Calculate the characteristic vibrational temperature of Cl_2 molecule. Given fundamental frequency of oscillation of $Cl_2 = 561.1\ cm^{-1}$. 6+2

8. a) Show that the phase space available to 1-D SHO having energy lying between E and $E + \delta E$ is $\partial A = 2\pi\sqrt{\frac{m}{k}}\partial E$.

Here A is phase space available to the oscillator having energy between 0 and E, m and k are mass and force constant, respectively. 3

Or

Consider an ideal gas containing N molecules at temperature T and volume V. Making use of the fact that the pressure of the gas is related to its kinetic energy, show that the fractional root mean square diviation of the pressure $\frac{\left[\overline{(\Delta P)^2}\right]^{1/2}}{P}$ is of the order of $N^{-\frac{1}{2}}$. $2\frac{1}{2}$

b) Obtain the expression of heat capacity of mono-atomic solid according to Einstein model. 3

c) What is the mean electronic internal energy of NO molecules at 293K? The electronically excited state of NO is 121.1 cm^{-1} above the ground state. Both excited and ground states are doubly degenerate. 3

M. Sc. Chemistry Examination, 2018

(2nd Semester)

Physical Chemistry

Paper - VIII

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answer script for each unit

UNIT - 2081

Answer ***any five*** questions :

1. Derive an expression of Eyring's equation for a bimolecular reaction by CTST. 5

2. Prove that the probability factor of a reaction between two diatomic molecules forming a linear complex is $P=(f_v/f_R)^4$, where f_v and f_R have their usual meanings. 5

3. Write down the London equation in terms of quantum mechanical energy of the triatomic molecule. Discuss about the calculation of potential energy surface by Sato's method. 2+3

4. Write a short note on 'quantum mechanical tunneling' of primary kinetic isotope effect. 5

5. a) Deduce Brönsted-Bjerrum equation considering the influence of ionic strength on the rate of reactions in solution. $2\frac{1}{2}$

   b) Discuss how the dielectric constant of a solvent influences the rate of a reaction between two ions. $2\frac{1}{2}$

6. a) Write down Hammett's acidity function and its utility. 3

   b) What is the relationship between the catalytic constant of an acid and the acid dissociation constant ? 2

UNIT - 2082

7. Answer ***any two*** :

   a) Find the expression of equilibrium constant of the gas phase reaction $A \rightleftarrows B + C$ in terms of relevant partition functions. Consider the following reaction $A(g) \rightleftarrows A^+(g) + e$ Calculate K_p at 4000 K and 1 Pa pressure. Given : i) Ionization potential of A is 4.102 eV ; ii) The ground state degeneracy of A, A^+ and electron is unity. 4+4

   b) Derive BET adsorption isotherm using the method of grand canonical ensemble.

   Evaluate thermal de Broglie wavelength and translation partition function for hydrogen atom at 300K kept in volume 22.414 dm^3. 5+3

   c) 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 distribition law.