Chemistry by Design
(AI) Agriculture and Industry
    Formulae and equations
        (a) *use the concept of amount of substance to perform calculations involving:*
         molecular formulae,

           Empirical formula
              The % compositions are taken as masses.
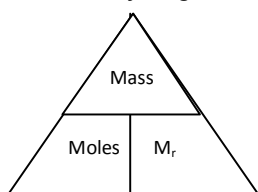   **The number of moles is calculated**
            ÷ by smaller to get the ratio
          Molecular Formula
             Either equal to Empirical formula or a simple multiple of it.
               The relationship between the formula mass of the empirical formula, and the relative molecular mass, and the empirical formula and the molecular formula is the same
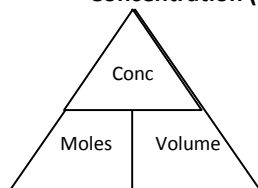
        masses of reagents,

        Moles = Mass / Molar mass

        volumes of gases,
          1 mole of gas under standard conditions occupies 24dm^3
        concentrations of solutions,
          Concentration (ppm) = (Mass of component/ Mass of solution) x 100,000

        Moles = Concentration / Volume

        percentage composition,
          % Composition of solids = (Molecular mass of one component/ total molecular mass) x 100
          % by volume= (Volume of one component/ total volume) x 100
        percentage yield
          Atom economy (%) = Mass of atoms in desired product / Mass of atoms in reactants
        balanced chemical equations (synoptic);
            There must be the same number of each element on each side of the equation.
            The oxidation states on each side must add up to the same value
      (b) *write and interpret balanced chemical equations (including ionic equations) with state symbols (synoptic);*
   Atomic structure
        (c) *work out the electronic configuration of atoms and ions up to Z = 36 and the outer sub-shell structures of atoms and ions of other elements, in terms of main energy levels, s-, p- and d-atomic orbitals and the elements' positions in the Periodic Table (synoptic);*
   **1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^6 is Krypton. Minus the number of electrons needed, starting with the 4p subshell until there is the correct number of electrons**

Bonding and structure

(d) suggest and explain the properties of substances in terms of their structure and bonding and position of their elements in the Periodic Table;
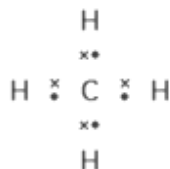
	GIANT LATTICE			COVALENT MOLECULAR	
	Ionic	**Covalent network**	**Metallic**	**Simple molecular**	**Macromolecular**
What substances have this type of structure?	Metals + non-metals	Some elements in group 4 and some of their compounds	Metals	Some non-metal elements and some non-metal/non-metal compounds	Polymers
Examples	Sodium Chloride, Calcium oxide	Diamond, Graphite, Silica	Sodium, Copper, Iron	Carbon Dioxide, Chlorine, Water	Poly(ethane), nylon, DNA
What type of particle does it contain?	Ions	Atoms	Positive ions surrounded by delocalised electrons	Small molecules	Long-chain molecules
How are the particles bonded together?	Strong ionic bonds; attraction between oppositely charged ions	Strong covalent bonds	Strong metallic bonds; attraction of atoms' nuclei for delocalised electrons	Weak intermolecular bonds between molecules; strong covalent bonds between the atoms within each molecule	Weak intermolecular bonds between molecules; strong covalent bonds between the atoms within each molecule

draw and use simple electron 'dot-and-cross' diagrams to show how atoms bond through ionic, covalent and dative covalent bonds and be able to describe a simple model of metallic bonding;
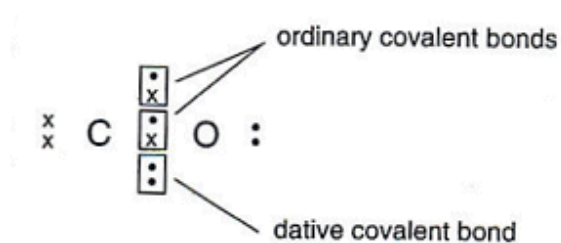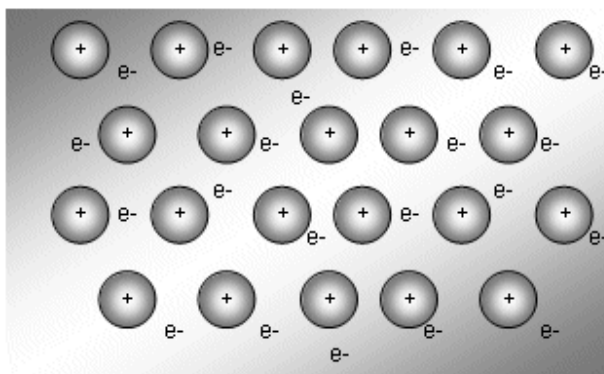
Ionic
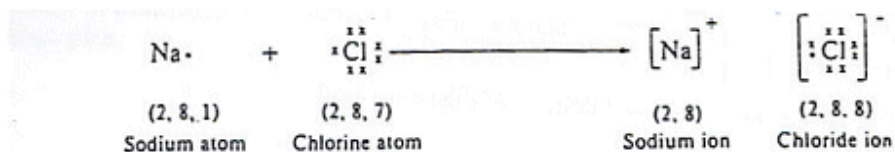
Covalent

Dative

Metallic

recall the typical physical properties (melting point, solubility in water, ability to conduct electricity) characteristic of giant lattice (metallic, ionic, covalent network) and simple molecular structure types (synoptic);

TYPICAL PROPERTIES					
	GIANT LATTICE			COVALENT MOLECULAR	
	Ionic	Covalent network	Metallic	Simple molecular	Macromolecular
Melting and boiling points	High	Very high	Generally high (except mercury)	Low	Moderate (often decompose on heating)
Hardness	Hard but brittle	Very hard (if 3D)	Hard but malleable	Soft	Variable; many are soft, but often flexible
Electrical conductivity	Conducts when molten or dissolved in water	Does not normally conduct (except graphite)	Conducts when solid or liquid	Do not conduct	Do not normally conduct
Solubility in water	Often soluble	Insoluble	Insoluble (but some react)	Usually insoluble, unless molecules contain groups which can hydrogen bond with water	Usually insoluble
Solubility in non-polar substances	Generally insoluble	Insoluble	Insoluble	Usually soluble	Sometimes soluble

