Registration Number:

Date & session:

ST. JOSEPH'S UNIVERSITY, BENGALURU -27

M. Sc. (CHEMISTRY) – II SEMESTER

SEMESTER EXAMINATION: APRIL 2023

(Examination conducted in May 2023)

CH 8321 – PHYSICAL CHEMISTRY II

(For current batch students only)

Time: 2 Hours **Max Marks: 50**

NOTE: This paper contains 2 printed pages, 3 parts, and 16 questions.

Data: Physical constants: h= 6.626×10^{-34} J s , $k_b = 1.38 \times 10^{-23}$ J K^{-1}, c= 3×10^8 m s^{-1}

PART-A

Answer any EIGHT of the following questions: **[2 x 8 = 16]**

1. State the linear law and write an expression for heat transfer by applying the same law.
2. Explain the Rabinowitch effect.
3. Write important features of RRK theory.
4. Explain the role of the co-catalyst in catalysis by BF_3 in the presence of moisture. (no need to give details of kinetics).
5. Write the initiation step and corresponding expression for the initial rate in the case of cationic polymerization
6. State two assumptions of Maxwell-Boltzmann statistics.
7. What is the significance of the partition function?
8. Write the partition function for the rotational motion.
9. Write an expression for the degeneracy of an atomic electronic level as per the Russell-Saunders coupling scheme. Explain the terms in it.
10. What is Konovalov's first law?

PART-B

Answer any TWO of the following questions **[12 x 2 = 24]**

11. a) The gas phase reaction $H_2 + I_2 \rightarrow 2HI$ is found to follow a second order kinetics. Its rate constant at 400 ^{0}C is 2.34 x 10^{-2} dm^3 mol^{-1} s^{-1}, E_a = 150 kJ mol^{-1}. Calculate at 400 ^{0}C, $\Delta^{\#}H^0$, $\Delta^{\#}S^0$, and $\Delta^{\#}G^0$.
    b) Derive an expression for entropy and its rate in a chemical reaction.
    c) Discuss the reasons for the first and second explosion limits in the gas-phase combustion reaction between hydrogen and oxygen. (5+4+3)
12. a) Derive an expression for the thermodynamic formulation of conventional transition state theory.
    b) Obtain an expression for the translational entropy of a monoatomic gas – Sakur Tetrode equation.
    c) Derive an expression for internal energy in terms of the partition function. (6+3+3)
13. a) How does chemical potential help deriving the following: i) Henry's law for gases dissolved in a liquid and ii) Raoult's law for a non-volatile solute in a liquid?

b) The energies of the first three energy levels of the fluorine atom, determined from spectroscopy, are as follows:

Energy level	Energy (cm^{-1})
$^2P_{3/2}$	0.0
$^2P_{1/2}$	404.0
$^2D_{5/2}$	102, 406.5

Calculate i) the electronic partition function and ii) the fractions of fluorine atoms in the three energy levels at 1000 K. **(6+6)**

PART-C

Answer any TWO of the following questions: [2 x 5 = 10]

14. The following mechanism was proposed for the decomposition of an organic molecule to form the compound Y:

$RX \rightarrow R + X$ …….(a)

$R + RX \rightarrow Y + Z$…….(b)

$Z \rightarrow R + L$ ……(c)

$2R \rightarrow P$ ……..(d)

k_1, k_2, k_3, k_4 are respective rate constants. Answer the following questions:

i) Identify the reactive intermediate involved in the second order propagation step.

ii) Apply steady-state approximation.

iii) Predict the overall order of the reaction.

iv) Write a generalized statement with respect to the overall order of such reaction kinetics.

15. The partial molal volumes of acetone and chloroform in a mixture in which the mole fraction of chloroform is 0.46 are 74.16 and 80.24 cm^3/mole, respectively. What is the volume of a solution of mass 1 kg.

16. a) The fundamental vibrational frequency of fluorine is 2.676×10^{13} Hz. Calculate the vibrational partition function at 25 °C. [$N=6.022 \times 10^{23}$ mol^{-1}, $h=6.626\times10^{-34}$ Js].

b) Write the mechanism for the polymerization of styrene catalyzed by potassium amide in liquid ammonia. (2+3)