

Equilibria, Energetics and Elements

1. Basic Terms

Rate of Reaction – Change of concentration of a reactant or product per unit time.

Order – The power in which the concentration of the reactant is raised in the rate equation.

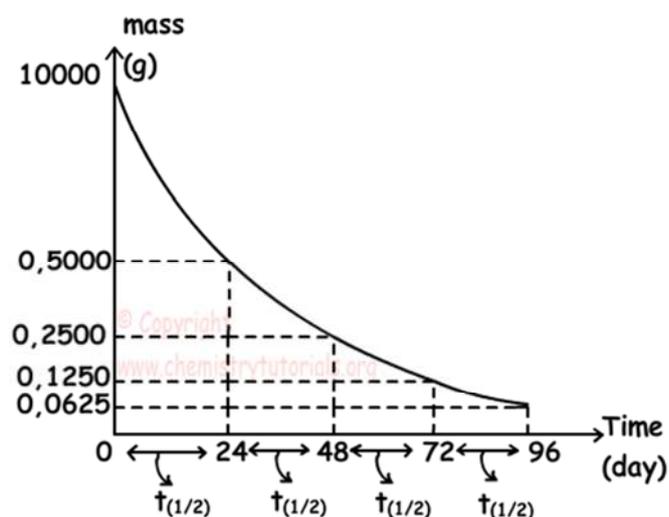
Half-life – The time taken for the concentration of a reactant to reduce by half

Rate determining step – The slowest step in the reaction mechanism of a multi-step reaction

2. Deducing Half Life and Rate of reaction from a graph.

The rate of reaction of a concentration-time graph is calculated by drawing a tangent to the line of best fit of a conc/time graph and dividing change of concentration by time.

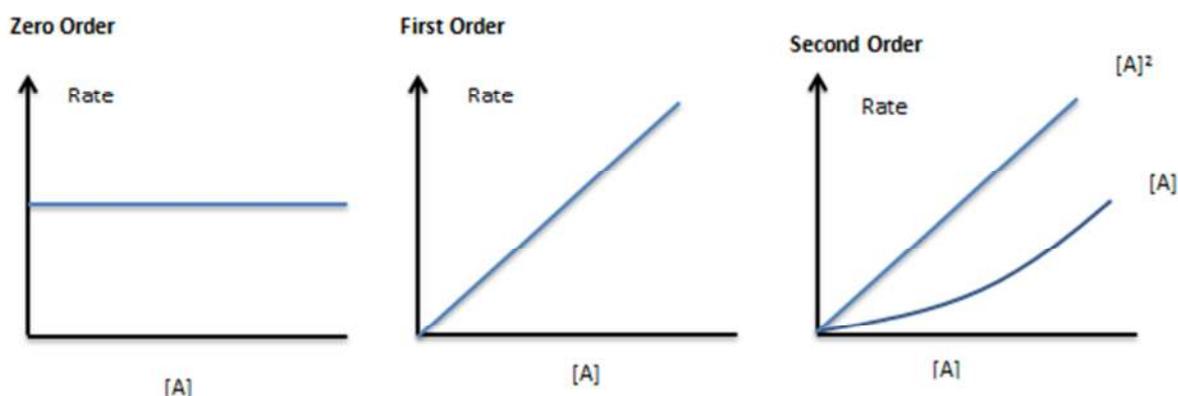
Half life can be deduced by intersecting a line graph each time the concentration has fallen by half and then drawing a line through the x – axis to determine the time taken.



E.g Every time the concentration decreases by half, the time taken is 24 seconds, meaning the half life is 24 seconds.

(c) state that the **half-life of a first-order reaction is independent of the concentration;**

3. Deducing order from a rate against concentration graph.



Zero order - rate is unaffected by changing the conc

First order - if [B] inc. x2, the rate also inc. x2 –
- if [B] inc. x3, the rate also inc. x3

Second order - if [B] inc. x2, the rate inc. x 2² = 4
- if [B] inc. x3, the rate inc. x 3² = 9

(e) determine, using the initial rates method, the order (0, 1 or 2) with respect to a reactant;

Initial rate = gradient of tangent drawn when t=0

Clock Reactions

- Measure time taken from the start of reaction until there is a visible change.
- Initial rate = 1/t
- Carry out series of clock reactions, varying each reactant.
- Plot graph of initial rate against initial concentration for each reactant.

4. Writing rate equations.

Order's can be determined from the powers outside square brackets.

E.g – $[Na_2S_2O_3]^1 [HCl]^0$

$Na_2S_2O_3$ is of the first order, and HCl of zero order

So

$k = [Na_2S_2O_3]^1 [HCl]^0$

5. Calculating orders of compounds

experiment	concentration of A	concentration of B	Rate
1	0.1M	0.1M	6×10^3
2	0.2M	0.1M	1.2×10^4
3	0.4M	0.1M	2.4×10^4
4	0.1M	0.2M	6×10^3
5	0.2M	0.2M	1.2×10^4

In experiments 1,2 and 3 the concentration of A changes while the concentration of B is kept constant. This means that the rate equation can be written as:

$$\text{Rate} = k[A]^m$$

For these three experiments. If we inspect the rate of experiments 1,2 and 3 we see that as the concentration of A is doubled so the rate doubles. In other words the order of reaction must be 1 so that whatever happens to the concentration must also happen in equal amounts to the rate.

Similar inspection of experiments 1 and 4 (or 2 and 5) show that while A is kept constant there is no effect on the rate when the concentration of B is changed. The order with respect to B must be 0.

The orders can now be substituted into the rate equation:

$$\text{Rate} = k[A]^1[B]^0$$

To obtain a value for the rate constant we simple substitute the values for one of the experiments above using the newly determined orders. (choose the experiment with the simplest numbers - in this case experiment 1)

Values from experiment 1

$$6 \times 10^3 = k \times [0.1]^1 \times [0.1]^0$$

$$k = 6 \times 10^3 / 0.1$$

$$\underline{k = 6 \times 10^4}$$

(g) calculate the rate constant, k, from a rate equation;

$$\text{Rate} = k[A]^m[B]^n$$

$$k = \frac{\text{Rate}}{[A]^m[B]^n}$$

See example above

6. Effect of temperature on a rate constant and rate of reaction.

- Raising the temperature speeds up most reactions by increasing the rate constant, k .
- For most reactions, every 10°C will double the rate \rightarrow This reflects the greater number of reacting particles that exceed the Activation energy.

7. Determining a rate equation consistent with the rate-determining step.

For the equation $\text{NO}_{2(g)} + \text{CO}_{(g)} \rightarrow \text{NO}_{(g)} + \text{CO}_{2(g)}$

If the results of an experiment show that the rate equation = $k[\text{NO}_2]^2$:

If a reactant appears in the rate equation, it is also found in the rate determining step. Therefore, so far we know:

1. Rate determining step = $\text{NO}_2 + \text{NO}_2 \rightarrow ? + ?$
2. 2nd step = $? + ? \rightarrow ? + ?$
3. Overall equation = $\text{NO}_{2(g)} + \text{CO}_{(g)} \rightarrow \text{NO}_{(g)} + \text{CO}_{2(g)}$

From the overall equation, we can see that CO is not in the rate determining step, so it must be in the 2nd step, as well as the CO_2

There is only 1 molecule of NO_2 in the overall equation, therefore a product of the 2nd step must be NO_2 (so the two NO_2 's cancel).

Therefore:

1. Rate determining step = $\text{NO}_2 + \text{NO}_2 \rightarrow ? + ?$
2. 2nd step = $? + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$
3. Overall equation = $\text{NO}_{2(g)} + \text{CO}_{(g)} \rightarrow \text{NO}_{(g)} + \text{CO}_{2(g)}$

After this. From the 2nd step we can see that there is an excess of 1 nitrogen and 3 oxygens on the right hand side. Therefore the reactant must be NO_3 .

This then tells us that the products in the RDS must be $\text{NO}_3 + \text{NO}$ to balance.

Our completed mechanism is therefore:

1. Rate determining step = $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}_2$
2. 2nd step = $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$
3. Overall equation = $\text{NO}_{2(g)} + \text{CO}_{(g)} \rightarrow \text{NO}_{(g)} + \text{CO}_{2(g)}$

8. Calculating concentration or amount at equilibrium.

For the reaction: $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

0.60 mol of H_2 was mixed with 0.40 mol of I_2 . The mixture was allowed to reach equilibrium and it was found that 0.28 mol of H_2 remained.

From this we can determine that 0.32 mol of H_2 was used.

Using stoichiometry, we can also deduce that 0.32 mol of I_2 was also used.

Therefore, remaining, is 0.28 mol of H_2 and 0.08 mol of I_2 .

The original total amount was $0.60 + 0.40$ which is 1 mol. We are now left with 0.28 mol of H_2 and 0.08 mol of I_2 , which means that 0.64 mol of HI must have been formed.

9. Calculating the units of K_c

$$K_c = \frac{\text{Products}}{\text{Reactants}}$$



$$\frac{(NH_3) (NH_3)}{(N_2) (H_2)(H_2)(H_2)} = \frac{(mol\ dm^{-3}) (mol\ dm^{-3})}{(mol\ dm^{-3}) (mol\ dm^{-3}) (mol\ dm^{-3}) (mol\ dm^{-3})}$$

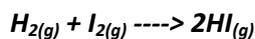
$$= \frac{(mol\ dm^{-3}) (mol\ dm^{-3})}{(mol\ dm^{-3}) (mol\ dm^{-3}) (mol\ dm^{-3}) (mol\ dm^{-3})}$$

$$= \frac{1}{(mol\ dm^{-3}) (mol\ dm^{-3})} = dm^6\ mol^{-2}$$

10. Calculating K_c

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

If the reaction



If there are

- 0.140 mol of H_2
- 0.0400 mol of I_2
- 0.320 mol of HI

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

There are no units as the $[mol\ dm^{-3}]^2$ is cancelled by each $mol\ dm^{-3}$ on the bottom.

$$\frac{0.320^2}{0.140 \times 0.0400} = 18.3$$

11. Effect of temperature on value of K_c in exo and endothermic reactions.

If the forward reaction is endothermic as the temperature increases, K_c increases.

