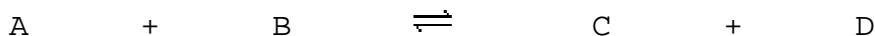


Chemical Equilibrium

Every reaction is, to some extent, reversible e.g.

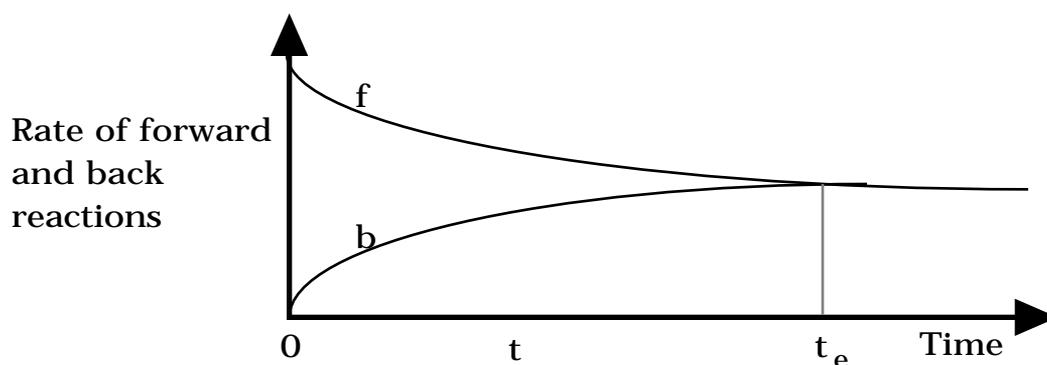


Consider the reaction :



Rate \propto concentration

Mix A and B



Time 0 A and B at maximum concentration so forward reaction proceeds at maximum rate.

No C or D so rate of back reaction is zero.

Time t A and B are being used up so rate of forward reaction decreases.

More C and D are becoming available so rate of back reaction increases.

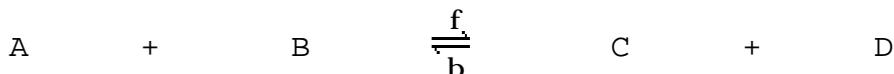
Time t_e When rate of forward reaction = rate of back reaction the concentration of A and B cannot get any less as they are being reformed as quickly as they are being used up. Similarly, the concentration of C and D cannot get any greater as they are being used again as quickly as they are generated. The concentrations now stay constant with time so the two rates stay constant. The reaction is said to have reached Equilibrium.

This is **Dynamic** equilibrium : the forward and back reactions continue at equal rates ; the concentrations stay constant though not necessarily equal.

Disturbing a reaction at Equilibrium

As equilibrium is attained when the rates of two opposing reactions become equal, any factor which causes the rates to become unequal will affect the equilibrium position.

For the general reaction



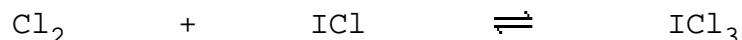
1. Make $\text{Rate}_f > \text{Rate}_b$
New equilibrium concentrations established are : more C and D ; less A and B.
2. Make $\text{Rate}_b > \text{Rate}_f$
New equilibrium concentrations established are : more A and B ; less C and D.

Factors which affect the equilibrium position

A. Concentration

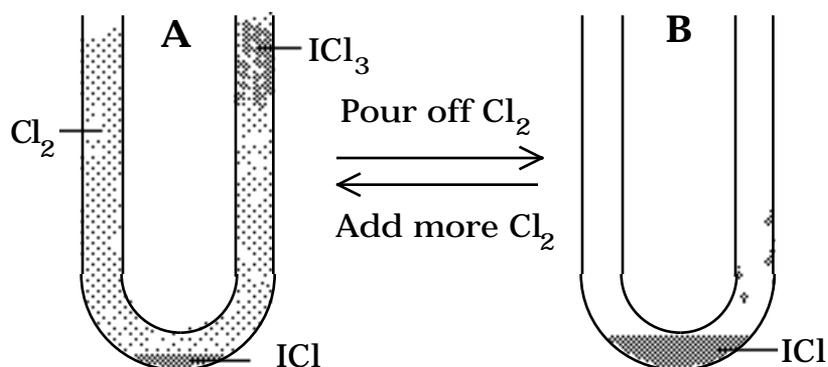
Example 1

Pass Chlorine gas over the brown liquid, Iodine monochloride. Yellow crystals of Iodine trichloride are formed :



Pour away Cl_2 from A : The forward reaction slows down and the equilibrium position moves towards the left.

Add more Cl_2 to B : The forward reaction speeds up and the equilibrium position moves to the right again.



Example 2

Reversible reactions can be made to go to completion if one of the products is removed to prevent a back reaction e.g. in the Haber process :



the Ammonia is removed by liquifaction. Also, Nitrogen and Hydrogen are recycled to further boost the forward reaction.

