ISC SEMESTER 2 EXAMINATION
SAMPLE PAPER - 4
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 = 1·987 cal deg^{-1} mol^{-1} = 8·314 JK^{-1} mol^{-1} = 0·0821 dm^3 atm K^{-1}mol^{-1}

1 l atm = 1 dm^3 atm = 101·3 J. 1 Faraday = 96500 coulombs.

Avogadro's number = 6·023 ·10^{23}.

Section-A

Question 1.

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

(temperature, concentration, pressure, basic, propanone, acidic, Propanal)

(i) The rate constant of a reaction depends on the _____ and is independent of the _____ of the reactants.

(ii) MnO is _____ whereas Mn_2O_7 is _____.

(iii) _____ will form the silver mirror, but _____ does not react.

Question 2.

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

(i) In which of the following coordination entities the magnitude of Δ_0 (CFSE in octahedral field) will be maximum?

(a) $[Co(CN)_6]^{3-}$ (b) $[Co(C_2O_4)_3]^{3-}$ (c) $[Co(H_2O)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$

(ii) Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is:

(a) Hydrazine in presence of feebly acidic solution

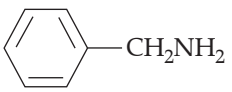
(b) Hydrocyanic acid

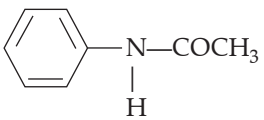
(c) Sodium hydrogen sulphite

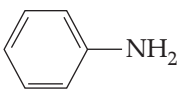
(d) A Grignard reagent

(iii) Which of the following compounds is most basic?

(a) 

(b) 

(c) 

(d) 

(iv) **Assertion:** Lyophilic sols are reversible sols.
Reason: Lyophilic sols can be reconstituted by simply remixing the dispersed phase and dispersion medium.

(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.

Describe with an example of each, the role of coordination compounds in:

(i) Biological systems (ii) Analytical chemistry

Question 4.

(i) Write chemical equations to illustrate each of the following named reactions:

(a) Clemmensen reduction (b) Hell-Volhard-Zelinsky reaction

OR

(ii) How will you bring about the following conversions:

(a) Propanone to Propene (b) Bromobenzene to 1-Phenylethanol

Question 5.

Name the products on hydrolysis of (i) sucrose and (ii) lactose.

Question 6.

State reasons for the following:

(i) Ethylamine is soluble in water whereas aniline is not soluble in water.

(ii) Primary amines have higher boiling points than tertiary amines.

Question 7.

What is essentially the difference between α-glucose and β-glucose? What is meant by pyranose structure of glucose?

Question 8.

The thermal decomposition of HCO_2H is a first order reaction with a rate constant of $2.4 \times 10^{-3}\ s^{-1}$ at a certain temperature. Calculate how long will it take for three-fourth of initial quantity of HCO_2H to decompose? (log 0.25 = – 0.6021)

Question 9.

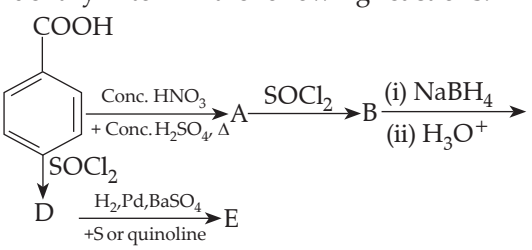
Complete and write chemical equations for the following reactions :

(i) Ethanamine to Ethanoic acid

(ii) Aniline into N-Phenylethanamide

Question 10.

Identify A to E in the following reactions:



Section-C

Question 11.

Answer the following questions:

(i) (a) A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value.

(b) Define pseudo first order reaction.

OR

Answer the following questions:

(ii) For the first order thermal decomposition reaction, the following data were obtained

$C_2H_5Cl_{(g)} \rightarrow C_2H_{4(g)} + HCl_{(g)}$

Time/sec	Total Pressure/atm
0	0.30
300	0.50

Calculate the rate constant.

(Given : log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)

Question 12.

(i) Account for the following :

(a) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.

(b) The enthalpy of atomization is lowest for Zn in 3*d* series of the transition elements.

(ii) How would you account for the following:

There is a greater range of oxidation states among the actinoids than among the lanthanides.

Question 13.

(i) What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when:

(a) $\Delta_0 > P$ (b) $\Delta_0 < P$

(ii) Draw one of the geometrical isomer of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically inactive.

Question 14.

(i) What is Gold number?

