2023	12	25

TS-C4

SEAT NUMBER

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XI & XII Science (CBSE/state)
IIT- JEE (Mains + Advance)
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2

(4 Pages)

calculator is not allowed.
5. All symbols having their usual meanings unless otherwise stated.
6. For each MCQ, correct answer must be written along with its alphabet.
7. Evaluation of each MCQ would be done for the first attempt only.

SECTION-A

Q.1 Select and write the correct answers to the following questions: **[10]**

1)In an allylic alcohol, $-OH$ group is directly attached to __________ carbon atom.

Ans:

c) sp^3 *hybridised* **(1)**

2)Magnetic moment 2.84 B.M is given by _____________.

Ans:

a) $¿^{2+¿¿}$ **(1)**

3)Which of the following exhibits isotropy?

Ans:

b) Quarts glass **(1)**

4)Which among the following has sulphur in +6 oxidation state?

Ans:

c) Oleum **(1)**

5)In a cyclic process

Ans:

b) $\Delta U=O, \Delta V=O, W\neq O$ **(1)**

6)The number of ions given by ¿ in aqueous solution is __________

Ans:

d) 4 **(1)**

7)The colour of transition metal compounds is attributed to

Ans:

c) incomplete (n-1)d subshell **(1)**

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8)The coordination number of [Co9$en¿_3¿¿^{3+¿¿}$ is

Ans:

b) 6 **(1)**

9)The vacant space in FCC unit cell is

Ans:

a) 26% **(1)**

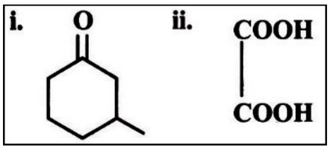
10) A plant cell shrinks when it is kept in

Ans:

b) a hypertonic solution **(1)**

Q.2 Answer the following questions in one sentence: [8]

(1) Write the IUPAC names of the following structures: (1)



Ans: i) 3-Methylcyclohexanone ii) 1- Ethanedioic acid

(2) Comment on hydrolysis product of disaccharides (1)

Ans:

Disaccharides give rise to two units of same or different monosaccharides on hydrolysis with dilute acids or specific enzymes.

(3) Write the IUPAC names of benzylamine (1)

Ans:

IUPAC name of benzylamine is phenylmethanamine.

(4) How are electrolytes classified? (1)

Ans:

The electrolytes are classified into strong and weak electrolytes. This classification is based on their extent of ionization in dilute aqueous solutions.

Strong Electrolyte:

The electrolytes ionizing completely or almost completely are strong electrolytes.

Example:

Strong acids, strong bases and salts

Weak Electrolyte:

The electrolytes which dissociate to a smaller extent in aqueous solution are weak electrolytes.

Example: Weak acids and weak bases

(5) What is the coordination number and oxidation state of metal iron in the complex ¿ **(1)**

Ans:

In complex $\left[Pt\left(NH_3\right)Cl_5\right]^{-¿¿}$, the coordination number of metal ion is 6 and oxidation state of metal ion is +4.

(6) Hydroboration-oxidation of propane gives __________. (1)

Ans:

Hydroboration-oxidation of propene gives propan-1-ol $\left(CH_3CH_2CH_2OH\right)$.

(7) Which amide does produce Ethanamine by Hofmann bromamide degradation reaction? **(1)**

Ans:

Propanamide $(C_2H_5CONH_2)$ produces Ethanamine by Hofmann bromamide degradation reaction.

(8) Calculate the pH of 0.01 M sulphuric acid. **(1)**

Ans:

The pH of 0.01 M sulphuric acid is 1.699.

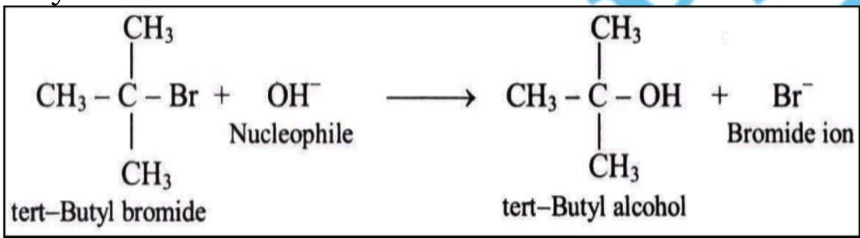
SECTION-B

Attempt any eight of the following questions: **[16]**

Q.3 Give a brief idea about S_n1 mechanism with the help of an example. **(2)**

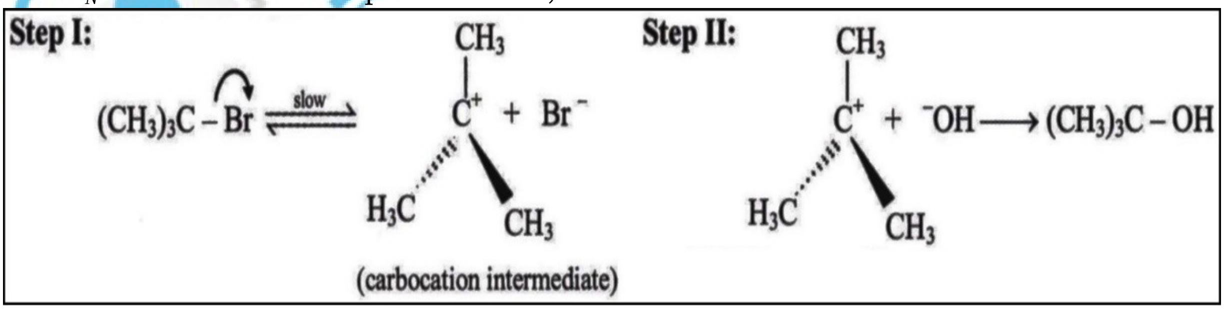
Ans:

1. S_N1 mechanism is a referred to as substitution nucleophilic unimolecular mechanism.
2. For example, the reaction between tert-butyl bromide and hydroxide ion to give tert-butyl alcohol.



