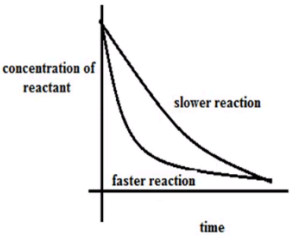
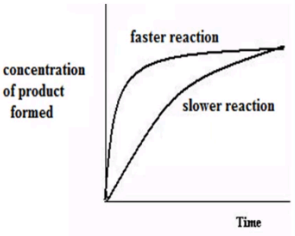
Topic 11 - Kinetics
11A - Further Kinetics

1- Techniques for measuring the rate of a reaction:

The rate of a reaction is the change in concentration of a species i.e. the reactants or products per unit time. The rate is always positive.





In a reaction, as the reaction progresses, the concentration of the product increases with time, whereas the concentration of the reactant decreases with time.

(1) How the concentration of a product *increases* with time.

$$\text{rate} = \frac{\text{change in concentration of product}}{\text{time}}$$

(2) How the concentration of a reactant *decreases* with time.

$$\text{rate} = -\frac{\text{change in concentration of reactant}}{\text{time}}$$

$$\text{rate} = \frac{d[\text{product}]}{dt}$$

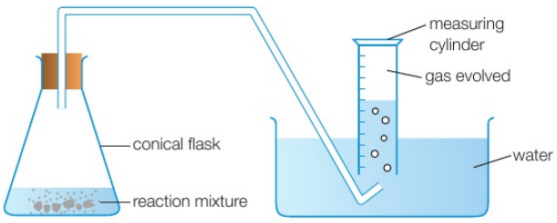
$$\text{rate} = -\frac{d[\text{reactant}]}{dt}$$

NOTE: The concentration of the reactant decreases with time, as a result, we usually get a negative value when measuring the rate. Since the rate is always positive, the negative sign shows us that the rate of a reaction is always positive.

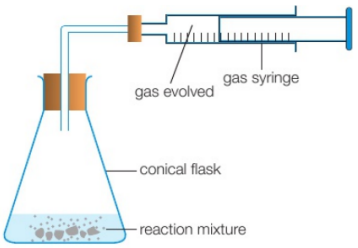
The units for rate = mol dm^{-3} s^{-1}

The rate of a reaction can be measured via several methods:

a) Measuring the volume of gas evolved:



▲ **fig A** Collecting a gas over water.



▲ **fig B** Collecting a gas in a gas syringe.

- The volume of gas evolved can be measured using two methods: Collecting the gas over water into the measuring cylinder and collecting the gas using a gas syringe.
- Reactions that produce gases that are soluble in water such as sulfur dioxide, carbon dioxide, nitrogen dioxide, etc.
- However, gas syringes have a greater degree of precision (Uncertainty = uncertainty/measured value) gas syringes would have a smaller absolute uncertainty, and therefore a smaller degree of uncertainty

b) Measuring the change in mass of a reaction mixture:

- This technique is suitable for gases with a high density - the greater the density of the gas, the greater the change mass, and therefore the lower the measurement uncertainty.

▲ **fig C** Cotton wool is placed in the neck of the flask to prevent the loss of liquid spray.

c) Colorimetry:
    - This technique gives us a quantitive measurement of the change in colour of the solution
    - The transmittance or absorbance of light is measured at various times. A calibration curve may convert the transmittance or absorbance to concentration.
    - For example $H_2 + Br_2 \rightarrow 2HBr$ Here, the reddish brown colour of the bromine will slowly disappear as the reaction proceeds. $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$ Here, the brown colour of the iodine solution will disappear slowly.

d) Analysis by titration:
    - This technique involves the use of a pipette to remove small samples or a reaction mixture at regular intervals. The small samples are known as aliquots.
    - The aliquot is then quenched (quenching is the process of rapidly cooling the aliquot to stop the reaction)
    - The aliquot is then titrated to determine the concentration of the reactants or products.
    - For example:
        - $CH_3COCH_3\ (aq) + I_2\ (aq) \rightarrow CH_3COCH_2I\ (aq) + H^+\ (aq) + I^-\ (aq)$
        - An acid catalyses this reaction. Initially, sodium hydrogen carbonate is added to the aliquot to remove the acid catalyst, which causes the reaction to stop. The remaining solution is then titrated with a standard solution of sodium thiosulfate - when you add sodium thiosulfate, the colour of the solution will change from brown to colourless

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

        - We cant use starch solution in this reaction, as starch solution is an indicator which means that the solution will turn blue black, the moment there is starch present

e) Measuring the electrical conductivity:
    - We use this method when the total number of ions in the solution changes over time.
    - The changes in the electrical conductivity are measured using a conductivity meter.

f) Changes in pressure:
    - The pressure of a reaction mixture will change if all the reactants and products are present as gases, and the number of moles of reactants and products changes over time.

g) Other methods of measuring the rate of a reaction include chirality (optical activity), changes in the volume of a liquid (dilatometry), and refractive index.

Iodine clock reaction:

- During this reaction, we add potassium iodide and sulfuric acid in a conical flask. This will result in the formation of iodine, potassium sulfate and water.

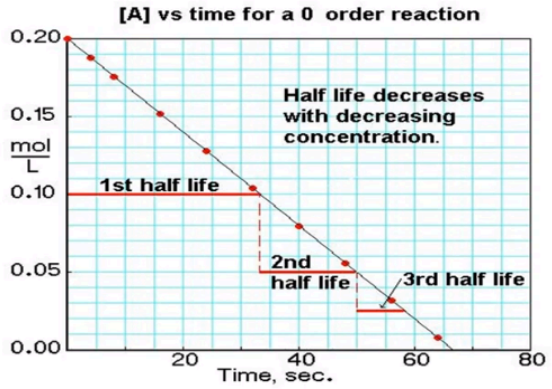
- The iodine then reacts with the sodium thiosulfate which results in the formation of sodium iodide and tetrathionate ions. When the sodium thiosulfate runs out, the excess iodine reacts with the scratch which causes the colour of the solution to change.

2 - Rate equations, rate constants and orders of reaction

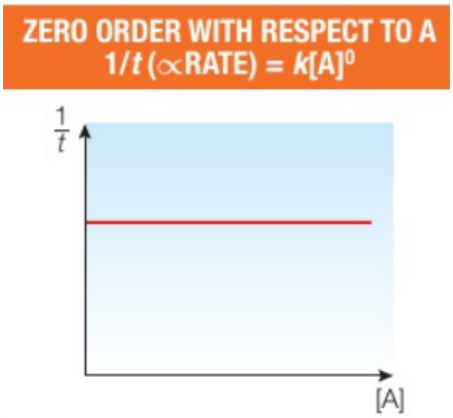
The rate of a reaction is dependent on the concentration of the reactants present. The order of a reaction tells us how the rate of the reaction is affected by the concentration of the reactant.

The rate equation is an equation that tells us how the rate of a reaction is affected by the concentration.

- The rate of a reaction concerning the concentration os its reactants can be affected in three ways which can be deduced by the order of the reactions.
- Zero-order reactions: in these types of reactions, the concentration doesn't affect the rate of the reaction
    - The concentration-time graph for a zero-order reaction:

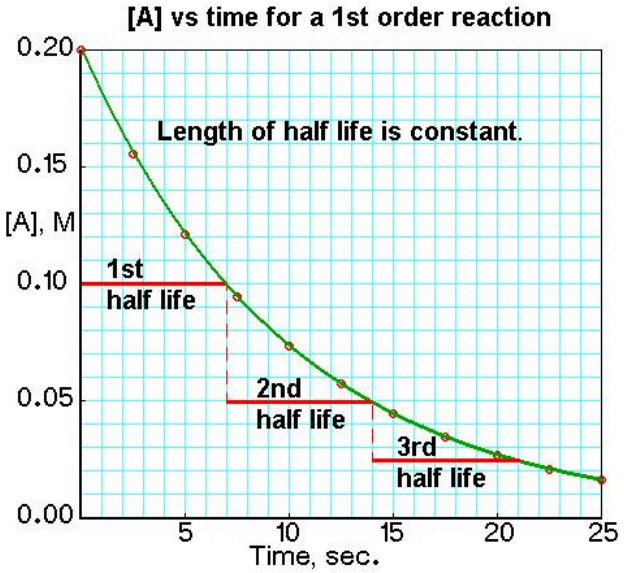


        - This shows us that, as the concentration of the reactant has no effect on the rate of the reaction - we know that the rate of the reaction = gradient of the graph, here we can see a constant gradient, as result we can say that a change in the conc of the reactant has no effect on the rate of the reaction
        - As the concentration decreases, the half-life decreases as well - this means that as the conc decreases, the time taken to reach half the initial conc decreases with time.
    - The rate concentration graph for a zero-order reaction:

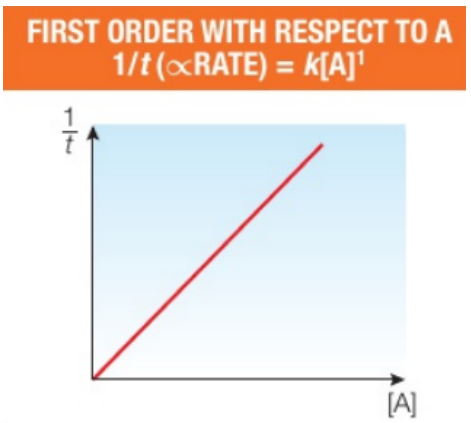


- Here, we can see that the rate of the reaction stays constant regardless of the conc of the reactant, which tells us that for zero order reactions, the conc of the reactant does not affect teh rate of the reaction

- First order reaction:
  - In these reactions, when the conc of the reactant increases by a factor of 1, the rate of teh reaction increases by a factor of 1 as well.
  - The concentration-time graph of a first order reaction:

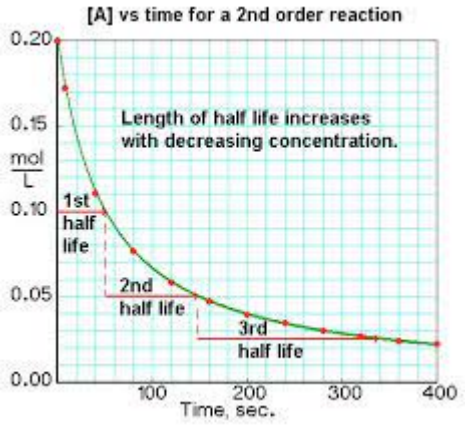


    - Based on this graph, at the conc of the reactnat decreases, the rate of the reaction decreases simulatneounsly as well. Thus the half life is constant, as the
  - The rate concentration graph for a first order reaction:

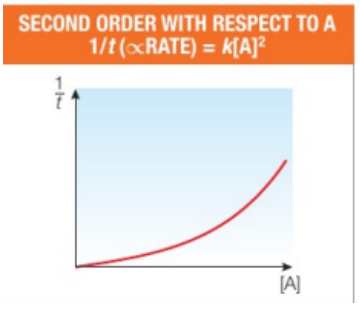


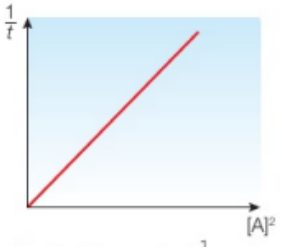
- Here, we can see that as the concentration increases, there is a linear increase in the rate as well, which suggests that if the concentration of the reactants increases by 1 then the rate of the reaction will increase by 1 as well

- Second-order reactions:
  - In these reactions, when the concentration of the reactants increases by 1 the rate will increase by a factor of 2.
  - The graph for concentration time of a second-order reaction would have an increasing half-life, i.e. the amount of time required to reach half the conc of the reactants would increase as the conc of the reactants decreases - this is because, in a second-order reaction,



  - The graph for rate against concentration would be an exponential graph wherein the rate increases exponentially as the concentration of the reactants increases.





- The rate equation tells us how the concentration of the reactants affects the rate of the rate of the reaction
- The rate of a reaction for a zero-order reaction: rate = k; for a first-order reaction rate = k[A]; lastly, for a second reaction: rate = $k[A]^2$
- The units for k will be different for every equation; whereas the units for the rate are fixed i.e. mol $dm^{-3}s^{-1}$

ORDER	UNIT
Zero	mol dm^{-3} s^{-1}
First	s^{-1}
Second	dm^3 mol^{-1} s^{-1}
Third	dm^6 mol^{-2} s^{-1}

table A

- Each reaction has its own rate equation
- The rate constant will only change if there is a change in temperature when the reaction is taking place.
- The overall order of the reaction is the sum of all the individual orders.

The units are obtained by rearranging the rate equation. For example, for a second order reaction:

$$k = \frac{\text{rate}}{[A]^2}$$

Inserting the units we obtain:

$$\frac{\text{mol dm}^{-3}\ \text{s}^{-1}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}$$

This cancels down to:

$$\frac{\text{s}^{-1}}{\text{mol dm}^{-3}}$$

which equates to dm^3 mol^{-1} s^{-1}.

The majority of reactions involve two or more reactants. If we call the reactants A, B and C, then the reaction may be first **order** with respect to A, first order with respect to B and second order with respect to C. The *overall* rate equation will be:

$$\text{rate} = k[A][B][C]^2$$

and the **overall order** of the reaction is four (1 + 1 + 2). Note that you are adding the powers.

For a general reaction in which the orders are m, n and p, we have:

$$\text{rate} = k[A]^m[B]^n[C]^p$$

The overall order of the reaction is $m + n + p$.