(ii) Explain what is observed when:

(a) An electric current is passed through a colloidal sol.

(b) When a beam of light is passed through a colloidal solution.

Answers

Section-A

Answer 1.

(i) temperature, concentration

Explanation :

The rate constant of a chemical reaction is defined as the rate of the reaction when concentration of all reactants are unity. Thus, it is independent of the concentration of reactants.

(ii) basic, acidic

Explanation :

MnO is basic and Mn_2O_7 is acidic because the oxide in the lower oxidation state of a metal is basic and oxide in the higher oxidation state of the metal is acidic. Thus, Mn in Mn_2O_7 is in +7 oxide state, therefore, it is acidic while Mn in MnO has +2 oxidation state, therefore, it is basic.

(iii) Propanal, propanone

Explanation :

When both propanal and propanone are treated with Tollen's reagent, only propanal gives metallic silver mirror test which can be seen as deposit on the walls of test tube while propanone does not react.

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+OH^-.$$
Propanal ↓
$$RCOO^- + 2Ag + 4NH_3 + 2H_2O$$
Silver mirror

$$CH_3COCH_3 + 2[Ag(NH_3)_2]^+ OH^-$$
Propanal ↓
No Silver mirror.

Answer 2.

(i) (a) $[CO(CN)_6]^{3-}$

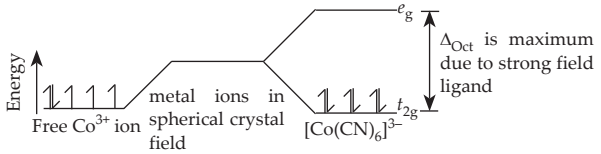
Explanation :

When the ligands are arranged in order of the magnitude of crystal field splitting, the arrangement, thus, obtained is called spectrochemical series.

Arranged in increasing field strength as

$I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NH_3 < en < NO_2^- < CN^- < CO$

From the list, it is clear that ligands after H_2O are weak field ligands while ligands after H_2O are strong field ligands.



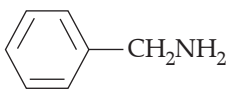
CFSE in octahedral field depends upon the nature of ligands. Stronger the ligands larger will be the value of Δ_{Oct}. Now in given complexes central metal is same and contains same number of *d*-electrons thus CFSE is decided by ligands. As among all ligands, CN^- is strongest ligand so splitting will be maximum here.

(ii) (a) Hydrazine in presence of feebly acidic medium.

Explanation :

The reaction of a carbonyl compound with hydrazine in the presence of feebly acidic medium involves nucleophilic addition and it is followed by elimination of water. The reaction can be represented as follows:

$$>C=O + H_2N-Z \longrightarrow \left[>C\begin{matrix}OH\\NHZ\end{matrix}\right] \xrightarrow[-H_2O]{H^+} >C=N-Z$$
Ammonia derivative

(iii) (b) 

Explanation :

Among the given compounds, benzyl amine is most basic due to localized lone pair of electrons on nitrogen atom while other compounds have delocalized lone pair of electron. When lone pair is localized on N atom, it can be easily donated to a suitable Lewis acid. On the other hand, if the lone pair of nitrogen is delocalized through resonance with aromatic nucleus, it cannot be easily donated to a Lewis acid. Thus, benzylamine is most basic.

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

Explanation :

Lyophilic sols are the colloidal sols which are directly formed by mixing substances like gum, gelatine, starch, rubber, etc., with a suitable dispersion medium. An important characteristic of these sols is that if the dispersion medium is separated from the dispersed phase, the sol can be reconstituted by simply remixing with the dispersion medium. This is the reason that these sols are also called as reversible sols. Hence, both assertion and reason are true and reason is the correct explanation for the assertion.

Section-B

Answer 3.

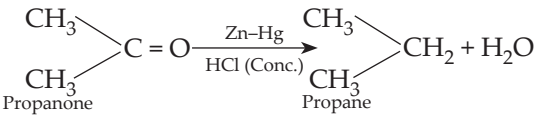
(i) **Role of coordination compounds in biological systems:** The process of photosynthesis is made possible by the presence of the chlorophyll pigment. This pigment is a coordination compound of magnesium. In the human biological system, several coordination compounds play important roles such as, the oxygen-carrier of blood, *i.e.*, haemoglobin, is a coordination compound of iron.

