

INTER B. SC. EXAMINATION, 2017

(1st Semester)

CHEMISTRY (HONOURS)

PAPER - V

PHYSICAL CHEMISTRY

Time : Two hours

Full Marks : 50

Use separate answerscript for each Group

GROUP - A

Answer any five questions

1. Write down, whether following statements are correct or incorrect.
 - a) Effect of pressure on boiling point and melting point of any substance is always positive.
 - b) For a mixture system, partial molar Gibbs free energy is component specific property whereas *Gibbs free energy* is system specific one.
 - c) Increase of temperature decreases the *pH* of pure water and it becomes acidic. As we know, the *pH* of pure water is 7.0 at 25 °C.
 - 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. 1×5

2. A reversible *Carnot Refrigerator* operating between 0 and 25 °C runs for 2 minute using 0.5 *hp* electrical motor. Find
 - i) the coefficient of performance (ψ) of the refrigerator,
 - ii) the amount of heat (in *J*) extracted from water, kept inside at 0 °C and
 - iii) 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 (*J K⁻¹ 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. For vaporization of 2 *mol* liquid water into its vapor at 100 °C and 1 *atm* pressure, find *W*, ΔU , ΔG , ΔS and ΔA . Given: normal boiling point of liquid water is 100 °C. 5

5. 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 , *entropy* change, $\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$. 3+2

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

7.
 - a) Explain with reason/s, effect of pressure on *Gibbs free energy* is positive but of temperature is negative.
 - b) K_p of a gas phase chemical is pressure independent but its K_x is pressure dependent, in general. Explain with reason/s. 2+3

8.
 - a) What's the final outcome of '*Nernst Heat Theorem*'?
 - b) State '*The third law of thermodynamics*' and what is the final conclusion of the process, '*Adiabatic demagnetization*'? 2+3

[Turn over

Group B

9. (a) What do you understand by the advancement of a chemical reaction? 1 $\frac{1}{2}$
- (b) Discuss in brief van't Hoff's differential method to determine the order of a reaction. 3
- (c) From the following data find the value of rate constant for the decomposition of H_2O_2 assuming a first order reaction. 3

Time (min)	0	10	20
v (mL)	22.8	13.8	8.2

Where, v = volume of KMnO_4 required for a definite volume of H_2O_2 solution.

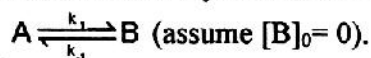
- (d) Calculate half life for the decomposition of N_2O_5 at 298 K and the fraction decomposed after 8 h (Given $k = 3.38 \times 10^{-5} \text{ s}^{-1}$). 2 $\frac{1}{2}$
- OR**
- A reaction is 25% completed in 25 minute. If it follows a first order kinetics, what would be the concentration at the end of another 50 minute? The initial concentration is $2 \times 10^4 \text{ mol L}^{-1}$.

10. (a) Consider the following mechanism for the thermal decomposition of acetaldehyde: 4
- $$\text{CH}_3\text{CHO} \xrightarrow{k_1} \cdot\text{CH}_3 + \cdot\text{CHO}$$
- $$\cdot\text{CH}_3 + \text{CH}_3\text{CHO} \xrightarrow{k_2} \text{CH}_4 + \cdot\text{CH}_2\text{CHO}$$
- $$\cdot\text{CH}_2\text{CHO} \xrightarrow{k_3} \cdot\text{CH}_3 + \text{CO}$$
- $$\cdot\text{CH}_3 + \cdot\text{CH}_3 \xrightarrow{k_4} \text{CH}_3\text{CH}_3$$

Show that the rate of formation of methane is 3/2 order with respect to acetaldehyde. What is the chain length of the reaction?

OR

Show how can you find the individual rate constants for the reversible first order reaction



- (b) Explain what will happen to rate of the reaction $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} + \text{Hg}^{2+} \rightarrow \text{Products}$ as the ionic strength of the solution is increased? 3
- (c) Justify on the basis of Lindemann mechanism the condition when unimolecular reactions will follow a second order kinetics. 3
11. (a) Starting from the Michaelis-Menten equation (derivation not required) for an enzyme catalyzed reaction, show how the Michaelis constant can be determined using Eadie's method. 2 $\frac{1}{2}$
- OR**
- What is a chain reaction? Under what condition(s) can there be explosion?
- (b) What are the requirements of chemical oscillations? 2 $\frac{1}{2}$
- OR**
- How does the polarity of a solvent affect the rate of a reaction?