- Reaction mechanisms:
  - The mechanism of a reaction, are the steps taken for the reaction to happen. I.e. suppose with a reaction between 8 moles of acid, 5 moles of iron, and one mole of a manganate ion. The probability of all the particles colliding and resulting in the formation of a product is very unlikely.
  - As a result, the reaction happens via a series of steps
  - We can assume a possible mechanism that is taking place, however, since we can't determine the order of a reaction without experimenting, we can't determine the actual mechanism
  - For example: A+B+ C → D + E
    - Based on this example, we can experimentally determine that the rate equation is rate = k[A][B]
    - This suggests that the concentration of C doesn't affect the rate of the reaction - i.e. it's zero order
    - A possible mechanism for this reaction would be

      Step 1: $A + B \rightarrow Z$ SLOW

      Step 2: $Z + C \rightarrow D + E$ FAST

    - The slowest step is always the rate-determining step, which in this case is Step 1. Therefore, the effect of conc of C on the rate is negligible

Determining the rate equation:

- The two methods of determining teh rate equation are continuous and experimental.
- Continuous method:
  - One reaction mixture is made up and samples of the reaction mixture are withdrawn at regular time intervals.
  - The reaction is stopped using quenching
  - The conc of the reactants is then determined using the process of titration.
  - Next, draw a conc time graph and determine the half-life
  - We know the is the half-life is decreasing then its a zero-order reaction, if its constant its a first order, if its increasing it second order

PRACTICAL SKILLS CP9A

A study of the acid-catalysed iodination of propanone

The reaction between propanone and iodine in aqueous solution may be acid catalysed:

$$I_2(aq) + CH_3COCH_3(aq) + H^+(aq) \rightarrow CH_3COCH_2I(aq) + 2H^+(aq) + I^-(aq)$$

The influence of the iodine on the reaction rate may be studied if the concentrations of propanone and hydrogen ions effectively remain constant during the reaction. This is achieved by using a *large excess* of both propanone and acid in the original reaction mixture. You will investigate this in **CP9A Following the rate of iodine–propanone reaction by a titrimetric method**.

Procedure

1 Mix 25 cm^3 of 1 mol dm^{-3} aqueous propanone with 25 cm^3 of 1 mol dm^{-3} sulfuric acid.

2 Start the stop clock *the moment you add* 50 cm^3 of 0.02 mol dm^{-3} iodine solution. Shake well.

3 Using a pipette, withdraw a 10 cm^3 sample and place it in a conical flask. Stop the reaction by adding a 'spatula-measure' of sodium hydrogen carbonate. Note the exact time at which the sodium hydrogen carbonate is added.

4 Titrate the remaining iodine present in the sample with 0.01 mol dm^{-3} sodium thiosulfate(VI) solution, using starch indicator.

5 Withdraw further 10 cm^3 samples at suitable time intervals (approx. 5 to 7 minutes) and treat them similarly, always noting the exact time at which the sodium hydrogen carbonate is added. Waste should be contained in a fume cupboard.

Treatment of results

The Lab Book can give additional guidance in the treatment and analysis of results.

- Plot a graph of titre against time. (The titre is proportional to the concentration of iodine.)
- Deduce from the graph the order of reaction with respect to iodine.

Analysis of results

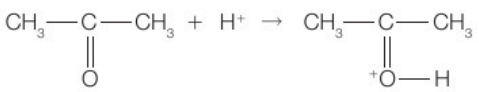
The graph produced shows that the reaction is zero order with respect to iodine.

Similar experiments show that the reaction is first order with respect to both propanone and hydrogen ions.

This gives us the following rate equation:

$$\text{rate} = k[CH_3COCH_3][H^+]$$

This would suggest the following reaction as the first step of the reaction:



Similar reactions in other mechanisms are very fast, so this reaction is unlikely to be the rate-determining step of this reaction.

11 - Kinetics

Rate of reaction:

- The rate of reaction can be expressed in two ways:
    - How the concentration of a product increases with time

$$\text{rate} = \frac{\text{change in concentration of product}}{\text{time}}$$

    - How the concentration of the reactant decreases with time

$$\text{rate} = -\frac{\text{change in concentration of reactant}}{\text{time}}$$

        - The negative sign in the expression shows that the concentration of the reactant is decreasing and therefore gives a positive value of the rate.
        - Rate is measured in units of concentration per unit time i.e. mol dm^{-3} s^{-1}

- The rate of reaction sometimes be called the overall rate fo reaction.

Techniques for measuring the rate of reaction:

- The rates of reactions can be measured by:
    - Measuring the volume of gas evolved
        - Collecting gas over water into a measuring cylinder - useful for larger volumes of gases collected.
        - Collection using a gas syringe. - greater degree of precision
    - Measuring the change in mass of a reaction mixture
        - The mass will change only is a gas has evolved form the reaction.
        - The technique is morep
    - Monitoring the change in intercity of the color of a reaction mixture (colorimetry)
    - Measuring the change in concentration of a reactant or product using titration.
    - Measuring the pH of a solution
    - Measuring the change in electrical conductivity of a reaction mixture.

Rate equation:

- We know that the rate of a reaction is the change in concentric of teh products or the reactions per unit time.
- Usually, the rate of a reaction is directly proportional to the concentration. However, this might not always be the case, as sometimes if the rate doubles the concentration can increase by a factor of 4.
- This can be represent using an equation which we call the rate equation:
    - rate = k [A]
        - Here, k is the proportionality constant,
        - A is the concentration of the reactnants

- Every reaction has its particular rate equation and its rate constant
- The rate constant can only change if there is a temperature change, as the temperature can affect the kinetic and thermal stability.

- There can be different type sof reactions i.e. first and second order reactions
- If there are two or more reactants the overall order of the reaction will be the sum of the individual orders of reactnats present in the reaction for example:

  rate = $k[A][B][C]^2$
  - In this reaction, teh overall order of the reaction will be 1+1+2 = 4

Units for rate constants can be obtained by rearranging the rate equation.

ORDER	UNIT
Zero	$mol\ dm^{-3}\ s^{-1}$
First	s^{-1}
Second	$dm^3\ mol^{-1}\ s^{-1}$
Third	$dm^6\ mol^{-2}\ s^{-1}$

Reaction mechanisms:
Some stoichiometric equations may consist of many models of reactions, for example, the reaction between manganate (VII) ions and iron (II) ions in an acid solution

MnO_4^- (aq) + $8H^+$ (aq) + $5Fe^{2+}$ (aq) → Mn^{2+} (aq) + $4H_2O$ (l) + $5Fe^{3+}$ (aq)

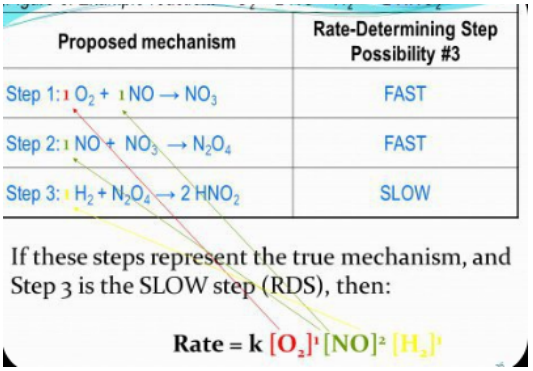
- The following reaction can't proceed in one step as the probability of 14 molecules colliding in the right orientation with the right amount of energy is fairly low, meaning that the rate of the reaction would be very slow
- However, this reaction takes place in steps which makes the overall reaction very fast under room temperature.
- The mechanism for the reaction can be deduced by looking at the order at which the individual reactants react with each other,
  - I.e. which molecule reacts first, and which reacts second with the intermediate created in the first.
- The mechanism of the reaction can only be found experimentally by finding out the relationship between the rate and concentration of the reactants.

- For example: for the reaction A + B + C → D + E
  - For which the experimentally determined rate equation is: rate = k[A][B]
  - This could suggest one of two things, either that the rate fo reaction with respect to the concentration of C is zero order, or that C is present in such a large excess that changes in its concentration is negligible and therefore has no measurable effect on the rate of the reaction.
  - If the reaction is zero order with respect to the concentration of C, then there must be a step involving a reaction between A and B that has an effect on the rate of the reaction - there must also be another step in which C reacts, but has no effect on the overall rate of the reaction.
  - This is possible by assuming that the reaction between A and B takes place before and the rate of the reaction between A and B is very slow.

- The slow step is the rate-determining step, this is because the rate is the change in concentration of reactants or products per unit of time, the slowest step would determine this/

Step 1:	$A + B \rightarrow Z$	SLOW
Step 2:	$Z + C \rightarrow D + E$	FAST

- Any species in or before the rate determining step will have an effect on the reaction and will appear in the rate equation.
- For example:
- Here, O_2 isn't present in the rate-determining step, however, it's present in the rate equation this is because:
    - Fast First Step: O2 reacts quickly with NO in step 1 to form NO3. Since it's fast, we can assume the concentration of NO3 remains relatively constant throughout the reaction.
    - Slow Consumption of NO3: The slow step (step 3) utilizes NO3 and H2 to form HNO2. As the reaction progresses, NO3 gets consumed, but it's constantly being replenished by the fast step 1 (as long as O2 is available).
    - Rate Depends on Available NO3: Because step 3 is slow and limits the overall reaction rate, the rate becomes dependent on the availability of NO3.
    - O2 indirectly controls NO3: Since O2 dictates the formation of NO3 (through the fast step 1), its concentration indirectly affects the rate of the overall reaction.



Therefore, even though O2 isn't directly involved in the slow step, its concentration influences the availability of NO3, which in turn controls the rate of the overall reaction. This explains why O2 appears in the rate equation.
In essence, the rapid first step acts like a "pre-equilibrium" that feeds the slow step with the necessary reactant (NO3). The rate law reflects the dependence on the overall process, even if some steps happen much faster.

- Once the reaction orders are known, the rate equation becomes more specific and can be used to predict the rate of the reaction at any given set of concentrations of the reactants.

3 - Determining the orders of reaction:

- The order of reactions can be determined via two methods both of which involves experiments rather than stochiometry:
    - Continuous method
    - Initial rate method

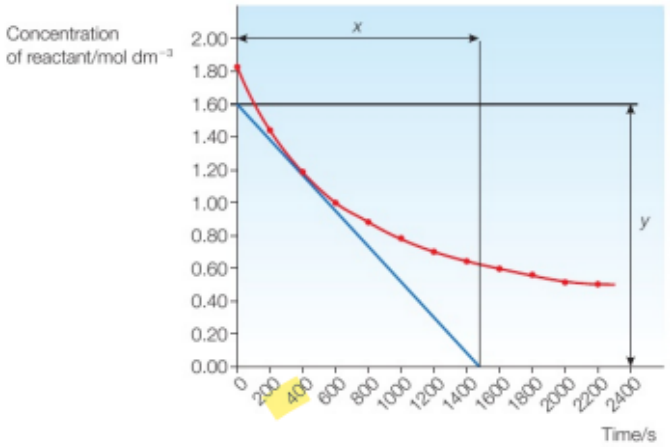
a) The continuous method:

- In this method, one reaction mixture is made up and samples of the reaction mixture are withdrawn at regular time intervals.
- The reaction in the sample is stopped, if necessary by quenching
- The concentration of the reactant is then determined by an appropriate experimental technique such as titration.
- The recorded concentration is used to draw a concentration time graph
- The second step is to find out the half life for the reaction at different concentrations.

- Half life:
  - Half-life is the time taken for the concentration of the reactant to fall to one-half of it's initial value.
  - Zero oder reactions = half-life decreases with decreasing concentration of the reactant
    - The graph for this has a straight line downwards, which suggests that the rate of the reaction is constant no matter what the conc of the reactant is
  - First-order reactions = half-life remains constant with decreasing concentration of the reactant
  - Second-order reactions = Half-life increases with decreasing concentration of the reactant.

Calculating rate from a concentration-time graph:

- The rate of a reaction at any given time can usually be determined by drawing a tangent at that time on the concentration-time graph of the reaction.
- For example:



- ▲ **fig C** Determining an instantaneous rate of reaction from a graph of concentration of reactant against time.

A tangent to the curve has been drawn at time = 400 s.

To find the rate at this time point, draw as large a triangle as possible and then measure x and y.

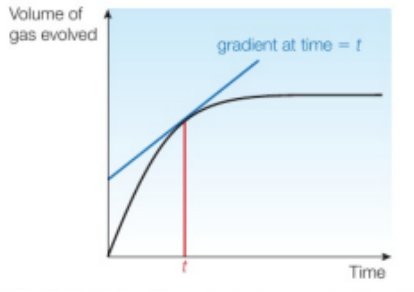
$x = 1470\,\text{s}$ and $y = -1.60\,\text{mol dm}^{-3}$.

$$\text{rate} = -\frac{\text{change in concentration of reactant}}{\text{time}}$$

$$= -\frac{-1.60\,\text{mol dm}^{-3}}{1470\,\text{s}} = 1.09 \times 10^{-3}\,\text{mol dm}^{-3}\,\text{s}^{-1}$$

Calculating rate from a volume time graph:

- In this graph, we record the volume of gas evolved in various time intervals and then plot a graph for acquired values
- Find the gradient of the graph, to determine the rate at a given time.
- The rate obtained is said to be the instantaneous reaction rate.



The initial rate method for determining the rate equation:

- In this method, several reaction mixtures are made up and the initial rate of the reaction measured
    - We use several reaction mixtures, as it can allow us to determine the rate with respect to one of the concentrations of the reactants in the reaction, but by adding the otehr reactant in excess, we can determine the rate of reaction with respect to one of the reactants only.
- In order to determine the rate equation using the initial concentration of the reactants, we keep the concentration of one of the reactants the same and the concentration of the other reactants different, i.e. we may double it or triple it and see how the rate changes accordingly.
    - Zero order = double conc; no change in rate
    - First order = double conc; double rate
    - Second order = double conc; rate = increases by a factor of 4.

