

1

QP Code :70167

[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**)
- (i) In Galvanic cell, any electrical work done is on the expense of **decrease in free energy**
 - (ii) In an electrochemical cell, the reduction reaction always takes place at the electrode which is at **higher reduction** potential.
 - (iii) Quinhydrone is a mixture of **equimolar mixture of quinone and hydroquinone**.
 - (iv) The least number of variable factors required to specify the mixture of gases are **two**.
 - (v) Clapeyron equation can be used to study the effect of pressure on **mp of solids and bp of liquids**.
 - (vi) The eutectic point of two component system is **non variant**,
 - (vii) Cr^{3+} ions form **yellow** color precipitate on addition of lead acetate and acetic acid.
 - (viii) Coordination no. of Fe in $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ is **six**.
 - (ix) The number of unpaired electrons in $[\text{Ni}(\text{CO})_4]$ is / are **Zero**
 - (x) **TiCl_4** among the following is used as a catalyst in the manufacture of polyethylene.
 - (xi) **Cobalt** among the following is ferromagnetic in nature.
 - (xii) According to IUPAC nomenclature, the name of the positively charged ligands end with the suffix **ium**.
 - (xiii) Reaction of phenyl magnesium bromide with dry ice followed by acid hydrolysis gives **benzoic acid**.
 - (xiv) Salicylic acid on heating strongly with soda lime gives **phenol**.
 - (xv) The weakest acid among the following **p-toluic acid**.
 - (xvi) Conversion of diester having α -hydrogen atom into cyclic β -keto ester on heating with base is known as **Dieckmann condensation**.
 - (xvii) Acetic acid when heated with P_2O_5 gives **acetic anhydride**.
- (B) State whether the following statements are true or false. (any **three**) 3
- (i) Valency of an ion can be determined by measuring an emf of an electrolyte concentration cell without transference -**False**
 - (ii) In one component system diagram along the curves, the system is bi-variant -**False**
 - (iii) Oxalate is a chelating ligand - **True**
 - (iv) Diamagnetic substances are attracted towards the magnetic field. ---**False**
 - (v) An intermediate formed in nucleophilic acyl substitution have tetrahedral structure -**True**
 - (vi) Formic acid is weaker acid than acetic acid -**False**
- (C) Match the column. (any **five**) 5
- (i) Invariant system
 - (ii) Salt bridge
 - (f) $F = 0$
 - (h) to minimize liquid junction

- | | | |
|-----------------------------|---|-----------|
| (iii) Patronite | (c) Ore of Vanadium | potential |
| (iv) Rutile | (d) Ore of Titanium | |
| (v) HVZ reaction | (d) α -halogen acid | |
| (vi) Sulfonation of benzene | (j) Electrophilic substitution reaction | |

2

2. Attempt any four of the following.

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(A) Explain - any two applications of Electrochemical series

Applications of Electrochemical series— (any two carrying 2½ mark each)

1) **To predict the relative oxidizing and reducing power**

In general,

Oxidizing agents have positive E° Values

- Higher the positive value, stronger will be the oxidizing agent that is placed below the hydrogen.

Reducing agents have negative E° values

Higher the negative value stronger will be the reducing agent that are placed above the hydrogen

2) **To predict the spontaneity of any redox reaction**

For any spontaneous reaction

$$\Delta G = -ve$$

Since,

$$\Delta G = -nFE_{\text{cell}}$$

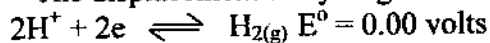
$\Rightarrow E_{\text{cell}}$ should be positive for spontaneous reaction.

The E_{cell} is calculated from the standard redox potentials by using the relation

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

3) **Displacement of hydrogen by metals from dil. Acids**

The displacement of hydrogen from an acid is a reduction process i.e.

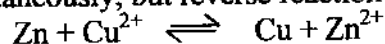


This is brought about by a metal whose reducing power is greater than that of hydrogen. Hence any metal placed above hydrogen in electrochemical series i.e. with negative std. reduction potential can displace hydrogen from a dil. acid.

Example : Zn, Mg, Ni.

4) **Displacement of metals from salt solution**

A metal with lower value of reduction potential can displace another metal with higher value of reduction potential. Example: Zinc displaces copper from its solution spontaneously, but reverse reaction is not feasible.



5) **Electropositive character of metals (tendency to form positive ions)**

Higher the electro positive character, greater is the stability of its oxide. Hence the stability of oxides of metals decreases in going from top to bottom of the series.

Example: Alkali metal oxides like Na_2O is more stable than Ag_2O , HgO etc.

6) **Calculation of standard cell potentials (E°_{Cell})**

The E°_{Cell} is calculated using $E^\circ_{\text{Cell}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{anode}}$

Where E°_{Cathode} is the standard reduction potentials of cathode

E°_{anode} is the standard reduction potentials of anode.

7) **Prediction of correct metallurgical method**

E° values of Cu, H_2O and Al are (+)0.34, (-)0.83 and (-) 1.66V.

Cu gets easily reduced when compared to H_2O and H_2O get reduced more easily than Al. Thus, copper is produced by electrolysis of aqueous CuSO_4 and aluminium cannot be produced from aqueous solution of aluminium.

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This is because when $Al^{3+}_{(aq)}$ is electrolyzed, only H_2O will be electrolysed and not Al^{3+} .

- (B) Derive Nernst equation for determination of emf of a galvanic cell. 5

Consider a general isothermal reaction which takes place in a galvanic cell is of the type-
 $aA + bB = cC + dD$

The free energy change ΔG associated with above reaction can be given by Van't Hoff isotherm as-

$$\Delta G = \Delta G^0 + RT \ln \frac{a_c^c \times a_d^d}{a_a^a \times a_b^b} \dots \dots \dots (1)$$

where a – activity of the particular species involved.

