

QP Code :70168

[Time : 3 Hours]

[Total Marks : 100]

Please check whether you have got the right question paper.

N.B. : 1. All Questions are compulsory.

2. Figures to the right indicate full marks.

3. Use of log-table/nonprogrammable calculator is allowed.

4. Answers for the same question as far as possible should be written together.

1. (A) Select the correct option and complete the following sentences. (any **twelve**) **12**
- (i) Substances with higher reduction potentials are strong **oxidising agents**.
 - (ii) All metals lying above in electrochemical series can liberate H₂ gas by reaction with **acids**.
 - (iii) In galvanic cell, electrons are given off by **anode** electrode.
 - (iv) A system with zero degrees of freedom is known as **non variant**.
 - (v) The eutectic temperature of lead silver system is **576K**
 - (vi) All metals lying below in electrochemical series can liberate H₂ gas by reaction with **bases**.
 - (vii) In first transition series **Cr** element has its 3d level exactly half filled.
 - (viii) Solution containing hydrated Ti³⁺ is **purple** in colour
 - (ix) Ni among following Shows ferromagnetism
 - (x) The complex [NiCN]₄²⁻ has **square planar** structure
 - (xi) Fe²⁺ salts show blue colour with **K- ferricyanide**.
 - (xii) The molecular formula of chromium carbonyl is **Cr(CO)₆**
 - (xiii) Due to presence of electron withdrawing group strength of carboxylic acid **increases**.
 - (xiv) Aromatic carboxylic acid on heating with soda lime forms **arene**.
 - (xv) Carboxylic acid is prepared from grignard reagent by action of **CO₂**.
 - (xvi) **Detergents** are salts of sulfonic acids.
 - (xvii) Naphthalene on reaction with concentrated H₂SO₄ at 160° C forms **2 – naphthalene sulphonic acid**.
 - (xviii) Nitro Benzene on reaction with oleum forms **m – nitro sulphonic acid**.
- (B) State whether the following statements are true or false. (any **three**) **3**
- (i) Any uni-univalent type salt can be used to prepare salt bridge - **FALSE**
 - (ii) Aqueous salt solution is a classic example of single phase system. **FALSE**
 - (iii) With increase in covalent character, acidic character of transition compounds increases - **True**
 - (iv) Ionisation isomerism is a form of stereoisomerism in coordination compounds- **False**
 - (v) Acetic acid is stronger than chloro acetic acid - **FALSE**
 - (vi) In IPSO substitution – SO₃H group is replaced by NO₂ group - **TRUE**

- (C) Match the column. (any **five**) 5
- | | |
|------------------------------------|---|
| (i) Salt bridge | (f) to minimize liquid junction potential |
| (ii) Clpyeron equation | (e) $\frac{dP}{dT} = \frac{\Delta H_f}{T(V_{liq.} - V_{vapour})}$ |
| (iii) SCN- | (b) Ambidentate ligand |
| (iv) Mo | (d) Half filled state |
| (v) Acyl nucleophilic substitution | (g) Forms tetrahedral intermediate |
| (vi) Reaction of different esters | (a) Crossed Claisen condensation |

2. Attempt any **four** of the following. 20

(A) Differentiate between concentration and chemical cells. 5

Any three differences – 3 marks

Example of type – 2 mark.

(B) Explain any two applications of Nernst equation in the study of galvanic cells? 5

Any two applications with example – 2 ½ mark each

(C) The emf of a cell $Zn | ZnSO_4 || CuSO_4 | Cu$ at 25°C is 0.3 V and the temperature coefficient of emf is -1.4×10^{-4} V per degree. Calculate the heat of reaction per mole for the reaction that taking place inside the cell. 5

$$\Delta H = nF \left[T \left(\frac{dE}{dT} \right)_P - E \right] \quad - 2 \text{ marks}$$

$$= 2 \times 96500 [298(1.4 \times 10^{-4}) - 0.03] \dots \dots \text{correct substitution} - 2 \text{ mks}$$

$$= -24843J = -24.843KJ \dots - 1 \text{ mk.}$$

(D) Justify the number of phases and components present in the following system – 5



The number of phases with justification - 2½ mks.