(ii) **Role of coordination compounds in analytical chemistry:** During salt analysis, a number of basic radicals are detected with the help of the colour changes they exhibit with different reagents. These colour changes are a result of the coordination compounds or complexes that the basic radicals form with different ligands. For example, when aqueous ammonia is added to the precipitate of AgCl, it dissolves due to the formation of soluble complex.

$$AgCl + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]Cl$$

Answer 4.

(i) (a) **Clemmensen reduction:** The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgum and concentrated hydrochloric acid.



(b) **Hell-Volhard-Zelinsky reaction:** Carboxylic acids react with chlorine or bromine in the presence of (red) phosphorus to give compounds in which α-hydrogen atom is replaced by halogen atom.

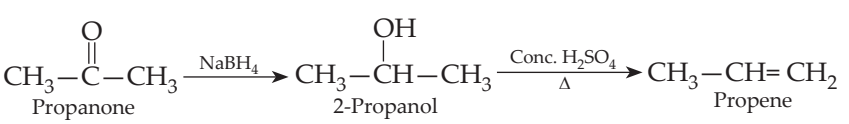
$$\underset{\text{Acetic Acid}}{CH_3COOH} + Cl_2 \xrightarrow[H_2O]{\text{Red P}} \underset{\text{Chloroacetic acid}}{ClCH_2 - COOH} + HCl$$

$$ClCH_2COOH + Cl_2 \xrightarrow[H_2O]{\text{Red P}} \underset{\text{Dichloroacetic acid}}{Cl_2CHCOOH} + HCl$$

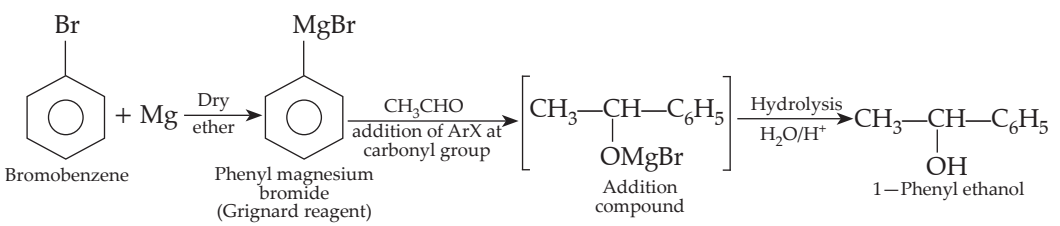
$$Cl_2CHCOOH + Cl_2 \xrightarrow[H_2O]{\text{Red P}} \underset{\text{Trichloroacetic acid}}{Cl_3CCOOH} + HCl$$

OR

(ii) (a) Propanone to Propene



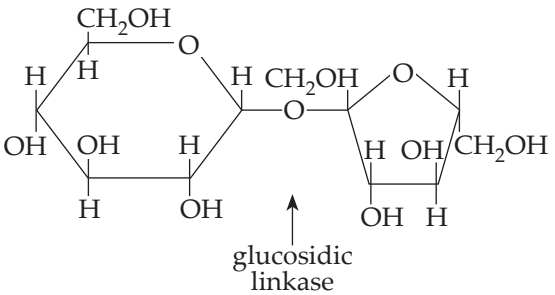
(b)



Answer 5.

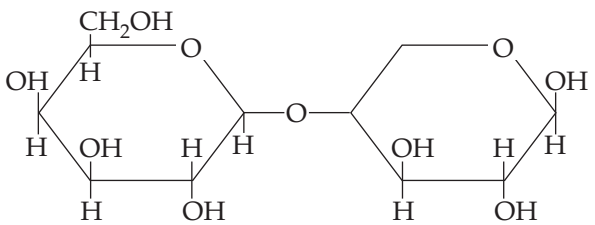
(i) Hydrolysis of Sucrose

$$\underset{}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{D(+)Glucose}}{C_6H_{12}O_6} + \underset{\text{D(–) Fructose}}{C_6H_{12}O_6}$$



(ii) Hydrolysis of Lactose

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{Galactose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$



Answer 6.

(i) Ethylamine is soluble in water due to the formation of intermolecular hydrogen bonds with water molecules. However, in aniline due to the presence of large hydrophobic aryl ($-C_6H_5$) group, the extent of hydrogen bonding decreases considerably and hence, ($-C_6H_5$) aniline is insoluble in water.

