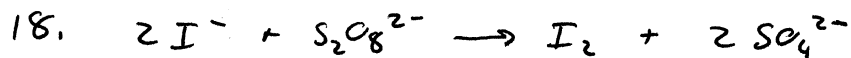


1. Ch 15, 16. k for $\text{H}\ddot{\text{O}}\cdot + \text{benzene} = 1.24 \times 10^{-12} \frac{\text{cm}^3}{\text{molecule}\cdot\text{sec}}$

$$1.24 \times 10^{-12} \frac{\text{cm}^3}{\text{molec}\cdot\text{sec}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} \times \frac{6.022 \times 10^{23} \text{ molec}}{1 \text{ mol}}$$

$$= 7.47 \times 10^8 \text{ L mol}^{-1}\text{sec}^{-1} = 7.47 \times 10^8 \text{ M}^{-1}\text{sec}^{-1}$$



a. conc. vs initial rate data $\Rightarrow 2 \times [\text{I}^-] \Rightarrow 2 \times \text{rate}$
 $2 \times [\text{S}_2\text{O}_8^{2-}] \Rightarrow 2 \times \text{rate}$

so

$$\text{rate} = -\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = -\frac{1}{2} \frac{d[\text{I}^-]}{dt} = k[\text{I}^-][\text{S}_2\text{O}_8^{2-}]$$

b. $3.91 \times 10^{-3} \text{ M}^{-1}\text{sec}^{-1}$ for first 4, $3.89 \times 10^{-3} \text{ M}^{-1}\text{sec}^{-1}$ for 5th
 the average is $3.91 \times 10^{-3} \text{ M}^{-1}\text{sec}^{-1}$,
 but conc. data has only 2 sig figs, so $3.9 \times 10^{-3} \text{ M}^{-1}\text{sec}^{-1}$
 (kind of a silly exercise - sorry.)

20. a. 1st-order in each; b. rate = $k[\text{Hb}][\text{CO}]$

c. $k = \frac{\text{rate}}{[\text{Hb}][\text{CO}]}$

0.280 $\mu\text{M}^{-1}\text{sec}^{-1}$ 1st set of data

0.281 " " 2nd " " "

0.280 " " 3rd " " "

ave = 0.280 $\mu\text{M}^{-1}\text{sec}^{-1}$

$$\times \frac{10^6 \mu\text{M}}{1 \text{ M}} = 0.280 \times 10^6 \text{ M}^{-1}\text{sec}^{-1}$$

$$= 2.80 \times 10^5 \text{ M}^{-1}\text{sec}^{-1}$$

d. plug 'n' chug ...

init. rate = 2.26 $\mu\text{M sec}^{-1}$

(= $2.26 \times 10^{-6} \text{ M sec}^{-1}$)

29. linear plot of $\ln[A]$ vs $t \Rightarrow$ 1st-order rxn, rate = $k[A]$

a.

integrated rate law: $\ln[A] = -kt + \ln[A]_0$

$$\text{slope} = -k = -2.97 \times 10^{-2} \text{ min}^{-1}$$

$$\text{so } k = 2.97 \times 10^{-2} \text{ min}^{-1} \times \frac{1 \text{ min}}{60 \text{ sec}}$$

$$= 4.95 \times 10^{-4} \text{ sec}^{-1}$$

b. $t_{1/2} = \frac{\ln 2}{k} = 1400 \text{ sec} = 23.3 \text{ min}$

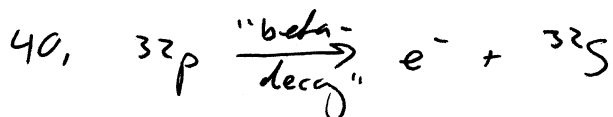
c.

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt \quad \text{plug in } k, [A]_0 = 2.00 \times 10^{-2} \text{ M}$$

$$\& [A] = 2.50 \times 10^{-3} \text{ M}$$

$$\Rightarrow t = 4200 \text{ sec} = 70 \text{ min}$$

also note that $0.25 \times 10^{-2} \text{ M}$ is $\frac{1}{8}$ init conc. -
so exactly 3 half-lives gets the rxn
to this point.



$$t_{1/2} = 14.3 \text{ days} \Rightarrow k = \frac{\ln 2}{t_{1/2}} = 0.0485 \text{ day}^{-1} \quad (\text{I'll leave}$$

