- (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 $Fe^{3+} \rightarrow Fe$.

Total number of printed pages-8

3 (Sem-4/CBCS) CHE HC1

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) [NiCl₄]²⁻
 - (d) $[AuCl_4]^{2-}$

(Choose the correct option)

8

(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)Cl₂Br₂]⁻ is

(a) 2

- (b) 4
- (c) 6

8

(Choose the correct option)

3 (Sem-4/CBCS) CHE HC1/G 2

(d)

- (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.

3 (Sem-4/CBCS) CHE HC1/G 3

- (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 $32,200 \text{ cm}^{-1}$ and the electron pairing energy is $17,600 \text{ cm}^{-1}$. 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

4

(i) The magnetic moment of $[Fe(CN)_6]^{3-}$ was found to be 1.9BM 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 [CoCl₄]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.

Contd.

3 (Sem-4/CBCS) CHE HC1/G

- 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

6

- (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=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 Fe²⁺ to reduce to Fe? Give reason.

3 (Sem-4/CBCS) CHE HC1/G 7

- H. (a) What is Hoffmann's exhaustive methylation ?
 - (b) Apply Hoffmann's exhaustive methylation and Emde's degradation to the following compound to get the final product :

4

11/2

1

10



Isoquinoline

- (c) What are different products you can expect when nicotine zinc chloride is distilled ? 1¹/₂
- (d) Find all the products of the following reaction :

(e) What are the therapeutic uses of reserpine ?

Total number of printed pages-12

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 : 1×7=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 :

 $RCH = NO_0 Na$

CHO

- (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 : 2×4=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

Imidazole

(g) Write the products of the following :

 $C_{10}H_{14} \overset{\bigoplus}{N_2}CH_3 \overset{\bigoplus}{I} \overset{\Delta}{\longrightarrow}$



(h) What do you mean by isoprene rule?

3 (Sem-4/CBCS) CHE HC2/G 3

- 3. Answer **any three** questions from the following : (A to H) 5×3=15
 - A. (a) Explain why aniline cannot undergo 1+1=2
 - (i) Friedel-Craft reaction
 - (ii) Nitration reaction with HNO3
 - (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 : 2¹/₂

 $H_{3}C \xrightarrow{(i) HNO_{3}, H_{2}SO_{4}} A \xrightarrow{Ac_{2}O} A \xrightarrow{(ii) H_{2}/Pd-C} A \xrightarrow{Ac_{2}O}$

$$B \xrightarrow{Br_2} C \xrightarrow{NaOH} D \xrightarrow{NaNO_2, HCl} E$$

(b) Identify P and propose a mechanism :

$$\bigvee_{N} + MeOOC - C \equiv C - COOMe \longrightarrow P$$

$$2^{\frac{1}{2}}$$

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



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

(c) Write the product P: 1

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

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

3 (Sem-4/CBCS) CHE HC2/G 5

Contd.

3 (Sem-4/CBCS) CHE HC2/G 4

- BOOD (b) Can vou prepare secondary amines using Gabriel's phthalimide synthesis ? Give 2 reasons.
 - Write the reactions involved in F. (a)Haworth synthesis of naphthalene. 3
 - (b) Identify A, B, C and D in the following reactions : CH_3 CrO_3 CH₃COOH A Na (ii) CH_CI

(iv)
$$(V_2H_5OH) \to D$$

- G Write the reaction mechanism of (a) synthesis of pyrrole by Hantzsch method.
 - Find the product of the following (b)reaction : 2

CHCl₂, KOH

3 (Sem-4/CBCS) CHE HC2/G 6

- 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
- Answer any three questions from the 4. following A to H : $10 \times 3 = 30$
 - (a) How will you ascertain the nature Α. of oxygen and number of double bonds in citral ? $1\frac{1}{2}+1\frac{1}{2}=3$
 - Write different steps involved in *(b)* the synthesis of citral from acetone and acetylene.
 - (c) Write the product and name it : 2



Write the sequence of reactions Β. (a)that takes place in the synthesis of quinoline by Doebner-Miller method. 5

3 (Sem-4/CBCS) CHE HC2/G 7 Contd.

(b) Find the products of the following :

2

LiAlH

Also name the products.

