# 5/H-23 (v) (Syllabus-2015)

#### 2017

(October)

### **CHEMISTRY**

( Honours )

(Chem-H-501)

*Marks* : 75

Time: 4 hours

The figures in the margin indicate full marks for the questions

# ( Part—A : Inorganic Chemistry—I )

( Marks: 38 )

- 1. (a) Find out the symmetry point group in  $PF_5$  and  $B_2H_6$  by indicating clearly in the structures the symmetry elements present in them. 2+2=4
  - (b) The following replicate results were obtained in measuring iron content of a sample:
    - 22.23%, 22.18%, 22.25%, 22.09%, 22.15%

Establish whether the result 22.09 is a valid measurement or not, given that

corresponding rejection quotient at 90% confidence limit for 5 observations is 0.64.

3

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2. (a) List down all the symmetry operations and symmetry elements present in [CO(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> ion.

OR

- (b) What type of error would you expect to occur while taking weight of a hygroscopic compound? What precautions may be taken to minimize such an error?
- 3. (a) Give the structural and chemical formulae of oxine and α-nitroso-β-naphthol. Discuss the applications of α-nitroso-β-naphthol in both qualitative and quantitative analyses.
  - (b) Outline the advantages and limitations of organic precipitants.
  - (c) What is argentometric titration? How is chloride determined by Volhard's method?

#### OR

formulae of cupron and dimethylglyoxime. Write some of the

important applications of both in qualitative and quantitative analyses.

2+2=4

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- (b) What is meant by masking and demasking of cations? Give examples. 11/2
- (c) What type of indicators is used in complexometric titration involving EDTA? How does this indicator function?
- 5. (a) What is Q-value of a nuclear reaction? What happens to Q-value when—
  - (i)  $m_{\rm R} > m_{\rm P}$ ;
  - (ii)  $m_{\rm R} < m_{\rm P}$ ?

(where  $m_R$  = mass of the reactants and  $m_P$  = mass of the products) 1+2+2=5

(b) How are radioisotopes separated by gaseous diffusion method?

#### OR

6. (a) Calculate the binding energy per nucleon (in MeV/nucleon) for the isotope <sup>56</sup><sub>26</sub>Fe.

Given the masses of

56<sub>Fe</sub> : 55.93494 a.m.u.

neutron: 1.008665 a.m.u.

proton : 1.00783 a.m.u.

electron: 0.00054859 a.m.u.

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(Turn Over)

- What are magic numbers? Why are the nuclei with magic number either proton or neutron or both extrastable?
- What are the factors that affect the **7.** (a) magnitude of crystal field stabilization energy parameter ( $\Delta_0$ ) in complexes?
  - Arrange the following complexes in increasing order of CFSE  $(\Delta_0)$  values and give explanation for your answer: 1+1+1=3

 $[Rh(NH_3)_6]^{3+}$ ,  $[Ir(NH_3)_6]^{3+}$ ,  $[Co(NH_3)_6]^{3+}$ 

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(c) Make the plot of hydration energies of M<sup>2+</sup> ions of first row transition metals and explain the important features.

#### OR

- 8. (a) Draw the splitting of d-orbital in a square planar system. Explain the magnetic behaviour of K<sub>2</sub>[Ni(CN)<sub>4</sub>] with 11/2+11/2=3 its help.
  - Calculate the CFSE ( $\Delta_0$ ) for Fe<sup>2+</sup> ion in high spin and low spin octahedral complexes.
  - Taking a suitable example explain the Jahn-Teller effect. (Continued)

9. (a) Describe the magnetic behaviour of K<sub>3</sub>[FeF<sub>6</sub>] and K<sub>3</sub>[Fe(CN)<sub>6</sub>] and explain their behaviour with help of crystal field theory.

What is Curie law? Why was it modified to give Curie-Weiss law? Explain.

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Draw qualitative diagrams indicating magnetic susceptibility as a function of temperature for (i) simple paramagnetic, (ii) ferromagnetic and (iii) antiferromagnetic substances.

#### OR

Give example of one paramagnetic and **10.** (a) one diamagnetic complex of Co3+ and calculate their spin-only magnetic moment  $\mu_s$ .

