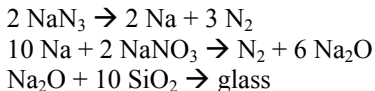## 10.37 Spring 2007 Homework 1
Due Wednesday, Feb. 14.

Problem 1. Airbags contain a mixture of NaN_3, $NaNO_3$, and SiO_2. When the vehicle is in a crash, the following reactions are initiated:

$2\ NaN_3 \rightarrow 2\ Na + 3\ N_2$
$10\ Na + 2\ NaNO_3 \rightarrow N_2 + 6\ Na_2O$
$Na_2O + 10\ SiO_2 \rightarrow glass$

a) If 150 g of NaN_3 are used in an airbag, how many grams of $NaNO_3$ and 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 NaN_3, Na, and Na_2O are all dangerous and toxic.

b) The most important species for airbag performance in a crash are NaN_3 and N_2, so there are two obvious definitions of conversion:

X_{NaN3} = (moles NaN_3 reacted)/(initial moles NaN_3)
and
X_{N2} = (moles of N_2)/(total moles of N_2 when all reactions are completed).

What units do X_{NaN3} and X_{N2} have? Does X_{NaN3} equal X_{N2}? If not, how different could they be?

There are three other related quantities, ξ_1, ξ_2, and ξ_3, the extents of reactions 1,2, and 3. Note that each ξ has units of moles. Write algebraic equations for each X in terms of the ξ'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 NaN_3), reaction 2 has a rate expression $r_2 = k_2[Na][NaNO_3]$, and reaction 3 has a rate expression $r_3 = k_3[Na_2O]/V$.

By the convention used in this course, all the r's have units of moles/second/liter. Write r_{N2}, the rate of production of 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=N_2, NaN_3, Na, $NaNO_3$, Na_2O, SiO_2, 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, 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:

$V = Vo + V_N * n_{N2}$
and under this condition the bag would expand depending on the rate at which gas is created:
$dV/dt = V_N * dn_{N2}/dt$

where V_N is the molar volume of a gas at atmospheric pressure (~22 liter/mole) and n_{N2} is the number of moles of N_2 in the airbag. The initial volume of the airbag Vo ~70 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:

$dR/dt < c_{sound}$
$c_{sound} \sim 300$ m/s   in air.

