ISC SEMESTER 2 EXAMINATION SAMPLE PAPER - 1 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 dm³ atm K⁻¹mol⁻¹

1 l atm = 1 dm³ atm = $101 \cdot 3$ 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: (first, zero, twice, lanthanoid, iron, copper, yellow, blue, benzophenone, transition)

(i) The half life of a ______ order reaction is independent of the initial concentration of reactants. For a first order reaction, the time required for 75% completion is ______ the half life time.

(ii) Mischmetal is well known alloy which consists of a _____ metal (about 95%), _____ (about 5%) and traces of S, C, Ca, Al etc.

(iii) Acetophenone will give the _____ precipitate of iodoform, but _____ will not react.

Question 2.

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

- (i) A magnetic moment at 1.73 BM will be shown by one among of the following :
 - (a) TiCl_4 (b) $[\text{CoCl}_6]^{4-}$ (c) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (d) $[\text{Ni}(\text{CN})_4]^{2-}$
- (ii) Which of the following reactions will not result in the formation of carbon-carbon bond?
 - (a) Reimer-Tiemann reaction

(b) Acetamide

- (b) Cannizzaro reaction (d) Friedel Crafts acylation
- (iii) Which one of the following on reduction with lithium aluminium hydride yields a secondary amine ?
 - (a) Methyl isocyanide
- (c) Methyl cyanide(d) Nitroethane

(c) Wurtz reaction

(iv) Assertion: Cu cannot liberate hydrogen from acids.

Reason: This is because it has positive electrode potential.

- (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.

Draw the structures of :

(i) $Ni(CO)_4$ (ii) Fe(CO)₅

Ouestion 4.

- (i) Write chemical equations to illustrate each of the following name reactions:
 - (a) Rosenmund reduction (b) Cannizzaro reaction

OR

- (ii) How will you bring about the following conversions? (Give equation).
 - (a) Phenol to benzaldehyde (b) Ethanal to but-2-enal

Question 5.

What are essential and non-essential amino acids? Give one example of each type. **Question 6.**

Give reasons for the following :

- (i) Aniline does not undergo Friedel-Crafts reaction.
- (ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

Question 7.

Mention the type of linkage responsible for the formation of the following :

- (i) Primary structure of proteins
- (iii) α -helix formation (ii) Cross-linkage of polypeptide chains (iv) β -sheet structure

Ouestion 8.

A reaction is first order in A and second order in B.

- (i) Write differential rate equation.
- (ii) How is rate affected when concentration of B is tripled?

Question 9.

Complete and write chemical equations for the following reactions :

- (i) $C_6H_5CONH_2$ to $C_6H_5NH_2$
- (ii) $C_6H_5NH_2$ to C_6H_5OH

Question 10.

Identify, A, B and C in the following sequence of reactions :

$$\underbrace{ \begin{array}{c} \mathsf{COOH} \\ + \mathrm{NH}_3 & \stackrel{\Delta}{\longrightarrow} \mathrm{A} \xrightarrow{\mathrm{Weakly}} \mathrm{B} \xrightarrow{\mathrm{Strong}} \mathrm{heating} \\ \mathsf{COOH} \end{array} } \mathsf{COOH}$$

Section-C

Question 11.

- (i) Answer the following :
 - (a) Rate constant 'k' of a reaction varies with temperature 'T' according to the equation :

$$\log k = \log A - \frac{E_a}{2.303R} \left(\frac{1}{T}\right)$$

where E_a is the activation energy. When a graph is plotted for log k vs $\frac{1}{T}$, a straight line with a

slope of – 4250 K is obtained. Calculate ' E_a ' for the reaction. $(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}).$

(b) In some cases it is found that a large number of colliding molecules have energy more than threshold energy, yet the reaction is slow, Why?

OR

(ii) Answer the following:

The decomposition of phosphine,

$$4PH_{3(g)} \rightarrow P_{4(g)} + 6H_{2(g)}$$

has the rate law, Rate = $k[PH_3]$.

The rate constant is $6.0 \times 10^{-4} s^{-1}$ at 300 K and activation energy is 3.05×10^5 J mol⁻¹. Calculate the value of rate constant at 310 K.

$$[Given : R = 8.314 JK^{-1} mol^{-1}]$$

Question 12.