$Rate = k[(CH_3)_3C - Br]$

3. The reaction follows a first-order kinetics. That is the rate of this reaction depends on concentration of only one species, which is the substrate molecule, tert-butyl bromide. Hence it is called substitution nucleophilic unimolecular, S_N1.
4. It can be seen in this reaction that concentration of only substrate appears in the rate equation; concentration of the nucleophile does not influence the reaction rate.
5. In other words, tert-butyl bromide reacts with hydroxide by a two-step mechanism. In the slow step C-X bond in the substrate undergoes heterolysis and in the subsequent fast step the nucleophile uses its electron pair to form a new bond with the carbon undergoing change.
6. The S_N1 mechanism is represented as,



Q.4 Write reaction to convert ethylamine into methylamine. **(2)**

Ans:

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$$CH_3-CH_2-NH_2 + HNO_2 \xrightarrow[ii.\,H_3O^+]{i.\,NaNO_2/HCl,\,273K} CH_3-CH_2-OH + N_2\uparrow H_2O$$

Ethylamine → Ethanol

$$CH_3-CH_2-OH + [O] \xrightarrow[dil.\,H_2SO_4,\,\Delta]{K_2Cr_2O_7} CH_3-COOH + H_2O$$

Acetic acid

$$CH_3-COOH + NH_3 \rightleftharpoons CH_3-COO^-NH_4^+ \xrightarrow[-H_2O]{\Delta} CH_3-CONH_2$$

Acetic acid, Ammanium carboxylate, Acetamide

$$CH_3-\overset{\overset{\large O}{\|}}{C}-NH_2 + Br_2 + 4KOH_{(aq)} \xrightarrow{\Delta} CH_3-NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

Acetamide → Methylamine

Q.5 State and explain: Effective atomic number (EAN) rule **(2)**

Ans:

1. EAN equals total number of electrons around the central metal ion in the complex.
2. EAN rule states that "a metal ion continues to accept electrons pairs till it attains the electronic configuration of the next noble gas".
3. If the EAN is equal to 18 (Ar), 36 (Kr), 54 (Xe) or 86 (Rn) then the EAN rule is obeyed.
4. EAN can be calculated with the following. Formula:

   EAN ¿ Number of electrons of metal ion + total number of electrons donated by ligands

   ¿ Atomic number of metal (Z) – Number of electrons lost by metal to form the ion (X) + Number of electrons donated by ligands (Y).

   ¿ $Z-X+Y$

   Eg: Consider, $\left[Co\left(NH_3\right)_6\right]^{3+}$¿¿

   Oxidation state of Cobalt is +3, six ligands donate 12 electrons.

   $Z=27, X=3, Y=12$

   EAN of Co^{3+}¿ $=Z-X+Y$ ¿ ¿ $27-3+12$ ¿ 36

Q.6 Distinguish between order and molecularity of a reaction. **(2)**

Ans:

	Order	Molecularity
1.	It is experimentally determined property.	It is theoretical entity.
2.	It is the sum of power of the concentration terms of reactants those appears in the rate equation.	It is the number of reactants molecules taking part in an elementary reaction.
3.	It may be an integer, fraction or zero.	It is integer.
4.	It is not based on balanced chemical equation.	It is based on balanced chemical equation.

Q.7 Classify the following carbohydrates into monosaccharides and polysaccharides. **(2)**

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Starch, glucose, glycogen, ribose, cellulose, fructose
Ans:
Monosaccharides: Glucose, ribose, fructose
Polysaccharides: Starch, glycogen, cellulose

Q.8 Construct a galvanic cell from the electrodes $Co^{3+¿|Co¿}$ **and** $Mn^{2+¿|Mn¿}$**.**
$E^0_{Co}=1.82\,V, E^0_{Mn}=-1.18\,V$. **Calculate** E^0_{cell} **(2)**

Ans:

Given: $E^o_{Co} = 1.82$ V, $E^o_{Mn} = -1.18$ V

To find: E^o_{Cell} and cell representation

Formula: $E^o_{Cell} = E^o_{Cathode} - E^o_{anode}$

Calculation: Electrode reactions are

At anode: $3(Mn_{(s)} \longrightarrow Mn^{2+}_{(aq)} + 2e^-)$

At cathode: $2(Co^{3+}_{(aq)} + 3e^- \longrightarrow Co_{(s)})$

The cell is composed of Mn (anode), $Mn_{(s)} \mid Mn^{2+}_{(aq)}$ and Co (cathode), $Co^{3+}_{(aq)} \mid Co_{(s)}$.

The cell is represented as: $\mathbf{Mn_{(s)} \mid Mn^{2+}_{(aq)} \| Co^{3+}_{(aq)} \mid Co_{(s)}}$

The standard electrode potential is given by

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = E^o_{Co} - E^o_{Mn} = 1.82\text{ V} - (-1.18\text{ V}) = \mathbf{3.00\text{ V}}$$

Q.9 Calculate the packing efficiency of metal crystal that has bcc structure. (2)

Ans:

Step 1: Radius of sphere (particle)

In bcc unit cell, particles occupy the corners and in addition one particle is at the centre of the cube.
The particle at the centre of the cube touches two corner particles along the diagonal of the cube. To obtain radius of the particle (sphere) Pythagoras theorem is applied.

