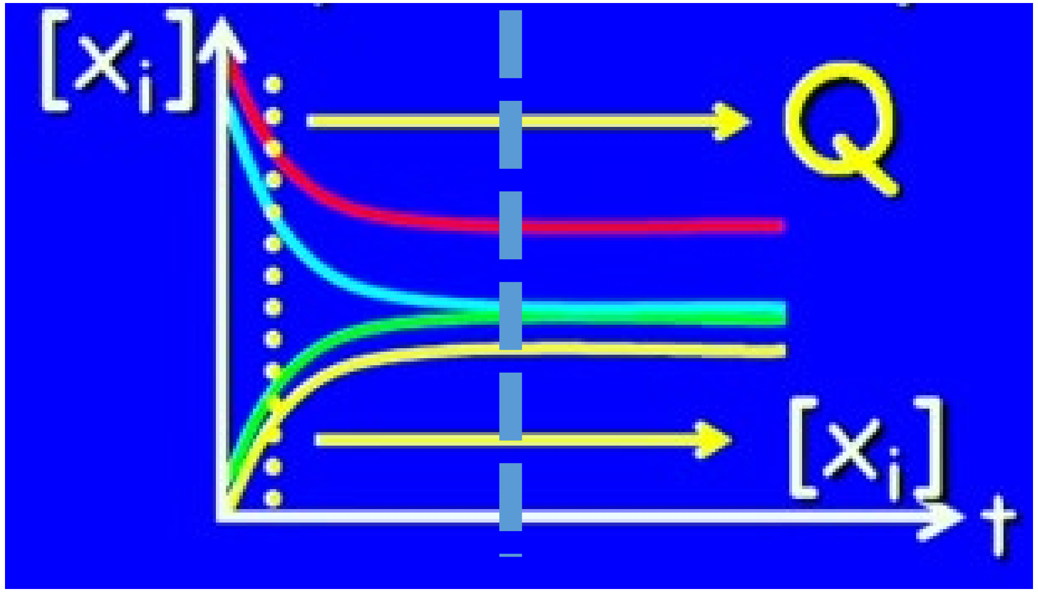
Chemical equilibrium

Law of mass action

$$aV + bX \rightleftharpoons cY + dZ$$

$$Q \sim \frac{products}{reactants} = \frac{[Y]^c[Z]^d}{[V]^a[X]^b}$$

Q: Reaction quotient, change with **time**



Q = a constant, $K(T)$, after reaching equilibrium at a given temperature

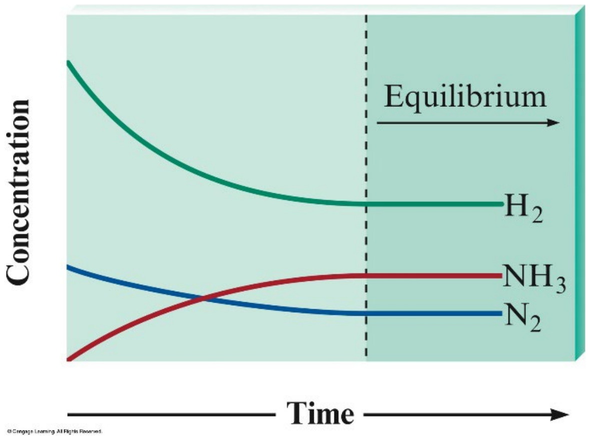
- The state where the **concentrations** of all **reactants and products** remain constant with time.
- On the molecular level, Equilibrium is a highly **dynamic** situation.

$Q < K$,
→ product

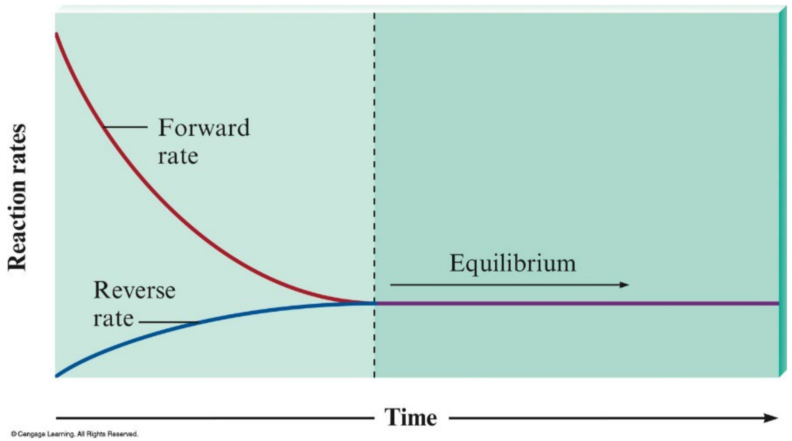
$Q = K$,
EQUILIBRIUM

$Q > K$,
Reactant ←

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$



Forward rate = Reverse rate



Forward reaction rate: $r_f = k_f[N_2][H_2]^3$

Reverse reaction rate: $r_r = k_r[NH_3]^2$

Equilibrium constant: $K_{eq} = \frac{k_f}{k_r} = \frac{[NH_3]^2}{[N_2][H_2]^3}$

General case

$$aV + bX \rightleftharpoons cY + dZ$$

$$\boxed{K_{eq} = \frac{k_f}{k_r} = \frac{[Y]^c[Z]^d}{[V]^a[X]^b}}$$

Calculating the K_{eq} : K_c and K_p

K_c: express the K_{eq} using molarity (mole/Liters (M))
K_p: express the K_{eq} using partial pressure

