Or

Derive an expression for entropy production and entropy flow in an open system.

6. Describe Lindemann-Hinshelwood theory of unimolecular reaction and compare it with Rice-Ramsperger-Kassel-Marcus theory.

Or

What are fast reactions ? Illustrate the technique used in studying kinetics of fast reactions.

Answer

M.Sc–Chem-IIS- (408)

2017

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

Answer any *four* questions. 4 × 4

1. (*a*) Prove that q and w are not state functions.

(*b*) One mole of N_2 gas in a cylinder at 300 K is allowed to expand isothermally against an external pressure of 5 atm from a volume of 1 dm^3 to a volume of 3 dm^3. Assuming ideality calculate q, w, Δu and ΔH.

(*c*) Derive the law of equiparation energy from 1st principle.

(*d*) For neon gas in 10 cm^3 box at 300 K calculate the number of available states with energy less than 3 KT.

(*e*) The rate constant for a reaction at 30 °C is exactly doubled the value at 20 °C. Calculate the activation energy.

(*f*) Write the general features of a fast reaction.

Or

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

(*a*) Define the term molar heat capacity at constant volume.

(*b*) Distinguish between isothermal and adiabatic process.

(*c*) Define canonical ensemble.

(*d*) Write the Onsagar's reciprocity relation.

(*e*) What is kinetic salt effect ?

(*f*) State first law of thermodynamics.

(*g*) What do you mean by the term relaxation time in fast reactions ?

(*h*) One mole of an ideal gas is expanded isothermally at 298 K until the volume is doubled. Find the values of ΔS_{gas} and ΔS_{total} when the expansion is carried out reversibly.

SECTION—B

Answer *all* questions. 16×4

3. What is fugacity ? How can you determine fugacity from (*i*) equation of state, and (*ii*) approximation method ?

Or

Discuss Nernst heat theorem and its application to solids.

4. (*a*) Describe an expression for molecular translational partition function of an ideal gas.

(*b*) Calculate the translational partition function for benzene (molar mass 78 gm/mol) in a volume of 1 m^3 at 25 °C.

Or

Maximizing the thermodynamic probability of a macrostate and involving Lagrange's undetermined multiplier derive the expression for Bose Einstein statistics.

5. Verify the Onsagar's reciprocal relations for a simple reversible reaction.