- **Electronegativity = power of atom to attract pair of electrons in a covalent bond, more electronegative to top right**

-> down group, electronegativity decreases = atomic radius increases, more shielding -> less electrostatic attraction

-> period, electronegativity increases = atomic radius decreases, increased nuclear charge, more electrostatic attraction

- Non - polar covalent bond – elements w identical electronegativities = equal sharing of electrons
- e- shared unequally between elements w different electronegativities leads to partial charges + polar covalent bond
- In a non – polar molecule polar bonds cancel each other out = usually linear, tetrahedral, octahedral

3.1.3.7 Forces between molecules

- **IM forces – forces of attraction between molecules, boiling points influenced by strength of IM forces**
- Dipole-dipole interactions – between polar molecules, attraction between atoms of opposing electronegativity
- Distribution of e- in atom constantly changes leading to dipole in non-polar molecules

-> distorts e- of neighbouring atoms - induced dipole forces

-> attraction between induced and temporary dipole = Van der Waals forces found between all molecules

- More e- = more SA, more chances of instantaneous dipole, larger dipole, more attraction, more energy to break
- Hydrogen bonding – large difference in electronegativity, creates dipole, between H+ and lone pair e- on F / O / N

3.1.4. Energetics

3.1.4.1Enthalpy Change Reactions don't occur spontaneously as atoms need to collide with sufficient energy

- **Exothermic – increase in temperature, combustion, making bonds, more energy released than supplied**
- **Endothermic – decrease in temperature, absorb energy from environment, more energy supplied, breaking bonds**
- Enthalpy change ^H = heat energy change measured under standard conditions - 298K and 100kPa
- Enthalpy of combustion = enthalpy change when mole of substance burnt completely in O2 - standard conditions
- Enthalpy of formation = enthalpy change when mole of substance formed from its elements - standard conditions

3.1.4.2 Calorimetry

- **Q = mc^T** + **^H = q/mol** Energy given out (kJ) / limiting moles of reactant (mol)
- Enthalpy changes experimentally = combusting known mass fuel + using heat given out to raise temperature of water
- Assumptions = 100% J transfer, density 1, solid doesn't change mass, no evaporation of fuel or water
- **Polystyrene cup = good insulator, prevents heat loss / gain**

-> adding lid helps reduce heat loss / makes temperature measurement difficult so adding more insulation is a solution

-> adding reactants quickly, as a powder with higher surface area, stirring chemicals = allow maximum temperature change

3.1.4.3 Hess's law Application of principle of conservation of energy

- Enthalpy change at constant pressure in reaction is independent of route taken + depends on initial and final states
- Enthalpies of formation = **enthalpy formation products – reactants**
- Enthalpies of combustion = **enthalpy combustion reactants - products**

3.1.4.4 Bond enthalpies – enthalpies of all elements in standard states is zero

- Mean bond - enthalpy change required to break one mole of covalent bonds averaged over a range of compounds
- Enthalpy change = energy required to break bonds in reactants – energy required to make bonds in products

3.1.5 Kinetics

3.1.5.1 Collision theory - particles must collide in correct orientation w enough KE to overcome specific activation energy

- **Collision energy – combined energy of colliding particles, changed by temperature**
- **Collision frequency – collisions between particles per second, changed by pressure / vol. / conc. / temp.**
- **Activation energy – minimum amount of energy required for reaction to occur, changed by catalyst**

3.1.5.2. Maxwell–Boltzmann distribution – of molecular energies in gases

- Energy v. Number of particles w Energy graph, Emp = most probable energy, area under graph is number of particles
- No particles have zero energy, there is a probable energy for particles in the gas, small number have high energies
- Majority of particles don't have enough activation energy to successfully react i.e. lower than activation energy
- Catalyst = provides alternative reaction pathway with lower activation energy but chemically unchanged
- Temperature increase – increased particles exceeding Ea, more successful collisions increases rate, same total

3.1.5.3 Effect of temperature on reaction rate

- **Rate of reaction – change in concentration of a substance per unit time**
- Faster reaction with increase – more kinetic energy, increased collision energy / frequency / successful collisions

3.1.5.4 Effect of concentration and pressure

- Pressure / conc. – faster reaction w increase, particles closer together, increased collisions so more successful

3.1.5.5 Catalysts

- Substance that increases rate of chemical reaction without being changed in chemical composition or amount

