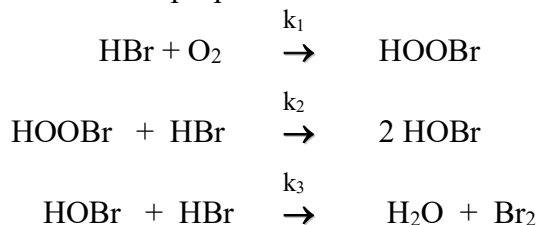


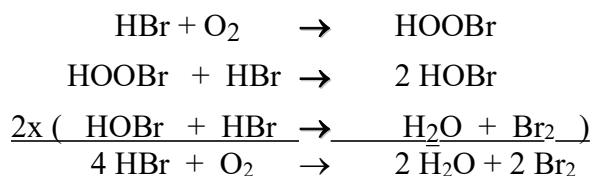
## Chapter 4 Problems

1. Consider the gas phase oxidation of HBr:  $4 \text{HBr} + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + 2 \text{Br}_2$ . The following mechanism has been proposed:



Assume all unidirectional steps. Comment on the validity of this mechanism.

*Answer:* The forward steps in a mechanism must add to give the overall stoichiometry of the reaction. To give the proper overall stoichiometry, the last step must be doubled.



The multiplier for a step in a mechanism is called the stoichiometric number. The stoichiometric number for Step 3 is 2. The next issue is that this mechanism can only hold far from equilibrium. Close to equilibrium a complete mechanism must include each step and its exact reverse.

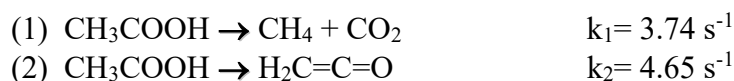
2. For the  $\text{H}_2 + \text{I}_2$  reaction,  $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$ , the empirical rate law is

$$v = \frac{d[\text{HI}]}{dt} = k [\text{H}_2][\text{I}_2]$$

The empirical rate law matches the stoichiometry of the reaction. Why can't you conclude that the mechanism is a simple single-step mechanism?

*Answer:* The reaction may occur by direct collisions of  $\text{H}_2$  and  $\text{I}_2$  molecules, but other mechanisms that have lower overall activation energies or larger pre-exponential factors may also be possible. The introductions to Chapters 3 and 4 discuss two alternate proposals. The direct molecular and rapid pre-equilibrium proposals are kinetically equivalent and therefore indistinguishable without additional experimental time course data for the concentrations of any and all reactive intermediates.

3. The gas phase decomposition of acetic acid at 1189 K proceeds by way of two parallel reactions:



What is the maximum ratio of  $\text{H}_2\text{C}=\text{C}=\text{O}$  to  $\text{CH}_4$  obtainable at this temperature?

*Answer:* The ratio of products during a parallel mechanism is always the same, Eq. 4.1.13:

$$\frac{[\text{CH}_4]}{[\text{H}_2\text{C}=\text{C}=\text{O}]} = \frac{k_1}{k_2} = \frac{3.74 \text{ s}^{-1}}{4.65 \text{ s}^{-1}}$$

4. The gas phase reaction,  $2 \text{NO} + 2 \text{H}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}$ , is known to have the rate law:

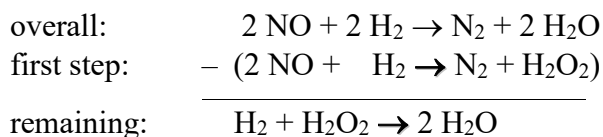
$$v = k [\text{NO}]^2[\text{H}_2]$$

Can this mechanism be a one-step mechanism? If not, suggest a possible two-step mechanism and suggest the rate determining step. You can use unidirectional elementary steps.

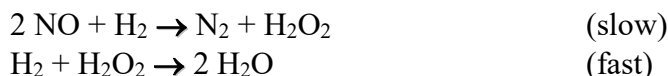
*Answer:* The reaction cannot have a simple one-step mechanism because the empirical rate law does not agree with the stoichiometry for the reaction. The rate law suggests (but does not require) that the rate determining step may be termolecular:



The product  $\text{H}_2\text{O}_2$  is suggested by the difference:  $2 \text{NO} + \text{H}_2 - \text{N}_2 = \text{H}_2\text{O}_2$ . This reaction produces stable products, which helps to justify the proposition. The hydrogen peroxide produced must be an intermediate since it does not appear in the overall reaction. To suggest the second step, we can “subtract” this first elementary step, Eq. 1, from the overall reaction, since sum of the mechanistic steps should give the overall stoichiometry:



This last step as an elementary process is a reasonable proposition for the second elementary step. For this mechanism to agree with the given empirical rate law, the first step must be the intrinsically slow step:



5. Use the finite difference approximation to integrate the rate law for a second order reaction,  $\text{A} + \text{B} \rightarrow \text{P}$  with a rate constant of  $0.05 \text{ M}^{-1} \text{ s}^{-1}$ . Choose the initial concentrations  $[\text{A}]_0 = 1.00 \text{ M}$  and  $[\text{B}]_0 = 0.50 \text{ M}$ . Integrate to at least 100 s. Use Excel for the integration. Compare to the exact expression and the results from the Web based “Kinetics Mechanism Simulation” applet or *MathCad* or *MatLab*.

*Answer:* Starting with the second-order rate law:

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

The finite-difference iteration formulas are:

$$\begin{aligned} [A](t + \Delta t) &= [A](t) - k[A](t)[B](t) \Delta t \\ \text{and } [B](t + \Delta t) &= [B](t) - k[A](t)[B](t) \Delta t \end{aligned}$$

The spreadsheet for  $\Delta t = 5$  s is:

A1	B	C	D	E	F
2					
3	[A] <sub>0</sub> =	1	M		
4	[B] <sub>0</sub> =	0.5	M		
5	k =	0.05	M <sup>-1</sup> s <sup>-1</sup>		
6	dt =	5	s		
7				exact	exact
8	t (s)	[A]	[B]	extent	[A]
9	0	1	0.5	0	1
10	5	0.875	0.375	0.105148	0.894852
11	10	0.792969	0.292969	0.181133	0.818867
12	15	0.73489	0.23489	0.238218	0.761782
13	20	0.691735	0.191735	0.282367	0.717633
14	25	0.658578	0.158578	0.317284	0.682716
15	30	0.632469	0.132469	0.345393	0.654607
16	35	0.611523	0.111523	0.368343	0.631657
17	40	0.594474	0.094474	0.3873	0.6127
18	45	0.580433	0.080433	0.403109	0.596891
19	50	0.568762	0.068762	0.416398	0.583602
20	55	0.558984	0.058984	0.427643	0.572357
21	60	0.550741	0.050741	0.437213	0.562787
22	65	0.543755	0.043755	0.445396	0.554604
23	70	0.537807	0.037807	0.452423	0.547577
24	75	0.532724	0.032724	0.458477	0.541523
25	80	0.528366	0.028366	0.463711	0.536289
26	85	0.524619	0.024619	0.468245	0.531755
27	90	0.52139	0.02139	0.472184	0.527816
28	95	0.518602	0.018602	0.475612	0.524388
29	100	0.51619	0.01619	0.4786	0.5214

The formula for C10 is: “=C9-\$C\$5\*C9\*D9\*\$C\$6”

and for D10 is “=D9-\$C\$5\*C9\*D9\*\$C\$6”.

The exact formula for the extent of the reaction is taken from the Chapter 3 Summary Table. The “Kinetics Mechanism Simulation” applet setup is:

Initial Conditions:

A<sub>0</sub>: 1 B<sub>0</sub>: 0.5 X<sub>0</sub>: 0 Y<sub>0</sub>: 0 P<sub>0</sub>: 0 Q<sub>0</sub>: 0 M: 1

(M and N are constant concentration reservoirs, such as a background gas, the vessel walls, or a constant f

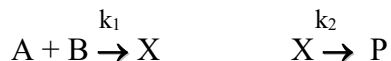
Plot Variables: A B P  Better plot quality (requires Java)

Maximum time: 150 Time steps: 750 Initialize Run Full Step Cl

and the applet result at 100 s is  $[A] = 0.5213$  M and  $[B] = 0.02134$  M. The error for the simple Excel version at 100 s is 2% and the error for the “Kinetics Mechanism Simulation” applet compared to the exact analytical integral is 0.02%. The error for the very simple Excel version is actually quite small given the simplicity of the approach. The error could be greatly decreased by choosing a smaller  $\Delta t$ . The  $\Delta t$  for the Web applet version is  $\Delta t = \text{max time}/750 = 0.20$  s, so it is

not surprising that the Web applet does better than the Excel version. However, the Web applet also uses a better approximation technique, which is the “4<sup>th</sup> order Runge–Kutta” algorithm, to further decrease errors. “Numerical Analysis” courses in Mathematics cover advanced methods for integrating differential equations.

