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978-0-521-78567-9 - Basic Physical Chemistry for the Atmospheric Sciences:
Second Edition: A Companion Text to "Introduction to Atmospheric Chemistry"

Peter V. Hobbs

Excerpt

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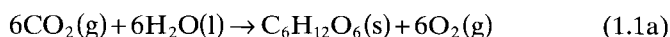
1

Chemical equilibrium

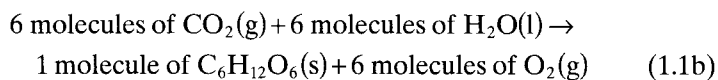
One of the major goals of chemistry is to predict what will happen when various substances come into contact. Will a chemical reaction occur, or will the substances just exist side by side? One way to approach this problem is through the concept of chemical equilibrium, which is the focus of this chapter.

1.1 Some introductory concepts

In a balanced equation for a chemical reaction, there are the same number of atoms of each element on the left side of the equation as there are on the right side. For example, the balanced equation for the chemical reaction representing photosynthesis is^{1,a}



In a balanced chemical equation (which we will often call a *reaction*), the relative numbers of the molecules involved in the reaction are given by the numerical coefficients preceding the chemical symbol for the molecule. Thus, Reaction (1.1a) indicates that six molecules of carbon dioxide, $\text{CO}_2(\text{g})$, react with six molecules of water, $\text{H}_2\text{O}(\text{l})$, to form one molecule of glucose, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$, and six molecules of oxygen, $\text{O}_2(\text{g})$



Reaction (1.1a) does not necessarily mean that if six molecules of $\text{CO}_2(\text{g})$ are mixed with six molecules of $\text{H}_2\text{O}(\text{l})$ they will react completely

^a Numerical superscripts in the text (1, 2, . . . , etc.) refer to *Notes* at the end of each chapter.

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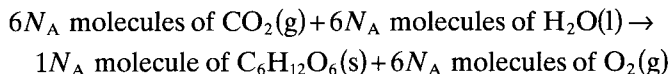
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and produce one molecule of $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$ and six molecules of $\text{O}_2(\text{g})$. Some chemical reactions proceed very quickly, others very slowly; and some never reach completion. However, what Reaction (1.1a) does tell us is that at any given instant in time the ratio of the numbers of molecules of $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$, and $\text{O}_2(\text{g})$ that have reacted is 6:6:1:6.

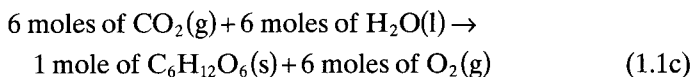
The relative masses of the various atoms are represented by their *atomic weights* (dimensionless) referenced to carbon-12 (i.e., a carbon atom containing six protons and six neutrons), where carbon-12 is arbitrarily assigned an exact atomic weight of 12. Atomic weights are listed in Appendix III. Similarly, the relative masses of molecules are represented by their *molecular weights* (dimensionless), where the molecular weight is obtained by adding together the atomic weights of all the atoms in the molecule. For example, since the atomic weights of hydrogen and oxygen are 1.008 and 15.999, respectively, the molecular weight of water (H_2O) is $(2 \times 1.008) + 15.999 = 18.015$.

One *gram-molecular weight* (abbreviation *mole* or *mol*) of any compound is a mass of that compound equal to its molecular weight in grams. Thus, 1 mole of water is 18.015 g of water. One mole of any compound contains the same number of molecules as one mole of any other compound.² The number of molecules in 1 mole of any compound is 6.022×10^{23} , which is called *Avogadro's number* (N_A). Since the volume occupied by a gas depends on its temperature, pressure, and the number of molecules in the gas, at the same temperature and pressure 1 mole of the gas of any compound occupies the same volume as 1 mole of the gas of any other compound. At *standard temperature and pressure* (STP), which are defined as 0°C and 1 bar ($= 10^5 \text{ Pa}$),³ the volume occupied by 1 mole of any gas is about 22.4 liters (L).

If we now multiply every term in the Relation (1.1b) by N_A we get



or,



Relations (1.1b) and (1.1c) demonstrate how we can move directly from a balanced chemical equation, such as Reaction (1.1a), to a statement about the relative numbers of molecules (1.1b) or the relative numbers of moles (1.1c) involved in the reaction.

