2023

(May/June)

CHEMISTRY

(Honours)

(Physical Chemistry—VI)

(Chem–H–603)

Marks : 38

Time : 2 hours

The figures in the margin indicate full marks for the questions

1. *(a)* Derive the following Maxwell relations starting from relevant thermodynamic equations : 2×2=4

(i) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

(ii) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

(b) Write notes on the following : 2×3=6

(i) Partial molar quantities

(ii) Residual entropy

(iii) Thermodynamic scale of temperature

OR

2. *(a)* State the third law of thermodynamics and explain its application in determining the entropy. 2+3=5

(b) What do you understand by chemical potential? Derive an expression, showing the variation of chemical potential with temperature and pressure. 1+2+2=5

3. *(a)* Explain the following phenomena in the presence of strong electrolytes : 3+2=5

(i) Relaxation effect

(ii) Electrophoretic effect

(b) For a cell reaction

$$Cd(s) + 2Ag^{+}(aq) \rightarrow Cd^{2+}(aq) + 2Ag(s)$$

the EMF of the cell is 0·6753 V at 25 °C and 0·6915 V at 0 °C. Calculate ΔG, ΔH and ΔS of the cell at 25 °C. (Given, $F = 96500$ C mol^{-1}) 1+2+2=5

OR

4. *(a)* Define activity and activity coefficient. 1½+1½=3

(b) Discuss the application of quinhydrone electrode in the determination of pH of a solution. 4

(c) What do you understand by the ionic strength of a solution? Calculate the ionic strength of a solution containing equal volume of 0·1 *M* $CaCl_2$ solution and 0·01 *M* NaCl solution. 1+2=3

5. *(a)* Write down the mathematical expression of Planck's radiation law in terms of wavelength and show the conditions under which it reduces to Wein's relation and Rayleigh-Jeans relation. 2+2+2=6

(b) A particle is confined within a box of width 1.00×10^{-14} m. Calculate its energy in the ground state and first-excited state in eV.

(1 eV= 1.602×10^{-19} J) 3

OR

6. *(a)* Write a short note on Einstein's explanation of temperature variation of heat capacities of monatomic solids. 5

(b) Mention the physical significances of the quantum numbers n, l and m. 4

7. *(a)* Explain thermodynamic probability of a system. Give the condition for thermodynamic probability to be maximum. 3+2=5

(b) Obtain the barometric distribution formula from the Boltzmann distribution expression. 2

(c) Calculate the number density for oxygen molecule at an altitude of 8 km above sea level at 25 °C ($g = 9 \cdot 8$ m/s^2). 2

OR

8. (a) What do you understand by partition function? Show that the total molecular partition function (Q) is the product of individual partition functions. 5

(b) Calculate the translational partition function of NO molecule at 300 K in a volume of 1000 m^3, assuming the gas to behave ideally. Given

$$k = 1 \cdot 38 \times 10^{-16} \text{ g cm}^2 \text{ s}^{-2}$$

$$h = 6 \cdot 625 \times 10^{-27} \text{ g cm}^{-2} \text{ s}^{-1}$$ 4

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