How would you account for the following :

- Metal-metal bonding is more extensive in the 4d and 5d series of transition elements than the 3d (i) series.
- (ii) Mn (III) undergoes disproportionation reaction easily.
- (iii) Co (II) is easily oxidised in the presence of strong ligands.

Question 13.

Explain the following :

- (i) Low spin octahedral complexes of nickel are not known.
- (ii) The π -complexes are known for transition elements only.
- (iii) CO is a stronger ligand than NH_3 for many metals.

Question 14.

Give reasons for the following observations :

- (i) NH_3 gas absorbs more readily than N_2 gas on the surface of charcoal.
- (ii) Powdered substances are more effective adsorbents.
- (iii) Leather gets hardened after tanning.



Section-A

Answer 1.

(i) first, twice

Explanation :

Half-life of a reaction is defined as time required to reduce the concentration of a reactant to one half of it's initial value.

$$k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$$

If amount reacted X = $\frac{a}{2}$ then $t = t_{\frac{1}{2}}$ Thus,

$$t_{\frac{1}{2}} = \frac{2.303}{t} \log\left(\frac{a}{a - a/2}\right)$$
$$= \frac{2.303}{k} \log 2$$
$$t_{\frac{1}{2}} = \frac{0.693}{k} \operatorname{sec.}$$

Thus, half-life period of a first order reaction is independent of the initial concentration of the reactant. \Rightarrow we know that (according to statement):

at
$$t(50\%) \Rightarrow t_{\frac{1}{2}} = \frac{2.303}{k} \log \frac{a_0}{a_0 - \frac{a_0}{2}} = \frac{2.303}{k} \log 2 ...(i)$$

$$t_{75\%} = \frac{2.303}{k} \log \frac{a_0}{a_0 - \frac{3}{4}a_0} = \frac{2.303}{k} \times \log 4$$
$$t_{75\%} = \frac{2.303}{k} 2\log 2 \qquad \dots (ii)$$

and

...

Now from equation (i) and (ii), we get,

$$t_{75\%} = 2 \times t_{1/2}$$

 \Rightarrow Hence, for a first order reaction, time required for 75% completion of a reaction is twice the half-life time.

(ii) lanthanoid, iron

Explanation:

Mischmetal consists of lanthanoid metal (about 95%) and iron (about 5%) and traces of S, C, Ca and Al. Mischmetal is used in Mg based alloy to produce bullets, shell etc.

(iii) Yellow precipitate, benzophenone

Explanation:

$$\begin{array}{c} C_{6}H_{5}COCH_{3} + 3NaOI \rightarrow C_{6}H_{5}COONa + CHI_{3} + 2NaOH \\ \text{(Acetophenone) (sod. hypoiodite)} & \text{Iodoform} \\ \text{(yellow ppt.)} \end{array}$$

 $C_6H_5COC_6H_5 + NaOI \rightarrow No \text{ yellow ppt.}$

(Benzophenone)

Answer 2.

(i) (c) $[Cu(NH_3)_4]^{2+}$

Explanation :

Oxidation state of Cu in $[Cu(NH_3)_4]^{2+}$ is + 2

 $Cu^{2+} = 3d^9$ 1 1 1 1 1

It has one unpaired electron (n = 1).

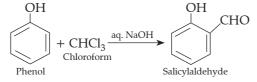
 $\mu = \sqrt{n(n+2)}$ BM

$$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$

(ii) (b) Cannizzaro reaction

Explanation:

Reimer-Tiemann reaction :



Cannizzaro reaction :

HCHO $\xrightarrow{50\% \text{ NaOH}}$ HCOO $^{\Theta}$ Na $^{\oplus}$ + CH₃OH Formaldehyde Sodium formate Methanol

Wurtz reaction :

 $\begin{array}{l} H_{3}C-I+2Na+I-CH_{3}\rightarrow CH_{3}-CH_{3}+2NaI\\ & \\ \text{Methyl iodide} \\ & \\ \end{array}$

Friedel-Crafts acylation :

$$\bigcirc + \operatorname{RCOCl} \xrightarrow{\operatorname{AlCl}_3} \bigcirc + \operatorname{HCl}$$

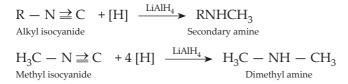
From the above examples, it is evident that C-C bond formation does not takes place in Cannizzaro reaction.

