SOLVED NUMERICAL 1

Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in an aqueous solution containing 20 % of $C_2H_6O_2$ by mass.

GIVEN DATA $A = H_2O$, $B = C_2H_6O_2$; 20 % by mass means 20 g in 100 g of solution : $W_B = 20$ g , $W_A = 80$ g , $M_A = 18$ g/mol , $M_B = 62$ g/mol

REQUIRED QUANTITY Mole fraction of ethylene glycol, x_B

RELEVANT FORMULA $n = \frac{W}{M}$, $x_B = \frac{n_B}{n_A + n_B}$

SUBSTITUTION

$$n_A = \frac{80}{18} , n_B = \frac{20}{62}$$

$$x_B = \frac{0.3226}{4.444 + 0.3226}$$

STEP-BY-STEP CALCULATION

$n_A = 4.44$ mol

$n_B = 0.32$ mol

$$x_B = \frac{0.3226}{4.767} = 0.0677$$

FINAL ANSWER $x_B \approx 0.068$ (rounded to 0.07)

SOLVED NUMERICAL 2

Calculate the molarity of a solution containing 5 g of NaOH in 450 mL of solution.

GIVEN DATA $W_B = 5$ g , $M_B = 40$ g/mol , $V_{A+B} = 450$ mL $= 0.45$ L

REQUIRED QUANTITY Molarity M

RELEVANT FORMULA $M = \frac{W_B}{M_B \times V_{A+B}\ (L)}$

SUBSTITUTION

$$M = \frac{5}{40 \times 0.45}$$

STEP-BY-STEP CALCULATION

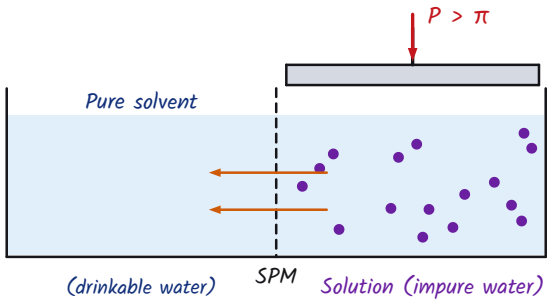
$$M = \frac{5}{18} = 0.2778 \text{ mol } L^{-1}$$

FINAL ANSWER $M = 0.278$ mol L^{-1} $= 0.278$ M

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Reverse osmosis and water purification

The direction of osmosis can be **reversed** if a pressure **larger than the osmotic pressure** is applied to the **solution side**. The pure solvent then flows **out of the solution** through the SPM. This phenomenon is called **reverse osmosis (R.O.)**.



Reverse osmosis : applied pressure P is greater than π

Real-Life Application

Desalination of sea water and purification of drinking water use reverse osmosis (R.O.) with a cellulose acetate SPM. The method is used in home R.O. water purifiers and in desalination plants.

SOLVED NUMERICAL 11

200 cm^3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of this solution at 300 K is 2.57×10^{-3} bar. Calculate the molar mass of the protein. ($R = 0.083$ L bar mol^{-1} K^{-1})

GIVEN DATA $w_B = 1.26$ g , $\pi = 2.57 \times 10^{-3}$ bar , $V = 200\ cm^3 = 0.2$ L , $T = 300$ K , $R = 0.083$ L bar mol^{-1} K^{-1}

REQUIRED QUANTITY Molar mass M_B of the protein

RELEVANT FORMULA $\pi V = \frac{w_B}{M_B} R T$ so $M_B = \frac{w_B R T}{\pi V}$

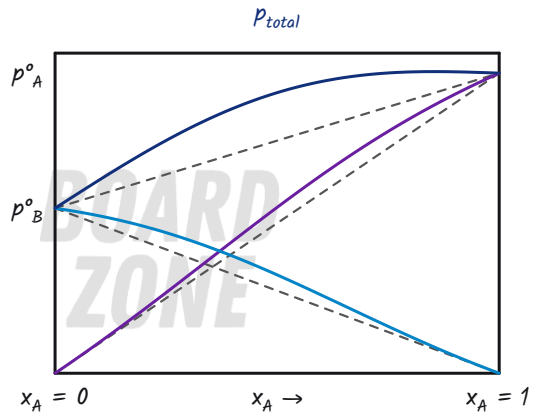
SUBSTITUTION $M_B = \frac{1.26 \times 0.083 \times 300}{2.57 \times 10^{-3} \times 0.2}$

STEP-BY-STEP CALCULATION $M_B = \frac{31.37}{5.14 \times 10^{-4}} = 6.10 \times 10^4$

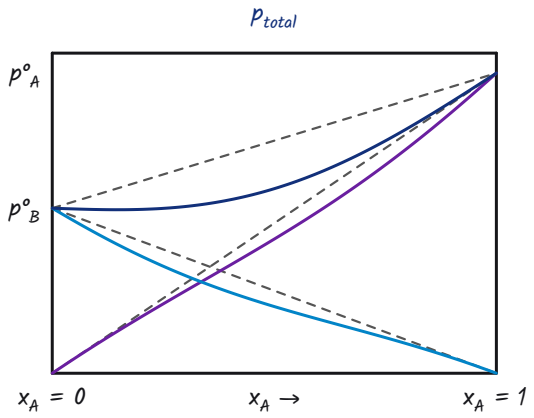
FINAL ANSWER $M_B \approx 6.1 \times 10^4$ g mol^{-1} (61 039 g mol^{-1})

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Examples of ideal solutions : *n*-hexane + *n*-heptane (nearly ideal), bromoethane + chloroethane, benzene + toluene, chlorobenzene + bromobenzene.



Positive deviation



Negative deviation

(dashed lines show the ideal behaviour ; solid curves show the real partial and total vapour pressures)

Chemical Reasoning

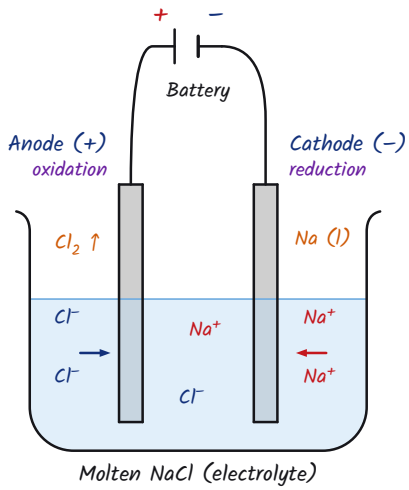
Positive deviation : the A–B attractions are **weaker** than A–A and B–B attractions, so molecules escape more easily and the vapour pressure is higher. **Negative deviation :** the A–B attractions are **stronger** than A–A and B–B (e.g. **hydrogen bonding**), so molecules escape less easily and the vapour pressure is lower.

Examples : Positive deviation : acetone + benzene, acetone + ethanol, ethanol + water. Negative deviation : phenol + aniline, chloroform + acetone (hydrogen bonding), nitric acid + water.

Difference between ideal and non-ideal solutions

Property	Ideal solution	Non-ideal : +ve deviation	Non-ideal : –ve deviation
Raoult's law	Obeyed	Not obeyed	Not obeyed
Total vapour pressure	$P_t = p_A + p_B$	$P_t > p_A + p_B$	$P_t < p_A + p_B$
ΔH of mixing	$\Delta H_{mix} = 0$	ΔH_{mix} = +ve (endothermic)	ΔH_{mix} = –ve (exothermic)
ΔV of mixing	$\Delta V_{mix} = 0$	ΔV_{mix} = +ve	ΔV_{mix} = –ve
Interactions	A–B = A–A = B–B	A–B < A–A or B–B (repulsion between A and B)	A–B > A–A or B–B (attraction between A and B)

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Electrolysis of molten NaCl in an electrolytic cell

Electrolysis of molten NaCl :

At anode (oxidation) : $2Cl^- \rightarrow Cl_2 + 2e^-$

At cathode (reduction) : $2Na^+ + 2e^- \rightarrow 2Na$

$$2NaCl\ (molten) \rightarrow 2Na + Cl_2$$

overall change : sodium metal at the cathode, chlorine gas at the anode

Exam Point of View

For electrolysis we must always use **D.C. (direct current)** and **not A.C.**, because with A.C. the polarity of the electrodes changes continuously and no net electrolysis takes place.

Electrochemical Cell (Galvanic or Voltaic Cell)

Electrochemical cell :- A device in which a **redox reaction is used to convert chemical energy into electrical energy**. Electricity can be obtained with the help of oxidation and reduction reactions in such a cell.

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Exam Point of View

*If **standard reduction potentials** are given, the electrode with the **higher** value is the cathode. For a feasible (spontaneous) cell **E°cell > 0**. Never change the sign of E° when you multiply a half reaction by a number.*

SOLVED NUMERICAL 1

Calculate the e.m.f. of the Daniell cell Zn | Zn^{2+} || Cu^{2+} | Cu if $E°(Zn^{2+}/Zn) = -0.76$ V and $E°(Cu^{2+}/Cu) = +0.34$ V.