The equilibrium yield on the right increases, and decreases on the left.

When the forward reaction is endothermic, the K_c value is greater than 1, so the products are favoured.

This is the other way round if the K_c value is less than 1 or when the forward reaction is exothermic.

Therefore, if K_c increases with temperature, the reaction is Endothermic, and vice versa.

12. Effect of concentration and pressure on K_c

The value of K_c is unaffected by changes in concentration or pressure, the higher the concentration of a reactant, the product increases proportionally, so there is no effect. The presence of a catalyst, also has no effect as the yield of reactant and product remains constant.

Le Chatelier's principle minimises the effect of changing concentration or pressure similarly to in AS chemistry. This allows the K_c value to stay the same.

13. Acids and Bases

Acid – A species which donates a proton

Base – A species that accepts a proton.

14. The role of H^+ in the reactions of acids.

Different acids may release different numbers of protons.

If the proton release is complete, a normal arrow is shown (\rightarrow); if the process is not complete, the reversible reaction arrows are shown.

The three types of acid are:

- 1. Monobasic – each molecule may release 1 proton (HCl)**
- 2. Dibasic – Each molecule may release 2 protons (H_2SO_4)**
- 3. Tribasic – Each molecule may release 3 protons (H_3PO_4)**

Carbonates

Acid_(aq) + Carbonate_(s) \rightarrow Salt_(aq) + $CO_{2(g)}$ + $H_2O_{(l)}$

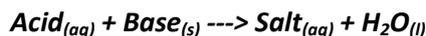
- 1. $2HCl_{(aq)} + CaCO_{3(s)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$**
- 2. $2H^+ + 2Cl^- + CaCO_{3(s)} \rightarrow Ca^{2+} + 2Cl^- + CO_{2(g)} + H_2O_{(l)}$**
- 3. $2H^+ + CaCO_{3(s)} \rightarrow Ca^{2+} + CO_{2(g)} + H_2O_{(l)}$**

Carbonate in Solution

Acid_(aq) + Carbonate_(aq) \rightarrow Salt_(aq) + $CO_{2(g)}$ + $H_2O_{(l)}$

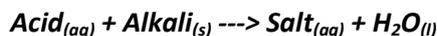
- 1. $2HCl_{(aq)} + Na_2CO_{3(aq)} \rightarrow 2NaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$**
- 2. $2H^+ + 2Cl^- + 2Na^+ + CO_3^{2-} \rightarrow 2Na^+ + 2Cl^- + CO_{2(g)} + H_2O_{(l)}$**
- 3. $2H^+_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)}$**

Bases



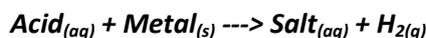
1. $2\text{HNO}_{3(aq)} + \text{MgO}_{(s)} \rightarrow \text{Mg}(\text{NO}_3)_{2(aq)} + \text{H}_2\text{O}_{(l)}$
2. $2\text{H}^+_{(aq)} + 2\text{NO}_3^-_{(aq)} + \text{MgO}_{(s)} \rightarrow \text{Mg}^{2+}_{(aq)} + 2\text{NO}_3^-_{(aq)} + \text{H}_2\text{O}_{(l)}$
3. $2\text{H}^+_{(aq)} + \text{MgO}_{(s)} \rightarrow \text{Mg}^{2+}_{(aq)} + \text{H}_2\text{O}_{(l)}$

Alkali's



1. $\text{H}_2\text{SO}_{4(aq)} + 2\text{KOH}_{(s)} \rightarrow \text{K}_2\text{SO}_{4(aq)} + 2\text{H}_2\text{O}_{(l)}$
2. $2\text{H}^+_{(aq)} + \text{SO}_4^{2-}_{(aq)} + 2\text{K}^+_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow 2\text{K}^+_{(aq)} + \text{SO}_4^{2-}_{(aq)} + 2\text{H}_2\text{O}_{(l)}$
3. $2\text{H}^+_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow 2\text{H}_2\text{O}_{(l)}$
4. $\text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)}$

Metals



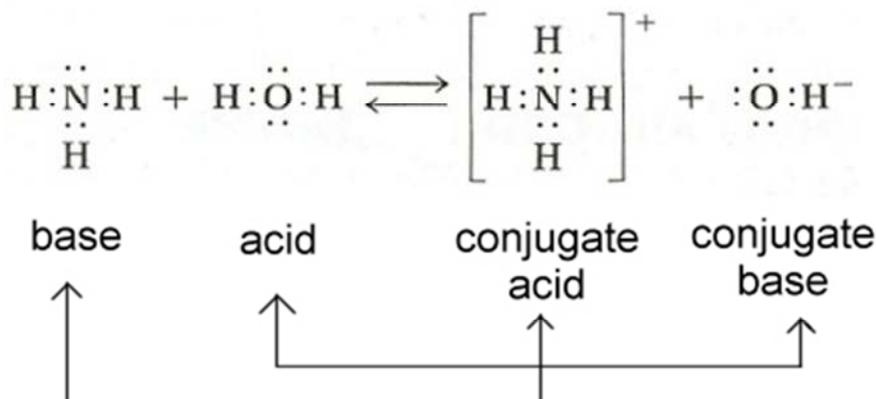
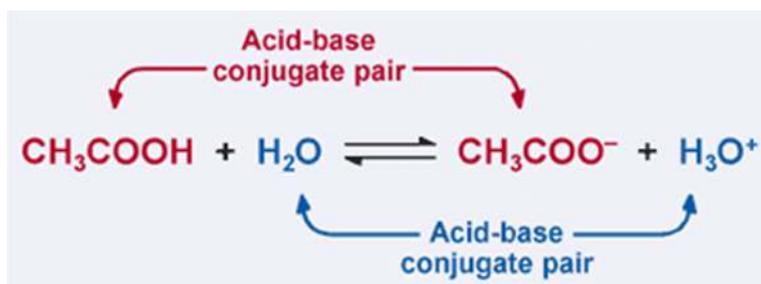
1. $2\text{HCl}_{(aq)} + \text{Mg}_{(s)} \rightarrow \text{MgCl}_{2(aq)} + \text{H}_{2(g)}$
2. $2\text{H}^+_{(aq)} + 2\text{Cl}^-_{(aq)} + \text{Mg}_{(s)} \rightarrow \text{Mg}^{2+}_{(aq)} + 2\text{Cl}^-_{(aq)} + \text{H}_{2(g)}$
3. $2\text{H}^+_{(aq)} + \text{Mg}_{(s)} \rightarrow \text{Mg}^{2+}_{(aq)} + \text{H}_{2(g)}$

15. Conjugate Acid-Base pairs.

Acid-Base pair – a pair of two species that transform into each other by gain or loss of a proton

In the forward reaction, the acid loses a proton to form its conjugate base.

The base accepts a proton to form its conjugate acid.



16. Differences between Strong and Weak acids

In aqueous solutions, acids dissociate and equilibrium it set up



**Strong acids are 100% dissociated in aqueous solution. There are few of these
Weak acids only partly dissociate in aqueous solutions**

17. Acid dissociation constant

The extend of acid dissociation is measured by the Acid dissociation constant, K_a .

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

The units for K_a are always mol dm^{-3}

A large K_a value indicated a lot of dissociation, a strong acid

A small K_a value indicates a small amount of dissociation, a weak acid.

18. K_a and pK_a

$$pK_a = -\log_{10}K_a$$

$$K_a = 10^{-pK_a}$$

A low value of K_a matched a high value of pK_a

A high value of K_a matches a low value of pK_a

The smaller the value of pK_a , the stronger the acid.

**(g) define pH as $pH = -\log[H^+]$;
 $[H^+] = 10^{-pH}$;**

pH values and $[H^+_{(aq)}]$:

pH	0	1	2	3	4	5	6	7	8
$[H^+_{(aq)}]/$ Mol dm^{-3}	10^0 (1)	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}

To convert from pH to $[H^+_{(aq)}]$ value on a calculator:

- Press the – button
- Log button
- Enter the pH value

To convert from $[H^+_{(aq)}]$ to pH:

- Press shift
- Press log
- Press –
- Enter the $[H^+_{(aq)}]$ value

Dilution of Acids

If an acid is diluted with water to twice its original volume, the concentration of H^+ ions decreases by half. If diluted to 3 times its volume, the value of H^+ ions is reduced to one third of its original value etc...

19. Ionic product of water

$$K_w = [H^+_{(aq)}][OH^-_{(aq)}]$$

At 25°C - $K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

20. Calculating pH of:

(i) strong monobasic acids,

Calculate the pH of 0.1M hydrochloric acid.

