

**B.Sc. Part-III (Honours) Examination, 2020**

**Subject: Chemistry**

**Paper: XI**

**(New Syllabus)**

**Time: 2 Hours**

**Full Marks: 50**

*The figures in the right hand margin indicate full marks.*

*Candidates are required to give their answers in their own words as far as practicable.*

**Group A**

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

(a) (i) Predict the trend in the value of transport number of an ion in pure water, NaCl and in tetraammonium butyl bromide.

(ii) Explain why  $\text{Li}^+$  has a lower value of ionic conductivity than  $\text{Na}^+$  and why the value of conductivity for  $\text{H}^+$  is so much higher than the value for both the  $\text{Na}^+$  and  $\text{Li}^+$  ions.

(b) At  $25^\circ\text{C}$  and pH 7, a solution containing compound A and its reduced form  $\text{AH}_2$  has standard electrode potential of  $-0.6\text{ V}$ . A solution containing B and  $\text{BH}_2$  has a standard potential of  $-0.16\text{ V}$ . If a cell were constructed with these systems as half cell,

(i) Is  $\text{AH}_2$  oxidized by B or  $\text{BH}_2$  oxidized by A under standard conditions?

(ii) What is the reversible emf of the cell?

(iii) What would be the effect of pH on the equilibrium ratio  $[\text{B}][\text{AH}_2]/[\text{A}][\text{BH}_2]$ ?

(c) (i) Draw the conductometric titration curves of the following reactions:

I. Acetic acid is titrated with sodium hydroxide solution.

II. Potassium chloride solution is titrated with silver nitrate solution.

(ii) The specific conductance of  $\text{SrSO}_4$  in a saturated solution at  $25^\circ\text{C}$  is estimated to be  $1.5 \times 10^{-4}\text{ ohm}^{-1}\text{cm}^{-1}$  and that of water be  $1.5 \times 10^{-6}\text{ ohm}^{-1}\text{cm}^{-1}$ . What is the solubility of this salt at  $25^\circ\text{C}$ ?

(d) (i) The e.m.f. of a cell formed by dipping two electrodes of a metal in two solutions of its salt with concentrations of 0.1M and 0.01M was observed to be 0.0295 V at 25°C. What is the valency of the metal, if liquid junction potential has been eliminated?

(ii) Describe briefly the principle of potentiometric titration with necessary graphical representation(s).

(e) (i) Calculate the separation of the (123) planes of an orthorhombic unit cell with  $a = 0.82$  nm,  $b = 0.94$  nm and  $c = 0.75$  nm.

(ii) The dipole moment of bromobenzene is calculated to be  $5.17 \times 10^{-30}$  C·m and its polarizability volume is  $1.5 \times 10^{-29}$  m<sup>3</sup>. Estimate its relative permittivity at 25°C when its density is  $1491$  kg·m<sup>-3</sup>.

2. Answer *any one* question from the following:

**10 × 1 = 10**

(a) (i) Write down the effect of pressure, temperature and viscosity over conductivity of an electrolyte.

(ii) Show graphically the variation of equivalent conductance with  $c^{1/2}$  (where  $c$  = concentration) for the following electrolytes:

KCl, NiSO<sub>4</sub>, BaCl<sub>2</sub>, CH<sub>3</sub>COOH.

(iii) From the given values of molar conductivity at infinite dilution, calculate  $\lambda_m^\infty$  for NH<sub>4</sub>OH.

$$\lambda_m^\infty \text{ for Ba(OH)}_2 = 457.6 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}.$$

$$\lambda_m^\infty \text{ for BaCl}_2 = 240.6 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}.$$

$$\lambda_m^\infty \text{ for NH}_4\text{Cl} = 129.8 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}.$$

(b) (i) Calculate the Weiss and Miller indices of a crystal plane which cuts through the crystal axes at  $(a, 2b, 2c)$ .

(ii) An element crystallizes in a body centered cubic lattice with a cell edge of 500 pm. The

density of the element is  $7.5 \text{ g}\cdot\text{cm}^{-3}$ . How many atoms are present in 300 g of the element?