Determining the order from a rate concentration graph:

- The initial rate method relies on approximate values for the initial rates of reactions, which is usually acceptable due to the integer nature of reaction rates.
- Time is measured for a fixed amount of product formed or reactant consumed, with the amounts typically remaining constant.
- Consequently, the rate of reaction is proportional to the reciprocal of time: rate $\propto$ 1/t.
- However, it's important to recognize that this assumption implies a constant rate throughout the reaction, which is often not the case; rates tend to decrease over time.
- Therefore, the rate calculated using this method represents the mean rate over time rather than the true initial rate of reaction.
- Rate-concentration graphs depict how the average rate of a reaction changes with varying concentrations of reactants.

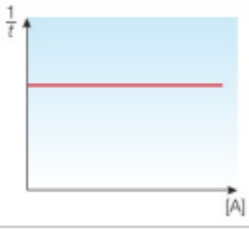
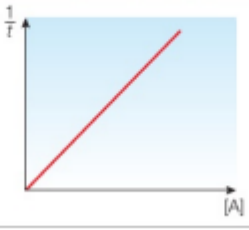
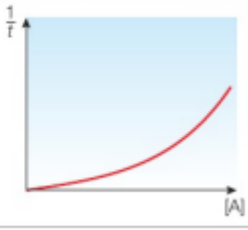
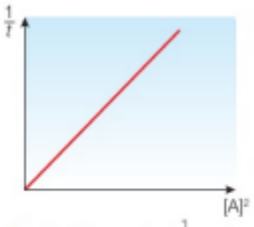
ZERO ORDER WITH RESPECT TO A $1/t\ (\propto \text{RATE}) = k[A]^0$	FIRST ORDER WITH RESPECT TO A $1/t\ (\propto \text{RATE}) = k[A]^1$	SECOND ORDER WITH RESPECT TO A $1/t\ (\propto \text{RATE}) = k[A]^2$
		

table C

- It is usually not possible to determine if a reaction is second order or not when the graph thats plotted is a rate, concentration graph. We usually plot, rate against concentration squared graph which gives us the following graph



▲ **fig E** A graph of $\frac{1}{t}$ against the square of the concentration of a reactant for a second order reaction.

Rate equations and mechanisms:

Rate mechanisms:

- For a reaction to take place, the particles first need to collide in the right rinitaoin and with sufficient energy.
- For reactions involving two reactants only i.e. P + Q → products; will give us a rate law of rate = k[P][Q]
- Such reactions are known as elementary reactions i.e. a reaction which is caused due to a sible collision between two particles.
- If we know that the reaction is elementary, we can deduce the rate law directly from the equation, as the rate is affect by the orientation and the energy of the molecules of the two reactants that are involved.
- If the reaction is not elementary i.e. involves more than two reactants, then its not possible to deduce the rate of the equation by looking at the stoichiometric equation only, as the rate at which some reacntnats react might not be the same as which the rate at which a different reacntnt reacts.
- For example, the decomposition of dinitrogen pentaoxide into nitrogen dioxide and oxygen is first order with respect to dinitogen pentaoxide, this is because it takes place via a series fo interconnected elementary reactions which we call the mechanism of the reaction.
- Another example of a non - elementary reaction is the free radical substitution between methane and chlorine, resulting in the formation of chloromethane

Step 1: $Cl_2 \rightarrow 2Cl\bullet$

Step 2: $Cl\bullet + CH_4 \rightarrow HCl + \bullet CH_3$

Step 3: $Cl_2 + \bullet CH_3 \rightarrow Cl\bullet + CH_3Cl$

The overall stoichiometric equation for the reaction is:

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

- In the above reaction, species such as chlorine free radical and the methyl free radical are the intermediates, as they do not appear in the overall equation of the reaction, but are involved in reactions that ultimately result in the reacntants being converted into the products

- If lets say that the rate equation for a reaction is rate = $k[NO_2]^2$ this suggests that only NO_2 is involved in the rate determining step, and that two molccules of NO_2 are involved in the step.
- The rate determining step is always the solwets step of the reaction.

Alkaline hydrolysus of halogneoalkanes:

- During the hydrolysis of halogenoalkane, the hydroxide ion acts as a nucleophile and replaces the halogen in the halogenoalkanes. The reaction is therefore described as nucleophilic substitution.
- Hydrolysis of tertiary halogenoalkanes:
  - The equation for the alkaline hydrolysis of 2-chloromthylpropane is
    $(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$
    rate = $k[(CH_3)_3CCl]$
  - Based on teh rate equation, the reaction is first order with respect to 2-chloromethylpropane but zero order with respect to the hydroxide ion.
  - This is because the 2-chloromethylpropane undergoes a slow ionisation, making it the rate-determining step.
    - This is because the methyl groups are known for being electron releasing, which means that its harder for the cation to form aka halide ion to leave the molecule.
    - (The methyl groups are electron-releasing, so thats why the greater the number of methyl groups present, the quicker the halide ion can take the electron and leave, rather than waiting for the nucleophile i.e. hydroxide ion to come and force the chloride ion out.)
    -

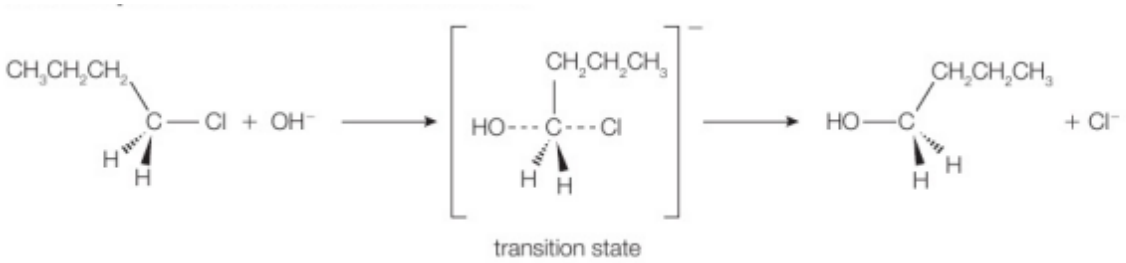
      Step 1: $(CH_3)_3CCl \rightarrow (CH_3)_3C^+ + Cl^-$ SLOW

      Step 2: $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ FAST

    - Once the cation has been formed, the hydroxide ion can easily attack the carbocation. Making the second step the faster step.
  - This type of mechanism is named S_N1 i.e. substitution nucleophilic unimolecular.
  - The rate-determining step is said to be unimolecular because there is only one reactant particle present i.e. $(CH_3)_3CCl$; the carbocation is the intermediate.

- Hydrolysis of a primary halogenoalkane:
  - The equation for the alkaline hydrolysis of 1-chlorobutane is:
    $CH_3CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2OH + Cl^-$
  - The experimentally determined rate equation for this reaction is:
    rate = $k[CH_3CH_2CH_2CH_2Cl][OH^-]$

- The reaction is first order with respect to each reactant, so both the particles are present in teh rate-determining step of the mechanism.



▲ **fig B** S_N2 mechanism of the alkaline hydrolysis of 1-chlorobutane.

- The reaction is S_N2 i.e. substitution nuclephilich bimoleculr.
- The rate-determining step is bimolecular because two reactant species are present.
- The complex in square brackets is the transition state rather than the intermediate.

Acid-catalyzed iodination of propanone:

- The reacion between propanone and iodine in an aqueous solution is usually catalysed by an acid.

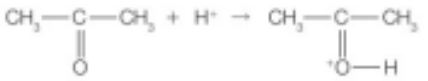
$$I_2(aq) + CH_3COCH_3(aq) + H^+(aq) \rightarrow CH_3COCH_2I(aq) + 2H^+(aq) + I^-(aq)$$

- The influence of iodine on the rate of the reaction can eb studied if the concnetraions of propanone and hydrogen ions remain constant during the reaction.
- This is done by adding a large excess of both the ketone and the acis to the original reaction mixture.
- Procedure:
  - Mix a set conc and volume of the ketonewith the same conc and vol of the acid
  - Start the stop clock the moment you add the iodine solution, and shake well
  - Using a pipette, withdraw a 10cm^3 sample and place it in a conical flask.
  - Stop the reaction by adding a sptual of sodium hydrogen carbonate. Note the exact time at which teh sodium hydrogen carbonate is added.
  - . **Titrate the remaining iodide present in the sample with 0.01 mol dm-3 of sodium thiosulfate (VI) solution, using a starch indicator:** After stopping the reaction with sodium hydrogen carbonate, the remaining iodide ions in the sample are titrated with a standardized solution of sodium thiosulfate (VI). This titration is carried out to determine the amount of iodine that has reacted with the thiosulfate. A starch indicator is added to the solution before titration begins. Starch forms a blue-black complex with iodine, but when all the iodine has reacted with the thiosulfate, the blue-black color disappears. Thus, the endpoint of the titration is reached when the blue-black color just disappears, indicating that all the iodine has been titrated.

  - Withdraw further 10cm^3 samples at suitable time intervals, and trest them similarly, always noting the time at which sodium hydrogencarbote is added.
- Results:

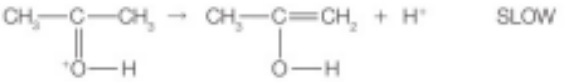
- The graph produces will show that the reaction is zero order with respect to iodine, and first order with respect to both propanone and hydrogen ions.
- This gives us the rate reaction:
  rate= $k[CH_3COCH_3][H^+]$

This would suggest the following reaction as the first step of the reaction:



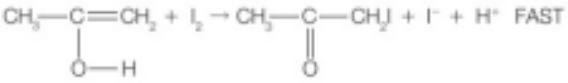
Similar reactions in other mechanisms are very fast, so this reaction is unlikely to be the rate-determining step of this reaction.

The second step probably controls the rate of the reaction and produces H^+ that, being a catalyst, is not used up in the reaction:



This rearrangement is likely to be very slow and hence is probably the rate-determining step of the reaction.

Iodine can now react in a fast step as follows:



The mechanism of the reaction can be verified by the following methods:

- Use a wider range of concentrations.
- Use instrumental analysis such as nmr can be used to show that acidificed propanone contains about one molecules in a million in the form $CH_3C(OH)=CH_2$
- Carry out the reaction with deuterated propane.

5 - Activation energy and catalysts:

- The activation energy is the energy that the colliding particles must have to reach the transition state, once the energy level of the reansiiton state has been reached, the particles react to form the product, and release energy.

- Catalysts:
  - A catalyst is a substance that increases the rate of a chemical reactio without changing itself, it provides an alternative route for the reaction to take place, which has a lower activation energy.
  - When a catalyst is present, the original rout eof the reaction is still available, however the fraction of particles taking the alternative route is grater, as a greater number of particle will possess/ a lower energy activation energy is more favourable.

  - Homogenous catalysts:
    - Thy are catalysts that are in teh same phase (solid, liquid, gas) as the reactnats. (only the reactnats, not the products)
    - Examples of reactions involving a homogenous catalyst involve:
      - The reaction between propanone and the iodine
      - The production of chlorine radicals from chloroflourocarbons, which is responsible for teh distrcuction of the ozone:
        - The UV rays from the sun results in the formation of chlorine free radicals from CFCs.
        - $CCl_2F_2(g) \xrightarrow{\text{ultraviolet radiation}} \bullet CClF_2(g) + Cl\bullet(g)$
        - The chlorine radicals then take part in a chain reaction with ozone (O_3)
        - $Cl\bullet(g) + O_3(g) \rightarrow ClO\bullet(g) + O_2(g)$
        - $ClO\bullet(g) + O_3(g) \rightarrow 2O_2(g) + Cl\bullet(g)$
        - Once the chlorine free radicals undergo a reaction with ozone, the chlorine free radical is regenerated, and remain unchanged in the reaction - thus acting as a catalyst.
        - Its a homogeneous ctalays as its a gas as well, similar to the reactants present.
        - The overall equation for the reaction is:
          $2O_3\ (g) \rightarrow 3O_2\ (g)$
      - Reaction between peroxydisulfate ions and iodide ions in aqueous solution:
        $S_2O_8^{2-}\ (aq) + 2I^-\ (aq) \rightarrow 2SO_4^{2-}\ (aq) + I_2\ (aq)$
        - The reaction is catalysexd by Fe^{2+} (aq) or Fe^{3+} (aq)
        - With Fe^{2+} (aq):

Step 1: $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

Step 2: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

-

- With Fe^{3+}:

step 1: $Fe^{3+} + 2I^- \rightarrow Fe^{2+} + I_2$

step 2: $S_2O_8^{2-} + Fe^{2+} \rightarrow 2SO_4^{2-} + Fe^{3+}$

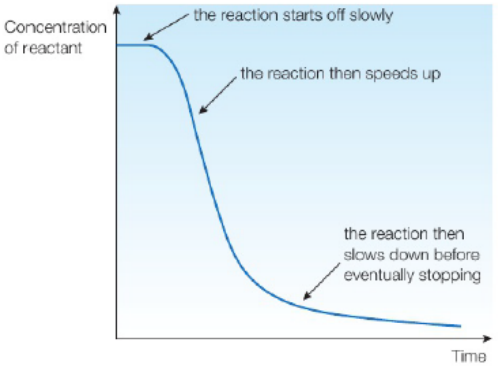
-

- Heterogeneous catalyst:
  - A hetrpgenus catalyst is a catalyst thats in a differe phase to that of the reactants.
  - Examples of such reactions include:
    - Haber process and the contact process
    - Haber process: the formation of ammonia:
      - N_2 (g) + $3H_2$ (g) ⇌ $2NH_3$ (g)
      - Iron = catalyst which forms metallix hydroides with the hydrogen molecules. The hydrogen atoms are held in spaces between the metal ions in the lattice.
      - The atoms of nitrogen are absorbed onto the surface of teh metal, and the process of catalsysi takes place in three stages:
        - Adsorption : the reactants are first absorbed onto the surface of the catalyst
        - Reaction: the reactnat molecules are held in positions that enable them to react together
        - Desorption: the product molecules leave the surface.
      - The rate of the reaction is controlled by how fast the reactnats are absorbed and how fast the products are desorbed. Once the surface of the iron is covered with molecules, there is no furtehe rincrease in reaction rate even if the pressure of the reactnats is increased.
  - They are also used in three way catalytic convertors, which cnverts unburned hydrocarbons into water and carbon dioxide; carbon and carbon monoxide into carbon dioxide; and oxides of nitrogen into oxygen and nitrogen.
- Autocatalysis:
  - In autoctalaysis, teh reaction is catalysed by one of its products.
  - For example: teh oxidation of ethandioci acid by acidified potassium manganate (VII).

$$5(COOH)_2(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$

-

- Th reaction is very slow under room temperature, however can be catalysed by Mn^{2+} .
- Initially the reaction starts off slow, however as soon as Mn^{2+} is prodcuded in a catalytic amount, the reaction rate increases.
- Initially, the reaction is very slow, as the catalyst begins to be formed in the mixture, teh reaction speeds up - it gets faster and faster as more and more catalyst are formed.
- Eventually the rate decreases in teh normal way as the concentrations of the reacntnsts decrease.