GIVEN DATA	$E°_{Zn^{2+}|Zn} = -0.76$ V (anode, since lower value) ; $E°_{Cu^{2+}|Cu} = +0.34$ V (cathode)
REQUIRED QUANTITY	E°cell
RELEVANT FORMULA	$E°_{cell} = E°_C - E°_A$
SUBSTITUTION	$E°_{cell} = 0.34 - (-0.76)$
STEP-BY-STEP CALCULATION	$E°_{cell} = 0.34 + 0.76 = 1.10$ V

FINAL ANSWER **E°cell = 1.10 V** *using oxidation potential of Zn (+0.76 V) + reduction of Cu (+0.34 V) gives the same*

SOLVED NUMERICAL 2

Find E°cell for the cell Cu | Cu^{2+} || Ag^+ | Ag given $E°(Ag^+/Ag) = 0.80$ V (cathode) and $E°(Cu^{2+}/Cu) = 0.34$ V (anode).

GIVEN DATA	$E°_C = 0.80$ V , $E°_A = 0.34$ V
REQUIRED QUANTITY	E°cell
RELEVANT FORMULA	$E°_{cell} = E°_C - E°_A$
SUBSTITUTION	$E°_{cell} = 0.80 - 0.34$
STEP-BY-STEP CALCULATION	$E°_{cell} = 0.46$ V

FINAL ANSWER **E°cell = 0.46 V** *positive, so the cell reaction is feasible*

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SOLVED NUMERICAL 14

How much charge is required for the oxidation of (i) 1 mol of H_2O to O_2 , (ii) 1 mol of FeO to Fe_2O_3 ?

GIVEN DATA (i) $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$ (ii) $Fe^{2+} \rightarrow Fe^{3+} + e^-$

REQUIRED QUANTITY Charge in coulomb

RELEVANT FORMULA $Q = n\,F$

SUBSTITUTION $Q = n \times 96500$

STEP-BY-STEP CALCULATION

(i) $O^{2-} \rightarrow O$: $n = 2$ so $Q = 2 \times 96500 = 193000\ C$

(ii) $Fe^{2+} \rightarrow Fe^{3+}$: $n = 1$ so $Q = 96500\ C$

FINAL ANSWER

(i) $2F = 1.93 \times 10^5\ C$

(ii) $1F = 9.65 \times 10^4\ C$

SOLVED NUMERICAL 15

A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 A for 20 minutes. What mass of Ni is deposited at the cathode ? (Molar mass of Ni = 59 g/mol)

GIVEN DATA $I = 5\ A$, $t = 20\ min = 1200\ s$, $Ni^{2+} + 2e^- \rightarrow Ni$, $n = 2$, $M = 59\ g/mol$

REQUIRED QUANTITY Mass of nickel

RELEVANT FORMULA $W = \frac{M\,I\,t}{n\,F}$

SUBSTITUTION $W = \frac{59 \times 5 \times 1200}{2 \times 96500}$

STEP-BY-STEP CALCULATION

$Q = 5 \times 1200 = 6000\ C$

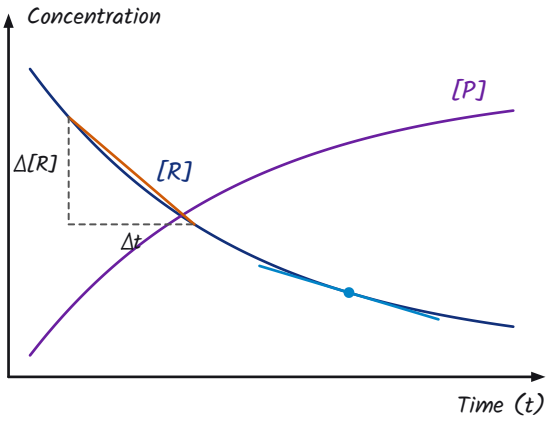
$W = \frac{59 \times 6000}{193000} = \frac{354000}{193000} = 1.834\ g$

FINAL ANSWER

$W = 1.83\ g$ of Ni deposited

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Unit of rate : $\frac{\text{mol } L^{-1}}{s}$, i.e. **mol L^{-1} s^{-1}** ($= M\ s^{-1}$). If the reactant is a gas and pressure is used, the unit is **atm s^{-1}** (or bar s^{-1}).



average rate = $-\Delta[R] / \Delta t$ (slope of the chord)

instantaneous rate = slope of the tangent at a point

Change of concentration with time : average rate (chord) and instantaneous rate (tangent)

- **Average rate** : the change in concentration of a reactant or product over a **finite time interval** (Δt).

- **Instantaneous rate** : the rate at a **particular instant** of time. It is the **slope of the tangent** to the concentration–time curve at that instant ($\Delta t \to 0$, i.e. $-\frac{d[R]}{dt}$).

Remember This

For the reaction $2N_2O_5 \to 4NO_2 + O_2$ the rate of reaction is $-\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$. So **$NO_2$ is formed 4 times as fast as the rate of reaction**, and N_2O_5 disappears 2 times as fast.

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Converting to common logarithm ($\ln x = 2.303 \log x$) :

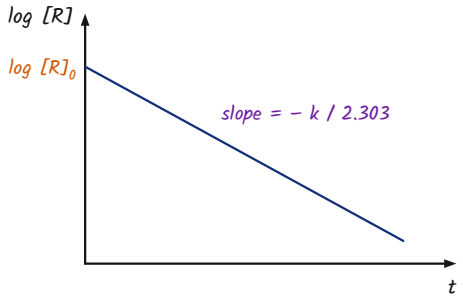
$$\log [A] = -\frac{k\,t}{2.303} + \log [A]_0$$

straight line : $y = mx + c$

$$\frac{k\,t}{2.303} = \log [A]_0 - \log [A]$$

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \quad , \quad t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

integrated rate law of a first order reaction ; $[A]_0$ = initial concentration , $[A]$ = concentration after time t



log [R] against t : a straight line of slope −k / 2.303

Half life ($t_{1/2}$)

Half life :- The **time taken by a reaction to reduce the concentration of a reactant to half of its initial concentration.**

For a first order reaction, put $[A] = \frac{[A]_0}{2}$ and $t = t_{1/2}$:

$$t_{1/2} = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/2}$$

$$t_{1/2} = \frac{2.303}{k} \log 2 = \frac{2.303 \times 0.3010}{k}$$

$\log 2 = 0.3010$

$$t_{1/2} = \frac{0.693}{k} = \text{constant}$$

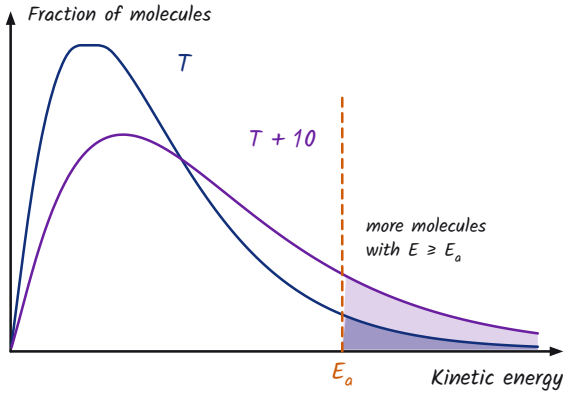
the half life of a first order reaction is **independent of the initial concentration**

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Effect of Temperature : Arrhenius Equation

The rate constant of a reaction **depends directly on temperature**. On observing many reactions it is found that for **every 10 °C rise in temperature the rate constant approximately doubles** (temperature coefficient ≈ 2 to 3).

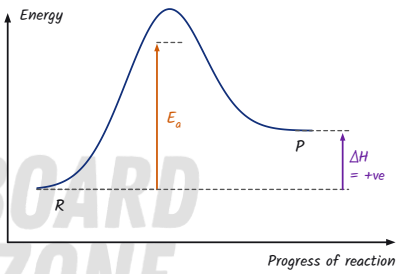
Why does temperature increase the rate ? On heating, the **number of molecules having energy greater than or equal to the activation energy (Ea)** increases (see the distribution curve), so the number of effective collisions increases.



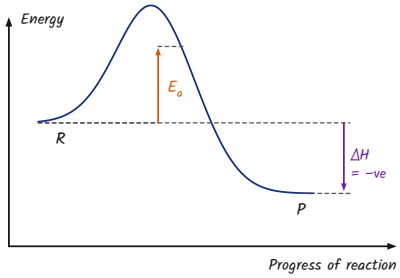
Distribution of kinetic energy : at T + 10 more molecules have energy ≥ Ea

Activation energy and the energy profile

Activation energy (Ea) :- The **minimum extra energy** which the reactant molecules must possess (over their average energy) so that the collision between them is effective and leads to products. It is the energy needed to reach the **activated complex (transition state)**.



