

Name of the Examination: First Semester End Semester Examination

Name of the Subject: Chemistry

Subject Code: CH1101

Date of Examination: 7<sup>th</sup> April, 2021.

Name of the Student: Tathagata Ghosh

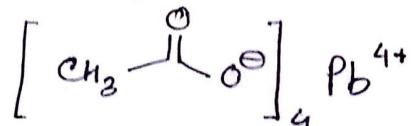
Examination Roll Number: 2020ITB065

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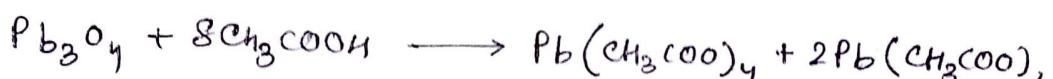
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Ans 1) Q1) i) The oxidative cleavage of 1,2-diol compounds by lead tetraacetate follows Criegee reaction. The Criegee oxidation is a glycol reaction in which vicinal diols are oxidized to form ketones and aldehyde using tetraacetate.

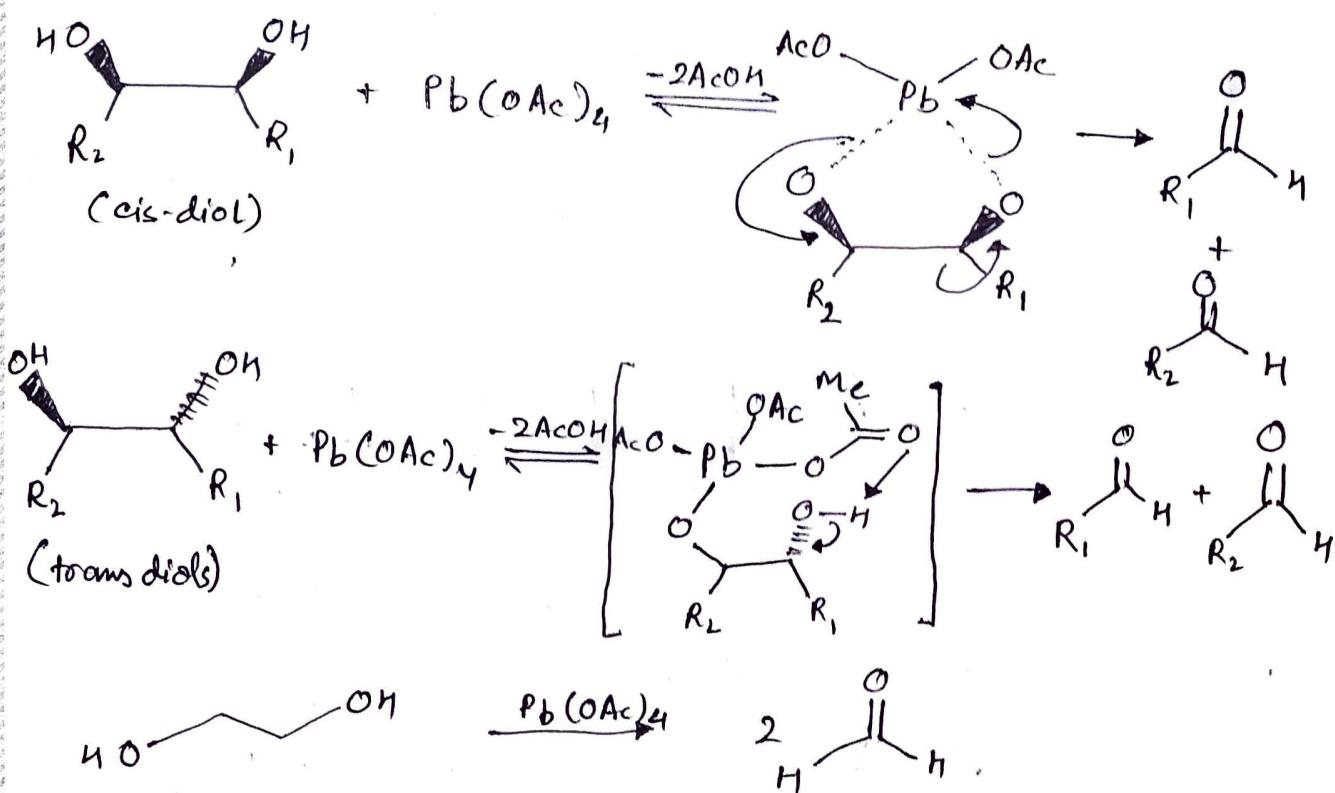
Chemical Formula:  $Pb(C_2H_3O_2)_4$



It is usually prepared by dissolving lead oxide in anhydrous acetic acid, heated until 55°- 65°C.



