RAFFLES INSTITUTION
YEAR 6 H2 CHEMISTRY 2016
Term 3 Revision –
Physical Chemistry Summary Notes

Topics

(A) Stoichiometry & Gases

(B) Atomic Structure

(C) Chemical Bonding

(D) Chemical Energetics

(E) Reaction Kinetics

(F) Chemical Equilibrium

(G) Acid–Base Equilibria

(H) Solubility Equilibria

(I) Electrochemistry

A1.   ATOMS, MOLECULES & STOICHIOMETRY and REDOX EQUATIONS

1) Know the definitions of the following terms!
 (i) Relative Atomic Mass based on the ^{12}C scale.
 (ii) Relative Isotopic Mass based on the ^{12}C scale.
 (iii) Relative Molecular Mass based on the ^{12}C scale.
 (iv) Relative Formula Mass based on the ^{12}C scale.
 (v) Mole (in terms of Avogadro constant)
 (vi) Empirical and Molecular formulae

2) Be able to calculate the relative atomic mass (A_r) of an element given the relative abundances of its isotopes.

$$\text{Average } A_r = \frac{\text{abundance x } A_r \text{ of isotope 1 + abundance x } A_r \text{ of isotope 2 + ...}}{\text{Total abundance}}$$

3) Calculate empirical and molecular formulae using combustion data or composition by mass.
 For combustion of hydrocarbons: $C_xH_y + (x + y/4)O_2 \longrightarrow xCO_2 + (y/2)H_2O$
 Be careful when approximating after obtaining the ratio of moles.

E.g.	1.2	:	1	=	6 : 5
1.25	:	1	=	5 : 4
1.33	:	1	=	4 : 3
1.5	:	1	=	3 : 2
1.67	:	1	=	5 : 3
1.75	:	1	=	7 : 4

In general, multiply by suitable factor to get nearest whole number and DO NOT SIMPLY ROUND UP/DOWN.

Ending no.	.2	.25	.33	.5	.67	.75
Multiply by	5	4	3	2	3	4

4) Write and /or construct balanced equations and perform calculations using mole ratios.
 Identify the limiting reagent!
 1 mole of gas at r.t.p. and s.t.p. occupies 24 dm^3 and 22.4 dm^3 respectively.
 No. of moles = mass/molar mass
 Concentration in mol dm^{-3} = no. of moles/volume of solution in dm^3
 Concentration in g dm^{-3} = mass/volume of solution in dm^3

5) 1 mole of a species contains 6.02×10^{23} particles of that species.
 1 mole of NH_3 contains 1 mole of N atoms and 3 moles of H atoms, 6.02×10^{23} N atoms and $3 \times 6.02 \times 10^{23}$ H atoms.

6) Be able to write balanced redox equations. (even if you've never seen the species before)
 To write a balanced **half-equation**:
 Step 1: Balance the **element** other than O and H.
 Step 2: Balance **O** using H_2O.
 Step 3: Balance **H** using H^+.
 Step 4: Add equal no. of moles of OH on both sides of half equation so as to completely neutralize all H$^+$. **(Step 4 is used only if in alkali/neutral conditions)**
 Step 5: Balance charges using **electrons**.

7) Be familiar with the following terminology:

Sulfur trioxide	SO_3	Nitrogen dioxide	NO_2
Sulfate/ sulfate (VI)	SO_4^{2-}	Nitrate/ nitrate (V)	NO_3^-
Sulfuric acid	H_2SO_4	Nitric acid	HNO_3
Sulfur dioxide	SO_2	Nitrogen oxide	NO
Sulfite/ sulfate (IV)	SO_3^{2-}	Nitrite/ nitrite (III)	NO_2^-
Sulfurous acid	H_2SO_3	Nitrous acid	HNO_2
Chromate (VI)	CrO_4^{2-}	Dichromate (VI)	$Cr_2O_7^{2-}$
Manganate (VII)	MnO_4^-	Manganese (II)	Mn^{2+}

8) Be familiar with these various common titrations.

(a) MnO_4^- with Fe^{2+} (purple MnO_4^- is reduced to colourless Mn^{2+}, Fe^{2+} is oxidized to Fe^{3+}.) $[MnO_4^- : Fe^{2+} = 1: 5]$

(b) MnO_4^- with H_2O_2 (purple MnO_4^- is reduced to colourless Mn^{2+}, H_2O_2 is oxidized to O_2.) $[MnO_4^- : H_2O_2 = 2: 5]$

Important note: In this case the half equation for H_2O_2 is $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ and NOT $H_2O_2 \rightarrow H_2O + O_2$, which shows the disproportionation of H_2O_2 as it is oxidized to O_2 as well as reduced to H_2O.

I $Cr_2O_7^{2-}$ with Fe^{2+} (orange $Cr_2O_7^{2-}$ is reduced to green Cr^{3+}, Fe^{2+} is oxidized to Fe^{3+}.) $[Cr_2O_7^{2-} : Fe^{2+} = 1:6]$

(d) A common 2-step reaction involving iodine.

(i) KI (a source of I^-), is oxidized by excess reagent to get I_2

(ii) I_2 formed from (i) is then titrated with $S_2O_3^{2-}$, where I_2 is reduced to I^- and $S_2O_3^{2-}$ is oxidized to $S_4O_6^{2-}$. $[I_2 : S_2O_3^{2-} = 1: 2]$

(e) $C_2O_4^{2-}$ as a reducing agent. How to write the equation for $C_2O_4^{2-}$ being oxidized? Product: CO_2. Use steps in point 7 above to write the half equation.

A2.   THE GASEOUS STATE

1) Be able to state basic assumptions of the kinetic theory of ideal gases, namely
   i)   Gases consist of <u>small particles of negligible volumes</u>.
   ii) The gaseous particles exert <u>no attractive forces</u> on each other.

2) Know the conditions necessary for a gas to approach ideality (i.e. low pressure and high temperature). This is because
   (a) at low pressure, the *volume of gas particles* of a real gas becomes negligible as compared to the volume occupied by the gas.
   (b) at high temperature, the gas particles are able to overcome most of the intermolecular forces of attraction.
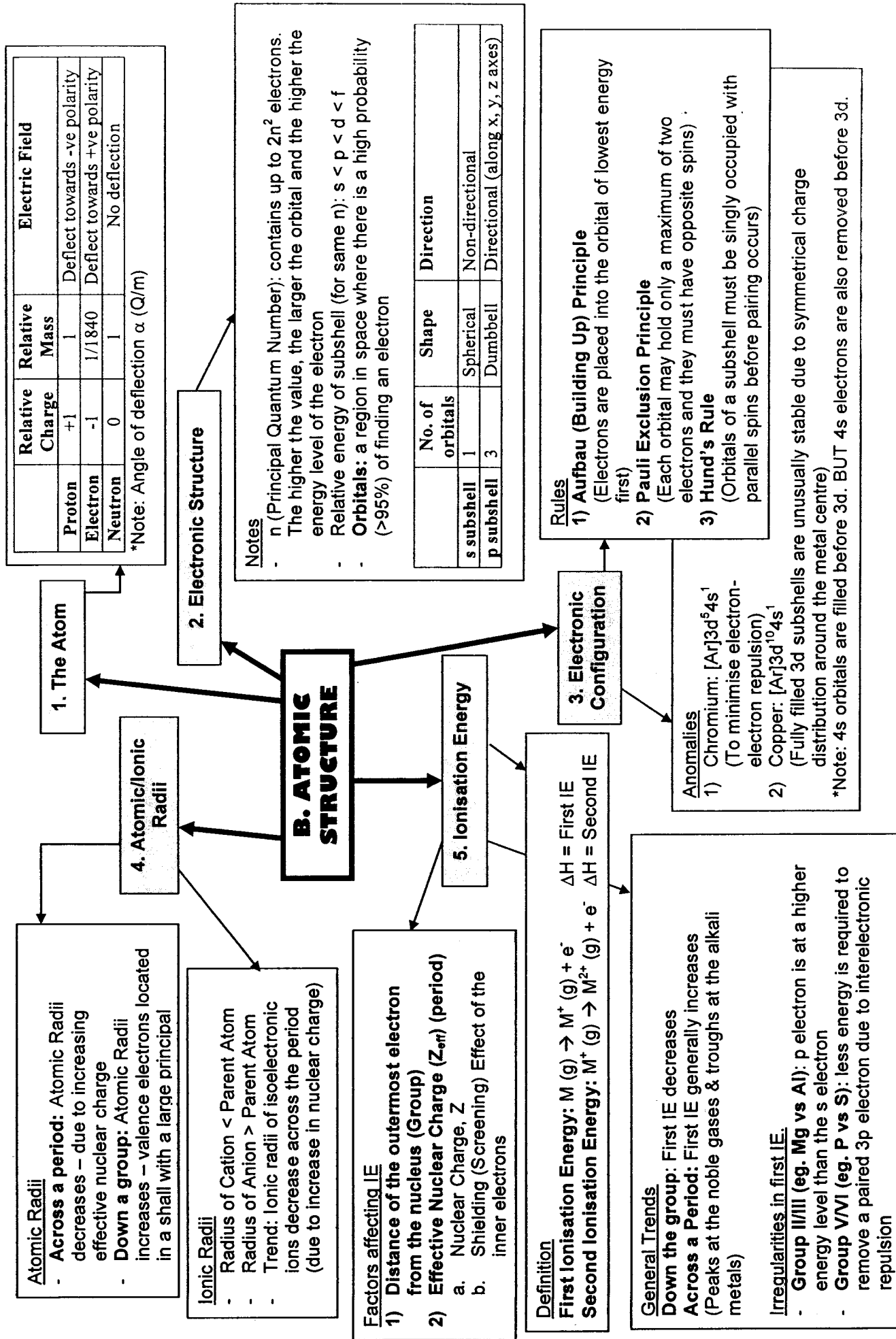
   Note that at these conditions of low pressure and high temperature, the real gas is able to behave close to the assumptions of an ideal gas (in point 1 above). Conversely, at high pressures and low temperatures, a real gas will deviate most greatly from ideality.

3) Gases with larger molecules (and thus electron cloud size) and stronger intermolecular attractive forces tend to deviate more from ideal gas behaviour.

4) State & use the general gas equation $pV = nRT$ in calculations, including the determination of M_r.
   Units are very important!!!!

Value of R	$8.31\ J\ K^{-1}\ mol^{-1}$	$0.082\ atm^{-1}\ mol^{-1}\ K^{-1}$
Pressure (p)	Pa or Nm^{-2} (1 atm = 1.013×10^5 Pa)	atm
Volume (V)	m^3 (1 cm^3 = $1 \times 10^{-6}\ m^3$; 1 dm^3 = $1 \times 10^{-3}\ m^3$)	dm^3
Temperature (T)	K (25° = 25 + 273 K)	K

B. ATOMIC STRUCTURE

1. The Atom

	Relative Charge	Relative Mass	Electric Field
Proton	+1	1	Deflect towards -ve polarity
Electron	-1	1/1840	Deflect towards +ve polarity
Neutron	0	1	No deflection

*Note: Angle of deflection α (Q/m)

2. Electronic Structure

Notes
- n (Principal Quantum Number): contains up to $2n^2$ electrons. The higher the value, the larger the orbital and the higher the energy level of the electron
- Relative energy of subshell (for same n): s < p < d < f
- Orbitals: a region in space where there is a high probability (>95%) of finding an electron

	No. of orbitals	Shape	Direction
s subshell	1	Spherical	Non-directional
p subshell	3	Dumbbell	Directional (along x, y, z axes)

3. Electronic Configuration

Rules
1) **Aufbau (Building Up) Principle** (Electrons are placed into the orbital of lowest energy first)
2) **Pauli Exclusion Principle** (Each orbital may hold only a maximum of two electrons and they must have opposite spins)
3) **Hund's Rule** (Orbitals of a subshell must be singly occupied with parallel spins before pairing occurs)

Anomalies
1) Chromium: $[Ar]3d^54s^1$ (To minimise electron-electron repulsion)
2) Copper: $[Ar]3d^{10}4s^1$ (Fully filled 3d subshells are unusually stable due to symmetrical charge distribution around the metal centre)

*Note: 4s orbitals are filled before 3d. BUT 4s electrons are also removed before 3d.

4. Atomic/Ionic Radii

Atomic Radii
- **Across a period:** Atomic Radii decreases – due to increasing effective nuclear charge
- **Down a group:** Atomic Radii increases – valence electrons located in a shall with a large principal

Ionic Radii
- Radius of Cation < Parent Atom
- Radius of Anion > Parent Atom
- Trend: Ionic radii of isoelectronic ions decrease across the period (due to increase in nuclear charge)

5. Ionisation Energy

Factors affecting IE
1) Distance of the outermost electron from the nucleus (Group)
2) Effective Nuclear Charge (Z_{eff}) (period)
   a. Nuclear Charge, Z
   b. Shielding (Screening) Effect of the inner electrons

Definition
First Ionisation Energy: M (g) $\rightarrow$ M$^+$ (g) + e$^-$ ΔH = First IE
Second Ionisation Energy: M$^+$ (g) $\rightarrow$ M^{2+} (g) + e$^-$ ΔH = Second IE

General Trends
Down the group: First IE decreases
Across a Period: First IE generally increases (Peaks at the noble gases & troughs at the alkali metals)

Irregularities in first IE
- **Group II/III (eg. Mg vs Al):** p electron is at a higher energy level than the s electron
- **Group V/VI (eg. P vs S):** less energy is required to remove a paired 3p electron due to interelectronic repulsion

1) When drawing **dot-cross diagrams**, note that

- All atoms in a molecule "want" to fulfil the OCTET rule – but this is NOT compulsory. E.g. BF_3 has only 6 electrons in the valence shell of B, and that is why it readily accepts a lone pair from NH_3 to form $BF_3.NH_3$ via coordinate (dative) bonding.
- General steps when drawing dot-cross diagrams for simple covalent molecules:
  (i) Satisfy all side atoms first. E.g. Cl is a side atom and needs 1 more electron to be shared with it. Hence the central atom forms a single bond with it.
  (ii) Account for all the electrons of the central atom. e.g. XeF_4: after forming 4 single bonds with F, I must draw 4 more electrons for Xe since it is from group 8 and should have 8 electrons around its valence shell.
  (iii) Check that, if the element is in period 1 or 2, that the central atom does not have more than a total of 8 shared electrons around it.
- Elements in period 3 (period containing P) and beyond can expand their octet and thus accommodate more than 8 valence electrons. When it is possible to expand its octet, the central atom would form double bonds with a side atom that needs to share 2 electrons (e.g. O) rather than coordinate (dative) bonds even if it has to accommodate more than 8 valence electrons. This is because double bonds are stronger than a single dative bond.
- For compounds XO_n, draw all the X-O bonds as double bonds if X is from period 3 and beyond. Otherwise, dative bonds may be drawn. For anions XO_n^{m-}, each of the negative charge is accommodated on m number of oxygen atoms, and these are singly bonded to the central atom. n-m number of oxygen atoms are then drawn as double bonds (if X is from period 3 and beyond), otherwise dative bonds may be drawn.
- For ionic bonding, the correct number of each ion should be indicated.
Remember to indicate the overall charge of any ions outside the square bracket.

2) Predicting shapes of molecules/ions.

Be clear about the **VSEPR** Theory- Regions of electron density arrange themselves as far apart as possible so as to minimize repulsion.
Find out the electron pair geometry based on total number of electron regions, and then determine the shape based on number of bond pairs and lone pairs. Note: the shape of the molecule and how the bond and lone pairs are arranged determine whether a molecule is polar. Symmetrically arranged => zero overall dipole moment =>non-polar

Factors affecting bond angles:

i) l.p.-l.p. repulsion > l.p.-b.p. repulsion > b.p.-b.p. repulsion
    Lone pairs exert greater repulsion as they are closer to the nuclei. E.g. 4 bond pairs: bond angle 109.5°, 3 bond pairs 1 lone pair: bond angle 107°; 2 bond pairs 2 lone pairs: bond angle 105°

ii) Electronegativity
    Atoms which are more electronegative than the central atom will draw the shared electron density further from the nucleus, resulting in a weaker repulsive force exerted by the bonding pair. Bond angle will be smaller.

iii) Size of the attached atoms
    A larger attached atom will have a larger electron cloud which will exert a repulsive force and prevent the attached atoms from coming too close together. Bond angle will be larger.

3) When explaining m.p. or b.p.

Structure	Giant Metallic	Giant Ionic	Giant Covalent	Simple Covalent (weak forces of interaction between molecules although they have **very strong covalent bonds within the molecule**. It is the intermolecular interactions that are being overcome during melting /boiling, not the covalent bonds)		
Type of bonds being overcome when melting and/or boiling	Strong forces of attraction between positive metallic cations and sea of delocalised electrons	Strong ionic bonds between oppositely charged ions	Strong covalent bonds between all atoms	Instantaneous dipole-induced dipole interactions (id-id) - for non-polar molecules, and essentially present in all molecules	Permanent dipole-permanent dipole interactions (pd-pd) - for polar molecules	Hydrogen bonds - molecules with H DIRECTLY bonded to F/O/N.
Remarks	When comparing m.p. of metals, the smaller the cation and the larger the number of delocalised electrons, the stronger the bond. i.e. strength of metallic bond α q⁺/r⁺	Bond strength determined by lattice energy.	Bond strength dependent on effectiveness of overlap. e.g. melting pt of C (diamond) higher than m.p. of Si.	NOTE: Hydrogen bonds > pd-pd > id-id **ONLY** if the molecules have similar electron cloud sizes. E.g. compounds with id-id interactions will have higher m.p./b.p. than compounds with pd-pd interactions if the electron cloud size of the molecule with id-id interactions is larger than that of the molecule with pd-pd interactions.		
m.p	Generally high			Generally low		

4) Ionic bond –
a) The strength of the ionic bond is indicated by the lattice energy of the ionic compound:

$$|\text{L.E.}| \ \alpha \ |(q_+ \ q_-) / (r_+ + r_-)|$$

From the relationship above, we can deduce that high charges and small inter-ionic distances will lead to a **more exothermic** L.E. and hence, a stronger ionic bond.

b) Ionic bonds are non-directional, i.e. there is no preferred orientation of the ions.

c) Ionic compounds usually:
i) Possess high m.p. and b.p. because all the ionic bonds need to be weakened / broken during a change of state.
ii) Are soluble in a polar solvent (e.g. water) but insoluble in a non-polar solvent (e.g. hexane). For the ionic compound to be soluble, the energy **released** from solvation (forming ion-solvent bonds) **must** be comparable with the energy **absorbed** for breaking up the lattice (α L.E.).
iii) Conduct electricity in the **molten** or **aqueous** states.

5) The covalent bond –

Usually formed between non-metallic atoms. Some **common exceptions: $FeCl_3$, $AlCl_3$, $BeCl_2$ are covalent** even though formed between metallic and non-metallic atoms. This covalent character is a result of the high charge density of the cation and polarisability of the anion. (AlF_3 is ionic due to the small anion which is not easily polarised).

The strength of the covalent bond is dependent on its bond energy (the energy required to break one mole of a particular bond in one mole of a gaseous substance) –

i) The higher the bond order, the stronger the covalent bond, e.g. C=C > C-C.
ii) **The smaller the orbitals involved, the less diffused the orbitals and the more effective the overlap and the stronger the covalent bond.** (most significant reason to account for strength of covalent bonds)
iii) The greater the difference in the electronegativity between the bonding atoms, the more polar the bond, the stronger the covalent bond (in general) because the resultant dipoles may reinforce the bond through added electrostatic attraction between the atoms.

6) Be able to describe and draw σ- and π-bonds.
σ-bonds are a result of head-on overlap, π-bonds are a result of side-on overlap. A single bond is made up of 1 σ-bond, while a double bond is made up of 1 σ-bond and 1 π-bond and a triple bond is made up of 1 σ-bond and 2 π-bonds.

7) Possible ways of forming a dimer
- through dative (coordinate bonding) e.g. Al_2Cl_6
- through hydrogen bonds e.g. $(HCOOH)_2$

8) Be able to account for the lower density of ice compared to water w.r.t. hydrogen bonding.

D. CHEMICAL ENERGETICS

You have to know **ALL** the definitions VERY WELL!!!!!

❏ Standard Enthalpy Change of *Reaction*, $\Delta H_r^{\ominus}$:

> The enthalpy change when molar quantities of reactants as <u>specified by the chemical equation</u> react to form products at 1 atmosphere pressure and 298 K temperature.

❏ Standard Enthalpy Change of *Formation*, $\Delta H_f^{\ominus}$:

> The enthalpy change when 1 mole of a pure compound in a specified state is formed from its <u>constituent elements</u> in their standard states, at 298 K and 1 atmosphere pressure.

❏ Standard Enthalpy Change of *Combustion*, $\Delta H_c^{\ominus}$:

> The heat energy *evolved* (ie exothermic) when 1 mole of the substance is completely burned in oxygen at 298 K and 1 atmosphere pressure.

❏ Standard Enthalpy Change of *Hydration*, $\Delta H_{hyd}^{\ominus}$:

> The heat energy *evolved* when 1 mole of the gaseous ion is dissolved in a large amount of water at 298 K and 1 atm.

❏ Standard Enthalpy Change of *Solution*, $\Delta H_{soln}^{\ominus}$:

> The heat change when 1 mole of solute is completely dissolved in enough solvent so that no further heat change takes place on adding more solvent (infinite dilution) at 298 K and 1 atm.

❏ Standard Enthalpy Change of *Neutralisation*, $\Delta H_{neut}^{\ominus}$:

> The heat change when an amount of acid neutralises a base to <u>form 1 mole of water</u> (in dilute aqueous solution) at 298 K and 1 atmosphere pressure.