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

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

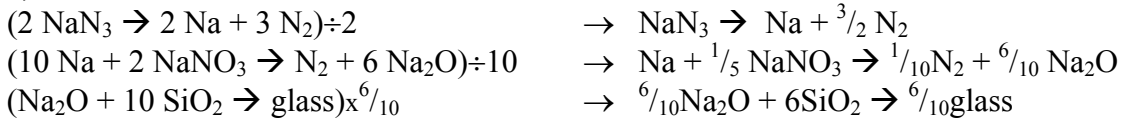So a reasonable approach to model this numerically is

```
if (V<Vo + V_N*n_N2)
        dV/dt = (36πV²)^(1/3)c_sound
else
        dV/dt = V_N * dn_N2/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, $k_2 \sim 10^6$ liter/mole-s, $k_3 \sim 10^5$ liter/s. Make and turn in a plot of X_{N2} vs. time, ξ_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 course website.

Problem 1 Solution

a)

(2 NaN$_3$ → 2 Na + 3 N$_2$)÷2	→ NaN$_3$ → Na + $^3/_2$ N$_2$
(10 Na + 2 NaNO$_3$ → N$_2$ + 6 Na$_2$O)÷10	→ Na + $^1/_5$ NaNO$_3$ → $^1/_{10}$N$_2$ + $^6/_{10}$ Na$_2$O
(Na$_2$O + 10 SiO$_2$ → glass)x$^6/_{10}$	→ $\underline{^6/_{10}$Na$_2$O + 6SiO$_2$ → $^6/_{10}$glass}$

Net reaction w/all Na safely sequestered as glass: NaN$_3$ + $^1/_5$NaNO$_3$ + 6SiO$_2$ → $^8/_5$N$_2$ + $^3/_5$ glass

$n_{NaN_3,o} = 150g \dfrac{1mol}{65g} = 2.3mol$

$n_{NaNO_3,o} = n_{NaN_3,o} \cdot \dfrac{1mol\ NaNO_3}{5mol\ NaN_3} = \dfrac{2.3}{5}mol = \boxed{0.46mol}$ or $m_{NaNO_3,o} = 0.46mol \dfrac{85g}{1mol} = \boxed{39g}$

$n_{SiO_2,o} = n_{NaN_3,o} \cdot \dfrac{6mol\ SiO_2}{1mol\ NaN_3} = 6 \cdot 2.3mol = \boxed{13.8mol}$ or $m_{SiO_2,o} = 13.8mol \dfrac{60g}{1mol} = \boxed{830g}$

b) X_{NaN3} and X_{N2} are dimensionless. X_{NaN3} does not equal X_{N2} during the reaction.

$X_{NaN_3} = \dfrac{2\xi_1}{n_{NaN_3,o}}$ $X_{N_2} = \dfrac{n_{N_2}}{n_{N_2,f}} = \dfrac{3\xi_1 + \xi_2}{\dfrac{8}{5}n_{NaN_3,o}}$

$X_{NaN_3} - X_{N_2} = \dfrac{2\xi_1}{n_{NaN_3,o}} - \dfrac{3\xi_1 + \xi_2}{\dfrac{8}{5}n_{NaN_3,o}} = \dfrac{\xi_1 - 5\xi_2}{8n_{NaN_3,o}}$

The difference between X_{NaN_3} and X_{N_2} will be determined by the kinetics of r_1 and r_2 (i.e. the rate of change of ξ_1 compared to ξ_2).

**c)** For no flows in/out and assuming a homogeneous reaction:

$$\frac{dn_A}{dt} = \sum_i \nu_{A,i}\frac{d\xi_i}{dt} = \sum_i \nu_{A,i} r_i V$$ Can report dn_i/dt using extents or reaction rates

Species	mol balance	dn_i/dt (using extents)	dn_i/dt (using reaction rates)
NaN_3	$n_{NaN_3} = n_{NaN_3,o} - 2\xi_1$	$\dfrac{dn_{NaN_3}}{dt} = -2\dfrac{d\xi_1}{dt}$	$\dfrac{dn_{NaN_3}}{dt} = -2r_1 V$
$NaNO_3$	$n_{NaNO_3} = n_{NaNO_3,o} - 2\xi_2$	$\dfrac{dn_{NaNO_3}}{dt} = -2\dfrac{d\xi_2}{dt}$	$\dfrac{dn_{NaNO_3}}{dt} = -2r_2 V$
SiO_2	$n_{SiO_2} = n_{SiO_2,o} - 10\xi_3$	$\dfrac{dn_{SiO_2}}{dt} = -10\dfrac{d\xi_3}{dt}$	$\dfrac{dn_{SiO_2}}{dt} = -10\,r_3 V$
Na	$n_{Na} = 2\xi_1 - 10\xi_2$	$\dfrac{dn_{Na}}{dt} = 2\dfrac{d\xi_1}{dt} - 10\dfrac{d\xi_2}{dt}$	$\dfrac{dn_{Na}}{dt} = (2r_1 - 10r_2)V$
N_2	$n_{N_2} = 3\xi_1 + \xi_2$	$\dfrac{dn_{N_2}}{dt} = 3\dfrac{d\xi_1}{dt} + \dfrac{d\xi_2}{dt}$	$\dfrac{dn_{N_2}}{dt} = (3r_1 + r_2)V$
Na_2O	$n_{Na_2O} = 6\xi_2 - \xi_3$	$\dfrac{dn_{Na_2O}}{dt} = 6\dfrac{d\xi_2}{dt} - \dfrac{d\xi_3}{dt}$	$\dfrac{dn_{Na_2O}}{dt} = (6r_2 - r_3)V$
Glass	$n_{glass} = \xi_3$	$\dfrac{dn_{glass}}{dt} = \dfrac{d\xi_3}{dt}$	$\dfrac{dn_{glass}}{dt} = r_3 V$

Rate of production of N_2: $r_{N_2} = 3 \cdot r_1 + r_2$