HCl (strong monoprotic acid) is fully dissociated. $HCl \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$

The $[H^+]$ is therefore the same as the original concentration of HCl i.e. 0.1M.

$$pH = -\log_{10} [H^+] = -\log_{10} (10^{-1}) = 1 \quad \text{AN:}$$

(ii) weak monobasic acids,

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

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

**e.g The concentration of HNO_2 , which is a weak acid, = $0.055 \text{ mol dm}^{-3}$
 $K_a = 4.7 \times 10^{-4} \text{ mol}$. Calculate the pH**



$$K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]} \quad \text{so} \quad K_a = \frac{[H^+_{(aq)}][NO_2^-_{(aq)}]}{[HNO_2(aq)]}$$

Or, since the acid partially dissociates:

$$K_a = \frac{[H^+_{(aq)}]^2}{[HA_{(aq)}]} \quad \text{so} \quad K_a = \frac{[H^+_{(aq)}]^2}{[HNO_2(aq)]}$$

Therefore: $[H^+_{(aq)}]^2 = K_a[HNO_2(aq)]$

$$[H^+_{(aq)}] = \sqrt{K_a[HNO_2(aq)]} = \sqrt{(4.7 \times 10^{-4} \times 0.055)} = 5.08 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = -\log(5.08 \times 10^{-3})$$

$$= 2.29$$

(iii) strong bases, using K_w :

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

Example – A solution of KOH has a concentration of $0.050 \text{ mol dm}^{-3}$. What is the pH?

$$[H^+(aq)] = \frac{K_w}{[OH^-(aq)]} \quad \text{At } 25^\circ\text{C} \text{ ----} \rightarrow K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^6$$

$$= \frac{1 \times 10^{-14}}{0.05} = 2 \times 10^{-13}$$

$$\text{pH} = -\log(2 \times 10^{-13}) \\ = 12.7$$

21. Calculating K_a

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

Or

$$K_a = \frac{[H^+(aq)]^2}{[HA(aq)]}$$

Example – A sample of $0.030 \text{ mol dm}^{-3}$ Methanoic acid, HCOOH , has a pH of 2.66. Calculate K_a

$$\text{Concentration} = 10^{-2.66} = 2.19 \times 10^{-3}$$

$$K_a = \frac{[2.19 \times 10^{-3}]^2}{[0.030]} \\ = 1.6 \times 10^{-4} \text{ mol dm}^{-3}$$

22. Buffer Solutions

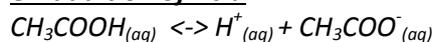
(k) describe a **buffer solution as a system that minimises pH changes on addition of small amounts of an acid or a base;**

(l) state that a **buffer solution can be made from:**

- a weak acid and a salt of the weak acid (Conjugate base) - eg $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$;
- a weak base + its chloride - eg Ammonia + Ammonium Chloride

An equilibrium mixture contains high amounts of undissociated weak acid and its conjugate base; this pushes the equilibrium position to the left resulting in low amounts of H^+ ions

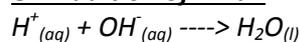
On addition of Acid



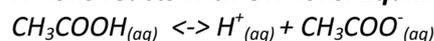
$[H^+(aq)]$ increases.

Conjugate base reacts with H^+ , shifting equilibrium to the left, minimising H^+ ions.

On Addition of Alkali



$[OH^-(aq)]$ increases. A small concentration of H^+ ions reacts with OH^- ions. Equilibrium of



is shifted to the right.

Method 2 (Using pOH)

$$\text{pOH} = -\log[OH^-(aq)]$$

$$\text{pOH} = -\log(0.050)$$

$$= 1.30$$

$$\text{pH} = 14 - 1.30 = 12.70$$

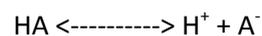
(m) explain the role of the conjugate acid–base pair in an acid buffer solution, eg $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$, in the control of pH;

The weak acid, HA and its conjugate base A^- are responsible for controlling pH.

- The weak acid, HA, removes added alkali
- The conjugate base, A^- , removes added acid.

On addition of an acid:

- $[\text{H}^+_{(\text{aq})}]$ is increased
- The conjugate base A^- reacts with the $\text{H}^+_{(\text{aq})}$ ions
- The equilibrium shifts to the left



On addition of an alkali

- $[\text{OH}^-_{(\text{aq})}]$ is increased
- A small concentration of H^+ ions react with the $\text{OH}^-_{(\text{aq})}$ ions
- HA dissociates, shifting the equilibrium to the right



(n) calculate the pH of a buffer solution, from the K_a value of a weak acid and the equilibrium concentrations of the conjugate acid–base pair;

For buffers:

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

E.g – Calculate the pH at 25°C of a buffer solution containing $0.050 \text{ mol dm}^{-3} \text{CH}_3\text{COOH}$ and $0.10 \text{ mol dm}^{-3} \text{CH}_3\text{COO}^- \text{Na}^+$
For CH_3COOH $K_a = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$

$$1 \quad [\text{H}^+_{(\text{aq})}] = K_a \times \frac{[\text{Conjugate Base}]}{[\text{Weak acid}]}$$

$$[\text{H}^+_{(\text{aq})}] = 1.7 \times 10^{-5} \times \frac{[0.050]}{[0.10]}$$

$$= 8.5 \times 10^{-6}$$

$$-\log(8.5 \times 10^{-6})$$

$$= 5.07$$

$$2 \quad \text{pH} = \text{p}K_a + \log \times \frac{[\text{Conjugate Base}]}{[\text{Weak acid}]}$$

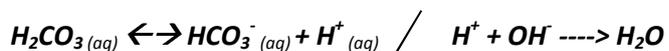
$$(\text{ where } \text{p}K_a = -\log K_a)$$

$$\text{pH} = -\log(1.7 \times 10^{-5}) + \log(0.10/0.050)$$

$$= 5.07$$

(o) explain the role of carbonic acid–hydrogencarbonate as a buffer in the control of blood pH;

If the human blood plasma falls below a pH of 7.35, acidosis occurs. If it rises above 7.45 alkalosis occurs



The pH of blood is controlled by the carbonic acid - hydrogencarbonate ions buffer

- Carbonic acid H_2CO_3 acts as a weak acid
- Hydrogencarbonate HCO_3^- acts as a conjugate base
- An increase in H^+ ions is removed by the conjugate base and moves the position of equilibrium to the left.
- An increase in OH^- ions reacts with the weak acid H_2CO_3 , it reacts with a small concentration of H^+ ions shifting the equilibrium position to the right.

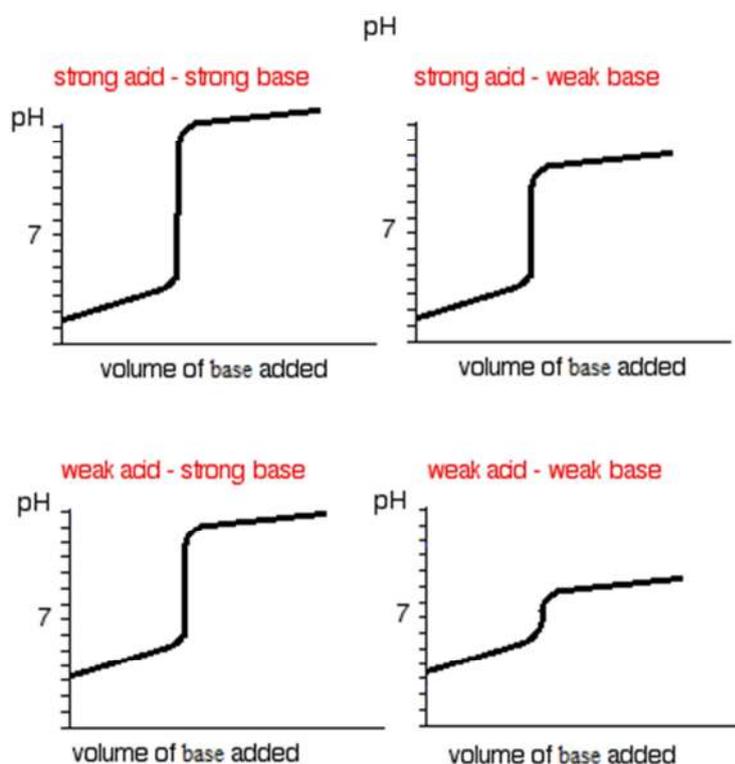
Carbonic acid is then converted to aqueous CO_2 through enzyme action.

After that, the aqueous CO_2 is converted to gaseous CO_2 in the lungs, where it is then exhaled

23. Graphs of Acid-base titrations

(p) for acid–base titration pH curves for strong and weak acids and bases:

(i) interpret, or sketch, their shapes,



When the base is first added, the pH only increases slightly as the acid is in great excess.

Within 1-2 cm³ of the equivalence point, the pH begins to rise more quickly, as the acid is in small amounts of excess.

There is eventually a very sharp increase caused by a small addition of the base. The centre of this almost vertical line is the equivalence point.

More base is then added to that the base is now in great excess.

24. Indicators

An acid-base indicator is a weak acid.

An indicator has one colour in acid form and one in its conjugate base form.

Methyl orange is red in acid and yellow in conjugate base form.

When there are equal amounts of the weak acid and conjugate base, the end point is reached.

Most indicators change colour over a range of 2 pH units:

- **Phenolphthalein – between 8.3 to 10.0**
- **Bromothymol blue – between 6.0 to 7.6**
- **Methyl Orange – between 3.1 to 4.4**

Indicator	High pH	Low pH
Phenolphthalein	Dark pink	Pale pink
Bromothymol blue	Dark blue	Yellow
Methyl Orange	Yellow	Orange

25. Enthalpy of Neutralisation

Enthalpy change of neutralisation – energy change that accompanies the neutralisation of an aqueous acid by an aqueous base to form one mole of $H_2O_{(l)}$ under standard conditions

Example – 25cm^3 of dilute nitric acid, of concentration 2.00 mol dm^{-3} , is added to 25 cm^3 of aqueous potassium hydroxide of concentration 2.00 mol dm^{-3} .

