; they are all connected by the stoichiometric equation, thus one single variable is enough to characterize the extent of the change of amounts of components according to the given stoichiometric equation. Mathematically, this can be formulated the following way. Let us denote the initial concentration (prior to the start of the reaction) for each component by n_{i0}, and express its instantaneous concentration during the reaction with the help of a variable ξ (Greek lowercase "ksi") depending on the progress of the reaction:

$$n_i = n_{i,0} + \nu_i \, \xi. \tag{8.9}$$

The variable ξ is called the *extent of reaction*. From the above definition, it is clear that ξ is an extensive quantity, and its unit is mole. It can be interpreted as the number of moles of the stoichiometric equation that has been converted from reactants to products. To formulate the condition of equilibrium, we need the increments n_i what we can get by differentiating (8.9):

$$\mathrm{d}n_i = \nu_i \, \mathrm{d}\xi. \tag{8.10}$$

Substituting this in (8.8), we obtain:

$$\sum_{i=1}^{R} \left(\mu_i^{\ominus} + RT \ln a_i\right) \nu_i \, \mathrm{d}\xi = 0. \tag{8.11}$$

The increment $\mathrm{d}\xi$ does not depend on the index i, thus it can be factored out from the sum. As $\mathrm{d}\xi$ can be chosen arbitrarily, the other factor of the product should be zero. Accordingly, the condition of equilibrium is simplified to:

$$\sum_{i=1}^{R} \nu_i \left(\mu_i^{\ominus} + RT \ln a_i\right) = 0. \tag{8.12}$$

An interesting property of this condition is revealed if we substitute here the chemical potential μ_i according to (8.7):

$$\sum_{i=1}^{R} \nu_i \mu_i = 0. \tag{8.13}$$

As we can see, the condition of chemical equilibrium has the same form as the stoichiometric equation (8.6), with the chemical potential μ_i in place of the formula A_i of the respective species.

Although (8.12) is appropriate to determine the equilibrium state, in common practice it is not this equation which is used, but a different form. To obtain this usual form, let us rearrange the equation and introduce some new notation. The rearranged equation we start with is the following:

$$\sum_{i=1}^{R} \nu_i \, \mu_i^{\ominus} = -\sum_{i=1}^{R} \nu_i \, RT \ln a_i. \tag{8.14}$$

Note that the standard chemical potentials $\mu_i^\ominus$ on the left-hand side are identical to the partial molar Gibbs potentials $G_i^\ominus$ that can be assigned to the standard states. Accordingly, we can write:

$$\sum_{i=1}^{R} v_i \mu_i^\ominus = \sum_{i=1}^{R} v_i G_i^\ominus = \Delta_\mathrm{r} G^\ominus. \tag{8.15}$$

The quantity $\Delta_\mathrm{r} G^\ominus$ thus defined is called the *standard reaction Gibbs potential*. (The result of the summation is denoted by the Greek letter Δ used for difference, as there are necessarily also negative stoichiometric numbers, thus this quantity is the difference of the standard Gibbs potential of the products and that of the reactants.) The product RT in (8.14) can be factored out from the sum, while the factor v_i of the logarithms can be written as the power of the arguments. Finally, the sum of logarithms obtained this way can be written as the logarithm of the product of the arguments, applying the usual notation Π (Greek upper case “pi”) for the product. Thus, we get the result:

$$\sum_{i=1}^{R} v_i RT \ln a_i = RT \sum_{i=1}^{R} \ln (a_i)^{v_i} = RT \ln \prod_{i=1}^{R} (a_i)^{v_i}. \tag{8.16}$$

Using this result, we can rewrite (8.14) in the following form:

$$\Delta_\mathrm{r} G^\ominus = -RT \ln \prod_{i=1}^{R} (a_i)^{v_i}. \tag{8.17}$$

The standard reaction Gibbs potential $\Delta_\mathrm{r} G^\ominus$ on the left-hand side does not depend on the composition, thus the product on the right-hand side is also composition independent. Consequently, the equilibrium condition can be formulated also with this product containing the *equilibrium activities* a_i:

$$K_a = \prod_{i=1}^{R} (a_i)^{v_i}. \tag{8.18}$$

The quantity thus defined is called the *equilibrium constant*, which is independent of the composition. The above result is commonly expressed in the form

$$-\Delta_\mathrm{r} G^\ominus = RT \ln K_a, \tag{8.19}$$

though the equivalent expression

$$K_a = \mathrm{e}^{-\frac{\Delta_\mathrm{r} G^\ominus}{RT}}. \tag{8.20}$$

is more straightforward to calculate the equilibrium constant.

Equations (8.19) and (8.20) have a wide range of application. If we know the equilibrium constant K_a and the dependence on composition of the activity of reactive species, we can calculate the equilibrium composition of the mixture when starting from any initial composition. The equilibrium constant can be determined with the help of (8.18) by measuring the equilibrium concentrations and knowing the respective activity coefficients. It can also be calculated from thermodynamic data. For this calculation, we only need to know the standard chemical potentials of the reactive species, according to (8.15) and (8.20). The calculation of the standard chemical potentials is discussed in Sect. 8.3.

8.1.1 Relation of the Equilibrium Constant and the Stoichiometric Equation

It is important to know some limitations of the application of the equilibrium constant. The most important limitation is that it *does not refer to a reaction, but to an actual form of the stoichiometric equation.* While demonstrating this property, we also show the application for an actual chemical reaction. Let us consider the formation of ammonia from its elements already mentioned in the introduction of this chapter. Consider the stoichiometric equation in the form of (8.3):

$$1\tfrac{1}{2}\,H_2 + \tfrac{1}{2}\,N_2 = NH_3. \tag{8.21}$$

The equilibrium constant and the standard reaction Gibbs potential can be given as follows:

$$K_{a,1} = \frac{a_{NH_3}}{\left(a_{H_2}\right)^{3/2}\left(a_{N_2}\right)^{1/2}} \qquad \Delta_{r,1}G^{\ominus} = \mu^{\ominus}_{NH_3} - \frac{3}{2}\mu^{\ominus}_{H_2} - \frac{1}{2}\mu^{\ominus}_{N_2}. \tag{8.22}$$

Consider next another stoichiometric equation for the same reaction, which does not contain fractional stoichiometric numbers but whole numbers only:

$$3H_2 + N_2 = 2NH_3. \tag{8.23}$$

The equilibrium constant and the standard reaction Gibbs potential for this reaction can be given as:

$$K_{a,2} = \frac{\left(a_{NH_3}\right)^2}{\left(a_{H_2}\right)^3 a_{N_2}} \qquad \Delta_{r,2}G^{\ominus} = 2\mu^{\ominus}_{NH_3} - 3\mu^{\ominus}_{H_2} - \mu^{\ominus}_{N_2}. \tag{8.24}$$

Comparing these with the previous quantities, we can state that $\Delta_{r,2}G^{\ominus}$ for reaction (8.23) is twice greater than $\Delta_{r,1}G^{\ominus}$ for reaction (8.21) – as we can expect. The two equilibrium constants are not identical either; $K_{a,2}$ is the square of $K_{a,1}$.

We can conclude from this example what has been already stated before; the equilibrium constant always characterizes the *stoichiometric equation*, not the *reaction itself*. We have also seen that, while the standard reaction Gibbs potential is *proportional* to the stoichiometric numbers in the equation, the equilibrium constant changes *exponentially*.

Note that the *direction* of the reaction also has a consequence on the value of the equilibrium constant. Obviously, if we would reverse the direction of the reactions in the stoichiometric equations (i.e., write the equations for the decomposition of ammonia), the standard reaction Gibbs potential would change sign, while the equilibrium constant would become the reciprocal of the original value.

There are often many simultaneous chemical reactions taking place in reactive mixtures (including those in living organisms), thus it is important to be able to describe simultaneous equilibria. In principle, this task is not more complicated than in case of a single reaction; for every reaction, the condition imposed by the corresponding equilibrium constant should hold. The concentrations of the common components in different reactions should, of course, be the same within the same phase, and the conservation of atoms (or amounts of elements) should always be fulfilled, as usually when writing stoichiometric equations. However, it is easy to find out that to write the condition of a simultaneous chemical equilibrium, only *independent reactions* should be taken into account.

