# 7. Equilibria

All reversible reactions reach an **dynamic equilibrium** state.

Many reactions are reversible
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The term dynamic means both forward and backward reactions are occurring simultaneously

**Two features of Dynamic Equilibrium**

1. **Forward** and **backward** reactions are occurring at **equal rates**.

2. The **concentrations** of reactants and products stays **constant**

We use the expression '**position of equilibrium**' to describe the composition of the equilibrium mixture.

If the position of equilibrium favours the reactants (also described as "towards the left") then the equilibrium mixture will contain mostly reactants.

**Le Chatelier's Principle**

We use Le Chatelier's principle to work out how changing external conditions such as temperature and pressure affect the position of equilibrium

Le Chatelier's principle states that if an external condition is changed the equilibrium will shift to oppose the change (and try to reverse it).

## Effect of Temperature on equilibrium

If temperature is increased the **equilibrium will shift to oppose** this and move in the **endothermic** direction to try and **reduce the temperature** by absorbing heat.

And its reverse

If temperature is decreased the **equilibrium will shift to oppose** this and move in the **exothermic** direction to try and **increase the temperature** by giving out heat.

Typical Exam question: What effect would increasing temperature have on the yield of ammonia?

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = \text{-ve exo}$$

Exam level answer : must include bold points

If temperature is increased the **equilibrium will shift to oppose** this and move in the **endothermic, backwards** direction to try to **decrease temperature**. The position of equilibrium will **shift towards the left,** giving a **lower yield of ammonia**.

Low temperatures may give a higher yield of product but will also result in slow rates of reaction. Often a compromise temperature is used that gives a reasonable yield and rate

## Effect of Pressure on equilibrium

Increasing pressure will cause the equilibrium to shift towards the side with **fewer moles of gas** to **oppose the change** and thereby **reduce the pressure.**

And its reverse

Decreasing pressure will cause the equilibrium to shift towards the side with **more moles of gas** to **oppose the change** and thereby increase the pressure.

If the number of moles of gas is the same on both sides of the equation then changing pressure will have no effect on the position of equilibrium
$$H_2 + Cl_2 \rightleftharpoons 2HCl$$

Typical Exam question: What effect would increasing pressure have on the yield of methanol?

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$$
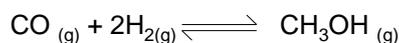
Exam level answer : must include bold points

If pressure is increased the **equilibrium will shift to oppose** this and move towards the side with **fewer moles of gas to try to reduce the pressure** . The position of equilibrium will **shift towards the right** because there are 3 moles of gas on the left but only 1 mole of gas on the right, giving a **higher yield of methanol**.

Increasing pressure may give a higher yield of product and will produce a faster rate. Industrially high pressures are expensive to produce ( **high electrical energy costs for pumping** the gases to make a high pressure) and the **equipment is expensive** (to contain the high pressures)

## Effect of Concentration on equilibrium

$$I_2 + 2OH^- \rightleftharpoons I^- + IO^- + H_2O$$
brown  colourless
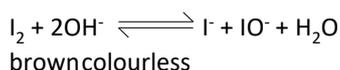
Increasing the concentration OH⁻ ions causes the **equilibrium to shift to oppose** this and move in the **forward** direction **to remove and decrease the concentration of OH⁻ ions**. The position of equilibrium will **shift towards the right,** giving a **higher yield of I⁻ and IO⁻**. ( The colour would change from brown to colourless)

Adding H⁺ ions reacts with the OH⁻ ions and reduces their concentration so the equilibrium shifts back to the left giving brown colour.

## Effect of catalysts on equilibrium

A catalyst has **no effect** on the position of equilibrium, but it will speed up the rate at which the equilibrium is achieved.

It does not effect the position of equilibrium because it speeds up the rates of the forward and backward reactions by the same amount.

## Importance of equilibrium to industrial processes

You should be able to apply the above ideas to given reactions

Common examples

**Haber process**

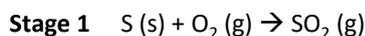$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = \text{-ve exo}$$

T= 450ºC, P= 200 – 1000 atm, catalyst = iron

Low temp gives good yield but slow rate: compromise temp used

High pressure gives good yield and high rate: too high a pressure would lead to too high energy costs for pumps to produce the pressure

**Contact process**

**Stage 1**    $S (s) + O_2 (g) \rightarrow SO_2 (g)$

**Stage 2** $SO_{2\,(g)} + \frac{1}{2} O_{2\,(g)} \rightleftharpoons SO_{3\,(g)}$ ΔH = -98 kJ mol⁻¹

T= 450ºC, P= 1 or 2 atm, catalyst = $V_2O_5$

Low temp gives good yield but slow rate: compromise moderate temp used

High pressure only gives slightly better yield and high rate: too high a pressure would lead to too high energy costs for pumps to produce the pressure

In all cases catalysts speeds up the rate allowing lower temp to be used (and hence lower energy costs) but have no effect on equilibrium

In all cases high pressure leads to **too high energy costs for pumps** to produce the pressure and **too high equipment costs** to have equipment that can withstand high pressures.

**Recycling unreacted reactants** back into the reactor can improve the overall yields of all these processes

Both methanol and ethanol can be used as fuels

# Equilibrium Equations

## Equilibrium constant Kc

For a generalised reaction

$$mA + nB \rightleftharpoons pC + qD$$

m,n,p,q are the stoichiometric balancing numbers

A,B,C,D stand for the chemical formula

Kc = equilibrium constant

$$Kc = \frac{[C]^p\,[D]^q}{[A]^m\,[B]^n}$$

[ ] means the equilibrium concentration

### Example 1

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)}$$

$$Kc = \frac{[NH_{3\,(g)}]^2}{[N_{2\,(g)}]\,[H_{2\,(g)}]^3}$$
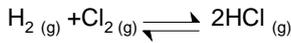
The unit of Kc changes and depends on the equation.

## Working out the unit of Kc

Put the unit of concentration (mol dm$^{-3}$) into the Kc equation

$$Kc = \frac{[NH_{3\,(g)}]^2}{[N_{2\,(g)}]\,[H_{2\,(g)}]^3} \rightarrow \quad Unit = \frac{[mol\ dm^{-3}]^2}{[mol\ dm^{-3}]\,[mol\ dm^{-3}]^3}$$

Cancel out units

$$\rightarrow \quad Unit = \frac{1}{[mol\ dm^{-3}]^2} \rightarrow \quad Unit = [mol\ dm^{-3}]^{-2}$$

$$\downarrow$$

**Unit = mol$^{-2}$ dm$^{+6}$**

### Example 2: writing Kc expression

$$H_{2\,(g)} + Cl_{2\,(g)} \rightleftharpoons 2HCl_{(g)}$$

$$Kc = \frac{[HCl_{(g)}]^2}{[H_{2\,(g)}]\,[Cl_{2\,(g)}]}$$

Working out the unit

$$\rightarrow \quad Unit\ Kc = \frac{[mol\ dm^{-3}]^2}{[mol\ dm^{-3}]\,[mol\ dm^{-3}]} \quad \textbf{= no unit}$$

## Calculating Kc

Most questions first involve having to work out the equilibrium moles and then concentrations of the reactants and products.
Usually the question will give the initial amounts (moles) of the reactants, and some data that will help you work out the equilibrium amounts.
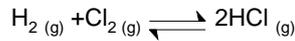
### Calculating the moles at equilibrium

moles of reactant at equilibrium
= initial moles – moles reacted

moles of product at equilibrium
= initial moles + moles formed

### Example 3

For the following equilibrium

$$H_{2\,(g)} + Cl_{2\,(g)} \rightleftharpoons 2HCl_{(g)}$$

In a container of volume 600cm$^3$ there were initially 0.5mol of $H_2$ and 0.6 mol of $Cl_2$.
At equilibrium there were 0.2 moles of HCl. Calculate Kc

|  | $H_2$ | $Cl_2$ | HCl |
|---|---|---|---|
| Initial moles | 0.5 | 0.6 | 0 |
| Equilibrium moles |  |  | 0.2 |

It is often useful to put the mole data in a table.

