ISC SEMESTER 2 EXAMINATION

SAMPLE PAPER - 5

CHEMISTRY PAPER 1 (THEORY)

Maximum Marks: 35

Time allowed: One and a half hour

Candidates are allowed an additional ***10 minutes*** *for* **only** *reading the paper.*

They must ***NOT*** *start writing during this time.*

All questions are compulsory

All working, including rough work, should be done on the same sheet as, and adjacent to the rest of the answer.

Balanced equations must be given wherever possible and diagrams where they are helpful.

When solving numerical problems, all essential working must be shown.

In working out problems, use the following data:

Gas constant $R = 1{\cdot}987\ \text{cal deg}^{-1}\ \text{mol}^{-1} = 8{\cdot}314\ \text{JK}^{-1}\ \text{mol}^{-1} = 0{\cdot}0821\ \text{dm}^3\ \text{atm K}^{-1}\text{mol}^{-1}$

$1\ \text{l atm} = 1\ \text{dm}^3\ \text{atm} = 101{\cdot}3\ \text{J}$. *1 Faraday = 96500 coulombs.*

Avogadro's number $= 6{\cdot}023 \cdot 10^{23}$.

Section-A

Question 1.

Fill in the blanks by choosing the appropriate word(s) from those given in the brackets:

(square root, BF_3, adenine, aniline , thiamine, ethylamine, universe, formic acid, directly, PCl_5, inner, outer, $BeCl_2$, CH_4, lanthanoids, actinoids, zinc blende, olefinic, aldol, antichlor, organometallic)

(i) The inner transition elements in which filling of 5f orbitals takes place are called as _______.

(ii) High spin complexes are _______ orbital complexes and low spin complex are _______ orbital complex.

(iii) Reduction of nitrobenzene using scrap iron in acidic medium produces _______.

Question 2.

Select and write the correct alternative from the choices given below:

(i) Lower amines are soluble in water due to :

(a) low molecular mass
(c) formation of hydrogen bonds with water
(b) formation of complexes
(d) affinity with water

(ii) Which of the following does not reacts with Hinsberg reagent?

(a) Ethyl amine
(c) $(CH_3)_3N$
(b) $(CH_3)_2NH$
(d) Propane-2-amine

(iii) The increase in surface area of adsorbent will:

(a) increase Physisorption
(b) increase Chemisorption
(c) increase both physisorption and chemisorption
(d) decrease both physisorption and chemisorption

(iv) **Assertion:** The unit of rate constant for second order reaction is $mol^{-1} L s^{-1}$.

Reason: Rate of second order reaction depends on concentration of reactant.

(a) Both assertion and reason are true and reason is the correct explanation of assertion.

(b) Both assertion and reason are true but reason is not the correct explanation for assertion.

(c) Assertion is true but reason is false.

(d) Assertion is false but reason is true.

Section-B

Question 3.

How does chemisorption depends on change in temperature? Comment on its specificity.

Question 4.

What are primary and secondary valencies according to Werner's theory of co-ordination compounds? Give examples of both.

OR

Define co-ordination number. What is co-ordination number of $[Fe(C_2O_4)_3]^{3-}$?

Question 5.

It has been found that for a reaction, a large number of colliding molecules have energy more than threshold value, yet the reaction is slow. Why?

Question 6.

What is electronic configuration of d-block elements? Why do they show variable oxidation states ?

Question 7.

Define ligands. How are they classified on basis of denticity? Give example.

Question 8.

Name one natural and one synthetic food preservative commonly used.

Question 9.

Give balanced equation for each of the following:

(i) Hydrogenation of benzoyl chloride in presence of $Pd/BaSO_4$.

(ii) Benzaldehyde with concentrated sodium hydroxide.

Question 10.

Give one chemical test for each to distinguish between the following pairs of compound:

(i) Propanal and propanone

(ii) Acetophenone and Benzophenone

Section-C

Question 11.

(i) With respect to the given co-ordination compound $[Co(NH_3)_6]^{3+}$, answer the following questions:

- (a) Write IUPAC name of the compound.
- (b) Is it a inner orbital complex or an outer orbital complex?
- (c) What is its primary and secondary valency?

OR

(ii) Answer the following questions with respect to given complex $[Fe(CN)_6]^{3-}$:

- (a) Is it a inner orbital complex or an outer orbital complex?
- (b) Is it paramagnetic or diamagnetic?
- (c) Predict its hybridization.

Question 12.

