Chapter 5
Chemical Equilibrium

Abstract Chemical reactions are irreversible processes that reach a state of equilibrium. Under well-defined conditions, this state of chemical equilibrium of a system is characterized by a unique composition, defined by the law of mass action.

Problems dealing with chemical equilibrium and the law of mass action are among those topics that students consider to be difficult. A general method based on the equilibrium extent of reaction is presented to tackle such problems in a systematic way. The selection of problems highlights different aspects of chemical equilibrium, such as equilibrium in parallel reactions, equilibrium in open and closed systems, or equilibrium in dilute solutions.

5.1 Basic Concepts

Under the condition of chemical equilibrium, the amounts of substances in a reaction mixture are constant with time. Note that this does not imply that the elementary reaction processes come to an end, but that a state is reached where the reaction rates of the forward and backward reaction are in balance. Problem 6.4 in Chap. 6 deals with this kinetic aspect of chemical equilibrium in detail. To characterize chemical equilibrium, the *extent of reaction* ξ introduced in Chap. 2 is a key quantity. In the state of chemical equilibrium, the reaction

$$\sum_j \nu_j X_j = 0 \tag{5.1}$$

reaches a special value ξ^{eq}. The equilibrium amount of substance n_j^{eq} of each species X_j participating in the reaction is given by (see also Eq. (2.6))

$$\boxed{n_j^{\mathrm{eq}} = n_j^0 + \nu_j\, \xi^{\mathrm{eq}} \qquad j = 1, 2, \ldots} \tag{5.2}$$

where n_j^0 is the initial amount of substance X_j. Once ξ^{eq} is known, *all* the amounts of substances can be determined by the set of equations Eq. (5.2). Four things are worth mentioning here. The determination of $n_j^{\mathrm{eq}} j = 1, 2, \ldots$ is not a multidimensional

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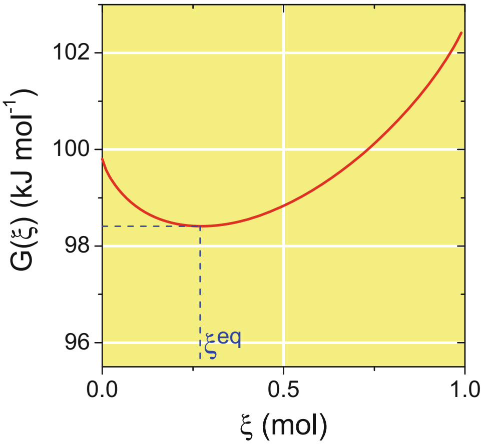

Fig. 5.1 Gibbs free energy as a function of extent of reaction in a concrete case of a chemical system. Equilibrium is reached as $G(\xi)$ reaches its minimum at ξ^{eq}

problem, as the quantities n_j do not vary independently. As already outlined in Chap. 2, the particle numbers strictly follow the reaction Eq. (5.1). Thus, the seeming complexity of typical textbook problems in chemical equilibrium is reduced in most cases to the determination of only one number, namely ξ^{eq}. Second, important for the correct identification of ξ^{eq} in many problems is the following inequality:

$$0 \leq \xi^{\mathrm{eq}} \leq \min \left\{ \frac{n_j^0}{|\nu_j|} \right\}_{\text{educts}} \tag{5.3}$$

It is based on the fact that the extent of reaction is by definition a positive mole number, and, as all n_j^{eq} are positive, ξ^{eq} cannot become larger than the smallest fraction $\frac{n_j^0}{|\nu_j|}$, formed by the initial amounts of all reactants and their stoichiometric numbers.[1] Problem 5.7 presents an application of Eq. (5.3). The third point to remember is that under well-defined conditions (e.g., constant pressure and temperature) the set $n_j^{\mathrm{eq}} j = 1, 2, \ldots$ is unique and does not change unless the external conditions are changed. The third point is that not only the particle numbers reach a constant value, the state of chemical equilibrium is also characterized by constant values of caloric state variables, in particular, the Gibbs free energy of the system, $G(\xi^{\mathrm{eq}})$. As shown for a concrete case in Fig. 5.1, this value is the minimum of the function $G(\xi^{\mathrm{eq}})$. Searching this minimum is equivalent to the formulation of the law of mass action.

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[1] See also the discussion of the *limiting reactant* in Problem 2.3.

5.1.1 The Law of Mass Action

The derivation of the **law of mass action** is found in the textbooks. In the absence of chemical equilibrium, a reaction is an irreversible process. Under the conditions of constant pressure and temperature, the system develops towards the minimum of its Gibbs free energy (see Eqs. (3.101) and (3.41)):

$$G = \sum_j \mu_j n_j, \tag{5.4}$$

$$dG_{p,T} \leq 0 \tag{5.5}$$

Here, μ_j is the *chemical potential*[2] of species X_j. Depending on the nature of the chemical system considered in a problem, the chemical potential is best expressed in terms of partial pressure (Eq. (3.105)) in the case of perfect gases participating in a reaction, in terms of *activity* (3.106) in the case of real solutions, or in terms of concentrations, or mole fractions. Then, insertion into Eq. (5.4) and application of the minimum condition $\left(\frac{\partial G}{\partial \xi}\right)_{p,T} \overset{!}{=} 0$ following from Eq. (5.5) leads to the law of mass action. Three common forms of the law of mass action are given in the following equations.

$$\boxed{\prod_j a_j^{\nu_j} = K = \exp\left(-\frac{\Delta g_r^0}{RT}\right)} \tag{5.6}$$

$$\boxed{\prod_j \left(\frac{p_j}{p^{\ominus}}\right)^{\nu_j} = K = \exp\left(-\frac{\Delta g_r^{\ominus}}{RT}\right)} \tag{5.7}$$

$$\boxed{\prod_j c_j^{\nu_j} = K_c} \tag{5.8}$$

In these equations a_j, p_j, and c_j denote activity, partial pressure, and concentration in the state of chemical equilibrium; ν_j is the stoichiometric coefficient of substance X_j. K is an **equilibrium constant** deduced from the value of the **standard molar Gibbs free energy of reaction** Δg_r^0. The standard state to which Δg_r^0 refers is indicated by the superscript 0. This nomenclature takes into account that, especially for reactions in the liquid phase, other standard states than that defined in Sect. 4.1.1

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[2] For the definition of the chemical potential see Eq. (3.100) at page 52.

might be used. For gas phase reactions, the standard state is related to standard pressure $p^{\ominus}$. The equilibrium constant K_c is not directly related to fundamental thermodynamic data. In problems dealing with gas phase reactions of perfect gases, the concentrations are easily expressed by the partial pressure, temperature, and the equation of state, $c_j = \frac{p_j}{RT}$. Thus, it is no difficult task to get the value of K_c from the general equilibrium constant K.

5.1.2 Temperature Dependency of the Equilibrium Constant

In many problems, the equilibrium constant is calculated based on thermochemical data tabulated at the reference temperature $T_1 = 298.15\,\mathrm{K}$. In concrete applications, however, the equilibrium constant needs to be calculated for a different temperature T_2. It can be rigorously shown that the following relation holds:

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta h_r^{\ominus}(T)}{RT^2} \tag{5.9}$$

Textbook and examination problems almost always assume that the standard molar heat of reaction is constant with temperature. This is an approximation. Integration of Eq. (5.9) then yields the simple relation called **Van’t Hoff reaction isobar**:

$$\boxed{\ln K(T_2) = \ln K(T_1) - \frac{\Delta h_r^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \tag{5.10}$$

5.1.3 Chemical Equilibrium in Dilute Solutions

Equilibrium of chemical reactions of acids and bases in dilute solutions is a frequently occurring topic. For a given reaction

$$\mathrm{AH(aq)} + \mathrm{H_2O} \overset{K}{\rightleftharpoons} \mathrm{A^-(aq)} + \mathrm{H_3O^+(aq)} \tag{5.11}$$

it is common to write the law of mass action in the following way:

$$K\, c_{\mathrm{H_2O}} = K_a = \frac{c_{\mathrm{A^-}} \cdot c_{\mathrm{H_3O^+}}}{c_{\mathrm{AH}}} \tag{5.12}$$

Here, AH is an acid, A^- its acetate ion, and it is assumed that the concentration of water ($55.55\,\mathrm{mol\,dm^{-3}}$) is much higher than the concentrations of all other substances. In this case, c_{H_2O} can be considered constant. By convention, the equilibrium constant and c_{H_2O} are then combined and their product is the *dissociation constant*[3] K_a. Moreover, it is common to write

$$\boxed{\mathrm{pH} = \mathrm{p}K_a + \log_{10} \frac{c_{A^-}}{c_{AH}}.} \tag{5.13}$$

Here,

$$\mathrm{pH} = -\log_{10} \frac{c_{H_3O^+}}{1\,\mathrm{mol\,dm^{-3}}} \tag{5.14}$$

is the pH value of the solution,[4]

$$\mathrm{p}K_a = -\log_{10} \frac{K_a}{1\,\mathrm{mol\,dm^{-3}}}. \tag{5.15}$$

Equation (5.13) is also called **Henderson-Hasselbalch equation**.

5.2 Problems

Problem 5.1 (Br_2 Decay) A reaction vessel is operated at a constant pressure of 10 mbar and a constant temperature of 1,500 K. The vessel initially contains $Br_2(g)$. Then the chemical equilibrium is established.

a. Write down the law of mass action for the reaction

$$Br_2(g) \overset{K}{\rightleftharpoons} 2Br(g) \tag{5.16}$$

b. The standard molar heats of formation of Br(g) and $Br_2(g)$ are 111.9 and 30.9 kJ mol^{-1} respectively. The standard molar Gibbs free energy of formation of Br(g) and $Br_2(g)$ is 82.4 and 3.1 kJ mol^{-1} respectively. Calculate the equilibrium constants at 298 and 1500 K. You may assume

(continued)

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[3] Whether the dissociation constant or the equilibrium constant is given in a concrete problem can be decided by a consideration of its physical dimension: although K in Eq. (5.11) is dimensionless, K_a in Eq. (5.12) has the dimension of a concentration.

[4] Strictly speaking, the definition of the pH value is based on activities rather than on concentrations.

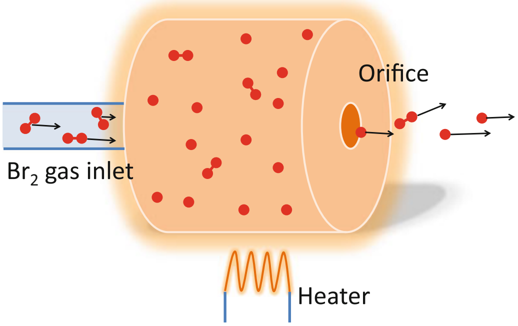

Fig. 5.2 Scheme of a Br atom beam source operating at constant pressure and high temperature

Problem 5.1 (continued)

that the standard molar heat of reaction is constant within the range 298 to 1,500 K.

c. Calculate the mole fractions and the partial pressure of Br(g) and Br_2(g) at 150 K. *Hint: express the partial pressure by the mole fraction and total pressure.*

d. To further increase the mole fraction of Br, would you increase or decrease the temperature? Would it be better to increase or to decrease the total pressure?