Endothermic reaction



Exothermic reaction

1. **Rate of reaction ∝ 1 / activation energy** : a reaction with a **lower Ea** is **faster**.
2. For an endothermic reaction $E_{a(f)} > E_{a(b)}$; for an exothermic reaction $E_{a(b)} > E_{a(f)}$ (f = forward , b = backward).
3. Ea is **not changed by temperature** ; it depends on the nature of the reaction and on the catalyst.

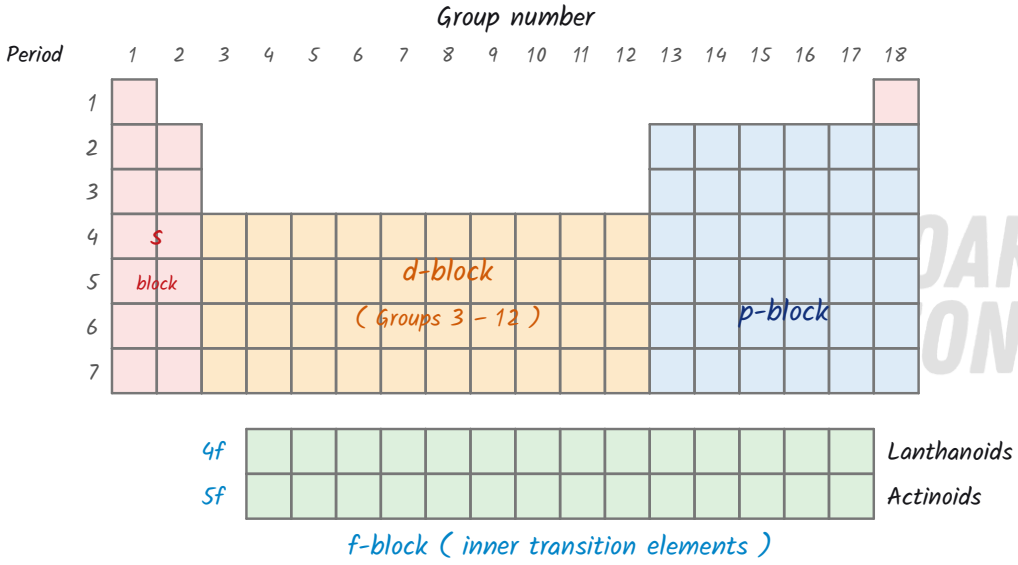
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Class 12 Chemistry | Chapter 4

The d- and f-Block Elements

The d- and f-Block Elements

The elements of **Groups 3 – 12** lie in the middle of the periodic table, between the s-block and the p-block. Their **last electron enters the penultimate (inner) d-orbital**, so they are called the **d-block elements**. They form **four series** : 3d (Sc – Zn) , 4d (Y – Cd) , 5d (La, Hf – Hg) and 6d (Ac, Rf – Cn).



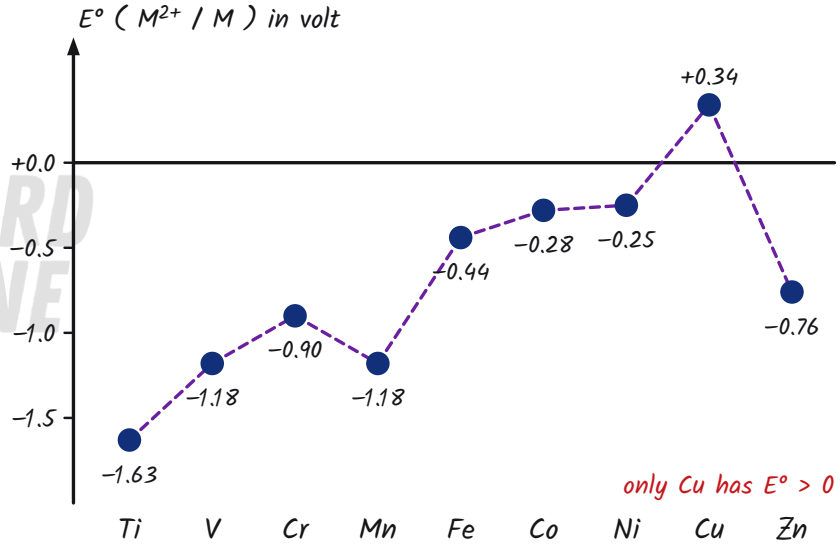
Position of the s-, p-, d- and f-blocks in the periodic table

Transition element :- An element which has an **incomplete d-subshell** either in its **neutral atom or in any of its common oxidation states**. (IUPAC)

- **Zn, Cd and Hg** have the configuration $(n-1)d^{10}ns^2$ in the atom **and** in their common ion (+2) . The d-subshell is **completely filled**, so they are **not** treated as transition elements (they are only d-block elements).
- **Cu** ($3d^{10}4s^1$) is a transition element because its **Cu^{2+} ion has $3d^9$**, an incomplete d-subshell.
- **Sc** ($3d^14s^2$) is a transition element because it has an incomplete d-subshell in the atom (Sc^{3+} is $3d^0$, but the atom counts).

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4. Standard electrode potentials



E° (M^{2+} / M) of the 3d series : irregular variation

- The E° values are **mostly negative** (M^{2+} is stable and M is a reducing agent) ; **only Cu is positive (+0.34 V)** because the sum of its enthalpy of atomisation and ionisation is **not balanced** by the hydration enthalpy. **Copper does not liberate H_2 from dilute acids.**
- **Mn and Zn have more negative E° than expected** : Mn^{2+} is **$3d^5$ (half-filled)** and Zn^{2+} is **$3d^{10}$ (completely filled)** , so these ions are extra stable.
- **E° (M^{3+} / M^{2+}) :** Mn^{3+} / Mn^{2+} = +1.57 V and Co^{3+} / Co^{2+} = +1.97 V are **very positive** (Mn^{2+} is d^5 , so Mn^{3+} is a strong oxidant) ; **Cr^{3+} / Cr^{2+} = −0.41 V is negative** (Cr^{3+} is d^3 with stable t_{2g}^3) , so **Cr^{2+} is strongly reducing** ; Fe^{3+} / Fe^{2+} = +0.77 V.
- **Mn^{3+} is unstable in water** and disproportionates ; **Ni^{2+} is the most stable** state of nickel.

5. Magnetic properties

Paramagnetic substances are attracted by a magnetic field because of **unpaired electrons**. **Diamagnetic** substances (all electrons paired) are weakly repelled. Most transition-metal ions are paramagnetic. The **spin-only magnetic moment** is :

$$\mu = \sqrt{n\,(n+2)}\ BM$$

n = number of unpaired electrons ; BM = Bohr magneton (the unit of magnetic moment)

Unpaired electrons (n)	1	2	3	4	5
μ (BM)	1.73	2.83	3.87	4.90	5.92

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Properties and oxidising action

- **Orange-red crystals**, m.p. 671 K. It is **moderately soluble in water**.
- **Strong oxidising agent in acid medium** : $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ ($E^\circ = 1.33$ V). **Orange → green (Cr^{3+})**.
- **Equivalent mass = molar mass ÷ 6** (6 electrons gained per ion) = 294.2 ÷ 6 = 49.03 g.

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

$$Cr_2O_7^{2-} + 8H^+ + 3H_2S \rightarrow 2Cr^{3+} + 3S + 7H_2O$$

$$Cr_2O_7^{2-} + 8H^+ + 3SO_3^{2-} \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

Exam Point of View

Q. Why is $K_2Cr_2O_7$ preferred to $Na_2Cr_2O_7$ as a primary standard in volumetric analysis ?

Ans. $Na_2Cr_2O_7$ is **hygroscopic** whereas $K_2Cr_2O_7$ is **not**, and it can be obtained **pure by crystallisation**. So a solution of exactly known concentration can be made from a weighed sample.

Real-Life Application

$K_2Cr_2O_7$ is used in **leather tanning , dyeing , photography (for screen printing) , chromyl chloride test** and as an oxidant in **volumetric titrations** (Fe^{2+}).

