Chapter 14. CHEMICAL EQUILIBRIUM

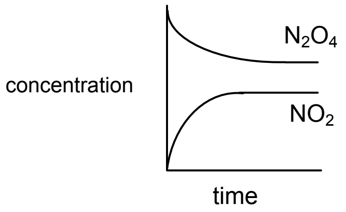
14.1 THE CONCEPT OF EQUILIBRIUM AND THE EQUILIBRIUM CONSTANT

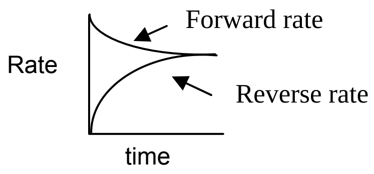
Many chemical reactions do not go to completion but instead attain a state of chemical equilibrium.

Chemical equilibrium: A state in which the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant.

⇒ Equilibrium is a dynamic process – the conversions of reactants to products and products to reactants are still going on, although there is no net change in the number of reactant and product molecules.

For the reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$





The Equilibrium Constant

For a reaction: **$aA + bB \rightleftharpoons cC + dD$**

equilibrium constant: $$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The **equilibrium constant, K_c,** is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients.

Example. Write the equilibrium constant, K_c, for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Law of mass action - The value of the equilibrium constant expression, K_c, is constant for a given reaction at equilibrium and at a constant temperature.

⇒ The equilibrium concentrations of reactants and products may vary, but the value for K_c remains the same.

Other Characteristics of K_c

1) Equilibrium can be approached from either direction.
2) K_c does not depend on the initial concentrations of reactants and products.
3) K_c does depend on temperature.

Magnitude of K_c

⇒ If the K_c value is large ($K_c >> 1$), the equilibrium lies to the right and the reaction mixture contains mostly products.

⇒ If the K_c value is small ($K_c << 1$), the equilibrium lies to the left and the reaction mixture contains mostly reactants.

⇒ If the K_c value is close to 1 ($0.10 < K_c < 10$), the mixture contains appreciable amounts of both reactants and products.

14.2 WRITING EQUILIBRIUM CONSTANT EXPRESSIONS

Calculating Equilibrium Constants, K_c

K_c values are listed without units ⇒ don't include units when calculating K_c.

If equilibrium concentrations are known, simply substitute the concentrations into the equilibrium constant expression:

Example. For the reaction, $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$, calculate K_c from the following equilibrium concentrations: [CO] = 0.0613 M; [H_2] = 0.1839 M; [CH_4] = 0.0387 M; [H_2O] = 0.0387 M.

Homogeneous equilibria: reactants and products exist in a single phase.

For the gas phase reaction: $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

The equilibrium constant with the concentrations of reactants and products expressed in terms of molarity, K_c, is:

$$\mathbf{K_c} = \frac{[NO_2]^2}{[N_2O_4]}$$

Gas Phase Expressions can also be expressed by K_p

⇒ The K_p expression is written using equilibrium partial pressures of reactants & products.

For the reaction given above, the K_p expression is:

$$\mathbf{K_p} = \frac{P_{NO_2}{}^2}{P_{N_2O_4}}$$

K_p is related to K_c

Since pressure and molarity are related by the Ideal Gas Law, the following equation relates K_p and K_c:

$$\mathbf{K_p = K_c(RT)^{\Delta n}}$$

where R = 0.0821 $\frac{L \cdot atm}{K \cdot mol}$; T = temperature in Kelvin

Δn = moles of gaseous products – moles of gaseous reactants

⇒ Note that $K_c = K_p$ when the number of gas molecules are the same on both sides.

Example. Does $K_c = K_p$ for (a) $H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$? (b) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$?

Example. For the reaction, $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ (a) write the equilibrium constant expression, K_p. (b) What is the value for K_p if $K_c = 2.8x10^2$ at 1000 K?