A reaction is independent if it cannot be constructed from other reactions taking place by addition or subtraction (i.e., by *linear combinations*). Was it possible to construct it this way, its standard reaction Gibbs potential $\Delta_r G^{\ominus}$ could also be calculated by additions and subtractions from other reactions' standard Gibbs potentials, while its equilibrium constant K_a could be calculated by multiplications and divisions. Thus, the reaction would not impose additional conditions for the equilibrium. In case of a few simple reactions, it is easy to find the number of independent reactions by inspection of the stoichiometric equations. However, this method becomes quite hopeless to apply if there are many reactions with common species in the system. In this case, the property that independent reactions are *linearly independent* offers the possibility to use standard algebraic methods to find their number. This can be done by determining the rank of the *stoichiometric matrix* of the reactions. (The columns of the stoichiometric matrix display the atoms of components, while its rows the components themselves. Elements of the rows express the number of the atoms corresponding to the actual column in the component corresponding to the actual row.) Independent reactions to take into account when imposing equilibrium conditions can usually be chosen several different ways. The only condition to choose them is that they should be independent of each other.

8.1.2 Affinity: The Driving Force of Chemical Reactions

The standard reaction Gibbs potential not only plays a determining role concerning the equilibrium but it is also a determining factor concerning chemical changes.

To demonstrate this, let us recall the differential of the Gibbs potential according to (8.4), but substitute the expression for dn_i from (8.10):

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \left(\sum_{i=1}^{R} \nu_i \mu_i\right) \mathrm{d}\xi + \sum_{i=R+1}^{K} \mu_i \mathrm{d}n_i = 0. \tag{8.25}$$

We have also rearranged terms so that the sum describing the change of the amounts of the R reacting species is separated from that of the nonreacting $K - R$ species. We know that the coefficients of the increments in the total differential are the partial derivatives of the G function with respect to the same variables as the increment. Consequently, the partial derivative of G with respect to ξ is the sum preceding the increment dξ, that is:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P,n_{j>R}} = \sum_{i=1}^{R} \nu_i \mu_i = \sum_{i=1}^{R} \nu_i G_i = \Delta_{\mathrm{r}} G. \tag{8.26}$$

Comparing this result with (8.5), we can state that the condition of chemical equilibrium can also be written in the alternative form

$$\Delta_{\mathrm{r}} G = \left(\frac{\partial G}{\partial \xi}\right)_{T,P,n_{j>R}} = 0. \tag{8.27}$$

Obviously, this form also expresses the fact that the reaction proceeds until a state is achieved where the Gibbs potential function has an extremum. In a stable equilibrium, it should be a minimum. Thus, we expect that the function should be *convex* as a function of the extent of reaction, which also means that, in a spontaneous reaction, the function should decrease. Consequently, the derivative $\left(\frac{\partial G}{\partial \xi}\right)_{T,P,n_{j>R}}$ is negative for values of ξ inferior to the equilibrium value and positive for those superior to the equilibrium value. (Note that it is negative for the reverse reaction, which actually takes place while approaching equilibrium from above the equilibrium state.) The absolute value of the derivative is monotonically decreasing as the reaction proceeds towards equilibrium and attains zero there. Due to this behavior, the quantity $-\left(\frac{\partial G}{\partial \xi}\right)_{T,P,n_{j>R}}$ can be considered as the measure in Gibbs potential of the distance from the equilibrium state, indicating the spontaneity of the reaction taking place from an initial state. In the early times of chemistry (the age of alchemy), the tendency of substances to react was called *affinity*, literally meaning a "relation by marriage". That was the reason why de Donder named the quantity $-\left(\frac{\partial G}{\partial \xi}\right)_{T,P,n_{j>R}}$ affinity, which is frequently used in thermodynamics. Thus, this expression in use for several centuries has been exactly defined and can also be measured. Indeed, we can understand the thermodynamic background of chemical reactions by examining the Gibbs potential of the reacting mixture.

To demonstrate this, let us discuss Fig. 8.1. The diagram shows the Gibbs potential of a gaseous mixture as a function of the extent of reaction ξ. Initially (at $\xi = 0$), the mixture consists of $n_{\mathrm{H_2}} = 1{,}5$ mol, $n_{\mathrm{N_2}} = 0{,}5$ mol and $n_{\mathrm{NH_3}} = 0$ mol. Obviously, if the reaction proceeds to completion (at $\xi = 1$), the mixture contains only 1 mol ammonia, and hydrogen and nitrogen are completely consumed. Using (8.9), we can write the actual composition of the mixture as a function of ξ:

$$n_{\mathrm{H_2}} = 1.5 - 1.5\,\xi \quad n_{\mathrm{N_2}} = 0.5 - 0.5\,\xi \quad n_{\mathrm{NH_3}} = \xi. \tag{8.28}$$

The total amount of species is the sum of the amounts of the three components, $2 - \xi$ mol, thus the mole fraction of the components is given in the following form:

$$x_{\mathrm{H_2}} = \frac{1.5 - 1.5\,\xi}{2 - \xi} \quad x_{\mathrm{N_2}} = \frac{0.5 - 0.5\,\xi}{2 - \xi} \quad x_{\mathrm{NH_3}} = \frac{\xi}{2 - \xi}. \tag{8.29}$$

Suppose that the reaction mixture behaves as an ideal mixture, thus we can apply the summation

$$G = \sum_{i=1}^{R} n_i\,\mu_i = \sum_{i=1}^{R} n_i\left(\mu_i^{\ominus} + RT\ln x_i\right) \tag{8.30}$$

for the actual mixture:

$$G = n_{\mathrm{H_2}}\mu_{\mathrm{H_2}}^{\ominus} + n_{\mathrm{N_2}}\mu_{\mathrm{N_2}}^{\ominus} + n_{\mathrm{NH_3}}\mu_{\mathrm{NH_3}}^{\ominus} + RT\left(n_{\mathrm{H_2}}\ln x_{\mathrm{H_2}} + n_{\mathrm{N_2}}\ln x_{\mathrm{N_2}} + n_{\mathrm{NH_3}}\ln x_{\mathrm{NH_3}}\right). \tag{8.31}$$

Figure 8.1 shows the function calculated using the above equation at the temperature of 500 K (226.85°C) and pressure of 1 bar (10^5 Pa). The standard chemical potentials of pure nitrogen and hydrogen are zero; that of pure ammonia is 4.800 kJ mol^{-1}; RT at this temperature is 4.157 kJ mol^{-1}. The equilibrium at this temperature is shifted towards the reactants.

Examining this diagram, we can have an insight into the thermodynamic background of why many reactions do not proceed until completion. Its origin is basically the fact that the Gibbs potential can decrease due to the mixing of the components of the reaction. This decrease is more important if there are more components. As we can see, this decrease already happens when mixing the reactants (1.5 mol hydrogen and 0.5 mol nitrogen in this case). This has the consequence that the Gibbs potential of the reacting mixture does not start from the sum of the standard Gibbs potentials of the reactants (zero in this case) but from the Gibbs potential of mixing that can be calculated using (8.31); in this case, from – 4.675 kJ mol^{-1}. If mixing would have been avoided before, as well as during the reaction (hydrogen and nitrogen were in separate phases and ammonia formed during the reaction in a third phase), the Gibbs potential of the three-phase

