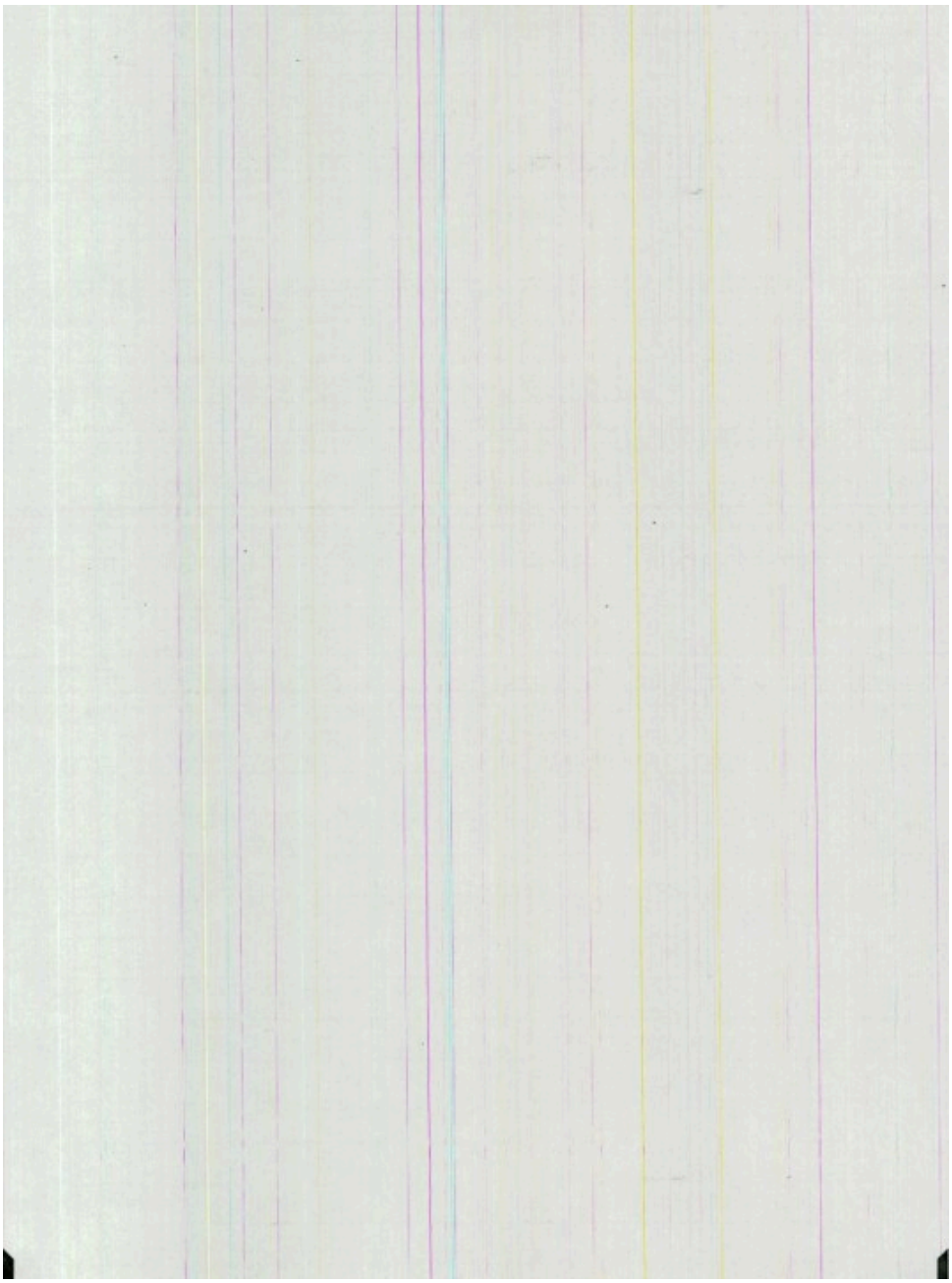
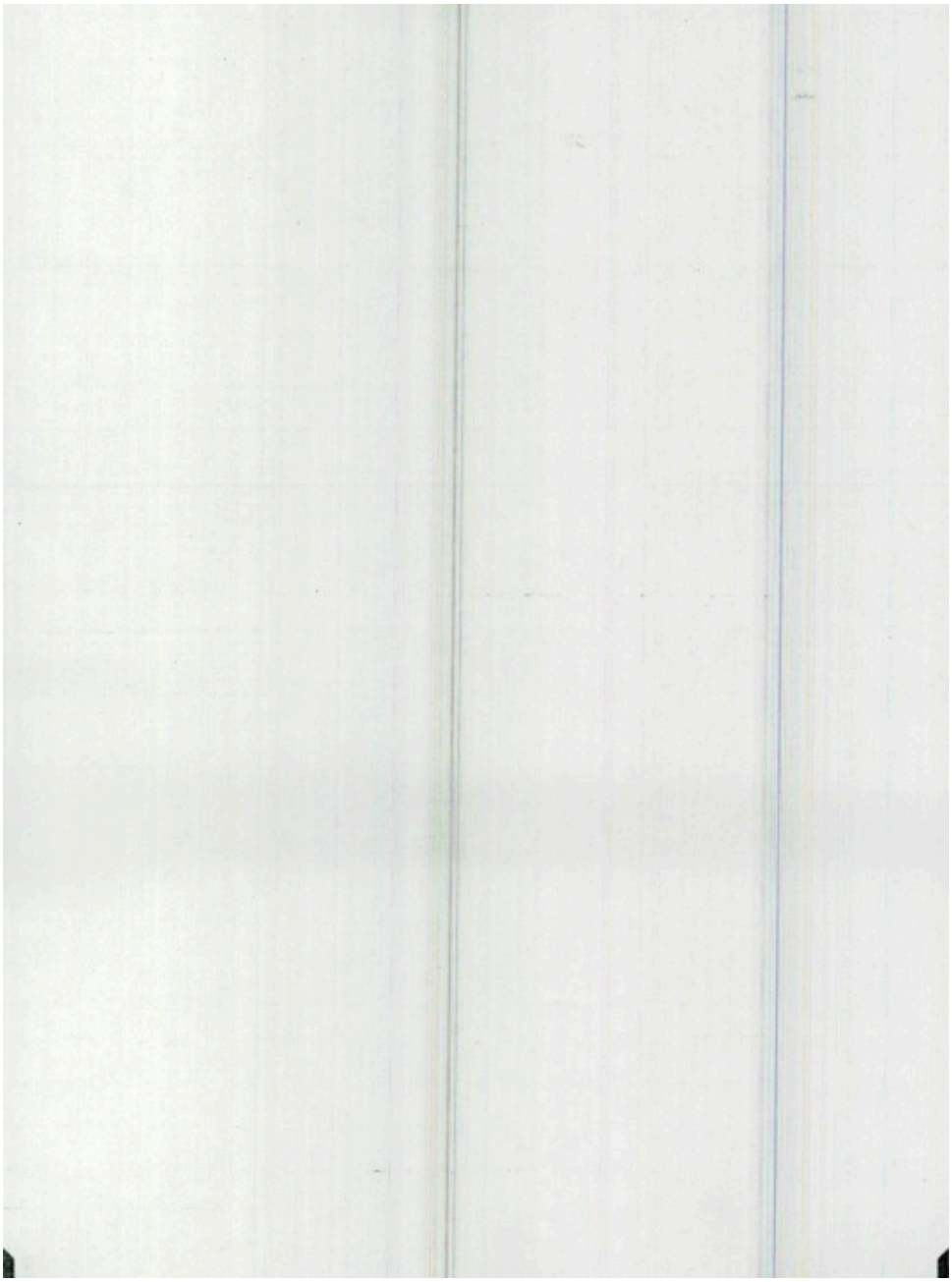
