B. Sc. CHEMISTRY EXAMINATION, 2024

(3rd Semester)

CHEMISTRY (CORE)

PAPER : CORE/CHEM/TH/07

Time : *Two Hours* *Full Marks* : 40

(*20 marks for each Unit*)

Use separate answer scripts for each Unit.

UNIT—3071 – P

Answer any four questions : **5×4**

1. Justify or criticize the following statements : 1×5

(a) Effect of pressure on boiling point and melting point of water is positive.

(b) For spontaneous changes, entropy change of the system is always positive.

(c) Effect of temperature on the magnitude of dimerization constant is always negative.

(d) Efficiency of *Carnot Heat Engine* and Coefficient of Performance of *Carnot Refrigerator* is always less than one.

(e) Internal energy change for isothermal expansion of *n mol van der Waals* gas is always positive.

2. A reversible *Carnot Refrigerator* operating between 0 and 25 ºC runs for 2 min using 0·5 hp electric motor. Find *(a)* the coefficient of performance (Ψ) of the refrigerator, *(b)* the amount of heat (in J) extracted from water, kept inside at 0 ºC and *(c)* the mass of ice produced.

Given : 1 hp = 746 W *& Enthalpy* of fusion of ice at 0 ºC and 1 atm is 80 cal g^{-1}. 1+2+2

3. *(a)* Mention factor(s) influences and does not influence the *Carnot efficiency*.

(b) Calculate ΔG when temperature of 2·0 mol of $N_2(g)$ increases from 298 to 348 K at constant pressure of 2 bar. Given : $S_m(\text{J K}^{-1}\text{ mol}^{-1}) = A + B\ln(T/K)$ for $N_2(g)$ where A = 25·1 and B = 29·3 in SI unit and both are independent of temperature. 2+3

4. Derive $\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n}$ and using this relation, show that for isothermal change of '$\underline{n}$' mol ideal gas from V_1 to V_2, the entropy change, $\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$. 3+2

11. For a particle of mass m moving freely in a cubic box of length l, explain the effect of distortion of the box along x-axis on the degeneracy of the level having energy value = $\frac{6h^2}{8ml^2}$. 3

12. Draw sketches showing the planes having Miller indices (011) and (002).

(OR)

The characteristic K_α lines for Cr, Fe and Ni have wavelengths of 2·29 Å, 1·94 Å and 1·66 Å respectively. Which of these may be used to determine a lattice spacing of 0·97 Å? 1½

13. Both NaCl and KCl crystallizes in fcc structure; but NaCl is fcc to X-ray, while KCl is simple cubic to X-ray. Clarify. 2½

14. What is the law of rational indices?

(OR)

What is the highest order (n) that can be observed in Bragg's reflection from a solid by X-ray of wavelength 'λ'? 1½

★ ★ ★

5. Derive *Clausius-Clapeyron equation* for ***liquid*** $\rightleftharpoons$ ***vapor*** equilibrium and *Trouton's Rule* from it, mentioning all assumption(s) and approximation(s). 3+2

6. *(a)* The molar work function (A_m) of a gas is expressed as :

$A_m = -\left(\frac{a}{V_m}\right) - RT\ln(V_m - b) + f(T)$; where a and b are constants. Obtain the expression of pressure of this gas.

(b) Derive : $\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_{P,n} = -\frac{H}{T^2}$; where each symbol bears usual meaning. 2+3

UNIT—3072 – P

Answer all questions :

7. Arrive at the Stefan-Boltzmann law from the Planck's equation of black-body radiation. 3

8. Examine whether the following are acceptable wave functions or not :

(a) $\cos^{-1} x\ [-1 \le x \le 1]$;

(b) $1/x\ [0 \le x \le \infty]$

(OR)

When lithium is irradiated with light, the kinetic energy of the ejected electrons is $2{\cdot}935 \times 10^{-19}$ J for λ = 300 nm and $1{\cdot}280 \times 10^{-19}$ J for λ = 400 nm. Calculate the Planck's constant. 2

9. Evaluate the commutator $\left[\frac{d^2}{dx^2} - x, \frac{d}{dx} + x^2\right]$.

(OR)

Check whether the set of functions, $\phi_m = \frac{1}{\sqrt{2\pi}}\exp(im\phi)$ where $m = 0, \pm 1, \pm 2, \ldots$ and $0 \le \phi \le 2\pi$, will form an orthonormal set or not. 3

10. Consider a particle with quantum number n, moving in a one-dimensional box of length l. Determine *(a)* the probability of finding the particle in the left quarter of the box and *(b)* the value of n for which this probability will be maximum. 2½+1

(OR)

The general structure of a porphyrin molecule is shown on the right side. The molecule is planar and one can approximate that the π electrons are confined inside a square box of perimeter 4000 pm. Calculate the wavelength of radiation absorbed corresponding to the lowest energy absorption of the molecule. 3½