- 2^{nd} **Electron affinity –** enthalpy change when n. of –1 gaseous ions gains an electron per ion to form –2 gaseous ions - ENDOTHERMIC as energy is required to overcome the repulsive forces between the negative ion and electron

Some trends

- Atomisation of metals - metal with the weaker metallic bonding has a more endothermic atomisation
- 1^{st} electron affinity becomes more exothermic down a group due to more shielding and more repulsion from e-
- Lattice formation more exothermic w smaller atomic radii = larger charge density = stronger electrostatic attraction
- Enthalpy of hydration less exothermic as ionic radius increases as lower charge density so weaker attraction
- In organic molecules solubility decreases as chain length increases because more VdW forces have to be overcome

Experimental value is more exothermic

- Indication that there are more and stronger bonds than only the ionic bonds involved
- Theoretical value assumes perfect ionic model – ions are spherical, and attraction is purely electrostatic
- Covalent character unconsidered – higher charge density of cation to anion causes anion to polarise
- Tendency for covalent character when: 1. Small cation 2. Multiple charges of cation / anion 3. Large anion

Enthalpy of solution – enthalpy change when n of ionic solid dissolves in enough water to separate into ions that don't interact

Enthalpy of hydration – enthalpy change when one mole of gaseous ions become hydrated

Dissolving a solid

- Endothermic – ions are separated to release them from crystal lattice or to overcome the IMF between molecules
- Exothermic – ions or molecules forming bonds with the polar water molecules
- Polar ends of water molecules are attracted to the cations and anions in the ionic lattice which disrupts the lattice

3.1.8.2 Free Gibbs energy and entropy change

- ΔS / entropy is a measure of disorder of the system, the more the disorder the more positive the entropy
- Total ΔS = total ΔS of products - ΔS of reactants, measured in J/K/mol so needs to be converted to K
- Entropy increases from s -> l -> g due to decreasing IMF and increases when gas molecules increase
- Entropy decreases when ionic solid lattice dissolves as ions dissociate so there is less order
- Entropy increases as temperature increases because the particles have more energy so have more disorder
- There is a larger entropy change during boiling than melting
- Balance between entropy and enthalpy determines feasibility of a reaction by: $\Delta G = \Delta H - T\Delta S \Rightarrow \Delta G = (-\Delta S)\,T + \Delta H$
- When $\Delta G = 0$ the minimum temperature can be found at which the reaction takes place
- For a reaction to be feasible, the value of ΔG must be zero or negative
- Exothermic reaction with positive entropy change – always feasible
- Exothermic reaction with negative entropy change – feasible at low temperatures
- Endothermic reaction with positive entropy change – feasible at high temperatures
- Endothermic reaction with negative entropy change – never feasible

3.1.9 Rate Equations

3.1.9.1 Rate equations

- Rate of reaction dependent on temperature, surface area, catalyst, pressure and concentration of reactants
- Rate of a chemical reaction is related to reactant concentration by rate equation: Rate = k[A]m [B]n

m and n are the orders of reaction = determined experimentally, restricted to 0 / 1 / 2, how concentration affects rate

- 0^{th} order = rate of reaction not affected by the reactant's concentration, it does not appear in the rate equation
- 1^{st} order = rate of reaction is proportional to the concentration of the reactant
- 2^{nd} order = rate of reaction is directly proportional to the concentration of the reactant squared
- Overall reaction order – sum of orders of the reactants that appear in the rate equation
- To work out reaction orders use experimental data and compare when one reactant has been changed

k is the rate constant, varies with temperature, increases with temperature, units calculated from rate equation

A / B are the reactants, concentrations measured in mol/dm^3 are inserted into the rate equation

1. **k = Ae^–Ea/RT** where A is the Arrhenius constant, Ea is the activation energy and T is the temperature in K

When temperature increases, -Ea/RT becomes smaller so becomes less negative so k becomes bigger \

1. **Lnk = lnA – Ea/RT therefore the graph equation -> lnk = -Ea/R * 1/T + lnA**
2. **Draw graph of lnk against 1/T, don't start at 0 but just before the data point**
3. **Look at data and calculate the range, count the number of squares given on the graph, range / squares = scale**
4. **6 marker experimental plan – measure 4 or 5 T, look up R, measure or deduce the rate to find the rate constant**

