3 (Sem–4/CBCS) CHE HC 1

2021

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.

GROUP–A

1.   Answer the following questions :   1×5=5

   (i)   What are ionophores ?

(ii) In biological systems, the metal ion involved in the dioxygen transport besides *Fe* is,

(a) Co

(b) Zn

(c) Mg

(d) Cu

(iii) $La^{3+}, Lu^{3+}, Yb^{2+}, Ce^{4+}$ are diamagnetic, while Sm^{3+} exhibits low paramagnetic behavior. Why ?

(iv) Determine the spin only magnetic moment (μ_s) of the compound, $Hg[Co(SCN)_4]$.

(v) The number of moles of $KMnO_4$ that will be needed to react completely with one mole of *Fe*(II) oxalate in acidic solution is _____.

2. Answer the following : 2×5=10

(i) Which of the following are expected to show Jahn-Teller distortion and why ?

(a) $[Cr(acac)_3]$

(b) $[CuCl_6]^{4-}$

(c) $[Co(CN)_6]^{4-}$
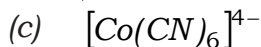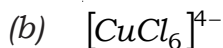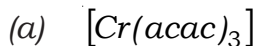
(ii) The complex $[NiCl_4]^{2-}$ contains two unpaired electrons while $[Ni(CN)_4]^{2-}$ is diamagnetic in nature. Propose structures for these two complex ions on the basis of CFT.

(iii) Why does the separation of lanthanide difficult ?

(iv) What are carboxypeptidases ? Give their structural features.

(v) Transition metals are less reactive than alkali and alkaline earth metals. Explain.

Contd.

3. Answer the following : 5×3=15

(i) How the energy level of *d*-orbital changes during distortion of an octahedral *Cu*(II) complex ? Discuss.

5

(ii) What is trigger mechanism for the cooperativity of oxygenation of hemoglobin ? Explain. 5

(iii) What is lanthanide contraction and what is its cause ? How the lanthanide contraction affects the basicity of ions ? 2+1+2=5

GROUP–B

4. Answer ***any three*** of the following :

10×3=30

(i) (a) Discuss the crystal field splitting pattern for a complex with a linear ligand environment. Assume that the ligands lie on the *z*-axis. 5

(b) Draw a qualitative crystal field splitting diagram in a cubic environment of ligands in reference to a tetrahedral field. 5

(ii) Explain the molecular mechanism of ion transport across membrane. 10

(iii) (a) Give the important oxidation states of lanthanides. How would you account for them ? Why M^+ and M^{2+} are less stable than M^{3+} in lanthanide series ?

$$1+2+3=6$$

(b) Discuss the +4 oxidation state of Cerium. 4

(iv) (a) Describe the preparation, properties and structure of chromium acetate monohydrate. Comment on its magnetic behavior. $1+2+2+2=7$

(b) How is $VOCl_2$ obtained from $VOCl_3$? Give appropriate chemical reactions. 3

(v) Discuss how the following metal ions cause toxicity :

As, Cd, Hg, Pb $\qquad 2\frac{1}{2}\times4=10$

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Total number of printed pages–7

3 (Sem–4/CBCS) CHE HC 2

2021

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.

Group–A

1. Answer all questions : 1×5=5

    (a) Arrange the following in order of decreasing basicity 1

    $$CH_3C\equiv N \quad , \quad H_3CHC=NH \quad , \quad CH_3CH_2NH_2$$

    (b) What product is obtained when 2, 4-hexanedione is heated with ammonium carbonate ? 1

    (c) Draw the structure of cocaine and give *one* medicinal use. 1

Contd.