For triangle FED, $\angle FED = 90^0$

$\therefore FD^2 = FE^2 + ED^2 = a_2 + a^2 = 2a^2$ .... (1)

(Because $FE = ED = a$)

For triangle AFD, $\angle AFD = 90^0$

$\therefore AF^2 = AD^2 + FD^2$ .... (2)

Substitution of equation (1) into (2) yields

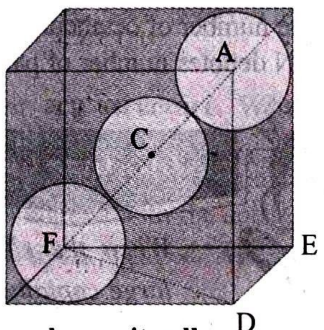
$AF^2 = a^2 + 2a^2 = 3a^2$ (Because AD=a)

¿ $AF = \sqrt{3}a$ .... (3)

From the figure, $AF = 4r$

Substitution for AF from equation (3) gives

$\sqrt{3}a = 4r$ and hence, $r = \frac{\sqrt{3}}{4}a$ .... (4)



bcc unit cell

Step 2: Volume of sphere

$$Volume\ of\ sphere\ particle = \frac{4}{3}\pi r^3$$

Substitution for r from equation (4) gives

$$Volume\ of\ one\ particle = \frac{4}{3}\pi \times \left(\frac{\sqrt{3}}{4}a\right)^3$$

$$¿\ \frac{4}{3}\pi \times \frac{(\sqrt{3})^3}{64}a^3 = \frac{\sqrt{3}\pi a^3}{16}$$

Step 3: Total volume of particles

Unit cell bcc contains 2 particles.

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Hence, volume occupied by particles in bcc unit cell ¿ $2 \times \frac{2\sqrt{3}\pi a^3}{16} = \frac{\sqrt{3}\pi a^3}{8}$ .... (5)

Step 4: Packing efficiency:

Packing efficiency

¿ $\frac{Volume\ occupied\ by\ particles \in unit\ cell}{Total\ volume\ of\ unit\ cell} \times 100$

¿ $\frac{\sqrt{3}\pi a^3}{8a^3} \times 100 = 68\%$

Thus, 68% of the total volume in bcc unit lattice is occupied by atoms and 32% is empty space or void volume.

Q.10 Write the important structural and functional difference between DNA and RAN. (2)

Ans:

	DNA	RNA
i.	DNA molecules contain several million nucleotides.	RNA molecules contain a few thousand nucleotides.
ii.	The sugar present in DNA is D-2-deoxyribose.	The sugar present in RNA is D-ribose.
iii.	DNA contains cytosine and thymine as pyrimidine bases.	RNA contains cytosine and uracil as pyrimidine bases.
iv.	DNA has double stranded α-helix structure.	RNA has single stranded α-helix structure.

Q.11 Distinguish between electrolytic and galvanic cells. (2)

Ans:

No.	Electrolytic cells	Galvanic cells
1	In electrolytic cell, a nonspontaneous reaction, known as electrolysis, is forced to occur by passing a direct current from an external source into the solution.	In galvanic (voltaic) cell a spontaneous chemical reaction produces electricity.
2	In these cells, electrical energy is converted into chemical energy.	In these cells, chemical energy is converted into electrical energy.
3	The anode of electrolytic cell is positive.	The anode of galvanic cell is negative.
4	The cathode of electrolytic cell is negative.	The cathode of galvanic cell is positive.

Q.12 What is pollution? Which are types of pollution? (2)

Ans:

1. Unnecessary and unacceptable changes in the environment due to natural events or human activities are known as pollution.
   OR
   Direct or indirect changes in physical, chemical and biological properties of air, water and soil that are harmful to humans and other living beings are called as pollution.
2. There are three main types of pollution: Air pollution, Water pollution and soil pollution.

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Q.13 Distinguish between crystalline solids and amorphous solids. **(2)**

Ans:

No.	Crystalline solids	Amorphous solids
1	The constituent particles are arranged in a regular and periodic manner.	The constituent particles are arranged randomly.
2	They have sharp and characteristic melting point.	They do not have sharp melting point. They gradually soften over a range of temperature.
3	They are anisotropic, i.e., have different physical properties in different direction.	They have isotropic, i.e., have same physical properties in all directions.
4	They have long range order.	They have only short range order.
Eg.	Ice, NaCl	Glass, rubber, plastics, etc.

Q.14 Define pH and pOH. Derive the relationship between pH and pOH. **(2)**

Ans:

1. The pH of a solution is defined as the negative logarithm to the base 10, of the concentration of $H^{+¿¿}$ ions in solution in $mol\ dm^{-3}$.
   pH is expressed mathematically as
   $pH=-\log_{10}¿$
2. Similarly, pOH of a solution can be defined as the negative logarithm to the base 10, of the molar concentration of $OH^{-¿¿}$ ions in solution.
   $pOH=-\log_{10}¿$
   Relationship between pH and pOH:
   The ionic product of water is given as:
   $K_w=¿$
   Now, $K_w=1\times10^{-14}\ at\ 298\ K$
   Thus, ¿
   Taking logarithm of both the sides, we write
   $\log_{10}¿$
   $-\log_{10}¿$
   Now, $pH=-\log_{10}¿$ and $pOH=-\log_{10}¿$
   $\therefore\ pH+pOH=14$

