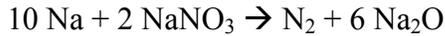
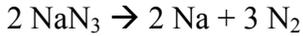


**10.37 Spring 2007 Homework 1**  
**Due noon Wednesday, Feb. 14.**

Problem 1. Airbags contain a mixture of  $\text{NaN}_3$ ,  $\text{NaNO}_3$ , and  $\text{SiO}_2$ . When the vehicle is in a crash, the following reactions are initiated:



a) If 150 g of  $\text{NaN}_3$  are used in an airbag, how many grams of  $\text{NaNO}_3$  and  $\text{SiO}_2$  must be included so that all of the sodium in the system can be safely sequestered as glass? Note the sodium-containing compounds  $\text{NaN}_3$ ,  $\text{Na}$ , and  $\text{Na}_2\text{O}$  are all dangerous and toxic.

b) The most important species for airbag performance in a crash are  $\text{NaN}_3$  and  $\text{N}_2$ , so there are two obvious definitions of conversion:

$$X_{\text{NaN}_3} = (\text{moles } \text{NaN}_3 \text{ reacted}) / (\text{initial moles } \text{NaN}_3)$$

and

$$X_{\text{N}_2} = (\text{moles of } \text{N}_2) / (\text{total moles of } \text{N}_2 \text{ when all reactions are completed}).$$

What units do  $X_{\text{NaN}_3}$  and  $X_{\text{N}_2}$  have? Does  $X_{\text{NaN}_3}$  equal  $X_{\text{N}_2}$ ? If not, how different could they be?

There are three other related quantities,  $\xi_1$ ,  $\xi_2$ , and  $\xi_3$ , the extents of reactions 1, 2, and 3. Note that each  $\xi$  has units of moles. Write algebraic equations for each  $X$  in terms of the  $\xi$ 's.

c) Suppose that reaction 1 has a rate expression  $r_1 = k_1/V$  (this reaction proceeds at a steady rate as a reaction front moves through the solid  $\text{NaN}_3$ ), reaction 2 has a rate expression  $r_2 = k_2[\text{Na}][\text{NaNO}_3]$ , and reaction 3 has a rate expression  $r_3 = k_3[\text{Na}_2\text{O}]/V$ .

By the convention used in this course, all the  $r$ 's have units of moles/second/liter. Write  $r_{\text{N}_2}$ , the rate of production of  $\text{N}_2$  per unit volume, in terms of  $r_1$ ,  $r_2$ , and  $r_3$ .

Write the equations for rate of change of the number of moles,  $dn_i/dt$ , for all the chemical species ( $i = \text{N}_2, \text{NaN}_3, \text{Na}, \text{NaNO}_3, \text{Na}_2\text{O}, \text{SiO}_2, \text{glass}$ ).

d) Of course the volume of the airbag,  $V$ , is dramatically changing during the course of the reaction due to the creation of a gas,  $\text{N}_2$ , inside the bag. If the bag can expand fast enough to so that the pressure inside the bag is similar to the pressure outside the bag, by the ideal gas law one would expect:

$$V = V_0 + V_N * n_{\text{N}_2}$$

and under this condition the bag would expand depending on the rate at which gas is created:

$$dV/dt = V_N * dn_{N_2}/dt$$

where  $V_N$  is the molar volume of a gas at atmospheric pressure ( $\sim 22$  liter/mole) and  $n_{N_2}$  is the number of moles of  $N_2$  in the airbag. The initial volume of the airbag  $V_0 \sim 70 \text{ cm}^3$ .

However there is a physical limit on how fast the airbag can expand. When an airbag is expanded by gas pressure, the radius of the bag cannot grow faster than the speed of pressure fronts in the gas, approximately the speed of sound:

$$dR/dt < c_{\text{sound}}$$

$$c_{\text{sound}} \sim 300 \text{ m/s in air.}$$

so there is an upper bound on how fast the airbag can grow; for a spherical airbag:

$$dV/dt = 4\pi R^2 dR/dt$$

$$\text{so } dV/dt < 4\pi (3V/4\pi)^{2/3} c_{\text{sound}} = (36\pi V^2)^{1/3} c_{\text{sound}}$$

So a reasonable approach to model this numerically is

if ( $V < V_0 + V_N * n_{N_2}$ )

$$dV/dt = (36\pi V^2)^{1/3} c_{\text{sound}}$$

else

$$dV/dt = V_N * dn_{N_2}/dt$$

endif

Using a numerical ODE solver in Matlab, solve the coupled system of differential equations for the  $n$ 's and  $V$ . Take  $k_1 \sim 10^3$  moles/s,  $k_2 \sim 10^4$  liter/mole-s,  $k_3 \sim 10^5$  liter/s. Make and turn in a plot of  $X_{N_2}$  vs. time,  $\xi_3$  vs. time and volume vs. time for the first 10 milliseconds of operation. Also, make and turn in a plot of volume vs. time for just the first 0.1 milliseconds of operation. Does the volume vs. time behavior make physical sense? If not, go back and modify your Matlab program to fix the non-physical  $dV/dt$  behavior.