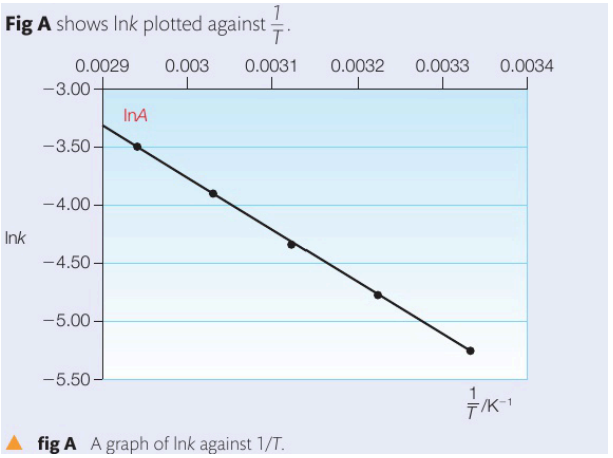


▲ **fig B** A graph of concentration against time for an autocatalysed reaction.

6 - The effect of temperature on the rate constant:

- An increase in temeprature leads to an increased rate of reaction due to the following reasons:
  - Greater fraction of molecules have energy equal to or more than teh activation energy required for the reaction to take place.
  - There is an overall increase in teh frequency of collisions between the reacting molecules.
- Arrhenius equation:

$$k = Ae^{\left(-\frac{E_a}{RT}\right)}$$



▲ **fig A** A graph of lnk against 1/T.

  - A is a constant, known as the pre exponential factor, which is a measure of the rate at which teh collisions occur irrespective of their energy.
  - E_a = activation energy of the reaction
  - R = gas constant = 8.41
  - T = the absolute temperature in helvin

- Taking the natural log of the Arrhenius equation, we get:

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$$

- In a graph of lnK against 1/T, a straight line is obtained which has a graident of $-E_a/R$
- We can the figure out the activation energy from this, the intercept with the vertical axis gives us the value for lnA

12 Entropy and energetics
12A - Intro to entropy

A reaction is said to be spontaneous if it can take place without any human intervention. The reverse of a sponateous reaction cannot be spontaneous as well.

When a reaction is in equilibrium, the amount of reaction and product do not have to be equal; it is the rate of the forward and the backward reaction which is equal.

There is always a position of equilibrium that is established in all reactions. For some reactions, the position of the equilibrium is far to the products side i.e. normal reactions wherein reactants are converted into products. Whereas in other reactions, the equilibrium is far to the right, when the reactants dont react at all.

- If a reaction doesn't occur at all we can say that the position of teh equilibrium of the reaction is far to the left

Exothermic and endothermic reactions:
- When the products have less energy than the reactants (exothermic reactions), we say that the products are more energetically stable than the reactants - energetically stable = stronger chemical bonds
- Low energy = more stability - by low energy, think of an electron in an atom - if we put in the energy, an electron gets excited which causes it to be unstable, however, once we remove the energy it becomes stable again
- When we have an exothermic reaction, the products of the reaction are usually more energetically stable, this can sometimes cause the reaction to be spontaneous; however for an endothermic reaction to be spontaneous, we need to consider the entropy, as the products formed are less energetically stable.

The second law of thermodynamics: the entropy of a closed system is already increasing - note that entropy similar to energy is something that can neither be created nor destroyed, so if the entropy of the system increases with time, the entropy of the surrounding decreases with time.

The entropy of a system can be measured using the following equation: $S=klnW$
- Here, W - number of ways a molecule can be arranged
- K = Boltzmann constant = 1.38×10^{-23} J K^{-1}
- The Boltzmann's constant X the avagradro's constant = the gas constant = 8.31. (from PV = nRT)
- Entropy (s) is measured in J K^{-1} mol^{-1}

Entropy is a measure of how spread out the molecule is - the more randomly spread out they are the greater the entropy.

Therefore, if there is an increase in heat energy, the more energy a substance has, the more energy a substance has, the more ways there are to distribute the energy. The more ways

there are to distribute energy, the higher the entropy. So, a higher temperature will lead to a greater entropy.

Perfect crystals:

- The entropy of a perfect crystal at the temperature of absolute zero (0K) is always zero according to the third law of thermodynamics
- This is because, teh particles are fixed and are not moving in any way, rotation or vibrating.

In a spontaneous reaction, occurs when the total entropy (entropy of system + entropy of surroundings) increases.

The total entropy is made up of two components:

- The entropy change of the system
- The entropy change of the surroundings

$\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$

A reaction can be spontaneous is the ΔS_{total} = positive = second law of thermodynamics

$\Delta S_{system} = \sum S \text{ (products)} - \sum S \text{ (reactants)}$

The standard entropy is the entropy of the system at 100kPa and 298K

$\Delta S_{surroundings} = -\frac{\Delta H}{T}$

According to this equation - an exothermic reaction would lead to an increase in entropy of the surroundings and vice versa. This makes sense, as an exothermic reaction leads to the release of energy, leading to energetically stable products - thus increasing the entropy of the surroundings.

According to both equations, the ΔS_{total} can only be positive if:

- If both the entropy of the system and surroundings are positive;
- If the $\Delta S_{surroundings}$ is negative and the ΔS_{system} is positive, however, the $\Delta S_{system} > \Delta S_{surroundings}$,
- If the ΔS_{system} is negative and the $\Delta S_{surroundings}$ is positive and the $\Delta S_{surroundings} > \Delta S_{system}$

Thermodynamic and kinetic stability:

- A reaction with a high activation energy that cannot happen spontaneously at room temperature is said to be kinetically stable but not feasible kinetically (something kinetically stable is kinetically non-feasible)
- However, a reaction with an overall positive entropy is said to be thermodynamically stable.
- If a reaction is thermodynamically unstable and kinetically stable the reaction will not take place under standard conditions.

Energetic stability = molecules with lower energy
Thermodynamic feasibility = +ve total entropy
Kinetic stability = activation energy.

Changes in entropy:

- As the state of the substance changes from a solid to gas the entropy of a system increases

  solid < liquid < gas

- The more complex/larger the molecule is the greater the entropy - this is because this would mean that the molecule would have more ways of arranging itself.
- An increase in the number of moles from reactants to products would lead to an increase in entropy of the system.

The entropy can be affected by the temperature - if the initial temperature of the system is very high, additional heat energy will not affect the entropy of the system. This is because in hot objects, the particles are already moving vigorously and the increased degree of movement is less for the hot object if extra heat is provided. For example freezing water:

- When freezing water, the entropy of the system decreases, whereas the entropy of the surroundings increases (as entropy is conserved) the reaction will be spontaneous, if the change in entropy of the surroundings is greater than the change in entropy of the system the reaction will be sponetous
- Change in total entropy at +5 degree celsius:

At +5 °C (278 K):

$$\Delta S_{\text{system}} = (47.9 - 69.9) = -22.0\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta S_{\text{surroundings}} = -\frac{-6010}{278}$$

$$= +\ 21.6\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta S_{\text{total}} = -0.4\ \text{J K}^{-1}\ \text{mol}^{-1}$$

-

- Change in total entropy at -5 degree celsius:

$$\Delta S_{\text{system}} = (47.9 - 69.9) = -22.0\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta S_{\text{surroundings}} = -\frac{-6010}{268}$$

$$= +22.4\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta S_{\text{total}} = +0.4\ \text{J K}^{-1}\ \text{mol}^{-1}$$

- Based on this we can see that the total change in entropy of the system has remained constant, however there is a change in entropy of the surroundings
- Eventhough the same amount of heat energy has been transferred to the surroundings, because the entropy of the surroundings has a higher temperature when at +5 degree celsius than at -5 degree celsius, teh change in entropy is smaller.
- At a greater temperature, we can see a lower change in entropy.

When an ionic solid dissolve in water:

- When an ionic solid dissolves in water two changes take place:
  - The lattic structure is broken down:

        - Endothermic process, equivalent to the reverse of the lattice energy
        - Results in an increased number of moles of particles present, so leads to an increased entropy of the salt.
    - The ions become hydrated
        - The hydration energy is the amount of energy released on dilution of one mole of gaseous ions - the hydration of ions is an exothermic process, i.e. heat energy is released.
        - It causes the water molecules to be more ordered, resulting in a decrease in entropy of the water.

To determine if an ionic solid is soluble in water, we need to look at both the changes in enthalpy and entropy:

The solubility of an ionic solid is determined by the total entropy change for the solid.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

Since $\Delta S_{surroundings} = -\frac{\Delta_{sol}H}{T}$

this expression becomes:

$$\Delta S_{total} = \Delta S_{system} - \frac{\Delta_{sol}H}{T}$$

The value of ΔS_{total}, and hence the solubility of the solid, depends on the values of three factors:

- the entropy change of the system, ΔS_{system}
- the enthalpy change of solution, $\Delta_{sol}H$
- the temperature, in kelvin, of the water, T.

Solubility trends in group 2:

- As we go down group two the solubility of metal hydroxides increases whereas the solubility of metal sulfates increases.
- Solubility of hydroxides:

METAL HYDROXIDE	$\Delta H^{\ominus}_{sol}$	$\Delta S^{\ominus}_{surroundings}$ /JK^{-1} mol^{-1}	HYDRATED CATION	STANDARD ENTROPY OF HYDRATED CATION / JK^{-1} mol^{-1}
$Mg(OH)_2$	+3	−10	$Mg^{2+}(aq)$	−138
$Ca(OH)_2$	−16	+54	$Ca^{2+}(aq)$	−53
$Sr(OH)_2$	−46	+154	$Sr^{2+}(aq)$	−33
$Ba(OH)_2$	−52	+174	$Ba^{2+}(aq)$	+10

- Here, we can see that as we go down the group, the standard enthalpy change of the solution decreases. This would then cause the entropy change of the surroundings to increase.
- Since the standard entropy of the hydroxide ion is going to be teh same for all the compounds, we can compare the standard entropy of the cations to compare the entropy change of the system.
- Here, as we go down the group, the standard entropy of the system increases, this favors the solubility - as the more positive the entropy = the total entropy would be positive.

Group 2 Metal sulfates:

METAL SULFATE	$\Delta H^{\ominus}_{sol}$	$\Delta S^{\ominus}_{surroundings}$ /JK^{-1} mol^{-1}	HYDRATED CATION	STANDARD ENTROPY OF HYDRATED CATION / JK^{-1} mol^{-1}
$MgSO_4$	−91	+305	$Mg^{2+}(aq)$	−138
$CaSO_4$	−18	+60	$Ca^{2+}(aq)$	−53
$SrSO_4$	−9	+30	$Sr^{2+}(aq)$	−33
$BaSO_4$	+19	−63	$Ba^{2+}(aq)$	+10

-
- The standard enthalpy change of the solution becomes less negative as we go down the group, which favours insolubility - as this causes the entropy change of the surroundings to be negative.
- As we go down the group, the values of the hydrated cation become less negative which favours solubility.
- Since the decrease in standard entropy of the hydrated cations is much less than the increase in the entropy of the surroundings, the group 2 sulfates become less valuable as we go down the group.

12B - Lattice energy and born haber cycles

Bond enthalpies are used to measure the strength of the covalent bonds in molecules
However, the lattice energy is used to measure the strength of the ionic lattice.

- The standard lattice energy is the energy change when one mole of the ionic solid is formed from its gaseous ions under standard states of 100KPa and 298K.
- Example:

The equation that represents the standard lattice energy of sodium chloride is:

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad \Delta_{LE}H^{\ominus} = -780\,kJ\,mol^{-1}$$

For magnesium chloride it is:

$$Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(s) \qquad \Delta_{LE}H^{\ominus} = -2526\,kJ\,mol^{-1}$$

Factors affecting the lattice energy:

- the charge: teh greater the charge the greater the lattice energy i.e. more exothermic
- Cation - to anion interactions: if there are more cations bonded to an anion and/or vice versa - the lattice energy will be greater
- Distance between the centers of the cations and their neighboring anions = the sum of the ionic radii. The greater the ionic radii, of the cation, the lower the polarizing power; whereas the greater the ionic radii of the anion, the greater the polarizability.

