

[This question paper contains 7 printed pages] **Your Roll No.** 2019

Sl. No. of Q. Paper: 7392JUnique Paper Code: 32171102 - OCName of the Course: B.Sc.(Hons.)<br/>ChemistryName of the Paper: Physical Chemistry - ISemester: I

Time : 3 Hours

Maximum Marks: 75

## Instructions for Candidates:

- (i) Write your Roll No. on the top immediately on receipt of this question paper.
- (ii) Attempt **six** questions in all.

(iii) Question No. 1 is compulsory.

(iv) Use of scientific calculator is permitted.

## **Physical constants:**

R= 8.314 J K<sup>-1</sup>mol<sup>-1</sup>

R= 0.082 lit atm K<sup>-1</sup> mol<sup>-1</sup>

k= 1.38x10<sup>-23</sup>J K<sup>-1</sup>

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Explain any **five** of the following :

1.

3×5=15

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- (a) Mean free path of gas molecules increases and number of collisions per unit time decreases with lowering of temperature.
- (b) Boyle temperatures of different gases are
- different. (c) pH of pure water is 6.63 at 50°C, but it is not
- acidic. (d) On passing H<sub>2</sub>S, Cus precipitates in acidic
- medium, but CoS precipitates in alkaline medium.
- (e) A crystal cannot have fivefold axis of symmetry.
- (f) Viscosity of liquids decreases and that of with increase in gases increases temperature.
- 2. (a) Draw the compressibility factor Z vs pressure curves for different gases at room temperature and for a particular gas at different temperatures. Describe the variation in Z as a function of nature of gas 5 temperature and pressure.
  - (b) Why does the Maxwell distribution curve of a gas show a maximum ? Derive the for average velocity of a gas using Maxwell distribution expression. 3

- (c) Calculate the fraction of molecules of  $N_2$  at 1 atm pressure and 315 K, when speeds are in the range of most probable speeds  $\pm 0.006$ cm per second. 4
- 3. (a) Derive the expression for kinetic theory of gases  $pv = \frac{1}{3}mNc^2$ . Why is this theory called kinetic theory ? 5
  - (b) What is equilibrium vapour pressure ? Why does it increase with the increase in temperature ? Why is it not possible to liquefy a gas above critical temperature ? 3
  - (c) What is the mean free path  $\lambda$  for oxygen molecules at temperature T= 300 K and P=1.00 atm ? Assume that the molecular diameter d= 290 pm and the gas is ideal. 4
- 4. (a) Starting from the Vander Waals equation,
  - derive the relations  $a = \frac{27R^2T_c^2}{64P_c}, b = \frac{RT_c}{8P_c}$ . Where  $T_{c_1} P_c$  are critical temperature and critical pressure of the gas and 'a' and 'b' are Vander Waals constants. 4

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- (b) Using Vander Waal's equation find the temperature at which 3 moles of  $SO_2$  will occupy a volume of 20 liters at a pressure of 2.1 M Pa. Given a=678.88 kPa dm<sup>6</sup> mol<sup>-2</sup> and b=5.6×10<sup>-2</sup> dm<sup>3</sup> mol<sup>-1</sup>.
- (c) Using the law of equipartition of energies, estimate the  $C_v$  and  $C_p$  of  $CCl_4$  and  $CO_2$ molecules.
- 5. (a) Derive the expressions for  $[H^+]$  for dilute solutions of strong monoprotic acid and concentrated solutions of weak monoprotic acids. 6
  - (b) Calculate the pH of a  $10^{-8}$  N solution of NaOH at room temperature.
  - (c) Degree of dissociation of Acetic acid in N/32 solution is 0.0236. What will be its degree of dissociation in 0.01N solution ?
- 2 6. (a) Derive relationships for the hydrolysis constant, degree of hydrolysis and the pH of a salt of strong acid and weak base. 3
  - (b) How does a solution of a weak acid and its salts act as a buffer ? Derive the expression for the pH of such a buffer and also derive the expression for the pH of this solution when some base is added to it. 3

