S1.3 a. rate $= k[A]^{3/2}$

$$-\frac{d[A]}{dt} = k[A]^{3/2}$$

$$\frac{1}{[A]^{3/2}}\, d[A] = -k\,dt$$

$$\int_{[A]_0}^{[A]_t} \frac{1}{[A]^{3/2}}\, d[A] = -k\int_0^t dt$$

$$\left.\frac{[A]^{-1/2}}{(-1/2)}\right|_{[A]_0}^{[A]_t} = -kt\Big|_0^t$$

$$\boxed{\frac{1}{[A]_t^{1/2}} - \frac{1}{[A]_0^{1/2}} = \frac{1}{2}kt}$$

At $t_{1/2}$ $[A]_t = \frac{1}{2}[A]_0$

so, $$\frac{1}{\left(\frac{[A]_0}{2}\right)^{1/2}} - \frac{1}{[A]_0^{1/2}} = \frac{1}{2}kt_{1/2}$$

$$\frac{2^{1/2}-1}{[A]_0^{1/2}} = \frac{1}{2}kt_{1/2}$$

$$\boxed{t_{1/2} = \frac{2}{k}\left(\frac{2^{1/2}-1}{[A]_0^{1/2}}\right)}$$

51.4

$SO_2Cl_2 \longrightarrow SO_2 + Cl_2 \qquad k_1 = 2.20\times10^{-5}\ s^{-1} \quad T = 593K$

1st order $\longrightarrow \quad -\frac{d[SO_2Cl_2]}{dt} = k[SO_2Cl_2]$

integrated rate law: $\ln\left(\frac{[SO_2Cl_2]_t}{[SO_2Cl_2]_0}\right) = -kt$

$t = 60\,min\left(\frac{60\,s}{1\,min}\right) = 3600\,s$

% dissociated $= \left(1 - \frac{[SO_2Cl_2]_t}{[SO_2Cl_2]_0}\right)100\%$

↑ so work out ratio $= \frac{[SO_2Cl_2]_t}{[SO_2Cl_2]_0}$

$\ln(\text{ratio}) = -(2.20\times10^{-5}\,s^{-1})(3600\,s) = -0.07920$

ratio $= 0.92386$

% diss. $= (1 - 0.92386)100\% = \boxed{7.61\%}$ (1 hour)

$t = 3\,hours = 3(3600\,s) = 10800\,s$

$\ln(\text{ratio}) = -(2.20\times10^{-5}\,s^{-1})(10800\,s) = -0.23760$

ratio $= 0.78852$

% diss. $= (1 - 0.78852)100\% = \boxed{21.1\%}$ (3 hours)

At $t_{1/2}$, ratio $= 0.5$:

$\ln(0.5) = -(2.20\times10^{-5}\,s^{-1})\,t_{1/2}$

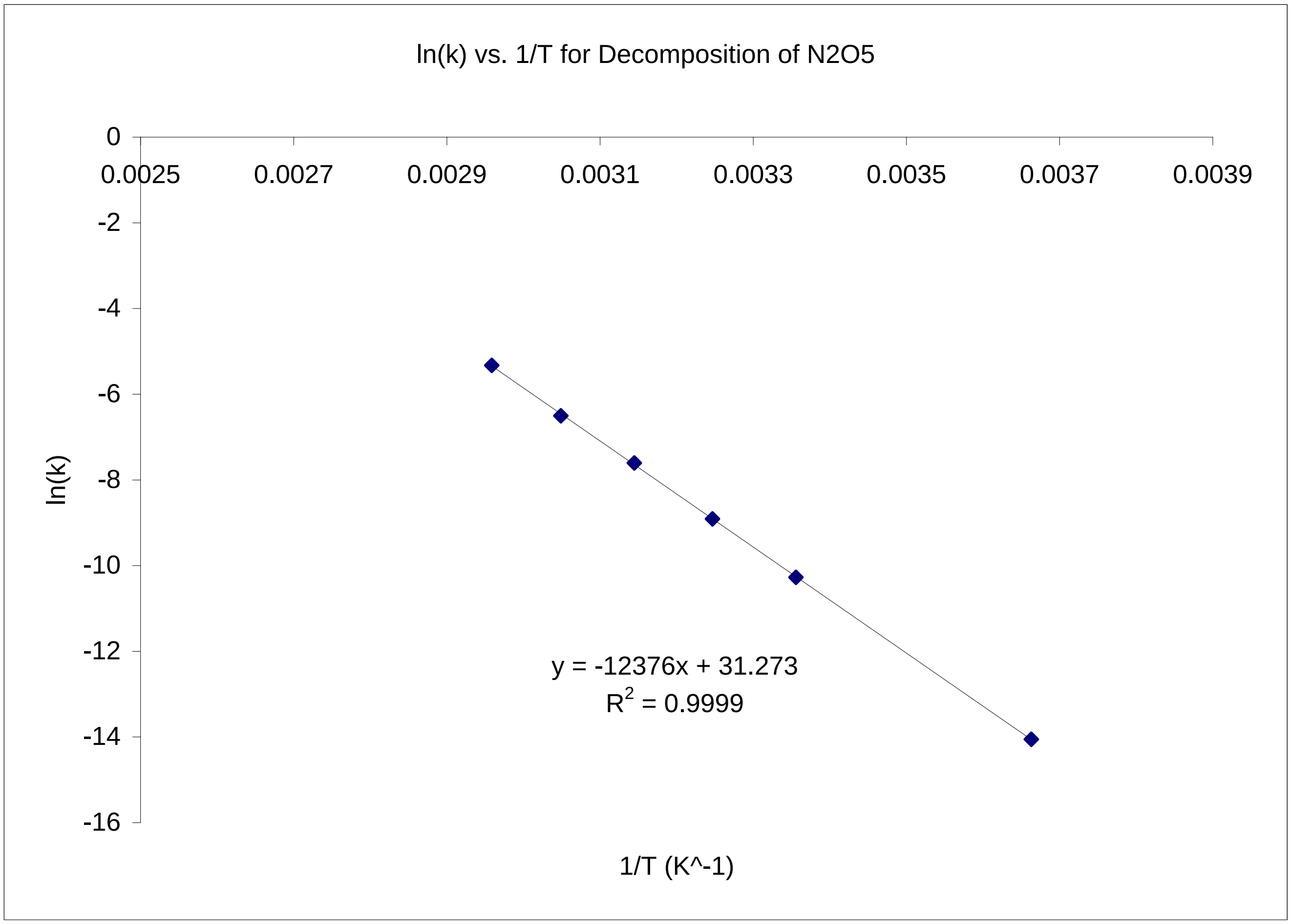
$t_{1/2} = 31506.7\,s = \boxed{8.75\,hr}$

or, for 1st order $t_{1/2} = \frac{0.693}{k}$

$t_{1/2} = \frac{0.693}{2.20\times10^{-5}\,s^{-1}}\left(\frac{1\,min}{60\,s}\right)\left(\frac{1\,hr}{60\,min}\right)$

$t_{1/2} = \boxed{8.75\,hr}$

T(K)	k(10^5 s-1)	1/T (K^-1)	ln(k)
273	0.0787	0.003663	-14.05504
298	3.46	0.003356	-10.27166
308	13.5	0.003247	-8.910236
318	49.8	0.003145	-7.60491
328	150	0.003049	-6.50229
338	487	0.002959	-5.324661



S 1.6 plot ln k vs. $1/T$

slope $= -E_a/R$

$$-12376\ K = -\frac{E_a}{8.3145\ J/mol \cdot K}$$

$$E_a = +102900\ J/mol = 103\ kJ/mol$$

intercept = ln A

$\ln A = 31.273$

$A = 3.81 \times 10^{13}\ s^{-1}$

S 1.7 a. $NO_3 + NO \longrightarrow 2\ NO_2$

$$rate = -\frac{d[NO_3]}{dt} = -\frac{d[NO]}{dt}$$

b. $rate = \frac{1}{2}\frac{d[NO_2]}{dt}$

c. $rate = k[NO_3][NO]$
(Unclear what c. is asking for)

H2.1 $\_A + \_B \longrightarrow P$

$A \times 2$, rate $\times 2$ $\rightarrow$ $[A]^1$

$B \times y$, rate $\times \sqrt{y}$ $[B]^{1/2}$

overall order $= 1 + \frac{1}{2} = \boxed{3/2 \ (c)}$

H2.3 $[A]_t = \frac{1}{x}[A]_0$

for 1st order, $t_{1/2}$ (drop [A] by ½) is indep. of [A], so test this as possible answer:

$$\ln[A]_t = \ln[A]_0 - kt_{1/x}$$

$$\ln\frac{[A]_0}{x} = \ln[A]_0 - kt_{1/x}$$

$$\ln\frac{[A]_0/x}{[A]_0} = -kt_{1/x}$$ → concentration cancels!

$$\ln\left(\frac{1}{x}\right) = -kt_{1/x}$$

$$t_{1/x} = +\frac{\ln x}{k}$$ → concentration independent, so

1st order time to decrease to any fraction of $[A]_0$ will be independent of $[A]_0$.