Using the balanced equation if 0.2 moles of HCl has been formed it must have used up 0.1 of $Cl_2$ and 0.1 moles of $H_2$ (as 1:2 ratio)

Work out the moles at equilibrium for the reactants

moles of reactant at equilibrium = initial moles – moles reacted

moles of hydrogen at equilibrium = 0.5 – 0.1 = 0.4    moles of chlorine at equilibrium = 0.6 – 0.1 = **0.5**

|  | $H_2$ | $Cl_2$ | HCl |
|---|---|---|---|
| Initial moles | 0.5 | 0.6 | 0 |
| Equilibrium moles | 0.4 | 0.5 | 0.2 |
| Equilibrium concentration (M) | 0.4/0.6 =0.67 | 0.5/0.6 =0.83 | 0.2/0.6 =0.33 |

If the Kc has no unit then there are equal numbers of reactants and products. In this case you do not have to divide by volume to work out concentration and equilibrium moles could be put straight into the kc expression

Work out the equilibrium concentrations

conc = moles/ vol (in dm$^3$)

Finally put concentrations into Kc expression

$$Kc = \frac{[HCl_{(g)}]^2}{[H_{2\,(g)}]\,[Cl_{2\,(g)}]}$$

$$Kc = \frac{0.33^2}{0.67 \times 0.83} \quad \textbf{= 0.196 no unit}$$

Example 4

For the following equilibrium

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2 NH_3 (g)$$

Initially there were 1.5 moles of $N_2$ and 4 mole of $H_2$ in a 1.5 dm³ container. At equilibrium 30% of the Nitrogen had reacted. Calculate Kc

|  | $N_2$ | $H_2$ | $NH_3$ |
|---|---|---|---|
| Initial moles | 1.5 | 4.0 | 0 |
| Equilibrium moles |  |  |  |

30% of the nitrogen had reacted = 0.3 x1.5 = 0.45 moles reacted. Using the balanced equation 3 x 0.45 moles of $H_2$ must have reacted and 2x 0.45 moles of $NH_3$ must have formed

Work out the moles at equilibrium for the reactants and products

moles of reactant at equilibrium = initial moles – moles reacted

moles of nitrogen at equilibrium = 1.5 – 0.45 = 1.05        moles of hydrogen at equilibrium =4.0 – 0.45 x3 = **2.65**

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium = 0 + (0.45 x 2) = 0.9

|  | $N_2$ | $H_2$ | $NH_3$ |
|---|---|---|---|
| Initial moles | 1.5 | 4.0 | 0 |
| Equilibrium moles | 1.05 | 2.65 | 0.9 |
| Equilibrium concentration (M) | 1.05/1.5 =0.7 | 2.65/1.5 =1.77 | 0.9/1.5 =0.6 |

Work out the equilibrium concentrations

conc = moles/ vol (in dm³)

Finally put concentrations into Kc expression

$$Kc= \frac{[NH_{3\,(g)}]^2}{[N_2 (g)\,][H_2 (g)]^3}$$

$$Kc = \frac{0.6^2}{0.7 \times 1.77^3} = \textbf{0.0927 mol}^{-2}\,\textbf{dm}^{+6}$$

## Effect of changing conditions on value of Kc

The larger the Kc the greater the amount of products.
If Kc is small we say the equilibrium favours the reactants

**Kc only changes with temperature**.
It does not change if pressure or concentration is altered.
A catalyst also has no effect on Kc

## Effect of Temperature on position of equilibrium and Kc

Both the **position of equilibrium** and the value of **Kc will change** it temperature is altered

In this equilibrium which is exothermic in the forward direction

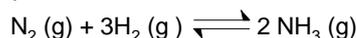$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2 NH_3 (g)$$
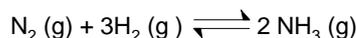
If temperature is increased the reaction will shift to oppose the change and move in the backwards endothermic direction. The position of equilibrium shifts left. The value of Kc gets smaller as there are fewer products.

## Effect of Pressure on position of equilibrium and Kc

The position of equilibrium will change it pressure is altered but the value of **Kc stays constant** as Kc only varies with temperature

In this equilibrium which has fewer moles of gas on the product side

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2 NH_3 (g)$$

If pressure is increased the reaction will shift to oppose the change and move in the forward direction to the side with fewer moles of gas. The position of equilibrium shifts right. The value of Kc stays the same though as only temperature changes the value of Kc.

Catalysts have **no effect** on the value of Kc or the position of equilibrium as they speed up both forward and backward rates by the same amount.

# Calculating the amounts of the equilibrium mixture from Kc

Using algebra it is possible to work out the amounts of each component in an equilibrium mixture using the value of Kc

Example 5

For the following equilibrium $\qquad$ $H_{2 (g)} + Br_{2 (l)} \rightleftharpoons 2HBr_{(g)}$

If 0.200 mol of $H_2$ and 0.200 mol of $Br_2$ are mixed and allowed to reach equilibrium. If Kc = 0.210 what are the equilibrium amounts of each substance.

$$Kc = \frac{[HBr_{(g)}]^2}{[H_{2\ (g)}][Br_{2\ (g)}]}$$

Make x = moles of $H_2$ that have reacted at equilibrium
V = volume of container

$$0.21 = \frac{(2x/V)^2}{(0.2-x)/V \cdot (0.2-x)/V}$$

This reaction is equimolar (same number of moles of reactant as products) so it is possible to cancel out the volume V

$$0.21 = \frac{(2x)^2}{(0.2-x) \cdot (0.2-x)}$$

$$0.21 = \frac{(2x)^2}{(0.2-x)^2}$$

Square root both sides

$$0.21 = \frac{2x}{0.2-x}$$

Rearrange to give x

0.458(0.2-x) = 2x

0.0917 - 0.458x = 2x

0.0917 = 2x + 0.458x

This example has been carefully set up to avoid the formation of a quadratic equation. It is not on the A-level syllabus to solve quadratic equations.

x = 0.0917/2.458
x = 0.0373

So at equilibrium
Moles of $H_2$ = 0.2000- 0.0373
$\qquad$ = 0.163 mol

Moles of $Br_2$ = 0.2000- 0.0373
$\qquad$ = 0.163mol

Moles of HBr = 2x 0.0373
$\qquad$ = 0.0746mol

## Partial Pressures and Kp

If a reaction contains gases an alternative equilibrium expression can be set up using the partial pressures of the gases instead of concentrations

### Partial Pressure

The partial pressure of a gas in a mixture is the pressure that the gas would have if it alone occupied the volume occupied by the whole mixture.

If a mixture of gases contains 3 different gases then the total pressure will equal the 3 partial pressure added together

$$P = p_1 + p_2 + p_3$$

partial pressure = mole fraction x total pressure
of gas 1                                              of gas 1

$$p_1 = x_1 \, P$$

### mole fraction

$$\text{mole fraction} = \frac{\text{number of moles of a gas}}{\text{total number of moles of all gases}}$$

For a 3 part mixture

$$x_1 = \frac{y1}{y_1 + y_2 + y_3}$$

**Example 6 :** A mixture contains 0.2 moles $N_2$, 0.5 moles $O_2$ and 1.2 moles of $CO_2$. If the total pressure is 3kPa. What are the partial pressures of the 3 gases?

