Equilibrium

- Some reactions go to completion
    - Reactants form products
    - No reactants left (unless in excess)
    - e.g. $Na_2CO_{3(aq)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + \underset{\text{gas escapes}}{CO_{2(g)}}$
- Some reactions never reach completion
    - At equilibrium reactant and product concentration remains constant indefinitely
    - Must be a closed system where reactants and products cannot escape but energy can be transferred to and from the system.
      e.g. $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$
    - Rate of forward reaction is equal to the rate of the reverse reaction

Equilibrium Constant

- Every equilibrium can be described by an equilibrium constant (K)
- Equilibrium constant (K) characterises the equilibrium composition of the reaction mixture
    - High K (above 1) – higher % of products in equilibrium mixture
    - Low K (below 1) – lower % of products in equilibrium mixture
- K is measured in terms of the concentration of species at equilibrium (or in terms of partial pressures in gas equilibrium)

For the reaction $aA + bB \rightleftharpoons cC + dD$

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

A, B, C & D are chemical formulae a, b, c & d are stoichiometric coefficients (numbers in equation)

- Homogeneous equilibrium is when all species are in the same state
- Heterogeneous equilibrium have species are in more than one state
- Equilibrium constant K has no units
- Equilibrium constant K is independent of the particular concentrations or pressures of species in a given reaction
- When a pure solid is present in an equation or a liquid is present as a solvent, its concentration, at a given temperature, doesn't vary to a measurable extent.
    - It is given the value of 1 in equilibrium equations (due to activity)

Effect of Changing Concentration

For example:

Dilute ethanoic acid has a pH=3.0 but adding a spatula of sodium ethanoate raises pH to 3.5

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

$$CH_3COONa_{(s)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

- $CH_3COO^-Na^+$ fully ionises on solution
- pH rises as $[H^+]$ falls
    - H^+ ions react with the increased concentration of CH_3COO^- ions to form molecules of CH_3COOH
    - Position of equilibrium shifts to LEFT but value of K remains constant

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

Equilibrium shifts to left

$$K = \frac{[CH_3COO^-] \times [H^+]}{[CH_3COOH]}$$

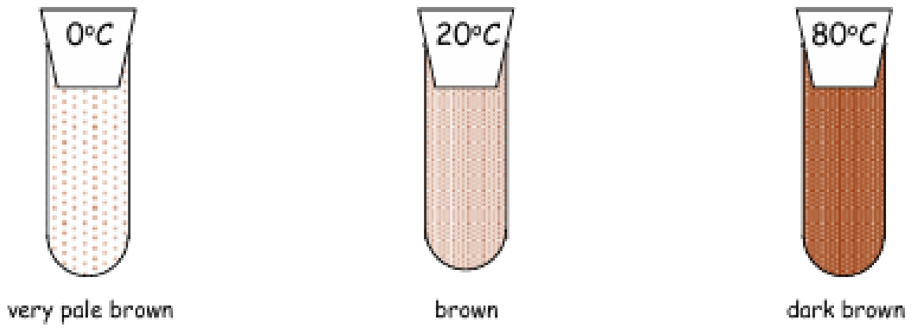
-
    - *increase* in $[CH_3COO^-]$ is balanced by *decrease* in $[H^+]$
      increase in $[CH_3COOH]$

    - Value of K remains constant by a combination of these changes

- The value of K remains constant (at the same temperature) as the equilibrium position shifts which results in changes in the concentrations of the species in the reaction
- Le Chatelier's Principle: "When a reaction at equilibrium is subjected to change, the composition alters in such a way as to minimise the effects of the change."

The Effects of Changing Temperature

$$\underset{\text{yellow}}{N_2O_{4(g)}} \rightleftharpoons \underset{\text{brown}}{2NO_{2(g)}} \qquad \Delta H = +ve$$



more N_2O_4 formed $\longleftrightarrow$ more NO_2 formed

- From colour changes, relative concentrations of N_2O_4 and NO_2 have changed with temperature changes
- Value of K has changed
- Value of K is dependant on temperature
- Values of K constants are quoted at particular temperatures

$$N_2O_{4(g)} \underset{\text{exothermic}}{\overset{\text{endothermic}}{\rightleftharpoons}} 2NO_{2(g)} \qquad \Delta H = +ve$$

$$K = \frac{[NO_2]^2}{[N_2O_4]}$$

- When temperature 20°C is *lowered* to 0°C
  - More N_2O_4 is formed (as exothermic reaction is favoured)
  - Brown colour (from NO_2) fades

$$K = \frac{\downarrow[NO_2]^2}{\uparrow[N_2O_4]} = \textit{decrease} \text{ in value of } K$$

- When temperature 20°C is *raised* to 80°C
  - More NO_2 is formed (as endothermic reaction is favoured)
  - Brown colour darkens (from more NO_2 produced)

$$K = \frac{\uparrow[NO_2]^2}{\downarrow[N_2O_4]} = \textit{increase} \text{ in value of } K$$

The Effects of Changing Temperature

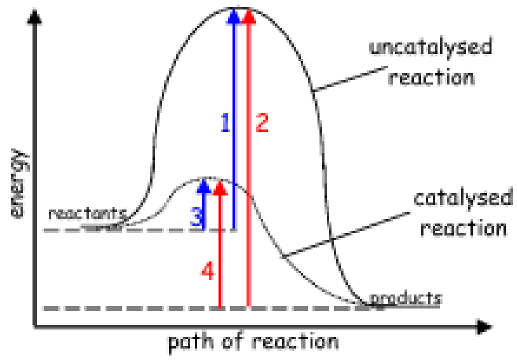
For endothermic reactions

Increase in temperature	*increase* in equilibrium constant K *increase* in product yield

For exothermic reactions

Increase in temperature	*decrease* in equilibrium constant K *decrease* in product yield

Effect of a Catalyst



1 E_a for forward uncatalysed reaction
2 E_a for reverse uncatalysed reaction
3 E_a for forward catalysed reaction
4 E_a for reverse catalysed reaction

- Catalysts lower activation energy E_a for both forward and reverse reactions by the same amount
- No change in the equilibrium concentration so position of equilibrium unchanged
- Equilibrium constant K is unaltered (at the same temperature)
- Catalysts speed up rate at which equilibrium is established

Equilibrium Constant K and Position of Equilibrium

- Value of K gives indication of how far equilibrium lies to the *left* or the *right* of a chemical reaction
    - High K means more products in the equilibrium mixture
    - Low K means more reactants in the equilibrium mixture
- K gives no indication about the rate at which dynamic equilibrium is established
- Catalysts do not increase percentage conversion of reactants to products
    - Catalysts only affect the speed at which equilibrium is attained
- For example

System	Value of K	Position of Equilibrium
$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]$	1.7×10^7 at 25°C	$K \gg 1$ Equilibrium lies to right (more products at equilibrium)
$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$	1.8×10^{-5} at 25°C	$K \ll 1$ Equilibrium lies to left (more reactants at equilibrium)
$N_2O_4 \rightleftharpoons 2NO_2$	0.87 at 55°C	$K \sim 1$ Equilibrium lies neither to left or right (similar amounts of reactants and products at equilibrium)