Solution 5.1 This problem deals with the dissociation of molecular bromine, which is in fact an endothermic reaction, as atomization of diatomic molecules requires energy for the breaking of its chemical bond. An application of this problem could be the construction of an atomic beam source for bromine atoms, as illustrated in Fig. 5.2. In **subproblem (a)**, we write down the law of mass action for the dissociation reaction of bromine, Eq. (5.16). Although bromine is a liquid under standard conditions, we only consider the gas phase reaction. Therefore, we use the representation with partial pressure (see Eq. (5.7)):

$$K = \exp\left(-\frac{\Delta g_r^{\ominus}}{RT}\right) = \frac{\left(\frac{p_{\mathrm{Br}}}{p^{\ominus}}\right)^2}{\frac{p_{\mathrm{Br}_2}}{p^{\ominus}}} = \frac{p_{\mathrm{Br}}^2}{p_{\mathrm{Br}_2} p^{\ominus}} \tag{5.17}$$

K is the equilibrium constant and $\Delta g_r^{\ominus}$ the molar Gibbs free energy of reaction. In **subproblem (b)** we calculate K for two different temperatures: for the reference temperature $T_1 = 298\,\mathrm{K}$, where thermochemical data are given, and, for later application, for a higher temperature $T_2 = 1500\,\mathrm{K}$. At the reference temperature, the standard molar heat of reaction is

$$\Delta h_r^{\ominus} = 2\Delta h_f^{\ominus}(\mathrm{Br}) - \Delta h_f^{\ominus}(\mathrm{Br_2}) = (2 \times 111.9 - 30.9)\ \mathrm{kJ\,mol^{-1}} = 192.9\,\mathrm{kJ\,mol^{-1}}. \tag{5.18}$$

This high positive value confirms our above thoughts on the endothermic nature of this reaction. The molar Gibbs free energy of reaction at the reference temperature is

$$\Delta g_r^{\ominus} = 2\Delta g_f^{\ominus}(\mathrm{Br}) - \Delta g_f^{\ominus}(\mathrm{Br_2}) = (2 \times 82.4 - 3.1)\ \mathrm{kJ\,mol^{-1}} = 161.7\,\mathrm{kJ\,mol^{-1}}. \tag{5.19}$$

Thus, at T_1, the reaction is not only endothermic, but also largely endergonic. We therefore expect a very small equilibrium constant:

$$K_1 = \exp\left(-\frac{\Delta g_r^{\ominus}(T_1)}{RT_1}\right) = 4.435 \times 10^{-29} \tag{5.20}$$

This is consistent with the notion that at room temperature almost no Br_2 molecule will decay spontaneously. If the temperature is raised to the much higher temperature T_2, we can expect that the vibrational degrees of freedom of the diatomic will be excited, involving an increased probability of dissociation. We therefore expect a higher equilibrium constant at T_2. We may assume that the molar heat of reaction is constant between T_1 and T_2. Therefore, we can use the *Van't Hoff reaction isobar* (Eq. (5.10)) and obtain

$$\ln K_2 = \ln K_1 - \frac{\Delta h_r^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5.21}$$

$$\ln K_2 = -65.2854 - \frac{192{,}900\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{1500\,\mathrm{K}} - \frac{1}{298\,\mathrm{K}}\right) = -2.8986 \tag{5.22}$$

Therefore, the equilibrium constant at 1,500 K is $K_2 = 0.0551$ and is thus many orders of magnitude greater than the room temperature value. A note here about calculus: an error often seen in examinations is the addition or division of terms with incompatible physical units. In this case, we need to pay attention to the correct insertion[5] of the heat of reaction $\Delta h_r^{\ominus} = 192.9\,\mathrm{kJ\,mol^{-1}}$, which is $192{,}900\,\mathrm{J\,mol^{-1}}$. Having obtained the equilibrium constant at 1500 K, we predict the mole fractions of bromine atoms and bromine molecules at this temperature in **subproblem (c)**. The total pressure is fixed at $p = 10\,\mathrm{mbar}$. Taking this into account, we can introduce

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[5] A frequently occurring error of novices is to add quantities with different units or, as in this case, to misapply the factor 10^3 hidden in the unit *kilo*joule (kJ).

the mole fractions x_{Br_2} and x_{Br} and write

$$p_{\mathrm{Br}_2} = x_{\mathrm{Br}_2} p; \qquad p_{\mathrm{Br}} = x_{\mathrm{Br}} p \tag{5.23}$$

Insertion of these relations into the law of mass action (Eq. (5.17)) yields

$$K_2 = \frac{x_{\mathrm{Br}}^2}{x_{\mathrm{Br}_2}} \frac{p}{p^{\ominus}}, \tag{5.24}$$

which contains the two unknown mole fractions. To determine the latter, we need additional equations. The strategy is, as outlined in Sect. 5.1, to determine the equilibrium extent of reaction ξ^{eq} and then to re-express the mole fractions sought by ξ^{eq}. We have (see Eq. (5.2))

$$n_{\mathrm{Br}_2} = n_{\mathrm{Br}_2}^0 - \xi^{\mathrm{eq}}; \qquad n_{\mathrm{Br}} = 0 + 2\xi^{\mathrm{eq}} \tag{5.25}$$

where we exploit the information that initially only molecular bromine is present in the vessel with an amount $n_{\mathrm{Br}_2}^0$. Using the definition of the mole fraction in Eq. (2.8) we can write

$$x_{\mathrm{Br}} = \frac{n_{\mathrm{Br}}}{n_{\mathrm{Br}} + n_{\mathrm{Br}_2}} = \frac{2\xi^{\mathrm{eq}}}{n_{\mathrm{Br}_2}^0 + \xi^{\mathrm{eq}}}; \qquad x_{\mathrm{Br}_2} = \frac{n_{\mathrm{Br}_2}^0 - \xi^{\mathrm{eq}}}{n_{\mathrm{Br}_2}^0 + \xi^{\mathrm{eq}}} \tag{5.26}$$

If we insert these expressions in Eq. (5.24), we obtain

$$K_2 = \frac{4\xi^{\mathrm{eq}2}}{\left(n_{\mathrm{Br}_2}^0 + \xi^{\mathrm{eq}}\right)^2} \frac{n_{\mathrm{Br}_2}^0 + \xi^{\mathrm{eq}}}{n_{\mathrm{Br}_2}^0 - \xi^{\mathrm{eq}}} \frac{p}{p^{\ominus}} \tag{5.27}$$

The latter equation can be simplified using the third binomial formula (Eq. (A.3)):

$$K_2 = \frac{4\xi^{\mathrm{eq}2}}{{n_{\mathrm{Br}_2}^0}^2 - \xi^{\mathrm{eq}2}} \frac{p}{p^{\ominus}} \tag{5.28}$$

This is an equation with only one unknown, ξ^{eq}. We can solve for ξ^{eq} and obtain

$$\xi^{\mathrm{eq}} = n_{\mathrm{Br}_2}^0 \sqrt{\frac{1}{\frac{4p}{K_2 p^{\ominus}} + 1}} = 0.7612 \times n_{\mathrm{Br}_2}^0 \tag{5.29}$$

With the value of K_2 from subproblem (b) and $p^{\ominus} = 100{,}000\,\mathrm{Pa}$ the root takes the value 0.7612. If we finally reinsert this result into the above expressions for the mole fractions Eq. (5.26), we obtain

$$x_{\mathrm{Br}} = \frac{2 \times 0.7612}{1 + 0.7612} = 0.8644; \qquad x_{\mathrm{Br}_2} = \frac{1 - 0.7612}{1 + 0.7612} = 0.1356 \tag{5.30}$$

The partial pressure of atomic bromine is thus $p_{\mathrm{Br}} = x_{\mathrm{Br}}p = 8.6\,\mathrm{mbar}$, and the partial pressure of $\mathrm{Br_2}$ is 1.4 mbar, accordingly. Hence, 86% of the particles in the vessel are atomic bromine, whereas only 14% of the particles are $\mathrm{Br_2}$ molecules.

Subproblem (d) deals with the question how the mole fraction of atomic bromine can be further increased. Concerning temperature, our results of subproblem (b) provide a clear answer: if we further increase the temperature, the equilibrium constant further increases because of the endothermic nature of the dissociation reaction, and hence the fraction of bromine atoms then increases further. But what about total pressure? Let us check the results of subproblem (c): the fraction of bromine is increased if the equilibrium extent of reaction ξ^{eq} is increased. We therefore analyze Eq. (5.29):

$$\lim_{p\to 0} \xi^{\mathrm{eq}} = n^0_{\mathrm{Br_2}} \lim_{p\to 0} \sqrt{\frac{1}{\frac{4p}{K_2 p^{\ominus}} + 1}} = n^0_{\mathrm{Br_2}} \tag{5.31}$$

At the limit of vanishing total pressure *all* bromine molecules dissociate. Reduction of total pressure thus increases the fraction of bromine atoms. As a consequence, we should operate the effusion source for atomic bromine at a high temperature and low total pressure.

Problem 5.2 (Equilibrium in Parallel Reactions I) Oxides of nitrogen are trace gases in the atmosphere with anthropogenic and natural sources. Consider the chemical equilibrium between NO, $\mathrm{NO_2}$ with the main components of clean air:

$$2\,\mathrm{NO(g)} + \mathrm{O_2(g)} \overset{K_1}{\rightleftharpoons} 2\,\mathrm{NO_2(g)} \tag{5.32}$$

$$\mathrm{N_2(g)} + \mathrm{O_2(g)} \overset{K_2}{\rightleftharpoons} 2\,\mathrm{NO(g)} \tag{5.33}$$

$$\mathrm{N_2(g)} + 2\mathrm{O_2(g)} \overset{K_3}{\rightleftharpoons} 2\,\mathrm{NO_2(g)} \tag{5.34}$$

a. Show that $K_3 = K_1 \times K_2$.
b. Clean air normally contains 78% $\mathrm{N_2}$ and 21% $\mathrm{O_2}$. Calculate the mole fraction and the concentration of NO and $\mathrm{NO_2}$ in clean air (total pressure 100,000 Pa, 298.15 K), assuming conditions of chemical equilibrium and $K_1 = 1.69 \times 10^{12}$, $K_2 = 4.2 \times 10^{-32}$.

Solution 5.2 This problem deals with nitrogen oxide, NO_x. These molecules occur as trace gases in the atmosphere. Although atmospheric processes, strictly speaking, never reach a state of equilibrium, we may ask if the observed abundance of these trace gases is roughly in accordance with the prediction from the law of mass action. For simplicity, only the molecules NO and $\mathrm{NO_2}$ are considered. The reaction laws

Eqs. (5.33) and (5.34) describe the formation of these oxides from the elements N_2 and O_2 in their standard states. Equation (5.32) describes the conversion of NO into NO_2 and vice versa. If we consider the chemical equilibrium for each of these parallel reactions, there must be relations among the equilibrium constants. In **subproblem (a)** we show that $K_3 = K_1 \times K_2$. We write down the law of mass action for each of these reactions and assume perfect gas behavior:

$$K_1 = \frac{\left(\frac{p_{NO_2}}{p^\ominus}\right)^2}{\left(\frac{p_{NO}}{p^\ominus}\right)^2 \frac{p_{O_2}}{p^\ominus}}; \qquad K_2 = \frac{\left(\frac{p_{NO}}{p^\ominus}\right)^2}{\frac{p_{N_2}}{p^\ominus}\frac{p_{O_2}}{p^\ominus}}; \qquad K_3 = \frac{\left(\frac{p_{NO_2}}{p^\ominus}\right)^2}{\frac{p_{N_2}}{p^\ominus}\left(\frac{p_{O_2}}{p^\ominus}\right)^2} \tag{5.35}$$

Therefore,

$$K_1 \times K_2 = \frac{\left(\frac{p_{NO_2}}{p^\ominus}\right)^2}{\left(\frac{p_{NO}}{p^\ominus}\right)^2 \frac{p_{O_2}}{p^\ominus}} \times \frac{\left(\frac{p_{NO}}{p^\ominus}\right)^2}{\frac{p_{N_2}}{p^\ominus}\frac{p_{O_2}}{p^\ominus}} = \frac{\left(\frac{p_{NO_2}}{p^\ominus}\right)^2}{\frac{p_{N_2}}{p^\ominus}\left(\frac{p_{O_2}}{p^\ominus}\right)^2} = K_3. \tag{5.36}$$

