Sample Question Paper - 21 Chemistry (043) Class- XII, Session: 2021-22 TERM II

Time allowed : 2 hours

General Instructions :

Read the following instructions carefully.

- 1. There are 12 questions in this question paper with internal choice.
- 2. SECTION A Q. No. 1 to 3 are very short answer questions carrying 2 marks each.
- 3. SECTION B Q. No. 4 to 11 are short answer questions carrying 3 marks each.
- 4. SECTION C Q. No. 12 is case based question carrying 5 marks.
- 5. All questions are compulsory.
- 6. Use of log tables and calculators is not allowed.

SECTION - A

- 1. Given reactions for the following (any two)
 - (a) Aniline with bromine water
 - (b) Controlled nitration of aniline
 - (c) Ethanamine with Hinsberg's reagent
- **2.** (a) Express the rate of the following reaction in terms of the formation of ammonia.
 - $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$
 - (b) For a reaction : $2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$; Rate = k Write the order and molecularity of this reaction.
- 3. Arrange the following
 - (a) In increasing order of boiling point : C_2H_5OH , $(CH_3)_2NH$, $C_2H_5NH_2$
 - (b) In increasing order of solubility in water : $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

SECTION - B

- 4. (a) Give reason :
 - (i) Sc (21) is a transition element but Ca (20) is not.
 - (ii) Fe^{2+} is much more easily oxidised to Fe^{3+} than Mn^{2+} to Mn^{3+} .
 - (b) Manganese exhibits the highest oxidation state of +7 among the 3*d* series of transition elements.
- 5. (a) For the reaction, $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$, the rate of formation of $NO_{2(g)}$ is 2.8×10^{-3} M s⁻¹. Calculate the rate of disappearance of $N_2O_{5(g)}$.
 - (b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction. (log 2 = 0.3010)

OR

The first order reaction take 100 minutes for completion of 60% of the reaction. Find the time when 90% of the reaction will be completed.

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Maximum marks : 35

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- 6. (a) Draw the structure of the compound named 4-methylpent-3-en-2-one.
 - (b) Complete the following reaction.

$$\operatorname{CH}_{3}\operatorname{CHO} \xrightarrow{\text{(i) } \operatorname{CH}_{3}\operatorname{MgBr}}_{\text{(ii) } \operatorname{H}_{3}\operatorname{O}^{+}} A \xrightarrow{\operatorname{Cu}/\Delta} B \xrightarrow{\operatorname{NH}_{2}\operatorname{NH}_{2}} C \xrightarrow{\operatorname{KOH/Glycol}}{\Delta} D$$

- (a) Write the reactions involved in the following:
 - (i) Hell-Volhard-Zelinsky reaction
 - (ii) Decarboxylation reaction
- (b) Describe the aldol condensation reaction.
- 7. (a) When a coordination compound $CrCl_3 \cdot 6H_2O$ is mixed with AgNO₃, 2 moles of AgCl are precipitated per mole of the compound. Write structural formula of the complex.
 - (b) Draw the crystal field spliting diagram for the complex $[Mn(CN)_6]^{4-}$.
- **8.** Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?
- 9. Assign a reason for each of the following observations :
 - (i) The transition metals (with the exception of Zn, Cd and Hg) are hard and have high melting and boiling points.
 - (ii) The ionisation enthalpies (first and second) in the first series of the transition elements are found to vary irregularly.
- 10. An organic compound (*A*) with molecular formula C_8H_8O forms an orange red precipitate with 2, 4-DNP reagent and gives yellow precipitate on heating with I_2 and NaOH. It neither reduces Tollens' reagent nor Fehling's reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (*B*) having molecular formula $C_7H_6O_2$. Identify the compounds (*A*) and (*B*) and explain the reactions involved.

OR

Give simple chemical tests to distinguish between the following pairs of compounds :

- (i) Benzaldehyde and benzoic acid
- (ii) Propanal and propanone.
- (iii)Ethanal and propanal
- 11. Calculate the emf of the following cell at 298 K : $Fe_{(s)}|Fe^{2+}(0.001 \text{ M})||H^{+}(1 \text{ M})|H_{2(g)}(1 \text{ bar}), Pt_{(s)}(Given E^{\circ}_{cell} = + 0.44 \text{ V})$

OR

In the plot of molar conductivity (Λ_m) *vs* square root of concentration $(c^{1/2})$, following curves are obtained for two electrolytes *A* and *B*.



Answer the following :

- (a) Predict the nature of electrolytes *A* and *B*.
- (b) What happens on extrapolation of Λ_m to concentration approaching zero for electrolytes A and B?