> for Cu(II) is normally 1.8-1.9 BM at room temperature but in dihydrate dicoppertetraacetate experimental value of  $\mu_{eff}$  is 1.4 BM. Explain.

magnetic by meant What susceptibility? How is it related to 11/2 magnetic moment?

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## ( Part—B : Organic Chemistry—I )

( Marks : 37 )

- 11. (a) Lower the  $pK_a$  value, stronger is the acid. Explain.
  - (b) Comment on the following observations:  $1\frac{1}{2}\times2=3$ 
    - (i) Formic acid is stronger than acetic acid.
    - (ii) p-nitrophenol has higher melting point than o-nitrophenol.
  - (c) Define acids and bases on the basis of Bronsted-Lowry concept.
  - (d) Arrange the following in order of increasing basicity or acidity:

(i) 
$$N$$
,  $N$ ,  $CH_3-C=N^2$ 

(ii) 
$$NO_2$$
 COOH  $NO_2$  ,  $NO_2$  ,  $NO_2$  (Continued)

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OR

- 12. (a) Electrophilic substitution reactions in naphthalene occur preferentially at  $C_1$ . Explain.
  - (b) Complete the following reaction with mechanism:

- (c) Give the Diels-Alder method of preparation of anthracene from 1,4-naphthaquinone.
- (d) Suggest the products of the following reactions: 1½×2=3

(i) 
$$OH \longrightarrow ArN_2X \longrightarrow POH/Cold$$

(ii) 
$$\bigcirc$$
 OH  $\longrightarrow$  ?

(Turn Over)

**13.** (a) Assign the R- and S-configuration of the following optical isomers:

(i) COOH (ii) CHO

H—C—OH

H—C—Cl

COOH

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- (b) Draw all the possible conformers of n-butane and arrange them in increasing order of energy.
- (c) Explain the stereochemical aspect of the bromination of Z-butene-2.
- (d) Draw the chair conformers of cis-1, 3-dimethyl cyclohexane. Which one is more stable and why?

#### OR

- 14. (a) What are the different types of dienes?

  Give example in each case.
  - (b) Complete the following reaction:

$$H_2C=CH-CH=CH_2+HX$$

What happens, when the products is heated above 60 °C?

(Continued)

- (c) What are natural and synthetic rubbers? Give examples.
- (d) Write one method of preparation of Nylon-66.
- 15. (a) Write the reaction mechanism of the formation of ester from acids.
  - (b) Predict the product of the following reactions with mechanism: 2×3=6

(i) 
$$CHO$$
 +  $(C_6H_5)_3P=CH_2 \longrightarrow ?$  (by Wittig reaction)

(ii) 
$$CH_3$$
— $C$ — $CH_2CH_3 + CH_2O + (CH_3)_2NH$ — $\longrightarrow$ ? (by Mannich reaction)

(iii) 
$$CH_3$$
 +  $C_6H_5COC1 \xrightarrow{AlCl_3}$ ?

(by Friedel-Crafts reaction)

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#### OR

16. (a) Suggest a suitable mechanism for the following transformations: 2×3=6

- (b) Why is NaBH<sub>4</sub> more selective than LiAlH<sub>4</sub>? Give one application of NaBH<sub>4</sub>.
- 17. (a) How is quinoline prepared by Skraup synthesis?

(b) Predict the correct products for the following reactions with mechanism:

 $2 \times 2 = 4$ 

(i) 
$$\bigcap_{N}$$
 + CHCl<sub>3</sub> + KOH $\longrightarrow$ ?

(c) Write down three basic principles of green chemistry.

#### OR

18. (a) How will you carry out the following conversions? 1½×4=6

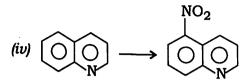
(i) 
$$\bigcirc$$
 CHO  $\longrightarrow$   $\bigcirc$  COOH

(ii) 
$$\bigcirc$$
  $\stackrel{\text{NH}_2}{\bigcirc}$   $\longrightarrow$   $\bigcirc$   $\stackrel{\text{Cl}}{\bigcirc}$ 

(iii) 
$$\bigcirc$$
 CN  $\longrightarrow$   $\bigcirc$  C—NH<sub>2</sub>

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HOOC



- (b) What do you mean by atom economy reaction? Cite an example.
- (c) What are microwave assisted reactions?

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