In **subproblem (b)**, we consider clean air with mole fractions $x_{N_2} = 0.78$ and $x_{O_2} = 0.21$. We determine the mole fractions and concentrations of NO and NO_2. We introduce the mole fractions using its definition in Chap. 2, Eq. (2.8), and the fact that under standard conditions the total pressure of air is simply the standard pressure:

$$x_i \overset{\text{Eq. (2.8)}}{=} \frac{n_i}{n_\text{total}} = \frac{p_i}{p_\text{total}} \overset{p_\text{total}=p^\ominus}{=} \frac{p_i}{p^\ominus} \tag{5.37}$$

Hence, the laws of mass action can be expressed in terms of mole fractions:

$$K_1 = \frac{x^2_{NO_2}}{x^2_{NO}\cdot x_{O_2}}; \qquad K_2 = \frac{x^2_{NO}}{x_{N_2}\cdot x_{O_2}}; \qquad K_3 = \frac{x^2_{NO_2}}{x_{N_2}\cdot x^2_{O_2}} \tag{5.38}$$

In the next step, we notice a considerable simplification of the problem if we recognize that there is excess nitrogen and oxygen. Hence, their mole fractions can thus be assumed to be constant. Therefore, x_{NO_2} and x_{NO} are best calculated using K_2 and K_3:

$$x_{NO} = \sqrt{K_2 x_{N_2} x_{O_2}} = \sqrt{4.2 \times 10^{-32} \times 0.78 \times 0.21} = 8.3 \times 10^{-17} \tag{5.39}$$

and

$$x_{NO_2} = \sqrt{K_3 x_{N_2} x^2_{O_2}} = \sqrt{7.1 \times 10^{-20} \times 0.78 \times 0.21^2} = 4.9 \times 10^{-11}. \tag{5.40}$$

Here, we have used the relation $K_3 = K_1 \times K_2$ shown in subproblem (a). Finally, we calculate concentrations. Using the equation of state for a perfect gas

(Eq. (2.12)), the definition of concentration (Eq. (2.9)), and Eq. (5.37), we obtain

$$c_{\mathrm{NO}} = \frac{p^{\ominus}}{RT} x_{\mathrm{NO}} = 3.3 \times 10^{-15}\,\mathrm{mol\,m^{-3}} \tag{5.41}$$

and

$$c_{\mathrm{NO_2}} = \frac{p^{\ominus}}{RT} x_{\mathrm{NO_2}} = 2.0 \times 10^{-9}\,\mathrm{mol\,m^{-3}} \tag{5.42}$$

The long-term concentration of NO_2 in the USA at the beginning of the twenty-first century[6] is about 50 ppb, (1 ppb = 10^{-9}). Hence, our result for nitrogen dioxide underestimates the real concentration by a factor of 25.

Problem 5.3 (Equilibrium in Parallel Reactions II) Consider the chemical equilibrium of a molecule that occurs in three different conformers, A, B, and C:

$$\mathrm{B} \overset{K_1}{\leftrightharpoons} \mathrm{A} \overset{K_2}{\rightleftharpoons} \mathrm{C} \tag{5.43}$$

The molar heats of reaction of A→B and A→C are −12, and $-16\,\mathrm{kJ\,mol^{-1}}$ respectively (see Fig. 5.3). For simplicity, assume that entropy differences between the conformers are negligible. Ignore all possible intermolecular interactions.

a. Write down the laws of mass action for both reactions and calculate the equilibrium constants both for room temperature (T_1) and for $T_2 = 700\,\mathrm{K}$.
b. Derive expressions for the mole fractions of each the three conformers in chemical equilibrium. Calculate x_A, x_B , and x_C for both temperatures T_1 and T_2. Under which condition is the abundance of the intermediate conformer A insignificantly small?

Solution 5.3 In Problem 5.2 we have dealt with a set of parallel reactions, in which equilibrium abundances of all substances could be easily calculated because there were excess amounts of several reactants. This led to a decoupling of the problem. But how do we proceed in the general case of coupled parallel reactions? In this

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[6] According to the United States Environmental Protection Agency (http://www.epa.gov).

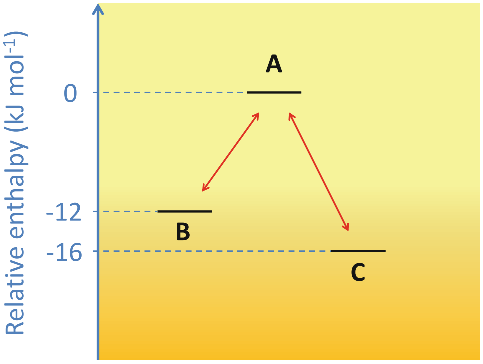
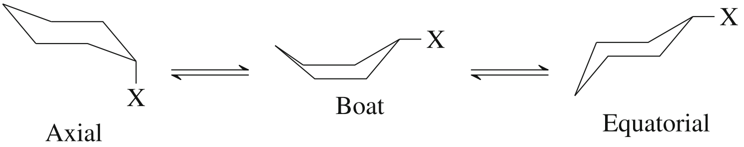


Fig. 5.3 Relative enthalpies of the three different conformers A, B, and C

problem, we shall consider three conformers A, B, and C of one substance in chemical equilibrium. An example could be a monosubstituted cyclohexane:



(5.44)

The molecule has two different stable chair conformations. In the axial conformation, the substituent group X is oriented perpendicularly with regard to the *seat* of the chair, whereas in the equatorial conformation, X is within this plane. Both geometries have a slightly different total energy. A transition from the axial into the equatorial conformation is caused by an internal *flipping* of the molecule into its energetically less favorable boat configuration. This brings the group X into the equatorial position. Then, by a second flipping at the opposite end, the molecule comes back into the equatorial chair position.

In **subproblem (a)**, we write down the laws of mass action and calculate equilibrium constants for both reactions. We use the amounts of substances n_A, n_B, and n_C to characterize the equilibrium:

$$K_1 = \frac{n_B}{n_A}; \qquad K_2 = \frac{n_C}{n_A} \tag{5.45}$$

If the molar entropies of A, B, and C are equal, the molar reaction entropy is zero and thus the molar Gibbs free energies of reaction are $\Delta g_1 = \Delta h_1 = -12\,\text{kJ mol}^{-1}$ and $\Delta g_2 = \Delta h_2 = -16\,\text{kJ mol}^{-1}$ respectively. The room temperature equilibrium constants are thus:

$$K_1(T_1) = \exp\left(-\frac{\Delta g_1}{RT_1}\right) = 126.56 \tag{5.46}$$

and

$$K_2(T_1) = \exp\left(-\frac{\Delta g_2}{RT_1}\right) = 635.43. \tag{5.47}$$

Equilibrium constants at $T_2 = 700\,\text{K}$ are calculated using Eq. (5.10). We obtain

$$\ln K_1(T_2) = \ln K_1(T_1) - \frac{\Delta h_1}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = 4.841 - 2.779 = 2.062 \tag{5.48}$$

and thus $K_1(T_2) = 7.86$. In the same way, we obtain $K_2(T_2) = 15.63$.

In **subproblem (b)**, we seek formulas predicting the abundances of the three conformers in chemical equilibrium. We assume that initially, all molecules are present in the conformer A with an amount n_A^0. Because A undergoes two different types of chemical reactions, we generalize Eq. (5.2) by introducing two different numbers, ξ_1 and ξ_2, representing the extent of reaction in these two reaction channels. Hence, in chemical equilibrium, the amounts of the conformers are:

$$n_\text{A} = n_\text{A}^0 - \xi_1^\text{eq} - \xi_2^\text{eq}; \qquad n_\text{B} = \xi_1^\text{eq}; \qquad n_\text{C} = \xi_2^\text{eq} \tag{5.49}$$

Insertion of these expressions in Eq. (5.45) yields

$$K_1 = \frac{\xi_1^\text{eq}}{n_\text{A}^0 - \xi_1^\text{eq} - \xi_2^\text{eq}}; \qquad K_2 = \frac{\xi_2^\text{eq}}{n_\text{A}^0 - \xi_1^\text{eq} - \xi_2^\text{eq}} \tag{5.50}$$

These two equations can be rearranged in a system of equation $\mathbf{A}\,\boldsymbol{\xi} = \mathbf{y}$ with $\mathbf{A}$ being a 2×2 matrix:

$$\begin{pmatrix} K_1 + 1 & K_1 \\ K_2 & K_2 + 1 \end{pmatrix} \begin{pmatrix} \xi_1^\text{eq} \\ \xi_2^\text{eq} \end{pmatrix} = \begin{pmatrix} K_1 n_\text{A}^0 \\ K_2 n_\text{A}^0 \end{pmatrix} \tag{5.51}$$

We use Cramer's rule (see Appendix Sect. A.3.17) to solve this system. By evaluating the determinant of the coefficient matrix $\mathbf{A}$ and the determinants of $\mathbf{A}_1$ and $\mathbf{A}_2$ with the first and second columns replaced by the 'vector' $\mathbf{y}$,

$$\det \mathbf{A} = \begin{vmatrix} K_1 + 1 & K_1 \\ K_2 & K_2 + 1 \end{vmatrix} = K_1 + K_2 + 1 \tag{5.52}$$

$$\det \mathbf{A}_1 = \begin{vmatrix} K_1 n_\text{A}^0 & K_1 \\ K_2 n_\text{A}^0 & K_2 + 1 \end{vmatrix} = K_1 n_\text{A}^0 \tag{5.53}$$

$$\det \mathbf{A}_2 = \begin{vmatrix} K_1 + 1 & K_1 n_\text{A}^0 \\ K_2 & K_2 n_\text{A}^0 \end{vmatrix} = K_2 n_\text{A}^0 \tag{5.54}$$

we obtain the solutions

$$\xi_1^{\text{eq}} = \frac{\det \mathbf{A}_1}{\det \mathbf{A}} = \frac{K_1}{K_1 + K_2 + 1} n_{\text{A}}^0 \tag{5.55}$$

and

$$\xi_2^{\text{eq}} = \frac{\det \mathbf{A}_2}{\det \mathbf{A}} = \frac{K_2}{K_1 + K_2 + 1} n_{\text{A}}^0 \tag{5.56}$$

Insertion of these results into Eq. (5.50) yields the amounts of the three conformers. Recognizing that the total amount of the substance is always n_{A}^0, we can compute the mole fractions sought:

$$x_{\text{A}} = \frac{n_{\text{A}}}{n_{\text{A}}^0} = \frac{1}{K_1 + K_2 + 1} \tag{5.57}$$

$$x_{\text{B}} = \frac{n_{\text{B}}}{n_{\text{A}}^0} = \frac{K_1}{K_1 + K_2 + 1} \tag{5.58}$$

$$x_{\text{C}} = \frac{n_{\text{C}}}{n_{\text{A}}^0} = \frac{K_2}{K_1 + K_2 + 1} \tag{5.59}$$

Using these formulae and the above calculated values for the equilibrium constants K_1 and K_2, the mole fractions for both temperatures can be determined. These are given in Table 5.1.

At 298 K only about one in a thousand molecules has the A conformation, and 83% of the molecules are B conformers. If the temperature is raised to 700 K, however, even conformer A, with the highest Gibbs free energy, has a notable abundance. Asked about the criterion when the abundance of this conformer is insignificantly small we refer to Eqs. (5.57)–(5.59): x_{A} becomes negligible over x_{B} and x_{C} if in the denominator $K_1 + K_2 \gg 1$. In this case, conformer A serves only as a *transition state* between the energetically more favorable conformers B and C. The problem then simplifies and can be treated as an equilibrium problem of the type $\text{B} \rightleftharpoons \text{C}$. Note also that the condition $K_1 + K_2 \gg 1$ is better met at room temperature than at T_2.