(d) What is the index of hydrogen deficiency of the compound given below ?   1
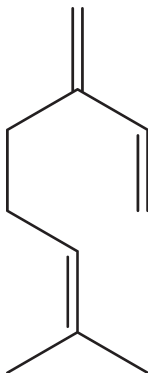
(e) Write the name and structure of *one* vitamin that contain a heterocyclic ring. Specify the heterocyclic ring.   1
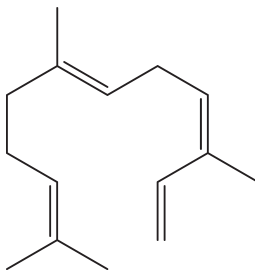
2. Answer **all** questions :   2×5=10

(a) Pyrrole is an extremely weak base. Explain.   2

(b) Pyridine is bad at electrophilic substitution. Why ?   2

(c) Can biphenyl form a picrate derivative ? Give reasons to justify your answer.   1+1=2

(d) What is the source of nicotine ? What class of alkaloid does it belong to ?   1+1=2

(e) Identify the isoprene units in the molecule given   2

3. Answer **any three** among *(a), (b), (c), (d)* and *(e)* :

    5×3=15

    (a) *(i)* Using appropriate chemical reactions to show that nicotine contains a pyridine nucleus.

    (ii) Suggest a synthesis of nicotine. Write the reactions involved.

    2+3=5

   *(b)* What are terpenes ? Describe their classification. Give *one* example of each classification.   1+4=5

    (c) *(i)* Explain why diazonium ion in a benzene ring cannot be used to direct incoming electrophile to the meta position.

    (ii) How can you convert aniline to 1, 3, 5-tribromobenzene ?

    (iii) Why are diazonium salts explosive in nature ?   2+2+1=5

(d) Predict the product(s) likely to be formed in the following reaction and identify the major one. Propose a mechanism for the same. 5


$$\xrightarrow[\text{H}^+]{\text{Me}_2\text{NH, HCHO}} \quad ?$$
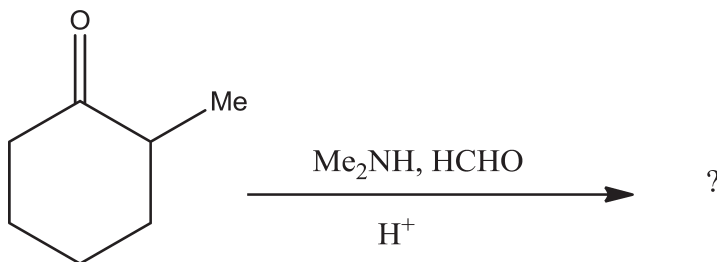
(e) What happens when citral reacts with (a) *Na-Hg* (b) NH_2OH (c) O_3 (d) $KMnO_4$; CrO_3 (e) $KHSO_4$? Write the reactions involved in each case. 5

Group–B

Answer *any three* questions among **4, 5, 6, 7** and **8** : 10×3=30

4. *(a)* Distinguish between a primary, secondary and tertiary amine. Write the reactions involved. 3

(b) Outline the reactions and reagents used to establish the structure of piperidine by exhaustive methylation and Hofmann elimination. 4

(c) Arrange methylamine, dimethylamine and trimethylamine in increasing order of basicity. Explain the proposed order. 3

5. *(a)* Arrange pyrrole, furan and thiophene in order of decreasing aromaticity and provide an explanation. 2

(b) Which position of furan is readily attacked by electrophiles and why? 3

(c) Starting with glycerol, suggest a method for the synthesis of quinoline. Write all the steps involved, explaining in brief each step. 5

6. *(a)* Predict the product of the following reaction. Propose a mechanism for the reaction, clearly mentioning each step in brief. 5
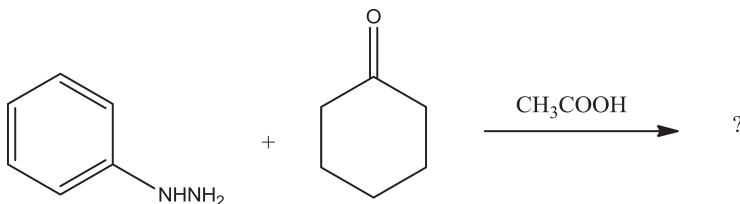
(b) What happens when 2+2=4

(i) Pyrrole reacts with *DMF* and *POCl$_3$* ?

