A2 Chemistry – Revision Notes
Unit 4 – Further Physical And Organic Chemistry

Reaction Kinetics

1. The rate of a chemical reaction is the change in concentration of a substance in unit time (units are $mol\ dm^{-3}\ s^{-1}$). It can only be found from experiment, not from the stoichiometric equation.
2. When a reaction occurs in more than one stage (e.g. in a mechanism), there will be one step that is slower, and will be the rate determining step.
3. The rate equation for a reaction with reactants A and B will be of the form $Rate = k\ [A]^m\ [B]^n$:
   a. k is the rate constant, with a value specific to the temperature.
   b. m and n are the orders of reaction with respect to A and B.
   c. The overall order is the sum of the individual orders ($m + n$).
4. Graphs of concentration against time for a reaction:
   a. Zeroth order – the concentration falls at a steady rate with time.
   b. First order – the concentration halves in equal time intervals.
   c. Second order – the concentration falls by a factor of four in equal time intervals.
5. Graphs of rate against concentration for a reaction:
   a. Zeroth order – the rate is unaffected by changes in concentration.
   b. First order – the rate doubles as the concentration doubles.
   c. Second order – the rate quadruples as the concentration doubles. Taking the common logarithm of the concentration will produce a linear graph with a gradient of 2.
6. In experiments, if you are determining the order with respect to a specific reactant, use an excess of the other reactants, so that their concentrations do not significantly change.
7. The initial rate method can be used to determine the rate equation:
   a. Vary the concentrations of reactants, and measure the initial rate of reaction as a tangent to the concentration-time curve at t = 0s.
   b. For a zeroth order, changing the concentration of reactant will have no effect on the rate. Doubling the concentration will cause the rate to double if it is of the first order, or quadruple if it is of the second order.
   c. If both reactants are doubled in concentration, then the effect on the rate will allow the overall order of reaction to be deduced.
8. An increase in temperature will always increase the rate of a reaction, as more molecules will have energy greater than or equal to the activation. The rate constant increases exponentially with temperature – a temperature rise of 10K approximately doubles the rate constant ($Q_{10} = 2$).

Equilibria, Acids And Bases

1. At equilibrium, there is no net change in the concentrations of reactants and products, due to equal and opposite tendencies for change in both directions.
2. A homogeneous system is one in which all the species present are in the same phase.
3. For any reversible reaction at equilibrium, e.g. $aA + bB \rightleftharpoons cC + dD$, the concentrations of the components are related by:

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

4. The value of K_c gives an indication of the position of equilibrium:
   a. $K_c < 1$ – the equilibrium position will be towards the left (more reactants).
   b. $K_c = 1$ – the equilibrium position will be in the middle (equal reactants and products).
   c. $K_c > 1$ – the equilibrium position will be towards the right (more products).
5. For a reaction completely in the gaseous phase, e.g. $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$, the equilibrium constant K_p can be used, whereby p(X) denotes the partial pressure of X:

$$K_p = \frac{p(C)^c\,p(D)^d}{p(A)^a\,p(B)^b}$$

6. The partial pressure of a gas is the pressure that a gas would exert if it were the only gas in the system. The sum of partial pressures gives the total pressure:
   a. The number of moles of a species A is denoted by n(A).
   b. The mole fraction of a species A, x(A), is defined as $x(A) = \dfrac{n(A)}{n_{tot}}$.
   c. The partial pressure of a species A, p(A), is defined as $p(A) = x(A) \times P_{tot}$.

