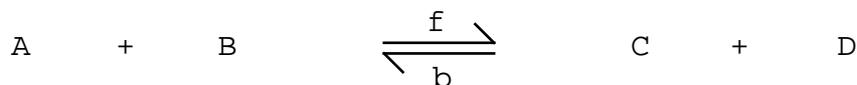


CHEMICAL EQUILIBRIUM

Every reaction is reversible:



A chemical reaction is in equilibrium when the composition of the reactants and products remains constant with time.

Since there is no further change in the concentrations of reactants or products, there is no further change in free energy i.e. $G = 0$. We must not confuse this value of G with $G_p - G_R$, often given the symbol G^0 to distinguish it from G .

$$\text{i.e. } G^0 = G_p - G_R$$

G = change in free energy as the reaction strives to reach equilibrium

Equilibrium is reached when the rate of the forward reaction equals the rate of the back reaction.

The rate of the forward reaction depends on the concentrations of the reactants:

$$\text{rate}_f \propto [A][B]$$

$$\Rightarrow \text{rate}_f = k_f[A][B] \quad \text{where } k_f = \text{rate constant for forward reaction}$$

The rate of the back reaction depends on the concentrations of the products:

$$\text{rate}_b \propto [C][D]$$

$$\Rightarrow \text{rate}_b = k_b[C][D] \quad \text{where } k_b = \text{rate constant for back reaction}$$

At equilibrium:

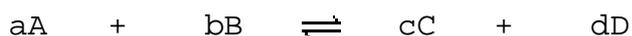
$$\text{rate}_f = \text{rate}_b$$

$$\Rightarrow k_f[A][B] = k_b[C][D]$$

$$\Rightarrow \frac{k_f}{k_b} = K = \frac{[C][D]}{[A][B]}$$

where K = the 'Equilibrium Constant'.

For the general reaction:



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

Concentrations may be expressed in moles or pressures.

The larger the value of K the greater the yield of products.

Notice that K is independent of particular concentrations or pressures in a given reaction. K is also unaffected by catalysts.

K does, however, change with temperature and, sometimes, pressure.

Example



Using Le Chatelier's principal, Energy (E) is a product and pressure (P) is a reactant:

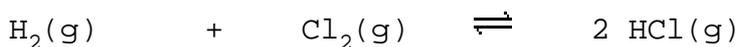


$$K = \frac{[C_2H_6]}{[C_2H_2][H_2]^2}$$

Increasing the temperature increases the energy E forcing the equilibrium to move to the left. This would reduce $[C_2H_6]$ and increase $[C_2H_2]$ and $[H_2]$. This would therefore reduce the value of K.

Increasing the pressure forces the equilibrium to move to the right increasing $[C_2H_6]$ and reducing $[C_2H_2]$ and $[H_2]$. This would therefore increase the value of K.

In reactions which do not involve a change in pressure, changing the pressure would have no effect on the equilibrium constant e.g.

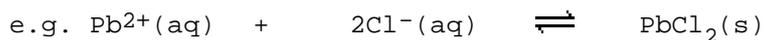


EXAMPLE 1

0.1 mol C_2H_4 was allowed to react with 0.04 mol CH_3COOH at 10°C . The total volume was made up to 1 litre with an inert solvent so that all reactants and products will be in the liquid phase.

This is described as 'homogeneous equilibrium' - all species are in the same phase.

In heterogeneous equilibrium the species are in more than one phase



When equilibrium had been established the mixture was found to contain 0.036 mol $\text{CH}_3\text{COOC}_2\text{H}_5$.

Calculate the equilibrium constant.

ANSWER :

The equilibrium concentrations are as follows:

$$\text{CH}_3\text{COOC}_2\text{H}_5 = 0.036 \text{ mol l}^{-1}$$

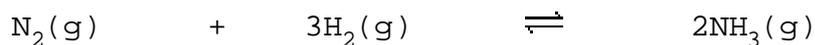
$$\begin{aligned} \text{C}_2\text{H}_4 &= 0.1 - 0.036 \\ &= 0.064 \text{ mol l}^{-1} \end{aligned}$$

$$\begin{aligned} \text{CH}_3\text{COOH} &= 0.04 - 0.036 \\ &= 0.004 \text{ mol l}^{-1} \end{aligned}$$

$$K = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{C}_2\text{H}_4][\text{CH}_3\text{COOH}]}$$

$$= \frac{(0.036)}{(0.064)(0.004)}$$

$$= \underline{140.63 \text{ mol l}^{-1}}$$

EXAMPLE 2

The total pressure of gas at equilibrium at 450 °C is 45 atm.