(i) How will you convert propanoic acid to acetic acid ?

(ii) What happens when formic acid is heated with Tollen's reagent?

Question 13.

In a reaction, $2A \longrightarrow$ Products, the concentration of A decreases from 0.7 mol L^{-1} to 0.6 mol L^{-1} in 10 minutes. Answer the following questions:

(i) Calculate the rate during this interval?

(ii) If half life period for the reaction is 6.93 s and reaction is first order with respect to A. Calculate rate constant.

(iii) What happens to rate of reaction, if concentration of A is doubled?

Question 14.

(i) Why is aniline less basic than methylamine?

(ii) How is the activation of benzene ring by amino group reduced by acetylated aniline during nitration ?

(iii) How is sulphanilic acid prepared from aniline?

Answers

Section-A

Answer 1.

(i) Actinides

Explanation:

The elements in which the last electron enters the 5f-orbital constitute the second inner transition series. They are also called actinides or actinoids because the series starts from the element actinium.

(ii) outer, inner

Explanation:

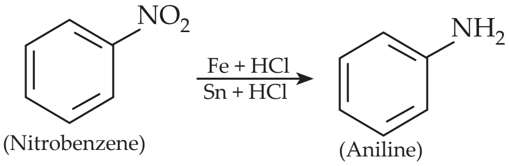
Inner orbital complexes use inner *d*-orbitals in hybridisation thus they have low spin while outer orbital complexes use outer *d*-orbitals in hybridisation thus they have high spin or spin free complex.

eg.: $[Co(NH_3]^{3+}$ is inner orbital complex thus hybridisation is d^2sp^3 and $[CoF_6]^{3-}$ used outer 4*d* orbitals in hybridisation (sp^3d^2) thus it is outer orbital complex.

(iii) Aniline

Explanation:

The reduction of nitrobenzene using scrap iron in acidic medium produces aniline. This reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.



Answer 2.

(i) (c) Formation of hydrogen bonds with water

Explanation:

Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. An increase in the size of hydrophobic alkyl part increases the molar mass of amines which results in a decrease in its solubility in water. Thus, higher amines are insoluble in water.

(ii) (c) $(CH_3)_3N$.

Explanation:

Tertiary amines (R_3N) does not react with Hinsberg reagent ($C_6H_5SO_2Cl$) as there are no freely available hydrogens on the amine group which can donate electrons to the Sulphur of the Hinsberg reagent.

(iii) (c) increase both physisorption and chemisorption

Explanation:

Since adsorption is a surface phenomenon, adsorption increases with the increase in the surface area of the adsorbent. More finely divided or rougher the surface of adsorbent, the greater will be the surface area and hence the greater will be the adsorption. Since, Physisorption and chemisorption both are directly proportional to surface area. Thus, on increasing the surface area of adsorbent both physisorption and chemisorption will increase.

(iv) (b) Both assertion and reason are true but reason is not the correct explanation for assertion.

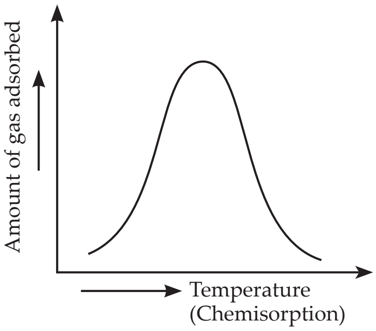
Explanation:

The unit of rate constant for second order reaction is $mol^{-1}\ L\ s^{-1}$ and the rate of second order reaction depends on initial concentration of reactant. Thus, both assertion and reason are true but reason is not the correct explanation for assertion.

Section-B

Answer 3.

In Chemisorption, with initial rise in temperature, the rate of adsorption increases but with further rise in temperature, adsorption starts decreasing after a certain limit. This is because an initial rise in temperature will provide the molecules necessary activation energy for chemical bond formation so rate of adsorption increases. At a certain temperature, all the bonds are formed and now the further increase in temperature will favour desportion *i.e.,* the rate of adsorption now starts decreasing.



Chemisorption is highly specific in nature and occurs only when there is possibility of bond formation between adsorbent and adsorbate.

Answer 4.

The ionisable valency in a coordination compound are called as primary valency. The primary or ionisable valency of the central metal atom or ion is satisfied by the anions. The oxidation number of central metal atom or ion is expressed by the primary valency. The non-ionisable valency in a coordination compound is called as secondary valency. The secondary valency of the central metal atom or ion is satisfied by the anion, neutral molecule or even by the cation. The number of secondary valency for a specific metal atom or ion is fixed. This specific value of secondary valency of the concern atom or ion is called coordination number .For example, in $[Cu(NH_3)_4]SO_4$, primary valency is 2 and secondary valency is 4.

