

Chemistry 4B Exam 1

Kshitij Chauhan

TOTAL POINTS

90 / 100

QUESTION 1

N₂O₅ Decomposition 20 pts

1.1 Calculate Rate Constant 10 / 10

- ✓ + **10 pts** Correct Answer with units and sig figs
- + **0 pts** Incorrect
- **2 pts** Wrong sig figs or No/wrong units
- **2 pts** Calculator Error
- + **2 pts** Has integrated first order rate expression
- + **2 pts** Plugs in $1/2^*$ original concentration
- + **2 pts** Rearranges and solves for k

1.2 Unreacted molecules 10 / 10

- ✓ + **10 pts** Correct answer
- + **2 pts** Writes out first order integrated rate expression
- + **2 pts** Converts 1 day into seconds (86,400)
- + **2 pts** Sets up equation to solve for unreacted molecules
- **2 pts** Click here to replace this description.
- + **0 pts** no points

QUESTION 2

Pyridine 20 pts

2.1 Diff Rate Expression 10 / 10

- ✓ + **10 pts** correct differential rate law by using method of initial rates
- + **3 pts** Writes differential rate law with variables in exponent
- + **2 pts** Sets up ratio of rate expressions and solves for order of CH₃I
- + **2 pts** Sets up ratio of rate expressions to solve for order of C₅H₄N
- + **0 pts** Incorrect
- **3 pts** Did not show all work

2.2 Rate Constant 10 / 10

- ✓ + **10 pts** Correct answer with units and sig figs
- + **2 pts** Writes correct differential rate equation with orders calculated in part a
- + **2 pts** Rearranges and solves for k
- + **2 pts** Plugs in correct values from any trial
- **2 pts** Wrong sig figs or wrong/no units
- **2 pts** Calculation or scientific notation error
- + **0 pts** Incorrect or blank

QUESTION 3

Iodine 10 pts

3.1 Calculate Concentration 10 / 10

- ✓ + **10 pts** Correct concentration with sig figs and units
- + **2 pts** Writes second order integrated rate law
- + **2 pts** Plugs in correct values
- **2 pts** Wrong sig figs or wrong / no units
- + **0 pts** Wrong integrated rate law
- **2 pts** Minor calculation error
- **2 pts** Contested rubric (no scoring error)

QUESTION 4

Isomerization Reaction 20 pts

4.1 Calculate Arrhenius Factor 8 / 10

- ✓ + **10 pts** Correct answer with units
- + **2 pts** Writes arrhenius equation
- + **2 pts** Rearranges and solves for A
- + **2 pts** Converts kJ to J or vice versa
- ✓ - **2 pts** Wrong/no units
- + **0 pts** Incorrect

4.2 Calculate Rate Constant 10 / 10

- ✓ + **10 pts** Correct final k with units

- **2 pts** wrong sig figs or wrong / no units
- + **7 pts** Right calculation with wrong numbers
- + **7 pts** Right calculation, arithmetic error
- **2 pts** Rounding error
- + **8 pts** Right calculation, k not evaluated
- + **0 pts** No credit

QUESTION 5

Steady State Assumption 15 pts

5.1 Rate Expression 15 / 15

- ✓ + **15 pts** Correct answer using steady state approx
- + **3 pts** Starts with correct differential rate law
- + **3 pts** Sets up steady state approx
- + **3 pts** Solves for [CI] in ss correctly
- + **0 pts** Incorrect
- **3 pts** Arithmetic Error / Missing Line
- **2 pts** Erroneous Superfluous Information

QUESTION 6

MM Kinetics 15 pts

6.1 Determine Constant 7 / 15

- ✓ + **7 pts** Correct value for k2 with units and sig figs
- + **8 pts** Correct value for km with unit and sig figs
- + **2 pts** Writes MM rate law
- + **3 pts** Simplifies rate for high [S]
- + **3 pts** Sets up ratio of rates to solve for km
- **2 pts** Wrong sig figs or no / wrong units
- + **0 pts** incorrect
- **2 pts** Small calculation error
- **2 pts** Contested the rubric and not a grading error

Chemistry 4B Exam 1
February 14, 2020
Professor Saykally

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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 to correct # of sig figs
- 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)

$$\text{rate} = k[\text{N}_2\text{O}_5]$$

$$t = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{t}$$

$$k = \frac{\ln 2}{4.03 \times 10^4 \text{ s}}$$

$$k = 1.72 \times 10^{-5} \text{ s}^{-1}$$

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

$$C = C_0 e^{-kt}$$

$$\frac{C}{C_0} = e^{-kt}$$

$$\frac{C}{C_0} = e^{-1.72 \times 10^{-5} \text{ s}^{-1} \cdot 1 \text{ day} \times \frac{24 \text{ hr}}{1 \text{ day}} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{60 \text{ s}}{1 \text{ min}}}$$

$$\frac{C}{C_0} = 0.226 \cdot 100\% = 22.6\% \text{ - percentage remaining}$$

$$\text{percentage that remain} = 22.6\% \text{ after a day}$$

(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:

Reaction	$[C_5H_5N]$ (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)

$$\text{rate} = k [C_5H_5N]^m [CH_3I]^n$$

$$\frac{1.00 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}}{3.00 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}} = \frac{k (2.00 \times 10^{-4} \text{ mol L}^{-1})^m (4.00 \times 10^{-4} \text{ mol L}^{-1})^n}{k (2.00 \times 10^{-4} \text{ mol L}^{-1})^m (2.00 \times 10^{-4} \text{ mol L}^{-1})^n}$$

$$2 = 2^m \Rightarrow m = 1$$

$$\frac{3.00 \times 10^{-6}}{7.50 \times 10^{-7}} = \frac{k (2.00 \times 10^{-4} \text{ mol L}^{-1})^m (2.00 \times 10^{-4} \text{ mol L}^{-1})^n}{k (1.00 \times 10^{-4} \text{ mol L}^{-1})^m (1.00 \times 10^{-4} \text{ mol L}^{-1})^n}$$

$$4 = 2^m 2^n \Rightarrow m = 1, n = 1$$

$$\boxed{\text{rate} = k [C_5H_5N] [CH_3I]}$$

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

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

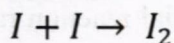
$$7.50 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} = k (1.00 \times 10^{-4} \text{ mol L}^{-1}) (1.00 \times 10^{-4} \text{ mol L}^{-1})$$

$$k = 7.50 \times 10^{-7} \frac{\text{mol}}{\text{L} \cdot \text{s}}$$

$$k = 7.50 \times 10^{-7} \frac{\text{mol}}{\text{L} \cdot \text{s}} \times \frac{1}{(1.00 \times 10^{-4} \text{ mol L}^{-1}) (1.00 \times 10^{-4} \text{ mol L}^{-1})}$$

$$\boxed{k = 75.0 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}}$$

(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)

$$\text{rate} = k[I]^2$$

$$k = 8.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$$

$$t = 2.0 \times 10^{-6} \text{ s}$$

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

$$\frac{1}{c} = \frac{1 + 2c_0kt}{c_0}$$

$$c = \frac{c_0}{1 + 2c_0kt}$$

$$c = \frac{1.00 \times 10^{-4} \text{ mol/L}}{1 + 2(1.00 \times 10^{-4} \text{ mol/L})(2.0 \times 10^{-6} \text{ s})(8.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1})}$$

$$c = 2.3 \times 10^{-5} \text{ M}$$

$$\boxed{[I] = 2.3 \times 10^{-5} \text{ M}}$$

(4) (20 points) The activation energy for the isomerization reaction of CH_3NC
 $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$
 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)

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

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln A = \ln k + \frac{E_a}{RT}$$

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

$$A = e^{\ln(0.41 \text{ s}^{-1}) + \frac{161 \text{ kJ mol}^{-1} \times 1000 \text{ J kJ}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 600 \text{ K}}}$$

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

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

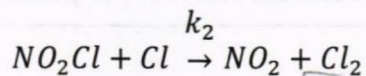
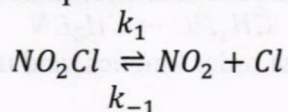
$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$k_2 = k_1 e^{-\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$k_2 = (0.41 \text{ s}^{-1}) e^{-\frac{161 \text{ kJ mol}^{-1} \times 1000 \text{ J kJ}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{1000} - \frac{1}{600}\right)}$$

$$k_2 = 1.7 \times 10^5 \text{ s}^{-1}$$

(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 .

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

Steady state approximation for $[\text{Cl}]$

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

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

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

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

(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 2.0×10^{-6} M, the maximum rate for substrate (NAG) reaction, found at high substrate concentration, is 1×10^{-6} mol L⁻¹ s⁻¹. The rate is reduced by a factor of 2 when the substrate concentration is reduced to 6.0×10^{-6} M. Determine the Michaelis-Menten constant K_m as well as k_2 for lysozyme.

when rate is half of maximum rate

$$[S] = K_m$$

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

when rate is maximum

$$\frac{d[P]}{dt} = k_2[E_0]$$

$$k_2 = \frac{1 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}}{2.0 \times 10^{-6} \text{ mol L}^{-1}}$$

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

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