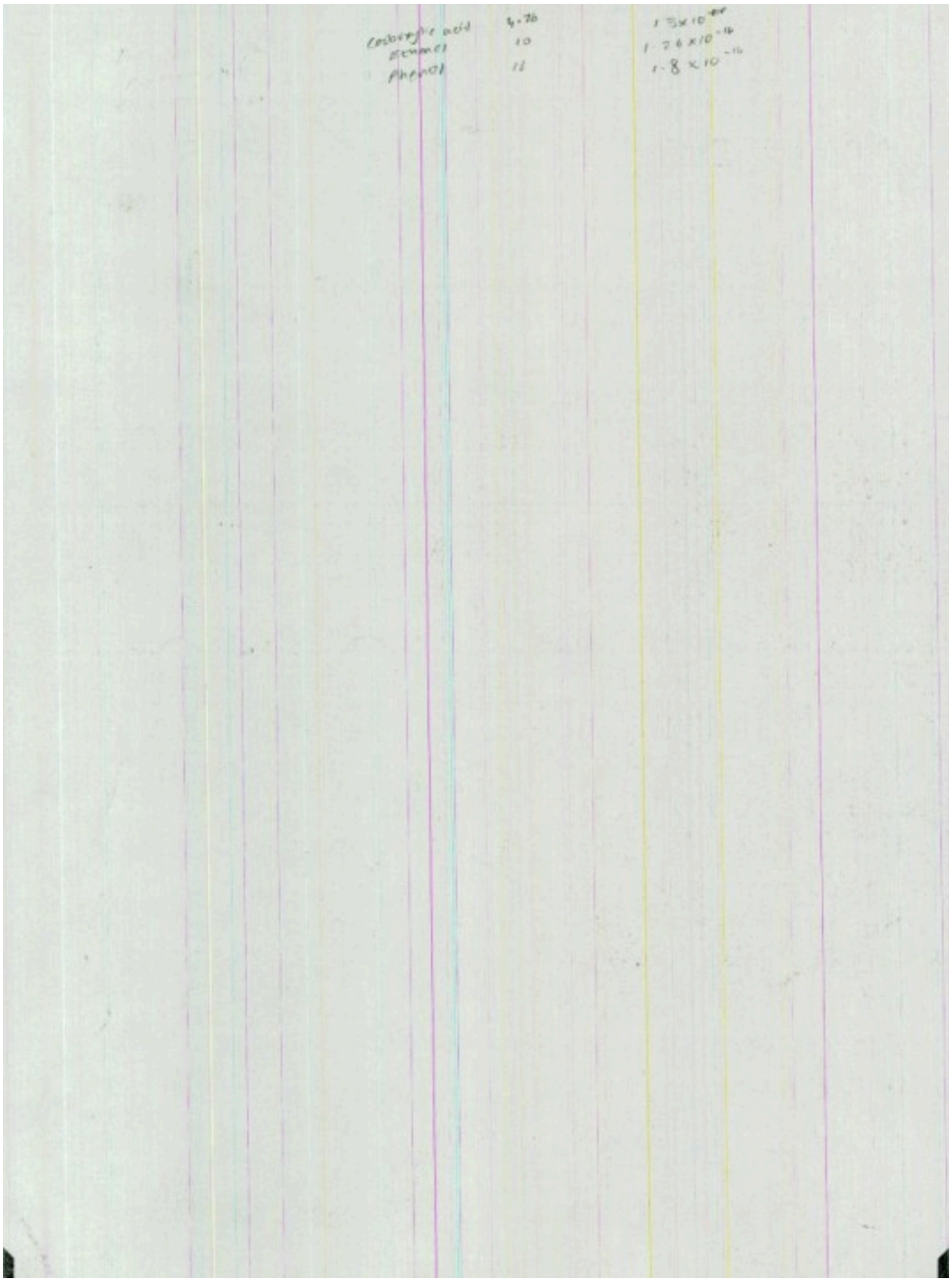






