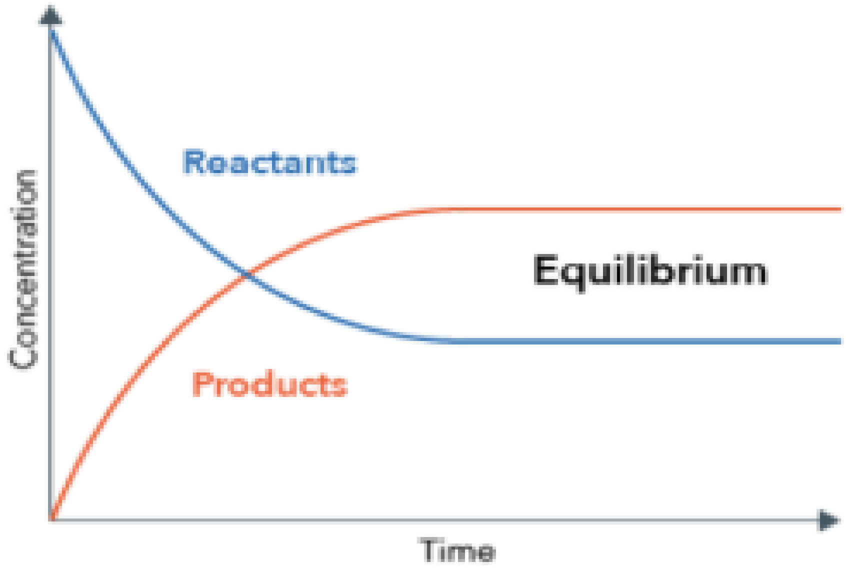
# Chapter 4

## Chemical equilibrium



- Chemical reactions can be
  - Complete (irreversible)
    - One way
    - At least one reactant disappear
    - Equation is represented by one arrow $\rightarrow$
  - Incomplete (reversible or limited)
    - Two ways
    - None of the reactants is totally consumed
    - Equation represented by 2 arrows $\rightleftarrows$

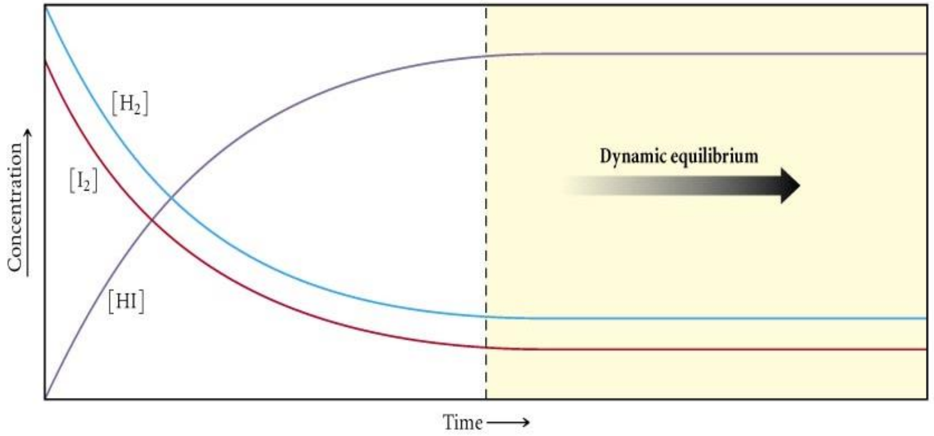
# 1- chemical equilibrium:

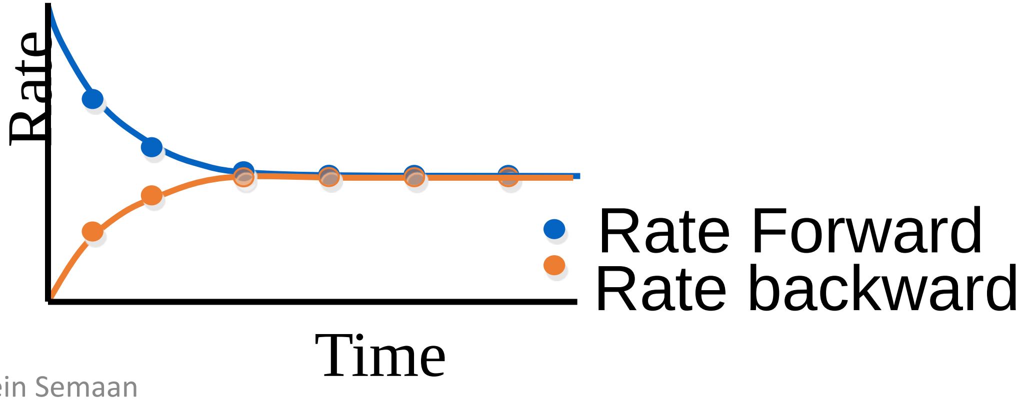
$$aA + bB \underset{\text{two}}{\overset{\text{one}}{\rightleftharpoons}} cC + dD$$

