3 (Sem–4/CBCS) CHE HC 1

2022

CHEMISTRY

(Honours)
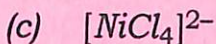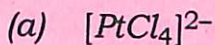
Paper : CHE–HC–4016

(Inorganic Chemistry–III)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Answer **any seven** questions from the following as directed : 1×7=7

(i) Which one of the following complex ions is tetrahedral ?

(a) $[PtCl_4]^{2-}$

(b) $[PdCl_4]^{2-}$

(c) $[NiCl_4]^{2-}$

(d) $[AuCl_4]^{2-}$

(Choose the correct option)

(ii) $[Cr(CN)_6]^{3-}$ is expected to be _____.

(diamagnetic/paramagnetic)

(Fill in the blank)

(iii) What happens when ammonium metavanadate is heated?

(iv) What is the oxidation number of Fe in $[Fe(H_2O)_5(NO)]^{2+}$?

(v) Which one of the following solutions will undergo higher depression of freezing point?

(a) $1M$ aqueous solution of $[Co(NH_3)_5Cl]Cl_2$

(b) $1M$ aqueous solution of $[Co(NH_3)_5Cl_2]Cl$

(vi) Number of possible isomers for the octahedral complex $[Co(en)Cl_2Br_2]^-$ is

(a) 2

(b) 4

(c) 6

(d) 8

(Choose the correct option)

(vii) Among the lanthanide hydroxides, $La(OH)_3$ is _____ basic and $Lu(OH)_3$ is _____ basic.   *(Fill in the blanks)*

(viii) Which metal play important role in glucose metabolism?

(ix) Name the metal that is present in cytochrome.

(x) Which one of the following oxides does not give rise to polyacids and polyanions?

(a) $V(V)$oxide

(b) $Cr(VI)$oxide

(c) $W(VI)$oxide

(d) $Mo(VI)$oxide

(Choose the correct option)

2. Answer *any four* questions from the following :   2×4=8

(i) Explain why actinides form oxocation while lanthanides don't.

(ii) Why is ORS given to patients suffering from diarrhoea?

(iii) Transition elements and their compounds are good catalysts. Explain.

(iv) Write the IUPAC name of $[(NH_3)_5Co-O_2-Co(NH_3)_5](NO_3)_4$ and the formula of diamminediaquadicyanidocobalt(III) chloride.

(v) Tetrahedral complexes are high spin. Explain.

(vi) Weak field ligands form high spin complexes and strong field ligands form low spin complexes. Why?

(vii) For a metal ion having d^6 configuration in an octahedral complex, the magnitude of crystal field splitting is $32,200 \ cm^{-1}$ and the electron pairing energy is $17,600 \ cm^{-1}$. Predict whether the complex will be high spin or low spin. Calculate the crystal field stabilization energy for the predictable spin state.

(viii) Why do transition elements show variable oxidation state?

3. Answer **any three** questions from the following: 5×3=15

(i) The magnetic moment of $[Fe(CN)_6]^{3-}$ was found to be 1.9 BM and of $[Fe(H_2O)^{3+}$ is 5.9 BM. Account for this observation with the help of valence bond theory.

(ii) Draw and justify the crystal field splitting diagram for $[CoCl_4]^{2-}$ and calculate CFSE.

(iii) Discuss about the stability of +2 oxidation state of the elements of the first transition series.

(iv) Most spinels involving Fe^{3+} have the inverse structure, whereas those of Mn^{2+} have normal arrangements. Why?

(v) In what ways magnetic properties of lanthanides are different than transition elements?

(vi) Write the structure and function of ferritin.

(vii) Name *two* chelating ligands used in chelate therapy and sketch their ligating sites and uses.

(viii) Write the chemistry of the well-known 'volcano' experiment. Explain the following observation:

CrO is basic, Cr_2O_3 is amphoteric while CrO_3 is fully acidic.

4. Answer *any three* questions from the following : 10×3=30

(i) What is the effect of π-donor and π-acceptor ligands on Δ_0? Explain on the basis of ligand field theory. 5+5=10

(ii) State Jahn-Teller theorem. Which d^n configuration leads to (i) weak, and (ii) strong Jahn-Teller distortion in octahedral complexes ? Explain why all six $Cu-OH_2$ distances in $[Cu(H_2O)_6]^{2+}$ are not equal. 2+2+6=10

(iii) Octahedral complexes are generally more stable and more common than tetrahedral complexes. Despite this, some tetrahedral complexes are formed and are stable. What are the reasons behind this ?

