(b) Calculate the characteristic rotational temperature and the rotational partition function for H_2 gas at $2727°C$ given that the moment of inertia of hydrogen gas molecule at this temperature is 4.6033×10^{-48} kg m^2. 6

5. Review the phenomenological laws leading to the onsager reciprocal relations. 16

Or

What is coupled and non-coupled reactions ? Discuss the entropy production in coupled phenomenon. 4 + 12

6. Discuss the Rice-Ramsperger-Karsel (RRK) theories of unimolecular reaction kinetic ? 16

Or

(a) Explain temperaturs jump method to study the fast reaction. 6

(b) Derive an expression for relaxation time (t). 10

2018

Time : 3 hours

Full Marks : 80

Answer from **both** the Sections as directed

The figures in the right-hand margin indicate marks

Candidates are required to answer in their own words as far as practicable

(PHYSICAL CHEMISTRY-II)

SECTION – A

1. Answer any *four* questions : 4 × 4

(a) Write the equation of partial molal valume, entropy, enthalpy and internal energy.

(b) Prove that

$$S = nR\left[\ln\frac{q}{N} + T\left(\frac{\partial \ln q}{\partial T}\right)_V + 1\right]$$

(2)

where S is entropy, q is partition function and N is the indipendent particles.

(c) Explain the electrokinetic phenomena.

(d) Write B-Z mechanism of oscillation reaction.

(e) Write the shortcomings of Lindemann theory of unimolecular reaction.

(f) Derive Gribbs Duhem equation.

Or

2. Answer *all* questions from the following : 2×8

(a) Write the concept of entropy and its unit.

(b) Define IIIrd law of thermodynamics.

(c) What is the law of equipartition of energy ?

(d) What is microscopic reversibility ?

(e) Define homogeneous catalysis with any one example.

(f) What is kinetic salt effect ?

(3)

(g) Write about thermodynamic probability.

(h) What is fast reaction ?

SECTION – B

Answer **all** questions : 16×4

3. What is meant by the term chemical potential ? How does chemical potential vary with temperature and pressure ? $4 + 12$

Or

Explain how the absolute entropy of a substance can be determined with the help of the IIIrd law of thermodynamics ?   16

4. Maximizing the thermodynamic probability of a macrostate and invoking Lagrange's undetermined multiplies, derive the expression for Maxwell-Boltzman statistics.   16

Or

(a) Discuss the vibrational partitions function.   10