

Chemistry 2710 Spring 2002 Test 1 Solutions

1.

$$\begin{aligned}\frac{dx}{dt} &= -kx. \\ \therefore k &= -\frac{1}{x} \frac{dx}{dt}.\end{aligned}$$

In this case, $-dx/dt = 651$ atoms/s. All we need to do is to calculate the number of atoms of ^{238}U (x) in the sample.

$$\begin{aligned}n_{238} &= (0.992832) \frac{0.0532 \text{ g}}{238.029229 \text{ g/mol}} = 2.22 \times 10^{-4} \text{ mol.} \\ \therefore x &= (2.22 \times 10^{-4} \text{ mol})(6.0221420 \times 10^{23} \text{ mol}^{-1}) = 1.34 \times 10^{20}. \\ \therefore k &= \frac{651 \text{ s}^{-1}}{1.34 \times 10^{20}} = 4.87 \times 10^{-18} \text{ s}^{-1}. \\ \therefore t_{1/2} &= \frac{\ln 2}{k} = \frac{\ln 2}{4.87 \times 10^{-18} \text{ s}^{-1}} = 1.42 \times 10^{17} \text{ s} \\ &\equiv \frac{1.42 \times 10^{17} \text{ s}}{(3600 \text{ s/h})(24 \text{ h/d})(365.25 \text{ d/y})} = 4.51 \times 10^9 \text{ y.}\end{aligned}$$

2. (a) The concentration of CH_3NNCH_3 increases by a factor of 3 from experiment 2 to experiment 1 and the rate increases in the same proportion. This is therefore a first-order reaction:

$$v = k[\text{CH}_3\text{NNCH}_3].$$

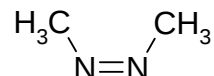
The rate constant can be obtained from either experiment. For instance:

$$k = \frac{v}{[\text{CH}_3\text{NNCH}_3]} = \frac{6.0 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}}{2.4 \times 10^{-2} \text{ mol/L}} = 2.5 \times 10^{-4} \text{ s}^{-1}.$$

(b)

$$\begin{aligned}v &\approx \frac{\Delta[\text{C}_2\text{H}_6]}{\Delta t} \\ \therefore \Delta t &\approx \frac{\Delta[\text{C}_2\text{H}_6]}{v} \\ &= \frac{10^{-4} \text{ mol/L}}{6.0 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}} = 17 \text{ s.}\end{aligned}$$

- (c) This reaction is almost certainly not elementary. In order for it to be an elementary reaction, both C-N bonds would have to break while the C-C bonds in ethane are made. However, a simple VSEPR model of the reactant shows that the two methyl fragments are quite far apart in the cis isomer:



(It's much worse in the trans isomer.) It seems highly unlikely that this bond could be made in the same step as the C-N bond breaking events.

3. (a) $2\text{NO}_{(\text{g})} + \text{Br}_{2(\text{g})} \rightarrow 2\text{NOBr}_{(\text{g})}$
 (b) For the overall reaction,

$$K = \frac{[\text{NOBr}]^2}{[\text{NO}]^2[\text{Br}_2]}.$$

Using the principle of detailed balance, for the individual elementary reactions, we have

$$\begin{aligned} k_1[\text{NO}][\text{Br}_2] &= k_{-1}[\text{NOBr}_2] \\ \text{and } k_2[\text{NOBr}_2][\text{NO}] &= k_{-2}[\text{NOBr}]^2 \end{aligned}$$

These can be rearranged to

$$\begin{aligned} \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]} &= \frac{k_1}{k_{-1}} \\ \text{and } \frac{[\text{NOBr}]^2}{[\text{NOBr}_2][\text{NO}]} &= \frac{k_2}{k_{-2}}. \end{aligned}$$

If we multiply these two equations together, we get

$$\frac{[\text{NOBr}]^2}{[\text{NO}]^2[\text{Br}_2]} = \frac{k_1 k_2}{k_{-1} k_{-2}}.$$

