

Chemistry 4B Exam 1
February 14, 2020
Professor Saykally

Name: _____
SID: _____
GSI: _____

Equations:

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

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{[S] + K_m}$$

$$\frac{1}{c} = \frac{1}{c_0} + 2kt$$

$$A = 2d^2 N_A \sqrt{\frac{\pi RT}{M}} P$$

$$k = A e^{-E_a/RT}$$

Rules:

- Work all problems to **3 significant figures**
- No lecture notes or books permitted
- No word processing, graphing, or programmable calculators
- Time: 50 minutes
- Total: 100 points
- **SHOW ALL WORK IN BOXES PROVIDED TO RECEIVE CREDIT**
- Answers with no work shown will receive no credit
- Periodic Table, Tables of Physical Constants, Equations, and Conversion Factors included

(1) (20 points) In lecture we studied the decomposition reaction of N_2O_5 :

(a) What is the rate constant, k , for the first-order decomposition of N_2O_5 (g) at 25°C if the half-life of N_2O_5 (g) at that temperature is 4.03×10^4 s? (10 points)

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

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

$$\ln\left(\frac{0.5c_0}{c_0}\right) = -kt$$

$$\ln(2) = kt \rightarrow t_{1/2} = \frac{\ln(2)}{k}$$

$$k = \frac{\ln(2)}{t_{1/2}} = \frac{0.6931}{4.03 \times 10^4 \text{ s}} = 1.72 \times 10^{-5} \text{ s}^{-1}$$

(b) What percentage of N_2O_5 molecules will not have reacted after 1 day? (10 points)

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

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

$$\frac{c}{c_0} = e^{-(1.72 \times 10^{-5} \text{ s}^{-1}) * (24 \text{ hrs} * \frac{3600 \text{ s}}{\text{hr}})}$$

$$\frac{c}{c_0} = 0.226$$

22.6% of molecules have not reacted after 1 day

(2) (20 points) In a study of the reaction of pyridine (C_5H_5N) with methyl iodide (CH_3I) in a benzene solution, the following set of initial reaction rates was measured at 25 °C for different initial concentrations of the two reactants:

<i>Reaction</i>	$[C_5H_5N]$ (mol L ⁻¹)	$[CH_3I]$ (mol L ⁻¹)	Rate (mol L ⁻¹ s ⁻¹)
1	1.00×10^{-4}	1.00×10^{-4}	7.50×10^{-7}
2	2.00×10^{-4}	2.00×10^{-4}	3.00×10^{-6}
3	2.00×10^{-4}	4.00×10^{-4}	6.00×10^{-6}

a) Write the differential rate expression for this reaction. *Show all work.* (10 points)

$$\text{Rate} = k[C_5H_5N]^x[CH_3I]^y$$

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{k[C_5H_5N]^x * 2[CH_3I]^y}{k[C_5H_5N]^x[CH_3I]^y}$$

$$2 = \frac{2 * [CH_3I]^y}{[CH_3I]^y} = 2^y \rightarrow y = 1$$

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{1}{4} = \frac{k[C_5H_5N]^x[CH_3I]^1}{k*2[C_5H_5N]^x*2[CH_3I]^1} = \left(\frac{1}{2}\right)^x \left(\frac{1}{2}\right) \rightarrow x = 1$$

$$\text{Rate} = k [C_5H_5N][CH_3I]$$

b) Calculate the rate constant and give its units. (10 points)

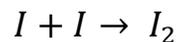
$$\text{Rate} = k [C_5H_5N][CH_3I]$$

$$7.50 \times 10^{-7} \frac{\text{mol}}{\text{L} \cdot \text{s}} = k * [1.00 * 10^{-4} \frac{\text{mol}}{\text{L}}][1.00 * 10^{-4} \frac{\text{mol}}{\text{L}}]$$

$$k = \frac{7.50 \times 10^{-7} \frac{\text{mol}}{\text{L} \cdot \text{s}}}{[1.00 * 10^{-4} \frac{\text{mol}}{\text{L}}][1.00 * 10^{-4} \frac{\text{mol}}{\text{L}}]}$$

$$k = 75.0 \frac{\text{L}}{\text{mol} \cdot \text{s}}$$

(3) (10 points) At 25°C in CCl₄ solvent, the reaction



is second-order in concentration of the iodine atoms. The rate constant k has been measured as $8.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. Suppose the initial concentration of I atoms is $1.00 \times 10^{-4} \text{ M}$. Calculate their concentration after $2.0 \times 10^{-6} \text{ s}$. (10 points)

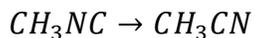
$$\frac{1}{c} = \frac{1}{c_0} + 2kt$$

$$\frac{1}{c} = \frac{1}{(1.00 \times 10^{-4} \text{ M})} + (2 * \left(8.20 \times 10^9 \frac{\text{L}}{\text{mol s}}\right) * (2.0 \times 10^{-6} \text{ s}))$$

$$\frac{1}{c} = 1.0 \times 10^4 \frac{\text{L}}{\text{mol}} + 3.28 \times 10^4 \frac{\text{L}}{\text{mol}} = 4.28 \times 10^4 \frac{\text{L}}{\text{mol}}$$

$$c = \frac{1}{4.28 \times 10^4 \frac{\text{L}}{\text{mol}}} = 2.3 \times 10^{-5} \text{ M}$$

(4) (20 points) The activation energy for the isomerization reaction of CH_3CN



is 161 kJ mol^{-1} ; the reaction obeys first order kinetics, and the rate constant at 600 K is 0.41 s^{-1} .