- A reversible reaction is a reaction, which takes place in the forward and backward direction. Such a reaction is partial does not go to completion.
- Direction one : forward direction.
- Direction two: backward direction.

| | $H_2$ | + $I_2$ $\rightleftharpoons$ | $2\,HI$ |
|---|---|---|---|
| T=0 min | 8 mol | 8 mol | 0 mol |
| T=16 min | 6 mol | 6 mol | 4 mol |
| T=32 min | 4 mol | 4 mol | 8 mol |
| T=48 min | 4 mol | 4 mol | 8 mol |

- As the reaction proceeds the quantity of reactants decrease.
- Once the quantity does not change an equilibrium state is established
- When the rate of forward direction is equal to the rate of backward reaction equilibrium state is reached.



- **<u>Definition:</u>**

- A state of equilibrium is characterized by an invariable composition of the reaction system.

## 2- Equilibrium constant:

- When a reversible reaction has attained equilibrium at a given temperature, the product of the molar concentrations of the products divided by the product of the molar concentration of the reactants, each concentration is raised to the power equal to the stoichiometric coefficient appearing in the balanced equation is a constant.

$$aA + bB \rightleftharpoons cC + dD$$

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

| | $H_2$ + | $I_2$ | 2 HI |
|---|---|---|---|
| T=0 min | 8 mol | 8 mol | 0 mol |
| T=16 min | 6 mol | 6 mol | 4 mol |
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$$Kc= \frac{[HI]^2}{[H_2]\ x\ [I_2]} = \frac{\frac{8}{V^2}^{2}}{\frac{4}{V} x \frac{4}{V}} = 4$$

- Kc depends on temperature
- Every reaction has its own equilibrium constant at a given temperature
- Kc is unaffected by any change in concentration of either products or reactants
- A large value for Kc indicates that large amount of reactants converted to products.(forward)
- A small value for Kc indicates that only a small fraction of reactants has been converted to products.(backward)
- if the reaction is inverted at the same conditions:

**cC + dD ⇌ aA + bB**

$$K'c = \frac{1}{k_C}$$

# 3- reaction quotient Qr

In a mixture containing both reactants and products not at equilibrium.

how can we determine in which direction it will proceed?

We must compare the current concentration ratios to the equilibrium constant $K_C$.

We calculate the reaction quotient Qr

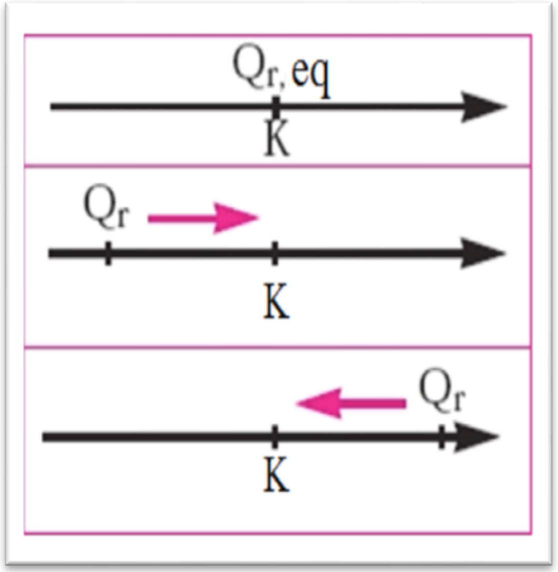
**aA + bB ⇌ cC + dD**

$$Q_r = \frac{[C]^c \, . \, [D]^d}{[A]^a \, . \, [B]^b}$$

Remark :

- If $Q = 0$, the reaction mixture contains only reactants, the reaction will go forward.
- If $Q = \infty$, a reaction mixture contains only products, the reaction will go backward.

