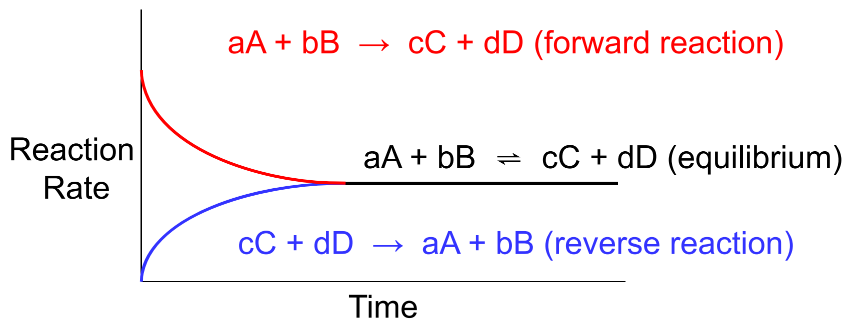
# Chemical Equilibrium

## Equilibrium

- involves reversible reactions
- Some reactions appear to go only in one direction – are said to go to completion.
- indicated by $\rightleftharpoons$
- All reactions are theoretically reversible but in some cases the reverse reaction is so slight or takes place so slowly that the reaction is considered irreversible.

# Homogeneous Equilibria

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



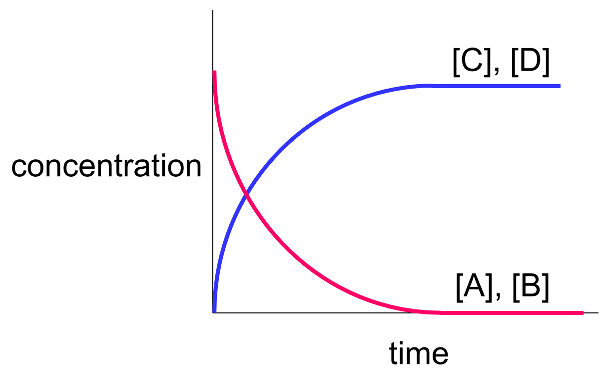

# At equilibrium:

- rate (forward reaction) = rate (reverse reaction)
- overall composition of reaction mixture does not change
- individual molecules go on reacting

  **dynamic equilibrium**

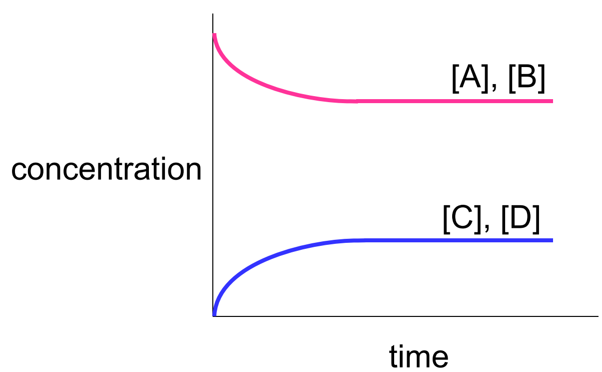
  As long as the temperature and pressure remain constant and nothing is added to or taken from the mixture, the equilibrium state remains unchanged.

$$aA + bB \rightarrow cC + dD$$



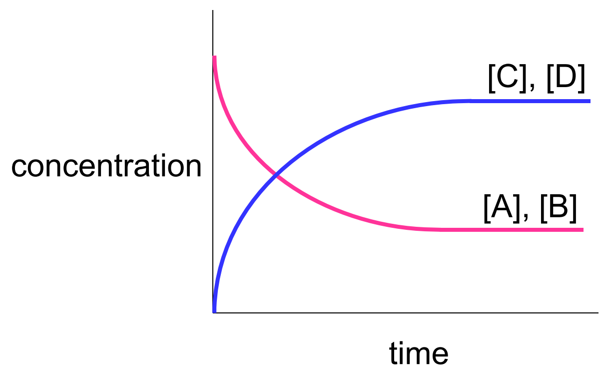

Reaction goes to completion.