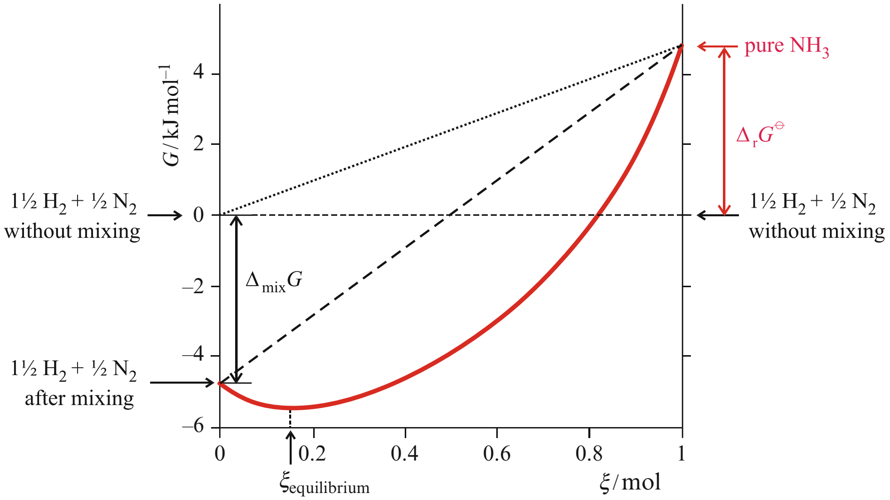

Fig. 8.1 Gibbs potential as a function of the extent of reaction ξ at the temperature of 500 K (226.85°C) and a pressure of 1 bar for the reaction 1½ H_2 + ½ N_2 = NH_3 in a mixture, where the initial state contains only 1½ mol H_2 and ½ mol N_2 without any NH_3

reacting system would change along the dotted line in the diagram. If reactants would have been allowed to mix but ammonia formed during the reaction would be accumulating in a separate phase, the Gibbs potential of the two-phase reacting system would change along the dashed line. As we can see from the diagram, in case of the single-phase (homogeneous) reacting mixture, the Gibbs potential of mixing (of H_2 and ½ N_2) is already present in the system, and the contribution due to mixing of the product is added during the reaction. This change is demonstrated by the thick solid curve, which shows the Gibbs potential of the reacting homogeneous mixture. The right-hand side of the diagram also shows the contribution of the standard reaction Gibbs potential $\Delta_r G^\ominus$; the rest of the change is due to mixing.

It can easily be concluded from the above discussion that the equilibrium composition can be in between the reactant ($\xi = 0$) and the product ($\xi = 1$) state, far from either of them, if the Gibbs potential of mixing is comparable to that of the reaction. In the example shown in the figure, $\Delta_r G^\ominus$ is 4.80 kJ mol^{-1}, while RT is 4.157 kJ mol^{-1}. The proximity of these two values enables mixing to compete with the change due to the reaction. Fig. 8.2 shows the Gibbs potential of mixing of the reaction mixture at 500 K anew, and a similar diagram valid at 298.15 K; in both cases calculated from (8.31) applying ideal mixture approximation, using data at 1 bar pressure. At the lower temperature of 298.15 K, $\Delta_r G^\ominus = -16.367$ kJ mol^{-1}, while RT is only 2.478 kJ mol^{-1}. As we can see from the figure, this difference is already sufficient to shift the equilibrium very close to completion of the reaction. Note that the Gibbs potential of mixing also means a smaller contribution to the overall Gibbs potential at the lower temperature; its value is merely – 2.776 kJ mol^{-1} compared to – 4.675 kJ mol^{-1}.

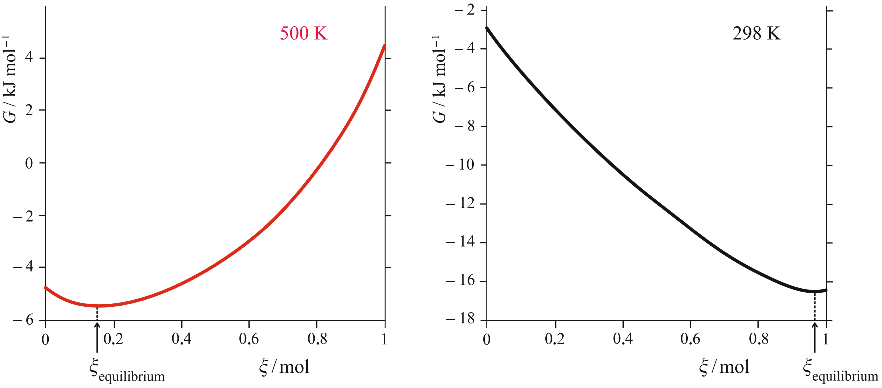

Fig. 8.2 Gibbs potential as a function of the extent of reaction ξ at temperatures 500 K (226.85°C) and 298.15 K (25°C) and a pressure of 1 bar for the reaction 1½ H_2 + ½ N_2 = NH_3 in a mixture where the initial state contains only 1½ mol H_2 and ½ mol N_2 without any NH_3. The equilibrium composition is close to the reactants at 500 K but it is shifted close to the product at 298.15 K

The higher the temperature, the more the equilibrium is shifted towards smaller extent of reaction. For example, at 1000 K, $\Delta_r G^{\ominus} = 61.91$ kJ mol^{-1}, while RT increases to 8.135 kJ mol^{-1}, which results in the extent of reaction in equilibrium of $\xi = 0.003$. This small conversion could not even be seen in the figure, it is so close to the pure reactants' state. (The temperature dependence of the equilibrium constant is discussed in detail in Section 8.4.) From the values discussed above, we can conclude that, at temperatures not much different from room temperature, reactants would not react in a detectable amount if the standard reaction Gibbs potential is 100 kJ mol^{-1} or higher. (The conversion is less than 10^{-10}.) Similarly, if the standard reaction Gibbs potential is –100 kJ mol^{-1} or lower, the reaction is practically completed in equilibrium. (The conversion differs less than 10^{-10} from 1.)

Note that a great affinity does not always mean that the reaction would take place in reality. The reason for this is the *activation barrier* meaning that the reaction could only occur via molecular interactions for which reactant molecules do not have enough energy at the given temperature. For example, most organic compounds are not in equilibrium in presence of oxygen, but the reaction with oxygen (burning) cannot take place due to the lack of sufficient energy of molecules. (To burn an organic substance, temperature must be raised above ignition temperature and conditions must be provided that heat delivered during the exothermic reaction could not dissipate easily, thus maintaining the necessary temperature.) The formation of ammonia from its elements shown in the previous figures does not take place either at room temperature, even if the equilibrium would be at quite high conversion. An efficient catalyst is needed in the mixture of N_2 and H_2 to make it possible for ammonia to form until equilibrium composition is achieved.

8.2 The Equilibrium Constant in Terms of Different Activities

In the previous section, we have stated that the equilibrium constant is only unique if the stoichiometric equation is given. We shall discuss now its dependence on the reference state; i.e., the choice of the standard state. Similarly to the discussion of mixture properties, we can base our analysis on the fact that the value of the chemical potential of a component does not depend on this choice, thus the equation

$$\sum_{i=1}^{R} \nu_i\, \mu_i = \sum_{i=1}^{R} \nu_i \left(\mu_i^{\ominus} + RT \ln a_i\right) = 0 \tag{8.32}$$

always holds. However – as discussed in Sect. 6.3.4 – the division of this value μ_i into a concentration-independent standard potential $\mu_i^{\ominus}$ and the concentration-dependent term $RT \ln a_i$ *does depend* on the reference state.

The choice of this state is based on practical aspects also when describing equilibria of reactions. In case of gas phase reactions, the pure substance is the reference state, and the relative activity is the fugacity divided by the total pressure. If there are reactants in a liquid-phase reaction, which are not liquid in their pure state, or whose solubility is limited in the reaction mixture, the practical reference state is the ideally dilute solution. The corresponding activity in this case may be either the rational activity on mole fraction basis, or relative activities on molarity or molality basis. To show the consequence of the actual type of activity used, let us write in (8.18) the activities expressed with the corresponding concentrations (or with the partial pressure):

$$K_a = \prod_{i=1}^{R} (f_i x_i)^{\nu_i} = \prod_{i=1}^{R} (x_i)^{\nu_i} \prod_{i=1}^{R} (f_i)^{\nu_i} = K_x K_f, \tag{8.33}$$

$$K_a = \prod_{i=1}^{R} (\gamma_{x,i} x_i)^{\nu_i} = \prod_{i=1}^{R} (x_i)^{\nu_i} \prod_{i=1}^{R} (\gamma_{x,i})^{\nu_i} = K_x K_{\gamma_x}, \tag{8.34}$$

$$K_a = \prod_{i=1}^{R} \left(\gamma_{c,i} \frac{c_i}{c^{\ominus}}\right)^{\nu_i} = \prod_{i=1}^{R} \left(\frac{c_i}{c^{\ominus}}\right)^{\nu_i} \prod_{i=1}^{R} (\gamma_{c,i})^{\nu_i} = K_c K_{\gamma_c}, \tag{8.35}$$

$$K_a = \prod_{i=1}^{R} \left(\gamma_{m,i} \frac{m_i}{m^{\ominus}}\right)^{\nu_i} = \prod_{i=1}^{R} \left(\frac{m_i}{m^{\ominus}}\right)^{\nu_i} \prod_{i=1}^{R} (\gamma_{c,i})^{\nu_i} = K_m K_{\gamma_m}, \tag{8.36}$$

$$\begin{aligned} K_a &= \prod_{i=1}^{R} \left(\varphi_i \frac{p_i}{P^{\ominus}}\right)^{\nu_i} = \prod_{i=1}^{R} \left(\frac{p_i}{P^{\ominus}}\right)^{\nu_i} \prod_{i=1}^{R} (\varphi_i)^{\nu_i} \\ &= \prod_{i=1}^{R} (p_i)^{\nu_i} \prod_{i=1}^{R} \left(\frac{1}{P^{\ominus}}\right)^{\nu_i} \prod_{i=1}^{R} (\varphi_i)^{\nu_i} = \frac{K_p K_{\varphi}}{(P^{\ominus})^{\Sigma \nu_i}}. \end{aligned} \tag{8.37}$$