Potassium Permanganate ($KMnO_4$)

Preparation from pyrolusite (MnO_2)

- **Fusion with KOH in the presence of air or an oxidising agent (KNO_3) gives dark-green potassium manganate :**

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

- **The manganate is oxidised to permanganate** either **electrolytically** (in alkaline solution) or **by a disproportionation in acid** :

$$MnO_4^{2-} \rightarrow MnO_4^- + e^- \text{ (electrolytic oxidation, green → purple)}$$

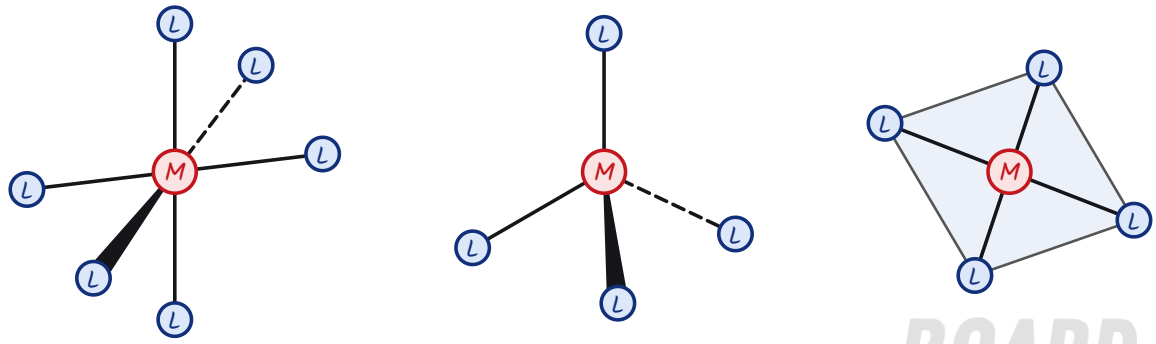
$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O \text{ (disproportionation)}$$

- **Laboratory method :** Mn^{2+} salts are oxidised by **peroxodisulphate** or **periodate** :

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

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Term	Meaning	Example : $[Co(NH_3)_5Cl]Cl_2$
Oxidation number of metal	the **charge** on the metal if all ligands are removed with their electron pairs	+3
Homoleptic / heteroleptic	a complex with **only one kind** of donor group / **more than one kind**	$[Co(NH_3)_6]^{3+}$ (homo) ; $[Co(NH_3)_4Cl_2]^+$ (hetero)



Octahedral (C.N. = 6) $[Co(NH_3)_6]^{3+}$ | Tetrahedral (C.N. = 4) $[NiCl_4]^{2-}$ | Square planar (C.N. = 4) $[Pt(NH_3)_2Cl_2]$

Common coordination polyhedra : octahedral , tetrahedral and square planar

Remember This

Coordination number = number of σ-bonds from the ligands, **not** the number of ligands. In $[Co(en)_3]^{3+}$ there are **3 ligands but C.N. = 6** (each en is **didentate**). Common values : **6 (octahedral) , 4 (tetrahedral or square planar)**.

SOLVED NUMERICAL 2

Find the oxidation number of the central metal and the coordination number in each : (a) $K_3[Fe(CN)_6]$ (b) $[Co(NH_3)_5Cl]Cl_2$ (c) $[Ni(CO)_4]$ (d) $[Cr(H_2O)_4Cl_2]^+$

GIVEN DATA Charges : $K^+ = +1$; $CN^- = -1$; NH_3 , CO , $H_2O = 0$; $Cl^- = -1$

REQUIRED QUANTITY Oxidation number (O.N.) and C.N.

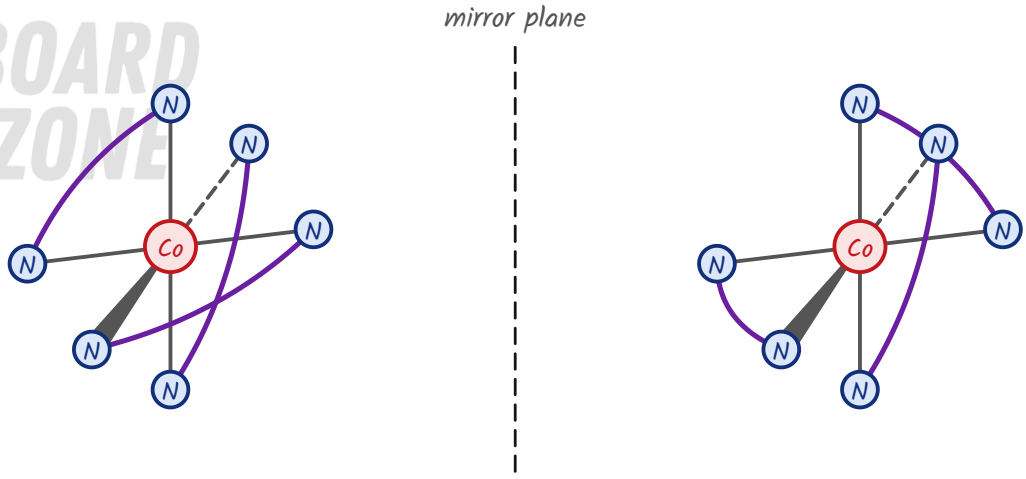
RELEVANT FORMULA Sum of the charges of metal and ligands = **overall charge** of the entity

SUBSTITUTION Let O.N. of the metal = x

solution continues on the next page

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(ii) Optical isomerism : two isomers which are **non-superposable mirror images** (**enantiomers**) and which **rotate the plane of polarised light in opposite directions** (**dextro (d) / laevo (l)**). They arise when the complex has **no plane or centre of symmetry** (it is **chiral**). Common in **octahedral complexes with didentate ligands**.



d - $[Co(en)_3]^{3+}$ l - $[Co(en)_3]^{3+}$

(mirror images that cannot be superposed)

Optical isomers of $[Co(en)_3]^{3+}$: the d- and l-forms are mirror images

- **Chiral :** $[Co(en)_3]^{3+}$, $[Cr(ox)_3]^{3-}$ and **cis-$[CrCl_2(en)_2]^+$** (d and l forms).
- **Achiral :** the **trans-$[CrCl_2(en)_2]^+$** isomer has a plane of symmetry , so it is **optically inactive**. So $[CrCl_2(en)_2]^+$ has **3 stereoisomers** in all (trans , cis-d , cis-l).
- **Square planar and tetrahedral** complexes with **simple unidentate** ligands do not show optical isomerism (they have a plane of symmetry).

Exam Point of View

Number of isomers (asked often) : $[Pt(NH_3)_2Cl_2] \rightarrow 2$; $[Co(NH_3)_4Cl_2]^+ \rightarrow 2$; $[Co(NH_3)_3Cl_3] \rightarrow 2$ (fac , mer) ; $[Co(en)_3]^{3+} \rightarrow 2$ (d , l) ; $[Co(en)_2Cl_2]^+ \rightarrow 3$; $[Ni(CO)_4]$, $[NiCl_4]^{2-}$ (tetrahedral) $\rightarrow 1$.

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Chemical Reasoning

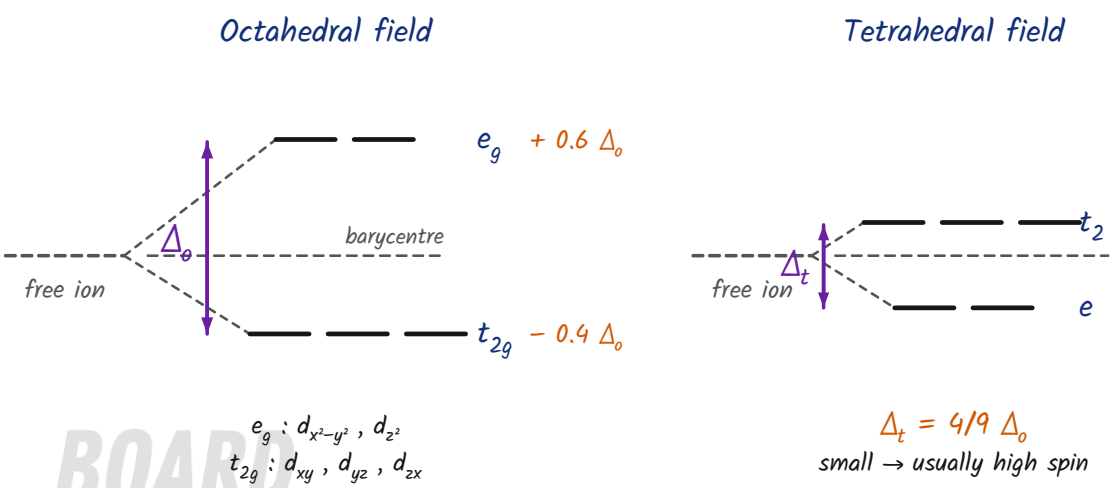
$[Ni(CN)_4]^{2-}$ is square planar and diamagnetic, but $[NiCl_4]^{2-}$ is tetrahedral and paramagnetic. CN^- is a strong field ligand : it forces the two unpaired $3d^8$ electrons to pair up, leaving one 3d orbital empty for **dsp^2**. **Cl^- is a weak field ligand** : it cannot pair them, so the **$3d^8$ configuration remains and sp^3 hybridisation** is used.

