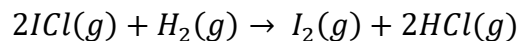


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- 1) (15 pts) The following kinetic data were obtained for the reaction:



Experiment	Initial Concentration (mmol L ⁻¹)		Initial Rate (mol L ⁻¹ s ⁻¹)
	[ICl] ₀	[H ₂] ₀	
1	1.5	1.5	3.7x10 ⁻⁷
2	3.0	1.5	7.4x10 ⁻⁷
3	3.0	4.5	2.2x10 ⁻⁶
4	4.7	2.7	??

- (a) Write the rate law for the reaction (5 pts)

$$\text{Rate} = k[\text{ICl}]_0^x [\text{H}_2]_0^y$$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k(2 * [\text{ICl}]_0^x)[\text{H}_2]_0^y}{k[\text{ICl}]_0^x [\text{H}_2]_0^y} = \frac{7.4x10^{-7}}{3.7x10^{-7}}$$

$$2 = 2^x \rightarrow x = 1$$

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{k[\text{ICl}]_0^x (3 * [\text{H}_2]_0^y)}{k[\text{ICl}]_0^x [\text{H}_2]_0^y} = \frac{2.2x10^{-6}}{7.4x10^{-7}}$$

$$3 = 3^y \rightarrow y = 1$$

$$\text{Rate} = k[\text{ICl}]_0^1 [\text{H}_2]_0^1$$

- (b) From the data, determine the value of the rate constant (5 pts)

*Choose data from any 1 experiment to plugin

Expt 1:

$$\text{Rate} = k[\text{ICl}]_0^1 [\text{H}_2]_0^1$$

$$3.7x10^{-7} \frac{\text{mol}}{\text{L} * \text{s}} = k(1.5x10^{-3} \text{M})^1 (1.5x10^{-3} \text{M})^1$$

$$k = \frac{3.7x10^{-7} \frac{\text{mol}}{\text{L} * \text{s}}}{(1.5x10^{-3} \text{M})^1 (1.5x10^{-3} \text{M})^1} = 0.164 \frac{\text{L}}{\text{mol} * \text{s}}$$

- (c) Predict the reaction rate for Experiment 4 (5 pts)

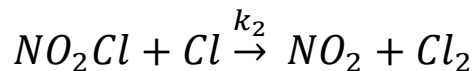
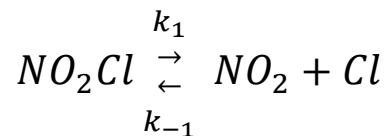
$$\text{Rate} = 0.164 \frac{\text{L}}{\text{mol} * \text{s}} (4.7x10^{-3} \text{M})(2.7x10^{-3} \text{M})$$

$$\text{Rate} = 2.09x10^{-6} \frac{\text{mol}}{\text{L} * \text{s}}$$

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2) (20 pts) The mechanism for the decomposition for NO_2Cl is:



Write out the differential rate law under the following conditions (make sure to eliminate intermediates from your answer):

a) high concentration of NO_2 (10 pts)

$$\begin{aligned} \text{Rate} &= \frac{d[Cl_2]}{dt} = \frac{d[NO_2]}{dt} = k_2[NO_2Cl][Cl] \\ \frac{d[Cl]}{dt} = 0 &= k_1[NO_2Cl] - k_{-1}[NO_2][Cl] - k_2[NO_2Cl][Cl] \\ [Cl] &= \frac{k_1[NO_2Cl]}{k_{-1}[NO_2] + k_2[NO_2Cl]} \\ \text{Rate} &= k_2[NO_2Cl][Cl] = \frac{k_1k_2[NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]} \end{aligned}$$

At high $[NO_2]$: $k_{-1}[NO_2] \gg k_2[NO_2Cl]$ and rate simplifies to:

$$\text{Rate} = \frac{k_1k_2[NO_2Cl]^2}{k_{-1}[NO_2]} = \frac{K_1k_2[NO_2Cl]^2}{[NO_2]}$$

b) low concentration of NO_2 (10 pts)

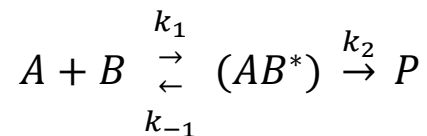
At low $[NO_2]$: $k_{-1}[NO_2] \ll k_2[NO_2Cl]$ and rate simplifies to:

$$\text{Rate} = k_1[NO_2Cl]$$

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3) (15 pts) A common scheme used to describe reactions in liquids is:



Write the expression for the rate law in the activation-controlled limit.