Trends in lattice energy:

COMPOUND	INTER-IONIC DISTANCE/nm	CHARGES ON THE IONS	LATTICE ENERGY/ kJ mol^{-1}
LiF	0.207	+1, −1	−1031
NaF	0.235	+1, −1	−918
CaF_2	0.233	+2, −1	−2630
Li_2O	0.214	+1, −2	−2814
MgO	0.212	+2, −2	−3791
Al_2O_3	0.193	+3, −2	−15 504

- **table A**
- The smaller the sum of the ionic radii of the anion and the cation, the more negative the value for the lattice energy.
- The greater the charge, teh the more exoethermic/ more negative the lattice energy is.
- The greate the number of cation-anion interactions, teh more exotehrmic the lattice energy is.

Standard enthalpy change of atomization $\Delta_{at}H^{\ominus}$

- The enthalpy change when one mole of gaseous atoms is formed from an element in its standard state under standard conditions of 298K and 100KPa
- It is an endothermic process
- Example:
    - $C(s) \rightarrow C(g)$
    - $1/2H_2\ (g) \rightarrow H(g)$

Electron affinity:

- The energy changes when each atom in one mole of atoms in the gaseous state gains an electron to form a -1 ion
- It is an exothermic process
- Example:
    - $Cl(g) + e^- \rightarrow Cl^-(g)$
- However, noble gases have positive first electron affinity, as energy is we need to given in energy to input an electron into a new valance shell - energy is required to overcome the repulsion between the electrons of the the fully filled valence shells.
- The 2nd electron affinity of all the elements is always endothermic. This is because energy is required to overcome the repulsion between the negative ion and the electron being added.
    - Example:

$$O^-\ (g) + e^- \rightarrow O^{2-}(g)$$

Born Haber cycle:

The cycle includes the following energy changes, all of which can be determined experimentally:

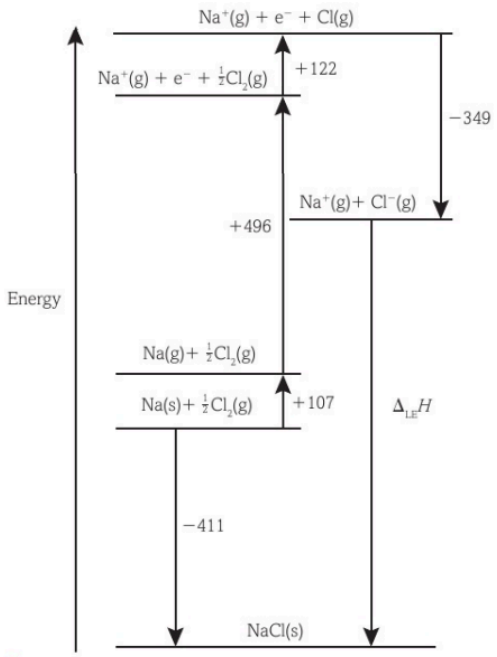
- The enthalpy change of formation of NaCl(s), $\Delta_f H[\text{NaCl(s)}] = -411\,\text{kJ mol}^{-1}$
- $\Delta_{at} H[\text{Na(s)}] = +107\,\text{kJ mol}^{-1}$
- the first ionisation energy, 1^{st} $IE[\text{Na(g)}] = +496\,\text{kJ mol}^{-1}$
- $\Delta_{at} H[\text{Cl}_2\text{(g)}] = +122\,\text{kJ mol}^{-1}$
- $EA[\text{Cl(g)}] = -349\,\text{kJ mol}^{-1}$

Applying Hess's Law to the cycle gives us:

$$+107 + 496 + 122 + (-349) + \Delta_{LE} H = -411$$

Hence:

$$\Delta_{LE} H[\text{NaCl(s)}] = -411 - 107 - 496 - 122 + 349\,\text{kJ mol}^{-1}$$
$$= -787\,\text{kJ mol}^{-1}$$



▲ **fig A** Born–Haber cycle for sodium chloride.

Experimental and theoretical lattice energies:

- The experimental lattice energy is calculated from the Born Haber cycle
- The theoretical lattice energy is calculated using the principles of electrostatics (coulomb's law = (q1q2)/(r1r2)
    - The type of lattice structure and the interionic distance can be found by x-ray crystallography.
    - While doing this, we usually make the following assumptions:
        - The ions are in contact with one another
        - The ions are perfectly spherical (they aren't distorted due to polarization)
        - The charge on each ion is evenly distributed around the centre so that each ion can be considered as a point charge.

Difference between the experiment and theoretical lattice energies:

COMPOUND	EXPERIMENTAL LATTICE ENERGY/kJ mol^{-1}	THEORETICAL LATTICE ENERGY/kJ mol^{-1}
NaF	−918	−912
NaCl	−780	−770
NaBr	−742	−735
AgF	−958	−920
AgCl	−905	−833
AgBr	−891	−816

table A

- We know that the ionic radius of a silver ion is larger than the ionic radius of the silver ion.
- While calculating the theoretical lattice energy we assume that the compound is 100% ionic and there isn't any covalent character present (polarization)

- Therefore, the greater distorted the electron could be on one of the compounds, the greater the differences in values between the theoretical and experimental values.
- The polarisation power of the cation is dependent on its ionic radius and charge - the lower the ionic radius and the greater the charge the greater the polarisation power. (the greater the charge density, the greater the polarisation power - charge density = charge/r^2)
- The polarizability of the anion depends on its ionic radius and charge - the greater the ionic radius and charge the greater the polarizability.

COMPOUND	CHARGE DENSITY OF CATION	EXPERIMENTAL LATTICE ENERGY/kJ mol^{-1}	THEORETICAL LATTICE ENERGY/kJ mol^{-1}	PERCENTAGE DIFFERENCE	EXTENT OF COVALENT BONDING
NaCl	$\frac{1}{(0.095)^2} = 111$	−780	−770	1.28	very little
$MgCl_2$	$\frac{2}{(0.060)^2} = 556$	−2526	−2326	7.92	more than in NaCl

table B

The charge density of the magnesium ion is larger than that of the sodium ion, resulting in greater polarisation of the chloride ion and greater covalent bonding in $MgCl_2$ than in NaCl.

COMPOUND	CHARGE OF ANION	RADIUS OF ANION/nm	EXPERIMENTAL LATTICE ENERGY/kJ mol^{-1}	THEORETICAL LATTICE ENERGY/kJ mol^{-1}	PERCENTAGE DIFFERENCE	EXTENT OF COVALENT BONDING
AgF	−1	0.133	−958	−920	3.97	fairly large
AgI	−1	0.215	−889	−778	12.49	greater than in AgF

table C

The larger iodide ion is more easily polarised, which leads to a greater degree of covalent bonding in silver iodide.

The enthalpy changes of solution:

- The enthalpy change that takes place when one mole of an ionic solid dissolves in water to form an infinitely dilute solution.
- For example

  $NaCl\ (s) \rightarrow Na^+\ (aq) + Cl^-\ (aq)$
- Upon dilution, the ions in the solution move further apart (endothermic process) and become more hydrated (exothermic process)
- Since the enthalpy change of solution involves both endothermic and exothermic processes, we cannot determine its value experimentally.
- The value can be both positive or negative

Enthalpy change of hydration:

- It's the enthalpy change when one mole of an ion in its gaseous state is completely hydrated by water - complete hydration takes place when the solution formed is at infinite dilution.
  - Example:

    $Na^+\ (g) \rightarrow Na^+\ (aq)$

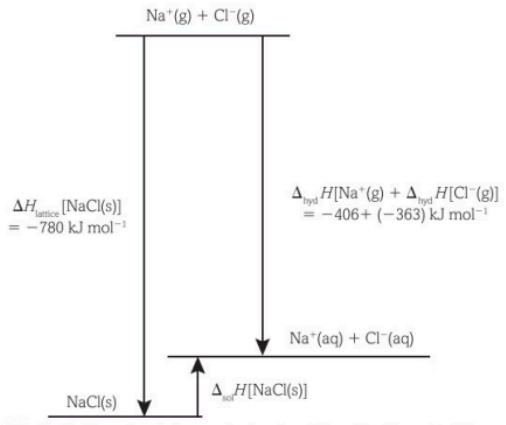
- When an ion is placed in water, it immediately interacts with the water molecules. The delta-positive side of teh water molecules interacts with the anion and vice versa
- This is known as ion-dipole interaction.

- The ion-dipole interactions exist in the hydrated chloride ion, but sometimes hydrogen bonds can be formed between the delta positive hydrogen atoms of the water molecules and the chloride ion.

Factors affecting the magnitude of the hydration enthalpy:

- The greater the charge, the greater the hydration enthalpy - as a greater charge would mean stronger forces of attraction with the polar water molecules.
- As we go down the group the hydration enthalpy decreases. This is because the ionic radius increases as we go down the group. This is because the larger the ions the lower the electrostatic forces of attraction between them and the water molecules.
    - Therefore, the greater the charge density, the more exothermic the hydration enthalpy would be

Relationship between the hydration enthalpy, enthalpy of solution, and the lattice enthalpy.



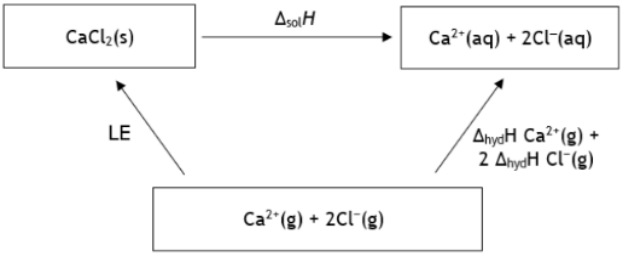
▲ **fig B** Energy level diagram for the dissolution of sodium chloride.

Applying Hess's Law:

$\Delta_{LE}H[NaCl(s)] + \Delta_{sol}H[NaCl(s)] = \Delta_{hyd}H[Na^+(g)] + \Delta_{hyd}H[Cl^-(g)]$

$\Delta_{sol}H[NaCl(s)] = -406 + (-363)\,kJ\,mol^{-1} - (-780)\,kJ\,mol^{-1}$

$= +11\,kJ\,mol^{-1}$



Explain why the difference between the theoretical and the experimental values of the lattice energy is very much greater for calcium iodide than for calcium chloride:

- Calcium chloride is almost completely ionic; calcium iodide has a partially covalent character; this is because iodide ions are larger than chloride ions, so they can be easily polarised.

13 - Chemical Equilibria

Homogenous reactions are reactions wherein both the reactants are in the same phase (i.e. solid, liquid or gas)

We know that when something is in equilibrium, the rate of the forward reaction is equal to the rate of the backward reaction.

- Due to Le Chaterlier's principle, we know that changes in conditions can cause the equilibrium to shift in either direction.
- The effect of the position of the equilibrium due to changes in concentration and pressure can be calculated quantitatively.

For the reversible reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

it can be shown experimentally that at equilibrium and at a given temperature:

$$\frac{[NO_2(g)]^2_{eq}}{[N_2O_4(g)]_{eq}} = \text{a constant}$$

- The constant is known as K_c - where c = equilibrium constant using concentrations.
- If we look at pressure it would be K_p - where p = equilibrium constant using parietal pressures
- The eq = concentration when the reaction is in equilibrium.

The equilibrium constant can only change if the temperature is changed. The concentrations don't affect the equilibrium constant.

Ways to obtain a value for the equilibrium constant:

- By experimentation
- Calculation using thermodynamic equations.

For a general reaction:

$$wA + xB \rightleftharpoons yC + zD$$

$$K_c = \frac{[C]^y_{eq}[D]^z_{eq}}{[A]^w_{eq}[B]^x_{eq}}$$

For convenience, the 'eq' sign is often not included, but is taken for granted.

How to obtain the equilibrium constant?

- In order to obtain the equilibrium constant, known amounts of reactants are allowed to reach equilibrium.
- The amount of the substances at equilibrium can either be measured or calculated stoichiometrically.

Heterogeneous reactions"

- They are reactions where the products and/or the reactants are in a different state/phase to one another.
- For example:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$
$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

- NOTE: we dont write the concentration of solids while writing the equation for K_c

2 - Equilibrium constant K_p

- The equilibrium constant, K_p describes the ratio of product and reactant concentrations at equilibrium in terms of partial pressures.
- For reactions involving gases, we make use of their partial pressure to determine the value for the K_p
- The particle pressure = the pressure that the gas would exert alone if it alone occupied the volume of the mixture
- The total pressure = sum of partial pressures of all the substances present in teh reaction.

If we have a mixture of two gases, A and B, then the total pressure, p, of the mixture is related to the partial pressures of A and B by the following equation:

$$p = p_A + p_B$$

where p_A = partial pressure of A and p_B = partial pressure of B.

For the general reaction:

$$wA(g) + xB(g) \rightleftharpoons yC(g) + zD(g)$$

we can define another equilibrium constant, K_p, in terms of partial pressures:

$$K_p = \frac{(p_C)^y (p_D)^z}{(p_A)^w (p_B)^x}$$

- To calculate the partial pressure:
  - Calculate the number of molar fractions of the molecule
  - This is done by the following equation:

$$\text{mole fraction of A} = \frac{\text{number of moles of A}}{\text{total number of moles of gas}}$$

  - Multiply the molar fraction by the total pressure to find the partial pressure of the substance.
-

- Heterogeneous reactions:
  - Similar to how we dont consider the molecules that are present as solids when calculating the partial pressure involving concentration, we dont involve, the solids while calculating the partial pressures here as well.
  - For example:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The equilibrium constant in terms of partial pressures is given by:

$$K_p = p_{CO_2(g)}$$

The equilibrium constant only changes if there are any changes in the temperature.