Common Mistakes

Limitations of VBT : it does **not** explain the **colour** of complexes, **does not give quantitative magnetic data**, and **does not explain the relative stability** or the **spectrochemical series**. It also says nothing about why $[Cu(NH_3)_4]^{2+}$ is square planar and not tetrahedral. These are explained by the **crystal field theory**.

2. Crystal field theory (CFT)

CFT treats the **metal–ligand bond as purely electrostatic** : ligands are **point negative charges (or dipoles)** and the metal ion a positive charge. In the free ion the five **d-orbitals are degenerate**. When ligands approach, the **degeneracy is lost** (splitting) because the d-orbitals pointing **toward** the ligands feel **more repulsion** than those between them.



Crystal field splitting of the d-orbitals in octahedral and tetrahedral fields

- **Octahedral :** d-orbitals split into **t_{2g} (dxy , dyz , dzx ; between the axes , lower energy , −0.4 Δ_o)** and **eg (dx^2-y^2 , dz^2 ; along the axes , higher energy , +0.6 Δ_o)**. Δ_o is the **crystal field splitting energy**.
- **Tetrahedral :** the order is **reversed** (e below , t_2 above) and **Δt = 4/9 Δ_o**. The splitting is **small, so tetrahedral complexes are always high spin**.

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- **By number of halogens :** mono-, di-, tri- and **polyhalogen** compounds (e.g. CH_2Cl_2 , $CHCl_3$, CCl_4).

- **By the carbon carrying X : primary (1°), secondary (2°)** and **tertiary (3°)** haloalkanes, according to whether that carbon is attached to one, two or three other carbon atoms.

Nomenclature of Haloalkanes and Haloarenes

Common name : alkyl group + halide (methyl chloride, ethyl bromide). **IUPAC name :** the halogen is a **prefix (Halo)** – fluoro-, chloro-, bromo-, iodo-.

- **Haloalkane :** name the **halogen first, then the alkane** (halo + alkane), choosing the longest chain and the **lowest locants** ; substituents are written in alphabetical order.

- **Haloarene :** name the **halogen first, then benzene** (halo + benzene). Two substituents are shown by **o- , m- , p-** or by the numbers 1,2 ; 1,3 ; 1,4.

Formula	Common name	IUPAC name
CH_3Cl	Methyl chloride	Chloromethane
$CH_3CH_2CH_2Br$	n-Propyl bromide	1-Bromopropane
$CH_3CHClCH_3$	Isopropyl chloride	2-Chloropropane
$(CH_3)_3CBr$	tert-Butyl bromide	2-Bromo-2-methylpropane
$CH_3–CCl_2–CH_3$	—	2,2-Dichloropropane
$CH_2=CH–Cl$	Vinyl chloride	Chloroethene
$CH_2=CH–CH_2Cl$	Allyl chloride	3-Chloropropene
C_6H_5Cl	Phenyl chloride	Chlorobenzene
$C_6H_5CH_2Cl$	Benzyl chloride	(Chloromethyl)benzene
CH_2Cl_2 , $CHCl_3$, CHI_3 , CCl_4	Methylene chloride, chloroform, iodoform, carbon tetrachloride	Dichloromethane, trichloromethane, triiodomethane, tetrachloromethane

Common Mistakes

For **chloromethane** no locant is written (there is only one carbon). Writing '1-chloromethane' is wrong. Locants are used only when the position can differ.

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SN1 : Substitution Nucleophilic Unimolecular

- Takes place in **two steps**. **Step 1 (slow, rate determining)** : the C–X bond breaks by itself to give a **carbocation** and X^-.
- **Step 2 (fast)** : the nucleophile attacks the **planar carbocation**.
- **Rate = k [R–X]** → first order (unimolecular).
- Favoured for **tertiary** halides because a 3° carbocation is the most stable (+I effect and hyperconjugation of three alkyl groups).

$$\text{Step 1 :} \quad (CH_3)_3C\text{–}Br \xrightarrow{\text{slow}} (CH_3)_3C^+ + Br^-$$

$$\text{Step 2 :} \quad (CH_3)_3C^+ + OH^- \xrightarrow{\text{fast}} (CH_3)_3C\text{–}OH$$

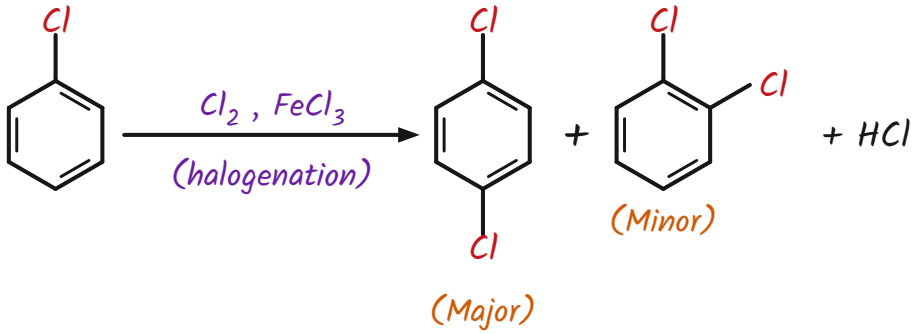
Order of the carbocation stability and hence of SN1 reactivity : **3° > 2° > 1° > CH_3X**. For SN2 the order is **exactly the opposite** : CH_3X > 1° > 2° > 3°.

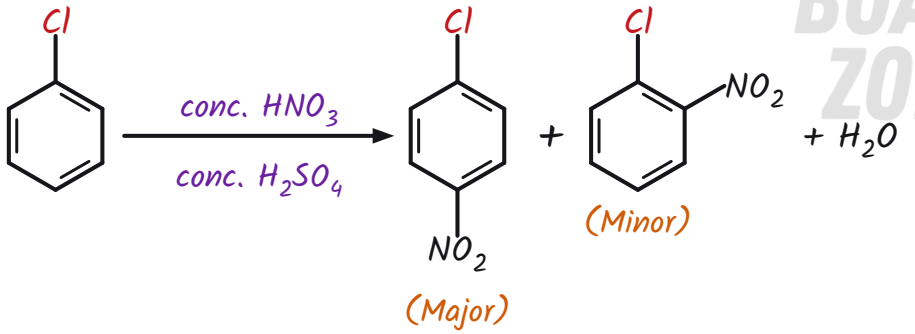
Factor	SN1	SN2
Order of reaction	First order (unimolecular)	Second order (bimolecular)
Rate law	k [R–X]	k [R–X] [Nu^-]
Number of steps	Two (carbocation intermediate)	One (pentavalent transition state)
Reactivity of R–X	3° > 2° > 1° > CH_3X	CH_3X > 1° > 2° > 3°
Leaving group	R–I > R–Br > R–Cl > R–F	R–I > R–Br > R–Cl > R–F
Nucleophile	Weak / neutral (H_2O , ROH) is enough	Strong and in high concentration
Solvent	Polar protic (water , alcohol)	Polar aprotic (acetone , DMF)
Stereochemistry	Racemisation	Inversion of configuration

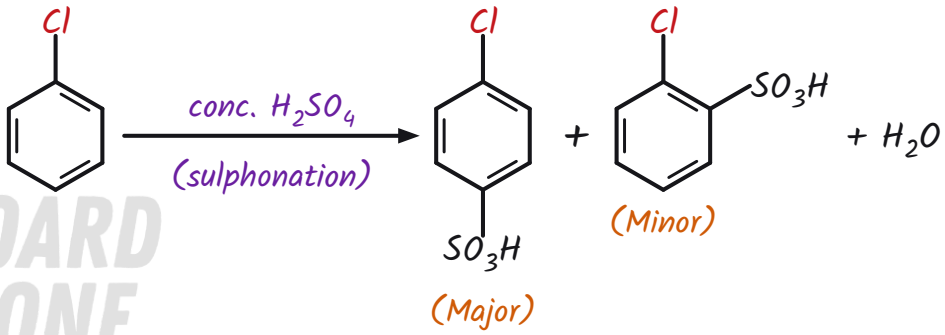
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B. Electrophilic substitution in haloarenes

Haloarenes undergo the usual electrophilic substitutions : **halogenation, nitration, sulphonation and Friedel–Crafts reactions**. The halogen is **deactivating** (strong –I effect makes the ring less reactive than benzene) but **ortho and para directing** (the +R effect of the lone pair increases electron density at o- and p-positions). The **para product is major** because it has less steric hindrance.







