

# CHEMICAL EQUILIBRIUM

## 10.1

Things you should know at the end of 10.1 are

1. That reversible reactions attain a state of dynamic equilibrium when the rates of the forward and reverse reactions are equal.
2. At equilibrium, the concentrations of the reactants and products remains constant although not usually equal.
3. Changes in concentration, pressure, and temperature can alter the position of equilibrium.
4. A catalyst speeds up the rate of attainment of equilibrium but does not affect the position of equilibrium.

A **reversible** chemical reaction reaches **equilibrium** when the **rate of the formation of products is equal to the rate of reforming reactants**.

Consider the formation of nitrogen monoxide: -



**At equilibrium the rate formation of nitrogen monoxide is equal to the rate at which ammonia and oxygen are being reformed.**

It is important to realise that the forward and back reactions do not stop when equilibrium is reached - nitrogen monoxide is still being formed and ammonia and oxygen are still being reformed. Since the reactions do not stop the process is described as being **dynamic**. It is equally important to realise that when equilibrium is reached this does **not** mean that the equilibrium mixture will contain 50% reactants and 50% products. This will very rarely be the case - the actual composition of the equilibrium mixture being controlled by a number of factors.

### FACTORS AFFECTING EQUILIBRIUM.

The effect of changing pressure, temperature and concentration conditions on the equilibrium position are summarised by **Le Chatelier's Principle** which states that

*"If a system in equilibrium is subjected to any change, the system will readjust to try to counteract the applied change."*

### Changing the Concentration

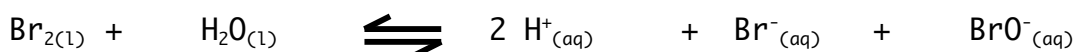
Consider the following reaction at equilibrium



An increase in the concentration of A [or B] will speed up the forward reaction increasing the concentration of C + D. **Le Chatelier's Principle** states that the system reacts to reduce the effect of this. Equilibrium will move to the right. This decreases the concentration of A. A new equilibrium will be established.

Likewise if one of the products is removed the reverse reaction will slow down causing equilibrium to move to the right.

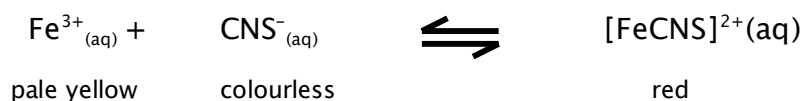
If we now consider the reaction



The solution will be brown owing to the colour of bromine molecules  $\text{Br}_{2(l)}$ . Adding water will move equilibrium to the right causing a decrease in brown colour as bromine molecules  $\text{Br}_{2(l)}$  react. Adding acid will cause equilibrium to move to the left increasing the number of bromine molecules  $\text{Br}_{2(l)}$  and hence the brown colour.

### Iron (III) ions and thiocyanate ions

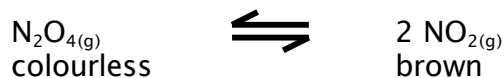
When separate solutions of  $\text{Fe}^{3+}_{(aq)}$  ions and thiocyanate ions are mixed a deep blood red colour is produced, equilibrium is established as shown



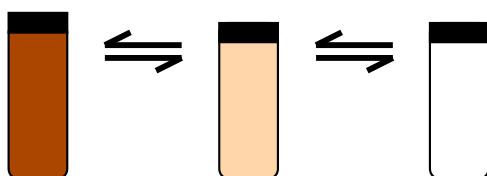
Adding FeCl<sub>3</sub> (Fe<sup>3+</sup>) causes equilibrium to move to the right (Deep red colour produced)  
 Adding OH<sup>-</sup>(aq) removes Fe<sup>3+</sup> as insoluble Fe(OH)<sub>3</sub> moves equilibrium to the left. {Pale orange colour produced}  
 Adding KCNS moves equilibrium to the right. (Deep red colour produced]

### Changing the temperature.

Consider the reaction the forward reaction is endothermic (takes in heat)



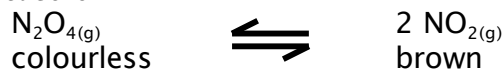
If we increase the temperature. **Le Chatelier's Principle** states that the system reacts to reduce the effect of this. i.e. reduce the temperature. It can do this by allowing the forward reaction (Endothermic) to take place. Increasing temperature will cause an increase in brown colour.



