

4.3: Gas Phase Equilibria and Heterogeneous Systems

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.

Whenever gases are involved in a reaction, the partial pressure of each gas can be used instead of its concentration in the equation for the reaction quotient because the partial pressure of a gas is directly proportional to its concentration at constant temperature.

Equilibrium Constant Expressions for Systems that Contain Gases

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction $aA + bB \rightleftharpoons cC + dD$, in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \quad (4.3.1)$$

Thus K_p for the decomposition of N_2O_4 (Equation 15.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \quad (4.3.2)$$

Like K , K_p is a unitless quantity because the quantity that is actually used to calculate it is an “effective pressure,” the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity. The “effective pressure” is called the fugacity, just as activity is the effective concentration.

This relationship between K_C and K_P can be derived from the ideal gas equation, where M is the molar concentration of gas, $\frac{n}{V}$.

$$PV = nRT \quad (4.3.3)$$

$$P = \left(\frac{n}{V} \right) RT \quad (4.3.4)$$

$$= MRT \quad (4.3.5)$$

Thus, at constant temperature, the pressure of a gas is **directly proportional** to its concentration. Using the partial pressures of the gases, we can write the reaction quotient for the system



by following the same guidelines for deriving concentration-based expressions:

$$Q_P = \frac{P_{C_2H_4} P_{H_2}}{P_{C_2H_6}} \quad (4.3.7)$$

In this equation we use Q_P to indicate a reaction quotient written with partial pressures: $P_{C_2H_6}$ is the partial pressure of C_2H_6 ; P_{H_2} , the partial pressure of H_2 ; and $P_{C_2H_4}$, the partial pressure of C_2H_4 . At equilibrium:

$$K_P = Q_P = \frac{P_{C_2H_4} P_{H_2}}{P_{C_2H_6}} \quad (4.3.8)$$

The subscript P in the symbol K_P designates an equilibrium constant derived using partial pressures instead of concentrations. The equilibrium constant, K_P , is still a constant, but its numeric value may differ from the equilibrium constant found for the same reaction by using concentrations.

Conversion between a value for K_c , an equilibrium constant expressed in terms of concentrations, and a value for K_P , an equilibrium constant expressed in terms of pressures, is straightforward (a K or Q without a subscript could be either concentration

or pressure).

The equation relating K_c and K_P is derived as follows. For the gas-phase reaction:



with

$$K_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \quad (4.3.10)$$

$$= \frac{([C] \times RT)^x ([D] \times RT)^y}{([A] \times RT)^m ([B] \times RT)^n} \quad (4.3.11)$$

$$= \frac{[C]^x [D]^y}{[A]^m [B]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \quad (4.3.12)$$

$$= K_c (RT)^{(x+y)-(m+n)} \quad (4.3.13)$$

$$= K_c (RT)^{\Delta n} \quad (4.3.14)$$

The relationship between K_c and K_P is

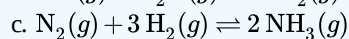
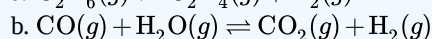
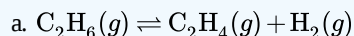
$$K_P = K_c (RT)^{\Delta n} \quad (4.3.15)$$

In this equation, Δn is the difference between the sum of the coefficients of the *gaseous* products and the sum of the coefficients of the *gaseous* reactants in the reaction (the change in moles of gas between the reactants and the products). For the gas-phase reaction $mA + nB \rightleftharpoons xC + yD$, we have

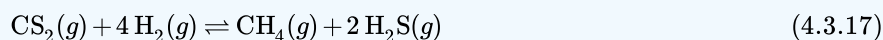
$$\Delta n = (x + y) - (m + n) \quad (4.3.16)$$

✓ Example 4.3.1: Calculation of K_P

Write the equations for the conversion of K_c to K_P for each of the following reactions:



d. K_c is equal to 0.28 for the following reaction at 900 °C:



What is K_P at this temperature?

Solution

(a) $\Delta n = (2) - (1) = 1$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^1 = K_c (RT)$$

(b) $\Delta n = (2) - (2) = 0$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^0 = K_c$$

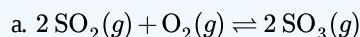
(c) $\Delta n = (2) - (1 + 3) = -2$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^{-2} = \frac{K_c}{(RT)^2}$$

d) $K_P = K_c (RT)^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$

? Exercise 4.3.1

Write the equations for the conversion of K_c to K_P for each of the following reactions, which occur in the gas phase:



- b. $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$
 c. $\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightleftharpoons 3\text{CO}_2(g) + 4\text{H}_2\text{O}(g)$
 d. At 227 °C, the following reaction has $K_c = 0.0952$:



What would be the value of K_p at this temperature?

Answer a

$$K_p = K_c (RT)^{-1}$$

Answer b

$$K_p = K_c (RT)$$

Answer c

$$K_p = K_c (RT);$$

Answer d

$$160 \text{ or } 1.6 \times 10^2$$



Video Discussing Converting K_c to K_p : https://youtu.be/_2WVnlqXrV4

Heterogeneous Equilibria

A heterogeneous equilibrium is a system in which reactants and products are found in two or more phases. The phases may be any combination of solid, liquid, or gas phases, and solutions. When dealing with these equilibria, remember that solids and pure liquids do not appear in equilibrium constant expressions (the activities of pure solids, pure liquids, and solvents are 1).

Some heterogeneous equilibria involve chemical changes:

Example 1



with associated equilibrium constant

$$K_c = [\text{Pb}^{2+}][\text{Cl}^-]^2 \quad (4.3.20)$$

Example 2



with associated equilibrium constant

$$K_c = \frac{1}{P_{\text{CO}_2}} \quad (4.3.22)$$

Example 3



with associated equilibrium constant

$$K_c = \frac{P_{\text{CS}_2}}{P_{\text{S}}^2} \quad (4.3.24)$$

Other heterogeneous equilibria involve phase changes, for example, the evaporation of liquid bromine, as shown in the following equation:



with associated equilibrium constant

$$K_c = P_{\text{Br}_2} \quad (4.3.26)$$

Summary

For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to K by the ideal gas constant (R), the temperature (T), and the change in the number of moles of gas during the reaction. An equilibrium system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \quad (4.3.27)$$

- Relationship between K_p and K :

$$K_p = K(RT)^{\Delta n} \quad (4.3.28)$$

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