There are two mechanisms proposed for Criegee oxidation based on the formation of vicinal diol.



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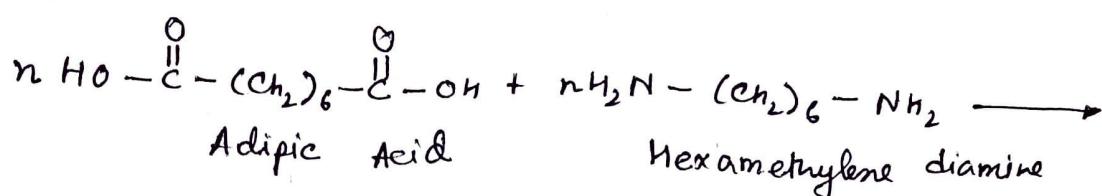
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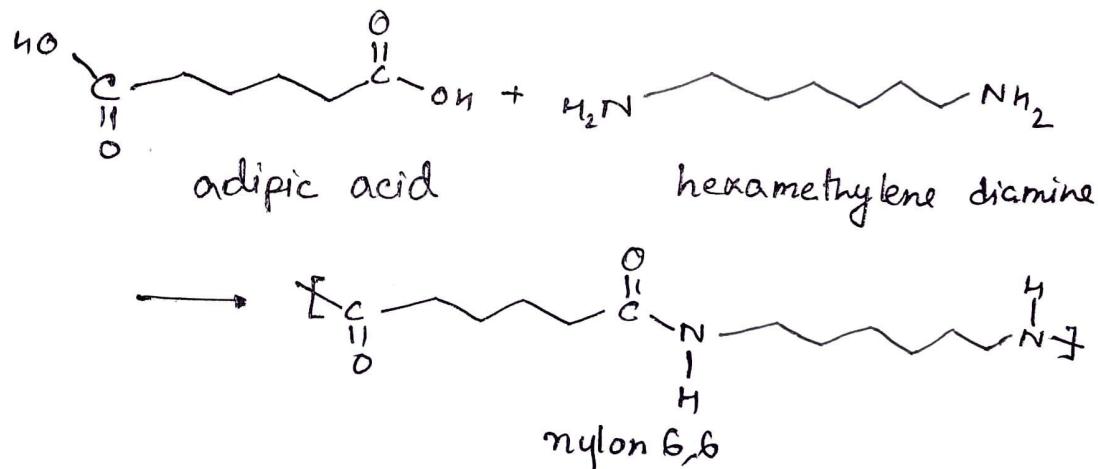
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### b) Preparation of Nylon 6,6 :-

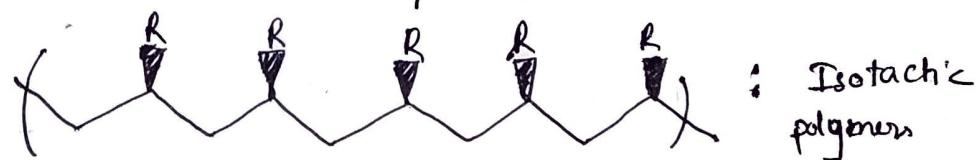


Reaction involved:-

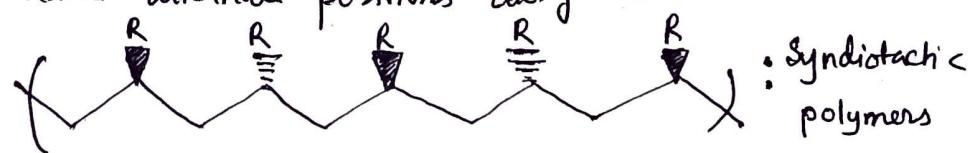


c) Polymers can be divided into 3 types on the basis of Tacticity

- Isotactic polymers: In isotactic macromolecules all the substituents are located on the same side of the micromolecular backbone.



- Syndiotactic polymers: In syndiotactic or syntactic macromolecules the substituents have alternate positions along the chain.