7. The value of K_c/K_p is constant for a specific reaction at a specific temperature. The temperature is the only condition that will cause a change in the value, and this relationship is exponential (pressure and concentration changes will change the position of equilibrium, but not the equilibrium constant):
   a. For an exothermic reaction, raising the temperature will result in fewer products and more reactants, hence K_c/K_p is smaller.
   b. For an endothermic reaction, raising the temperature will result in more products and fewer reactants, hence K_c/K_p is bigger.
   c. A catalyst does not affect the position of equilibrium or the value of K_c/K_p – it only affects the reaction kinetics.
8. An acid is defined as a species that releases $H^+(aq)$ ions, and has a pH lower than 7. A base will neutralise an acid to form a salt and water only (normally metal oxides or hydroxides). An alkali is a soluble base.
9. The Brønsted-Lowry definition of acids and bases:
   a. An acid is a proton donor.
   b. A base is a proton acceptor.
10. The Lewis definition of acids and bases:
    a. An acid is an electron acceptor.
    b. A base is an electron donor.
11. An H^+ ion by itself is not able to exist (it is not stable), so it will combine with water molecules to form hydronium ions, $H_3O^+(aq)$.
12. Any reaction between an acid and a base forms an acid-base equilibrium, whereby the acid donates a proton to form its conjugate base, and the base accepts the proton to form its conjugate acid. A conjugate (acid/base) pair differ only by one proton.
13. pH is defined as: $pH = -\log[H_3O^+(aq)]$. pH values are usually given to 2 decimal places.
14. For a strong acid, always assume complete dissociation into ions. The value of $[H_3O^+]$ will therefore be given by the concentration of acid, multiplied by the number of moles of protons released by one mole of acid.
15. The ionic product of water is defined as $K_w = [H_3O^+(aq)][OH^-(aq)]$:
    a. At 298K, $K_w = 1.0 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$.
    b. The conditions are neutral when $[H_3O^+] = [OH^-]$, but the pH changes with temperature as the value of K_w changes (the pH is only exactly 7 at 298K).
    c. For a strong alkali, the concentration of OH^- ions will be proportional to the concentration of alkali, hence the concentration of H_3O^+ ions can be calculated using the ionic product of water, and consequently the pH can be calculated.
16. For a mixture of an acid and an alkali, calculate the number of moles of H_3O^+ from the acid, and OH^- from the alkali, then calculate the excess after neutralisation. This can consequently be used to calculate the pH of the solution.
17. A weak acid or base only partially dissociates (ionises) in aqueous solution.
18. For the weak acid equilibrium, $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$:
    a. The acid dissociation constant is defined as $K_a = \dfrac{[H_3O^+(aq)][A^-(aq)]}{\left[HA(aq)\right]}$.
    b. $pK_a = -\log K_a$
    c. The smaller the value of K_a and the higher the value of pK_a, the weaker the acid.
    d. You can assume that $[H_3O^+] = [A^-]$, and that $[HA]$ at equilibrium is approximately the same as that before dissociation, resulting in the expression $[H_3O^+]^2 = [HA]_{tot} K_a$.
19. A buffer solution is one that is able to oppose changes in pH when small amounts of acid or base are added, or if it is diluted with water:
    a. An acidic buffer is a mixture of a weak acid and its salt (e.g. ethanoic acid and sodium ethanoate), maintaining a pH below 7:
       i. Ethanoic acid – $CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$ (equilibrium to the left).
       ii. Sodium ethanoate – $CH_3COONa \rightleftharpoons Na^+ + CH_3COO^-$ (equilibrium to the right).
       iii. When the ethanoate ions from the salt are added to the weak acid, the position of equilibrium of the acid is 'pushed' even further to the left – resulting in an excess of both the acid and its conjugate base.
       iv. Added H^+ ions will react with the ethanoate ions, but as they are in excess, the equilibrium will only shift slightly, and the pH is maintained.
       v. Added base will react with the ethanoic acid, but as the acid is also in excess, the equilibrium will only shift slightly, and the pH is maintained.

    b. A basic buffer is a mixture of a weak base and its salt (e.g. ammonia and ammonium chloride), maintaining a pH above 7:

       i. The equilibrium can be written as $NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$.

       ii. From this, $K_a = \dfrac{[H^+][NH_3]}{[NH_4^+]}$.

       iii. If $[NH_3] = [NH_4^+]$ then $pH = pK_a$ for the equilibrium.

    c. The pH of a buffer solution is dependant upon the value of K_a, and the ratio of the concentrations of the conjugate acid/base pair.

20. The equivalence point for an acid-base titration corresponds to the mixing together of stoichiometrically equivalent amounts of acid and base. At equivalence, the pH will be 7.0 for a strong acid and a strong base, less than 7.0 for a strong acid and a weak base, and greater than 7.0 for a weak acid and a strong base. A graph of pH against volume added during a titration results in a pH curve:
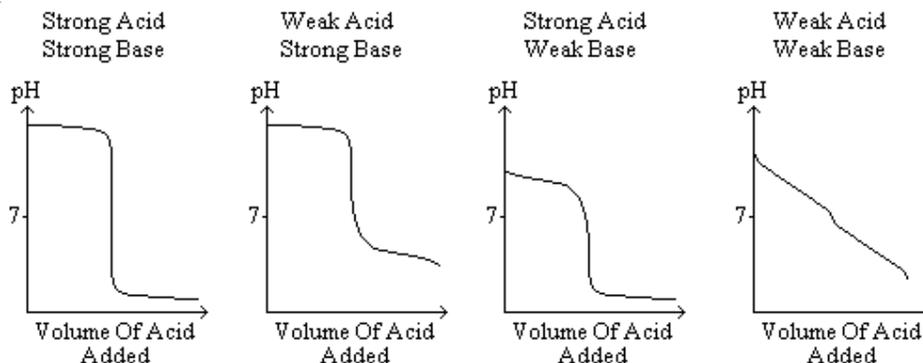
21. Weak, diprotic, acids and bases will produce two end points in a titration, as the ions form separately and sequentially (for a strong diprotic acid such as H_2SO_4, it is fully ionised, so there is only one end point). Different indicators can be used to distinguish between the end points, which occur in a 1:2 ratio. For sodium carbonate, the equilibria are:

    a. $Na_2CO_3 + H^+ \rightleftharpoons NaHCO_3 + Na^+$ (1st end point)

    b. $NaHCO_3 + H^+ \rightleftharpoons Na^+ + CO_2 + H_2O$ (2nd end point)

22. An indicator is a weak acid, whose conjugate base is a different colour:

    a. $HIn + H_2O \rightleftharpoons H_3O^+ + In^-$

    b. Adding acid moves the equilibrium to the left to form colour A. Adding alkali pushes the equilibrium to the right to form colour B.

    c. At the end point, $[In^-] = [HIn]$, so $pH = pK_a$, and the pH at which the indicator changes colour is determined by its K_a value.

    d. Phenolphthalein is colourless in acids (HIn), and purple in bases (In^-), and has a pH range of 8.2 to 10.0. It is used for weak acid–strong base titrations.

    e. Methyl Orange is pink in acids (HIn), and yellow in bases (In^-), and has a pH range of 3.2 to 4.4. It is used for strong acid–weak base titrations.

