

DEPARTMENT OF CHEMISTRY
SCHOOL OF CHEMICAL AND LIFESCIENCES, JAMIA HAMDARD
MSc. CHEMISTRY, SEMESTER-II EXAMINATIONS-2022
PAPER CODE: MCHCC-201
PAPER TITLE: PHYSICAL CHEMISTRY-II

(Write your Roll No. at the top immediately on receipt of this question paper)

Time: 3 hours

Maximum Marks: 75

Attempt all questions. All parts of a question must be attempted in continuation. Start answer of a fresh question on a new page. Cite examples and draw labelled diagrams whenever necessary.

Q1. Attempt all the questions.

(1x15=15)

Section A: Select the most suitable answer from the given choice:

- (i) The decay of a substance X in atmosphere is a first order reaction, whereas the decay of substance Y is a second order reaction. Which of the above substances will persist for a longer time in the atmosphere?
(a) X (b) Y
(c) both X and Y for the same duration (d) none of the above
- (ii) The rate constant for a reaction at 30 °C is exactly twice the value at 20 °C. Its activation energy is
(a) 25.6 kJ mole⁻¹ (b) 51.2 kJ mole⁻¹
(c) 102.4 kJ mole⁻¹ (d) 205.8 kJ mole⁻¹
- (iii) The half-life of a first order reaction ($A \rightarrow P$) is given by
(a) $t_{1/2} = (\ln 2)/k$ (b) $t_{1/2} = (\ln 2)/k[A]_0$
(c) $t_{1/2} = 1/k[A]_0$ (d) $t_{1/2} = (1/2)/k[A]_0$
- (iv) Generally, for many reactions the $\ln k$ against $1/T$ gives a straight line with a negative slope indicating that an increase in $\ln k$ results from
(a) a decrease in $1/T$ (b) an increase in $1/T$
(c) a decrease in T (d) none of the above, it is independent of temperature
- (v) For a reaction $X + Y \rightarrow Z$, rate $\propto [X]$. Its molecularity and order are respectively
(a) 2 and 1 (b) 2 and 2 (c) 1 and 1 (d) 1 and 2
- (vi) At absolute zero of temperature, the partition function
(a) $q = 0$ (b) $q = 1$ (c) $q = -1$ (d) $q = \infty$
- (vii) The canonical ensemble partition function of N indistinguishable entities is related to their molecular partition function by
(a) $Q = q^N$ (b) $Q = \frac{q^N}{N!}$ (c) $Q = Nq^N$ (d) $Q = N! q^N$

Section B: State whether the statements are True or False:

- (viii) Partition function is a dimensionless quantity (True / False)
(ix) Spontaneous process leads to the most probable state of the system. (True / False)

Section C: Fill in the blank with an appropriate answer:

- (x) The possible number of ways of distribution of 2 fermions among 4 energy states is _____.
- (xi) The possible number of ways of distribution of 2 bosons among 4 energy states is _____.
- (xii) Partition function increases with _____ in temperature.
- (xiii) The charge of a hydrophilic part of an amphoteric surfactant is controlled by the _____ of the solution.
- (xiv) Hydrophobic interactions describe the relation between water and _____.
- (xv) The cleaning agents in shampoo are _____.

Q2. Attempt any three of the following questions:

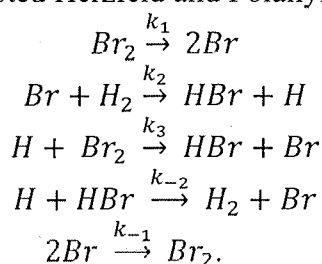
(3x5=15)

- A. A sample of milk kept at 25 °C is found to sour 40 times as rapidly as when it is kept at 4 °C. Estimate the activation energy for the souring process.
- B. Discuss the basis of the collision theory of reaction rate. What is the physical significance of the steric factor?
- C. Derive an expression for the rate constant of a bimolecular gas phase reaction of unlike molecules as per the hard sphere collision theory.
- D. What is 'kinetic salt effect'? Derive an equation expressing the kinetic salt effect.
- E. The rate constant for the base hydrolysis of pentaamine bromo-cobalt (III) cation varies with ionic strength (I) and the slope of the best-fit straight-line plot of $\log(k/k_0)$ against $I^{1/2}$ is -2.04. Find the charge number of the second ion if the first ion involved in the activated complex is OH^- ion.

Q3. Attempt any three of the following questions:

(3x5=15)

- A. Derive the rate law for the consumption of H_2 or Br_2 for thermal hydrogen-bromine reaction on the basis of accepted Herzfeld and Polanyi mechanism given by



- B. What is a catalyst? Explain the term homogeneous catalysis and discuss briefly the mechanism of catalysis.
- C. Describe the relaxation method for the study of the kinetics of a fast reaction.
- D. Discuss the salient features of the Rice-Ramsperger-Kassel-Marcus theory and its edge over the Rice-Ramsperger-Kassel theory.
- E. What is the basic assumption of the Lindemann-Hinshelwood mechanism of unimolecular reactions? Derive the Lindemann-Hinshelwood rate law.

Q4. Attempt any three of the following questions:

(3x5=15)

- A. What is the difference between the time average and the ensemble average? Characterize different kinds of ensembles according to their thermodynamic criteria.
- B. Show that the average energy of the system of independent particles in terms of partition function is given by

$$\bar{E} = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)$$

- C. Using the partition function, show that the molar translational energy of a gas is given by

$$E_{t,m} = \frac{3}{2} RT$$

- D. Using the partition function, show that $PV = NkT$.
- E. What are the fermions and the bosons? Derive the Bose-Einstein distribution law.

Q5. Attempt any three of the following questions

(3x5=15)

- A. What are surface active agents? Briefly discuss their surface activity in aqueous solution.
- B. Give a detailed classification of surfactants based on the charge of their head groups with examples.
- C. How does the nature of the hydrophobic group affect the critical micelle concentration of a surfactant?
- D. Apply the mass-action model to non-ionic surfactants and jot down the expression for standard free energy of micellization. What is the advantage of this model over the phase separation model?
- E. What are micelles? When do reverse micelles form?

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