<u>EQUILIBRIUM</u>

A system that is at equilibrium has the following properties.

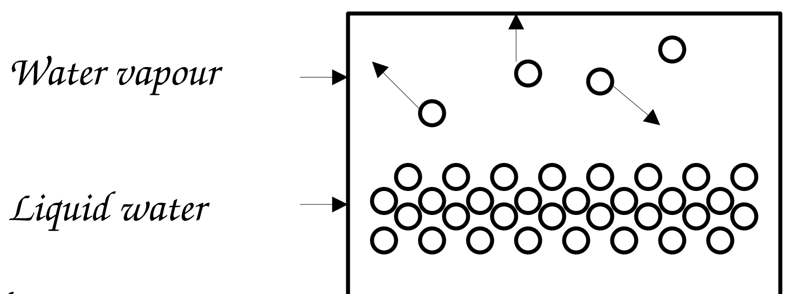
1. *The rates of the forward and reverse reactions are equal.*
2. *The concentrations of all species in the system are constant.*

Nb: For equilibrium to occur it must be a closed system and the temperature must remain constant.

At equilibrium both the forward and reverse reaction occur at a molecular level but they are occurring at the same rate but in opposite directions. This is why it is called ***DYNAMIC EQUILIBRIUM****.*

<u>PHASE EQUILIBRIA:</u>

$H_2O\ (l) \leftrightarrow H_2O\ (g)$



If some water is placed in a closed container at a constant temperature, some of the liquid will evaporate and become a gas. As soon as some gas is formed there is the possibility that it will condense back into a liquid.

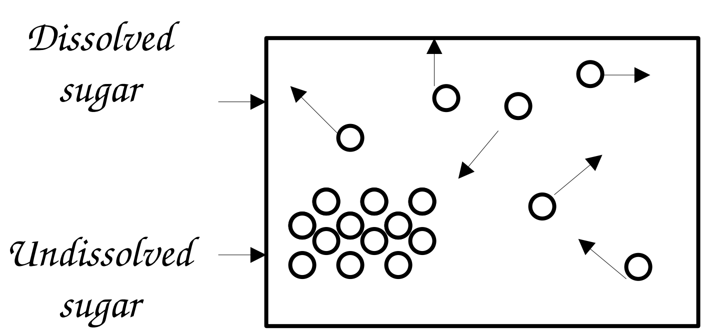
After a period of time the rates of evaporation and condensation will become equal and the system has reached equilibrium.

If the temperature is increased, the extra energy will increase the rate of evaporation. After time a new equilibrium position will be reached.

<u>SOLUTION EQUILIBRIA:</u>

$C_{12}H_{22}O_{11}\ (s) \leftrightarrow C_{12}H_{22}O_{11}\ (aq)$

sugar



When a solid solute is placed in water it will start to dissolve. If there is excess solute, a saturated solution is formed, then the macroscopic properties will become constant. Some of the dissolved solid can also crystallises out of solution.

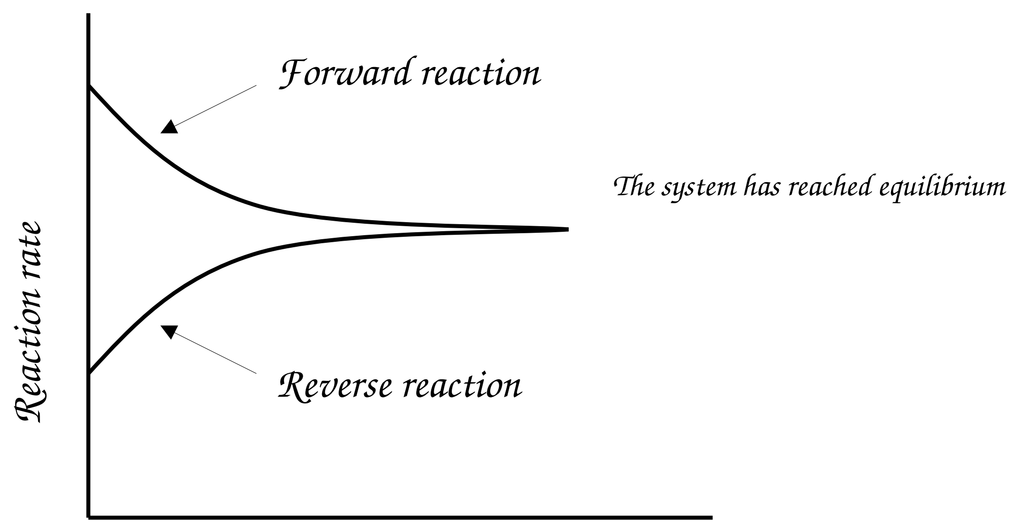
When the rate of dissolving and crystallising become constant the solution is at equilibrium.

*For a **solution** to reach equilibrium it must be a saturated solution and the temperature must be kept constant.*

CHEMICAL EQUILIBRIUM:

$$N_2O_4\ (g) \leftrightarrow 2NO_2\ (g)$$

Colourless Brown



EQUILIBRIUM CONSATANT:

$$aA + bB \leftrightarrow cC + dD$$

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

Solids and liquids are not included as they do not have a concentration ($molL^{-1}$).

Example:

$$N_2O_4\ (g) \leftrightarrow 2NO_2\ (g)$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 0.213 \text{ at } 100^\circ C$$

The value of the equilibrium constant stays the same as long as the temperature remains constant.