Nomenclature And Isomerism

1. Functional groups in addition to those in CHM3:

| Homologous Series	Prefix / Suffix	Functional Group
Acid chloride	-oyl chloride	
Acid anhydride	-oic anhydride	
Nitro	nitro-	$- NO_2$
Phenyl	phenyl-	
Secondary amine	*N*-alkylamino-	$- NH - R$
Tertiary amine	*N,N*-dialkylamino-	

2. When naming cyclic compounds, add the prefix *cyclo-* to the name of the carbon chain that forms the ring. Cycloalkanes can exhibit geometric isomerism, if two adjacent carbon atoms each have two different groups attached. As with alkenes, this leads to *cis* and *trans* isomers.
3. When functional groups are placed around a cycloalkane or an aromatic, the lowest number carbon atom should be used for the principle functional group. For a benzene ring, the positions can be indicated relative to the principle functional group:
    a. *Ortho (o-)* – on the carbon next to the principle functional group.
    b. *Meta (m-)* – on the second carbon from the principle functional group.
    c. *Para (p-)* – on the carbon opposite the principle functional group.
4. Some aromatic compounds can be given alternative names for simplification:
    a. Methylbenzene à toluene.
    b. Hydroxybenzene à phenol.
5. If a beam of light is passed through a polaroid filter, the light emerging will have vibrations only in a single plane. Some compounds have the ability to rotate the plane of plane-polarised light, and are optically active. This can be measured using a polarimeter.
6. An optically active compound must be chiral (having no centre of symmetry), due to having a chiral carbon atom that has four different functional groups attached. The two optical isomers (enantiomers) are non-superimposable mirror images of one another, and have the same chemical properties, but often react differently in biological systems:
    a. Dextrorotary (D-, +) – rotation to the right (usually used in biological systems).
    b. Laevorotary (L-, –) – rotation to the left.
7. A racemate (racemic mixture) is mixture containing equal concentration of both optical isomers. There is no net rotation of plane-polarised light.
8. Diastereomers are stereoisomeric structures that are not enantiomers (usually having substantially different chemical and physical properties).
9. Tautomerism is where two isomeric forms of a compound form a dynamic equilibrium, due to the changing position of an atom or feature. For a keto-enol taut, the equilibrium occurs between a ketone, and an alkene with an OH group.

The Carbonyl Group
1. Compounds containing the carbonyl group (C=O) can be formed from the oxidation of alcohols. This requires the presence of either acidified $KMnO_4$ or acidified $K_2Cr_2O_7$ oxidising agent, and is can be carried out in a pear-shaped flask using a condenser:
    a. Primary alcohols:
        i. Heat gently, with the condenser slanting into a collecting flask, to distil off the product. This results in the formation of an aldehyde.
        ii. Boil gently (with an excess of oxidising agent and acid) under reflux, with the condenser upright, to completely oxidise the alcohol into a carboxylic acid. The product can then distilled off.
    b. Secondary alcohols – can be oxidised to a ketone.
    c. Tertiary alcohols – cannot be oxidised.
2. Alcohols have higher boiling points than aldehydes or ketones, due to hydrogen bonding caused by the OH group. Carboxylic acids have an even higher boiling point, as the C=O group withdraws more electrons from the OH oxygen, increasing the polarity of the bond and the strength of the hydrogen bonding.
3. To test between aldehydes and ketones, use Tollen's reagent or Fehling's solution – an aldehyde will be oxidised to a carboxylic acid, and reduce the species in the reagent, whereas a ketone cannot be oxidised.
4. To reduce an aldehyde or a ketone, use a reducing agent of either $NaBH_4$ (aq) or $LiAlH_4$ (in dry ether, then add H_2O to hydrolyse the product). Alternatively a reducing agent of H_2 / Ni catalyst can be used (although this will also reduce alkenes). $NaBH_4$ and $LiAlH_4$ provide a source of hydride (H^-) ions, which are able to carry out a nucleophilic attack of the carbonyl carbon atom:
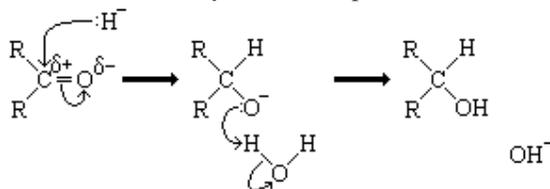
5. Hydrogen cyanide can react with an aldehyde or a ketone with a nucleophilic addition mechanism. This results in the formation of a racemic mixture of a hydroxy*alkan*nitrile. KCN is normally used in preference to HCN, due to HCN being extremely toxic:
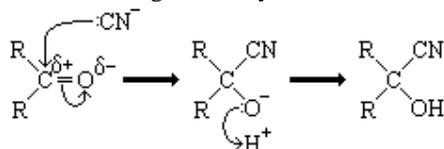

