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BSK1133 PHYSICAL CHEMISTRY

CHAPTER 6
CHEMICAL EQUILIBRIUM

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Description

Aims

- To discuss the equilibrium state of chemical and physical equilibrium.
- To express and calculate equilibrium constants for homogeneous equilibria, heterogeneous equilibria and multiple equilibria.
- To discuss the factors that may affect the position of equilibrium.
- To learn the Le Châtelier's principle in the prediction of changes.

Description

Expected Outcomes

- ❖ Able to describe the equilibrium state of chemical and physical equilibrium.
- ❖ Able to express and calculate the equilibrium constants.
- ❖ Able to study the factors that may affect the position of an equilibrium.
- ❖ Able to apply the Le Châtelier’s principle.

References

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Contents

6.1 The Concept of Equilibrium

The Concept of Equilibrium and the Equilibrium Constant

I. Introduction

- **Chemical equilibrium** can be obtained when the **rates** of the forward and reverse reactions must be equal. In addition, the **concentrations of the** reactants and products are unchanged.

  Example: $2NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$

- **Physical equilibrium** is referring equilibrium of two phases with the same substance.

  Example: $H_2O\,(l) \rightleftharpoons H_2O\,(g)$

II. Equilibrium Constant

a) Homogeneous Equilibria – same phase of reacting species.

$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ $\quad K_c = \frac{[NO_2]^2}{[N_2O_4]}$

- ✓ K_c shows the reacting species (gas) (units = **molarity**, **moles per liter** and **partial pressure)**.

- ✓ **Pressure** of a gas is to **concentration in mol/L** of gas (at constant temperature) $\mathbf{P} = (\frac{n}{V})\mathbf{RT}$ $\quad K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$
- ✓ P_{NO_2} and $P_{N_2O_4}$ are equilibrium partial pressure (atm).
- ✓ K_p shows equilibrium concentration expressed in terms of **pressure**.
- ✓ $K_c \neq K_p$ cause their units of expression are different.

Example: $\quad H_2\,(g) + Br_2\,(g) \rightleftharpoons 2HBr\,(g)$

Since Δ n = 2 – 2 = 0, therefore, $K_p = (0.0821T)^{\Delta n}\, K_c$

$K_p = (0.0821T)^0\, K_c$

$K_p = K_c$ (Special Case for this reaction where $K_p = K_c$)

Explanation: **Assume ideal gas behaviour**

aA (g) $\rightleftharpoons$ bB (g) (a,b = stoichiometric coefficients)

$$K_c = \frac{[B]^b}{[A]^a} \qquad K_p = \frac{P_B^b}{P_A^a} \qquad K_c \neq K_p$$

$$P_A = \frac{n_A RT}{V} \qquad P_B = \frac{n_B RT}{V}$$

P_A = partial pressure of A
P_B = partial pressure of B
V = volume of the container in liters

$\frac{n_A}{V}$ and $\frac{n_B}{V}$ have units of mol/L. Thus, can be replaced by [A] and [B].

Substitute in K_p

$$K_p = \frac{\left(\frac{n_B RT}{V}\right)^b}{\left(\frac{n_A RT}{V}\right)^a} = \frac{\left(\frac{n_B}{V}\right)^b}{\left(\frac{n_A}{V}\right)^a}(RT)^{b-a} = \frac{[B]^b}{[A]^a}(RT)^{\Delta n}$$

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

$$\boxed{K_p = (0.0821T)^{\Delta n}\,K_c}$$

Where $\Delta n = b - a$ (moles of gaseous products – moles of gaseous reactants)
Pressures are usually expressed in atm, hence, gas constant R is 0.0821 atm L/(K mol).

b) Heterogeneous Equilibria

- Refer to a reversible reaction where **different phases of reactants and products that are in**.

$$CaCO_3\,(s) \leftrightharpoons CaO\,(s) + CO_2\,(g) \qquad K'_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

K'_c is used as symbols to differentiate it from final equilibrium constant at the end.

- **SPECIAL:** "Concentration" (means density) of a solid does not depend on **how much** of the substance is present.