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

- C. (a) Write the method of synthesis of α -terpineol from *p*-toluidic acid.
 - (b) Write the products when
 α-terpineol undergoes following
 series of oxidation reaction : 4

$$\begin{array}{ccc} \alpha - terpineol & \frac{KMnO_4}{alKali} & I & \frac{CrO_3}{CH_3COOH} & II \\ \hline & -H_2O & KMnO \end{array}$$

2

4

3 (Sem-4/CBCS) CHE HC2/G 8

- 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 ?
 - (d) Write on medicinal importance of morphine along with side effects.
 - (a) Write different resonating structures of isoquinoline. 2
 - (b) Suggest mechanism of Bischler-Napieralskiol synthesis of isoquinoline.
 - (c) Find the final products of the following reaction.



(d) Compare the basicities of isoquinoline with pyridine.

3 (Sem-4/CBCS) CHE HC2/G 9

E.

Contd.

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2

2



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





3 (Sem-4/CBCS) CHE HC2/G 10

Total number of printed pages-11

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: 1×7=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.

A) Whet are meant by electronic polarisation and atomic polarisation ?

What is drift velocity of ions in solution 2 What is abnormal transference number 2 Give one example, 2+3=5

bi) The standard efectivede potentials

of Pb/Pb^{*} and Pi/I^{*}/I₂ are -0.126 volt and + 0.536 volt respectively. When a galvanic colits 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 2

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- (e) What is the relationship between molar conductivity and equivalent conductivity of an electrolyte $A_x B_y$?
- (f) The conductivity of N/10KCl 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) CH₃Cl
 - (iv) NH₃

(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 BaCl₂ are $2.481 \times 10^{-2} Sm^2 mol^{-1}$,

 $1.265 \times 10^{-2} Sm^2 mot^{-1}$ and

- $2.80 \times 10^{-2} Sm^2 mol^{-1}$ respectively. Calculate molar conductance at infinite dilution of $Ba(OH)_2$.
- (d) Given, $E^{o}Cu^{2+}|Cu=0.34V$ and

 $E^{\circ}Al^{3+} | Al = -1.66V$. Calculate the equilibrium constant of the following reaction at 298 K: $2Al(s) + 3CuSO_4(aq) \rightleftharpoons Al_2(SO_4)_3(aq)$

 $\mu_4(aq) \leftarrow A\iota_2(SO_4)_3(aq) + 3Cu(s)$

3 (Sem-4/CBCS) CHE HC 3/G 3

- (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

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- (ii) Write the electrode reaction of calomel electrode when the cell acts as cathode. Give the expression for potential of a calomel electrode.
 - (d) (i) Calculate the mean ionic activity coefficient of $0.01 \ M \ Na_2 SO_4$ 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 :

 $E^{o}_{Al^{3+}|Al} = -1.66V$ 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

Sem - //CBCS) CHE

- (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

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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) AgNO3 against KCl.

2+2+2+2=10

3 (Sem-4/CBCS) CHE HC 3/G 7

- Write Nernst equations for the (c) (i) potentials of Zn-electrode and Cuelectrode in the Daniell cell. Hence find an expression for the e.m.f. of the Daniell cell at any given 2+2=4temperature.
 - (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 $Fe + 2Fe^{3+} \Rightarrow 3Fe^{2+}$ is spontaneous or not. 4+2=6
- Deduce the relationship between (d) (i) ion mobility and molar conductance of an electrolyte. 4
 - What do you mean by activity (ii) coefficient ? Taking an example, discuss how mean ionic activity coefficient can be found out from e.m.f. measurement. 1+3=4

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

 $Pb(Hg)(a_1 = 0.2) | Pb(NO_3)_2(aq)$

 $|Pb|Hg(a_2 = 0.02)$

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

- Explain a method of measurement of magnetic susceptibility of a substance. 4
- Explain how the dipole moment of (f) (i) 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

3 (Sem-4/CBCS) CHE HC 3/G 9

(e) (i)

(ii)

3 (Sem-4/CBCS) CHE HC 3/G 8

(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 $387.9 \times 10^{-4} Smol^{-1}m^2$, 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 $61.92 \times 10^{-4} Sm^2 mol^{-1}$ 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.

S ITHM - AVCBACKI CHE HO 3/0

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

 (ii) What is drift velocity of ions in solution ? What is abnormal transference number ? Give one example.

(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

2

3 (Sem-4/CBCS) CHE HC 3/G 10