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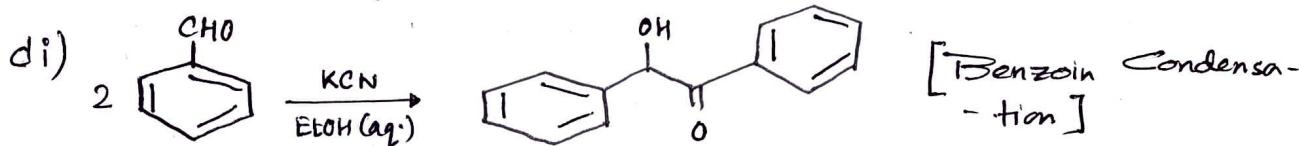
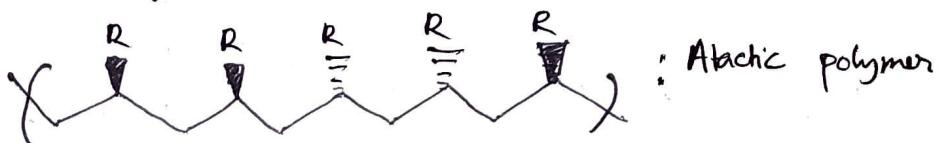
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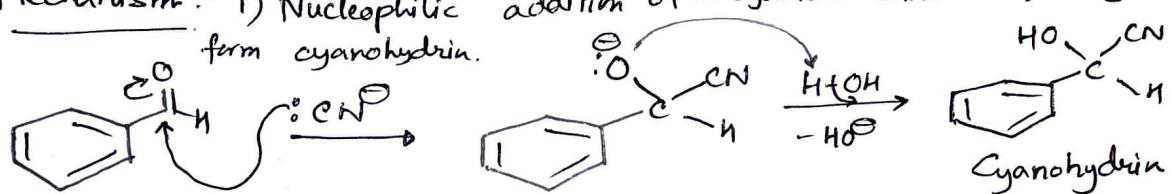
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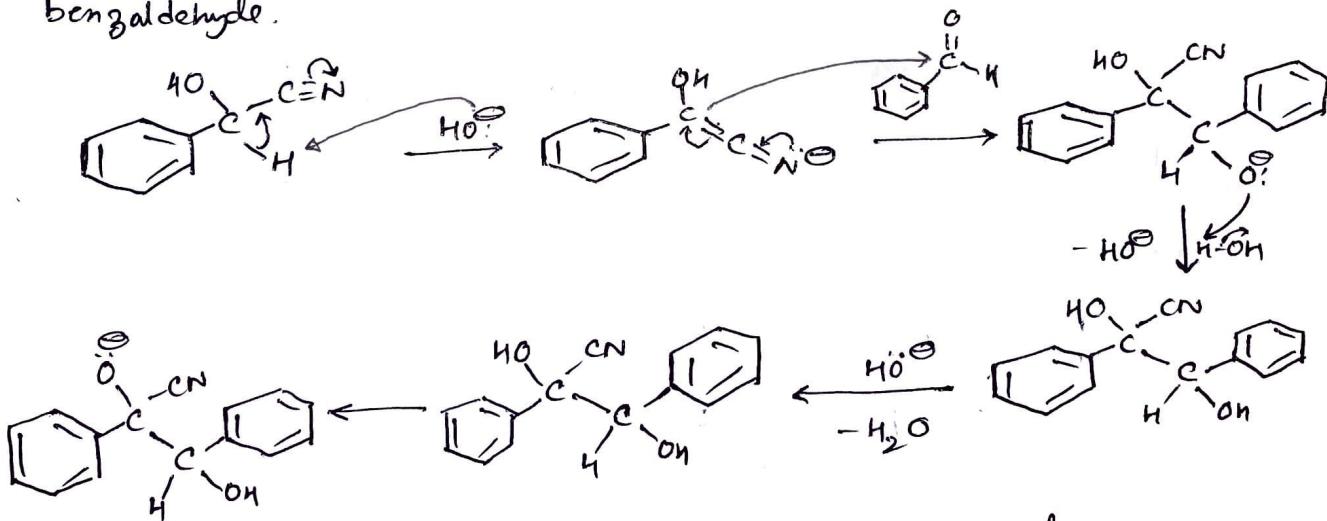
Atactic polymers: In atactic macromolecules the substituents are placed randomly along the chain. No order of arrangement is observed.