Heterogeneous Equilibria and Solvents in Homogeneous Equilibria

Heterogeneous equilibria: reactants and products are present in more than one phase.

pure solids and liquids: concentrations of pure solids and liquids are fixed by their density and molar mass (both constants) and do not vary with the amount.

$$[\ ] = M = \frac{Density}{Molar\ Mass} \qquad M = \frac{mol}{L} = \frac{g}{ml} \times \frac{10^3\ ml}{1L} \times \frac{mol}{g}$$

⇒ Thus, the concentrations of solids and liquids are incorporated in the K_c value; they are not part of the variable K_c expression:

Example. Write the K_c expression for $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

- **Omit concentration terms for solids and liquids from K_c and K_p expressions; only include terms for gases (g) and aqueous substances (aq).**

Example. Write the K_c expression for the following reaction:

$$3Cu_{(s)} + 2NO_3^-{}_{(aq)} + 8H^+{}_{(aq)} \rightleftharpoons 3Cu^{2+}{}_{(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$$

Modifying Equilibrium Constant Expressions:

A. Changing stoichiometric coefficients:

1) $2SO_2 + O_2 \rightleftharpoons 2SO_3$ $\qquad K_1 =$

2) $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$ $\qquad K_2 =$

⇒ If we multiply an equation by a factor, we must raise its K to that power to get the new K.

B. Reversing the reaction:

3) $2SO_3 \rightleftharpoons 2SO_2 + O_2$ $\qquad K_3 =$

⇒ K is the reciprocal of the K value for the reverse reaction.

C. Adding Equations for Multiple Equilibrium Reactions:

1. $A + 2B \rightleftharpoons C$ $\qquad K_1 =$

2. $A + D \rightleftharpoons B$ $\qquad K_2 =$

3. $2A + B + D \rightleftharpoons C$ $\qquad K_3 =$

⇒ When we add equations to get a new equation, the new K is the product of the other K's.

Example. $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$ $\qquad K_c = 1.7\times10^{27}$

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\qquad K_c = 1.5\times10^{2}$

Calculate the value of K_c for $4NH_{3(g)} + 3O_{2(g)} \rightleftharpoons 2N_{2(g)} + 6H_2O_{(g)}$

14.3 THE RELATIONSHIP BETWEEN CHEMICAL KINETICS AND CHEMICAL EQUILIBRIUM

For the reaction $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

Rate of forward reaction = Rate of reverse reaction

$$k_f[N_2O_4] = k_r[NO_2]^2$$

Rearrange: $\frac{[NO_2]^2}{[N_2O_4]} = \frac{k_f}{k_r} = K_c$

Thus, the equilibrium constant is simply the ratio of the forward and reverse rate constants which are both constant values at a given temperature.

14.4 WHAT DOES THE EQUILIBRIUM CONSTANT TELL US?

Predicting the Direction of Reaction

The **reaction quotient, Q,** is the resulting value when we substitute reactant and product concentrations into the equilibrium expression.

1. If $Q > K$, the reaction will go to the left.
   - The ratio of products over reactants is too large & the reaction will move toward equilibrium by forming more reactants.
2. If $Q < K$, the reaction will go to the right.
   - The ratio of products over reactants is too small & the reaction will move toward equilibrium by forming more products.
3. If $Q = K$, the reaction mixture is already at equilibrium, so no shift occurs.

Example. For the reaction, $B \rightleftharpoons 2A$, $K_c = 2$. Suppose 3.0 moles of A and 3.0 moles of B are introduced into a 2.00 L flask. (a) In which direction will the reaction proceed to attain equilibrium? (b) Will the concentration of B increase, decrease or remain the same as the system moves towards equilibrium?

Calculating Equilibrium Concentrations

Use ICE Tables To Solve Equilibrium Problems For K_c Or Equilibrium Amounts:

1. I = initial concentration: Initial concentration of reactants are usually given; initial [Product]'s are assumed to be 0 unless otherwise specified.

2. C = change in concentration: Assign change as the variable x; use the stoichiometry of the reaction to assign changes for all species.