Example: $[CaCO_3]$ and $[CaO]$ are constant and combine with K'_c to form final equilibrium constant.

$$\frac{[CaCO_3]}{[CaO]} K'_c = Kc = [CO_2] \quad \text{(new equilibrium constant)}$$

In thermodynamic, ***concentration*** replace with ***activity*** of pure solid or liquid = 1. Thus,

$$\boxed{K_c = [CO_2] \text{ or } K_p = P_{CO_2}}$$

c) Multiple Equilibria

Example: These equilibria can be split into two steps:

$$H_2A \leftrightharpoons HA^- + H^+ \qquad K_1 = \frac{[HA^-][H^+]}{[H_2A]}$$

$$HA^- \leftrightharpoons A^{2-} + H^+ \qquad K_2 = \frac{[A^{2-}][H^+]}{[HA^-]}$$

K_1 and K_2 are examples the equilibrium constants for each step. Next, we can write out the overall reaction equation, which is a sum of these two steps:

$$H_2A \rightleftharpoons A^{2-} + 2\ H^+ \qquad K_c = \frac{[A^{2-}][H^+]^2}{[H_2A]}$$

K_c is equal to the product of the equilibrium expressions for the two reaction steps. Thus,

$$K_c = K_1K_2$$

d) The Form of K and the Equilibrium Equation

Condition I

$N_2O_4\,(g) \leftrightharpoons 2NO_2\,(g)$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \text{ x } 10^{-3}$$

$2NO_2\,(g) \leftrightharpoons N_2O_4\,(g)$

$$K_c' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K_c} = \frac{1}{4.63 \text{ x } 10^{-3}} = 216$$

- $K_c K_c' = 1$. (Must specify the equilibrium equation).

Condition II

$\frac{1}{2}N_2O_4\,(g) \leftrightharpoons NO_2\,(g)$

$$K_c'' = \frac{[NO_2]}{[N_2O_4]^{\frac{1}{2}}}$$

$N_2O_4\,(g) \leftrightharpoons 2NO_2\,(g)$

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

- $K_c'' = \sqrt{K_c}$, since $K_c = 4.63 \text{ x } 10^{-3}$, Hence, $K_c'' = 0.0680$

SUMMARY

✓ $K_p = (0.0821T)^{\Delta n} K_c$

✓ Equilibrium constant (K_p or K_c) is unitless.

6.2 Relate the Kinetics in Chemical Equilibrium

Relate Kinetics and Chemical Equilibrium

a) A single elementary step

$$A + 2B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} AB_2$$

rate constant

Forward: rate$_f$ = $k_f[A][B]^2$ **Reverse: rate$_r$ = $k_r[AB]^2$**

At equilibrium (no net changes): **rate$_f$ = rate$_r$**

$$K_c = \frac{k_f}{k_r} = \frac{[AB_2]}{[A][B]^2}$$

b) More than one elementary step

Step 1: $2B \underset{k'_r}{\overset{k'_f}{\rightleftharpoons}} B_2$

Step 2: $A + B \underset{k''_r}{\overset{k''_f}{\rightleftharpoons}} AB_2$

Overall reaction: $A + 2B \rightleftharpoons AB_2$ **(Example of multiple equilibria)**

$$\boldsymbol{K' = \frac{k'_f}{k'_r} = \frac{[B_2]}{[B]^2}} \qquad \boldsymbol{K'' = \frac{k''_f}{k''_r} = \frac{[AB_2]}{[A][B_2]}}$$

Overall reaction: $\boldsymbol{K_c = K'K'' = \frac{[AB_2]}{[A][B]^2}}$

6.2 Relate the Kinetics in Chemical Equilibrium

Le Chatelier's Principle

- It states that if external stress is introduced to an equilibrium system, the system will adjust to offset it and achieve a new equilibrium position.
- It helps in prediction of the position of an equilibrium reaction when a change of conditions (concentration, pressure, volume and temperature) occurs.
- When a new equilibrium reaches, the concentrations of reactants and products remain constant.

Forward Reaction

$A\,(g) + 3B\,(g) \rightleftharpoons C\,(g) + D\,(g) \quad \Delta H = -328\ kJ/mol$

Factors	**Position of Equilibrium**	
	shift to right	**shift to left**
Concentration	Increase (substance A)	Decrease (substance A)
Pressure	Increase	Decrease
Temperature	Decrease	Increase
Catalyst	Unchange	

Conclusion

- ***Chemical equilibrium*** is referring different substances as reactants and products in an equilibrium, whereas, ***physical equilibrium*** is equilibrium between two same phases of same composition of reactants and products.

- Equilibrium constants is used as an indicator to show relative amount between reactants and products.

- The direction where an equilibrium reaction will shift is assessed by Le Châtelier’s Principle when an occurrence of varying conditions.

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