COD

(iii) (a) Methyl isocyanide

Explanation:

Alkyl isocyanides on reduction with lithium aluminium hydride forms secondary amines containing methyl as one of the alkyl groups. For example, methyl isocyanide undergoes reduction with LiAlH₄ to form a secondary amine, *i.e.*, dimethyl amine.



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

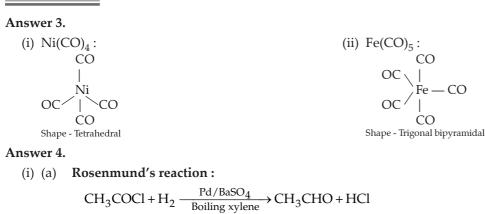
Explanation :

Ethanoyl chloride

(Acetyl chloride)

Copper cannot liberate hydrogen from acid's because it has positive electrode potential. Only metals having negative electrode potential can liberate hydrogen gas. Hence, both assertion and reason are correct and reason is the correct explanation of the assertion.

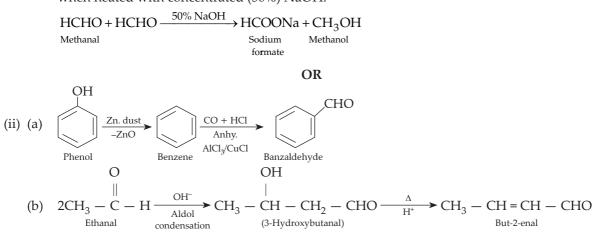
Section-B



(b) **Cannizzaro's reaction :** Aldehydes which do not contain α-H atom undergo disproportionation when heated with concentrated (50%) NaOH.

Ethanal

(Acetaldehyde)

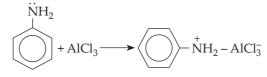


Answer 5.

Amino acids which cannot be synthesised in the body and must be obtained through diet are known as essential amino acids, *e.g.*, valine and leucine. There are ten essential amino acids. Amino acids which can be synthesised in the body are known as non-essential amino acids, *e.g.*, alanine and glutamic acids.

Answer 6.

(i) In Friedel - Crafts reaction, AlCl₃ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence, aniline does not undergo Friedel - Crafts reaction.



(ii) (CH₃)₂NH is more basic than (CH₃)₃N in an aqueous solution. This is because (CH₃)₂NH₂⁺ is hydrated to a greater extent than (CH₃)₃NH⁺. As the number of methyl groups increases, the extent of hydration decreases due to steric hindrance. Greater is the extent of hydration, greater is the stability of ion and greater is the basic strength of amine.

Answer 7.

- (i) Primary structure of protein Peptide bond (or linkage)
- (ii) Cross linkage of polypeptide chain Polypeptide linkage
- (iii) α-helix formation Hydrogen bond
- (iv) β -sheet structure Intermolecular hydrogen bonds

Answer 8.

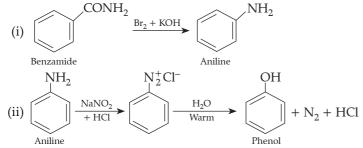
(i) Differential rate equation of reaction is $\frac{dx}{dt} = k[A]^{1}[B]^{2} = k[A][B]^{2}$

- (ii) When concentration of B is tripled, it means concentration of B becomes [3 × B]
 - $\therefore \quad \text{New rate of reaction, } \frac{dx'}{dt} = k[A][3B]^2$

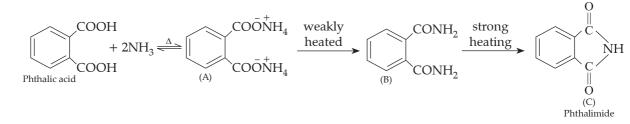
$$= 9k[A][B]^2 = 9\left(\frac{dx}{dt}\right)$$

i.e., the rate of reaction will become 9 times.

Answer 9.



Answer 10.



Section-C

Answer 11.