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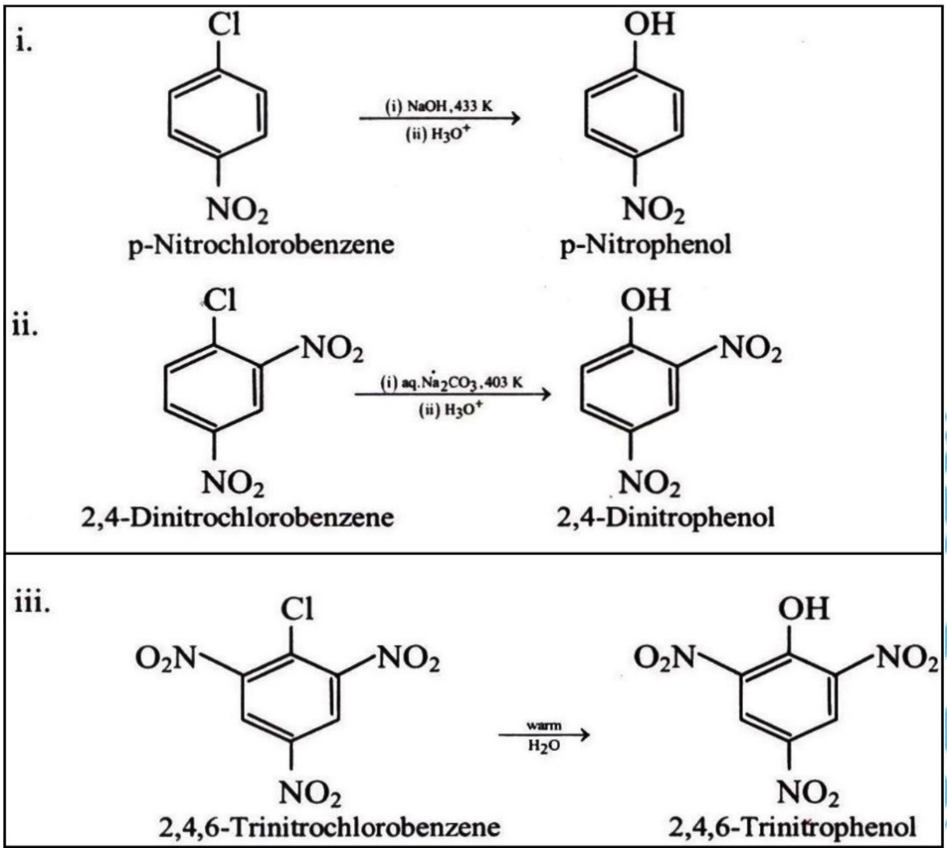
SECTION-C

Attempt any eight of the following questions:
[24]

Q.15 How will you convert the following: **(3)**

1) p-Nitrochlorobenzene to p-nitrophenol
2) 2,4-Dinitrochlorobenzene to 2,4-dinitrophenol
3) 2,4,6-Trinitrochlorobenzene to 2,4,6-trinitrophenol

Ans:

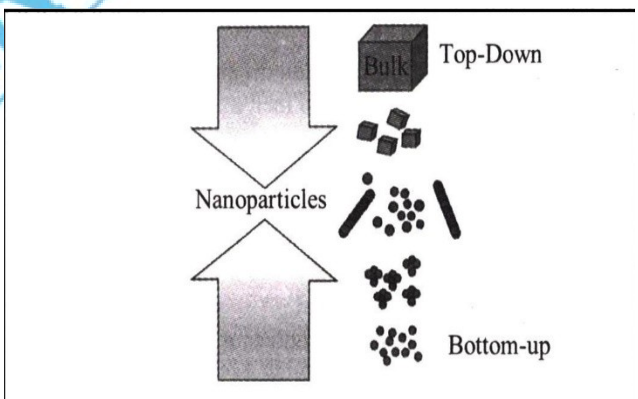


Q.16 Explain the two approaches that are followed for the synthesis of nanomaterials. Draw a suitable schematic illustration representing the two approaches. (3)

Ans:

Following are the two approaches to the synthesis of nanomaterials:

1. **Bottom-up approach:**
   In this approach, molecular components arrange themselves into more complex assemblies atom by atom, molecule by molecule and cluster by cluster from the bottom.
   Example:
   Synthesis of nanoparticles by colloidal dispersion
2. **Top-down approach:**
   In this approach, nanomaterials are synthesized from bulk material by breaking the material in stepwise manner.
   The bulk solids are dis-assembled into finer pieces until they are constituted of only few atoms.



Schematic illustration of the preparation of nanoparticles

Q.17 A first order reaction takes 40 minutes for 30% decomposition. Calculate its half-life. (3)

Ans:

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Given: $[A]_0 = 100\%$, $[A]_t = 100–30 = 70\%$, t = 40 min

To find: Half life of reaction ($t_{1/2}$)

Formula: $k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$

Calculation: Substitution of these in above

$$k = \frac{2.303}{t}\log_{10}\frac{100}{70}$$

$$= \frac{2.303}{40\ \text{min}}\ \log_{10}(1.429)$$

$$= \frac{2.303}{40\ \text{min}} \times 0.155 = 0.008924\ \text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.008924\ \text{min}^{-1}} = \mathbf{77.66\ min}$$

Q. 18 a) Give reason: When the bottle of soft drink is opened, effervescence is observed.
b) Give reason: Gases like NH_3 and CO_2 do not obey Henry's law.
(3)

Ans:

a)

1. Before sealing the bottle of soft drink, it is pressurised with a mixture of air, CO_2 saturated with water vapour.
2. Because of high partial pressure of CO_2, its amount dissolved in soft drink is higher than the solubility of CO_2 under normal conditions.
   Hence, when the bottle of soft drink is opened, excess dissolved CO_2 comes out with effervescence.

b)

1. Gases like NH_3 and CO_2 react with water as follows:
   $NH_3 + H_2O \rightleftharpoons NH_4^{+¿+OH^{-¿¿}}$
   $CO_2 + H_2O \rightleftharpoons H_2CO_3$
2. Because of these reactions, NH_3 and CO_2 gases have higher solubilities than expected by Henry's law.
   Hence, Gases like NH_3 and CO_2 do not obey Henry's law.

Q.19 Sketch and explain the operation and working of dry cell (Leclanche' cell). (3)

Ans:

Dry cell: It is a cell without liquid component, but the electrolyte is not completely dry. It is a viscous aqueous paste.

1. **Construction:**

a. The container of the cell is made of zinc which serves as anode ¿. It is lined from inside with a porous to separate it from the other material of the cell.

b. An inert graphite rod in the centre of the cell immersed in the electrolyte paste serves as cathode ¿. It is surrounded by a paste of manganese dioxide (MnO_2) and carbon black.

c. The rest of the cell is filed with an electrolyte. It is a moist paste of ammonium chloride (NH_4Cl) and zinc chloride $(ZnCl_2)$. Starch is added to make the paste thick so that it does not leaks.

d. The cell is sealed at the top to prevent drying of the paste by evaporation of moisture.