3 - Factors affecting the equilibrium constant:

- Temperature:
  - As the temperature increases, the K_p decreases for an exothermic reaction.
  - However, for an endothermic reaction, as the temperature increases the K_p increases as well.

THERMICITY OF REACTION	INCREASE IN TEMPERATURE	DECREASE IN TEMPERATURE
exothermic	*K* decreases	*K* increases
endothermic	*K* increases	*K* decreases

table B

  - If the equilibrium constant changes with a temperature change, then the amount of products and reactants gets affected as well.
  - When the equilibrium constant increases, the amount of product increases, and the amount of reactants decreases.
- Concentration:
  - The only thing that can change the equilibrium constant is the temperature, when there is a change in teh concentration of the components, the Q_c (reaction quotient) changes.

For a general reaction:

$$wA + xB \rightleftharpoons yC + zD$$

the reaction quotient, Q_c, is given by the expression:

$$Q_c = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

  - At equilibrium, $Q_c = K_c$,
  - When there is a change in the concentration, the reaction composition will change causing Q_c to change. Until the reaction comes back to equilibrium again.
- Pressure:
  - Similar to concentration, the pressure doesn't affect the equilibrium constant
  - If the partial pressure of only the products or reactants changes then similar to a change in K_c the K_p will either increase or decrease.

- However, if the total pressure of the system is changed, then the Q_p value will change as well.

Consider the reaction:

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

for which:

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$$

Suppose the equilibrium partial pressures of nitrogen, hydrogen and ammonia are a, b and c atm, respectively. Then:

$$K_p = \frac{c^2}{ab^3}$$

If the total pressure is suddenly doubled, the partial pressures of nitrogen, hydrogen and ammonia will be doubled to $2a$, $2b$ and $2c$ respectively:

$$Q_p = \frac{(2c)^2}{2a \times (2b)^3} = \frac{4c^2}{16ab^3}$$

The value of Q_p is now one-quarter of the value of K_p. In order to re-establish equilibrium the numerator has to increase, with a subsequent decrease in the denominator, until $Q_p = K_p$. This is achieved by some nitrogen and hydrogen reacting to form more ammonia.

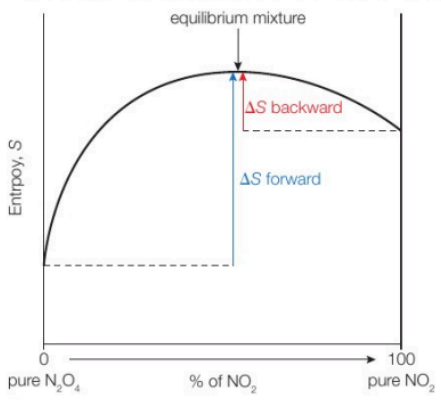
Hence, an increase in pressure increases the equilibrium yield of ammonia by shifting the equilibrium to the right.

- Adding a catalyst:
  - A catalyst does not take part in the reaction, and can therefore not affect the equilibrium constant.

5 - Relating entropy to equilibrium constants:

- We know that $\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$
- And the total change in teh trophy is positive for all spontaneous reactions.
- When there is a change in temperature, the ΔS_{system} doesn't change much, however, the $\Delta S_{surroundings}$ change, causing the total change in entropy to change as well.
- In a reversible reaction both the forward and backward reactions can spontaneously take place, suggesting that ΔS_{total} is always positive.

- For example



▲ **fig C** A graph of entropy against percentage NO_2 in a mixture of N_2O_4 and NO_2.

  - Both N_2O_4 and NO_2 have a lower entropy than the entropy at the equilibrium position.
  - Thus the change in entropy is positive from both directions.
  - At equilibrium, the total entropy is zero this is because:

$$\Delta S_{total}\,[\text{forward reaction}] = \Delta S_{total}\,[\text{backward reaction}]$$

- The relationship between the total entropy of the reaction and the equilibrium constant is therefore given by:

$$\Delta S_{\text{total}} = R \ln K$$

  - Here, K can be K_c or K_p and R = gas constant = 8.13

As mentioned above, $\Delta S_{\text{total}} = R \ln K$.

Rearranging the equation gives us:

$$\ln K = \frac{\Delta S_{\text{total}}}{R}$$

So:

$$K = e^{\Delta S_{\text{total}} / R}$$

-

14 - Acid-Base Equilibria

The BrØnsted Lowery theory describes acids and bases in terms of protons.

- An acid = proton donor
- Base = proton acceptor

A substance with hydrogen that carries a slight positive charge can act as an acid. For example, when it is bonded to a highly electronegative atom

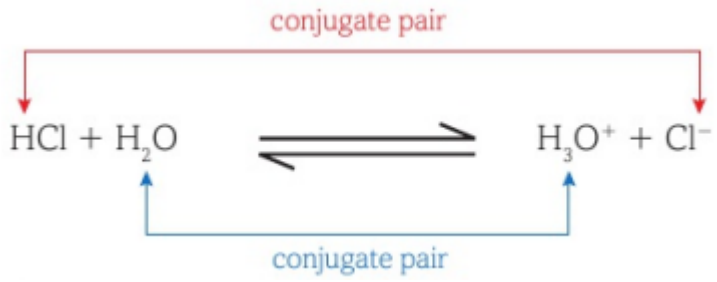
For a substance to accept the proton, the base has to contain a lone pair of electrons so that it can form a dative covalent bond with the proton.

Conjugate acid and base pairs:

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

- The HCl donates a proton to the H_2O
- The H_2O accepts the proton as it behaves as a base.
- In the reverse reaction, the H_3O^+ behaves as an acid by donating a proton to the Cl^-
- Whereas, the Cl^- behaves as a base by accepting the proton

The HCl and Cl^- ; H_2O and H_3O^+ are conjugate acid-base pairs.



The (base 1) Cl^- is the conjugate base of (acid 1) HCl; (base 1) H_2O is the conjugate base of (acid 1) H_3O^+

A monobasic or monoprotic acid is an acid that can donate only one proton
A diprotic or dibasic acid is an acid that can donate two protons

Amphoteric substances are those that can behave as both acids and bases.

Strong and weak acids:

- A strong acid is an acid that disassociates completely in an aqueous solution.
- For example:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

- A weak acid on the other hand is an acid that partially disaccociates in an aqueous solution.
- For example:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

Hydrogen ion concentration and pH:

- The pH of a solution is the potential of hydrogen, the greater the hydrogen ion concentration in the solution the lower the pH of the solution.
- We know that the greater the H^+ ions in a solution the more acetic the solution is (link it to teh definition of acids and how acids need to have a +ve charge on the hydrogen ion for it to be an acid)
- However since it is very hard to measure the concentration of the H^+ ions in the solution, we use the pH scale to figure out the acidity of the solution

$$pH = -\lg [H^+] \qquad \text{or} \qquad pH = \lg \frac{1}{[H^+]}$$

(In chem, p stands for "the negative decimal logarithm of")

- We can also use this equation to figure out the hydrogen ion concentration.
- The ion concentration is usually equal to the concentration of the acid since it is a strong acid.

Weak acids:

- We know that weak acids disassociate partially only, so in this case, the hydrogen ion concentration will not be equal to the concentration of the acid, as a significant amount of H^+ ion is undissociated.
- The acid dissociation constant = K_a is used for weak acids

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

When we apply the equilibrium law to this reaction we obtain:

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

- We can calculate the hydrogen ion concentration using the K_a and get the pH of the solution.
    - The hydrogen ion concentration of an aqueous solution of ethanoic acid of concentration 0.05mol/dm^3 given that the K_a of ethanoic acid is 1.74×10^{-5} at 298K

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]}$$

Every time a molecule of CH_3COOH dissociates, a CH_3COO^- ion and a H^+ ion are formed.

This means that $[CH_3COO^-(aq)] = [H^+(aq)]$.

So, the expression for K_a can be simplified to:

$$K_a = \frac{[H^+(aq)]^2}{[CH_3COOH(aq)]}$$

$$K_a = \frac{[H^+(aq)]^2}{0.0500} = 1.74 \times 10^{-5}\,\text{mol dm}^{-3}$$

$$[H^+(aq)] = \sqrt{(0.0500 \times 1.74 \times 10^{-5})} = 9.33 \times 10^{-4}\,\text{mol dm}^{-3}$$

This gives a pH of 3.03.

- The concentrations in the expression for the K_a are the equilibrium constants.
- If K_a is very small, then the concentration of the undissociated acid at equilibrium is very similar to the initial concentration of the acid. This is because, if K_a is small: then

the product of the concentration of the ions is much smaller than the concentration of the aid, which suggests that the the acid is very weak as the concentration of H^+ ions will be very low.

K_a and pK_a values:

$$pK_a = -\log(K_a)$$

- The larger the value of K_a the stronger the acid
- The smaller the value of pK_a the stronger the acid.

Calculating the pH of a dibasic acid:

$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$
$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

- Here, when sulfuric acid is dissolved in an aqueous solution, it disassociates into hydrogen ion and hydrogen sulfate ion
- The concentration of the hydrogen ion and the hydrogen sulfate is going to be equal to the concentration of the acid itself since its a strong acid
- However, the hydrogen sulfate ion is a weak acid, and therefore disassociates into sulfate ions and hydrogen ions n a reversible reaction.

- Since we know the K_a, hydrogen sulfate concentration, we can figure out the pH of the solution.

$$K_a\,(HSO_4^-) = 0.0100 = (0.500 - x)x/0.500$$

Solving this quadratic equation gives $x = 0.0098$.

- Based on the calculation, the contribution of the H^+ ions from the HSO_4^- ions is negligible.

3 – Ionic product of water, K_w

- Dissociation of water:
  - Pure water disassociates by itself as
    $H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$

- If we apply the equilibrium law to the reaction above:

$$\frac{[H^+(aq)][OH^-(aq)]}{[H_2O(l)]} = \text{a constant}$$

- The concentration of water is constant at a given temperature, as the expression can also be written as: $[H^+(aq)][OH^-(aq)] = \text{a constant}$

- This constant is known as K_w = the ionic product of water.
  - $K_w = 1 \times 10^{-14}\ mol^2\ dm^{-6}$ at 298K

- In a neutral solution, the hydrogen ion concentration is equal to the hydroxide ion concentration. Therefore:

At 298 K, $[H^+(aq)] = 1.00 \times 10^{-7}\ mol\ dm^{-3}$ $[(1.00 \times 10^{-14})^{1/2}]$

So, the pH of pure water at 298 K is 7.00 $[-\lg (1.00 \times 10^{-7})]$

- Similar to calculating the pK_a from K_a we can calculator the pK_w from the K_w by finding the -log(K_w)

pH of aqueous solutions of strong bases:

- When a large amount of strong acid is dissolved in water, it produces many hydrogen ions to the point that the hydrogen ions from water become insignificant.
- However, if the acid is present in every small concentration (0.01 mol/dm^3 or less)

- When we dissolve a strong base in water, there are usually some H^+ ions from water, which would cause it to have a pH. While calculating the pH we ignore the OH^- conc of the water, and use the OH^- conc of the base dissolved, which will be equal to the conc of the base itself.
- We then use the K_w of water to figure out the H^+ conc via which we find the pH

A sodium hydroxide solution of concentration $0.100\ mol\ dm^{-3}$ therefore has a hydroxide ion concentration of $0.100\ mol\ dm^{-3}$.

If $[OH^-(aq)] = 0.100\ mol\ dm^{-3}$ and $[H^+(aq)][OH^-(aq)] = 1.00 \times 10^{-14}\ mol^2\ dm^{-6}$, then

$[H^+(aq)] = 1.00 \times 10^{-14} / 0.100\ mol\ dm^{-3}$

$= 1.00 \times 10^{-13}\ mol\ dm^{-3}$

The pH of this solution is therefore 13.0.

pH of salts:

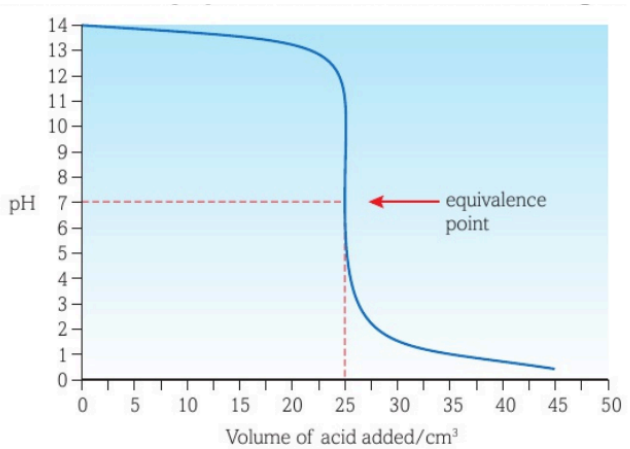
Salt of a strong acid and a strong base	pH = 7
Salt of a weak acid and a strong base	pH > 7
Salt of a strong acid and weak base	pH < 7
Salt of a weak acid and a weak base	Depends of the strengths of the acid and bases" - $K_a = K_b$, pH = 7 - $K_a > K_b$, pH < 7 - $K_a < K_b$ pH > 7

- When we dilute acid in the water, the more the diluted the solution is the greater the pH of the solution. As mentioned earlier, at a very small conc of acid, we consider the conc of H^+ ions from the water as well which would make the pH go very close to 7 but not above 7
- This can also be seen when experimenting with a weak acid as well, however, the following has a large uncertainty, as:
    - We assume that the conc of the acid in the equilibrium is identical to the original conc of the acid that we use.
    - A small error in the measurement of pH can give us different values for the K_a

14B - Acid-Base titrations, pH curves, and indicators

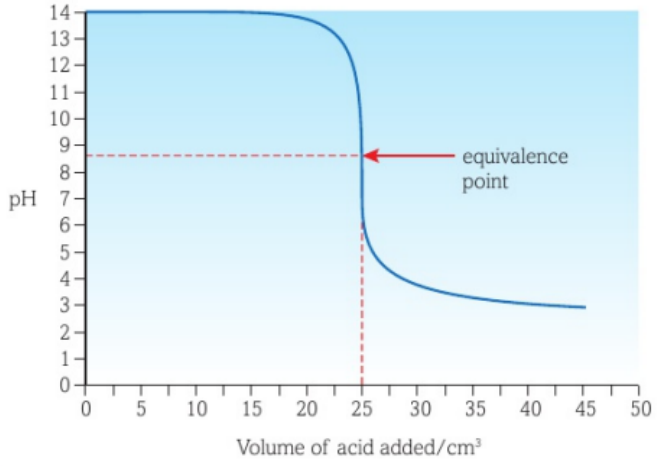
Acid-base titrations:

- The endpoint of a titration is when the indicator changes color.
- The equivalence point is when the acid and base have reacted together in the exact proportions as dictated by the stochiometric equation
- The pH at the equivalence point depends on the acid or base used, for example, the pH of the salt of a strong acid and base will be different from the pH of the salt of a weak acid and/or base:
    - Titrating strong acid with a strong base:



▲ **fig B** pH curve for a strong acid–strong base titration.