3. E = equilibrium concentration: E = I + C

⇒ Note, values in ICE tables can be in terms of moles or Molarity (or atm for K_p), but values used in the K_c expression must be in terms of Molarity (or atm for K_p).

Example. When 0.250 mol SO_2 and 0.200 mol O_2 are placed in a 10.0 L vessel at 1000 K, the equilibrium mixture was found to contain 0.162 mol SO_3. Calculate K_c for this reaction:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

Method to find equilibrium concentrations

1) Set up the ICE table.
2) Set up the K_c expression; substitute equilibrium concentrations from the ICE table into K_c.
3) Solve for x; plug the solution for x back into the equilibrium concentration expressions.

Perfect square problem to solve for x

⇒ Take the square root of both sides when the math expression is a perfect square.

Example. At 430 °C, $K_p = 54.3$ for the following reaction: $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
A mixture of H_2 at a pressure of 0.500 atm and I_2 at a pressure of 0.500 atm is placed in a container at 430 °C. Calculate the equilibrium partial pressures of HI, H_2 and I_2.

Quadratic Formula Example

For this reaction, $H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$, $K_c = 1.15\text{x}10^2$ at a certain temperature.
Suppose 3.000 moles of H_2 and 6.000 moles of F_2 are placed in a 3.000 L container. What are the equilibrium concentrations of H_2, F_2 and HF?

14.5 FACTORS THAT AFFECT CHEMICAL EQUILIBRIUM

Le Chatelier's Principle: If a system at equilibrium is disturbed by an external stress, the system adjusts to partially offset the stress as the system attains a new equilibrium position.

Changes in Concentration

- ⇒ Adding a reactant or product, the equilibria shifts away from the increase in order to consume part of the added substance.
- ⇒ Removing a reactant or product, the equilibria shifts toward the decrease to replace part of the removed species.

E.g. For $H_2 + I_2 \rightleftharpoons 2HI$, does the equilibria shift left or right if we: a) add H_2? b) remove I_2?

a)

b)

Changes in Volume and Pressure

Because the pressure of gases is related directly to the concentration by P = n/V, changing the pressure by increasing/decreasing the volume of a container will disturb an equilibrium system.

- ⇒ If P increases (V decreases), the system shifts to the side with a smaller number of gas molecules (this effectively reestablishes equilibrium by decreasing the pressure).
- ⇒ If P decreases (V increases), the system shifts to the side with a greater number of gas molecules.

Example. For $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, does the equilibrium shift left or right if the pressure is increased?

Changes in Temperature

Heat can be considered a reactant in an endothermic rxn and a product in an exothermic rxn.

Endothermic ($\Delta H > 0$) $R + \text{Heat} \rightleftharpoons \text{Products}$

Exothermic ($\Delta H < 0$) $R \rightleftharpoons \text{Products} + \text{Heat}$

Recall that both K_c and the position of the equilibrium system will vary with temperature:

- K_c is larger when the reaction shifts right. This occurs if T is increased for an Endothermic Reaction or T is decreased for an Exothermic reaction.
- K_c is smaller when the reaction shifts left. This occurs if T is decreased for an Endothermic Reaction or T is increased for an Exothermic reaction.

Example. If the temperature is decreased for the reaction: $2CO_2 \rightleftharpoons 2CO + O_2$, $\Delta H = 566$ kJ.

a) Will the equilibrium shift left or right? b) Does K_c become larger or smaller?

Effect of a Catalyst

- ⇒ Catalysts lower E_a for the reaction, so a catalyst decreases the amount of time taken to reach equilibrium for both the forward and reverse reactions.
- ⇒ The catalyst does not affect the equilibrium concentrations of reactants and products in the equilibrium mixture; thus, the K_c value does not change.

Choosing Optimum Conditions

Le Chatelier's principle can be used to select optimum conditions to form a substance.

e.g. To form more NH_3, predict the optimum conditions for temperature and pressure.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -91.8 \text{ kJ}$$