EX. The following equilibrium concentrations were observed for the Haber process, $N_{2(g)} + 3\,H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ at 127 °C,
$[NH_3] = 3.1 \times 10^{-2}\ M$; $[N_2] = 8.5 \times 10^{-1}\ M$; $[H_2] = 3.1 \times 10^{-3}\ M$
Calculate K

$$K = K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[3.1\times10^{-2}]^2}{[8.5\times10^{-1}][3.1\times10^{-3}]^3} = 3.8 \times 10^{-4}$$

EX. The following equilibrium concentrations were observed for the Haber process, $2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$ at 25 °C,
$P_{NOCl} = 1.2$ atm; $P_{NO} = 5.0 \times 10^{-2}$ atm; $P_{Cl_2} = 3.0 \times 10^{-1}$ atm.
Calculate K

$$K = K_p = \frac{P_{NOCl}{}^2}{P_{NO}{}^2 P_{Cl2}} = \frac{(1.2)^2}{[5.0\times10^{-2}]^2[3.0\times10^{-1}]} = 1.9 \times 10^{-3}$$

Conversion between K_p and K_c

$$K_p = \frac{P_{NOCl}{}^2}{P_{NO}{}^2 P_{Cl2}} = \frac{([NOCl]\times RT)^2}{([NO]\times RT)^2([Cl_2]\times RT)} = \frac{([NOCl])^2}{([NO])^2([Cl_2])} \times \frac{(RT)^2}{(RT)2(RT)} = K_c \times \frac{1}{(RT)}$$

General case

$$aV + bX \rightleftharpoons cY + dZ$$

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

Δn = the sums of coefficient of product – the sums of reactant in **gas** phase

TABLE Relations Between Equilibrium Constants

Chemical equation	Equilibrium constant
$a\,A + b\,B \rightleftharpoons c\,C + d\,D$	K_1
$c\,C + d\,D \rightleftharpoons a\,A + b\,B$	$K_2 = 1/K_1 = K_1^{-1}$
$na\,A + nb\,B \rightleftharpoons nc\,C + nd\,D$	$K_3 = K_1^{n}$

For a reaction that can be expressed as the sum of other reactions, the equilibrium constant is the product of the equilibrium constants of the component reactions.

The equilibrium constant for the reaction $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ has the value $K = 2.5 \times 10^{10}$ at 500K? Find the value of the following reaction at 500K

- $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$
- $SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$
- $3SO_2(g) + \frac{3}{2}O_2(g) \rightarrow 3SO_3(g)$

The concentration of the oxides of nitrogen are monitored in air-pollution reports. At 298K,

- $NO(g) + \frac{1}{2} O_2(g) \rightarrow NO_2(g)$ $K = 1.3 \times 10^{6}$
- $\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \rightarrow NO(g)$ $K = 6.5 \times 10^{-16}$
- Find the equilibrium constant K for the reaction

  $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$

Heterogeneous Equilibria

Position of a heterogeneous equilibrium does **NOT** depend on the amounts of pure solids or liquids present

$$2KClO_{3(s)} \rightleftharpoons 2KCl_{(s)} + 3O_{2(g)}$$

$$2H_2O_{(l)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$$

Unit of K_{eq} ?? K_{eq} is **unit less** !! Corrections for non-ideal behavior of the substances

Application of the Equilibrium Constant

Calculating the concentrations (pressures) of reactants and products at equilibrium

How ???

Small *x* approximation:
When the reaction is strongly product (K_c >10^4) or reactant (K_c <10^{-4}) favored

1) Assume the reaction goes 100% to product or reactants
2) ICE table
3) Solve for *x*, assume *x* is small
4) Check the answer → equilibrium constant back into K_c

For $10^{-4} < K_c < 10^4$, can't do approximation, solve it using $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ if needed

With $I_{2(g)}$ initial concentration of 0.45 *M* and $K_c = 5.6 \times 10^{-12}$, calculate the concentration of $I^-_{(g)}$ at equilibrium

With $NO_{(g)}$ and $Cl_{2(g)}$ initial concentration of 2.0 *M* and $K_c = 6.25 \times 10^{4}$, calculate the concentration of $NOCl_{(g)}$ at equilibrium

3 moles of $H_{2(g)}$ and 6 moles of $F_{2(g)}$ are mixed in a 3.000L flask and $K_c = 1.15\times10^2$, calculate the concentration of each species at equilibrium

Le Chatelier's Principle

If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.

How reaction direction is affected by **concentration**, **temperature**, and **pressure**.

Predict the effect of compression on the equilibrium composition of the following reaction mixtures in which the equilibria has been established

- $2PbS(s) + 3O_2\,(g) \leftrightarrow 2PbO(s) + 2SO_2(g)$
- $H_2\,(g) + I_2\,(g) \leftrightarrow 2HI(g)$

$N_2\,(g) + 3H_2\,(g) \leftrightarrow 2NH_3(g)$

- $\Delta H_r° = -92.22$ kJ/mol

$N_2\,(g) + 3H_2\,(g) \leftrightarrow 2NH_3(g) + \text{Heat}$