(iv) Discuss the +IV oxidation state of cerium. Explain, why Ce(III) can be easily oxidized to Ce (IV) ? 8+2=10

(v) Write the structure and function of haemoglobin. What change occurs in the heme group of haemoglobin in going from deoxy to oxy form ? 5+5=10

(vi) Write the structure, function and mechanism of carbonic anhydrase. 3+3+4=10

(vii) Compare the chemistry of the transition elements of the second and third series with that of the first series considering the following features : 2+2+2+2+2=10
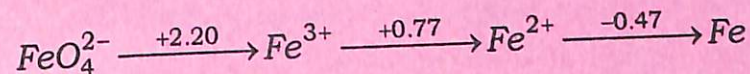
(a) Atomic and ionic radii

(b) Oxidation state

(c) Aqueous chemistry

(d) Metal-metal bonding

(e) Magnetic property

(viii) Given below is the Latimer diagram of Fe in acidic medium :

$$FeO_4^{2-} \xrightarrow{+2.20} Fe^{3+} \xrightarrow{+0.77} Fe^{2+} \xrightarrow{-0.47} Fe$$

On the basis of this diagram answer the following questions : 2+2+1+2+3=10

(a) Predict the strongest oxidising agent and the strongest reducing agent.

(b) Is there *any* thermodynamic tendency of Fe^{2+} to reduce to Fe ? Give reason.

(c) Write the half reaction for the conversion of FeO_4^{2-} to Fe^{3+}.

(d) What is a disproportionation reaction ? Is there *any* oxidation state of iron which undergoes disproportionation ? Explain.

(e) Calculate the skip-step *emf* for $Fe^{3+} \rightarrow Fe$.

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3 (Sem–4/CBCS) CHE HC2

2022

CHEMISTRY

(Honours)

Paper : CHE–HC–4026

(Organic Chemistry –III)

Full Marks : 60

Time : Three hours
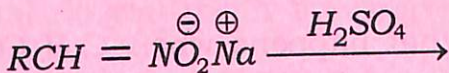
The figures in the margin indicate full marks for the questions.

1. Answer *any seven* from the following :

    $1 \times 7 = 7$

    (i) Write the IUPAC nomenclature of pyrrole.

    (ii) What product can you expect if furfural is heated at 200 °C in presence of Pd-C ?
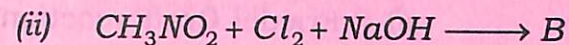
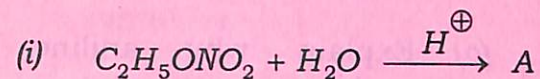   *(ii)* Write the products of the following :

    $$RCH = \overset{\ominus}{N}\overset{\oplus}{O_2}Na \xrightarrow{H_2SO_4}$$

(iv) Name the intermediate compound formed in Hofmann's degradation of amide to amine.

(v) The rate of electrophilic substitution reactions of heterocyclic compounds is slower than benzene. Why ?

(vi) Why are alkyl isocyanides insoluble in water ?

(vii) Why is naphthalene less aromatic than benzene ?

(viii) How many number of isoprene units are present in citral ?

(ix) Which position of indole is more susceptible to electrophilic substitution ?

(x) Which bond of phenanthrene is readily attacked by reagents ?

2. Answer *any four* questions from the following : $2 \times 4 = 8$

(a) How can 'yellow oil' be prepared from a secondary amine ? Give reaction.

(b) What happens when $C_6H_5CON_3$ is heated ? Write the mechanism of the reaction.

(c) Identify A and B in the following reactions, also write their names :

(i) $C_2H_5ONO_2 + H_2O \xrightarrow{H^{\oplus}} A$
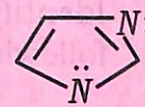
(ii) $CH_3NO_2 + Cl_2 + NaOH \longrightarrow B$

(d) Compare the aromaticities of furan and pyrrole and give explanations.

(e) Thiophene is less reactive than furan. Explain.

(f) Compare the basicities of the following :

Pyrrole   and   Imidazole

(g) Write the products of the following :

$C_{10}H_{14} \overset{\oplus}{N_2}CH_3\overset{\ominus}{I} \xrightarrow{\Delta}$

Nicotine methiodide

(h) What do you mean by isoprene rule ?