(Section B)

Q. No. 2 Part (i) FEASABILITY OF REDOX REACTION

we can split this ~~half~~ redox reaction into two half reactions:

⊙ $Fe \rightarrow Fe^{2+}$: oxidation halfreaction as oxidation state increased which occurs at anode half-cell

⊙ $Pb^{2+} \rightarrow Pb$: reduction half reaction as oxidation state decreased which occurs in cathode half-cell.

$Fe \rightarrow Fe^{2+} + 2e^-$ Oxidation half reaction :: $E_{anode} = -0.44\ V$

$Pb^{2+} + 2e^- \rightarrow Pb$ reduction half-reaction :: $E_{cathode} = -0.13\ V$

The emf of cell : $E_{cell} = E_{cathode} - E_{anode}$

$E_{cell} = E_{Pb} - E_{Fe}$

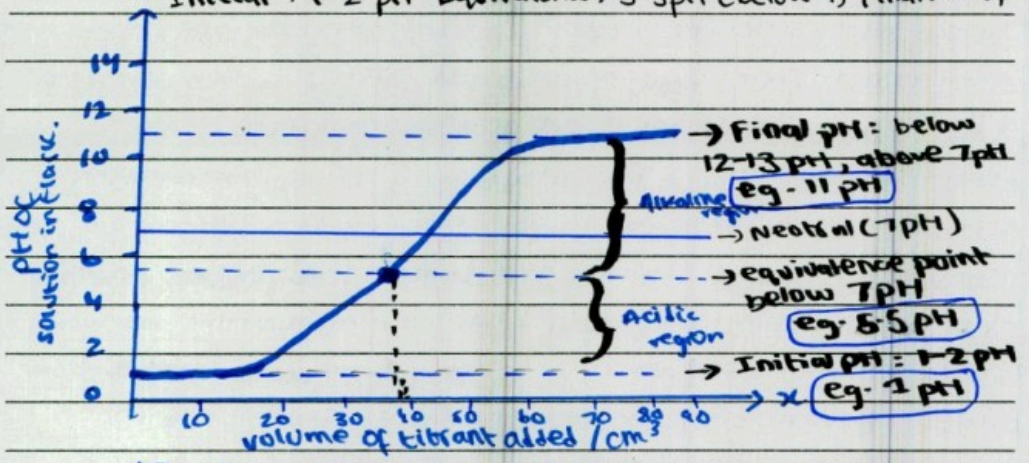
$E_{cell} = -0.13\ V - (-0.44\ V)$

$E_{cell} = \underline{0.31\ V}$

⊙ Since emf of cell is positive, reaction is feasible. Since the iron has greater tendency to lose electrons, it ~~has~~ is negative anode.

Q. No. 2 Part (ii) TITRATION CURVE

Initial : 1-2 pH Equivalence: 5·5pH (below 7) Final: 12-13pH



consider ~~20~~ 40 cm^3 of 0·1 M NH_3 and 0·1 M HCl to get at just a volume for consideration of 40 cm^3

weak base $NH_3 + HCl \rightleftarrows NH_4Cl$ strong conjugate base

(Section B)

Q. No. 2 Part (iii) — **Electrolysis Products**

As electricity is passed through the molten NaCl,

CATHODE (−): $2Na^{+}_{(aq)} + 2e^- \rightarrow 2Na_{(s)}$ (reduction half reaction)

ANODE (+): $2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$ (oxidation half reaction)

$2Na^{+}_{(aq)} + 2Cl^-_{(aq)} \rightarrow 2Na_{(s)} + Cl_{2(g)}$ (overall reaction)

+ Sodium ions are reduced to **sodium metal** at the cathode as it gains electrons, and no other ions eg. H^+ are present as electrons from the anode through battery come.

