

# Chemical Equilibrium and pH

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Equilibrium



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# Equilibrium



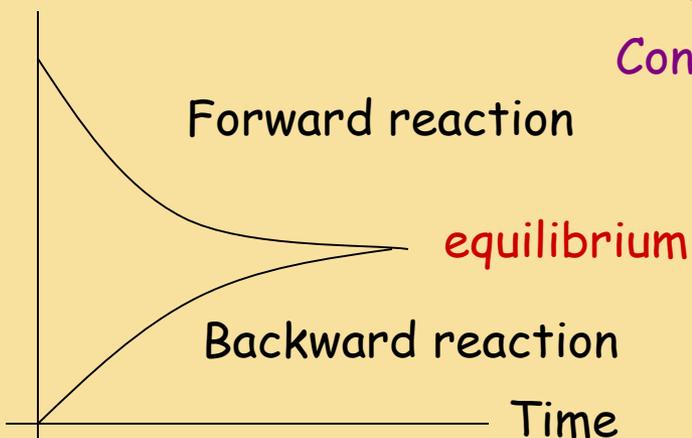
A reversible reaction goes both ways, with both products and reactants existing together. The final equilibrium position is the same whether you start with the products or reactants.

Eventually the rate for the forward reaction equals the backward rate. (graph 1)  
A state of **dynamic equilibrium** is reached. (in a closed system).

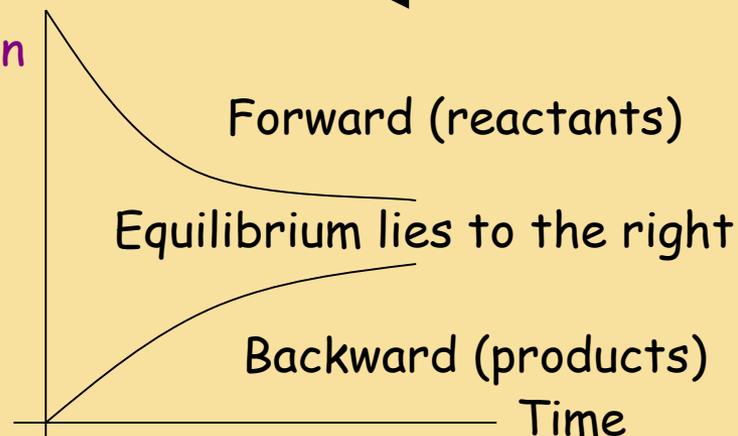
Depending on the percentage of products to reactants, the equilibrium is said to lie to the left or right. With **graph 2** there are more reactants than products.

Graph 1

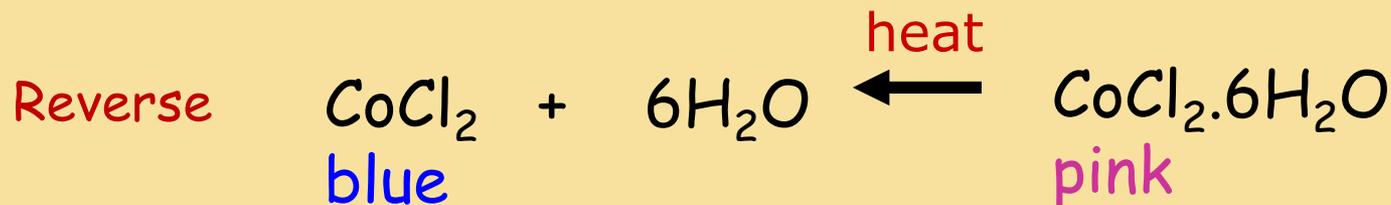
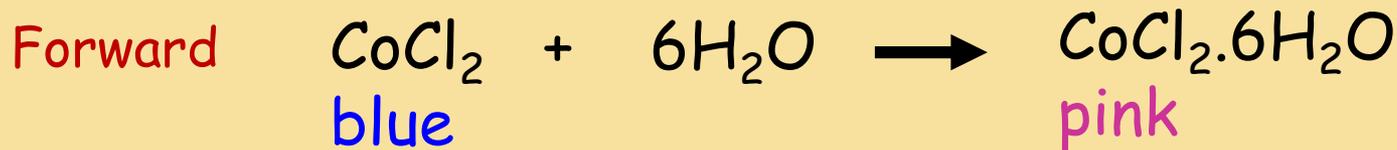
Reaction rate



Graph 2  
Concentration



# Reversible Reactions



No matter which side of the equation you start from the concentrations in the equilibrium mixture will be the same and the forward and backward rates will be the same.