### Changing the pressure

The pressure exerted by a gas is caused by free moving particles hitting the walls of the vessel. An increase in the number of particles will cause an increase in the pressure. A decrease in particles an decrease in pressure.

Consider the reaction



1 vol

2 vol

Increasing the pressure, **Le Chatelier's Principle** states that the system reacts to reduce the effect of this. i.e. reduce the pressure. The system will do this by moving equilibrium to the left, reducing the brown colour.

### Using a catalyst

A catalyst speeds up a chemical reaction by lowering the Activation energy; it will however also lower the activation energy of the reverse reaction. Thus a catalyst will not change the position of equilibrium. A catalyst does however speed up the time taken to reach equilibrium.

## EQUILIBRIUM AND AQUEOUS SOLUTIONS.

### WATER DISSOCIATION.

When water is purified by repeated distillation its conductivity falls to a constant, but consistent value. Even the purest water has a tiny conductivity indicating that even the purest water contains a small number of ions.

This is evidence that water forms ions as a result of its own dissociation i.e.





The concentration of ions is very small and the equilibrium for this reaction lies very far to the left.

### CONCENTRATION OF IONS IN NEUTRAL SOLUTIONS.

In pure water and neutral solutions such as sodium chloride solution the concentration of the  $\text{H}^+_{(aq)}$  ions is equal to the concentration of the  $\text{OH}^-_{(aq)}$  ions, both having a concentration of  $1 \times 10^{-7} \text{ mol l}^{-1}$ .

This gives pure water a pH value of 7.

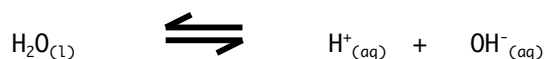
## ACIDIC SOLUTIONS.

## 10.2

Things you should know at the end of 10.2 are

1. The pH scale is a continuous range from below zero to above 14.
2. Integral values of pH from 0 to 14 can be related to concentrations of  $\text{H}^+_{(aq)}$  in  $\text{mol l}^{-1}$ .
3. In water and aqueous solutions with a pH value of 7 the concentrations of  $\text{H}^+$  and  $\text{OH}^-$  are both  $10^{-7} \text{ mol l}^{-1}$  at  $25^\circ\text{C}$ .
4. The concentrations of  $\text{H}^+$  and  $\text{OH}^-$  in a solution can be calculated from the concentration of the other by using  $[\text{H}^+_{(aq)}][\text{OH}^-_{(aq)}] = 10^{-14} \text{ mol}^2 \text{ l}^{-2}$ .
5. In water there is an equilibrium between water molecules and  $\text{H}^+_{(aq)}$  and  $\text{OH}^-_{(aq)}$ .
6. In aqueous solution strong acids are completely dissociated but weak acids are only partly dissociated.
7. Equimolar solutions of strong and weak acids differ in pH, conductivity and rate of reaction but not in stoichiometry of reactions.
8. The weakly acidic nature of solutions of ethanoic acid, sulphur dioxide and carbon dioxide can be shown by reference to equilibrium reactions.

In acidic and alkaline solutions the  $\text{H}^+_{(aq)}$  and  $\text{OH}^-_{(aq)}$  ions arise from sources other than dissociation of water. Nevertheless, in the system



the product  $[\text{H}^+][\text{OH}^-]$  remains constant at  $1 \times 10^{-14} \text{ mol}^2 \text{ l}^{-2}$

Thus it is possible to determine both the hydrogen ion concentration  $[\text{H}^+]$  and the hydroxide ion concentration  $[\text{OH}^-]$  in any source since: -

$$[\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14} \text{ mol}^2 \text{ l}^{-2}$$

For example, in  $0.01 \text{ M HCl}$  solution the concentration of  $[\text{H}^+] = 0.01 \text{ mol l}^{-1}$

$$\text{but since } [\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14} \text{ mol}^2 \text{ l}^{-2}$$

$$[\text{OH}^-] = 1 \times 10^{-12} \text{ mol l}^{-1}$$

pH	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$[\text{H}^+_{(aq)}]$	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$	$10^{-7}$	$10^{-8}$	$10^{-9}$	$10^{-10}$	$10^{-11}$	$10^{-12}$	$10^{-13}$	$10^{-14}$

### pH Measurements

$$\text{pH} = -\log[\text{H}^+_{(aq)}]$$

equation not needed for higher but can help

### CALCULATIONS USING pH.

1. What is the hydrogen ion concentration in solutions with the following pH values?

a) pH = 5

b) pH = 11.