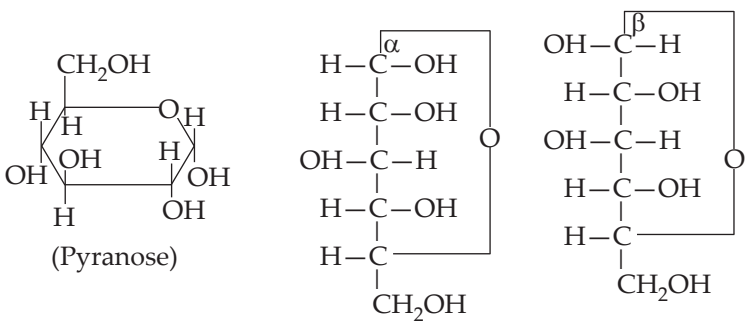
(ii) Primary amines have higher boiling points than tertiary amines. This is because H-bonding is most extensive in 1° amines in which two H-atoms are directly attached to N (R-NH_2) which take part in H-bonding. On the other hand, in 3° amine has no H-bonding is possible as no H-atom (R_3N) is directly attached to nitrogen. As we know that H-bonding leads to stronger intermolecular forces and hence higher boiling points. Thus, intermolecular hydrogen bonding is the reason behind the higher boiling point of primary amine as compared to the tertiary amine.

Answer 7.

α-glucose and β-glucose are two cyclic hemiacetal forms of glucose which differ only in the configuration of hydroxyl group (–OH) at anomeric C_1carbon. Such isomers are called anomers.

Pyranose structure of glucose: The six membered cyclic structure of glucose is called pyranose structure in which six membered ring contains oxygen atom and because of its resemblance with pyran it is called as pyranose.

α-D-glucose and β-D-glucose are stereoisomers. They differ in 3-dimensional configuration of atoms/ groups at one or more positions.



Answer 8.

Half life for a first order reaction is $\frac{0.693}{K}$.

Thus,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.4 \times 10^{-3}\ s^{-1}} = 288.75 \text{ sec.}$$

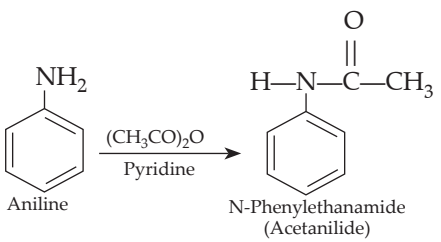
Hence, $t_{3/4} = 2 \times t_{1/2} = 577.50$ sec.

Answer 9.

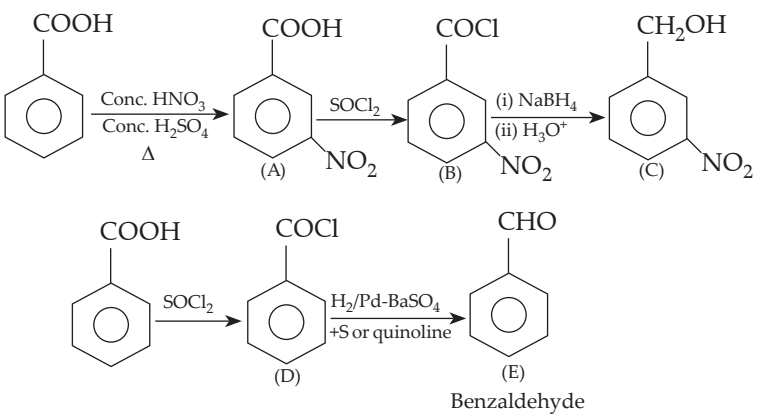
(i) $CH_3-CH_2-NH_2 \xrightarrow[HCl]{NaNO_2} [CH_3-CH_2-N_2^+Cl^-] \xrightarrow{H_2O} CH_3-CH_2-OH \xrightarrow[H^+]{KMnO_4} CH_3COOH$

Ethanamine — Ethanoic acid

(ii)



Answer 10.



Section-C

Answer 11.

(i) (a) Here $t = 40$ min, $t_{1/2} = ?$

Let $a = 100$ $\therefore$ $x = 30\%$ of $100 = 30$

Using the formula,

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$\Rightarrow \quad 40 = \frac{2.302}{k} \log \frac{100}{100-30}$$

$$40 = \frac{2.303}{k} \log \frac{100}{70}$$

$$\Rightarrow \quad 40 = \frac{2.303}{k} (\log 10 - \log 7)$$

$$40 = \frac{2.303}{k}(1-0.8451)$$

$$\Rightarrow \quad 40 = \frac{2.303}{k} \times 0.1549 \Rightarrow k = \frac{0.357}{40} = 0.0089 \text{ min}^{-1}$$

$$\therefore \quad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0089} = 77.86 \text{ min}$$