Table 5.1 Mole fractions of the three conformers A, B, and C in chemical equilibrium at 298 and at 700 K

Temperature (K)	x_{A}	x_{B}	x_{C}
298	0.0013	0.1659	0.8328
700	0.0408	0.3209	0.6382

Table 5.2 Standard molar heats of formation and standard Gibbs free energy of formation of some compounds at 298.15 K

Molecule	$\Delta h_f^{\ominus}$ (kJ mol^{-1})	$\Delta g_f^{\ominus}$ (kJ mol^{-1})
$CO(g)$	−110.5	−137.2
$CO_2(g)$	−393.5	−394.4
$H_2(g)$	0	0
$H_2O(g)$	−241.8	−228.6

Problem 5.4 (Water-Gas Shift Reaction) The water-gas shift reaction

$$CO(g) + H_2O(g) \overset{K}{\rightleftharpoons} CO_2(g) + H_2(g) \tag{5.60}$$

is widely used to reduce the content of carbon monoxide in hydrogen gas.

a. Write down the law of mass action for the given reaction. From thermochemical data found in Table 5.2, calculate the equilibrium constants at 298.15 and at 400 K. Does a catalyst influence the chemical equilibrium?
b. A reactor contains a mixture of CO and H_2 with an initial proportion $n^0_{CO}:n^0_{H_2} = 0.1:0.9$. Then, $H_2O(g)$ is added at a temperature of 400 K and the chemical equilibrium is established. Calculate the initial proportion $n^0_{H_2O}:n^0_{H_2}$ necessary to reduce the equilibrium proportion $n^{eq}_{CO}:n^{eq}_{H_2}$ to 0.01:0.99.

Solution 5.4 Some examination problems for chemical equilibrium require the consideration of *extra* constraints apart from the law of mass action and the set of equations given in Eq. (5.2). Such an extra constraint may be the request for a special composition of the system in the state of equilibrium. In this case, the obvious task is to determine the initial composition of the system. This problem offers an example in which we deal with the water gas shift reaction Eq. (5.60), which is used in industrial scale production of high purity syngas[7]. In **subproblem (a)** we write down the law of mass action using partial pressures:

$$K = \exp\left(-\frac{\Delta g_r^{\ominus}}{RT}\right) = \frac{\frac{p_{CO_2}}{p^{\ominus}}\frac{p_{H_2}}{p^{\ominus}}}{\frac{p_{CO}}{p^{\ominus}}\frac{p_{H_2O}}{p^{\ominus}}} = \frac{p_{CO_2}p_{H_2}}{p_{CO}p_{H_2O}} \tag{5.61}$$

---

[7] Syngas or synthesis gas is a mixture of hydrogen and carbon monoxide.

Now, we determine the equilibrium constant from the thermochemical data in Table 5.2. The standard molar heat of reaction is:

$$\begin{aligned}\Delta h_r^\ominus &= \sum_i \nu_i \Delta h_f^\ominus(i) = \Delta h_f^\ominus(\mathrm{CO_2}) + \Delta h_f^\ominus(\mathrm{H_2}) - \Delta h_f^\ominus(\mathrm{CO}) - \Delta h_f^\ominus(\mathrm{H_2O}) \\ &= -41.2\,\mathrm{kJ\,mol^{-1}}\end{aligned} \tag{5.62}$$

The standard molar Gibbs free energy of reaction is:

$$\begin{aligned}\Delta g_r^\ominus &= \sum_i \nu_i \Delta g_f^\ominus(i) = \Delta g_f^\ominus(\mathrm{CO_2}) + \Delta g_f^\ominus(\mathrm{H_2}) - \Delta g_f^\ominus(\mathrm{CO}) - \Delta g_f^\ominus(\mathrm{H_2O}) \\ &= -28.6\,\mathrm{kJ\,mol^{-1}}\end{aligned} \tag{5.63}$$

Hence, the equilibrium constant at the reference temperature $T_1 = 298.15\,\mathrm{K}$ is

$$K(T_1) = \exp\left(-\frac{\Delta g_r^\ominus}{RT}\right) = 102{,}443. \tag{5.64}$$

The equilibrium constant at $T_2 = 400\,\mathrm{K}$ is calculated using Van't Hoff's reaction isobar (Eq. (5.10)):

$$\ln K(T_2) = \ln K(T_1) - \frac{\Delta h_r^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = 7.3053 \tag{5.65}$$

Hence, at 400 K the equilibrium constant is $K(T_2) = 1,488$ and thus considerably smaller compared with the room temperature value. This is consistent with the fact that the water gas shift reaction is exothermic. Like many reactions of high technical relevance, the water gas shift reaction is conducted on the surface of a catalyst. We answer the question, does a catalyst influence the equilibrium, with a no. The Gibbs free energy of reaction, from which the equilibrium constant is calculated, does not depend on the reaction pathway. The presence and the nature of the catalyst only influence reaction rates, and not the composition of the system in chemical equilibrium.

In **subproblem (b)**, we determine how much water vapor needs to be added to a 0.1:0.9 mixture of CO and H_2 to achieve a reduction of the CO content to 1% as the equilibrium is established. We first define the initial ratio

$$R_0 = \frac{n^0_{\mathrm{CO}}}{n^0_{\mathrm{H_2}}} = \frac{1}{9} \tag{5.66}$$

expressed by unknown initial amounts n^0_{CO} and $n^0_{\mathrm{H_2}}$, which are not given. Do we need to know them? No, because, with regard to the composition, it should not matter if we are dealing with 1 mol or with 100 t of gas mixture. In the same way, we define the equilibrium ratio

$$R_{\mathrm{eq}} = \frac{n_{\mathrm{CO}}^{\mathrm{eq}}}{n_{\mathrm{H_2}}^{\mathrm{eq}}} \overset{!}{=} \frac{1}{99} \tag{5.67}$$

Finally, we define a third ratio

$$R_x = \frac{n_{\mathrm{H_2O}}^0}{n_{\mathrm{H_2}}^0} \tag{5.68}$$

It is the initial ratio of water vapor and hydrogen sought. Now, we introduce the equilibrium extent of reaction ξ^{eq}. Using Eq. (5.2) and recognizing that initially there is no carbon dioxide present in the vessel, we write

$$n_{\mathrm{H_2}}^{\mathrm{eq}} = n_{\mathrm{H_2}}^0 + \xi^{\mathrm{eq}}; \quad n_{\mathrm{CO_2}}^{\mathrm{eq}} = \xi^{\mathrm{eq}}; \quad n_{\mathrm{H_2O}}^{\mathrm{eq}} = n_{\mathrm{H_2O}}^0 - \xi^{\mathrm{eq}}; \quad n_{\mathrm{CO}}^{\mathrm{eq}} = n_{\mathrm{CO}}^0 - \xi^{\mathrm{eq}} \tag{5.69}$$

We insert these relations into Eq. (5.67) and obtain

$$R_{\mathrm{eq}} = \frac{n_{\mathrm{CO}}^0 - \xi^{\mathrm{eq}}}{n_{\mathrm{H_2}}^0 + \xi^{\mathrm{eq}}} = \frac{R_0 n_{\mathrm{H_2}}^0 - \xi^{\mathrm{eq}}}{n_{\mathrm{H_2}}^0 + \xi^{\mathrm{eq}}} \tag{5.70}$$

Solving for ξ, we obtain, after some rearrangements:

$$\xi^{\mathrm{eq}} = \frac{R_0 - R_{\mathrm{eq}}}{R_{\mathrm{eq}} + 1} n_{\mathrm{H_2}}^0 \overset{\mathrm{def}}{=} B n_{\mathrm{H_2}}^0 = 0.1 \times n_{\mathrm{H_2}}^0. \tag{5.71}$$

This equation relates the extent of the reaction to the quantities given and the unknown $n_{\mathrm{H_2}}^0$. The next step is to exploit the law of mass action. We assume perfect gas behavior and therefore a proportionality of the partial pressure and amount of the substance. As a consequence,

$$K(T_2) = \frac{n_{\mathrm{H_2}}^{\mathrm{eq}} n_{\mathrm{CO_2}}^{\mathrm{eq}}}{n_{\mathrm{H_2O}}^{\mathrm{eq}} n_{\mathrm{CO}}^{\mathrm{eq}}} = \frac{\xi^{\mathrm{eq}} \left(n_{\mathrm{H_2}}^0 + \xi^{\mathrm{eq}}\right)}{\left(n_{\mathrm{CO}}^0 - \xi^{\mathrm{eq}}\right)\left(n_{\mathrm{H_2O}}^0 - \xi^{\mathrm{eq}}\right)} = \frac{B n_{\mathrm{H_2}}^0 \left(n_{\mathrm{H_2}}^0 + B n_{\mathrm{H_2}}^0\right)}{\left(n_{\mathrm{CO}}^0 - B n_{\mathrm{H_2}}^0\right)\left(n_{\mathrm{H_2O}}^0 - B n_{\mathrm{H_2}}^0\right)} \tag{5.72}$$

We recognize that we can factor out $n_{\mathrm{H_2}}^0$ in numerator and denominator and obtain:

$$K(T_2) = \frac{B(1+B)}{(R_0 - B)(R_x - B)} \tag{5.73}$$

Apart from the sought ratio R_x, this equation only contains known quantities. Solving for R_x we obtain:

$$R_x = \frac{B(1+B)}{K(T_2)(R_0 - B)} + B = \frac{0.1 \times 1.1}{1488 \times (\frac{1}{9} - 0.1)} + 0.1 = 0.107 \qquad (5.74)$$

About more than 10% water vapor has to be added to the gas mixture and nearly all the water is converted to hydrogen gas, whereas carbon monoxide is oxidized. Further analysis would show that greater purification, e.g., CO:H_2 = 1:999, would require a disproportionate addition of water ($B = 0.11$, $R_x = 0.18$) and subsequent removal of the excess water.

Problem 5.5 (Dehydrogenation of Methanol) Formaldehyde is produced on an industrial scale via the dehydrogenation of methanol on silver catalysts:

$$CH_3OH(g) \overset{\text{Ag catalyst}}{\rightleftharpoons} H_2CO(g) + H_2(g) \qquad (5.75)$$

a. Write down the law of mass action for the given reaction. Calculate the equilibrium constants at 298.15 and 920 K from the thermochemical data given in Table 5.3.
b. At a temperature of 920 K, a reactor with a movable piston contains a silver catalyst and is filled at standard pressure with methanol. The initial volume of the reactor is 1 dm^3. Then, the chemical equilibrium is established. Assume perfect gas behavior of reactants and products. Calculate the partial pressures of all gases in the state of chemical equilibrium and determine the work done by the piston. Is this process reversible?

Solution 5.5 Here, we have another problem of chemical equilibrium that requires the consideration of additional conditions. In this problem, the total pressure is constant, whereas the volume may change as the reaction proceeds. As we are dealing with a dissociation reaction where the number of molecules increases, we expect that the volume increases by an upward movement of the piston (see Fig. 5.4).