❏ Standard Enthalpy Change of *Atomisation*, $\Delta H_{at}^{\ominus}$:

> The enthalpy change when 1 mole of atoms in the <u>gas phase</u> is formed from the <u>element</u> in the defined physical state under standard conditions.

❏ *Bond energy*

> The **bond energy** of a X-Y bond is the <u>average energy</u> absorbed when 1 mole of X-Y <u>bonds are broken in gaseous state</u>. The stronger the bond, the higher the bond energy.

❏ *Bond dissociation energy:*

> **Bond Dissociation Energy** of a X-Y bond is the energy required to break 1 mole of that particular X-Y bond in a particular compound in gaseous state.

❏ *Lattice Energy*

> **Lattice energy** is the enthalpy change when one mole of a pure solid ionic compound is formed from its constituent gaseous ions under standard conditions.

❑ *First Ionisation Energy:*

First ionisation energy is the energy required to remove 1 mole of electrons from one mole of gaseous atoms in the ground state to form one mole of gaseous unipositive charged cations.

❑ *First Electron Affinity:*

First electron affinity is the energy change when 1 mole of electrons are added to one mole of atoms in the gaseous state to form one mole of gaseous X^- ions.

❑ *Second Electron Affinity:*

Second electron affinity is the energy change when 1 mole of electrons are added to one mole of gaseous X^- ions to form one mole of gaseous X^{2-} ions.

Summary of problem solving approach for Chemical Energetics

1. $q = mc\Delta T$
2. Shortcuts: Use of formulae/ bond energies.
3. Hess' Cycle
4. Energy Level Diagram

1. **Step 1**: Using $q = mc\Delta T$ to find heat energy released/ absorbed.
   It is easy to identify when to use this equation. The question will mention that there is a rise in temperature in the solution, and immediately this equation should come to mind.
   However, many students do not understand what the symbols represent.

(c)-Specific heat capacity of water	(m) mass
quantity of heat required to raise the temperature of 1g of water by 1 K. The heat energy released or absorbed is used to raise or lower the temperature of water. The mass is thus **mass of SOLUTION ONLY**.	the mass that is computed must be the **mass of SOLUTION ONLY** (aqueous solutions consist mainly of water) and does not include mass of any solids.

Step 2: Finding enthalpy change of reaction using $\Delta H = q/n$
Note: n = no. of moles of <u>limiting reagent</u>

2. Use of formulae/ bond energies
   (short-cut; actually can be derived using Hess' cycle).

   (a) $\Delta H_{rxn} = \Sigma \Delta H_f(\text{products}) - \Sigma \Delta H_f(\text{reactants})$
   Qn: When do we use this equation?
   Ans: When data given is in the form of ΔH_f.

   Example: *(Pls verify your answers with your friends.)*
   The yellow gas chlorine dioxide, ClO_2, has been used for many years as a flour-improving agent in bread-making. It can be made in the laboratory by the following reaction:
   $2AgClO_3(s) + Cl_2(g) \rightarrow 2AgCl(s) + 2ClO_2(g) + O_2(g)\Delta H$, zero.
   Calculate and comment on, the value of $\Delta H_f^\ominus(ClO_2)$, given the following data:
   $\Delta H_f^\ominus(AgClO_3) = -25 kJmol^{-1}$
   $\Delta H_f^\ominus (AgCl) = -127 kJmol^{-1}$ [3] N92/I/4(a)
   Important Note: ΔH_f of elements in their standard states = 0
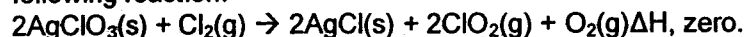
(b)   Using bond energy data from *Data Booklet*.
Qn: When do we use this method?
Ans: When the question asks you to use bond energy values from the *Data Booklet*.

Step 1: Draw out the FULL structural formulae of all species in the chemical equation. This is so that you can see all the bonds and not miss out on any bonds.

Step 2: Refer to *Data Booklet* for bond energy values. Write them in a table form.

Bonds broken (+ve)	Bonds formed (-ve)

Step 3: Remember that energy is required to break bonds and energy is released when bonds are formed. Therefore all values in the bonds broken column should be **positive**, while all values in the bonds formed column should be **negative**. To find the overall enthalpy for reaction in question, simply add the summation of the 2 columns together.

Example: *(Pls verify your answers with your friends.)*
Hydrogen is used in large quantities in industry to convert nitrogen into ammonia, for use in fertilizers. One method of manufacturing hydrogen is to pass methane and steam over a heated nickel catalyst.
$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H_1 = + 206 kJmol^{-1}$
(i)   Use the value of ΔH_1 above, and bond energy values from the Data Booklet, to calculate the total bond energy in the carbon monoxide molecule.
(ii)   Suggest why the bond energy you have calculated in (i) is larger than either of the carbon-oxygen bond energies in the *Data Booklet*.
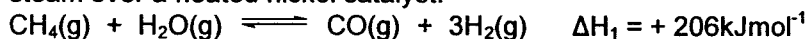
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Note: A very common question asked is why bond energy value differs from that found in the Data Booklet. Reason: Bond energy values in the Data Booklet are <u>average values</u>.

3. Hess' Cycle
Qn: When do we use this method?
Ans: For almost ALL thermochemistry questions except for those which specify that an energy level diagram must be drawn.

A Hess' cycle looks like this:
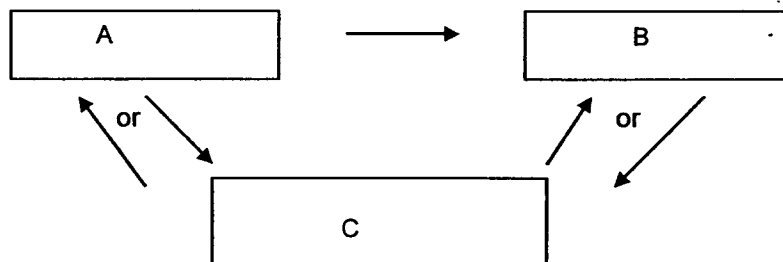
Step 1: Write down the equation for the enthalpy change in question. Reactants at A, products at B.

Step 2: **Decide what should be written for C**. You will decide what C should be depending on the **information that is provided**. If the question provides you with enthalpy of atomization values, for example, there will be atoms at C. If the question gives you enthalpy of combustion values, then you will have the products of the combustion of the species at A and B at C. Species at A, B and C must **all balance** with each other.

Step 3: Draw the arrows. The direction of the arrows will depend on the information given. This requires a thorough knowledge of the different enthalpy definitions. Plug in the values of the different enthalpies next to the arrows.

Step 4: Use your knowledge of vectors to work out the enthalpy change in question.

4. Energy level diagrams
   Qn: When do we use this method?
       Ans: When the question asks explicitly for an energy level diagram.
       Typically used when lattice energy is involved.
       Thorough knowledge of enthalpy definitions needed.
       Relevant data that can be obtained from Data Booklet:
   - 1st ionization energy
   - 2nd ionization energy
   - bond energy

An energy level diagram looks like this, with varying number of steps/ energy levels:
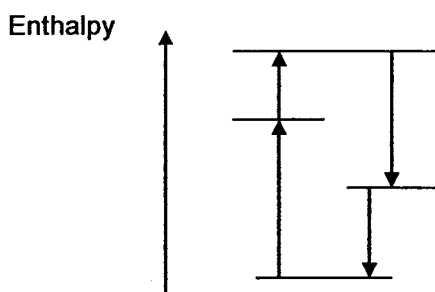
Enthalpy

The cycle must be complete. i.e. forms one full circle.
    (i)   Each step represents one enthalpy change.
    (ii)   An arrow pointing upwards represents an endothermic reaction.
    (iii)   An arrow pointing downwards represents an exothermic reaction.
    (iv)   Labelling of numbers on y-axis not needed, just label each enthalpy change. If there is a 0 labelled on the y-axis, that would represent the **ELEMENTS** at **standard conditions**.

E. Kinetics Summary

1. Know the definitions!

(i)	rate of reaction	The *change in concentration* of a **reactant** *or* **product** with time. i.e. rate at a given time $t = -\frac{d[reactant]}{dt} = \frac{d[product]}{dt}$.
(ii)	rate equation	The rate equation or rate law is a mathematical equation that shows how the rate of reaction is dependent on the concentrations of the reactants; it relates the rate of the reaction to the concentration of reactants raised to the appropriate power. E.g. rate = $k[A]^m[B]^n$
(iii)	order of reaction	① The order of reaction with respect to a reactant is the power to which the concentration of that reactant is raised to in the rate law. ② The overall order of reaction is the sum of the powers to which the concentrations of the reactants are raised to in the rate law.
(iv)	rate constant	The rate constant, k is a **proportionality constant** in the rate equation of the reaction.
(v)	half-life of a reaction	The time required for the concentration of a limiting reactant to decrease to half of its initial concentration.
(vi)	rate-determining step	The *slowest* step in the sequence of steps leading to the formation of the product.
(vii)	activation energy, E_a	The minimum amount of energy that the reactant particles must possess before they can collide successfully to form products
(viii)	catalyst	A substance which **increases the rate** of a chemical reaction without itself undergoing any permanent chemical change. It is **regenerated** at the end of the reaction.

2. Determining orders of reaction and rate equations

a. Observing initial rates data (Direct comparison)

If rate remains constant when concentration is doubled => zero order
If rate doubles when concentration is doubled => 1st order
If rate quadruples when concentration is doubled => 2nd order

(e.g. when concentration of a reactant is doubled while keeping concentration of the other reactants constant, rate doubles => order 1 with respect to the reactant)

b. Mathematical equations (Indices method)

Usually used because (a) is not feasible due to more complicated numbers

e.g. $\frac{\text{initial rate of experiment 2}}{\text{initial rate of experiment 1}} = \frac{k[A]_2^a[B]_2^b}{k[A]_1^a[B]_1^b}$

c.	**Graphical data**

Example: $2H_2O_2 \xrightarrow{OH^-} 2H_2O + O_2$
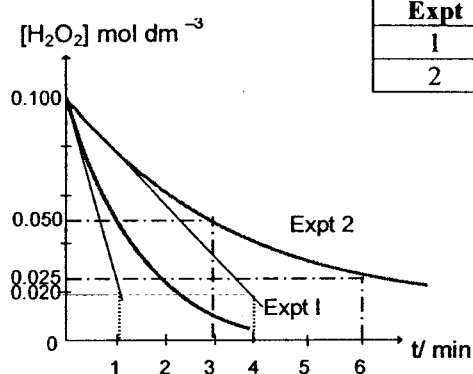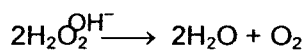
[H_2O_2] mol dm^{-3}

Expt	[H_2O_2] / mol dm^{-3}	Initial [OH$^-$] / moldm^{-3}
1	0.1	0.1
2	0.1	0.05

Solution
- To find order of reaction with respect to H_2O_2, use one of the graphs and find the half life. If half life is constant, order is 1 wrt H_2O_2.
- To find order of reaction with respect to OH$^-$, draw a tangent at t = 0 for both expts and compare the value of the gradient (which represents rate) when [OH$^-$] in expt 2 is half that in expt 1. If grad of curve from expt 2 is half that in expt 1, order wrt OH$^-$ is 1.

3.   Pseudo-order reactions.

Consider a reaction in which rate = k[A][B]
If [A] is essentially constant, then rate = k'[B] where k' = k[A].

(a) This occurs
   (i)   when A is present in large excess such that its concentration hardly changes
   (ii)   if A is a catalyst.

(b) This is a pseudo first order reaction wrt to A. If a graph of [B] against time was plotted,
   (i)   the graph will have a constant half life ($t_{1/2}$)
   (ii) $t_{1/2}$= ln2/k' = ln2/(k[A]). The true rate constant k can be found.

4.   Using rate law to determine mechanism

Verify that a suggested reaction mechanism is consistent with the experimentally observed kinetics. The slow step is the rate-determining step and must contain the correct ratio of reactants in the rate equation.

When predicting the order of reaction from a reaction mechanism, the rate equation should only contain reactants and NOT INTERMEDIATES.

5.   Collision theory

Using microscopic processes to explain the phenomenon of reaction and its rate. Reactions only occur if there are effective collisions, i.e.
(i)   reactant molecules colliding with $E > E_a$ and
(ii)   the correct orientation.

Factors affecting the rate of a reaction:

Concentration / Pressure	:	Higher concentration / pressure increases the frequency of effective collisions.
Temperature (T)	:	At higher T, the fraction of reactant molecules with $E > E_a$ increases. Use Maxwell-Boltzmann Distribution curve to explain.
Presence of catalyst	:	A catalyst provides an alternative reaction pathway of lower E_a and more reactant molecules have energy greater than or equal to E_a, leading to a higher frequency of effective collisions and hence a higher reaction rate. (use Maxwell-Boltzmann Distribution Curve to explain).

6. Catalysis

Two modes of catalysis:
(a) Homogeneous (catalyst and reactants are in the <u>same</u> phase)
(b) Heterogeneous (catalyst and reactants are in <u>different</u> phase)

(a) Heterogeneous catalysis

(i) Important steps in heterogeneous catalysis

Step 1	*Adsorption* of the reactant particles onto the ***active sites*** on the surface of the catalyst. - *Weak bonds form between the reactant particles and the catalyst.* - *Surface concentration of the reactants is increased.*
Step 2	Reaction at the surface. - *The **activation energy** of this process **is lower** than that of the uncatalysed reaction **because the bonds within the reactant particles are weakened by the adsorption effects**, thereby reducing the energy required to disrupt them* - *The reactant particles are brought into **close contact** and are **properly orientated** for reaction*
Step 3	Desorption of the reactants or products from the surface.

(ii) Examples of heterogeneous catalysis

Haber Process
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
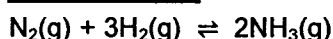
Conditions: 250 atm, 450°C, Fe

Catalytic converter
- As the gases enter, the oxides of nitrogen (NO and NO_2) are reduced to N_2 by the excess CO present, with rhodium acting as the catalyst.

$$2NO + CO \xrightarrow{\text{Rh}} N_2 + CO_2$$
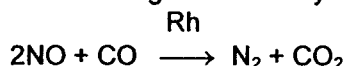
- The CO is also oxidised to CO_2 with platinum and palladium as the catalysts.

$$\frac{1}{2} O_2 + CO \xrightarrow{\text{Pt/Pd}} CO_2$$
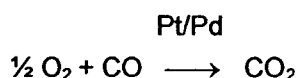
- The unburnt hydrocarbons are oxidised to CO_2 and H_2O with platinum and palladium as the catalysts.

(b)   Homogeneous catalysis

- Reaction catalysed by Fe^{3+}:

  Step 1: $2I^-$ (aq) + $2Fe^{3+}$ (aq) $\longrightarrow$ I_2 (aq) + $2Fe^{2+}$ (aq)

                    catalyst   intermediate

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

            Intermediate   catalyst regenerated
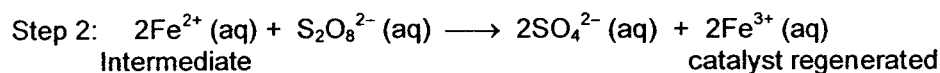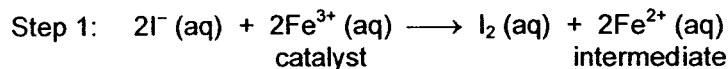
  The catalysed reaction proceeds via a 2-step route. Each step involves a reaction between oppositely charged ions which have a natural tendency to attract each other. This lowers the activation energy and enhances the reaction rate. ($E_{cell} > 0$ for each step of the reaction)

- Enzymes catalyse reactions by providing an alternative reaction pathway with a lower activation energy. To bring this about, the enzyme forms a complex with the substrate or substrates (reactants) of the reaction. Thus a simple picture of the enzyme action is:

  substrate + enzyme $\longrightarrow$ enzyme/substrate complex $\longrightarrow$ enzyme + products

  Once the products of the reaction are formed, they are released and the enzyme is free to form a new complex with more substrate.

F.   Chemical Equilibrium

Reversible Reactions and Dynamic Equilibrium

1.   Irreversible reactions are reactions that take place in <u>one direction</u> almost exclusively.

Eg: Burning of magnesium in air:
$2Mg\ (s) + O_2\ (g) \rightarrow 2MgO\ (s)$

Only the forward reaction takes place.
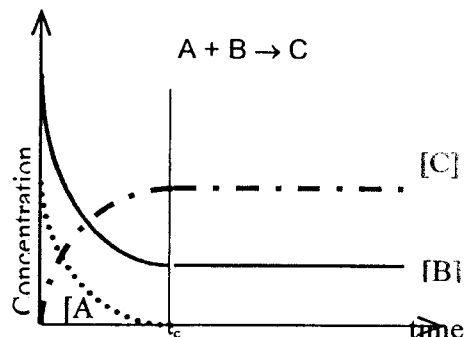
2.   Reversible reactions are reactions that take place in <u>both</u> directions ($\rightleftharpoons$) at comparable rates.

Eg: Rxn of SO_2 with O_2 :
$2\ SO_2\ (g) + O_2\ (g) \rightleftharpoons 2\ SO_3\ (g)$

Both the forward and backward reaction akes place simultaneously.
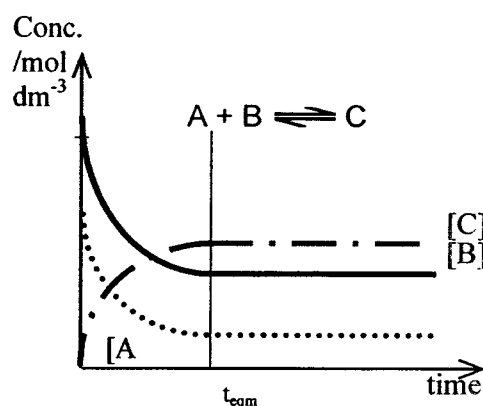
3.   For reversible reactions, the system can reach a stage in which the **rate of forward reaction = rate of backward reaction** so that **no macroscopic changes are observed**. The system is said to be at equilibrium. Since microscopic changes are still occurring, the system is said to be in *dynamic equilibrium*.

4.   Equilibrium is only achieved in a *closed* system. An open system which allows matter to escape or enter cannot reach equilibrium unless there is absolutely <u>no gain or loss</u> of materials from or to the surroundings.

5.   Once equilibrium is reached, the system will remain in this state, until conditions affecting rate of forward/ backward reaction is altered. (eg, temperature, pressure, concentration of reactant/product)

Law of Chemical Equilibrium and Equilibrium Constants

1. **Reaction Quotient** (or mass action expression)
    (a) For a reversible reaction represented by a A + b B $\rightleftharpoons$ c C + d D,

Reaction Quotient, $Q_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

[X] is instantaneous concentration (in mol dm^{-3})of **X** <u>at time t</u>

(b) From time = 0 till time = t_{eqm}, the reaction quotient changes as the concentrations of reactants and products change until equilibrium is reached.

2. Law of Chemical Equilibrium (or law of mass action)

(a) For a reversible reaction represented by $a A + b B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} c C + d D$,

At time = t, Rate of forward reaction, $R_f = k_f [A]_t^a [B]_t^b$

Rate of backward reaction, $R_b = k_b [C]_t^c [D]_t^d$

At equilibrium, $R_f = R_b$

$\Rightarrow k_f [A]^a[B]^b = k_b [C]^c[D]^d$ (subscript 'eqm' is left out for convenience)

Hence, reaction quotient, $Q_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b} = \dfrac{k_f}{k_b} = K_c$, Equilibrium constant

(b) Relationship between, Q_c, K_c and equilibrium

$Q_c < K_c$	$Q_c = K_c$	$Q_c > K_c$
System not at eqm. Forward rxn is favoured and Q_C increases until $Q_c = K_c$.	System at equilibrium	System not at eqm. Backward reaction is favoured and Q_C decreases until $Q_c = K_c$.

(c) Equilibrium constant **is a constant at a fixed temperature**. Hence, **the value of equilibrium constant will not change unless temperature changes**. The effect of temperature on the value of equilibrium constant is shown in the table below:

ΔH of forward reaction	>0 (endothermic)	= 0	<0 (exothermic)
Effect of K_c when temperature ↑	K_c ↑	No change	K_c ↓
Effect of K_c when temperature ↓	K_c ↓	No change	K_c ↑

Types of Equilibrium Constants

Equilibrium Constant	Reactions	Example	Expression & Units
K_c, involving concentrations in mol dm^{-3}	Reactions involving gases or aqueous solutions	$2VO^{2+}$ (aq) + Cu (s) + $4H^+$ (aq) $\rightleftharpoons 2V^{3+}$ (aq) + Cu^{2+} (aq) + $2H_2O$ (l)	$K_c = \dfrac{[V^{3+}(aq)]^2[Cu^{2+}(aq)]}{[VO^{2+}(aq)]^2[H^+(aq)]^4}$
	Reactions involving liquids	CH_3COOH (l) + CH_3OH (l) $\rightleftharpoons CH_3COOCH_3$ (l) + H_2O (l)	$K_c = \dfrac{[CH_3COOCH_3(l)][H_2O(l)]}{[CH_3COOH(l)][CH_3OH(l)]}$
K_p, involving partial pressure	Reactions involving gases	$3H_2$ (g) + N_2 (g) $\rightleftharpoons 2NH_3$ (g)	$K_p = \dfrac{(P_{NH_3})^2}{(P_{H_2})^3 P_{N_2}}$

Some points to take note when writing expressions for Equilibrium Constants

1. In general, for a a reversible reaction represented by $a A + b B \rightleftharpoons c C + d D$,

$K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ or $K_p = \dfrac{P_C^c P_D^d}{P_A^a P_B^b}$ (for gaseous reactions only)

2. Leave out substances whose concentration is a constant (eg solids, immsicible liquids or water in reactions occurring in aqueous solutions) for K_c or whose partial pressure is very low and constant (eg solids or liquids) for K_p.