6. Use the finite difference approximation to integrate the rate law for the two step mechanism:



with rate constants  $k_1 = 0.05 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_2 = 0.2 \text{ s}^{-1}$ . Choose the initial concentrations  $[A]_0 = 1.00$  and  $[B]_0 = 0.50 \text{ M}$ . Use  $\Delta t = 1 \text{ s}$  for a maximum time of at least 50 s. Use Excel and compare to the results from the Web based “Kinetics Mechanism Simulation” applet or *MathCad* or *MatLab*. A useful comparison is to find the maximum concentration of the reactive intermediate.

*Answer:* We can extend the spreadsheet from Problem 5. The additional rate laws are:

$$\frac{d[X]}{dt} = k_1 [A][B] - k_2 [X] \quad \frac{d[P]}{dt} = k_2 [X]$$

The corresponding iteration formulas are:

$$[A](t + \Delta t) = [A](t) - k_1 [A](t)[B](t) \Delta t$$

$$[B](t + \Delta t) = [B](t) - k_1 [A](t)[B](t) \Delta t$$

$$[X](t + \Delta t) = [X](t) + k_1 [A](t)[B](t) \Delta t - k_2 [X](t) \Delta t$$

$$[P](t + \Delta t) = [P](t) + k_2 [X](t) \Delta t$$

The first part of the spreadsheet for  $\Delta t = 1 \text{ s}$  is:

A1	B	C	D	E	F	G
2						
3	[A] <sub>0</sub> =	1	M			
4	[B] <sub>0</sub> =	0.5	M			
5	k <sub>1</sub> =	0.05	M <sup>-1</sup> s <sup>-1</sup>			
6	k <sub>2</sub> =	0.2	s <sup>-1</sup>			
7	dt =	1	s			
8						check
9	t (s)	[A]	[B]	[X]	[P]	[A]+[X]+[P]
10	0	1	0.5	0	0	1
11	1	0.975	0.475	0.025	0	1
12	2	0.951844	0.451844	0.043156	0.005	1
13	3	0.93034	0.43034	0.056029	0.013631	1
14	4	0.910321	0.410321	0.064841	0.024837	1
15	5	0.891645	0.391645	0.070549	0.037805	1
16	6	0.874185	0.374185	0.0739	0.051915	1
17	7	0.857829	0.357829	0.075475	0.066695	1
18	8	0.842482	0.342482	0.075728	0.08179	1
19	9	0.828055	0.328055	0.075009	0.096936	1
20	10	0.814473	0.314473	0.07359	0.111938	1
21	11	0.801666	0.301666	0.071678	0.126656	1
22	12	0.789574	0.289574	0.069434	0.140991	1
23	13	0.778142	0.278142	0.06698	0.154878	1
24	14	0.767321	0.267321	0.064405	0.168274	1
25	15	0.757065	0.257065	0.06178	0.181155	1
26	16	0.747334	0.247334	0.059155	0.193511	1
27	17	0.738092	0.238092	0.056566	0.205342	1

The formula for [A] in C11 is: “=C10- $k_1$ \*C10\*D10”

for [B] in D11 is “=D10- $k_1$ \*C10\*D10”

for [X] in E11 is “=E10+ $k_1$ \*C10\*D10- $k_2$ \*E10”

and [P] in F11 is “=F10+ $k_2$ \*E10”.

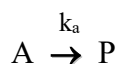
We also added a column to act as an error check, [A]+[X]+[P], from the mass balance during the reaction. This column should always give [A]<sub>0</sub>. The “Kinetics Mechanism Simulation” applet setup is:

The initial part of the applet output is:

time	A	B	X	P
0	1	0.5	0	0
2.5	0.9428	0.4428	0.04416	0.01302
5	0.8948	0.3948	0.06388	0.04135
7.5	0.8539	0.3539	0.07029	0.07582
10	0.8187	0.3187	0.06975	0.1115
12.5	0.7883	0.2883	0.06582	0.1459
15	0.7617	0.2617	0.06047	0.1779
17.5	0.7382	0.2382	0.05476	0.207
20	0.7175	0.2175	0.04921	0.2333
22.5	0.6991	0.1991	0.04408	0.2568
25	0.6826	0.1826	0.03946	0.2779

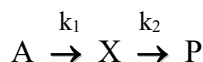
The maximum concentration for the reactive intermediate from the simple Excel version is 0.0757 M at 8.0 s, while the more accurate applet version gives 0.0703 M at about the same time. At 10 s, where we have data for both approaches, the error is 6%. So the  $\Delta t = 1$  s is too long and the Excel simulation should be repeated with much shorter  $\Delta t$ . The Web applet used  $\Delta t = 75$  s/750 = 0.10 s, so the result of the Web applet should be much more accurate.

