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.

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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 5.86×10^{-6} mol dm^{-3} s^{-1}

$$2N_2O\ (g) \rightarrow 2\ N_2\ (g) + O_2\ (g)$$

Calculate values for $\frac{d[N_2O]}{dt}$, $\frac{d[N_2]}{dt}$ and $\frac{d[O_2]}{dt}$ (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 $e^{-Ea/RT}$.

i. Propose a relationship between the rate constant and temperature.

ii. 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. ($R = 8.314\ J\ K^{-1}\ mol^{-1}$)

(25 marks)

3. a) The gas-phase reaction of $2\ N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is assumed to occur by the following mechanism:

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3 \qquad \text{(fast)}$$

$$NO_2 + NO_3 \xrightarrow{k_{-1}} N_2O_5 \qquad \text{(fast)}$$

$$NO_2 + NO_3 \xrightarrow{k_2} NO_2 + O_2 + NO \qquad \text{(slow)}$$

$$NO + N_2O_5 \xrightarrow{k_3} 3NO_2 \qquad \text{(fast)}$$

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 $H_2 + 2ICl \rightarrow I_2 + 2HCl$ ($\Delta H = -218\ kJ\ mol^{-1}$) is assumed to occur in the following two elementary reactions.

i. $H_2 + ICl \rightarrow HI + HCl$ (slow)

ii. $HI + ICl \rightarrow I_2 + HCl$ (fast)

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 (x) 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 <x>

(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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