d) See the Matlab solution provided. Plots showing X_{N_2} vs. time, ξ_3 vs. time, and volume vs. time are copied below.
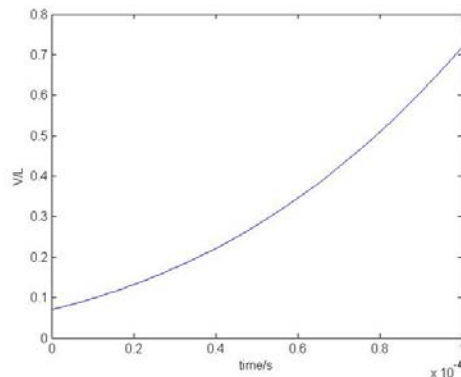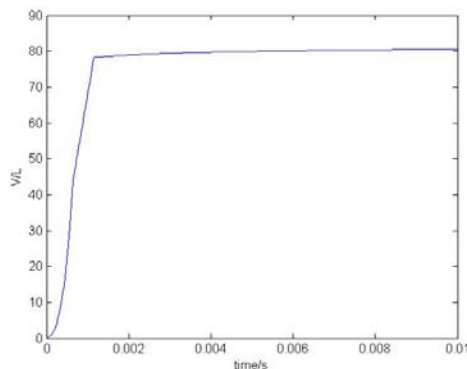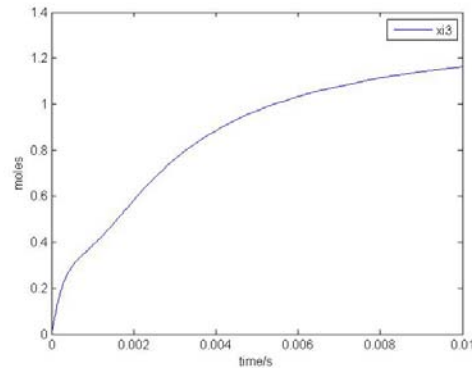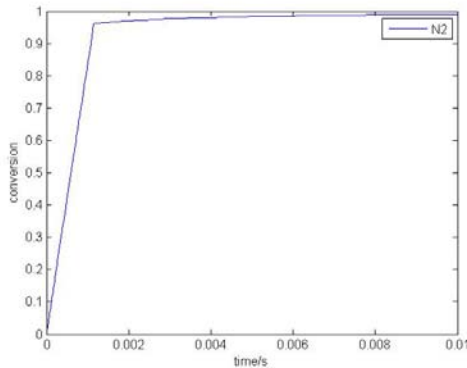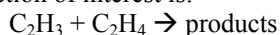
<u>Problem 2.</u> One of the students in this class recently measured the reaction of vinyl radical (C_2H_3) with ethene (C_2H_4), a reaction important in flames, pyrolysis, and polymerization reactors. Vinyl radical absorbs purple light, so the amount of light absorbed is proportional to the concentration 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

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

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 temps and pressures.

The reaction of interest is:
$$C_2H_3 + C_2H_4 \rightarrow \text{products}$$
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.

$$-r_{C2H3} = (k_0 + k[C_2H_4])[C_2H_3] \qquad \text{(Eq. 2)}$$

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 $[C_2H_3]$:

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

a) Write out the algebraic relationship between τ and k. Fit the measured signal for the nth experiment S_n to this form:

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

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

b) Use Matlab to plot $1/\tau_n$ vs. $[C_2H_4]_n$, where τ_n is the exponential decay time constant determined by fitting the data from the nth 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 $[C_2H_3]_o$, 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 r_0). Because of these simplifications, this type of experiment is very widely use'd to determine rate constants.

Problem 2 Solution

a) $-r_{C_2H_3} = -\dfrac{d[C_2H_3]}{dt}$

Eq 5

Substitute Eq 3 into Eq 5

$-r_{C_2H_3} = -\dfrac{d[C_2H_3]}{dt} = -\dfrac{d\left([C_2H_3]_o e^{-t/\tau}\right)}{dt} = [C_2H_3]_o\left(\dfrac{1}{\tau}\right)e^{-t/\tau}$

Eq 6

Substitute Eq 3 into Eq 2:

$-r_{C_2H_3} = \left(k_0 + k[C_2H_4]\right)[C_2H_3] = \left(k_0 + k[C_2H_4]\right)[C_2H_3]_o e^{-t/\tau}$

Eq 7

Set Eq 6 = Eq 7 and simplify:

$[C_2H_3]_o\left(\dfrac{1}{\tau}\right)e^{-t/\tau} = \left(k_0 + k[C_2H_4]_o\right)[C_2H_3]_o e^{-t/\tau}$ $\rightarrow$ $\boxed{\tau = \dfrac{1}{k_0 + k[C_2H_4]_o}}$

Eq 8

algebraic relationship between τ and k

Substitute Eq 3 into Eq 1:

$S(t) = b + m[C_2H_3](t) = b + m[C_2H_3]_o e^{-t/\tau}$

Eq 9

Substitute Eq 8 into Eq 9:

$S(t) = b + m[C_2H_3]_o e^{-t/\tau} = b + m[C_2H_3]_o e^{\left(\frac{-t}{\frac{1}{k_0 + k[C_2H_4]_o}}\right)}$

Eq 10

Compare Eq 10 and Eq 4 to define:

$\boxed{B_n = b}$ $\qquad$ $\boxed{A_n = m[C_2H_3]_o}$ $\qquad$ $\boxed{\tau_n = \dfrac{1}{k_0 + k[C_2H_4]_{o,n}}}$

Only τ_n depends on k and $[C_2H_4]_{o,n}$.

b) See the Matlab solution provided. To determine k, fit $1/\tau_n$ vs. $[C_2H_4]_{o,n}$ to a straight line. Slope = k (L/mol-s), y-intercept = k_0 (1/s). Figures from Matlab are copied below.

$k = 1.11 \times 10^7$ L/mol-s

Vinylethene 1

Vinylethene 2

Vinylethene 3