The number of components with justification - 2½ mks.

(E) Derive Gibbs phase rule thermodynamically.

Correct derivation – 5 mks.

(F) The boiling point of a given solvent is 352.2K at $1.013 \times 10^5 \text{ N m}^{-2}$. Calculate the boiling point of the given solvent at $0.63 \times 10^5 \text{ N m}^{-2}$. (molar heat of vaporization of a solvent at 352.2 K is 31.8 kJ mol^{-1} ; $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

Given -

$$T_2 = 352.2K \quad P_2 = 1.013 \times 10^5 \text{ N m}^{-2} \quad P_1 = 0.63 \times 10^5 \text{ N m}^{-2}$$

$$T_1 = ?$$

$$\Delta H_v = 31.8 \text{ kJ mol}^{-1} = 31.8 \times 10^3 \text{ J mol}^{-1}, \quad R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \quad -- 1 \text{ mk}$$

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{vap}}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] - 1 \text{ mks.}$$

Correct substitution of respective values – 2 marks

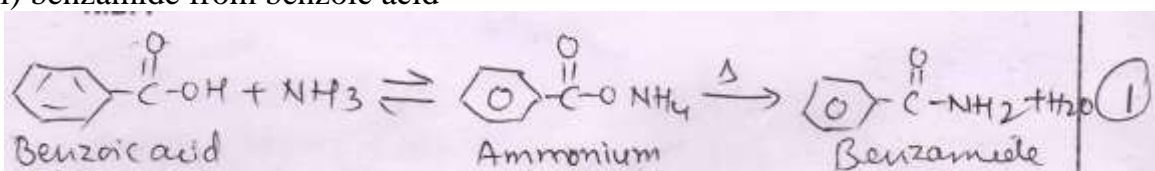
$$T_1 = 1/0.002963 = 337.49 = 337.5 \text{ K} \quad \text{Correct answer} - 1 \text{ mks}$$

3. Attempt any **four** of the following. 20

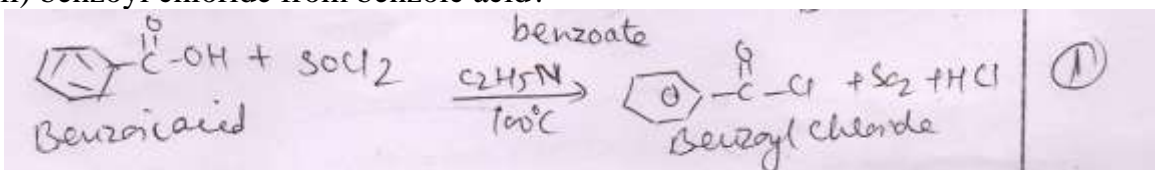
- (A) Explanation of two terms - 2 marks each 05
 One example each $\frac{1}{2}$ mark each
- (B) Names of oxides of Titanium and Vanadium -1 $\frac{1}{2}$ mark each =03 05
 Any two properties of oxide of Titanium and Vanadium - $\frac{1}{2}$ mark each =02
- (C) Any five evidences of formation of coordination compounds- 1 mark each 05
- (D) Colour property of transition metals- Explanation with examples on the basis of i. 05
 Presence of unpaired electrons
 ii. d-d transition of electrons
 iii. Splitting of d orbitals and absorption of light of certain wavelength
- (E) **Werner's Theory** – postulates 03 marks
 Examples 02 marks
- (F) Note on variable oxidation state of transition metals- Brief account -03 marks
 Examples w.r.t. oxidation states - 02 marks