2. What is the pH of the following solutions?

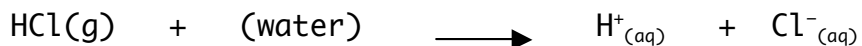
a)  $[H^+] = 1 \times 10^{-8} \text{ mol}^{-1}$

b)  $[OH^-] = 1 \times 10^{-4} \text{ mol}^{-1}$

## STRONG AND WEAK ACIDS

A strong acid is one, which in aqueous solution is completely ionised (dissociated), whereas a weak acid is one, which in aqueous solution is only partially ionised.

When hydrogen chloride gas is bubbled into water the hydrogen chloride molecules are completely ionised in aqueous solution producing many hydrogen and chloride ions.



When concentrated propanoic acid, which is composed almost entirely of uncharged molecules, is added to water only some of the propanoic acid molecules ionise.



As the equilibrium for this reaction lies well to the left most of the propanoic acid molecules remain as uncharged molecules.

	HCl	CH <sub>3</sub> CH <sub>2</sub> COOH
Reaction with Mg		
Titration of 10 cm <sup>3</sup> 0.1M acid with 0.1M NaOH		
Conductivity		
pH		

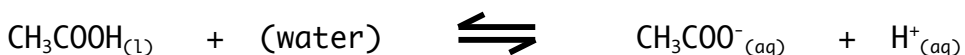
A **strong acid** in aqueous solution is completely ionised (dissociated), whereas a **weak acid** in aqueous solution is only **partially ionised**.

### CARBOXYLIC ACIDS ARE WEAK ACIDS

The carboxylic acids are weak acids they are only partly ionised in aqueous solution.

The carboxylic acids are weak acids due to the partial ionisation of the O-H group adjacent to the carbonyl group i.e. only a few of the O-H bonds next to the carbonyl group in the acid molecules break apart to form ions.

Consider the addition of ethanoic acid to water



The equilibrium for this reaction lying far to the left

The carboxylic acids are not the only examples of weak acids. The inorganic acids, carbonic and sulphurous acids are also weak acids.

**Sulphurous acid. (H<sub>2</sub>SO<sub>3</sub>).**

Sulphurous acid is formed when sulphur dioxide gas is bubbled through water.



The equilibrium for this reaction lies far to the left

### Carbonic acid

Carbonic acid is formed when carbon dioxide dissolves in water.



The equilibrium for this reaction lies far to the left.

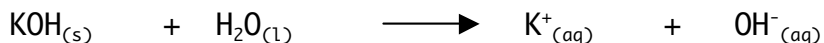
## STRONG AND WEAK BASES 10.3

Things you should know / be able to do at the end of 10.3 are

1. In aqueous solution strong bases are completely ionised whilst weak bases are only partly ionised.
2. Equimolar solutions of strong and weak bases differ in pH and conductivity but not in stoichiometry.

Metal oxides and metal hydroxides are bases. When a metal oxide dissolves in water it forms a solution of the metal hydroxide (alkali).

A strong base in aqueous solution is completely ionised. For example, potassium hydroxide is a strong base as it completely ionises in solution.



A weak base in aqueous solution is only partially ionised.

For example, ammonia is a weak base.



The equilibrium for this reaction lies far to the left.

### AMINES

Amines, like ammonia, are weak bases. This is not surprising since amines are related to ammonia. An amine can be considered as an ammonia ( $\text{NH}_3$ ) molecule in which one of the hydrogen atoms has been replaced by an alkyl group i.e.  $\text{RNH}_2$ .

Consider what happens when methylamine is dissolved in water.



The equilibrium for this reaction lies well to the left.

SOLUTION.	PH	Conductivity	Volume needed to neutralise 10cm <sup>3</sup> of 0.1M HCl.
0.1 M NaOH			
0.1 M NH <sub>3</sub>			
0.1 M CH <sub>3</sub> NH			

## ACID, NEUTRAL and BASIC SALTS 10.4

A salt is a substance formed when an acid is neutralised by reaction with a base (or alkali solution). When a salt is dissolved in water it can have

- 1 no effect on the pH of the water - a neutral salt.
- 2 make the pH fall - an acidic salt.
- 3 raise the pH - a basic salt.

A simple rule to determine the effect that a salt will have on the pH of water is

A neutral salt is formed when a strong acid reacts with a strong base.