(e) describe the shapes of molecules and ions with up to six electron pairs (any combination of bonding and lone pairs), draw 'dot-and-cross' diagrams, and explain these shapes in terms of electron repulsion theory (synoptic);

Groups of electrons will arrange themselves to be as far away from each other as possible in the space
Bond angles of 109°
4 groups of electrons
Tetrahedral
4 bonding pairs
Pyramidal
3 bonding pairs, 1 lone pair
Bent
2 bonding pairs, two lone pairs
Bond angles of 120°
3 groups of electrons
Planar triangular
3 bonding pairs
2 bonding pairs, 1 double bond
Bond angles of 180°
Two groups of electrons
Linear
2 bonding pairs
Triple bond, 1 bonding pair
2 double bonds

Chemistry by Design

Rates of reaction

(f) describe and explain the effect of temperature, pressure and catalysts on the rate of a reaction (synoptic);

Increasing the temperature increases the rate of reaction, because not only are there more collisions, because the molecules have more kinetic energy, but more of the collisions are successful, because the molecules have the required activation enthalpy for the reaction to occur.

Decreasing temperature does the opposite

Increasing the pressure increases the rate of reaction because the molecules are closer together, so there are more collisions

Decreasing the pressure does the opposite

A catalyst provides an alternative pathway for the reaction with a lower activation enthalpy.

Equilibrium

(g) describe and explain the way in which changes of temperature and pressure and addition of catalysts affect the magnitude of the equilibrium constant and the position of equilibrium (latter synoptic);

The only thing that affects the equilibrium constant is temperature

	Exothermic reaction	Endothermic reaction
Temperature increases	Value of K_c decreases	Value of K_c increases
Temperature decreases	Value of K_c increases	Value of K_c decreases

Temperature moves the position of equilibrium towards the endothermic reaction

Pressure moves the position of equilibrium towards the side with fewer molecules

The addition of a catalyst does not affect equilibrium

(h) use principles of equilibrium and rates of reaction to suggest and explain the most economical operating conditions for an industrial process;

For industrial processes, the rate of reaction is very important- ideally the most amount of product possible is desired. Increasing the rate of reaction is done by increasing pressure and temperature. However, in equilibrium reactions, increasing the temperature favours the endothermic reaction, and increasing the pressure favours the side with the least molecules, which may be the reactants, rather than the products. Therefore, there must be a compromise, with enough temperature and pressure to make enough of the products, but not too much of the reactants.

(i) write an expression for the equilibrium constant, Kc, for a given homogeneous reaction;

In the reaction aA+bB ⇌ cC + dD

$$K_c= \ [C]^c \ [D]^d \ / \ [A]^a \ [B]^b$$

(j) calculate one of the values in an equilibrium constant equation, given the others;

Redox

(k) calculate oxidation states and explain and write equations and half-equations for redox reactions (synoptic)

including those involved in the interconversion of the following compounds in the nitrogen cycle:

nitrogen gas,

N_2

nitrate(V) ion,

NO_3^-

nitrate(III) ion,

NO_2^+

ammonium ion,

NH_4^+

oxides of nitrogen;

Dinitrogen (I) oxide

N_2O

Nitrogen (II) oxide

NO

Nitrogen (IV) oxide

NO_2

define oxidation and reduction in terms of loss and gain of electrons;

use systematic nomenclature to name and interpret the names of inorganic compounds [ie copper(II) sulfide, lead(II) nitrate(V), potassium manganate(VII), not complex ions];

Inorganic chemistry and the Periodic Table

(l) recall the following aspects of nitrogen chemistry:

structure and bonding in:

nitrogen gas,

Triple bond

ammonia

N attached by covanlent bonds to 3 Hs. Lone pair

the ammonium ion,

As ammonia, but with a dative bond to the fourth hydrogen

the appearance and names of the oxides of nitrogen,

N_2O,

Dinitrogen (I) oxide (Nitrous oxide)
Straight molecule

NO,

Nitrogen (II) oxide (nitrogen monoxide)
Straight molecule

NO_2;

Nitrogen (IV) oxide (Nitrogen dioxide)
Bent, symmetrical molecule

(m) calculate from given data the percentage yield and the atom economy of an industrial process and suggest the effect of the process on the environment;

Higher % yield and atom economy mean that less energy can be used, and fewer reactants need to be purchased. Less energy use reduced greenhouse gas emissions

(n) discuss given examples of industrial processes in terms of: costs of raw materials, energy costs, costs associated with plant, co-products and by-products, principles of green chemistry;

The costs want to be kept as low as possible to decrease outgoings and increase profit.

The production of co-products and by-products reduce the atom economy, but if they have a use then they can be sold

The principles of green chemistry are:

Minimise waste
Reduce energy consumption
Reduce feedstock consumption

(o) discuss the benefits and risks associated with given industrial processes in terms of:

benefits to society of the product(s),

hazards involved with the raw materials:

reactants,
products and by-products,
explosions,
acidic gases,
flammable gases,
toxic emissions;

(p) discuss the facts and ethics associated with the ways in which chemists are involved in developments to improve food production, including:

(i) providing extra nutrients,

(ii) controlling soil pH,

(iii) controlling pests.