# Le Chatelier's principle

In the chemical industry many reactions are in equilibrium.  
e.g. Haber Process, Synthesis Gas manufacture, Contact Process  
and Nitric Acid manufacture.

Concentration, pressure and temperature can all affect the position of the equilibrium. Their effect can be predicted using **Le Chatelier's Principle**. This states:

'If a system at equilibrium is subjected to a change, the system will adjust to oppose the effect of the change.'

**Catalysts** do not change the equilibrium position. Catalysts speed up **both** the forward and backward reactions. So the state of equilibrium will be reached **quicker**, but the amounts of the products and reactants will stay the same.



# Le Chatelier's Principle

## 1. Changing concentration



To increase the proportion of the products you can:

(i) Increase the concentration of reactants

By increasing the concentration of  $\text{Fe}^{3+}(\text{aq})$  the forward reaction will increase producing more products, however, the reverse reaction will also increase until the equilibrium is reached again.

The new equilibrium position will have moved to the right in order to reduce the increased concentration of  $\text{Fe}^{3+}(\text{aq})$ . So the **deep red darkens**

(ii) Decrease the concentration of products.

By reducing the concentration of  $\text{Fe}^{3+}(\text{aq})$ , the equilibrium will shift to the left in order to try and replace the  $\text{Fe}^{3+}(\text{aq})$  ions that have been removed. So the **pale yellow darkens**.



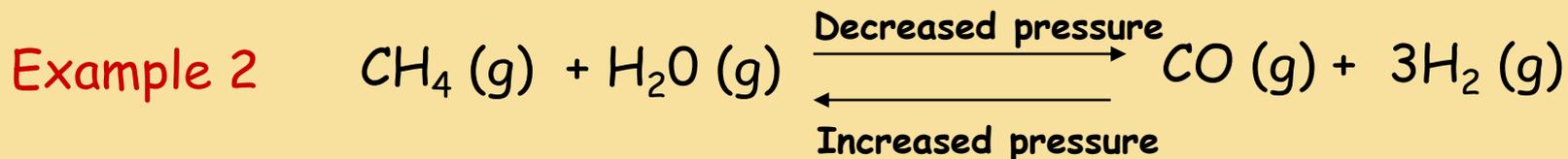
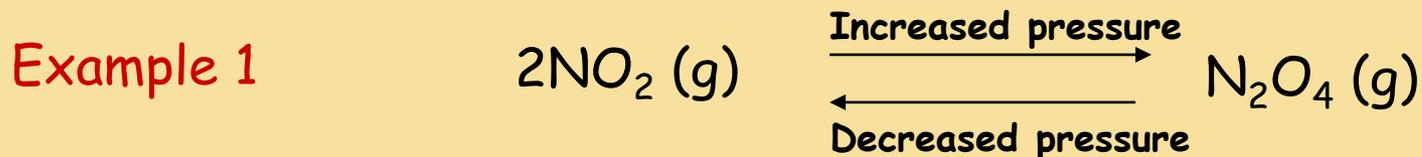
# Le Chatelier's Principle

## 2. Changing Pressure

Pressure **only** effects the equilibrium in reactions which **involve gases where the number of moles of gas change**.

Increasing the pressure will cause a shift to an equilibrium mixture towards a smaller number of gas molecules. i.e. less molecules would mean less overall pressure, in effect reducing the overall pressure.

