

Chemistry 2710 Spring 2001 Test 1 Solutions

1.

$$\frac{db}{dt} \approx \frac{\Delta b}{\Delta t} = \frac{1.4 \times 10^{-4} \text{ mol/L}}{3.5 \text{ s}} = 4.0 \times 10^{-5} \text{ molL}^{-1}\text{s}^{-1}$$
$$\therefore v = \frac{1}{3} \frac{db}{dt} \approx 1.3 \times 10^{-5} \text{ molL}^{-1}\text{s}^{-1}$$

2. (a) $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$

(b) $v = k_1[\text{N}_2\text{O}_4]^2$

(c) The empirical equilibrium constant for the overall reaction (expressed in terms of concentrations) is

$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

According to the principle of detailed balance, at equilibrium,

$$k_1[\text{N}_2\text{O}_4]^2 = k_{-1}[\text{N}_2\text{O}_4][\text{N}_2\text{O}_4^*]$$

and $k_2[\text{N}_2\text{O}_4^*] = k_{-2}[\text{NO}_2]^2$

These equations can be rearranged to

$$\frac{[\text{N}_2\text{O}_4^*]}{[\text{N}_2\text{O}_4]} = \frac{k_1}{k_{-1}}$$

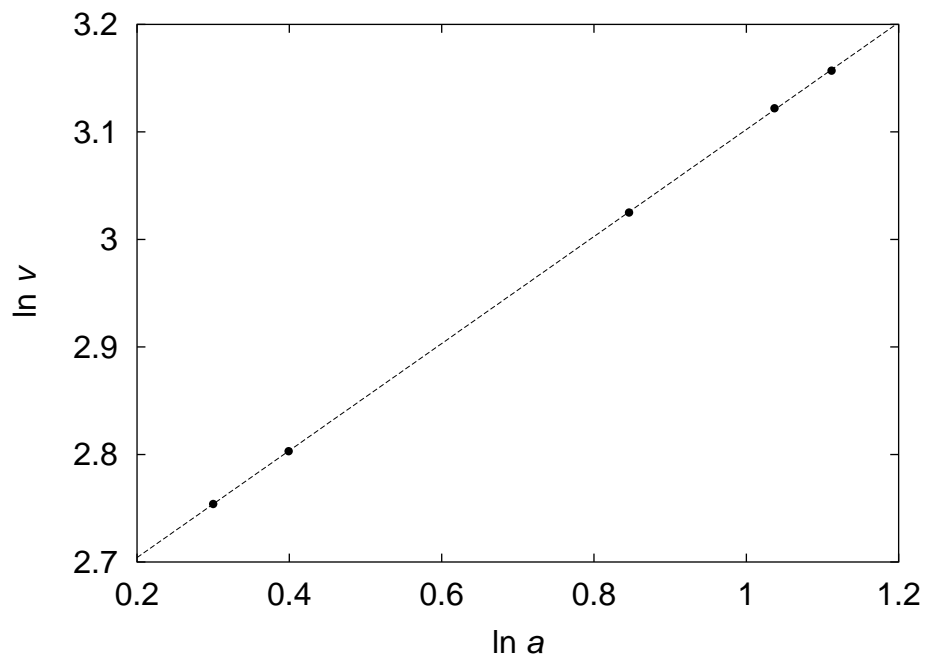
and $\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4^*]} = \frac{k_2}{k_{-2}}$

If we multiply these equations together, we get

$$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = K = \frac{k_1 k_2}{k_{-1} k_{-2}}$$

3. Since we have several points, it is probably best to use van't Hoff's method. In van't Hoff's method, we plot $\ln v$ against $\ln a$.