Table 5.3 Standard molar heats of formation and standard molar entropies of some compounds at 298.15 K

Molecule	$\Delta h_f^\ominus$ (kJ mol^{-1})	$s^\ominus$ (J K^{-1} mol^{-1})
$CH_3OH(g)$	−201.0	+239.9
$H_2CO(g)$	−108.6	+218.8
$H_2(g)$	0	+130.7

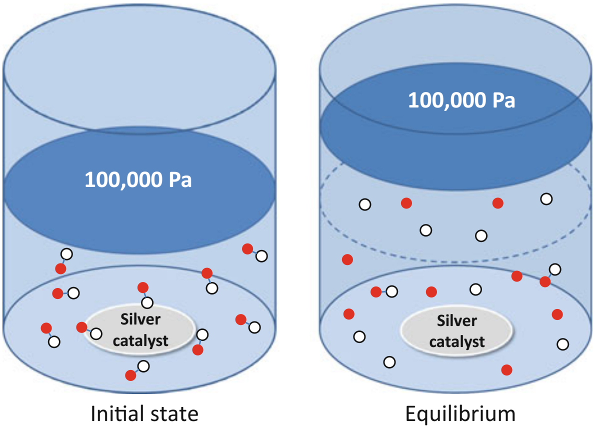


Fig. 5.4 Dissociation reaction at constant pressure

Thus, work is done during this process. The goal of **subproblem (a)** is to calculate the equilibrium constants from thermochemical data in Table 5.3. Here, standard heats of formation and standard entropies of the reactants and products are given. At the reference temperature $T_1 = 298.15\,\mathrm{K}$ the standard molar reaction enthalpy is:

$$\begin{aligned}\Delta h_r^\ominus &= \Delta h_f^\ominus(\mathrm{H_2CO}) + \Delta h_f^\ominus(\mathrm{H_2}) - \Delta h_f^\ominus(\mathrm{CH_3OH}) \\ &= (-108.6 + 0 + 201.0)\ \mathrm{kJ\,mol^{-1}} = +92.4\,\mathrm{kJ\,mol^{-1}}\end{aligned} \tag{5.76}$$

The standard molar reaction enthalpy is:

$$\begin{aligned}\Delta s_r^\ominus &= s^\ominus(\mathrm{H_2CO}) + s^\ominus(\mathrm{H_2}) - s^\ominus(\mathrm{CH_3OH}) \\ &= (+218.8 + 130.7 - 239.9)\ \mathrm{J\,K^{-1}\,mol^{-1}} = +109.6\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned} \tag{5.77}$$

The standard molar Gibbs free energy of reaction at this temperature is thus:

$$\Delta g_r^\ominus = \Delta h_r^\ominus - T_1 \Delta s_r^\ominus = +59.7\,\mathrm{kJ\,mol^{-1}} \tag{5.78}$$

Therefore, the reaction is endothermic, and also endergonic at this temperature, consistent with a very small equilibrium constant, which is:

$$K(T_1) = \exp\left(-\frac{\Delta g_r^\ominus}{RT_1}\right) = \exp(-24.11) = 3.38 \times 10^{-11}. \tag{5.79}$$

The equilibrium constant at the higher temperature $T_2 = 920\,\text{K}$ is calculated using Eq. (5.10) under the assumption that $\Delta h_r^{\ominus}$ is constant between T_1 and T_2:

$$\ln K(T_2) = \ln K(T_1) - \frac{\Delta h_r^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = -24.11 + 25.21 = 1.10 \tag{5.80}$$

Hence, the equilibrium constant at 920 K is $K(T_2) = 3.01$ and the reaction is exergonic. For the calculation of the partial pressures in **subproblem (b)** we thus expect that most of the methanol is dissociated in the state of chemical equilibrium, whereas the volume of the reaction vessel is essentially filled with hydrogen and formaldehyde in equal amounts (see Fig. 5.4). Introducing the partial pressures p_{F}, p_{H}, p_{M} of formaldehyde, hydrogen, and methanol respectively, we write down the law of mass action for the reaction:

$$K(T_2) = \frac{\frac{p_{\text{F}}}{p^{\ominus}}\frac{p_{\text{H}}}{p^{\ominus}}}{\frac{p_{\text{M}}}{p^{\ominus}}} = \frac{n_{\text{F}}n_{\text{H}}}{n_{\text{M}}}\frac{RT_2}{p^{\ominus}} \tag{5.81}$$

Here, we have expressed partial pressures by the respective amounts of substances using the perfect gas equation of state. Following the basic procedure outlined above in Sect. 5.1, we write down the set of equations describing the change of the amounts of reactants and products (Eq. (5.2)). We take into account that at first only methanol, with an initial amount of n_{M}^0, is present in the reactor, whereas the amounts of the products formaldehyde and hydrogen are zero:

$$n_{\text{M}}^{\text{eq}} = n_{\text{M}}^0 + \xi^{\text{eq}} \qquad n_{\text{F}}^{\text{eq}} = \xi^{\text{eq}} \qquad n_{\text{H}}^{\text{eq}} = \xi^{\text{eq}} \tag{5.82}$$

We calculate n_{M}^0 from the initial volume V^0 and pressure $p^{\ominus}$ using the state of equation of a perfect gas:

$$n_{\text{M}}^0 = \frac{p^{\ominus}V^0}{RT_2} = 0.013\,\text{mol} \tag{5.83}$$

We recognize that not only the amounts of methanol, formaldehyde, and hydrogen depend on the extent of reaction, but also the volumes: because of Dalton's law of additivity of the partial pressures we can write:

$$p^{\ominus} = p_{\text{M}} + p_{\text{F}} + p_{\text{H}} = \frac{RT_2}{V}(n_{\text{M}} + n_{\text{F}} + n_{\text{H}})\,. \tag{5.84}$$

Solving for V we obtain:

$$V = \frac{RT_2}{p^{\ominus}}(n_{\text{M}} + n_{\text{F}} + n_{\text{H}}) \overset{\text{Eq. (5.82)}}{=} \frac{RT_2}{p^{\ominus}}\left(n_{\text{M}}^0 + \xi^{\text{eq}}\right)\,. \tag{5.85}$$

Now, we insert the last equation and Eq. (5.82) into the law of mass action (Eq. (5.81)) and obtain:

$$K(T_2) = \frac{\xi^{\mathrm{eq}\,2}}{\left(n_\mathrm{M}^0 + \xi^\mathrm{eq}\right)\left(n_\mathrm{M}^0 - \xi^\mathrm{eq}\right)} \overset{\text{Eq. (A.3)}}{=} \frac{\xi^{\mathrm{eq}\,2}}{n_\mathrm{M}^{0\;2} - \xi^{\mathrm{eq}\,2}} \tag{5.86}$$

We can solve this equation for the extent of reaction:

$$\xi^\mathrm{eq} = n_\mathrm{M}^0 \sqrt{\frac{K(T_2)}{1 + K(T_2)}} = 0.011\,\mathrm{mol} \tag{5.87}$$

Using Eq. (5.85)we calculate the volume in the state of equilibrium and obtain $V = 1.87 \times 10^{-3}\,\mathrm{m}^3$. At constant pressure the work is thus:

$$W = p^\ominus \left(V - V^0\right) = -87\,\mathrm{J} \tag{5.88}$$

The partial pressure of hydrogen and formaldehyde is computed using the equation of state and the equilibrium amounts of these substances:

$$p_\mathrm{F} = p_\mathrm{H} \overset{\text{Eq. (5.82)}}{=} \xi^\mathrm{eq} \frac{RT_2}{V} = 46{,}422\,\mathrm{Pa}. \tag{5.89}$$

Methanol has an equilibrium partial pressure of:

$$p_\mathrm{M} = \left(n_\mathrm{M}^0 + \xi^\mathrm{eq}\right) \frac{RT_2}{V} = 7157\,\mathrm{Pa} \tag{5.90}$$

We can check our result by summing the partial pressures. Our results confirm our expectation that most of the methanol is converted to formaldehyde and hydrogen. Discussing the results in a seminar group, one of the students was astonished about the fact that work is done in this reaction, even though it is endothermic. Is this really a contradiction? What would you have answered? The last question of the problem is about reversibility. The process is irreversible. If a state of chemical equilibrium is reached, it cannot be reversed without changing the external conditions.

Problem 5.6 (Temperature Dependence of Equilibrium Constants) The often-made assumption of a constant heat of reaction leading to Van't Hoff's reaction isobar in the form of Eq. (5.10) is an approximation.

a. Use Kirchhoff's law on the heat of reaction and derive an expression for the equilibrium constant at a temperature of T_2 if the equilibrium constant

(continued)

Table 5.4 Polynomial representation of constant pressure molar heat capacities of various gases, valid in the temperature range between 298 and 800 K

Molecule	a_0 (J K^{-1} mol^{-1})	a_1 (J K^{-2} mol^{-1})	a_2 (J K^{-3} mol^{-1})	a_3 (J K^{-4} mol^{-1})
$CO(g)$	31.08	-1.452×10^{-2}	3.1415×10^{-5}	-1.4973×10^{-8}
$CO_2(g)$	18.86	7.937×10^{-2}	-6.7834×10^{-5}	2.4426×10^{-8}
$H_2(g)$	22.66	4.381×10^{-2}	-1.0835×10^{-4}	1.1710×10^{-7}
$H_2O(g)$	33.80	-0.795×10^{-2}	2.8228×10^{-5}	-1.3115×10^{-8}

Problem 5.6 (continued)

at a temperature of T_1 is given. Assume the constant pressure heat capacity in the form $c_p(T) = \sum_{k=0} a_k T^k$, valid in the interval between T_1 and T_2.

b. Consider the water-gas shift reaction (Eq. (5.60)). Use information from Problem 5.4 and the data given in Table 5.4 to calculate the equilibrium constant at various points in the temperature range between $T_1 = 298.15$ and 500 K. Compare with approximative results using Van't Hoff's reaction isobar Eq. (5.10) and thereby check the validity of the results in Problem 5.4.

Solution 5.6 As stated in Sect. 5.1.2, the assumption of a constant reaction enthalpy can be a crude approximation if larger temperature intervals are considered. In the concrete case of the water-gas shift reaction, we check the difference between an approximative and the more precise treatment. In **subproblem (a)**, the goal is the generalized form of the Van't Hoff reaction isobar with a temperature-dependent heat of reaction, $\Delta h_r(T)$. Integration of Eq. (5.9) yields:

$$\int_{K(T_1)}^{K(T_2)} d\ln K = \int_{T_1}^{T_2} \frac{\Delta h_r(T)\,dT}{RT^2}. \tag{5.91}$$

According to Kirchhoff's law (see Eq. (4.6), on page 73),

$$\Delta h_r(T) = \Delta h_r(T_1) + \int_{T_1}^{T} \Delta c_p(\tau)\,d\tau \tag{5.92}$$

where $\Delta h_r(T)$ is the value of the heat of reaction at the reference temperature T_1, and $\Delta c_p(\tau) = \sum_i \nu_i c_{p;i}(\tau)$. The left side of Eq. (5.91) is easily integrated. Inserting Kirchhoff's law (Eq. (5.92)), we obtain:

$$\ln K(T_2) = \ln K(T_1) + \int_{T_1}^{T_2} \frac{\Delta h_r(T_1)}{RT^2}\,dT + \int_{T_1}^{T_2} \frac{1}{RT^2} \int_{T_1}^{T} \Delta c_p(\tau)\,d\tau\,dT \tag{5.93}$$

Using a polynomial representation of the molar heat $\Delta c_p(\tau) = \sum_k \Delta a_k \tau^k$ with $\Delta a_k = \sum_i \nu_i a_{k;i}$, we can write:

$$\ln K(T_2) = \ln K(T_1) + \frac{\Delta h_r(T_1)}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} + \int_{T_1}^{T_2} \frac{dT}{RT^2} \sum_{k=0} \frac{\Delta a_k}{k+1} \left(T^{k+1} - T_1^{k+1}\right) \tag{5.94}$$

Sorting the terms with regard to the dependence on T, we obtain:

$$\begin{aligned} \ln K(T_2) &= \ln K(T_1) + \frac{\left[\Delta h_r(T_1) - \sum_{k=0} \frac{\Delta a_k}{k+1} T_1^{k+1}\right]}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \\ &\quad + \frac{\Delta a_0}{R} \int_{T_1}^{T_2} \frac{dT}{T} + \sum_{k=1} \frac{\Delta a_k}{(k+1)R} \int_{T_1}^{T_2} T^{k-1}\, dT \end{aligned} \tag{5.95}$$

The integrals are now evaluated using the integral table in the appendix (Sect. A.3.7):

$$\begin{aligned} \ln K(T_2) &= \ln K(T_1) - \frac{\left[\Delta h_r(T_1) - \sum_{k=0} \frac{\Delta a_k}{k+1} T_1^{k+1}\right]}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ &\quad + \frac{\Delta a_0}{R} \ln \frac{T_2}{T_1} + \sum_{k=1} \frac{\Delta a_k}{k(k+1)R} \left(T_2^k - T_1^k\right) \end{aligned} \tag{5.96}$$

This is our generalized form for evaluating the equilibrium constant at a temperature of T_2.