3. Answer **any three** questions from the following : (A to H) $5 \times 3 = 15$
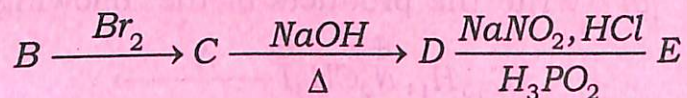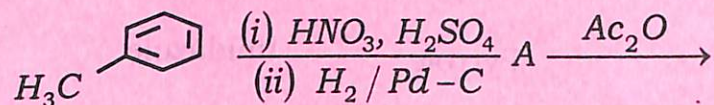
A. (a) Explain why aniline cannot undergo $1+1=2$
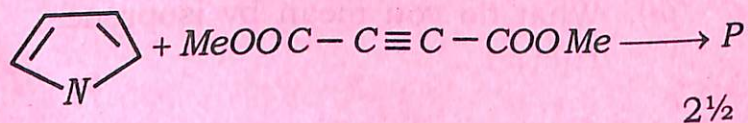
    (i) Friedel-Craft reaction

    (ii) Nitration reaction with HNO_3

  (b) Discuss about kinetically and thermodynamically controlled product of napthalene, when it undergoes sulphonation reaction with conc. H_2SO_4 at $80°C$ and $160°C$.   3

B. (a) Identify A, B, C, D and E in the following : $2\frac{1}{2}$

$$H_3C-\langle\text{benzene}\rangle \xrightarrow[\text{(ii) } H_2/Pd-C]{\text{(i) } HNO_3, H_2SO_4} A \xrightarrow{Ac_2O}$$

$$B \xrightarrow{Br_2} C \xrightarrow[\Delta]{NaOH} D \xrightarrow[H_3PO_2]{NaNO_2, HCl} E$$

  (b) Identify P and propose a mechanism :

$$\langle\text{pyrrole}\rangle + MeOOC-C\equiv C-COOMe \longrightarrow P$$
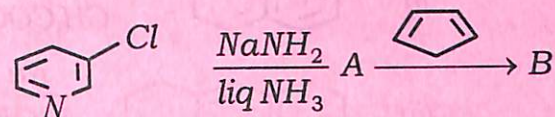
$2\frac{1}{2}$

C. (a) Write the sequence of reactions involved in the Fischer indole synthesis.   2

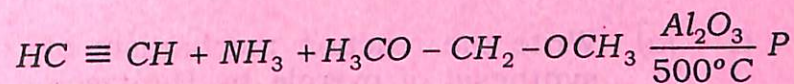 (b) Why is catalytic reduction of thiophene difficult ?   1

  (c) Compare and explain the basicity of indole and quinoline.   2

D. (a) Find the product of the following reactions :   2

$$\langle\text{pyridine}\rangle\text{-}Cl \xrightarrow[liq\ NH_3]{NaNH_2} A \xrightarrow{\langle\text{cyclopentadiene}\rangle} B$$

  (b) Compare the basicities of 2-methyl pyridine and 3-methyl pyridine.   2

  (c) Write the product P :   1

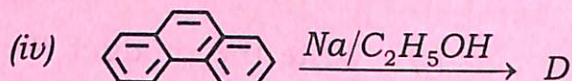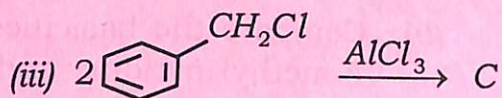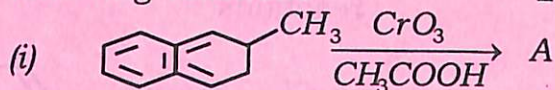$$HC \equiv CH + NH_3 + H_3CO - CH_2 - OCH_3 \xrightarrow[500°C]{Al_2O_3} P$$

E. (a) Write the mechanism of diazotization of an aromatic amine.   3

(b) Can you prepare secondary amines using Gabriel's phthalimide synthesis ? Give reasons. 2
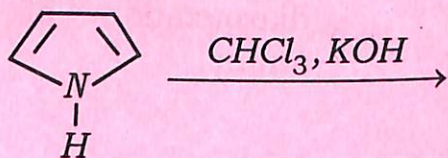
F. *(a)* Write the reactions involved in Haworth synthesis of naphthalene. 3

