Chemistry 4B Exam 1
February 14, 2020
Professor Saykally

Name:______________________________
SID:______________________________
GSI:______________________________

Equations:

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

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

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

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

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

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)

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

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

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

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

$$k = \frac{\ln(2)}{t_{1/2}} = \frac{0.6931}{4.03x10^4 s} = 1.72x10^{-5}\ s^{-1}$$

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

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

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

$$\frac{c}{c_0} = e^{-\left(1.72x10^{-5}s^{-1}\right)*\left(24\ hrs*\frac{3600s}{hr}\right)}$$

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

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:

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)

$$Rate = k[C_5H_5N]^x[CH_3I]^y$$

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

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

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

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

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

Rate = k $[C_5H_5N][CH_3I]$

$$7.50x10^{-7}\,\frac{mol}{L*s^{-1}} = k * [1.00 * 10^{-4}\,\frac{mol}{L}][1.00 * 10^{-4}\,\frac{mol}{L}]$$

$$k = \frac{7.50x10^{-7}\frac{mol}{L*s^{-1}}}{[1.00*10^{-4}\frac{mol}{L}][1.00*10^{-4}\frac{mol}{L}]}$$

$$k = 75.0\,\frac{L}{mol*s}$$

(3) **(10 points)** At 25°C in CCl_4 solvent, the reaction

$$I + I \rightarrow I_2$$

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

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

$$\frac{1}{c} = \frac{1}{(1.00x10^{-4}\ M)} + (2 * \left(8.20x10^9 \frac{L}{mol\ s}\right) * (2.0x10^{-6} s))$$

$$\frac{1}{c} = 1.0x10^4 \frac{L}{mol} + 3.28x10^4 \frac{L}{mol} = 4.28x10^4 \frac{L}{mol}$$

$$c = \frac{1}{4.28x10^4 \frac{L}{mol}} = 2.3x10^{-5}\ M$$

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

$$CH_3NC \rightarrow CH_3CN$$

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)

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

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

$$A = \frac{0.41\ s^{-1}}{\exp\left(-1.61x10^5 J\ mol^{-1}/(8.3145\ J\ mol^{-1}K^{-1})(600K)\right)}$$

$$A = 4.3x10^{13}\ s^{-1}$$

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

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

$$k = (4.3x10^{13}s^{-1}) * \exp\left(-1.61x10^5 J\ mol^{-1}/(8.3145\ J\ mol^{-1}K^{-1})(1000K)\right)$$

$$k = 1.7x10^5 s^{-1}$$

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

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

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

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

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

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

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

$$[Cl]_{ss}(k_{-1}[NO_2] + k_2[NO_2Cl]) = k_1[NO_2Cl]$$

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

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

$$\boldsymbol{Rate = \frac{d[Cl_2]}{dt} = \frac{k_1 k_2[NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]}}$$

(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 x 10^{-6} M, the maximum rate for substrate (NAG) reaction, found at high substrate concentration, is 1 x 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 x 10^{-6} 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] >> k_M, so we can write:

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

$$k_2 = \frac{Max\ Rate}{[E]_0} = \frac{1x10^{-6}\ mol\ L^{-1}\ s^{-1}}{2.0x10^{-6}\ mol\ L^{-1}} = 0.5\ s^{-1}$$

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

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

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

$$\frac{1}{2} = \frac{[6.0x10^{-6}M]}{k_M + [6.0x10^{-6}M]}$$

$$k_M = 2[6.0x10^{-6}M] - [6.0x10^{-6}M]$$

$$k_M = 6.0x10^{-6}M$$