Secondary valence refers to coordination number. Since copper is coordinated to 4 ammonia ligands, secondary valence is 4. Primary valence is satisfied by anions. Since sulphate ion has −2 charge, primary valence is 2.

OR

The coordination number (CN) of a metal atom or ion in a given complex may be defined as the number of ligand donor atoms to which the metal is bonded directly. Coordination number of Fe ion in $[Fe(C_2O_4)_3]^{3-}$ is 6 as it is attached to three bidentate ligands.

Answer 5.

The reason could be improper orientation of the molecules. For a reaction to occur, colliding molecules should have sufficient kinetic energy i.e. threshold frequency and proper orientation so as to lead to formation of products.

Answer 6.

The general electronic configuration of *d*-block elements can be written as $(n\text{-}1)d^{1-10}\ ns^{1-2}$. Where *n* is the valence shell and (n-1) is penultimate shell.

Transition elements show variable state oxidation in their compounds because their valence electrons are in two different sets of orbitals, i.e., (n-1)*d* and *ns* and there is a very small energy difference in between (n-1)*d* and ns orbitals. As a result, electrons of (n-1)*d* orbitals as well as ns-orbitals take part in bond formation. Thus, transition elements have variable oxidation states.

Answer 7.

A ligand is an ion or molecule, which donates a pair of electrons to the central metal atom or ion to form a coordination complex. The number of ligating (linking) atoms present in a ligand is called denticity.

On the basis of denticity, ligands can be of following types:

1. **Monodentate ligands:** These ligands donate one pair of electron to the central metal atom or ion. Example: Cl^-
2. **Bidenate ligand:** These ligands donate two pair of electrons to the central metal atom or ion. Example: C_2O_4
3. **Polydentate:** These ligands donate more than two pairs of electrons to the central metal atom or ion. Example: EDTA.

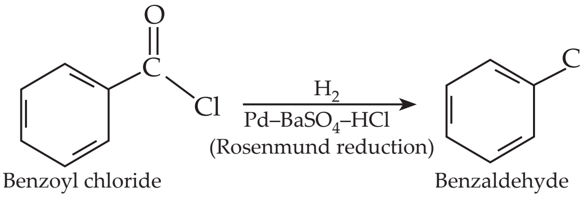
Answer 8.

Natural preservatives are additives that slow the growth of spoilage organisms like mould or bacteria in food. They are derived from natural sources and their common examples are table salt, sugar, vinegar etc.

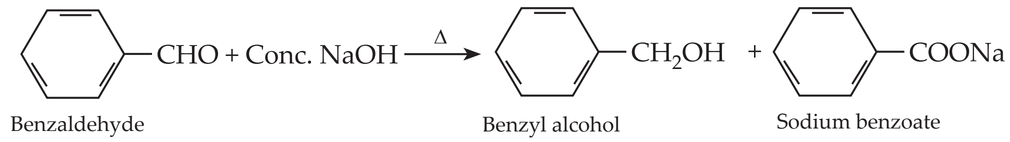
Artificial preservatives are chemical substances that may be sprayed on the outside of a food, or added to foods to retard spoilage, discoloration, or contamination by bacteria and other disease organisms. They are chemical substances which are derived artificially and their common examples are salts of sorbic acid, propanoic acid etc.

Answer 9.

(i)



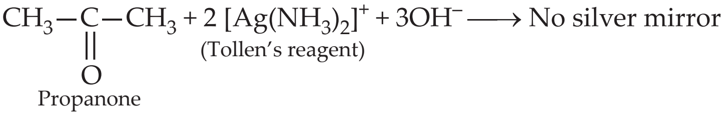
(ii)



Answer 10.

