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

ii) Calculate the characteristic vibrational temperature of N_2 molecule. The fundamental frequency of oscillation of N_2 molecule is $2357.6\ cm^{-1}$. 4+1

e) i) Find the fractional fluctuation of energy in a canonical ensemble.

ii) For harmonic oscillator;

$$\left[\overline{(\Delta E)^2}\right]^{\frac{1}{2}} = \frac{h\nu \exp\left(-h\nu/2k_bT\right)}{1-\exp\left(-h\nu/k_bT\right)};$$

Show that at absolute zero $\left[\overline{(\Delta E)^2}\right]^{\frac{1}{2}} = 0$ and at high temperature $\left[\overline{(\Delta E)^2}\right]^{\frac{1}{2}} = k_bT$. The terms have their usual significance. 3+2

Ex/SC/CHEM/PG/CORE/TH/VIII/2023

M. Sc. (Chemistry) Examination, 2023

(2nd Semester)

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. What do you understand by a potential energy surface? Draw a potential energy contour diagram of such a surface for a reaction $A + BC \rightarrow AB + C$ that proceeds through the formation of a linear activated complex and explain all the important features of it. $1\frac{1}{2}+4\frac{1}{2}$

Or

What is meant by the kinetic isotope effects? Draw the possible potential-energy profiles for reactions of the type

$$RH + R' \rightarrow R + HR'$$
$$RD + R' \rightarrow R + DR'$$

based on the semiclassical treatment (in the absence of quantum-mechanical tunneling). Find out an approximate value for the semiclassical ratio of the rate constants and compare them (consider the energy values of C—H bonds). $1\frac{1}{2}+2+2\frac{1}{2}$

2. Derive the conventional transition state theory (CTST) equation for the rate constant of a bimolecular elementary reaction by treating the motion through the col as a very loose vibration. 6

Or

Apply CTST to the reaction between two atoms, $A+B \rightleftharpoons AB^{\neq} \rightarrow$ Products, and hence show that the expression of the rate constant (in molar unit) is identical with the one obtained directly from the simple hard sphere collision theory. 6

3. Consider the "double-sphere" model for a reaction between two ions, of charges Z_Ae and Z_Be, in a medium of dielectric constant ε, and hence prove that the logarithm of rate constant varies linearly with the reciprocal of the dielectric constant. 5

4. Based on the CTST, show that the temperature dependency of the rate constant of trimolecular reaction $2NO + Cl_2 \rightarrow 2NOCl$ can be approximately given by $k \propto T^{3.5} e^{-E_0/RT}$. 3

Or

Mention in brief the operational principle of flow techniques 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 Fermi-Dirac 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 significance. 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.

b) i) Show that the phase space available to 1-D SHO having energy between E to $E + \partial E$ is $\partial A = 2\pi \sqrt{m/k}\,\partial E$. Here A = phase space available to the oscillator having energy between 0 to E, m=mass and k=force constant.

ii) Calculate the characteristic rotational temperature for N_2 molecule. The internuclear distance of N_2 is 109.76 pm. 3+2

c) i) Derive Sackur-Tetrode equation.

ii) Calculate translational contributions to molar entropy and molar Gibbs free energy for helium at 25°C. 3+2

[Turn over