In the examples below, increasing the pressure in **example 1** will cause the equilibrium to move to the right in an attempt to reduce the overall number of molecules, the opposite is true of **example 2**



# Le Chatelier's Principle

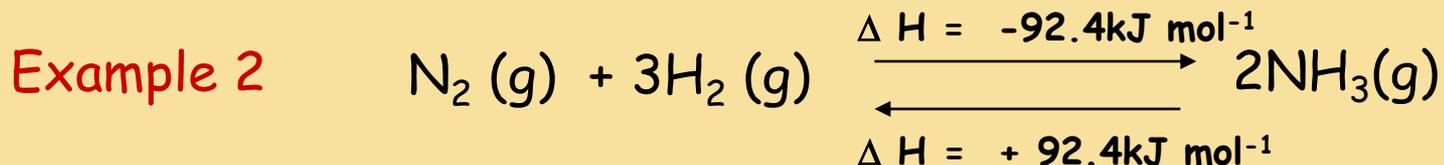
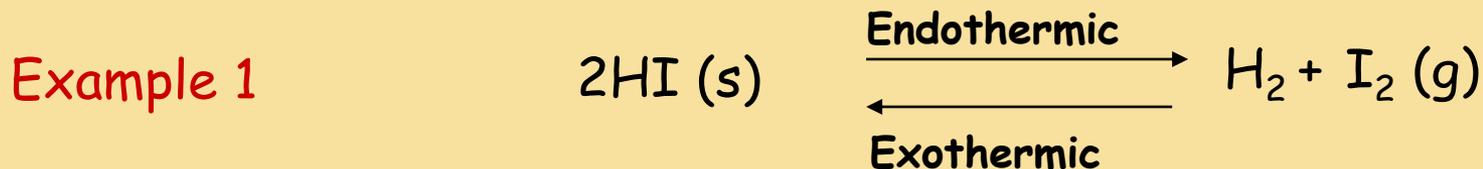
## 3. Changing Temperature

Chemical reactions are either **exothermic** or **endothermic**.

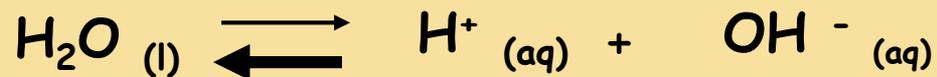
**Reversible reactions are exothermic in one direction and endothermic in the other.**

An increase in temperature shifts the equilibrium position to a mixture which is formed by absorbing thermal energy. i.e. the equilibrium moves in the direction which will remove the added thermal energy.

In **example 1**, if the **temperature is increased** the equilibrium will move to the **right**, as this is endothermic, so removing the increase of thermal energy. The opposite is true in **example 2**.



# Equilibrium, Water and pH



**Covalent water** exists in equilibrium with tiny traces of **ionic water**, with the equilibrium to the **left**. This is true for aqueous solutions as well.

In fact only 1 in every 555 million water molecules dissociates (ionises).

Water can conduct electricity. Even in its pure form, it will conduct electricity very slightly because some ions are free to move.

## pH

This value depends on the **concentration of hydrogen ions** in solution

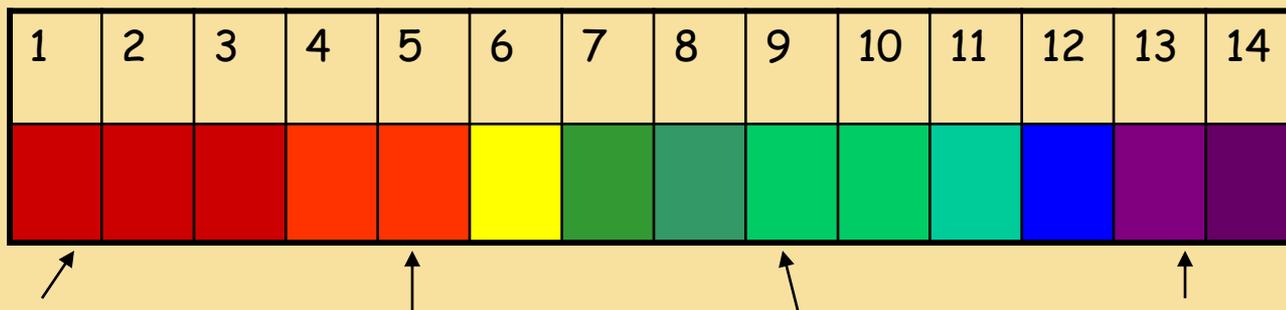
The concentration of  $\text{H}^+$  ions in **pure water** is  $1 \times 10^{-7} \text{ mol l}^{-1}$  a pH of 7. This is true for water at  $25^\circ\text{C}$ .