The pressure of the individual gases present (partial pressures) are:

$$\text{N}_2(\text{g}) \quad 10.35 \text{ atm}$$

$$\text{H}_2(\text{g}) \quad 31.05 \text{ atm}$$

$$\text{NH}_3(\text{g}) \quad 3.60 \text{ atm}$$

(a) Calculate the equilibrium constant.

$$\begin{aligned} K &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\ &= \frac{[3.60]^2}{[10.35][31.05]^3} \\ &= \underline{4.18 \times 10^{-5} \text{ atm}^{-2}} \end{aligned}$$

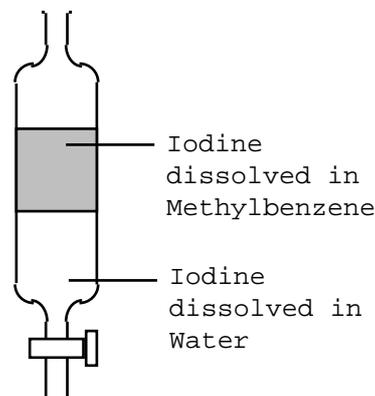
(b) The partial pressure of $\text{H}_2(\text{g})$ is increased to 35.00 atm. Calculate the new partial pressure of $\text{NH}_3(\text{g})$ at equilibrium.

$$\begin{aligned} [\text{NH}_3] &= (\sqrt{K [\text{N}_2][\text{H}_2]^3}) \\ &= \sqrt{(4.18 \times 10^{-5} \times 10.35 \times [35.00]^3)} \\ &= \underline{4.31 \text{ atm}} \end{aligned}$$

SOLVENT EXTRACTION

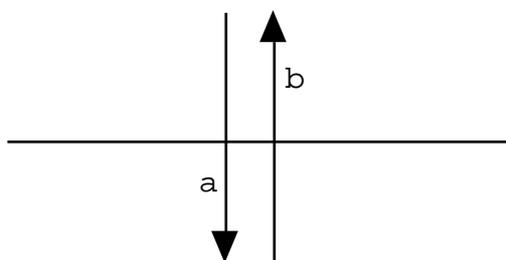
If a solute is in contact with two liquids which do not mix,

e.g. Iodine in contact with Water and Methylbenzene,



an equilibrium is eventually established when the rate (a) of diffusion of Iodine from the Methylbenzene into the Water is the same as the rate (b) of diffusion of Iodine from the Water into the Methylbenzene:

I_2 (in Methylbenzene)



I_2 (in Water)

$$K = \frac{[I_2 \text{ in Methylbenzene}]}{[I_2 \text{ in Water}]}$$

This particular equilibrium constant, K , is known as the Partition Coefficient. It depends on the two immiscible liquids involved, the solute and the temperature.

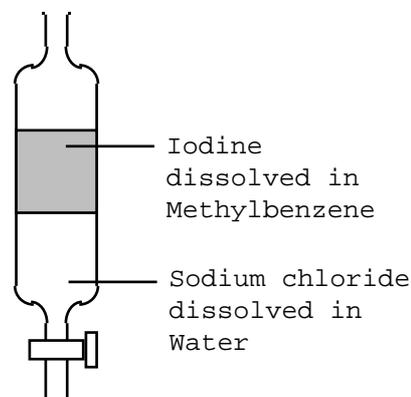
Iodine is much more soluble in Methylbenzene than in Water. The value of the partition coefficient is quite high.

Solvent extraction is a technique which makes use of this partitioning of a solute between two liquids.

Say we had a mixture of Iodine contaminated with Sodium chloride. We can extract the Iodine from this mixture by shaking the mixture in a separating funnel containing Methylbenzene and Water.

Most of the Iodine will diffuse into the Methylbenzene layer.

Sodium chloride is much more soluble in Water than in Methylbenzene - most of the Sodium chloride will diffuse into the Water layer.