As we see, the expressions K_x, K_c, K_m, and K_p calculated using concentrations (or partial pressures) instead of the activities should be multiplied by the expressions K_f, K_{γ_x}, K_{γ_c}, K_{γ_m}, and $K_{\varphi}\,(P^{\ominus})^{\Sigma \nu_i}$ calculated using the respective activity coefficients to get the concentration-independent equilibrium constant K_a. In the expression $K_\varphi\,(P^\ominus)^{\Sigma\nu_i}$, $P^\ominus$ is the reference pressure (the standard pressure) and $\Sigma\nu_i$ is the sum of stoichiometric numbers, which is the change in number of moles in one mole stoichiometric equation.

Accordingly, if we consider the reactive mixture to be an ideal mixture, we use the approximation of the "true" activities by the concentrations, and we can consider the *apparent equilibrium constants* K_x, K_c, and K_m as concentration independent within this approximation. However, the apparent equilibrium constant K_p expressed with partial pressures is not always pressure independent, even if the gas mixture can be considered as an ideal mixture. If the sum of stoichiometric numbers $\Sigma\nu_i$ is zero, K_p can be considered constant within the ideal approximation. If it is not zero (i.e., in case of gas reactions resulting in change of the total amounts of the reactive components), even in ideal mixtures, only another apparent equilibrium constant, namely

$$K = \frac{K_p}{(P^\ominus)^{\Sigma\nu_i}} \tag{8.38}$$

can be considered as pressure and concentration independent. Of course if the standard pressure $P^\ominus$ is unity, $(P^\ominus)^{\Sigma\nu_i}$ is also identically unity. (This is the case if the standard pressure is 1 bar and partial pressures are also given in bar units. As this is typically the case when activities on concentration basis $c^\ominus$ or $m^\ominus$ are given – i.e., $c^\ominus = 1\,\mathrm{mol\,dm^{-3}}$ and $m^\ominus = 1\ \mathrm{mol\,kg^{-1}}$ – K_c and K_m do not require a similar correction.)

It is obvious from the above considerations that the apparent equilibrium constants K_x , K_c , K_m, and K_p are different in case of the ideal mixture approximation. However, they are also different if we do not use the ideal mixture approximation, as different activities in (8.33)–(8.37) are calculated based on different standard states. Accordingly, explicit forms of (8.17) can be given as follows:

$$\sum_{i=1}^{R} \nu_i\,\mu_i^* = -RT\ln\prod_{i=1}^{R} (f_i\,x_i)^{\nu_i}, \tag{8.39}$$

$$\sum_{i=1}^{R} \nu_i\,\mu_{x,i}^\ominus = -RT\ln\prod_{i=1}^{R} (\gamma_{x,i}\,x_i)^{\nu_i}, \tag{8.40}$$

$$\sum_{i=1}^{R} \nu_i\,\mu_{c,i}^\ominus = -RT\ln\prod_{i=1}^{R} \left(\gamma_{c,i}\,\frac{c_i}{c^\ominus}\right)^{\nu_i}, \tag{8.41}$$

$$\sum_{i=1}^{R} \nu_i\,\mu_{m,i}^\ominus = -RT\ln\prod_{i=1}^{R} \left(\gamma_{m,i}\,\frac{c_i}{m^\ominus}\right)^{\nu_i}, \tag{8.42}$$

$$\sum_{i=1}^{R} \nu_i\,\mu_i^*(P^\ominus) = -RT\ln\prod_{i=1}^{R} \left(\varphi_i\,\frac{p_i}{P^\ominus}\right)^{\nu_i}. \tag{8.43}$$

The left-hand side of these equations can be called the reaction standard Gibbs potential $\Delta_r G^\ominus$, but we should keep in mind that its actual expression, thus its actual value is also different for different cases. Calculating the equilibrium constant using the relative activities $f_i\, x_i$ has the consequence that the chemical potentials of pure components μ_i^* are used in the proper phase, at the actual pressure and temperature in the expression $\Delta_r G^\ominus = \sum_{i=1}^{R} \nu_i\, \mu_i^*$ to calculate the reaction standard Gibbs potential. Similarly, in (8.40) the reaction standard Gibbs potential is calculated from $\mu_{x,i}^\ominus$, referenced to infinitely dilute solutions; in (8.41), it is calculated from $\mu_{c,i}^\ominus$ (at $c^\ominus = 1\,\mathrm{mol\,dm^{-3}}$ in a hypothetical ideal solution referenced to infinite dilution), while in (8.42), from $\mu_{m,i}^\ominus$ (at $m^\ominus = 1\ \mathrm{mol\,kg^{-1}}$ in a hypothetical ideal solution referenced to infinite dilution). In (8.43), $\Delta_r G^\ominus$ is calculated from the chemical potentials $\mu_i^*(P^\ominus)$ of the pure species at the standard pressure $P^\ominus$.

From the above considerations, we can conclude that the value of the equilibrium constant K_a depends not only on the actual form of the stoichiometric equation but also on the reference state of the chemical potential, that is, the type of the standard chemical potential. This ambiguity is even more complicated if the reaction does not take place in a single (homogeneous) phase but in at least two phases. In this case, it should also be decided, in which phase the equilibrium condition will be formulated. There are also cases where the equilibrium condition – thus the equilibrium constant and the reaction standard Gibbs potential – is given taking into account more than one phase. In some cases, not all the activities within the same phase are expressed on the same concentration basis.

As an example, let us consider the formation of carbonic acid from water and carbon dioxide:

$$\mathrm{CO_2}(l) + \mathrm{H_2O}(l) = \mathrm{H_2CO_3}(l). \tag{8.44}$$

Each component is present in the liquid phase, thus it can be the reference state. It is practical to reference the activities of CO_2 and H_2CO_3 to infinite dilution, but that of the H_2O to the pure water. According to (8.18) and (8.15), the equilibrium constant and the standard reaction Gibbs potential can then be written as:

$$K_a = \frac{\gamma_{x,\mathrm{H_2CO_3}}\, x_{\mathrm{H_2CO_3}}}{f_{\mathrm{H_2O}}\, x_{\mathrm{H_2O}}\ \gamma_{x,\mathrm{CO_2}}\, x_{\mathrm{CO_2}}} \qquad \Delta_r G^\ominus = \mu_{\mathrm{H_2CO_3}}^\ominus - \mu_{\mathrm{H_2O}}^* - \mu_{\mathrm{CO_2}}^\ominus. \tag{8.45}$$

As there are mole fractions of the components in the expression of the equilibrium constant, the activity coefficient of water is referenced to the pure component, but in the case of CO_2 and H_2CO_3, to the virtual "pure" components as if they were in the same state as in an infinitely dilute solution. Trying to interpret the standard reaction Gibbs potential, we only could imagine it as the change in Gibbs potential when from 1 mol "pure carbon dioxide" of the same state as in an infinitely dilute solution and 1 mol pure water 1 mol "pure carbonic acid" of the same state as in an infinitely dilute solution would be formed. Of course such reaction does not exist in practice, due to the limited solubility of both CO_2 and H_2CO_3 in water. (Even if they existed in a pure liquid state, this state would not be identical to that of the respective species in an infinitely dilute solution.) For this reason, it is better to interpret the standard reaction Gibbs potential simply as *a constant* referring to a specified stoichiometric equation *and* specified standard states, without associating to it an actual change in Gibbs potential during an actual reaction.