4. Attempt any **four** of the following. 20

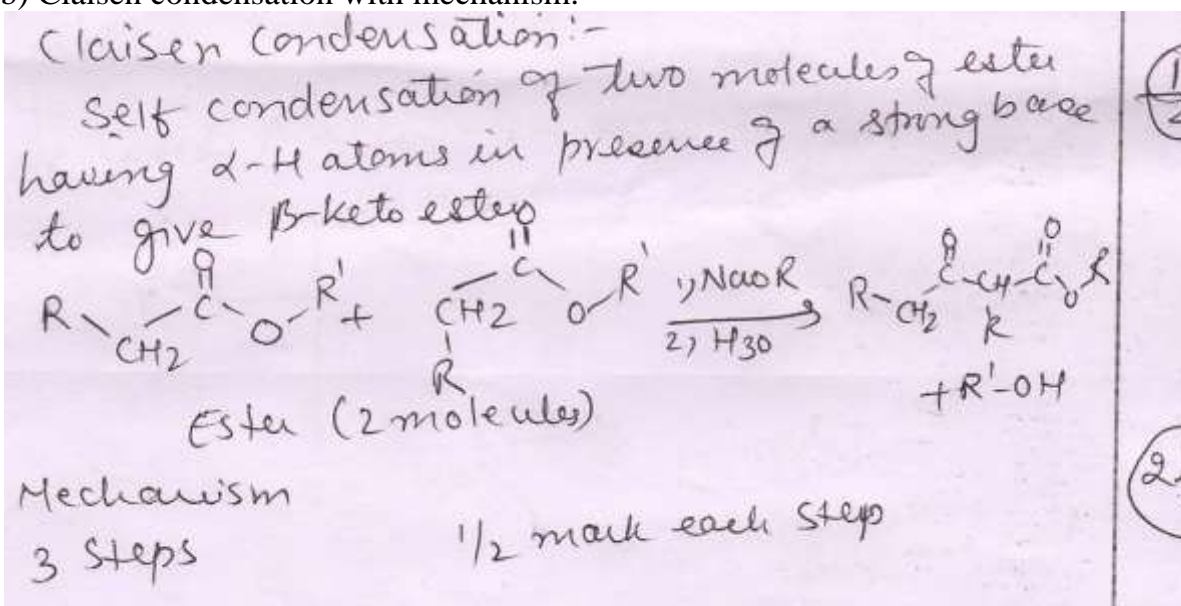
- (A) a) How will you prepare—
 i) benzamide from benzoic acid-



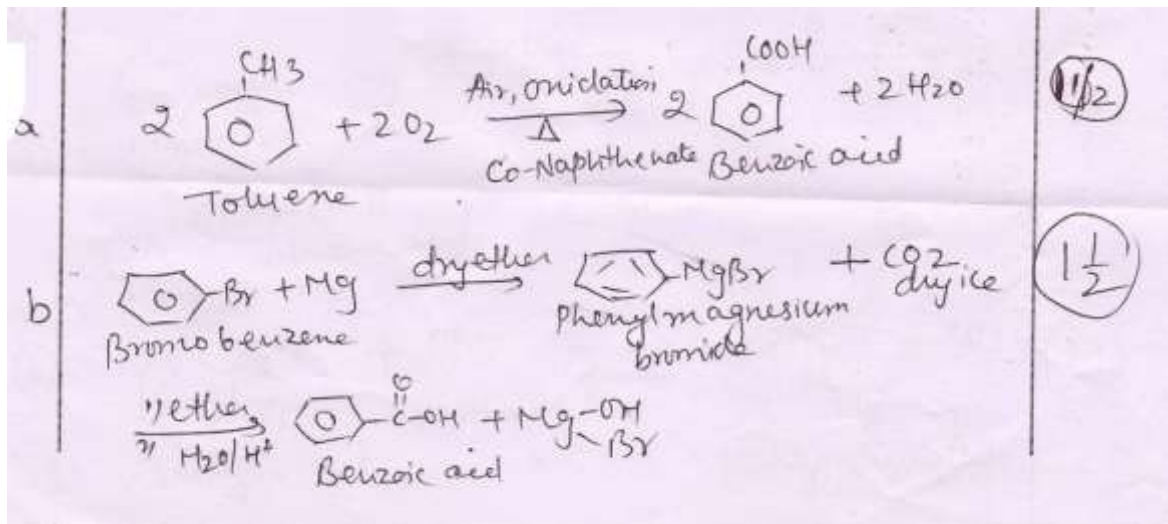
- ii) benzoyl chloride from benzoic acid?