For example, barium nitrate is a neutral salt made by reacting together barium hydroxide and nitric acid

An acidic salt is formed when a strong acid reacts with a weak base.

For example, ammonium sulphate is an acidic salt made by reacting together ammonium hydroxide (ammonia solution) and sulphuric acid.

A basic salt is formed when a weak acid reacts with a strong base.

For example, sodium ethanoate is a basic salt made by reacting together sodium hydroxide with ethanoic acid.

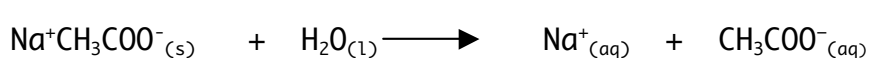
Acid	+	Alkali	=>	Salt	+	water
strong		strong		pH = 7	+	H <sub>2</sub> O
strong		weak		pH < 7	+	H <sub>2</sub> O
weak		strong		pH > 7	+	H <sub>2</sub> O
weak		weak		?	+	H <sub>2</sub> O

### EXPLAINING ACIDIC AND BASIC SALTS. 10.5

The acidity or alkalinity of a salt solution can be explained in terms of the shift in the water equilibrium.

#### Sodium ethanoate solution

Sodium ethanoate solution has a pH greater than 7, sodium ethanoate is a basic salt. Sodium ethanoate, like all sodium salts, is soluble in water and so when sodium ethanoate dissolves in water it completely ionises to give sodium (Na<sup>+</sup>) and ethanoate (CH<sub>3</sub>COO<sup>-</sup>) ions.

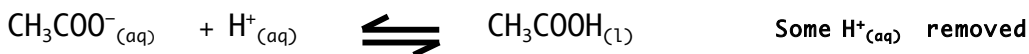


**Note** All soluble salts are totally ionised.

In water the following equilibrium exists



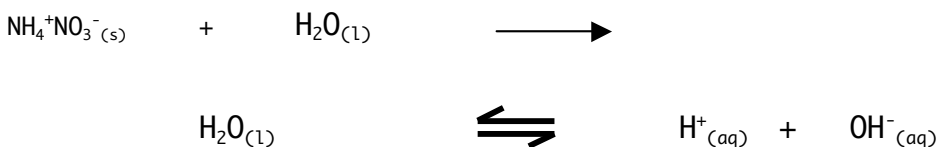
And so there will be Na<sup>+</sup><sub>(aq)</sub>, CH<sub>3</sub>COO<sup>-</sup><sub>(aq)</sub>, H<sup>+</sup><sub>(aq)</sub> and OH<sup>-</sup><sub>(aq)</sub> ions present in the solution.



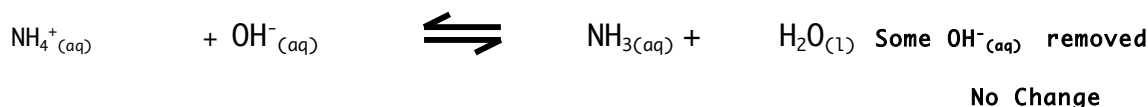
The [OH<sup>-</sup><sub>(aq)</sub>] will be greater than [H<sup>+</sup><sub>(aq)</sub>] i.e. alkaline. As [H<sup>+</sup><sub>(aq)</sub>] ions are removed the water equilibrium will move to the right to ensure that [H<sup>+</sup><sub>(aq)</sub>] x [OH<sup>-</sup><sub>(aq)</sub>] = 10<sup>-14</sup>

#### Ammonium nitrate solution

Ammonium nitrate will have a pH of .....



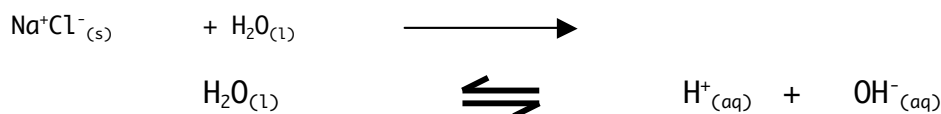
Ions in solution will be .....



The  $[\text{OH}^-_{(aq)}]$  will be ..... than  $[\text{H}^+_{(aq)}]$  i.e. ....

### Sodium chloride solution

Sodium chloride will have a pH of .....



The  $[\text{OH}^-_{(aq)}]$  will be ..... to the  $[\text{H}^+_{(aq)}]$  i.e. ....