The formation of carbonic acid can also be described by a different reaction if we allow for gas-phase carbon dioxide to be present:

$$CO_2(g) + H_2O(l) = H_2CO_3(l) \tag{8.46}$$

This equation is of more practical importance, especially if we write the concentration of carbon dioxide in the form of partial pressure, and that of carbonic acid and water in molar concentration. The corresponding equilibrium constant and the reaction standard Gibbs potential can be written as follows:

$$K_a = \frac{\gamma_{c,\mathrm{H_2CO_3}}[\mathrm{H_2CO_3}]}{\gamma_{c,\mathrm{H_2O}}[\mathrm{H_2O}] \quad \varphi_{\mathrm{CO_2}}(p_{\mathrm{CO_2}}/P^{\ominus})} \qquad \Delta_\mathrm{r}G^{\ominus} = \mu^{\ominus}_{c,\mathrm{H_2CO_3}} - \mu^{\ominus}_{c,\mathrm{H_2O}} - \mu^{\ominus}_{\mathrm{CO_2}}. \tag{8.47}$$

Stoichiometric formulae in brackets represent the values of molar concentration in mol dm^{-3} unit of the corresponding species, while $p_{\mathrm{CO_2}}$ is the *partial pressure* of carbon dioxide in the gas phase. Accordingly, in the expression of the reaction standard Gibbs potential, the standard chemical potential $\mu^{\ominus}_{c,i}$ of both carbon dioxide and water are referenced to a mixture in which the concentration of the given component is 1 mol dm^{-3}, but in the same (virtual) state as in an infinitely dilute solution. At the same time, the standard chemical potential $\mu^{\ominus}_{\mathrm{CO_2}}$ is the chemical potential of the *pure CO$_2$ gas* at the standard pressure $P^{\ominus}$, given that it behaves as an ideal gas at this pressure and the actual temperature. (If we apply the ideal gas approximation at the actual partial pressure for the carbon dioxide, the value of $\varphi_{\mathrm{CO_2}}$ is unity – thus it can be omitted from the product –, and we can write the chemical potential $\mu^{*}_{\mathrm{CO_2}}$ of the pure gas at pressure $P^{\ominus}$.)

The gas phase chemical potential can be written in the equilibrium conditions – according to the stoichiometric equation (8.46) – as it is *the same as that of the dissolved carbon dioxide*, due to the phase equilibrium between the gas and the liquid, and the free passage of CO_2 between the two phases. We can proceed the same way for every *heterogeneous reaction* if the reactive components mix. However, it should always be clear what concentration is used and in which phase, as the corresponding standard chemical potentials should be used in the expression for the reaction standard Gibbs potential.

8.2.1 Heterogeneous Reaction Equilibria of Immiscible Components

As explained at the end of Sect. 8.1.2, *mixing* of the components also plays a role in determining the equilibrium composition of the reaction mixture, in addition to the reaction standard Gibbs potential. If this mixing does not involve some of the reacting components (i.e., they do not mix with other reactive species), the consequence of their mixing should not be included in the equilibrium condition. We should keep in mind that mixing is always unlimited in the gas phase, thus nonmixing reactive components can only be present in condensed phases. To describe corresponding equilibrium conditions, let us start from the general equilibrium condition for a reaction:

$$\sum_{i=1}^{R} \nu_i \mu_i = 0. \tag{8.48}$$

Let us separate the sum for the r gas phase components, and the other $R - r$ condensed phase components that do not mix with each other:

$$\sum_{i=1}^{r} \nu_i \mu_i + \sum_{i=r+1}^{R} \nu_i \mu_i = 0. \tag{8.49}$$

If the $R - r$ species in the second sum are not present in the gas phase,[2] and they do not mix in the condensed (usually solid) phase, their chemical potential is independent of composition. Taking this into account and expressing the gaseous components' chemical potential with their fugacity, we get the following form:

$$\sum_{i=1}^{r} \nu_i \mu_i^{\ominus} + RT \sum_{i=1}^{r} \nu_i \ln \varphi_i \left(\frac{p_i}{P^{\ominus}} \right) + \sum_{i=r+1}^{R} \nu_i \mu_i = 0. \tag{8.50}$$

The second term of the above equation can be expressed with the usual notation:

$$RT \sum_{i=1}^{r} \nu_i \ln \varphi_i \left(\frac{p_i}{P^{\ominus}} \right) = RT \ln \prod_{i=1}^{r} \left(\frac{\varphi_i p_i}{P^{\ominus}} \right) = RT \ln K'. \tag{8.51}$$

Rearranging this, we get the result:

$$- \sum_{i=1}^{r} \nu_i \mu_i^{\ominus} - \sum_{i=r+1}^{R} \nu_i \mu_i = RT \ln K'. \tag{8.52}$$

This result is quite similar to the usual equation describing chemical equilibrium. Its peculiarity is that, for the nonmixing condensed-phase species, it is not the

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[2] Strictly speaking, the "nonvolatile" solid or liquid species are also present in the gas phase, even if their quantity is undetectable. The effect of these tiny quantities in mixing can be readily neglected, thus it is not necessary to take their contribution into account. These tiny amounts would not play a perceptible role in determining the equilibrium of the reaction either; the reaction is typically much faster than the evaporation of the "nonvolatile" species.

standard chemical potential at the standard pressure $P^{\ominus}$,which is written in the sum, but the chemical potential at the actual pressure of the reaction mixture. Let us examine how we can calculate this chemical potential from the standard chemical potential at the standard pressure $P^{\ominus}$. According to (6.31), the chemical potential at constant pressure and composition (in this case, in the pure state) can be calculated using the following expression:

$$\mu_i = \mu_i^{\ominus} + \int_{P^{\ominus}}^{p} v_i \, \mathrm{d}P = \mu_i^{\ominus} + v_i \left(p - P^{\ominus}\right). \tag{8.53}$$

During integration, it is supposed that the molar volume v_i does not depend on temperature – a fairly good approximation for solids even in a wide pressure range. We can apply another approximation; the molar volume v_i of solids is so small that the product $v_i \left(p - P^{\ominus}\right)$ can be neglected compared to the standard chemical potential $\mu_i^{\ominus}$. Consequently, the sum of the products $v_i\ \mu_i$ is approximately the same as that of $v_i \mu_i^{\ominus}$ at pressures not too much higher than $P^{\ominus}$:

$$\sum_{i=r+1}^{R} \nu_i \mu_i = \sum_{i=r+1}^{R} \nu_i \mu_i^{\ominus} + \left(p - P^{\ominus}\right) \sum_{i=r+1}^{R} \nu_i v_i \cong \sum_{i=r+1}^{R} \nu_i \mu_i^{\ominus}. \tag{8.54}$$

In condensed phases, the difference of the molar volume of products and reactants $\sum_{i=r+1}^{R} \nu_i v_i$ is also negligible compared to the difference of the standard chemical potentials, thus – at moderately high pressures – the following equation can be considered as valid:

$$-\Delta_{\mathrm{r}} G^{\ominus} = \sum_{i=r+1}^{R} \nu_i \mu_i^{\ominus} = RT \ln K'. \tag{8.55}$$

In other words, the *reduced equilibrium constant K'* can be expressed using the reaction standard Gibbs potential for the original stoichiometric equation.

Let us illustrate the above general principles by the example of the *calcination of limestone*. The stoichiometric equation can be written as:

$$\mathrm{CaCO3}(s) = \mathrm{CaO}(s) + \mathrm{CO_2}(g). \tag{8.56}$$

The gas phase contains only CO_2 from the reactive species, while $CaCO_3$ and CaO are in the solid phase but they do not mix. According to the above described results, the reduced equilibrium constant and the reaction standard Gibbs potential can be written as:

$$K' = \varphi_{\mathrm{CO_2}} \left(p_{\mathrm{CO_2}} / P^{\ominus}\right) \quad \Delta_{\mathrm{r}} G^{\ominus} = \mu^*_{\mathrm{CaCO_3}}(s) - \mu^*_{\mathrm{CaO}}(s) - \mu^{\ominus}_{\mathrm{CO_2}}\left(P^{\ominus}\right). \tag{8.57}$$

These expressions include only the approximation valid for the solids at moderate pressures; properties of the CO_2 gas are properly taken into account by the fugacity coefficient and the standard chemical potential referenced to the hypothetical ideal gas behavior. Note that the validity does not depend on the actual quantity of the reactive species in the solid phase; it is essential only that some quantity be present to maintain equilibrium.