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Preparation of Alcohols

1. From alkenes

- **Acid-catalysed hydration :** water adds to the double bond in the presence of an acid (**Markovnikov's rule**). The reaction goes through a **carbocation** (3 steps : protonation of the alkene , attack of H_2O on the carbocation , loss of H^+).
- **Hydroboration – oxidation :** diborane adds to the alkene and the trialkylborane is oxidised by H_2O_2 / NaOH. The **net result is anti-Markovnikov addition of water** — the product is the **1° alcohol**. It occurs with **no rearrangement**.

$$CH_3-CH=CH_2 + H_2O \xrightarrow[\text{Markovnikov}]{H^+} CH_3-CH(OH)-CH_3 \quad \text{propan-2-ol}$$

$$CH_3-CH=CH_2 \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ B_2H_6} CH_3CH_2CH_2-OH \quad \text{propan-1-ol (anti-Markovnikov)}$$

2. From carbonyl compounds (by reduction)

Aldehydes give **1° alcohols** and **ketones** give **2° alcohols** with **H_2 / Ni , $NaBH_4$ or $LiAlH_4$**. **Carboxylic acids and esters** are reduced to 1° alcohols by **$LiAlH_4$** ($NaBH_4$ does **not** reduce acids).

$$R-CHO + H_2 \xrightarrow[\text{or } NaBH_4 \text{ or } LiAlH_4]{Ni\ /\ Pt\ /\ Pd} R-CH_2-OH \quad \text{1° alcohol}$$

$$R-CO-R' + H_2 \xrightarrow[\text{or } NaBH_4 \text{ or } LiAlH_4]{Ni\ /\ Pt\ /\ Pd} R-CH(OH)-R' \quad \text{2° alcohol}$$

$$R-COOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-OH \quad \text{1° alcohol}$$

$$R-COOR' \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2OH + R'OH$$

Remember This

$NaBH_4$ is mild and selective : it reduces **–CHO and >C=O** but not –COOH or –COOR. **$LiAlH_4$** is a very strong reducing agent and must be used in **dry ether** (it reacts violently with water). Carboxylic acids are directly reduced to alcohols by **$LiAlH_4$** or by **B_2H_6**.

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Compound	Formula	Molar mass (g mol^{-1})	b.p. (K)
Ethanol	C_2H_5OH	46	351

Chemical Reasoning

Ethanol (46 g mol^{-1} , b.p. 351 K) boils far above methoxymethane (same mass , 249 K) because ethanol molecules are linked by **O–H···O hydrogen bonds** and a lot of energy is needed to break them, while the ether has only weak dipole–dipole attractions.

Phenol : colourless , **hygroscopic** crystalline solid (m.p. 316 K , b.p. 455 K) which turns **pink-red in air and light** due to slow oxidation ; it is **corrosive** and has a **characteristic odour**.

Chemical Reactions of Alcohols

Alcohols react by **cleavage of the O–H bond** (acidic nature , esterification) or by **cleavage of the C–O bond** (substitution , dehydration). The ease of **O–H cleavage** is **1° > 2° > 3°** ; the ease of **C–O cleavage (carbocation stability)** is **3° > 2° > 1°**.

1. Reactions involving the O–H bond

- **Acidic nature :** alcohols react with **active metals (Na , K)** to give **alkoxides and H_2**. They are **weaker acids than water** ($pK_a \approx 16 - 19$) because the alkyl group is **electron-releasing** and destabilises the alkoxide ion. **Acidity : CH_3OH > 1° > 2° > 3°.**

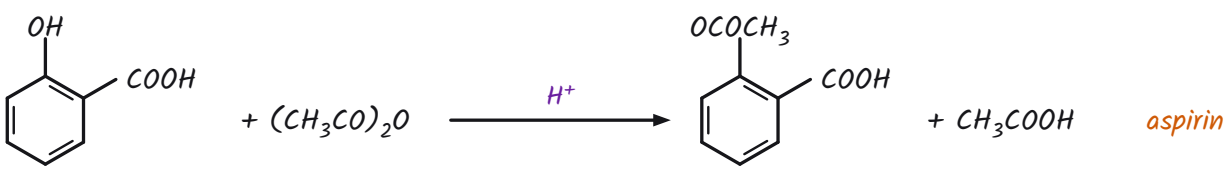
$$2\ R\text{–}O\text{–}H + 2\ Na \longrightarrow 2\ R\text{–}O^-Na^+ + H_2$$ sodium alkoxide

$$2\ C_2H_5OH + 2\ Na \longrightarrow 2\ C_2H_5ONa + H_2$$

- **Esterification :** alcohols react with **carboxylic acids** (conc. H_2SO_4 ; reversible) or with **acid chlorides / anhydrides** (pyridine ; irreversible) to form **esters**. **Aspirin** is made by acetylation of salicylic acid.

$$R\text{–}OH + R'COOH \xrightarrow{\text{conc. } H_2SO_4} R'COOR + H_2O$$ ester

$$R\text{–}OH + (R'CO)_2O \xrightarrow{\text{pyridine}} R'COOR + R'COOH$$



aspirin

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SOLVED NUMERICAL 1

Sodium metal (excess) reacts with 4.6 g of ethanol. Calculate the volume of hydrogen gas liberated at STP (C = 12 , H = 1 , O = 16 ; molar volume = 22.4 L mol⁻¹).

GIVEN DATA mass of C_2H_5OH = 4.6 g ; M (C_2H_5OH) = 46 g mol⁻¹

REQUIRED QUANTITY Volume of H_2 at STP

RELEVANT FORMULA $2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$ (2 mol alcohol : 1 mol H_2)

SUBSTITUTION $n_{H_2} = \frac{1}{2} \times n_{C_2H_5OH}$; $V = n \times 22.4$

STEP-BY-STEP CALCULATION

$$n_{C_2H_5OH} = \frac{4.6}{46} = 0.10 \text{ mol}$$

$$n_{H_2} = \frac{0.10}{2} = 0.050 \text{ mol}$$

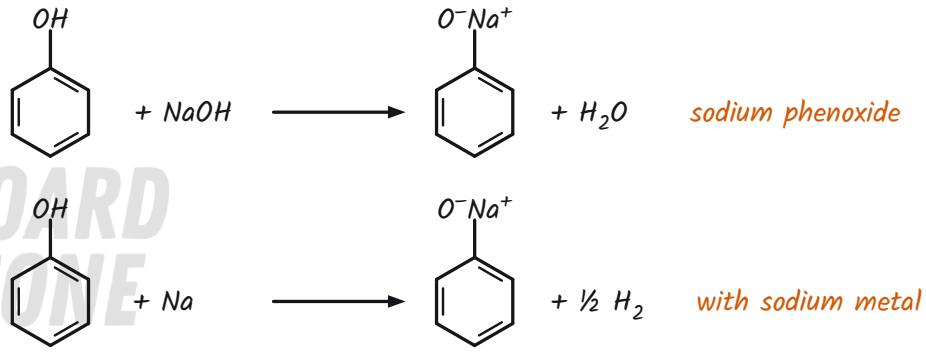
$$V = 0.050 \times 22.4 = 1.12 \text{ L}$$

FINAL ANSWER $V(H_2) = 1.12$ L at STP

Chemical Reactions of Phenols

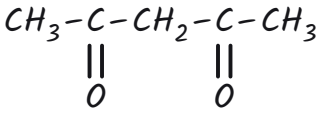
1. Acidic nature of phenol

Phenol is **more acidic than alcohols and water** (pK_a = 10.0) because the **phenoxide ion is stabilised by resonance** (the negative charge is **delocalised over the ring** : ortho and para carbons) whereas an alkoxide ion has its charge localised on oxygen. Phenol is **neutralised by NaOH** (not by $NaHCO_3$) and **liberates H_2 with Na**.

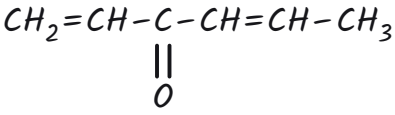


- **Electron-withdrawing groups ($-NO_2$, $-Cl$)** at the o- / p-positions **increase acidity** (they stabilise the phenoxide ion).
- **Electron-donating groups ($-CH_3$, $-OCH_3$) decrease acidity**.
- **The effect is strongest at the o- and p-positions** (resonance) and smaller at the m-position (only the −I effect).

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Pentane-2,4-dione



Hexa-1,4-dien-3-one

Carboxylic acids

- Suffix **–oic acid** (alkane – e + oic acid) ; the **–COOH carbon is always C-1**. Ring acids : **–carboxylic acid** (cyclohexane**carboxylic acid**).

- Two –COOH groups : **–dioic acid** (ethane**dioic** acid) ; for benzene compounds : benzene-1,2-**dicarboxylic** acid (phthalic acid).

- Substituents are written alphabetically with locants (2-chloro-4-ethylhexanoic acid).