(b) Identify A, B, C and D in the following reactions : 2

(i) $\xrightarrow[CH_3COOH]{CH_3\ CrO_3}$ A

(ii) $\xrightarrow[EtOH]{Na}$ B

(iii) $2\ \text{(}CH_2Cl\text{)} \xrightarrow{AlCl_3}$ C

(iv) $\xrightarrow{Na/C_2H_5OH}$ D

G *(a)* Write the reaction mechanism of synthesis of pyrrole by Hantzsch method. 3

(b) Find the product of the following reaction : 2

$\underset{H}{\underset{N}{\text{pyrrole}}} \xrightarrow{CHCl_3,\ KOH}$

H. How will you distinguish 1°, 2° and 3° nitroalkanes ? What products are obtained when nitrobenzene is reduced in (i) acidic medium, and (ii) alkaline medium ? 3+2=5

4. Answer *any three* questions from the following A to H : 10×3=30

A. *(a)* How will you ascertain the nature of oxygen and number of double bonds in citral ? 1½+1½=3

(b) Write different steps involved in the synthesis of citral from acetone and acetylene. 5

(c) Write the product and name it : 2

$\xrightarrow{K_2CO_3,\ H_2PO}$?

with CHO group
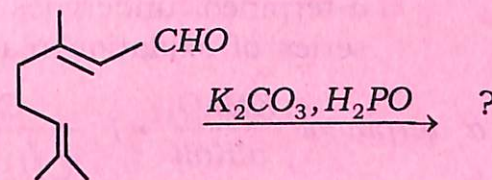
B. *(a)* Write the sequence of reactions that takes place in the synthesis of quinoline by Doebner-Miller method. 5

Contd.

(b) Find the products of the following : 2

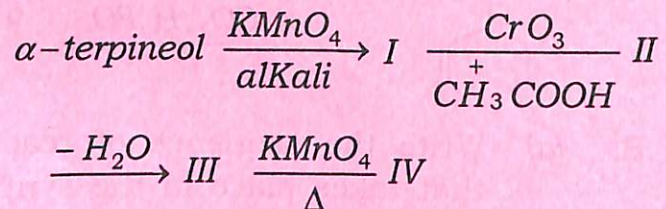$$B \xleftarrow{\ LiAlH_4\ } \quad \text{[quinoline]} \quad \xrightarrow{\ Pt\,/\,ACOH\ } A$$
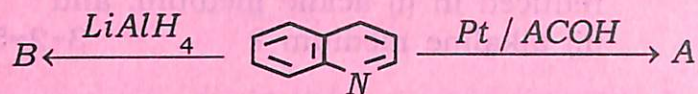
Also name the products.

(c) Which position of quinoline is more susceptible to undergo electrophilic substitution reaction ? Explain with proper reasoning. 3

C. (a) Write the method of synthesis of α-terpineol from *p*-toluidic acid. 4

(b) Write the products when α-terpineol undergoes following series of oxidation reaction : 4

$$\alpha-terpineol \xrightarrow[alKali]{KMnO_4} I \xrightarrow[\substack{+\\CH_3COOH}]{CrO_3} II$$

$$\xrightarrow{-H_2O} III \xrightarrow[\Delta]{KMnO_4} IV$$

(c) What conclusion can you draw from the above oxidation reactions ? 2

D. (a) Write how alkaloids can be extracted from plants. 2

(b) Write the reactions to ascertain the nature of N-atoms in nicotine. 3

(c) How can you show the presence of pyrrolidine ring in nicotine ? 4

(d) Write on medicinal importance of morphine along with side effects. 1

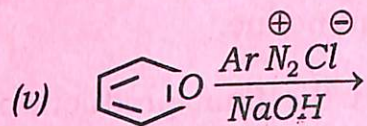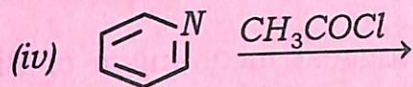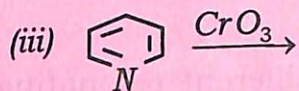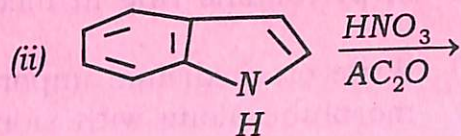E. (a) Write different resonating structures of isoquinoline. 2
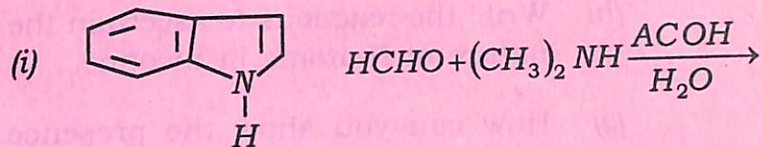
(b) Suggest mechanism of Bischler-Napieralskiol synthesis of isoquinoline. 4