6. A nitrile can undergo two main reactions:
   a. It can be hydrolysed to a carboxylic acid in the presence of water and an acid catalyst (usually HCl). This results in the production of an ammonium salt.
   b. It can be reduced to a primary amine by catalytic hydrogenation with H_2 and Ni.
7. Carboxylic acids are weak acids, so they are only partially dissociated in solution. This produces a low concentration of H_3O^+ ions, but the concentration is sufficient to displace CO_2 from aqueous carbonate ions.
8. Esters can be formed by the reaction of a carboxylic acid and an alcohol, in the presence of a strong acid catalyst (concentrated H_2SO_4). This is a condensation, or esterification reaction. The structure is that of the carboxylic acid, but with the hydrogen replaced by the alkyl group from the alcohol. Esters have no free OH groups, so cannot form hydrogen bonds – they are immiscible with water, volatile, and have lower melting and boiling points than carboxylic acids.
9. Uses of esters:
   a. Solvents – for polar organic compounds. They can be easily separated from solutes, due to their high volatility (e.g. in nail varnish, the ester evaporates quickly).
   b. Plasticisers – they are incorporated into thermoplastic polymers, allowing movement of the polymer chains, and greater flexibility of the material.
   c. Food flavourings – some esters smell nice (there are also a large number that do not!), and can be used to provide artificial fruit flavourings.
10. Esters can be hydrolysed to an alcohol and a carboxylate salt using excess aqueous NaOH, and heating. Naturally occurring esters (oils and fats) can be hydrolysed to produce soaps and glycerol.
11. Soaps are salts of long-chain fatty acids (e.g. stearic acid with 18C). The hydrolysis of fats and oils to produce soaps is saponification. Soaps act as anionic detergents, as the negative carboxyl group is hydrophilic and the carbon chain is hydrophobic, so forms a layer around fats and oils to emulsify them. A strong acid (e.g. HCl) will convert soaps to fatty acids.
12. Acid chlorides can be synthesised from carboxylic acids, using PCl_5:
$$R–COOH \,(l) + PCl_5 \,(s) \rightarrow R–COCl \,(s) + PCl_3O \,(l) + HCl \,(g)$$
13. Acid chlorides and acid anhydrides will undergo acylation reactions, with a nucleophilic addition-elimination mechanism. For the reaction of an acid chloride with ammonia (in excess):
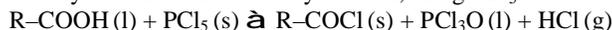
Addition   *Elimination*   *Deprotonation*
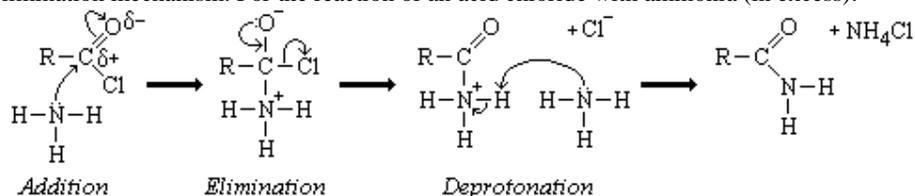
14. The major acylation reactions of acid chlorides are as follows (these must all be carried out in anhydrous conditions, except for the reaction with water!):
   a. Water → carboxylic acid $RCOCl + H_2O \rightarrow RCOOH + HCl$
   b. Alcohol → Ester $RCOCl + R_2OH \rightarrow RCOOR_2 + HCl$
   c. Ammonia → Amide $RCOCl + 2NH_3 \rightarrow RCONH_2 + NH_4Cl$
   d. Primary amine → *N*-substituted amide $RCOCl + 2R_2NH_2 \rightarrow RCONHR_2 + CH_3NH_3^+Cl^-$
15. For acid anhydrides, a carboxylic acid is produced rather than HCl, and an alkanoate salt rather than a chloride salt. Note that the ammonium salts are only produced if an excess of ammonia or the primary amine is used – otherwise HCl (or a carboxylic acid) will be produced.
16. In the preparation of aspirin, acylation is used in the conversion of salicylic acid (2-hydroxy benzoic acid) into aspirin. The hydroxyl group is acylated with ethanoic anhydride. Salicylic acid can be produced by the reaction of phenol with CO_2 (the Kolbe process).
17. In industrial processes, acid anhydrides are used rather than acid chlorides, because:
   a. They are cheaper than the acid chlorides.
   b. Carboxylic acid is produced rather than HCl (difficult and expensive to deal with).
   c. Acid anhydrides react more slowly, so the reaction is easier to control (not violent).