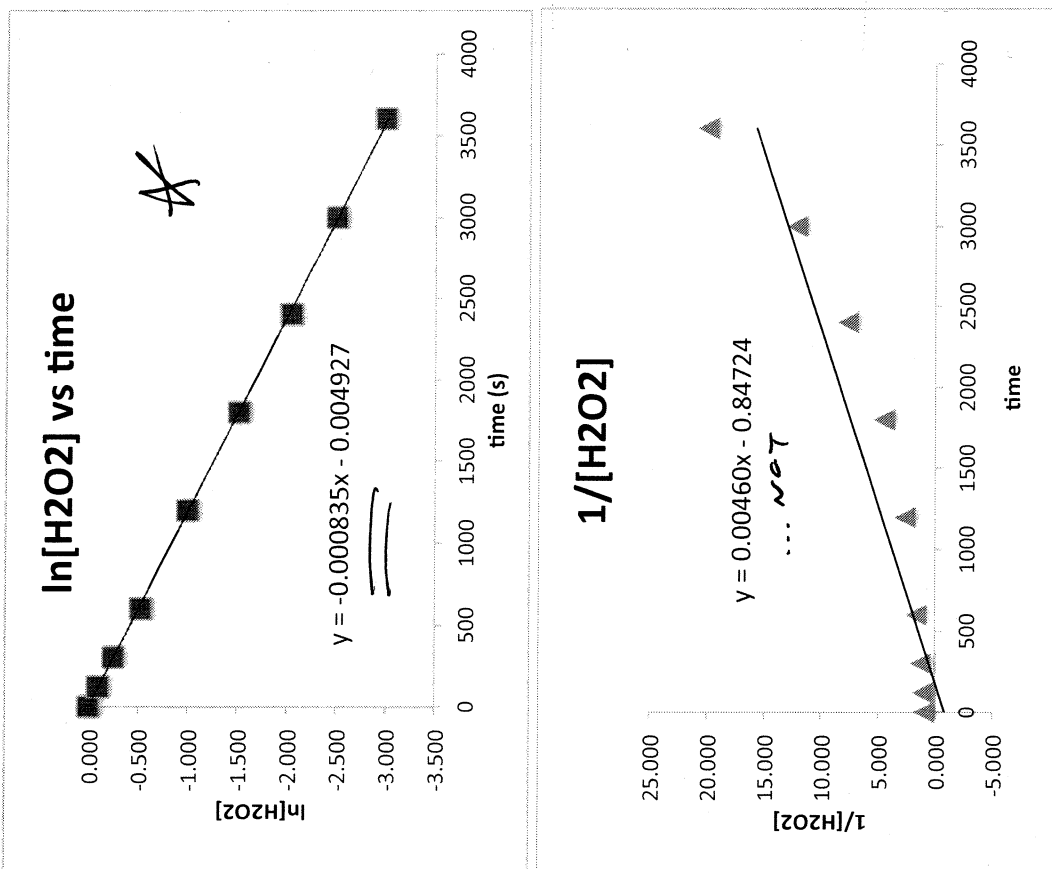
$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

↑
for 95% decay, "[A]" = 5%
so this ratio is 20

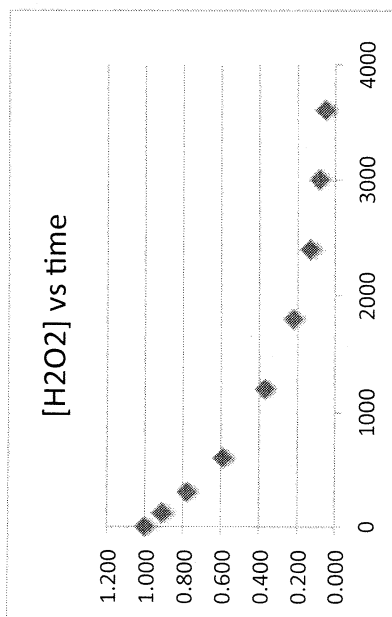
$$t = 61.8 \text{ days} \left(\times \frac{1 \text{ month}}{30.437 \text{ days}} = 2.03 \text{ months} \right)$$

this in units of
per day since
the result we
want will probably
be in days.)

2. Ch 15 31. If 1st-order, a plot of $\ln[H_2O_2]$ vs t will be linear
 $(\ln[H_2O_2] = -kt + \ln[H_2O_2]_0)$
 If 2nd-order, a plot of $1/[H_2O_2]$ vs t will be linear
 $(1/[H_2O_2] = kt + 1/[H_2O_2]_0)$



time (s)	[H2O2] (M)	ln[H2O2]	1/[H2O2]
0	1.000	0.000	1.000
120	0.910	-0.094	1.099
300	0.780	-0.248	1.282
600	0.590	-0.528	1.695
1200	0.370	-0.994	2.703
1800	0.220	-1.514	4.545
2400	0.130	-2.040	7.692
3000	0.082	-2.501	12.195
3600	0.050	-2.996	20.000