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




reactant molecules > product molecules
not much forward reaction

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




reactant molecules < product molecules
forward reaction favourable,
reaction goes to the right

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

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

$K_c$ ≡ equilibrium constant

[ ] ≡ molarity **at** equilibrium

K does vary with temperature

K > 1 products favoured, forward reaction favoured

K < 1 reactants favoured, reverse reaction favoured

## Interpreting the equilibrium constant

- If $K_c$ for a reaction,

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

  is large, the equilibrium mixture is mostly products.
- If $K_c$ is small, the equilibrium mixture is mostly reactants.
- When $K_c$ is around 1, the equilibrium mixture contains appreciable amounts of both reactants and products.

## Example

For the reaction

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

$$K_c = \frac{[SO_3]}{[SO_2][O_2]^{1/2}} = 25.0 \text{ at } 600\ ^\circ C$$

Calculate the value of $K_c$ for each of the following reactions, at the same temperature:

- $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
- $SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)$

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

| | Starting Conc. | Equil. Conc. | $K_c$ |
|---|---|---|---|
| **Exp I** | 0.1000 M CO<br>0.3000 M $H_2$ | 0.0613 M CO<br>0.1839 M $H_2$<br>0.0387 M $CH_4$<br>0.0387 M $H_2O$ | 3.93 |

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

| | Starting Conc. | Equil. Conc. | $K_c$ |
|---|---|---|---|
| **Exp II** | 0.2000 M CO<br>0.3000 M $H_2$ | 0.1522 M CO<br>0.1566 M $H_2$<br>0.0478 M $CH_4$<br>0.0478 M $H_2O$ | 3.91 |

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

| | Starting Conc. | Equil. Conc. | $K_c$ |
|---|---|---|---|
| **Exp III** | 0.1000 M $CH_4$ | 0.0613 M CO | |
| | 0.1000 M $H_2O$ | 0.1839 M $H_2$ | 3.93 |
| | | 0.0387 M $CH_4$ | |
| | | 0.0387 M $H_2O$ | |

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

When 1.000 mol CO and 3.000 mol $H_2$ are placed in a 10.00 $dm^3$ vessel at 1200 K and allowed to come to equilibrium, the mixture is found to contain 0.387 mol $H_2O$.

What is the molar composition of the equilibrium mixture? That is, how many moles of each substance are present?

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

| | | | | |
|---|---|---|---|---|
| Starting | 1.000 | 3.000 | 0 | 0 |
| Change | -x | -3x | +x | +x |
| Equil. | 1.000 - x | 3.000 - 3x | x | x = 0.387 |

CO = (1.000 – 0.387) mol = 0.613 mol

$H_2$ = (3.000 – 3 × 0.387) mol = 1.839 mol

$CH_4$ = x mol = 0.387 mol

# Reaction Quotient, $Q_c$

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

Takes the same form as $K_c$ but is written for reactions **not** at equilibrium.

## Predicting the direction of reaction

- $Q > K$ to establish equilibrium reverse reaction is favoured
- $Q < K$ to establish equilibrium forward reaction is favoured
- $Q = K$ at equilibrium

## Example

A 50.0 $dm^3$ reaction vessel contains 1.00 mol $N_2$, 3.00 mol $H_2$, and 0.500 mol $NH_3$. Will more ammonia, $NH_3$, be formed or will it dissociate when the mixture goes to equilibrium at 400 °C? The equation is

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

$K_c$ is 0.500 at 400 °C.

