PHYSICAL CHEMISTRY (SAMPLE ASSIGNMENT)

1. A high-temperature study of the decomposition of SO Cl into SO and Cl , followed the reaction in time by measuring the system's

total pressure at constant volume.

Is the rate law first or second order in ? What is the rate law?

2 2 (g)

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time (hr)	P_{tot} (kPa)
0	11.07
3	14.79
6	17.26
9	18.90
12	19.99
15	20.71

$[SO_2Cl_2]$

Solution: *First, we need to find the partial pressure of SO^2Cl^2 $^{(g)}$ from the total pressure. We know:*

$$P_{tot} = P_{SO_2Cl_2} + P_{SO_2} + P_{Cl_2}$$

and given the stoichiometry of the reaction:

$$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

We know that for each mole of SO^2Cl^2 that decomposes, we get one mole of SO^2 and one mole of Cl^2, so:

$$P_{SO_2}(t) = P_{SO_2Cl_2}(0) - P_{SO_2Cl_2}(t)$$

$$P_{Cl_2}(t) = P_{SO_2Cl_2}(0) - P_{SO_2Cl_2}(t)$$

Plugging these into our expression for P_{tot} we get:

$$P_{tot}(t) = P_{SO_2Cl_2}(t) + P_{SO_2Cl_2}(0) - P_{SO_2Cl_2}(t) + P_{SO_2Cl_2}(0) - P_{SO_2Cl_2}(t)$$

So:

$$P_{tot}(t) = 2P_{SO_2Cl_2}(0) - P_{SO_2Cl_2}(t)$$

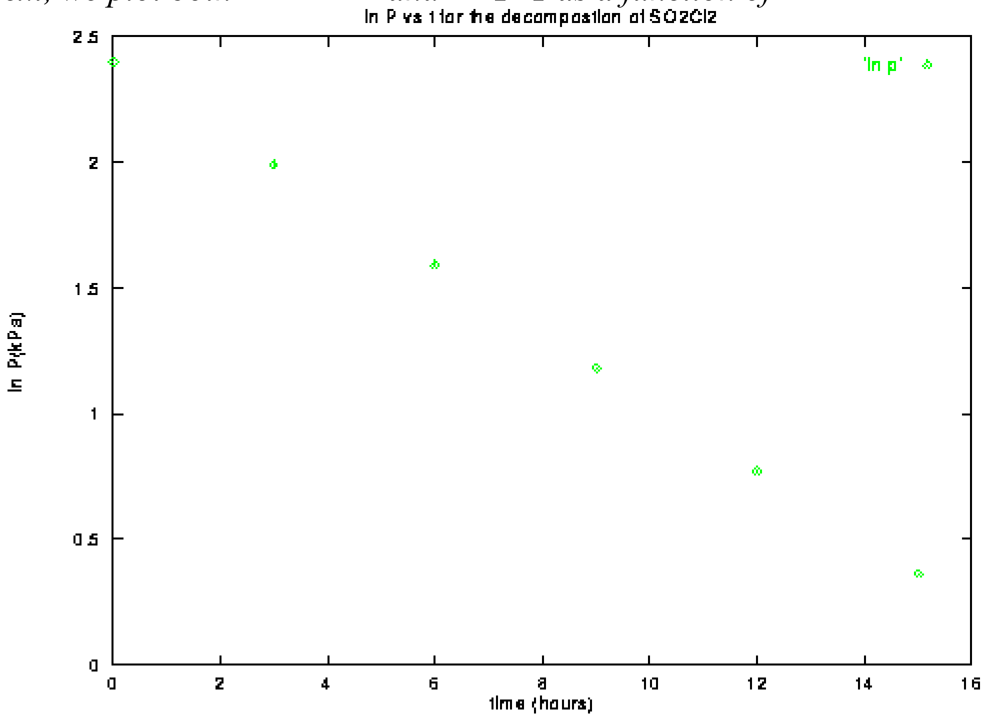
So:

$$P_{SO_2Cl_2}(t) = 2P_{SO_2Cl_2}(0) - P_{tot}(t)$$

Using P_{tot} *at time = 0, as our initial pressure of* SO^2Cl^2*,* $P_{SO_2Cl_2}(0)$ *we obtain the following:*

time (hr)	P_{tot} (kPa)	$P_{SO_2Cl_2}$ (kPa)
0	11.07	11.07
3	14.79	7.35
6	17.26	4.88
9	18.90	3.24
12	19.99	2.15
15	20.71	1.43

Next, we plot both $\ln P_{SO_2Cl_2}$ *and* $\frac{1}{P_{SO_2Cl_2}}$ *as a function of*



t.