Relationship between K and equation written

Expression for K is dependent on the equation written:

Equation	Expression for K	Relation to K_1
$3H_2$ (g) + N_2 (g) $\rightleftharpoons$ $2NH_3$ (g)	$K_1 = \dfrac{[NH_3(g)]^2}{[H_2(g)]^3[N_2(g)]}$	--------
$\dfrac{3}{2}H_2$ (g) + $\dfrac{1}{2}N_2$ (g) $\rightleftharpoons$ NH_3 (g)	$K_2 = \dfrac{[NH_3(g)]}{[H_2(g)]^{\frac{3}{2}}[N_2(g)]^{\frac{1}{2}}}$	$K_2 = \sqrt{K_1}$
$2NH_3$ (g) $\rightleftharpoons$ $3H_2$ (g) + N_2 (g)	$K_3 = \dfrac{[H_2(g)]^3[N_2(g)]}{[NH_3(g)]^2}$	$K_3 = (1 / K_1)$
$3H_2$ (g) + N_2 (g) $\rightleftharpoons$ $2NH_3$ (l)	$K_4 = \dfrac{1}{[H_2(g)]^3[N_2(g)]}$	--------

Le Chatelier's Principle and Using it to Predict Shift in Position of Equilibrium

1. Le Chatelier's Principle states that if a system in equilibrium is subjected to a change which disturbs the equilibrium, the system responds in such a way to counteract the effect of the change.
2. Predict and explain the effect of the following changes on the yield of NH_3 for the reaction:

   $3H_2$ (g) + N_2 (g) $\rightleftharpoons$ $2NH_3$ (g), $\Delta H < 0$

No	Change	Effect of yield of NH_3	Reason
1	Adding more N_2	↑	Forward rxn favoured to decrease [N_2].
2	Using more iron catalyst	no change	The Fe catalyst affects the forward and backward reaction to the same extent.
3	Increasing temperature	↓	Backward reaction favoured to remove heat.
4	Higher pressure	↑	Forward rxn favoured as it gives less gaseous molecules so that pressure is decreased.
5	Using a reaction vessel of a larger volume	↓	↑ in volume decreases total concentration. Backward rxn favoured as it gives more gaseous molecules to ↑ total concentration.

Problems on Equilibrium Involving Gases

1. Useful formulae:
   (a) Partial pressure of a gas = mole fraction of gas x total pressure

   $P_A = X_A P_{total}$ where $X_A = \dfrac{\text{no of mol of A}}{\text{total no of mol}} = \dfrac{n_A}{n_{total}}$

   (b) Degree of dissociation of A, $\alpha = \dfrac{\text{amt of A dissociated}}{\text{initial amt of A}}$

(c) For a gaseous mixture made up of gases A and B with mole fraction of X_A and X_B respectively, (Note: $X_B = 1 - X_A$)

Apparent $M_r = X_A \times M_r$ of A $+ X_B \times M_r$ of B

When mass and total number of mol of a gaseous mixture is given, apparent $M_r = \dfrac{mass}{n_{total}}$ (n_{total} is often found using $pV = nRT$ equation)

G. Acid Base Equilibria

(I) Definitions (Know definitions of these terms):

Terms	Definition
Bronsted acid	Proton donor in aq. solution
Bronsted base	Proton acceptor in aq. solution
Strong acid/base	Fully dissociated Note: concentration of acid $\neq$ strength
Weak acid/base	Partially dissociated
pH	$= -\lg[H^+]$
pOH	$= -\lg[OH^-]$
K_w	$= [H^+][OH^-] = 1.0 \times 10^{-14}$ $mol^2 dm^{-6}$ at 298 K
K_a	Acid dissociation constant, indicator of strength of acid. Higher $K_a \rightarrow$ stronger acid. $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ $K_a = \dfrac{[H^+][A^-]}{[HA]} \, mol \, dm^{-3}$
pK_a	$= -\lg K_a$
pK_b	Base dissociation constant, indicator of strength of base. Higher $K_b \rightarrow$ stronger base
pK_b	$= -\lg K_b$
K_w	$= K_a K_b$ applies only for acid-conjugate base pair

(II) Calculations of pH for Different Types of Solutions

Solutions with pH < 7	Solutions with pH > 7
1. **Strong acid**: Calculate pH of a solution of dilute H_2SO_4 with concentration of 0.025 mol dm^{-3}. $[H^+ (aq)] = 2 \times 0.025 = 0.0500$ mol dm^{-3} pH = $-\log [H^+ (aq)] = 1.30$	1. **Strong base**: Calculate pH of a solution of aqueous $Ba(OH)_2$ with concentration of 0.025 mol dm^{-3}. $[OH^- (aq)] = 2 \times 0.025 = 0.0500$ mol dm^{-3} pOH = $-\log [OH^- (aq)] = 1.30$; pH = 14–pOH = 12.7
2. **Weak acid, HA**: Calculate pH of a solution of aq CH_3COOH with concentration of 0.050 mol dm^{-3} given K_a of CH_3COOH is 1.8×10^{-5} mol dm^{-3} Let $[H^+ (aq)]$ at eqm be a mol dm^{-3}. Ignoring H^+ from self-ionisation of water, $[CH_3COO^-(aq)] = a$ mol dm^{-3} $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$	2. **Weak base, B**: Calculate pH of a solution of aq NH_3 with concentration of 0.050 mol dm^{-3} given K_b of NH_3 is 1.74×10^{-5} mol dm^{-3} Let $[OH^- (aq)]$ at eqm be a mol dm^{-3}. Ignoring OH^- from self-ionisation of water, $[NH_4^+ (aq)] = a$ mol dm^{-3} $H_2O(l) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Initial conc^n/ mol dm^{-3}	0.050	–	–		Initial conc^n/ mol dm^{-3}	0.050	–	–
Eqm conc^n/ mol dm^{-3}	0.050–a	a	a		Eqm conc^n/ mol dm^{-3}	0.050–a	a	a

$K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \dfrac{a^2}{0.050-a} \approx \dfrac{a^2}{0.050}$ (since 0.050 >>a) $[H^+ (aq)] = a \approx \sqrt{K_a[HA]_0} = 9.487 \times 10^{-4}$ mol dm^{-3} pH = $-\log (9.487 \times 10^{-4}) = 3.02$	$K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]} = \dfrac{a^2}{0.050-a} \approx \dfrac{a^2}{0.050}$ (since 0.050 >>a) $[OH^- (aq)] = a \approx \sqrt{K_b[B]_0} = 9.327 \times 10^{-4}$ mol dm^{-3} pOH = $-\log (9.327 \times 10^{-4}) = 3.03$; pH = 14–pOH = 10.97

SALT HYDROLYSIS CALCULATIONS

Solutions with pH < 7	Solutions with pH > 7
3. **Salt of weak base, BH^+ (strong conjugate acid)**: Calculate pH of a solution of aq NH_4Cl with concentration of 0.050 mol dm^{-3} given K_b of NH_3 is 1.74×10^{-5} mol dm^{-3} Let $[H^+ (aq)]$ at eqm be a mol dm^{-3}. Ignoring H^+ from self-ionisation of water, $[NH_3 (aq)] = a$ mol dm^{-3} $NH_4^+ (aq) \rightleftharpoons NH_3 (aq) + H^+(aq)$	3. **Salt of weak acid, A^- (strong conjugate base)**: Calculate pH of a solution of aq CH_3COONa with concentration of 0.050 mol dm^{-3} given K_a of CH_3COOH is 1.8×10^{-5} mol dm^{-3} Let $[OH^- (aq)]$ at eqm be a mol dm^{-3}. Ignoring OH^- from self-ionisation of water, $[CH_3COOH (aq)] = a$ mol dm^{-3} $H_2O + CH_3COO^- \rightleftharpoons CH_3COOH + OH^-$

Initial conc^n/ mol dm^{-3}	0.050	–	–		Initial conc^n/ mol dm^{-3}	0.050	–	–
Eqm conc^n/ mol dm^{-3}	0.050–a	a	a		Eqm conc^n/ mol dm^{-3}	0.050–a	a	a

$K_a = \dfrac{K_w}{K_b} = \dfrac{[NH_3][H^+]}{[NH_4^+]} = \dfrac{a^2}{0.050-a} \approx \dfrac{a^2}{0.050}$ (since 0.050 >>a) $[H^+ (aq)] = a \approx \sqrt{\dfrac{K_w}{K_b}[BH^+]_0} = 5.361 \times 10^{-6}$ mol dm^{-3} pH = $-\log (5.361 \times 10^{-6}) = 5.27$	$K_b = \dfrac{K_w}{K_a} = \dfrac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \dfrac{a^2}{0.050-a} \approx \dfrac{a^2}{0.050}$ (since 0.050 >>a) $[OH^- (aq)] = a \approx \sqrt{\dfrac{K_w}{K_a}[A^-]_0} = 5.270 \times 10^{-6}$ mol dm^{-3} pOH = $-\log (5.270 \times 10^{-6}) = 5.28$; pH = 14–pOH = 8.72

BUFFERS CALCULATIONS	
4. **Acid buffer made up of weak acid and its salt, HA and A⁻**: Calculate pH of a mixture made of 20 cm³ of 0.050 mol dm⁻³ aq CH_3COOH and 40 cm³ of 0.030 mol dm⁻³ aq CH_3COONa. (K_a of $CH_3COOH = 1.8 \times 10^{-5}$ mol dm⁻³) After mixing, $[CH_3COOH] = \dfrac{20}{20+40} 0.050 = 0.01667$ mol dm⁻³ $[CH_3COO^-] = \dfrac{40}{20+40} 0.030 = 0.020$ mol dm⁻³ $pH = pK_a + \log \dfrac{[A^-]}{[HA]}$ $= -\log(1.8 \times 10^{-5}) + \log \dfrac{0.020}{0.01667} = 4.82$	4. **Alkaline buffer made of weak base and its salt, B and BH⁺**: Calculate pH of a mixture made of 20 cm³ of 0.050 mol dm⁻³ aq NH_3 and 40 cm³ of 0.030 mol dm⁻³ aq NH_4^+. (K_b of $NH_3 = 1.74 \times 10^{-5}$ mol dm⁻³) After mixing, $[NH_3] = \dfrac{20}{20+40} 0.050 = 0.01667$ mol dm⁻³ $[NH_4^+] = \dfrac{40}{20+40} 0.030 = 0.020$ mol dm⁻³ $pOH = pK_b + \log \dfrac{[BH^+]}{[B]}$ $= -\log(1.74 \times 10^{-5}) + \log \dfrac{0.020}{0.01667} = 4.84$ $pH = 14 - pOH = 9.16$

(III) Explanation of how buffer works using equations:

Acid Buffer: made up of weak acid HA and its salt NaA	Alkaline Buffer: made up of weak base B and its salt (eg BH⁺Cl⁻)
On addition of H⁺: A^- (aq) + H^+ (aq) ⟶ HA(aq) *Single arrow to show removal of H⁺* A^- present reacts with H^+ so that [H⁺] remains approximately constant and pH is maintained. On addition of OH⁻: HA (aq) + OH⁻(aq) ⟶ A^-(aq) + H_2O (l) HA present reacts with OH⁻ so that [OH⁻] remains approximately constant and pH is maintained. Large reservoir of HA and A⁻ present is able to cope with small amount of H⁺ and OH⁻ added.	On addition of H⁺: B (aq) + H^+ (aq) ⟶ BH^+ (aq) B present reacts with H^+ so that [H⁺] remains approximately constant and pH is maintained. On addition of OH⁻: BH^+ (aq) + OH⁻(aq) ⟶ B(aq) + H_2O (l) BH^+ present reacts with OH⁻ so that [OH⁻] remains approximately constant and pH is maintained. Large reservoir of B and BH⁺ present is able to cope with small amount of H⁺ and OH⁻ added.

(IV) Application: Role of H_2CO_3/HCO_3^- in controlling pH of blood

Buffer system in human blood: $H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$

On addition of H⁺: $HCO_3^-(aq) + H^+(aq) \longrightarrow H_2CO_3(aq)$

On addition of OH⁻: $H_2CO_3(aq) + OH^-(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$
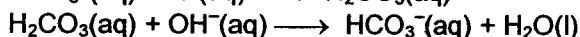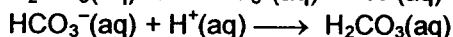
Regions in Titration Curve

Titration Curve of Weak Acid vs Strong Base (WA-SB)	Titration Curve of Weak Base vs Strong Acid (WB-SA)

Region	①	②
Contents	Weak acid, HA	Mixture of HA and A^-
$[H^+]$ or pH	$[H^+] \approx \sqrt{K_a[HA]_0}$	$pH = pK_a + \lg \dfrac{[A^-]}{[HA]}$ $= pK_a + \lg \dfrac{n_{OH^- added}}{n_{HA}{}^\circ - n_{OH^- added}}$ At $\frac{1}{2}V_E$: $pH = pK_a$ (max buffer capacity)
Region	③ (equivalence pt)	④
Contents	Salt of weak acid, A^-	Excess base
$[OH^-]$ or pOH	$[OH^-] \approx \sqrt{\dfrac{K_w}{K_a}[A^-]_0}$	$[OH^-] = \dfrac{\text{amt of xs } OH^-}{Vol}$

Region	①	②
Contents	Weak base, B	Mixture of B & HB^+
$[OH^-]$ or pOH	$[OH^-] \approx \sqrt{K_b[B]_0}$	$pOH = pK_b + \lg \dfrac{[BH^+]}{[B]}$ $= pK_b + \lg \dfrac{n_{H^+ added}}{n_B{}^\circ - n_{H^+ added}}$ At $\frac{1}{2}V_E$: $pH = pK_a = 14 - pK_b$ (max buffer capacity)
Region	③ (equivalence pt)	④
Contents	Salt of weak base, BH^+	Excess acid
$[H^+]$ or pH	$[H^+] \approx \sqrt{\dfrac{K_w}{K_b}[BH^+]_0}$	$[H^+] = \dfrac{\text{amt of xs } H^+}{Vol}$

Note: you should still show clear and proper workings and not just apply these formulae blindly.

(I) K_{sp} and solubility

General Example - A_bB_a made up of A^{a+} & B^{b-}	Specific Example - $Ca_3(PO_4)_2$
1. For a sparingly soluble compound A_bB_a: A_bB_a (s) + aq $\rightleftharpoons$ bA^{a+}(aq) + aB^{b-} (aq); $K_{sp} = [A^{a+}]^b[B^{b-}]^a$	Eg calcium phosphate: $Ca_3(PO_4)_2$ $Ca_3(PO_4)_2$ (s) + aq $\rightleftharpoons$ $3Ca^{2+}$(aq) + $2PO_4^{3-}$ (aq); $K_{sp} = [Ca^{2+} (aq)]^3[PO_4^{3-} (aq)]^2$
2. If solubility of A_bB_a in water is s mol dm^{-3}, $[A^{a+}] = bs$ mol dm^{-3}, $[B^{b-}] = as$ mol dm^{-3}	If solubility of $Ca_3(PO_4)_2$ is 2.6×10^{-6} mol dm^{-3}, $[Ca^{2+} (aq)] = 3 \times 2.6 \times 10^{-6} = 7.8 \times 10^{-6}$ mol dm^{-3} $[PO_4^{3-} (aq)] = 2 \times 2.6 \times 10^{-6} = 5.2 \times 10^{-6}$ mol dm^{-3}
3. If solubility of A_bB_a in water is s mol dm^{-3}, $K_{sp} = [A^{a+}]^b[B^{b-}]^a = (bs)^b(as)^a = b^b a^a s^{(a+b)}$	If solubility of $Ca_3(PO_4)_2$ is 2.6×10^{-6} mol dm^{-3}, $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$ $= (3 \times 2.6 \times 10^{-6})^3(2 \times 2.6 \times 10^{-6})^2$ $= 1.3 \times 10^{-26}$ mol^5 dm^{-15}
4. If solubility product of A_bB_a in water is K_{sp}, then its solubility s = $\sqrt[a+b]{\dfrac{K_{sp}}{b^b a^a}}$	Given K_{sp} of $Ca_3(PO_4)_2 = 1.3 \times 10^{-26}$ mol^5 dm^{-15}, calculate its solubility. Let its solubility be s mol dm^{-3} $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3s)^3(2s)^2 = 108\, s^5$ $s = \sqrt[5]{\dfrac{K_{sp}}{3^3 2^2}} = \sqrt[5]{\dfrac{1.3 \times 10^{-26}}{3^3 2^2}} = 2.61 \times 10^{-6}$ mol dm^{-3}

(II) Ionic Product, K_{sp} and Precipitation

1. Precipitation occurs when ionic product is greater than K_{sp}.

Ionic product = $[M^+(aq)]\,[X^-(aq)]$	Remark	Precipitation?
$IP < K_{sp}$	The solution is unsaturated.	No!
$IP = K_{sp}$	The solution is saturated.	No
$IP > K_{sp}$	The solution is beyond saturation upon mixing.	Yes!

Note: Ionic product and K_{sp} have the same expression. The only difference is for IP, the concentration terms are the concentration **at a particular instant**, but for K_{sp}, **equilibrium** concentrations are used.

2. To predict whether precipitation occurs when two solutions, one containing cations and the other containing anions of a sparingly soluble salt, calculate
   (i) the new concentration of the cation and anion **immediately after mixing**
   (ii) ionic product
   If ionic product > K_{sp}, then precipitation occurs.

(III)   Change in solubility of a sparingly soluble salt

1. The solubility of a sparingly soluble salt is decreased in the presence of its cation or anion. This is known as the <u>common ion effect</u>. For example, solubility of silver iodide is decreased in the presence of silver ions or iodide ions.

2. The solubility of a sparingly soluble salt may be increased by adding a reagent which reacts with its cation or anion. The phenomenon can either be explained using Le Chatelier's Principle or ionic product. Some examples:

Sparingly soluble salt	Reagent added to increase its solubility	Remarks
Silver chloride $AgCl\ (s) + aq \rightleftharpoons$ $Ag^+(aq) + Cl^-(aq)$	Aq NH_3 $Ag^+(aq) + 2NH_3\ (aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$	K_{sp} of AgCl is not so low so that it is soluble in xs aq NH_3. However, AgBr and AgI are insoluble in xs aq NH_3 as their K_{sp} are too low.
Barium chromate: $BaCrO_4\ (s) + aq \rightleftharpoons$ $Ba^{2+}(aq) + CrO_4^{2-}(aq)$	Dilute nitric acid $2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons$ $\qquad Cr_2O_7^{2-}(aq) + H_2O\ (l)$	Ag_2CrO_4 also dissolves in dil HNO_3 due to the reaction between CrO_4^{2-} and H^+.
Copper(II) hydroxide $Cu(OH)_2\ (s) + aq \rightleftharpoons$ $Cu^{2+}(aq) + 2OH^-(aq)$	Aq NH_3 $Cu^{2}(aq) + 4NH_3\ (aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$ $[Cu^{2+}]$ decreases due to formation of $Cu(NH_3)_4^{2+}$ complex → equilibrium position for $Cu(OH)_2\ (s) + aq \rightleftharpoons$ $Cu^{2+}(aq) + 2OH^-(aq)$ shifts right → ppt $Cu(OH)_2(s)$ dissolve	Zinc hydroxide also dissolves in excess aq NH_3 due to the formation of $Zn(NH_3)_4^{2+}(aq)$

Assessment Objectives	Remarks
(a) describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state).	Oxidation = loss of electrons/ ↑ in oxidation state Reduction =gain of electrons/ ↓ in oxidation state

(b) define the terms:
  (i) standard electrode (redox) potential, $E^\ominus$
  (ii) standard cell potential, $E^\ominus_{cell}$
	$E^\ominus$, of a standard half-cell is defined as the potential of that half-cell relative to a standard hydrogen half-cell, under standard conditions.
	
	$E^\ominus_{cell}$ is the potential difference between 2 half-cells under standard conditions

(c) describe the standard hydrogen electrode.
 	
(d) describe methods used to measure the standard electrode potentials of
  (i) metals or non-metals in contact with their ions in aqueous solution
  (ii) ions of the same element in different oxidation states
	Draw the experimental set-up to help you in your description.

(e) calculate a standard cell potential by combining two standard electrode potentials.	$E^\ominus_{cell} = E^\ominus_{Red} - E^\ominus_{Ox}$ (where $E^\ominus_{Red} = E^\ominus$ of substance reduced and $E^\ominus_{Ox} = E^\ominus$ of substance oxidised)

(f) use standard cell potentials to
  (i) explain/predict the direction of electron flow from a simple cell;
  (ii) predict the feasibility of a reaction
	(i) ½–cell with bigger $E^\ominus$ is the [R] ½–cell and hence cathode. The other ½–cell with smaller $E^\ominus$ is the [O] ½–cell and hence anode. Electron flows from anode to cathode.
	
	(ii) In predicting feasibility of a reaction, first identify relevant ½–eqn and compute $E^\ominus_{cell}$. Reaction is energetically feasible if $E^\ominus_{cell} > 0$

(g) Understand the limitations in the use of standard cell potentials to predict the feasibility of a reaction.	Limitations = rxn may be kinetically slow, conditions not std and side rxn may occur.
(h) construct redox equations using the relevant half-equations (including the use of Fe^{3+} / Fe^{2+}, MnO_4^- / Mn^{2+} and $Cr_2O_7^{2-}$ / Cr^{3+} as examples of redox systems).	MnO_4^- reduced to Mn^{2+} under acidified medium and to MnO_2 under weakly acidic/ neutral/ weakly alkaline conditions. Under strongly alkaline conditions, MnO_4^- is reduced to MnO_4^{2-}.
(i) predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ion.	Changes that ↑E_{Red} or ↓E_{Ox} increase E_{cell}. Changes that ↓E_{Red} or ↑ E_{Ox} decrease E_{cell}.