But we know that, any electrical work done by a cell is on the expense of decreasing in chemical free energy and can be given as

$$- \Delta G = n f E_{cell} \text{ hence, } \Delta G = - n f E_{cell}$$

where, negative sign indicates the decrease in free energy,
 E_{cell} – electromotive force (emf)

nf – number of Faradays

$$\text{Similarly, } - \Delta G^0 = n f E_{cell}^0 \text{ hence, } \Delta G^0 = - n f E_{cell}^0$$

On substituting the above values in equation (1), we get

$$-nFE_{cell} = -nFE^0_{cell} + RT \ln \frac{a_c^c \times a_d^d}{a_a^a \times a_b^b}$$

$$-nFE_{cell} = -nFE^0_{cell} + RT \ln Qa$$

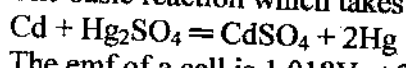
where, Qa is the reaction quotient in terms of activities.

Dividing the above equation by the term $-nF$ and converting it into common logarithm, it becomes

$$E_{cell} = E^0_{cell} - \frac{2 \cdot 303RT}{nF} \log Qa$$

The above equation is known as the Nernst equation for the emf of a cell.

- (C) The basic reaction which takes place in cell is - 5



The emf of a cell is 1.018V at 298K. Its temperature coefficient at constant pressure is $(-3.9) \times 10^{-5} \text{ VK}^{-1}$. Calculate ΔG , ΔS and ΔH for the given cell reaction of Weston Cell.

From the given cell reaction $n = 2$ - 1mk

$$\Delta G = -nFE = -2 \times 96500 \times 1.018 = 1.964 \times 10^5 J$$

$$\Delta S = nF \left(\frac{dE}{dT} \right)_p - 1mk$$

$$\Delta S = 2 \times 96500 \times (-4 \times 10^{-5}) = -7.72 \text{ JK}^{-1} - 1mk$$

$$\Delta H = -nFE + \left[nFT \left(\frac{dE}{dT} \right)_p \right] - 1mk$$

$$= -2 \times 96500 \times 1.018 + [2 \times 96500 \times 298 (-4 \times 10^{-5})] = -1.99 \times 10^5 J - 1mk$$

- (D) State and explain the phase rule and the terms involved in it. 5

Correct statement of phase rule.....2 marks.

Terms involve-

Component – with explanation in short– 1 mark

Phase - with explanation in short – 1 mark

Degrees of Freedom - with explanation in short – 1 mark

- (E) Define congruent melting point. Explain with labelled diagram for sodium –potassium system. 5

Congruent Melting Point-- A solid compound is said to have congruent melting point if it remain present in its solid phase up to its melting point and at which it melts to produce a

liquid whose composition is same as that of the original solid compound. – 1 mk.

Correct labelled phase diagram of sodium – potassium system – 1 mk.

Explanation of phase diagram in detail – 3 mks.

(F) 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 2.74×10^4 J mol⁻¹. 5

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

$T_2 = 306K$; $T_1 = ?$

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

Substituting these values in Clausius – Clapeyron equation—

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

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

$$\therefore T_1 = 252K - 1mk$$

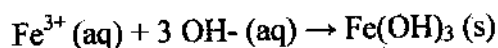
3. Attempt any four of the following.

(A) i) Give the characteristic properties of transition elements. 03

Metals, good conductors of heat and electricity, have metallic lustre, hard, strong ductile, form alloys, variable oxidation states, form coordination compounds, high M.P and B.P, form colored compounds, have good catalytic property.....

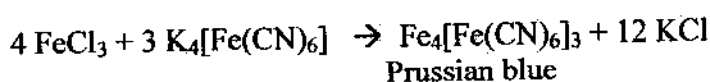
ii) Write the tests by which presence of iron can be detected in the given salt. (any two tests also will do) 02

- To Fe³⁺ (aq) add ammonium hydroxide .It gives reddish brown precipitate of ferric hydroxide



- To 10 drops of Fe³⁺ (aq) solution, add 0.5 M K₄Fe(CN)₆ dropwise . It gives a dark blue precipitate of ferric ferrocyanide (Prussian blue).

Ex:



- To 10 drops of Fe³⁺ solution, add 1 or 2 drops of 0.5 M KNCS. The solution becomes deep red (blood red coloration) due to formation of [FeNCS]²⁺.



(B) i) Name the first five elements of 3d series of transition elements and give their electronic configuration 03

- Names of the first five elements and their electronic configuration

ii) Give an account of the special stability of d⁰, d⁵ and d¹⁰ configurations with reference to first transition series. 02

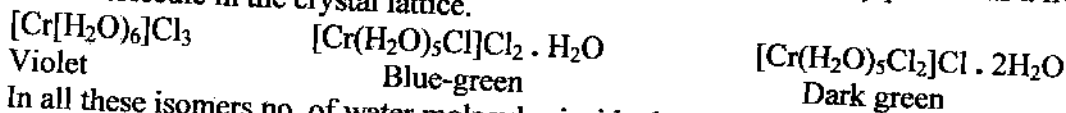
Examples of Transition elements having valence configuration of d⁰, d⁵ and d¹⁰ configurations, show their electronic configuration in each of the examples and account for their stability

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(C) **Explain the isomerism exhibited by $[\text{Co}(\text{Cl})_3(\text{NH}_3)_3]$ complex.** 2.5
 $[\text{Co}(\text{Cl})_3(\text{NH}_3)_3]$ complex shows Geometric isomerism. The isomers here are called facial and meridional isomers. Explain why they are called as 'fac' and 'mer' isomers. Structures of facial and meridional isomers of $[\text{Co}(\text{Cl})_3(\text{NH}_3)_3]$ complex are to be shown.

ii) What is hydrate isomerism? Explain with a suitable example. 2.5

Hydrate isomerism also called as Solvate isomerism: These isomers differ by whether or not the water molecule is directly bonded to the metal ion or merely present as a free water molecule in the crystal lattice.



