

[4]

- d) i) Derive Langmuir adsorption isotherm using statistical mechanical approach.
- ii) Calculate the characteristic vibrational temperature of N₂ molecule. The fundamental frequency of oscillation of N₂ molecule is 2357.6 cm⁻¹. 4+1
- e) i) Find the fractional fluctuation of energy in a canonical ensemble.
- ii) For harmonic oscillator;

$$\left[\overline{(\Delta E)^2} \right]^{\frac{1}{2}} = \frac{hv \exp\left(-\frac{hv}{2k_b T}\right)}{1 - \exp\left(-\frac{hv}{k_b T}\right)};$$

Show that at absolute zero $\left[\overline{(\Delta E)^2} \right]^{\frac{1}{2}} = 0$ and

at high temperature $\left[\overline{(\Delta E)^2} \right]^{\frac{1}{2}} = k_b T$. 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.

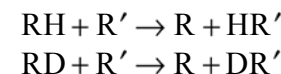
UNIT – 2081

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



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). $1\frac{1}{2} + 2 + 2\frac{1}{2}$

[Turn over

[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, $A + B \rightleftharpoons AB^\ddagger \rightarrow$ 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 $Z_A e$ and $Z_B e$, 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

[3]

UNIT – 2082

5. Answer **any four** questions:
- a) Show that the equilibrium distribution of particles following the Fermi-Dirac Statistics is given by $n_i = \frac{g_i}{e^{\alpha} e^{\beta \epsilon_i} + 1}$, 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 $\partial A = 2\pi \sqrt{\frac{m}{k}} \partial E$. 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