(iii) At  $25^\circ\text{C}$  and 1 atm, for the cell  $(\text{Pt})\text{H}_2 | \text{HCl}(0.1\text{M}) | \text{AgCl}-\text{Ag}$ , the e.m.f. of the cell is calculated to be 0.35252 V and the temperature co-efficient is estimated to be  $-1.8 \times 10^{-4} \text{ V}/^\circ\text{C}$ . Calculate the changes in free energy, enthalpy and entropy for the cell reaction occurring in above mentioned cell.

(iv) Write down the point group and symmetry elements that the following molecules can have:

$\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$

### Group B

3. Answer *any three* questions from the following:

**5 × 3 = 15**

(a) (i) Test whether  $f(y) = 3y^2 - 1$  is an eigenfunction of the operator ( $\hat{A}$ ):

$\hat{A} = - (1 - y^2) (d^2/dy^2) + 2y (d/dy)$ . If so, find the eigenvalue.

(ii) Find the commutator for the operators,  $x^2$  and  $d^2/dx^2$ .

(b) (i) Test whether the operator, namely,  $-i(\hbar/2\pi)(d/dx)$  is linear or not?

(ii) Calculate the probability of finding a particle in an one dimensional box in the region between  $(1/4)L$  and  $(3/4)L$  (where  $L$  = length of the box).

(c) Evaluate  $\langle x \rangle$  and  $\langle x^2 \rangle$  for the particle in an one dimensional box.

(d) (i) Explain why the rotational spectrum is observed for  $\text{ICl}$  but not for  $\text{I}_2$  or  $\text{Cl}_2$ .

(ii) The radiation absorbed by  $^{12}\text{C}^{16}\text{O}$  during a vibrational transition occurs at  $2168 \text{ cm}^{-1}$ . Calculate the force constant of the bond, assuming that  $^{12}\text{C}^{16}\text{O}$  behaves as a simple harmonic oscillator (Given:  $m(^{12}\text{C}) = 1.993 \times 10^{-26} \text{ kg}$ ,  $m(^{16}\text{O}) = 2.657 \times 10^{-26} \text{ kg}$ ).

(e) (i) Classify radiative and non-radiative transitions in the following photophysical phenomena:

Internal Conversion, Fluorescence, Phosphorescence, Intersystem Crossing.

(ii) Discuss the effects of following factors over fluorescence:

Temperature, solvent viscosity and dissolved oxygen.

4. Answer *any one* question from the following:

**10 × 1 = 10**

(a) (i) Which of the following functions is (are) an eigen function of the operator  $d^2/dx^2$ :

$kx^2$ ,  $\sin(kx)$ ,  $\exp(kx)$ ,  $\exp(ikx)$ .

(Give the eigen value(s) wherever appropriate).

(ii) A system is defined by the following wave function:

$$\psi(x) = A \cos(2\pi x/L) \text{ for } -L/4 \leq x \leq L/4.$$

Determine the normalization constant A. What is the probability that the particle will be found between  $x = 0$  and  $x = L/8$ ?

(iii) Determine whether each of the following functions is acceptable or not as a wave function over the indicated regions:

I.  $\cos x$  over  $(0, \infty)$ ; II.  $e^x$  over  $(-\infty, \infty)$ ; III.  $e^{-x}$  over  $(0, \infty)$ ; IV.  $\tan \theta$  over  $(0, 2\theta)$ .

(b) (i) Prove that the momentum operator corresponding to  $p_x$  is a Hermitian operator.

(ii) Determine the degree of degeneracy of the energy level  $21h^2/8mL^2$  of a particle in a cubical box. Write down all the possible degeneracies.

(iii) Absorption of  $H^{35}Cl$  occurs in the far infrared near wave number of  $200 \text{ cm}^{-1}$ , and the spacing between the neighbouring lines is estimated to be  $20.89 \text{ cm}^{-1}$ . Find the moment of inertia and the internuclear distance in  $H^{35}Cl$  (reduced mass of  $H^{35}Cl = 1.627 \times 10^{-27} \text{ kg}$ ).