(j) state the possible advantages of developing other types of cell, e.g. the H_2/O_2 fuel cell and improved batteries (as in electric vehicles) in terms of smaller size, lower mass and higher voltage.	Learn how to draw H_2/O_2 fuel cell and write equations for the reactions at anode/ cathode.
(k) state the relationship between the Faraday constant, the Avogadro constant and the charge on the electron, $F = Le$.	–
(l) predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration.	Zinc and metals more reactive than it cannot be obtained from electrolysis of their aqueous solutions. Water is reduced instead: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ Cl^- is oxidised at the anode if concentrated solution is used; I^- and Br^- are oxidised at anode from aq solutions. Sulfate and nitrate ions are not discharged. Instead water is oxidised: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
(m) calculate: (i) the quantity of charge passed during electrolysis; (ii) the mass and/or volume of substance liberated during electrolysis, including those in the electrolysis of H_2SO_4 (aq), Na_2SO_4 (aq).	$Q = I \times t$ or $Q = nF$ where Q = quantity of charge in coulombs I = current in amperes t = time in seconds F = Faraday's Constant
(n) explain, in terms of the electrode reactions, the industrial processes of: (i) the anodising of aluminium; (ii) the electrolytic purification of copper.	Learn description and how to draw experimental set up as well.

Equations showing discharge of H_2 and O_2 from aqueous solutions

Discharge of H_2 at cathode		Discharge of O_2 at anode	
Type of aq solution electrolysed	Equation	Type of aq solution electrolysed	Equation
Acidic eg dil H_2SO_4	$2H^+ (aq) + 2e^- \rightarrow H_2$	Acidic eg dil H_2SO_4	$2H_2O$ (l) $\rightarrow O_2(g)+ 4H^+ (aq)+ 4e^-$
Neutral eg aq Na_2SO_4	$2H_2O$ (l)+ $2e^- \rightarrow H_2$ (g)+ $2OH^-$ (aq)	Neutral eg aq Na_2SO_4	$2H_2O$ (l) $\rightarrow O_2(g)+ 4H^+ (aq)+ 4e^-$
Alkaline eg aq KOH	$2H_2O$ (l)+ $2e^- \rightarrow H_2$ (g)+ $2OH^-$ (aq)	Alkaline eg aq KOH	$4OH^- (aq) \rightarrow O_2(g)+ 2H_2O$ (l) + $4e^-$

RI YEAR 5 – 6 ORGANIC CHEMISTRY SUMMARY

A Formulae

Types of Formulae	Compound		
	2-methylpent-1-ene	4-cyanocyclohexanol	3-ethyl-4-nitrobenzoic acid
Empirical Formula (simplest formula)	CH_2	$C_7H_{11}ON$	$C_9H_9O_4N$
Molecular Formula (shows no. of atoms of each element)	C_6H_{12}	$C_7H_{11}ON$	$C_9H_9O_4N$
Structural Formula (shows arrangement of atoms without ambiguity)	$H_2C{=}C(CH_3){-}CH_2CH_2CH_3$	HO–⬡–CN	structure (C_2H_5, NO_2, HOOC–)
Displayed Formula/ Full Structural Formula (shows all bonds and atoms in open chains but for rings, symbols such as ⬠ & ⬡ are acceptable)	full structure	H–O–⬡–C≡N	full structure
Skeletal Formula (Straight lines represent the C-C bonds. C & H atoms are not explicitly shown.)	skeletal structure	HO–⬡–≡N	skeletal structure (NO_2, –COOH)

B Hybridisation, Resonance and Delocalisation

Hybridisation	Delocalisation and Resonance (for species/ compounds ≠ metal)
Hybridisation = mixing of orbitals resulting in hybrid orbitals formed. Each hybrid orbital has a big lobe and a small lobe.	Delocalisation = movement of electrons beyond the attraction of two bonding atoms due to side-on overlaps of 3 or more p/d orbitals (⇒ π bond (s) present in species with delocalisation of e⁻) eg benzene
Hybridisation allows geometries such as linear, trigonal planar, tetrahedral, trigonal bipyramidal and octahedral to be possible thus minimising repulsion between electron pairs. Three types of hybrid orbitals are encountered in H2 chem:	Resonance = same attachment of atoms but different arrangement of electrons, eg NO_2 ↔ benzene

Type	Remarks	Shape & Diagram
sp³	4 hybrid orbitals. No unhybridised p orbital ⇒ no π bond. For an atom with 4 regions of electron density.	Tetrahedral 109°
sp²	3 hybrid orbitals. 1 unhybridised p orbital ⇒ may form 1 π bond. For an atom with 3 regions of electron density.	Trigonal planar 120°
sp	2 hybrid orbitals. 2 unhybridised p orbital ⇒ may form 2 π bonds. For an atom with 2 regions of electron density.	Linear 180°

1. Species with delocalised electrons exhibit resonance and species that exhibit resonance have delocalised electrons.

2. How to recognise species which have delocalisation of electrons/resonance:
   (a) Species contain conjugated double bonds (ie at least two double bonds alternating with single bonds) **OR**
   (b) 'Bond Structure" diagrams of species can be drawn in more than 1 way

3. Which of the following species contain delocalised electrons/ show resonance?

(i) [seven-membered ring with two double bonds]

(ii) [seven-membered ring with two double bonds]

(iii) $CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_3$

(iv) $CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH{=}CH_2{-}CH_3$

(v) H–C–H (with H's)

(vi) H–C–H

(vii) N≡N⁺—N⁻

Isomerism

Structural isomerism
(exhibited by substances with the same molecular formula but different structural formulae)

Stereoisomerism
(exhibited by substances with same structural formula but different spatial arrangement of atoms.)

Functional Group Isomerism

eg

CH_3CH_2OH & CH_3OCH_3

Positional Isomerism

eg

&
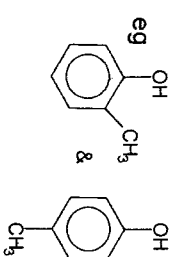
Straight chain vs branching

eg

$CH_3CH_2CH_2CH_3$ & CH_3CHCH_3
$\qquad\qquad\qquad\qquad\quad CH_3$

Geometric (Cis-trans) Isomerism
(caused by restriction of rotation due to double bond or ring.)

Optical Isomerism
(present in molecules with no plane of symmetry)

Chiral Carbon
Chiral carbon is sp³ hybridised and has four different groups attached to it. Mark the chiral carbons in the molecule shown below with an "*" (there are eight):

Optical isomerism = existence of 2 cpds with the same structural formula but differ in being non-superimposable mirror images of each other.
Geometric Isomerism = existence of 2 cpds with the same structural formula but have different spatial arrangement eg due to restricted rotation about a double bond or ring structure.
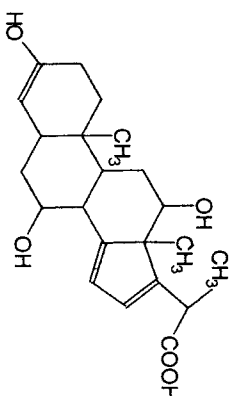
Found in alkenes when the two groups attached to each of the two carbons in the double bond are different.

eg

Compounds with 2 or more chiral carbons may not exhibit optical isomerism if a plane of symmetry is present in the molecule:

eg

or
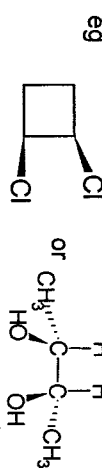
Such compounds are called meso compounds.

Found in rings when the two groups attached to two ring carbon atoms are different.

eg

Compounds with only one chiral carbon exhibit optical isomerism:

eg

A compound that exhibits optical isomerism has two enantiomers (mirror images which are non-superimposable). If only one enantiomer is present, the compound is optically active and rotates plane-polarised light. If both enantiomers are present but in unequal proportions, the mixture still rotates plane-polarised light but the angle of rotation is smaller than that of the pure enantiomer. If both the enantiomers are present in equal proportions, the mixture is called a racemic mixture and shows no optical activity (ie does not rotate plane-polarised light).

D Mechanism

Free Radical Substitution in Alkanes: eg Bromination of ethylbenzene. Alkane reacted with Br_2 in uv light.

Initiation:	Propagation:	Termination: (Three possible steps)
$Br_2 \xrightarrow{uv} 2Br\bullet$	(a) $C_6H_5-CH_2CH_3 + Br\bullet \longrightarrow C_6H_5-\overset{\bullet}{C}HCH_3 + HBr$ (b) $C_6H_5-\overset{\bullet}{C}HCH_3 + Br_2 \longrightarrow C_6H_5-CHBrCH_3 + Br\bullet$ Then (a), (b), (a), (b)...	(i) $2Br\bullet \longrightarrow Br_2$ or (ii) $C_6H_5-\overset{\bullet}{C}HCH_3 + Br\bullet \longrightarrow C_6H_5-CHBrCH_3$ or (iii) $2\ C_6H_5-\overset{\bullet}{C}HCH_3 \longrightarrow C_6H_5-CH(CH_3)-CH(CH_3)-C_6H_5$
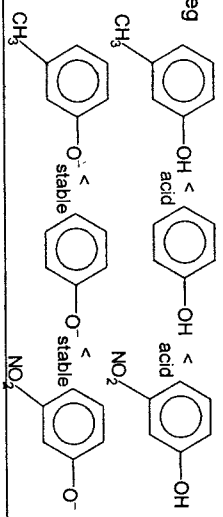
Electrophilic Addition in Alkenes	Electrophilic Substitution in Arenes	Nucleophilic Substitution in Halogenoalkanes	Nucleophilic Addition in Carbonyl Compounds
eg Bromination of propene	eg Bromination of ethylbenzene	eg KCN and 2-chlorobutane	eg HCN and butanone
Alkene reacted with bromine in CCl_4 or bromine water	Arene reacted with bromine in the presence of $FeBr_3$.	Halogenoalkane warmed with KCN dissolved in alcohol.	Aldehyde or ketone reacted with HCN with a small amount of base (or KCN).

Electrophilic Addition in Alkenes

Addition of electrophile - formation of carbocation (Markovnikov's Rule):

$CH_3-CH=CH_2 \xrightarrow{slow} CH_3-\overset{+}{C}H-CH_2-Br + Br^-$

$Br\ \delta+$
$Br\ \delta-$

Addition of nucleophile:

$CH_3-\overset{+}{C}H-CH_2-Br \xrightarrow{fast} CH_3-CH-CH_2-Br$ (with Br, Br)

$:\overset{..}{B}r^-$

If bromine water is used, H_2O can act as a nucleophile and bromohydrin is formed as the major product:

$CH_3-\overset{+}{C}H-CH_2-Br \xrightarrow{fast} CH_3-CH-CH_2-Br$
$\overset{..}{O}H_2$, $+\overset{+}{O}H_2$
$\xrightarrow{-H^+} CH_3-CH-CH_2-Br$
OH

Electrophilic Substitution in Arenes

Generation of electrophile:
$Br_2 + FeBr_3 \longrightarrow Br^+ + FeBr_4^-$

Addition into benzene ring (position dependent on group which is already present): $C_6H_5-CH_2CH_3$

$+ Br^+ \xrightarrow{slow}$ (ring with + and H, Br, CH_2CH_3)

$+ FeBr_4^-$

Loss of H$^+$: (ring with + , H, Br, CH_2CH_3) $\xrightarrow{fast}$ (Br, CH_2CH_3) $+ HBr + FeBr_3$

Nucleophilic Substitution in Halogenoalkanes

Since chloroethane is a secondary RX, the reaction can proceed via S_N2 or S_N1

S_N2 mechanism:

$NC:^- + \overset{\delta+}{C}\cdots\overset{\delta-}{Cl}$ (with CH_2CH_3, H, CH_3) $\longrightarrow \left[NC\overset{\delta-}{\cdots}C\overset{\delta-}{\cdots}Cl \right]^{\ddagger}$ (with CH_3, CH_2CH_3, H) $\longrightarrow$ $NC\cdots C\cdots + Cl^-$ (with CH_2CH_3, CH_3, H)

Product from S_N2 is optically active if reactant RX is optically active.

S_N1 mechanism:

(with CH_2CH_3, CH_3, H, Cl) $\xrightarrow{slow}$ $\overset{+}{C}$ (with CH_2CH_3, CH_3, H) $+ Cl^-$

$NC^- + \overset{+}{C}$ (with CH_2CH_3, CH_3, H) $\xrightarrow{fast}$ $NC\cdots C$ (with CH_2CH_3, CH_3, H) or $C\cdots CN$ (with CH_2CH_3, CH_3, H)

Racemic mixture

Nucleophilic Addition in Carbonyl Compounds

Generation of nucleophile:
$HCN + OH^- \longrightarrow CN^- + H_2O$ (for NaOH)
or $KCN \longrightarrow K^+ + CN^-$ (for KCN)

Addition of CN$^-$:

$\overset{\delta-}{O}=\overset{\delta+}{C}$ (with CH_3, CH_2CH_3) $\xrightarrow{slow}$ O^- — C (with CH_3, CH_2CH_3, CN)
$:CN^-$

Extraction of H$^+$ from HCN:

$\overset{..}{O}^-$ — C — CN (with CH_3, CH_2CH_3) $+ H-CN \xrightarrow{fast}$ OH — C — CN (with CH_3, CH_2CH_3) $+ CN^-$

The carbonyl C is sp^2 hybridised. CN^- can add to either face with equal likelihood so that the resultant product forms a racemic mixture. Hence even though the product has one chiral carbon, it shows no optical activity.

E Acidity

1. A weak acid dissociates incompletely in water: HA (aq) $\rightleftharpoons$ H$^+$ (aq) + A$^-$ (aq). The more stable the anion, the greater is the dissociation and hence the stronger is the acid.

2. In general, | alcohol acid | < | water acid | < | phenol acid | < | carboxylic acid |

Compound	Alcohol, ROH	Phenol	Carboxylic acid, RCOOH
Anion	Alkoxide, RO$^-$	Phenoxide,	Carboxylate ion, RCOO$^-$
Stability of anion and relative acidity	The alkyl group is electron-donating so that the negative charge on O in RO$^-$ is more intensified compared to OH$^-$. Hence RO$^-$ is destabilised by the electron-donating R group so that alcohols are weaker acids than water.	The p-orbital of O overlaps with the π-electron cloud of the benzene ring so that the negative charge on O delocalises into the benzene ring. The dispersal of negative charge stabilises the phenoxide ion so that phenol is a stronger acid than water.	Carboxylate ion has 2 resonance structures: R—C(=O)O$^-$ $\rightleftharpoons$ R—C(O$^-$)=O The 2 resonance structures are equivalent and negative charge is delocalised over two electronegative O atoms resulting in the carboxylate ions being greatly stabilised so that carboxylic acid is more acidic than phenol.
Reaction with Na	Effervescence of hydrogen: ROH (l) + Na (s) ⟶ RO$^-$Na$^+$ (s) + ½H$_2$ (g)	Vigorous rxn with evolution of hydrogen: C$_6$H$_5$OH + Na ⟶ C$_6$H$_5$O$^-$Na$^+$ (s) + ½H$_2$ (g)	Explosive rxn with evolution of hydrogen: RCOOH + Na ⟶ RCOO$^-$Na$^+$ (s) + ½H$_2$ (g)
Rxn with aq NaOH	No reaction. Alcohol is not acidic enough to react with OH$^-$.	Neutralisation reaction and phenol dissolves (to form 1 miscible layer) C$_6$H$_5$OH (s) + NaOH (aq) → C$_6$H$_5$O$^-$Na$^+$(aq) + H$_2$O (l)	Neutralisation reaction: RCOOH(aq) + NaOH(aq) → RCOO$^-$Na$^+$(aq) + H$_2$O (l)
Rxn with aq Na$_2$CO$_3$	No reaction. Alcohol is not acidic enough to react with CO$_3$$^{2-}$.	No reaction. Phenol is not acidic enough to react with CO$_3$$^{2-}$.	Evolution of CO$_2$: 2RCOOH + Na$_2$CO$_3$ → 2RCOO$^-$Na$^+$ + H$_2$O + CO$_2$ (g)
Variation of acidity within class of compound	Primary alcohol > Secondary acid alcohol	> Tertiary alcohol Primary acid > Secondary alcohol	e$^-$-donating groups, if present in phenol, reduce the delocalisation of negative charge of O into benzene ring thus decreasing the stability of phenoxide ion and its acidity. Conversely, e$^-$-withdrawing groups enhance the delocalisation of negative charge of O into benzene ring thus increasing the stability of phenoxide ion and its acidity.	An electron-donating group intensifies the –ve charge and decreases the acidity of a carboxylic acid while an electron-withdrawing group disperses the –ve charge and increases its acidity (same as phenol).

Variation of acidity eg (alcohol structures):

CH$_3$CH$_2$CH$_2$—C(H)(H)—O$^-$ stable > CH$_3$CH$_2$—C(CH$_3$)(H)—O$^-$ stable > CH$_3$—C(CH$_3$)(CH$_3$)—O$^-$ stable

CH$_3$CH$_2$CH$_2$—C(H)(H)—OH acid > CH$_3$CH$_2$—C(CH$_3$)(H)—OH acid > CH$_3$—C(CH$_3$)(CH$_3$)—OH acid

Phenol eg:

OH < (CH$_3$-phenol) OH < (phenol) OH

stable < (CH$_3$-phenoxide) O$^-$ < (phenoxide) O$^-$ < (NO$_2$-phenoxide) O$^-$ stable

Carboxylic acid Eg:

CH$_3$COOH acid < CH$_2$ClCOOH acid < CH$_2$FCOOH;

CH$_2$FCH$_2$COOH acid < CH$_3$CHFCOOH
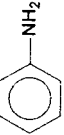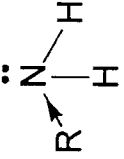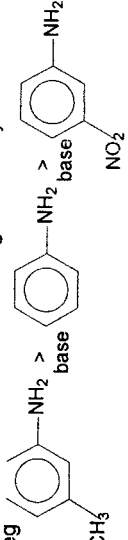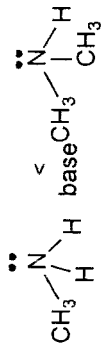
F Basicity

1. A base is a lone-pair donor. The more available the lone pair of electrons is for donation, the stronger is the base.

2. In general, | amide | $<$ | phenylamine | $<$ | ammonia | $<$ | aliphatic amine |
   | | | | base | | base | | base | | base |
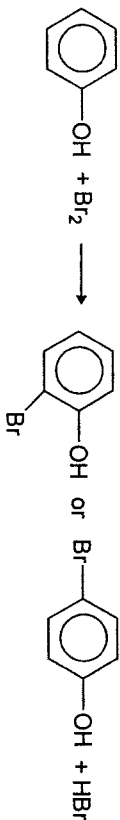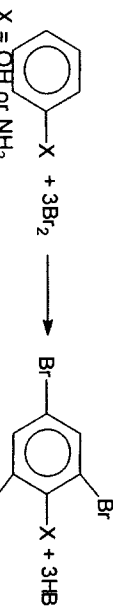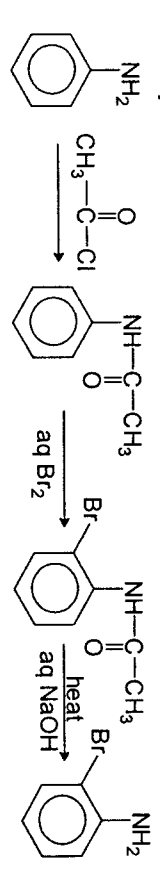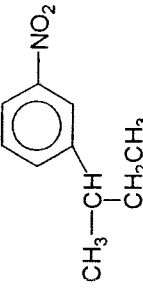
Compound	Amide, $R-\overset{\overset{O}{\|}}{C}-NH_2$	Phenylamine, —NH₂	Aliphatic amine, RNH₂
Availability of lone pair of electrons on N	Amide has 2 resonance structures; $R-\overset{\overset{O}{\|}}{C}-NH_2 \longleftrightarrow R-\overset{\overset{O^-}{\|}}{C}=\overset{+}{N}H_2$ Due to resonance, the lone pair of e⁻ on N is less available for protonation so that amide is neutral and less basic than phenylamine. Another explanation: p-orbital of N overlap with p-orbitals of carbonyl group resulting in delocalisation thus making lp on N less available.	The p-orbital of N overlaps with the π-electron cloud of the benzene ring so that the lone pair of electrons on N delocalise into the benzene ring. This decreases the availability of the lone pair of electrons on N for donation to a H⁺ (protonation). Hence phenylamine is a weaker base than ammonia.	Aliphatic amines contain alkyl groups. The alkyl group is electron donating and enhances the availability of the lone pair for protonation so that aliphatic amines are stronger bases than ammonia.
Variation of basicity within class of compound	—	e⁻-donating groups, if present in phenylamine, reduce the delocalisation of lone pair of e⁻ on N into benzene ring thus increasing the availability of the lone pair of e⁻ for protonation thus increasing its basicity. Conversely, e⁻-withdrawing groups enhance the delocalisation of lone pair of e⁻ on N into benzene ring thus decreasing availability of the lone pair of e⁻ for protonation thus decreasing its basicity. eg	As no of alkyl groups on N ↑, the availability of lone pair e⁻ for protonation is even more enhanced so that: 	Primary amine	$<$	Secondary amine	 base eg Tertiary amines are weaker bases than primary amines as the three bulky alkyl groups cause the lone pair of electrons on N to be less available due to steric hindrance.
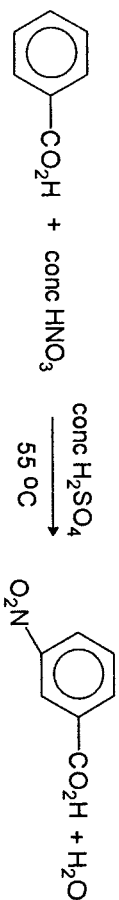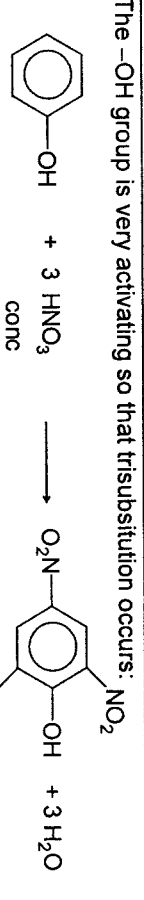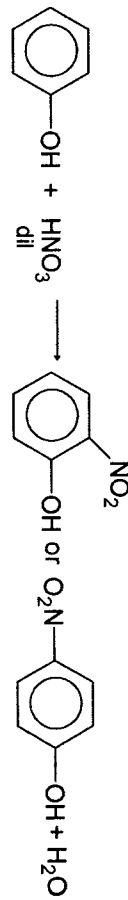
G Physical Properties of Organic Compounds (Rough Guide, may vary due to branching of alkyl groups, class of alcohol, amine or amide etc)