(b) **Pseudo first order reactions**—The reactions that have higher order true rate law but are found to behave as first order are called pseduo first order reactions.

$$\underset{}{eg\text{–}} \underset{(aq)}{CH_3COOCH_3} + \underset{(l)}{H_2O} \rightarrow \underset{(aq)}{CH_3COOH} + \underset{(aq)}{CH_3OH}$$

In above example of acid hydrolysis of methyl acetate, the reaction is expected to have second order kinetics (according to rate law equation). However, experimentally the reaction is found to follow first order kinetics because water as solvent is present in such a large excess that its concentration remains constant.

$$\text{rate} = k\,[CH_3COOCH_3] \times [H_2O]$$

$$\therefore \quad \text{rate} = k\,[CH_3COOCH_3] \qquad \{\because [H_2O] = \text{constant}\}$$

Thus, this bimolecular reaction which appears of second order is actually pseudo first order reaction.

OR

(ii) The given reaction is:

$$C_2H_5Cl_{(g)} \longrightarrow C_2H_{4(g)} + HCl_{(g)}$$

At time $t = 0$	0.30 atm	0	0
At time $t = 300$ sec	$0.30-x$	x	x

Total pressure $= 0.30 - x + x + x = 0.50$

or $0.30 + x = 0.50$

$\therefore\ x = 0.50 - 0.30 = 0.20$

$\therefore$ Initial pressure, $P_0 = 0.30$ atm

Pressure of C_2H_5Cl after 300 sec, $P_t = 0.30 - 0.20 = 0.10$ atm

Using formula for first order reaction,

$$k = \frac{2.303}{t}\log\frac{P_0}{P_t}$$

$$k = \frac{2.303}{300}\log\frac{0.30}{0.10}$$

$$k = \frac{2.303}{300}\log 3 = \frac{2.303 \times 0.4771}{300} = 3.66 \times 10^{-3}\ \text{sec}^{-1}$$

Answer 12.

(i) (a) It is known that half-filled and fully-filled orbitals are more stable. The electronic configuration of Mn^{2+} is $3d^5$ which is half filled and stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily. Whereas, the electronic configuration of Fe^{2+}, is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$. Thus, Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.

(b) The valence shell electronic configuration of Zn is $3d^{10}4s^2$. Due to the absence of unpaired electrons in ns and (n–1)*d* shells, the d-d interactions are negligible and therefore, the interatomic electronic bonding is the weakest in zinc. The element therefore, has lowest enthalpy of atomisation (126 kJ mol^{-1}) in the 3*d* transition series of elements.

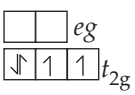
(ii) Actinides exhibit larger oxidation states than lanthanides, because of the very small energy gap between 5*f*, 6*d* and 7*s* subshells as compared to 4*f*, 5*d* and 6*s* orbitals in case of lanthanoids. Thus, the outermost electrons get easily excited to the higher energy levels, giving variable oxidation states.

Answer 13.

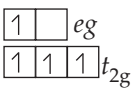
(i) The difference between the t_{2g} and eg splitted *d*-orbitals is called as the crystal field splitting energy 4*s*. It is denoted by Δ .

For octahedral Δ_0 for tetrahedral it is Δ_t and for square planar Δ_{sp} (For electric configuration of d^4).

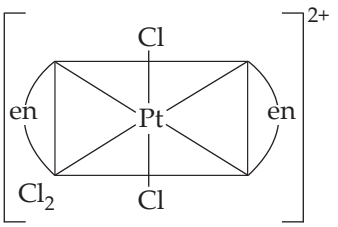
(a) When $\Delta_0 > P$, the electronic configuration is $t_{2g}^4 eg^0$



(b) When $\Delta_0 < P$, the electronic configuration is $t_{2g}^3\ eg^1$



(ii) Trans-isomer is optically inactive due to the presence of plane of symmetry.



trans–$[PtCl_2(en)_2]^{2+}$ is optically inactive

Answer 14.

(i) The number of milligrams of protective colloid which is just sufficient to prevent the coagulation of 10 ml standard gold solution when 1 ml of 10% solution of NaCl is added to it, is called as gold number. For example: gold number of gelatin = 0.005 — 0.01.

(ii) (a) On passing an electric current through a colloidal sol., colloidal particles move towards the oppositely charged electrode where they lose their charge and gets coagulated. This process is known as electrophoresis.

(b) When a beam of light is passed through a colloidal sol, colloidal particles scatter light and path of light becomes visible. This is known as Tyndall effect.

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