The temperature increases from 22°C to 35.5°C

- 1. The Enthalpy change must be calculated using $Q=mc\Delta T$**
 - a. $m = \text{mass of surroundings}$**
 - i. $25 + 25 = 50$**
 - b. $c = \text{specific heat capacity which is usually } 4.18\text{ J g}^{-1}\text{ K}^{-1}$**
 - c. $\Delta T = 35.5 - 22 = +13.5^\circ\text{C}$**
 - d. $mc\Delta T = 50 \times 4.18 \times 13.5$**
 - i. $= + 2821.5\text{ J}$**
 - ii. The temperature has increased so an exothermic reaction occurs, therefore the heat lost by the system is $- 2821.5\text{ J}$**
- 2. Calculate the number of moles that reacted.**
 - a. $n(\text{HNO}_3) = c \times V$**
 - b. $2 \times (25 \div 1000) = 0.0500\text{ mol}$**
 - c. $n(\text{KOH}) = c \times V$**
 - d. $2 \times (25 \div 1000) = 0.0500\text{ mol}$**
- 3. Scale the quantities to match molar quantities.**
 - a. In this case the moles of the two reactants are the same, so there is no limiting reagent.**
 - b. Therefore 1 mol of HNO_3 reacts with 1 mole of KOH .**

- c. $\Delta H = Q \div n$
- $-2821.5 \div 0.0500$
 - $= -56430 \text{ J}$
 - $\Delta H = -56.4 \text{ kJ}$

4. Work out enthalpy change of neutralisation to form 1 mole of H_2O

- $\text{HNO}_3(\text{aq}) + \text{KOH}(\text{aq}) \rightarrow \text{KNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- $\text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{K}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{K}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$
- $\Delta H_{\text{neut}} = -56.4 \text{ kJmol}^{-1}$

In weak acids, ΔH_{neut} is sometimes less negative. They only dissociate partially, the molecules do this by breaking O-H bonds which requires energy. This means the enthalpy is slightly less exothermic.

Module 2: Energy

26. Lattice Enthalpy

The enthalpy change that accompanies the formation of 1 mole of ionic compounds from its gaseous ions under standard conditions.

Lattice enthalpy is an exothermic change and indicates the strength of the lattice - a more negative value means the electrostatic forces are stronger.

(b) use the lattice enthalpy of a simple ionic solid (ie NaCl, MgCl₂) and relevant energy terms to:

It is first important to understand these terms:

Standard Enthalpy of formation – one mole of a compound formed from its constituent elements in their standard states.

Standard enthalpy of atomisation – one mole of gaseous atoms formed from its element in standard states.

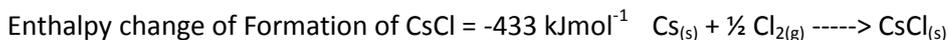
First ionisation energy – energy needed to form 1 mole of gaseous 1^+ atoms through the removal of 1 mole of electrons from an atom in its gaseous state.

First electron affinity - energy needed to form 1 mole of gaseous 1^- atoms through the addition of 1 mole of electrons from an atom in its gaseous state

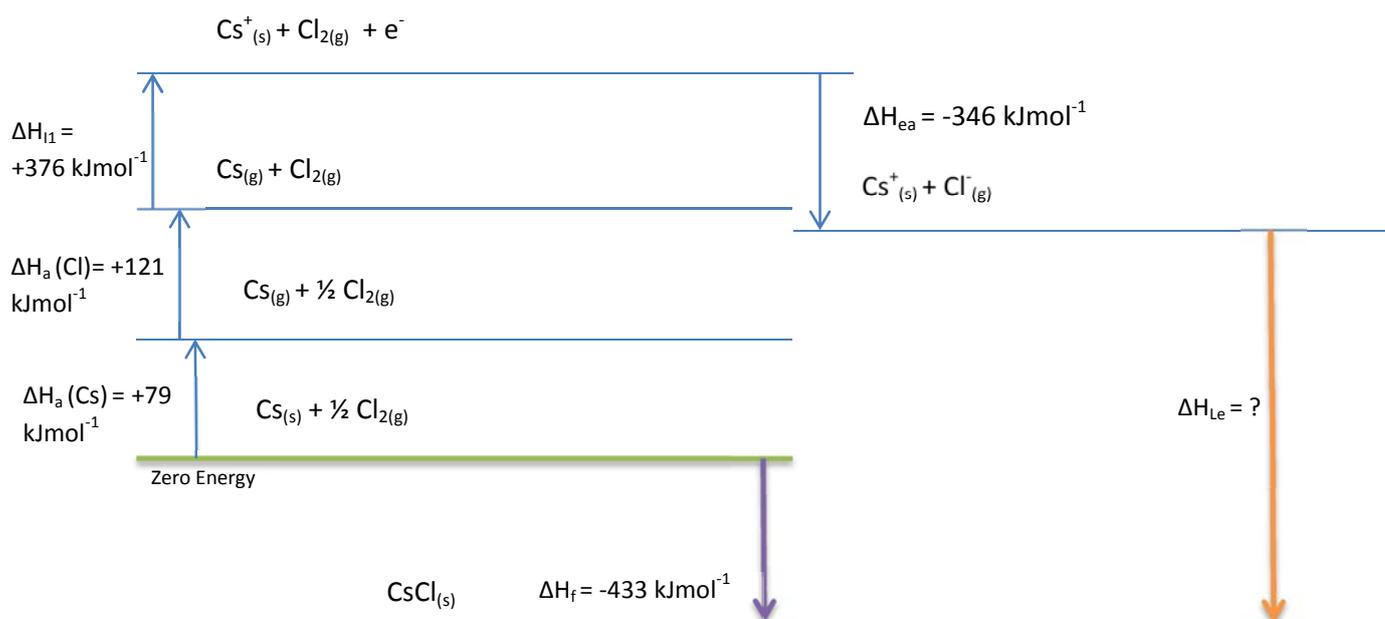
27. Born-Haber cycles

- (i) construct Born–Haber cycles,
 (ii) carry out related calculations;

Born Haber Cycles



- **The enthalpy of formation value at zero energy must first be added.**
- **The Lattice enthalpy must then be added.**
- **The cycle must then be completed by inserting the enthalpy values.**



- **The formula Sum of anticlockwise = sum of clockwise can then be used.**

- $-433 = 79 + 121 + 376 + (-346) + \Delta H_{Le}$
- $\Delta H_{Le} = -433 - 79 - 121 - 376 + 346$
- $\Delta H_{Le} = -663 \text{ kJmol}^{-1}$

- However, take into account stoichiometric values.

- For example, if the elements at zero energy are $2\text{Na}_{(s)} + \frac{1}{2} \text{O}_{2(g)} \rightarrow \text{Na}_2\text{O}_{(s)}$, if an enthalpy of atomisation is $108 \text{ kJmol}^{-1} (\text{Na}_{(s)} \rightarrow \text{Na}_{(g)})$ then when calculating using *Sum of anticlockwise = sum of clockwise*, the value of 108 must be multiplied by 2 etc.

28. Enthalpy of Solution and Hydration

Standard enthalpy change of solution – enthalpy change when one mole of a compound is completely dissolved in water under standard conditions.

Standard Enthalpy change of hydration – Enthalpy change when one mole of isolated gaseous ions is dissolved in water forming one mole of aqueous ions under standard conditions.

(d) use the enthalpy change of solution of a simple ionic solid (ie NaCl, MgCl₂) and relevant energy terms (enthalpy change of hydration, and lattice enthalpy), to:

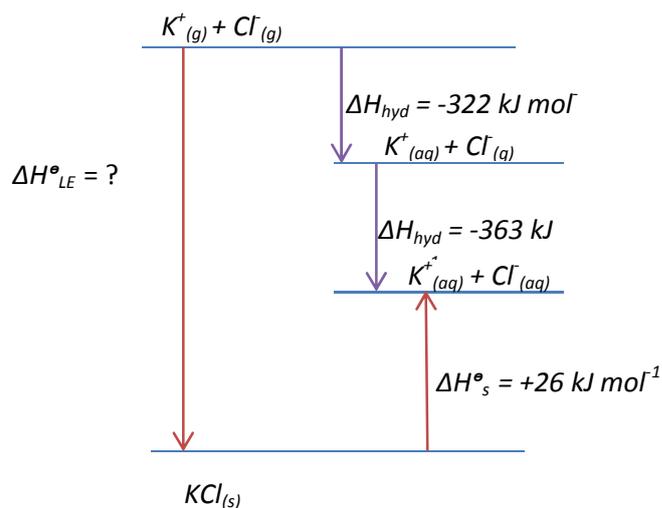
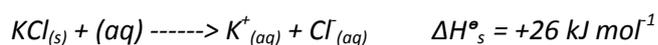
(i) construct Born–Haber cycles,

(ii) carry out related calculations;

Enthalpy change of Solution and Hydration

Given the values of Hydration and Solution, it is possible to calculate the Lattice Enthalpy

E.g – Calculate the Lattice Enthalpy given:



Using Hess' law, Sum Anticlockwise = Sum Clockwise

$$\Delta H^{\circ}_{\text{LE}} + \Delta H^{\circ}_s = \Delta H_{\text{hyd}(1)} + \Delta H_{\text{hyd}}$$

$$? + 26 = -322 + -363$$

$$? = -322 -363 - 26$$

$$= -711 \text{ kJ mol}^{-1}$$

29. Ionic charge and radius and its effect of lattice enthalpy and enthalpy of hydration.

A large exothermic value for a lattice enthalpy means there is a large electrostatic force of attraction. Two factors affecting this are ionic size and ionic charge.