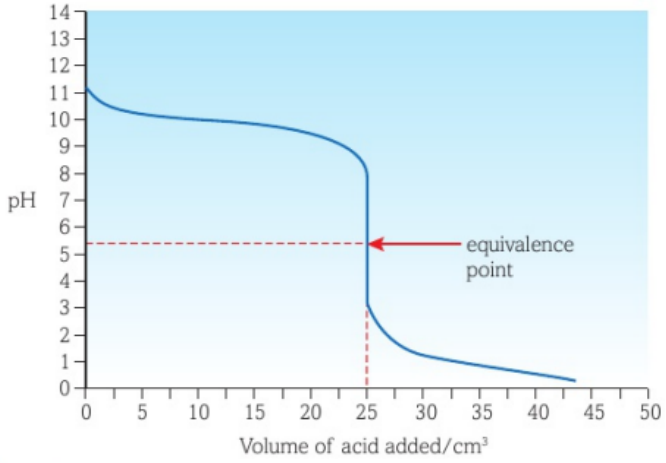
- Titrating a weak acid with a strong base:



▲ **fig C** pH curve for a weak acid–strong base titration.

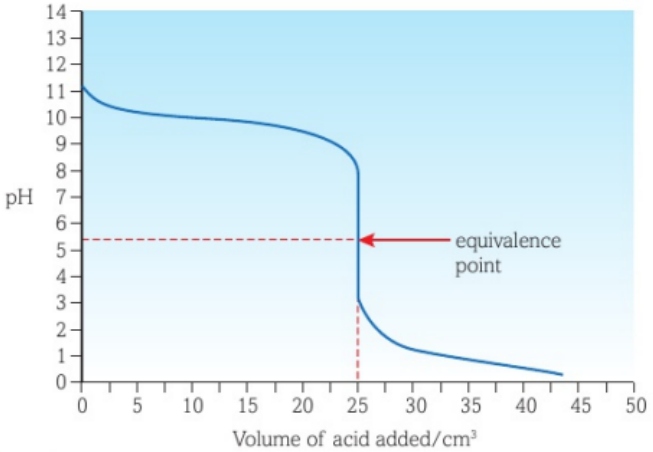
-

- Titrating a strong acid with a weak base:



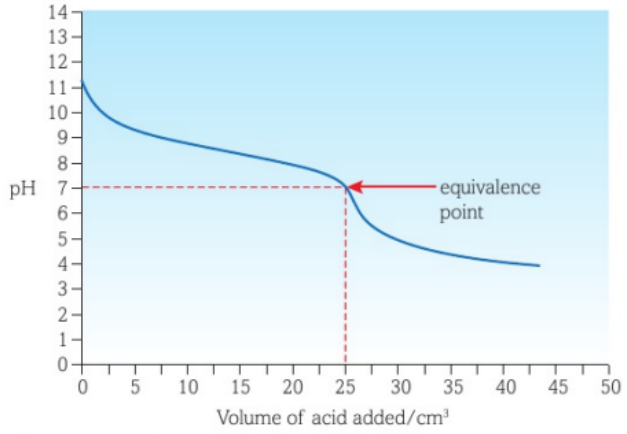
▲ **fig D** pH curve for a strong acid–weak base titration.

- Titrating a strong acid with a weak base:



▲ **fig D** pH curve for a strong acid–weak base titration.

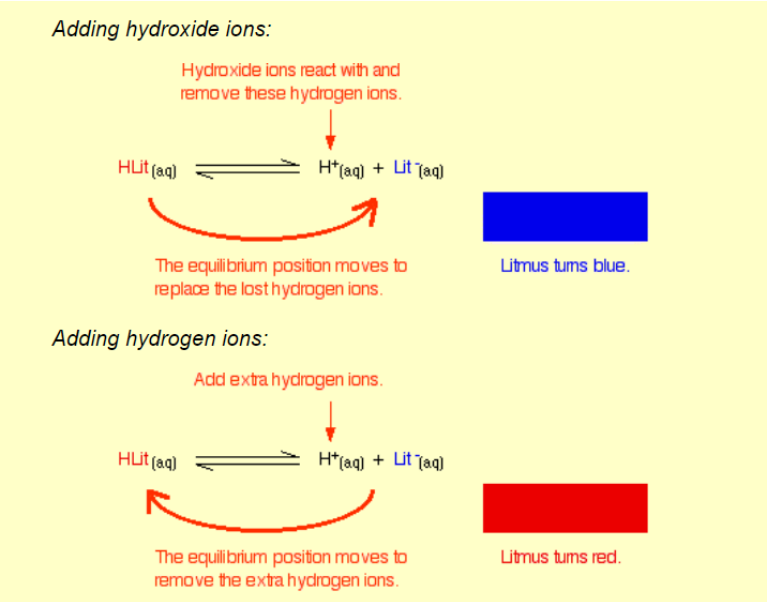
- Titrating a weak acid with a weak base:



▲ **fig E** pH curve for a weak acid–weak base titration.

- We usually use different indicators for different reactions:
  - Most acid-base indicators are either weak acid or base.
  - So when we put an indicator into the solution, it disassociates into the hydrogen ion and its conjugate base:

    $HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$
  - The molecules HIn and In^- have different colours in an aqueous solution, which results in different colours, when we put in the indicators.



  - Since the reaction is reversible when there is a high concentration of hydrogen ions, the equilibrium would shift to the side with a lower concentration to counteract the change; causing the colour to change.
  - There will be a stage when the [HIn (aq)] = [In^-(aq)] when the inidactor will appear as its usual colour. The pH at this stage can be determined using the equilibrium constnat K_{In} for the given indicator.
  - For example for methyl orange:

$$K_{In} = \frac{[H^+(aq)][In^-(aq)]}{[HIn(aq)]} = 2.00 \times 10^{-4}\,mol\,dm^{-3}$$

- This would give us the pH at the halfway stage at which the indicator would change colour. At this stage, the pH = pK_{In} as well (the half way point on the titration graph at which there is a colour change)
- I.e. a color change will only occur when there is

pH range indicator:

- The red color of the methyl orange, for example, will appear only when the [HIn(aq)] is ten times [In^-(aq)] and vice versa.
- The approximate pH at which this happens can be found using the following calculation

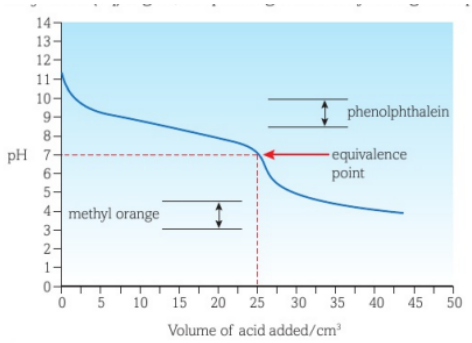
When $[HIn(aq)] = 10[In^-(aq)]$:

$$\frac{[H^+(aq)][In^-(aq)]}{10[In^-(aq)]} = 2.00 \times 10^{-4}\ \text{mol dm}^{-3}$$

$$[H^+(aq)] = 2.00 \times 10^{-3}\ \text{mol dm}^{-3}$$

- Which would give us a pH of 2.70 which shows us when the red color first predominates
- When we do a similar calculator, to find when the yellow appears we would get 4.70
- Between both the values, we will see a shade of both the colors.

- Since the pH at the equivalence point is not the same for all reactions, the pH range can be used to decide which indicator to use
  - If the pH range of the indicator falls within the steep range of the titration curve, it can be used.
  - This is usually applicable to most reactions except for a reaction between a weak acid and weak base, as there is no prominent steep section to the curve, which means that other methods can be used such as:
    - Temperature changes (thermometric titration)
    - Electrical conductivity changes



▲ fig I Weak acid–weak base pH curve.

Titration curves of diprotic curves:

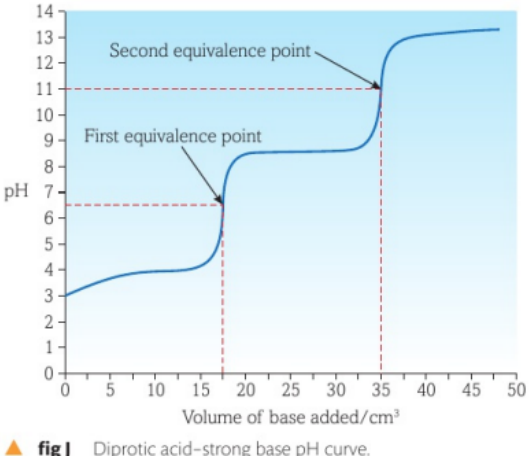
- A diprotic acid is an acid that produces two protons per acid molecule, such as H_2SO_4
- Since the disassociate in two different stages, the titration curves have two equivalence points.

A diprotic acid dissociates in water in two stages:

Stage 1: $H_2X(aq) \rightarrow H^+(aq) + HX^-(aq)$

Stage 2: $HX^-(aq) \rightarrow H^+(aq) + X^{2-}(aq)$

- At the first equivalence point, the H^+ ions from the first disassociation react with the base



▲ fig I Diprotic acid–strong base pH curve.

- However, during the second equivalence point, the H^+ ions from both the reactions (i.e. stage 1 and stage 2 of disassociation) have reacted
- Therefore, the volume of the base the second equivalence point is exactly twice the first equivalence point.

From the beginning of the reaction to the first equivalence point:

$$H_2X + NaOH \rightarrow NaHX + H_2O$$

From the first equivalence point to the second equivalence point:

$$NaHX + NaOH \rightarrow Na_2X + H_2O$$

From the beginning of the reaction through to the second equivalence point (overall reaction):

$$H_2X + 2NaOH \rightarrow Na_2X + 2H_2O$$

Buffer solution:

- To create a buffer we use:
  - A weak acid and its conjugate base
  - A weak base and its conjugate acid
- The conjugate base or acid is usually in the form of a soluble salt, for example, the conjugate acid/base with potassium or sodium eg, sodium methanoate
- When we mix both the weak acid/base and the salt of the conjugate acid/base:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

$$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

- The pH of the buffer depends on the concentration of both the acid and its conjugate base.

Calculating the pH of a buffer solution:

- To calculator the pH of a buffer solution, we assume that the extent of disassociation of the weak acid is negligible and assume that all of it has the conc of the carboxylate ions is made from the carboxylate salt.
- When we mix both solutions, the volume doubles, therefore, the concentration halves.
- Example calculation, wherein 1 mol/dm^3 of salt and 1 mol/dm^3 of acid are mixed together.
  - We assume that the extent of dissociation of the acid is negligible. Since the volume of the mixture doubles, the concentration of the ethanoic acid halves to 0.5 mol/dm^3
  - The concentration of ethanoate ions is also therefore 0.5 mol/dm^3 due to a change in the volume of the solution

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

  - To calculate the pH:

At 298 K,

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]} = 1.74 \times 10^{-5}\,\text{mol dm}^{-3}$$

Rearranging this equation and substituting values for $[CH_3COOH(aq)]$ and $[CH_3COO^-(aq)]$ gives:

$$[H^+(aq)] = (1.74 \times 10^{-5} \times 0.500)/0.500\,\text{mol dm}^{-3}$$
$$= 1.74 \times 10^{-5}\,\text{mol dm}^{-3}$$

This gives a pH for the buffer solution of 4.76.

How do buffers work?

- When a small amount of acid is added to the buffer, the H^+ ions of the buffer react with the carboxylate salt ions, which results in teh formation of the weak acid. (remember that when a weak acid disassociates, it forms carboxylate ion and the H^+ ions, here since there is a high concentration of the H^+ ions the equilibrium will be shifted to the left i.e. the side with the weak acid where it's not disaccociated)
- When a small amount of the base is added, the OH^- ions react with the acid which results in the formation of CH_3COO^- and H_2O
- This results in the new equilibrium mixture being established, wherein the concentration of the acid and carboxylate ions have changed slightly. This would cause the pH to change however it will be very minimal.
- This is because:

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]}$$

Rearranging this equation gives:

$$[H^+(aq)] = K_a \times \frac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$$

- The ratio of the weak acid to the carboxylate ion remains constant
    - When you add 0.1 mol/dm^3 of acid to a container consisting of 0.5mol/dm^3 of a weak acid and its conjugate base for example, the concentration of the acid will increase to 0.6 which will cause the concentration of the carboxylate ions to decrease by 0.1, making it 0.4. Thus giving us a constant ratio.