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Excerpt

[More information](#)*Equilibrium constants*

3

Exercise 1.1. An important chemical reaction in atmospheric, earth, and ocean sciences is that of dissolved carbon dioxide with liquid water to form carbonic acid, $\text{H}_2\text{CO}_3(\text{l})$,

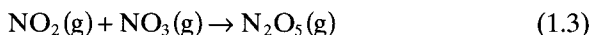


Calculate the mass of carbonic acid that forms for every kilogram of carbon dioxide that reacts with liquid water.

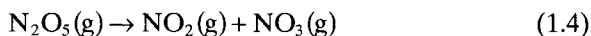
Solution. From the balanced chemical equation (1.2) we see that for every mole of carbon dioxide that reacts with water one mole of carbonic acid is formed. Since the molecular weight of CO_2 is 44.01, the number of moles of CO_2 in 1 kg is $1000/44.01 = 22.72$. Therefore, 22.72 moles of carbonic acid will form for every kilogram of CO_2 that reacts with water. The molecular weight of carbonic acid is 62.02; therefore, the number of grams of carbonic acid in 22.72 moles is $(22.72 \times 62.02) = 1409$. Therefore, for every kilogram of CO_2 that reacts with water 1.409 kg of carbonic acid are formed.

1.2 Equilibrium constants

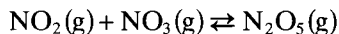
A vapor is in equilibrium with its liquid when the rate of condensation is equal to the rate of evaporation. An analogous state of equilibrium exists in a chemical system when the rate at which the reactants combine to form products is equal to the rate at which the products decompose to form the reactants. For example, a reaction that plays a role in tropospheric and stratospheric chemistry is



However, some of the N_2O_5 molecules so formed break up again



Reaction (1.3) is called the *forward* reaction and Reaction (1.4) the *reverse* reaction. Reactions (1.3) and (1.4) can be combined as follows



At every temperature there exists partial pressures of the gases for which the forward and reverse reactions occur at the same rate; under these conditions, the system is said to be in *chemical equilibrium*.

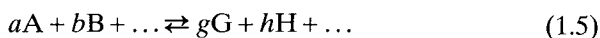
A general chemical reaction can be represented by

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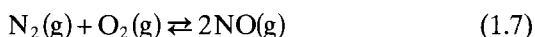
where A, B, ... and G, H, ... represent the chemical *reactants* and *products*, respectively, and *a, b, ...* and *g, h, ...* their coefficients in the balanced chemical equation. If Reaction (1.5) is in chemical equilibrium, and if the reactants and products are ideal gases or are present as solutes in an ideal solution,⁴ then

$$\frac{[G]^g [H]^h \dots}{[A]^a [B]^b \dots} = K_c \quad (1.6)$$

where [A], [B], ... and [G], [H], ... represent the equilibrium concentrations of the reactants and products, and K_c is called the *equilibrium constant* for the forward reaction (or, simply, the equilibrium constant for the reaction).⁵ Equilibrium constants for some chemical reactions are given in Appendix IV. The value of K_c for a chemical reaction depends only on temperature (see Section 2.2), not on the concentrations of the chemical species or the volume or pressure of the system.

The concentrations in Eq. (1.6) may be expressed in *molarity* (M). For a gas the molarity is the number of *moles* of gas per liter of air; for a solution, it is the number of moles of solute per liter of solution. If any of the reactants or products are pure liquids or pure solids, their concentrations (i.e., densities) are essentially constant, compared to the large changes that are possible in the concentrations of the gases. Therefore, the concentrations of liquids and solids are incorporated into the value of K_c . The practical consequence of this is that the concentration of any pure liquid or pure solid may be equated to unity in Eq. (1.6).

Exercise 1.2. At 2000°C the value of K_c for the reaction



is 1.0×10^{-4} . If the equilibrium concentrations of $O_2(g)$ and $NO(g)$ are 50 M and 0.030 M, respectively, what is the equilibrium concentration of $N_2(g)$?

Solution. Application of Eq. (1.6) to Reaction (1.7) yields

$$K_c = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]}$$

Therefore,

$$1.0 \times 10^{-4} = \frac{(0.030)^2}{[N_2(g)](50)}$$

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[More information](#)

Equilibrium constants

5

and,

$$[\text{N}_2(\text{g})] = 0.18 \text{ M}$$

At 25°C the value of K_c for Reaction (1.7) is only 1×10^{-30} ! This implies that the equilibrium concentration of $\text{NO}(\text{g})$ is very low at normal temperatures and that the equilibrium "lies to the left" of Reaction (1.7), favoring the reactants. Hence, in the troposphere, negligible quantities of $\text{NO}(\text{g})$ are produced by Reaction (1.7).