3.1.9.2 Determination of rate equation

- Experimentally determined relationship - ^rate = k ^[X] ^[Y]

Development over time

- 19th century – artificial polymers such as artificial silk and hard rubber synthesised
- 20th century – further developments -> Kevlar and Nylon synthesised
- Developments still being made for cheaper production and better function

Polymer name	Everyday name	Uses
Polyethene	**Polythene**	**LDPE** • **Loosely packed due to branching = small SA, less area of contact = weak Van der Waal forces** • **Flexible, soft, low melting point = bags / cling film** **HDPE** • **Tightly packed = big SA, more area of contact = strong Van der Waals forces** • **Stiffer, stronger, rigid, high melting point = bottles**
Polychloroethene	**PVC**	**Window frames** **Strong but brittle** • **Polar covalent bonds between C and Cl** • **Permanent dipole forces between molecules = strong** • **Brittle = like charges repel as chains come together**

3.3.5 Alcohols

3.3.5.1 Alcohol production

Electrophilic addition of sulfuric acid to ethene and then hydrolysis

Produced industrially by hydration of alkenes with conc. phosphoric acid catalyst, 300 – 600 degrees, 70atm

Produced industrially by fermentation of glucose, yeast, no air, 30 – 40 degrees

- Ethanol produced by fermentation separated by fractional distillation = biofuel = carbon-neutral, 6 moles CO2 taken in, 2 moles produced / 4 moles after burning – however energy for transport and irrigation not taken into account

Hydration	Fermentation
Advantages • Faster, purer product, continuous process Disadvantages • High tech equipment and ethene is non-renewable • High energy costs to maintain high pressures	Advantages • Sugar is renewable and low-level technology Disadvantages • Slow batch process and depletes land for crops • Impure ethanol needs purification by distillation

3.3.5.2 Oxidation of Alcohols – hot water bath and not bunsen burner as highly flammable

- Classified as primary, secondary and tertiary – oxidation dependent on number of C-H bonds / available bonds
- Primary alcohols can be oxidised to aldehydes (H-C=O heat + distilled) which can be further oxidised to carboxylic acids (heat under reflux, change the position of the condenser = vertical)
- Boiling points – carboxylic acid > primary alcohol > aldehyde – carboxylic has two polar bonds for hydrogen bonding
- Secondary alcohols can be oxidised to ketones – O=C, tertiary alcohols are not oxidised
- Acidified potassium dichromate (VI) and dilute sulfuric acid = orange dichromate ion reduces to green chromium ion
- [O] - to produce mole of water, add 2 before the symbol for oxidation of aldehyde to carboxylic acid

3.3.5.3 Elimination – dehydration = water removal

- Alkene produced, concentrated H2SO4 used as a catalyst, heat under reflux
- Neighbouring carbon atoms must have H groups attached – varying number = more than one isomeric product
- 1.Lone pair on O donated to H+ 2. e- in bond donated to O+ 3. Water removed 4. e- from H to C 5. H+ removed
- Alkenes produced = addition polymers without using monomers derived from crude oil

3.3.6 Organic analysis

3.3.6.1 Identification of functional groups by test-tube reactions

- Alcohol – potassium dichromate turns green from orange for primary and secondary alcohols
- Aldehyde can be further oxidised, reducing agent so property used to distinguish aldehydes from ketones

Fehling's – red precipitate for aldehyde, Cu2+ blue solution forms Cu2O red precipitate

Tollen's – 1. 2AgNO3 + NaOH -> Ag2O + 2NaNO3 +H2O 2. 4NH3 + Ag2O -> 2[Ag(NH3)2]+ , silver mirror

- Carboxylic acid – solid sodium hydrogencarbonate in test tube added to acid for effervescence
- Alkene – aqueous bromine water changes colour from orange to colourless

3.3.6.2 Mass Spectrometry

- Used to determine molecular formula of a compound

- Molecular ion then fragments into cation + free radical
- Higher Mr than actual molecule has low % abundance and can be ignored
- High resolution – used to determine molecular formula of compound from accurate mass of molecular ion (5 d.p.)
- Relative intensity of molecular ions depending on the ratio of isotopes present in the atmosphere

3.3.6.3 Infrared Spectroscopy - Shows what bonds are present / absent in molecule to suggest functional groups

Bonds have unique frequency, absorb same frequency so radiation emerging has missing frequencies of the bonds in sample

