# 3/EH-23 (iii) (Syllabus-2015)

## 2016

(October)

### **CHEMISTRY**

( Elective/Honours )

## (General Chemistry-III)

(Chem-EH-301)

*Marks*: 56

Time: 3 hours

The figures in the margin indicate full marks for the questions

#### SECTION—I

(Inorganic)

( Marks : 18 )

- 1. (a) Explain why the atomic and ionic radii of the alkaline-earth metals are lower as compared to alkali metals. How do they differ from alkali metals based on the above observation?

  11/4-17/2=3
  - (b) How do the acidic and basic characters of oxides of the s- and p-block elements change on moving across a period and down the group?

### OR

2.	(a)	What is inert-pair effect? Give a reason					
		why on moving down the group the					
		lower oxidation state of group 13					
		elements becomes more stable.	:				

- (b) Give one method of preparation and one use of the following compounds: 1½×2=3
  - (i) Potassium iodide (ii) Lead tetraacetate
- (c) Explain why phosphorus forms pentahalides but nitrogen does not form pentahalides.
- 3. (a) Give reasons for the following:  $1\frac{1}{2} \times 2=3$ 
  - (i) Cations of transition elements have a higher tendency to form complexes.
  - (ii) The second and the third rows of transition elements resemble each other more closely than they resemble the first row transition elements.
  - (b) What is lanthanide contraction? Explain the cause of lanthanide contraction. 3

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<b>4.</b>	(a)	What are transuranic elements?					Write
				preparation			
		transu	iranio	element.			

- (b) Explain the separation of lanthanides by ion-exchange method.
- (c) What is the number of ions per mole of the complex CoCl<sub>3</sub>·5NH<sub>3</sub> in aqueous solution?
- 5. (a) What is meant by effective atomic number? Calculate the effective atomic number of cobalt in  $[Co(NH_3)_6]^{3+}$ .

  (Atomic number of cobalt = 27) 1+1=2
  - (b) Give the IUPAC nomenclature of the following: ½×3=1½
    - (i)  $[Ag(NH_3)_2]C1$
    - (ii) [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>
    - (iii) (NH<sub>4</sub>)<sub>3</sub>[Cr(NCS)<sub>6</sub>]
  - (c) What is chelating ligand? Write down the applications of chelate formation. 21/2

## OR

6. (a) Give an example and draw the structure of an octahedral complex of the type [M(aa)<sub>3</sub>]. What type of isomerism will it exhibit?

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(Turn Over)

11/2

2

- (b) Using valence-bond theory, predict the structure and magnetic behaviour of [Mn(CN)<sub>6</sub>]<sup>4-</sup> and also mention whether it is an outer or inner orbital complex and high-spin or low-spin complex. 2½
- (c) What relationship exists between the crystal-field splitting energy  $(\Delta_0)$  and pairing energy (P) in determining whether a given complex will be high spin or low spin?

SECTION—II

## (Organic)

(Marks: 19)

7. (a) Name the following compounds according to IUPAC nomenclature: ½×2=1

(b) Arrange the following in decreasing order of pK<sub>a</sub>: 1½

Benzoic acid, 4-nitrobenzoic acid, 4-methoxybenzoic acid

(c) Complete the following reactions with mechanisms: 2×2=4

(i) OH 
$$CH_3OH \rightarrow ? + H_2O$$

(ii) 
$$CH_3Br \xrightarrow{2Li, Et_2O}$$
 ?  $\xrightarrow{CO_2}$  ?  $\xrightarrow{H_2O/H^+}$ 

(d) Why is Grignard reagent prepared under anhydrous conditions? 1½

(e) 
$$CH_3$$
  $CH_3$   $CH_2$   $OH_3$   $OH_4$   $II$ 

Although I and II are isomers, the boiling point of I is lower than II. Explain.

OR

- 8. (a) Discuss with an example the difference between tautomerism and resonance. 11/2
  - (b) "Acid chlorides give a pungent smell in air." Explain.

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(Turn Over)

1½

2

(c) Starting from ethylacetoacetate, how would you synthesize the following compounds? 1½×2=3

(i) Cinnamic acid

(ii) Ethyl methyl ketone

(d) Complete the following reactions with mechanisms: 2×2=4

(ii) 
$$_{2CH_3} \circ CH_3 \xrightarrow{1) C_2H_5O \cap Na^+} ?$$

9. (a) "Ethylamine is soluble in water whereas aniline is not." Explain.