Formula	Common name	IUPAC name
$HCOOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid
$CH_3(CH_2)_3COOH$	Valeric acid	Pentanoic acid
$CH_2=CH-COOH$	Acrylic acid	Propenoic acid
$CH_3CH=CHCOOH$	Crotonic acid	But-2-enoic acid
$HOOC-COOH$	Oxalic acid	Ethanedioic acid
$HOOC-CH_2-COOH$	Malonic acid	Propanedioic acid
$HOOC-(CH_2)_2-COOH$	Succinic acid	Butanedioic acid
$HOOC-(CH_2)_3-COOH$	Glutaric acid	Pentanedioic acid
$HOOC-(CH_2)_4-COOH$	Adipic acid	Hexanedioic acid
C_6H_5COOH	Benzoic acid	Benzenecarboxylic acid
$o\text{-}C_6H_4(COOH)_2$	Phthalic acid	Benzene-1,2-dicarboxylic acid

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(ii) Fehling's test

Fehling's solution A (aqueous $CuSO_4$) + B (alkaline sodium potassium tartrate). **Aliphatic aldehydes** give a **red-brown precipitate of Cu_2O. Aromatic aldehydes (benzaldehyde) and ketones do not.**

BOARD ZONE

$$R\text{-}CHO + 2\ Cu^{2+} + 5\ OH^- \xrightarrow{\Delta} R\text{-}COO^- + Cu_2O\downarrow + 3\ H_2O$$

red-brown ppt

$$CH_3CH_2CHO + Cu^{2+} \xrightarrow{OH^-} CH_3CH_2COO^- + Cu_2O\downarrow$$

Exam Point of View

Q. Give a chemical test to distinguish propanal from propanone, and benzaldehyde from acetophenone.

Ans. Propanal gives the silver mirror (Tollens) and the red-brown ppt (Fehling) ; **propanone** gives neither. **Benzaldehyde** gives Tollens' test but **not** Fehling's ; **acetophenone** (a methyl ketone) gives the **iodoform test** while benzaldehyde does not.

BOARD ZONE

(iii) Haloform reaction : the iodoform test

Methyl ketones ($CH_3CO\text{-}R$), **ethanal** and **methyl carbinols** [$CH_3CH(OH)\text{-}R$, ethanol included] react with **NaOI** (I_2 + NaOH) to give a **yellow precipitate of iodoform (CHI_3)** and the sodium salt of an acid with **one carbon less.**

$$CH_3\text{-}CO\text{-}R + 3\ NaOX \longrightarrow R\text{-}COONa + CHX_3 + 2\ NaOH$$

$$CH_3\text{-}CHO + NaOI \longrightarrow HCOONa + CHI_3\downarrow$$

yellow ppt

BOARD ZONE

$$CH_3\text{-}CO\text{-}CH_3 + NaOI \longrightarrow CH_3COONa + CHI_3\downarrow$$

$$CH_3CH_2\text{-}CO\text{-}CH_3 + NaOI \longrightarrow CH_3CH_2COONa + CHI_3\downarrow$$

$$CH_3CH_2\text{-}CHO + NaOI \longrightarrow \text{no yellow ppt}$$

Common Mistakes

Propanal (CH_3CH_2CHO) does **not** give the iodoform test : it has no $CH_3\text{-}C{=}O$ group. Only **ethanal** among aldehydes does. Also, a ketone like pentan-3-one gives no iodoform.

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(b) Formation of anhydrides

$$2\ R\text{-}COOH \xrightarrow[\Delta]{P_2O_5 \text{ or conc. } H_2SO_4} R\text{-}CO\text{-}O\text{-}CO\text{-}R + H_2O$$

$$2\ CH_3COOH \xrightarrow[\Delta]{P_2O_5} (CH_3CO)_2O + H_2O$$

(c) Esterification

Fischer esterification : *carboxylic acid + alcohol with a* ***few drops of conc.*** H_2SO_4 *(or dry HCl) →* ***ester + water****. The reaction is* ***reversible****.*

$$R\text{-}COOH + R'OH \xrightarrow[\Delta]{\text{conc. } H_2SO_4} R\text{-}COOR' + H_2O$$

$$CH_3COOH + C_2H_5OH \xrightarrow[\Delta]{\text{conc. } H_2SO_4} CH_3COOC_2H_5 + H_2O$$

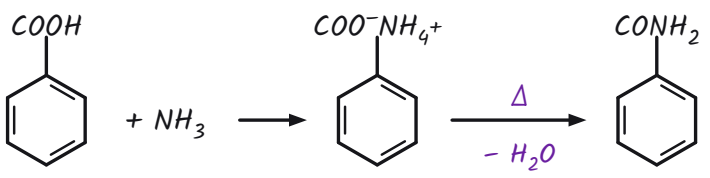
Exam Point of View

Q. *Why is conc.* H_2SO_4 *used in esterification, and why is the ester distilled off as it forms ?*

Ans. *Esterification is* ***reversible****. Conc.* H_2SO_4 *is a* ***catalyst and dehydrating agent****: it removes the water formed and shifts the equilibrium towards the ester. The ester must be* ***removed / distilled off as it forms****, because in the presence of water and acid, on heating, it* ***hydrolyses back*** *into the acid and alcohol.*

(d) Formation of amides

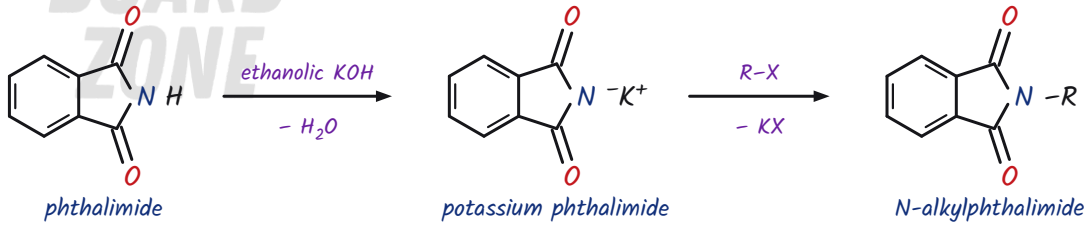
$$R\text{-}COOH + NH_3 \longrightarrow R\text{-}COO^-\ NH_4^+ \xrightarrow[-\ H_2O]{\Delta} R\text{-}CO\text{-}NH_2$$



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5. Gabriel phthalimide synthesis

Phthalimide with **ethanolic KOH** forms its **potassium salt**, which on heating with an **alkyl halide** gives an **N-alkylphthalimide**. **Alkaline hydrolysis** then liberates the **pure primary amine**.



$$\text{N-alkylphthalimide} \xrightarrow[\Delta]{\text{(aq) NaOH}} \underset{\text{1° amine}}{R\text{–}NH_2} + \underset{\text{sodium phthalate}}{C_6H_4(COONa)_2}$$

Exam Point of View

Q. Why can aniline not be prepared by the Gabriel phthalimide synthesis ?

Ans. Aryl halides do not undergo nucleophilic substitution with the phthalimide anion (the C–X bond has partial double-bond character). The Gabriel method is used only for **1° aliphatic amines**.

6. Hofmann bromamide degradation

A primary **amide** is heated with **Br_2 and NaOH (or KOH)** and gives a **primary amine with one carbon atom less** : the series is **descended**.

$$R\text{–}CO\text{–}NH_2 + Br_2 + 4\ NaOH \longrightarrow R\text{–}NH_2 + Na_2CO_3 + 2\ NaBr + 2\ H_2O$$

$$CH_3\text{–}CO\text{–}NH_2 + Br_2 + 4\ KOH \longrightarrow CH_3\text{–}NH_2 + K_2CO_3 + 2\ KBr + 2\ H_2O$$

Remember This

Hofmann bromamide : amine has **one carbon less** than the amide. Nitrile reduction : amine has **one carbon more** than the alkyl halide. Amide reduction : **same** number of carbons.

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- **Aliphatic 1° amines** give an unstable diazonium salt, which at once gives the **alcohol** with the evolution of N_2.

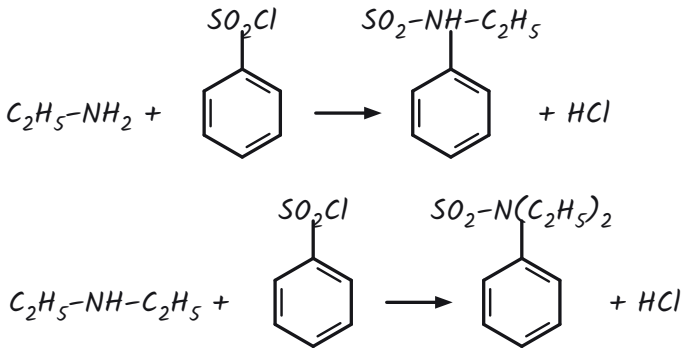
- **Aromatic 1° amines** give a **stable diazonium salt** at **273–278 K** ; on warming with water this changes to **phenol**.

- **Secondary amines (aliphatic or aromatic)** give **N-nitrosoamines**, which are **yellow oily liquids**.