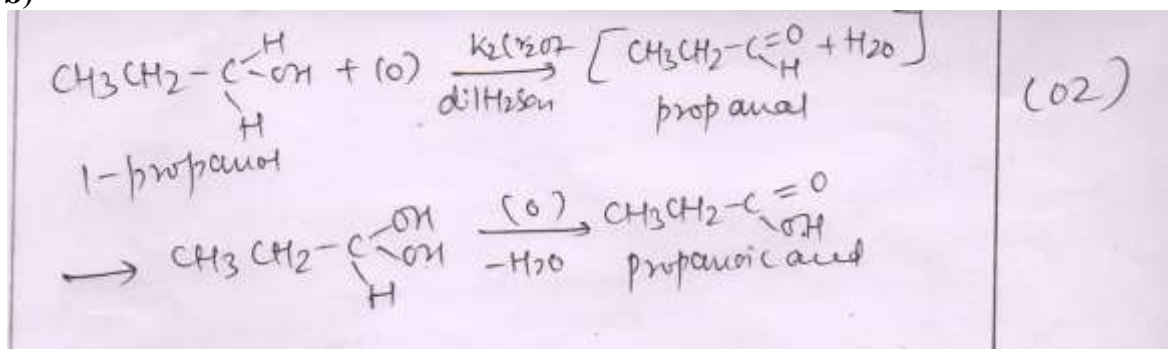
- b) Claisen condensation with mechanism.