Note that the plot of $\ln P_{SO_2Cl_2}$ *as a function of t is linear, so the reaction is first order.*

2. (3 pts) One of the hazards of nuclear explosions is the generation of ^{90}Sr and its subsequent incorporation in place of calcium in bones. This nuclide emits β rays of energy 0.55 MeV, and has a half-life of 28.1 years. Suppose 1.00 μg was ingested by a newly born child. How much will remain after (a) 18 yr (b) 70 yr, if none is lost metabolically?

Solution:

$$[A] = [A]_o e^{-kt}$$

Find k using the half-life:

$$\frac{0.5[A]_o}{[A]_o} = e^{-kt_{1/2}}$$

$$\ln 0.5 = -kt_{1/2}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{28.1\ years} = 2.45 \times 10^{-2}\ years^{-1}$$

$$[A]_{18\ years} = [A]_o e^{-kt} = (1.00 \times 10^{-6}\ g)e^{-(2.45\times10^{-2}\ years^{-1})(18\ years)} = 6.41 \times 10^{-7}\ g = 0.641$$

$$[A]_{70\ years} = [A]_o e^{-kt} = (1.00 \times 10^{-6}\ g)e^{-(2.45\times10^{-2}\ years^{-1})(70\ years)} = 1.78 \times 10^{-7}\ g = 0.178$$

3. A reaction:

$$2A \rightarrow$$

has a second order rate law with $k = 3.50 \times 10^{-4}\ L\ mol^{-1}\ s^{-1}$. Calculate the time required for the concentration of A to change from 0.260 M to 0.011 M.

Solution: *Using the integrated rate law for a second order equation, we find:*

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$$

so:

$$t = \frac{\frac{1}{[A]_t} - \frac{1}{[A]_o}}{k} = \frac{\frac{1}{0.011\ L\ mol^{-1}} - \frac{1}{0.260\ L\ mol^{-1}}}{3.50 \times 10^{-4}\ L\ mol^{-1}\ s^{-1}} = 2.48 \times 10^{5}\ s \times \frac{1\ hour}{3600\ s} \times \frac{1\ day}{24\ hours} = 2.88\ d$$

4. The data below correspond to the formation of urea from ammonium cyanate, $NH_4CNO \rightarrow NH_2CONH_2$. Initially 22.9 g of ammonium cyante was dissolved in enough water to prepare 1.00 L of solution. Determine the order of the reaction, the rate constant, and the mass of ammonium cyanate left after 300 min.

t (min)	m_{urea} (g)
0	0
20.0	7.0
50.0	12.1
65.0	13.8
150	17.7

Solution: *As the molecular weights are the same for ammonium cyanate and urea, and 1 mole of ammonium cyanate forms 1 mole of urea, the mass of urea* *at any time is equal to the mass of ammonium cyante consumed. We could use mass or molarity for the plots. We'll use molarity here. First, we need the initial concentration of ammonium cyanate:*

$$[NH_4CNO]_o = \frac{22.9\ g}{60.35\ g\ mol^{-1} \div 1.00\ L} = 0.379\ M$$

We can calculate the concentration of ammonium cyanate at any time given the mass of urea produced:

$$[NH_4CNO]_t = 0.379\ M - \left(\frac{m_{urea} g}{60.35\ g\ mol^{-1}} \div 1.00\ L\right)$$

Calling NH_4CNO ``A'', we can calculate $[A]$, $\ln[A]$, and $\frac{1}{[A]}$ and plot each vs. time. By using linear regression, we can confirm that the $\frac{1}{[A]}$ vs. time is linear. In addition to linear regression, blowing up the 0th and 1st order plots clearly demonstrates the curvature.

Using the slope from the second order plot we can find k:

$$k = slope = 0.0597\ M^{-1}\ min^{-1}$$

After 300 minutes we have:

$$m_{NH_4CNO} = [NH_4CNO]_{300} \times 1.00\ L \times 60.35\ g\ mol^{-1}$$

$$[NH_4CNO]_{300} = \frac{1}{kt + \frac{1}{[NH_4CNO]_o}} = \frac{1}{(0.0597\ M^{-1}\ min^{-1})(300\ min) + \frac{1}{0.379\ M}} = 4.87 \times 10^{-2}$$

so:

$$m_{NH_4CNO} = 4.87 \times 10^{-2}\ M \times 1.00\ L \times 60.35\ g\ mol^{-1} = 2.94\ g$$

5. (2 pts) The rate of consumption of B in the reacton

$$A + 3B \rightarrow C + 2$$

is $1.25 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}$. State the reaction rate, and the rates of formation or consumption of A, C and D.

Solution: *We know:*

$$-\frac{d[B]}{dt} = 1.25 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}$$

so:

$$rate = -\frac{1}{3}\frac{d[B]}{dt} = 4.17 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$$

$$-\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = 4.17 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$$

$$\frac{d[C]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = 4.17 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$$

$$\frac{d[D]}{dt} = -\frac{2}{3}\frac{d[B]}{dt} = 8.33 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$$