In the case of chemical reactions involving only gases, it is often more convenient to express the equilibrium constant for the reaction in terms of the partial pressures of the reactants and products instead of their molarities. However, before doing this we must review the ideal gas equation.

Laboratory experiments show that for a wide range of conditions the pressure (p), volume (V), and temperature (T) of all gases follow closely the same relationship, which is called the *ideal gas equation*. In SI units (see Appendix I), the ideal gas equation can be written in the following forms. For mass m (in kilograms) of a gas

$$pV = mRT \quad (1.8a)$$

where p is in pascals, V in cubic meters, T in K ($\text{K} = ^\circ\text{C} + 273.15 \approx ^\circ\text{C} + 273$), and R is the gas constant for 1 kg of a gas. The value of R depends on the number of molecules in 1 kg of the gas, and therefore varies from one gas to another. Since $m/V = \rho$, where ρ is the density of the gas,

$$p = R\rho T \quad (1.8b)$$

For 1 kg of gas ($m = 1$), Eq. (1.8a) becomes

$$p\alpha = RT \quad (1.8c)$$

where α is the specific volume of the gas (i.e., the volume occupied by 1 kg of the gas). One mole of any gas contains the same number of molecules (N_A). Therefore, the gas constant for 1 mole is the same for all gases and is called the *universal gas constant* R^* ($8.3143 \text{ J deg}^{-1} \text{ mol}^{-1}$). Therefore,

$$pV = nR^*T \quad (1.8d)$$

where n is the number of moles of the gas, which is given by

$$n = \frac{1000m}{M}$$

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[More information](#)

where $1000m$ is the number of grams of the gas and M the molecular weight of the gas. Also,

$$R^* = M \frac{R}{1000} \quad (1.8e)$$

where R is divided by 1000 to obtain the gas constant for 1 g of gas. It can be seen from Eq. (1.8d) that at constant temperature and pressure the volume occupied by any gas is proportional to the number of moles (and therefore the number of molecules) in the gas. The gas constant for 1 molecule of any gas is also a universal constant, called the *Boltzmann constant* k . Since the gas constant for N_A molecules is R^*

$$k = \frac{R^*}{N_A} = \frac{8.3143}{6.022 \times 10^{23}} = 1.381 \times 10^{-23} \text{ J deg}^{-1} \text{ molecule}^{-1} \quad (1.8f)^6$$

For a gas containing n_0 molecules per cubic meter, the gas equation can be written

$$p = n_0 k T \quad (1.8g)$$

In chemistry, it is common because it is convenient, to depart from SI units in the gas equation and, instead, to express pressure in atmospheres and volume in liters (T is still in K). In this case, for n_A moles of gas A with pressure p_A and volume V_A we can write the ideal gas equation as

$$p_A V_A = n_A R_c^* T \quad (1.8h)$$

where R_c^* is the universal gas constant in "chemical units" (indicated by the subscript c); the value of R_c^* is $0.0821 \text{ L atm deg}^{-1} \text{ mol}^{-1}$. Since n_A/V_A is the number of moles of the gas per liter, that is, the molarity $[A]$ of the gas

$$[A] = \frac{n_A}{V_A} = \frac{p_A}{R_c^* T} \quad (1.8i)$$

Exercise 1.3. Carbon dioxide occupies about 354 parts per million by volume (ppmv) of air. How many CO_2 molecules are there in 1 m^3 of air at 1 atm and 0°C ?

Solution. Let us calculate first the number of molecules in 1 m^3 of any gas at 1 atm and 0°C (which is called the *Loschmidt number*). This is given by n_0 in Eq. (1.8g) with $p = 1 \text{ atm} = 1013 \times 10^2 \text{ Pa}$, $T = 273 \text{ K}$ and $k = 1.381 \times 10^{-23} \text{ J deg}^{-1} \text{ molecule}^{-1}$. Therefore,

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Excerpt

[More information](#)*Equilibrium constants*

7

$$\text{Loschmidt number} = \frac{1013 \times 10^2}{(1.381 \times 10^{-23})273} = 2.69 \times 10^{25} \text{ molecule m}^{-3}$$

