B.Sc.(Honours) Examination, 2019

Semester-IV (CBCS)
Chemistry (Honours)
Core Course: CC-10
(Physical Chemistry)

Time: Three Hours **Full Marks: 60**

Questions are of value as indicated in the margin.

Group-A

Answer ***any two*** questions.

1. a) Show that for a H-like atom the potential energy is given by $V(r) = -\frac{ze'^2}{r}$. Symbols have usual meaning. 2

   b) Write down the expression of energy levels for a H-like atom explaining the terms. Show that the energy expression can be written as $E_n = -\left(\frac{1}{2}\frac{e'^2}{a_0}\right)\cdot\frac{1}{n^2}$ where a_0 = Bohr radius. 2

   c) What do you mean by radial distribution function (RDF) plot? What is its significance? Derive the algebraic expression for RDF for H-like atoms. Obtain a special expression of RDF which is valid only for S-orbitals. 2+2+2+2

   d) Draw the RDF plot of ψ_{2S} orbital of hydrogen atom. Determine the locations of two maxima. Discuss the physical significance of emergence of two maxima. 1+3+2

2. a) The θ-equation for diatomic rigid rotor is given by

   $$\frac{1}{\sin\theta}\frac{d}{d\theta}\left[\sin\theta\frac{dS}{d\theta}\right]+\left(\lambda-\frac{m^2}{\sin^2\theta}\right)S=0$$

   Using suitable mathematical transformation convert above equation to the form

   $$\left(1-x^2\right)\frac{d^2S}{dx^2}-2x\frac{dS}{dx}+\left(\lambda-\frac{m^2}{1-x^2}\right)S=0.$$ 4

   b) Derive the selection rule for allowed transitions in diatomic rigid rotor when the external field is applied along z-direction. 4

   c) Discuss what do you mean by space quantization of orbital angular momentum vector. 2

   d) "The existence of zero-point energy of LHO agrees with the uncertainty principle" – Justify. 2

   e) The wave function for LHO is given by

   $$\psi_v\left(\sqrt{\beta}x\right)=\left(\frac{\beta^{1/2}}{2^v v!\sqrt{\pi}}\right)^{1/2} H_v\left(\sqrt{\beta}x\right)e^{-\beta x^2/2},\ \text{where } \beta=\frac{\sqrt{mk}}{\hbar}.$$

   Using appropriate recurrence relation and orthogonality property of Hermite polynomial show that <x> = 0. What is the physical reason behind zero value of average position? 4+2

3. a) Draw the phase diagram of a two-component system exhibiting simple eutectic behavior. 3

   b) What is the lever rule and deduce it from pressure vs composition diagram for the binary liquid mixture. 4

   c) Explain why the congruent and incongruent melting points are invariant points. 3

   d) Predict the sequence of steps that takes place when the pressure on the binary liquid mixture at constant temperature is gradually lowered. 2

   e) Show that it is not possible to separate the constituents from an azeotropic mixture following ordinary fractional distillation. 3

P.T.O.

f) What is the difference between the critical solution temperature and mutual solubility temperature? 3

4. a) Element X exists in three solid allotropic modifications, known as 1,2 and 3. In the vicinity of 1-2-3 triple point $S_{m,2} > S_{m,3} > S_{m,1}$ and $V_{m,3} > V_{m,1} > V_{m,2}$, where S and V stand for entropy and volume, respectively. Sketch an arrangement of the three two-phase equilibrium lines around the 1-2-3 triple point on a pressure-temperature diagram considering all given information. Label all the lines and axes. 4

b) Why the solid-liquid line is not almost vertical but slightly tilted? 3

c) Compute the number of components, degrees of freedom and number of phases in the following systems:

i) $Fe(S) + H_2O(g) \rightleftharpoons FeO(S) + H_2(g)$

ii) A pure substance at its critical point.

iii) A solution containing Na^+, Cl^-, Ag^+, NO_3^-, AgCl(S) and H_2O. 4.5

d) What do you mean by the terms 'binodal curve' and 'plait point'? 3

e) Draw phase diagrams of a three-component system involving water and two solid salts with an ion in common for the crystallization of pure components. 3.5

Group-B

Answer ***any two*** questions.

1. a) Define electrochemical systems with two examples. 3

b) Find an expression for change in free energy of a phase of an electrochemical system. Based on this define electrochemical potential. 3

c) Derive the phase equilibrium condition for two phases α and β in contact with a closed electrochemical system. 2

d) 2g of benzoic acid dissolved in 25g of benzene, $k_f = 4.9$ k kg mol^{-1}, produces a freezing point depression of 1.62 k. Calculate the molar mass of the benzoic acid. Compare this with the molar mass obtained from the formula of benzoic acid C_6H_5COOH and explain the result. 2+0.5+1.5

2. a) Using the cell diagram state the IUPAC conventions for the cell EMF and the reaction. 3

b) Derive an expression to calculate the freezing point depression in terms of molal concentration of solute. 5

$$2Cu^+ \rightleftharpoons Cu + Cu^{2+}$$

c) The equilibrium constant for the reaction is 3.4×10^{12} at 25°C. Calculate the standard oxidation potential for $Cu \rightarrow Cu^+ + e^-$. The standard oxidation potential for $Cu \rightarrow Cu^{2+} + 2e^-$ is – 0.337 V. 4

3. a) Symbolize the galvanic cell. Mention the significance of the symbol. 1+4

b) Using an example express EMF of a cell in terms of mean ionic activity coefficient. 3

c) Express the chemical potential of both solvent and solute in a binary mixture of dilute solution in terms of their concentrations. Do you expect this result? 1+1.5+1.5

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