Chemistry 549
Spring 2004
Problem Set 1
Due Monday, Feb. 2

Read Chapter 1.

Do Problems 1.4, 1.8, and 1.9 in the textbook. Also do the following problems:

1. Consider the following network of first order reactions, with the indicated rate constants:

$$x \rightarrow z, \quad k_1$$

$$x \rightarrow y, \quad k_2$$

$$y \rightarrow z, \quad k_3$$

A. Derive the general result for x(t), y(t), z(t), assuming that x(0) = 1, y(t) = 0, z(t) = 0.

B. Show that $z(t=\infty)=1$

C. Show that in the limit of $k_1 t << 1, \quad k_2 t << 1, \quad k_3 t << 1$, the following results are true:

$$y(t) = k_2 t$$
$$z(t) = k_1 t$$

D. Show that in the limit of $k_1 t >> 1, \quad k_2 t << 1, \quad k_3 t << 1$, the following results are true:

$$y(t) = \frac{k_2}{k_1} e^{-k_3 t}$$
$$z(t) = 1$$

E. Show that in the limit of $k_1 t << 1, \quad k_2 t >> 1, \quad k_3 t << 1$, the following results are true:

$$y(t) = e^{-k_3 t}$$
$$z(t) = k_3 t$$

F. Show that in the limit of $k_1 t << 1, \quad k_2 t << 1, \quad k_3 t >> 1$, the following results are true:

$$y(t) = \frac{k_2}{k_3} e^{-k_{12}t}$$
$$z(t) = k_{12}t$$

where $k_{12} = k_1 + k_2$.

2. Consider the first order reaction

$$A \rightarrow B, \quad k_1$$

$$B \rightarrow A, \quad k_2$$

Derive an exact expression for A(t).

3. A certain molecule has an extinction coefficient of 1,000 liter mol^{-1} cm^{-1} (base e) at a wavelength of 800 nm. Suppose the molecule is in the gas phase and is irradiated with a pulsed laser having a radius of 1 mm. What must the energy of the laser pulse be to excite 10% of the molecules in its path?