Total moles of gas = 0.5 + 1.2 + 0.2
= 1.9

| mole fraction of $N_2$ | = 0.2/1.9 =0.105 | mole fraction of $O_2$ | = 0.5/1.9 =0.263 | mole fraction of $CO_2$ | = 1.2/1.9 =0.632 |

| Partial pressure of $N_2$ | =0.105x 3 =0.315 | Partial pressure of $O_2$ | = 0.263 x 3 =0.789 | Partial pressure of $CO_2$ | = 0.632 x 3 =1.896 |

### Writing an expression for $K_p$

$$N_2 \, (g) + 3H_2 \, (g) \rightleftharpoons 2 NH_3 \, (g)$$

$$Kp = \frac{p^2 NH_3}{p \, N_2 \; p^3 H_2}$$

$p$ means the partial pressure of that gas

Kp = equilibrium constant

Only include gases in the $K_p$ expression. Ignore solids, liquids, and aqueous substances.

### Working out the unit of Kp

Put the unit of pressure(kPa) into the Kp equation

$$Kp = \frac{p^2 NH_{3\,(g)}}{p N_{2\,(g)} \; p^3 H_{2\,(g)}}$$

Cancel out units

$$\text{Unit} = \frac{kPa^2}{kPa \; kPa^3}$$

$$\text{Unit} = \frac{1}{kPa^2}$$

$$\text{Unit} = kPa^{-2}$$

However, if the equation is written the other way round, the value of Kp will be the inverse of above and the units will be $kPa^2$.
It is important therefore to write an equation when quoting values of Kp.

**Example 7**

For the following equilibrium $N_2$ (g) + 3$H_2$ (g) $\rightleftharpoons$ 2 $NH_3$ (g)

1 mole of $N_2$ and 3 moles of $H_2$ are added together and the mixture is allowed to reach equilibrium. At equilibrium 20% of the $N_2$ has reacted. If the total pressure is 2kPa what is the value of Kp?

|  | $N_2$ | $H_2$ | $NH_3$ |
|---|---|---|---|
| Initial moles | 1.0 | 3.0 | 0 |
| Equilibrium moles |  |  |  |

20% of the nitrogen had reacted = 0.2 x1.0 = 0.2 moles reacted. Using the balanced equation 3 x 0.2 moles of $H_2$ must have reacted and 2x 0.2 moles of $NH_3$ must have formed

Work out the moles at equilibrium for the reactants and products

moles of reactant at equilibrium = initial moles – moles reacted

moles of nitrogen at equilibrium = 1.0 – 0.2 = 0.8      moles of hydrogen at equilibrium =3.0 – 0.20 x3 = **2.40**

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium = 0 + (0.2 x 2) = 0.4

|  | $N_2$ | $H_2$ | $NH_3$ |
|---|---|---|---|
| Initial moles | 1.0 | 3.0 | 0 |
| Equilibrium moles | 0.80 | 2.40 | 0.40 |
| Mole fractions | 0.8/3.6 =0.222 | 2.40/3.6 =0.667 | 0.40/3.6 =0.111 |
| Partial pressure | 0.222 x2 = 0.444 | 0.667 x2 =1.33 | 0.111 x2 = 0.222 |

Finally put concentrations into Kp expression

$$Kp= \frac{p^2 NH_{3\ (g)}}{pN_{2\ (g)}\ p^3H_{2\ (g)}}$$

$$Kp = \frac{0.222^2}{0.444 \times 1.33^3} = 0.0469\ kPa^{-2}$$

**Heterogeneous equilibria for Kp**

Kp expressions only contain gaseous substances. Any substance with another state is left out

$CaCO_{3\ (s)}$ $\rightleftharpoons$ $CaO_{(s)}$ + $CO_{2\ (g)}$

$Kp = p\ CO_2$

Unit kPa

## Effect of changing conditions on value of Kc or Kp

The larger the Kc the greater the amount of products.
If Kc is small we say the equilibrium favours the reactants

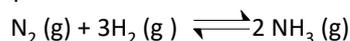> **Kc and Kp only change with temperature**.
> It does not change if pressure or concentration is altered.
> A catalyst also has no effect on Kc or Kp

## Effect of Temperature on position of equilibrium and Kc

> Both the **position of equilibrium** and the value of **Kc or Kp will change** it temperature is altered

> In this equilibrium which is exothermic in the forward direction
>
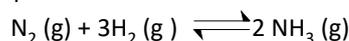> $$N_2 (g) + 3H_2 (g) \rightleftharpoons 2 NH_3 (g)$$
>
> If temperature is increased the reaction will shift to oppose the change and move in the backwards endothermic direction. The position of equilibrium shifts left. The value of Kc gets smaller as there are fewer products.

## Effect of Pressure on position of equilibrium and Kp

> The position of equilibrium will change it pressure is altered but the value of **Kp stays constant** as Kp only varies with temperature

> In this equilibrium which has fewer moles of gas on the product side
>
> $$N_2 (g) + 3H_2 (g) \rightleftharpoons 2 NH_3 (g)$$
>
> If pressure is increased the reaction will shift to oppose the change and move in the forward direction to the side with fewer moles of gas. The position of equilibrium shifts right. The value of Kp stays the same though as only temperature changes the value of Kp.

> Increasing pressure does not change $K$p.
> The increased pressure increases the pressure terms on bottom of $K$p expression more than the top. The system is now no longer in equilibrium so the equilibrium shifts to the right increasing mole fractions of products and decreases the mole fractions of reactants. The top of $K$p expression therefore increases and the bottom decreases until the original value of $K$p is restored

$$Kp = \frac{p^2 NH_3}{p\,N_2\, p^3 H_2}$$

$$Kp = \frac{x^2 NH_3 . P^2}{x\,N_2.P\ x^3 H_2.P^3}$$

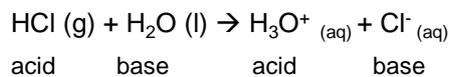$$Kp = \frac{x^2 NH_3 . P^2}{x\,N_2\ x^3 H_2.\ P^4}$$

Where P is total pressure and x mole fraction

## Ionic Equilibria

### Bronsted-Lowry Definition of acid Base behaviour

A **Bronsted-Lowry acid** is defined as a substance that can **donate a proton**.
A **Bronsted-Lowry base** is defined as a substance that can **accept a proton**.

$HCl$ (g) + $H_2O$ (l) → $H_3O^+$ (aq) + $Cl^-$ (aq)

acid        base        acid        base

Each acid is linked to a conjugate base on the other side of the equation.

### Calculating pH

**pH  = - log [H$^+$]**

Where [H$^+$] is the concentration of hydrogen ions in the solution.

## Calculating pH of strong acids

Strong acids **completely dissociate**

The concentration of hydrogen ions in a monoprotic strong acid will be the same as the concentration of the acid.

For HCl and $HNO_3$ the [H$^+$(aq)] will be the same as the original concentration of the acid.

For 0.1M HCl the pH will be –log[0.1] =1.00

Always give pH values to **2d.p**. In the exam

### Finding [H$^+$] from pH

**[H$^+$]  =  1 x 10$^{-pH}$**

On most calculators this is done by pressing

Inv (or 2$^{nd}$ function)→ log → - number(pH)

Example 8
What is the concentration of HCl with a pH of 1.35?
[H$^+$]  =  1 x 10$^{-1.35}$ = 0.045M

## Ionic Product for water

In all aqueous solutions and pure water the following equilibrium occurs: $H_2O$ (l) ⇌ H$^+$ (aq) + OH$^-$ (aq)

This equilibrium has the following equilibrium expression

$$Kc= \frac{[H^+_{(aq)}][OH^-_{(aq)}]}{[H_2O(l)]}$$

Rearrange to

Kc x [$H_2O$ (l)]  = [H$^+$ (aq)][OH$^-$ (aq)]

Because [$H_2O$ (l)] is much bigger than the concentrations of the ions, we assume its value is constant and make a new constant Kw

**Kw  = [H$^+$ (aq) ][OH$^-$ (aq) ]**

Learn this expression

At 25$^o$C  the value of Kw for all aqueous solutions is 1x10$^{-14}$ mol$^2$dm$^{-6}$

The Kw expression can be used to calculate [H$^+$ (aq)] ions if we know the [OH$^-$ (aq)] ions and vice versa.