# Equilibrium constant, $K_p$

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

- This is a gas phase reaction and we can use partial pressures instead of concentration, i.e. $K_p$.

partial pressure $\propto$ [ ]

$$P_A = \frac{n_A}{V_A}RT$$

$$= [A]RT$$

# $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

$$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]} = 9.7 \times 10^{-4}$$

$$K_p = \frac{P_{PCl5}}{P_{PCl_3}P_{Cl_2}} = 1.2 \times 10^{-5}$$

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

$\Delta n$ = (moles of gaseous products) – (moles of gaseous reactants)

# Heterogeneous Equilibria

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

$$K_c = \frac{[H_2]^4}{[H_2O]^4} \quad \text{or} \quad K_p = \frac{P_{H_2}^4}{P_{H_2O}^4}$$

- As long as some solid is present (no matter how much), equilibrium is reached in the same way.
- The equilibrium law for a heterogeneous reaction is written **without** concentration terms for **pure** solids or liquids.

# Homogeneous Equilibria in Solution

alcohol + acid $\rightleftharpoons$ ester + water

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]}$$

When water is a reactant or product but is **not** present in excess as the solvent, its concentration must be included in the equilibrium constant expression.

## Reactions in dilute aqueous solution

Here water is the solvent and is in great excess:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_c = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_c = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

## Factors that influence equilibria

- Le Chatelier's Principle

If a system at equilibrium is subjected to a stress, the system will react in a way that tends to relieve the stress.

- Two factors cause the equilibrium to shift:
  - concentration
  - temperature

## Changing the amounts of products or reactants

- Can be changed either by changing the amount of a particular substance or the volume that it is contained in.
- Changing the volume causes a change in pressure.

## Adding or removing a reactant or product

The reaction shifts in a direction that will partially remove a substance that has been added or partially replace a substance that has been removed.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Remove water?

| | | | | |
|---|---|---|---|---|
| Original equi. | 0.613 | 1.839 | 0.387 | 0.387 |
| Remove $H_2O$ | 0.613 | 1.839 | 0.387 | 0 |
| New Equil. | 0.491 | 1.473 | 0.509 | 0.122 |

Equilibrium shifts to the right (forward direction). $K_c$ does not change.

## Changing the volume

Reducing the volume of a gaseous reaction mixture shifts the equilibrium in whichever direction will, if possible, decrease the number of molecules of gas.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

- Reduce the volume at constant T
- Equilibrium shifts to the right $\longrightarrow$ to decrease the moles of gas and reduce the pressure.

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

- Increase the pressure by decreasing the volume
- Shifts to the left (reverse reaction)

$\longleftarrow$

- Solids and liquids are incompressible and are not much affected by pressure changes.

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

- Does not respond to pressure changes.

## Changing the temperature

- Increasing the temperature shifts an equilibrium in a direction that produces an endothermic change (which absorbs heat).

## Increasing temperature

- Exothermic reaction

  $A + B \rightleftharpoons C + D + \text{heat}$

  $\xleftarrow{\hspace{6em}}$

- Endothermic reaction

  $A + B + \text{heat} \rightleftharpoons C + D$

  $\xrightarrow{\hspace{6em}}$

## K changes with temperature

- If the forward reaction in an equilibrium is exothermic, raising the temperature causes the equilibrium constant to become smaller.

- The opposite change in K occurs if the forward reaction is endothermic.

# Agents that do not affect the position of equilibrium

- catalyst
  - affects both the forward and reverse reactions equally and does not affect the position of the equilibrium
  - causes no change in the value of K or in the concentrations at equilibrium
- adding an inert gas at constant volume

# Example

Consider the reaction:

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g);$$

$$\Delta H = 28 \text{ kJ}$$

Describe what happens to the composition of the equilibrium mixture and to $K_c$ with each of the following changes to the system at equilibrium:

(a) Addition of oxygen gas

(b) An increase in temperature

(c) Reduction of the volume of the reaction container

(d) Addition of a catalyst

(e) Removal of HCl(g) from the reaction vessel.

## Calculating equilibrium concentrations

- Consider the reaction

  $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$.