As the size of ionic radius increases, the attraction between ions decreases. So the lattice enthalpy becomes less negative, or less exothermic.

As the ionic charge increases, however, the forces of attraction are greater. This causes the ionic radius to decrease, making the lattice enthalpy more negative, or more exothermic.

The Enthalpy changes of formation differ with charge and radius the same as the lattice enthalpies.

30. Entropy

(a) explain that **entropy is a measure of the 'disorder' of a system, and that a system becomes energetically more stable when it becomes more disordered;**

(b) explain the difference in magnitude of entropy:

(i) of a solid and a gas,

Solid materials are generally in rigid lattice structures, so are often very organised and strongly ordered, so have a lower entropy.

Gas molecules move about constantly, hence are less ordered than those particles of a solid so have a, generally, higher entropy.

(ii) when a solid lattice dissolves,

When a solid dissolves in a lattice, the energy is changing from being localised to delocalised, entropy increases when the particles become more disorganised, so entropy increases.

(iii) for a reaction in which there is a change in the number of gaseous molecules;

Where there is an increase in the number of gaseous particles, they become more spread out and disorganised, hence entropy increases.

(c) calculate the entropy change for a reaction given the entropies of the reactants and products;

$$\Delta S = \text{Sum of } S^\circ_{(\text{products})} - \text{Sum of } S^\circ_{(\text{reactants})}$$

If a change makes a system more random, ΔS is positive

If a change makes a system less random, ΔS is negative.

31. When do processes take place?

The tendency of a process to take place depends on temperature, T , the entropy change in the system, ΔS , and the enthalpy change, ΔH , with the surroundings;

Many exothermic processes take place at room temperature, the enthalpy content of the system decreases during the reaction and is released to the surroundings, becoming more stable.

Some endothermic reactions take place at room temperature. The enthalpy content of the system increases during the reaction, also increasing stability.

(e) explain that the balance between entropy and enthalpy changes is the free energy change, ΔG , which determines the feasibility of a reaction;

For a reaction to be feasible:

ΔG must be $-ve$. If it is negative at low temperatures, the reaction is feasible at low temperatures, and the same for high temperatures.

(f) state and use the relationship

$$\Delta G = \Delta H - T\Delta S;$$

32. Spontaneous reactions

Endothermic reactions may only take place spontaneously when:

- ΔS is positive
- Temperature is high enough so that $T\Delta S > \Delta H$

These two values can be calculated using the formulae:

1. $\Delta S = \text{Sum of } S^\circ_{(\text{products})} - \text{Sum of } S^\circ_{(\text{reactants})}$

2. $\Delta G = \Delta H - T\Delta S;$

33. Redox reactions and half equations

Redox – A reaction in which oxidation and reduction occurs.

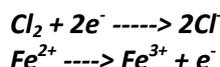
Oxidation Number – A measure of the number of electrons that an atom uses to bond with atoms of another element.

Half-reaction- Either the oxidation or reduction reaction component of a redox reaction

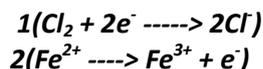
Oxidising agent – The substance in a reaction which is reduced.

Reducing Agent – The substance in a reaction which is oxidised

Two half equations can be added together in order to form a full redox equation.
For example:



For two half equations to be added to form a full redox equation, the electrons must balance on each side. This means that there must be 2 electrons, for this equation, on each side.



The half equations are now balanced so can be added to form:



34. Interpret and make predictions for reactions involving electron transfer.

Oxidation numbers make it easy to account for electrons and make it easy to balance complex redox reactions.

For example:

Hydrogen Iodide, HI, is oxidised to iodine, I₂, by concentrated Sulphuric Acid H₂SO₄; this is then reduced to Hydrogen Sulphide H₂S.

1. We can deduce the formula from the question
 - a. $\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{I}_2 + \text{H}_2\text{S}$ → This must then be balanced
2. We must then balance the equation, using each reaction pathway,
 - a. $\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{I}_2 + \text{H}_2\text{S}$
 - b. We have 1x I on the left side, but we need 2, so HI is multiplied by 2.
 - c. $2\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{I}_2 + \text{H}_2\text{S}$
 - d. We then look at the individual oxidation numbers
 - e. $2\text{HI} \longrightarrow \text{I}_2$
 - i. The I on the left has an oxidation state of 2 x -1 (H combined is always +1)
 - ii. The I on the right has an oxidation of 0, as it is an un-combined element.
 - iii. -2 → 0 is equal to a oxidation value of +2
 - f. $\text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{S}$
 - i. The S on the left has an oxidation state of +6 (H = 2 x +1 and O = 4 x -2)
 - ii. The S on the right has an oxidation state of -2 (H is always +1 combined)
 - iii. +6 → -2 is equal to a reduction value of -8
 - g. The oxidation numbers must then be balanced: we can do this by multiplying the oxidation value of '2HI → I₂' by 4.
3. By doing this, we get the equation:
 - a. $8\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow 4\text{I}_2 + \text{H}_2\text{S}$
4. However, this equation is not balanced, there are 10 H's on the LHS and only 2 on the RHS, there are also 4 O's on the LHS and none on the RHS
 - a. Therefore the equation must be:
$$8\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow 4\text{I}_2 + \text{H}_2\text{S} + 4\text{H}_2\text{O}$$

35. Standard Electrode potential.

The emf of a half cell compared to the standard hydrogen half cell, measure at 298K with solution concentrations of 1 mol dm⁻³ and a gas pressure of 1 atmosphere (100kPa)

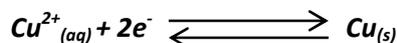
The more negative this value, the higher the tendency to lose electrons

36. Measuring standard electrode potentials of:

(i) metals or non-metals in contact with their ions in aqueous solution,

A half cell consists of an element in two oxidation states – e.g, a metal placed in an aqueous solution of its ions.

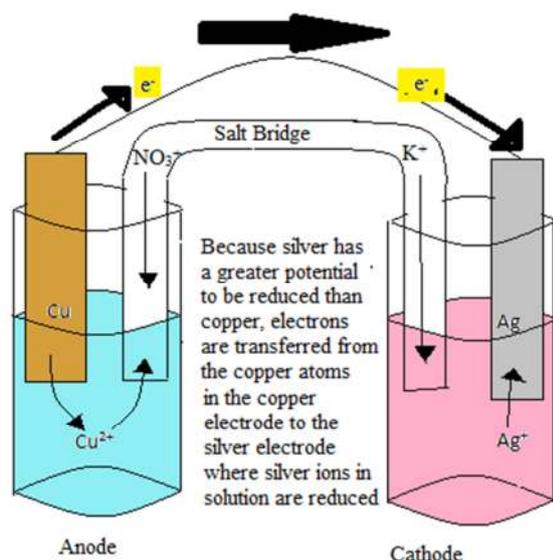
An example is a copper half cell:



A copper half cell consists of a solution of Copper ions with a strip of copper in.

An equilibrium exists where the forward reaction is reduction, and the reverse is oxidation.

An electrochemical cell can be made by connecting two half cells with different electrode potentials, e.g one half cell releases electrons and one gains electrons.



The wire connects the two metals, allowing transfer of electrons between the two half cells. The Salt bridge connects the two solutions, allowing ions to be transferred between half cells. It is usually a strip of filter paper soaked in an aqueous solution that does not react with the half cell solutions, usually KNO₃ or NH₄NO₃

The equilibrium which releases electrons more readily becomes the negative electrode, electrons flow along the wire to the other electrode.

The equations of redox are:

1. $\text{Ag}^{+}_{(aq)} + e^- \rightarrow \text{Ag}_{(s)}$
2. $\text{Cu}^{2+}_{(aq)} + 2e^- \rightarrow \text{Cu}_{(s)}$

Due to that fact that, in this reaction, copper releases electrons more rapidly than silver, so is oxidised, therefore it's equation moves to the left.



This means that silver gains electrons, so the reaction moves to the right.

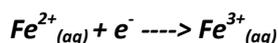


(ii) ions of the same element in different oxidation states;

A metal ion; metal ion half cell with different oxidation states can be formed.

- A standard half cell of this state is made up of a solution containing the same element with different oxidation states in equal concentrations (an equimolar solution)
- An inert platinum electrode allows electrons to pass in and out of the half cell via a connecting wire.

An example of this would be Fe^{2+} and Fe^{3+} :



37. Calculating a standard cell potential by combining two standard electrode potentials

The standard electrode potential $E^{\circ}_{cell} = E^{\circ}(\text{positive terminal}) - E^{\circ}(\text{negative terminal})$

E.g



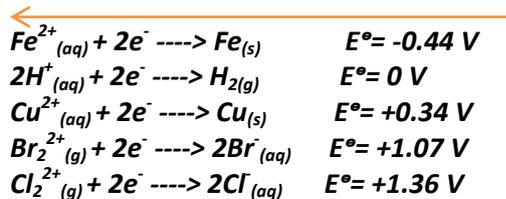
Therefore $E^{\circ}_{cell} =$

$$0.80 - 0.34 = 0.46 \text{ V}$$

38. Feasibility of reactions

We can predict feasibility of a reaction by looking at the standard cell potentials.

In these 5 reactions:



The top equation has the highest tendency to release electrons and shift to the left, and vice versa for the bottom.

From this, we can predict that $Fe_{(s)}$ would react with every species below it, and on the left side of every equation; also $Cu_{(s)}$ would also react with the species below it on the left hand side of the equation.

39. Limitations of predictions made using standard cell potentials in terms of kinetics and concentration.

Non-standard conditions may alter the value of the electrode potential.