In all these isomers no. of water molecules inside the coordination sphere and outside the coordination sphere differ. Accordingly the no. Of chlorides precipitated per mol also differs.

(D) **Account for the following:**

i) Magnetic moment of transition elements is determined by using spin only formula only. 03

The magnetic moment is dependent on both spin and orbital angular momentum contributions of the total no. of unpaired electrons present in the species. In case of complexes of the elements of 4d and 5d transition series, both the types of contributions make the magnetic momentum of the complexes. The magnitude of the paramagnetism is expressed as an effective magnetic moment, μ_{eff} . And is calculated by the equation

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

where S = Sum of the spin Quantum nos

L = Sum of the orbital angular Quantum nos

But in case of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. Therefore, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula which is given as:

$$\mu_{s.} = \sqrt{4S(S+1)}$$

or

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

where n is the number of unpaired electrons and μ is the magnetic moment in units of Bohr magneton (BM)..

ii) Lanthanum though is a d block element, is always considered as a member of f block elements. 02

Lanthanum is the first element of the 3rd transition series, and the 5d orbitals start getting filled from lanthanum. And so, it has the configuration $[\text{Xe}]5d1 6s2$. The 4f orbitals get filled from the next element (cerium) only.

But still it is studied along with f block elements because it shows very close resemblances in its physical and chemical properties with those off-block elements of 4f series. Not only that, it also occurs along with minerals of f-block elements. Hence chemistry of 'La' is studied along with f block elements.

(E) **Comment on the following statements**

i) Colour of transition metal compounds can be explained on the basis of d-d transition of electrons. 03

The colours exhibited by transition metal complexes are due to d-d transitions (i.e. the energy difference in orbital configuration corresponds to the visible region).

Transition elements are usually characterised by partially filled d orbitals., these d orbitals are degenerate, means they all have the same energy .

However when the metal bonds with any anion or with other ligands, the d orbitals split into two sets of different energy levels.

when light is absorbed , the unpaired d electrons in transition metal species undergo d-d transition i.e They move from the lower d energy state to higher d energy state.

During this d-d transition process, the electrons absorb certain energy from the visible radiation and emit the remainder of energy as colored light. The color of ion is the complementary of the color absorbed by it. hence, colored ion is formed due to d-d transition which falls in the visible region for all transition metal compounds and complexes.

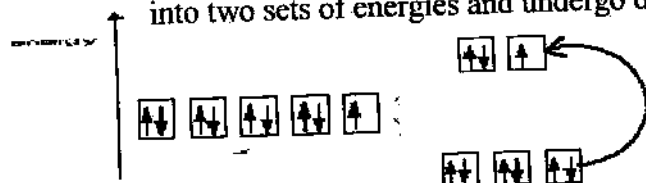
The colour can vary with change in

- i) oxidation state of the metal
- ii) ligand
- iii) co-ordination number
- iv) no. of unpaired electrons
- v) changing the transition metal itself.

ii) **Cu²⁺ salts are coloured but Zn²⁺ salts are colourless.**

Cu(+II) has d⁹ electronic configuration . In presence of white light the d orbitals split up into two sets of energies and undergo d-d transition as shown below.

02



Since the d levels are incompletely filled, the electrons can get excited from lower level to higher level by absorbing energy of a particular radiation from (yellow color) visible region and emits it's complimentary color.i.e blue . Hence cupric salts are blue in color.

In case of Zn²⁺ ions – they have d¹⁰ electronic configuration whose d-orbitals are completely filled. So there is no vacancy in the d orbitals to undergo d-d transition. Hence no absorption of light from visible region. Hence their salts are colorless.

(F) **What are inner orbital and outer orbital complexes? Explain the same with the help of [Fe (H₂O)₆]³⁺ and [Fe (CN)₆]³⁻. Comment on their magnetic properties.**

Inner Orbital Complex

If the complex is formed by use of inner d-orbitals for hybridisation (written as d²sp³), it is called **inner orbital complex** .In the formation of inner orbital complex , the electrons of the metal are forced to pair up and hence the complex will be either **diamagnetic** or will have lesser number of unpaired electrons. Such complexes are **Low Spin**

01

Complexes.

For example, [Fe(CN)₆]³⁻ is **inner orbital complex**.

Outer Orbital Complex

If the complex is formed by use of outer d-orbitals for hybridisation (written as sp³d²), it is called as **outer orbital complex**. Outer orbital complex will have larger number of unpaired electrons since the configuration of the metal ion remains undisturbed. Such complex is also called **high spin complexes**.

01

For example, [Fe(H₂O)₆]³⁺ is **outer orbital complex**.

In the complex, [Fe(H₂O)₆]³⁺ and [Fe(CN)₆]³⁻, the oxidation state of Fe is +3.

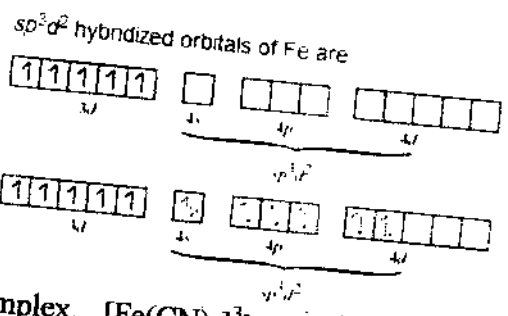
Orbitals of Fe+3 ion:

↑	↑	↑	↑	↑	↑				
t _{2g}						e _g			

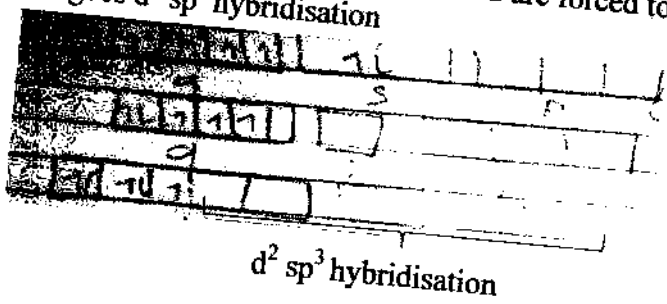
In the complex, [Fe(H₂O)₆]³⁺ there are 6 H₂O ligands .Experimentally it is found that it is paramagnetic. Hence all the 5 unpaired electrons remain unpaired. It undergoes sp³d² hybridisation.

