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:

$$2NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2\,(rapid);\ \Delta H = x$$

$$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2\,(slow)$$

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) $S_2O_8^{2-} + I^- \rightarrow$ Product

ii) $C_{12}H_{22}O_{11} + OH^- \rightarrow$ Product

b) Calculate $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ 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^{-1}. 2+3

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 μ_{JT} is zero for an ideal gas.

ii) 2 moles of an ideal monatomic gas ($r = 1{\cdot}67$) at 300 K and $10{\cdot}13\times10^5$ Nm^{-2} is allowed to expand to $1{\cdot}013\times10^5$ Nm^{-2} by a reversible adiabatic process. Calculate the final temperature, Δu and ΔH. (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: $2H_2(g)+C_2H_2(g)=C_2H_6(g)$, if the bond energies are:

$\in_{H-H}= 433$ kJ mol^{-1}, $\in_{C-C}= 336$ kJ mol^{-1}

$\in_{C\equiv C}= 812$ kJ mol^{-1} and $\in_{C-H}= 416$ kJ mol^{-1}

3+2

e) For laminar flow of a liquid, prove that the co-efficient 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 (rate) versus log (concentration of reactant) for an n-th order reaction.

ii) log (initial rate) versus log(substrate concentration) at low substrate concentration for an enzyme catalyzed reaction.

b) The reaction A $\rightarrow$ 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 l/r versus l/[S] are 3.5×10^2 s and 5×10^4 $mol^{-1}Ls$ respectively, where r and [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 2.5×10^{-9} $molL^{-1}$. 2+3

4. a) The hydrolysis of a substance is simultaneously catalyzed by H^+ and 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 $[H^+]=\left[\frac{k_{OH^-}}{k_{H^+}}\cdot K_w\right]^{\frac{1}{2}}$; the terms have their usual significances.