### Finding pH of pure water

Pure water/ neutral solutions are **neutral** because the **[H$^+$ (aq) ] = [OH$^-$(aq)]**
Using Kw = [H$^+$ (aq) ][OH$^-$ (aq) ] then when neutral  Kw = [H$^+$ (aq) ]$^2$
and  [H$^+$(aq) ] = √Kw
At 25$^o$C [H$^+$(aq) ] =  √1x10$^{-14}$ = 1x10$^{-7}$ so pH = 7

Example 9 : Calculate the pH of  water at 50$^o$C given that $K_w$ = 5.476 x 10$^{-14}$ mol$^2$ dm$^{-6}$ at 50$^o$C
[H$^+$(aq) ] =  √Kw =  √5.476 x 10$^{-14}$ =2.34 x 10$^{-7}$ mol dm$^{-3}$
pH = - log 2.34 x 10$^{-7}$ = **6.6**
It is still neutral though as [H$^+$ (aq) ] = [OH$^-$ (aq)]

At different temperatures to 25$^o$C the pH of pure water changes. Le Chatelier's principle can predict the change.  The dissociation of water is endothermic so increasing the temperature would push the equilibrium to the right giving a bigger concentration of H$^+$ ions and a lower pH.

## Calculating pH of a Strong Base

For bases we are normally given the concentration of the hydroxide ion.

To work out the pH we need to work out $[H^+(aq)]$ using the Kw expression.

Strong bases completely dissociate into their ions.
$NaOH \rightarrow Na^+ + OH^-$

Example 10: What is the pH of the strong base 0.1M NaOH
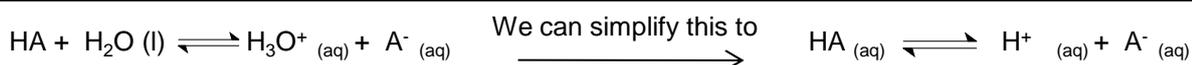
Assume complete dissociation.

$Kw = [H^{+ (aq)}][OH^{- (aq)}] = 1 \times 10^{-14}$

$[H^+(aq)] = Kw / [OH^{- (aq)}] = 1 \times 10^{-14} / 0.1 = 1 \times 10^{-13}$ M

$pH = -\log[1 \times 10^{-13}] = \textbf{13.00}$

## Weak Acids

Weak acids only **slightly dissociate** when dissolved in water, giving an equilibrium mixture.
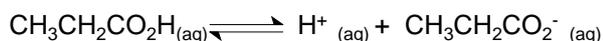
$HA + H_2O\ (l) \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$    We can simplify this to    $HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$

**Weak acids dissociation expression**

$$Ka = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA\ (aq)]}$$

The $K_a$ for ethanoic acid is $1.7 \times 10^{-5}$ mol dm$^{-3}$.

The larger ka the stronger the acid.

**Example 11** Write an equation for dissociation of propanoic acid and its ka expression

$$CH_3CH_2CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CH_2CO_2^-_{(aq)}$$

$$Ka = \frac{[H^+_{(aq)}][CH_3CH_2CO_2^-_{(aq)}]}{[CH_3CH_2CO_2H_{(aq)}]}$$

**pKa**
Sometimes Ka values are quoted as pKa values
$pKa = -\log Ka$   so $Ka = 10^{-pKa}$

## Calculating pH of a Weak Acid

To make the calculation easier two assumptions are made to simplify the Ka expression:

1) $[H^+_{(aq)}]_{eqm} = [A^-_{(aq)}]_{eqm}$ because they have dissociated according to a 1:1 ratio.

2) As the amount of dissociation is small we assume that the initial concentration of the undissociated acid has remained constant.
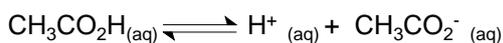
So $[HA_{(aq)}]_{eqm} = [HA_{(aq)}]_{initial}$

$$Ka = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA\ (aq)]}$$

Simplifies to $\downarrow$

$$Ka = \frac{[H^+_{(aq)}]^2}{[HA_{(aq)}]_{initial}}$$

**Example 12** What is the pH of a solution of 0.01M ethanoic acid (ka is $1.7 \times 10^{-5}$ mol dm$^{-3}$)?

$$CH_3CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CO_2^-_{(aq)}$$

$$Ka = \frac{[H^+_{(aq)}][CH_3CO_2^-_{(aq)}]}{[CH_3CO_2H_{(aq)}]} \longrightarrow Ka = \frac{[H^+_{(aq)}]^2}{[CH_3CO_2H_{(aq)}]_{initial}} \rightarrow 1.7 \times 10^{-5} = \frac{[H^+_{(aq)}]^2}{0.01}$$

$[H^+_{(aq)}]^2 = 1.7 \times 10^{-5} \times 0.01$

$[H^+_{(aq)}] = \sqrt{1.7 \times 10^{-7}} = 4.12 \times 10^{-4}$

$pH = -\log[H^+] = -\log(4.12 \times 10^{-4})$

$pH = 3.38$

**Example 13** What is the concentration of propanoic acid with a pH of 3.52 (ka is $1.35 \times 10^{-5}$ mol dm$^{-3}$)?

$$CH_3CH_2CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CH_2CO_2^-_{(aq)}$$

$[H^+] = 1 \times 10^{-3.52} = 0.000302$M

$$Ka = \frac{[H^+_{(aq)}][CH_3CH_2CO_2^-_{(aq)}]}{[CH_3CH_2CO_2H_{(aq)}]} \longrightarrow Ka = \frac{[H^+_{(aq)}]^2}{[CH_3CH_2CO_2H_{(aq)}]_{initial}} \rightarrow 1.35 \times 10^{-5} = \frac{[0.000302]^2}{[CH_3CH_2CO_2H_{(aq)}]_{initial}}$$
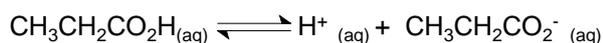
$[CH_3CH_2CO_2H_{(aq)}] = 9.12 \times 10^{-8} / 1.35 \times 10^{-5}$    $[CH_3CH_2CO_2H_{(aq)}] = 6.75 \times 10^{-3}$ M

## pH Calculations involving Neutralisation Reactions

These can be quite complex calculations working out the pH of a partially neutralised acid or the pH of the solution if too much alkali has been added and has gone past neutralisation. The method differs if the acid is strong or weak for the partially neutralised case.

### Strong Acid and Strong Base Neutralisations

Work out moles of original acid
Work out moles of base added
Work out which one is in excess

If excess acid →

Work out new concentration of excess $H^+$ ions
$[H^+] = \dfrac{\text{moles excess } H^+}{\text{total volume (dm}^3)}$

$pH = -\log [H^+]$

Total volume = vol of acid + vol of base added

If excess alkali →

Work out new concentration of excess $OH^-$ ions
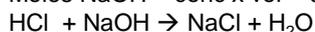$[OH^-] = \dfrac{\text{moles excess } OH^-}{\text{total volume (dm}^3)}$

$[H^+] = K_w / [OH^-]$

$pH = -\log [H^+]$

Total volume = vol of acid + vol of base added

**Example 14** 15cm$^3$ of 0.5M HCl is reacted with 35cm$^3$ of 0.55M NaOH. What will be the pH of the resulting mixture?