In **subproblem (b)**, we apply this equation to the water gas shift reaction already studied in Problem 5.4. At the reference temperature $T_1 = 298.15\,\mathrm{K}$, the equilibrium constant, obtained from thermochemical data, is $K(T_1) = 102{,}443$. The standard molar reaction enthalpy is $\Delta h_r(T_1) = -41.2\,\mathrm{kJ\,mol^{-1}}$. From the coefficients given in Table 5.4, we determine the quantities Δa_i, $i = 0, \ldots, 3$, for the reaction $CO + H_2O \longrightarrow CO_2 + H_2$. We obtain

$$\Delta a_0 = (18.86 + 22.66 - 31.08 - 33.80)\,\mathrm{J\,K^{-1}\,mol^{-1}} = -23.36\,\mathrm{J\,K^{-1}\,mol^{-1}} \tag{5.97}$$

and, in the same way, $\Delta a_1 = 0.14565\,\mathrm{J\,K^{-2}\,mol^{-1}}$, $\Delta a_2 = -2.35827 \times 10^{-4}\,\mathrm{J\,K^{-3}\,mol^{-1}}$, and $\Delta a_3 = 1.69614 \times 10^{-7}\,\mathrm{J\,K^{-4}\,mol^{-1}}$. Using Eq. (5.96), we can now calculate for arbitrary T_2. The results are depicted in Fig. 5.5 (*solid line*). For comparison, the *dashed line* represents the value of the equilibrium constant according to Eq. (5.10). In particular, the corrected value of the equilibrium constant at 400 K is 1,433. The uncorrected value, used in Problem 5.4, is 1,488. Therefore, the systematic error in this case is about 4%. If the temperature intervals become larger, of course, the deviations become more significant.

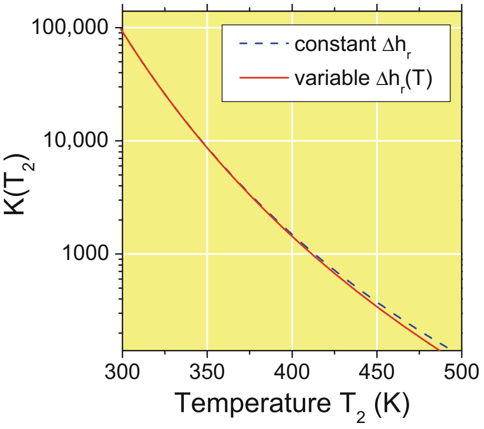


Fig. 5.5 Equilibrium constant for the water gas shift reaction as a function of temperature. Note the logarithmic scaling

Problem 5.7 (Determination of Reaction Enthalpy and Reaction Entropy) Dimethyl ether (CH_3–O–CH_3) is a possible replacement for diesel fuel. Dimethyl ether is produced from methanol using a suitable catalyst:

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \tag{5.98}$$

a. Measurements of the equilibrium K constant as a function of temperature yield the following empirical law:

$$\ln K(T) = \frac{2051.7}{\frac{T}{\mathrm{K}}} - 1.5587 \tag{5.99}$$

Determine the molar heat of reaction Δh_r and the reaction enthalpy Δs_r of the reaction. You may assume that both Δh_r and Δs_r are constant within the temperature range 498 to 623 K.

b. 2 g methanol are filled in a vessel with a volume of 1 dm^3. The vessel, containing a catalyst, is sealed and heated to 250 °C and the chemical equilibrium is established according to Eq. (5.99). Calculate the equilibrium partial pressures of the gases assuming ideal behavior.

Solution 5.7 The measurement of equilibrium constants as a function of temperature is one way of determining reaction enthalpies and reaction entropies. The procedure is quite similar to the evaluation of the heat of vaporization and the entropy of vaporization discussed in Problem 3.10. In **subproblem (a)** we deal with the synthesis of dimethyl ether from methanol. Equation (5.99) is the empirical relationship between the equilibrium constant and temperature, fitted to experimental data. Usually, the logarithm of the measured equilibrium constant

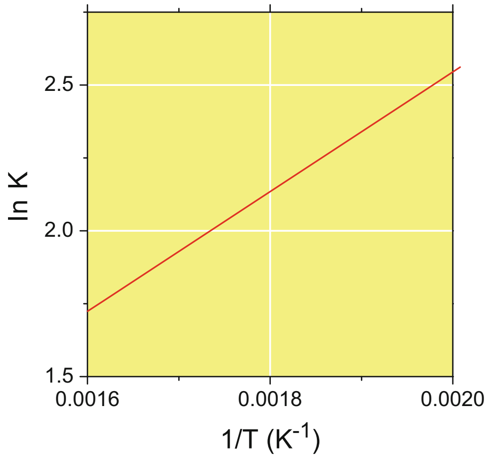


Fig. 5.6 Graphical representation of Eq. (5.99) in the temperature range between 625 and 500 K

plotted against the reciprocal temperature exhibits a linear behavior, which is shown in Fig. 5.6, where we have plotted the function Eq. (5.99) in this way. The relation to Δh_r and Δs_r is established, taking into account the law of mass action Eq. (5.7),

$$K = \exp\left(-\frac{\Delta g_r}{RT}\right) \tag{5.100}$$

and, moreover, the relation:

$$\Delta g_r(T) = \Delta h_r - T\Delta s_r. \tag{5.101}$$

Hence,

$$\ln K = -\frac{\Delta h_r}{R}\frac{1}{T} + \frac{\Delta s_r}{R} \tag{5.102}$$

Comparison with Eq. (5.99) reveals

$$\Delta h_r = -R \times 2015.7\,\mathrm{K} = -16.8\,\mathrm{kJ\,mol^{-1}} \tag{5.103}$$

and

$$\Delta s_r = R \times (-1.5587) = +13.0\,\mathrm{J\,K^{-1}\,mol^{-1}} \tag{5.104}$$

In **subproblem (b)**, we shall calculate the partial pressures of dimethyl ether, water, and methanol in the state of chemical equilibrium at 523.15 K. Using Eq. (5.99), we calculate the equilibrium constant for this temperature and obtain $K(523.15\,\mathrm{K}) = 10.624$. The following procedure is similar to our solution of Problem 5.5b. If p_D, p_W, and p_M are the equilibrium partial pressures of dimethyl ether, water, and methanol respectively, the law of mass action is

$$K \overset{\text{Eq. (5.7)}}{=} \frac{p_{\mathrm{D}} p_{\mathrm{W}}}{p_{\mathrm{M}}^2} = \frac{n_{\mathrm{D}} n_{\mathrm{W}}}{n_{\mathrm{M}}^2}, \tag{5.105}$$

where n_{D}, n_{W}, and n_{M} are the amounts of substances. Introducing the equilibrium extent of reaction, ξ (we omit the superscript 'eq'), we can write:

$$n_{\mathrm{M}} = n_{\mathrm{M}}^0 - 2\xi; \qquad n_{\mathrm{D}} = n_{\mathrm{W}} = \xi \tag{5.106}$$

where n_{M}^0 is the initial amount of methanol in the vessel. The molar mass of methanol is $M_{\mathrm{M}} = 31.05\,\mathrm{g\,mol^{-1}}$ and its initial mass is $m = 2\,\mathrm{g}$. Thus, the initial amount is $n_{\mathrm{M}}^0 = \frac{m}{M_{\mathrm{M}}} = 0.0624\,\mathrm{mol}$. We insert Eq. (5.106) into Eq. (5.105) and obtain the conditional equation for ξ:

$$K = \frac{\xi^2}{\left(n_{\mathrm{M}}^0 - 2\xi\right)^2} = \frac{\xi^2}{{n_{\mathrm{M}}^0}^2 - 4 n_{\mathrm{M}}^0 \xi + 4\xi^2} \tag{5.107}$$

Solving for ξ we obtain a quadratic equation:

$$(4K-1)\,\xi^2 - 4 n_{\mathrm{M}}^0 K \xi + K {n_{\mathrm{M}}^0}^2 = 0 \tag{5.108}$$

with the two solutions

$$\xi_{1,2} = \frac{4 n_{\mathrm{M}}^0 K \pm \sqrt{16 {n_{\mathrm{M}}^0}^2 K^2 - 4(4K-1) K {n_{\mathrm{M}}^0}^2}}{2(4K-1)} = n_{\mathrm{M}}^0 \frac{2K \pm \sqrt{K}}{4K-1} \tag{5.109}$$

The two solutions are $\xi_1 = 0.5906 \times n_{\mathrm{M}}^0$ and $\xi_2 = 0.4335 \times n_{\mathrm{M}}^0$. Here, we have to decide which of the two solutions is the correct one according to the problem. The decision is possible using Eq. (5.3), which poses the requirement that ξ leads to positive values for all reactants. Applied to our problem, where we have only one reactant,

$$0 \le \xi \le \frac{n_{\mathrm{M}}^0}{2} \tag{5.110}$$

Hence the first solution, ξ_1, is rejected, and thus $\xi = 0.4335 \times n_{\mathrm{M}}^0 = 0.0271\,\mathrm{mol}$. With this result and Eq. (5.106), we obtain the equilibrium mole numbers of all substances $n_{\mathrm{M}} = 0.0083\,\mathrm{mol}$, $n_{\mathrm{W}} = n_{\mathrm{D}} = 0.02705\,\mathrm{mol}$. With the equation of state and the given volume $V = 10^{-3}\,\mathrm{m^{-3}}$ the equilibrium partial pressures are

$$p_{\mathrm{M}} = \frac{RT}{V} n_{\mathrm{M}} = 36{,}103\,\mathrm{Pa}; \qquad p_{\mathrm{W}} = p_{\mathrm{D}} = 117{,}660\,\mathrm{Pa} \tag{5.111}$$

It is advisable to insert these partial pressures again in Eq. (5.105) to test if our results are correct. The fraction $\frac{p_D p_W}{p_M^2}$ is 10.621, in very good agreement with the equilibrium constant $K = 10.624$ on which our calculation was based. The small deviation is a contaminant from round-off errors during the calculation.

Problem 5.8 (A Simple Model of Acid Rain) A simple model of the acidity of rain water is based on the solution of atmospheric carbon dioxide in water:

$$\mathrm{CO_2(g)} \overset{K_0}{\rightleftharpoons} \mathrm{CO_2(aq)} \tag{5.112}$$

$$\mathrm{CO_2(aq)} + \mathrm{H_2O(l)} \overset{K_1}{\rightleftharpoons} \mathrm{H_2CO_3(aq)} \tag{5.113}$$

$$\mathrm{H_2CO_3(aq)} + \mathrm{H_2O(l)} \overset{K_{a2}}{\rightleftharpoons} \mathrm{HCO_3^-(aq)} + \mathrm{H_3O^+(aq)} \tag{5.114}$$

Given that $K_0 = 1$, $K_1 = 3.0 \times 10^{-5}\,\mathrm{l\,mol^{-1}}$, $K_{a2} = 2.5 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$, and a CO_2 concentration of $14.6\,\mu\mathrm{mol\,l^{-1}}$ in clean air, calculate the pH value of raindrops. Hint: autoprotolysis of water and the deprotonation of HCO_3^- can be ignored.