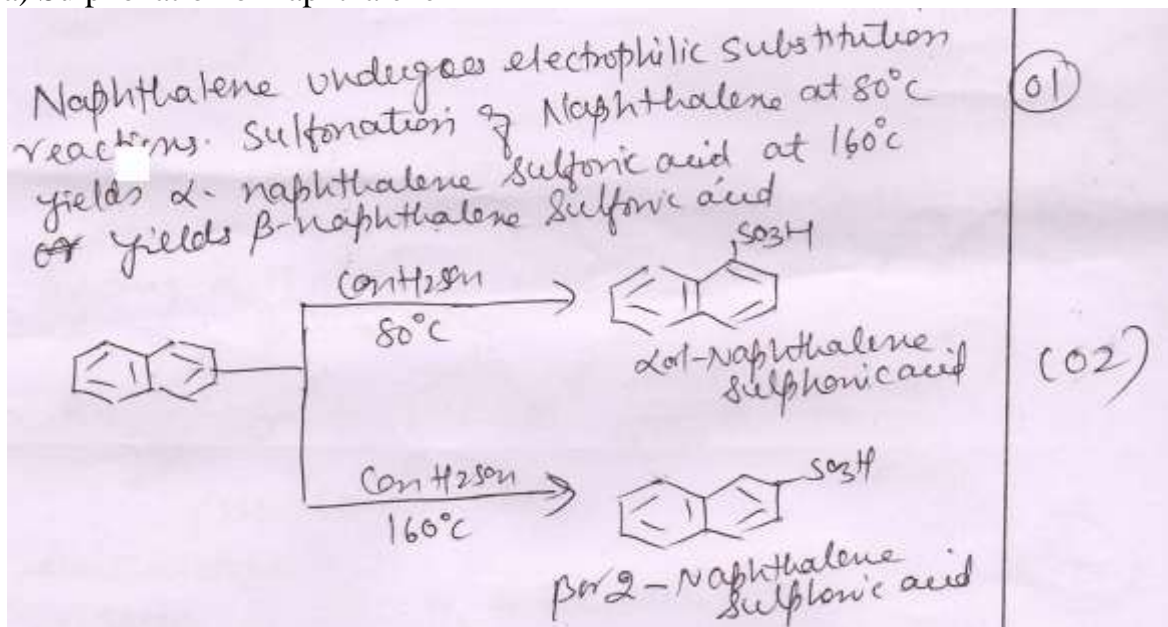
- (B) a) Benzoic acid preparation -



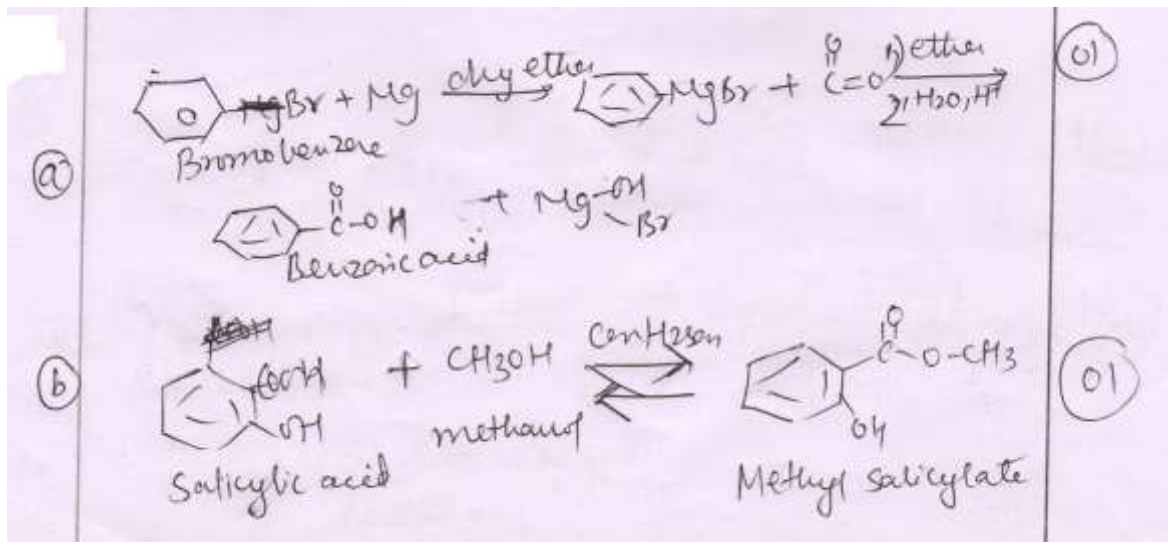
b)



(C) a) Sulphonation of naphthalene



b)



(D) a)

IPSO substitution

Aromatic ring in which $-SO_3H$ group is attached undergoes electrophilic substitution reaction in the same way as the ring carrying strongly electron attracting gr.