- Frequency depends on atom mass in bond, bond strength, vibration – symmetrical / asymmetrical stretch or bend
- 'Fingerprinting' allows identification of a molecule by comparison of spectra – unique for each compound
- O-H - broad peak in alcohols (3230-3550), acid – very broad / jagged (2500-3000)
- C=O - aldehyde / ester / ketone / carboxylic acid – sharp, strong, almost 0 transmission (1680-1750)
- CO_2 / CH_4 – bonds absorb + re-emit IR -> increases temperature of planet = greenhouse gases -> warm earth for life
- More CO_2 - more re-emission of IR so mean temperature is rising = global warming

Peak at …, bond … is present, there is not a peak in the range …, bond … is not present, suggests it is …

3.3.7 Optical isomerism – stereoisomerism and occurs as a result of chirality in molecules in molecules with single chiral centre

- Asymmetric C atom is chiral and gives rise to optical isomers known as enantiomers = 4 different groups bonded to it

Enantiomers = non-super imposable mirror images that differ in their effect on plane polarised light

- Same physical properties
- Each rotates plane polarised light in different directions – clockwise / anti-clockwise = determined experimentally

Racemic mixture / racemate - a mixture of equal amounts of enantiomers

- Plane polarised light unaffected by racemate / would rotate by an enantiopure sample

Many drugs sold are enantiopure and they work by binding to amino acid receptors in the body

Amino acids are chiral / our bodies are enantiopure = beneficial as small doses are required for drug to be effective

3.3.8 Aldehydes and ketones

- Carbonyl is the functional group C=O – planar bond, aldehydes are readily oxidised into carboxylic acids
- Aldehyde – the carbonyl group is at the end of the C chain, ketone – carbonyl group is within the C chain
- Fehlings solution – blue solution to red precipitate for aldehydes only, Tollens – silver mirror for aldehyde

Nucleophilic addition reactions – attraction to partial positive C atom, combines with another molecule to form larger one

Cyanide ions – produces hydroxynitrile products that are isomeric products

- HCN – low concentration of cyanide ions as partial dissociation, in alkaline reflux to shift eqbm to the right, gaseous at room temperature, to minimise danger use fume cupboard and wear gloves
- KCN and H_2SO_4 – acidic reflux as a source of protons, soluble cyanide salt – high concentration of cyanide ions

Racemic mixture formed after nucleophilic addition: planar C=O group, attacked from either side, with equal probability

Aldehydes can be reduced to primary alcohols, and ketones to secondary alcohols, using $NaBH_4$ in aqueous solution

- 2[H] - aqueous alcoholic solution, nucleophilic addition where H- acts as the nucleophile

Hydrogen acts as a reducing agent, Pt / Ni acts as a catalyst -> makes an alcohol (can reduce C=C / C=O)

3.3.9 Carboxylic acids and derivatives

3.3.9.1 Carboxylic acids and esters

Carboxylic acids - weak acids but liberate CO_2 from carbonates

- Carboxylate ions – negative charge is shared over the whole of the carboxylate group
- Form 2 H bonds per molecule = dimer with larger VdW forces between molecules = more energy to overcome forces

Carboxylic acid + base -> salt + water

Carboxylic acid + carbonate -> salt + water + carbon dioxide

Esters – carboxylic acids and alcohols react, in the presence of an acid catalyst, to give esters

- Common uses of esters: in solvents, plasticisers, perfumes and food flavourings
- Molecules with one hydroxy and one carboxyl group on either end can self-esterify to form a cyclic ester
- Vegetable oils and animal fats are esters of propane-1,2,3-triol

Saturated fats – regular, fit neatly together so bigger SA, stronger VdW forces, higher m.p, solid at room temperature

Unsaturated fats – don't fit neatly, smaller SA, weaker VdW forces, lower m.p, liquid at room temperature

- Hydrolysis of esters under acidic and alkaline conditions

Acidic – ester + water <-> carboxylic acid + alcohol (reversible reaction that goes to completion w acid catalyst under reflux)

Alkaline – ester + NaOH <-> carboxylate ion + alcohol (non-reversible, carboxylate ion can react w acid to form carboxylic acid)

- Vegetable oils / fats hydrolysed in alkaline conditions to give soap (salts of long-chain carboxylic acids) + glycerol

Fat / oil + 3NaOH -> glycerol + 3 sodium salts