  Suppose you start with 1.00 mol each of carbon monoxide and water in a 50.0 $dm^3$ vessel. How many moles of each substance are in the equilibrium mixture at 1000 °C? The equilibrium constant $K_c$ at this temperature is 0.58.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$$\text{starting conc. } [CO]=[H_2O]= \frac{1.00 \text{ mol}}{50.0 \text{ dm}^3} = 0.0200 \text{ mol dm}^{-3}$$

| | $CO(g)$ | $H_2O(g)$ | $CO_2(g)$ | $H_2(g)$ |
|---|---|---|---|---|
| Starting conc. | 0.0200 | 0.0200 | 0 | 0 |
| Change | -x | -x | +x | +x |
| Equil. Conc. | 0.0200 - x | 0.0200 -x | x | x |

- $K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$
- $= \frac{(x)^2}{(0.0200-x)^2} = 0.58$
- $\frac{x}{0.0200-x} = 0.76$
- $x = 0.0152 - 0.76x$
- $x = 0.0087$

- $[CO] = [H_2O] = 0.0113 \text{ mol dm}^{-3} \times 50.0 \text{ dm}^3 = 0.57 \text{ mol}$
- $[CO_2] = [H_2] = 0.0087 \text{ mol dm}^{-3} \times 50.0 \text{ dm}^3 = 0.43 \text{ mol}$

# Example

- Suppose that in the preceding example 0.060 mol each of CO and $H_2O$ are mixed with 0.100 mol each of $CO_2$ and $H_2$. What will the concentrations of all the substances be when the mixture reaches equilibrium at the same temperature?

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

| | CO(g) | $H_2O(g)$ | $CO_2(g)$ | $H_2(g)$ |
|---|---|---|---|---|
| **Initial Conc.** | 0.060 | 0.060 | 0.100 | 0.100 |
| **Change** | -x | -x | +x | +x |
| **Equi. Conc.** | 0.060 - x | 0.060 - x | 0.100 + x | 0.100 + x |

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = 0.58$$

$$\frac{(0.100 + x)^2}{(0.060 - x)^2} = 0.58$$

$$\frac{(0.100 + x)}{(0.060 - x)} = 0.76$$

$$0.100 + x = 0.0457 - 0.76x$$

$$1.76x = -0.0543$$

$$x = -0.0309 \text{ mol}$$

$$
\begin{aligned}
\text{mol CO} &= 0.060 - (-0.0309) \\
&= 0.091 \\
&= \text{mol } H_2O
\end{aligned}
$$

$$
\begin{aligned}
\text{mol } CO_2 &= 0.100 - 0.0309 \\
&= 0.069 \\
&= \text{mol } H_2
\end{aligned}
$$

$$[CO] = [H_2O] = \frac{0.091\ \text{mol}}{50.0\ \text{dm}^3} = 1.8 \times 10^{-3}\ \text{mol dm}^{-3}$$

$$[CO_2] = [H_2] = \frac{0.069\ \text{mol}}{50.0\ \text{dm}^3} = 1.4 \times 10^{-3}\ \text{mol dm}^{-3}$$

$Q_c$ = 2.78 > $K_c$, therefore reaction goes to left.

## Example

- Consider the reaction

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

Suppose 1.00 mol $H_2$ and 2.00 mol $I_2$ are placed in a 1.00 $dm^3$ vessel. How many moles of substances are in the gaseous mixture when it comes to equilibrium at 458 °C? The equilibrium constant $K_c$ at this temperature is 49.7.

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

| | $H_2(g)$ | $I_2(g)$ | $2HI(g)$ |
|---|---|---|---|
| **Starting conc.** | 1.00 | 2.00 | 0 |
| **Change** | -x | -x | +2x |
| **Equi. Conc.** | 1.00 - x | 2.00 -x | 2x |

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

- $= \frac{(2x)^2}{(1.00 - x)(2.00 - x)} = 49.7$
- $4x^2 = 49.7(2 - 3x - x^2)$
- $= 99.4 - 149.1x + 49.7x^2$
- $45.7x^2 - 149.1x + 99.4 = 0$
- $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

- $x$ = 2.33 or 0.93
- $[H_2]$ = 1.00 – 0.93 = 0.07 mol
- $[I_2]$ = 2.00 – 0.93 = 1.07 mol
- [HI] = 1.86 mol