6 Chemical equilibrium
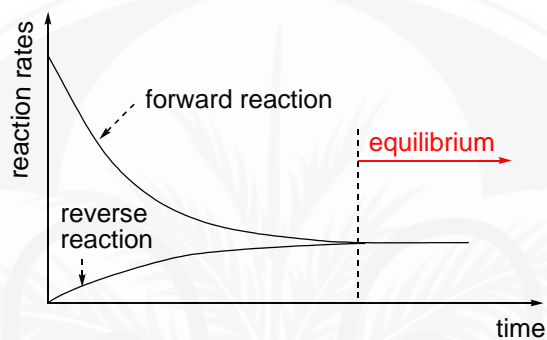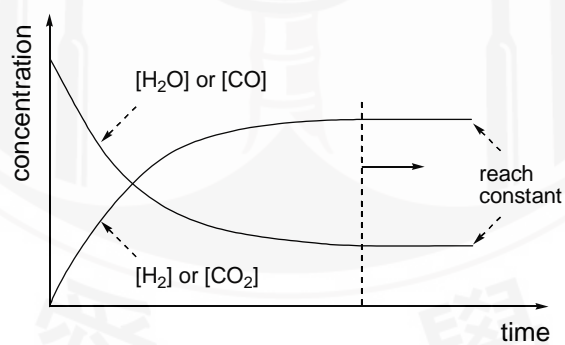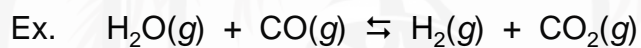
※ Equilibrium is dynamic
   forward reaction rate = reverse reaction rate
   → reach equilibrium

Follow the concentration
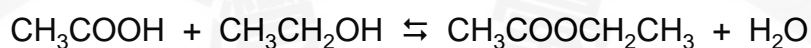
Ex. $H_2O(g) + CO(g) \leftrightarrows H_2(g) + CO_2(g)$

※ The equilibrium constant

1862   Berthlot and Saint-Gilles

$$CH_3COOH + CH_3CH_2OH \leftrightarrows CH_3COOCH_2CH_3 + H_2O$$

　　　　1 : 1　　　　　　　66.5% conversion
　　　　1 : 12　　　　　　93.2% conversion

1846   Guldberg and Waage

Law of mass action

$$j\mathbf{A} + k\mathbf{B} \leftrightarrows l\mathbf{C} + m\mathbf{D}$$
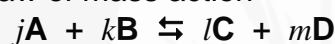
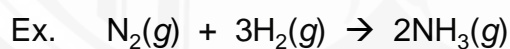At equilibrium

$$K = \frac{[C]^l[D]^m}{[A]^j[B]^k}$$

└── Equilibrium constant (T dependent)

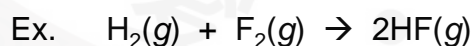Depends on ini. conc., equilibrium position may be different

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For gas: $PV = nRT$ ⇨ $P = \frac{n}{V}RT = cRT$

　　　　　　　　　　　　　　└── concentration

　　　　　　⇨ $c = \frac{1}{RT}P$

$$K_P = K(RT)^{\Delta n} \qquad (\Delta n = l + m - j - k)$$

Ex.　$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

$$K = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{P_{NH_3}^2}{P_{H_2}^3 P_{N_2}} \bullet \frac{(\frac{1}{RT})^2}{(\frac{1}{RT})^3(\frac{1}{RT})} = K_P(RT)^2$$

Ex.　$H_2(g) + F_2(g) \rightarrow 2HF(g)$

$$K = \frac{[HF]^2}{[H_2][F_2]} = K_P \qquad K \neq K_P \text{ unless } (l+m) = (j+k)$$

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※ Heterogeneous equilibria

Ex.　　$CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g)$
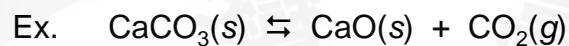
The conc. of pure solid (and liquid) does not change

→　　as if constant

$$K' = \frac{[CO_2][CaO]}{[CaCO_3]} \implies [CO_2] = \frac{K'[CaCO_3]}{[CaO]} = K$$

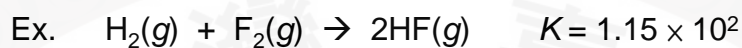Equilibrium position does not depend on the amt. of *s* and *l*

※ Applications

Reaction quotient (*Q*)
　　　　same mathematical expression as *K*
　　　　using initial concentration

1. When $Q = K$:　equilibrium
2. $Q > K$:　　　　shift to the left
3. $Q < K$:　　　　shift to the right

Note: reaction rate and equilibrium are not related

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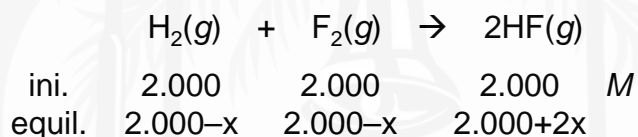
Ex.　　$H_2(g) + F_2(g) \rightarrow 2HF(g)$　　　$K = 1.15 \times 10^2$

In a 1.500 L flask, add 3.000 mol of each component
What are the equilibrium concentrations?

Soln.

Ini. conc.　　$[H_2]_o = [F_2]_o = [HF]_o = \dfrac{3.000 \text{ mol}}{1.500 \text{ L}} = 2.000 \ M$

$$Q = \frac{[HF]^2}{[H_2][F_2]} = \frac{(2.000)^2}{(2.000)^2} = 1.000 < K$$

Reaction will shift to the right

$$H_2(g) \quad + \quad F_2(g) \quad \rightarrow \quad 2HF(g)$$

ini.　　　2.000　　　　2.000　　　　　2.000　　M
equil.　　2.000–x　　　2.000–x　　　2.000+2x

$$Q = \frac{(2.000 + 2x)^2}{(2.000 - x)(2.000 - x)} = K = 1.15 \times 10^2$$

$x = 1.53$
$[H_2] = 2.000 - 1.53 = 0.47 \ M = [F_2]$
$[HF] = 2.000 + 2(1.53) = 5.06 \ M$

※ Le Châtelier's principle

Equilibrium position will shift in a direction that tends to reduce the change

Factors effecting equilibrium
• Concentration
• Pressure (for gaseous reaction)
    At constant V: add an inert gas → increase P_T
                    → does not change partial pressure
                    → no change of equilibrium
    Reduce the V: P increases
                    equilibrium shifts to the smaller V side
                    → $P \downarrow$
• Temperature (treat E as a reaction component)
    Exothermic (放熱) reaction: treat E as product
    Endothermic (吸熱) reaction: treat E as reactant