OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Degree Examination Part III

CHM 305 - Chemical Kinetics
Harmattan Semester Examination (2023/2024 Session)

Time Allowed: 2 hrs **Date: 17th February 2025**

INSTRUCTION: ATTEMPT ALL QUESTIONS

Constants: $R = 8.314\ J.K^{-1}.mol^{-1}$, $k_b = 1.3805 \times 10^{-23}\ J.K^{-1}$, $h = 6.626 \times 10^{-34}\ J.s$, $N_A = 6.022 \times 10^{23}\ mol^{-1}$; $1\ \AA = 1.0 \times 10^{-8}\ cm$

QUESTION ONE

(a) The anti-cancer drug cis-platin hydrolyses in water with a first-order rate constant of 6.0×10^{-3} min^{-1} at pH 7.0 and 25 °C. (i) What is the half-life for the hydrolysis reaction under these conditions? (ii) If a freshly prepared solution of cis-platin has a concentration of 0.060M, what will be the concentration after 8 half-lives? (iii) What is the percent completion of the reaction after 8 half-lives?

(b) (i) What are the 3 important criteria required in experimental measurement of reaction rates for kinetic study?

(ii) List any ~~three~~ four (4) physical methods of measuring reaction rates

(iii) State the advantages of stopped flow technique over continuous flow method.

[15 marks]

QUESTION TWO

(a) Calculate the entropy of activation for a bimolecular gas reaction occurring at 827 °C given that the rate constant is 145.5 $dm^6\ mol^{-2}\ s^{-1}$ and the activation energy is 184 $kJ\ mol^{-1}$.

(b) Assuming $q_t = 10^8, q_r = 10,\ q_v = 1\ and\ \frac{k_bT}{h} = 10^{13}$, determine the expression for the value of rate constant for $A + B \rightarrow X^{\neq}$ in litres $mole^{-1}$ sec^{-1} if A and B are atoms.

(c) Consider the conversion of cyclopropane to propene which follows the mechanism:

cyclopropane + cyclopropane $\xrightarrow{k_1}$ cyclopropane* + cyclopropane

cyclopropane* + cyclopropane $\xrightarrow{k'_1}$ cyclopropane + cyclopropane

cyclopropane* $\xrightarrow{k_2}$ prop-1-ene (where cyclopropane* is an activated molecule). Write the overall rate expression for the reaction. Determine the order for this reaction when (i) $k_2 >> k'_1$[cyclopropane] and (ii) k'_1[cyclopropane] >> k_2.

[20 marks]

QUESTION THREE

(a) What is a chain reaction?

(b) The gas-phase reaction of $H_2 + Br_2$ follows a five-step mechanism to produce HBr. The mechanism of the reaction is as follows

$$Br_2 \xrightarrow{k_1} 2Br^\bullet$$

$$Br^\bullet + H_2 \xrightarrow{k_2} HBr + H^\bullet$$

$$H^\bullet + Br_2 \xrightarrow{k_3} HBr + Br^\bullet$$

$$H^\bullet + HBr \xrightarrow{k_4} H_2 + Br^\bullet$$

$$2Br^\bullet \xrightarrow{k_5} Br_2$$

Using steady-state approximation, determine the concentration of the chain carriers (intermediates)

(c) The proposed mechanism for ethane decomposition is:

$$C_2H_6 \xrightarrow{k_1} 2\,{}^\bullet CH_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (I)$$

$${}^\bullet CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + {}^\bullet C_2H_5 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (II)$$

$${}^\bullet C_2H_5 \xrightarrow{k_3} C_2H_4 + H^\bullet \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (III)$$

$$H^\bullet + C_2H_6 \xrightarrow{k_4} H_2 + {}^\bullet C_2H_5 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (IV)$$

$$H^\bullet + {}^\bullet C_2H_5 \xrightarrow{k_5} C_2H_6 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (V)$$

(i) Identify the chain steps involved in (I), (II) and (V)

(ii) In one equation (for each), show the steady state for methyl radical, ethyl radical, and hydrogen atom

(iii) in one equation, show the rate of production of ethylene.

ion.

[15 marks]

QUESTION FOUR

(a) Using the concept of *cage effect*, briefly differentiate between gas-phase reactions and reactions in solution.

(b) Suppose that we have a solution of two uncharged reactant molecules, A and B, with radii r_A and r_B. The rate constant k_d of the elementary diffusion-controlled reaction, A + B → P, is given by $k_d = 4\pi N_A(r_A + r_B)(D_A + D_B)$. In a limit where the diffusion coefficient and radii of two reactants are equivalent, demonstrate that the rate constant for a diffusion-controlled reaction can be written as $k_d = \frac{8RT}{3\eta}$.

(c) In aqueous solution at 25°C and pH 7.4, the diffusion coefficient for hemoglobin (radius =3.4Å) is $7.6 \times 10^{-7}\,cm^2s^{-1}$, and the diffusion coefficient for O_2 (radius =2.0Å) is $2.2 \times 10^{-5}\,cm^2s^{-1}$. The rate constant for the binding of O_2 to hemoglobin is $4.0 \times 10^7\,M^{-1}s^{-1}$. Is this a diffusion-controlled reaction?

(d) Estimate the rate constant for a diffusion-controlled reaction in water at 298 K, given that the viscosity of water is 8.9×10^{-4} Jsm^{-3}.

[20 marks]

$\frac{cm^3}{1} = \left(\frac{10^{-2} m}{1cm}\right)^3 \times \left(\frac{1dm}{10^{-1} m}\right)^3$

$\frac{10^{-6}}{10^{-3}}$