It is common practice also to consider the gas phase reactant as an ideal gas, and ignore the division by the standard pressure $P^{\ominus}$ in the equilibrium constant. This leads to the simplified formulae that can be seen in many textbooks and handbooks:

$$K' = p_{\mathrm{CO_2}} \quad \Delta_r G^{\ominus} = \mu^*_{\mathrm{CaCO_3}}(s) - \mu^*_{\mathrm{CaO}}(s) - \mu^*_{\mathrm{CO_2}}(g). \tag{8.58}$$

However, it is important to know that $p_{\mathrm{CO_2}}$ (and, in general, partial pressures in similar expressions) should be understood as the *value* of pressure in the unit of the pressure at which the chemical potential of the pure component in the expression of $\Delta_r G^{\ominus}$ is determined (usually 101 325 Pa, or 1 bar $= 10^5$ Pa). Within this approximation, the partial pressure of carbon dioxide at which the reaction is in equilibrium can be calculated from the equilibrium constant K' using (8.20). If the partial pressure of CO_2 at the actual temperature is less than this, $CaCO_3$ will *completely decompose*. This is the case during lime burning when fresh air flows to burn the coal sweeps the carbon dioxide from the hot reaction zone, thus the product is pure quicklime (CaO). If the partial pressure of CO_2 is higher than the equilibrium pressure, the reaction is reversed; $CaCO_3$ is formed from calcium oxide and carbon dioxide. In case the partial pressure is continuously maintained above the equilibrium level, the reverse reaction also proceeds to completion. (Contrarily to homogeneous reactions where mixing does not allow the reaction to complete in either direction.)

The results can readily be applied also for reactions when the gas phase contains more than one reacting species. It can be illustrated by the reaction

$$\mathrm{C}(s) + \mathrm{CO_2}(g) = 2\,\mathrm{CO}(g), \tag{8.59}$$

where carbon is only present in the solid phase and neither CO nor CO_2 present in the gas phase dissolve in it. Applying the ideal gas mixture approach for the gas phase and omitting the division by $P^{\ominus}$, the reduced equilibrium constant and the standard Gibbs potential of the reaction can be written the following way:

$$K' = \frac{(p_{\mathrm{CO}})^2}{p_{\mathrm{CO_2}}} \quad \Delta_r G^{\ominus} = 2\mu^*_{\mathrm{CO}}(g) - \mu^*_{\mathrm{C}}(s) - \mu^*_{\mathrm{CO_2}}(g). \tag{8.60}$$

During this reaction, the equilibrium ratio of the partial pressures of CO and CO_2 will always be adjusted to the value prescribed by the equilibrium constant (if the temperature is high enough that the reaction of the two gases in contact with coal can proceed). The condition for the equilibrium to be achieved requires, of course, that there should be enough coal to be oxidized, or there should be enough carbon monoxide to disproportionate; depending on the actual direction of the reaction. A continuous flow of CO_2 will result in the complete transformation of the coal to carbon monoxide.

Heterogeneous reactions are also important in the formation of minerals in rocks. At large depths in the earth crust, pressure can be so high that the pressure dependence of the chemical potential of the solid reactants cannot be neglected. By analyzing the composition of the reactive species, it is possible to determine the pressure acting on the rocks by the time the minerals have been formed. For this reason, these rocks are also called *geobarometers*.

8.3 Calculation of the Equilibrium Constant from Thermodynamic Data

As already mentioned, the equilibrium constant can be determined by measuring the concentrations of the reacting species and substituting them into the expression of the equilibrium constant. To do so, it is necessary to have the physical realization of the reaction mixture at equilibrium, and experimentally determine all the relevant concentrations. If there exist thermodynamic data for the reacting components, (8.20) largely facilitates the task; the equilibrium constant can be calculated from the reaction standard Gibbs potential.

In this section, we explore the possibility to calculate the reaction standard Gibbs potential from measurable thermodynamic quantities. According to (8.15), the necessary quantities to be calculated are the standard chemical potentials of the reacting species.

We can use (6.9) to calculate standard chemical potentials $\mu_i^\ominus$ as:

$$\mu_i^\ominus = H_i^\ominus - TS_i^\ominus. \tag{8.61}$$

In this equation, $H_i^\ominus$ is the standard partial molar enthalpy while $S_i^\ominus$ is the standard partial molar entropy at the pressure $P^\ominus$, in a state according to the standard (i.e., in its pure state or at unit concentration).

Thus, $H_i^\ominus$ is either the molar enthalpy of the pure substance or the partial molar enthalpy of the component after mixing. Knowing the thermodynamic properties of the actual mixture, we can use (6.125) to calculate the enthalpy of mixing, from which we can calculate $H_i^\ominus$ in the mixture. One of the tasks is thus to determine the standard enthalpy of pure substances at a given temperature T. Let us see first that to do so, it is sufficient to know the standard enthalpy at an arbitrary temperature and the function c_P, the constant-pressure heat capacity at the pressure $P^\ominus$. According to (4.25), it is possible then to calculate the standard enthalpy at any other temperature:

$$H_i^\ominus(T_2) = H_i^\ominus(T_1) + \int_{T_1}^{T_2} c_{P,i}^\ominus \, \mathrm{d}t. \tag{8.62}$$

Thus, it is sufficient to determine the molar enthalpy at one single temperature, using calorimetric measurements. According to this condition, we usually find molar enthalpies $H_i^{\ominus}$ calculated using the above equation at the temperature of 25°C, i.e., at 298.15 K, called usually as *standard heats of formation*. The background of this name is that the molar enthalpy is the enthalpy of formation of a given substance from its elements, as the enthalpy of pure elements in their stable state at the standard pressure (of 1 bar) is zero by definition. The usual symbol for the standard heat of formation is $\Delta_f H_i^{\ominus}$. We recall here that the scale of the internal energy – and thus of all other energy-like state functions derived from it – is not unique; there is always an arbitrary additive constant involved. The additive constant mentioned at the end of Sect. 2.1.1 is also fixed using the mentioned convention. Fixing the scale of enthalpy instead of the internal energy is supported by practical reasons. On the one hand, standard enthalpies are more directly related to the calculation of equilibrium constant – as seen from (8.61). On the other hand, it is easier to determine the heat effect of reactions at a constant pressure (i.e., $\Delta_r H$) than at constant volume (i.e., $\Delta_r U$).

Having seen the method to calculate standard partial molar enthalpies $H_i^{\ominus}$, let us explore how to calculate standard partial molar entropies $S_i^{\ominus}$. Recalling that the scale of entropy – contrarily to that of the energy – is uniquely determined, its temperature dependence can be written based on (4.41) as

$$S_i^{\ominus}(T) = S_0(T_0 = 0) + \int_0^T \frac{c_{P,i}^{\ominus}}{T} \mathrm{d}T. \tag{8.63}$$

Knowing that S_0 (T_0 = 0) – according to Postulate 4 – the standard partial molar entropy can always be calculated if the constant-pressure molar heat capacity c_P is available. It is important to know how to proceed if there is a phase-transition below the temperature of the upper limit of integration. In this case, we only integrate until the temperature of the phase transition, then add the entropy of the phase transition, and then continue integration from the temperature of the phase transition but with the heat capacity c_P of the newly formed phase.

Summing up, we can state that we need the standard enthalpies (of formation) $H_i^{\ominus}$ and the constant-pressure molar heat capacities $c_{P,i}^{\ominus}$ (at the standard pressure $P^{\ominus}$) of the reacting species to calculate the reaction standard Gibbs potential $\Delta_r G^{\ominus}$. The heat-capacity function should be applicable from around 0 K until the temperature, where we want to calculate $\Delta_r G^{\ominus}$. The calculation can be formalized in a compact equation, using the following notation:

$$\Delta_r H^{\ominus} = \sum_{i=1}^{R} \nu_i H_i^{\ominus} \quad \Delta_r C_P^{\ominus} = \sum_{i=1}^{R} \nu_i c_{P,i}^{\ominus} \quad \Delta_r S^{\ominus} = \sum_{i=1}^{R} \nu_i S_i^{\ominus}. \tag{8.64}$$

The compact form then reads as:

$$\Delta_r G^{\ominus}(T) = \Delta_r H^{\ominus}(T) + \int_{298.15\mathrm{K}}^{T} \Delta_r C_P^{\ominus} \, \mathrm{d}t - T \int_{0\mathrm{K}}^{T} \frac{\Delta_r C_P^{\ominus}}{T} \mathrm{d}t. \tag{8.65}$$

Note that the second integral includes also the entropy changes of eventual phase transitions. T is the temperature at which we want to get $\Delta_r G^\ominus$ while t is the integration variable referring to temperature.

