

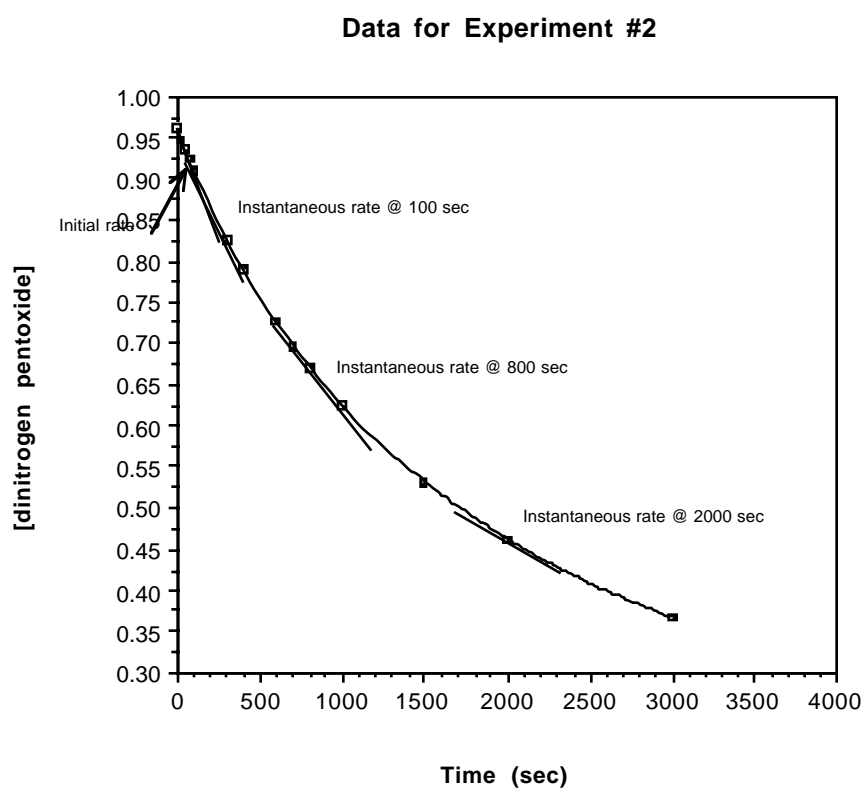
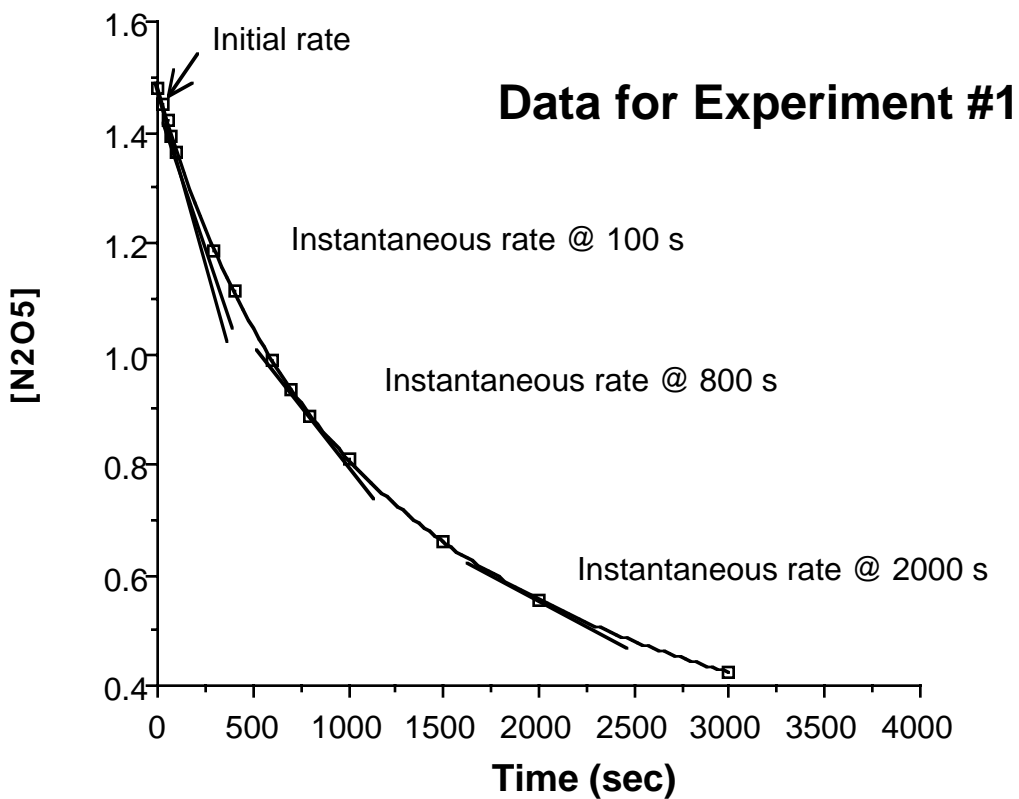
ALL work must be shown to receive full credit. **Due at the beginning of lecture on Monday, October 8, 2001.**