Buffer Solution

- To the previous buffer solution of pH 4.76, we add 0.01 mol HCl
- This gives 0.01 moles of H^+ ions
- Therefore:
    - $[CH_3COOH] = 0.510$ mol dm^{-3}
    - $[CH_3COO^-] = 0.490$ mol dm^{-3}
- This gives $[H^+]$ of 1.81×10^{-5}
- Therefore the new pH is 4.74

Water

- At 298 K, the pH of water is 7 so $[H^+]$ is 1.00×10^{-7}
- We add 0.01 mol HCl
- This gives 0.01 moles of H^+ ions
- Therefore:
    - $[H^+] = 1.00 \times 10^{-7} + 0.01$
- This gives $[H^+]$ of 1.00001×10^{-2}
- Therefore the new pH is 2.00

Handerson - Hasselbalch equation:

- According to the above equations, we can say that the concentration of the carboxylate ion is the same as the concentration of the salt used.
- Thus it can be written as $[H^+] = K_a \times [\frac{acid}{salt}]$
- If we were to take -logs from both sides, we would get:

$$-\lg [H^+(aq)] = -\lg K_a - \lg \frac{[acid]}{[salt]}$$

$$pH = pK_a - \lg \frac{[acid]}{[salt]}$$

$$pH = pK_a + \lg \frac{[salt]}{[acid]}$$

-

- Since the pK_a is constant at a given temperature, teh pH of teh solution depends on the ratio of the acid and salt

Buffer made from a weak base and its conjugate acid:

- When we use a buffer made from a weak base and its conjugate acid, we can use the same equation, except that the acid is replaced with the concentration of the base, and the salt is replaced with the concentration of the conjugate acid.

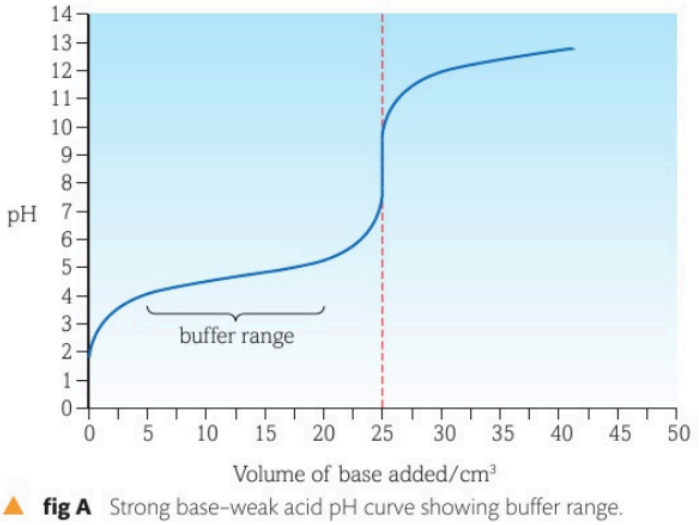
To make a buffer solution with:

- pH less than 7 = weak acid + conjugate base
- pH more than 7 = weak base + conjugate acid

Te buffer capacity = a measure of the amount of acid or base required to change significantly the pH of the food or a solution of an acid and a base.

3 - Buffer solutions and pH curves:

- On a pH curve, the buffer range is the part where the pH changes gradually.



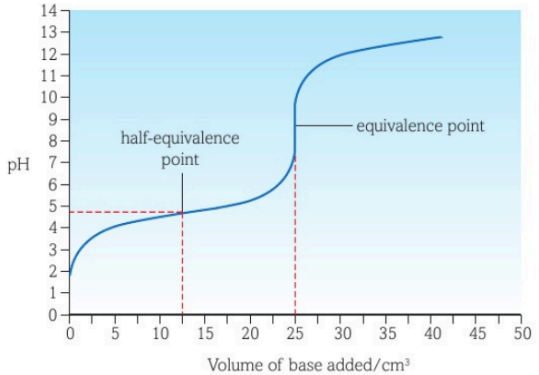
▲ **fig A** Strong base–weak acid pH curve showing buffer range.

- Determining the K_a from the pH curve:
  - The pH at half the volume of the base/acid than at the equivalence point = pK_a value of the acid.

The volume at the equivalence point is 25 cm^3, so the volume at the half-equivalence point is 12.5 cm^3. The pH when 12.5 cm^3 of base is added is 4.80.

The pK_a of the acid = 4.80

K_a for the acid = $10^{-4.80} = 1.58 \times 10^{-5}$ mol dm^{-3}



▲ **fig B** Strong base–weak acid pH curve showing equivalence and half-equivalence points.

- Why is this?
    - At the half equivalence point, the conc of the acid and salt will be exactly half the conc of the acid and salt than at the equivalence point.

    - At this point, the solution contains a mixture of the weak acid and its conjugate base (in the case of titrating a weak acid with a strong base) or a weak base and its conjugate acid (in the case of titrating a weak base with a strong acid). This combination of a weak acid/base and its conjugate pair is what forms a buffer solution.

$$pH = pK_a + \lg \frac{[salt]}{[acid]}$$

At the half-equivalence point:

$$[salt] = [acid], \text{ so } [salt]/[acid] = 1$$

The logarithm to the base 10 of 1 (lg 1) = 0.

So, the equation becomes:

$$pH = pK_a$$

- We can use a different method to find the pK_a of the acid as well:

This method has been called the 'half-volume method'.

- Using a volumetric pipette, place 25.0 cm^3 of an aqueous solution of the weak acid into a conical flask.
- Add a few drops of phenolphthalein indicator.
- Titrate against a solution of aqueous sodium hydroxide until the end point colour is obtained.
- Note the volume of sodium hydroxide required. This is the minimum volume required to completely react with the acid.
- Use a fresh 25.0 cm^3 sample of the same aqueous solution of the weak acid and the same aqueous solution of sodium hydroxide, but this time do not add the phenolphthalein.
- Add only *half* the volume of sodium hydroxide required to react with the acid.
- Measure the pH of this solution. This pH value is equal to the pK_a value of the acid.

-

Buffer solutions: (detailed explanation)

A buffer solution is a solution that resists changes in pH when small amounts of an acid or a base are added to it. Buffers are typically composed of a weak acid and its conjugate base, or a weak base and its conjugate acid.

Let's take an example of a buffer solution made from a weak acid, HA, and its conjugate base, A^-. When you mix the weak acid with its conjugate base in solution, some of the weak acid dissociates into its ions, releasing H^+ ions, while the conjugate base captures some of those H^+ ions:

$HA \rightleftharpoons H^+ + A^-$

The equilibrium is established between the weak acid and its ions. Now, if you add a small amount of a strong base (like NaOH) to this solution, the hydroxide ions (\(OH^-\)) from the base will react with the H^+ ions from the weak acid:

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

This reaction will remove some of the H^+ ions from the solution. However, according to Le Chatelier's principle, the equilibrium will shift to the left to counteract the loss of H^+ ions, causing more weak acid molecules to dissociate, thus replenishing the H^+ ions:

$HA \rightleftharpoons H^+ + A^-$

Similarly, if you add a small amount of a strong acid to the solution, the excess H^+ ions will react with the conjugate base, forming more weak acid molecules:

$H^+ + A^- \rightarrow HA$

Again, the equilibrium will shift to the right to counteract the increase in H^+ ions.

In both cases, the presence of the weak acid and its conjugate base allows the solution to resist changes in pH. This is because the equilibrium can shift to either side to maintain a relatively constant concentration of H^+ ions, thus keeping the pH stable.

- We can demonstrate this using calculations:
- $$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]} \qquad [H^+(aq)] = K_a \times \frac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$$

The conjugate base thats used needs to be soluble in water, usually all sodium compounds are soluble in water

How do you calculate the pH of a buffer solution:

- Lets say that we create a buffer with equal volumes of 1mol/dm^3 of ethanoic acid and 1 mol/dm^3 of sodium ethanoite at 298K.
- If we assume that the dissociation of the weak acid is negligianle, then the concentration of the acdi will be 0.5 mol/dm^3 (sicne the volume of the solution doubles, the concentration halves)

- Therefore, the concentration of the ethanote ions from teh conjugate base is considered to be equal to the amount of base that was added i.e. 0.5mol/dm^3 (since the volume has doubled)
- At 298K:

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]} = 1.74 \times 10^{-5}\,\text{mol dm}^{-3}$$

  - If we rearrange this equation, and input the concentrations of the carboxylate ions, and rearrange it to find the H+ concentration, we can find the pH of the buffer.

How can we show that the pH resists change in pH ?

- So we know that a buffer is made up of an acid and its conjugate base. When we add an acid to the solution, the equlirbium of the dissociation of the acid will shit the left, reducing the number of H+ ions in teh solution, thus causing teh pH to remain stable.

  As a result; with acid and base

  $CH_3COO^- + H^+ \rightarrow CH_3COOH$

  $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$
- Overall, the concentration of the acid would increase, and there would be a difference between the initial pH and the final pH however this effect is very minimal.
- If we look at the equation of to calculate the amount of H+ ions that are present in the solution:

$$[H^+(aq)] = K_a \times \frac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$$

So, we know that there is relatively large number/large reservoir of acid present in the solution, and the extent of dissociation of the acid is very small/negligible. There is also a relatively large reservoir of the carboxylate ion present as well, from the disaccoiaiton of the conjugate base that has been added.

- However, when we add an acid or a base, as a result of teh alrge resiovior of the acid and the conjugate base thats present, the ratio between the two remains fairly unchange , which means that the H+ ion constanrtaio wont change massively.
- Therefore, the pH wont change massively as well; this can be demeonstrated by calculating the pH before and afte the addition the acid and the base,
- We can see this in the exmaple below:

The buffer solution is made by mixing equal volumes of 1.00 mol dm^{-3} ethanoic acid and 1.00 mol dm^{-3} sodium ethanoate at 298 K. The initial pH of the buffer solution is calculated to be 4.76.

Then, let's imagine we have 1 dm^3 of this solution and we add 1.00×10^{-2} (0.0100) mol of HCl to it. The text says to make the math easier, we will assume that the volume of the solution does not change.

The added 0.0100 mol of HCl provides 0.0100 mol of H+ ions. These will react with the CH3COO- ions in the buffer in a 1:1 molar ratio according to the following equation:

CH3COO- (aq) + H+ (aq) → CH3COOH (aq)

The amount of CH3COOH present will now have increased from 0.500 to 0.510 mol.

The amount of CH3COO- present will have decreased from 0.500 to 0.490 mol.

So, the new concentrations of acid and base present are: [CH3COOH(aq)] = 0.510 mol dm^-3 and [CH3COO- (aq)] = 0.490 mol dm^-3

The new hydrogen ion concentration is given by the following equation: [H+ (aq)] = 1.74 × 10^-5 × (0.510 / 0.490) = 1.81 × 10^-5 mol dm^-3

The new pH is calculated to be -log(1.81 × 10^-5) = 4.74 (to 3 significant figures).

The pH has changed by 0.02 units from 4.76 to 4.74, which demonstrates the buffering capacity of the solution.

Conversely, if we add a strong acid to lets say water for example:

- We know that the pH of the deaionsed water is 7 at room tempetrature, so this would give us:

The pH, at 298 K, of deionised water is 7.00 so:

$$[H^+(aq)] = 1.00 \times 10^{7}\,\text{mol dm}^{-3}$$

Adding 0.0100 mol of H^+ ions gives:

$$[H^+(aq)] = (1.00 \times 10^{-7} + 0.0100) = 1.00001 \times 10^{-2}\,\text{mol dm}^{-3}$$

The new pH is given by:

$$\text{pH} = -\lg (1.00001 \times 10^{-2}) = 2.00$$

The pH has dropped by 5 units as opposed to 0.02 units with the buffer solution. A considerable difference!

We can also use the henderson - hasselblach's equation to calculate the pH of a buffer; where in we take the log of the previous equation:

$$[H^+(aq)] = K_a \times \frac{[\text{acid}]}{[\text{salt}]}$$

If we take the logarithm to base 10 of both sides of this equation we get:

$$\lg [H^+(aq)] = \lg K_a + \lg \frac{[\text{acid}]}{[\text{salt}]}$$

Or:

$$-\lg [H^+(aq)] = -\lg K_a - \lg \frac{[\text{acid}]}{[\text{salt}]}$$

Or:

$$\text{pH} = \text{p}K_a - \lg \frac{[\text{acid}]}{[\text{salt}]}$$

Or:

$$\text{pH} = \text{p}K_a + \lg \frac{[\text{salt}]}{[\text{acid}]}$$

Buffers made from weak bas and their conjugate acid:

- These kind of buffers have a pH greater than 7. An example of this includes a solution of ammonia and ammonium chloride.

  $NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$

  This would provide us with a mixture of high concentration of the ammonium ion an dthe ammonia.

- When we add an acid to the mixture:
  $NH_3 + H^+ \rightarrow NH_4^+$
- When we add a base to the mixture:
  $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

Extra points:

- The statement "If Ka is very small" implies that the acid is weak, and only a small fraction of it ionizes in water.
- When Ka is small, the numerator of the Ka expression (the product of ion concentrations) is much smaller than the denominator (the concentration of the undissociated acid).
- As a result, the concentration of the undissociated acid ([HA] [HA]) at equilibrium is very similar to its initial concentration.

- when we say that the reactants are more energetically stable, we mean that the chemical bonds in the reactants are stronger or require less energy to break compared to the bonds in the products. In an exothermic reaction, the released energy is typically in the form of heat, and the products are considered to be at a lower energy state (more stable) than the reactants. The reactants, therefore, are often said to be more energetically stable because they have stronger bonds and are at a higher potential energy state before the reaction occurs.