Moles HCl = conc x vol = 0.5 x 0.015 = 0.0075mol
Moles NaOH = conc x vol = 0.55 x 0.035 = 0.01925
HCl + NaOH → NaCl + $H_2O$
Moles of NaOH in excess = 0.01925 – 0.0075= 0.01175 (as 1:1 ratio)
$[OH^-] = \dfrac{\text{moles excess } OH^-}{\text{total volume (dm}^3)}$

= 0.01175/ 0.05 = 0.235M
$[H^+] = K_w / [OH^-]$
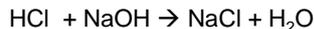= 1x10$^{-14}$ / 0.235 = 4.25x10$^{-14}$
$pH = -\log [H^+]$
= -log 4.25x10$^{-14}$
= 13.37

**Example 15** 45cm$^3$ of 1M HCl is reacted with 30cm$^3$ of 0.65M NaOH. What will be the pH of the resulting mixture?

Moles HCl = conc x vol = 1 x 0.045 = 0.045mol
Moles NaOH = conc x vol = 0.65 x 0.030 = 0.0195
HCl + NaOH → NaCl + $H_2O$
Moles of HCl in excess = 0.045-0.0195 = 0.0255 (as 1:1 ratio)
$[H^+] = \dfrac{\text{moles excess } H^+}{\text{total volume (dm}^3)}$

= 0.0255/ 0.075 = 0.34M
$pH = -\log [H^+]$
= -log 0.34
= 0.47

### Weak Acid and Strong Base Neutralisations

Work out moles of original acid
Work out moles of base added
Work out which one is in excess

If excess acid →

Work out new concentration of excess HA
$[HA] = \dfrac{\text{initial moles HA} - \text{moles } OH^-}{\text{total volume (dm}^3)}$

Work out concentration of salt formed $[A^-]$
$[A^-] = \dfrac{\text{moles } OH^- \text{ added}}{\text{total volume (dm}^3)}$
Rearrange ka = $\dfrac{[H^+][A^-]}{[HA]}$ to get $[H^+]$

$pH = -\log [H^+]$

If excess alkali use the same method with excess alkali and strong acid above

**Example 16** 55cm$^3$ of 0.5M $CH_3CO_2H$ is reacted with 25cm$^3$ of 0.35M NaOH. What will be the pH of the resulting mixture?

$CH_3CO_2H + NaOH → CH_3CO_2Na + H_2O$

ka is 1.7 x 10$^{-5}$ mol dm$^{-3}$

Moles $CH_3CO_2H$ = conc x vol =0.5x 0.055 = 0.0275mol
Moles NaOH = conc x vol = 0.35 x 0.025 = 0.00875

Moles of $CH_3CO_2H$ in excess = 0.0275-0.00875 = 0.01875 (as 1:1 ratio)

$[CH_3CO_2H] = \dfrac{\text{moles excess } CH_3CO_2H}{\text{total volume (dm}^3)}$

= 0.01875/ 0.08 = 0.234M

$[CH_3CO_2^-] = \dfrac{\text{moles } OH^- \text{ added}}{\text{total volume (dm}^3)}$

= 0.00875/ 0.08 = 0.109M

$ka = \dfrac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$

$[H^+] = ka \times [CH_3CO_2H] / [CH_3CO_2^-]$
= 1.7 x 10$^{-5}$ x 0.234 / 0.109
= 3.64 x 10$^{-5}$

$pH = -\log [H^+]$
= -log 3.64 x 10$^{-5}$
= 4.44

## Working out pH of a weak acid at half equivalence

When a weak acid has been reacted **with exactly half the neutralisation volume of alkali**, the above calculation can be simplified considerably.

$$ka = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$

At half neutralisation we can make the assumption that $[HA] = [A^-]$

So $[H^+_{(aq)}] = ka$

And **pH = pka**

**Example 17**

What is the pH of the resulting solution when **25cm³ of 0.1M** NaOH is added to **50cm³ of 0.1M** $CH_3COOH$ (ka $1.7 \times 10^{-5}$)

From the volumes and concentrations spot it is half neutralisation (or calculate)

**pH = pka = -log (** $1.7 \times 10^{-5}$ ) = 4.77

## Diluting an acid or alkali

### pH of diluted strong acid

$$[H^+] = [H^+]_{old} \times \frac{old\ volume}{new\ volume}$$

$$pH = -\log[H^+]$$

### pH of diluted base

$$[OH^-] = [OH^-]_{old} \times \frac{old\ volume}{new\ volume}$$

$$[H^+] = \frac{K_w}{[OH^-]}$$

$$pH = -\log[H^+]$$

**Example 18** Calculate the new pH when 50.0 cm³ of 0.150 mol dm⁻³ HCl is mixed with 500 cm³ of water.

$$[H^+] = [H^+]_{old} \times \frac{old\ volume}{new\ volume}$$

$$[H^+_{(aq)}] = 0.150 \times \frac{0.05}{0.55}$$

$$[H^+_{(aq)}] = 0.0136$$

$$pH = -\log[H^+]$$
$$= -\log 0.0136$$
$$= 1.87$$

## Buffer Solutions

A Buffer solution is one where the pH does **not change significantly** if **small** amounts of acid or alkali are added to it.

An **acidic** buffer solution is made from a **weak acid** and a **salt of that weak acid** ( made from reacting the weak acid with a strong base).

Example : ethanoic acid and sodium ethanoate

$$CH_3CO_2H_{(aq)} \quad and \quad CH_3CO_2^-Na^+$$

A **basic** buffer solution is made from a weak base and a salt of that weak base ( made from reacting the weak base with a strong acid).

Example :ammonia and ammonium chloride $NH_3$ and $NH_4^+Cl^-$

### How Buffer solutions work

In an ethanoic acid buffer

$$CH_3CO_2H_{(aq)} \rightleftharpoons CH_3CO_2^-_{(aq)} + H^+_{(aq)}$$

Acid                    conjugate base

In a buffer solution there is a much higher concentration of the salt $CH_3CO_2^-$ ion than in the pure acid.

The buffer contains a reservoir of HA **and** A⁻ ions

If **small amounts of acid is added** to the buffer: Then the above equilibrium will shift to the left removing nearly all the H⁺ ions added,

$$CH_3CO_2^-_{(aq)} + H^+_{(aq)} \rightarrow CH_3CO_2H_{(aq)}$$

As there is a large concentration of the salt ion in the buffer the ratio $[CH_3CO_2H]/[CH_3CO_2^-]$ stays almost constant, so the pH stays fairly constant.

$$[H^+_{(aq)}] = Ka\frac{[CH_3CO_2H_{(aq)}]}{[CH_3CO_2^-_{(aq)}]}$$

If **small amounts of alkali is added** to the buffer. The OH⁻ ions will react with H⁺ ions to form water.

$$H^+ + OH^- \rightarrow H_2O$$

The Equilibrium will then shift to the right to produce more H⁺ ions.

$$CH_3CO_2H_{(aq)} \rightleftharpoons CH_3CO_2^-_{(aq)} + H^+_{(aq)}$$

Some ethanoic acid molecules are changed to ethanoate ions but as there is a large concentration of the salt ion in the buffer the ratio $[CH_3CO_2H]/[CH_3CO_2^-]$ stays almost constant, so the pH stays fairly constant.

Learn these explanations carefully and be able to write the equilibrium to illustrate your answer.

## Calculating the pH of Buffer Solutions

We still use the weak acids dissociation expression

$$Ka= \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]}$$

But here we assume the $[A^-]$ concentration is due to the added salt only

Normally we rearrange to →

$$[H^+_{(aq)}] = Ka\ \frac{[HA_{(aq)}]}{[A^-_{(aq)}]}$$

The salt content can be added in several ways: a salt solution could be added to the acid or some solid salt added. A buffer can also be made by partially neutralising a weak acid with alkali and therefore producing salt.