Water-soluble organic acids can be separated from water-insoluble impurities by shaking with Ethoxyethane/Water. The organic acids diffuse into the Water layer; the impurities diffuse into the Ethoxyethane.

PROBLEM

- (a) 25.0 cm³ of a solution of Butanedioic acid in Water required 37.0 cm³ of 0.1 mol l⁻¹ Sodium hydroxide for complete reaction:



Calculate the concentration of the Butanedioic acid.

ANSWER:

$$\begin{aligned} \text{No. of m.moles of NaOH} &= 37.0 \times 0.1 \\ &= 3.70 \text{ m.moles} \\ \Rightarrow \text{No. of m.moles C}_2\text{H}_4(\text{COOH})_2 \text{ in } 25.0\text{cm}^3 &= 1.85 \text{ m.moles} \\ \Rightarrow \text{molarity} &= \frac{1.85}{25} \\ &= \underline{0.074 \text{ mol l}^{-1}} \end{aligned}$$

- (b) 25.0 cm³ of the same solution of Butanedioic acid in Water was now shaken with 25.0 cm³ Ethoxyethane and allowed to come to equilibrium at 25 °C.

The 25.0 cm³ aqueous (Water) layer now requires only 31.0 cm³ of 0.1 mol l⁻¹ Sodium hydroxide for complete reaction.

Calculate the partition coefficient:

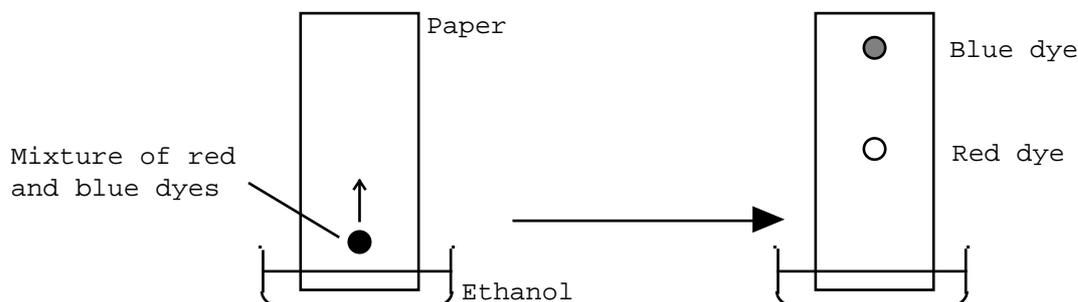
$$K = \frac{[\text{Butanedioic acid in Water}]}{[\text{Butanedioic acid in Ethoxyethane}]}$$

ANSWER :

$$\begin{aligned} \text{No. of m.moles of NaOH} &= 31.0 \times 0.1 \\ &= 3.10 \text{ m.moles} \\ \\ \Rightarrow \text{No. of m.moles } \text{C}_2\text{H}_4(\text{COOH})_2 \text{ in } 25.0\text{cm}^3 \text{ Water} &= 1.55 \text{ m.moles} \\ \\ \Rightarrow \text{molarity of } \text{C}_2\text{H}_4(\text{COOH})_2 \text{ in } 25.0\text{cm}^3 \text{ Water} &= \frac{1.55}{25} \\ &= \underline{0.062 \text{ mol l}^{-1}} \\ \\ \Rightarrow \text{No. of m.moles } \text{C}_2\text{H}_4(\text{COOH})_2 \text{ in } 25.0\text{cm}^3 \text{ Ethoxyethane} &= 1.85 - 1.55 \\ &= 0.30 \text{ m.moles} \\ \\ \Rightarrow \text{molarity of } \text{C}_2\text{H}_4(\text{COOH})_2 \text{ in } 25.0\text{cm}^3 \text{ Ethoxyethane} &= \frac{0.30}{25} \\ &= \underline{0.012 \text{ mol l}^{-1}} \\ \\ \Rightarrow K = \frac{[\text{Butanedioic acid in Water}]}{[\text{Butanedioic acid in Ethoxyethane}]} \\ \\ \Rightarrow K = \frac{0.062}{0.012} \\ &= \underline{5.17} \end{aligned}$$

PAPER CHROMATOGRAPHY

Put a tiny spot of a mixture of red and blue dyes at the end of a piece of paper and dip the paper into Ethanol. The Ethanol flows up the paper, dissolves the dyes and carries them up the paper.