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In the complex, $[\text{Fe}(\text{CN})_6]^{3-}$, electrons are forced to pair up as shown below. Hence it undergoes $d^2 sp^3$ hybridisation

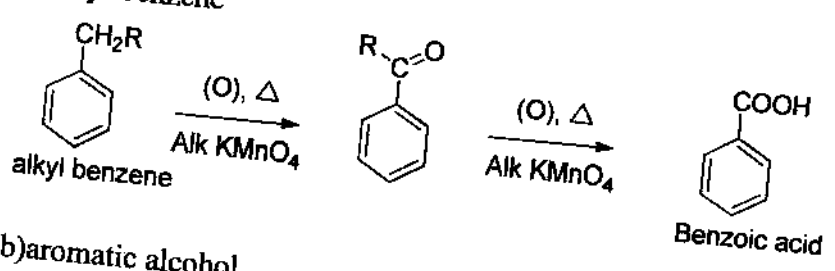


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4. Attempt any four of the following.
 (A) (i) Preparation of benzoic acid from

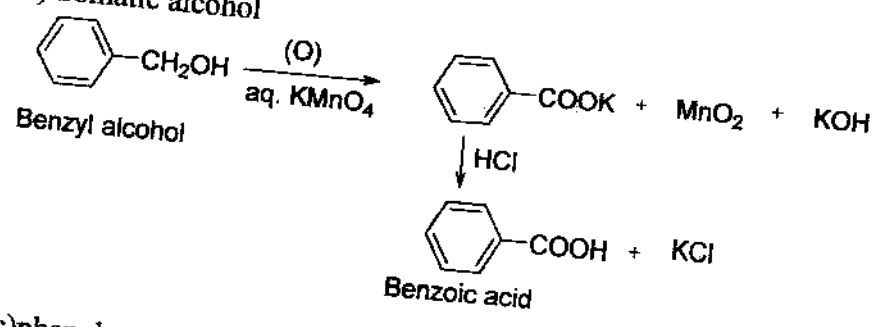
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a) alkyl benzene



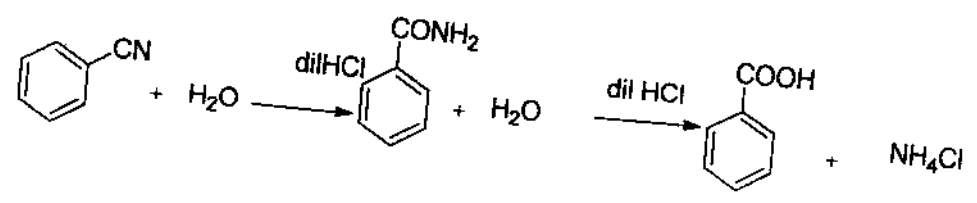
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b) aromatic alcohol



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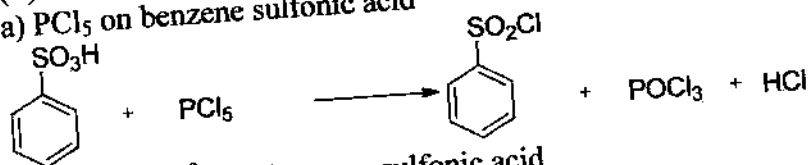
c) phenyl cyanide



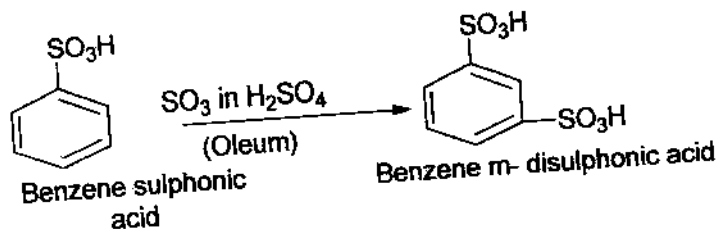
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(ii) Action of

a) PCl_5 on benzene sulfonic acid



b) oleum at 90°C on benzene sulfonic acid



(B) Nucleophilic acyl substitution is a nucleophilic substitution at acyl carbon atom by a nucleophile where X is a leaving group like $-\text{NH}_2, -\text{Cl}, -\text{Br}, -\text{COOR}, -\text{OR}$ etc.

The carbonyl group of carboxylic acids and their derivatives undergo nucleophilic addition-elimination. The nucleophile attacks the carbonyl group to form a tetrahedral intermediate from the trigonal structure.

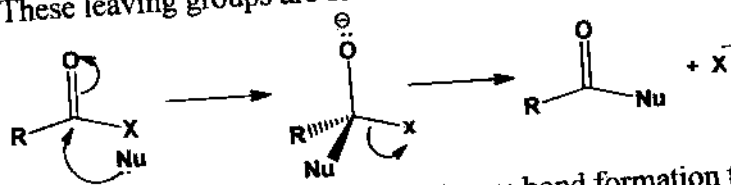
The tetrahedral intermediate eliminates a leaving group (X). The carbonyl group is regenerated; the net effect is an acyl substitution.

To undergo nucleophilic addition-elimination the acyl compound must have a good leaving group or a group that can be converted into a good leaving group.