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SECTION - C

12. Read the passage given below and answer the following questions.

Hardy Schulze rule states that the precipitating effect of an ion on dispersed phase of opposite charge increases with the valency of the ion. The higher the valency of the flocculating ion, the greater is its precipitating power. Thus, for the precipitation of As_2S_3 sol (-ve sol) the precipitating power of Al^{3+} , Ba^{2+} and Na^+ ions is of the order, $Al^{3+} > Ba^{2+} > Na^+$. Similarly, for precipitating Fe(OH)₃ sol (+ve sol) the precipitating power of $[Fe(CN)_6]^{3-}$, SO_4^{2-} and Cl^- is of the order, $[Fe(CN)_6]^{3-} > SO_4^{2-} > Cl^-$. The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in 2 hours is called flocculation value. The smaller the flocculation value, the higher will be the coagulating power of the ion. The minimum mass of the protective colloid (lyophilic colloid) in milligrams that must be added to 10 mL of a standard red gold sol so that no coagulation occurs when 1 mL of 10% NaCl solution is rapidly added to it is called the gold number of the protective colloid.

- (a) The gold number of four protective colloids *A*, *B*, *C* and *D* are 0.03, 0.003, 10 and 30 respectively. What will be the order of protective power of these colloids?
- (b) Which of the following ions has least flocculating value for positive sol? Cl⁻, SO₄²⁻, [Fe(CN)₆]⁴⁻
- (c) Which of the following colloidal solutions is positively charged? TiO₂, As₂S₃, Starch sol
- (d) The coagulation value in millimoles per litre of electrolytes used for the coagulation of As_2S_3 are as below : I. NaCl = 52 II. KCl = 50 III. $BaCl_2 = 0.69$ IV. $MgSO_4 = 0.72$ Give the correct order of their flocculating power.

OR

Why Fe(OH)₃ sol is more easily coagulated by Na₃PO₄ in comparison to KCl?

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(b) Since Rate = $k[NH_3]^0$

The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.

In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration.

However, two molecules of ammonia react to give products thus, the molecularity is two.

(a) (CH₃)₂NH < C₂H₅NH₂ < C₂H₅OH
(b) C₆H₅NH₂ < (C₂H₅)₂NH < C₂H₅NH₂

Amines can form hydrogen bonds with water and are therefore soluble in it. However, the solubility decreases if the mass of the hydrocarbon part increases. 4. (a) (i) Sc(21) is a transition element but Ca(20) is not because Sc has incompletely filled 3*d* orbitals. (ii) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3^{rd} electron cannot be lost easily. In case of Fe²⁺, electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.

(b) As manganese has maximum number of unpaired electrons (5) in 3*d* subshell in addition to 2 electrons in the 4*s* subshell, it can use the 7 electrons for bonding purpose. Thus, it exhibits +7 oxidation state.

5. (a) Given,
$$\frac{d[NO_2]}{dt} = 2.8 \times 10^{-3} \text{ M s}^{-1}$$

According to rate law expression,

$$-\frac{1}{2} \frac{d[N_2O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\therefore -\frac{d[N_2O_5]}{dt} = \frac{2}{4} \times 2.8 \times 10^{-3}$$

$$\frac{-d[N_2O_5]}{dt} = \frac{1}{2} \times 2.8 \times 10^{-3} = 1.4 \times 10^{-3} \text{ M s}^{-1}$$

(b) $t_{50\%}$ or $t_{1/2} = 30$ minutes

$$\Rightarrow k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

$$t_{90\%} = \frac{2.303}{k} \log \frac{100}{100 - 90} = \frac{2.303}{0.0231} \log 10$$

$$= 99.69 \text{ minutes}$$

OR

For the first order reaction,
Rate constant,
$$k = \frac{2.303}{100} \log \frac{a}{a-x}$$

For 60% completion of the reaction, if a = 100%

$$a - x = 100 - 60 = 40\%$$

Then, $k = \frac{2.303}{100} \log \frac{100}{40}$...(i)

For 90% completion of the reaction,

$$a = 100\%$$

and $a - x = 100 - 90 = 10\%$
Then, $k = \frac{2.303}{t} \log \frac{100}{10}$...(ii)
Substituting the value of k in eq. (ii),

we have,
$$\frac{2.303}{100} \log \frac{100}{40} = \frac{2.303}{t}$$
 [:: log10=1]
or $\frac{1}{t} = \frac{1}{100} \log \frac{100}{40}$

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

$$CH_{3}COOH + Cl_{2} \xrightarrow{\text{Red P}} ClCH_{2} \xrightarrow{} COOH + HCl$$
Acetic acid
Chloroacetic acid

(ii) Decarboxylation : Sodium or potassium salt of carboxylic acids on heating with soda lime (NaOH and CaO), loses a molecule of carbon dioxide and alkanes are obtained as products.

$$R - C - O^{-}Na^{+} + NaOH \xrightarrow{CaO} R - H + Na_{2}CO_{3}$$

(b) Aldol condensation : Two molecules of an aldehyde or ketones having at least one α -hydrogen atom condense in the presence of a dilute alkali to give β -hydroxyaldehyde or β -hydroxyketone which upon heating give α , β -unsaturated aldehyde or ketone.

