

EX/SC/CHEM/UG/CORE/TH/07/2024

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.

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(2)

- (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 °C 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 °C and (c) the mass of ice produced.

Given : 1 hp = 746 W & *Enthalpy* of fusion of ice at 0 °C 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 N₂(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 N₂(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 ' 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

(5)

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

★ ★ ★

(3)

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

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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) $\cos^{-1} x$ [$-1 \leq x \leq 1$];

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

(OR)

When lithium is irradiated with light, the kinetic energy of the ejected electrons is 2.935×10^{-19} J for $\lambda = 300$ nm and 1.280×10^{-19} J for $\lambda = 400$ nm. Calculate the Planck's constant. 2

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(4)

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

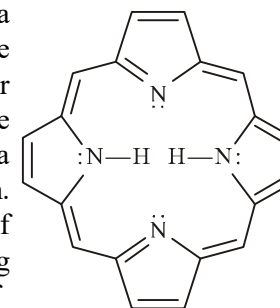
(OR)

Check whether the set of functions, $\phi_m = \frac{1}{\sqrt{2\pi}} \exp(im\phi)$ where $m = 0, \pm 1, \pm 2, \dots$ and $0 \leq \phi \leq 2\pi$, 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



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