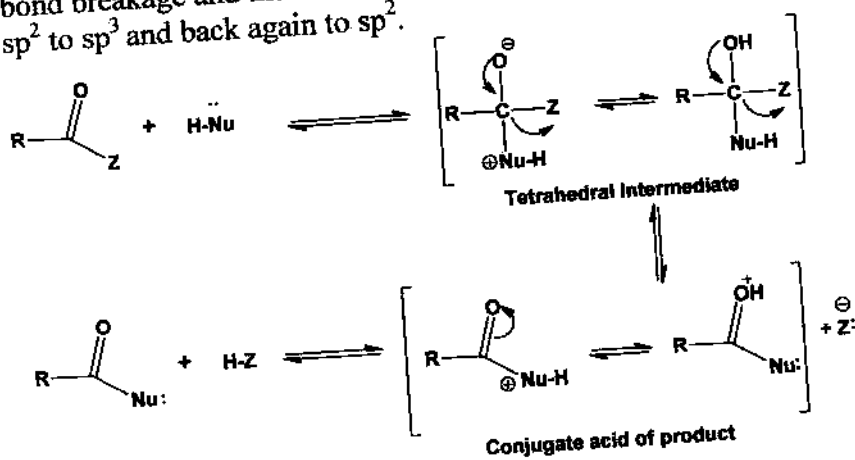
Acid chlorides react after losing chloride ion. Anhydrides react after losing a carboxylate ion.

Esters, carboxylic acids and amides react after losing alcohol, water and amine molecules respectively.

These leaving groups are formed by protonation of the acyl compound.

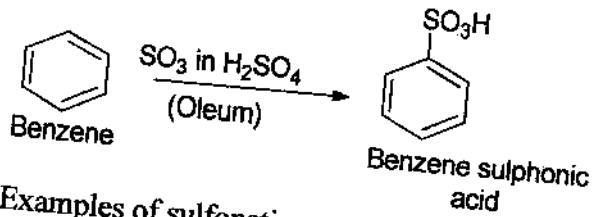


In this mechanism there are two stages; bond formation takes place initially followed by bond breakage and the carbonyl carbon atom undergoes a change in hybridisation from sp^2 to sp^3 and back again to sp^2 .



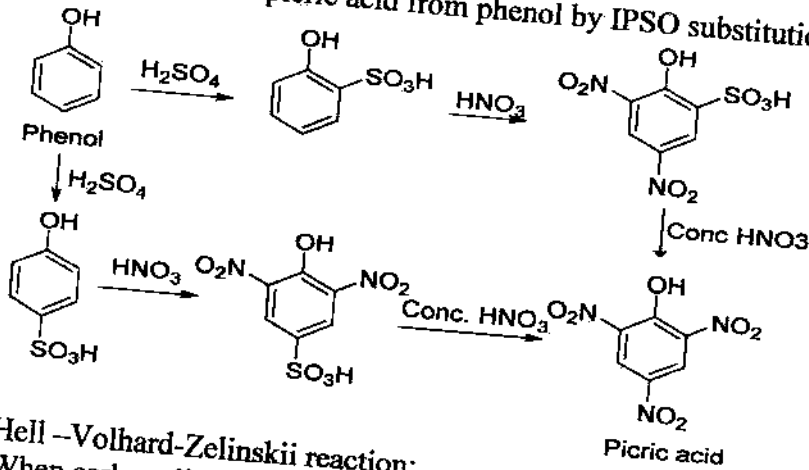
Where $\text{Z}=\text{NH}_2$
 $\text{Nu}=\text{OH}$

(C) (i) Introduction of sulfonic acid group in aromatic ring is known as aryl sulfonation.

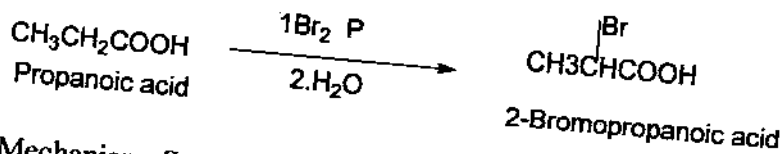


Examples of sulfonating agents: Conc. H_2SO_4 , Fuming sulphuric acid

(ii) Preparation of picric acid from phenol by IPSO substitution via sulfonation



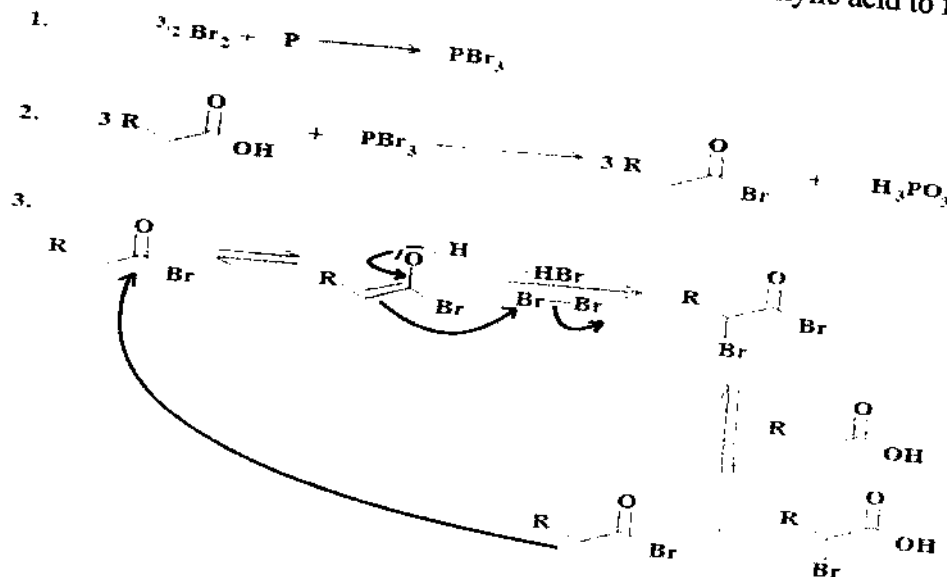
(D) Hell-Volhard-Zelinskii reaction:
 When carboxylic acid is heated with Cl_2 or Br_2 in presence of red phosphorus the α -hydrogen atom is substituted by halogen atom giving α -halogen acid.
 e.g.