+ Cl^- chlorine ions are oxidized to chlorine gas at anode by losing two electrons (one per ion) ~~so its reduction potential~~

+ Cathode (−): sodium metal + Anode (+): chlorine gas

Q. No. 2 Part (iv) — **GROUP II REACTIVITY**

• Group II elements have a general valence configuration of ns^2 where n = number of shells. So they have two valence electrons in their outermost shell, which they lose to form **positively charged cations** with a charge of +2. They get oxidised hence, act as reducing agents.

• Reactivity depends upon **ionization energy**. Lower the ionization energy, means minimum energy for valence electron removal to form reactive ions. Group I elements have **lower ionization energy** than group II elements as Group 1 have a greater atomic and ionic size due to lower nuclear attraction so Group 1 are **more reactive** than Group II and are stronger reducing agents. Group 1 reacts so vigorously with water that liberated H_2 catches fire while Group II show slower reaction. GI: $2Na_{(s)} + H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_2$

GII: $Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_2 + H_2$ → Be and Mg don't even react with cold water.

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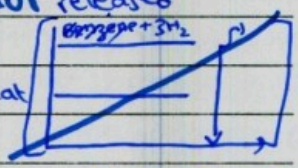
Q. No. 2 Part (v) COLOURLESS COMPLEXES

Transition elements show colour when their ions in solid or aqueous form have **incomplete d-subshell** so when white light passes through, characteristic photon of a specific wavelength and energy is absorbed (if absorbed) to allow the electron to be excited from lower energy state to higher energy state by **d-d electronic transition** as the approach of ligands and interaction of d orbital with ligands' lone pair caused **d-d splitting** in which d orbitals acquire have different energy states, eg. in octahedral t_{2g} is lower ($3d_{xy}, 3d_{yz}, 3d_{xz}$) and eg is higher energy ($3d_{x^2-y^2}, 3d_{z^2}$). (CFE)

→ Due to absorption of photon, colour disappears and complementary colour is transmitted ★ while in d^0 configuration: ① There is no unpaired electron in lower energy state but mainly **no valency in higher energy d-orbitals where low energy electron can get excited to, so no photon absorbed, no colour disappeared all transmitted** – so colourless compounds.

Q. No. 2 Part (vi) RESONANCE ENERGY

- Experimentally, hydrogenation of 1,3,5-cyclohexatriene requires **-360 KJ/mol** energy which is released as cyclohexene requires **120 KJ/mol** (120×3 = 360) as 3 double bond in 1,3,5-cyclohexatriene, the enthalpy of hydrogenation of benzene is only **-208 KJ/mol** released experimentally using 20-30 atm etc.

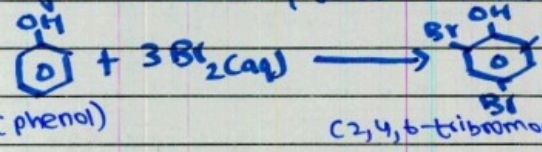


- The energy difference is called **resonance energy** 360 − 208 = **152 KJ/mol** because benzene is highly stabilized due to the **delocalization and continuous rotation of the 6 π electrons** from its unhybridized-p orbitals. This forms a highly stable aromatic ring which cannot be broken easily – **hydrogenation being addition** reaction is not favoured; benzene wants to maintain aromatic conjugated ring; more energy and harsh conditions to break it.

(Section B)

Q. No. 2 Part (vii) REACTION OF PHENOL

- When phenol reacts with bromine water, it forms **white solid** precipitate of 2,4,6- tribromophenol and HBr released while the orange-brown colour of solution decolorizes as bromine is used up.



(phenol) (2,4,6-tribromophenol) (hydrogen bromide)

- Phenol is more reactive than benzene due to **resonance (+R)** donating effect of hydroxyl group which delocalizes electrons into benzene's aromatic ring increasing electron density on all carbon atoms making it highly ~~electrophilic~~ attractive to incoming electrophiles. OH- **is ring-activating** and increases electron density mainly at 2, 4 positions of benzene so Br^+ can attack ring. Benzene has **extremely stable aromatic ring**, not as electron-rich, so vigorous reactions to make it more reactive while phenol reacts at room temperature.