- If $Q > K$, the reaction will shift in the backward direction:
  [products] ↓ and [reactants] ↑
- If $Q < K$, the reaction will shift in the forward direction:
  [products] ↑ and [reactants] ↓
- If $Q = K$, the reaction is at equilibrium:
  no change in [products] and [reactants]



# Application :

For the reaction: $CH_{4\,(g)} + 2\ H_2S_{\ (g)} \leftrightarrow CS_{2\,(g)} + 4\ H_{2\,(g)}$
$K_c = 3.59$ at 900 °C.
1- For each of the following measured concentrations determine whether the reaction is at equilibrium.
2- If not at equilibrium, in which direction will the reaction proceed to get to equilibrium?

| | Expt 1 | Expt 2 | Expt 3 |
|---|---|---|---|
| $[CH_4]$ | 1.15 | 1.07 | 1.10 |
| $[H_2S]$ | 1.20 | 1.20 | 1.49 |
| $[CS_2]$ | 1.51 | 0.90 | 1.10 |
| $[H_2]$ | 1.08 | 1.78 | 1.68 |

| | Expt 1 | Expt 2 | Expt 3 |
|---|---|---|---|
| $[CH_4]$ | 1.15 | 1.07 | 1.10 |
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| $[CS_2]$ | 1.51 | 0.90 | 1.10 |
| $[H_2]$ | 1.08 | 1.78 | 1.68 |

$$Q = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}$$

$$Q_{\text{exp}\,t\,1} = \frac{(1.51)(1.08)^4}{(1.15)(1.20)^2} = 1.24 < K_c \quad \text{proceeds forward}$$

$$Q_{\text{exp}\,t\,2} = \frac{(0.90)(1.78)^4}{(1.07)(1.20)^2} = 5.86 > K_c \quad \text{proceeds backward}$$

$$Q_{\text{exp}\,t\,3} = \frac{(1.10)(1.68)^4}{(1.10)(1.49)^2} = 3.59 = K_c \quad \text{equilibrium}$$

# 4- degree of conversion (α):

$\alpha$=amount of substance of the reactant dissociated/amount of substance of the reactant present initially

$$\alpha = \frac{n\,(\text{dissociated})}{n\,(\text{initial})}$$

$$0<\alpha<1$$

**α increase in forward direction**

## Table in terms of x :

For the following equation draw a table in terms of x

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

| | $N_2$ | $3H_2$ | $2NH_3$ |
|---|---|---|---|
| T=0 | 1 mol | 3 mol | 0 |
| variation | -x | -3x | +2x |
| T | 1-x | 3-3x | 2x |

**<u>Table in terms of α :</u>**

**α is the degree of conversion of** $N_2$

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

| | $N_2$ | $3H_2$ | $2NH_3$ | |
|---|---|---|---|---|
| T=0 | 1 mol | 3 mol | 0 | |
| variation | -α | -3α | +2α | |
| T | 1-α | 3-3α | 2α | nt=4-2α |

**α = ndissociated/ n initial = ndissociated/1**

**So n dissociated = 1 α**

**A.S.R**

**$n(H_2)=3n(N_2)$**

**$n(NH_3)= 2n(H_2)$**

## Table in terms of α :

**α is the degree of conversion of $H_2$ (limiting reactant)**

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

| | $N_2$ | $3H_2$ | $2NH_3$ | |
|---|---|---|---|---|
| T=0 | 2 mol | 4 mol | 0 | |
| variation | $-4\alpha/3$ | $-4\alpha$ | $+8\alpha/3$ | |
| T | $2-4\alpha/3$ | $4-4\alpha$ | $8\alpha/3$ | $n_t=6-8\alpha/3$ |

**α = ndissociated/ n initial = ndissociated/4**

**So n dissociated = 4 α**

**A.S.R**

**$n(H_2)/3=n(N_2)$**

**$n(NH_3)= 2n(H_2)/3$**