2. **Working (Cell Reactions):**

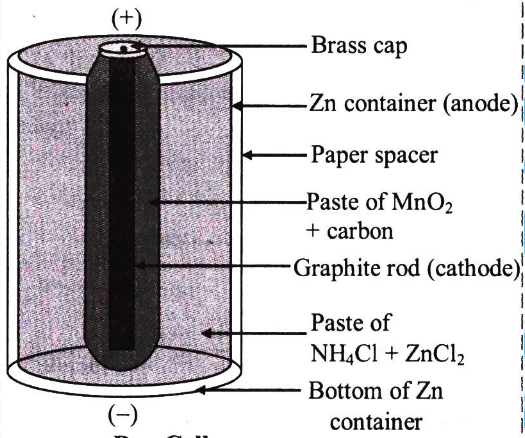
a. Oxidation at anode: When the cell operates the current is drawn from the cell and metallic zinc is oxidized to zinc ions.

$Zn_{(s)} \rightarrow Zn_{(aq)}^{2+¿+2e^{-¿¿}}$

b. Reduction at cathode: The electrons liberated in oxidation at anode flow along the container and migrate to cathode. At cathode, NH_4^{+} ions are reduced.
Hydrogen gas produced in reduction reaction is oxidized by MnO_2 and prevents its collection on cathode.
$H_{2(g)} + 2MnO_{2(s)} \rightarrow Mn_2O_{3(s)} + H_2O_{(l)}$
The net reduction reaction at cathode is combination of these two reactions.
$2NH_{4(aq)}^{+} + 2MnO_{2(s)} + 2e^{-} \rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$

c. **Net Cell Reaction:** The net cell reaction is sum of oxidation at anode and reduction at cathode.
$Zn_{(s)} + 2NH_{4(aq)}^{+} + 2MnO_{2(s)} \rightarrow Zn_{(aq)}^{2+} + Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$
The ammonia produced combines with Zn^{2+} to form soluble compound containing complex ion.
$Zn_{(aq)}^{2+} + 4NH_{3(aq)} \rightarrow [Zn(NH_3)_4]_{(aq)}^{2+}$

3. **Diagram:**



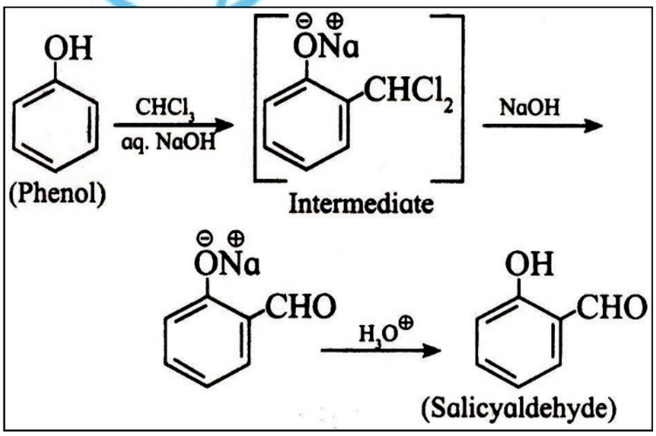
Dry Cell

4. **Uses:** Dry cell is used as a source of power in flashlights, portable radios, tape recorders, clocks, etc.

Q.20 Explain: Reimer- Tiemann reaction **(3)**

Ans:

When phenol is treated with chloroform in aqueous sodium hydroxide solution followed by hydrolysis with acid, salicylaldehyde is formed. This reaction is known as Reimer-Tiemann reaction.

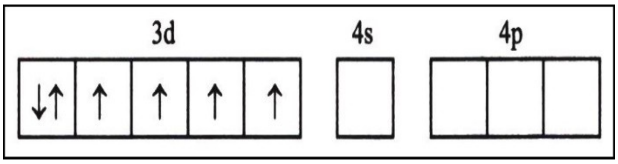


If carbon tetrachloride is used in place of chloroform, salicylic acid is formed.

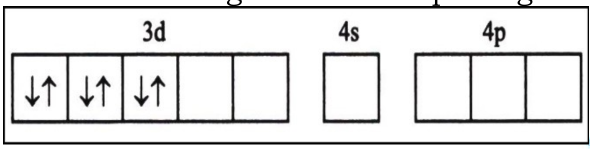
Q.21 Explain the structure of octahedral low spin complex, ¿¿. **(3)**

Ans:

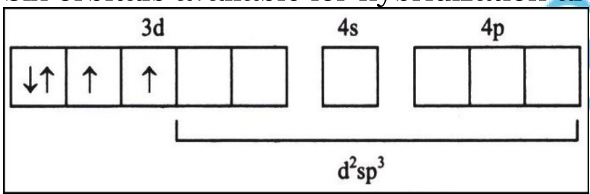
1. Oxidation state of Cobalt is +3.
2. Valence shell electronic configuration of Co^{3+}¿¿ is represented in box diagram as shown below:



3. Number of ammine ligands is 6, number of vacant metal ion orbitals required for bonding with ligands must be six.
4. Complex is low spin, so pairing of electrons will take place prior to hybridization.
5. Electronic configuration after pairing would be

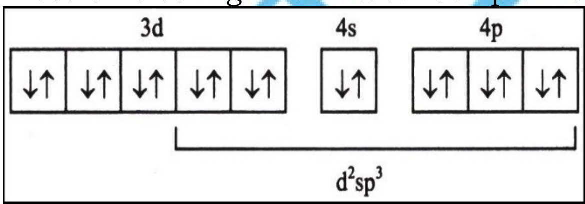


6. Six orbitals available for hybridization are two 3d, one 4s, three 4p orbitals



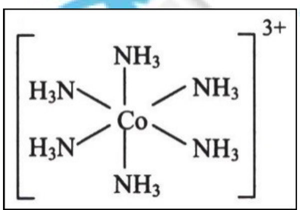
The orbitals for hybridization are decided from the number of ammine ligands which is six. Here $(n-1)d$ orbitals participate in hybridization since it is the low spin complex.