PS5.1. The following data was collected for the reaction



Experiment #1		Experiment #2	
time (sec)	Conc.(M)	time (sec)	Conc.(M)
0	1.480	0	0.960
25	1.450	25	0.947
50	1.421	50	0.935
75	1.393	75	0.923
100	1.366	100	0.911
300	1.185	300	0.826
400	1.111	400	0.790
600	0.988	600	0.726
700	0.936	700	0.697
800	0.889	800	0.671
1000	0.808	1000	0.624
1500	0.659	1500	0.531
2000	0.556	2000	0.462
3000	0.424	3000	0.367

a) Plot the data for Exp. #1 and graphically estimate



PS5.1. (Continued)

i) the initial rate

$$\frac{\Delta y}{\Delta x} = \frac{1.48 - 1.42}{0 - 50} = 1.20 \times 10^{-3} \frac{\text{M}}{\text{s}}$$

ii) the instantaneous rate at 100 sec? 800 sec? 2000 sec?

at 100 s instantaneous rate is $1.02 \times 10^{-3} \frac{\text{M}}{\text{s}}$

at 800 s instantaneous rate is $4.33 \times 10^{-3} \frac{\text{M}}{\text{s}}$

at 2000 s instantaneous rate is $1.69 \times 10^{-4} \frac{\text{M}}{\text{s}}$

iii) the time it takes for half of the N_2O_5 to react

half-life is approximately 1150 s

b) Repeat a) for Exp #2

i) the initial rate

$$\frac{\Delta y}{\Delta x} = \frac{0.960 - 0.947}{0 - 25} = 5.20 \times 10^{-4} \frac{\text{M}}{\text{s}}$$

ii) the instantaneous rate at 100 sec? 800 sec? 2000 sec?

at 100 s instantaneous rate is $4.3 \times 10^{-4} \frac{\text{M}}{\text{s}}$

at 800 s instantaneous rate is $2.6 \times 10^{-4} \frac{\text{M}}{\text{s}}$

at 2000 s instantaneous rate is $7.8 \times 10^{-5} \frac{\text{M}}{\text{s}}$

iii) the time it takes for half of the N_2O_5 to react

half-life is approximately 1800 s

c) By what factor did the initial concentration change in going from Exp #1 to Exp #2?

$$\frac{1.48 \text{ M}}{0.960 \text{ M}} = 1.54$$

d) By what factor did the initial rate change in going from Exp #1 to Exp #2?

$$\frac{1.20 \times 10^{-3} \frac{\text{M}}{\text{s}}}{5.20 \times 10^{-4} \frac{\text{M}}{\text{s}}} = 2.31$$

PS5.1. (Continued)

e) What is the order of the reaction with respect to N_2O_5 ?

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k_2[\text{N}_2\text{O}_5]_2^m}{k_1[\text{N}_2\text{O}_5]_1^m}$$
$$2.31 = (1.54)^m$$
$$m = 2$$

f) How did the half-life change for the two experiments?

The half-life increased by a factor of about 1.54.

g) Determine the rate constant for the reaction including units.