(i) (a) Given : Slope, m = -4250 K,

Using formula,

$$\log k = \log A - \frac{E_a}{2.303 R} \left(\frac{1}{T}\right)$$

[straight line equation]

Comparing with
$$y = mx + a$$

$$\frac{E_a}{303 \text{ R}} = \frac{-4250}{1}$$

$$E_a = 2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 4250 \text{ K}$$

$$= 81,375.35 \text{ J mol}^{-1} = 81.37 \text{ kJ mol}^{-1}$$

(b) The main reason behind the reaction to be slow even after a large number of colliding molecules have energy more than threshold energy for a reaction, is because of the improper alignment of the molecules which are colliding.

(ii)
$$k_1 = 6.0 \times 10^{-4} \, s^{-1}, \, T_1 = 300 \, \text{K}, \, \text{E}_a = 3.05 \times 10^5 \, \text{J mol}^{-1}$$

 $k_2 = ?, \, \text{T}_2 = 310 \, \text{K}$

OR

2.

Using Arrhenius equation,

or

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \text{ R}} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{k_2}{k_1} = \frac{3.05 \times 10^5 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \times \left[\frac{310 - 300}{300 \times 310} \right]$$

$$\log \frac{k_2}{k_1} = \frac{3.05 \times 10^5 \text{ J mol}^{-1} \times 10 \text{ K}}{1780684.2 \text{ JK}^{-1} \text{ mol}^{-1}}$$

$$\log \frac{k_2}{k_1} = 1.71$$

$$\log \frac{k_2}{k_1} = 1.71$$

$$\log \frac{k_2}{k_1} = 3.01 \times 10^2 \text{ s}^{-1}$$

Answer 12.

- (i) The 4*d* and 5*d* series of the transition metals have more frequent metal-metal bonding in their compounds than do the 3*d* metals because of higher enthalpies of atomisation of 4*d* and 5*d* as compared to 3*d*.
- (ii) Disproportionation reaction are those in which the same substance undergoes oxidation as well as reduction. Since, Mn in its +2 oxidation state is more stable as compared to +3 oxidation state due to half-filled *d*-orbital, Mn(III) disproportionate easily to Mn(II).
- (iii) Co^{2+} ions are easily oxidised to Co^{3+} ions in the presence of strong field ligand because the crystal field stabilisation energy of Co^{3+} ions with a d^6 configuration is higher than d^7 configuration. In presence of strong ligand the d^- orbitals of metal gets splits up into two set of orbitals that is t_{2g} and e_g . The half-filled or fully filled t_{2g} is more stable than other configuration. This is because it gives maximum amount of low energy of t_{2g} orbital. Lower the energy more is the stabilisation. This is the reason that Co^{2+} ions are easily oxidised in the presence of strong ligand.

Answer 13.

- (i) Nickel does not form low spin octahedral complexes because 'Ni' has electronic configuration 3d⁸ 4s², in which two inner *d*-orbitals are not available which are required to form d²sp³ hybridization. Hence, Ni does not form low spin complexes.
- (ii) Transition metal form complexes with ligands due to availability of vacant *d*-orbitals. These ligands have vacant π orbitals. The transition metals form π complexes because they have t_{2g} of correct symmetry which allows them to overlap with the vacant π orbitals of these ligands, forming π bonds. This bonding is known as back bonding. Hence, the presence of *d*-orbitals of proper symmetry in transition metals allows the formation of pi complexes.
- (iii) CO is a stronger ligand than NH_3 for many metals because in case of CO back bonding takes place in which the central metal uses its filled *d* orbital with empty anti bonding π^* molecular orbital of CO.

Answer 14.

(i) Higher the critical temperature of gas, more readily it can get adsorbed on the surface of an adsorbent due to stronger Van der Waals' forces.

 NH_3 (132° C) has a higher critical temperature than dinitrogen (– 147° C). Thus, NH_3 gas adsorbs more readily than N_2 gas on the surface of charcoal.

- (ii) A finely divided substance or powdered substances are more effective as adsorbent because
 - (a) It has more surface area so more adsorption occurs.
 - (b) The number of active sites (active centres) becomes more and the extent of adsorption increases.
- (iii) Animal skin leather is colloidal in nature and has positively charged particles whereas tanning consists of negatively charged colloidal particles. When leather is soaked in tanning mutual coagulation takes place and as a result, leather gets hardened.