Mechanism: Step 1: Formation of PBr_3

2: PBr_3 reacts with carboxylic acid to give acyl halide

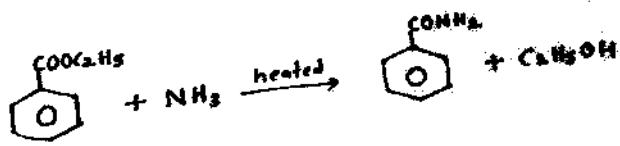
3: Enol form of acyl halide reacts with bromine to give dibromo derivative & Dibromo derivative reacts with unreacted carboxylic acid to form α -halogen acid.





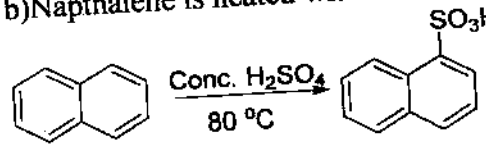
(E) a) Ethyl benzoate is heated with ammonia

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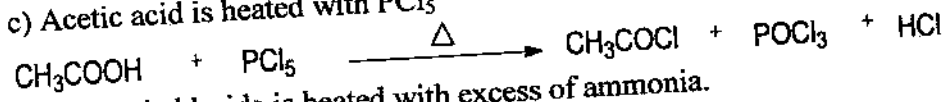
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b) Naphthalene is heated with conc. H₂SO₄ at 80°C



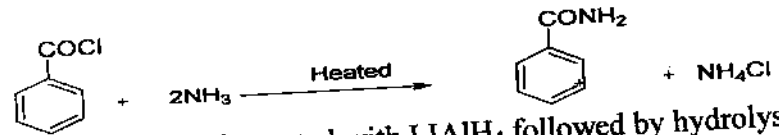
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c) Acetic acid is heated with PCl₅



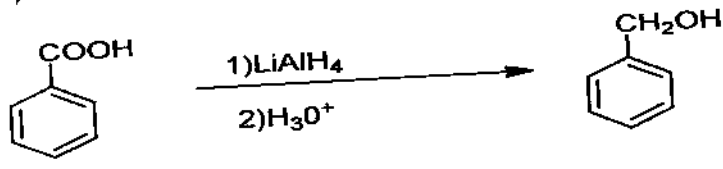
d) Benzoyl chloride is heated with excess of ammonia.

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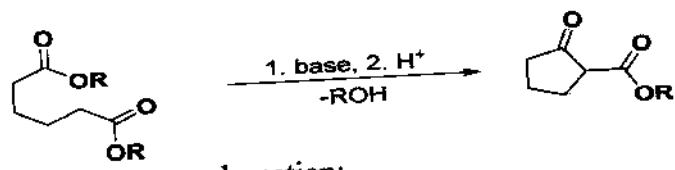


e) Benzoic acid is treated with LiAlH₄ followed by hydrolysis.

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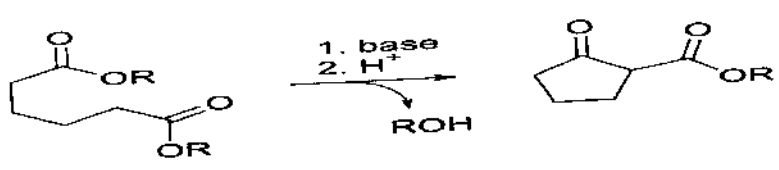


Dieckmann condensation:

Conversion of a diester having α -hydrogen atom into a cyclic β -keto ester is known as Dieckmann condensation.

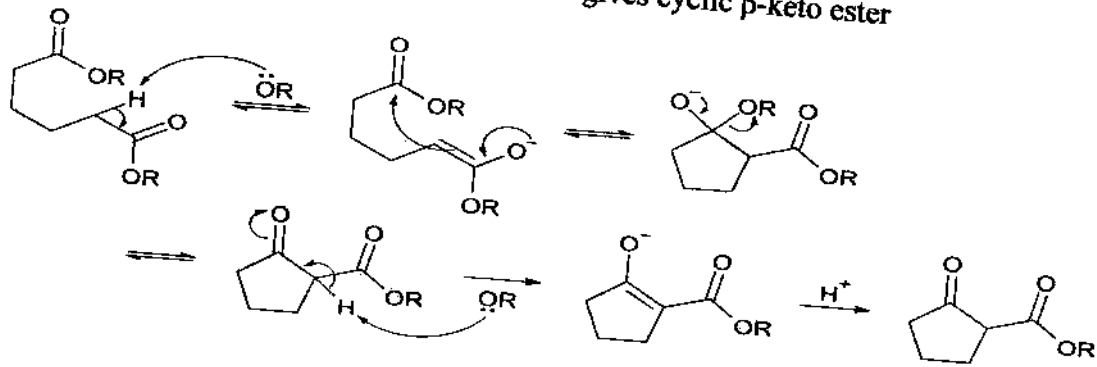
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This is base catalysed formation of a cyclic β -keto ester from a diester.



Step 1: α -hydrogen atom of one of the ester group is removed by the base to form a carbanion which changes into enolate ion.

Step2: The nucleophilic addition of enolate ion to carbonyl carbon of other ester molecule followed by a loss of alkoxide ion gives cyclic β -keto ester



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5.

Attempt any four of the following.