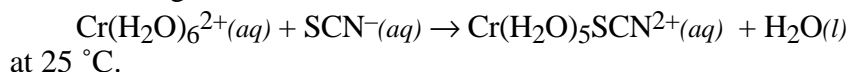
$$\text{rate} = k[\text{N}_2\text{O}_5]^2$$
$$k = \frac{\text{initial rate}}{[\text{N}_2\text{O}_5]^2}$$
$$= \frac{1.20 \times 10^{-3} \frac{\text{M}}{\text{s}}}{(1.48 \text{ M})^2}$$
$$= 5.48 \times 10^{-4} \text{ M}^{-1}\cdot\text{sec}^{-1}$$

h) What would the initial rate be if the initial concentration of N_2O_5 is 1.225 M? 0.475 M?

$$\text{rate} = k[\text{N}_2\text{O}_5]^2 = 5.48 \times 10^{-4} \text{ M}^{-1}\cdot\text{sec}^{-1} [1.225]^2 = 8.22 \times 10^{-4} \text{ M}\cdot\text{sec}^{-1}$$

$$\text{rate} = k[\text{N}_2\text{O}_5]^2 = 5.48 \times 10^{-4} \text{ M}^{-1}\cdot\text{sec}^{-1} [0.475]^2 = 1.24 \times 10^{-4} \text{ M}\cdot\text{sec}^{-1}$$

PS5.2. The following initial rate data were collected for the reaction



Exp. #	$[\text{Cr}(\text{H}_2\text{O})_6^{2+}(\text{aq})]$	$[\text{SCN}^-]$	initial rate $\left(\frac{\text{M}}{\text{s}}\right)$
1	$1.85 \times 10^{-4} \text{ M}$	0.25 M	9.25×10^{-11}
2	$4.56 \times 10^{-4} \text{ M}$	0.25 M	2.28×10^{-10}
3	$4.56 \times 10^{-4} \text{ M}$	0.101 M	9.25×10^{-11}

a) Determine the reaction order for $\text{Cr}(\text{H}_2\text{O})_6^{2+}(\text{aq})$ and SCN^- .

The reaction is first order for $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ and first order for SCN^- .

To determine the order with respect to $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ experiments 1 and 2 will be used since the concentration of SCN^- is constant.

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k_2[\text{Cr}(\text{H}_2\text{O})_6^{2+}]_2^m[\text{SCN}^-]_2^n}{k_1[\text{Cr}(\text{H}_2\text{O})_6^{2+}]_1^m[\text{SCN}^-]_1^n}$$

the rate constant and $[\text{SCN}^-]$ are constant.

$$\frac{2.28 \times 10^{-10} \frac{\text{M}}{\text{s}}}{9.25 \times 10^{-11} \frac{\text{M}}{\text{s}}} = \left(\frac{4.56 \times 10^{-4} \text{ M}}{1.85 \times 10^{-4} \text{ M}} \right)^m$$

$$2.46 = (2.46)^m$$

$$1 = m$$

To determine the order of the reaction with respect to SCN^- experiments 2 and 3 can be used.

$$\frac{\text{rate}_2}{\text{rate}_3} = \frac{k_2[\text{Cr}(\text{H}_2\text{O})_6^{2+}]_2^1[\text{SCN}^-]_2^n}{k_3[\text{Cr}(\text{H}_2\text{O})_6^{2+}]_3^1[\text{SCN}^-]_3^n}$$

$$\frac{2.28 \times 10^{-10} \frac{\text{M}}{\text{s}}}{9.25 \times 10^{-11} \frac{\text{M}}{\text{s}}} = \left(\frac{0.25}{0.101} \right)^n$$

$$2.46 = 2.47^n \quad n = 1$$

b) Determine the overall order of the reaction.

The reaction is second order overall. overall order = m + n = 2

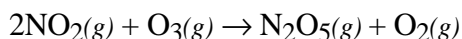
c) Write the specific rate law for the reaction.

$$\text{rate} = k[\text{Cr}(\text{H}_2\text{O})_6^{2+}]^1[\text{SCN}^-]^1$$

d) Determine the rate constant for the reaction (include units).