Solution 5.8 This simple application of the law of mass action deals with the acidity of rain water. Even in clean air—free from atmospheric trace gases such as SO_2 or NO_x—carbon dioxide is present and is thus dissolved in rain water forming carbonic acid (see Fig. 5.7). The equilibrium between gaseous CO_2 and dissolved CO_2 is described by the so-called Ostwald solubility coefficient, which we assume

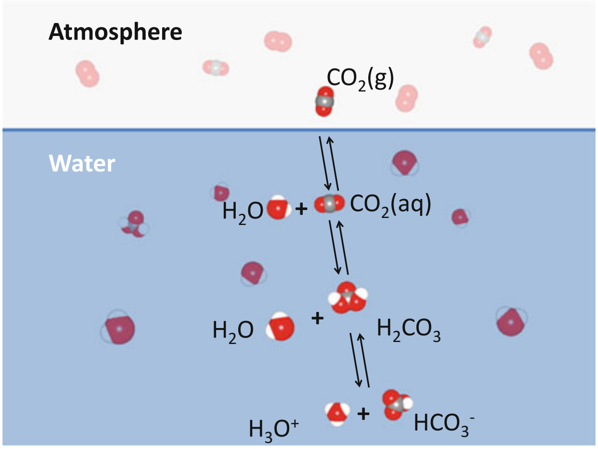


Fig. 5.7 Dissolution and dissociation of atmospheric CO_2 in water (schematic)

to be $K_0 = 1$. A fraction of the dissolved CO_2 reacts to carbonic acid, H_2CO_3. After deprotonation HCO_3^- is formed (Eq. (5.112)), which causes the production of hydronium ions and thus a decrease in the pH value. For simplicity, we ignore the autoprotolysis of the solvent water and, moreover, the fact that additional H_3O^+ ions are formed by the reaction $HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$. This is because the equilibrium constant for this reaction is orders of magnitude smaller than K_2. We write down the law of mass action for the first reaction:

$$K_0 = \frac{c_{CO_2}^{aq}}{c_{CO_2}^{g}} \tag{5.115}$$

Here, $c_{CO_2}^{g} = 14.6\,\mu\text{mol}\,\text{l}^{-1}$ is the given concentration of atmospheric CO_2, and $c_{CO_2}^{aq}$ is the concentration of physically dissolved CO_2 in water. The law of mass action for the second equilibrium reaction is

$$K_1 = \frac{c_{H_2CO_3}}{c_{CO_2}^{aq} \cdot c_{H_2O}} \tag{5.116}$$

The dissociation of carbonic acid is characterized by the dissociation constant K_{a2}, which is defined above in Eq. (5.12) and is more commonly used to describe the dissociation of acids in dilute solutions:

$$K_{a2} = \frac{c_{HCO_3^-} \cdot c_{H_3O^+}}{c_{H_2CO_3}} \tag{5.117}$$

If we solve Eq. (5.115) for $c_{CO_2}^{aq}$ and insert this concentration into Eq. (5.116), we obtain

$$c_{H_2CO_3} = K_1 c_{CO_2}^{aq} c_{H_2O} = K_0 K_1 c_{CO_2}^{g} c_{H_2O} \tag{5.118}$$

Because no other acids are present (perfectly clean water) and autoprotolysis is ignored, $c_{HCO_3^-} = c_{H_3O^+}$. The concentration of the solvent water, which is largely in excess, is $c_{H_2O} = 55.555\,\text{mol}\,\text{l}^{-1}$. Therefore, insertion of Eq. (5.118) into Eq. (5.117) yields:

$$c_{H_3O^+} = \sqrt{K_0 K_1 K_{a2} c_{CO_2}^{g} c_{H_2O}} = 2.47 \times 10^{-6}\,\text{mol}\,\text{l}^{-1} \tag{5.119}$$

With the definition of the pH value (Eq. (5.14)), we obtain pH $= 5.6$ for clean air rain water. Hence, because of the presence of atmospheric natural CO_2, rain water is already acid. Recapitulating our method of solving this problem it is worth mentioning the following: in this problem the abundance of atmospheric CO_2 takes a constant value regardless of how much CO_2 is dissolved in water. Thus, the initial concentration and the equilibrium concentration of carbon dioxide are identical. The same is true for the concentration of water. Therefore, the calculation of $c_{H_3O^+}$ can

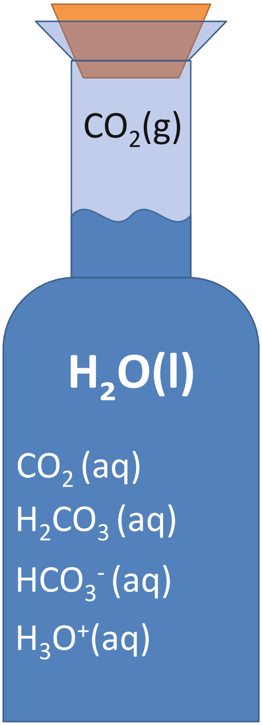


Fig. 5.8 Chemical equilibrium between gaseous and dissolved CO_2 in a sealed bottle of water

be carried out in a straightforward way. When deciding whether we have to balance floating concentrations using the concept of the extent of reaction (Eq. (5.2)) or whether it is justified to assume constant concentrations, the following question may also be helpful: is the system under consideration an *open system* or a *closed system*? In the present problem concerning atmospheric CO_2 we have an open system—the carbon dioxide of the entire atmosphere is in equilibrium with the dissolved carbon dioxide in a small rain drop. Now, consider the more complicated case of a sealed bottle of mineral water where the gas phase in the small volume between the water surface and the crown seal is in equilibrium with the dissolved gas (see Fig. 5.8). In this more complicated case, we have a closed system and we must distinguish between initial concentration and equilibrium concentration.

Problem 5.9 (CO_2 Dissolution in a Closed Bottle of Water) A sealed bottle with a total volume of 1 l contains 0.95 l of clean water (see Fig. 5.8). Initially, the gas phase between the water surface and the sealing contains carbon dioxide at a total pressure of 2 bar at room temperature. Then the chemical equilibrium according to Eq. (5.112) is established. Use the

(continued)

Problem 5.9 (continued)
values for the equilibrium constants given in Problem 5.8 and determine the concentrations of dissolved CO_2, H_2CO_3, and HCO_3^- along with the pH value of the water under the conditions of chemical equilibrium. Assume a density of water of $1\,\mathrm{g\,cm^{-3}}$ and the ideal behavior of gaseous carbon dioxide. *Hints: You may ignore the autoprotolysis of the solvent water. It is assumed that you have already dealt with Problem 5.8.*

Solution 5.9 This problem again picks up on the problem of carbon dioxide solvation in water (see Fig. 5.7). As stated in the discussion of the solution to Problem 5.8, the solvation of a finite amount of CO_2 in a closed system requires a treatment using floating concentrations, which is the method we must follow now. Moreover, it is a good idea to use a representation of the laws of mass action (Eqs. (5.115)–(5.117)) involving amounts of substances. With the volumes of the gas phase and the water, $v_g = 0.05\,\mathrm{l}$ and $v_l = 0.95\,\mathrm{l}$, we can introduce new equilibrium constants κ_0, κ_1, and κ_3, and write:

$$\kappa_0 = K_0 \frac{v_l}{v_g} = \frac{n_{\mathrm{CO_2}}^{\mathrm{aq}}}{n_{\mathrm{CO_2}}^{g}}, \tag{5.120}$$

$$\kappa_1 = K_1 c_{\mathrm{H_2O}} = \frac{n_{\mathrm{H_2CO_3}}}{n_{\mathrm{CO_2}}^{\mathrm{aq}}}, \tag{5.121}$$

and

$$\kappa_2 = v_l K_{a2} = \frac{n_{\mathrm{HCO_3}} n_{\mathrm{H_3O}}}{n_{\mathrm{H_2CO_3}}}, \tag{5.122}$$

where $\kappa_0 = K_0 \frac{0.95}{0.05} = 19$, $\kappa_1 = K_1 c_{\mathrm{H_2O}} = 3.0 \times 10^{-5}\,\mathrm{l\,mol^{-1}} \times 55.555\,\mathrm{mol\,l^{-1}} = 1.667 \times 10^{-3}$, and $\kappa_2 = v_l K_{a2} = 0.95\,\mathrm{l} \times 2.5 \times 10^{-4}\,\mathrm{mol\,l^{-1}} = 2.375 \times 10^{-4}\,\mathrm{mol}$. The mole numbers in Eqs. (5.120)–(5.122) are understood to be equilibrium mole numbers. These depend on the equilibrium extents of reaction for

$$\mathrm{CO_2(g)} \overset{\kappa_0}{\rightleftharpoons} \mathrm{CO_2(aq)}$$

$$\mathrm{CO_2(aq)} + \mathrm{H_2O(l)} \overset{\kappa_1}{\rightleftharpoons} \mathrm{H_2CO_3(aq)}$$

$$\mathrm{H_2CO_3(aq)} + \mathrm{H_2O(l)} \overset{\kappa_2}{\rightleftharpoons} \mathrm{HCO_3^-(aq)} + \mathrm{H_3O^+(aq)}$$

which simultaneously reach chemical equilibrium. Therefore, we introduce the equilibrium extents of reaction ξ_0, ξ_1, and ξ_2 associated with the equilibrium constants κ_0, κ_1, and κ_2 respectively. According to Eq. (5.2), we set up the equations for the mole numbers as follows:

$$n^{g}_{CO_2} = n^{0}_{CO_2} - \xi_0 \tag{5.123}$$

$$n^{aq}_{CO_2} = \xi_0 - \xi_1 \tag{5.124}$$

$$n_{H_2CO_3} = \xi_1 - \xi_2 \tag{5.125}$$

$$n_{H_3O} = n_{HCO_3} = \xi_2 \tag{5.126}$$

Here, $n^0_{CO_2}$ is the initial mole number of gaseous CO_2, and we take into account the fact that all other substances have initial mole numbers of zero. Treating CO_2 as a perfect gas,

$$n^0_{CO_2} = \frac{p^0 V_g}{RT} = \frac{2\times 10^5\,\mathrm{Pa}\times 0.05\times 10^{-3}\,\mathrm{m}^3}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\times 298\,\mathrm{K}} = 4.034\times 10^{-3}\,\mathrm{mol}. \tag{5.127}$$

In the next step, we insert Eqs. (5.123)–(5.126) into Eqs. (5.120)–(5.122) and obtain the following set of three equations for the three unknowns ξ_0, ξ_1, and ξ_2:

$$\kappa_0 = \frac{\xi_0 - \xi_1}{n^0_{CO_2} - \xi_0}; \qquad \kappa_1 = \frac{\xi_1 - \xi_2}{\xi_0 - \xi_1}; \qquad \kappa_2 = \frac{\xi_2^2}{\xi_1 - \xi_2} \tag{5.128}$$

The strategy is to eliminate two of the unknowns and obtain an equation for one extent of reaction. Therefore, we take the first equation and solve for ξ_0:

$$\xi_0 = \frac{\kappa_0 n^0_{CO_2} + \xi_1}{\kappa_0 + 1} \tag{5.129}$$

Insertion into the middle expression of Eq. (5.128) yields

$$\kappa_1 = \frac{\xi_1 - \xi_2}{\frac{\kappa_0 n^0_{CO_2}}{\kappa_0+1} + \left(\frac{1}{\kappa_0+1} - 1\right)\xi_1} = \frac{1}{A}\frac{\xi_1 - \xi_2}{n^0_{CO_2} - \xi_1} \tag{5.130}$$

where we have defined $A = \frac{\kappa_0}{\kappa_0+1} = \frac{19}{20}$. We can solve Eq. (5.130) for ξ_1 and insert this into the third expression of Eq. (5.128):

$$\xi_1 = \frac{A\kappa_1 n^0_{CO_2} + \xi_2}{1 + A\kappa_1} \tag{5.131}$$

$$\kappa_2 = \frac{\xi_2^2}{\frac{A\kappa_1 n^0_{CO_2} + \xi_2}{1+A\kappa_1} - \xi_2} \tag{5.132}$$