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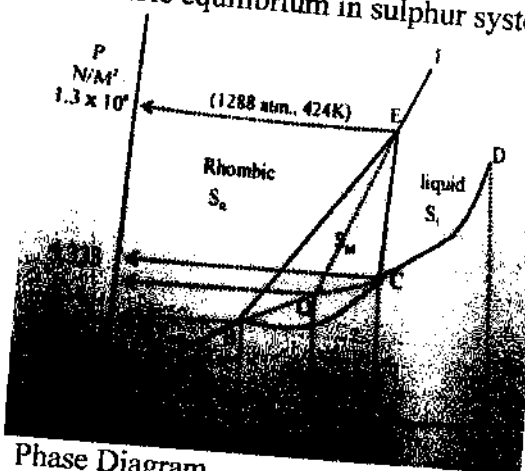
(A) Explain the origin of liquid junction potential and show how it can be minimized. Consider two solutions of the same electrolyte having different activities say a_1 and a_2 , such that $a_1 \neq a_2$, separated from one another by means of porous partition. A concentration gradient exists across the boundary and therefore, the ions from more concentrated solution will have a tendency to diffuse into the less concentrated one. Since the different ions have different velocities, the rate of diffusion of each ion will be proportional to its speed of ions. If the anions diffuse more rapidly than the cations, they will diffuse ahead into the dilute solution, leaving the latter negatively charged and the concentrated solution positively charged which will result in the formation of an electrical double layer of positive and negative charges at the junction of the two solutions. Therefore liquid junction potential or diffusion potential can be defined as the potential which develops when two solutions of an electrolyte having different concentrations are in contact with each other.

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The liquid junction potential can be minimize conveniently by using a salt bridge.

(B) Give a brief account of meta-stable equilibrium in sulphur system.

Metastable equilibrium in sulphur system :



5

Phase Diagram

Description ----- 1 Mark

Metastable equilibria ----- 4 Marks

Metastable equilibria : A phase diagram of sulphur system is as in fig. In the phase diagram there are four areas, six curves, four triple points.

There are three metastable equilibria. The dotted lines BO, Co, EO indicates metastable equilibria.

The dotted line BO is the sublimation curve of metastable rhombic sulphur. At any point

on this line, rhombic sulphur (S_R) and vapour sulphur (S_V) are in metastable equilibrium. As the conversion of rhombic sulphur to monoclinic sulphur (S_M) involves molecular rearrangement, which is a slow process, hence heating must be gradual and sufficient time must be allowed for the transition to take place. But if the heating is rapid then the transition of rhombic sulphur to monoclinic sulphur cannot take place and the sublimation curve of rhombic sulphur extends beyond point B till point O (387K) is reached, which is the melting point of metastable rhombic sulphur.

The dotted line CO is the vapour pressure curve of metastable liquid sulphur. At any point on this line liquid sulphur (S_L) and vapour sulphur (S_V) are in metastable equilibrium. Thus if the liquid sulphur is cooled rapidly along DC then solid monoclinic sulphur may not appear at point C and the vapour pressure curve of liquid sulphur extends beyond point C and till point O is reached, which is the melting point of metastable rhombic sulphur.

The dotted line EO is the fusion curve of metastable rhombic sulphur.

At any point on this line rhombic sulphur (S_R) and liquid sulphur (S_L) are in metastable equilibrium. This curve gives the effect of pressure on m.p. of metastable rhombic sulphur.

- (C) i) Name the different oxides of vanadium. Mention the oxidation state of vanadium in each of them. 03

Names of the oxides, their formula and the oxidation state of 'V' in each of them.

(for any three oxides)

- ii) Write a note on use of Ti^{3+} salts in titrimetric analysis. 02

Brief information about the use of Ti^{3+} salts in volumetric analysis.

(Determination of Fe^{3+} and also organic nitro compounds.)

- (D) Explain the following terms with suitable examples.

- i) ligand ii) coordination number iii) ambidentate ligand iv) double salt

1 × 4
= 04

Definition for each term ----- 1 mark each

Giving for examples -----

01

Ligands

are the species which can donate electron pairs to the central metal of the complex forming coordinate bonds. Metals are electron acceptors. Ligands may be neutral or negatively charged species with electron pairs available. Ex : Water is a neutral ligand. Cl^- is a negatively charged ligand. NO^+ is a positively charged ligand. Water with its two lone pairs of electrons.

Coordination No :

The no of ligands coordinated to the central metal ion is called coordination no. Example : In $[Ni(CO)_4]$ coordination no of Nickel is 4

Ambidentate ligands

Ligands with more than one donor atom are known as ambidentate, such as the thiocyanate ion, NCS^- , which can bind to the metal center with either the nitrogen or sulphur atoms. Examples of ambidentate ligands include NO_2^-/ONO^- (O and N), and SO_3^{2-}/OSO_2^{2-} (O and S). But when they act as donor atoms they use only one of the two donor atoms at a time instead of both.

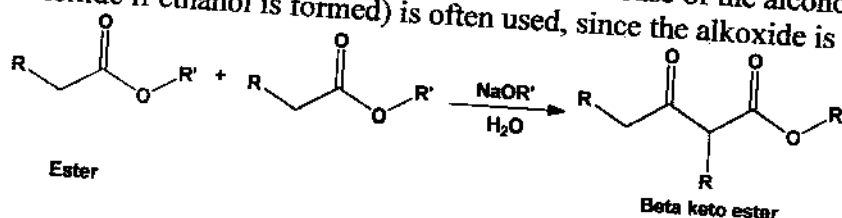
A double salt

is an addition compound that is stable in the solid state but that which breaks up into its constituent ions in the dissolved state. These compounds exhibit individual properties of

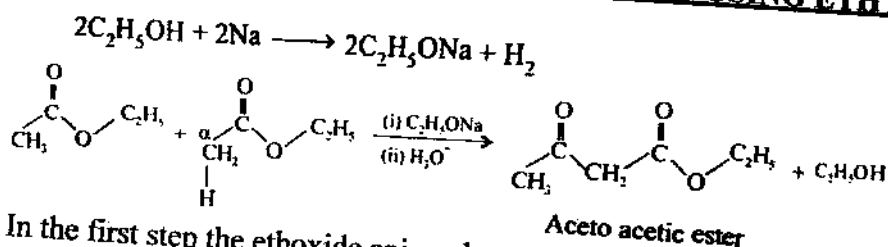
13 their constituents. For e.g. $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ breaks into Fe^{2+} , NH_4^+ , and SO_4^{2-} ions. Hence, it gives a positive test for Fe^{2+} ions.