Pesticides can increase crop yields by killing pests, but they need to be biodegrable, otherwise they will accumulate in the food chain and cause harm to the top predator

GM crops can be developed to give crops with desirable characteristics, but some people have objections to scientists altering genes, and the effects of GM crop on health are unknown

Chemistry by Design

(CD) Colour by Design

    Bonding and structure

      (a) <u>*explain the term electronegativity:*</u>

The degree to which an atom of an element attracts electrons

<u>*recall qualitatively the electronegativity trends in the Periodic Table;*</u>

More electronegative towards the top right

<u>*use relative electronegativity values to predict bond polarity in a covalent bond;*</u>

The electrons in a bond will be nearer to the more electronegative atom, meaning that it will be δ-, and the less electronegative atom will be δ+

<u>*decide whether a molecule is polar or nonpolar from its shape and the polarity of its bonds;*</u>

In tetrachloromethane, there are four dipoles, but because the chlorine atoms are arranged symmetrically, there is no overall dipole.

<u>*explain, give examples of and recognise in given examples the following types of intermolecular bonds:*</u>

    instantaneous dipole–induced dipole bonds (including dependence on branching and chain length of organic molecules),

Very weak. often between molecules which don't usually have a dipole. They are continuously breaking and reforming

    permanent dipole–permanent dipole bonds,

In bonds between atoms with different electronegativities. The δ+ atom from one molecule is attached to the δ- atom from the other molecule and a bond forms. These are stronger than instantaneous dipole-induced dipole

    hydrogen bonds (synoptic);

Occurs between a Hydrogen atom attached to either an Oxygen, Nitrogen or Flourine molecule, and the lone pair on another Oxygen, Nitrogen or Flourine molecule. Very strong types of permanent dipole-permanent dipole bonds

(b) suggest and explain in terms of intermolecular bonds, ionic attractions and covalent bonding, how some dyes attach themselves to fibres;

Direct dyes attach to cotton via hydrogen bonds

Acid dyes attach to protein fibres, e.g. silk, via ionic bonds

Other dyes attach to fabrics using a mordant- this forms a complex, linking fibre and dye together

Fibre-reactive dyes form strong covalent bonds with cotton fabrics

(c) describe and explain the structure of a dye molecule in terms of the chromophore and:

The chromophore is two benzene rings attached by -N=N-

(i) functional groups that modify the chromophore,

-NH$_2$ groups have lone pairs of electrons that can interact with the chromophores to produce colour

(ii) functional groups that affect the solubility of the dye,

-OH groups can hydrogen bond with water

(iii) functional groups that allow the dye to bond to fibres;

-SO$_3^-$ groups on a dye molecule can interact with NH$_3^+$ groups on a protein chain

    Organic functional groups

(d) recall ***that fats and oils consist mainly of mixed esters of propane-1,2,3-triol with varying degrees of unsaturation;***

(e)

(i) recognise arenes and their derivatives (aromatic compounds),

Arenes usually contain a benzene ring

(ii) describe the delocalisation of electrons in these compounds,

The p-electron on each carbon atom overlaps with those on both sides of it. This produces a system of pi bonds which are spread out over the whole carbon ring. Because the electrons are no longer held between two carbon atoms, but spread over the whole ring, they are said to be delocalised

(iii) explain how delocalisation accounts for their characteristic properties [limited to undergoing substitution (often slowly) rather than addition reactions];

The benzene ring is electron rich, so attracted electrophiles. The delocalisation makes the ring very stable, so, so maintain the stability, substitution, rather than addition, occurs. The characteristic reaction with benzene is electrophilic substitution

*(f) understand that **our knowledge of science progresses by the development of increasingly refined models to explain concepts and observations and that the nature of scientific knowledge is often tentative**;*

*understand that **various models have been proposed to explain the bonding in aromatic compounds** and discuss how various representations of benzene account for its properties and molecular shape;*

A representation of benzene contains three double bonds. This structure would decolourise bromine water, so it cannot be correct as benzene does not.

Organic reactions

(g) describe and explain the following electrophilic substitution reactions of arenes, naming the benzene derivatives formed:

(i) halogenation of the ring,

Benzene reacts far less readily with the halogens, due to its additional stability, so a halogen carrier catalyst must be used.
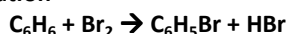
Chlorination

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$
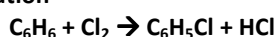
Room temperature

Anhydrous $AlCl_3$ catalyst

Forms chlorobenzene

Bromination

$$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$$

Room temperature

Iron (III) bromide or iron filling catalyst

Forms bromobenzene

As the halogen molecule approaches the benzene ring, the delocalised electrons repel the electrons in the halogen-halogen bond, so the halogen molecule becomes polarised. The presence of the catalyst helps the polarisation of the halogen

(ii) nitration,

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$
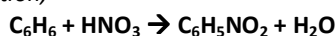
(Conc H_2SO_4 catalyst, 50-55°C)

HNO_3 is not an electrophile. It reacts with the Sulfuric acid in the first step of the reaction to form the positive NO_2^+, which then goes on to react with benzene to form nitrobenzene

(iii) sulfonation,

Concentrated sulfuric acid reacts with benzene when heated under reflux for several hours to produce Benzene sulfonic acid. The electrophile is SO_3

(iv) Friedel–Crafts alkylation and acylation (including use of ionic liquids);

Alkylation

Benzene reacts with halogenoalkanes under reflux in the presence of anhydrous aluminium chloride to give alkyl benzenes. The catalyst polarises the molecule as before.

Acylation

As above, but benzene reacts with acyl chlorides to give ketones

Ionic liquids are green solvents that can act as combined solvent/catalyst systems. They have many properties which make them suitable for potential solvents for synthesis

Ionic salts with melting points of under 300°C, often under room temperature

They are liquids over a wide temperature range

Show very good dissolution properties for most organic and inorganic compounds

Usually have high thermal stability up to 200°C

Non-flammable

Not expensive

Easy to prepare

(h) describe and explain the formation of diazonium compounds and coupling reactions that these undergo to form azo dyes;

Nitrous acid (HNO_2) is produced by reacting sodium nitrate with dilute HCl.

Phenlyamine then reacts with nitrous acid at a temperature below 5°C to produce benzene diazonium chloride. This is a benzene ring attached to a positive nitrogen, which has a triple bond with another nitrogen molecule. The negative chlorine is attracted to the positive nitrogen

The diazonium ion then acts as a weak electrophile and will react with another aromatic compound, such as phenylamine or phenol under alkaline conditions (to make the ring more negative) in a coupling reaction to give an azo dye.