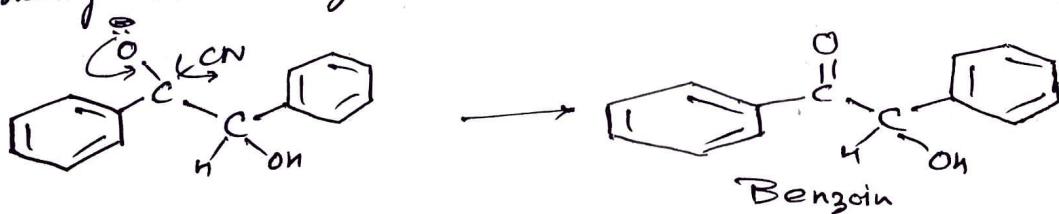
Mechanism:- i) Nucleophilic addition of a cyanide with benzaldehyde to form cyanohydrin.



ii) Condensation reaction between the cyanohydrin and a second benzaldehyde.



iii) Rearrangement reaction removing the cyano group resulting in a benzoin



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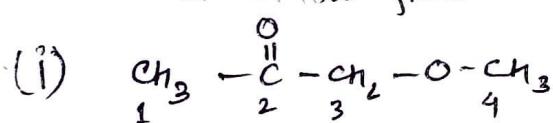
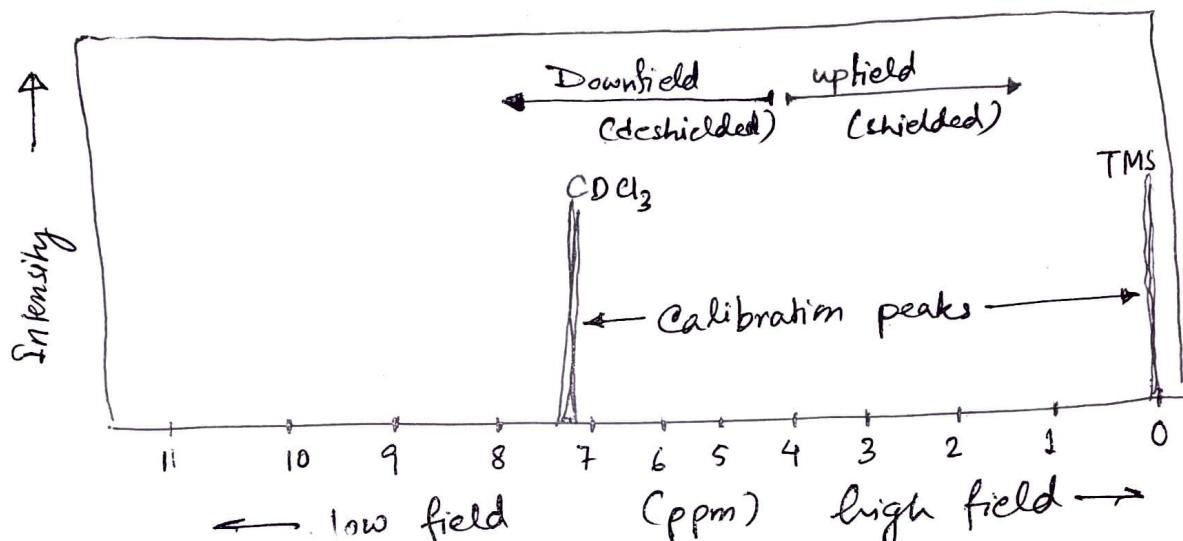
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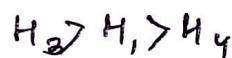
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Ans) The position of a signal along the axis of an NMR spectrum is called its chemical shift. The chemical shift of each signal gives information about the structural environment of the nuclei producing that signal. In NMR spectroscopy, the chemical shift is the reagent frequency. The positive on the plot at which the nuclei absorbs is called the chemical shift.



Relation of chemical shift:

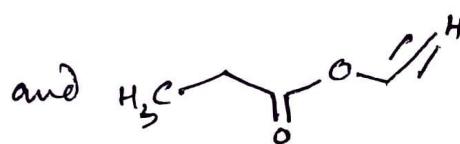
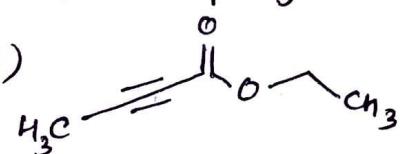


For C<sub>1</sub>, multiplicity is 1.