7. Electronic configuration after complex formation.



8. As all electrons are paired the complex is diamagnetic.

Structure of the complex $[Co(NH_3)_6]^{3+}$¿¿ :



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Q.22 Define the following: **(3)**

1. Pyrometallurgy 2. Hydrometallurgy 3. Electrometallurgy

Ans:

1. **Pyrometallurgy:** A process in which the ore is reduced to metal at high temperature using reducing agents like carbon, hydrogen, aluminium, etc. is called pyrometallurgy.
2. **Hydrometallurgy:** The process of extracting metals from the aqueous solution of their salts using suitable reducing agent is called hydrometallurgy.
3. **Electrometallurgy:** A process in which metal is extracted by electrolytic reduction of molten (fused) metallic compound is called electrometallurgy.

Q.23 How is polythene manufactured? Give their properties and uses. **(3)**

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Ans:

Low Density Polyethylene (LDP):

1. LDP is obtained by polymerization of ethylene under high pressure (1000 - 2000 atm) and temperature (350 - 570 K) in presence of traces of O_2 or peroxide as initiator.

$$CH_2 = CH_2 \xrightarrow[\text{peroxide at 350 - 370K, 1000 - 2000 atm}]{\text{Traces of } O_2} LDP$$

2. The mechanism of this reaction involves free radical addition and H-atom abstraction. The latter results in branching.
3. As a result, the chains are loosely held and the polymer has low density.

Properties of LDP:

1. LDP films are extremely flexible, but tough, chemically inert and moisture resistant.
2. It is poor conductor of electricity with melting point $100^0 C$.

Uses of LDP:

1. LDP is mainly used in preparation of pipes for agriculture, irrigation, domestic water line connections as well as insulation to electric cables.
2. It is also used in submarine cable insulation.
3. It is used in producing extruded films, sheets, mainly for packaging and household uses like in preparation of squeeze bottles, attractive containers etc.

High-Density Polyethylene (HDP):

1. It is essentially a linear polymer with high density due to close packing.

$$CH_2 = CH_2 \xrightarrow[\text{6 - 7 atm, catalyst}]{\text{333 K - 343 K}} HDP$$

2. HDP is obtained by polymerization of ethene in presence of Zieglar-Natta catalyst, which is a combination of triethyl aluminium with titanium tetrachloride at a temperature of 333K to 343K and a pressure of 6-7 atm.

Properties of HDP:

1. HDP is crystalline, melting point in the range of $144-150^0 C$.
2. It is much stiffer than LDP and has high tensile strength and hardness.
3. It is more resistant to chemicals than LDP.

Uses of HDP:

1. HDP is used in manufacture of toys and other household articles like buckets, dustbins, bottles, pipes etc.
2. It is used to prepare laboratory wares and other objects where high tensile strength and stiffness is required.

Q.24 Calculate pH and pOH of 0.01 M HCl solution. **(3)**

Ans:

Given: Concentration of HCl solution = 0.01 M

To find: pH and pOH

Formulae: i. $pH = -\log_{10}[H_3O^+]$ ii. $pH + pOH = 14$

Calculation: HCl is a strong acid. It dissociates almost completely in water as:

$$HCl_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Hence, $[H_3O^+] = c = 0.01\ M = 1 \times 10^{-2}\ M$

From formula (i),

$pH = -\log_{10}[H_3O^+] = -\log_{10}[1 \times 10^{-2}] = \mathbf{2}$

From formula (ii),

$pH + pOH = 14$

$\therefore$ $pOH = 14 - pH = 14 - 2 = \mathbf{12}$

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Q.25 Explain the trends in ionization enthalpies of d block elements. (3)

Ans:

1. The ionization enthalpies of transition elements are intermediate between those of s-block or p-block elements. This suggests that transition elements are less electropositive than elements of group 1 and 2.
2. As the atomic number increases across a transition series, the first ionization energy increases with some irregularities.
3. Ionization enthalpies shown for a given element there is substantial increase from the first ionization enthalpy IE_1 to the third ionization enthalpy IE_3.
4. The atoms of elements of third transition series possess filled 4f- orbitals. 4f orbitals show poor shielding effect on account of their peculiar diffused shape. As a result, the valence electrons experience greater nuclear attraction. A greater amount of energy is required to ionize elements of the third transition series.

Q.26 The rate constant for a first order reaction are $0.6\,s^{-1}$ at 313 K and 0.045 s^{-1} at 293 K. What is the activation energy? (3)

Ans:

Given: $k_1 = 0.6\ s^{-1}$, $T_1 = 313$ K, $k_1 = 0.045\ s^{-1}$, $T_2 = 293$ K,

To find: Activation energy (E_a)

Formula: $\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

Calculation: $\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

Substituting the given values

$$\log_{10}\frac{0.6}{0.045} = \frac{E_a}{2.303 \times 8.314\ J\ K^{-1}\ mol^{-1}} \times \left[\frac{313\ K - 293\ K}{293 K \times 313\ K}\right]$$

$$\log_{10} 13.33 = \frac{E_a}{2.303 \times 8.314\ J\ mol^{-1}} \times \frac{20}{293 \times 313}$$

$$1.1248 = \frac{E_a}{19.15\ J\ mol^{-1}} \times 2.18 \times 10^{-4}$$

$$E_a = \frac{1.1218 \times 19.15}{2.18 \times 10^{-4}}\ J\ mol^{-1} = 98810\ J\ mol^{-1} = \mathbf{98.8\ kJ\ mol^{-1}}$$

SECTION-D

Attempt any three of the following question: [12]

Q.27 a) Define path function. Give examples. (4)

b) State Hess's law of constant heat summation. Illustrate with an example. State its applications.

Ans:

a) The properties which depend on the path are called path functions.

