

U. G. 4th Semester Examination 2022

CHEMISTRY (Honours)

Paper Code : CEMH DC-8

Physical Chemistry

[CBCS]

Full Marks : 25

Time : Two Hours

The figures in the margin indicate full marks.

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

Answer any **five** questions from the following:

1×5=5

- (a) The vapor pressure of a given liquid will decrease if
- (i) Surface area of the liquid is decreased
 - (ii) The volume of the liquid in the container is decreased
 - (iii) The volume of the vapor phase is decreased
 - (iv) The temperature is decreased
- (b) If a salt-bridge is removed between the half-cells, the voltage
- (i) Increases rapidly
 - (ii) Decreases to zero
 - (iii) Does not change
 - (iv) Fluctuates
- (c) 6.0 g of Urea was dissolved in 9.9 moles of water. If the vapor pressure of pure water is P° , the vapor pressure of the solution is
- (i) $0.10 P^\circ$
 - (ii) $1.10 P^\circ$
 - (iii) $0.90 P^\circ$
 - (iv) $0.99 P^\circ$

[P.T.O.]

(d) The triple point of carbon dioxide occurs at a temperature of -56°C and a pressure of 5.1 atm. The critical temperature of the gas is 31°C . Under which of the following conditions will carbon dioxide therefore most likely exist as a liquid

(i) -25°C and 10 atm

(ii) -56°C and 10 atm

(iii) 33°C and 10 atm

(iv) -25°C and 5.1 atm

(e) The ionic activity coefficient of Ca^{+2} and F^{-} are 0.72 and 0.28 respectively. Find the mean activity coefficient of CaF_2 .

(i) 0.3836

(ii) 0.2563

(iii) 0.1536

(iv) 0.5732

(f) At μ vs T curve correct order of slopes of solid, liquid and gas phases are

(i) $S > L > G$

(ii) $G > S > L$

(iii) $L > G > S$

(iv) $G > L > S$

(g) The correct normalized wavefunction for one of the sp^2 hybrid orbitals is

(i) $\frac{1}{3}\psi_{2s} + \frac{1}{3}\psi_{2p_x} + \frac{1}{3}\psi_{2p_y}$

(ii) $\frac{1}{\sqrt{3}}\psi_{2s} + \frac{2}{\sqrt{3}}\psi_{2p_x} + \frac{1}{\sqrt{6}}\psi_{2p_y}$

(iii) $\frac{1}{\sqrt{3}}\psi_{2s} + \frac{1}{\sqrt{2}}\psi_{2p_x} + \frac{1}{\sqrt{6}}\psi_{2p_y}$

(iv) $\frac{1}{\sqrt{3}}\psi_{2s} + \frac{2}{2\sqrt{3}}\psi_{2p_x} + \frac{1}{\sqrt{6}}\psi_{2p_y}$

(h) When the concentration of K^+ across a cell membrane drops from 0.01 M to 0.001 M, the potential difference across the membrane is

- (i) 0.0 V
- (ii) 0.0059 V
- (iii) 0.059 V
- (iv) 0.59 V

2. Answer any **four** questions: 2×4=8

- (a) For a one-component system, the triple point is invariant, whereas the freezing point is variable — explain.
- (b) Lowering of vapour pressure of a liquid does not occur when a volatile solute is dissolved in it?—Justify or criticize.
- (c) The ϕ dependent part of spherical harmonics $F(\phi)$ for a rigid rotator satisfy the following expression: $[d^2F(\phi)/d\phi^2] = -m^2$, where m is constant. From this expression, derive normalised form of $F(\phi)$.
- (d) Calculate the percent ionic character of HCl. The dipole moment and bond-distance of HCl are 1.03D and 127.5 pm respectively.
- (e) Prove that \vec{L} is conserved if $\vec{\tau}$ is equal to zero.

3. Answer any **two** questions: 2×6=12

- (a)
 - (i) Deduce thermodynamically van't Hoff equation for osmotic pressure, mentioning the assumptions involved.
 - (ii) Define radial distribution function (rdf) and give the plot corresponding to the following wave function against r/a_0 : $\psi = A(2a_0 - r)\exp(-r/2a_0)$ 3+3
- (b)
 - (i) Outline the self-consistent field (SCF) method of Hartree as applicable to the many-electron atoms. Explain how in the SCF method the multi-electron problem is effectively reduced to one-electron problem.
 - (ii) For a binary liquid mixture, assuming Duhem-Margules equation, derive Konowaloff's rule. 2+2+2
- (c)
 - (i) A potentiometer equipped with a glass-saturated calomel electrode gave a reading of 0.0232 V at 25°C for a pH 2.5 buffer. What is the pH of another buffer for which the same potentiometer reads 0.111 V.
 - (ii) Two liquids **A** and **B** form an ideal solution. At 60°C, the vapour pressure of a solution consisting of 2 mole of **A** and 3 mole of **B** is 280 mm Hg. On addition of further one mole of **A** to this solution at same temperature, the vapour pressure rises to 300 mm of Hg. Calculate the vapour pressure of pure **A** and pure **B**.

[P.T.O.]

- (iii) Prove that $[\widehat{L}_x, \widehat{L}_y] = i\hbar\widehat{L}_z$ 2+2+2
- (d) (i) Removal of Water from a mixture by “freeze drying” involves cooling below 0°C, reduction of pressure below the triple point, and subsequent warming. How do you explain.
- (ii) Explain on which factors does Orientation Polarizability depend and how.
- (iii) Camphor has the molecular weight 152.23 and density 0.99 g cm⁻¹ between 0°C and 100° C. The dielectric constant of camphor at 0°C and 60°C are 12.5 and 10.0 respectively. Find out the polarizability and dipole moment of the molecule. 2+2+2
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