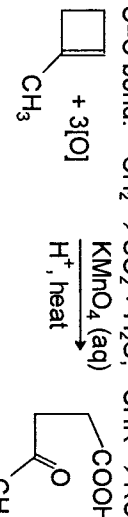| Type of Organic Cpds	Hydrocarbon (alkane, alkene & arene)	Halogeno-alkanes	Alcohol	Phenol	Carbonyl Cpd (aldehyde & ketone)	Carboxylic acid	Ester	Amine, phenylamine	Amide
Dominant IMF	Mostly id-id interactions	pd-pd interactions	Hydrogen bonding	Hydrogen bonding	pd-pd interactions	Hydrogen bonding	pd-pd interactions	H bonding except 3° amine	Hydrogen bonding
State at rm temp	≤ 4 C = gas > 5 C = liquid	Mostly liquids	≤ 6 C = liquid > 7 C = solid	solid	Mostly liquids	≤ 6 C = liquid > 7 C = solid	Mostly liquids	Mostly liquids	HCONH₂ (l) > 2 C = solid
Interactions with water	Van der Waals forces	Van der Waals forces	H bonding	H bonding	H bonding (not extensive)	H bonding	H bonding (not extensive)	H bonding	H bonding
Solubility in water	Insoluble	Insoluble	≤ 4 C soluble	Limited solubility	Mostly insoluble	≤ 6 C soluble	Insoluble	≤ 5 C soluble	≤ 4 C soluble
Conductivity of aq solution	—	–	Does not conduct	Conducts	–	Conducts	–	Conducts	Does not conduct
Effect on litmus	No change	No change	No change	Blue → red	No change	Blue → red	No change	Red → blue	No change

H Reagents In Organic Chemistry

Reagent	Conditions	Organic Cpds that react	Product (s) formed & observations	Type of Reaction	Equations and Remarks
	uv light (note: Cl₂ also undergoes FRS with alkanes in uv light to form chloroalkane)	Alkane	Bromoalkane Decolourisation of bromine and white fumes of HBr observed.	Free Radical Substitution	Eg $C_6H_5CH_2CH_3 + Br_2 \xrightarrow{uv} C_6H_5CHBrCH_3 + HBr$ Any compounds with H attached to a saturated C may undergo FRS. Variety of products formed. To favour monobromination, use excess of the alkane. Major product is the one that is formed via the more stable alkyl radical intermediate. Stability of alkyl radical: $CH_3{\bullet} < R{-}\overset{H}{\underset{H}{C}}{\bullet} < R{-}\overset{H}{\underset{R}{C}}{\bullet} < R{-}\overset{R}{\underset{R}{C}}{\bullet}$ Stability due to a benzene ring is equivalent to two alkyl groups.
Bromine	Br₂ in CCl₄	Alkene	Dibromoalkane Decolourisation of brown Br₂	Electrophilic addition	Eg: $CH_3CH{=}CH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$ This is used as a distinguishing test for alkenes.
		Phenol	2– or 4–bromophenol Decolourisation of brown Br₂	**Easy** electrophilic substitution (Electrophilic subsb on a highly activated benzene ring in the absence of catalyst)	Eg: ⬡–OH + Br₂ → ⬡–OH or Br–⬡–OH + HBr
	Aq Br₂	Alkene	Bromohydrin Decolourisation of orange Br₂	Electrophilic addition	Major product is bromohydrin rather than dibromoalkane because H₂O is used as the solvent. Addition follows Markovnikoff's Rule (may be explained by stability of carbocation.) Eg: $CH_3CH{=}CH_2 + Br_2 + H_2O \rightarrow CH_3CH(OH)CH_2Br + HBr$ Decolourisation of bromine water is used as a distinguishing test for alkenes.
		Phenol or phenylamine	2,4,6-tribromophenol or 2,4,6-tribromophenylamine Decolourisation of orange Br₂ and formation of white ppt.	**Easy** electrophilic substitution	⬡–X + 3Br₂ → Br–⬡(Br)(Br)–X + 3HBr X = OH or NH₂ Both –OH and –NH₂ activates the benzene ring towards electrophilic substitution so that the catalyst FeBr₃ is not required. This is used as a distinguishing test for phenol and phenylamine.
		N-phenyl-ethanamide ⬡–N(H)–C(=O)–CH₃	Br–⬡–N(H)–C(=O)–CH₃ or ⬡(Br)–N(H)–C(=O)–CH₃ Decolourisation of orange Br₂	**Easy** Electrophilic substitution	The –NHCOCH₃ is less activating than the –NH₂ group so that monosubstitution occurs. Hence to convert phenylamine to 2- or 4-bromophenylamine, –NH₂ is first converted to –NHCOCH₃ before bromination. Then the –NHCOCH₃ is hydrolysed back to –NH₂ as shown by the rxn scheme below: ⬡–NH₂ $\xrightarrow{CH_3-C(=O)-Cl}$ ⬡–NH–C(=O)–CH₃ $\xrightarrow{aq\ Br_2}$ Br–⬡–NH–C(=O)–CH₃ $\xrightarrow[aq\ NaOH]{heat}$ Br–⬡–NH₂

Reagent	Conditions	Organic Cpds that react	Product formed &observation	Type of Reaction	Equations and Remarks
Br_2	$FeBr_3$ or $AlBr_3$ as catalyst. (If Cl_2 and $FeCl_3$ is used, chlorination occurs)	Benzene	Bromobenzene Decolourisation of Br_2 with formation of white fumes.	Electrophilic substitution	Eg [benzene] $+ Br_2 \xrightarrow[\text{or } AlBr_3]{FeBr_3}$ [benzene]—Br + HBr. If another group, G, is already present on the benzene ring, substitution is at 2,4 position if G = alkyl group, halogen, $-OH$, $-OR$, $-NH_2$, $-NHR$, $-NR_2$, $-NHCOR$ and at 3– position if G = $-COOH$, $-COOR$, $-COR$, $-NO_2$
Hydrogen halide: HCl or HBr	Anhydrous conditions	Alkene	Halogenoalkane	Electrophilic addition	Addition follows Markovnikov's Rule (may be explained by stability of carbocation). Eg: $CH_3CH=CH_2 + HCl \rightarrow CH_3CHClCH_3$
Conc H_2SO_4	xs conc H_2SO_4, 170 °C	Alcohol	Alkene	Dehydration (elimination)	Product formed follows Sayzeff's Rule (more substituted alkene is major product because of their greater stability). Eg $CH_3CH(OH)CH_2CH_3 \xrightarrow[\text{170 °C}]{\text{xs conc } H_2SO_4} CH_3CH=CHCH_3 + H_2O$
	1. Add cold conc H_2SO_4 2. Add water and warm	Alkene	Alcohol	Hydration (electrophilic addition followed by nucleophilic substitution)	Addition follows Markovnikov's Rule (may be explained by stability of carbocation). Eg: $CH_3CH=CH_2 + H_2SO_4 \rightarrow CH_3CH(OSO_3H)CH_3$; $CH_3CH(OSO_3H)CH_3 + H_2O \rightarrow CH_3CH(OH)CH_3 + H_2SO_4$. Usually, only one equation is used for this two step reaction: $CH_3CH=CH_2 + H_2O \xrightarrow[\text{2. } H_2O, \text{ warm}]{\text{1. conc } H_2SO_4} CH_3CH(OH)CH_3$
	Used as a catalyst for esterification. heat	Alcohol + Carboxylic Acid	Ester	Esterification	Eg $RCOOH + ROH \xrightarrow[\text{Warm/ reflux}]{\text{conc } H_2SO_4} RCOOR' + H_2O$
Al_2O_3	Heat	Alcohol	Alkene	Dehydration, (elimination)	Product formed follows Saytzeff's Rule (more substituted alkene is major product because of their greater stability). Eg $CH_3CH(OH)CH_2CH_3 \xrightarrow{Al_2O_3, \text{ heat}} CH_3CH=CHCH_3 + H_2O$
Halogenoalkane, AlX_3/ FeX_3 (not in syllabus)	–	Benzene or substituted benzene	Alkylated benzene	Electrophilic Substitution (Friedal Crafts Alkylation)	If another group, G, is already present on the benzene ring, substitution is at 2,4 position if G = alkyl group, halogen, $-OH$, $-OR$, $-NH_2$, $-NHR$, $-NR_2$, $-NHCOR$ and at 3– position if G = $-COOH$, $-COOR$, $-COR$, $-NO_2$ eg [benzene]—NO_2 + $CH_3CHBrCH_2CH_3 \xrightarrow{FeBr_3}$ [benzene]—NO_2 + HBr (with CH_3—CH—CH_2CH_3 substituent)
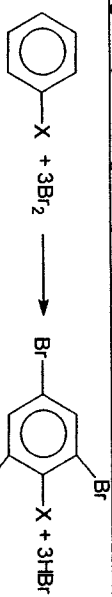
Reagent	Conditions	Organic Cpds that react	Product formed & observation	Type of Reaction	Equations and Remarks
Conc HNO_3	Conc H_2SO_4, 55/60 °C for benzene, 30 °C for methylbenzene	Benzene or substituted benzene	Nitrobenzene (appears as a yellow oil with almond smell)	Electrophilic Substitution (Nitration)	If another group, G, is already present on the benzene ring, substitution is at 2,4 position iif G = alkyl group, halogen, –OH, –OR, –NH₂, –NHR, –NR₂, –NHCOR and at 3– position if G = –COOH, –COOR, –COR, –NO₂ eg [ring]–CO₂H + conc HNO₃ $\xrightarrow[\text{55 °C}]{\text{conc } H_2SO_4}$ O₂N[ring]CO₂H + H₂O
	Room temperature, no catalyst needed	Phenol	2,4,6-trinitrophenol	**Easy** electrophilic substitution (Nitration)	The –OH group is very activating so that trisubstitution occurs: [ring]–OH + 3 HNO₃ (conc) → O₂N[ring with NO₂]OH + 3 H₂O If dil HNO₃ is used instead of con nitric acid, mononitration occurs: –OH + HNO₃ (dil) → [ring]OH or O₂N[ring]OH+ H₂O
Na_2CO_3 (aq)	room temperature	Carboxylic acid	Carboxylate salt. Effervescence of CO_2.	Acid-base reaction	2RCOOH + CO₃²⁻ → 2RCOO⁻ + CO₂ + H₂O This is used as a test for carboxylic acid. Acyl chloride will also give CO₂ but fumes of HCl is also observed: RCOCl + H₂O → RCOOH + HCl 2H⁺ + CO₃²⁻ → CO₂ + H₂O
NaOH (KOH can also be used in place of NaOH)	Aq NaOH, room temperature	Carboxylic acid and phenol	RCOO⁻ or phenoxide .If RCOOH has six or more C atoms, the acid is originally insoluble. On addition of aq NaOH, the insoluble phenol or acid dissolves.	Acid-base reaction	Acid with 6C or more and phenol are insoluble in water. Reaction wth NaOH produces the ionic salt which dissolves in water due to stronger ion-dipole interactions formed between the salt andwater: RCOOH + OH⁻ ⟶ RCOO⁻ (aq) + H₂O C₆H₅OH + OH⁻ ⟶ C₆H₅O⁻ (aq) + H₂O This can be used to distinguish insoluble carboxylic acids or phenol from other compounds. (NB: phenoxide ion, C₆H₅O⁻ may also be called phenate)
	Aq NaOH, heat	Halogeno-alkane	Alcohol	Nucleophilic Substitution	RX +OH⁻ (aq) $\xrightarrow{\text{heat}}$ ROH + X⁻ X directly attached to benzene ring cannot be substituted by OH⁻ due to partial double bond character (since lone pair of electrons on X delocalised into benzene ring as p-orbital of X overlaps with π-electron cloud of benzene).

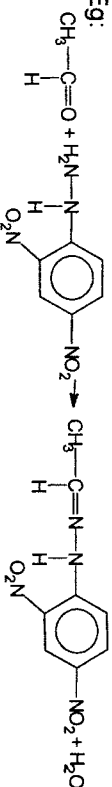| Reagent	Conditions	Organic Cpds that react	Product formed & observation	Type of Reaction	Equations and Remarks
NaOH	Aq NaOH, heat	(i) Ester (ii) Amide (iii) Nitrile	Carboxylate salt and (i) alcohol or (ii) NH_3/amine or (iii) NH_3. For (ii) and (iii), alkaline gas that turned moist red litmus paper blue was evolved.	Hydrolysis	$RCOOR' + OH^- \longrightarrow RCOO^- + R'OH$ $RCONHR' + OH^- \longrightarrow RCOO^- + R'NH_2$ $RCN + OH^- + H_2O \longrightarrow RCOO^- + NH_3$ The evolution of ammonia from nitrile and primary amide and the evolution of amines from sec and tert amides (provided these amines are volatile, 5C or less) on warming with aq NaOH may be used as a distinguishing test for amide and nitrile against other classes of compounds.
	Alcoholic NaOH, heat	Halogeno-alkane	Alkene	Elimination (dehydro-halogenation)	Product formed follows Saytzeff's Rule (more substituted alkene is major product because of their greater stability). Alcoholic NaOH Eg $CH_3CHBrCH_2CH_3 \longrightarrow CH_3CH=CHCH_3 + H_2O$
Sodium alkoxide	heat	Halogeno-alkane	Ether	Nucleophilic Substitution	$RX + R'O^- \longrightarrow ROR' + X^-$ (solvent used is ROH) Sodium alkoxide is obtained by reacting the appropriate alcohol with Na: $2ROH + 2Na \longrightarrow 2R'O^-Na^+ + H_2$
Conc NH_3	In ethanol, heat in a sealed tube	Halogeno-alkane	Amine	Nucleophilic Substitution	$RX + NH_3 \longrightarrow RNH_2 + HX$ Primary amine formed. NH_3 needed to be used in excess to favour formation of 1° amine. With excess RX, R_2NH, R_3N or $R_4N^+X^-$ may be formed.
NH_3	–	Acid halide	Amide	Nucleophilic Substitution	$RCOX + NH_3 \longrightarrow RCONH_2 + HX$ Primary amide formed.
KCN (or NaCN)	Aqueous alcoholic KCN, heat	Halogeno-alkane	Nitrile	Nucleophilic Substitution	$RX + CN^- \longrightarrow RCN + X^-$ Alcohol is used as a solvent to dissolve both CN^- and RX. The resultant compound has one C more than the starting RX. This is an important synthesis step allowing length of C chain to be extended by 1. RCN can be hydrolysed to RCOOH (warming RCN with dil acid) or reduce to RCH_2NH_2 (using $LiAlH_4$). HCN cannot be used as it is not strong enough a nucleophile to react with RX.
HCN	Trace amt of KCN or small amount of aq NaOH, cold	Carbonyl compound (ie aldehyde or ketone)	Cyanohydrin	Nucleophilic addition	$R-\overset{O}{\underset{\parallel}{C}}-R' + HCN \xrightarrow{\text{trace KCN}} R-\overset{OH}{\underset{CN}{\underset{\mid}{C}}}-R'$ R, R' = H, alkyl or aryl Cyanohydrin may be hydrolysed (by warming with dil acid) to give 2-hydroxycarboxlic acid or reduced to 2-hydroxyamine. This reaction allows an increase of one carbon in carbon chain length.
Dilute acid (HCl, HNO_3 or H_2SO_4)	heat acid with compound	(i) Ester (ii) Amide (iii) Nitrile	Carboxylic acid and (i) alcohol or (ii) NH_4^+/amine salt or (iii) NH_4^+	Hydrolysis	$RCOOR' + H_2O \longrightarrow RCOOH + R'OH$ $RCONHR' + H_2O + H^+ \longrightarrow RCOOH + R'NH_3^+$ $RCN + H_2O + H^+ \longrightarrow RCOOH + NH_4^+$

Reagent	Conditions	Type of Organic Cpds that react	Product formed & observation	Type of Reaction	Equations and Remarks
RCOCl (RCOBr may also be used)	Room temperature (either pri or sec)	(i) alcohol (ii) phenol (iii) amine	(i) ester (ii) phenolic ester (iii) amide formation (condensation)	(i) and(ii) esterification; (iii) amide formation (condensation)	(i) $RCOCl + R'OH \rightarrow RCOOR' + HCl$ (ii) $RCOCl + C_6H_5OH \rightarrow RCOOC_6H_5 + HCl$ (ii) $RCOCl + R'NH_2 \rightarrow RCONHR' + HCl$ To convert phenol to phenolic ester, acid chloride must be used. Carboxylic acids are not reactive enough to react with phenol. To convert amine to amide, acid chloride is needed. Carboxylic acid does not react with amine to form amide (unless under industrial conditions) but merely neutralises it.
Aq KMnO₄	Cold dil alkaline	Alkene	Diol. Formation of black MnO_2.		Eg $CH_3CH=CH_2 + H_2O + [O] \rightarrow CH_3CH(OH)CH_2OH$
		Alkene (C=C)	CO_2, carboxylic acid or ketone. Decolourisation of purple KMnO₄		C=C bond cleaves. Final product dependent on groups attached to each C in the C=C bond: $=CH_2 \rightarrow CO_2 + H_2O$; $=CHR \rightarrow RCOOH$; $=CRR' \rightarrow RCOR'$. Eg [structure] $+ 3[O] \xrightarrow[H^+, \text{heat}]{KMnO_4 \text{(aq)}}$ [structure with COOH and C=O, CH₃]
		Alkyl benzene	Benzoic acid and CO_2		Alkylbenzene will be oxidized to benzoic acid, eg $C_6H_5CH_2CH_2CH_3 + 9[O] \rightarrow C_6H_5COOH + 2CO_2 + 3H_2O$ The alkyl group needed to have a H atom on C attached to benzene ring for alkylbenzene to be oxidised. Hence, $C(CH_3)_3C_6H_5$ would not be oxidised.
		HCOOH, and ethanedioic acid.	CO_2 and H_2O	Oxidation	These are the only two common carboxylic acids which can be oxidized by KMnO₄: $HCOOH + [O] \rightarrow CO_2 + H_2O$ $HOOC-COOH + [O] \rightarrow 2CO_2 + H_2O$
	Add dilute H₂SO₄, and KMnO₄ to the compound and heat	aldehyde, 1° or 2° alcohol	Carboxylic acid (from aldehyde & 1° ROH) & ketone (fr 2° ROH)		$RCHO + [O] \rightarrow RCOOH$ $RCH_2OH + 2[O] \rightarrow RCOOH + H_2O$ $RCH(OH)R' + [O] \rightarrow RCR'=O + H_2O$
		Esters which hydrolyses to form HCOOH, ethanedioic acid, CH₃OH, 1° or 2° alcohol	CO_2 (from HCOOH, ethanedioic acid or CH₃OH, pri or sec alcohol),decolourisation of KMnO₄ observed.		heat with dil H₂SO₄, hydrolyses the ester into an acid and alcohol. if either the acid or alcohol can undergo oxidation (acid = HCOOH or ethanedioic acid; alcohol = CH₃OH, pri or sec alcohol),decolourisation of KMnO₄ observed. Eg (1) $HCOOC(CH_3)_3 + H_2O \rightarrow HCOOH + C(CH_3)_3OH$ $HCOOH + [O] \rightarrow CO_2 + H_2O$ (2) $CH_3COOCH_2CH_2CH_3 + H_2O \rightarrow CH_3COOH + CH_3CH_2CH_2OH$ $CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2COOH + H_2O$
		Phenylketone and 3° ROH with phenyl gp attached to hydroxyl C.	Benzoic acid		Phenyl ketone and 3° alcohol with phenyl gp attached to hydroxyl C contain a benzene ring and can be oxidised to benzoic acid by heating with KMnO₄/H⁺: eg $C_6H_5COCH_2CH_3 + 7[O] \rightarrow C_6H_5COOH + 2CO_2 + 2H_2O$ $C_6H_5C(OH)(CH_3)_2 + 8[O] \rightarrow C_6H_5COOH + 2CO_2 + 3H_2O$