(i) Propanal and propanone can be easily distinguished by Tollen's test. Propanal will give positive tollen's test and will form silver mirror on reacting with tollen's reagent. On the other hand, propanone, being a ketone, will not form any silver mirror with tollen's reagent.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{(Tollen's reagent)}}{2[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow \underset{\text{Propanoate ion}}{CH_3CH_2COO^-} + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$



$$\underset{\text{Propanone}}{CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3} + \underset{\text{(Tollen's reagent)}}{2\,[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow \text{No silver mirror}$$

(ii) Acetophenone and Benzophenone can be distinguished by using iodoform test. Acetophenone due to presence of terminal $-COCH_3$ group will give positive iodoform test and will give yellow coloured precipitate on reaction with alkaline iodine solution. On the other hand, benzophenone will not show iodoform reaction.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + \underset{\substack{\text{Sodium}\\\text{hypoiodite}}}{3NaOI} \longrightarrow \underset{\substack{\text{Sodium}\\\text{benzoate}}}{C_6H_5COONa} + \underset{\substack{\text{Iodoform}\\\text{(yellow ppt)}}}{CHI_3\downarrow} + 2NaOH$$

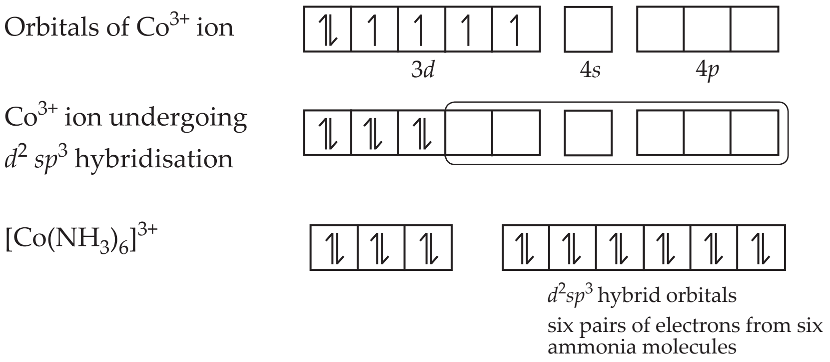
$$\underset{\text{Benzophenone}}{C_6H_5COCH_3} + NaOI \longrightarrow \text{No yellow ppt of } CHI_3$$

Section-C

Answer 11.

(i) (a) Hexaamminecobalt(III) ion

(b) In $[Co(NH_3)_6]^{3+}$ Co is in +3 state and has configuration $3d^6$. In the presence of NH_3, $3d$ electrons pair up leaving two d-orbitals empty. Hence, the hybridization is d^2sp^3 forming an inner orbital complex.



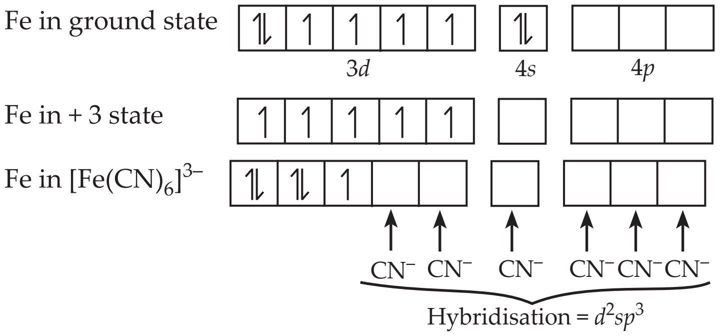
(c) Primary valency is zero because there is no ion outside coordination sphere and secondary valency is 6 because there are six monodentate ligand attached with cobalt metal ion.

OR

(ii) (a) It is an inner orbital complex because inner 3d orbitals are used by the central metal atom for the hybridisation. Also, as CN is a strong field ligand therefore will form low spin complex by using inner 3-d-orbitals. Thus, $[Fe(CN)_6]^{3-}$ is an inner orbital complex.

(b) Fe has $4s^23d^6$ configuration and therefore Fe^{3+} will be $3d^5$. Upon pairing it has one unpaired electron that makes it paramagnetic complex.

(c) In $[Fe(CN)_6]^{-3}$ complex CN is a strong field ligand therefore will form low spin complex by using inner $3d$-orbitals. Since it has octahedral geometry as there are 6 ligands, so its hybridization will be d^2sp^3.



Answer 12.