B. Pressure (affects gas reactions only)

Since pressure \propto no. of molecules of gas

it can be treated as a reactant or product in gas reactions (symbol P)

Example 1

The equilibrium which exists between Dinitrogen tetroxide N_2O_4 , a pale yellow gas, and Nitrogen dioxide NO_2 , a brown gas.



Pressure is therefore a product of the forward reaction :



Hence, increasing the pressure speeds up the back reaction giving more N_2O_4 and less NO_2 at equilibrium (fig a).

Decreasing the pressure speeds up the forward reaction giving more NO_2 and less N_2O_4 at equilibrium (fig b).

Pressure : > 1 atm.



fig. (a)
more N_2O_4
less NO_2

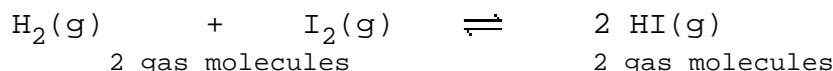
1 atm.



< 1 atm.



fig. (b)
more NO_2
less N_2O_4

Example 2

Pressure does not alter in either direction so changing it has no effect on the equilibrium position.

Example 3

In the Haber process :



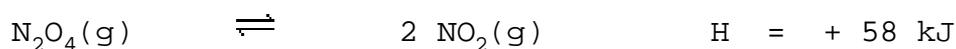
Pressure is a reactant in the forward reaction :



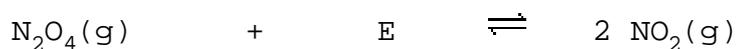
Increasing the pressure produces more Ammonia at equilibrium.
500 atm. is used.

C. Temperature

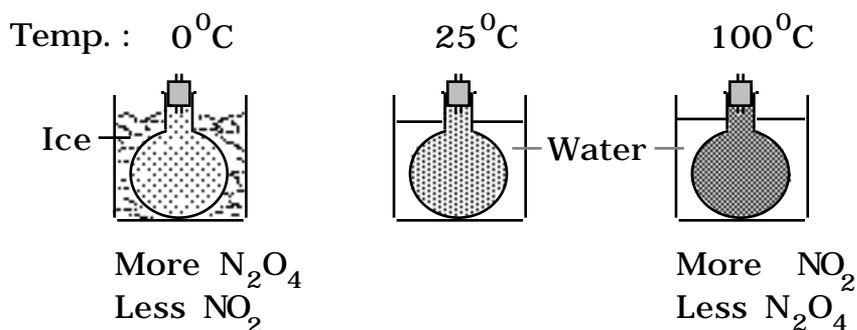
Example 1



Energy could be regarded as a reactant in the forward reaction i.e.

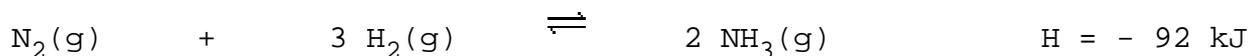


So, increasing the energy (e.g. by heating) should shift the equilibrium to the right.



Example 2

In the Haber process :

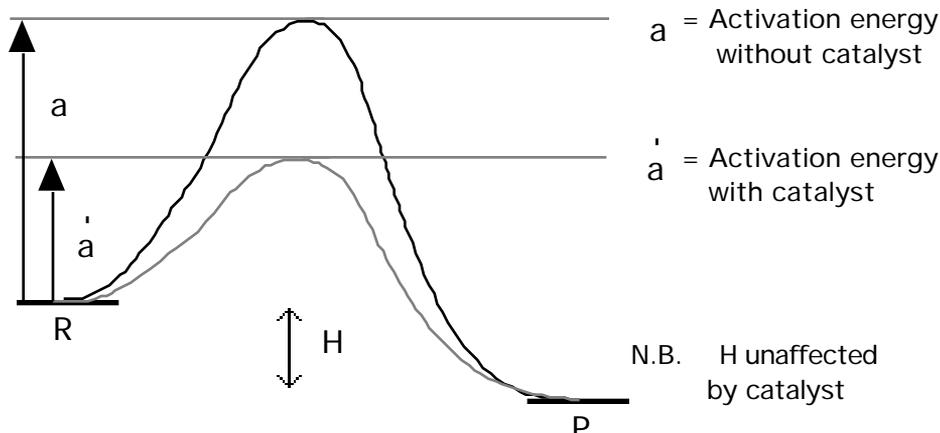


energy is a product of the forward reaction :



so increasing the energy, by raising the temperature, would force the equilibrium to the left reducing the yield of Ammonia ! Hence the temperature should be kept low. However, the lower the temperature, the slower the reaction ! The solution is a compromise : the temperature is kept as low as possible (450 °C) and an Iron catalyst is used to speed up the reaction.