Reagent	Conditions	Type of Organic Cpds that react	Product formed & observation	Type of Reaction	Equations and Remarks
Aq $K_2Cr_2O_7$	Add dil H_2SO_4 and aq $K_2Cr_2O_7$ to compound and heat	HCOOH, aldehyde, 1° & 2° alcohols, and esters which form oxidisable products on hydrolysis.	Products same as $KMnO_4$. Observation: Colour change from orange to green.	Oxidation	Potassium dichromate(VI) is a weaker oxidizing agent than $KMnO_4$ and is usually not used to oxidize alkenes, alkylbenzenes and ethanedioic acid.
	Add dil H_2SO_4 and aq $K_2Cr_2O_7$ to compound. Immediate distillation	Primary alcohol	Aldehyde	Oxidation	$RCH_2OH + [O] \longrightarrow RCHO + H_2O$
H_2	Ni, heat	Alkene	Alkane	Addition/ reduction	$RCH{=}CHR' + H_2 \longrightarrow RCH_2CH_2R'$
		Nitrile, RCN	Primary amine	reduction	$RCN + 2H_2 \longrightarrow RCH_2NH_2$
		Aldehyde and ketone	Primary and secondary alcohol	Reduction	$RCHO + H_2 \longrightarrow RCH_2OH$ $RCR'O + H_2 \longrightarrow RCH(OH)R'$ (does not reduce RCOOH !!)
LiAlH$_4$ in dry ether	Room temp	(i) Nitrile, (ii) aldehyde, (iii) ketone and (iv) carboxylic acid	(i) Primary amine, (ii) primary alcohol, (iii) secondary alcohol and (iv) primary alcohol.	Reduction	$RCN + 4[H] \longrightarrow RCH_2NH_2$ $RCHO + 2[H] \longrightarrow RCH_2OH$ $RCR'O + 2[H] \longrightarrow RCH(OH)R'$ $RCOOH + 4[H] \longrightarrow RCH_2OH + H_2O$
NaBH$_4$ in methanol	Room temp	aldehyde, ketone	primary alcohol, secondary alcohol	Reduction	$RCHO + 2[H] \longrightarrow RCH_2OH$ $RCR'O + 2[H] \longrightarrow RCH(OH)R'$
Sn and conc HCl	Reflux	Nitrobenzene	Phenylamine	Reduction	$C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 + 2H_2O$ (aq NaOH is used in 2nd step to liberate free amine from amine salt, $C_6H_5NH_3^+$ Cl^-)
PCl$_5$	anhydrous	Alcohol	Chloroalkane	N. Substitution	$ROH + PCl_5 \longrightarrow RCl + HCl + POCl_3$
	anhydrous	Carboxylic acid	Acyl chloride	N. Substitution	$RCOOH + PCl_5 \longrightarrow RCOCl + HCl + POCl_3$ PCl$_5$ replaces OH group in ROH or RCOOH with Cl
PCl$_3$ or PBr$_3$	anhydrous	Alcohol	Chloroalkane/ bromoalkane	N. Substitution	$3ROH + PX_3 \longrightarrow 3RX + H_3PO_3$ where X = Br or Cl
	anhydrous	Carboxylic acid	Acid chloride/ bromide	N. Substitution	$3RCOOH + PX_3 \longrightarrow 3RCOX + H_3PO_3$ where X = Br or Cl PX$_5$ replaces OH group in ROH or RCOOH with X where X = Br or Cl
SOCl$_2$	anhydrous	Alcohol	Chloroalkane	N. substitution	$ROH + SOCl_2 \longrightarrow RCl + HCl + SO_2$ SOCl$_2$ replaces OH group in ROH with Cl

# I Reagents used to Test for Various Functional Groups

Reagent	Type of Organic Cpds that react	Test and Conditions	Observations	Equation and Remarks
aq KMnO$_4$ + dil H$_2$SO$_4$ (Note: This test is not specific and more specific tests are usually preferred)	Alkene (C=C)			Eg: $CH_3CH=CH_2 + 5[O] \rightarrow CH_3COOH + CO_2 + H_2O$
	Alkyl benzene			Eg: $C_6H_5CH_2CH_3 + 6[O] \rightarrow C_6H_5COOH + CO_2 + 2H_2O$
	HCOOH, ethanedioic acid, aldehyde, primary or secondary alcohol	Heat compound with acidified KMnO$_4$ (aq) (dil H$_2$SO$_4$ is used for acidification)	Purple KMnO$_4$ was decolourised.	HCOOH and ethanedioic acid are oxidised to CO$_2$ and H$_2$O. Aldehydes and primary alcohols are oxidised to carboxylic acids while secondary alcohols are oxidised to ketones. Eg $(CH_3)_2CHOH + [O] \rightarrow (CH_3)_2C=O + H_2O$
	Ester which hydrolyses to give oxidisable acids (ie HCOOH or ethanedioic acid) or methanol, primary or secondary alcohol.			Ester hydrolyses to form acid and alcohol on being warmed with dil H$_2$SO$_4$. If either the acid or alcohol can be oxidized, KMnO$_4$ will be decolourised. Eg $CH_3COOCH_3 + H_2O + H^+ \rightarrow CH_3COOH + CH_3OH$ $CH_3OH + 3[O] \rightarrow CO_2 + 2H_2O$
Bromine	Alkene (C=C)	React compound with Br$_2$ in CCl$_4$	Brown Br$_2$ was rapidly decolourised.	Eg: $CH_3CH=CH_2 + Br_2 \rightarrow CH_3CH_2BrCH_2Br$
	Alkene (C=C)		Orange / brown Br$_2$ was rapidly decolourised.	Addition follows Markovnikov's Rule Eg: $CH_3CH=CH_2 + Br_2 + H_2O \rightarrow CH_3CH(OH)CH_2Br + HBr$
	Phenol and phenylamine	React compound with aqueous bromine	Orange / brown Br$_2$ was decolourised, white fumes of HBr and white ppt.	[benzene ring]—X $+ 3Br_2 \longrightarrow$ Br—[benzene ring with Br]—X $+ 3HBr$ where X = OH or NH$_2$
	Benzene	React compound with bromine and FeCl$_3$ as catalyst in the dark	Brown Br$_2$ was decolourised.	Alkenes, phenol and phenylamine will also decolourise bromine. This test is used to distinguish compound with benzene rings from those that do not have benzene ring and C=C bond, eg benzene from cyclohexane.
Aqueous Na$_2$CO$_3$	Carboxylic acid	Add aq Na$_2$CO$_3$ to compound	Effervescence of CO$_2$ [gave white ppt with aq Ca(OH)$_2$].	Eg: $2CH_3COOH + CO_3^{2-} \rightarrow 2CH_3COO^- + H_2O + CO_2$ Acyl chloride will also give effervescence of CO$_2$ too but fumes of HCl is also evolved: Eg: $CH_3COCl + H_2O + \rightarrow CH_3COOH + HCl$ $2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$
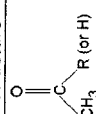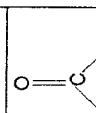
Reagent	Type of Organic Cpds that react	Test and Conditions	Observations	Equation and Remarks
Aqueous NaOH	Phenol	Add aq NaOH to compound	Insoluble phenol dissolves to form a colourless soln (1 miscible layer).	Phenol is sparingly soluble but on conversion to sodium phenoxide by reaction with aq NaOH, will dissolve: C_6H_5OH (s) + NaOH (aq) $\rightarrow C_6H_5O^-Na^+$ (aq) + H_2O (l) This test can be used to distinguish phenol from solids that are insoluble in aq NaOH but will not be able to distinguish phenol from benzoic acid.
	Amine salt	Add aq NaOH to a solution of the compound. Warm gently.	A gas that turned moist red litmus paper as evolved (for volatile amine - with 5 C or less eg CH_3NH_2) or an organic layer separates out (non-volatile amines such as phenylamine)	Eg: $CH_3NH_3^+$ (aq) + OH^- (aq) $\rightarrow CH_3NH_2$ (g) + H_2O (l) Eg: $C_6H_5NH_3^+$ (aq) + OH^- (aq) $\rightarrow C_6H_5NH_2$ (l) + H_2O (l)
	Ammonium salt	Add aq NaOH to a solution of the compound. Warm gently.	A gas that turns moist red litmus paper blue was evolved.	Ammonia was formed. The gentle warming was necessary to drive the soluble NH_3 out of solution. Eg: NH_4^+ (aq) + OH^- (aq) $\rightarrow NH_3$ (g) + H_2O (l)
	Amide	Add aq NaOH to the compound. Heat strongly	After some time of warming, a gas that turns moist red litmus paper blue was evolved.	Only amides that hydrolyse to give volatile ammonia or amines (5C or less) will give a gas that turns moist red litmus blue. The strong heating is needed to hydrolyse the amide bond: Eg $CH_3CON(CH_3)_2 + OH^- \rightarrow CH_3COO^- + NH(CH_3)_2\uparrow$
Aqueous NaOH (with dil HNO_3 & aq $AgNO_3$)	Halogenoalkane	Heat cpd with aq NaOH. Cool. Acidify with dil HNO_3. Add aq $AgNO_3$.	White ppt of AgCl (for RCl) Cream ppt of AgBr (for RBr) Yellow ppt for AgI (for RI)	Eg: $C_6H_5CH_2Cl + OH^- \rightarrow C_6H_5CH_2OH + Cl^-$, Ag^+ (aq) + Cl^- (aq) $\rightarrow$ AgCl (s) Test is negative if Cl, Br or I is directly attached to benzene ring.
aq $AgNO_3$	Acid halide	Add aq $AgNO_3$ to compound at r.t.	White fumes seen with formation of ppt: White ppt of AgCl (for RCOCl) Cream ppt of AgBr (for RCOBr) Yellow ppt for AgI (for RCOI)	Eg: $RCOCl + H_2O \rightarrow RCOOH$ (aq) + HCl (aq) Ag^+ (aq) + Cl^- (aq) $\rightarrow$ AgCl (s)
Sodium	Alcohol	Add sodium to compound	Effervescence of H_2 (gas extinguished lighted splinter with a pop sound)	Eg: $C_2H_5OH + Na \rightarrow C_2H_5O^-Na^+ + \frac{1}{2}H_2$ (g) Note that Na should not be used unless there is no other alternative as it reacts explosively with water, phenol and carboxylic acid. A better test for alcohol with a $CH_3CH(OH)$– group is the CH_3 test (warming with aq alkaline I_2).

Reagent	Type of Organic Cpds that react	Test and Conditions	Observations	Equation and Remarks
Iodine solution + aq NaOH	Alcohol with $CH_3C(OH)H$— gp or carbonyl cpd with CH_3CO— gp	Warm compound with aqueous iodine and aqueous NaOH	Yellow ppt of CHI_3 formed.	$RCH(OH) CH_3 + 4I_2 + 6OH^- \rightarrow RCOO^- + CHI_3 (s) + 5I^- + 5H_2O$ $RCOCH_3 + 3I_2 + 4OH^- \rightarrow RCOO^- + CHI_3 (s) + 3I^- + 3H_2O$ The pdt is a carboxylate salt with one C less than the starting alcohol (ethanol of a secondary 2-ol) or carbonyl cpd (ethanal or methylketone). Note that methyl esters or amides **DO NOT** give CHI_3 with I_2/OH^-.
Neutral $FeCl_3$ (aq)	Phenol	Add neutral $FeCl_3$ (aq) to the compound	Violet complex formed.	$6 C_6H_5OH + Fe^{3+} \rightarrow [Fe(C_6H_5O)_6]^{3-} + 6H^+$
2,4-dinitrophenyl hydrazine (2,4–DNPH or Brady's reagent)	Carbonyl cpds (aldehyde or ketone)	Add 2,4-dinitrophenylhydrazine to compound	Orange ppt formed.	Eg: Note: esters, amides, carboxylic acids **give NO ppt** with 2,4-dinitrophenylhydrazine even though they contain C=O group.
Fehling's solution	Aliphatic aldehyde	Warm cpd with Fehling's solution.	Reddish brown ppt of Cu_2O formed.	$RCHO + 2Cu^{2+} + 5OH^- \rightarrow RCOO^- + Cu_2O + 3H_2O$ A carboxylate salt with the same number of C as the aldehyde is formed. Methanoic acid (with the H–C=O group) also reacts with Fehling's solution (and Tollens' rgt), itself being oxidised to CO_3^{2-}. $HCOOH + 2Cu^{2+} + 6OH^- \rightarrow CO_3^{2-} + Cu_2O + 4H_2O$ Benzaldehyde (aromatic aldehydes) **DOES NOT** react with Fehling's solution.
Tollens' reagent	Aldehyde	Warm cpd with Tollens' solution.	Silver mirror formed.	$RCHO + 2Ag(NH_3)_2^+ + 3OH^- \rightarrow RCOO^- + 2Ag + 4NH_3 + 2H_2O$ A carboxylate salt with the same no of C as the aldehyde is formed. Benzaldehyde reacts with Tollens' reagent with much less ease and a grey ppt may be obtained instead of a silver mirror. Methanoic acid is oxidised to carbonate ion: $HCOOH + 2Ag(NH_3)_2^+ + 4OH^- \rightarrow CO_3^{2-} + 2Ag + 4NH_3 + 3H_2O$

J SUMMARY OF COMMON REAGENTS
Table 1: Common reagents used for identifying various functional groups

Organic Compound	Alkene	Alkyl benzene	Halogenoalkane	Alcohol			Phenol	Carbonyl compound				Carboxylic acid
				1°/2°	3°	Alcohol with $CH_3CH(OH)$ – structure		Aldehyde	Benzaldehyde	Ketone	Carbonyl with CH_3CO- structure	
Functional Group	$C=C$	(toluene)	RX	ROH (RCH_2OH or R_2CHOH)	R_3COH		(phenol)	$RCHO$	C_6H_5CHO	$RCOR$		$RCOOH$
Example	$CH_2=CH_2$	CH_3 (on ring)	CH_3CH_2Br	$CH_3(CH_2)_2OH$	$(CH_3)_3COH$	CH_3CH_2OH	(phenol, OH)	CH_3CH_2CHO	(benzaldehyde, CHO)	$(C_2H_5)_2CO$	CH_3COCH_3	CH_3COOH
Br₂(aq)	decolourise						Decolourise, white ppt					
FeCl₃ neutral							Violet colouration					
KMnO₄/H₂SO₄, heat	Purple MnO₄⁻ decolourise	Purple MnO₄⁻ decolourise		Purple MnO₄⁻ decolourise		Purple MnO₄⁻ decolourise		Purple MnO₄⁻ decolourise	Purple MnO₄⁻ decolourise			
K₂Cr₂O₇/H₂SO₄, heat				Orange → green		Orange → green		Orange → green	Orange → green			
Na				H₂ evolved	H₂ evolved	H₂ evolved	H₂ evolved					H₂ evolved
NaOH(aq)							Phenol dissolves					Heat evolved
Na₂CO₃(aq)												CO₂ evolved
I₂(aq)/NaOH(aq), heat						Yellow ppt (iodoform)					Yellow ppt (iodoform)	
2,4-DNPH								Orange ppt	Orange ppt	Orange ppt	Orange ppt	
Tollens' reagent, warm								Silver mirror	Silver mirror			
Fehling's solution, warm								Reddish brown ppt				
NaOH(aq), heat, cool, acidify, AgNO₃(aq)			White ppt ⇒ X = Cl, Cream ppt ⇒ X = Br, Yellow ppt ⇒ X = I									

R = alkyl group

- Test for RCOX: Add water, white fumes of HX formed. OR Add aqueous AgNO₃. White fumes and white, cream or yellow ppt for X = Cl, Br or I respectively.
- Test for salts of amine, eg $RNH_3^+NO_3^-$. Heat gently with aq NaOH. If R contains 5C or less, gase evolved turned moist red litmus paper blue. For R with 6 C or more, a immiscible layer formed.
- Test for amide: $RCONH_2$ Heat strongly with aq NaOH. Gas evolved turned moist red litmus paper blue.

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Table 2: Reactions with common oxidising agents
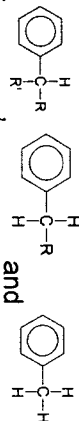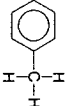
	KMnO₄(aq), H₂SO₄(aq), heat	K₂Cr₂O₇(aq), H₂SO₄(aq), heat	KMnO₄(aq), NaOH(aq), heat	KMnO₄(aq), NaOH(aq), Cold	Remarks/Equations
Alkene	✓ Purple KMnO₄ decolourised	✗	✓ Purple KMnO₄ decolourised, brown MnO₂ ppt	✓ Purple KMnO₄ decolourised, brown MnO₂ ppt	CO₂ may be produced for terminal alkenes. E.g. $CH_3CH=CH_2 + 5[O] \rightarrow CH_3COOH + CO_2 + H_2O$. Oxidative cleavage of alkenes with hot KMnO₄.
Alkybenzene	✓ Purple KMnO₄ decolourised	✗	✓ Purple KMnO₄ decolourised; benzoate salt formed	✗	$C_6H_5CH_2CH_3 + 6[O] \rightarrow C_6H_5COOH + CO_2 + 2H_2O$. Oxidation only occurs when alkyl side-gp has H atom on C attached to benzene ring, i.e. [benzene ring with C bonded to H, R] and [benzene ring with C bonded to H, H]
1°/2° Alcohol	✓ Purple KMnO₄ decolourised	✓ Orange K₂Cr₂O₇ turns green	✓ Purple KMnO₄ decolourised	✗	1° alc are oxidised to carboxylic acids. 1° alc are oxidised to aldehydes using K₂Cr₂O₇/H⁺ and heat with immediate distillation. 2° alc are oxidised to ketones. E.g. $(CH_3)_2CHOH + [O] \rightarrow (CH_3)_2C=O + H_2O$
3° Alcohol	✗	✗	✗	✗	3° alcohols are generally resistant to oxidation except for 3° alcohols with phenyl gp attached to hydroxyl C contain a benzene ring and can be oxidised to benzoic acid by warming with KMnO₄/H⁺: E.g. $C_6H_5C(OH)(CH_3)_2 + 8[O] \rightarrow C_6H_5COOH + 2CO_2 + 3H_2O$
Benzaldehyde	✓ Purple KMnO₄ decolourised	✓ Orange K₂Cr₂O₇ turns green	✓ Purple KMnO₄ decolourised; benzoate salt formed	✗	E.g. $C_6H_5CHO + [O] \rightarrow C_6H_5COOH$
Aldehyde	✓ Purple KMnO₄ decolourised	✓ Orange K₂Cr₂O₇ turns green	✓ Purple KMnO₄ decolourised; salt formed	✗	Aldehydes are oxidised to carboxylic acids. E.g. $CH_3CHO + [O] \rightarrow CH_3COOH$
Ketone	✓ Purple KMnO₄ decolourised for phenyl ketones	✗	✗	✗	Most ketones are resistant to oxidation except for phenyl ketones which can be oxidised to benzoic acid by warming with KMnO₄/H⁺: E.g. $C_6H_5COCH_2CH_3 + 7[O] \rightarrow C_6H_5COOH + 2CO_2 + 2H_2O$
Ester	✓ Purple KMnO₄ decolourised;	✗	✓ Purple KMnO₄ decolourised	✗	Warming with dil H₂SO₄, hydrolyses the ester into an acid and alcohol. If either the acid or alcohol can undergo oxidation (acid = HCOOH or ethanedioic acid; alcohol = CH₃OH, 1° or 2° alcohol), decolourisation of KMnO₄ observed. E.g. (1) $HCOOC(CH_3)_3 + H_2O \longrightarrow HCOOH + C(CH_3)_3OH$; $HCOOH + [O] \longrightarrow CO_2 + H_2O$ (2) $CH_3COOCH_2CH_2CH_3 + H_2O \longrightarrow CH_3COOH + CH_3CH_2CH_2OH$; $CH_3CH_2CH_2OH + 2[O] \longrightarrow CH_3CH_2COOH + H_2O$

Table 3: Reactions with common reducing agents

	H₂, Ni, heat	LiAlH₄, dry ether	NaBH₄ in methanol	Sn/conc HCl	Remarks/Equations
Alkene	✓	✗	✗	✗	Reaction can be considered as catalytic hydrogenation/addition/reduction (but **NOT** electrophilic addition). E.g. $RCH{=}CHR' + H_2 \longrightarrow RCH_2CH_2R'$
Benzene	✓*	✗	✗	✗	*Benzene will be reduced to cyclohexane only when heated with H_2, Ni under high temperature and pressure (100–200°C, 1500 psi) $C_6H_5 + 3H_2 \longrightarrow C_6H_{12}$
Nitrobenzene	✗	✗	✗	✓	E.g. $C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 + 2H_2O$ phenylamine formed NaOH(aq) is used to liberate free amine $(C_6H_5NH_2)$ from amine salt $(C_6H_5NH_3{}^+Cl^-)$formed.
Nitrile	✓	✓	✗	✗	Reduction of nitrile always leads to formation of 1° amine. H_2/Ni, heat: $RCN + H_2 \longrightarrow RCH_2NH_2$ LiAlH₄, dry ether: $RCHO + 2[H] \longrightarrow RCH_2OH$
Aldehyde	✓	✓	✓	✗	H_2/Ni, heat: $RCHO + H_2 \longrightarrow RCH_2OH$ LiAlH₄, dry ether or NaBH₄ $RCHO + 2[H] \longrightarrow RCH_2OH$
Ketone	✓	✓	✓	✗	H_2/Ni, heat: $RCOR' + H_2 \longrightarrow RCH(OH)R'$ LiAlH₄, dry ether or NaBH₄ $RCOR' + 2[H] \longrightarrow RCH(OH)R'$
Carboxylic Acid	✗	✓	✗	✗	Carboxylic acid cannot be reduced by H_2/ Ni. Need to use LiAlH₄. $RCOOH + 4[H] \longrightarrow RCH_2OH + H_2$

Table 4: Common reagents used to identify some acidic compounds

	Na(s)	NaOH(aq)	Na$_2$CO$_3$(aq) or NaHCO$_3$(aq)	PCl$_5$	Remarks/Equations
Alcohol	✓ H$_2$ evolves	✗	✗	✓ white fumes of HCl	PCl$_5$ cannot distinguish between alcohol and carboxylic acid. ROH + PCl$_5$ → RCl + POCl$_3$ + HCl
Phenol	✓ H$_2$ evolves	✓ Phenol dissolves	✗	✗	C$_6$H$_5$OH (s) + NaOH (aq) → C$_6$H$_5$O$^-$Na$^+$ (aq) + H$_2$O (l) This test can be used to distinguish phenol from solids that are insoluble in aq NaOH but will not be able to distinguish phenol from benzoic acid.
Carboxylic Acid	✓ H$_2$ evolves	✓	✓ CO$_2$ evolves	✓ white fumes of HCl	E.g. 2CH$_3$COOH + CO$_3$$^{2-}$ → 2CH$_3$COO$^-$ +H$_2$O + CO$_2$ Acid chloride will also give effervescence of CO$_2$ with aq Na$_2$CO$_3$ too but fumes of HCl is also evolved: E.g. CH$_3$COCl + H$_2$O + → CH$_3$COOH+ HCl 2H$^+$ + CO$_3$$^{2-}$→CO$_2$ + H$_2$O

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Table 5: Common reagents used to identify carbonyl compounds

	2,4-DNPH	Tollens' regent, warm $[Ag(NH_3)_2]^+$, OH^-	Fehling's reagent, warm Cu^{2+}, OH^-	$I_2(aq)$, $NaOH(aq)$, warm	Remarks/Equations
Aldehyde (aliphatic)	✓ Orange ppt	✓ Ag mirror	✓ Reddish brown ppt of Cu_2O	✓ (see remarks) Yellow ppt of CHI_3 only for CH_3CHO	Ethanal is the only aldehyde that gives yellow ppt of CHI_3 when heated with aq. alkaline I_2.
Benzaldehyde (aromatic aldehydes : CHO gp bonded directly to benzene ring)	✓ Orange ppt	✓ Ag mirror	✗	✗	Benzaldehyde **DOES NOT** react with Fehling's solution.
Ketone	✓ Orange ppt	✗	✗	✓ (see remarks) Yellow ppt of CHI_3 only for methyl ketones (CH_3CO-)	Only ketones with CH_3CO— unit give yellow ppt of CHI_3 when heated with aq. alkaline I_2.