(E) **Claisen Condensation** occurs between an ester molecule and a carbonyl compound in the presence of a strong base alkoxide. The carbonyl compound can also be another ester molecule or another carbonyl compound, resulting in the formation of a β -keto ester or a β -diketone.

At least one of the reagents must be enolizable (have an α -proton and be able to undergo deprotonation to form the enolate anion). The base used must not interfere with the reaction by undergoing nucleophilic substitution or addition with a carbonyl carbon. For this reason, the conjugate sodium alkoxide base of the alcohol formed (e.g. sodium ethoxide if ethanol is formed) is often used, since the alkoxide is regenerated.



MECHANISM OF CLAISEN CONDENSATION USING ETHYL ACETATE

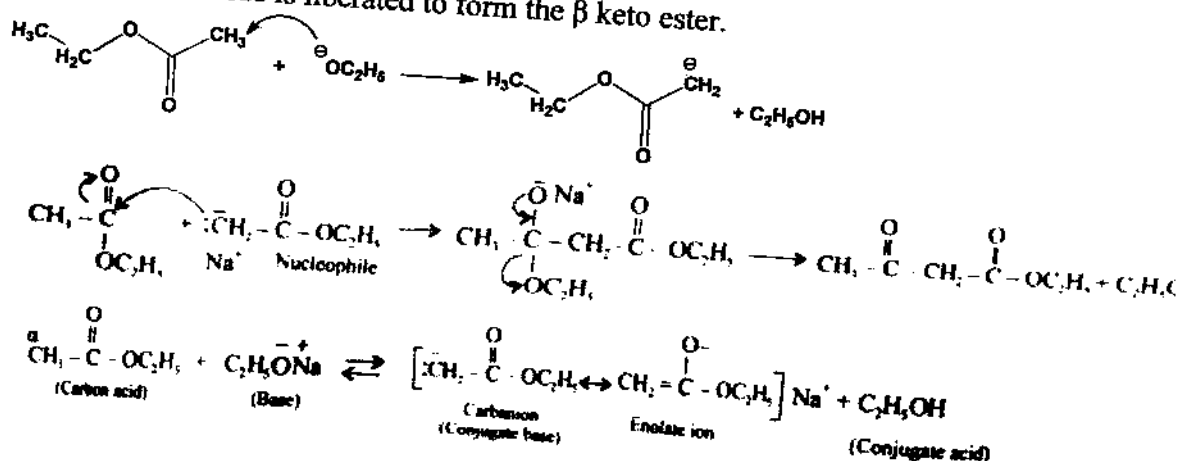


In the first step the ethoxide anion abstracts a hydrogen atom to form ethanol and carbanion (nucleophile).

The nucleophile attacks the carbon atom of the carbonyl group of the second ester molecule.

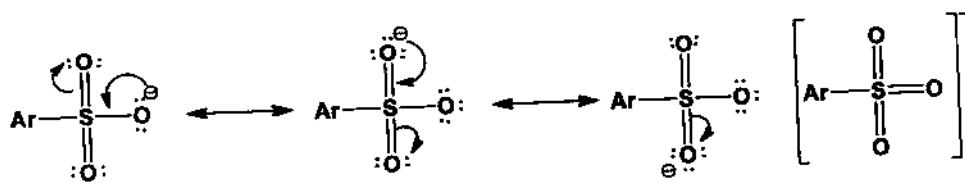
This carbanion is resonance stabilized.

Finally the ethoxide is liberated to form the β keto ester.

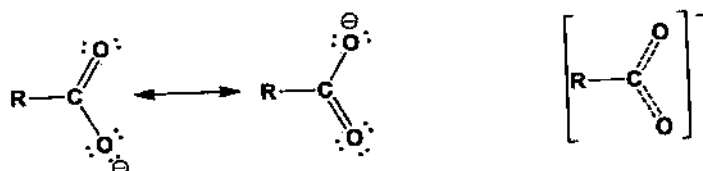


(F) (i) Sulphonic acids are stronger than carboxylic acids. Benzene sulfonic acid is more acidic than benzoic acid. Strength of an acid depends on its tendency to lose a proton to give the conjugate base of the acid. More stable is the conjugate base in both, the resonance stabilized anion, more is the acidic strength. In the case of sulphonic acids the sulphonate anion is more stable due to the dispersal of

negative charge over three oxygen atoms whereas in the carboxylic acid anion the negative charge is delocalized over two oxygen atoms. Hence the sulphonate anion is more stable than carboxylate anion



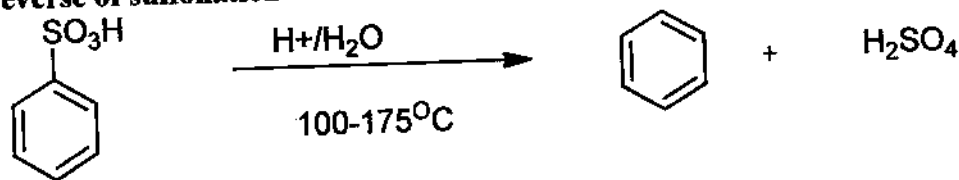
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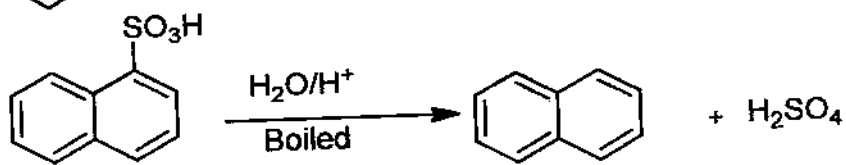
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(ii) When aromatic sulfonic acid is heated with dil. acid at about 100-175°C under pressure an aromatic hydrocarbon and sulphuric acid is formed. This reaction is exact reverse of sulfonation and is known as desulfonation.

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