Modern analytical techniques

(i) explain the origins of colour in transition metal complexes in terms of the splitting of the d orbitals by the ligands and transitions between the resulting electronic energy levels (details of how the d electrons split in a particular complex are not required);

The 3d subshell can accommodate 10 electrons in 5 orbitals which, in an isolated ion, will all have the same energy. They are <u>degenerate</u>. Once complexes are formed, however, the orbitals are no longer degenerate. Two orbitals become of higher energy that the other three, known as <u>d-orbital splitting</u>. If a transition metal complex has at least one electron in a lower 3d orbital, and at least one space in an upper 3d orbital, an electron can be promoted from a lower to a higher energy orbital. The coloured light with energy equal to that of the energy difference between the two sets of orbitals will be absorbed, and all other colours will be transmitted.

(j) explain the origins of colour (and UV absorption) in organic molecules in terms of:

(i) transitions between electronic energy levels,

As with inorganic molecules, the transition of electrons between energy levels causes the absorbance of some colour and the transmittance of the complementary colour

(ii) the relationship between the extent of delocalisation in the chromophore and the energy absorbed;

The more delocalised a system is, the less energy the electrons need to become excited. The energy is available when the molecule absorbs UV light

(k) describe and explain the general principles of gas–liquid chromatography:

(i) sample injected into inert carrier gas stream,

(ii) column consisting of high boiling liquid on porous support,

(iii) detection of the emerging compounds (sometimes involving mass spectroscopy),

(iv) distinguishing compounds by their retention times;

Smaller molecules move through the column faster than larger molecules

(l) understand the techniques used to identify the materials used in a painting, including:

(i) gas–liquid chromatography,

The area under a peak corresponds to the amount of that component in a mixture. So if the peak is high, there is a lot of that component present, and if it is low, there is very little

(ii) atomic emission spectroscopy,

Seen when a chemical burns with a coloured flame. The spectrum shows the emissions of energy by electrons, after they absorb a photon of energy and are promoted to higher energy levels, and then drop back to the lower energy levels, emitting energy

The energy emitted by each of the atoms has a definite frequency related to the difference in energy levels

The lines on the emission spectrum correspond to the emission of energy by the electrons

(iii) visible spectroscopy (reflection and absorption),

UV is either shone through a solution and the wavelengths absorbed are measured, osrshone on the surface of solids and any reflected light is analysed.

The wavelengths that aren't absorbed are reflected, and this is that colour that the compound appears

and explain and predict given results from these techniques.

(O) The Oceans

   Bonding and structure

   Candidates should be able to:

   (a) explain the hydrogen bonding in water and explain the unusual physical properties of water that arise from this:

   (i) anomalous boiling point among hydrides of Group 6,

It takes a lot of energy to break the hydrogen bonds between water molecules

   (ii) specific heating capacity,

As above

   (iii) enthalpy change of vaporisation,

As above

   (iv) density change on melting;

Ice is less dense than liquid water. This is because ice has a very open hydrogen bonded structure. As the temperature rises about 273K, the water molecules have more kinetic energy, and some of the hydrogen bonds break, disrupting the lattice structure and allowing the molecules to come closer together and the density to increase. A maximum density is reach at 277K

   (b) explain the factors (including intermolecular bonds and ion–dipole forces) determining the relative solubility of a solute in aqueous and non-aqueous solvents and explain the hydration of ions;

The bonds within the solute have to be strong enough to overcome the hydrogen bonds in water. Non-polar substances have instantaneous dipole-induced dipole bonds, which are weaker than hydrogen bonds, so they don't dissolve. Ionic bonds are stronger than hydrogen bonds, so salt, for example, dissolves in water.

Like dissolves like, so non-polar substances (e.g. candle wax) dissolve in non-polar solvents (e.g. hexane), and polar solids (e.g. salt) dissolve in polar solvents (e.g. water).

Like also mixes with like. A pair of polar liquids will mix and be miscible, but a polar liquid and a non-polar liquid (e.g. water and hexane) will be immiscible.

A pair of non-polar liquids, such as hexane and octane, will mix completely because they both have instantaneous dipole-induced dipole bonds, and when they are mixed these forces extend throughout the mixture

Molecules such as low molecular mass alcohols and carboxylic acids will also dissolve in, or be miscible with, water, as they have polar –OH groups which can hydrogen bond with the –OH groups in water.

   Energetics

   (c) For the following terms: enthalpy change of solution, lattice enthalpy, enthalpy change of solvation (hydration) of ions:

   (i) explain and use these terms,

Enthalpy change of Solution

The enthalpy change when 1 mole of the compound dissolves in a stated amount of water (under standard conditions)

Lattice enthalpy

The enthalpy change when 1 mole of an ionic compound is formed from its gaseous ions under standard conditions. Always negative. Is a measure of ionic bond strength

Enthalpy change of solvation

The enthalpy change when 1 mole of the gaseous ions dissolve in water (under standard conditions) to produce a solution of 1moldm^{-3}

(ii) describe the solution of an ionic solid in terms of an enthalpy cycle involving these terms,
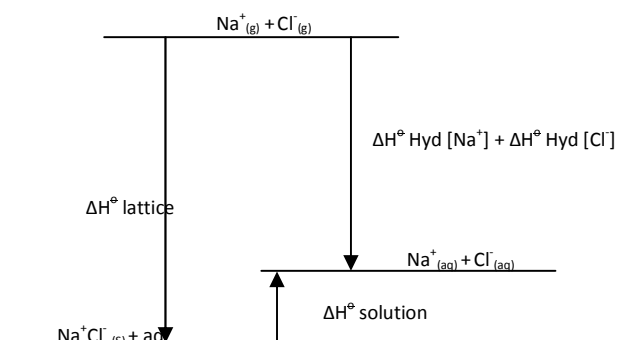
(iii) use these enthalpy cycles to perform calculations;

Hess' law states that the enthalpy change for a reaction is the same, no matter how many steps occur in that reaction. This means that any route can be taken to calculate individual parts of the enthalpy changes.