For C<sub>3</sub>, multiplicity is 1. } singlet

For C<sub>4</sub>, multiplicity is 1.

Ans f) i)



For first compound there is resonance which leads to lowering in bond order and bond strength also decreases thus wave number decreases and simultaneously wavelength increases. Whereas there is no such resonance in second compound. So, wavelength

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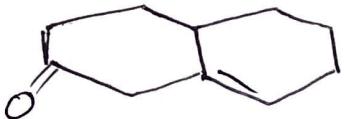
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of first compound is more than second compound.

ii)



and



For second compound there is resonance which leads to lower in bond order and <sup>bond</sup> strength also decreases thus wave number decreases and simultaneously wavelength increases. Whereas there is no such resonance in first compound. So, wavelength of second compound is more than first compound.

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Ans 2a) Essential criteria for a radioelement to be chosen for use a radiodiagnostic agent or a radiotherapeutic agent:-

(i) They should be short lived.

(ii) They should radiate low energy  $\gamma$ -photons and no  $\alpha$  or  $\beta$  photons.

(iii) Their degraded products should not be toxic and these should be easily excreted from the body.

(iv) The compound should be sufficiently stable to allow their distributions among the affected parts and detection by counter.

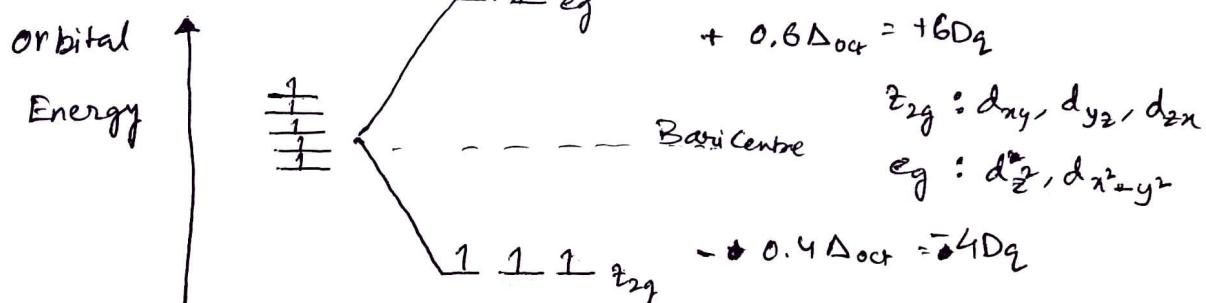
Examples of radionuclides as

i) Radiodiagnostic agents and radiotracers: The exact location of a tumour in brain can be detected by using

$^{131}\text{I}$  and  $^{32}\text{P}$

ii) Radiotherapeutic agents: The  $\gamma$ -radiation of  $^{60}\text{Co}$  can destroy the tumour cell.  $^{67}\text{Ga}$  is also able to destroy tumour cell by its  $\gamma$ -radiations.

b) The crystal field splitting diagrams for a  $d^5$  metal ion in octahedral high spin:-



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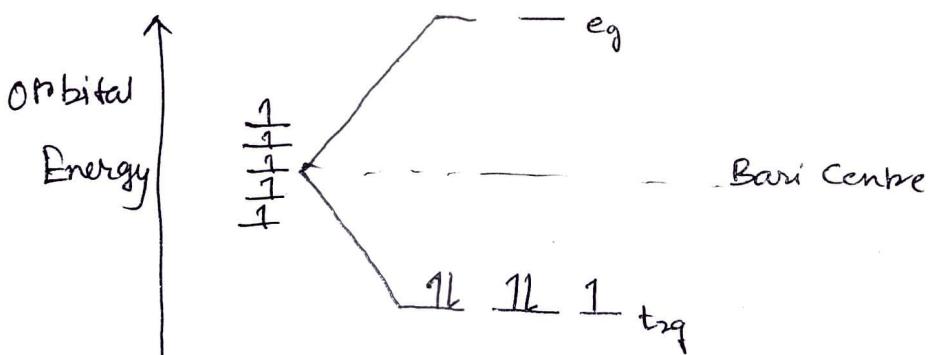
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In presence of high spin:  $t_{2g}^3 e_g^2$

$$\begin{aligned} (\text{CFSE})_{\text{high spin}} &= (\text{no. of } e^- \text{ in } e_g \times 6 D_q) - (\text{no. of } e^- \text{ in } t_{2g} \times 4 D_q) \\ &\quad + nPE \quad (\text{PE : Pairing Energy}) \\ &= 2 \times 6 D_q - 3 \times 4 D_q + 0.PE \\ &= 0 D_q \end{aligned}$$