Aromatic Chemistry

1. Benzene is a colourless, volatile liquid, and is immiscible with water (although it can be used as an organic solvent). Kekulé proposed a structure for benzene with alternating single and double bonds, that occurred as a resonance structure – this was shown to be wrong:
    a. The Kekulé structure predicts four isomers of dibromobenzene, however there are only actually three, as 1,6-dibromobenzene and 1,2-dibromobenzene are not separate isomers.
    b. Benzene is not as reactive as would be expected if it contained three double bonds. It does not decolourise bromine water, as alkenes do.
    c. The enthalpy of hydrogenation of benzene would be expected to be about three times the value for cyclohexene, due to containing three double bonds. In actuality, it is considerably lower, and hence benzene is more stable than expected.
    d. Using X-Ray diffraction to calculate the bond lengths in benzene, it was found that they are all the same length (half way between double and single bonds) – thus benzene cannot contain a mixture of single and double bonds.
2. Linus Pauling developed the delocalised structure of benzene – all the carbons are bonded together with single σ bonds, with a cloud of delocalised π electrons above and below the ring.
3. The high electron density around the benzene ring leaves it open to electrophilic attack. It does not undergo electrophilic addition, as this would disrupt the ring structure and is not energetically favoured. Instead, it will undergo electrophilic substitution (E^+ represents the electrophile):
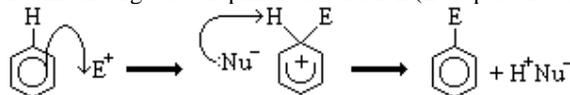
4. The nitration of benzene requires concentrated nitric acid and a concentrated sulphuric acid catalyst, carried out at 50°C:
    a. $HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$
    b. $H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O$
    c. $E^+ = NO_2^+; Nu^- = HSO_4^-$
5. Nitrobenzene can be converted to aminobenzene (phenylamine) by reducing the NO_2 group to an NH_2 group, using a reducing agent of Fe or Sn with moderately concentrated HCl. Phenylamine is used in the production of azo dyes (with a functional group of –N=N–), by converting it into benzenediazonium chloride, and then reacting these together in a coupling reaction. The aromatic groups and the azo group together are called a chromophore (chromophoric group).
6. The nitration of benzene is used in the explosives industry, for the production of TNT (2,4,6-trinitrotoluene) from toluene (methylbenzene). The positive inductive effect of the methyl group favours substitution of the ortho and para positions.
7. The Friedel-Crafts alkylation of benzene requires a haloalkane, and an $AlCl_3$ or $FeCl_3$ catalyst, carried out at about 40°C in anhydrous conditions:
    a. $RCl + AlCl_3 \rightleftharpoons R^+ + AlCl_4^-$
    b. $E^+ = R^+; Nu^- = AlCl_4^-$
8. Uses of Friedel-Crafts alkylation:
    a. Methylbenzene is used in the manufacture of explosives (TNT).
    b. Ethylbenzene is used in the production of polystyrene:
        i. Benzene does not react directly with chloroethane, so a mixture of ethene and HCl is used.
        ii. Dehydrogenation of ethylbenzene (with Fe_2O_3 at 600°C) produces phenylethene.
        iii. Polymerisation of phenylethene produces polystyrene.
    c. 2-phenylpropane (cumene) is oxidised to form phenol and propanone:
        i. Propanone is used as a solvent in medicine and cosmetic applications.
        ii. Phenol is used as a coupling agent in the dye-making industry.
9. The Friedel-Crafts acylation of benzene requires an acid chloride, and an $AlCl_3$ or $FeCl_3$ catalyst, carried out at about 40°C in anhydrous conditions:
    a. $RCOCl + AlCl_3 \rightleftharpoons RCO^+ + AlCl_4^-$
    b. $E^+ = RCO^+; Nu^- = AlCl_4^-$
10. Ethylbenzene can be prepared from the acylation of benzene with ethanoyl chloride, which first produces phenylethanone. This is then reduced using H_2/Ni to form ethylbenzene.

Amines

1. An amine is defined as being primary, secondary or tertiary according to the number of alkyl groups bonded to the nitrogen atom. Side chains are given the prefix *N-* (rather than a number).

2. Primary and secondary amines (with short alkyl groups) are soluble in water as they are able to form hydrogen bonds with water molecules, due to the presence of the N–H bond. As the order of the amine increases, the boiling point decreases (as the molecules cannot pack as closely together). The boiling points of amines are lower than those of the respective alcohols, due to weaker hydrogen bonding.

3. Ammonia and amines act as Brønsted-Lowry bases, as the nitrogen atom is able to accept a proton. Amines are weak bases, as they only partially react with water in solution:
   a. $RNH_2(aq) + H_3O^+(aq) \rightleftharpoons RNH_3^+(aq) + H_2O(l)$
   b. Primary aliphatic amines are stronger bases than ammonia, due to the positive inductive effect of the alkyl group. This provides a greater electron density around the nitrogen atom, increasing the availability of the lone pair, so that it can react more readily.
   c. Aromatic aryl amines are weaker bases than ammonia, as the lone pair of electrons on the nitrogen atom interacts with the delocalised π electrons in the benzene ring. This decreases the availability of the lone pair for accepting a proton.
   d. Aromatic compounds where the amine group is not directly bonded to benzene have a similar base strength to the aliphatic amines, as the nitrogen electrons are not dissociated.

