M. Sc. Chemistry Examination, 2019

(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 ***all*** the questions :

1. a) What do you understand by a potential energy surface? Show a 3D diagram of such a surface together with the potential energy contour diagram for a collinear reaction A+BC $\rightarrow$ AB+C. What does the minimum energy path signify? Hence comment about the "col" or "Saddle" point. 2+3+2

OR

What is meant by the kinetic isotope effect ? Based on the semiclassical treatment (in the absence of quantum-menchanical tunneling) of primary kinetic isotope effect, draw the possible potential - energy profiles for reactions of the type,

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

Find out an approximate value for the semiclassical ratio of the rate constants and compare them (condiser the energy values of C—H bonds). What will happen to this ratio when effect of tunneling is considered ?

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

b) Show that the Hammett relationships are equivalent to the existence of linear relationships between the free energies of activation for different series of reactions. Under what instances one observes a poor agreement in reference to the expected pattern ? 3+2

2. a) What are the main assumptions of the conventional transition state theory (CTST) ? Derive the CTST equation for the rate constant of a bimolecular elementary reaction by treating the motion through the 'col' as a very loose vibration. 2+5

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

c) The ionization constants of benzoic acid and p-chlorobenzoic acid in water are 6.30×10^{-5} and 1.07×10^{-4}, respectively. In 60% aqueous acetone, the alkaline hydrolysis of methyl p-chlorobenzoate is 3.95

c) Calculate the number of ways of distribition of 2 particles among 4 energy states when (i) particles are distinguishable and there is no restrction on the occupancy of the energy state (boltzons); (ii) particles are fermions and (iii) particles are bosons. 3

times as fast as that of the unsubstituted ester. Calculate the Hammett substituent constant for the p-chloro group and the reaction constant for the hydrolysis reaction. 3

OR

Mention in brief the operational principle of continuous flow method to study the kinetics of fast reactions. 3

UNIT - 2082

3. Answer ***any two*** :

a) Obtain the expression of heat capacity of monatomic solid according to Einstein's model. Also find the values of limiting heat capacity as $T \to 0$ and $T \to \infty$. 8

b) Derive Langmuir adsorption isotherm using statistical mechanical approach. Calculate the configurational entropy of localized adsorption if the fraction of surface area covered is (i) 1/100, (ii) 1/8 5+3

c) 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 significances. Also show that for a system in which $\frac{g_i}{n_i} \gg 1$, the equilibrium distribution becomes equivalent to using Boltzmann distribution law.

[Turn over

Iodine has many low lying vibrational states which are 213.3, 425.39, 636.27, 845.93 and 1054.38 cm^{-1} above the zero point energy level. Find the partition function of idoine by direct summation at 300K. Also calculate average vibrational energy of iodine at the said temperature. 4+4

4. Answer all :

a) If the root mean squre deviation in energy is defined as $\left(\overline{(\Delta E)^2}\right)^{\frac{1}{2}} = \left[\overline{E^2} - \overline{E}^2\right]^{\frac{1}{2}}$. 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 $\beta = 1/k_B T$

OR

The heat capacity C_v is defined in terms of partition function as $C_v = \frac{N}{K_B T^2} \frac{\partial}{\partial \beta}\left(\frac{1}{z}\frac{\partial z}{\partial \beta}\right)$. Show that $\frac{C_v}{R} = \frac{\overline{(\Delta E)^2}}{(k_B T)^2}$. 3

b) Calculate the rotational partition function for HCL at 25^0C. The rotational constant of HCL is 10.59 cm^{-1}. Also calculate the characteristic rotational temperature of HCl 3