- How can the pH of solutions be calculated (c)before, at and after the equivalent point for the titration of strong acid with weak base? Why is Phenolphthalein not a suitable indicator for this titration ?
- (d) Calculate the pH of a solution containing 20ml 0.1N HCl and 25 ml 0.1 M NH4OH ? 2
- 7. (a) Solubility of  $BaSO_4$  at 25°C is 0.0023 g/lit. Calculate its solubility product. What will be its solubility in a solution containing 10 gm of  $(NH_4)_2SO_4$  is added to it. Molecular Weight of  $BaSO_4$  is 233 gm/mol. 4
  - (b) What are Millar indices ? Why are these preferred over the Weiss indices for the designation of planes in a crystal ? Write the Millar indices of the planes with intercepts : 6

- (c) List and describe the symmetry elements of 2 C<sub>6</sub>H<sub>6</sub>.
- 8. (a) Describe different planes in primitive, face centered and body centered cubic crystals. Compute their interplanar distances.

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<sup>(</sup>i) 1a, 3b, -1c (ii) 2a, 3b, 4c

(b) Following  $\theta$  values obtained when a cubic crystal is subjected to X rays of wave length 153.9pm. 4

θ/degree 13.70 15.89 22.75 26.91 28.25 33.15 37.00 37.60 41.95

Identify the type of cubic lattice, determine edge length and index the lines.

- (c) Why are the X rays suitable for determining the crystal structure ? 2
- 9. (a) Explain how some liquids including water rise in a capillary ? Derive the formula for the rise of a liquid in a capillary.

(b) The radius of a given capillary is 1.05×10<sup>-4</sup> m. A liquid whose density is 0.80 g/cm<sup>3</sup> rises up to a height of 6.25×10<sup>-2</sup> m, calculate the surface tension of liquid assuming the contact angle to be zero. 2

(c) Derive the formula for the coefficient of viscosity of liquid. What will happen to the viscosity of a liquid if the radius of the capillary of the viscometer used for its measurement is doubled ? 3 (d) Why does the boiling point of a liquid vary with external pressure? Derive the relation

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$$\ln \frac{p_2}{p_1} = \Delta H_{vap} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

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[This question paper contains 3 printed pages.]

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Sr. No. of Question Paper	:	8590	J
Unique Paper Code	:	32171101	JAD NU COL
Name of the Paper	:	Inorganic Chemistry	AND ARY
Name of the Course	:	B.Sc. (H) Chemistr	y LIBRON ?
Semester	:	I	Ann. New "
Duration: 3 Hours		Ν	/aximum Marks : 75

1. Write your roll number on the top immediately e on receipt of this question paper

- 2. Attempt six questions in all.
- 3. Question number one is compulsory.
- 4. The questions should be numbered in accordance with the number in the question paper.

5. Calculator and lock tables may be used.

1. Explain any five of the following

(I) Ionic radii of  $Na^+$  and  $Cu^{2+}$  ions are almost similar.

- (II) An electron moving in an orbital dose not slow down gradually.
- (III) Electron affinity of Nitrogen is lower than Oxygen.
- (IV) HF is liquid whereas HCl is a gas.
- (V)  $H_2$  is known while  $He_2$  is not.
- (VI) BeCl<sub>2</sub> has zero dipole movement while H<sub>2</sub>S has some.

(3x5=15)

- Draw radial probability distribution curve for 1s,4p,5s,4d. What are 2. (I) radial and angular wave functions?
  - Drive the Born-Lande's equation for lattice energy of a crystal lattice. (II)
  - Explain significance of Azimuthal quantum number. (6, 4, 2)
- Calculate Z\* (effective nuclear charge- Slater's rule) for 2s and 4s electrons. 3. (I)
  - During ionization of atoms having ns and (n-1)d electrons, the electron of ns (II) orbital lost first. Why?
  - Find out electron gain enthalpy using following data: (III)

(III)

Enthalpy of formation	:382 KJ mol <sup>-1</sup>	
Lattice Energy	:759 KJ mol <sup>-1</sup>	
Ionization Enthalpy	: 494 KJ mol <sup>-1</sup>	
Dissociation Energy Cl <sub>2</sub>	: 121 KJ mol <sup>-1</sup>	
Sublimation Energy (Na)	: 108 KJ mol <sup>-1</sup>	(3,3,6)

Draw molecular orbital energy level diagram of  $O_2^-$  and  $NO^+$ . Which has 4. (I) higher bond energy?

or

Draw molecular orbital energy level diagram of NO<sup>-</sup> and HCl. Which has higher bond energy?