7. (a) For one mole of the compound, two moles of AgCl are precipitated which indicates two ionisable chloride ions in the complex. Hence, its structural formula is $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$

(b) $[Mn(CN)_6]^{4-}$ contains Mn^{2+} ion with $3d^5$ configuration, C.N. = 6, octahedral geometry, CN^- (strong field ligand) hence, $\Delta_a > P$.

$$\underbrace{1 + 1 + 1}_{t + 1} \underbrace{-e_g}_{t_2} \Delta_o > P$$

Hence, pairing of electrons in t_{2g} orbitals takes place. It has only one unpaired electron.

8. Phenoxide ion has the following resonating structures :



Carboxylate ion has the following resonating structures.

$$R - C \underbrace{\bigcirc}^{O} \longleftrightarrow R - C \underbrace{\bigcirc}^{O} \equiv \begin{bmatrix} R - C \underbrace{\bigcirc}^{O} \end{bmatrix}$$

(i) Phenoxide ion is a resonance hybrid of structures I to V, which are non equivalent resonance structures. On the other hand, the conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures. Therefore, the carboxylate ion tends to be more stable than the phenoxide ion and hence has higher acidity.

(ii) The negative charge rests on the electronegative O atom in carboxylate ion. The presence of negative charge on an electronegative atom makes the ion more stable. For the same reason $RCOO^-$ is more stable than the phenoxide ion where the carbon has negative charge on it. For the above two reasons carboxylate ion is more stable and hence carboxylic acid has higher acidity than phenol.

9. (i) As we move along transition metal series from left to right (*i.e.*, Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Hence, the atomic volume decreases. At the same time, atomic mass increases. Hence, the density from titanium (Ti) to copper (Cu) increases. The atoms of transition metals have strong metallic bonds between them, thus these have high melting and boiling points.

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(ii) Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3*d*-configurations (e.g., d^0 , d^5 , d^{10} are exceptionally stable).

10. (*A*) forms, 2, 4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' or Fehling reagent, (*A*) must be a ketone. (*A*) responds to iodoform test.

Compound (*B*), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (*B*) indicates that it should be benzoic acid and compound (*A*) should, therefore, be a monosubstituted aromatic methyl ketone.





(i) Benzaldehyde and benzoic acid can be distinguished by sodium bicarbonate test.

Benzoic acid will give efferve scence with NaHCO₃ but benzaldehyde will not react.

(ii) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

Propanal will form the silver mirror, but propanone does not react.

(iii)

NaOI	CH ₃ CHO	$CH_3CH_2CHO \longrightarrow$
	Ethanal	Propanal
	gives iodoform test.	No reaction

11. $\operatorname{Fe}_{(s)} |\operatorname{Fe}^{2+}(0.001 \text{ M})|| \operatorname{H}^{+}(1 \text{ M}) |\operatorname{H}_{2(g)}(1 \text{ bar})| \operatorname{Pt}_{(s)}$ Reactions :

Anode :
$$\operatorname{Fe}_{(s)} \longrightarrow \operatorname{Fe}_{(aq)}^{+} + 2e$$

Cathode : $2\operatorname{H}_{(aq)}^{+} + 2e^{-} \longrightarrow \operatorname{H}_{2(g)}$

Cell reaction : $Fe_{(s)} + 2H^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + H_{2(g)}$ n = 2.

Using Nernst equation at 298 K

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}] \times p_{\text{H}_2}}{[\text{H}^+]^2}$$

For the given cell,

$$\begin{split} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = E^{\circ}_{\text{H}^{+}/\text{H}_{2}} - E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} \\ &= 0 - (-0.44) = + 0.44 \text{ V} \\ \text{Given} : [\text{Fe}^{2+}] &= 0.001 \text{ M}; [\text{H}^{+}] = 1 \text{ M}; p_{\text{H}_{2}} = 1 \text{ bar} \\ \text{Putting in Nernst equation} \end{split}$$

$$E_{\text{cell}} = 0.44 - 0.0295 \log \frac{0.001 \times 1}{1^2}$$

= 0.44 - 0.0295 log 10⁻³
= 0.44 - [(0.0295) × (-3)]
= 0.44 + 0.0885 = 0.53 V
OR

(a) Electrolyte *A* is a strong electrolyte while electrolyte *B* is a weak electrolyte.

(b) For electrolyte *A*, the plot becomes linear near high dilution and thus can be extrapolated to zero concentration to get the molar conductivity at infinite dilution.

For weak electrolyte *B*, Λ_m increases steeply on dilution and extrapolation to zero concentration is not possible. Hence, molar conductivity at infinite dilution cannot be determined.

12. (a) Lesser is the gold number, greater is the protective power.

(b) Charge of $[Fe(CN)_6]^{4-}$ is highest, hence, it will be most effective for the coagulation of positive colloids. More is the coagulating power lesser will be the flocculating value.

(c) TiO_2

(d) Coagulation value is inversely proportional to their flocculating power. Correct order is I < II < IV < III

OR

Ferric hydroxide is a positively charged sol hence ions carrying negative charge can coagulate it. Since PO_4^{3-} has higher negative charge than Cl⁻ hence it is more effective for coagulation.

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