(a) Calculate the Arrhenius factor A for this reaction (10 points)

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

$$A = \frac{k}{e^{\frac{-E_a}{RT}}}$$

$$A = \frac{0.41 \text{ s}^{-1}}{\exp(-1.61 \times 10^5 \text{ J mol}^{-1} / (8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(600 \text{ K}))}$$

$$A = 4.3 \times 10^{13} \text{ s}^{-1}$$

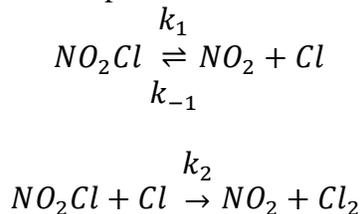
(b) Calculate the rate constant for this reaction at 1000 K . (10 points)

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

$$k = (4.3 \times 10^{13} \text{ s}^{-1}) * \exp(-1.61 \times 10^5 \text{ J mol}^{-1} / (8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(1000 \text{ K}))$$

$$k = 1.7 \times 10^5 \text{ s}^{-1}$$

(5) (15 points) The mechanism for decomposition of NO_2Cl is:



By making a steady state approximation for $[\text{Cl}]$, express the rate of appearance of Cl_2 in terms of the concentrations of NO_2Cl and NO_2 .

$$\text{Rate} = \frac{d[\text{Cl}_2]}{dt} = k_2[\text{NO}_2\text{Cl}][\text{Cl}]$$

$$\frac{d[\text{Cl}]}{dt} = k_1[\text{NO}_2\text{Cl}] - k_{-1}[\text{NO}_2][\text{Cl}] - k_2[\text{NO}_2\text{Cl}][\text{Cl}] = 0$$

$$k_{-1}[\text{NO}_2][\text{Cl}] + k_2[\text{NO}_2\text{Cl}][\text{Cl}] = k_1[\text{NO}_2\text{Cl}]$$

$$[\text{Cl}]_{ss}(k_{-1}[\text{NO}_2] + k_2[\text{NO}_2\text{Cl}]) = k_1[\text{NO}_2\text{Cl}]$$

$$[\text{Cl}]_{ss} = \frac{k_1[\text{NO}_2\text{Cl}]}{k_{-1}[\text{NO}_2] + k_2[\text{NO}_2\text{Cl}]}$$

$$\text{Rate} = \frac{d[\text{Cl}_2]}{dt} = k_2[\text{NO}_2\text{Cl}][\text{Cl}]_{ss}$$

$$\text{Rate} = \frac{d[\text{Cl}_2]}{dt} = \frac{k_1 k_2 [\text{NO}_2\text{Cl}]^2}{k_{-1}[\text{NO}_2] + k_2[\text{NO}_2\text{Cl}]}$$

(6) (15 points) The enzyme lysozyme kills certain bacteria by attacking a sugar called *N*-acetylglucosamine (NAG) in their cell walls. At an enzyme concentration of $2.0 \times 10^{-6} \text{ M}$, the maximum rate for substrate (NAG) reaction, found at high substrate concentration, is $1 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$. The rate is reduced by a factor of 2 when the substrate concentration is reduced to $6.0 \times 10^{-6} \text{ M}$. Determine the Michaelis-Menten constant K_m as well as k_2 for lysozyme.

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{k_M + [S]}$$

At high substrate concentration $[S] \gg k_M$, so we can write:

$$\text{Max Rate} = \frac{d[P]}{dt} = k_2[E]_0$$

$$k_2 = \frac{\text{Max Rate}}{[E]_0} = \frac{1 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}}{2.0 \times 10^{-6} \text{ mol L}^{-1}} = 0.5 \text{ s}^{-1}$$

$$k_2 = 0.5 \text{ s}^{-1}$$

Now, we take a ratio of our rate expressions to solve for k_M :

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

$$\frac{1}{2} = \frac{[6.0 \times 10^{-6} \text{ M}]}{k_M + [6.0 \times 10^{-6} \text{ M}]}$$

$$k_M = 2[6.0 \times 10^{-6} \text{ M}] - [6.0 \times 10^{-6} \text{ M}]$$

$$k_M = 6.0 \times 10^{-6} \text{ M}$$