(c) Find the final products of the following reaction. 2

$$\text{[isoquinoline]} \xrightarrow[(O)]{KMnO_4}$$
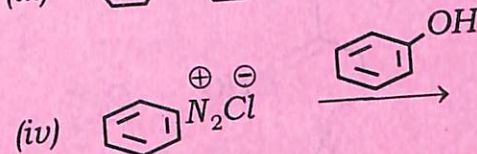
(d) Compare the basicities of isoquinoline with pyridine. 2

F. Write the products of the following reactions : 2×5=10

(i) $HCHO + (CH_3)_2 NH \xrightarrow{\dfrac{ACOH}{H_2O}}$

(ii) $\xrightarrow{\dfrac{HNO_3}{AC_2O}}$

(iii) $\xrightarrow{CrO_3}$

(iv) $\xrightarrow{CH_3COCl}$

(v) $\xrightarrow{\dfrac{Ar \overset{\oplus}{N_2} \overset{\ominus}{Cl}}{NaOH}}$

G. (a) Compare the basicities of furan, pyrrole and thiophene with proper explanations. 3

(b) Furan is less reactive than pyrrole. Explain. 2

(c) Find the products of the following reactions : 1×5=5

(i) $+$ $\longrightarrow$

(ii) $+$ $\xrightarrow{\substack{(i)\ AlCl_3 \\ (ii)\ Zn\ dust}}$

(iii) $+ CH_3COCl \longrightarrow$

(iv) $\xrightarrow{\hspace{2cm}}$

(v) $\xrightarrow{\substack{(1)\ RLi, H^+ \\ (2)\ [O]}}$
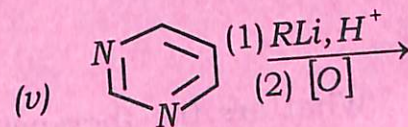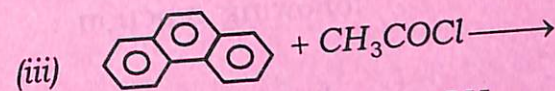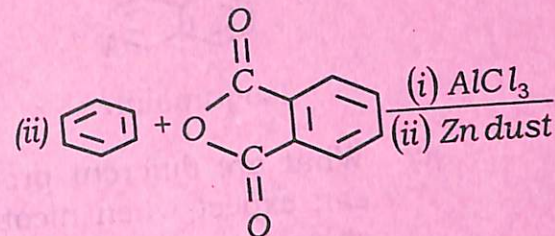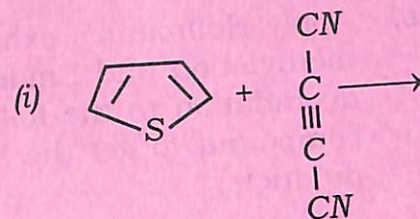
H. (a) What is Hoffmann's exhaustive methylation ? 2

(b) Apply Hoffmann's exhaustive methylation and Emde's degradation to the following compound to get the final product : 4
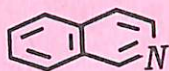
Isoquinoline

(c) What are different products you can expect when nicotine zinc chloride is distilled ? 1½

(d) Find all the products of the following reaction : 1½

(e) What are the therapeutic uses of reserpine ? 1

_____

3 (Sem–4/CBCS) CHE HC 3

2022

CHEMISTRY

(Honours)

Paper : CHE–HC–4036

(Physical Chemistry–IV)

Full Marks : 60

Time : Three hours

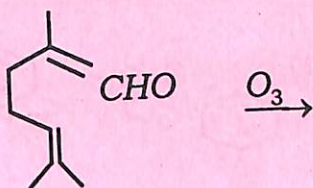*The figures in the margin indicate full marks for the questions.*

1. Answer **any seven** of the following questions : $1\times7=7$

   (a) Define specific conductance of an electrolyte.

   (b) Under what conditions will a galvanic cell send no current in the outer circuit ?

   (c) What is the charge in coulombs on CO_3^{2-} ion ?

   (d) Define Wien effect.

(e) What is the relationship between molar conductivity and equivalent conductivity of an electrolyte A_xB_y ?