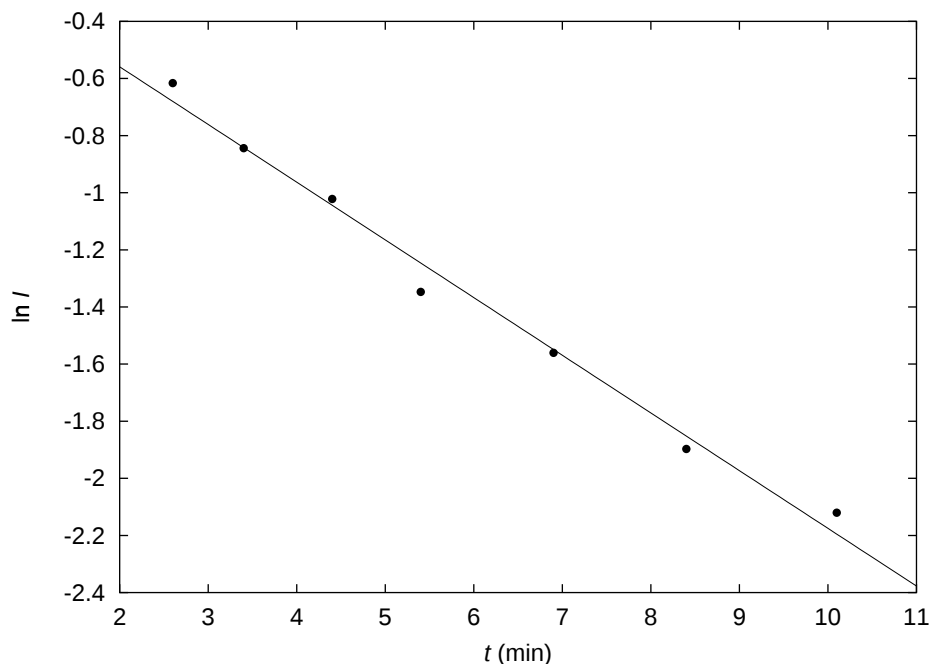
The equilibrium constant is therefore

$$K = \frac{k_1 k_2}{k_{-1} k_{-2}}.$$

4. (a) The rate constant is the absolute value of the slope of a graph of $\ln I$ vs t , where I is the EPR intensity. We must therefore calculate $\ln I$:

t (min)	2.6	3.4	4.4	5.4	6.9	8.4	10.1
$\ln I$	-0.6162	-0.8440	-1.0217	-1.3471	-1.5606	-1.8971	-2.1203

Although a graph isn't required, here's mine, just to convince you that the behavior is that of a first-order process:



The slope of the line of best fit is -0.202 min^{-1} so the rate constant is

$$k = 0.202 \text{ min}^{-1}.$$

The half-life is therefore

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{0.202 \text{ min}^{-1}} = 3.43 \text{ min}.$$

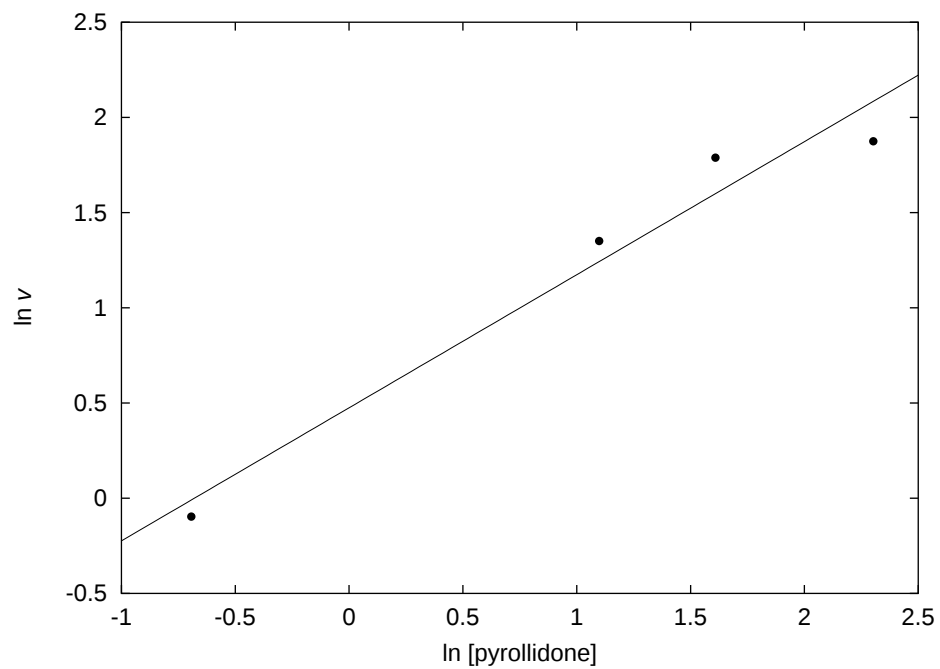
(b)

$$\begin{aligned} x &= x_0 e^{-kt} \\ \therefore \ln \left(\frac{x}{x_0} \right) &= -kt \\ \therefore t &= \frac{1}{k} \ln \left(\frac{x_0}{x} \right) \\ &= \frac{1}{0.202 \text{ min}^{-1}} \ln \left(\frac{1}{0.01} \right) = 22.8 \text{ min}. \end{aligned}$$

5. The best way to handle this question is to use van't Hoff's method, i.e. to plot $\ln v$ vs $\ln[\text{pyrrolidone}]$. If the data obey a simple rate law, this should give a straight line.

$\ln[\text{pyrrolidone}]$	-0.6931	1.0986	1.6094	2.3026
$\ln v$	-0.0965	1.3507	1.7884	1.8749

Here is my plot:



The data do *not* fit a straight line, therefore the rate does not obey a simple power law.