It deactivates the ring & is meta directing

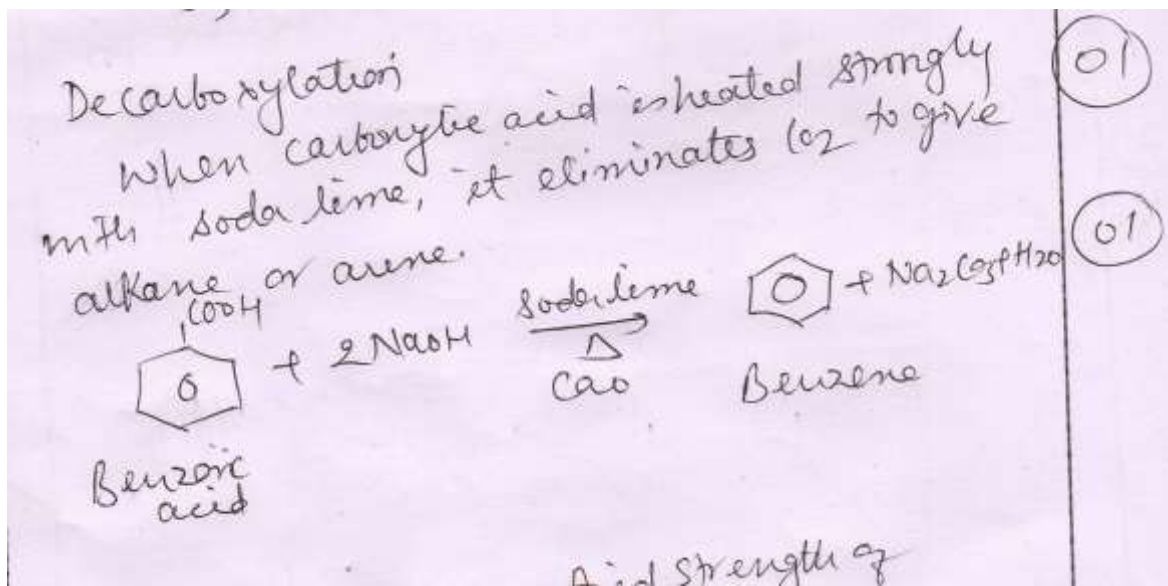
This type of electrophilic attack in aromatic sulfonic acids which results in replacement of $-SO_3H$ gr by H-atom is known as ~~IPSO~~

IPSO substitution

c1ccc(S(=O)(=O)O)cc1 + c1ccc([N+](=O)[O-])cc1 $\xrightarrow{\Delta}$ c1ccc(O)cc1[N+](=O)[O-] + H_2SO_4

(02) (01)

b)



(E) a)

Effect of substituents on Acid strength of Aliphatic acids

1) presence of electron withdrawing substituents
 eg like F, Cl, Br, CN, NO₂ (-I effect)
 \therefore helps to release proton \therefore strength of acid increases
 Explanation with example

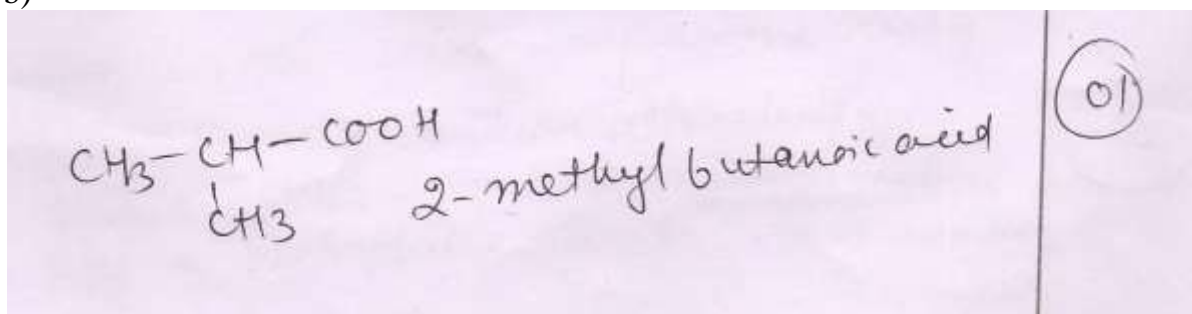
(02)

2) presence of electron donating group
 +I effect
 \therefore release of proton is difficult
 Explanation with example