4. Ammonia and amines both have a lone pair of electrons on the nitrogen atom, so they are able to act as nucleophiles and ligands (electron pair donors). Amines can react in two main ways:
   a. Nucleophilic substitution with a haloalkane – further substitution can take place to form a secondary amine, tertiary amine, and finally a quaternary ammonium salt (where four groups are bonded to the nitrogen to form a cation).
   b. Acylation with an acid chloride or anhydride – this produces an *N*-substituted amide.

5. An excess of haloalkane will result in a high yield of quaternary ammonium salts. These can be manufactured using long chain haloalkanes to produce cationic surfactants (the positive charge on the nitrogen is attracted to negatively charged surfaces such as glass, hair, fibres, metals and plastics). These can be used in fabric and hair conditioners, leather softeners, sewage flocculants (bringing particles to the surface), corrosion inhibitors, emulsifiers and disinfectants.

6. Primary aliphatic amines can be prepared in two main ways:
   a. Nucleophilic substitution of ammonia with a haloalkane – an excess of ammonia is used to give a high yield of the primary amine, although further substitution can take place.
   b. Nucleophilic substitution of cyanide ions with a haloalkane – this produces a nitrile, which can be reduced to an amine using either catalytic hydrogenation (H_2/Ni) or $LiAlH_4$ in dry ether ($NaBH_4$ is not a strong enough reducing agent). This gives a higher yield (no further substitution), and increases the length of the carbon chain by one.

7. Aromatic amines can be produced by the nitration of benzene to form nitrobenzene. This is then reduced to aminobenzene by catalytic hydrogenation (H_2/Ni) or Sn/Fe with moderately concentrated HCl (in this case, NaOH must be added afterwards, to deprotonate the phenylamine).

Amino Acids
1. Amino acids are bifunctional organic compounds, containing both the amino group and the carboxylic acid group. There are 20 naturally occurring amino acids, which have the amino group on the carbon next to the carboxyl group (α-amino acids). These differ only in their R group:

$$R-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}-C\underset{OH}{\overset{O}{<}}$$

2. All amino acids have optical isomers (except for glycine, where R = H), but only the D-isomers occur naturally in body proteins.

3. Amino acids act as both acids and bases, and so in alkaline solution the carboxylic acid group is deprotonated, and in acidic solution the amino group is protonated. Amino acids can never exist as uncharged compounds, so at its isoelectric pH (unique for each amino acid), where it has no net charge, it forms a zwitterion (or amphion), whereby the amino group is protonated and the carboxylic acid group is deprotonated:

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N^+}}-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-C\underset{O^-}{\overset{O}{<}}$$

4. Two amino acids can react in a condensation reaction to form a peptide (or amide) group – the CONH group – containing a peptide bond (C–N). Many condensation reactions can take place to form a polypeptide or polyamide, which is the primary structure of a protein. Hydrogen bonding

can occur between N–H and C=O groups to form a helical shape (the secondary structure). The tertiary structure is the characteristic three-dimensional shape of the protein (fibrous or globular).

5. Polypeptides can be hydrolysed into their constituent amino acids by hydrolysing the peptide bonds between them. This requires heating the polypeptide with 5M HCl for 24 hours.

Polymers

1. There are two types of polymer (synthetic polymers are plastics):
    a. Addition (chain-growth) – a double bond in the monomer is broken to bond with other monomers, forming a long chain polymer.
    b. Condensation (step-growth) – the monomers have two different functional groups that react together, resulting in the loss of small molecules (e.g. H_2O).
2. Thermosetting polymers char or burn on heating, whereas thermoplastic polymers melt or soften on heating.
3. Poly(ethene) is an addition polymer, and has two types:
    a. LDPE (low density) – there are many branches from the polymer chains, resulting in a softer material, with a low melting point. It is used for packaging and electrical insulation.
    b. HDPE (high density) – there is very little branching, so the straight chains can get closer together, resulting in a stronger and more rigid material, with a higher melting point. It is produced using a Ziegler catalyst (organometallic).
4. PVC (polyvinyl chloride) is stronger than poly(ethene), as the chlorine provides permanent dipoles in the molecules, resulting in stronger intermolecular forces. PVC is brittle though, as the big chlorine atoms mean that the chains cannot move past one another.
5. There are three different types of addition polymer:
    a. Isotactic – the functional groups are evenly spaced on the same side of the chain.
    b. Syndiotactic – the functional groups are evenly spaced and alternate between sides.
    c. Atactic – the functional groups are randomly positioned.
6. A polymer can be made stronger by adding an electronegative atom (stronger intermolecular forces) or by increasing the number of cross-linkages (e.g. using sulphur – vulcanised rubber).
7. Addition polymerisation usually involves a free radical mechanism, and is carried out at a high temperature and pressure, and with a catalyst. The repeating unit is enclosed in square brackets, with the letter *n* to denote a large number of repeats. Common addition polymers are:
    a. Poly(ethene) or polythene – bags, packaging, insulating electric wires.
    b. Poly(phenylethene) or polystyrene – packaging, insulation.
    c. Poly(chloroethene) or PVC – window frames, guttering.
    d. Poly(tetrafluoroethene) or Teflon – waterproofing, non-stick surfaces.
    e. Poly(ethenyl ethanoate) or PVA – paints, adhesives.
8. There are two main types of condensation polymer:
    a. Polyesters – A dicarboxylic acid and a diol react to form the monomer.
    b. Polyamides (polypeptides) – the monomer is either an amino acid, or a mixture of a dicarboxylic acid and a diamine.
9. Nylon-6,6 is a polyamide formed from the reaction of hexanedioic acid and hexane-1,6-diamine at 250°C. Nylon-6 is formed from the amino acid 6-aminohexanoic acid. In the condensation reaction, water is formed from the OH of the carboxylic acid and an H from the amino group.
10. Terylene, PET, or poly(ethyleneterephthalate) is a polyester formed from benzene-1,4-dicarboxylic acid, and ethane-1,2-diol. The water is produced from the acid OH and an H from the alcohol. If the dimethyl ester of the acid is used, methanol is evolved as a gas.
11. Addition polymers are non-biodegradable, as they are chemically inert, but they are highly flammable, so can sometimes be recycled (if the different types are separated first). Condensation polymers can undergo hydrolysis to break them down into their component monomers, so they are biodegradable.