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RAFFLES INSTITUTION
Year 6 H2 CHEMISTRY 2016
Inorganic Chemistry Revision

1. Summary

1.1 Periodicity Summary

Periodicity: Trends Across Period 3

A. Elements (Na, Mg, Al, Si, P, S, Cl₂, Ar)

B. Oxides (Na₂O, MgO, Al₂O₃, SiO₂, P₄O₆/P₄O₁₀, SO₂/SO₃, Cl₂O₇)

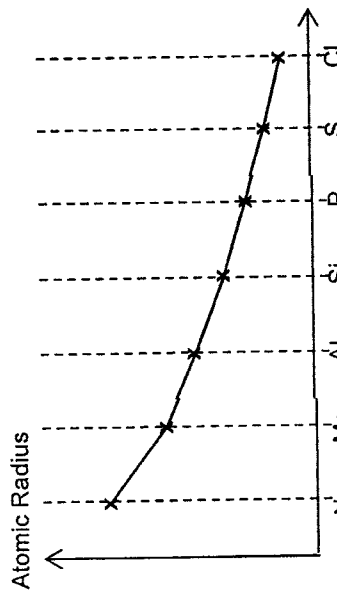**C. Chlorides (NaCl, MgCl₂, AlCl₃, SiCl₄, PCl₃/PCl₅, SCl₂/S₂Cl₂)**

C1. Types of Chlorides:

- NaCl & MgCl₂: ionic chlorides. High mp and bp.
- AlCl₃, SiCl₄, PCl₃/PCl₅, SCl₂/S₂Cl₂ are all covalent with simple molecular structures. Mp and bp low due to weak IMF.
- Bp: AlCl₃ (actually Al_2Cl_6 ∵ of dimerisation, highest no. of e⁻)> PCl₃ (∵ of pd–pd interactions)>SiCl₄ >S₂Cl₂
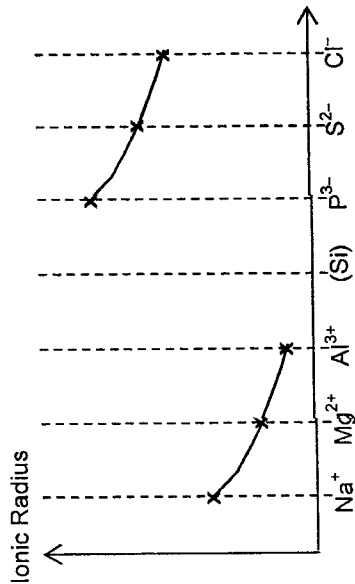
C2. Reaction of Chlorides with Water (Graph C2)

- NaCl is ionic & soluble. Dissolves in H₂O to give NaCl (aq) : (pH = 7)
  $$NaCl\ (s)+aq \rightarrow NaCl\ (aq)$$
- MgCl₂ & AlCl₃ dissolve in water to give Mg²⁺ & Al³⁺. The aq ions exist as aqua complexes and hydrolyse in water:
  $$[Mg(H_2O)_6]^{2+} \rightleftharpoons [Mg(H_2O)_5(OH)]^+ + H^+$$
  (pH ≈6.5)
  $$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H^+$$
  (pH ≈3)
- SiCl₄, PCl₅ and S₂Cl₂ hydrolyses in water: (pH ≈2 ∵ HCl is strong acid.)
  $$SiCl_4\ (l)+ 2H_2O\ (l) \rightarrow SiO_2(s) + 4HCl\ (aq)$$

Refer to Graph B3 and C3 for melting points of oxides and chlorides

B1. Types of Oxides (Rxn with acids and bases):

- Na₂O & MgO: ionic oxides. Basic oxides that react with acids but not bases:
  $$Na_2O(s) +2H^+(aq) \rightarrow 2Na^+(aq) +H_2O(l)$$
  $$MgO(s) +2H^+(aq) \rightarrow Mg^{2+}(aq) +H_2O(l)$$
- Al₂O₃: ionic oxide with high covalent character. Amphoteric oxide tt reacts with acids & bases:
  $$Al_2O_3(s) +6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$$
  $$Al_2O_3(s) +2OH^-(aq) + 3H_2O(l) \rightarrow 2Al\ (OH)_4^-(aq)$$
- SiO₂: Covalent oxide with giant molecular structure. Acidic oxide that reacts with conc NaOH:
  $$SiO_2(s) +2OH^-(aq) \rightarrow SiO_3^{2-}(aq) + H_2O(l)$$

B2. Reaction of Oxides with Water (Graph B2)

- Na₂O is ionic & soluble. Reacts with H₂O to form aq NaOH: (pH ≈ 12)
  $$Na_2O(s) +H_2O(l) \rightarrow 2NaOH\ (aq)$$
- MgO: ionic oxide &sparingly soluble (pH ≈ 9):
  $$MgO(s)+H_2O(l) \rightleftharpoons Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq)+2OH^-(aq)$$
- Al₂O₃ & SiO₂: insoluble in H₂O ⇒ after adding Al₂O₃ & SiO₂ to H₂O, pH of resultant mixture = 7.
- P₄O₁₀, SO₃ and Cl₂O₇ reacts with water to give oxoacids (pH ≈ 2)
  $$P_4O_{10}(s) +6H_2O(l) \rightarrow 4H_3PO_4\ (aq)$$

Chemical Properties

A5. 1st Ionisation Energy (Graph A5):

- 1st IE generally ↑ across period due to ↑ Z_{eff} as number of protons ↑ but shielding ≈ constant. 2 exceptions:
1) 1st IE of Mg>Al because e⁻ of Al removed from a 3p orbital which is higher in energy than 3s orbital where e⁻ of Mg is removed from.
2) 1st IE of P>S because e⁻ of S removed from a paired orbital and is aided by e⁻–e⁻ repulsion.

A6. Rxn with O₂

Element	Deg of Rxn	Oxide formed
Na	vigorous	Na₂O
Mg	vigorous	MgO
Al	vigorous at 1st then slow	Al₂O₃
Si	slow	SiO₂
P	vigorous	P₄O₆ &/or P₄O₁₀
S	slow	SO₂ &/or SO₃

A7. Rxn with Cl₂

Element	Deg of Rxn	Chloride formed
Na	vigorous	NaCl
Mg	vigorous	MgCl₂
Al	vigorous	AlCl₃
Si	slow	SiCl₄
P	slow	PCl₃ &/or PCl₅
S	slow	SCl₂ &/or S₂Cl₂

A8. Variation in Oxidation No. of Oxides and Chlorides

- [O] no. of Na, Mg and Al in oxide and chlorides are fixed at +1, +2 and +3 respectively as the metals loses or shares (only for AlCl₃) their valence e⁻(s) in bonding.
- Si shares its 4 valence e⁻ in oxide and chloride formation so its [O] no. is +4.
- P forms P₄O₆ & PCl₃ with [O] no. of +3 by sharing 3 e⁻ to achieve octet configuration. It can also expand its octet by promoting one 3s e⁻ to 3d subshell to form P₄O₁₀ and PCl₅ with [O] no.+5
- S forms SO₂ with [O] no. +4 by promoting one 3p e⁻ to 3d subshell and SO₃ with [O] no. +₆) promoting one 3s and one 3p e⁻ to 3d subshell.

Physical Properties

A1. Atomic radius (Graph A1)

↓ across period due to ↑ Z_{eff} as number of protons ↑ but shielding ≈ constant.

A2. Ionic Radius (Graph A2)

- Cationic radius (r⁺) ↓ from Na⁺ to Al³⁺ as Na⁺, Mg²⁺ & Al³⁺ are isoelectronic but nuclear charge ↑ from Na⁺ to Al³⁺. Anionic radius (r⁻) ↓ from P³⁻ to Cl⁻ as P³⁻, S²⁻ & Cl⁻ are isoelectronic from P to Cl. Also, ↓ in −ve charge ⇒ ↓ in electronic repulsion.
- r₊ < r⁻ ∵ period 3 cations has one shell less than anions.

A3. Melting point (Graph A3)

- Element changes from metals (Na, Mg, Al) to non-metals with giant cmolecular structure (Si) and simple molecular structure (P₄, S₈, Cl₂ and Ar).
- Mp of Na, Mg and Al are high with mp of Na<Mg<Al ∵ ↑ no. of delocalised e⁻ so that metallic bond strength↑.
- Mp of Si very high ∵melting involves breaking strong Si–Si bond.
- Mp of P₄, S₈, Cl₂ and Ar low ∵ weak id–id interactions between molecules.

A4. Electrical Conductivity (Graph A4)

- Na, Mg and Al are metals and are good electrical conductors. Electrical conductivity ↑ from Na to Al ∵ ↑ no. of delocalised e⁻.
- Si is a semi-conductor and conducts electricity minimally.
- P, S, Cl₂ and Ar are insulators of electricity.

A1: Variation of Atomic Radius for Period 3 Elements

Atomic Radius

Na Mg Al Si P S Cl

A2: Variation of Ionic Radius for Period 3 Elements

Ionic Radius

Na⁺ Mg²⁺ Al³⁺ (Si) P³⁻ S²⁻ Cl⁻

A3: Variation of Melting Points for Period 3 Elements

Melting Point

Na Mg Al Si P₄ S₈ Cl₂

A4: Variation of Electrical Conductivity for Period 3 Elements

Electrical Conductivity

Na Mg Al Si P S Cl

0

B2: Variation of pH of resultant mixture when Period 3 Oxide is added to water

pH

Na₂O MgO Al₂O₃ SiO₂ P₄O₁₀ SO₃ Cl₂O₇

7

B3: Variation of Melting Points for Period 3 Oxides

Melting Point

covalent oxide with giant covalent structure

covalent oxide with simple molecular structure

Ionic oxide

Na₂O MgO Al₂O₃ SiO₂ P₄O₁₀ SO₃ Cl₂O₇

A4: Variation of 1ˢᵗ Ionisation Energy for Period 3 Elements

1ˢᵗ Ionisation Energy

Na Mg Al Si P S Cl

C2: Variation of pH of resultant mixture when Period 3 Chloride is added to water

pH

NaCl MgCl₂ AlCl₃ SiCl₄ PCl₅ S₂Cl₂ Cl₂

7

C3: Variation of Melting Points for Period 3 Chlorides

covalent chloride with simple molecular structure

Ionic chloride

Melting Point

NaCl MgCl₂ AlCl₃ SiCl₄ PCl₅ S₂Cl₂ Cl₂

1.2 Group II Summary

A. Elements:

Be, Mg, Ca, Sr, Ba

Solubility of common ionic compounds:

- All ammonium, potassium and sodium compounds are soluble.
- All nitrates are soluble.
- All halides ($X^- = Cl^-$, Br^- or I^-) are soluble except AgX and PbX_2.
- All sulphates are soluble except $PbSO_4$ and $BaSO_4$.
- All carbonates are insoluble except carbonates of NH_4^+, K^+ and Na^+.
- All hydroxides are insoluble except Gp I hydroxides (eg NaOH and KOH) and $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$. Metal oxides have similar solubility as metal hydroxides.

Reactions of Common Cations with aq NaOH:

- No ppt, no NH_3 on warming $\Rightarrow$ H^+, Na^+, K^+
- No ppt, NH_3 on warming $\Rightarrow$ NH_4^+
- White ppt insoluble in xs aq NaOH $\Rightarrow$ Group II cations: Mg^{2+}, Ca^{2+}, Ba^{2+}
- White ppt soluble in xs aq NaOH $\Rightarrow$ Pb^{2+}, Al^{3+}, Zn^{2+}
- White ppt insoluble in xs aq NaOH, turns brown on standing $\Rightarrow$ Mn^{2+}
- Greyish green ppt soluble in xs aq NaOH $\Rightarrow$ Cr^{3+}
- Dirty green ppt, insoluble in xs aq NaOH $\Rightarrow$ Fe^{2+}
- Reddish brown ppt, insoluble in xs aq NaOH $\Rightarrow$ Fe^{3+}
- Blue ppt. insoluble in xs aq NaOH $\Rightarrow$ Cu^{2+}

Reactions of Common Cations with aq NH₃:

- No ppt $\Rightarrow$ H^+, Na^+, K^+, Ca^{2+}, Ba^{2+}
- White ppt insoluble in xs aq NH_3 $\Rightarrow$ Mg^{2+}, Pb^{2+}, Al^{3+}
- White ppt soluble in xs aq NH_3 $\Rightarrow$ Zn^{2+} [due to formation of $Zn(NH_3)_4^{2+}$ (aq)]
- White ppt insoluble in xs aq NH_3, turns brown on standing $\Rightarrow$ Mn^{2+}
- Greyish green ppt, insoluble in xs aq NH_3 $\Rightarrow$ Cr^{3+}
- Dirty green ppt, insoluble in xs aq NH_3 $\Rightarrow$ Fe^{2+}
- Reddish brown ppt, insoluble in xs aq NH_3 $\Rightarrow$ Fe^{3+}

Test for Anions:

- CO_3^{2-}: reacts with H^+ to give CO_2.
- SO_3^{2-}: reacts with H^+ to give SO_2.
- NO_3^-: reacts with Al foil and aq NaOH on heating to give NH_3.
- SO_4^{2-}: reacts with aq $Ba(NO_3)_2$ to give white ppt, insoluble in dil HNO_3.
- CrO_4^{2-}: turns from yellow to orange on addition of H^+
- Cl^-: reacts with aq $AgNO_3$ to give white ppt, insoluble in dil HNO_3.
- Br^-: reacts with aq $AgNO_3$ to give cream ppt, insoluble in dil HNO_3.
- I^-: reacts with aq $AgNO_3$ to give yellow ppt, insoluble in dil HNO_3.

Test for Gases:

- H_2: extinguishes lighted splinter with a 'pop' sound.
- O_2: relights a glowing splinter
- CO_2: forms a white ppt with aq $Ca(OH)_2$
- SO_2: decolourises aq $KMnO_4$
- Cl_2: turns moist blue litmus red then bleach it.
- NH_3: turns moist red litmus blue.

Group II Chemistry

A1. Reactivity as Reducing Agent:

- Group II metals lose e^- in their rxn: $M \rightarrow M^{2+} + 2e^-$, ie they become oxidised and hence act as reducing agents (RA)
- Strength of a RA depends on its ease to be oxidised.
- Greater ease of oxidation $\Rightarrow$ greater strength as RA.
- Since [O] involves loss of e^-, strength of RA $\uparrow$ when ease of loss of e^- $\uparrow$.
- Ease of loss of e^- $\uparrow$ down Gp II as valence e^- is further from nucleus and shielded by more filled inner quantum shells.
- Hence reactivity as RA $\uparrow$ down Gp II

A2. Reaction with Water:

Element	Deg of Rxn	Equations
Mg	Very slow rxn with cold water.	–
Ca	Readily	M(s) + $2H_2O(l)$ --> $M(OH)_2$ (aq) + H_2(g)
Sr	Vigorously	
Ba	Very vigorously	

A3. Reaction with Air:

Element	Deg of Rxn	Equations
Mg	Ignites above mp	2M(s) + O_2(g) --> 2MO(s)
Ca	Ignites on heating	
Sr	Ignites spontaneously	
Ba		

B. Type of Gp II oxides

- BeO is amphoteric and reacts with both acids and bases:
  $BeO + 2H^+ \rightarrow Be^{2+} + H_2O$
  $BeO + 2OH^- \rightarrow Be(OH)_4^{2-}$
- All other gp II oxides are basic and reacts with acids but not bases.

C. Thermal Stability of Group II Cpds containing oxoanions

- Thermal stability $\uparrow$ down Gp II.
- Cation size $\uparrow$ down Gp II resulting in $\downarrow$ in charge density and hence polarising power.
- Anion electron cloud is polarised to a smaller extent by cation resulting in $\downarrow$ weakening of covalent bond in anion.
- Hence a higher temperature is needed for decomposition of oxoanion to oxide.
- Decomposition of Nitrate on Heating:
  $M(NO_3)_2$ (s) $\rightarrow$ MO(s) + $2NO_2$(g) + $\frac{1}{2}O_2$ (g)
- Decomposition of Carbonate on Heating:
  MCO_3 (s) $\rightarrow$ MO(s) + CO_2(g)

D. Uses of Gp II Compounds

- MgO used as refractory material to line furnaces due to its high melting point.
- Lime (CaO) used to neutralize acidic soil.
  NB: Lime/ Quicklime = CaO; Slaked lime = $Ca(OH)_2$ (s); Limewater = $Ca(OH)_2$ (aq); Limestone = $CaCO_3$.

1.3 GROUP VII SUMMARY

Overview: Key reactivity for halogens is <u>redox</u> reactions.
(1) Oxidizing power trend
(2) Reaction with hydrogen
(3) Displacement of halide by more reactive halogen
(4) Reaction with water
   (oxidation of water, disproportionation)
(5) Reaction with thiosulfate
(6) Disproportionation in alkalis
   (oxidize S O.S $+2 \to +6$ or $+2.5$)
   (O.S $O \to +1, -1,$ or $+5, -1$)

Aside from F_2, typically Cl_2 is most reactive and most oxidizing.
It is best to have the skills to derive and balance the equations quickly, rather than memorizing them by rote.

(1) Oxidizing power
A substance that is readily reduced would oxidize another substance in a redox reaction.=> top of the group: more +ve E, higher oxidizing power.

Best oxidizing agent [OA]
↓
$F_2 + 2e^- \rightleftharpoons 2F^- \quad E^o = +2.87\ V$
$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \quad E^o = +1.36\ V$
$Br_2 + 2e^- \rightleftharpoons 2Br^- \quad E^o = +1.07\ V$
$I_2 + 2e^- \rightleftharpoons 2I^- \quad E^o = +0.54\ V$
↑
Weak Ox. agent   **Good reducing agent**
                 (since backward rxn takes place easily)
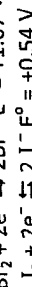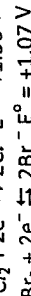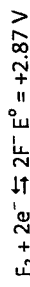
(2) Reaction with H₂
All react to give HX.
F_2: violent explosion. No heat or light required.
Cl_2: Violent explosion. UV light or heat to start reaction.
Br_2: Slow reaction. Heat and catalyst required.
I_2: Slow, incomplete/reversible reaction.

(3)<u>Displacement of halide by more reactive halogen</u>
Cl_2 displaces Br^-, I^-. Br_2 displaces I^-.
Eg: $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$

(4) Reaction with water
F_2 oxidizes H_2O to give O_2 and HF
Cl_2 disproportionates to +1 and -1 O.S.
Br_2 does not react.
I_2 dissolves in I^-(aq) by forming I_3^-(aq)
   $I_2(s) + I^-(aq) \rightleftharpoons I_3^-(aq)$
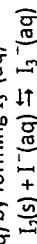
How to remember the equations?
- For redox reactions, you need to know the **oxidation states**
=> **formula of starting materials and products.**
- If O.S is known, the identity of the halide/halate can be determined. O.S of X increases by +2 for every O atom added. i.e.