- **Tertiary aliphatic amines** simply dissolve in HNO_2 forming **trialkylammonium nitrite salts**.

Reaction with Aryl Sulphonyl Chloride : Hinsberg Test

Hinsberg's reagent is **benzenesulphonyl chloride ($C_6H_5SO_2Cl$)**. It distinguishes **1°, 2° and 3° amines**.



Amine	Result with $C_6H_5SO_2Cl$ / aqueous alkali
1° amine	sulphonamide has an **acidic N–H → soluble in alkali**
2° amine	sulphonamide has **no H on N → insoluble in alkali**
3° amine	**does not react** with the reagent

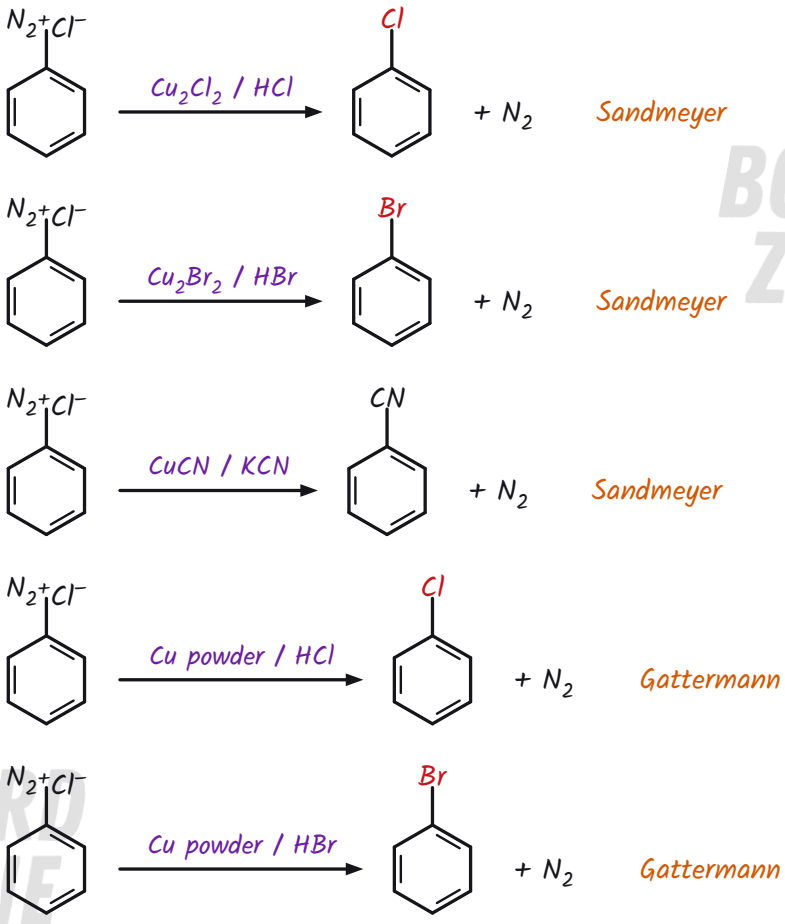
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Chemical properties

Reactions are of two types : (a) reactions **involving removal of N_2** and (b) reactions **retaining the diazo group**.

(a) Replacement of the diazonium group

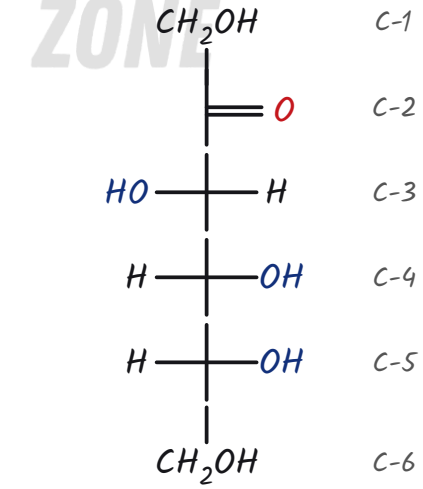
Sandmeyer reaction : Cl^- , Br^- and CN^- are introduced with **Cu(I)** ions (Cu_2Cl_2 , Cu_2Br_2 , CuCN). **Gattermann reaction :** Cl^- and Br^- are introduced with the **halogen acid and copper powder**. The **Sandmeyer reaction gives a better yield**.



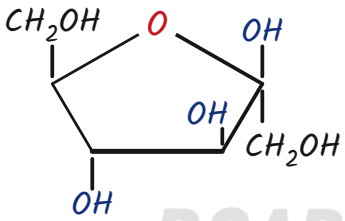
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Fructose ($C_6H_{12}O_6$)

Fructose is an important **ketohexose**, obtained with glucose from the hydrolysis of **sucrose**. It is found in fruits, honey and vegetables, is the **sweetest sugar** (fruit sugar) and is **laevorotatory** (laevulose).



D-(−)-fructose (open chain)



β-D-fructofuranose (five-membered ring)

The –OH on **C-5** adds to the **C-2 keto group** to form a **five-membered furanose ring**.

Remember This

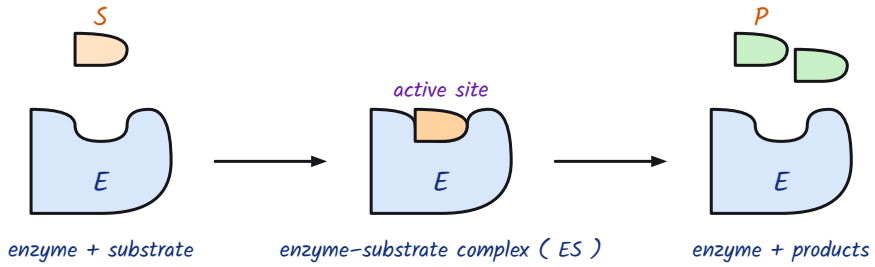
Glucose : aldohexose , **pyranose** ring (6-membered). **Fructose** : ketohexose , **furanose** ring (5-membered). Both are **reducing sugars** (fructose isomerises to glucose in basic medium).

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Enzymes (Bio-catalysts)

Biochemical reactions are catalysed by **enzymes**. **Almost all enzymes are globular proteins**. They are **highly specific** for a particular reaction and substrate and are named after the compound they act on (**maltase** hydrolyses maltose) or the reaction they bring about (an **oxidoreductase** catalyses oxidation of one substrate with reduction of another).

Mechanism (lock and key) : the **substrate fits the active site** of the enzyme, forming an **enzyme–substrate complex**, which gives the product and the free enzyme.



$$E + S \rightleftharpoons ES \text{ (complex)} \longrightarrow E + P$$

Vitamins

Organic compounds **essential in small amounts for normal growth** and health. They are **not synthesised by animals** (vitamin D can be made in the skin in sunlight) and must be supplied through food.

Water-soluble vitamins	Fat-soluble vitamins
vitamin B-complex and vitamin C (not stored, except B_{12} which is stored in the liver)	**vitamin A** (retinol) , **D** (calciferol) , **E** (tocopherol) , **K** (phylloquinone)

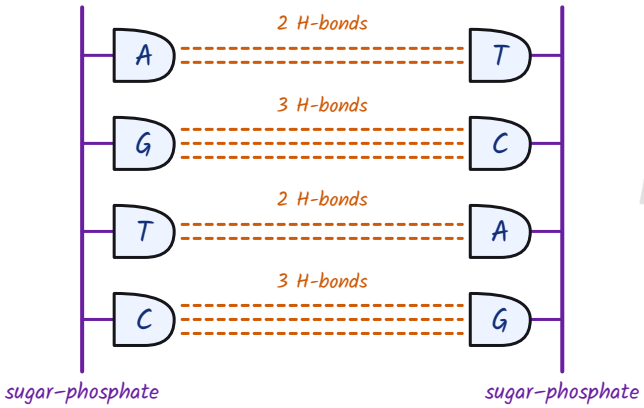
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sugar + base ⟶ nucleoside + H_3PO_4 ⟶ nucleotide $\xrightarrow{\text{polymerisation}}$ nucleic acid

Structure of DNA and RNA

- **DNA :** two chains are wound about each other (**double helix**) and held by **hydrogen bonds between pairs of bases**. The strands are **complementary : A pairs with T (two H-bonds)** and **C pairs with G (three H-bonds)**.

- **RNA :** a **single-stranded** helix which sometimes folds back on itself. Three types : **messenger RNA (m-RNA) , ribosomal RNA (r-RNA) and transfer RNA (t-RNA)**.



Differences between DNA and RNA

	DNA	RNA
Strands	double stranded helix	single stranded
Bases	A , T , G , C	A , U , G , C
Sugar	2-deoxyribose	ribose
Replication	can replicate itself	cannot replicate itself
Protein synthesis	does not synthesise protein	synthesises protein
Heredity	passes characters from parent to offspring	does not pass characters to offspring

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