For example, work (W) and heat (Q).

b)

1. The law states that, "Overall the enthalpy change for a reaction is equal to sum of enthalpy changes of individual steps in the reaction".
2. **Illustration:**

a. The enthalpy change for a chemical reaction is the same regardless of the path by which the reaction occurs. Hess's law is a direct consequence of the fact that enthalpy is state function. The enthalpy change of a reaction depends only on the initial and final states and not on the path by which the reaction occurs.

b. To determine the overall equation of reaction, reactants and products in the individual steps are added or subtracted like algebraic entities.

c. Consider the synthesis of NH_3,

1. $2H_{2(g)} + N_{2(g)} \longrightarrow N_2H_{4(g)},\ \Delta_r H_1^\circ = +95.4\ kJ$
2. $N_2H_{4(g)} + H_{2(g)} \longrightarrow 2NH_{3(g)},\ \Delta_r H_2^\circ = -187.6\ kJ$

$$3H_{2(g)} + N_{2(g)} \longrightarrow 2NH_{3(g)},\ \Delta_r H^\circ = -92.2\ kJ$$

d. The sum of the enthalpy changes for steps (1) and (2) is equal to enthalpy change for the overall reaction.

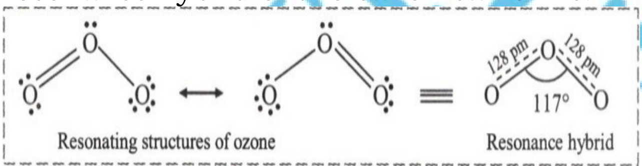
Q.28 a) Describe the structure of ozone. Give its uses. **(4)**

b) What is the action of following on SO_2?

1) Cl_2 **2)** O_2 **3)** $NaOH$ **4)** Na_2SO_3

Ans:

a) Structure of Ozone: Ozone (O_3) is an angular molecule. The two $O-O$ band lengths in the ozone molecule are identical, 128 pm and the $O-O-O$ bond angle of about 117^0. It is a resonance hybrid of two canonical forms.



Uses of Ozone:

1. Ozone is used for air purification at crowded places like cinema halls, tunnels, railways, etc.
2. In sterilizing drinking water by oxidising all germs and bacteria.
3. For bleaching ivory, oils, starch, wax and delicate fabrics such as silk.
4. In the manufacture of synthetic camphor, potassium permanganate, etc.

b)

1. **Reaction with Cl_2:** Sulfur dioxide reacts with chlorine in the presence of charcoal (catalyst) to form sulfuryl chloride.
   $SO_{2(g)} + Cl_{2(g)} \xrightarrow{charcoal} SO_2Cl_{2(l)}$
2. **Reaction with O_2:** Sulfur dioxide is oxidised by dioxygen in presence of vanadium (V) oxide to sulfur trioxide.
   $2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$
3. **Reaction with NaOH:** Sulfur dioxide readily reacts with sodium hydroxide solution to form sodium sulfite.
   $2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$
4. **Reaction with Na_2SO_3:** Sulfur dioxide reacts with sodium sulfite solution to form sodium hydrogen sulfite.
   $Na_2SO_3 + H_2O_{(l)} + SO_2 \rightarrow 2NaHSO_3$

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Q.29 a) Write a note on Cannizzaro reaction. **(4)**

b) How will you prepare carboxylic acids by hydrolysis of the following?

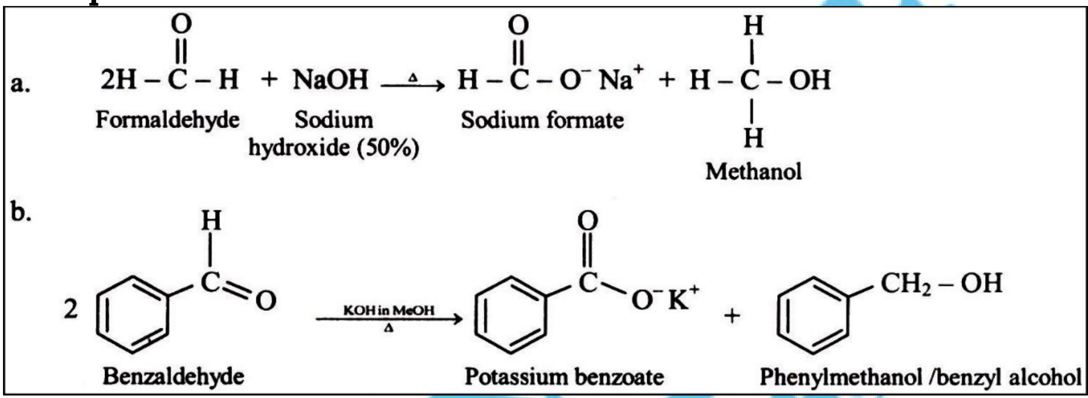
1) Acyl chlorides 2) anhydrides 3) esters

Ans:

a)

1. This reaction is given only by aldehydes having no $\alpha -$¿hydrogen atom.
2. Aldehydes undergo self -oxidation and reduction reaction on heating with concentrated alkali.
3. In cannizzaro reaction one molecule of an aldehyde is reduced to alcohol and at the same time second molecule is oxidized to carboxylic acid salt. This is an example of disproportionation reaction.

Example:



b)

1. **By Hydrolysis of Acyl Chlorides:**
   Acyl chlorides on hydrolysis with water give carboxylic acids. This method is useful for preparation of aliphatic as well as aromatic acid.

$$\underset{\text{Acyl chloride}}{R-COCl} + H_2O \longrightarrow \underset{\text{Carboxylic acid}}{R-COOH} + H-Cl$$

2. **By Hydrolysis of Anhydrides:**
   Anhydrides on hydrolysis with water give carboxylic acids.

$$\underset{\text{Anhydride}}{R-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-R} + H_2O \longrightarrow 2\underset{\text{Carboxylic acid}}{R-\overset{\overset{O}{||}}{C}-O-H}$$

3. **By Hydrolysis of Esters:**
   Carboxylic acids can be obtained from esters either by acid hydrolysis or alkaline hydrolysis.

a. **Acid Hydrolysis of Ester:** Esters on hydrolysis with dilute mineral acid like dilute HCl or dilute H_2SO_4 give the corresponding carboxylic acid.

$$\underset{\text{Ester}}{R-\overset{\overset{O}{||}}{C}-O-R'} + H_2O \xrightarrow[\Delta]{\text{dil.}H_2SO_4} \underset{\text{Carboxylic acid}}{R-\overset{\overset{O}{||}}{C}-O-H} + \underset{\text{Alcohol}}{R'-OH}$$

b. **Alkaline Hydrolysis of Ester** using dilute alkali like dilute NaOH or dilute KOH form solution of water-soluble sodium or potassium salt of the acid (carboxylate). On acidification with concentrated HCl, free acid is formed.