This expression can be written as a quadratic equation for ξ_2,

$$\xi_2^2 + C\xi_2 - Cn^0_{\mathrm{CO_2}} = 0; \qquad C = \frac{A\kappa_1\kappa_2}{1 + A\kappa_1} = \frac{\kappa_0\kappa_1\kappa_2}{1 + \kappa_0\,(\kappa_1 + 1)} \tag{5.133}$$

We obtain the roots of the quadratic equation using Eq. (A.4) and obtain

$$\xi_{2;1,2} = \frac{-C \pm \sqrt{C^2 + 4Cn^0_{\mathrm{CO_2}}}}{2} \tag{5.134}$$

As $C = 3.75447 \times 10^{-7}$ mol is positive, we can exclude the solution with the minus sign in front of the root. Hence,

$$\xi_2 = \frac{\sqrt{C^2 + 4Cn^0_{\mathrm{CO_2}}} - C}{2} = 3.8730 \times 10^{-5}\,\mathrm{mol} \tag{5.135}$$

Having obtained this result, we use Eq. (5.131) and obtain $\xi_1 = 4.50471 \times 10^{-5}$ mol. Insertion of this result into Eq. (5.129) then yields $\xi_0 = 3.83455 \times 10^{-3}$ mol. Using Eqs. (5.123)–(5.126), we can now calculate all mole numbers:

$$\begin{aligned} n^g_{\mathrm{CO_2}} &= n^0_{\mathrm{CO_2}} - \xi_0 = 1.9945 \times 10^{-4}\,\mathrm{mol} \\ n^{\mathrm{aq}}_{\mathrm{CO_2}} &= \xi_0 - \xi_1 = 3.789503 \times 10^{-3}\,\mathrm{mol} \\ n_{\mathrm{H_2CO_3}} &= \xi_1 - \xi_2 = 6.3171 \times 10^{-6}\,\mathrm{mol} \\ n_{\mathrm{H_3O}} = n_{\mathrm{HCO_3}} &= \xi_2 = 3.7930 \times 10^{-5}\,\mathrm{mol} \end{aligned}$$

As a consistency test we can add up all equilibrium mole numbers of CO_2 containing species and obtain $n^g_{\mathrm{CO_2}} + n^{\mathrm{aq}}_{\mathrm{CO_2}} + n_{\mathrm{H_2CO_3}} + n_{\mathrm{HCO_3}} = 4.0340001 \times 10^{-3}$ mol, which, according to Eq. (5.127), is just the initial amount of gas phase CO_2. In addition, these mole numbers satisfy the three laws of mass action Eqs. (5.120), (5.121), and (5.122). If we inspect these data, we see that the dominant amount of CO_2 is physically dissolved as CO_2(aq), whereas only about 2×10^{-4} mol remain in the gas phase, which corresponds to an equilibrium pressure of only $p = \frac{n^g_{\mathrm{CO_2}}RT}{V_g} = 9883$ Pa and a concentration of $c^g_{\mathrm{CO_2}} = 3.99 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$. The concentrations of the dissolved species are $c^{\mathrm{aq}}_{\mathrm{CO_2}} = 3.99 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$, $c_{\mathrm{H_2CO_3}} = 6.65 \times 10^{-6}\,\mathrm{mol\,l^{-1}}$, and $c_{\mathrm{HCO_3^-}} = c_{\mathrm{H_3O^+}} = 4.08 \times 10^{-5}\,\mathrm{mol\,l^{-1}}$. Hence, the pH value of the water under equilibrium conditions is 4.4.

Problem 5.10 (Dissociation of Trichloroacetic Acid) Under normal conditions, trichloroacetic acid (TCA) forms crystals with a sharp odor. 5 g of TCA are dissolved in 1 dm^3 perfectly clean water, and the dissociation equilibrium is established:

$$\mathrm{CCl_3COOH(aq)} + \mathrm{H_2O(l)} \overset{K_a}{\rightleftharpoons} \mathrm{CCl_3COO^-(aq)} + \mathrm{H_3O^+(aq)} \qquad (5.136)$$

a. The dissociation constant of the reaction is $K_a = 0.30$. Determine the equilibrium concentrations of dissociated and undissociated TCA, the pH value of the solution, and the degree of dissociation defined as $\alpha = \frac{c_{\mathrm{TCA}^-}}{c^0_{\mathrm{TCA}}}$, where c_{TCA^-} is the equilibrium concentration of dissociated TCA, and c^0_{TCA} is the initial concentration of undissociated TCA.
b. Show that the degree of dissociation reaches a value of 1 in the limit $c^0_{\mathrm{TCA}} \to 0$.

Hint: You may ignore the autoprotolysis of the solvent water.

Solution 5.10 This problem is a typical application of chemical equilibrium in dilute solutions (compare Sect. 5.1.3). Although strong acids such as HCl dissociate completely, a weak acid such as acetic acid ($\mathrm{CH_3COOH}$) is only partially dissociated. In TCA, the hydrogens of the methyl group are replaced by the more electronegative chlorine, which affects the bonding in the carboxyl group. As a consequence, TCA has a higher dissociation constant than acetic acid. Given $K_a = 0.3$, we determine the equilibrium concentrations and the degree of dissociation of TCA in **subproblem (a)** according to the reaction:

$$\mathrm{TCA(aq)} + \mathrm{H_2O(l)} \overset{K_a}{\rightleftharpoons} \mathrm{TCA^-(aq)} + \mathrm{H_3O^+(aq)} \qquad (5.137)$$

Analogous to Eq. (5.12), we can write

$$K_a = \frac{c_{\mathrm{TCA}^-} \cdot c_{\mathrm{H_3O^+}}}{c_{\mathrm{TCA}}} \qquad (5.138)$$

We can assume that initially no $\mathrm{H_3O^+}$ and $\mathrm{TCA^-}$ ions are present in the solution. Hence, $c^0_{\mathrm{H_3O^+}} = c^0_{\mathrm{TCA}^-} = 0$. To determine the initial concentration of TCA we have to consider its molar mass, $M_{\mathrm{TCA}} = 163.38\,\mathrm{g\,mol^{-1}}$. If $m = 5$ g of TCA are dissolved in 1 dm^3 water, then $c^0_{\mathrm{TCA}} = \frac{5\,\mathrm{g}}{163.38\,\mathrm{g\,mol^{-1}}\ 1\,\mathrm{dm^3}} = 0.0306\,\mathrm{mol\,dm^{-3}}$. In the next step we have to set up the equations for the equilibrium concentrations analogous to Eq. (5.2):

$$c_{\mathrm{TCA}} = c^0_{\mathrm{TCA}} - \tilde{\xi} \tag{5.139}$$

$$c_{\mathrm{TCA}^-} = c_{\mathrm{H_3O}^+} = \tilde{\xi} \tag{5.140}$$

Note that the concentration of the solvent water is taken as a constant contained in the dissociation constant K_a. The concentration $\tilde{\xi} = \frac{\xi^{\mathrm{eq}}}{1\,\mathrm{dm}^3}$ is related to the equilibrium extent of reaction. Insertion of these equations into Eq. (5.138) yields

$$K_a = \frac{\tilde{\xi}^2}{c^0_{\mathrm{TCA}} - \tilde{\xi}} \tag{5.141}$$

If we solve for $\tilde{\xi}$ we obtain the quadratic equation

$$\tilde{\xi}^2 + K_a\tilde{\xi} - K_a c^0_{\mathrm{TCA}} = 0 \tag{5.142}$$

with the roots

$$\tilde{\xi}_{1,2} = \frac{\pm\sqrt{K_a^2 + 4K_a c^0_{\mathrm{TCA}}} - K_a}{2} \tag{5.143}$$

The meaningful mathematical solution is the one that yields a positive concentration. Hence, we can exclude the solution with the negative sign in front of the square root and obtain

$$\tilde{\xi} = \frac{\sqrt{K_a^2 + 4K_a c^0_{\mathrm{TCA}}} - K_a}{2} = 0.0280\,\mathrm{mol\,dm^{-3}} \tag{5.144}$$

Reinserting this result into Eqs. (5.139) and (5.138) yields $c_{\mathrm{TCA}^-} = c_{\mathrm{H_3O}^+} = 0.028\,\mathrm{mol\,dm^{-3}}$ and $c_{\mathrm{TCA}} = 2.61 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$. Hence, the *pH* value of the solution is $\mathrm{pH} = -\log_{10} c_{\mathrm{H_3O}^+} = 1.6$. The degree of dissociation is

$$\alpha = \frac{c_{\mathrm{TCA}^-}}{c^0_{\mathrm{TCA}}} = \frac{0.0280}{0.0306} = 0.915. \tag{5.145}$$

Thus, more than 90% of the TCA is dissociated.

Moving to **subproblem (b)** we deal with the question of how the degree of dissociation is affected by the initial concentration of TCA; more precisely, we study the case $\alpha(c^0_{\mathrm{TCA}})$ as $c^0_{\mathrm{TCA}} \to 0$. We have already dealt with the analogous problem for a gas phase reaction in Problem 5.1. A superficial inspection of Eq. (5.144) shows that $\tilde{\xi} \to 0$ and thus $c_{\mathrm{TCA}^-} \to 0$ in the limit $c^0_{\mathrm{TCA}} \to 0$. However, this

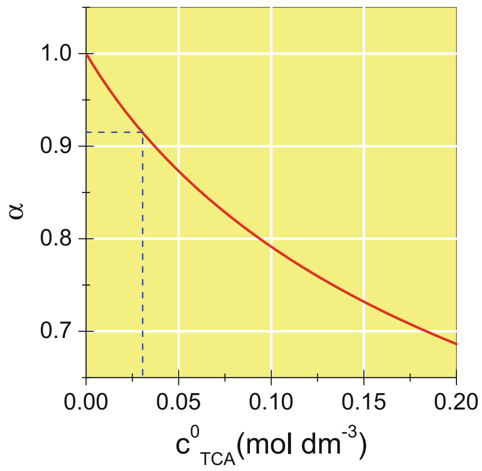


Fig. 5.9 Degree of dissociation of trichloroacetic acid as a function of initial concentration. The *dashed lines* indicate the situation treated in subproblem (a)

does not mean that the degree of dissociation reaches zero. We have to consider the

$$\lim_{c^0_{\mathrm{TCA}}\to 0} \alpha = \lim_{c^0_{\mathrm{TCA}}\to 0} \frac{\tilde{\xi}}{c^0_{\mathrm{TCA}}} = \lim_{c^0_{\mathrm{TCA}}\to 0} \frac{K_a}{2c^0_{\mathrm{TCA}}} \left(\sqrt{1 + \frac{4c^0_{\mathrm{TCA}}}{K_a}} - 1 \right) \tag{5.146}$$

Using the power series expansion of $\sqrt{1+x} = 1 + \frac{1}{2}x - \cdots$ (see Eq. (A.59)), we obtain

$$\lim_{c^0_{\mathrm{TCA}}\to 0} \alpha = \lim_{c^0_{\mathrm{TCA}}\to 0} \frac{K_a}{2c^0_{\mathrm{TCA}}} \left(1 + \frac{2c^0_{\mathrm{TCA}}}{K_a} - 1 \right) = 1 \tag{5.147}$$

Thus, at the limit of infinite dilution of the acid, the degree of dissociation reaches a value of 1, which means that *all* TCA molecules are deprotonated. The limiting behavior of $\alpha(c^0_{\mathrm{TCA}})$ is illustrated in Fig. 5.9.