- Using VSEPR theory give the shape of POCl<sub>3</sub>, SF<sub>6</sub>, BrF<sub>4</sub>, NH<sub>3</sub>. (II)
- What is Fajan's Rule ? Explain why lithium halides are covalent in spite of the (III) fact that Li is an alkali metal. (4X3)
- 5. (I) First ionization energy of Be is greater than Li but position is reversed in case of second ionization energy of Be and Li. Why?
  - Why P-Nitrophenol has higher boiling point than O-nitrophenol phenol? (II)
  - Write short note on following (any three) (III)

a. Londen or dispersion forces

c. HF is liquid HCl is gas

b. Diple-dipole interaction

d. Hybridization (3,3,2x3)

- 6. (I) Explain Conductivity of metals and semiconductors using band theory.
  - (II) What was the velocity of a beam of electron if they are display a de-Broglie wavelength of 100 A<sup>o</sup>
  - (III)  $\psi$  has no physical significance and  $\psi^2$  has. Explain.
  - (IV) Be and N in second period and Mg and P in third period of the periodic table have higher ionization energy than expected. Justify
  - (V) What do you understand by equivalent and non-equivalent hybrid orbital's give one example of each
  - (VI) Bond angle of  $CH_4$  is higher than  $NH_3$ . Explain. (2X6)
- 7. (I) Draw neatly labelled molecular orbital diagram of  $N_2^-$  and  $O_2^{2^+}$  with bond order and magnetic behaviour.
  - (II) Write Schrödinger equation for Hydrogen atom. Explain terms involved in it and write conditions for physical significance of the equation.
  - (III) What are Slater rules, calculate the Z\* effective nuclear charge for the valence electrons in G, Z is equal to 31. (4X3)
- 8. (I) First ionization enthalpy of Oxygen is less than that of Nitrogen. Give reason.
  - (II) Which of following is more covalent and why?

CuCl or KCl

- (III) Define electro negativity according to Mullikan Scale.
- (IV) If a solid "A<sup>+</sup>B<sup>-</sup>" has a structure similar to NaCl. Consider the radius of anion as 250 pm. Find the ideal radius of the cation in the structure. Is it possible to fit a cation C<sup>+</sup> of radius 180 pm in the tetrahedral site of the structure "A<sup>+</sup>B<sup>-</sup>"?

(3,2,2,5)

(1500)

This question paper contains 4+2 printed pages]



Duration : 3 Hours

Maximum Marks : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt six questions in all.

Question No. 1 is compulsory.

Use of scientific calculator and log tables is permitted.

1. Explain briefly, any *five* statements of the following :

- (a) An ideal gas is not expected to show any cooling on free expansion.
- (b) Addition of detergents decreases the surface tension of water.

iii

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- (c) K<sup>+</sup> ions and Cl<sup>-</sup> ions are indistinguishable by X-ray diffraction.
- (d) Identify the type of lattice planes shown in the following figures :



(e) The viscosity of gas increases with temperature while that of liquid decreases with temperature.

ii<sup>-</sup>

- (f) Can pH of an aqueous solution be less than 0 or more than 14 at 25°C ?
- (g) Phenolphthalein is not a suitable indicator for a strong acid-weak base titration.
- (a) Starting from the postulates of kinetic theory of gases, derive the Kinetic Gas Equation pV = mNû<sup>2</sup>/3, where symbols have their usual meaning.
  - (b) What is law of corresponding states ? Derive the reduced equation of state for van der Waals equation of state.

