MATH 3511 Bennethum

Supplemental ODE Homework Problems

These are homework problems involving modeling kinetics. The exact assignment (which problems are due when) will be announced in class.

1. Consider the reaction

$$NO_3 + NO \rightarrow 2NO_2$$

which is an elementary process.

   (a) Write the rate expression for the rate of disappearance of NO_3 and NO.

   (b) Write the rate expression for the appearance of NO_2.

   (c) Show how the rate constants in (a) and (b) are related.

2. Consider the simple reaction

$$A + A \rightarrow \text{products.}$$

   (a) Derive the ODE governing this equation.

   (b) Solve the equation to the point where you would know what to plot to determine the rate coefficient, k.

3. Consider the simple reaction

$$3A \rightarrow \text{products.}$$

   (a) Derive the ODE governing this equation.

   (b) Solve the equation to the point where you would know what to plot to determine the rate coefficient, k.

4. Consider the simple reaction

$$2A + B \rightarrow C$$

   (a) Derive the ODE governing the rate of loss of $[A]$ in terms of (i) $[A]$ and $[B]$, and then (ii) in terms of a single variable, x, assuming the initial concentrations of $[A]$, $[B]$, and $[C]$ are a, b, and 0, respectively.

   (b) Write the integral equation.

   (c) Solve the equation to the point where you would know what to plot to determine the rate coefficient, k. You may want to use technology....

5. Consider the simple reaction

$$A + B + C \rightarrow D.$$

Derive the integral form of the rate expression. Do not solve.

6. Write the rate equation for the production of $[HI]$ given the simple reaction

$$H_2 + 2I \xrightarrow{k} 2HI$$

in terms of $[I]$, $[H_2]$, and $[HI]$. Then write a suitable integral form of the rate expression. Do not solve.

7. Consider the simple reaction

$$A \xrightarrow{k} B \xrightarrow{k} C.$$

Note that the rate coefficients are identical.

   (a) As in class, set up the ODE's and solve to determine $[A]$, $[B]$, and $[C]$. Assume $[A]_0 = a$, $[B]_0 = b$, and $[C]_0 = 0$.

   (b) Would it be appropriate to assume that $[B]$ is at steady-state? Explain.

8. Consider the simple reaction

$$A + B \underset{k'}{\overset{k}{\rightleftarrows}} X + B$$
$$X \xrightarrow{k_2} C + D$$

   (a) Write the chemical rate equations for $[A]$ and $[X]$.

   (b) Employing the steady-state approximation for the intermediate, X, show that the effective rate equation of $[A]$ is

$$\frac{d[A]}{dt} = -k_{\text{eff}}[A][B].$$

   Give an expression for k_{eff} in terms of k, k', k_2, and $[B]$.

Solutions

1a) $\frac{d[NO_3]}{dt} = -k_1[NO_3][NO]$, $\frac{d[NO]}{dt} = -k_1[NO_3][NO]$.

1b) $\frac{1}{2}\frac{d[NO_2]}{dt} = k_2[NO_3][NO]$.

1c) $k_1 = k_2$ for how they are written here.

2a) $\frac{1}{2}\frac{d[A]}{dt} = -k[A]^2$

2b) $\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$. Plot $\frac{1}{[A]}$ vs t. Slope is $2k$, y-int is $\frac{1}{[A]_0}$.

3a) $\frac{1}{3}\frac{d[A]}{dt} = -k[A]^3$

3b) $\frac{1}{[A]^2} = \frac{1}{[A]_0^2} + 6kt$. Plot $\frac{1}{[A]^2}$ vs t. Slope is $6k$, y-int is $\frac{1}{[A]_0^2}$.

4a) $\frac{1}{2}\frac{d[A]}{dt} = -k[A]^2[B]$, $\frac{dx}{dt} = k(a-2x)^2(b-x)$

4b) $\frac{dx}{(a-2x)^2(b-x)} = kdt$

4c) $\frac{1}{(a-2b)}\left(\frac{1}{a} - \frac{1}{[A]}\right) + \frac{1}{(a-2b)^2}\ln\left(\frac{b[A]}{a[B]}\right) = kt$. Plot left-hand side of solution vs t. Slope is k. Note that if $a = 2b$ then this equation is no longer valid.

6) $\frac{d[HI]}{dt} = 2k[H_2][I]^2$, $\frac{dx}{([H_2]_0 - x)([I]_0 - 2x)^2} = 2kdt$.

7a) $[A] = [A]_0 e^{-kt}$, $[B] = [A]_0 kte^{-kt}$, $[C] = [A]_0 - [A] - [B] = [A]_0 - e^{-kt}([A]_0 + kt)$.

8b) $k_{\text{eff}} = -\left[k + \frac{k'k[B]}{k[B] + k_2}\right]$