N.B. A catalyst lowers the energy barrier of both forward and back reactions by exactly the same amount and therefore speeds up both forward and back reactions equally.



A catalyst therefore speeds up the time taken to reach equilibrium but has **no effect on the equilibrium position.**

Equilibrium in Aqueous Solutions

Water is ionised according to the equilibrium expression :



The position of this equilibrium lies well over to the left.

In 1 litre of Water, at 25 °C there are only 10^{-7} moles of H^+ and 10^{-7} moles of OH^- i.e.

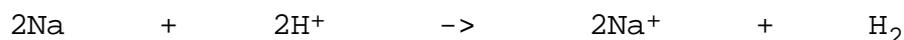
$$[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ mol l}^{-1}$$

Like all equilibria, this one can be disturbed e.g.

- (a) Increase $[\text{H}^+]$ to $10^{-6} \text{ mol l}^{-1}$; $[\text{OH}^-]$ drops to $10^{-8} \text{ mol l}^{-1}$; equilibrium moves to the left.
- (b) Decrease $[\text{H}^+]$ to $10^{-8} \text{ mol l}^{-1}$; $[\text{OH}^-]$ rises to $10^{-6} \text{ mol l}^{-1}$; equilibrium moves to the right.

N.B. $[\text{H}^+][\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{ l}^{-2}$ [at 25 °C]

- (c) Add Sodium to Water



$[\text{H}^+]$ is reduced ; $[\text{OH}^-]$ consequently rises; equilibrium moves to the right.

pH

The pH scale is a continuous scale ranging from below 0 to above 14. The higher the pH the lower $[\text{H}^+]$.

$$\text{pH} = -\log [\text{H}^+]$$

Example 1 Calculate the pH of a solution whose $[\text{H}^+] = 10^{-7} \text{ mol l}^{-1}$

Answer : $\text{pH} = -\log [\text{H}^+] = -\log(10^{-7}) = 7$

N.B. This is a **neutral** solution :

$$\text{pH} = 7 \text{ and } [\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ mol l}^{-1}$$

Example 2 Calculate the pH of a solution whose $[\text{H}^+] = 0.004 \text{ mol l}^{-1}$

Answer : $\text{pH} = -\log [\text{H}^+] = -\log(0.004) = 2.398$

N.B. This is an **acidic** solution :

$$\text{pH} < 7 \text{ and } [\text{H}^+] > [\text{OH}^-]$$

Example 3 Calculate the pH of a solution whose
 $[\text{OH}^-] = 2 \times 10^{-3} \text{ mol l}^{-1}$

Answer : $[\text{H}^+][\text{OH}^-] = 10^{-14}$

$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]} = \frac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}$$

$$\text{pH} = -\log [\text{H}^+] = -\log(5 \times 10^{-12}) = \underline{11.3}$$

N.B. This is an **alkaline** solution :

$\text{pH} > 7$ and $[\text{H}^+] < [\text{OH}^-]$

Example 4 Calculate the pH of a solution whose $[\text{H}^+] = 5 \text{ mol l}^{-1}$

Answer : $\text{pH} = -\log [\text{H}^+] = -\log(5) = \underline{-0.7}$

Example 5 Calculate the pH of a solution
 whose $[\text{H}^+] = 5 \times 10^{-15} \text{ mol l}^{-1}$

Answer : $\text{pH} = -\log [\text{H}^+] = -\log(5 \times 10^{-15}) = \underline{14.3}$

Example 6

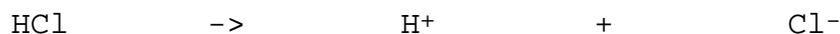
Complete the table below.

$[\text{H}^+] \text{ mol l}^{-1}$	$[\text{OH}^-] \text{ mol l}^{-1}$	Calculated pH
0.1		
	0.01	
0.0001		
	0.00001	

Strong and Weak Acids

Acids are proton (H^+) donors.

A strong acid dissociates completely in Water e.g. Hydrogen chloride



1 litre of a 1M solution of Hydrogen chloride (Hydrochloric acid) contains 1 mole of H^+ .

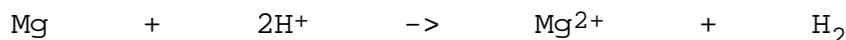
A weak acid only partially dissociates e.g. Ethanoic acid



Dissociation is difficult. The two ions have a tendency to recombine. Equilibrium is established when the rate of dissociation is equal to the rate of recombination.

1 litre of a 1M solution of Ethanoic acid contains only 0.004 moles of H^+ .

Consequently, a solution of Ethanoic acid has a higher pH, lower electrical conductivity and a slower reaction with Magnesium :



than an equimolar solution of the stronger Hydrochloric acid.

Since there are less H^+ in the Ethanoic acid, the reaction is slower.