$$\begin{aligned} \text{Rate} &= \frac{d[P]}{dt} = k_2[AB^*] \\ \frac{d[AB^*]}{dt} &= 0 = k_1[A][B] - k_{-1}[AB^*] - k_2[AB^*] \\ [AB^*] &= \frac{k_1[A][B]}{k_{-1} + k_2} \end{aligned}$$

$$\text{Rate} = \frac{d[P]}{dt} = \frac{k_1 k_2 [A][B]}{k_{-1} + k_2}$$

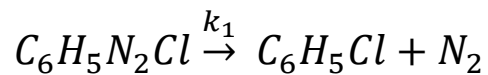
In the activation – controlled limit $k_2 \ll k_{-1}$

$$\text{Rate} = \frac{k_1 k_2 [A][B]}{k_{-1}} = K_1 k_2 [A][B]$$

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- 4) (15 pts) The decomposition of benzene diazonium chloride



follows first order kinetics with a rate constant of $4.3 \times 10^{-5} \text{ s}^{-1}$ at 20°C . If the initial partial pressure of $C_6H_5N_2Cl$ is 0.0088 atm, calculate its partial pressure after 10.0 hours.

$$c = c_0 e^{-kt}$$

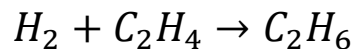
$$c = 0.0088 \text{ atm} * \exp \left(-4.3 \times 10^{-5} \text{ s} * 10.0 \text{ hrs} * \frac{3600 \text{ s}}{\text{hr}} \right)$$

$$c = 0.00187 \text{ atm} = 1.87 \times 10^{-3} \text{ atm}$$

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- 5) (10 pts) Estimate the steric factor P for the following reaction at 355° C



given the following experimental factors: $A = 1.24 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$, $\sigma = 0.50 \times 10^{-18} \text{ m}^2$, and $\mu = 1.9 \times 10^{-3} \text{ kg mol}^{-1}$

$$A = \sigma * P * N_A \sqrt{\frac{8RT}{\pi\mu}}$$

$$P = \frac{A}{N_A \sigma} * \sqrt{\frac{\pi\mu}{8RT}}$$

$$= \frac{1.24 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1} * 0.50 \times 10^{-18} \text{ m}^2} * \sqrt{\frac{\pi * 1.9 \times 10^{-3} \text{ kg mol}^{-1}}{8 * 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} * 628.15 \text{ K}}} * \frac{1 \text{ m}^3}{1000 \text{ L}}$$

$$P = 1.56 \times 10^{-6}$$

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- 6) **(10 pts)** The hydrolysis of sucrose is a part of the digestive process. To investigate how strongly the rate depends on our body temperature, calculate the rate constant for the hydrolysis of sucrose at 35.0°C, given that $k=1.0 \text{ mL mol}^{-1} \text{ s}^{-1}$ at 37.0°C (normal body temperature), and the activation energy of the reaction is 108 kJ mol^{-1} .

$$k = Ae^{\frac{-E_a}{RT}}$$

$$\frac{k_{35 \text{ C}}}{k_{37 \text{ C}}} = \frac{Ae^{\frac{-E_a}{RT(35 \text{ C})}}}{Ae^{\frac{-E_a}{RT(37 \text{ C})}}}$$

$$k_{35 \text{ C}} = k_{37 \text{ C}} * e^{\frac{-E_a}{R}(\frac{1}{308 \text{ K}} - \frac{1}{310 \text{ K}})}$$

$$k_{35 \text{ C}} = 1.0 \text{ mL mol}^{-1} * e^{\frac{-108 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}(\frac{1}{308 \text{ K}} - \frac{1}{310 \text{ K}})} = 0.762 \text{ mL mol}^{-1}$$

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- 7) **(15 pts)** Certain bacteria use the enzyme penicillinase to decompose penicillin and render it inactive. The Michaelis–Menten constants for this enzyme and substrate are:

$$K_m = 5.3 \times 10^{-5} \text{ mol L}^{-1}$$

$$k_2 = 2.6 \times 10^3 \text{ s}^{-1}.$$

- a) At what substrate concentration will the rate of decomposition be half of the maximum rate? Must show all work for full credit (10 pts)

$$\frac{\text{Rate}}{\text{Max Rate}} = \frac{\frac{k_2[E]_0[S]}{K_m + [S]}}{k_2[E]_0}$$

$$\frac{1}{2} = \frac{[S]}{K_M + [S]}$$

$$K_M + [S] = 2[S] \rightarrow K_M = [S]$$

$$[S] = 5.3 \times 10^{-5} M$$

- b) What is the significance of k_2 in the Michaelis-Menten model of enzyme kinetics (one sentence)? (5 pts)

k_2 is the turnover number, which tells us the number of substrate molecules converted to product per enzyme per second