(iv) In a photochemical experiment it is observed that  $5.78 \times 10^{-5} \text{ mol}$  of uranyl oxalate is decomposed at a wavelength of  $300 \text{ nm}$  emitted by a lamp in one hour. When acetone was irradiated with the same lamp for 10 hours, the amount of acetone decomposed was found to be  $2.32 \times 10^{-4} \text{ mol}$ . What is the quantum yield for the acetone decomposition under the same condition?

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**Group A**

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

(a) (i) The trend in the individual ionic conductivities of some alkali metal ions may be arranged as  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$  - Comment.

(ii) If a potential gradient of  $100 \text{ V} \cdot \text{cm}^{-1}$  is applied to a 0.01M solution of NaCl, what are the speeds of  $\text{Na}^+$  and  $\text{Cl}^-$  ions? (The molar ionic conductivities of  $\text{Na}^+$  and  $\text{Cl}^-$  ions are given as 50.1 and  $76.4 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ , respectively).

(b) (i) Draw the conductometric titration curves of the following reactions:

I. Acetic acid is titrated with sodium hydroxide solution.

II. Potassium chloride solution is titrated with silver nitrate solution.

(ii) The specific conductance of  $\text{SrSO}_4$  in a saturated solution at  $25^\circ\text{C}$  is estimated to be  $1.5 \times 10^{-4}$  and that of water be  $1.5 \times 10^{-6} \text{ ohm}^{-1} \text{cm}^{-1}$ . What is the solubility of this salt at  $25^\circ\text{C}$ ?

(c) How the rate constant of following reactions would vary with  $(\text{ionic strength})^{1/2}$ :

I.  $2\text{I}^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{I}_2 + 2\text{SO}_4^{2-}$ .

II. Inversion of sucrose solution.

III.  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} + \text{OH}^- \rightarrow [\text{Co}(\text{NH}_3)_5\text{OH}]^{2+} + \text{Br}^-$ .



(d) (i) The dependence of osmotic pressure ( $\pi$ ) over molar mass ( $M_r$ ) of a polymer substance may be expressed as follows:

$\pi = RT [(\rho/M_r) + B\rho^2 + D\rho^3 + \dots]$ , the terms have their usual significance. Neglecting the contribution of third term in the above expression, calculate the value of  $M_r$ . Show the graphical plot in this connection.

(ii) A polymer solution contains equal number of molecules of molecular weights  $20,000 \text{ g. mol}^{-1}$  and  $30,000 \text{ g. mol}^{-1}$ . Calculate the mass average and number average molecular weights.

(e) Give an outline for the measurement of entropy of a substance utilizing the concept of third law of thermodynamics. Show the graphical variation of  $C_P$  vs.  $\log T$  and  $C_P/T$  vs.  $T$  in this connection.

2. Answer *any one* question from the following:

**10 × 1 = 10**

(a) (i) The Arrhenius dissociation constant of propionic acid is  $1.35 \times 10^{-5}$ . Calculate the degree of dissociation and the concentration of  $\text{H}^+$  ions in a 0.005 molar solution.

(ii) Calculate the mean ionic activity coefficient of a 0.001 molal solution of (I)  $\text{Na}_2\text{SO}_4$  and (II)  $\text{K}_3\text{Fe}(\text{CN})_6$  at  $25^\circ\text{C}$ , with the help of Debye-Hückel limiting law.

(iii) The specific conductance of a salt solution of  $\text{TlBr}$  is  $2.16 \times 10^{-4} \text{ ohm}^{-1}\text{cm}^{-1}$  and that of water  $0.04 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$ . The equivalent conductance at infinite dilution is  $138.2 \text{ ohm}^{-1}\text{cm}^2$ . Find out the solubility of  $\text{TlBr}$  in g per litre at the same temperature.

(iv) Predict the sign of e.m.f. for spontaneous and non-spontaneous reactions.

(b) (i) (ii) At  $25^\circ\text{C}$  and 1 atm, for the cell  $(\text{Pt})\text{H}_2 | \text{HCl}(0.1\text{M}) | \text{AgCl}-\text{Ag}$ , the e.m.f. of the cell is calculated to be 0.35252 V and the temperature co-efficient is estimated to be  $-1.8 \times 10^{-4} \text{ V}/^\circ\text{C}$ .