N.B. Although the weak acid reacts more slowly, all the H^+ available does eventually react e.g. the volume of Hydrogen gas given off in both reactions is the same.

More examples of weak acids

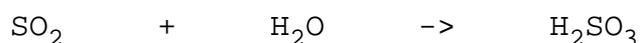
- Carbonic acid H_2CO_3
This is formed when Carbon dioxide reacts with Water :



Carbonic acid dissociates as follows :



- Sulphurous acid H_2SO_3
This is formed when Sulphur dioxide reacts with Water :



Sulphurous acid dissociates as follows :



Strong and Weak Bases

Bases are proton acceptors.

Strong bases (e.g. the oxide ion O^{2-}) accept protons readily

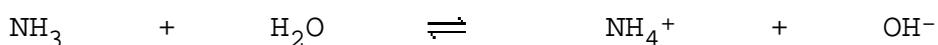
e.g. reaction of oxide ion with Water



There is little reversal ; solutions are strongly alkaline (pH 13-14) and good conductors of electricity since there are so many ions.

Weak bases (e.g. Ammonia NH_3) accept protons less readily e.g.

reaction of Ammonia with Water

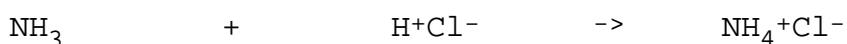


There is a tendency for the two ions to recombine. Equilibrium is established when the rate of formation of ions is equal to the rate at which they recombine.

Most of the OH^{-} recombine so the solution is only weakly alkaline (pH 9-12) and a poor conductor of electricity since there are so few ions.

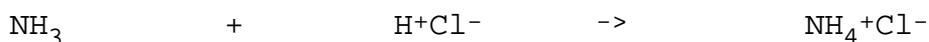
Reaction of Bases with Acids

Both strong and weak bases react completely although the weak base reacts more slowly e.g.



pH of Salt Solutions in Water

1. Salts of a strong acid (e.g. HCl) and a weak base (e.g. NH₃)

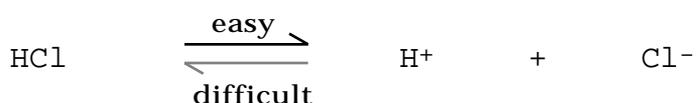


A solution of Ammonium chloride in Water contains four ions :

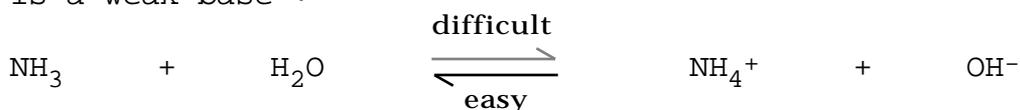


(H⁺ and OH⁻ from the ionisation of H₂O)

There is no tendency for H⁺ and Cl⁻ to combine since HCl is a strong acid :



There is however a tendency for OH⁻ and NH₄⁺ to react since NH₃ is a weak base :

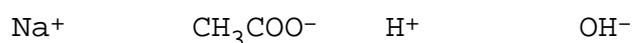


So, NH₄⁺ and OH⁻ combine leaving excess H⁺ - the solution is slightly **acidic**.

2. Salts of a weak acid (e.g. CH₃COOH) and a strong base (e.g. OH⁻)



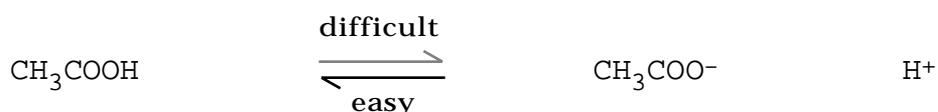
A solution of Sodium ethanoate in Water contains four ions :



There is no tendency for Na⁺ and OH⁻ to combine since Na⁺OH⁻ is completely soluble in Water :



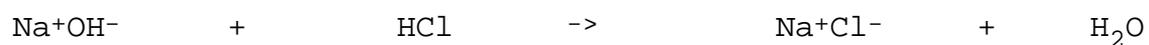
There is however a tendency for CH₃COO⁻ and H⁺ to react since CH₃COOH is a weak acid :



So, CH₃COO⁻ and H⁺ combine leaving excess OH⁻ ; the solution is slightly **alkaline**.

N.B. A Sodium stearate (Soap) solution in Water is alkaline because Sodium stearate is the salt of a weak acid (Stearic acid) and strong base (Sodium hydroxide).

3. Salts of a strong acid (e.g. HCl) and a strong base (e.g. OH⁻)



A solution of Sodium chloride in Water contains four ions :



There is no tendency for Na⁺ and OH⁻ to combine.

There is no tendency for H⁺ and Cl⁻ to combine.

Neither H⁺ nor OH⁻ is removed so their concentrations remain equal ; the solution is **neutral**.