(d) explain entropy changes in a qualitative manner, interpreting entropy as a measure of the number of ways that molecules and their associated energy quanta can be arranged (part synoptic);

Entropy is a measure of disorder. The more ways the particles can be arranged, the higher the entropy. The entropy of gases is higher than liquids, a mixture higher than the unmixed constituents, and the entropy of solids is lowest of all

(e)

(i) recall the expressions:

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$$
$$\Delta S_{surr} = -\Delta H/T$$

(ii) be able to perform calculations using these expressions,

The units of entropy are $Jmol^{-1}K^{-1}$. This means that ΔH must be converted to J before the ΔS_{surr} can be calculated.

(iii) explain the tendency for a reaction to occur in terms of the sign of ΔS_{tot};

When ΔS_{tot} is positive, the reaction is spontaneous

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

$$\Delta S^{\ominus}_{sys} = \Sigma \Delta S^{\ominus}_{Products} - \Sigma \Delta S^{\ominus}_{Reactants}$$
$$\therefore \Delta S_{tot} = (\Sigma \Delta S^{\ominus}_{Products} - \Sigma \Delta S^{\ominus}_{Reactants}) + (-\Delta H/T)$$
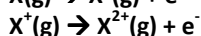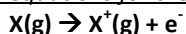
Inorganic chemistry and the Periodic Table

(g)

(i)   recall the meaning of the term ionisation enthalpy,

The energy needed to remove one electron from each of one mole of isolated gaseous ions of an element

(ii) write equations for the successive ionisations of an element,

X(g) → X⁺(g) + e⁻
X⁺(g) → X²⁺(g) + e⁻

and interpret periodic and group trends in the properties of elements in terms of ionisation enthalpy (synoptic);

Ionisation enthalpies for group 0 elements are the highest because they have a full outer shell and are unreactive.

Ionisation enthalpies for group 1 elements are the lowest because they have only one outer shell electron

The ionisation enthalpy increases across a period because the nuclear charge increases, so it takes more energy to remove an electron

The ionisation enthalpy decreases down a group. This is because the outermost electron is further from the nucleus, and the filled electron shells shield the charged nucleus from the outermost electrons

(h) recall and explain the relationship between the position of an element in the Periodic Table and the charge on its ion;

Elements on the left of the periodic table must lose electrons to have a full outer shell, so they are positively charged. Elements on the right of the periodic table must gain electrons to have a full outer shell, so they are negatively charged. Group 0 elements are uncharged and Group 4 elements can be positive or negative

(i) recall the names and formulae of

NO_3^-,

Nitrate ion

SO_4^{2-},

Sulfate ion

CO_3^{2-},

Carbonate ion

OH^-,

Hydroxide ion

NH_4^+,

Ammonium ion

HCO_3^-;

Bicarbonate

write formulae for compounds formed between these ions and other given anions and cations (synoptic);

The oxidation states must add up to the same number on each side, and there must be the same number of each molecule on each side of an equation

Equilibria

(j) describe acids in terms of the Brønsted–Lowry theory as proton donors and bases as proton acceptors (synoptic)and explain and use the terms conjugate acid and conjugate base;

Conjugate acid

When basic ion acts as an acid. The base accepts a proton from the acid, and it's conjugate acid can then donate the proton
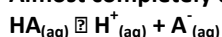
Conjugate base

When an acid ion acts as a base. The acid donates a proton to and acid, and then the conjugate base can accept the proton again

$$NH_{3(aq)} + H_2O\ (l) \rightleftharpoons NH_4^+{}_{(aq)} + OH^-$$

Base   Acid   Conjugate Conjugate
**   Acid   Base**
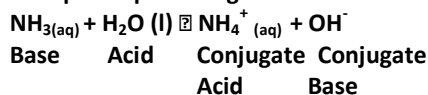
(k) explain and use the terms strong acid, strong base, writing equations for their ionisation in water;

Strong acid

Almost completely dissociates in water

$$HA_{(aq)} \rightleftharpoons H^+{}_{(aq)} + A^-{}_{(aq)}$$

(l) explain and use the terms

weak acid (writing equations for their ionisation in water),

Only partially dissociates in water

$$K_a = [H]^2 / [HA]$$

acidity constant ('dissociation constant') Ka,

Value of the equilibrium constant for an acid's dissociation into ions

$$K_a = [H^+]\ [A^-]/[HA]$$

pKa;

Used for weak acids. The smaller the value of pK_a, the stronger the acid

$$pK_a = -\log K_a$$

(m) explain and use the term pH and use given data to calculate the pH of:

pH =-log[H$^+_{(aq)}$]

(i) strong acids,

pH =-log[H$^+_{(aq)}$]

(ii) strong bases, using Kw (value will be given),

pH=-log(K$_w$ /[OH$^-$])

(iii) weak acids (including calculating any of the terms pH, Ka and concentration from any two others, being aware of the approximations made in using a simple equation);

K$_a$= [H$^+_{(aq)}$]^2/ [HA]

pH=-log(K$_a$)

∴ pH= -log (√(K$_a$ x [HA$_{(aq)}$]))

Assuming that:

[H$^+$] = [A$^-$]

Equilibrium [acid] = initial [acid]

(n) for buffer solutions based on solutions of weak acids and their salts:

(i) explain the meaning of the term buffer,

A buffer solution is one which will resist changes in pH due to the addition of small amounts of acid or alkali

(ii) explain how buffers work (including in everyday applications),

In the example of a buffer made from Ethanoic acid and sodium ethanoate there are two equilibriums

1. **CH$_3$COOH ⇌ CH$_3$COO$^-$ + H$^+$**
   CH$_3$COO$^-$Na$^+$ ⇌ CH$_3$COO$^-$ + Na$^+$
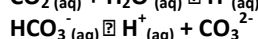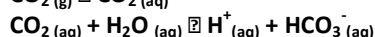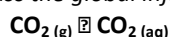2. **H$_2$O ⇌ H$^+$ + OH$^-$**

When more hydrogen ions are added to the system, in the form of adding an acid, this disrupts equilibrium 1. They combine with ethanoate ions to form more Ethanoic acid molecules- the equilibrium has shifted to the left. This removes nearly all of the H$^+$ ions from the solution and almost restores the original pH.