-1	+1	+3	+5	+7
X^-	XO^-	XO_2^-	XO_3^-	XO_4^-

- The balanced equations can easily be derived.

*Note. Fast redox eqn balancing method
<u>Balancing Redox equations</u>
*Note. The best way to remember the reactions is to note:
(1) type of reaction., (2) for redox, note the Oxidation state(O.S) reached.

(1) use ΔO.S for each atom oxidized or reduced to determine no. of e^- transferred.
(2) use LCM(lowest common multiple) of the no. of e^- transferred to find stoichiometric ratio of [R] and [O] agents.
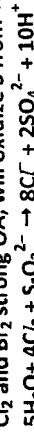(3) balance LHS and RHS charge with charged particles available (usually H^+ or OH^-)
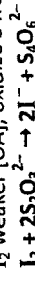(4) balance O and H atoms with H_2O last.
See next section for example with $S_2O_3^{2-}$

(5) Reaction with thiosulfate
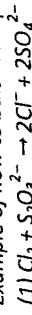Cl_2 and Br_2 strong OA, will oxidize S from +2 to +6
$5H_2O+ 4Cl_2 + S_2O_3^{2-} \rightarrow 8Cl^- + 2SO_4^{2-} + 10H^+$

I_2 weaker [OA], oxidize S from +2 to +2.5
$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$
*Standard and in databook.

Example of how to balance equations:
(1) $Cl_2 + S_2O_3^{2-} \rightarrow 2Cl^- + 2SO_4^{2-}$
    (0)   (+2)   (-1)   (+6)
$Cl(0 \rightarrow -1)$ 1 eln gain; $S(+2 \rightarrow +6)$ 4 eln lost.
So LCM is 4, ratio of Cl:S is 4:1 Thus
(2) $4Cl_2 + S_2O_3^{2-} \rightarrow 8Cl^- + 2SO_4^{2-}$
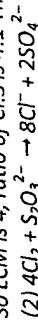
(3)Balance charge with H^+. excess 10 -ve charge on RHS so:
$4Cl_2 + S_2O_3^{2-} \rightarrow 8Cl^- + 2SO_4^{2-} + 10H^+$

(4) Balance O and H with H_2O. so:
$5H_2O+ 4Cl_2 + S_2O_3^{2-} \rightarrow 8Cl^- + 2SO_4^{2-} + 10H^+$
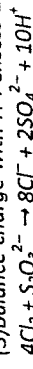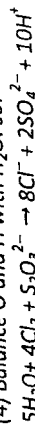
(6) Disproportionation in alkali
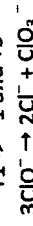Cl_2, good OA, but difficult to oxidize. so at rtp disproportionates in alkaline solutions.
Cold or rtp, Cl_2 0 → +1 and -1
   $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$
On warming. Further disproportionation
              +1 -> -1 and +5
   $3ClO^- \rightarrow 2Cl^- + ClO_3^-$
Overall/or Cl_2 in hot OH-: 0 -> -1 and +5
   $3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$
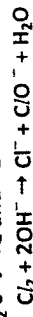
Br_2, I_2 more easily oxidized to higher O.S
        0 → +5 and -1
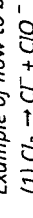 $3X_2 + 6OH^- \rightarrow 5X^- + XO_3^- + 3H_2O$
T>15 °C for Br_2.
How to remember the equations?
Same redox method used in previous section can be used for any reaction here.
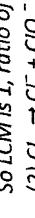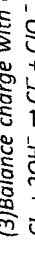*Example of how to balance equations:*
(1) $Cl_2 \rightarrow Cl^- + ClO^-$
    (0) (-1)   (+1)
$C(0 \rightarrow -1)$ 1 eln gain; $Cl(0 \rightarrow +1)$ 1 eln lost.
So LCM is 1, ratio of $Cl^-:ClO^-$ is 1:1 Thus
(2) $Cl_2 \rightarrow Cl^- + ClO^-$
(3)Balance charge with OH⁻. excess 2 -ve charge on RHS so:
$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^-$
(4) Balance O and H with H_2O. so:
   $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$
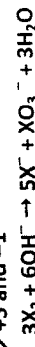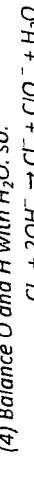
X₂ in hot OH⁻

Example of how to balance equations:

(1) $Cl_2 \rightarrow Cl^- + ClO_3^-$
   (0) (-1) (+5)

$Cl(0 \rightarrow -1)$ 1 eln gain; $Cl(0 \rightarrow +5)$ 5 eln lost.
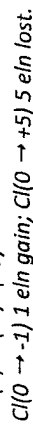
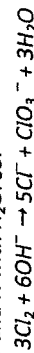So LCM is 5, ratio of Cl^- :ClO_3^- is 5:1 Thus
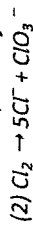
(2) $Cl_2 \rightarrow 5Cl^- + ClO_3^-$

Balance Cl atoms $3Cl_2 \rightarrow 5Cl^- + ClO_3^-$

(3) Balance charge with OH^-. excess 6 -ve charge on RHS so:

$3Cl_2 + 6 OH^- \rightarrow 5Cl^- + ClO_3^-$

(4) Balance O and H with H_2O. so:
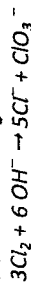
$$3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$$

If counter-ion is to be included, simply add to balance off against all ions. For eg. if NaOH was used, add Na^+ to balance of all the anions.

Thus:

$$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

(7) Physical Properties of halogens

- Colour intensifies down the group.

Boiling point

- b.p. increases down the group as size of electron cloud increases, van der Waals' forces between X_2 molecules increase.

b.p: $F_2 < Cl_2 < Br_2 < I_2$
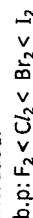
X-X Covalent bond strength.

- F-F bond is unusually weak. The F-F bond is very short and the atoms are close together. The lone pair electrons on both atoms repel and push the atoms apart, weakening the bond.

- The X-X bond down the group weakens, since the atoms become larger down the group and orbital overlap is less effective. Thus Cl-Cl bond is strongest amongst X_2 molecules.

X-X covalent bond strength: F-F << Cl-Cl > Br-Br > I-I

Properties of halides

(1) hydrogen halides: physical properties, acidity
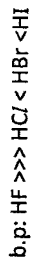
(2) halide salts,
- reaction with conc. H_2SO_4
- precipitation reactions (Ag^+)

(1) Hydrogen halides

Boiling point

- **b.p. is especially high for H-F, since there are strong hydrogen bonds between HF molecules.**

- b.p is lowest for H-Cl < H-Br < H-I. Since the size of electron cloud increases down the group, the strength of the van der Waals' forces increase down the group for HX.

b.p: HF >>> HCl < HBr <HI

H-X covalent bond strength

The H-X covalent bond weakens down gp VII. As the X atom becomes larger, orbital overlap with H atom becomes poorer.

Cov bond strength: H-F> H-Cl > H-Br > H-I

Stability

- H-Br decomposes slightly with heat.

- H-I is least stable and decomposes easily with heat

Acidity

- H-F bond is strongest and so HF is a weaker acid, ionizing less readily.

- HCl, HBr, HI are all strong acids and ionize completely in water. However relatively, acid strength of HF << HCl < HBr < HI

(2) Halide salts

Reaction with c. H_2SO_4

H_2SO_4 has 2 roles

- Acid => acid base reaction possible

- S atom at +6 O.S. Thus it <u>can be reduced</u> and has limited oxidizing power.

Thus

(1)

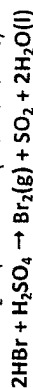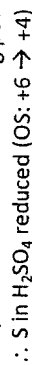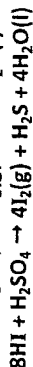With any halide salt eg. NaX, protonation to HX occurs first:
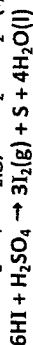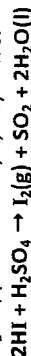
$H_2SO(l) + NaX(s) \rightarrow HX(g) + NaHSO$
     White fumes evolved.

(2)

HCl/Cl^- has a poor reducing power and no further redox reactions observed.

HBr/Br^- has moderate reducing power,

∴ S in H_2SO_4 reduced (OS: +6 → +4)

$2HBr + H_2SO_4 \rightarrow Br_2(g) + SO_2 + 2H_2O(l)$
    Reddish brown liquid, fumes evolved.

HI/I^- has good reducing power, and will reduce S atom in H_2SO_4 (O.S +6 → +4, 0, -2). Thus:

$2HI + H_2SO_4 \rightarrow I_2(g) + SO_2 + 2H_2O(l)$

$6HI + H_2SO_4 \rightarrow 3I_2(g) + S + 4H_2O(l)$

$8HI + H_2SO_4 \rightarrow 4I_2(g) + H_2S + 4H_2O(l)$

How to remember the equations?
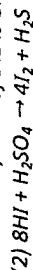
Same redox method used in previous section can be used for any reaction here.

Example, HI with H_2SO_4 to reduce S (OS +6 → -2)

(1) $HI + H_2SO_4 \rightarrow I_2 + H_2S$
  (-1)   (+6) (0)   (-2)
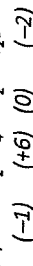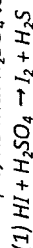
$I(-1 \rightarrow 0)$ 1 eln lost; $S(+6 \rightarrow -2)$ 8 eln gain.
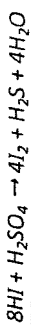
So LCM is 8, ratio of I :S is 8:1 Thus

(2) $8HI + H_2SO_4 \rightarrow 4I_2 + H_2S$

(make sure all the I and S atoms are balanced)

(3) Balance charge: not necessary since all neutral

(4) Balance O and H with H_2O. so:

$$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$$

Precipitation of silver halides, AgX

All halides form precipitates with Ag^+:

$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$
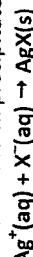
AgCl – white ppt, AgBr – cream ppt, AgI – yellow ppt

AgI has the smallest K_{sp} and lowest solubility.

Excess $NH_3(aq)$ can dissolve AgCl by forming silver diammine

(l) $[Ag(NH_3)_2]^+(aq)$ complex.

$Ag^+(aq) + NH_3 (aq) \rightarrow [Ag(NH_3)_2]^+(aq)$
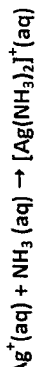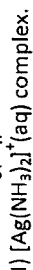
$[Ag^+(aq)]$ drops and IP falls below K_{sp} of AgCl hence, AgCl ppt dissolves.

First Row Transition Elements

A transition element is defined as an <u>element that possesses an incomplete d subshell in at least one of its stable ions</u>. Scandium is not a transition metal as its only common ion Sc^{3+} does not possess d electron. Zinc is also not a transition metal as it contains a full 3d subshell in its only oxidation state +2. Note: Cr and Cu has one 4s electron only as it is more energetically favourable for them to have a half-filled or fully filled 3d subshell.

Element	(Sc)	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	(Zn)
Electronic configuration	$[Ar]3d^14s^2$	$[Ar]3d^24s^2$	$[Ar]3d^34s^2$	$[Ar]3d^54s^1$	$[Ar]3d^54s^2$	$[Ar]3d^64s^2$	$[Ar]3d^74s^2$	$[Ar]3d^84s^2$	$[Ar]3d^{10}4s^1$	$[Ar]3d^{10}4s^2$

Essentially for TEs, the special properties arise from the presence of d-electrons and d orbitals: eg catalytic property, colour.

Physical Trends

1st 3 TMs have <u>smaller atomic radii</u> than s-block metals: S-block metals use inner shell s and p electrons for shielding while s, p and d electrons are used for shielding in TMs. d-orbitals are more diffuse and the d electrons provide poor shielding effect; thus TMs experience a higher effective nuclear charge.

Later TMs have <u>almost constant atomic radii</u> and <u>1st I.E.</u>: Across the d-block, nuclear charge increases but shielding effect increases as additional electrons are added to the penultimate (inner) 3d subshell. The increase in shielding effect offsets the increase in nuclear charge and effective nuclear charge increases gradually. Hence the atomic radii and first I.E. are almost constant.

note there is no contradiction between the first two points. For the latter TMs, the 4s electrons are repelled out, as well as the d-subshell having a higher electron density; thus shielding effect from d electrons is insignificant in earlier TMs while significant for latter TMs.

TMs have <u>higher melting points</u> and <u>boiling points</u> as well as <u>higher electrical conductivity</u>: The 4s and 3d electrons are available for delocalization, hence there are more delocalized electrons and cations have higher charge. Metallic bonding is stronger due to these and smaller cationic radii compared to s-block metals. There are also more delocalized electrons to conduct electricity.

Variable Oxidation State

TMs have variable oxidation states (OS) as the <u>3d and 4s electrons are very similar in energy</u>. When TMs lose electrons, they lose the 4s electrons first and the +2 OS is common. The M^{4+} ion is rare and in higher oxidation states, the element is usually not found in the free metal ion but covalently bonded or as oxyanions, e.g. MnO_4^-.

Catalytic Properties

Catalysts: provide alternate reaction path with lower Ea. Itself not consumed in net reaction. 2 types:

<u>Homogeneous</u>: Same phase (eg in aq solution) involves rapid conversion from one oxidation state to another oxidation state. Eg. Fe^{2+} in the reaction between I^- and $S_2O_8^{2-}$.
The metal ion acts as an electron carrier. Higher OS cation oxidizes one reagent, while lower OS cation reduces another.
-*uncatalysed reaction*: slow because of high Ea. For eg I^- and $S_2O_8^{2-}$ both –ve charged and repel.
-*catalysed reaction*: multiple steps, new reaction path.
Eg: Fe^{3+} oxidizes I^- to give Fe^{2+} and I_2.
Fe^{2+} then reduced $S_2O_8^{2-}$ to SO_4^{2-}. Each step has lower Ea, since oppositely charged ions which attract are involved, thus the reaction is faster. $E°_{cell}$ for each step can be calculated to show feasibility.

<u>Heterogeneous</u>:. Depends on the availability of vacant low-lying orbitals. and availability of d electrons for bonding with reactants.
E.g. Fe in Haber process, Ni in hydrogenation of alkenes, MnO_2 in decomposition of H_2O_2, V_2O_5 in Contact Process.
-diffusion, adsorption on surface (bond breaking within reagent molecules, effective orientation of reactants), -reaction (new bonds form to give products), -diffusion(product molecules leave)

Formation of Complex Ions

TM ions have high charge densities and can attract ligands, which are neutral molecules or anions containing lone pairs. The ligands form dative covalent bonds with the central metal ion to form complex ions.

Coordination Number	Examples	Shape
6	$[Fe(CN)_6]^{3-}$, $[Cu(edta)]^{2-}$	Octahedral
4	$[CuCl_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$	Square planar or tetrahedral
2	$[Ag(NH_3)_2]^+$, $[CuCl_2]^-$	Linear

Key concepts:
1) Ligand exchange. Takes place when more stable complexes can be formed. Expect to see colour change, etc

2) E° will be different. For eg
$Fe^{3+}(aq)(E° = +0.77 V)$ vs $[Fe(CN)_6]^{3-}(aq)$ $(E° = +0.36 V)$
-ve charge complex repels electrons and less easily reduced

$Fe^{3+}(aq)(E° = +0.77 V)$ vs $Fe(OH)_3(s)$ $(E° = -0.56 V)$
Stronger ligand (the OH^-) increases electron density on metal centre, decreased ease of reduction. Also the Fe(III) centre is stabilized by electron donated from ligand.

3) Formation of complex ions can "extract" the metal ion from solution and thus enable the ppt of the ion to dissolve. Eg:
-excess conc Cl^- dissolves $PbCl_2$, forms $[PbCl_4]^{2-}$
- addition of aq. NH_3 dissolves AgCl ppt., forms $[Ag(NH_3)_2^+]$
- excess NH_3 dissolves $Cu(OH)_2$. Net reaction:
$4NH_3(aq) + Cu(OH)_2(s) \rightarrow [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$
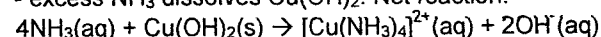
Coloured Complexes

In the gaseous or free ion, the five d orbitals are degenerate (of equal energy). In the presence of ligands, the d orbitals are split into two distinct levels, creating an energy gap. The energy difference between the levels corresponds to a particular wavelength in the visible region of the spectrum. When light falls on the complex, light with wavelength and energy corresponding to the energy gap are absorbed and the d electrons are promoted from the lower energy d orbitals to the higher higher energy d orbitals (d-d transition). The complex exhibits the colour complementary to that of the absorbed wavelengths.

The splitting of the d orbitals depends on the nature of the TM, its oxidation state, the shape of the complex and the nature of the ligands, hence different complexes have different colours. If the d orbitals are completely empty (Sc^{3+}) or completely full (Cu^+ or Zn^{2+}), no transitions within the d levels can take place and the complexes are colourless.

Vanadium	
$VO_2^+/[VO_2(H_2O)_4]^+$	yellow
$VO^{2+}/[VO(H_2O)_5]^{2+}$	blue
$V^{3+}/[V(H_2O)_6]^{3+}$	green
$V^{2+}/[V(H_2O)_6]^{2+}$	violet
VF_5	white
VF_4	lime green
VF_3	yellow green
VF_2	blue
VCl_4	red-brown
VCl_3	red-violet
VCl_2	pale green

Chromium	
$Cr^{2+}/[Cr(H_2O)_6]^{2+}$	blue/sky-blue
$Cr^{3+}/[Cr(H_2O)_6]^{3+}$ (aq)	green
$[Cr(H_2O)_6]^{3+}$ solid salt	violet
CrO_4^{2-}	yellow
$Cr_2O_7^{2-}$	orange
$Cr(OH)_3/[Cr(OH)_3(H_2O)_3]$	green ppt
$[Cr(OH)_6]^{3-}$	deep green

Manganese	
$Mn^{2+}/[Mn(H_2O)_6]^{2+}$	pale pink
$Mn(OH)_2$	off-white ppt/buff ppt
$Mn_2O_3.xH_2O$	brown ppt
$MnCl_4^{2-}$	green-yellow
MnO_2	black solid
MnO_4^-	deep purple
$[Mn(CN)_6]^{3-}$	dark red

Iron	
$[Fe(CN)_6]^{3-}$	orange-brown
$[Fe(CN)_6]^{4-}$	yellow
$Fe(OH)_3/[Fe(OH)_3(H_2O)_3]$	reddish brown
$Fe(OH)_2/[Fe(OH)_2(H_2O)_4]$	dirty green
$Fe_2O_3.xH_2O$	reddish brown
$FeCO_3$	white
$Fe^{3+}/[Fe(H_2O)_6]^{3+}$ (aq)	yellow
$[Fe(H_2O)_6]^{3+}$ (solid salt)	lilac
$[Fe(H_2O)_6]^{2+}$	pale green
$[Fe(SCN)(H_2O)_5]^{2+}$	blood red
$[Fe(CN)_6]^{4-} + Fe^{2+}$	Prussian blue ppt
$[Fe(CN)_6]^{3-} + Fe^{3+}$	Turnbull's blue ppt
$Fe_4[Fe(CN)_6]_3.15H_2O$	dark blue ppt (same as above)

Cobalt	
$[Co(NH_3)_6]^{3+}$	golden brown
$[Co(NH_3)_5(H_2O)]^{3+}$	bright red
$[Co(NH_3)_5Cl]^{2+}$	purple
$[Co(NH_3)_4Cl_2]^+$ cis	deep violet
$[Co(NH_3)_4Cl_2]^+$ trans	green
$[CoCl_4]^{2-}$	blue
$[Co(H_2O)_6]^{2+}$	pink
$Co(OH)_2$	blue ppt
$[Co(NH_3)_6]^{2+}$	pale brown

Nickel	
$[Ni(H_2O)_6]^{2+}$	green
$[Ni(NH_3)_6]^{2+}$	blue
$[Ni(CN)_4]^{2-}$ sq planar	yellow
$[NiCl_4]^{2-}$	blue
$Ni(OH)_2/[Ni(OH)_2(H_2O)_4]$	pale green ppt
$Ni(DMG)$ DMG = dimethylglyoxime	red ppt

Copper	
Cu(I) compounds (except below)	white solids
Cu_2O	red ppt
Cu_2S	black solid
CuI	cream ppt
$CuCN$	white ppt
$[Cu(CN)_4]^{3-}$	colorless
$[CuCl_2]^-$	colorless
CuO	black solid
$CuCO_3$	green solid
$CuCl_2$ (anhydrous)	dark brown
$CuCl_2.2H_2O$	blue-yellow
$Cu^{2+}/[Cu(H_2O)_6]^{2+}$	pale blue
$[Cu(NH_3)_4]^{2+}/[Cu(NH_3)_4(H_2O)_2]^{2+}$	deep blue
$Cu(OH)_2/[Cu(OH)_2(H_2O)_4]$	blue ppt
$[CuCl_4]^{2-}$	yellow
$[Cu(edta)]^{2-}$	pale blue

Silver	
Ag(I) charged complexes	colorless usually
$[Ag(H_2O)_2]^+$, $[Ag(NH_3)_2]^+$ $[Ag(S_2O_3)_2]^{3-}$, $[Ag(CN)_2]^-$	colorless
$AgCl$	white ppt
$AgBr$	cream ppt
AgI	yellow
Ag_2S	black ppt

Metal Ion Centre	Usual Co-ord. No.
Cu^+, Ag^+ (d^{10})	2 (linear)
Cu^{2+} (d^9)	4 (tetrahedral or sq. planar)
Ni^{2+}, Pt^{2+} (d^8)	4 (sq. planar)
Others	6 (octahedral)