Since, at the same temperature and pressure, the volumes occupied by gases are proportional to the numbers of molecules in the gases, we can write

$$\begin{aligned} & \frac{\text{Volume occupied by CO}_2 \text{ molecules in air}}{\text{Volume occupied by air}} \\ &= \frac{\text{Number of CO}_2 \text{ molecules in 1 m}^3 \text{ of air}}{\text{Total number of molecules in 1 m}^3 \text{ of air}} \end{aligned}$$

Therefore,

$$354 \times 10^{-6} = \frac{\text{Number of CO}_2 \text{ molecules in 1 m}^3 \text{ of air}}{2.69 \times 10^{25}}$$

Hence, the number of CO₂ molecules in 1 m³ of air is $(354 \times 10^{-6}) \times (2.69 \times 10^{25}) = 9.52 \times 10^{21}$.

We can now derive an expression for the equilibrium constant for a chemical reaction involving only gases in terms of the partial pressures of the gases. From Eqs. (1.6) and (1.8i)

$$K_c = \frac{[p_G/R_c^*T]^g [p_H/R_c^*T]^h \dots}{[p_A/R_c^*T]^a [p_B/R_c^*T]^b \dots} = \frac{p_G^g p_H^h \dots}{p_A^a p_B^b \dots} (R_c^*T)^{\Delta n}$$

or,

$$K_c = K_p (R_c^*T)^{\Delta n} \quad (1.9a)$$

where,

$$K_p = \frac{p_G^g p_H^h \dots}{p_A^a p_B^b \dots} \quad (1.9b)$$

and,

$$\Delta n = (a + b + \dots) - (g + h + \dots) \quad (1.9c)$$

K_p is generally used as the equilibrium constant in problems involving gaseous reactions. As in the case of K_c , terms for pure liquids and solids do not appear in the expression for K_p , and the coefficients for these

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[More information](#)

terms are taken to be zero in the expression for Δn . Note that the units, as well as the numerical values, of K_c and K_p may differ. For example, for Reaction (1.3) the units of K_c are those of

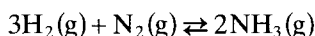
$$\frac{[\text{O}_3(\text{g})]}{[\text{O}(\text{g})][\text{O}_2(\text{g})]} \text{ or } \frac{\text{M}}{(\text{M})(\text{M})} = \text{M}^{-1}, \text{ the units of } K_p \text{ are}$$

$$\frac{p_{\text{O}_3}}{(p_{\text{O}})(p_{\text{O}_2})} \text{ or } \frac{\text{atm}}{(\text{atm})(\text{atm})} = \text{atm}^{-1}.$$

Nevertheless, it is common practice in chemistry not to indicate the units of equilibrium constants, with the understanding that when K_c is used the concentrations are in molarity, and when K_p is used the partial pressures are in atmospheres.

Exercise 1.4. Ammonia, $\text{NH}_3(\text{g})$, is produced commercially from the reaction of hydrogen, $\text{H}_2(\text{g})$, and atmospheric nitrogen, $\text{N}_2(\text{g})$, at high temperatures. If $\text{H}_2(\text{g})$, $\text{N}_2(\text{g})$, and $\text{NH}_3(\text{g})$ attain equilibrium at 472°C when their concentrations are 0.12 M, 0.04 M, and 0.003 M, respectively, calculate the values of K_c and K_p for the reaction at 472°C .

Solution. The balanced chemical equation for the reaction is



Hence, from Eq. (1.6)

$$K_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{H}_2(\text{g})]^3 [\text{N}_2(\text{g})]} = \frac{(0.003)^2}{(0.12)^3 (0.04)} = 0.1$$

From Eq. (1.9a)

$$K_c = K_p (R_c^* T)^{\Delta n}$$

where $K_c = 0.1$, $R_c^* = 0.0821 \text{ L atm deg}^{-1} \text{ mol}^{-1}$, $T = 745\text{K}$ and, from Eq. (1.9c), $\Delta n = (3 + 1) - (2) = 2$. Therefore,

$$K_p = \frac{0.1}{(0.0821 \times 745)^2} = 3 \times 10^{-5}$$

1.3 Reaction quotient

If the general chemical reaction represented by Eq. (1.5) is not in equilibrium, we can still formulate a ratio of concentrations that has the same form as Eq. (1.6). This is called the *reaction quotient*, Q

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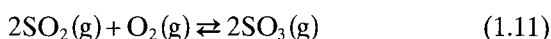
Reaction quotient

9

$$Q = \frac{[G]^g [H]^h \dots}{[A]^a [B]^b \dots} \quad (1.10)$$

Clearly, if $Q = K_c$, the reaction is in chemical equilibrium. If $Q < K_c$, the reaction is not in equilibrium, and it will proceed in the forward direction until $Q = K_c$. If $Q > K_c$, the reaction will proceed in the reverse direction until $Q = K_c$.

