B. Sc. Chemistry Examination, 2023

(1st Year, 2nd Semester)

CHEMISTRY (CORE)

Paper: Core/Chem/Th/04

Time : Two Hours Full Marks : 40

(20 marks for each unit)

Use a separate answer script for each unit.

UNIT - 2041-P

1. Answer any ***three*** :

   a) Mention the correct and incorrect statement of the following.

      i) Algebraic summation of heat involvement (dq) and work involvement (dw) of any process is perfect differential.

      ii) Work involved for any adiabatic process is imperfect differential.

      iii) Ideal gas can't have critical (T_c), Boyle (T_B) and inversion (T_i) temperatures.

      iv) For closed system and for ideal gas, H=f(T) only.

      v) Joule-Thomson expansion leads always lowering of temperature.

      vi) For a reaction, ΔH is always greater than its ΔU.

      vii) C_V is independent of T for ideal gas.

viii) Enthalpy of diamond is assigned zero, by convention, at 1 bar and 298 K.

b) i) State and explain of *Zeroth law of thermodynamics*.

ii) Bodies A & B are in thermal contact. Are temperatures of A & B same? Are enthalpies of A & B same? Give your answer with justification. 2+2

c) 2 mol ideal gas has been expanded from 10.0 to 20.0 L at constant 27 °C (i) reversibility and (ii) against a constant final pressure. Calculate work involved (in SI unit) for each case and comment on your findings. 4

d) i) Define *enthalpy of formation* and *combustion* of liquid benzene with appropriate chemical equation.

ii) *Enthalpy of neutralization of any strong acid and any strong base are always same.* –Justify. 2+2

e) The $\Delta_r H^\circ$ for the reaction: $A_2(g) + 2B_2(g) = 2AB_2(g)$; is 425 kJ mol^{-i} at 300 K. Find its value at 310 K. Given:

$C^o_{p,m}(A_2, g) = 32.0 + 1.04 \times 10^{-2}(T/K)$,

$C^o_{p,m}(B_2, g) = 45.2 + 2.06 \times 10^{-2}(T/K)$ and

b) For the consecutive first order reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ the values of k_1 and k_2 are 45 h^{-1} respectively. (i) How much time will be required for the concentration of B to reach maximum? (ii) What will be the maximum concentration of B if the initial concentration of A is 1 and L^{-1}? 3+2

6. a) The reaction $2NO + O_2 \xrightarrow{k} 2NO_2$, the rate constant k is observed to decrease with increase in temperature. Is it violation of the Arrhenius equation? Justify your answer.

b) For a complex reaction the experimental rate constant is $k = [k_1 k_2 k_3 / k_4]^{\frac{1}{2}}$, where k_1, k_2, k_3 and k_4 are the rate constants of the elementary steps in the mechanism with respective activation energies E_1, E_2 and E_4. Write down the expression of overall activation energy in terms of E_1, E_2, E_3 and E_4. 3+2

7. a) 'A unimolecular gaseous reaction shows second order kinetics at low pressure' : Explain with Lindermann mechanism.

b) Predict the effect of increase of ionic strength on the rate constant for each of the following reactions:

i) $Pt(NH_3)_2Cl_2 + OH^- \rightarrow$ Product

ii) $[Pr(NH_3)_3Cl]^+ + NO_2^- \rightarrow$ Product 3+2

$C^{o}_{p,m}(AB_2, g) = 61.2 + 2.58\times10^{-2}(T/K)$

(all in J K^{-1} $mole^{-1}$) 4

2. Answer any **two** :

a) Justify or criticize the following statements with reasons.

i) Magnitude of capillary rise for a given wetting liquid depends on temperature only.

ii) Viscosity coefficient of a given liquid is dependent on its density at constant. 2+2

b) Derive the *Laplace equation* for a perfectly spherical liquid drop and interpret. Which one is more stable drop of smaller size or larger size? And why? 4

c) Surface tension of water at 293 K is 72.75×10^{-3} Nm^{-1}. Calculate rise of column in a glass tube of radius of 0.005 cm. Assume density of water at 293 K is 1.0 g cm^{-3} and '*g*' at the place of experiment is 980 cm s^{-2}. 4

UNIT - 2042-P

Answer any four questions:

3. a) Find the time required for the decomposition of $\frac{n}{n-1}$th fraction of the initial amount of A undergoing the first order reaction A→product.

b) For the thermal decomposition of acetaldehyde into methane and carbon monoxide the proposed mechanism is

$$CH_3CHO \xrightarrow{k_1} \bullet CH_3 + \bullet CHO$$

$$\bullet CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + \bullet CH_2CHO$$

$$\bullet CH_2CHO \xrightarrow{k_3} \bullet CH_3 + CO$$

$$\bullet CH_3 + \bullet CH_3 \xrightarrow{k_4} CH_3CH_3$$

Show that the order of formation of methane is $1\frac{1}{2}$. 2+3

4. a) Show that the enzyme catalyzed reaction is first order and zero order with respect to the substrate at low and high concentration of substrate respectively.

b) For enzyme catalyzed reaction, in Eadie plot, the y-axis intercept is 1.0532×10^{-2} min^{-1} and the x-axis intercept is 13.463×10^{-6} mol $L^{-1}min^{-1}$. Find Michaelis-Menten constant and also the turn over number if the initial concentratin of the enzyme is 4×10^{-6} mol L^{-1}. 2+3

5. a) For the reversible (first order opposed by first order) reaction $A \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} B$ derive the integrated rate equation $\ln\frac{x_e}{x_e - x} = (k_1 + k_{-1})t$ where x = concentration of B at any time t and x_e = equilibrium concentration of B.