Contd.

(ii) Phenethylamide is treated with $POCl_3$?

Write the reactions involved.

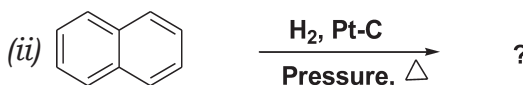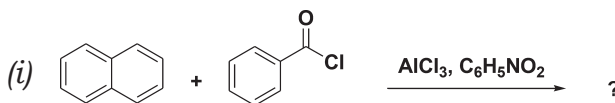(c) Name a medicinal compound in which quinoline is an important component. 1

7. (a) "Naphthalene undergoes electrophilic substitution generally at 1-position." Explain. 3

(b) How can you obtain 2-Naphthyl amine starting from β-naphthol? Show the mechanistic steps involved. 3

(c) How Elbs reaction can be utilized to synthesize anthracene? Why does anthracene undergo addition reaction comparatively easier than other similar aromatic systems? 3+1=4

8. (a) Predict the product of the following reactions: 4×1=4

(i)   + $\xrightarrow{AlCl_3, C_6H_5NO_2}$?

(ii) $\xrightarrow[\text{Pressure}, \triangle]{H_2, \text{Pt-C}}$?

(iii) + $\xrightarrow[\Delta]{\text{Xylene}}$?

(iv) $\xrightarrow{\begin{array}{l}\text{1. O}_3 \\ \text{2. H}_2\text{O} \\ \text{3. KMnO}_4\end{array}}$?
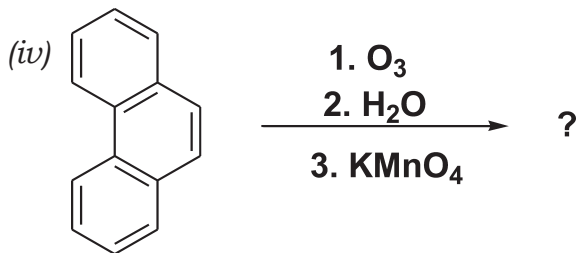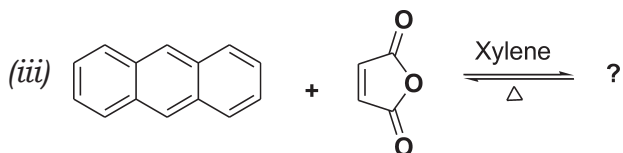
(b) Describe the Friedlander's method of synthesis of quinoline.　　3

(c) Distinguish between the isoprene and special isoprene rule.　　3

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3 (Sem–4/CBCS) CHE HC 3

2021

CHEMISTRY

(Honours)

Paper : CHE–HC–4036

(Physical Chemistry–III)

Full Marks : 60

Time : Three hours

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

GROUP–A

1. Answer the following questions :   1×5=5

    (a) Define molar conductivity of an electrolyte.

(b) Equivalent conductance Λ_e and molar conductance Λ_m of $BaSO_4$ are related as —   (*Choose the correct option*)

(i) $\Lambda_e = \dfrac{\Lambda_m}{2}$

(ii) $\Lambda_e = \Lambda_m$

(iii) $\dfrac{\Lambda_e}{2} = \Lambda_m$

(iv) $\Lambda_e = \dfrac{\Lambda_m}{4}$

(c) Write the Faraday's first law of electrolysis.

(d) Define Wien effect.

(e) Calculate dipole moment of *NaCl* is found to be 11.3 *D* and its experimental dipole moment is 8.5 *D*. Calculate the per cent ionic character of *NaCl*.