This means if you know the concentration of one substance (at equilibrium) you can calculate the other.

Also if the concentration of a reactant changes the new concentration of other substances can be calculated.

$$H_2\,(g) + I_2\,(g) \leftrightarrow 2HI(g)$$

$$3K = \frac{[HI]^2}{[H_2][I_2]} = 57 \text{ at } 425^\circ C$$

What does the equilibrium constant say about the system?

If K is large –

If K is small –

If K is close to 1 –

Le Chatelier's Principle

If a chemical system at equilibrium is subjected to a change in conditions, the system will adjust to establish equilibrium in such a way to partially counteract the imposed change.

There are three main ways to change the conditions of an equilibrium system.

Concentration, Pressure, Temperature.

Temperature:

An increase in the temperature of the system will favour the endothermic reaction.

A decrease in the temperature of the system will favour the exothermic reaction.

In your own words explain why.

Concentration:

An increase in the concentration of a reactant or product of the system will favour the direction, which will decrease the concentration of that substance.

A decrease in the concentration of a reactant or product of the system will favour the direction, which will increase the concentration of that substance.

If an equilibrium system involves one or more gaseous reactants or products the partial pressure of these substances is a measure of their concentration.

An increase in the partial pressure of a gaseous reactant or product of the system will favour the direction, which will decrease the partial pressure of that gaseous substance.

Pressure

If the external pressure of a system at equilibrium is changed the volume will be altered.

If decreasing the volume of the system increases the pressure it will favour the direction, which will reduce the pressure. This can be achieved by favouring the production of fewer moles of gaseous substances.

If increasing the volume of the system decreases the pressure it will favour the direction, which will increase the pressure. This can be achieved by favouring the production of more moles of gaseous substances.

If there are the same number of moles of gaseous substances in the reactants and products a change in the external pressure will favour neither direction.

Factors which effect the rate and equilibrium position.

Change made to the system	Effect on the Yield (amount of product)	Effect on the rate of reaction

Temperature ***Exothermic reaction***		
Endothermic reaction		
Concentration of reactants		
Pressure of the system		
Partial pressure of a reactant or product		
Catalyst		
Sub-division of reactants.		

Factors which effect the rate and equilibrium position.

Change made to the system	***Effect on the Yield (amount of product)***	***Effect on the rate of reaction***
Temperature ***Exothermic reaction***	***Increases temp decreases yield***	***Increased temp increases the rate of all reactions***
Endothermic reaction	***Increases temp increases yield***	
Concentration of reactants	***Increase in conc favours the direction which consumes extra***	***Increase in conc increases reaction rate.***

Pressure of the system	Increase in pressure favours less moles of gas	Increase in pressure increases rate
Partial pressure of a reactant or product	Increase in partial pressure favours direction which consumes	Increase in partial pressure increases rate
Catalyst	No effect just gets to equilibrium quicker	Increase rate of forward & reverse
Sub-division of reactants.	No effect	Increase in SA increases rate

In Industry chemist must find a compromise between the factors that favour a fast reaction and the factors that favour a high yield of the product.

THE HABER PROCESS (Ammonia production)

The main use of ammonia in WA is to make fertilisers and explosives in the form of ammonium nitrate and ammonium sulfate.

$$N_2 + 3H_2 \Leftrightarrow 2NH_3 + 92kJmol^{-1}$$

The factors that favour a **high reaction rate** are:

- **High temperature**
- **High Pressure**
- **Addition of a catalyst** (Fe/Fe_2O_3 ie rusty iron)

The factors that favour a **high yield** are:

- **Low temperature** (favours the forward reaction that is exothermic)
- **High pressure** (favours the forward reaction due to the 4:2 mole ratio of gases)

The actual conditions used are:

- **500°C, 350atm, Fe/Fe_2O_3 catalyst.**

The ammonia is liquefied under pressure and the unused N_2 and H_2 gas are recycled.

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

THE CONTACT PROCESS (Sulfuric acid production)

The main uses of H_2SO_4 are in the production of fertilisers and explosives, batteries and many industrial processes.

To start the process sulfur can be burnt or the roasting of zinc blend (ZnS ore).

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

The second step involves the oxidation of SO_2

$$2SO_2 + O_2 \Leftrightarrow 2SO_3 + heat$$

*The factors that favour a **high reaction rate** are:*

- **High temperature**
- **High Pressure**
- **Addition of a catalyst (V_2O_5 Vanadium oxide)**

*The factors that favour a **high yield** are:*

- **Low temperature** *(favours the forward reaction that is exothermic)*

- **High pressure** *(favours the forward reaction due to the 3:2 mole ratio of gases)*

The actual conditions used are:

- ***600°C, 1atm, V_2O_5 catalyst.***

This is quick but gives a low yield, the gas is removed and cooled to 400°C, which gives a high yield.

The SO_3 cannot be dissolved in water because it forms a mist when it comes near water that cannot be condensed.

The SO_3 is then dissolved in concentrated (18M) H_2SO_4 to produce oleum, and the oleum is diluted and some is removed and the rest recycled.

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4 \quad (98\% \text{ or } 18M)$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 5H_2O \rightarrow \underbrace{Ca(H_2PO_4)_2.H_2O + CaSO_4.2H_2O}_{\text{superphosphate}}$$