- (3)
- (c) The critical constants for water are 647 K, 22.09 MPa and 0.0566 dm<sup>3</sup> mol<sup>-1</sup>. Calculate the values of van der Waals constants a, b and R and also explain the abnormal value of R.
- (a) Write the mathematical expression for the Maxwell distribution of molecular speeds for a gas and explain briefly the terms involved. Derive the mathematical expression for the most probable speed of a gas molecule.
- (b) The mean free path of molecules in a gas increases and the number of collisions per unit time decreases with lowering of pressure if temperature is kept constant. Explain.
- (c) The average speed at  $T_1$ K and most probable speed at  $T_2$  K of CO<sub>2</sub> is 9 × 10<sup>2</sup>m s<sup>-1</sup>. Calculate the value of  $T_1$  and  $T_2$ . 5.3.4
- (a) Describe the powder diffraction method to determine crystal structure. Explain the significance of missing lines in the analysis of crystal structure using powder diffraction method.

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- (b) Evaluate the Miller indices for the planes with the following intercepts :
  - (*i*) 0a, 2b, 2c
  - (*ii*) a, 1/3b, 1/4c
  - (*iii*) -2a, 3b, 4c
- (c) Show that a 5-fold rotation axis of symmetry cannot exist in a crystal.5,3,4
- (a) How does viscosity of a liquid vary with temperature ? Give the mathematical expression of the same and define each term.
  - (b) Define surface tension of liquid and give its SI units, and describe a method for its experimental determination.
  - (c) If the flow time for the two liquids A and B through the same capillary is in the ratio of 4 : 5 and the densities in the ratio of 2 : 1. What is the ratio of their viscosities ?
  - 6. (a) Show that the concentration of  $H_3O^+$  in an aqueous solution of a monoprotic acid HA can be computed from the following expression :

$$K_{a} = \frac{[H_{3}O^{+}]^{3} - [H_{3}O^{+}]K_{w}}{[H_{3}O^{+}][HA]_{o} - [H_{3}O^{+}]^{2} + K_{w}}$$

Under what conditions can the following expressions be used :

$$K_a = \frac{[H_3O^+]^2}{[HA]_o - [H_3O^+]}$$

$$K_a = \frac{[H_3O^+]^2}{[HA]_o}$$

- (b) Define different types of buffer solutions. Derive Henderson-Hasselbalch equation for pH of acidic and basic buffer.
- (c) What is pH of a solution obtained by mixing 50 mL, 0.1M HCl with 50 mL, 0.1 M NH<sub>4</sub>OH. (Given :  $pK_b$  of NH<sub>4</sub>OH = 4.74).
- (a) Define solubility and solubility product. Express solubility product of the given salts in terms of the solubility of ions :
  - (i) PbCl, and

7.

(*ii*)  $\operatorname{Fe}_{3}(\operatorname{PO}_{4})_{2}$ 

1 . . . . . .

(b) Show that the pH of an aqueous solution of salt formed from a strong acid and weak base is given by :

$$pH = 7 - \frac{1}{2}(pK_b + \log c)$$

- (c) Will a precipitate form if equal volumes of 0.01 M AgNO<sub>3</sub> and 0.0004 M NaCl are mixed ? Given  $K_{sp}$  of AgCl =  $1.7 \times 10^{-10} M^2$ .
- 8. (a) Write the van der Waals equation in the virial form and evaluate the second virial coefficient.
  - (b) Calculate the volume occupied by 2.0 mol of  $N_2$  at 400 K and 10.1325 MPa pressure if  $p_r V_r/T_r$  is equal to 2.21.
  - (c)Calculate at 25°C the exact pH of a solution of (a) 0.001M NaOH, and (b) 10-7 M NaOH.4,4,4]

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- 9. Write short notes on any four :
  - (i) Law of equipartition of energy
  - (ii) Rotating crystal method withdulos softed
  - (iii) Theory of Acid-base indicators
  - (iv) Continuity of States
  - (v) Cleansing action of detergents.

 $4 \times 3$ 

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20 Roll No.