The pH scale is continuous, going from below 0 to 14



# Acids and Alkalis

pH



Strong acid	Weak acid
Fully dissociated in aqueous solution	Not fully dissociated in aqueous solution

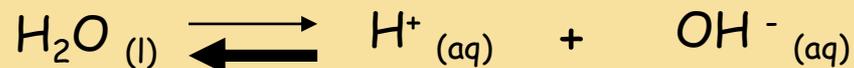
Weak alkali	Strong alkali
Not fully dissociated in aqueous solution	Fully dissociated in aqueous solution

<b>Dilute</b>	<b>Concentrated</b>
A little solute in a large amount of water. e.g. $0.2 \text{ mol l}^{-1}$	A lot of solute in a small amount of water. e.g. $2.0 \text{ mol l}^{-1}$



# Concentration and pH

The pH range, (p comes from the German word Potenz meaning power and H from  $[H^+]$ ) (square brackets indicate concentration), can vary from -1 to 15.



When pure water dissociates one  $H^+$  ion is produced for every  $OH^-$  ion.

So  $[H^+] = [OH^-]$       Since the pH is 7 so  $[H^+] = [OH^-] = 10^{-7} \text{ mol l}^{-1}$

i.e.  $[H^+]_{(aq)} = 10^{-7} \text{ mol l}^{-1}$       and  $[OH^-]_{(aq)} = 10^{-7} \text{ mol l}^{-1}$

The **Ionic Product** for water is the product of the concentration of the hydrogen and hydroxide ions.

$$\begin{aligned} \text{Ionic Product for water} &= [H^+]_{(aq)} \times [OH^-]_{(aq)} = 10^{-7} \times 10^{-7} \\ &= \mathbf{10^{-14} \text{ mol}^2 \text{ l}^{-2}} \end{aligned}$$



# $[OH^-]$ , $[H^+]$ and pH

The table below shows the relationship between  $[OH^-]$ ,  $[H^+]$  and pH .

$[H^+]$ aq mol l <sup>-1</sup>	$[H^+]$ mol l <sup>-1</sup>	pH	$[OH^-]$ aq mol l <sup>-1</sup>	$[OH^-]$ aq mol l <sup>-1</sup>
0.1	$1 \times 10^{-1}$	1	$1 \times 10^{-13}$	
0.001	$1 \times 10^{-3}$	3	$1 \times 10^{-11}$	
0.00001	$1 \times 10^{-5}$	5	$1 \times 10^{-9}$	
0.0000001	$1 \times 10^{-7}$	7	$1 \times 10^{-7}$	0.0000001
	$1 \times 10^{-9}$	9	$1 \times 10^{-5}$	0.00001
	$1 \times 10^{-11}$	11	$1 \times 10^{-3}$	0.001
	$1 \times 10^{-13}$	13	$1 \times 10^{-1}$	0.1

Note the relationship between  $[H^+]$  and the pH value.



# Strong and Weak Acids

**Acids** are substances which **dissociate** in water to form  $H^+$  ions.

**Strong Acids**, e.g.  $HCl$ ,  $H_2SO_4$  and  $HNO_3$ . These are molecular compounds

These acids **dissociate completely**. The acid is strongly ionised.



$H_3O^+$  ion is usually written as  $H^+(aq)$

The relationship between pH and hydrogen ion concentration:

$[H^+](aq)$ mol $l^{-1}$	$[H^+](aq)$ mol $l^{-1}$	pH
10	$1 \times 10^1$	-1
0.001	$1 \times 10^{-3}$	3
0.000001	$1 \times 10^{-6}$	6

0.1 mol  $l^{-1}$  of  $HCl$  would contain 0.1 mol of hydrogen ions ( $H^+(aq)$ ).

This would mean the concentration of hydrogen ions would be  $1 \times 10^{-1}$ .

Its pH would be 1



# Strong and Weak Acids

Weak Acids, e.g.  $\text{CH}_3\text{COOH}$ ,  $\text{HCOOH}$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{SO}_3$

These acids **only partially dissociate**. The acid is only partially ionised.