Equation (8.65) reflects the fact that the equilibrium constant of chemical reactions is uniquely determined, and that to calculate it, it is sufficient to know the relevant reaction enthalpies and the heat capacity functions. Practical calculations are usually even more simple, as in thermodynamic tables containing necessary standard enthalpies of formation $H_i^\ominus$, we can also find the standard entropies of formation $S_i^\ominus$ – calculated using (8.63), usually at 298.15 K. In terms of these data, we can use the following formula to calculate $\Delta_r G^\ominus$:

$$\Delta_r G^\ominus(T) = \Delta_r H^\ominus(298.15\mathrm{K}) + \int_{298.15\,\mathrm{K}}^{T} \Delta_r C_P^\ominus\,\mathrm{d}t - T\Delta_r S^\ominus(298.15\mathrm{K}) - T\int_{298.15\,\mathrm{K}}^{T} \frac{\Delta_r C_P^\ominus}{T}\,\mathrm{d}t. \tag{8.66}$$

If there exist thermodynamic data containing $H_i^\ominus$ and $S_i^\ominus$ values at the actual temperature T, we can even avoid doing the integrations.

The equation

$$\Delta_r G^\ominus(T) = \Delta_r H^\ominus(T) - T\Delta_r S^\ominus(T), \tag{8.67}$$

which is equivalent to (8.61) and was also used when writing (8.65), elucidates an important property of the reaction standard Gibbs potential $\Delta_r G^\ominus$. It is readily seen from the equation that the quantity that determines the equilibrium of the reaction at temperatures not much higher then zero is the heat of the reaction $\Delta_r H^\ominus$, as the product $T\Delta_r S^\ominus$ is very small compared to $\Delta_r H^\ominus$. As the temperature is raised, the contribution of the product $T\Delta_r S^\ominus$ becomes higher and higher. Supposing that $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ do not change significantly with temperature (which is usually a good approximation at around room temperature up to even a few hundreds of K), we can say that the product $T\Delta_r S^\ominus$ increases proportionally to temperature. This applies approximately also for the formation of ammonia discussed in Sect. 8.1.2. The value of $\Delta_r G^\ominus$ for this reaction, relative to (8.21) is –16.367 kJ/mol at 298.15 K, but it is only 4.80 kJ/mol at 500 K. At the same temperatures, the value of $\Delta_r H^\ominus$ changes from – 45.90 kJ/mol to only – 49.86 kJ/mol, and $\Delta_r S^\ominus$ from – 99.05 kJ/(mol K) to only –109.32 kJ/(mol K), respectively.

It is worth mentioning the great importance in the thermodynamics of chemical reactions of Postulate 4 that fixes the scale of entropy. It would be impossible to determine an eventual arbitrary additional constant for the entropies of individual components. To determine the entropy differences between different components is also not feasible – contrarily to differences of energy or enthalpy. Thus, without the knowledge of the entropy scale provided by Postulate 4, the equilibrium constant of chemical reactions could not be determined in a unique way.

8.4 Temperature and Pressure Dependence of the Equilibrium Constant

Although we have dealt with the temperature dependence of the equilibrium constant in the previous section, it is practical to apply a simpler and more straightforward formalism for this purpose. To derive the temperature and pressure dependence of the equilibrium constant, we can start from (8.19) written in the following form:

$$\ln K_a = -\frac{1}{R}\frac{\Delta_r G^{\ominus}}{T}. \tag{8.68}$$

Based on this, the temperature dependence of ln K_a can be derived from the known dependence of $\Delta_r G^{\ominus}$. The total differential of $\Delta_r G^{\ominus}$ can be written, according to (4.22), as:

$$\mathrm{d}\,\Delta_r G^{\ominus} = -\Delta_r S^{\ominus}\mathrm{d}T + \Delta_r V^{\ominus}\mathrm{d}P. \tag{8.69}$$

(There are only two terms in the equation as the standard Gibbs potential does not depend on composition.) We can readily see in the equation that the derivatives with respect to temperature and pressure are the following:

$$\left(\frac{\partial\,\Delta_r G^{\ominus}}{\partial T}\right)_P = -\Delta_r S^{\ominus} \qquad \left(\frac{\partial\,\Delta_r G^{\ominus}}{\partial P}\right)_T = \Delta_r V^{\ominus} \tag{8.70}$$

Starting from (8.68) we can find another expression for the temperature dependence of ln K_a. Let us start with the differentiation of the equation:

$$\left(\frac{\partial \ln K_a}{\partial T}\right)_P = -\frac{1}{R}\frac{\partial}{\partial T}\left(\frac{\Delta_r G^{\ominus}}{T}\right)_P. \tag{8.71}$$

We can apply for the derivative on the right-hand side the *Gibbs–Helmholtz equation*:

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_P = \left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{H}{T^2}. \tag{8.72}$$

Thus, (8.71) can be written in the following form:

$$\left(\frac{\partial \ln K_a}{\partial T}\right)_P = \frac{\Delta_r H^{\ominus}}{RT^2}. \tag{8.73}$$

As temperature is still included in the derivative, it is worth to change the variable of derivation using

$$\frac{\mathrm{d}(1/T)}{\mathrm{d}T} = -\frac{1}{T^2} \qquad \rightarrow \qquad \frac{1}{T^2}\mathrm{d}T = -\mathrm{d}\left(\frac{1}{T}\right) \tag{8.74}$$

This variable change results in the following expression:

$$\left(\frac{\partial \ln K_a}{\partial (1/T)}\right)_P = -\frac{\Delta_r H^\ominus}{R}. \tag{8.75}$$

Both (8.73) and (8.75) are usually called *van't Hoff equation*. It is straightforward to use the last form, from which we readily see that for exothermal reactions (for which $\Delta_r H^\ominus$ is negative) the equilibrium constant decreases with increasing temperature (i.e., *when* $1/T$ decreases). Similarly, for endothermic reactions (for which $\Delta_r H^\ominus$ is positive), the equilibrium constant increases with increasing temperature (i.e., *when* $1/T$ decreases). The simplicity of (8.75) is reflected also in the common practice to plot the temperature dependence of the logarithm of K_a in the form of $\ln K_a$ *versus* $1/T$. If we accept the approximation that $\Delta_r H^\ominus$ does not depend on temperature, we can expect that experimentally determined values are all along a straight line whose slope is $-\Delta_r H^\ominus/R$. From the experimental data, we can also determine the value of $\Delta_r H^\ominus$. However, it is not a good practice to determine this from the estimation of the slope of the linearized $\ln K_a$ *versus* $1/T$ function as this can lead to the distortion of the estimation of $\Delta_r H^\ominus$. A more correct procedure is to estimate the parameter $\Delta_r H^\ominus$ directly from the K_a *versus* T function, taking into account the experimental errors of the individual K_a values. This procedure leads to an unbiased estimate of $\Delta_r H^\ominus$. This function can be obtained by indefinite integration of (8.75) after having separated its variables:

$$\ln K_a = -\frac{\Delta_r H^\ominus}{R}\frac{1}{T} + \ln A. \tag{8.76}$$

The undetermined integration constant has been chosen as $\ln A$, which leads to a simple expression of the $K_a - T$ function:

$$K_a = A\mathrm{e}^{-\frac{\Delta_r H^\ominus}{RT}} \tag{8.77}$$

The two parameters to estimate from the experimental data are $\Delta_r H^\ominus$ in the exponent and the factor of the exponential, A. Note that this procedure is the reverse of determining the equilibrium constant from calorimetric data; in this case, the heat of reaction is calculated from the measurement of equilibrium concentrations.

The definite integration of (8.75) leads to the following result:

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \tag{8.78}$$

This is readily rearranged in the usual form

$$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right), \tag{8.79}$$

which can be used to calculate the equilibrium constant at temperature T_2 if we know its value at temperature T_1. (The condition of validity is of course that the temperature dependence of $\Delta_r H^\ominus$ be negligible in the range between T_1 and T_2.)

