

**B. Sc. (CHEMISTRY) EXAMINATION, 2022**

( 1st Year, 2nd Semester )

**CHEMISTRY (CORE)****PAPER – 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 four* questions:

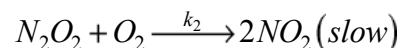
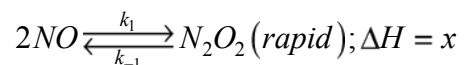
- a) i) Test the cyclic rules for  $\left(P + \frac{a}{v^2}\right)v = RT$ , where the terms bear usual significances.
- ii) Prove that the work done in isothermal reversible expansion is greater than that in irreversible expansion for a given change of state. 2+3
- b) Using the thermodynamic equation of state:  $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$ , prove that  $C_p - C_v = \frac{Tv\alpha^2}{\beta}$ , where the terms bear usual significances. 5
- c) i) Prove that the Joule Thomson co-efficient,  $\mu_{JT} = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T$ .

Explain why  $\mu_{JT}$  is zero for an ideal gas.

[ Turn over

- b) A sample of milk kept at 27°C is found to sour 40 times as rapidly as when it is kept at 4°C. Estimate the activation energy for the souring process. 3+2

5. The reaction  $2NO + O_2 \rightarrow 2NO_2$  proceeds through the following elementary steps:



Derive the differential rate expression and mention the overall order of the reaction. What can be said about the sign of  $x$  if the overall rate constant is found to decrease as temperature increases? 3+2

6. a) Predict the effect of increase of ionic strength on the rate constant for each of the following reactions:
- i)  $S_2O_8^{2-} + I^- \rightarrow \text{Product}$
- ii)  $C_{12}H_{22}O_{11} + OH^- \rightarrow \text{Product}$
- b) Calculate  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for the second order reaction  $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$  at 500 K. Given  $A = 2.0 \times 10^9 s^{-1}$  and the energy of activation is 111 kJ mol<sup>-1</sup>. 2+3

[ 2 ]

- ii) 2 moles of an ideal monatomic gas ( $\gamma = 1.67$ ) at 300 K and  $10.13 \times 10^5 \text{ Nm}^{-2}$  is allowed to expand to  $1.013 \times 10^5 \text{ Nm}^{-2}$  by a reversible adiabatic process. Calculate the final temperature,  $\Delta u$  and  $\Delta H$ . (2+1)+2
- d) i) Justify the statement with necessary derivation – “The formation and maintenance of smaller bubbles will need greater values of excess pressure than the larger ones”
- ii) Calculate the enthalpy change for the reaction:  $2\text{H}_2(\text{g}) + \text{C}_2\text{H}_2(\text{g}) = \text{C}_2\text{H}_6(\text{g})$ , if the bond energies are:  
 $\epsilon_{\text{H-H}} = 433 \text{ kJ mol}^{-1}$ ,  $\epsilon_{\text{C-C}} = 336 \text{ kJ mol}^{-1}$   
 $\epsilon_{\text{C=C}} = 812 \text{ kJ mol}^{-1}$  and  $\epsilon_{\text{C-H}} = 416 \text{ kJ mol}^{-1}$   
 3+2
- e) For laminar flow of a liquid, prove that the coefficient of viscosity of the liquid,  $\eta = \frac{\pi PR^4}{8l(dv/dt)}$ , where the terms bear usual significances. 5

**UNIT: 2042-P**

Answer *any four* questions.

2. a) Draw the following plots and state the values of the slope and the intercept for each
- i)  $\log(\text{rate})$  versus  $\log(\text{concentration of reactant})$  for an n-th order reaction.

[ 3 ]

- ii)  $\log(\text{initial rate})$  versus  $\log(\text{substrate concentration})$  at low substrate concentration for an enzyme catalyzed reaction.
- b) The reaction  $\text{A} \rightarrow \text{Products}$  is “3/2” order with respect to A. Deduce the integrated rate law. Find the expression of half-life period. 2+3
3. a) At what value of  $K_M$  does the rate of an enzyme catalyzed reaction obeying Michaelis-Menten kinetics become one-eighth of its maximum value?
- b) The slope and intercept of the plot of  $1/r$  versus  $1/[\text{S}]$  are  $3.5 \times 10^2 \text{ s}$  and  $5 \times 10^4 \text{ mol}^{-1}\text{Ls}$  respectively, where  $r$  and  $[\text{S}]$  are the rate and substrate concentration of an enzyme catalyzed reaction obeying Michaelis-Menten kinetics. Estimate the Michaelis constant ( $K_M$ ) and turn over number when the initial enzyme concentration is  $2.5 \times 10^{-9} \text{ molL}^{-1}$ . 2+3
4. a) The hydrolysis of a substance is simultaneously catalyzed by  $\text{H}^+$  and  $\text{OH}^-$  ions. The reaction is first order with respect to all the species. Write down the expression of the rate constant and hence show that the rate is minimum when  $[\text{H}^+] = \left[ \frac{k_{\text{OH}^-}}{k_{\text{H}^+}} \cdot K_w \right]^{\frac{1}{2}}$ ; the terms have their usual significances.

[ Turn over