(b) Why is it necessary to use concentrated H<sub>2</sub>SO<sub>4</sub> in nitration of benzene? 1½

(c) Complete the following reactions:  $2\times2^{-2}$ (i)  $H_3$ C  $NH_2$  1)  $Br_2/KOH$  ?

(ii) 
$$\frac{1) \text{ NaNO}_2/\text{HCl(0 °C)}}{2) \text{ Cu/KCN}}$$
?

(d) Why is diazotization of aniline always carried out in ice-cold solution?

(e) "The basic strength of amines in aqueous solution is different from gaseous phase." Explain.

OR ·

10. (a) Why is it difficult to prepare pure amines by ammonolysis of alkyl halides?

(b) Why does —NO<sub>2</sub> group increase the electrophilic character at *ortho*- and *para*-positions and not at *meta*-position? Explain with structures. 1½

(c) How will you make the following conversions? 1½×2=3

(i) Benzene to aniline

(ii) Aniline to p-hydroxyazobenzene

(d) Complete the following reaction:  $2 \times \frac{\text{CHCl}_3}{\text{KOH}}$ ?

(e) Give reason why aryl diazonium ions are more stable than alkyl diazonium ions.

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11/2

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(Continued)

## (Physical)

SECTION-III

( Marks: 19)

11.	(a)	Derive	the exp	ression	for	entro	entropy	
	•	change	of an id	eal gas	in	terms	of	
	tempera		ture and	volume	chai	nge.		

(b) Calculate the efficiency of a Carnot's engine working between the temperatures 110 °C and 25 °C.

(c) State Le Chatelier's principle and discuss the effect of pressure on the reaction

 $PCl_5 \rightleftharpoons PCl_3 + Cl_2$  2

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(Continued)

(d) State and explain the law of mass action.

### OR

- 12. (a) Derive the Gibbs-Helmholtz equation. 3
  - (b) State Trouton's rule. 1½
  - (c) The value of  $K_p$  for the equilibrium  $2H_2O(g)+2Cl_2(g) \rightleftharpoons 4HCl(g)+O_2(g)$  is 0.035 atm at 400 °C when the partial pressure is expressed in atmosphere. Calculate the value of  $K_c$  for the same reaction.

(d) Derive van't Hoff equation for temperature dependence of equilibrium constant in terms of  $K_c$ .

**13.** (a) Distinguish between order and molecularity of a reaction.

(b) Derive an expression for the rate constant of a first-order reaction. Show that the half-life of a first-order reaction is independent of the initial concentration of the reactant. 2+1=3

(c) What do you understand by lowering and relative lowering of vapour pressure? 1+1=2

(d) A solution containing 4 g of a non-volatile organic solute per 100 ml solution was found to have an osmotic pressure equal to 500 cm of mercury at 27 °C. Calculate the molecular weight of the solute.

#### OR

14. (a) For a particular reaction, the rate constant k is  $2.8 \times 10^{-5}$  lit  $\text{mol}^{-1}\text{sec}^{-1}$  at 300 K and  $7.0 \times 10^{-1}$  lit  $\text{mol}^{-1}\text{sec}^{-1}$  at 400 K. Calculate the energy of activation for the reaction.

(Given R = 1.98 cal  $\text{mol}^{-1}\text{deg}^{-1}$ )

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(b) The differential form of the rate of a reaction is

$$\frac{dx}{dt} = k(a-x)^2$$

Obtain the integrated form of the rate equation.

- (c) Define boiling point of a liquid. Why is boiling point of a solvent less than that of its solution?

  1+1=2
- (d) Explain reverse osmosis.

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2016

(October)

**BOTANY** 

(Elective/Honours)

( Angiosperm Taxonomy, Economic Botany, Ethnobotany and Phytogeography )

(BOT-ELH-301)

Marks: 56

Time: 3 hours

The figures in the margin indicate full marks for the questions

Answer Question No. 1 which is compulsory and four questions, selecting one from each Section

- 1. Write short notes on the following:  $4\times4=16$ 
  - (a) Barriers to plant migration
  - (b) Spikelets of Poaceae
  - (c) Processing of rubber
  - (d) Rules of priority

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(Turn Over)