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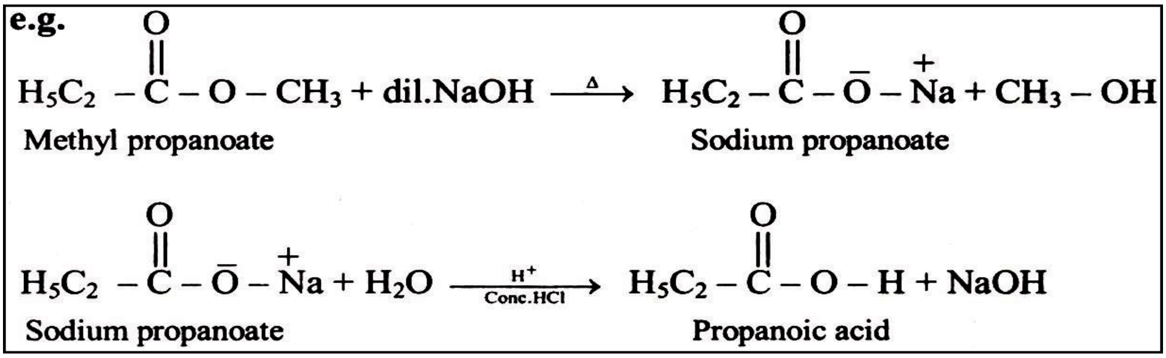

Q.30 300 mmol of an ideal gas occupies 13.7 dm^3 at 300 K. Calculate the work done when the gas is expanded until its volume has increased by 2.3 dm^3 (a) isothermally against a constant external pressure of 0.3 bar (b) isothermally and reversibly (c) into vacuum. **(4)**

Ans:

Given: Number of moles = n = 300 mmol

Initial volume = V_1 = 13.7 dm^3

Increase in volume = ΔV = 2.3 dm^3

Temperature = T = 300 K,

Pressure (P_{ext}) = 0.3 bar

To find: Work done under different conditions

Formulae:

i. $W = -P_{ext}\,\Delta V$

ii. $W_{max} = -2.303\ nRT \log_{10} \frac{V_2}{V_1}$

Calculation: i. Using formula (i),

$W = -P_{ex}\,\Delta V$

$= -\ 0.3\ bar \times 2.3\ dm^3$

$= -\ 0.69\ dm^3\ bar$

$= -\ 0.69\ dm^3\ bar \times \frac{100\ J}{dm^3\ bar}$

$= \mathbf{-\ 69\ J}$

ii. $n = 300\ mmol = 300 \times 10^{-3}\ mol = 0.3\ mol$

Final volume = $V_2 = V_1 + \Delta V = 13.7\ dm^3 + 2.3\ dm^3 = 16\ dm^3$

Using formula (ii),

$W_{max} = -\ 2.303\ nRT \log_{10} \frac{V_2}{V_1}$

$= -\ 2.303 \times 0.3\ mol \times 8.314\ J\ K^{-1} mol^{-1} \times 300\ K \times \log_{10} \frac{16}{13.7}$

$= -\ 2.303 \times 0.3 \times 8.314\ J \times 300 \times 0.0674$

$= \mathbf{-\ 116.1\ J}$

iii. When gas is expanded in vacuum, $P_{ext} = 0$. Hence, W = **0**

Q.31 a) Write a note on Stephen reaction. **(4)**

b) Explain the preparation of aliphatic and aromatic ketones from acyl chloride using dialkyl cadmium.

Ans:

a)

Nitriles are reduced to imine hydrochloride by stannous chloride in presence of hydrochloric acid which on acid hydrolysis give corresponding aldehydes. This reaction is called Stephen reaction.

$$R-C\equiv N+2[H]\xrightarrow{SnCl_2,HCl}R-HC=NH.HCl\xrightarrow{H_3O^+}R-CHO+NH_4Cl$$

Alkane nitrile — Imine hydrochloride — Aldehyde

e.g. $$H_3C-C\equiv N+2[H]\xrightarrow[\text{(reduction)}]{SnCl_2,HCl}CH_3-HC=NH.HCl\xrightarrow{H_3O^+}CH_3-CHO+NH_4Cl$$

Ethanenitrile — Ethanimine hydrochloride — Ethanal

b)

Ketones are obtained from acyl chloride by reaction with dialkyl cadmium which is prepared by the treatment of cadmium chloride with Grignard reagent. The reaction can be represented as,

$$2R-MgX+CdCl_2\longrightarrow R_2Cd+2Mg(X)Cl$$

Grignard reagent — cadmium chloride — Dialkyl cadmium

$$2R'-COCl+R_2Cd\longrightarrow 2R'-CO-R+CdCl_2$$

Acyl chloride — Ketone

e.g. i. Ethanoyl chloride to propanone

$$2CH_3-COCl+(CH_3)_2Cd\longrightarrow 2CH_3-CO-CH_3+CdCl_2$$

Ethanoyl chloride — Dimethyl cadmium — Propanone (Acetone)

ii. Benzoyl chloride to acetophenone

$$2C_6H_5-COCl+(CH_3)_2Cd\longrightarrow C_6H_5-CO-CH_3+CdCl_2$$

Benzoyl chloride — Dimethyl cadmium — Acetophenone