2. Answer the following questions :   2×5=10

(a) A current of 0.5 ampere is passed for 30 minutes through a voltameter containing copper sulphate solution. Calculate the weight of copper deposited at the cathode. (At. wt. of Cu = 63.6u).

(b) Explain how degree of dissociation of a weak electrolyte can be calculated from the measurement of conductance.

(c) For a salt of weak acid, show that the degree of dissociation is $\alpha = \sqrt{\left(\dfrac{K_w}{K_a.C} \right)}$.

The symbols signify the usual meanings.

(d) Write the electrode reactions and cell reaction for the following cell _____
$Pt, H_2(1atm) | HCl(c_1) | AgCl(s); Ag$

(e) For pH determination the quinhydrone electrode works satisfactorily only at _____ pH values.

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

(a) Define molar conductivity at infinite dilution. State and explain Kohlrausch law of independent migration of ions.
                                        1+4=5

(b) Explain asymmetric effect and electrophoretic effect for strong electrolytes. Give Debye-Huckel-Onsagar equation for uni-uniequivalent electrolyte, explaining the terms involved in it.   3+2=5

(c) Give the conditions for a reversible cell. Give *one* example each of a reversible cell and irreversible cell.   3+2=5

(d) Name *two* metals that can be extracted by electrolysis method. With the help of a suitable example explain how electrolysis can be used in metallurgy.
                                        1+4=5

(e) Define the terms dipole moment and molar polarisability. Explain why ethyl chloride has dipole moment of 2.05 *D* but chlorobenzene has the dipole moment of 1.70 *D*.   3+2=5

GROUP–B

4. Answer **any three** of the following :

$$10 \times 3 = 30$$

(a) (i) Explain how equivalent conductivities of hydrochloric acid and acetic acid vary with concentration at constant temperature. The specific conductance of water at 298 K is 5.8×10^{-8} $S\ cm^{-1}$. Calculate the degree of dissociation of water. Given that Λ^0 for water at 298 K is 548.6 $S\ cm^2\ eq^{-1}$ and density of water is 0.997 $g\ cm^{-3}$. 3+2=5

(ii) What is drift velocity of ions in solution ? Explain why H⁺ ion has the highest mobility in aqueous solution. 2+3=5

(b) (i) Explain the term transference number of ions. Explain the Hittorf's method of measurement of transference number of ions. Give the basis for calculation of transference number of ions in the Hittorf's method. 1+5=6

Contd.

(ii) A solution of hydrochloric acid was electrolysed in a transport cell using platinum electrode. Analysis of cathode solution gave the following results :

Mass of Cl^- ions before electrolysis = 0.160 g per 20 g of water.

Mass of Cl^- ions after electrolysis = 0.146 g per 20 g of water.

A silver coulometer connected in series showed a deposit of 0.28 g of Ag.

Calculate the transport number of Cl^- ions.

(eq.wt. of $Cl = 35.5$ g eq^{-1}; eq. wt. of $Ag = 107.8$ g eq^{-1})　　　　4

(c) *(i)* The equivalent conductivities of HCl, $NaCl$ and CH_3COOH at infinite dilutions are 426.16, 126.45 and 91.0 S cm^2 eq^{-1} respectively. If the degree of dissociation of $0.1N$ acetic acid 0.001, calculate the equivalent conductance of acetic acid at this concentration.　　4

(ii) Mention *two* advanatges of conductometric titration. Explain the variations of conductivity against volume of base added for the following conductometric titrations : HCl vs NH_4OH and acetic acid vs $NaOH$. 2+2+2=6

(d) (i) Define standard reduction potential. Represent the standard hydrogen electrode with its potential. With the help of a suitable example explain how standard reduction potential of any other electrode can be measured. 1+1+4=6

(ii) Explain how $\Delta G^o, \Delta H^o$ and ΔS^o of a cell reaction can be determined from the measurement of standard *emf* of a cell. 4

(e) (i) Explain the principle of acid-base titrations by potentiometric method. 6

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

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