Organic Analysis

1. Saturated hydrocarbons (alkanes) tend to burn with a clean flame, whereas unsaturated hydrocarbons (alkenes and aromatics) tend to burn with a sooty flame.
2. Alkenes decolourise bromine water (orange to colourless), whereas alkanes and aromatics do not.
3. Carboxylic acids dissolve in water as a weakly acidic solution, whereas amines are weak alkalis.
4. Alcohols and carboxylic acids react with Na (s) to produce hydrogen gas.
5. Carboxylic acids will react with Na_2CO_3 to produce CO_2 gas.
6. Aldehydes and ketones react with Brady's reagent (2,4-dinitrophenylhydrazine in sulphuric acid) to produce an orange-red precipitate (carboxylic acids and alcohols do not react).

7. Aldehydes will form a brick red precipitate or a silver precipitate when warmed with Fehling's solution or Tollen's reagent respectively. Ketones do not react.
8. Primary and secondary alcohols and aldehydes can be oxidised by acidified $K_2Cr_2O_7$ (orange to green) or $KMnO_4$ (purple to colourless) respectively. Tertiary alcohols and ketones do not react.
9. Carboxylic acids react with ethanol and a concentrated H_2SO_4 catalyst to form an ester.
10. Alcohols react with ethanoic acid and a concentrated H_2SO_4 catalyst to form an ester.
11. Haloalkanes can be hydrolysed with dilute NaOH (aq), then after adding nitric acid and silver nitrate solution, a precipitate will appear (fluoroalkanes are not detected, as AgF is water soluble):
    a. Chloroalkanes – white precipitate (AgCl), dissolves in dilute ammonia.
    b. Bromoalkanes – cream precipitate (AgBr), dissolves in concentrated ammonia.
    c. Iodoalkanes – yellow precipitate (AgI), insoluble in dilute and concentrated ammonia.
12. Acyl chlorides react vigorously with $AgNO_3$ (aq) to form a white AgCl precipitate.
13. Amines and amino acids produce a dark-blue soluble complex with copper (II) ions and excess ammonia. Aromatic amines tend to form green, insoluble complexes.
14. Adding hydroxide ions to an amine causes the indicator to change colour more rapidly (with less hydroxide) than with an amino acid, as there is no carboxylic acid group to react with the alkali.