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{Cr}(\text{H}_2\text{O})_6^{2+}]^1[\text{SCN}^-]^1} \\ &= \frac{9.25 \times 10^{-11} \frac{\text{M}}{\text{s}}}{[1.85 \times 10^{-4} \text{ M}]^1[0.25 \text{ M}]^1} \\ &= 2.00 \times 10^{-6} \text{ M}^{-1} \cdot \text{sec}^{-1} \end{aligned}$$

PS5.3. The following initial rate data were collected for the reaction



at 100 °C.

Exp. #	[NO ₂]	[O ₃]	initial rate $\left(\frac{\text{M}}{\text{s}}\right)$
1	.65 M	.80 M	2.61 x 10 ⁴
2	1.10 M	.81 M	4.40 x 10 ⁴
3	1.70 M	1.55 M	1.32 x 10 ⁵

a) Determine the reaction order for NO₂ and O₃.

The reaction is first order for NO₂ and first order for O₃.

To determine the order with respect to NO₂ experiments 1 and 2 will be used since the concentration of O₃ is effectively constant.

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k_2[\text{NO}_2]_2^m[\text{O}_3]_2^n}{k_1[\text{NO}_2]_1^m[\text{O}_3]_1^n}$$

the rate constant and [O₃] are constant.

$$\frac{4.40 \times 10^4 \frac{\text{M}}{\text{s}}}{2.61 \times 10^4 \frac{\text{M}}{\text{s}}} = \left(\frac{1.10 \text{ M}}{0.65 \text{ M}}\right)^m$$

$$1.68 = (1.69)^m$$

$$1 = m$$

To determine the order of the reaction with respect to O₃ experiments 2 and 3 can be used.

$$\frac{\text{rate}_3}{\text{rate}_2} = \frac{k_3[\text{NO}_2]_3^1[\text{O}_3]_2^n}{k_2[\text{NO}_2]_2^1[\text{O}_3]_2^n}$$

$$\frac{1.32 \times 10^5 \frac{\text{M}}{\text{s}}}{4.40 \times 10^4 \frac{\text{M}}{\text{s}}} = \left(\frac{1.70}{1.10}\right)^1 \left(\frac{1.55}{0.81}\right)^n$$

$$3.00 = 1.55 \cdot 1.94^n$$

$$1.94 = 1.94^n$$

$$n = 1$$

The reaction is second order overall. overall order = m + n = 2

c) Write the specific rate law for the reaction.

$$\text{rate} = k[\text{NO}_2]^1[\text{O}_3]^1$$

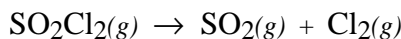
d) Determine the rate constant for the reaction (include units).

$$k = \frac{\text{rate}}{[\text{NO}_2]^1[\text{O}_3]^1}$$

$$= \frac{2.61 \times 10^4 \frac{\text{M}}{\text{s}}}{[0.65 \text{ M}]^1[0.80 \text{ M}]^1}$$

$$= 5.02 \times 10^4 \text{ M}^{-1} \cdot \text{sec}^{-1}$$

PS5.4. The reaction



follows simple first order kinetics. If the $[\text{SO}_2\text{Cl}_2]_0$ is 0.582 M,

- a) calculate the rate constant for the reaction if it takes 1.25×10^2 s for the concentration of SO_2Cl_2 to fall to 0.309 M.

$$\ln \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = -kt \qquad \ln \frac{[0.309 \text{ M}]}{[0.582 \text{ M}]_0} = -k(1.25 \times 10^2)$$

$$\ln 0.531 = -k(1.25 \times 10^2)$$

$$-0.633 = -k(1.25 \times 10^2)$$

$$k = 5.06 \times 10^{-3} \text{ s}^{-1}$$

- b) calculate the half-life for the reaction. (When the $[\text{SO}_2\text{Cl}_2]_0 = 0.582 \text{ M}$.)

$$t_{1/2} = \frac{0.693}{k} \qquad t_{1/2} = \frac{0.693}{5.06 \times 10^{-3} \text{ s}^{-1}} = 137 \text{ s}$$

- c) how long will it take for the $[\text{SO}_2\text{Cl}_2]$ to fall to 0.219 M?