Q. No. 2 Part (viii) ACIDITY COMPARISON

Acidity refers to how easily H^+ is lost, and stability of conjugate base after deprotonation ~~since, pKa = -log Ka, acidity $\propto \frac{1}{pKa}$.~~

(1) CH_3COOH < $CH_2ClCOOH$ (2) ethanoic acid is less acidic than 2-chloroethanoic acid. The **chlorine** bonded to carbon next to carboxyl group is **electron-withdrawing group** via (-I) inductive effect, so it decreases the electron density between O-H bond, weakening it allowing it to break easily in comparison to CH_3COOH hydroxyl bond where alkyl group (-R) here methyl is **electron-donating** group pushing electrons towards oxygen atom strengthening O-H bond by **+I effect**. So in $CH_2ClCOOH$, H^+ is lost easily and the negative charge on alkoxide after deprotonation is also **reduced** stabilizing ethanoate ion due to Cl^- inductive effect while in CH_3COOH, H^+ not lost easily ∴ less acidic and ethanoate ion is **destabilized** as O is electron-rich → higher tendency to gain H^+ back.

2. chloro

(Section B)

Q. No. 2 Part (ix) — **POLYMERIZATION**

① convert acetylene into vinyl chloride:

$$H-C\equiv C-H + HCl \xrightarrow{HgCl_2} \underset{H}{\overset{H}{\diagdown}}C=C\underset{H}{\overset{Cl}{\diagup}}$$

② **Addition polymerization** of vinyl chloride at temperature 40–60° C and 13 atm pressure, where the double-bond backbone is lost to form a saturated **polyvinylchloride** polymer.

$$n\ \underset{H}{\overset{H}{\diagdown}}C=C\underset{H}{\overset{Cl}{\diagup}} \xrightarrow[13\,atm]{40\text{-}60^{\circ}C} \left[\begin{array}{cc} H & Cl \\ | & | \\ C & -C \\ | & | \\ H & H \end{array}\right]_n$$

where n = number of molecules

→ PVC is used in gramophone records, corrugated roofing materials etc. It is **non-biodegradable** as its non-polar and saturated, with stable long chain.

Q. No. 2 Part (x) — **FACTORS - ENZYME ACTIVITY**

① **Temperature**: Temperature impacts kinetic energy and bonding of the enzymes proteins structure. Low temperature below optimum means inactive enzyme, at optimum temperature → maximum activity due to great and high enzyme-substrate collisions, while after it, the enzyme is denatured as bonding (secondary mainly) is broken – no activity. eg. optimum for ptyalin enzyme is 37°C.

② **pH**: Enzymes work in narrow range of pH as it changes **charges on acidic and basic groups so the bonding that holds structure can be disrupted** if pH changes outside optimum range (where it works best). eg. Pepsin works at 2 pH but denatured at 8 pH and so.

③ **Substrate concentration**: Until the **active site state where enzyme** and substrate are in equilibrium, the rate of enzyme activity increases with increasing substrate concentration as more ES (enzyme-substrate) complex form – while temperature and pH remain constant.

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Q. No. 2 Part (xi) MOLECULAR ION PEAK

- Molecular ion peak symbol : $[M^+]$
- The peak with the **greatest m/z** ratio in a molecule's mass spectrum excluding peaks due to heavier isotopes is called the molecular ion peak. It represents m/z ratio and the abundance of the molecular ion formed **as neutral molecule loses exactly one electron** & **upon bombardment** of other electron. Since electron has negligible mass compared to molecule, molecular ion peak's m/z ratio represents the **molecular mass** of the compound → IMPORTANCE
- most ions have +1 charge so $m/z = \frac{m}{+1} \approx$ molecular mass. eg. molecular ion of n-pentane is $CH_3CH_2CH_2CH_2CH_3^+$ ion with m/z ration = 72 which is same as pentane's molecular mass.

Q. No. 2 Part (xii) PRINCIPLE OF IR + USAGE

- when an organic compound consisting of functional group of hetero atom has **infrared radiation (4000 cm^{-1} to 625 cm^{-1})** irradiated on it, the electric component of radiation interacts with dipole moment of the bond. If **natural frequency** of bond or collection of bond matches with IR radiation, absorption occurs causing bond to vibrate with greater amplitude and & polarity increases, so greater bond polarity, more stronger IR absorption.

→ Each functional group absorbs characteristic IR frequency allowing recognition using IR spectrum's bands.

USE: Identification of **functional group** in an organic compound eg. Absorption in 1700 - 1725 cm^{-1} causes strong sharp peak in spectrum revealing **ketone** functional group.

(Section B)

Q. No. 2 Part (xiii) — DEUTERATED SOLVENTS

Deuterated solvents such as D_2O (deuterium oxide) and deuterated acetone ($(CD_3)_2CO$) are used to prevent interference of solvent during analysis as they contain NMR-inactive ^2D which have even number of protons and neutrons, and ~~paired~~ do not have a spin, so no dipole magnetic moment and no interaction with external magnetic field which causes no NMR signals to be produced.

→ This ensures that no unnecessary ^1H signals are found from solvents so NMR spectrum becomes easier and less complex to read. Solvent has high concentration compared to sample, so otherwise too many unrequired signals. Non-polar solvents like CS_2 and CCl_4 can also be used.

Q. No. 2 Part (xiv) — PESTICIDES

* Pesticides: natural or synthetic chemicals that are used to control growth and spread of pests such as insects, weeds, rodents, fungi etc. in plants by inhibiting their growth or killing them completely. They have various mechanisms to do so such as paralysis of and disruption of nervous system by insecticides or causing uncontrolled growth by using plant-based pesticides such as "Dicamba".

