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 N_2 (*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 N_2 (*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

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 $k= 3.38\times10^{-5}\ s^{-1}$). $2\frac{1}{2}$

OR

A reaction is 25% completed in 25minute. If it follows a first order kinetics, what would be the concentration at the end of another 50 minute? The initial concentration is 2×10^{4} mol L^{-1}.

10. (a) Consider the following mechanism for the thermal decomposition of acetaldehyde: 4

$$CH_3CHO \xrightarrow{k_1} {}^{\cdot}CH_3 + {}^{\cdot}CHO$$

$${}^{\cdot}CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + {}^{\cdot}CH_2CHO$$

$${}^{\cdot}CH_2CHO \xrightarrow{k_3} {}^{\cdot}CH_3 + CO$$

$${}^{\cdot}CH_3 + {}^{\cdot}CH_3 \xrightarrow{k_4} CH_3CH_3$$

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 $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$ (assume $[B]_0= 0$).

(b) Explain what will happen to rate of the reaction $[Co(NH_3)_5Br]^{2+} + Hg^{2+} \rightarrow$ 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?