$$\ln \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = -kt \qquad \ln \frac{[0.219 \text{ M}]}{[0.582 \text{ M}]_0} = -5.06 \times 10^{-3} \text{ s}^{-1}(t)$$

$$\ln 0.376 = -5.06 \times 10^{-3} \text{ s}^{-1}(t)$$

$$-0.977 = -5.06 \times 10^{-3} \text{ s}^{-1}(t)$$

$$t = 193 \text{ s}$$

- d) what is the $[\text{SO}_2\text{Cl}_2]$ after 350 s? (When $[\text{SO}_2\text{Cl}_2]_0 = 0.156 \text{ M}$.)

$$\ln \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = -kt \qquad \ln \frac{[\text{SO}_2\text{Cl}_2]}{[0.156 \text{ M}]_0} = -5.06 \times 10^{-3} \text{ s}^{-1}(350$$

s)

$$\ln [\text{SO}_2\text{Cl}_2] - \ln[0.156 \text{ M}]_0 = -1.77$$

$$\ln [\text{SO}_2\text{Cl}_2] = -1.77 + \ln[0.156 \text{ M}]_0 = -3.63$$

$$\ln [\text{SO}_2\text{Cl}_2] = -3.63$$

$$[\text{SO}_2\text{Cl}_2] = e^{-3.63} = 0.0266 \text{ M}$$

- e) calculate the fraction of SO_2Cl_2 that remains after 160 s.

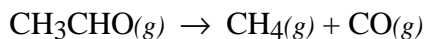
$$\ln \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = -kt \qquad \ln \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = -5.06 \times 10^{-3} \text{ s}^{-1}(160 \text{ s})$$

$$\ln \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = -0.810$$

$$\frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = e^{-0.810}$$

$$\frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = 0.445 \qquad [\text{SO}_2\text{Cl}_2]_t = 0.445[\text{SO}_2\text{Cl}_2]_0$$

PS5.5. The reaction



follows simple second order kinetics. When the $[\text{CH}_3\text{CHO}]_0 = 0.0120 \text{ M}$ the half-life is 8.75 s.

a) Calculate the rate constant for the reaction.

$$t_{1/2} = \frac{1}{k[\text{CH}_3\text{CHO}]_0} \quad k = \frac{1}{t_{1/2}[\text{CH}_3\text{CHO}]_0}$$
$$k = \frac{1}{8.75 \text{ s}(0.0120 \text{ M})} = 9.52 \text{ s}^{-1}\cdot\text{M}^{-1}$$

b) How long will it take for the $[\text{CH}_3\text{CHO}]$ to fall from 0.0120 M to $2.45 \times 10^{-3} \text{ M}$?

$$\frac{1}{[\text{CH}_3\text{CHO}]} - \frac{1}{[\text{CH}_3\text{CHO}]_0} = kt$$
$$\frac{1}{2.45 \times 10^{-3} \text{ M}} - \frac{1}{0.0120 \text{ M}} = 9.52 \text{ M}^{-1}\cdot\text{s}^{-1} (t)$$
$$t = 34.1 \text{ s}$$

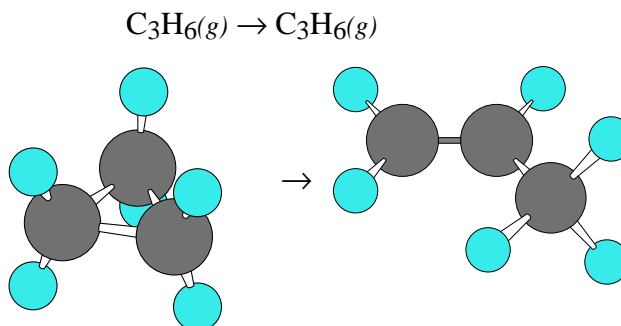
c) What is the $[\text{CH}_3\text{CHO}]$ after 7.0 minutes if $[\text{CH}_3\text{CHO}]_0 = 0.245 \text{ M}$?