When a base is added, this disturbs equilibrium 2. The extra OH$^-$ ions combine with H$^+$ ions to form H$_2$). This reduces the hydrogen ion concentration, so equilibrium 1 moves to the right, and the Ethanoic acid molecules ionise to restore the equilibrium

(iii) carry out buffer solution calculations;

[H$^+$] = K$_a$ x ([acid] / [salt])

(o) discuss the global influence of the dissolving of carbon dioxide in water,

CO$_2$ $_{(g)}$ ⇌ CO$_2$ $_{(aq)}$

CO$_2$ $_{(aq)}$ + H$_2$O $_{(aq)}$ ⇌ H$^+_{(aq)}$ + HCO$_3^-$ $_{(aq)}$

HCO$_3^-$ $_{(aq)}$ ⇌ H$^+_{(aq)}$ + CO$_3^{2-}$

So, the more carbon dioxide in the sea, the more acidic the sea is

discuss and explain the benefits and risks associated with various approaches to reducing atmospheric CO$_2$ levels including:

more economical use of fuels,

the use of alternative fuels (including hydrogen),

capture and storage of CO$_2$

and increased photosynthesis.

Chemistry by Design
(MD) Medicines by Design
    Bonding and structure
        (a) describe and explain the structure and action of a given pharmacologically active material in terms of:
            (i) the pharmacophore and groups that modify it,
                The pharmacophore is the part of the natural molecule which produces a biological response.
                Different group can illicit different responses as they interact differently with the receptor sites
            (ii) its interaction with receptor sites,
                Phamacophores are complementary to receptor sites in the body.
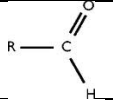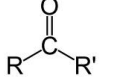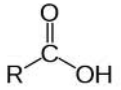   *(iii) the ways that species interact in three dimensions (size, shape, bond formation, orientation);*
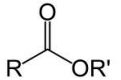   **They have a specific three dimensional structure which allows the pharmacophore to bind to**
                the receptor site at several point to produce a response.
    Organic functional groups
        (b) recall and use systematic nomenclature for naming and interpreting names of compounds met earlier in the specification (AS and A2) (synoptic);
            See below
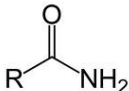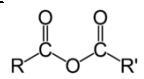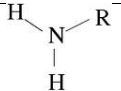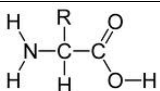   *(c) recognise and draw structures for individual functional groups mentioned elsewhere in the specification (AS and A2) within a polyfunctional molecule (synoptic); hence make predictions about its properties;*
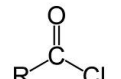
Name	General Formula	Functional Group	Nomenclature
Alkane	C_nH_{2n+2}		-ane
Alkene	C_nH_{2n}	C=C	-ene
Primary alcohol	$C_nH_{2n+1}OH$	CH_2OH	-ol
Secondary alcohol	$C_nH_{2n+1}OH$	R-CHOH	-ol
Tertiary alcohol	$C_nH_{2n+1}OH$	R-CR'OH	-ol
Halogenoalkane	$C_nH_{2n+1}X$ (X is halogen)	-X	Bromo- Chloro- -ene Floro-
Aldehyde	$C_nH_{2n+1}O$		-al
Ketone	$C_nH_{2n+1}O$		-one
Carboxylic Acid	R-COOH		-oic acid
Ester	R-COO-R'		Alcohol –yl Acid -oate
Acyl Chloride	R-COCl		-yl chloride
Amide	$R-CONH_2$		-Amide
Acid Anhydride	R-COOCOR'		-oic anhydride
Amine	$R-NH_2$		-amine
Nitrile	R-CN	$R-C\equiv N$	-Nitrile
Amino acid	$HOOCCH(R)NH_2$		Amino- -oic acid

Organic reactions

(d) <u>recall organic reactions and reaction conditions mentioned elsewhere in the specification</u> *(AS and A2) (synoptic);*
use these with any further given reactions, to suggest and explain synthetic routes for preparing organic
compounds including simple examples of retrosynthesis;

See below

(e) <u>use the following terms to classify organic reactions:</u>

<u>addition,</u>

Atoms or groups join to two atoms joined by a multiple bond. The product is a single molecule

<u>condensation,</u>

Two molecules combine to form a bigger molecule, and a smaller molecule is eliminated

<u>elimination,</u>

Two groups or atoms on neighbouring carbon atoms are removed, leaving a multiple bond between the two carbon atoms

<u>substitution,</u>

A group is substituted for another one, usually a nucleophile

<u>oxidation,</u>

Either combination with oxygen, a reaction in which an atom, ion or molecule loses electrons, or a reaction where the overall oxidation number of an element increases