The crystal field splitting diagrams for d<sup>5</sup> metal ion in octahedral spin and low spin environments:



In presence of low spin:  $t_{2g}^5 e_g^0$

$$\begin{aligned} (\text{CFSE})_{\text{low spin}} &= (\text{no. of } e^- \text{ in } e_g \times 6 D_q) - (\text{no. of } e^- \text{ in } t_{2g} \times 4 D_q) \\ &\quad + nPE \\ &= -5 \times 4 D_q + 2 PE \\ &= -20 D_q + 2 PE \end{aligned}$$

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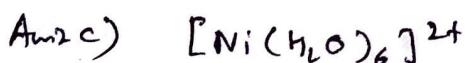
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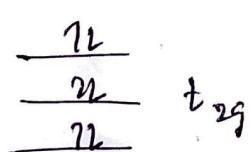
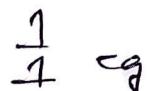
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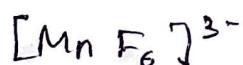


$$\text{Ni}^{2+} = 3d^8 4s^0$$



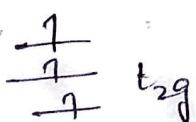
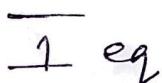
It is symmetric so no

John Teller Distortion.

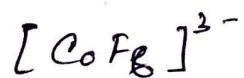


$$\text{Mn}^{3+} = 3d^5$$

∴ F is a weak field ligand so unpaired



There is no symmetry so John Teller Distortion will occur and as the last electron enters the eg where the orbitals directly face the axis so high John Teller effect.



$$\text{Co}^{3+} = 3d^6$$

∴ F is a weak field ligand so unpaired

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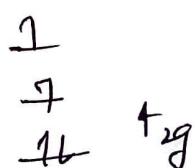
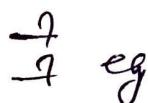
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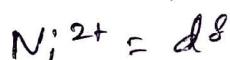
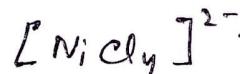
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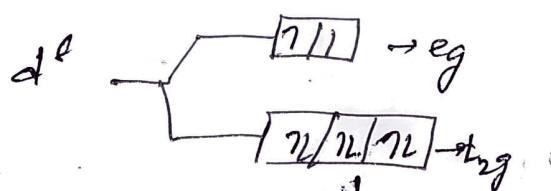
If it is not symmetrical so John Teller effect will occur but as the last electron enters  $t_{2g}$  where the orbitals do not directly face the orbitals so low

John Teller Distortion.

Ans 2 d) John.,



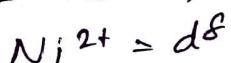
Cl is a weak field so it remains unpaired



$$\text{no. of single electron} = 2$$

$$\text{So } \mu = \sqrt{n(n+2)} = \sqrt{8} \quad (\text{B.M}) \neq 0$$

So paramagnetic in nature



CN<sup>-</sup> is a strong field ligand and so it

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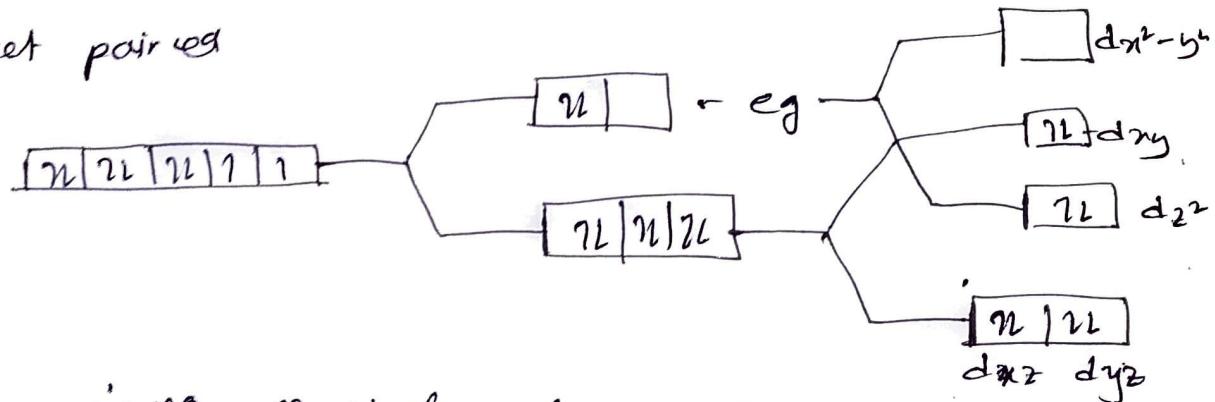
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get paired