We also assume the Initial concentration of the acid has remained constant, because amount that has dissociated or reacted is small.

---

**Example 19:** making a buffer by adding a salt solution

What would be the pH of a buffer made from $45cm^3$ of 0.1M ethanoic acid and $50cm^3$ of 0.15 M sodium ethanoate (Ka = $1.7 \times 10^{-5}$) ?

Work out the moles of both solutions
Moles ethanoic = conc x vol = 0.1 x 0.045 = 0.0045mol
Moles sodium ethanoate = conc x vol = 0.15 x 0.050 = 0.0075

We can enter moles of acid and salt straight into the equation as they both have the same new final volume

$$[H^+_{(aq)}] = Ka\ \frac{[HA_{(aq)}]}{[A^-_{(aq)}]}$$

$$[H^+_{(aq)}] = 1.7 \times 10^{-5} \times \frac{0.0045}{0.0075} \quad \Rightarrow \quad [H^+_{(aq)}] = 1.02 \times 10^{-5}$$

pH = − log [H$^+$]
= -log $1.02 \times 10^{-5}$
= 4.99

---

**Example 20** : making a buffer by adding a solid salt

A buffer solution is made by adding 1.1g of sodium ethanoate into 100 cm$^3$ of 0.4M ethanoic acid. What is its pH? Ka = $1.7 \times 10^{-5}$

Work out the moles of both solutions
Moles ethanoic = conc x vol = 0.4 x 0.1 = 0.04mol
Moles sodium ethanoate = mass/Mr= 1.1/82 = 0.0134

We can enter moles of acid and salt straight into the equation as they both have the same new final volume

$$[H^+_{(aq)}] = Ka\ \frac{[HA_{(aq)}]}{[A^-_{(aq)}]}$$

$$[H^+_{(aq)}] = 1.7 \times 10^{-5} \times \frac{0.04}{0.0134} \quad \Rightarrow \quad [H^+_{(aq)}] = 5.07 \times 10^{-5}$$

pH = − log [H$^+$]
= -log $5.07 \times 10^{-5}$
= 4.29

---

If a buffer is made by adding sodium hydroxide to partially neutralise a weak acid then follow the method below

---

**Example 21**  $55cm^3$ of 0.5M $CH_3CO_2H$ is reacted with $25cm^3$ of 0.35M NaOH. What will be the pH of the resulting buffer solution?

$$CH_3CO_2H + NaOH \rightarrow CH_3CO_2Na + H_2O$$

Moles $CH_3CO_2H$ = conc x vol =0.5x 0.055 = 0.0275mol
Moles NaOH = conc x vol = 0.35 x 0.025 = 0.00875
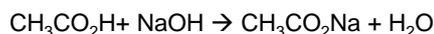
ka is $1.7 \times 10^{-5}$ mol dm$^{-3}$

Moles of $CH_3CO_2H$ in excess = 0.0275-0.00875 = 0.01875 (as 1:1 ratio)

$$[CH_3CO_2H] = \frac{\text{moles excess } CH_3CO_2H}{\text{total volume (dm}^3)}$$

= 0.01875/ 0.08 = 0.234M

$$[CH_3CO_2^-] = \frac{\text{moles OH}^-\ \text{added}}{\text{total volume (dm}^3)}$$

= 0.00875/ 0.08 = 0.109M

$$ka = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$

$[H^+]$ = ka x[ $CH_3CO_2H$ ] / [$CH_3CO_2^-$]
= $1.7 \times 10^{-5}$ x 0.234 / 0.109
= $3.64 \times 10^{-5}$

pH = − log [H$^+$]
= -log $3.64 \times 10^{-5}$
= 4.44

**Calculating change in pH of buffer on addition of small amount of acid or alkali**

If a small amount of alkali is added to a buffer then the moles of the buffer acid would reduce by the number of moles of alkali added and the moles of salt would increase by the same amount so a new calculation of pH can be done with the new values.

$$CH_3CO_2H_{(aq)} + OH^- \rightarrow CH_3CO_2^-{}_{(aq)} + H_2O_{(l)}$$

If a small amount of acid is added to a buffer then the moles of the buffer salt would reduce by the number of moles of acid added and the moles of buffer acid would increase by the same amount so a new calculation of pH can be done with the new values.

$$CH_3CO_2^-{}_{(aq)} + H^+ \rightarrow CH_3CO_2H_{(aq)}$$
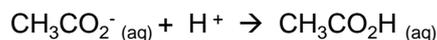
**Example 22:** 0.005 mol of NaOH is added to 500cm$^3$ of a buffer where the concentration of ethanoic acid is 0.200 mol dm$^{-3}$ and the concentration of sodium ethanoate is 0.250 mol dm$^{-3}$ . (Ka = 1.7 x 10$^{-5}$)

Calculate the pH of the buffer solution after the NaOH has been added.

**Work out the moles of acid and salt in the initial buffer solution**
Moles ethanoic acid= conc x vol = 0.200 x 0.500 = 0.100mol
Moles sodium ethanoate = conc x vol = 0.25 x 0.500 = 0.125mol

**Work out the moles of acid and salt in buffer after the addition of 0.005mol NaOH**
Moles ethanoic acid = 0.100 - 0.005 = 0.095 mol
Moles sodium ethanoate = 0.125 +0.005 = 0.130 mol

$$[H^+{}_{(aq)}] = Ka \frac{[CH_3COOH_{(aq)}]}{[CH_3COO^-{}_{(aq)}]}$$

We can enter moles of acid and salt straight into the equation as they both have the same new final volume

$$[H^+{}_{(aq)}] = 1.7 \times 10^{-5} \times \frac{0.095}{0.130} \rightarrow [H^+{}_{(aq)}] = 1.24 \times 10^{-5}$$

$$pH = -\log[H^+]$$
$$= -\log 1.24 \times 10^{-5}$$
$$= 4.91$$

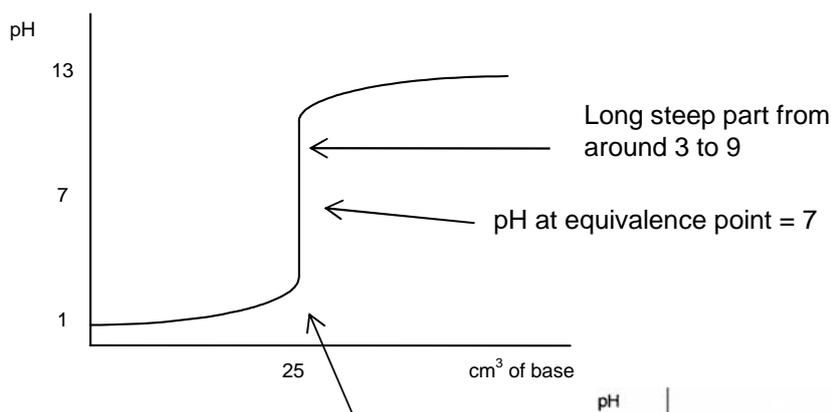## Titration curves

### Constructing a pH curve

1. Transfer 25cm³ of acid to a conical flask with a volumetric pipette
2. Measure initial pH of the acid with a pH meter
3. Add alkali in small amounts (2cm³) noting the volume added
4. Stir mixture to equalise the pH
5. Measure and record the pH to 1 d.p.
6. Repeat steps 3-5 but when approaching endpoint add in smaller volumes of alkali
7. Add until alkali in excess

**Calibrate** meter first by measuring known pH of a buffer solution. This is necessary because pH meters can lose accuracy on storage.