$$\frac{1}{[\text{CH}_3\text{CHO}]} - \frac{1}{[\text{CH}_3\text{CHO}]_0} = kt$$
$$\frac{1}{[\text{CH}_3\text{CHO}]} - \frac{1}{0.245 \text{ M}} = 9.52 \text{ M}^{-1}\cdot\text{s}^{-1} (7 \text{ min}) \left(\frac{60 \text{ s}}{1 \text{ min}} \right)$$
$$\frac{1}{[\text{CH}_3\text{CHO}]} = 3998 \text{ M}^{-1} + \frac{1}{0.245 \text{ M}}$$
$$[\text{CH}_3\text{CHO}] = 2.50 \times 10^{-4} \text{ M}$$

d) How long will it take for the $[\text{CH}_3\text{CHO}]$ to decrease to 0.166 of its original concentration when the $[\text{CH}_3\text{CHO}]_0 = 0.245 \text{ M}$?

$$\frac{1}{[\text{CH}_3\text{CHO}]} - \frac{1}{[\text{CH}_3\text{CHO}]_0} = kt$$
$$\frac{1}{0.0407 \text{ M}} - \frac{1}{0.245 \text{ M}} = 9.52 \text{ M}^{-1}\cdot\text{s}^{-1} (t)$$
$$t = 2.15 \text{ s}$$

PS5.6. C_3H_6 re-arranges from a cyclic structure to a straight chain structure according to the following equation;



- the rate constant for the decomposition is $5.5 \times 10^{-4} \text{ s}^{-1}$ at 500°C .
- a) What is the order of the reaction?

1st order based on the unit of the rate constant

- b) How long would it take for 15.00 % of a sample of C_3H_6 to decompose at 500°C and 1 atm?

Since the reaction is first order we do not need to know the initial concentration of $C_3H_6(g)$. The time required for 15% of a sample to react is equivalent to the time when the concentration of $C_3H_6(g)$ is 85% of the initial $C_3H_6(g)$ concentration. That is,

$$[C_3H_6]_t = 0.85 [C_3H_6]_0$$

$$\frac{\ln [C_3H_6]_t}{[C_3H_6]_0} = -kt$$

$$\frac{\ln 0.85 [C_3H_6]_0}{[C_3H_6]_0} = -5.5 \times 10^{-4} \text{ sec}^{-1} \text{ (time)}$$

$$\ln 0.85 = -5.5 \times 10^{-4} \text{ sec}^{-1} \text{ (time)}$$

$$-0.163 = -5.5 \times 10^{-4} \text{ sec}^{-1} \text{ (t)}$$

$$295 \text{ sec} = \text{time}$$

If the students need a concentration it can be calculated using $PV=nRT$ recall

$$PV = nRT \quad \text{or} \quad \frac{n}{V} = \frac{P}{RT}$$

$$M = \frac{1 \text{ atm}}{0.0821 \frac{\text{L} \cdot \text{atm} (298 \text{ K})}{\text{mol} \cdot \text{K}}}$$

$$[C_3H_6]_0 = 0.0409 \text{ M}$$

So 15% reacting leaves 85% unreacted

$$[C_3H_6]_t = 0.0348 \text{ M}$$

$$\frac{\ln 0.0348}{0.0409} = -5.5 \times 10^{-4} \text{ sec}^{-1} \text{ (time)}$$

$$\ln 0.85 = -5.5 \times 10^{-4} \text{ sec}^{-1} \text{ (time)}$$

$$\ln 0.85 = -5.5 \times 10^{-4} \text{ sec}^{-1} \text{ (time)}$$

$$295 \text{ sec} = \text{time}$$

- c) What is the half-life of the reaction?
The half-life of the reaction is

$$t_{1/2} = \frac{0.693}{k}$$

$$= \frac{0.693}{5.5 \times 10^{-4} \text{ sec}^{-1}}$$

$$= 1.26 \times 10^3 \text{ sec}$$

- d) How long would it take for 15.00 % of a sample of C_3H_6 to decompose at 500 °C and 10 atm?

For first order reactions, the time required for a specific amount of reaction to occur is independent of the initial concentration. Therefore, the time is identical to part b). If the $[\text{C}_3\text{H}_6]_0$ is determined it should be

$$M = \frac{P}{RT}$$

$$= \frac{10 \text{ atm}}{0.0821 \frac{\text{L}\cdot\text{atm} (298 \text{ K})}{\text{mol}\cdot\text{K}}}$$

$$= 0.409 \text{ M}$$

Performing the same calculations as used in part b) will yield the same answer as part b).