∴ no. of single electron = 0

so,  $\mu = 0$ . B.M.

It is diamagnetic in nature.

2e) In  $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$  the oxidation state of Ru is 3+ whereas in  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$  the oxidation state of Ru is 2+. we know that as the oxidation state of metal atom increases value of  $\Delta_o$  increases  
∴  $\Delta_o$  value for  $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$  is greater than  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$

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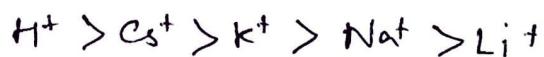
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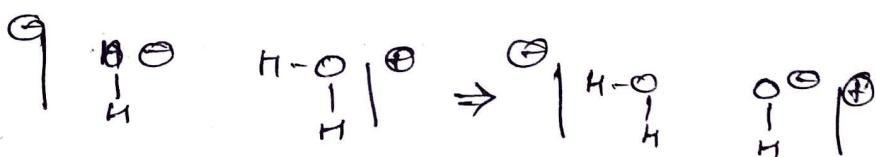
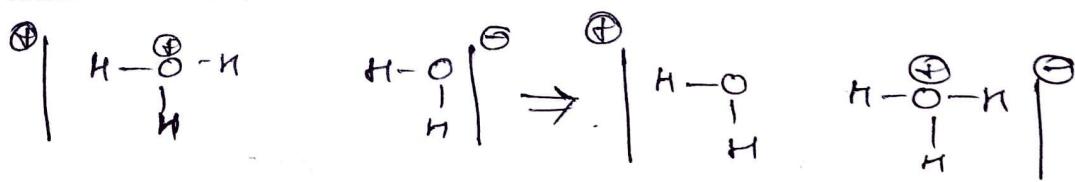
Ans 3a) The increasing order of ionic mobilities of alkali cations is



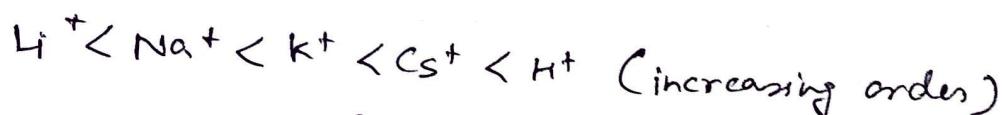
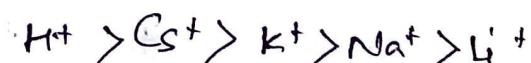
The low ionic mobility of  $\text{Li}^+$  is due to its high degree of hydration. Since it is very small, it has high degree of hydration. ~~Since its~~ very so, its mobility is low.  $\text{Cs}^+$  is very large, hence it has low degree of hydration and high ionic mobility. Ionic mobility increases as the size of cation increases.

The exceptional high ionic mobility of  $\text{H}^+$  in water is due to fastness proton ~~jam~~ mechanism. Hence  $\text{H}^+$  and  $\text{HO}^-$  have high ionic mobilities. So, the  $\text{H}^+$  ion has high ionic mobility than  $\text{Cs}^+$ .

