10.59 cm^{-1}. Calculate the rotational partition function of HCl at : 6

(i) 100 K

(ii) 500 K

OR

Maximizing the thermodynamic probability of a macrostate and involving Lagrange's undetermined multiplier derive the expression for Maxwell Boltzmann statistics. 16

5. Derive Onsagar's reciprocal relations from the principle of microscopic reversibility. 16

OR

Use Onsagar's reciprocal relations to study the electrokinetic effects. 16

6. Discuss the kinetics of consecutive reactions. 16

OR

Describe the study of fast reactions by stop flow method and relaxation method. 16

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2016

Time : 3 hours

Full Marks : 80

The figures in the right-hand margin indicate marks.

Answer from both the Sections as directed.

(Physical Chemistry – II)

Section – A

1. Answer any **four** of the following : 4×4 = 16

   (a) Establish the relationship between heat capacity at constant volume and at constant pressure.

   (b) One mole of an ideal gas is expanded isothermally at 298K until the volume is tripled. Find the value of ΔS_{gas} and ΔS_{total} under the following conditions :

   (i) Expansion is carried out reversibly.

   (ii) Expansion if free.

   (c) Based on collision state theory, define the following terms :

   (i) Collision number

   (ii) Collision frequency factors

(d) Discuss the influence of ionic strength on the rate of ionic reaction.

(e) Calculate the partition function and average energy of the system for two Bose particles each of which can occupy any of the two energy levels 0 and ε.

(f) Derive the van der Waals equation from viral equation of state.

OR

2. Answer **all** questions from the following :

$$2 \times 8 = 16$$

(a) Define the term heat capacity.

(b) State Zeroth law of thermodynamics.

(c) Define microcanonical ensemble.

(d) Which thermodynamics variabes are held constant in each system of canonical ensemble ?

(e) What do you mean by non-equilibrium thermodynamics ?

(f) Give an example of oscillatory reaction.

(g) Estimate the diffusion controlled rate constant for the recombination of iodine

atoms in n-hexane solution at $25^\circ C$. Give that η for hexane is 0.325 CP.

(h) Derive a relation between half-life and temperature for nth order reaction, where $n > 2$.

Section – B

Answer **all** questions.

3. Write the laws of thermodynamics. How will you determine entropy by the third law of thermodynamics ?   16

OR

Define partial molar properties ? Discuss briefly various methods used to determine the partial molar properties.   16

4. (a) Derive the expression for rotational partition function of an ideal diatomic gas.   10

(b) The rotational constant of gaseous HCl determined from microwave spectroscopy is