0.1 mol l<sup>-1</sup> of  $\text{CH}_3\text{COOH}$  has a pH of 3.

This suggests the weak acid has a lower  $[\text{H}^+]$  than 0.1 mol l<sup>-1</sup> of HCl.

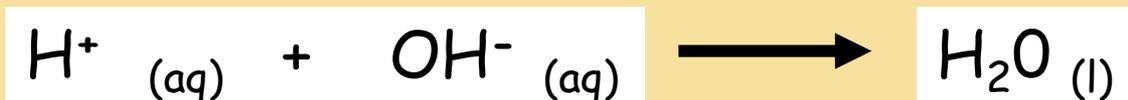
Comparison of strong and weak acids. Consider 0.1 mol l<sup>-1</sup> of:

	HCl (Strong)	$\text{CH}_3\text{COOH}$ (Weak)
pH	1	3
Conductivity	High	Low
Reaction with Mg	Fast	Slow
Reaction with $\text{CaCO}_3$	Fast	Slow



# Strong and Weak Acids

The neutralisation of an acid by an alkali can be represented by:



If you titrate 25 ml of 1.0 mol l<sup>-1</sup> HCl against 1.0 mol l<sup>-1</sup> NaOH, what volume of NaOH would you need?

$$V_{\text{acid}} \times C_{\text{acid}} = V_{\text{alk}} \times C_{\text{alk}} \quad \text{So } 25 \times 1 = 25 \times \text{Vol of NaOH} \quad \text{Ans: 25 ml NaOH}$$

What happens if you use 1.0 mol l<sup>-1</sup> of weak acid instead? **Ans: 25 ml NaOH**

## The reason

As  $\text{OH}^-$  ions are being added to the weak acid,  $\text{H}^+$  ions are being used up. However, as the  $\text{H}^+$  ions are used up, more of the weak acid will dissociate to replace the  $\text{H}^+$  ions that have been used up. This will, in turn, produce more  $\text{H}^+$  ions, which in turn will use up more  $\text{OH}^-$  ions. This will continue until all the molecules of the weak acid have dissociated.



# Stoichiometry of Reactions

Stoichiometry of a reaction means the numerical proportions of the substances involved.



Even though a 1 mol l<sup>-1</sup> NaOH solution has about 250 times the concentration of hydroxide ions as 1 mol l<sup>-1</sup> NH<sub>4</sub>OH, the mass of Iron(III) hydroxide precipitate, in both reactions, is the same.

## The reason

As Fe<sup>3+</sup> ions are added to the weak acid, OH<sup>-</sup> ions are used up. However, as the OH<sup>-</sup> ions are used up, more of the weak base will dissociate producing more OH<sup>-</sup> ions, which in turn will use up more Fe<sup>3+</sup> ions. This will continue until all the molecules of the weak base have dissociated.



# Strong and Weak Bases

**Bases** are substances which can react with  $H^+$  ions (aq) to form water.

**Strong bases** are ionic and **dissociate completely**.



**Weak bases** do not dissociate completely.



Only around 0.4% of the  $NH_4OH$  molecule, dissociates.

Comparison of strong and weak bases, consider  $0.1 \text{ mol l}^{-1}$  of:

	NaOH (strong)	Ammonia (Weak)
pH	13	11-12
Conductivity	High	low





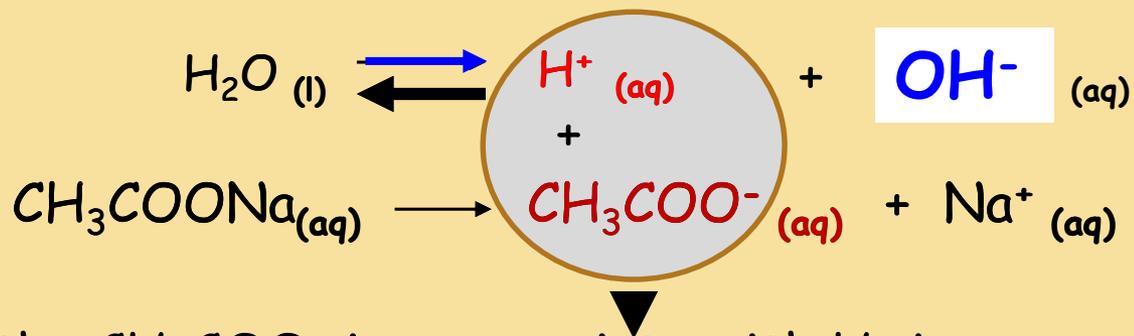
# Aqueous solutions

## Salts solutions

When salts dissolve in water they become fully ionised. Sometimes these ions can disturb the water equilibrium giving an acidic or alkaline solution. This interaction is called **hydrolysis**.

