ChE 528
Problem Set 6
Due Thursday 10/16/2003

1. The multiple reaction sequence

$$P \xrightarrow{k_0} A \qquad k_0 = 10^{-3}\ s^{-1}$$

$$A \xrightarrow{k_u} B \qquad k_u = 10^{-2}\ s^{-1}$$

$$A + 2B \xrightarrow{k_1} 3B \qquad k_1 = 25 \times 10^{8}\ dm^6/mol^2 \cdot s$$

$$B \xrightarrow{k_2} C \qquad k_2 = 1.0\ s^{-1}$$

is carried out in a batch reactor with pure P initially at a concentration of 0.1 mol/dm^3. It appears the first reaction is slow w.r.t. the other reactions, i.e. the half life is ca. 2 hr.

a) Assume pseudo steady state w.r.t. A and B.
Show

(1) $C_P = C_{P_0} e^{-k_0 t}$

(2) $C_{A_{SS}} = \dfrac{k_2^2 k_0}{\left(k_1 k_0^2 C_P^2 + k_2^2 k_u\right)} C_P$

(3) $C_{B_{SS}} = \dfrac{k_0}{k_2} C_P$

Put the equations in dimensionless form by letting

$$\square = \left(\frac{k_1}{k_2}\right)^{1/2} C_P \qquad \square = \frac{k_0}{k_2}$$

$$\square = \left(\frac{k_1}{k_2}\right)^{1/2} C_A \qquad \square_u = \frac{k_u}{k_2}$$

$$\square = \left(\frac{k_1}{k_2}\right)^{1/2} C_B \qquad \square = \square\square$$

$$\square = k_2 t$$

to show

$$\square_{SS} = \square$$

$$\square_{SS} = \frac{\square}{\left(\square^2 + \square_u\right)}$$

b) Plot $\square$, $\square_{SS}$, and $\square_{SS}$ as a function of time up to a time of 5000 sec ($\square$ = 5000)

(1) At what time are $\square_{SS}$ and $\square_{SS}$ equal? What does this signify?

(2) At what time is $\square_{SS}$ a maximum?

(3) What is the corresponding dimensionless concentration of P? What does $\square_{SSmax}$ signify?

c) Now use Polymath to solve the full combined mole balance and rate law equations to plot $\square$, $\square$, and $\square$ as a function of time up to a **maximum time t = 1500** seconds ($\square = 1500$).

First show the mole balances can be put in the form

$$\frac{d\square}{d\square} = \square\square\square$$

$$\frac{d\square}{d\square} = \square\square\square$$

$$\square = \square_0 e^{\square\square\square}$$

$$\frac{d\square}{d\square} = \square\square\square\square\square^2\ \square\square_u\square$$

$$\frac{d\square}{d\square} = \square\square^2 + \square_u\square\ \square\square$$

$$\square_0 = 5000\ ,\quad \square = 10^{-3}$$

$$\square_0 = \square\square_0 = \frac{k_0}{k_2}\left(\frac{k_1}{k_2}\right)^{1/2} C_{P_0}$$

$$\square_0 = \square\square_0 = 5$$

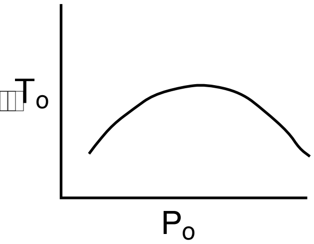
$$\square_u = 10^{-2}$$

$$\square = k_2 t = \frac{1.0}{s} t = \frac{t}{s}$$

How does the full solution compare with the pseudo steady state analysis you carried out in part (b)?

2. Load the aerosol PFR from Polymath on the web in the aerosol reactor exercise section of the web module. Warning: These equations are very "stiff" and as a result the program may crash for certain combinations of variables.
   a) For a cooling rate of 500 K/s and an initial temperature of 1550°C, plot particle diameter, (d_p) nucleation rate, ($r_N\square$), and ($r_N\square n^*$), condensation rate, ($r_C\square$) and ($r_C\square\, N\, \square d_P^2$), molecule concentrations (n_m) and (n_{ms}), saturation ratio, S, molecules per nuclei, (n^*), gas velocity, (U), gas density, ($\square_g$), number of particles, (N), and flocculation rate (r_F) as a function of time (moving with the fluid) and of distance down the reactor.
   b) Study the number of particles, Al concentration and particle diameter in the exit stream as a function of cooling rate between 100°C/s and 1500°C/s for an initial temperature of 1600°C.
   c) Study the number of particles, Al concentration and particle diameter in the exit stream as a function of pressure between 0.1 atm and 100 atm for an initial temperature of 1600°C and cooling rate 1000°C/s.
   d) Study the number of particles, Al concentration and particle diameter in the exit stream as a function of initial temperature between 1550°C and 1625°C for 1 atm pressure cooling rate 1000 K/s.
   e) For a cooling rate of 1000 K/s find the relationship between inlet temperature and pressure.
   f) Explore the problem to see the effect of the various operational variables. on dp, ($r_C\square\, N\, \square d_P^2$), ($r_N\square n^*$), r_F, etc.

e.g.



for which e.g. $d_p = 500$nm.

Summarize (a) through (f) by writing a couple of paragraphs describing what you found. Use sketches where appropriate to discuss trends, and such things as the operation of the APFR and how to vary the particle sizes.

3. It is proposed to replace the carrier gas by helium. Assume the helium is saturated with aluminum at the entrance to the reactor.
   a) What changes do you need to make in the polymath code given in the CD and in the appendix? Before carrying out any computer runs, discuss qualitatively what differences using Helium rather than Argon.
   b) Compare your plots (He versus Ar) of the number of Al particles as a function of time. Explain the shape of the plots. Print out your Polymath code and plot.
   c) How does the final value of d_p compare with that when the carrier gas was Argon? Explain.
   d) Compare the time at which the rate of nucleation reaches a peak in the two cases [carrier gas = Ar and He]. Explain the comparison.

   For parts (b) and (c), <u>write down</u> or <u>sketch</u> the results as appropriate.

   <u>Data for a He molecule:</u>

   Mass = 6.64×10^{-27} kg
   Volume = 1.33×10^{-29} m^3
   Surface area = 2.72×10^{-19} m^2
   Bulk density = 0.164 kg/ m^3, at normal temperature (25°C) and pressure (1 atm)

4. Extra Credit.
   Make a list of the things that can be improved or are unclear on the aerosol reactor web module.