Negative impact 1: Pesticide Resistence → in which pests become resistant to pesticides by natural selection and evolution so pesticide usage in-effective and stronger and more toxic pesticides are used. **2. Loss of Biodiversity** → Broad-spectrum pesticides target beneficial insects such as earthworms and pollinators causing die-offs and imbalance in ecosystem.

(Section C)

Q. No. 3 (Page 1)

SN1 MECHANISM

It is a nucleophilic substitution reaction in which the halide ion / halogen group is replaced by incoming nucleophile in a "two-step" mechanism. It is a unimolecular reaction.

① Slow / Rate-Determining Step:

The water molecule's OH^- acts as the nucleophile:

$$H\ddot{-}OH \rightarrow H^+ + OH^-$$

The hydroxyl group is nucleophile. In first step, the tert-butyl bromide undergoes reversible ionization into the **carbonium ion and halide ion** after heterolytic cleavage

(A) $(CH_3)_3C\ddot{-}Br \overset{\text{slow}}{\rightleftharpoons} (CH_3)_3C^+ + \ddot{Br}^-$ (Br carries shifted lone pair)

tert-butyl bromide ⇌ carbonium ion + bromide ion (leaving group)

(B) The carbonium ion here is a **highly stable tertiary carbocation** - a planar structure with sp^2 hybridized carbon, carrying a positive charge. The alkyl groups are electron-donating groups. Although weak, they donate electrons towards positive carbon by **inductive effect (+I) and hyperconjugation**, which decreases central carbon's positive charge and helps to stabilize it. Hyperconjugation bring their **sigma bond electrons.**

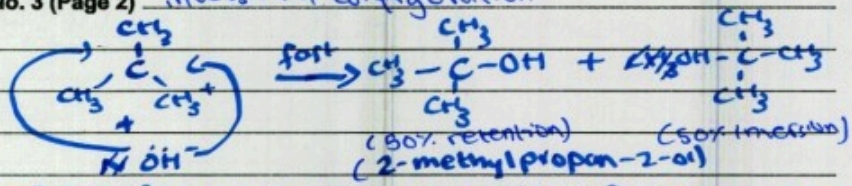
→ This planar structure allows attack of nucleophile in next page.

② Attack of Nucleophile:

Since there is a p-orbital (unhybridized) that lies perpendicular to plane of carbonium ion, there's equal probability that nucleophile donates electrons from left or right side. So the nucleophilic attack forms a **saturated product**. There's 50% retention and 50%

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Q. No. 3 (Page 2) inversion in configuration



(50% retention) (50% inversion)

(2-methylpropan-2-ol)

⊙ **Retention**: OH^- attacks electrophilic carbon from same side where bromide ion departed

⊙ **Inversion** : OH^- attacks from opposite side to bromide departure

⊙ So **racemic mixture** is obtained with both molecules, through this fast step.

KINETIC EVIDENCE

→ Experimentally, the rate of reaction is independent of **concentration of nucleophile**, it only changes as concentration of tert-butyl bromide is varied:

Rate ∝ [tert-butyl bromide]

Hence, **Rate** = k **[tert-butyl bromide]**

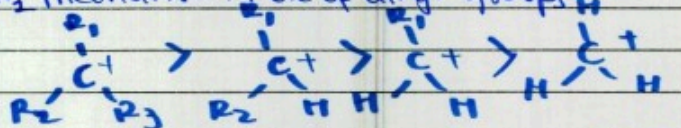
(k = constant; [tert-butyl bromide] = concentration of substrate)

or

general : Rate = k [substrate]

So this S_N1 mechanism is **first order reaction**, making it **unimolecular**.

S_N1 mechanism: Role of alkyl groups



3^0 > 2^0 > 1^0 > methyl

The more the alkyl groups, the more stable the carbocation so tertiary carbocation is most stable

(Section C)

Q. No. 3 (Page 3) and favours S_N1 mechanism more as it is product of rate- determining step. Anything that stabilizes it favours formation and reaction rate increases.

(Section C)

Q. No. 4 (Page 1)

TRANSITION METALS

Definition: metals found in d- block of periodic table that have incomplete d-subshells in their most stable ionic states. They show gradual change from the highly reactive and electronegative Group I and II elements to electropositive p-block, first group-13 (Boron family). It consists of: **Scandium, Titanium, Vandium, Chromium, Mongenese, Iron, Cobalt, Nickel, Copper, Zinc.** Zinc is pseudo-transition metal as it has a $3d^{10}$ configuration.

There metals show variable oxidation states, high melting and boiling points, high strength, colored compounds etc.

① TREND OF MELTING POINT: Being metals, melting points depend on the strength of metallic bonding between delocalized electrons and the positively charged nuclei. metallic bonding in turn depends on number of unpaired electrons for bonding. They show greater melting point than s-group metals due to involvement of both 3d and 4s electrons.