<u>reduction,</u>

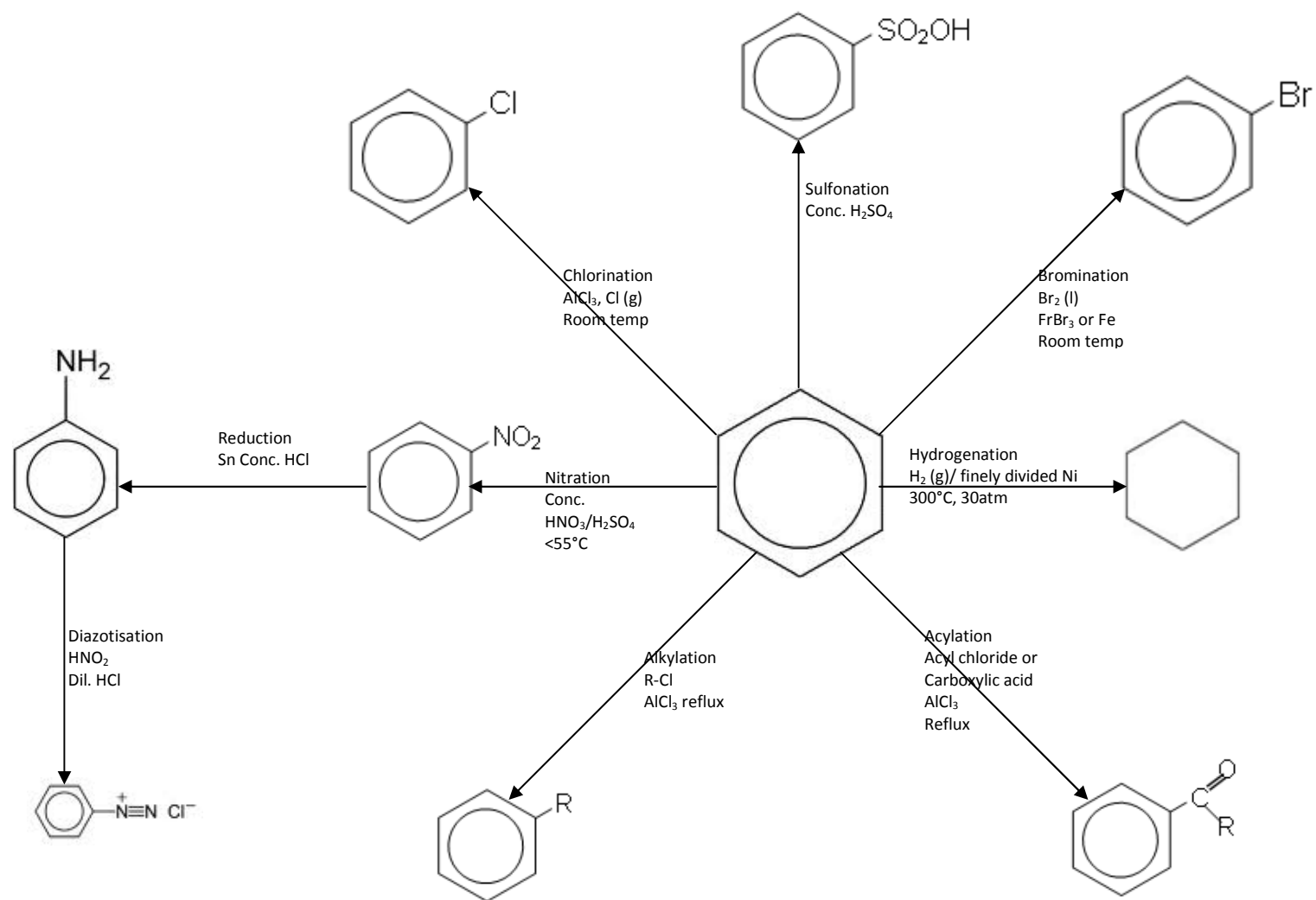**Either the removal or oxygen from, or the addition of oxygen to a compound, a reaction where an atom, ion or molecule gains electrons, or a reaction where the overall oxidation number of an element decreases**

<u>hydrolysis (synoptic);</u>

The reaction of water with a substance, resulting in the formation of a new element-oxygen bond

ALKANE

NITRILE

Ni, 150°C, 5atm or Pt, room temp and pressure

H_2

Radical substitution

Br_2 UV light

Nucleophilic substitution

KCN

ALKENE

Electrophilic addition
HBr
Room temp

HALOGENOALKANE

Nucleophilic substitution

Heat in a sealed tube

AMINE

Acyl chloride
Acylation

High temp and pressure

Addition polymerisation

Hot c. H_2SO_4 or Al_2O_3
Dehydration

Steam
300°C, 60atm
H_3PO_4 or c. H_2SO_4
then water
Electrophilic addition

Nucleophilic substitution

H_2O
or
reflux

Nucleophilic substitution

C. HBr or HCl
Reflux

POLY(ALKENE)

PRIMARY ALCOHOL

ACID ANHYDRIDE

SECONDARY AMIDE

$K_2Cr_2O_7/H_2SO_4$
Distil
Oxidation

Carboxylic acid
Conc. H_2SO_4
Reflux
Esterification

Acyl chloride anhydrous
Acylation

Alcohol
Acylation

Amine
Room temp.

Acylation

CYANOHYDRIN

HCN

ALDEHYDE

Nucleophilic addition

ESTER

Alcohol
Acylation

ACYL CHLORIDE

NaCN
cold
Nucleophilic addition

$K_2Cr_2O_7/H_2SO_4$
Reflux
Oxidation

Alcohol
Conc. H_2SO_4
Esterification
Condensation

Reflux
$H^+_{(aq)}$ or $OH^-_{(aq)}$
Hydrolysis

Conc.
Ammonia
Room temp

Acylation

KETONE

CARBOXYLIC ACID

Reflux
$H^+_{(aq)}$ or $OH^-_{(aq)}$
Hydrolysis

PRIMARY AMIDE

$NaBH_4$
Reduction

$K_2Cr_2O_7/H_2SO_4$
Distil
Oxidation

Reflux
$H^+_{(aq)}$ or $OH^-_{(aq)}$

SECONDARY ALCOHOL

Acylation

SO₂OH

Cl

Br

Sulfonation
Conc. H₂SO₄

Chlorination
AlCl₃, Cl (g)
Room temp

Bromination
Br₂ (l)
FrBr₃ or Fe
Room temp

NH₂

Reduction
Sn Conc. HCl

NO₂

Hydrogenation
H₂ (g)/ finely divided Ni
300°C, 30atm

Nitration
Conc.
HNO₃/H₂SO₄
<55°C

Diazotisation
HNO₂
Dil. HCl

Alkylation
R-Cl
AlCl₃ reflux

Acylation
Acyl chloride or
Carboxylic acid
AlCl₃
Reflux

N≡N Cl⁻

R

C
O
R

Reaction mechanisms

(f) use and explain the following terms:

radical,

A chemical species with an unpaired electron

electrophile,

Negative species which accepts an electron pair in order to bond to the nucleophile

nucleophile,

An atom or molecule that is electron-rich and is attracted to centres of positive charge.

