ii) Write down the expression of heat capacity of mono-atomic solid according to Einstein model and find the values of limiting heat capacity as $T \to \infty$. 3+2

M. Sc. (Chemistry) Examination, 2022

(2nd Semester, CBCS)

Physical Chemistry

Paper – VIII

Time : Two hours Full Marks : 40

Use a separate answer script for each Unit.

UNIT – 2081

Answer ***all*** the questions.

1. Justify and draw a perspective view of the potential energy surface together with its potential energy contour diagram for the reaction: $A + BC \to AB + C$ that proceeds through the formation of a linear activated complex. 6
2. Derive the conventional transition state theory equation for the rate constant of a bimolecular elementary reaction by treating the motion through the col as a translational motion. 5
3. What are the Hammett's relationships? Prove that there is a linear relationship between the Gibbs energies of activation for one homologous series of reactions and those for another. 2+4=6
4. Discuss in brief the various indicators of "quantum mechanical tunneling" in primary kinetic isotope effect.

Or

Mention in brief the operational principle of relaxation methods to study the kinetics of fast reactions. 3

UNIT – 2082

5. Answer ***any four*** questions.

a) Show that the equilibrium distribution of particles following the Bose-Einstein Statistics is given by $n_i = \frac{g_i}{e^{\alpha} e^{\beta \varepsilon i} - 1}$, where α, β are constants and other terms have their usual significances. Also show that for a system in which $\frac{g_i}{n_i} \gg 1$, the equilibrium distribution can be computed by using Boltzmann distribution law. 3+2

b) i) Find the number of phase cells in a given energy range (0 to E) of harmonic oscillator having fundamental frequency of oscillation ν.

ii) Calculate the rotational partition for HCl at 27°C. The rotational constant of HCl is 10.59 cm^{-1}. 3+2

c) i) Show that the entropy of a system involving indistinguishable particles is given by $S = Nk_b \left[\ln\left(\frac{q}{N}\right) + T\left(\frac{\partial \ln q}{\partial T}\right)_V + 1 \right]$; the terms have their usual significance.

ii) Calculate the characteristic vibrational temperature of Cl_2 molecule. Given fundamental frequency of oscillation of Cl_2 = 561.1 cm^{-1}. 3+2

d) i) Derive Langmuir adsorption isotherm using statistical mechanical approach.

ii) Evaluate thermal de Broglie wavelength and translation partition function for hydrogen atom at 300 K kept in volume 22.414 dm^3. 4+1

e) i) If the root mean square deviation in energy is defined as $\left(\overline{(\Delta E)^2}\right)^{\frac{1}{2}} = \left[\overline{E^2} - \bar{E}^2\right]^{\frac{1}{2}}$ show that $\overline{(\Delta E)^2} = \frac{1}{z}\left(\frac{\partial^2 z}{\partial \beta^2}\right) - \frac{1}{z^2}\left(\frac{\partial z}{\partial \beta}\right)^2$, where Z is the partition function and $\beta = 1/k_b T$.

ii) Consider that argon gas is adsorbed on a solid according to Langmuir adsorption isotherm at 200 K. If U_0 is 1500 cal mol^{-1} and $\nu_x = \nu_y = \nu_z = 5x10^{12} s^{-1}$. Calculate the surface coverage when pressure (P) of the gas is 1 atm. 3+2

f) i) Find the expression of equilibrium constant of the gas phase reaction: $A + B \rightleftarrows C$ in terms of relevant partition function.