From titanium to vandium, number of unpaired electrons increase so the metallic bonding strengthens with vanadium having **4 unpaired electrons** involved in metallic bonding. However, chromium has electronic configuration $[Ar]\ 4s^1\ 3d^5$ so the stability of half-filled 3d orbital means electrons don't readily participate in metallic bonding and melting point drops so.

melting point increased from Ti to V but dropped at Cr.

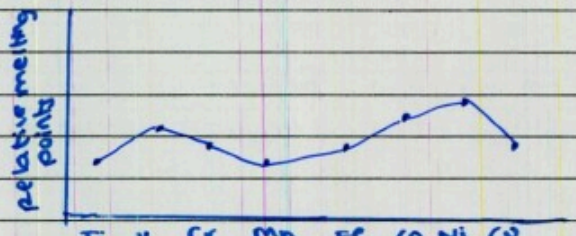
(Section C)

Q. No. 4 (Page 2)

① Manganese has electron configuration: $[Ar]4s^2 3d^5$, so the s and d orbital electrons do not readily participate in metallic bonding and melting point **drops alot**, as less energy required to break the weaker intermolecular forces.

② From manganese to nickel, the melting points **start increasing again** as number of electrons from metallic bonding start increasing. However at copper, due to stability of $3d^{10}$ ($[Ar]4s^1 3d^{10} \rightarrow Cu$) orbital, electrons don't participate in metallic bonding so melting point decreases once again.

However, generally **melting points increases across 1st row of transition element**.



③ **TREND IN ATOMIC RADIUS**:

The atomic radius generally **decreases** across first row of transition metals but this decrease is **not as steep** as main group elements because the electrons being added to 3d subshell are not as effective in shielding against nuclear attraction.

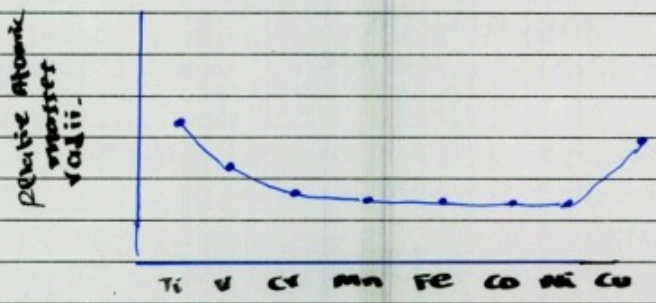
① From Titanium till chromium, the atomic radius decreases because the shielding effect is not affected and valence shell is pulled close by nucleus **where**

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Q. No. 4 (Page 3) nuclear charge increasing with atomic number.

① In the middle, from chromium till nickel, decrease in atomic radius is not as pronounced because the shielding effect effectiveness and increased nuclear attraction counterbalance each other, so atomic radius is almost constant.

② From Nickel to copper, atomic radius increases because of full filled copper's 3d subshell which effectively shields valence shell from nuclear attraction. Shielding effects increasing dominance means atomic radius increases.



(Section C)

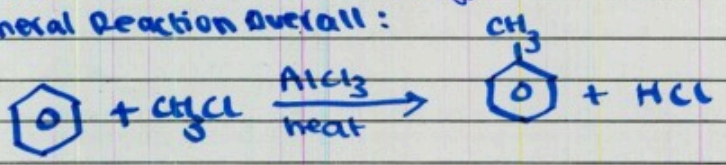
Q. No. 5 (Page 1)

Alkylation: Mechanism

Definition:

Friedel-Craft Alkylation is the introduction of an alkyl group into benzene by reacting it with an alkyl halide, in the presence of heat and anhydrous aluminium (III) chloride as a catalyst

General Reaction Overall:

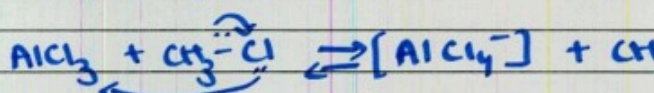


benzene + methylchloride → methylbenzene + hydrogen chloride

MECHANISM

Step 1: Electrophile Generation & Role of Lewis Acid:

- The $AlCl_3$ acts as a lewis acid because the central aluminium has an empty p-orbital and incomplete octet so it accepts a lone pair of electrons from the reagent of methyl chloride from chloride ion. This causes polarization of C–Cl bond in methylchloride causing heterolytic cleavage, producing electrophile CH_3^+ (alkyl cation) → methyl cation. so **lewis Acid ($AlCl_3$) is the catalyst and electrophile generator.**

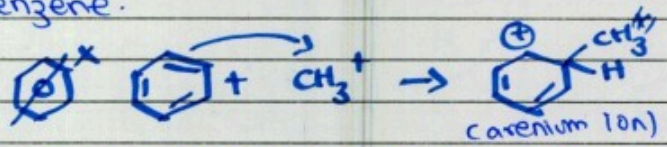


- CH_3Cl is a lewis base as it donates lone pair of electrons to the $AlCl_3$ forming $AlCl_4^-$ base.