The pressure dependence of the equilibrium constant can be obtained directly from the partial derivative shown in (8.70):

$$\left(\frac{\partial \ln K_a}{\partial P}\right)_T = -\frac{\Delta_r V^\ominus}{RT}. \tag{8.80}$$

According to this result, the equilibrium constant increases with increasing pressure if the *reaction standard volume* $\Delta_r V^\ominus = \sum_{i=1}^{R} \nu_i V_i^\ominus$ is negative, that is, the volume decreases when the reaction proceeds. Conversely, it decreases with increasing pressure if the volume decreases when the reaction proceeds. In case of gas reactions, if there is a change in the stoichiometric numbers summed on the two sides of the equation ($\Sigma \nu_i$ is nonzero), this leads to important pressure dependence. (Cf. Sect. 8.2). If $\Sigma \nu_i$ is zero, then the volume will not change, thus the equilibrium constant is pressure independent within the ideal mixture approximation. In condensed phases, the volume change is typically much smaller than in a gas reaction, thus the pressure dependence is also smaller.

Supposing that the pressure dependence of $\Delta_r V^\ominus$ itself is negligible within the studied pressure range, experimental values in a plot of ln K_a *versus P* should be along a straight line whose slope is proportional to $-\Delta_r V^\ominus$. Accordingly, the standard reaction volume $\Delta_r V^\ominus$ can be estimated from these data. For condensed-phase reactions where the volume change is small, a special device made of diamond – the diamond anvil cell (DAC) – is used, as the deformation of diamond is very small even at large pressures. The DAC consists of two small high-quality gem diamonds of the shape of an anvil, and there is a little cavity between the two where solids and liquids can be compressed to ultrahigh pressures of several GPa, that is, to several tens of millions of the atmospheric pressure. The anvils are compressed using a first-class lever and a screw. In case of liquid samples, there is a gasket between the two anvils, which withstands lateral pressure but deforms in the direction of the axis of pressure. Using this device, equilibria of reactions in great depths of Earth can be studied.

8.4.1 The Le Châtelier–Braun Principle

Let us apply (8.25) for a chemical reaction, omitting the change of the nonreactive species:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \left(\sum_{i=1}^{R} \nu_i \mu_i\right) \mathrm{d}\xi = 0. \tag{8.81}$$

This equation formulates the condition of the minimum of Gibbs potential in equilibrium. Taking into account (8.26), we can rewrite the above equation in the following form:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \left(\frac{\partial G}{\partial \xi}\right)_{T,P} \mathrm{d}\xi = 0. \tag{8.82}$$

Let us differentiate both sides with respect to the extent of reaction ξ:

$$\mathrm{d}\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = -\left(\frac{\partial S}{\partial \xi}\right)_{T,P} \mathrm{d}T + \left(\frac{\partial V}{\partial \xi}\right)_{T,P} \mathrm{d}P + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,P} \mathrm{d}\xi = 0. \tag{8.83}$$

At constant pressure ($\mathrm{d}P = 0$), we get the following expression:

$$\left(\frac{\partial \xi}{\partial T}\right)_P = \frac{\left(\frac{\partial S}{\partial \xi}\right)_{T,P}}{\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,P}}. \tag{8.84}$$

At constant temperature and pressure, we can substitute $\partial H/T$ in place of ∂S:

$$\left(\frac{\partial \xi}{\partial T}\right)_P = \frac{\frac{1}{T}\left(\frac{\partial H}{\partial \xi}\right)_{T,P}}{\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,P}} \tag{8.85}$$

If the temperature is constant ($\mathrm{d}T = 0$), we get the following expression:

$$\left(\frac{\partial \xi}{\partial P}\right)_T = -\frac{\left(\frac{\partial V}{\partial \xi}\right)_{T,P}}{\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,P}}. \tag{8.86}$$

The Gibbs potential should be minimal in equilibrium, which is equivalent to the criterion of *stability* (cf. Sect. 7.1):

$$\mathrm{d}^2 G > 0 \tag{8.87}$$

One of the conditions of this inequality is that $(\partial^2 G/\partial \xi^2)_{T,P}$ should be positive. Due to this condition, we can conclude from (8.85) that

$$\text{if} \quad \left(\frac{\partial H}{\partial \xi}\right)_{T,P} > 0, \quad \text{then} \quad \left(\frac{\partial \xi}{\partial T}\right)_P > 0. \tag{8.88}$$

Accordingly, if the reaction is endothermic, an increase in temperature results in a shift of the equilibrium towards the products. Conversely, in case of an exothermic reaction, the equilibrium shifts towards the reactants if the temperature increases.

Similarly, from (8.86) we can conclude that

$$\text{if} \quad \left(\frac{\partial V}{\partial \xi}\right)_{T,P} > 0, \quad \text{then} \quad \left(\frac{\partial \xi}{\partial P}\right)_{T} < 0. \tag{8.89}$$

This has the consequence that, if the forward reaction results in an increase of the volume, then the equilibrium shifts towards the products when the pressure is increased. Conversely, in case of a reaction which decreases the volume, the equilibrium shifts towards the reactants when the pressure is increased. These results are of course in agreement with the conclusions made of the temperature- and pressure-dependence of the equilibrium constant as stated in Sect. 8.4.

The above principle can be derived for thermodynamic equilibria in general. It has been described first independently by Le Châtelier and Braun[3] also in connection with chemical reactions, which is the reason why it is called the *Le Châtelier–Braun principle*. Its general form reads as follows: any change in the conditions of equilibrium prompts an opposing consequence in the responding system to diminish the effect of the change.

For a chemical reaction it means that the increase of temperature induces the endothermic reaction whose heat effect counterbalances the increase of temperature. If the pressure is increased, it favors the reaction which decreases the volume, thus counteracting the increase of pressure. If the concentration of a reacting component is increased, the reaction induced will decrease the concentration of this species.

Problems

1. The equilibrium constant of a particular chemical reaction in the vicinity of $T = 502.3$ K can be calculated using the following equation:

$$\ln K = 1 - 1\,000 \left(\frac{T}{\mathrm{K}}\right)^{-1} + 20\,000 \left(\frac{T}{\mathrm{K}}\right)^{-2}.$$

Calculate the standard reaction enthalpy and entropy at the given temperature.

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[3] The French chemist Henri Louis Le Châtelier (1850–1936) had presented his results, concerning the response of chemical reactions to changes in conditions, in 1885 to the French Academy, and published them in 1888. Independently of him, the German physicist Karl Ferdinand Braun (1850–1918) published similar results in 1877. (Braun received the Nobel prize in 1909 for his contribution to the development of the "wireless telegraph" – the radio – together with Marconi.) It is interesting to note that Le Châtelier has cited in his publication the result described in the book of van't Hoff published in 1884 (*Études de dynamique chimique*), which correctly describes the change of the chemical equilibrium constant with temperature. (It is a characteristic of the humble and understanding personality of van't Hoff that – despite this fact – he later cited this result as Le Châtelier's principle.)

Solution: Let us start with the form of the van't Hoff equation according to (8.73):

$$\left(\frac{\partial \ln K_a}{\partial T}\right)_P = \frac{\Delta_r H^{\ominus}}{RT^2}.$$

As we can see, by calculating the derivative of ln K with respect to the temperature from the given formula, we readily obtain the reaction enthalpy (7.652 kJ mol^{-1}). The reaction entropy can be calculated using the following relation:

$$\Delta_r S^{\ominus} = \frac{\Delta_r H^{\ominus} - \Delta_r G^{\ominus}}{T}.$$

The missing $\Delta_r G^{\ominus}$ can be calculated using the relation (8.19):

$$-\Delta_r G^{\ominus} = RT \ln K_a$$

The result is $\Delta_r S^{\ominus} = 7.655 \mathrm{J}/(\mathrm{mol\,K})$.

2. The equilibrium constant of a particular chemical reaction is doubled when elevating the temperature from 200 K to 300 K. Calculate the reaction enthalpy (considering it as independent of temperature in this range).

Solution: Let us apply this time the definite integral form of the van't Hoff equation according to (8.78):

$$\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

Solution of this equation yields $\Delta_r H^{\ominus} = 3.458\,\mathrm{kJ/mol}$.

Further Reading

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