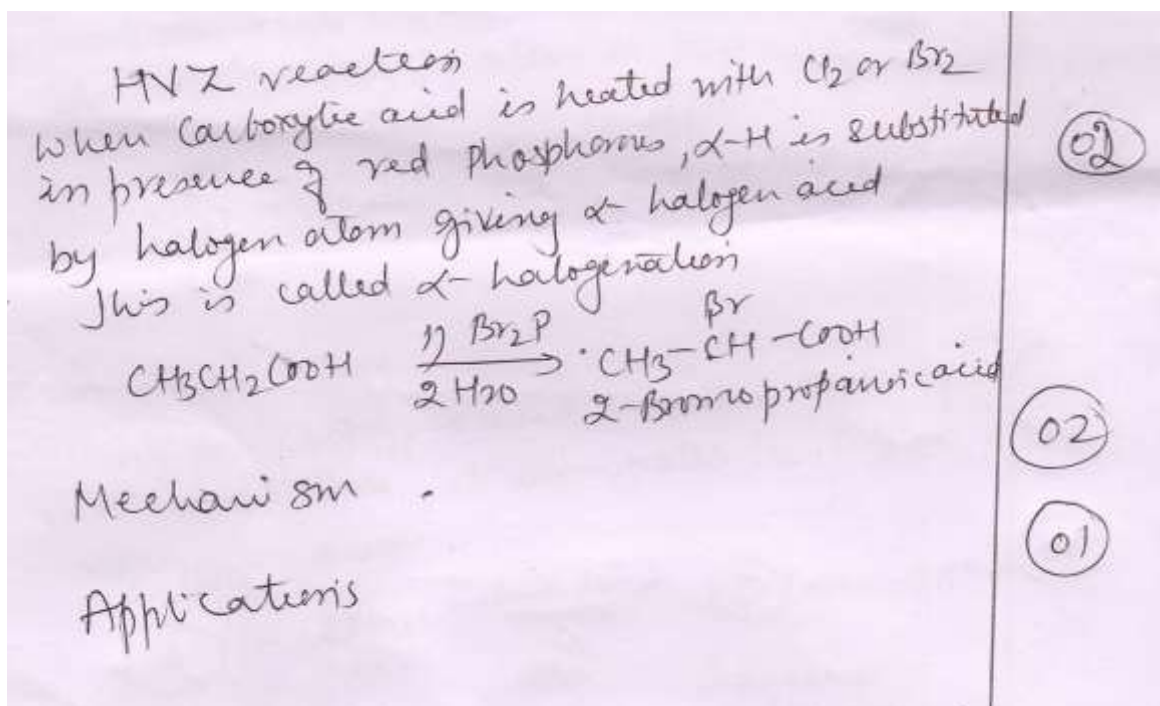
Marks

(02)

b)



(F)



5. Attempt any **four** of the following.

20

(A) What are the advantages and disadvantages of Quinhydrone electrode in the determination of pH? **5**

Any three advantages – 3 mks

Any 2 disadvantages – 2 mks.

(B) Ether boils at 306K at 1.00×10^5 Pa pressure. At what temperature will it boil at a pressure of 9.85×10^3 Pa? Given that the molar enthalpy of vaporization of ether is $2.74 \times 10^4 \text{ J mol}^{-1}$.

Given that $\Delta H_{\text{vap}} = 2.74 \times 10^4 \text{ J mol}^{-1}$. - **1mk**

$T_2 = 306\text{K}$; $T_1 = ?$

$p_2 = 1.00 \times 10^5 \text{ Pa}$ $p_1 = 9.85 \times 10^3 \text{ Pa}$

Substituting these values in Clausius – Clapeyron equation—

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{\text{vap}}}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] - \mathbf{1mk}$$

$$\log \frac{1.00 \times 10^5 \text{ Pa}}{9.85 \times 10^3 \text{ Pa}} = \frac{2.74 \times 10^4 \text{ J mol}^{-1}}{2.303R} \left[\frac{306 - T_1}{T_1 \cdot 306} \right] - \mathbf{2mk}$$

$\therefore T_1 = 252\text{K}$ -**1mk**

(C) Representation in tabular form **04 marks**

Names of elements with special stability **01 mark**

(D)

1) Fischer's Esterification
Acid catalyzed esterification is known as Fischer's esterification
Any Examples