1. **Salts of a weak acid and a strong alkali** gives an **alkaline** solution.  
e.g. soaps

In sodium ethanoate,  $\text{CH}_3\text{COONa}$ , not all the molecules ionise in water, some  $\text{CH}_3\text{COO}^-$  and  $\text{Na}^+$  ions associate with each other.



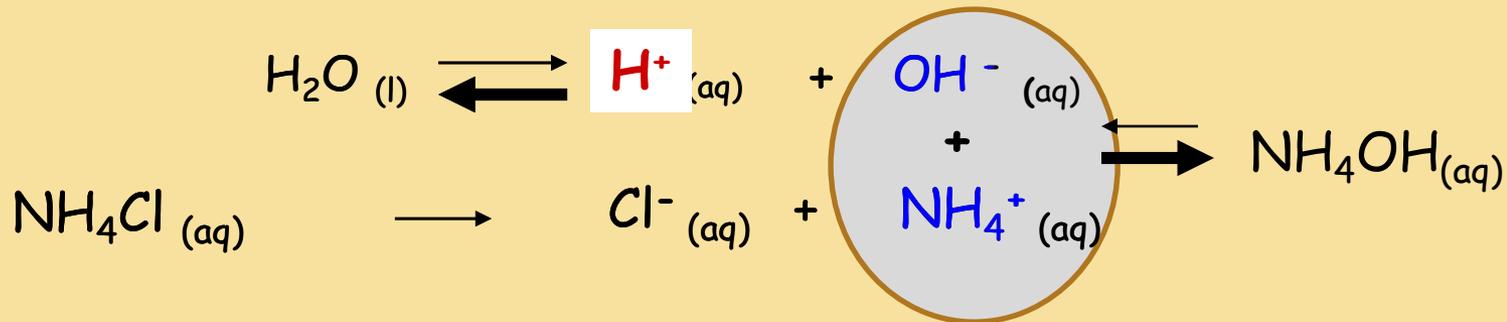
Some of the  $\text{CH}_3\text{COO}^-$  ions associate with  $\text{H}^+$  ions, so removing the  $\text{H}^+$ . This causes more  $\text{H}_2\text{O}$  to dissociate and so an excess of  $\text{OH}^-$  ions results.



# Aqueous solutions

2. Salts of a strong acid and a weak alkali gives an acidic solution.

When ammonium chloride  $\text{NH}_4\text{Cl}$ , is added to water not all of the molecules ionise. Some  $\text{Cl}^-$  and  $\text{NH}_4^+$  ions associate with each other.



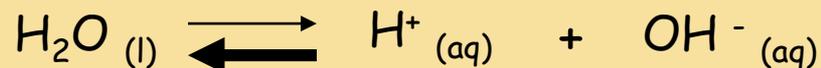
Some of the  $\text{NH}_4^+$  ions associate with  $\text{OH}^-$  ions, so removing them. (remember the position of the equilibrium for ammonium hydroxide solution, is to the left.) This causes more  $\text{H}_2\text{O}$  to dissociate and so an excess of  $\text{H}^+$  ions results.

The  $\text{H}^+$  and  $\text{Cl}^-$  ions have no tendency to join because  $\text{HCl}$  is a strong acid.



# Salts made from a strong acid and a strong base

## Sodium Chloride



Both the sodium ions and the chloride ions will not associate with either the hydrogen or hydroxide ions. Because both HCl and NaOH, being a strong acid and a strong alkali, are completely dissociated into their respective ions.

So the concentration of  $[\text{H}^+]$  and  $[\text{OH}^-]$  ions are unaffected.

For this reason, sodium chloride solution has a pH of 7.