**Submit your Matlab program(s) to the 10.37 the course website.**

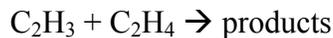
Problem 2. One of the students in this class recently measured the reaction of vinyl radical ( $C_2H_3$ ) with ethene ( $C_2H_4$ ), a reaction important in flames, pyrolysis, and polymerization reactors. Vinyl radical absorbs purple light, so the amount of light absorbed is proportional to the concentration of the vinyl radical. In each experiment the student measured the time variation in the amount of purple light passing through his constant volume sample using a photodetector. The voltage signal from the photodetector is linearly related to the absorbance, which is proportional to  $[C_2H_3]$ , so

$$\text{Signal}(t) = b + m[C_2H_3](t) \quad \text{Eq. (1)}$$

where  $b$  is an uninteresting number related to how well the electronics baseline was zeroed out before each experiment.

He performed similar experiments many times, each time with different initial concentrations of ethene in the sample. From these experiments, he extracted the rate constant “ $k$ ” at various temperatures and pressures.

The reaction of interest is:



This reaction is very exothermic, so the reaction is essentially irreversible (i.e. when equilibrium is achieved the vinyl concentration is too small to detect). You expect this reaction to follow elementary-step kinetics, i.e.

$$-r_{C_2H_3} = (k_0 + k[C_2H_4])[C_2H_3] \quad \text{(Eq. 2)}$$

$k_0$  accounts for all other first-order loss processes of  $C_2H_3$  in the experiment (e.g. unimolecular reaction). Because the initial concentration of  $C_2H_3$  is much smaller than the concentration of  $C_2H_4$ , it is reasonable to assume that the concentration of  $C_2H_4$  does not vary significantly during each experiment. Therefore one expects a simple exponential decay of  $[C_2H_3]$ :

$$[C_2H_3] = [C_2H_3]_0 e^{-t/\tau} \quad \text{(Eq. 3)}$$

a) Write out the algebraic relationship between  $\tau$  and  $k$ . Fit the measured signal for the  $n$ th experiment  $S_n$  to this form:

$$S_n(t) = B_n + A_n \exp(-t/\tau_n) \quad \text{(Eq. 4)}$$

Give expressions for  $A_n$ ,  $B_n$ , and  $\tau_n$  in terms of  $b$ ,  $m$ ,  $[C_2H_3]_0$ ,  $k_0$ ,  $k$ , and  $[C_2H_4]_{0,n}$ . Which of the three fit parameters  $A_n$ ,  $B_n$ , and  $\tau_n$  depends on  $k$  and  $[C_2H_4]_0$ ?

b) Use Matlab to plot  $1/\tau_n$  vs.  $[C_2H_4]_n$ , where  $\tau_n$  is the exponential decay time constant determined by fitting the data from the  $n$ th experiment. How can you use this plot to determine the rate constant “ $k$ ”?

Your assignment is to compute the rate constant “ $k$ ” for the reaction of interest from the student’s data, contained in files `vinylethene1`, `vinylethene2`, and `vinylethene3` on the 10.37 course website. In each file the first column is the time in seconds, and the second column is the measured signal  $S_n$ . The first dataset is for  $[C_2H_4]=6.7 \times 10^{-4}$  M, the second for  $[C_2H_4]=4 \times 10^{-4}$  M and the third for  $[C_2H_4]=1.33 \times 10^{-4}$  M.

Turn in the value of “ $k$ ” you derived from modeling the student’s experimental data (don’t forget to specify the units of “ $k$ !”), and also turn in plots comparing your model predictions using this “ $k$ ” with the experimental data.

**Submit your Matlab program(s) to the 10.37 course website.**

N.B. Notice that in this type of “pseudo-first-order” experiment, one can determine “ $k$ ” without knowing  $[C_2H_3]_0$ , the calibration constant “ $m$ ” relating the signal to  $[C_2H_3]$ , what the products of the reaction are, nor what the competing reactions are (that contribute to  $k_0$ ). Because of these simplifications, this type of experiment is very widely used to determine rate constants.