(f) The conductivity of $N/10\,KCl$ solution at $20°C$ is $0.0212\ S\ cm^{-1}$ and the resistance of the cell containing this solution is 55 ohms. The cell constant in cm^{-1} is

(i) 4.6

(ii) 0.616

(iii) 2.17

(iv) 1.166

(Choose the correct option)

(g) Define magnetic susceptibility.

(h) Which of the following molecules would have zero dipole moment ?

(i) m-dichlorobenzene

(ii) p-dichlorobenzene

(iii) CH_3Cl

(iv) NH_3

(Choose the correct option)

(i) What is magnetic permeability ?

(j) Fluorine cannot be prepared from fluorides by chemical oxidation. Why ?

2. Answer *any four* of the following questions :

$2×4=8$

(a) Explain why mobility of H^+ ion is highest in aqueous solution.

(b) Write the reaction that takes place in Ag–AgCl electrode. Also write Nernst equation for the same.

(c) The molar conductances at infinite dilution of $NaOH$, $NaCl$ and $BaCl_2$ are

$2.481×10^{-2}\ Sm^2mol^{-1}$,

$1.265×10^{-2}\ Sm^2mol^{-1}$ and

$2.80 ×10^{-2}\ Sm^2mol^{-1}$ respectively.

Calculate molar conductance at infinite dilution of $Ba(OH)_2$.

(d) Given, $E°Cu^{2+}\,|\,Cu = 0.34\,V$ and

$E°Al^{3+}\,|\,Al = -1.66\,V$. Calculate the equilibrium constant of the following reaction at $298\ K$:

$$2Al(s)+3CuSO_4(aq) \rightleftharpoons Al_2(SO_4)_3(aq)$$
$$+3Cu(s)$$
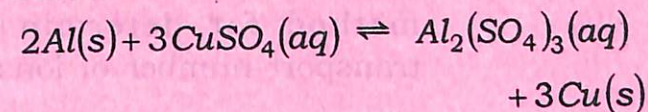
(e) Explain why mobility of Li^+ is less than that of K^+ ion aqueous medium.

(f) Explain the terms 'induced polarization' and 'orientation polarization'.

(g) What is dipole moment ? What are its units ?

(h) The dipole moment of $NH_3(g)$ is 1.46D. If the angle HNH is 108°, calculate the bond moment of N–H bond.

3. Answer *any three* of the following questions :   5×3=15

(a) Using Debye-Huckel theory discuss about different factors that affect the speed of ion when an electric field is applied.

(b) Deduce an expression for the e.m.f. of the concentration cell with transference :

$$Pt(s)\,|\,H_2(1atm)\,|\,HCl(a_1):HCl(a_2)\,|\,H_2(1atm)\,|\,Pt(s)$$
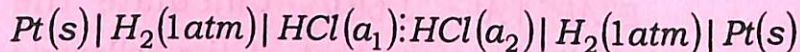
(c) (i) Explain the moving boundary method for determination of transport number of ions.   3

(ii) Write the electrode reaction of calomel electrode when the cell acts as cathode. Give the expression for potential of a calomel electrode.   2

(d) (i) Calculate the mean ionic activity coefficient of 0.01 M Na_2SO_4 solution in water at 298 K.   3

(ii) Calculate the standard free energy change associated with the reaction :   2

$$2Al(s)+3ZnSO_4(aq) \rightarrow Al_2(SO_4)_3(aq)+3Zn(s)$$
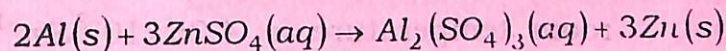
Given :

$$E^o_{Al^{3+}|Al} = -1.66V \text{ and}$$

$$E^o_{Zn^{2+}|Zn} = -0.76V$$

(e) What is meant by polarizability of a molecule ? Derive the Clausius–Mossotti equation.   1+4=5

(f) What information regarding the structure of molecules can be obtained from the knowledge of their dipole moments ? What are meant by bond moment and group moment ?   3+2=5

(g) Give a brief account of Lorentz-Lorentz equation.

(h) Calculate the solubility product of the sparingly soluble salt CaF_2 from the following data :

The molar ionic conductances (at infinite dilution) of Ca^{2+} and F^- ions are 104×10^{-4} and $48 \times 10^{-4} Sm^2 mol^{-1}$ respectively. The specific conductance of the saturated solution of CaF_2 at room temperature is $4.25 \times 10^{-3} Sm^{-1}$ and the specific conductance of water used for preparing the solution is $2 \times 10^{-4} Sm^{-1}$.