Le Chatelier's principle may kick in; if electrons are added or removed from the equilibrium, the electrode potential may become more positive or negative due to the changing equilibrium position.

The reaction rate cannot be predicted by using these potentials, as the Activation energy is too high, so the reaction is too slow. Also, the actual conditions used may vary from the standard conditions, which may affect the electrode potentials. This means the standard value may not be valid.

40. Modern Storage cells.

Electrochemicals are used widely today as a source of electrical energy. Cells can be divided into 3 types.

- 1. Non-Rechargeable – provide electrical energy until the chemicals have reacted to such extent that the potential difference falls.**
- 2. Rechargeable – The chemicals in the cell react similarly to above, the reaction can then be reversed during charging and the cell can be used again (Nickel and Cadmium & Lithium ion)**
- 3. Fuel Cells – cell reaction uses an external supply of a fuel as an oxidant, which are consumed constantly. They will provide electrical energy so long as there is a supply of fuel and oxidant.**

(j) explain that a fuel cell uses the energy from the reaction of a fuel with oxygen to create a voltage;

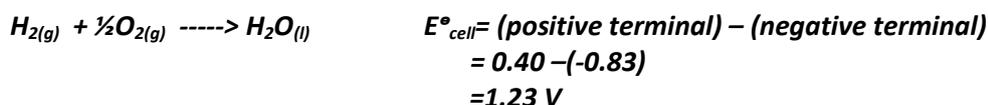
A fuel cell uses energy from the reaction with a fuel and oxygen to create a voltage. The reactants flow in and the products flow out while the electrolyte remains in the cell. These fuel cells can work continuously as long as the fuel and oxygen continue to flow into the cell

41. Changes that take place in a hydrogen oxygen fuel cell.

In a hydrogen-oxygen fuel cell, the hydrogen terminal is more negative. This system provides the electrons. Therefore the redox equation is:



Overall:



42. Development of fuel cells

(l) outline that scientists in the car industry are developing fuel cell vehicles (FCVs), fuelled by:

- (i) hydrogen gas,**
- (ii) hydrogen-rich fuels;**

These are an alternative to our current finite oil-based fuels.

43. Advantages of fuel cell vehicles

(m) state advantages of FCVs over conventional petrol or diesel-powered vehicles, in terms of:

- (i) less pollution and less CO₂,**
- (ii) greater efficiency;**

44. Storage of hydrogen in FCV's

(i) as a liquid under pressure, - a very low storage temperature is needed however.

(ii) adsorbed on the surface of a solid material.

(iii) absorbed within a solid material;

45. Limitations of fuel cells.

(i) storing and transporting hydrogen, in terms of safety, feasibility of a pressurised liquid and a limited life cycle of a solid 'adsorber' or 'absorber.

(ii) limited lifetime of current fuel cell (requiring regular replacement and disposal) and high production costs,

(iii) use of toxic chemicals in their production (see also unit F322: 2.4.2);

(p) comment that a 'hydrogen economy' may contribute largely to future energy needs but limitations include:

- (i) public and political acceptance of hydrogen as a fuel,**
- (ii) handling and maintenance of hydrogen systems,**
- (iii) initial manufacture of hydrogen, requiring energy.**

Module 3: Transition Elements

46. Electronic configuration of Transition elements.

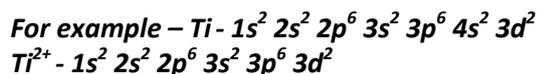
The electron configuration of transition metals are more complicated than at AS. The transition metals are known as d block which means they fill until the d orbitals.

The first row of the d block, beginning with Scandium, has a configuration of $[Ar] 4s^2 3d^1$. This means the orbitals of lower energy than the 4s orbital are all filled.

Element Name and Symbol	Atomic Number	Common Oxidation States	Electron Configuration	
Scandium (Sc)	21	+3	Sc: $[Ar] 4s^2 3d^1$	Sc: $[Ar] \begin{array}{c} \uparrow\downarrow \\ 4s \end{array} \quad \underbrace{\begin{array}{c} \uparrow \quad _ \quad _ \quad _ \\ 3d \end{array}}$
Titanium (Ti)	22	+4	Ti: $[Ar] 4s^2 3d^2$	Ti: $[Ar] \begin{array}{c} \uparrow\downarrow \\ 4s \end{array} \quad \underbrace{\begin{array}{c} \uparrow \quad \uparrow \quad _ \quad _ \\ 3d \end{array}}$
Vanadium (V)	23	+2, +3, +4, +5	V: $[Ar] 4s^2 3d^3$	V: $[Ar] \begin{array}{c} \uparrow\downarrow \\ 4s \end{array} \quad \underbrace{\begin{array}{c} \uparrow \quad \uparrow \quad \uparrow \quad _ \\ 3d \end{array}}$
Chromium (Cr)	24	+2, +3, +6	Cr: $[Ar] 4s^1 3d^5$	Cr: $[Ar] \begin{array}{c} \uparrow \\ 4s \end{array} \quad \underbrace{\begin{array}{c} \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\ 3d \end{array}}$
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: $[Ar] 4s^2 3d^5$	Mn: $[Ar] \begin{array}{c} \uparrow\downarrow \\ 4s \end{array} \quad \underbrace{\begin{array}{c} \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\ 3d \end{array}}$
Iron (Fe)	26	+2, +3	Fe: $[Ar] 4s^2 3d^6$	Fe: $[Ar] \begin{array}{c} \uparrow\downarrow \\ 4s \end{array} \quad \underbrace{\begin{array}{c} \uparrow\downarrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\ 3d \end{array}}$
Cobalt (Co)	27	+2, +3	Co: $[Ar] 4s^2 3d^7$	Co: $[Ar] \begin{array}{c} \uparrow\downarrow \\ 4s \end{array} \quad \underbrace{\begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow \quad \uparrow \quad \uparrow \\ 3d \end{array}}$
Nickel (Ni)	28	+2	Ni: $[Ar] 4s^2 3d^8$	Ni: $[Ar] \begin{array}{c} \uparrow\downarrow \\ 4s \end{array} \quad \underbrace{\begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow \quad \uparrow \\ 3d \end{array}}$
Copper (Cu)	29	+2	Cu: $[Ar] 4s^1 3d^{10}$	Cu: $[Ar] \begin{array}{c} \uparrow \\ 4s \end{array} \quad \underbrace{\begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ 3d \end{array}}$
Zinc (Zn)	30	+2	Zn: $[Ar] 4s^2 3d^{10}$	Zn: $[Ar] \begin{array}{c} \uparrow\downarrow \\ 4s \end{array} \quad \underbrace{\begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ 3d \end{array}}$

Two exceptions of this are Copper and chromium, however. In Chromium, the 3d and 4s orbitals only have 1 electron in each, none are full. In Copper, the 4s orbital only has 1 electron, and the 3d orbitals are full.

Also, the 4s electrons are of lower energy than 3d orbitals so are filled first. However, after the electrons occupy the orbitals, 4s has a higher energy level. This means in forming ions, the 4s not only is filled first, but also becomes deprived first.



The 4s electrons are lost first, to form the states configuration or Titanium $^{2+}$.

(b) describe the elements Ti–Cu as transition elements, ie d-block elements that have an ion with an incomplete d sub-shell;

47. Oxidation states of Transition elements

With exception to Scandium, all the first row of transition elements may form ions with a 2+ oxidation state; in most cases this is due to the 2 4s electrons being lost. However, the 3d electrons can also be lost when an atom forms a stable ion.

The oxidation states are not always +2, however, and can be calculated using oxidation number rules learned in AS.

These are common oxidation states and colours of d-block ions.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
	+5	+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

(ii) the formation of coloured ions,

When white light passes through a solution, some wavelengths of light are absorbed. The wavelengths that are not absorbed are reflected, and we see a mixture of these.

A lot of coloured inorganic compounds contain transition metal ions; colour is linked partially to filled d orbitals of transition metal ions.

(iii) the catalytic behaviour of the elements and/or their compounds;

Transition metals are effective catalysts.

- **They provide a surface on which a reaction may take place via adsorption, reaction, desorption etc.**
- **They have the ability to change oxidation states by gaining or losing electrons. They may then form intermediates by binding to reactants as part of a chemical pathway, lowering activation energy.**

48. Precipitation reactions of Transition elements

Precipitation reactions occur when soluble ions in separate mixtures are mixed together to form an insoluble compound.

Equation	Colour and state before	Colour and state after
$\text{Cu}^{2+}_{(aq)} + 2\text{OH}^{-}_{(aq)} \rightarrow \text{Cu}(\text{OH})_{2(s)}$	Pale blue solution	Pale blue precipitate
$\text{Co}^{2+}_{(aq)} + 2\text{OH}^{-}_{(aq)} \rightarrow \text{Co}(\text{OH})_{2(s)}$	Pink Solution	Blue precipitate Beige in presence of air
$\text{Fe}^{2+}_{(aq)} + 2\text{OH}^{-}_{(aq)} \rightarrow \text{Fe}(\text{OH})_{2(s)}$	Pale green solution	Green precipitate Rusty brown on surface in presence of air
$\text{Fe}^{3+}_{(aq)} + 3\text{OH}^{-}_{(aq)} \rightarrow \text{Fe}(\text{OH})_{3(s)}$	Pale yellow solution	Rusty brown solution

49. Ligands and Coordinate bonds.

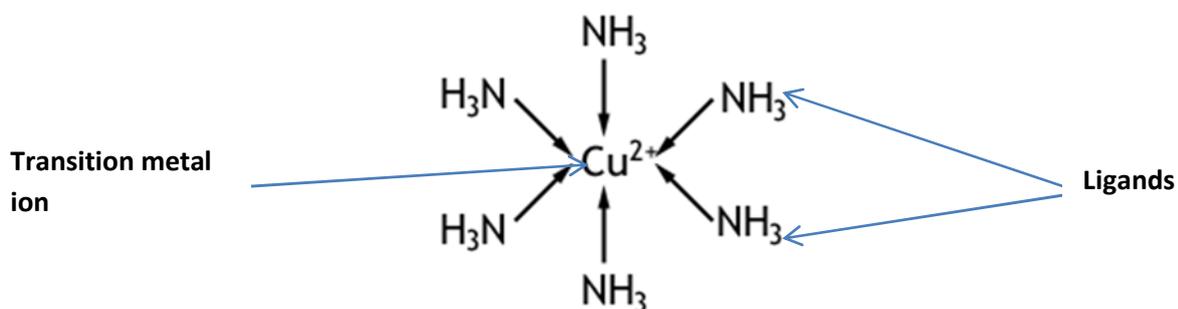
Ligand – A molecule or ion that can donate a pair of electrons with the transition metal ion to form a coordinate bond.