Exercise 1.5. If 0.80 mole of $\text{SO}_2(\text{g})$, 0.30 mole of $\text{O}_2(\text{g})$, and 1.4 mole of $\text{SO}_3(\text{g})$ simultaneously occupy a volume of 2L at 1000K, will the mixture be in equilibrium? If not, in what direction will it proceed to establish equilibrium? Consider only the species $\text{SO}_2(\text{g})$, $\text{O}_2(\text{g})$, and $\text{SO}_3(\text{g})$ in the reaction



with $K_c = 2.8 \times 10^2$.

Solution. The reaction quotient for Reaction (1.11) is

$$Q = \frac{[\text{SO}_3(\text{g})]^2}{[\text{SO}_2(\text{g})]^2 [\text{O}_2(\text{g})]}$$

To evaluate the initial value of Q we must determine their initial molarities. These are: for $\text{SO}_2 = 0.80/2 = 0.40\text{M}$, for $\text{O}_2 = 0.30/2 = 0.15\text{M}$, and for $\text{SO}_3 = 1.4/2 = 0.70\text{M}$.

Hence,

$$Q = \frac{(0.70)^2}{(0.40)^2 (0.15)} = 20$$

Since this value of Q is not equal to K_c (namely, 2.8×10^2), the initial mixture is not in equilibrium. Moreover, since $Q < K_c$, Reaction (1.11) will proceed in the forward direction.

Exercise 1.6. What are the equilibrium concentrations of $\text{SO}_2(\text{g})$, $\text{O}_2(\text{g})$, and $\text{SO}_3(\text{g})$ in Exercise 1.5?

Solution. If y moles (or $\frac{y}{2}\text{M}$) of $\text{SO}_3(\text{g})$ are formed, it follows from Reaction (1.11) that y moles (or $\frac{y}{2}\text{M}$) of $\text{SO}_2(\text{g})$ and $\frac{y}{2}$ moles (or $\frac{y}{4}\text{M}$) of $\text{O}_2(\text{g})$ disappear. If this change establishes chemical equilibrium we have

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[More information](#)

Reaction	$2\text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g})$	$\rightleftharpoons$	$2\text{SO}_3(\text{g})$
Initial concentrations	0.40 M		0.15 M		0.70 M
Change in concentrations	$-\frac{y}{2}\text{M}$		$-\frac{y}{4}\text{M}$		$\frac{y}{2}\text{M}$
Equilibrium concentrations	$\left(0.40 - \frac{y}{2}\right)\text{M}$		$\left(0.15 - \frac{y}{4}\right)\text{M}$		$\left(0.70 + \frac{y}{2}\right)\text{M}$

Hence the equilibrium constant for this reaction is

$$K_c = \frac{[\text{SO}_3(\text{g})]^2}{[\text{SO}_2(\text{g})]^2 [\text{O}_2(\text{g})]} = \frac{\left(0.70 + \frac{y}{2}\right)^2}{\left(0.40 - \frac{y}{2}\right)^2 \left(0.15 - \frac{y}{4}\right)}$$

Since $K_c = 2.8 \times 10^2$ at 1000°C , we have

$$2.8 \times 10^2 = \frac{\left(0.70 + \frac{y}{2}\right)^2}{\left(0.40 - \frac{y}{2}\right)^2 \left(0.15 - \frac{y}{4}\right)}$$

Rearranging and simplifying yields

$$-70y^3 + 153y^2 - 115y + 25 = 0$$

The reader may verify by substitution that an approximate solution to this cubic equation is $y = 0.37$. Hence, the equilibrium concentrations of $\text{SO}_2(\text{g})$, $\text{O}_2(\text{g})$, and $\text{SO}_3(\text{g})$ are approximately 0.21 M, 0.057 M, and 0.89 M, respectively.

1.4 LeChatelier's principle

The way in which a system at equilibrium will respond to an imposed change can be predicted in a qualitative sense by *LeChatelier's principle*, which states that *if a system at equilibrium is subjected to a disturbance that changes any of the factors that determine its state of equilibrium, the*