$\ln a$	0.300	0.399	0.846	1.037	1.112
$\ln v$	2.754	2.803	3.025	3.122	3.157

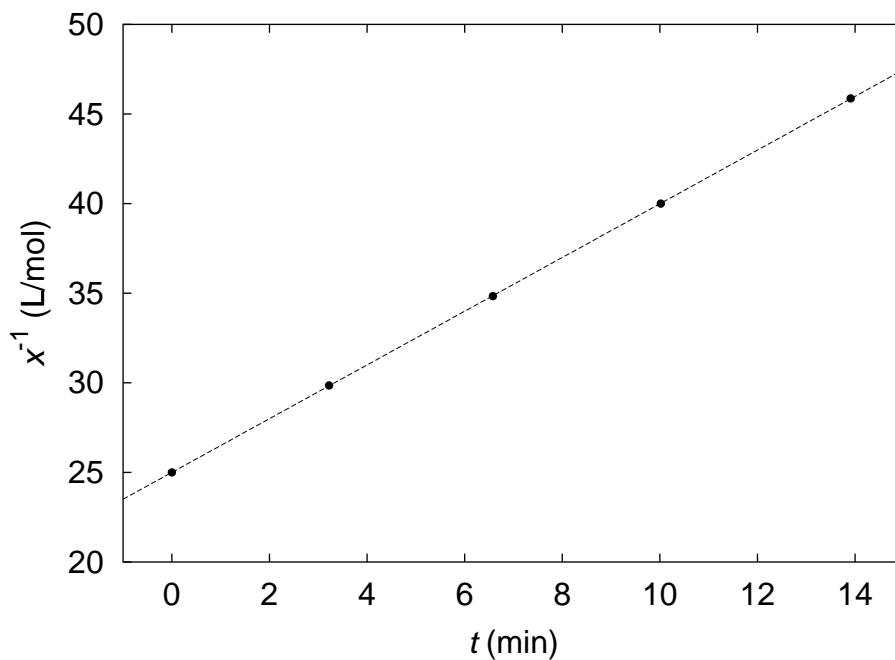


The plot is nicely linear so the reaction does have a simple rate law. The slope of the plot is 0.50, so the order of the reaction is $\frac{1}{2}$.

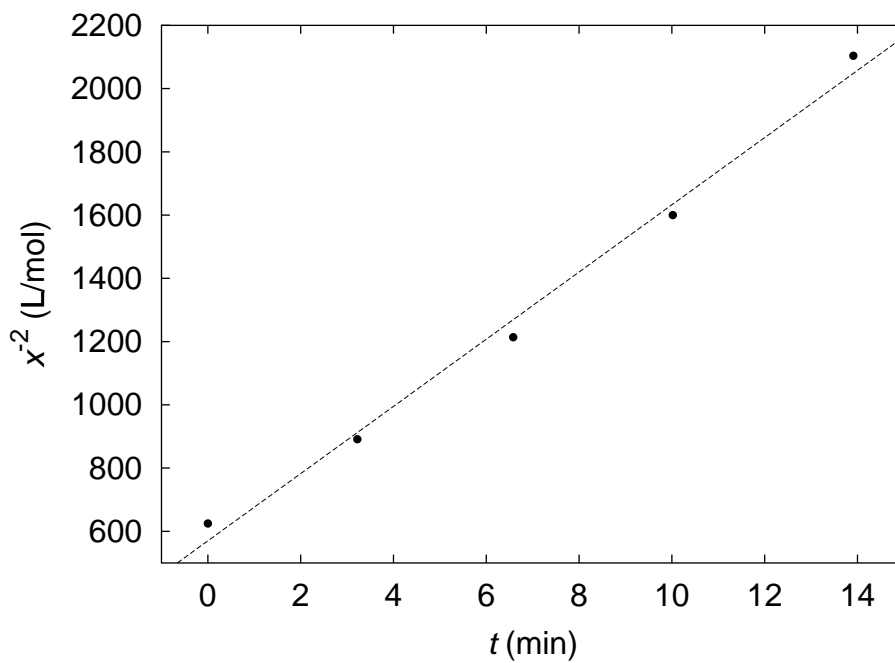
4. (a) We first need to calculate x as a function of t : The amount of Z produced is twice the amount of X used, i.e. $z = 2(x_0 - x)$ or $x = x_0 - \frac{1}{2}z$. Thus we have

t (min)	0	3.22	6.58	10.02	13.91
x (mol/L)	0.0400	0.0335	0.0287	0.0250	0.0218

If the reaction is second order in X, a plot of $1/x$ vs t should be linear, which indeed it is:



If the reaction were third order, a plot of $1/x^2$ vs t would be linear:



The data clearly don't fit a line when plotted in this form, so we can eliminate the possibility that the reaction is third order in x .

The slope of the second-order plot is the rate constant:

$$k = 1.50 \text{ L mol}^{-1} \text{ min}^{-1}.$$

(b) We can rearrange the second-order integrated rate law to the form

$$t = \frac{1}{k} \left(\frac{1}{x} - \frac{1}{x_0} \right).$$

In this case,

$$t = \frac{1}{1.50 \text{ L mol}^{-1} \text{ s}^{-1}} \left(\frac{1}{10^{-6} \text{ mol/L}} - \frac{1}{0.2 \text{ mol/L}} \right) = 6.7 \times 10^5 \text{ min}.$$

This is over a year, so this probably won't be practical as it stands.

5. First, rearrange the equation to the form

$$t = \frac{1}{2k} \left\{ \ln \left(\frac{1 + \frac{[D]}{[L]}}{1 - \frac{[D]}{[L]}} \right) - \ln \left(\frac{1 + \frac{[D]_0}{[L]_0}}{1 - \frac{[D]_0}{[L]_0}} \right) \right\}.$$

We would want to measure D to L ratios for a particular amino acid from a set of biological samples of known ages. Ideally, these samples would be chemically similar to those whose ages we would eventually want to analyse (e.g. we would use eye lenses to calibrate the method for dating other eye lenses). Since rate constants depend on temperature, the thermal histories of the calibration and analytical samples would also, ideally, be similar. We could then plot t as a function of

$$x = \ln \left(\frac{1 + \frac{[D]}{[L]}}{1 - \frac{[D]}{[L]}} \right).$$

The slope of this plot should be $1/(2k)$.