Calculate the changes in free energy, enthalpy and entropy for the cell reaction occurring in above mentioned cell.

(ii) The rate of an acid catalyzed reaction may be expressed as follows:

$$dx/dt = k_H \cdot C_{H^+} + k_{OH^-} \cdot C_{OH^-}$$

(neglecting the value of  $k_{water}$ ).

Write down the expression of overall rate constant ( $k_{overall}$ ). How the expression of  $k_{overall}$  is modified when the whole experiment is performed independently in (i) appreciable acid medium and (ii) in appreciable alkaline medium. Demonstrate the plot of  $\log k$  vs. pH in each of the cases as mentioned above.

### Group B

3. Answer *any three* questions from the following:

**5 × 3 = 15**

(a) (i) Determine all the possible multiplicities for an atom in the configuration  $1s^2 2s^2 2p^2$ .

(ii) Determine the degree of degeneracy of the energy level  $21h^2/8mL^2$  of a particle in a cubical box. Write down all the possible degeneracy.

(b) (i) Test whether  $f(y) = 3y^2 - 1$  is an eigen function of the operator ( $\hat{A}$ ):

$$\hat{A} = -(1 - y^2) (d^2/dy^2) + 2y (d/dy). \text{ If so, find the eigen value.}$$

(ii) Find the commutator for the operators,  $x^2$  and  $d^2/dx^2$ .

(c) (i) Test whether the operator, namely,  $-i(h/2\pi)(d/dx)$  is linear or not?

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(ii) The radiation absorbed by  $^{12}C^{16}O$  during a vibrational transition occurs at  $2168 \text{ cm}^{-1}$ .

Calculate the force constant of the bond, assuming  $^{12}C^{16}O$  behaves as a simple harmonic

oscillator (Given:  $m(^{12}\text{C}) = 1.993 \times 10^{-26}$  kg,  $m(^{16}\text{O}) = 2.657 \times 10^{-26}$  kg).

(e) (i) Using the principle of equipartition of energy, calculate the average energy of ammonia molecule.

(ii) Write down all the possible electronic transitions in formaldehyde molecule and arrange them in increasing order of energy.

4. Answer *any one* question from the following:

**10 × 1 = 10**

(a) (i) Find out the longest wavelength of light just able to eject a least bound photo electron from copper (work function copper is 4.3 eV).

(ii) A system is defined by the following wavefunction:

$$\psi(x) = A \cos(2\pi x/L) \text{ for } -L/4 \leq x \leq L/4.$$

Determine the normalization constant A. What is the probability that the particle will be found between  $x = 0$  and  $x = L/8$ ?

(iii) Determine whether each of the following functions is acceptable or not as a wavefunction over the indicated regions:

I.  $\cos x$  over  $(0, \infty)$ ; II.  $e^x$  over  $(-\infty, \infty)$ ; III.  $e^{-x}$  over  $(0, \infty)$ ; IV.  $\tan \theta$  over  $(0, 2\theta)$ .

(iv) Prove that the momentum operator corresponding to  $p_x$  is a Hermitian operator.

(b) (i) Calculate the number of rotational and vibrational degrees of freedom in the following molecules:

Xe, HCl, CS<sub>2</sub>.

(ii) Absorption of H<sup>35</sup>Cl occurs in the far infrared near wave number of 200 cm<sup>-1</sup>, and the spacing between the neighbouring lines is estimated to be 20.89 cm<sup>-1</sup>. Find the moment of inertia and the internuclear distance in H<sup>35</sup>Cl (reduced mass of H<sup>35</sup>Cl =  $1.627 \times 10^{-27}$  kg).

(iii) In a photochemical experiment it is observed that  $5.78 \times 10^{-5}$  mol of uranyl oxalate is decomposed at a wavelength of 300 nm emitted by a lamp in one hour. When acetone was irradiated with the same lamp for 10 hours, the amount of acetone decomposed was found to be  $2.32 \times 10^{-4}$  mol. What is the quantum yield for the acetone decomposition under the same condition?

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