(i)
$$\begin{tikzcd}
\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \arrow[r, "NH_3\text{(excess)}", "\Delta"'] & \underset{\text{(Propionamide)}}{CH_3CH_2CONH_2} \arrow[r, "Br_2/KOH", "\text{(Hoffmann bromide (reaction)}"'] & CH_3CH_2NH_2\ \text{(Ethylamine)} \arrow[d, "NaNO_2/HCl"] \\
\underset{\text{Ethanoic acid}}{CH_3COOH} & CH_3CH_2OH \arrow[l, "KMnO_4/H^+"'] & {[CH_3CH_2\overset{+}{N_2}\overset{-}{Cl}]} \arrow[l, "H_2O"']
\end{tikzcd}$$

(ii) Formic acid (HCOOH) is not a true acid, it contains both aldehyde as well as carboxyl group (–COOH) and it behaves as a reducing agent. Therefore, formic acid reduces Tollen's reagent to metallic silver. The reaction can be represented as follows:

$$\underset{\text{Tollen's reagent}}{2AgNO_3 + 2NH_4OH} \longrightarrow Ag_2O + 2NH_4NO_3 + H_2O$$

$$\underset{\text{Formic acid}}{Ag_2O + HCOOH} \xrightarrow{\Delta} \underset{\text{Silver mirror}}{2Ag + CO_3 + H_2O}$$

Answer 13.

(i) Rate of reaction = Rate of disappearance of A $= -\frac{1}{2}\frac{\Delta[A]}{\Delta t}$

$$\text{Rate} = -\frac{1}{2}\frac{[A_2]-[A_1]}{t} = -\frac{1}{2}\frac{0.6-0.7}{10}$$

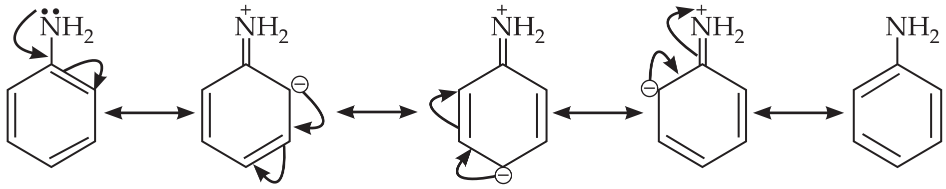
$$\therefore \qquad \text{Rate} = -\frac{1}{2}\times\frac{-(0.1)}{10} = \frac{0.1}{20} = \frac{1}{200} = 0.005 = 5 \times 10^{-3} \text{ mol lit}^{-1} \text{ m}^{-1}$$

(ii)
$$k = \frac{0.693}{t_{12}}$$
$$k = \frac{0.693}{6.93s}$$
$$k = 0.1s^{-1}$$

(iii) Since, the reaction is first order reaction and the rate of first order reaction is directly proportional to the concentration of reactants the rate of reaction will also double.

Answer 14.

(i) Due to resonance in aniline, the lone pair of electrons on nitrogen of aniline get delocalised over benzene ring and thus is less available for protonation.

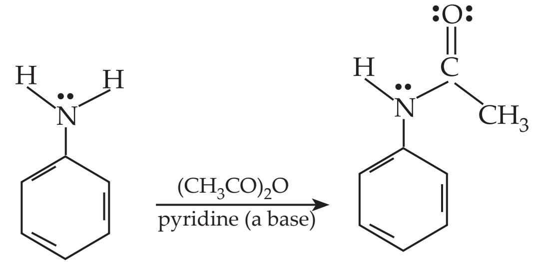


Resonance in Aniline

On the other hand, in case of methylamine, lone pair on nitrogen of amine group is readily available for protonation. Thus, methylamine is more basic than aniline or aniline is weaker base than methyl amine

$$\underset{\text{Methylamine}}{CH_3-\ddot{N}H_2}$$

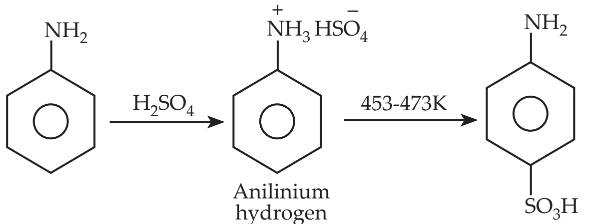
(ii) Amino group is electron releasing group and therefore, activates benzene ring as electron pair on nitrogen group gets delocalized in ring, making ortho and para position electron rich. When aniline is acetylated with acetyl chloride, acetanilide is formed which means the $-NH_2$ group gets converted to $-NHCOCH_3$, the carbonyl group being electron withdrawing, does not let nitrogen of amine to give its electron pair to benzene ring for delocalization. Thus, it leads to deactivation of benzene ring. Hence, activation of benzene by $-NH_2$ group can be reduced by treating the compound with acetyl chloride.



Aniline
Strongly Activated
Aromatic Ring

Acetanilide
Less Activated
Aromatic Ring

(iii) Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which on heating with sulphuric acid at 453 - 473 K produces sulphanilic acid



Anilinium
hydrogen
sulphate

Sulphanilic acid

❑❑