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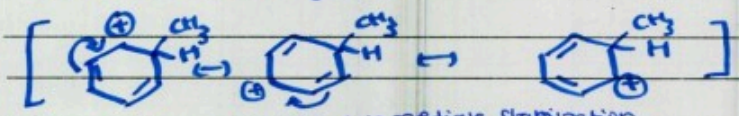
Q. No. 5 (Page 2) **STEP 2: Attack of Electrophile on Aromatic Ring:**

- The CH_3^+ attacks the electron-rich aromatic ring of benzene - so two pi-electrons are used to form a sigma covalent bond with CH_3^+ forming a uni-positive intermediate called arenium ion / **sigma complex** which contains 4 π electrons and a positive charge delocalized over 5 carbon on benzene.



(arenium ion)

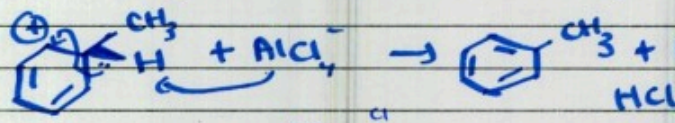
Arenium ion **lost aromatic ring** and undergoes resonance stabilization.



cation-intermediate stabilization.

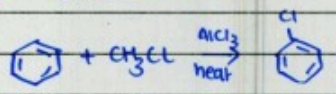
STEP 3: Regeneration of catalyst and Deprotonation:

- The $AlCl_4^-$ base comes close as heterolytic cleavage of C-H bond causes the proton to be removed. The two δ electrons are used to restore the aromatic ring of benzene. $AlCl_4^-$ abstracts the proton to regenerate the catalyst $AlCl_3$.



$+ AlCl_4^- \rightarrow CH_3 + AlCl_3 + HCl.$

General:

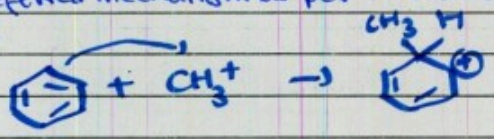


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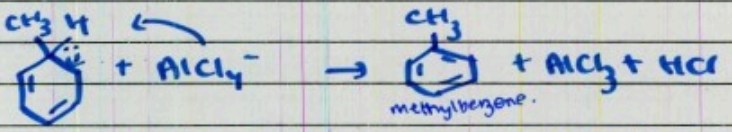
Q. No. 5 (Page 3) 8½

Preferred mechanism as per initial reaction given.

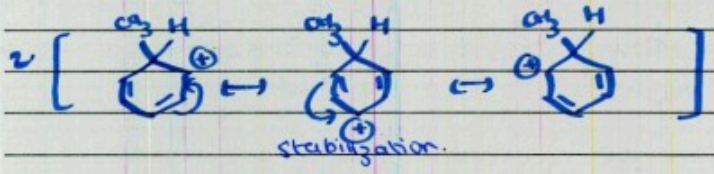
2.



3.



* Better suited at this position to show mechanism where



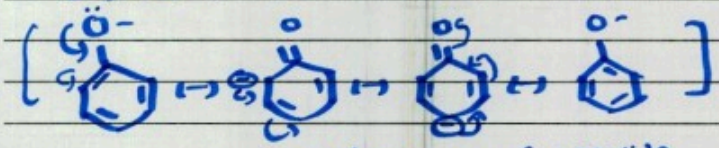
(Section C)

Q. No. 6 (Page 1)

ACIDIC STRENGTH

- Acidity depends on: Ka value, ease of H^+ loss and stability of base

(1) Phenol: After deprotonation, the phenoxide ion forms undergoes resonance destabilization as the negative charge on alkoxide ion is delocalized over the benzene structure, so it is stabilized. The value of Ka is 1.3×10^{-10}



stabilization of phenoxide

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

Since the acidity is directly proportional to Ka, Phenol is stronger. Since structure is stabilized, less tendency to regain lost proton, as oxygen doesn't have negative charge in resonant structures.

(2) Water: It is amphoteric: undergoes auto-ionization acting as the base and acid.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

The hydroxide ion is more stable than the ethanoate ion but less stable than the phenoxide ion as there is no electron donating group like ethanoate ion but no resonance like phenoxide ion.

The Ka of water is: 1.8×10^{-16}

$K_{a\,water} < K_{a\,phenol}$ So water is less acidic.

(3) Ethanol: The negative charge on alkoxide after deprotonation in ethanoate ion is localized, so no

(Section C)

Q. No. 6 (Page 2) resonance-stabilization. Also alkyl group acts as electron donating group pushing electrons towards oxygen, increasing tendency to gain the proton. The Ka value is 1.26×10^{-16}

$K_a$ethanol $<$ $K_a$water $<$ $K_a$phenol.

$1.26 \times 10^{-16} < 1.8 \times 10^{-16} < 1.3 \times 10^{-10}$

$CH_3CH_2OH \rightarrow CH_3CH_2O^- + H^+$

$\delta+$ $\delta-$

* $CH_3-CH_2-O^-$

no resonance stabilized structure;
localized negative charge

* Hydroxide ion :

$\ddot{O}-H^-$ → no resonance occurs

(Section C)

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