50. Complex ions and coordinate numbers

Complex Ion – a transition metal ion bonded to one or more ligands by coordinate bonds.

Coordination number – The total number of coordinate bonds formed between a central metal ion and it's ligands.

E.g - $[\text{Cu}(\text{NH}_3)_6]^{2+}$



In this example, the co-ordination number is 6 as there are 6 coordinate bonds.

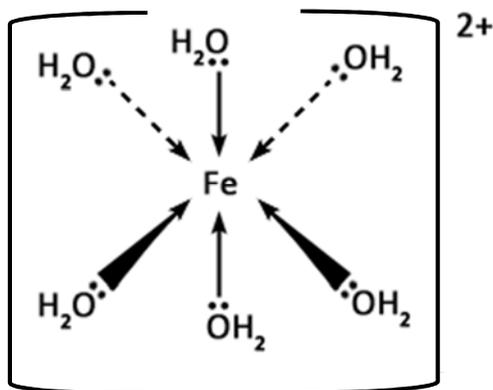
51. Monodentate Ligands

Monodentate ligands donate just 1 pair of electrons to the central metal ion.

Name of Ligand	Formula	Charge
Water	$:\text{OH}_2$	None
Ammonia	$:\text{NH}_3$	None
Thiocyanate	$:\text{SCN}^-$	-1
Cyanide	$:\text{CN}^-$	-1
Chloride	$:\text{Cl}^-$	-1
Hydroxide	$:\text{OH}^-$	-1

(g) state and give examples of complexes with sixfold coordination with an octahedral shape;

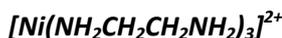
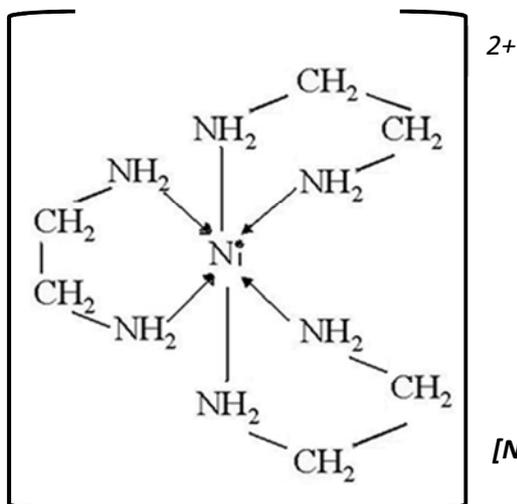
The most common shape of complex ion is the octahedral shape. They have 6 coordinate bonds. 4 of the ligands are in the same plane, 1 is above and 1 below. All bond angles are 90°



(h) explain and use the term bidentate ligand (eg $NH_2CH_2CH_2NH_2$, 'en');

52. Bidentate Ligands

Bidentate ligands can donate 2 lone pairs of electrons to the central metal ion to form 2 coordinate bonds.



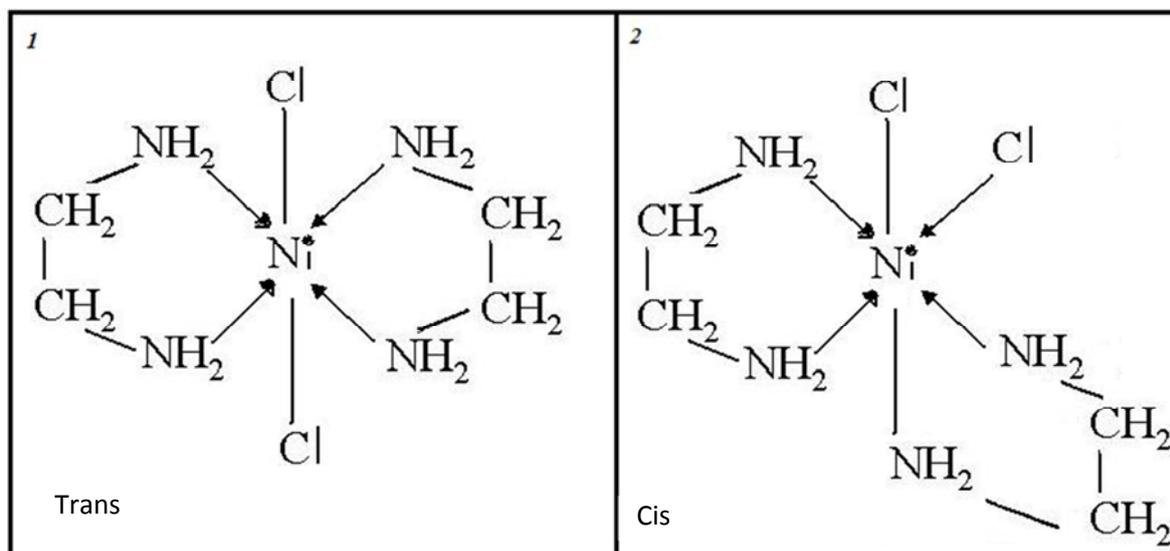
An example of this is ethane-1-2-diamine ($NH_2CH_2CH_2NH_2$) – this is often shortened to 'en'

Here, each nitrogen atom donates its lone pair to the central metal ion. This is also an example of an octahedral complex ion. Each 'en' ligand donates 2 lone pairs and there are 3 'en' ligands; there are therefore 6 coordinate bonds.

53. Stereoisomerism in Ligands

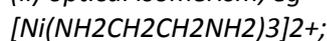
(i) *cis-trans isomerism,*

Cis-trans isomerism is demonstrated in this complex ion



In trans, the bidentate ligands are opposite each other, whereas in cis they are next to each other.

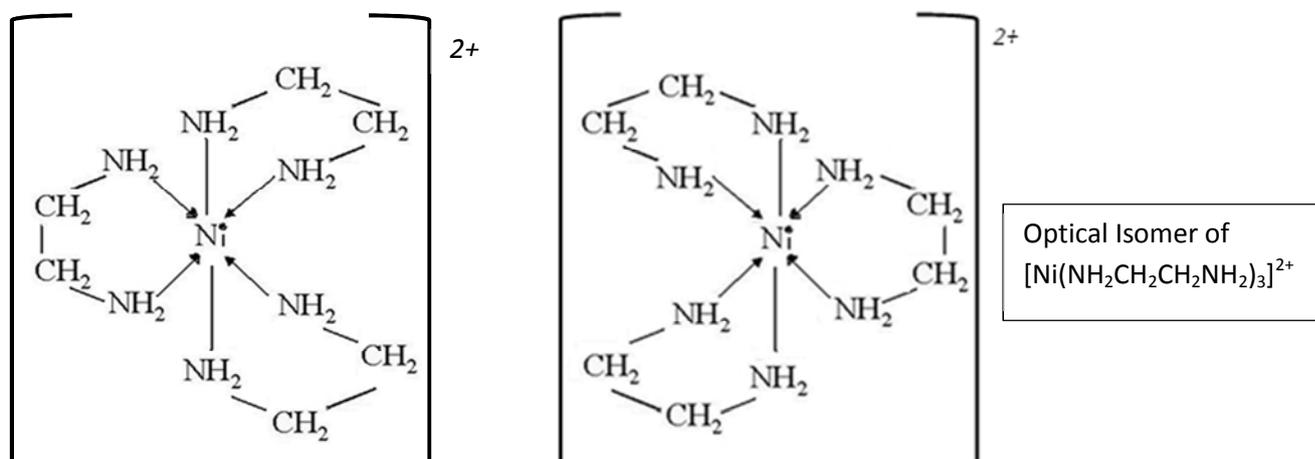
(ii) *optical isomerism, eg*



Optical isomers in transition element chemistry is usually associated with octahedral complexes that contain multidentate ligands.

The requirements for optical isomerism are:

1. **A complex with 3 molecules, ions of a bidentate ligand**
2. **A complex with 2 molecules or ions of a bidentate ligand, and two molecules or ions of a monodentate ligand.**
3. **A complex with one hexadentate ligand**



54. Cis-platin

Cis-platin is the cis complex of $[PtCl_2(NH_3)_2]$

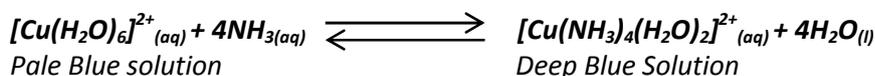
Cancer is the rapid and uncontrollable division of cells. Cis-platin acts by binding to the DNA of the cancerous cells- the cells are then prevented from reproducing by this change. This leads to the death of the cancer containing cells.