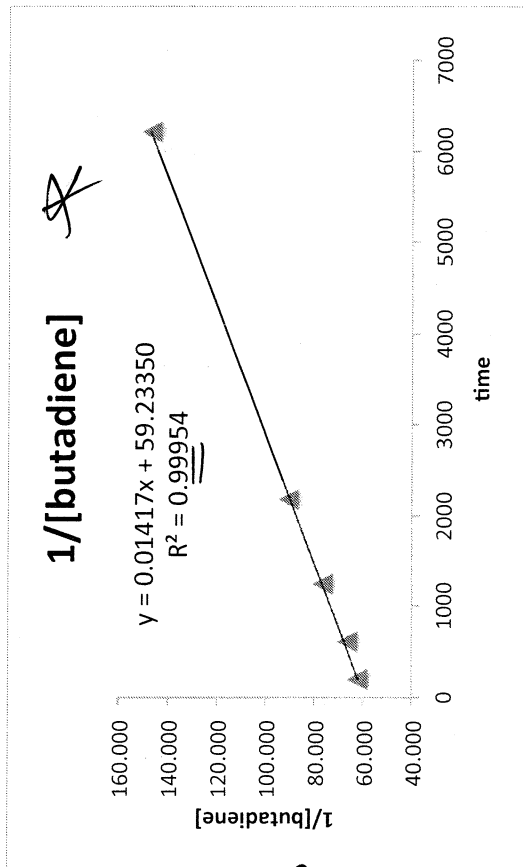
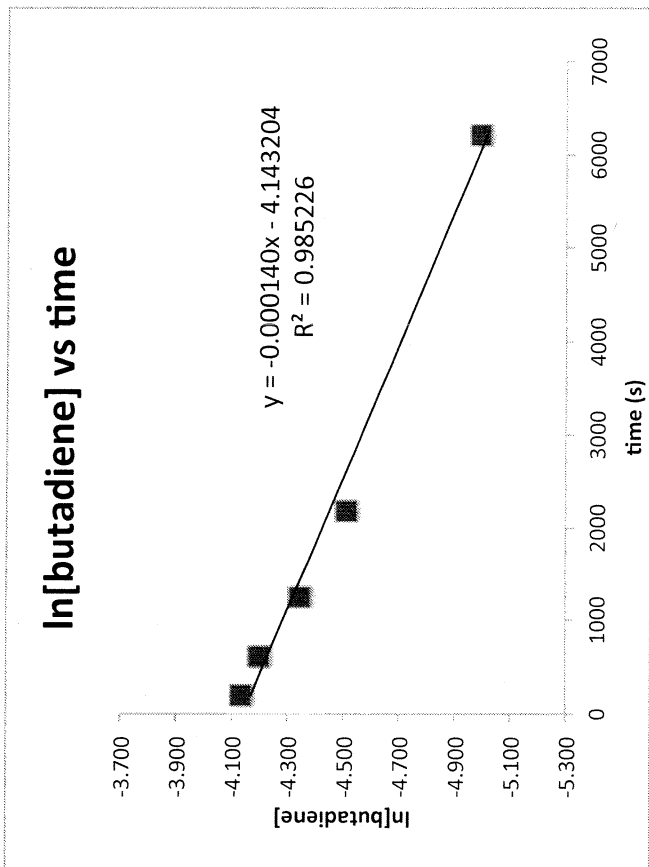
$$k = 8.35 \times 10^{-4} \text{ sec}^{-1}$$

at $t = 4000 \text{ sec}$,

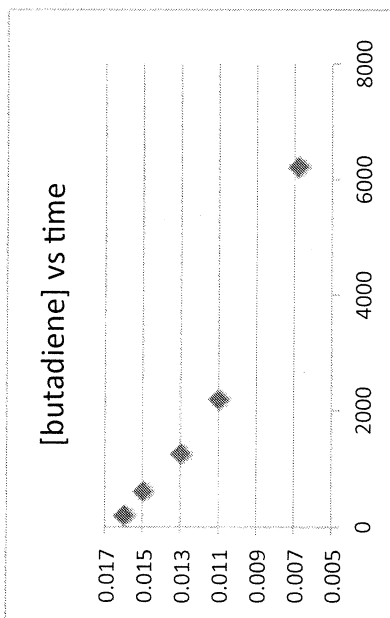
$$\ln[H_2O_2] = -3.34$$

$$\text{so } [H_2O_2] = 0.035 \text{ M}$$

32. This is tough because that $\ln[\text{butadiene}]$ vs t plot is close to linear. The $1/[\text{but.}]$ vs t plot has a better correlation coefficient (R^2 value), but this data set could really benefit from a few more points!



time (s)	[C4H6] (M)	$\ln[C4H6]$	$1/[C4H6]$
195	0.016	-4.135	62.500
604	0.015	-4.200	66.667
1246	0.013	-4.343	76.923
2180	0.011	-4.510	90.909
6210	0.007	-4.991	147.059



↑
2nd-order -

$$\text{rate} = -\frac{1}{2} \frac{d[\text{but.}]}{dt} = k[\text{but.}]^2$$

\equiv
integrated rate law is:

$$\frac{1}{[\text{but.}]} = 2kt + \frac{1}{[\text{but.}]_0}$$

$$\text{slope} = 0.01417 = 2k$$

$$k = 7.1 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$$