*carbocation,*

An ion containing a positively charged carbon

saturated,

An organic structure which contains no Carbon-Carbon double (or sometimes triple) bonds

unsaturated (synoptic);

an organic molecule which contains Carbon-Carbon double (or sometimes triple) bonds

(g) use the following terms to classify organic reactions according to their reaction mechanisms:

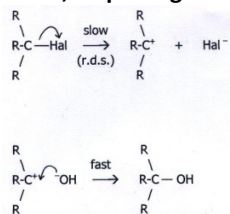*(i) radical substitution*,*

Substitution takes place as a result of an attack by a radical
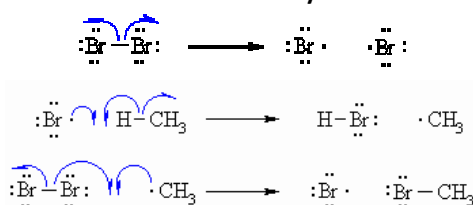
(ii) electrophilic addition,*

An electrophile attacks a pi bond resulting in the formation of two new covalent bonds
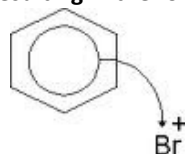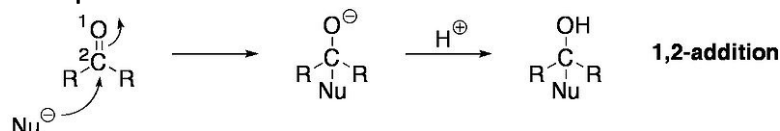

(iii) nucleophilic substitution,*

A nucleophile reacts with a compound, displacing another compound

(iv) electrophilic substitution,

Substitution that takes place as a result of an attack by an electrophile

(v) nucleophilic addition,*

A pi bond is removed by the formation of two new covalent bonds by the addition of a nucleophile

*be able to describe and explain the mechanisms of these processes in terms of bond polarisations and 'curly arrows' (synoptic);
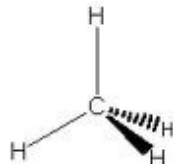
Isomerism

(h) draw and interpret skeletal, structural and full structural formulae as representations of molecules;
use the concept of repulsion of areas of electron density to deduce the bond angles in organic molecules (including double bonds) (no treatment of small deviation of angle due to lone pair repulsion required);

See previous

relate molecular shape to structural formulae and use wedges and dotted lines to represent 3D shape;

recognise where E/Z isomerism occurs, explaining it in terms of **lack of free rotation about C=C bonds when there are two different groups on each carbon;**
draw and interpret diagrams to represent E/Z isomers for alkenes which have the same groups on both sides of the double bond (**E – opposite sides of bond; Z – same side of bond***); in such molecules, describe* **'E' as 'trans' and 'Z' as 'cis'** *and extend this cis-trans nomenclature to other, more complicated, alkenes (knowledge of Cahn–Ingold–Prelog priority rules will not be required);*
explain and use the term chiral as applied to a molecule;

A molecule that has a non-superimposable mirror image

explain that **enantiomers are non-superimposable mirror image molecules** *(synoptic);*

Applications

(i) describe and explain the role of chemists in:

(i) designing and making new compounds for use as pharmaceuticals,

Scientists start by developing a biological understanding of the disease or condition that they want to cure
They then find a 'lead compound' which provides a lead
Sometimes the idea for the lead compound comes from research into chemical processes in the body, other times it is based on traditional remedies

(ii) ethical testing,

A detailed protocol is developed before trialling can start
Sets out the purpose of the research
Explains who the trial will be conducted and the results analysed
All human participants in clinical trials confirm their willingness to participate after being informed of the aspects of the trial that are relevant to their decision to participate
Scientists are trying to reduce the use of animals in drug testing, so chemists and biochemists may work on using alternative techniques, such as using isolated tissues and cell cultures

(iii) the application of computer modelling techniques in the design of medicines;

Computer modelling can be used to produce a 3D map which allows chemists to view the possible ways in which a molecule can bind to a receptor site and this shortens the time needed to design new drugs

Modern analytical techniques

(j) describe and explain how proton nuclear magnetic resonance spectra (NMR) can be used for the elucidation of molecular structure (including splitting patterns up to quartets – using the 'n + 1' rule; further explanation of splitting not required);

Hydrogen nuclei absorb energy and this changes the direction of their spin. The amount of energy this takes depends on the environment of the hydrogen ions.

> **E.g. in ethanol there is three environments $-CH_3$, $-CH_2$ and $-OH$. The hydrogens in each of these groups will come into resonance at different times**

Generally, the more the electrons are attracted away from the proton (i.e. near an electronegative molecule) the higher (further left) the chemical shift value

The size of the peak is directly proportional to the number of resonating protons

The peaks are split according to the number of protons on adjacent carbon atoms, with n adjacent protons giving a peak split into (n+1) parts. The relative heights of the peaks are as follows

> **Singlet- 1**
> **Doublet- 1:1**
> **Triplet- 1:2:1**
> **Quadruplet- 1:3:3:1**

(k) explain how a combination of spectroscopic techniques [MS, IR (synoptic) and NMR] can be used to elucidate the structure of organic molecules.

Mass spectroscopy shows the molecular mass of the compound, as well as any ions

IR spectroscopy can be used, in conjunction with a data sheet, to show any major bonds in the molecule

NMR shows the number of proton environments, if they are near electronegative molecules, if they are near other protons, and if so, how many