4. Answer **any three** of the following questions : 10×3=30

(a) (i) A solution of HCl was electrolysed in a Hittorf cell using Pt electrodes. The analysis of the solution from the cathode compartment before and after electrolysis indicated the masses of HCl as $1.82 \times 10^{-4} kg$ and $1.67 \times 10^{-4} kg$ respectively. At the same time the mass of Ag deposited at the cathode of the coulometer in the same circuit was found to be $2.52 \times 10^{-4} kg$. Calculate the transport number of each ion. 4

(ii) Write what you mean by concentration cell. Taking the example of hydrogen electrode, explain how concentration cells are classified. Explain in which type of cell liquid junction potential will be maximum. 1+3+2=6

(b) What is the principle underlying conductometric titrations ? Discuss the titration curves obtained in the titration of :

(i) a strong acid with a strong base;

(ii) a strong acid with a weak base;

(iii) a mixture of HCl and CH_3COOH with $NaOH$;

(iv) $AgNO_3$ against KCl. 2+2+2+2+2=10

(c) (i) Write Nernst equations for the potentials of Zn-electrode and Cu-electrode in the Daniell cell. Hence find an expression for the e.m.f. of the Daniell cell at any given temperature. 2+2=4

(ii) For the reaction $Fe^{3+} + 3e^- \rightleftharpoons Fe$, standard electrode potential is -0.036 V and the standard electrode potential for the reaction $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ is 0.771 V. Calculate the standard electrode potential for the reaction $Fe^{2+} + 2e^- \rightleftharpoons Fe$. Predict whether the reaction $Fe + 2Fe^{3+} \rightleftharpoons 3Fe^{2+}$ is spontaneous or not. 4+2=6

(d) (i) Deduce the relationship between ion mobility and molar conductance of an electrolyte. 4

(ii) What do you mean by activity coefficient ? Taking an example, discuss how mean ionic activity coefficient can be found out from e.m.f. measurement. 1+3=4

(iii) Calculate the EMF of the following electrode concentration cell at 298K : 2

$$Pb(Hg)(a_1 = 0.2)\,|\,Pb(NO_3)_2(aq)$$
$$|\,Pb\,|\,Hg(a_2 = 0.02)$$
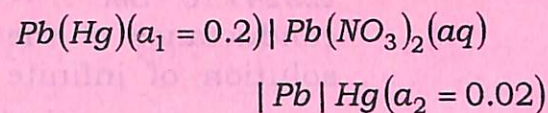
(e) (i) Discuss the principle underlying potentiometric titrations. Discuss the variation of potential with volume of NaOH added in the titration against HCl ? In what respect potentiometric titrations are better than simple volumetric titrations ? 2+2+2=6

(ii) Explain a method of measurement of magnetic susceptibility of a substance. 4

(f) (i) Explain how the dipole moment of a gaseous molecule can be determined by using the Debye equation. 6

(ii) Estimate the refractive index of water, given that the polarizability volume of water molecule at optical frequencies is $1.5 \times 10^{-24} cm^3$. 4

(g) (i) Conductivity of a 0.02 $mol\ ohm^{-3}$ solution of acetic acid at 298K is $2.324 \times 10^{-2}\ Sm^{-1}$. If the molar conductance of the acetic acid solution of infinite dilution is $387.9 \times 10^{-4}\ S mol^{-1} m^2$, calculate the degree of dissociation of acetic acid in the solution at 298K. 3

(ii) The molar ionic conductance at infinite dilution of silver ions is $61.92 \times 10^{-4} S m^2 mol^{-1}$ at 25°C. Calculate the ionic mobility of silver ions at 25°C at infinite dilution. 3

(iii) In an electrolysis experiment, a current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold salt and second cell contains copper sulphate solution. 9.85g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode in the second cell. Also calculate the magnitude of the current in ampere. 4

(h) (i) What are meant by electronic polarisation and atomic polarisation ? 2

(ii) What is drift velocity of ions in solution ? What is abnormal transference number ? Give one example. 2+3=5

(iii) The standard electrode potentials of Pb/Pb^{2+} and $Pt/I^-/I_2$ are -0.126 volt and $+0.536$ volt respectively. When a galvanic cell is constructed using 0.1 molar concentrations of the respective ions, Pt is found to be the cathode. What is the voltage generated in the cell ? 3

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