55. Ligand Substitution

Ligand Substitution – a reaction in which one ligand in a complex ion is replaced by another ligand.

(i) $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and $[CuCl_4]^{2-}$ from $[Cu(H_2O)_6]^{2+}$.

Aqueous solution of Copper (II) ions contains $[Cu(H_2O)_6]^{2+}$ complex ions. This can react with an excess of aqueous ammonia solution.

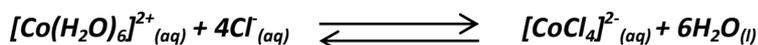


4 of the water ligands are replaced by ammonia ligands – this is ligand substitution as only 1 type of ligand has been replaced by another.

In this reaction, the copper oxygen bonds are longer than the copper nitrogen bonds, so a distorted octahedral shape is formed.

(ii) $[CoCl_4]^{2-}$ from $[Co(H_2O)_6]^{2+}$;

If Hydrochloric acid is added to Cobalt (II) ions in solution, it's pale pink colour turns into a dark blue solution.



The concentrated hydrochloric acid provides a high amount of chloride ions. The 6 water molecules in the complex ions are replaced by 4 chloride ions.

56. Iron in Haemoglobin

Red blood cells carry oxygen efficiently since they contain haemoglobin, which is a complex protein consisting of 4 polypeptide chains.

Each chain consists of 4 non protein groups called haem. Each haem group has an Fe^{2+} ion at its centre – oxygen can bind to this.

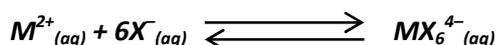
This occurs because:

- There are 4 coordinate bonds between the Fe^{2+} ion and the nitrogen atoms in the haem.
- A further protein bond forms to the protein, globin.
- A final coordinate bond is formed to an oxygen molecule, which is then transported.

57. Stability Constant:

Of a complex ion is the equilibrium constant for the formation of the complex ion in a solvent from its constituent ions;

(n) deduce expressions for the stability constant, K_{stab} , of a ligand substitution, eg



$$K_{stab} = \frac{[MX_6^{4-}_{(aq)}]}{[M^{2+}_{(aq)}][X^{-}_{(aq)}]^6}$$

The K_{stab} constant is theoretically the same as the K_c constant. Water is left out in these equations as essentially, all species are dissolved in water. It is largely in excess and the concentration remains virtually constant.

(o) relate ligand substitution reactions of complexes to stability constants and understand that a large K_{stab} results in formation of a stable complex ion;

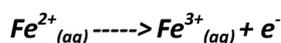
A large stability constant indicates the position of an equilibrium lies to the right. Complex ions with high stability constants are more stable than those with lower values.

A large value also means the ion is easily formed.

58. Redox in transition elements.

Transition elements have variable oxidation states; this means they can partake in both oxidation and reduction reactions.

For example, Iron has two common oxidation states, Fe^{2+} and Fe^{3+} . In the presence of air, Fe^{2+} readily turns into Fe^{3+}



Manganese can also exist in many oxidation states, most notably in 2^{+} and 7^{+} . MnO_4^{-} is a strong oxidising agent. An example is shown below



Manganese is found in both 7^{+} and 2^{+} states so has been reduced, whereas Iron has been oxidised from 2^{+} to 3^{+}

(q) carry out redox titrations, and carry out structured calculations, involving MnO_4^- and $\text{I}_2/\text{S}_2\text{O}_3^{2-}$.

Example:

20cm³ of a solution of Iron(II) salt required 21 cm³ of 0.0165 mol dm⁻³ potassium manganate(VII) for complete oxidation in acid solution.

1. Calculate number of moles of manganate (VII) used in the titration.
2. Calculate number of moles of Iron (II) in the titrated solution.
3. Calculate the concentration of Fe^{2+} in the titrated solution.

First refer to the equation:



- $N(\text{MnO}_4^-) = cv$
 - $0.0165 \times (21/1000)$
 - $= 3.47 \times 10^{-4} \text{ mol}$
- There are 5 Fe^{2+} 's to every 1 MnO_4^-
 - $5 \times 3.47 \times 10^{-4} \text{ mol}$
 - $= 1.73 \times 10^{-3} \text{ mol}$
- $N = cv$
 - $C = n/V$
 - $\frac{1.73 \times 10^{-3} \times 1000}{20}$
 - $= 0.0866 \text{ mol dm}^{-3}$

These questions are often tested, so three relevant half equations must be learned, as well as the whole equation.

$\text{Fe}^{2+} (\text{aq}) \longrightarrow \text{Fe}^{3+} (\text{aq}) + \text{e}^-$	Half equation (1)
$\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O} (\text{l})$	Half equation (2)
$\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{Fe}^{2+} (\text{aq}) \longrightarrow \text{Mn}^{2+} (\text{aq}) + 5\text{Fe}^{3+} (\text{aq}) + 4\text{H}_2\text{O} (\text{l})$	Full equation (3) 1+2 = 3

59. Non Structured titration calculations

There are 3 standard titration type questions

Calculating molar mass and formula of an Iron (II) salt.

Question: A student weighed out 2.950g of hydrated iron (II) sulphate, $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$ and dissolved it in 50 cm^3 of Sulphuric acid. This solution was poured into a 250 cm^3 volumetric flask and made up to the mark with distilled water. 2.5 cm^3 of this solution was titrated against 0.0100 mol dm^{-3} potassium manganate (VII), KMnO_4 , and 21.2 cm^3 of the MnO_4^- solution was used.

1. Calculate n on MnO_4^- used in the titration.
2. Deduce in moles, the amount of Fe^{2+} that was used in the titration if 25 cm^3 of the solution is used.
3. Deduce the amount in moles of Fe^{2+} in 250 cm^3 of solution.
4. Determine the M_r of the iron(II) salt
5. Determine the value of x and the formula of the hydrated salt.

❖ $N = cv$

- $0.0100 \times (21.2/1000)$
- $2.12 \times 10^{-4} \text{ mol}$

❖ Molar ratio of MnO_4^- to $\text{Fe}^{2+} = 1:5$

- $2.12 \times 10^{-4} \times 5 = 1.06 \times 10^{-3} \text{ mol}$

❖ In 25 cm^3 there is $1.06 \times 10^{-3} \text{ mol}$, so to calculate amount in 250 cm^3

- $1.06 \times 10^{-3} \text{ mol} \times 10$
- $1.06 \times 10^{-2} \text{ mol}$

❖ $n = m/M_r$

- $M_r = m/n$
- $2.950/1.06 \times 10^{-3} \text{ mol}$
- 278.3 g mol^{-1}

❖ Calculate molar mass of FeSO_4

- $55.8 + 32.1 + 4(16)$
 - 151.9g

- $278.3 - 151.9$
 - = 126.4 g

➤ Molar mass of H_2O

- $16 + 2 = 18$
- $126.4/18$

• 7

➤ The formula must therefore be

- $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Calculating percentage mass of iron in tablets

A 0.325g iron tablet was dissolved in some water containing dilute sulphuric acid. 12.10 cm³ of 0.00200 mol dm⁻³ potassium manganate(VII) solution was titrated until a pale pink colour was observed.

Calculate the percentage mass of iron in the tablets.

1. $n(\text{MnO}_4^-) = c \times V$
 - a. $= 0.00200 \times (12.10/1000)$
 - b. $= 2.46 \times 10^{-5} \text{ mol}$
2. $n(\text{Fe}^{2+})$
 - a. $2.46 \times 10^{-5} \text{ mol} \times 5$ (using the equation)
 - b. $= 1.21 \times 10^{-4} \text{ mol}$
3. $n = m/M_r$
 - a. $m = n \times M_r$
 - b. $1.21 \times 10^{-4} \text{ mol} \times 55.8$
 - c. $= 0.00675\text{g}$
4. $\% = \text{mass of iron} / \text{mass of tablet}$
 - a. $(0.00675/0.325) \times 100$
 - b. $= 2.08\%$

Oxidising Hydrogen Peroxide

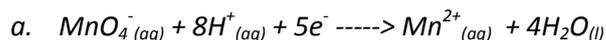
A 25.0 cm³ portion of hydrogen peroxide was poured into a 250 cm³ volumetric flask and made up to the top with water.

A 25 cm³ portion of this solution was acidified and titrated against 0.0200 mol dm⁻³ potassium manganate (VII) solution.

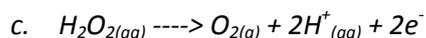
38.00 cm³ of the manganate solution was required for complete oxidation.

Calculate the concentration of original hydrogen peroxide solution.

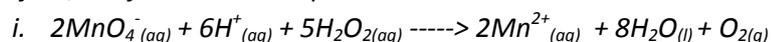
1. The equation required is



b. However, there is hydrogen peroxide in this equation which is being oxidised.



d. Therefore, the full balanced equation is:



2. $n(\text{MnO}_4^-) = cV$

a. $0.0200 \times (38/1000)$

b. $7.60 \times 10^{-4} \text{ mol}$

3. Amount of $\text{MnO}_4^- : \text{H}_2\text{O}_2 = 2:5$ ratio

a. $\text{H}_2\text{O}_2 = 7.60 \times 10^{-4} \text{ mol} \times 2.5$

b. $1.90 \times 10^{-3} \text{ mol}$

4. Concentration of $\text{H}_2\text{O}_2 = n/V$

a. $(1.90 \times 10^{-3} \text{ mol} \times 1000) / 25$

b. $0.0760 \text{ mol dm}^{-3}$

5. Solution was diluted at the start,

a. 0.0760×10

b. $=0.760 \text{ mol dm}^{-3}$