## Concentration and pH

## 10.6

We have already seen that  $\text{pH} = -\log [\text{H}^+_{(aq)}]$  and also that  $[\text{H}^+_{(aq)}] \times [\text{OH}^-_{(aq)}] = 10^{-14}$   
We can use these to determine the pH of both acids and alkalis.  
Using one or both formula determine the pH of

- 1 a) 0.1 M hydrochloric acid.  
b) 0.3 M Hydrochloric acid.  
c) 0.5 M Sulphuric acid ( Note  $\text{H}_2\text{SO}_4 \Rightarrow 2\text{H}^+ + \text{SO}_4^{2-}$ )  
d) 0.5 M nitric acid  
e) A solution where  $[\text{H}^+_{(aq)}] = 10^{-9} \text{ mol l}^{-1}$   
f) A solution containing 1.96g of sulphuric acid in 500  $\text{cm}^3$  of solution.
- 2 a) 0.1 M sodium hydroxide.  
b) 0.005 M barium hydroxide.  
c) 10 M potassium hydroxide.
3. Calculate the concentration of hydrogen ions in
  - a) a solution of pH 4
  - b) a solution of pH 3.5
4. Calculate the concentration of hydroxide ions in
  - a) a solution of pH = 9
  - b) a solution of pH = 11

## Changing Conditions

## 10.7

We have looked already [10.1]at changing conditions of an equilibrium mixture. In this we are going to look at specific examples.

Factors which may affect the position of equilibrium are

1. Catalysts
2. Concentrations (solutions)
3. Pressure (gases)
4. Temperature

### Catalysts

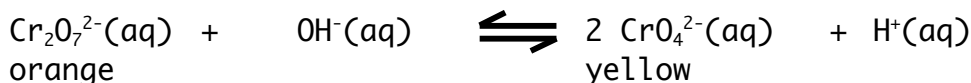
Shortens the time a system takes to reach equilibrium but has no effect on its position.  
According to **Le Chatelier's Principle**

**Concentrations**

To raise the proportion of product, chemists have two options

- a) Add more reactant.
- b) Remove some product.

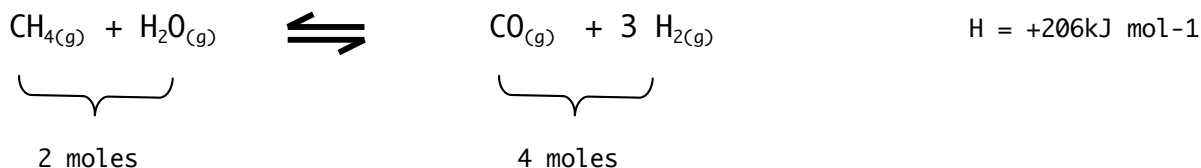
Consider the reaction



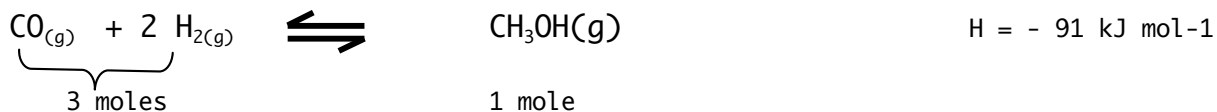
When sodium hydroxide ( $\text{NaOH}_{[\text{aq}]}$ ) is added. ....  
 When hydrochloric acid ( $\text{HCl}_{[\text{aq}]}$ ) is added. ....  
 When  $\text{Cu}^{2+}_{(\text{aq})}$  ions are added. ....

**Pressure**

Increasing the pressure causes a shift to an equilibrium mixture with a smaller number of moles of gas molecules



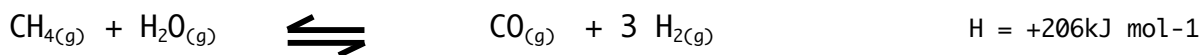
Increasing pressure would cause equilibrium to shift to the .....



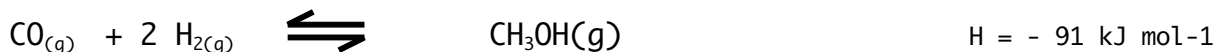
Increasing pressure would cause equilibrium to shift to the .....

**Temperature**

An increase in temperature shifts the equilibrium position to a mixture which is formed by absorbing heat



Raising temperature from 50°C to 200°C would shift equilibrium to the .....



Raising temperature from 50°C to 200°C would shift equilibrium to the .....