Why do the dyes separate?

The dyes are partitioned between two phases:

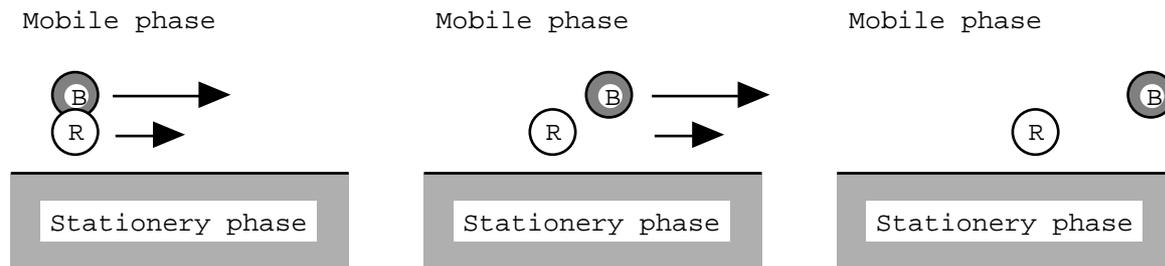
- The Stationery Phase

In paper chromatography' this is the water held on the paper.

- The Mobile Phase

In this case - Ethanol.

The Ethanol dissolves the two dyes and begins to drag them along the paper. The BLUE dye is less strongly attracted to the stationary phase than the RED dye. The BLUE dye therefore moves faster along the paper and thus separates from the RED dye:



Paper chromatography can be used to separate many solids e.g. amino acids and sugars.

GAS-LIQUID CHROMATOGRAPHY (GLC)

GLC is used to separate gases and volatile liquids.

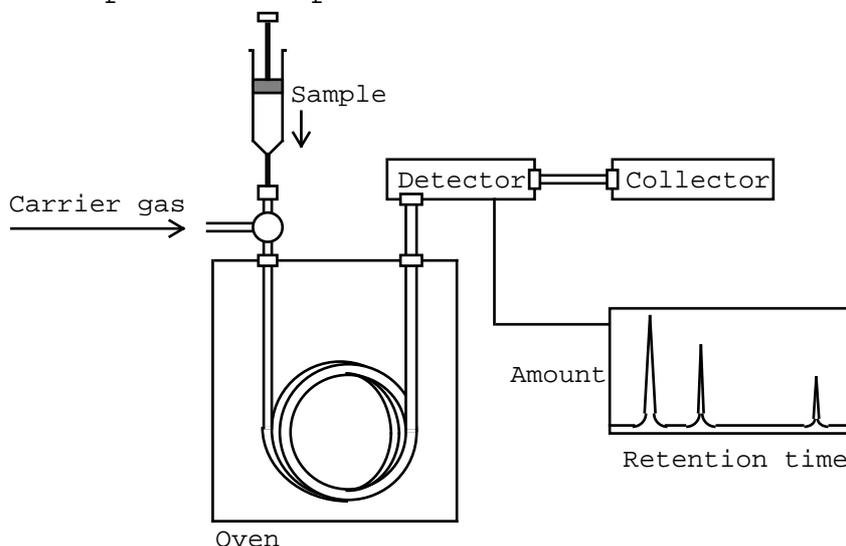
The mobile phase is a gas known as the 'carrier' gas, usually Nitrogen or Helium. The carrier gas drags the mixture into a heated coil packed with the stationary phase - a liquid (e.g. a silicone oil) held on a solid support (e.g. Celite).

Careful control of the oven temperature ensures that volatile liquids in the mixture quickly become gaseous. The gas mixture is then carried through the coils by the carrier gas. Each component is attracted to the stationary phase by different amounts. Weakly attracted components flow more quickly and begin to separate from more strongly attracted components.

Each component is detected as it emerges from the other end of the coil. The detector records the time taken to travel through the coil (retention time) and the amount of each component as a peak on a chart.

Retention times can be used to identify the individual components.

The separated components are collected.



GLC is used to measure accurately the amount of alcohol in a driver's blood.