Most pH probes are calibrated by putting probe in a set buffer (often pH 4) and pressing a calibration button/setting for that pH. Sometimes this is repeated with a second buffer at a different pH

Can also improve accuracy by **maintaining** constant temperature

### Strong acid – Strong base
e.g. HCl and NaOH



Long steep part from around 3 to 9

pH at equivalence point = 7

There are 4 main types of curve
1. Strong acid and strong base
2. Weak acid and strong base
3. Strong acid and weak base
4. Weak acid and weak base

You may also have to work out the neutralisation volume from titration data given in the question. These are done by standard titration calculations.

The Key points to sketching a curve:
Initial and final pH
Volume at neutralisation
General Shape (pH at neutralisation)



The equivalence point lies at the mid point of the extrapolated vertical portion of the curve.
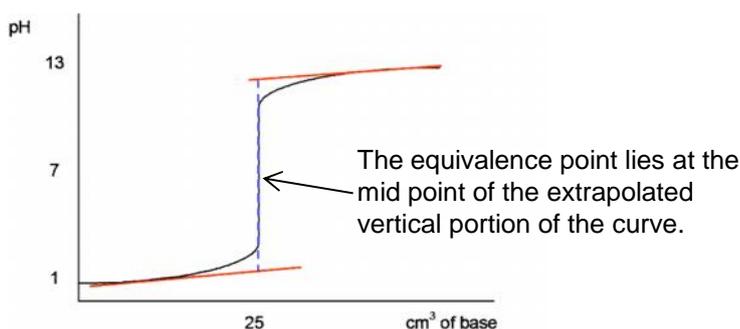
### Weak acid – Strong base
e.g. $CH_3CO_2H$ and NaOH

At the start the pH rises quickly and then levels off. The flattened part is called the buffer region and is formed because a buffer solution is made



Equivalence point >7

Steep part of curve >7 (around 7 to 9)

pH starts near 3
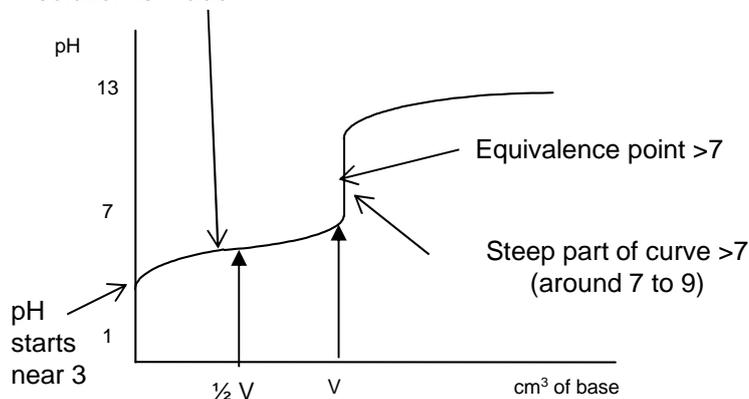
**Half neutralisation volume**

For weak acids

$$Ka = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]}$$
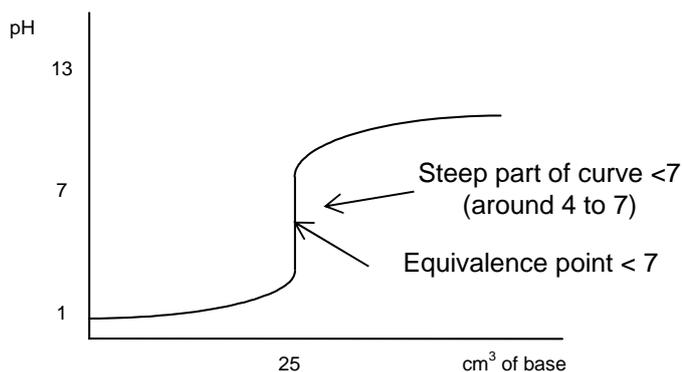
At ½ the neutralisation volume the [HA] = [A⁻]

So Ka= [H⁺] and pKa = pH

If we know the Ka we can then work out the pH at ½ V or vice versa.

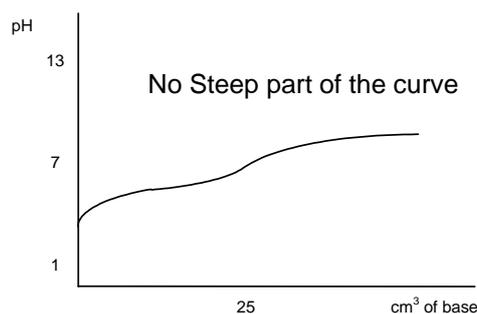If a pH curve is plotted then the pH of a weak acid at half neutralisation (½ V) will equal the pKa

## Strong acid – Weak base
e.g. HCl and NH$_3$

pH

13

7

1

25    cm$^3$ of base

Steep part of curve <7 (around 4 to 7)

Equivalence point < 7

## Weak acid – Weak base
e.g. CH$_3$CO$_2$H and NH$_3$

pH

13

7

1

No Steep part of the curve

25    cm$^3$ of base

## Choosing an Indicator

Indicators can be considered as weak acids. The acid must have a different colour to its conjugate base

An indicator changes colour from HIn to In$^-$ over a narrow range. Different indicators change colours over different ranges.

The end-point of a titration is defined as the point when the colour of the indicator changes colour

The end-point of a titration is reached when [HIn] = [In$^-$]. To choose a correct indicator for a titration one should pick an indicator whose end-point coincides with the equivalence point for the titration.

## How indicators work

$$HIn\ (aq) \rightleftharpoons In^-_{(aq)} + H^+_{(aq)}$$
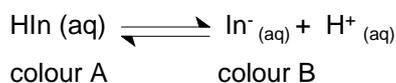
colour A            colour B

We can apply Le Chatelier to give us the colour.

In an acid solution the H$^+$ ions present will push this equilibrium towards the reactants. Therefore colour A is the acidic colour.

In an alkaline solution the OH$^-$ ions will react and remove H$^+$ ions causing the equilibrium to shift to the products. Colour B is the alkaline colour.
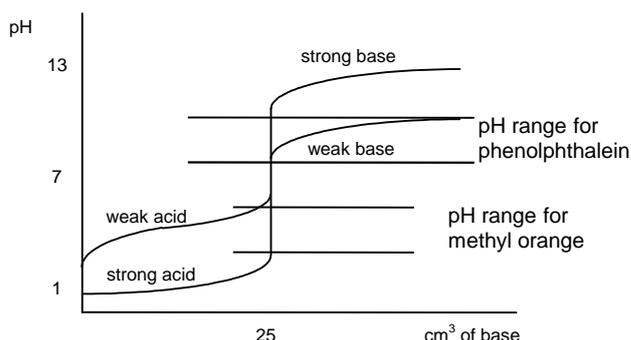
An indicator will work if the pH range of the indicator lies on the **steep** part of the titration curve. In this case the indicator will change colour rapidly and the colour change will correspond to the neutralisation point.

