b) Calculate the translation contribution to internal energy, enthalpy, entropy and Gibbs free energy for helium at 25°C.

c) Show that the entropy of a monoatomic gas is given by

$$S_t = Nk\left[\ln\left\{\frac{kT}{P}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right\}+\frac{5}{2}\right].$$ The terms have their usual significance.

Ex/MSc/CH/2/2081/102/2017

M. Sc. Chemistry Examination, 2017

(2nd Semester)

Physical Chemistry

Paper - VIII

Time : Two hours | Full Marks : 50

(25 Marks for each Unit)

Use a separate answerscript for each unit.

UNIT – 2081

Answer ***any five*** questions : 5×5

1. Derive an expression of the rate constant for a unimolecular reaction and write down the value of the rate constant for that reaction under low temperature and high vibrational frequency.

2. Estimate the probability factors of the following reactions from Eyring's equation.

   i) reaction between two atoms

   ii) reaction between two polyatomic molecules.

3. Explain the unusual dependence of the rate constant of the reaction, $2NO + O_2 \rightarrow 2NO_2$ on temperature with the help of CTST.

4. Discuss the essential features of 'potential energy surface'.

5. Show that the Hammett equation leads to linear free energy relationship. What is Taft's equation ?

6. Deduce an expression of the relaxation time for the following rapid reaction :

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y + Z$$

Where the concentrations of the products are different.

UNIT – 2082

7. Answer ***any two*** of the following questions :

a) Give the statistical mechanical derivation of Langmiur adsorption isotherm. Sodium metal ionizes as $Na(g) \rightleftharpoons Na^+(g) + e$. With the help of statistical mechanics calculate the value of equilibrium constant at 1000 K. Given the ionization potential of Na is 5.14 eV. 5+3

b) 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 constnats and other terms have their significance. Also show that for a system in which $\frac{g_i}{n_i} >> 1$, the equilibrium distribution can be computed by using Boltzmann distribution law. Calculate the characteristic vibrational temperature of Cl_2 molecule. Given $\overline{\nu_o} = 561{\cdot}1\ cm^{-1}$ for Cl_2 molecule. 5+1+2

c) Find both high temperature and low temperature limiting forms of heat capacity of monoatomic solid according to Debye model. At 60 K the heat capacity of copper is $8.7 Jk^{-1} mol^{-1}$. Prdict C_v at 4K using (i) Einstein and (ii) Debye at low temperature limits. Which result agrees better with the experimental value of 5.78×10^{-3} JK^{-1} mol^{-1} ? 4+4

8. Answer ***all*** the questions : ×3

a) Show that the relative fluctuation in energy in canonical ensemble is given by $\left[\frac{\overline{(\Delta E)^2}}{\overline{E}}\right]^{\frac{1}{2}} = N^{-\frac{1}{2}}$. N is the total number of systems in the ensemble.

Or

The heat capacity, C_v is defined in terms of the partition function as $C_v = \frac{N}{kT^2}\frac{\delta}{\delta\beta}\left(\frac{1}{z}\frac{\delta z}{\delta\beta}\right)$. Show that $\frac{C_v}{R} = \left[\frac{\overline{(\Delta E)^2}}{(kT)^2}\right]$. The terms have their usual significance.

[Turn over