

RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. in Applied Sciences
Second Year - Semester II Examination – January/February 2023
CHE 2201–PHYSICAL CHEMISTRY II

Time: Two (2) hours

Answer all questions.

The use of a non-programmable calculator is permitted.

1. a) A certain amount of pure solid PCl_5 was kept in a closed vessel. Calculate the number of phases, number of components, and degrees of freedom in a system containing a mixture of PCl_5 (s), PCl_3 (g) and Cl_2 (g) obtained because of partial dissociation of PCl_5 (s).
(25 marks)
- b) Draw a fully labeled phase diagram for water and draw a tie line to obtain the temperature of the triple point T_3 , the normal boiling point T_b and freezing point T_f on the temperature axis.
(25 marks)
- c) Explain the following:
 - i. Fractional distillation ii. Number of theoretical plates with a suitable temperature-composition phase diagram.
(20 marks)
 - ii. Draw a temperature-composition phase diagram for a pair of partially miscible liquids hexane (P) and nitrobenzene (Q). A mixture of 50 g of P and 50 g of Q was prepared at 290 K. The upper critical temperature is 293 K. The point $X_Q = 0.41$, $T = 290$ K occurs in the two-phase region of the phase diagram. The tie line cuts the phase boundaries at $X_Q = 0.35$ and $X_Q = 0.83$, and $T = 290$ K. What are the compositions of the phases, and in what proportion do they occur? (Relative atomic weight of C = 12, H = 1, O = 16, N = 14)
(30 marks)
2. a) With appropriate reaction energy profile diagrams, differentiate between a reaction intermediate and an activated complex.
(30 marks)
- b) Under certain experimental conditions, the rate of the following reaction is $5.86 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

$$2\text{N}_2\text{O} (\text{g}) \rightarrow 2 \text{N}_2 (\text{g}) + \text{O}_2 (\text{g})$$

Calculate values for $\frac{d[\text{N}_2\text{O}]}{dt}$, $\frac{d[\text{N}_2]}{dt}$ and $\frac{d[\text{O}_2]}{dt}$
(15 marks)

- c) Substance R decomposes to product P. Experimentally prove that the decomposition is first order reaction. The time for half change of A is 60 s. Calculate the rate constant. How much of R will be left after 180 s?

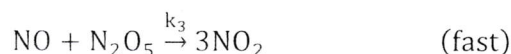
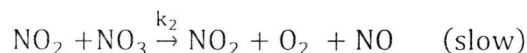
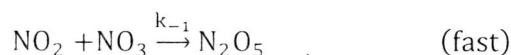
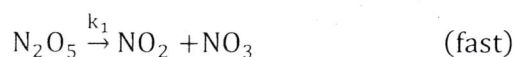
(30 marks)

- d) Arrhenius suggested that the rates of most reactions vary with temperature in such a way that the rate constant is directly proportional to $e^{-E_a/RT}$.

- Propose a relationship between the rate constant and temperature.
- The rate constant of a reaction at 400 K and 200 K are 0.04 and 0.02 s⁻¹ respectively. Calculate the value of activation energy. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

(25 marks)

3. a) The gas-phase reaction of $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ is assumed to occur by the following mechanism:



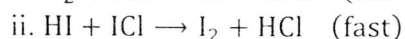
Derive the rate law associated with the above mechanism.

(25 marks)

- b) Account the effect of catalysts on the rate of reactions.

(25 marks)

- c) The reaction of $\text{H}_2 + 2\text{ICl} \rightarrow \text{I}_2 + 2\text{HCl}$ ($\Delta H = -218 \text{ kJ mol}^{-1}$) is assumed to occur in the following two elementary reactions.



Draw a labeled diagram of potential energy vs. reaction progress for the above overall reaction.

(20 marks)

- d) Write the Clausius–Clapeyron equation for sublimation of a solid and outline its significance. The vapour pressure of a liquid at 50° C is equal to 12330 N m⁻². If the average value of the enthalpy of vaporization between 50°C and the normal boiling point of the liquid is 42.74 kJ mol⁻¹. Estimate the boiling point of the liquid.

(30 marks)

4. a) Explain what is meant by the following terms:

- i. Operator.
- ii. Expectation value of a quantum state.

(20 marks)

b) i. Which of the functions x^2 , e^{kx} are eigen functions of d/dx and d^2/dx^2 and what are their eigenvalues?

ii. The position $\langle x \rangle$ of a wave of function between 0 and 2π is given by:

$$\Psi(x) = \sqrt{\frac{1}{2\pi}} e^{inx}$$

Give the complex conjugate for the wave function and calculate the expectation value $\langle x \rangle$
(50 marks)

c) Write the Schrodinger equation for the probability of finding a particle at some positions x , y , and z . Identify all terms there in.

(15 marks)

d) Ten electrons are trapped in a three-dimensional potential well with a length of one side equals to 'a'. Calculate the minimum energy of the system.

$$E = \frac{\pi^2 h^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2)$$

(15 marks)

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