S. No. of Question Paper:8842-Unique Paper Code:217103Name of the Paper:Organic Chemistry-I (CHHT-102)Name of the Course:B.Sc. (H) ChemistrySemester:IDuration:3 HoursMaximum Marks:75

LIBRARY .

## Instructions for Candidates:

- Write your Roll No. on the top immediately on receipt of this question paper.
- Answer any six questions.
- Attempt all the parts and sub parts of a question together.
- Question No. 1 carries 15 marks (Question Nos. 2 to 8 carry 12 marks each).
- 1. (a) Giving reasons, arrange the following in order of increasing stability.

(b) Arrange the following in order of decreasing acidity with suitable reason.

CI-CH<sub>2</sub>-COOH CI-CH-COOH CI-COOH

(c) Give the mechanism of the following transformation.



(d) Predict the structures of major products A to F in the following reactions.

(i) 
$$Conc. H_2SO_4$$
 A  $O_3$  B

(ii)  $C \xrightarrow{Na} H_3C - C \equiv C - CH_3 \xrightarrow{H_3} D$ (iii)  $Liq. NH_3$   $H_3C - C \equiv C - CH_3$   $H_3$ 

(iii) E 
$$HBr = H_3C - CH = CH_2 = HBr = F$$
  
(iii) (3.3.3.6)

2. (a) Assign the following as aromatic/antiaromatic with suitable explanation.

(b) Assign the R/S configurations and stereochemical relationship to the following compounds.



(c) Giving reasons, arrange the following in order of increasing dipole moment.



(d) What do you mean by "optically active substance"? Assign the following compounds as optically active/inactive.



3. (a) Giving reasons, arrange the following in order of increasing rate towards aromatic electrophilic substitution reactions.

(3,3,3,3)



- (b) Describe the Hofmann-elimination reaction with suitable example.
- (c) Draw the conformations of cyclohexane and relate their energies through potential energy diagram.
- (d) Predict the structures of major products A to C in the following reactions.



(2,3,4,3)

- 4. (a) Explain the reaction and mechanism involved in the hydroboration-oxidation of 1-propene.
  - (b) Give the E/Z notation in the following compound.



- (c) Explain the mechanism of free radical halogenations of an alkane.
- (d) Predict the structures of major products in the following reactions,



5. (a) Giving reason, arrange the following in order of increasing boiling point.

$$H_{3}C-CH_{2}-CH_{2}-CH_{2}-CH_{3}$$

$$H_{3}C-CH-CH_{2}-CH_{3}$$

$$H_{3}C-CH_{2}-CH_{3}$$

$$H_{3}C-CH_{2}-CH_{3}$$

$$H_{3}C-CH_{2}-CH_{3}$$

$$H_{3}C-CH_{3}$$

(b) Classify the following into electrophiles and nucleophiles with explanation.

(b) Classify the torus  $\bigcirc$   $H_3C-C\equiv O^{\textcircled{}}$ ,  $H_3C-NH_2$ ,  $CBr_2$ ,  $CO_2$ ,  $NO_2$ ,  $NH_2$ (c) Giving reasons, arrange the following in order of increasing stability. (3.2,3,4)

CH3

(d) Predict the structures of major products A to D in the following reactions.



6. Explain the following:

(a) 1-Propyne is less reactive than 1-propene towards electrophilic addition reactions.

(b) Iodoethane is less reactive than chloroethane in Friedel-Craft's alkylation of benzene.

(c) Ethane-1,2-diol is more stable in Gauche conformation than its Anti conformation.

(3,3,3,3)

(3.3.6)

(d) Dipole moment of chloroethane is higher than chloroethene.

7. (a) Giving reasons, arrange the following in order of increasing stability.



(b) Draw the Lischer projection formulae of the following.



(c) Give the reaction and mechanism of the following:

(i) Ozonolysis of 2-butene.

(ii) Friedel-Craft's acylation of benzene.

8. Write shot notes on the following (any four).

(a) Baeyer strain theory.

(b) Markovnikov's addition to alkenes.

(c) Wurtz reaction.

(d) Optical Isomerism.

(e) Inductive and electromeric effects.

(3,3,3,3)