Mechanism :-



Hence the order of ionic mobilities



b)  $\mu_{\text{Na}^+} = 7.623 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{s}^{-1}$

i) Ionic Conductance ( $\gamma_{\text{Na}^+}$ ) =  $\mu_{\text{Na}^+} F$

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$$\Rightarrow \lambda_{\text{Na}^+} = 7.623 \times 10^{-8} \times 96500 \\ = 7.356 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}$$

i) Ionic conductance of  $\text{Cl}^- (\lambda_{\text{Cl}^-}) = M_{\text{Cl}^-} \times F$

$$\Rightarrow \lambda_{\text{Cl}^-} = 4.239 \times 10^{-8} \times 96500 \\ = 4.09 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}$$

ii) Transport number of  $\text{Na}^+$  ( $t_{\text{Na}^+}$ ) =  $\frac{\lambda^o_{\text{Na}^+}}{\lambda^o_{\text{NaCl}}}$

$$= \frac{7.356 \times 10^{-3}}{127 \times 10^{-4}} \\ = 0.579$$

Since the  $t_{\text{Na}^+} + t_{\text{Cl}^-} = 1$

$$\Rightarrow t_{\text{Cl}^-} = 1 - t_{\text{Na}^+} = 0.421$$

Transport number of  $\text{Na}^+ = 0.579$

Transport number of  $\text{Cl}^- = 0.421$

c) i) As an external electric field is applied, the central ion moves in one direction, but the ionic atmosphere does not get enough time to adjust the spherically symmetrical arrangement around the central ion, and it lags behind.

This causes a retardation in the motion of the central ion, since the anions in behind are more in number than the one in front of the central ion. Thus the ionic

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atmosphere become assymetrical due to this motion of the central ion. This effect on the velocity of the central ion is known as assymmetric effect.

### i) Irreversible Cell

→ If we reverse the mode of operation, the exact equations are not reversed.

→ e.g. Dry Cell or Lechandru Cell

d) Given:-



Anode :-



$$E^\circ_{\text{Fe}^{2+}/\text{Fe}^{3+}} = -0.771 \text{ V}$$

Cathode :-



$$\Delta G_1 = -F \times E^\circ_{\text{Fe}^{2+}/\text{Fe}^{3+}}$$

Cell reaction:-



$$\Delta G_2 = -2F E^\circ_{\text{Fe}^{2+}/\text{Fe}}$$

$$\Delta G_3 = \Delta G_1 + \Delta G_2$$



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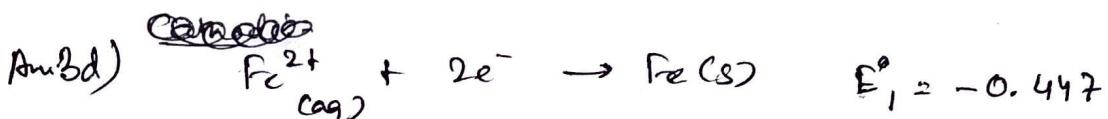
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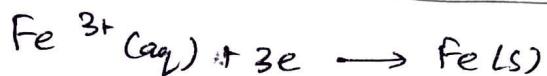
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$$\Delta G_1 = -2 \times E_1^\circ \times F$$



$$\Delta G_2 = -1 \times E_2^\circ \times F$$



$$\Delta G_3 = \Delta G_1 + \Delta G_2$$

$$\Rightarrow -3 \times F \times E_{\text{cell}}^\circ = -2 \times F \times E_1^\circ$$

$$- 1 \times E_2^\circ \times F$$

$$\Rightarrow +3E_{\text{cell}}^\circ = 2 \times E_1^\circ + E_2^\circ$$

$$\Rightarrow E_{\text{cell}}^\circ = \frac{2 \times E_1^\circ + E_2^\circ}{3}$$

$$\Rightarrow E_{\text{cell}}^\circ = \frac{-2 \times 0.447 + 0.771}{3}$$

$$\Rightarrow E_{\text{cell}}^\circ = \frac{-0.123}{3}$$

$$\Rightarrow E_{\text{cell}}^\circ = 0.041 \text{ V (Ans)}$$

$$RT \ln k_{\text{eq}} = nF E_{\text{cell}}^\circ$$

$$\Rightarrow \ln k_{\text{eq}} = \frac{nF}{RT} E_{\text{cell}}^\circ \quad | \text{Taking } T = 25^\circ \text{C} \\ = 298 \text{ K}$$

$$\Rightarrow \ln k_{\text{eq}} = 0.0591 \times 0.041$$

$$\Rightarrow \ln k_{\text{eq}} = \underline{\text{calculated value}} \quad 7.26 \times 10^{-3}$$

$$\Rightarrow k_{\text{eq}} = \underline{\text{calculated value}} \quad 1.0073$$

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