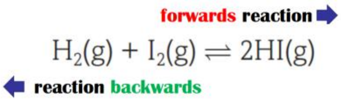
7. Equilibria

King

考点一：What is equilibrium?

7.1 State some examples of reversible reactions, which are an essential feature of equilibrium systems
7.2 Recognise different types of equilibria (both physical and chemical)
7.3 Distinguish between homogeneous and heterogeneous equilibria
7.4 List the characteristics of the equilibrium state

1. Some **reactions** are **reversible** — they go both ways. Symbol $\rightleftharpoons$ show the reversible reaction. This reaction can go in either direction — —forwards reaction or backwards/reverse reaction



$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(i) Characteristics of reversible reactions

(a) These reactions can be started from either side,

(b) These reactions are never complete,

(c) These reactions have a tendency to attain a state of equilibrium,

(d) This sign ($\rightleftharpoons$*) represents the reversibility of the reaction,*

(e) Free energy change in a reversible reaction is zero ($\Delta G = 0$*),*

(ii) Examples of reversible reactions

(a) Neutralisation between an acid and a base either of which or both are weak e.g.,

$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H2O$

(b) Salt hydrolysis, e.g., $FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 6HCl$

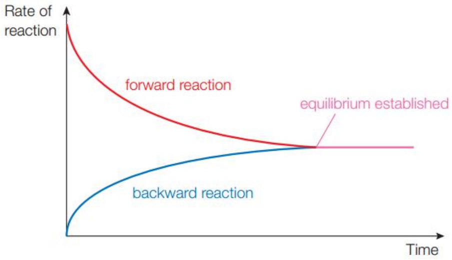
(c) Thermal decomposition, e.g., $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

(d) Esterification, e.g., $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

(e) Evaporation of water in a closed vessel, e.g., $H_2O(l) \rightleftharpoons H_2O(g)$

(f) Other reactions, e.g., $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + Q$; $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

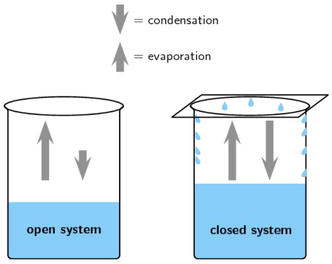
As the reactants get **used up**, the **forward reaction** slows down — and as more product is formed, the **reverse reaction** speeds up. After a while, the forward reaction will be going at exactly the **same rate** as the backward reaction. This is called **dynamic equilibrium**



2. Types of equilibria

Physical Equilibrium

If in equilibrium opposing processes involve only physical changes, then the equilibrium is called **physical equilibrium**. For example, equilibrium between water and vapor in evaporation of water.



Water ↔ Vapor

Chemical Equilibrium

If in equilibrium opposing processes involve chemical changes, then the equilibrium is called **chemical equilibrium**. For example, equilibrium between acetic acid, water and acetate and hydronium ions. Equation is given below –

$$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO^{2-} + H_3O^+$$

3. Homogeneous and heterogeneous equilibria

Homogeneous equilibria – In these types of equilibrium reactants and products are found in same phase.

Example:

(i) $C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + \underset{liquid\quad phase}{H_2O(l)}$

(ii) $N_2(g) + 3H_2(g) \rightleftharpoons 2\ \underset{gas\quad phase}{NH_3(g)}$

(iii) $2SO_2(g) + O_2(g) \rightleftharpoons 2\ \underset{gas\quad phase}{SO_3(g)}$

Heterogeneous equilibria – In these types of equilibrium reactants and products are found in different phases.

Example : (i) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(ii) $2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$

(iii) $H_2O(l) \rightleftharpoons H_2O(g)$

(iv) $Ca(OH)_2(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$

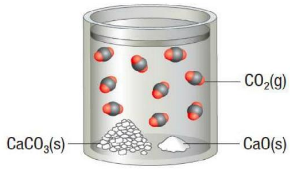
Note : The equilibrium expression for heterogeneous reactions does not include the concentrations of pure solids because their concentrations remain constant.

Reactions involving only gasses or only solutions

$$N_2O_{4\,(g)} \rightleftharpoons 2\ NO_{2(g)} \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

Reactions involving different phases (s, l, g, aq) of matter

$$CaCO_{3\,(s)} \rightleftharpoons CO_{2\,(g)} + CaO_{(s)} \qquad K_C = [CO_2]$$



Characteristics of the equilibrium

- Both forward and backward reactions are continuously occurring.
- The rate of the forward reaction is equal to the rate of the backward reaction.

Rate of forward reaction = Rate of backward reaction

- The concentrations of reactants and products remain constant.

考点二： Le Châtelier’s principle

7.5 State Le Châtelier’s principle and apply it to the effect on equilibrium systems of (a) changing concentration, (b) changing temperature, (c) changing pressure and (d) using catalysts.

7.6 Use equilibrium principles to predict the conditions necessary for optimizing yields in continuous industrial processes run under steady state conditions.

7.10 State what is meant by the common ion effect, and demonstrate its use in solubility calculations and in buffer

4. Le Châtelier's principle

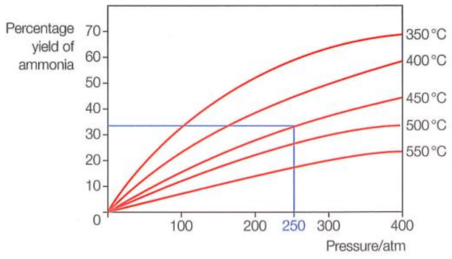
> If there's a change in **concentration**, **pressure** or **temperature**, the equilibrium will move to help **counteract** the change.

Effect of change in **concentration** – If a reaction is at equilibrium and concentration of any reactant is increased then the equilibrium will shift in forward direction. While if concentration of any product is increased then the reaction will shift in the backward direction. If the concentrations are decreased, then the reverse happens.