Spectroscopy
1. Mass spectrometry uses the varying mass-to-charge (m/z) ratios of ions, and their varying degrees of deflection in a magnetic field, in order to determine their relative abundances:
    a. The main peaks on the mass spectrum are caused by the parent molecule and fragments of it, although some minor peaks can be caused by rearrangements.
    b. The peak at the maximum m/z value is the parent molecular ion, $M^{+\bullet}$ (a radical cation), which has an m/z value equal to the M_r of the molecule.
    c. The parent ion can fragment into a cation and a radical – $M^{+\bullet} \grave{a} \ X^+ + Y^{\bullet}$ – only the cation is detected, as it can be accelerated by the electric field and deflected by the magnetic field. Further fragmentation of X^+ (or Y^+ if it is formed) can take place.
    d. The notation $(M – R)^+$ refers to the parent ion losing the group R (as $R^{\bullet}$).
    e. The heights of peaks on the mass spectrum are shown as percentages of the height of the largest peak (the base peak). The more abundant the fragment is, the more stable it will be, and the easier it will be to form it (the weaker the broken bond is).
    f. Molecular ions that are two m/z units apart in a 3:1 intensity ratio will be due to the presence of chlorine, occurring as roughly 75% ^{35}Cl and 25% ^{37}Cl.
    g. Molecular ions that are two m/z units apart in a 1:1 intensity ratio will be due to the presence of bromine, occurring as roughly 50% ^{79}Br and 50% ^{81}Br.
    h. Fragmentation usually occurs as the weaker bonds break (e.g. C–C, C–O and O–H), whereas the stronger bonds remain unbroken (e.g. C–H and C=O). Some common stable ions formed as a result of fragmentation are as follows:
        i. CH_3 (m/z =15)
        ii. NH_2 (m/z = 16)
        iii. OH (m/z = 17)
        iv. C_2H_5 (m/z = 29)
        v. C_6H_5 (m/z 77)
    i. Alcohols will readily eliminate water from the parent ion, to form a peak at $(M – H_2O)^{+\bullet}$.
    j. Alkanes tend to give peaks at $(M – R)^+$, where R is an alkyl group.
    k. Ketones tend to form stable acylium cations (RCO^+).
2. Infra-red spectroscopy uses the characteristic absorption wavelengths of photons for different bonds in order to identify a compound:
    a. Covalent bonds are able to vibrate, by either stretching or bending, and they do this at a resonant frequency for each pattern of vibration. This corresponds to a specific wavelength in the infra-red spectrum, which can be absorbed by the bond electrons. Thus the intensity of each wavelength of infra-red light passing through a sample is recorded and compared to that through a blank (the background), to give an absorption spectrum.
    b. The scale for an infra-red spectrum is given in terms of the wavenumber ν, which is defined as $1/\lambda$. The units are given in cm^{-1}.
    c. The region of the spectrum below 1500 cm^{-1} (to the right) is the fingerprint region, which can be very complex. This is unique to each compound, and so comparison with a database can be used to determine the identity of the compound.
    d. The higher wavenumber region of the spectrum is very useful in determining particular functional groups, which can aid identification:

       i.   O–H (alcohol) gives a broad absorption around 3300 cm^{-1}, due to H-bonding.

      ii.   O–H (acid) gives a very broad absorption around 2800 cm^{-1}.

     iii.   C=O gives a sharp absorption at about 1700 cm^{-1}.

     iv.   C≡N gives a small, sharp absorption at about 2250 cm^{-1}.

   e. The most useful information can often be the absence of particular functional groups, as this eliminates possibilities as to the identity of the compound.

3. Nuclear magnetic resonance (NMR) spectroscopy gives the most information of the spectroscopic analyses, with regard to the positions and numbers of protons (hydrogen atoms) in the molecule:

   a. Nuclei spin, and thus create a magnetic field around them, as they are charged. If they are placed within a magnetic field, they all line up either in the same direction (lower energy) or in the opposite direction (higher energy) to the magnetic field. The very small energy gap between these states corresponds to radio frequency waves. Normally a fixed magnetic field is used, and the frequency of applied radio waves (causing resonance) is modified, in order to scan the sample and detect the effects.

   b. The chemical shift, δ, is measured in ppm (parts per million), and depends upon the amount of shielding of the protons by electrons – the more shielding, the higher the field strength needed for resonance, and the lower the δ value.

   c. The amount of shielding depends upon the environment of the protons – if they are next to an electronegative atom (e.g. in COOH) then there will be deshielding and a high δ value (downfield), whereas if they are next to an atom with low electronegativity (e.g. in CH_3) there will be more shielding and a lower δ value (upfield).

   d. The δ value is determined as relative to a standard of TMS (tetramethylsilane – $Si(CH_3)_4$):

       i.   This gives a strong signal due to 12 protons in the same environment.

      ii.   Si is less electronegative than carbon, so the signal is upfield of other organic molecules (δ is defined as 0.0ppm).

     iii.   It is inert and non-toxic, cheap, and is volatile (can be evaporated afterwards).

   e. The area under each peak on the NMR spectrum is proportional to the number of protons it represents (in the same environment), and this ratio is given by the integration curve.

   f. A high resolution NMR spectrum is able to show splitting of individual peaks, due to being adjacent to other protons in a different environment:

       i.   The number of splits is $n + 1$ where the number of adjacent protons is n ($n + 1$ rule). The splitting pattern is given by the $(n + 1)$th line of Pascal's triangle.

      ii.   A triplet (1:2:1) indicates that the protons are adjacent to a CH_2 group.

     iii.   A quartet (1:3:3:1) indicated that the protons are adjacent to a CH_3 group.

     iv.   An ethyl group (CH_2CH_3) is indicated by a triplet and a quartet, with integration curves in a 3:2 ratio.

      v.   If there is no splitting, then the protons are not adjacent to any different protons (a singlet) – e.g. the H in an OH group.

     vi.   If the protons are next to two different types of proton, then there will be splitting of the splitting pattern (e.g. a quartet of triplets).

    vii.   The splitting of peaks is called the coupling effect.

4. It is often most useful to compare the results of all three spectroscopic analyses, as they give different types of information, and to also use chemical analytical tests, in order to determine the identity of a compound.