01

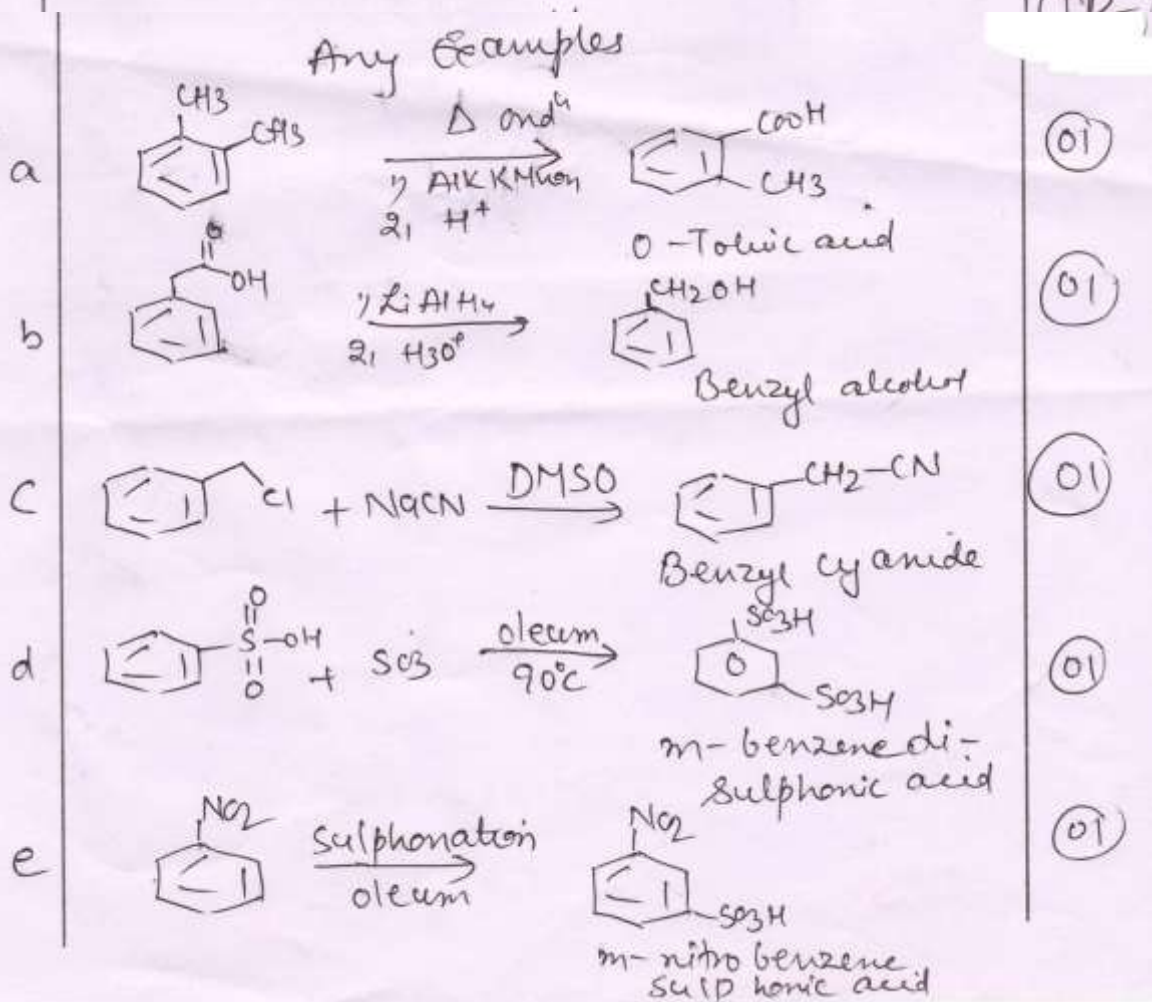
1/2

2) Ammonolysis
Ester when heated with ammonia, acid amide and an alcohol is obtained
This is called ammonolysis

01

1/2

(E)



01

01

01

01

01