Effect of change in **temperature** - Exothermic reactions are favoured by low temperature whereas endothermic reactions are favoured by high temperature.

Effect of change in **pressure** – Change in pressure will not have any effect if moles of reactants and products are the same. When pressure is increased then reaction will shift in the direction having smaller number of moles and vice – versa.

5. **Industrial processes** 鱼和熊掌不可兼得



温度角度：Because it's an exothermic reaction, lower temperatures favour the forward reaction（high yield）But lower temperatures mean a slower rate of reaction. So the 450 ºC is a compromise between maximum yield and a faster reaction.

压强角度：Higher pressures favour the forward reaction. Increasing the pressure also increases the rate of reaction. But high pressures are expensive to produce. You need stronger pipes and containers to withstand high pressure.So the 250 atmospheres is a compromise between maximum yield and expense.

考点三：Equilibrium law expression

7.7 Write the equilibrium law expression (either K_c or K_p as appropriate) for a reversible reaction

7.8 Write the standard equilibrium law expressions used for K_{SP} , K_a, K_b and K_w, and the modified equilibrium law expressions used for heterogeneous reactions in general

7.9 Perform calculations using equilibrium law expressions

6. Equilibrium law expression

K, constant 常数，只受温度影响！

- *If the reaction is reversed, the value of the equilibrium constant is inverse.*

$$K_{\text{forward reaction}} = \frac{1}{K_{backward \quad reaction}}$$

- *If an equation having equilibrium constant K is divided by 2, the equilibrium constant for the new equation is the square root of K (that is, √K).*

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \text{ and } SO_3(g) \rightleftharpoons SO_2(g) + 1/2O_2(g)$$

$$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2} \text{ and } K' = \frac{[SO_2][O_2]^{1/2}}{[SO_3]};\ K' = \sqrt{K} \text{ or } (K)^{1/2}$$

- *If an equation having equilibrium constant K is multiplied by 2, the equilibrium constant for the new equation is the square of K (that is, K^2)*
- *If an equation having equilibrium constant K is written in two steps (having equilibrium constant K1 and K2) then K1 × K2 = K.*

$N_2(g) + O_2(g) \rightleftharpoons 2NO\ (g)$; (Equilibrium constant = K_1)

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$; (Equilibrium constant = K_2)

Now, $K = \frac{[NO]^2}{[N_2][O_2]}$ and $K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$

Therefore, $K_1 \times K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K$

- *The value of the equilibrium constant is not affected by the addition of a catalyst to the reaction. This is because the catalyst increases the speed of the forward reaction and the backward reaction to the same extent.*

K_c , concentration

$$aW + bX \rightleftharpoons cY + dZ$$

$$K_c = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$$

K_a , acid

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \qquad Ka = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$$

K_b , base

$$HB + H_2O \leftrightarrows B^+ + OH^-$$

$$Kb = [B^+][OH^-]/[BOH]$$

K_p , pressure

$$wA(g) + xB(g) \rightleftharpoons yC(g) + zD(g) \qquad K_p = \frac{(p_C)^y(p_D)^z}{(p_A)^w(p_B)^x}$$

$$\underbrace{p_A = x_A}_{\text{mole fraction of A}}\underbrace{p}_{\text{total pressure}}$$

$$\text{mole fraction of A} = \frac{\text{number of moles of A}}{\text{total number of moles of gas}}$$

K_w , water

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad Kw = [H^+(aq)][OH^-(aq)]$$

K_{sp} , solubility product

$$A_aB_{b(s)} \rightleftharpoons aA^+{}_{(aq)} + bB^-{}_{(aq)}$$

$$K_{sp} = [A^+]^a[B^-]^b$$

7. Common ion effect

The **common ion effect** describes the effect on equilibrium that occurs when a common ion (an ion that is already contained in the solution) is added to a solution. The common ion effect generally decreases solubility of a solute. It also can have an effect on buffering solutions, as adding more conjugate ions may shift the pH of the solution.

Calculate its solubility of AgBr in g/L (K_{sp} = 7.7 x 10^{-13}) in:

$$AgBr (s) \rightleftharpoons Ag^+ (aq) + Br^-$$

(a) pure water

(b) 0.0010 M NaBr

(a) pure water

$$AgBr\ (s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

$$K_{sp} = [Ag^+][Br^-] = 7.7 \times 10^{-13}$$

$$x^2 = 7.7 \times 10^{-13}$$

$$x = 8.8 \times 10^{-7}\ M = 1.7 \times 10^{-4}\ g/L$$ solubility of AgBr

(b) 0.0010 *M* NaBr

$$AgBr\ (s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

$$K_{sp} = [Ag^+][Br^-] = 7.7 \times 10^{-13}$$

$$[Ag^+]\ (0.0010) = 7.7 \times 10^{-13}$$

$$[Ag^+] = 7.7 \times 10^{-10}\ M = 1.4 \times 10^{-7}\ g/L$$ solubility of AgBr

Le Chatelier's principle: *the solubility is less in a solution of NaBr than in pure water*

8. 求 Kc 的方法：ICE

0.100 mol of N_2O_4 is placed into a 0.100 dm^3 flask and allowed to reach equilibrium with NO_2 at 398 K. At equilibrium, there is 0.071 mol of N_2O_4. Calculate K_c at this temperature

	$N_2O_4(g)$	⇋	$2NO_2(g)$
I	**1.00**		0
C	（0.29）		0.58
E	**0.71**		0.58

$$Kc = \frac{[NO_2(g)]^2}{N_2O_4(g)]} = \frac{0.582^2}{0.71} = 0.474\ \mathrm{mol\ dm^{-3}}$$