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

$$2ICl(g) + H_2(g) \rightarrow I_2(g) + 2HCl(g)$$

	Initial Concentration (mmol L^{-1})		
Experiment	$[ICl]_0$	$[H_2]_0$	Initial Rate (mol L^{-1} s^{-1})
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)

$$Rate = k[ICl]_0{}^x[H_2]_0{}^y$$

$$\frac{Rate\ 2}{Rate\ 1} = \frac{k(2 * [ICl]_0{}^x)[H_2]_0{}^y}{k[ICl]_0{}^x[H_2]_0{}^y} = \frac{7.4x10^{-7}}{3.7x10^{-7}}$$

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

$$\frac{Rate\ 3}{Rate\ 2} = \frac{k[ICl]_0{}^x(3 * [H_2]_0{}^y)}{k[ICl]_0{}^x[H_2]_0{}^y} = \frac{2.2x10^{-6}}{7.4x10^{-7}}$$

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

$$Rate = k[ICl]_0{}^1[H_2]_0{}^1$$

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

*Choose date from any 1 experiment to plugin

Expt 1:

$$Rate = k[ICl]_0{}^1[H_2]_0{}^1$$

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

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

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

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

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

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

$$NO_2Cl \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NO_2 + Cl$$

$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2$$

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)

$$Rate = \frac{d[Cl_2]}{dt} = \frac{d[NO_2]}{dt} = k_2[NO_2Cl][Cl]$$

$$\frac{d[Cl]}{dt} = 0 = k_1[NO_2Cl] - k_{-1}[NO_2][Cl] - k_2[NO_2Cl][Cl]$$

$$[Cl] = \frac{k_1[NO_2Cl]}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$

$$Rate = k_2[NO_2Cl][Cl] = \frac{k_1k_2[NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$

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

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

b) low concentration of NO_2 (10 pts)

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

$$Rate = k_1[NO_2Cl]$$

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

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (AB^*) \overset{k_2}{\rightarrow} P$$

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

$$Rate = \frac{d[P]}{dt} = k_2[AB^*]$$

$$\frac{d[AB^*]}{dt} = 0 = k_1[A][B] - k_{-1}[AB^*] - k_2[AB^*]$$

$$[AB^*] = \frac{k_1[A][B]}{k_{-1} + k_2}$$

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

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

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

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

$$C_6H_5N_2Cl \overset{k_1}{\rightarrow} C_6H_5Cl + N_2$$

follows first order kinetics with a rate constant of 4.3x10^{-5} 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.

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

$$c = 0.0088atm * \exp\left(-4.3x10^{-5}s * 10.0\ hrs * \frac{3600\ s}{hr}\right)$$

$$c = 0.00187\ atm = 1.87x10^{-3}atm$$

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

$$H_2 + C_2H_4 \rightarrow C_2H_6$$

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

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

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

$$= \frac{1.24x10^{6} L\ mol^{-1} s^{-1}}{6.023x10^{23} mol^{-1} * 0.50x10^{-18} m^2} * \sqrt{\frac{\pi * 1.9x10^{-3} kg\ mol^{-1}}{8 * 8.3145\ Jmol^{-1} K^{-1} * 628.15\ K}} * \frac{1m^3}{1000L}$$

$$P = 1.56x10^{-6}$$

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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 mL mol^{-1} s^{-1} at 37.0°C (normal body temperature), and the activation energy of the reaction is 108 kJ mol^{-1}.

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

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

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

$$k_{35\,C} = 1.0\,mL\,mol^{-1} * e^{\frac{-108x10^3 J\,mol^{-1}}{8.3145\,J\,mol^{-1}K^{-1}}(\frac{1}{308\,K} - \frac{1}{310\,K})} = 0.762\,mL\,mol^{-1}$$

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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)

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

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

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

$$[S] = 5.3x10^{-5}M$$

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