PS5.7. The second-order thermal decomposition of hydrogen bromide, $\text{HBr}(g)$, has a half-life of 2.74 s at a given temperature when the initial concentration of HBr is 0.0714 M.

- a) What is the concentration of hydrogen bromide after 3.16 s?

$$t_{1/2} = \frac{1}{k[\text{HBr}]_0} \quad k = \frac{1}{t_{1/2}[\text{HBr}]_0}$$

$$k = \frac{1}{2.74 \cdot \text{s}(0.0714 \text{ M})} = 5.11 \text{ s}^{-1} \cdot \text{M}^{-1}$$

$$\frac{1}{[\text{HBr}]} - \frac{1}{[\text{HBr}]_0} = kt$$

$$\frac{1}{[\text{HBr}]} - \frac{1}{0.0714 \text{ M}} = 5.11 \text{ M}^{-1} \cdot \text{s}^{-1} (3.16 \text{ s})$$

$$\frac{1}{[\text{HBr}]} = 14.0 \text{ M}^{-1} + \frac{1}{0.0714 \text{ M}}$$

$$[\text{HBr}] = 3.32 \times 10^{-2} \text{ M}$$

- b) How long will it take for 20.0 % of the sample to decompose?

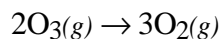
$$[\text{HBr}]_t = 0.80[\text{HBr}]_0 = 0.80 (0.0714 \text{ M}) = 0.0571 \text{ M}$$

$$\frac{1}{[\text{HBr}]} - \frac{1}{[\text{HBr}]_0} = kt$$

$$\frac{1}{0.0571 \text{ M}} - \frac{1}{0.0714 \text{ M}} = 5.11 \text{ M}^{-1} \cdot \text{s}^{-1} (t)$$

$$t = 0.686 \text{ s}$$

PS5.8. The rate constant for the gas phase decomposition of ozone



is $0.0140 \text{ M}^{-1}\cdot\text{sec}^{-1}$ at 80°C .

- a) How long will it take for 90 % of a sample of ozone to decompose given that the initial concentration is $6.00 \times 10^{-3} \text{ M}$?

$$\frac{1}{[\text{O}_3]_t} - \frac{1}{[\text{O}_3]_0} = kt$$

$$0.10 \cdot 6.00 \times 10^{-3} \text{ M} = 6.00 \times 10^{-4} \text{ M remaining}$$

$$\frac{1}{[6 \times 10^{-4} \text{ M}]} - \frac{1}{6 \times 10^{-3} \text{ M}} = 0.0140 \text{ M}^{-1}\cdot\text{s}^{-1} (t)$$

$$1500 \text{ M}^{-1} = 0.0140 \text{ M}^{-1}\cdot\text{s}^{-1} (t)$$

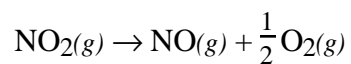
$$t = \frac{1500 \text{ M}^{-1}}{0.0140 \text{ M}^{-1}\cdot\text{s}^{-1}} = 1.19 \times 10^5 \text{ seconds}$$

- b) What is the half-life of the reaction for this initial concentration?

$$t_{1/2} = \frac{1}{k[\text{O}_3]_0}$$

$$t_{1/2} = \frac{1}{0.0140 \text{ M}^{-1}\cdot\text{s}^{-1}(6.00 \times 10^{-3} \text{ M})} = 1.19 \times 10^4 \text{ s}$$

PS5.9. In the reaction



the $[\text{NO}_2]$ was followed with time and the data shown below was obtained.

Time(s)	$[\text{NO}_2](\text{M})$
0	0.0831
4.2	0.0666
7.9	0.0567
11.4	0.0497
15	0.0441

Determine the order of the reaction and its half-life. (Include graphs of your data to support your conclusion. Be sure all plots are included.)

PS5.10a. Draw the Lewis structure and name the following compounds;



2, 3, 3-trimethylhexane



2, 5, 5, 8-tetramethylnonane

PS3.10b. Draw the structure which corresponds with each of the following names.