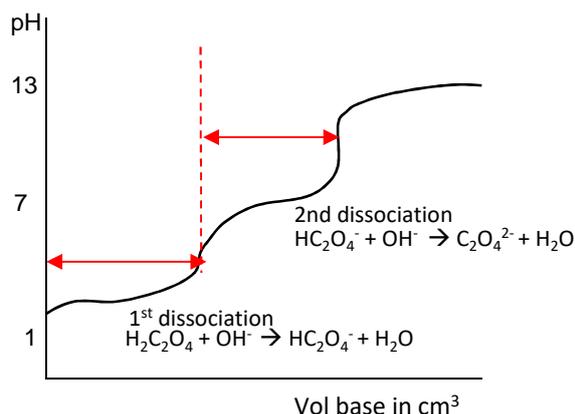Only use phenolphthalein in titrations with strong bases but not weak bases-

Colour change: colourless acid → pink alkali

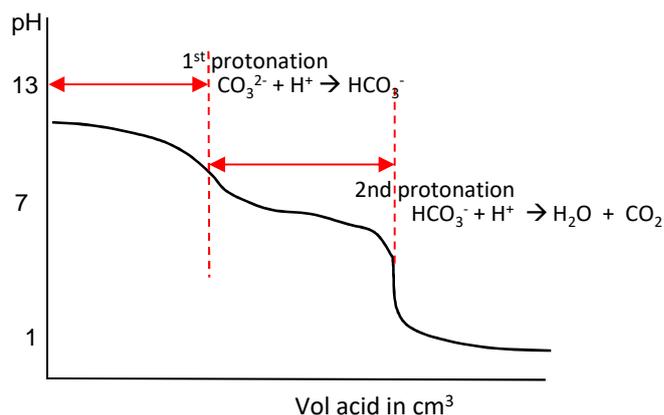Use methyl orange with titrations with strong acids but not weak acids
Colour change: red acid → yellow alkali
(orange end point)

pH

13

7

1

strong base

weak base

pH range for phenolphthalein

weak acid

strong acid

pH range for methyl orange

25    cm$^3$ of base

## Diprotic acid with base

pH



Vol base in cm³

Diprotic acids will give a two part pH curve with two end points. Different indicators can be used to find out the two end points.

## Diprotic base with acid

pH



Vol acid in cm³

## Partition coefficients
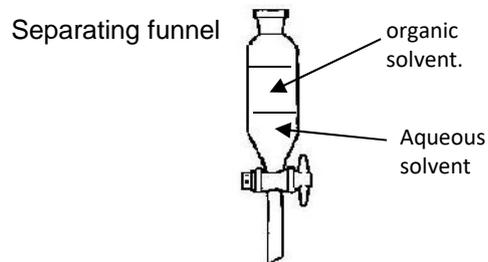
Solvent extraction splits a solute between two immiscible liquid solvents. The solute will be split between the two solvents in an equilibrium.

Solute in aqueous solvent ⇌ Solute in organic solvent

The partition coefficient $K_{pc}$ can be calculated from the equilibrium expression

$$K_{pc} = \frac{[\text{ solute in organic}]}{[\text{ solute in aqueous}]}$$

Separating funnel — organic solvent.

— Aqueous solvent

The concentration term is usually mol dm⁻³. As the expression has the same substance in both terms it is also possible to use g dm⁻³ or g cm⁻³

$K_{pc}$ is defined as equilibrium constant for the solution of a solute between two immiscible solvents

---

**Example 23**
3.56g of phenylamine was produced in an experiment. It was present in 30cm³ of an alkaline solution. The phenylamine was extracted by addition of 50cm³ of an organic solvent dichloromethane. After the extraction, the dichloromethane layer contained 3.01g of phenylamine.
Calculate the partition coefficient, $K_{pc}$, of phenylamine between dichloromethane and water.

mass left in water layer = 3.56 − 3.01 = 0.55 g

$$K_{pc} = \frac{(3.01/50)}{(0.55/30)} = 3.28$$

---

**Example 24**
The partition coefficient of substance Y between ether and water is 35.0
A solution contains 3.50 g of Y dissolved in 0.500 dm³ of water.
Calculate the mass of Y that can be extracted from this aqueous solution by mixing it with 0.050 dm³ of ether.
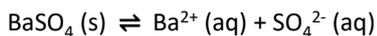
mass left in water layer = 3.50 − x

$$K_{pc} = \frac{(x/0.05)}{((3.5-x)/0.50)} = 35$$

$$\frac{10x}{(3.5-x)} = 35$$

x=2.72g

# Solubility Product

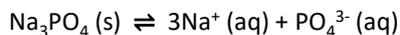Consider the dissolving of a solid in water as an equilibrium

$$BaSO_4 \text{ (s)} \rightleftharpoons Ba^{2+} \text{ (aq)} + SO_4^{2-} \text{ (aq)}$$

An equilibrium expression can be written for the reaction

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

Note the $BaSO_4$ (s) does not appear in the expression. In a heterogeneous equilibrium, concentration terms for solids are not included because they are constant

Note the case where multiple ions are dissociated

$$Na_3PO_4 \text{ (s)} \rightleftharpoons 3Na^+ \text{ (aq)} + PO_4^{3-} \text{ (aq)}$$

$$K_{sp} = [Na^+]^3[PO_4^{3-}]$$

The value of $K_{sp}$ is corresponds to the case where it is a **saturated solution** (i.e. the maximum amount of solute that can be dissolved in a solvent)
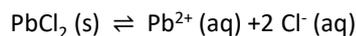
## Unit of K$_{sp}$

Like other equilibrium constants the unit of $K_{sp}$ will vary depending on the expression.

$$\begin{aligned} K_{sp} &= [Na^+]^3 [PO_4^{3-}] \\ &= [mol\ dm^{-3}]^3 [mol\ dm^{-3}] \\ &= mol^4 dm^{-12} \end{aligned}$$

**Example 25**
A saturated solution of $PbCl_2$ has the concentration of $[PbCl_{2\ (aq)}]$ of $3.5 \times 10^{-2}$ mol dm$^{-3}$ Calulcate the $K_{sp}$ for this solution.

$$PbCl_2 \text{ (s)} \rightleftharpoons Pb^{2+} \text{ (aq)} + 2Cl^- \text{ (aq)}$$

if $[PbCl_2] = 3.5 \times 10^{-2}$ then $[Pb^{2+}] = 3.5 \times 10^{-2}$ and $[Cl^-] = 7.0 \times 10^{-2}$

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

$$\begin{aligned} K_{sp} &= (3.5 \times 10^{-2}) \times (7.0 \times 10^{-2})^2 \\ &= 1.715 \times 10^{-4}\ mol^3\ dm^{-9} \end{aligned}$$

**Example 26**
The Ksp for silver phosphate, $Ag_3PO_4$, is $1.25 \times 10^{-20}$ . Calculate $[Ag^+(aq)]$ in a saturated solution of $Ag_3PO_4$.

$$K_{sp} = [Ag^+]^3 [PO_4^{3-}]$$

make $[PO_4^{3-}] = y$ and therefore $[Ag+] = 3y$

$$K_{sp} = [3y]^3 [y] = 27y^4$$
$$y = (K_{sp} / 27)^{¼}$$

$$y = (1.25 \times 10^{-20} / 27)^{¼} = 4.64 \times 10^{-6}\ mol\ dm^{-3}$$
$$\begin{aligned} [Ag+] &= 3y \\ &= 1.39 \times 10^{-5}\ mol\ dm^{-3} \end{aligned}$$

**Case where concentrations are less than those of a saturated solution**
If the ionic concentrations, put into the $K_{sp}$ expression, give a value less than the solubility product, then the solution is not saturated. No solid precipitate would be seen

## Common Ion Effect

If a mixture of salts present has an ion in common then they will have an effect on each other's solubility.

If sodium chloride solution is added to a solution of lead chloride then the increased concentration of chloride ions will shift the lead chloride equilibrium to the left

$$PbCl_2 \text{ (s)} \rightleftharpoons Pb^{2+} \text{ (aq)} + 2Cl^- \text{ (aq)}$$
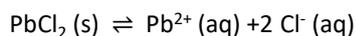
The solubility of the lead chloride would therefore decreases and more solid would be produced

The solubility of $Ca(OH)_2$ in 0.1 mol dm$^{-3}$ NaOH is lower than that in water.
It is less soluble in NaOH due to the common hydroxide ion effect. It causes the equilibrium
$$Ca(OH)_2 \text{ (s)} \rightleftharpoons Ca^{2+} \text{ (aq)} + 2OH^- \text{ (aq)}$$

to be shifted to the left by the higher hydroxide ion concentration