7. The purpose of this exercise is to understand the statement: “the intrinsically slow step is the rate determining step.” (a) Plot the integrated time course for the first-order mechanism:



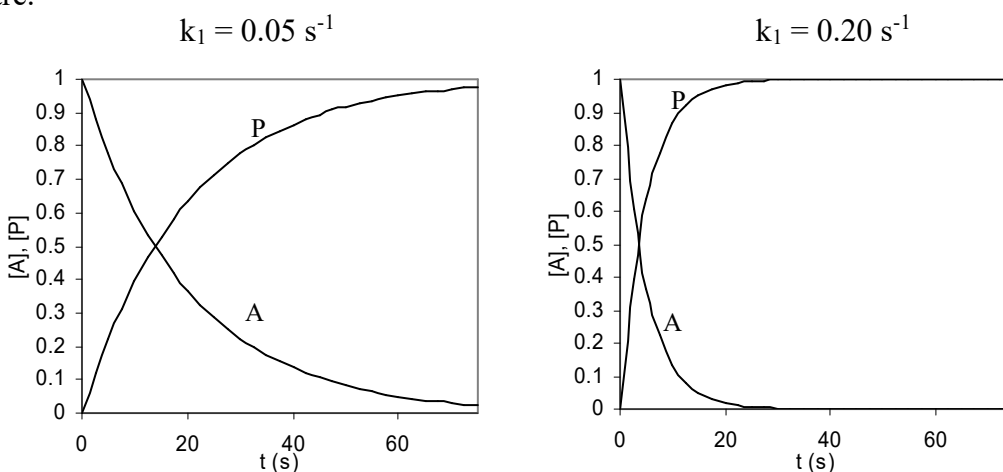
using  $k_a = 0.05 \text{ s}^{-1}$  and  $0.20 \text{ s}^{-1}$ . Plot both [A] and [P] for each case. Use an initial concentration of  $[A]_0 = 1$ . Use the Web based “Kinetics Mechanism Simulation” applet or *MathCad* or *MatLab*.

(b) Similarly find the integrated time course for the consecutive first-order mechanism:



Use  $k_1 = 0.2 \text{ s}^{-1}$  and  $k_2 = 0.05 \text{ s}^{-1}$ . Predict the step that will be the rate determining step. Plot the time course for A, X, and P. To which curve in part (a) does the disappearance of A correspond,  $k=0.05$  or  $k=0.20 \text{ s}^{-1}$ ? To which curve in part (a) does the appearance of product correspond? According to the plot, which step is the rate determining step? Is the intrinsically slow step the rate determining step?

*Answer:* Using the Web based “Kinetics Mechanism Simulation,” the single-step first-order plots are:



(b) The “Kinetics Mechanism Simulation” applet setup is:

A  +  +  = X  +  +   $k_f=0.2$   $k_r=0$

X  +  +  = P  +  +   $k_f=0.05$   $k_r=0$

**Initial Conditions:**

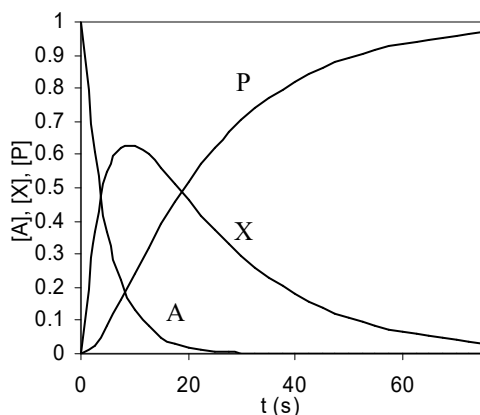
$A_0:$    $B_0:$    $X_0:$    $Y_0:$    $P_0:$    $Q_0:$    $M:$

(M and N are constant concentration reservoirs, such as a background gas, the vessel walls, or a constant flow)

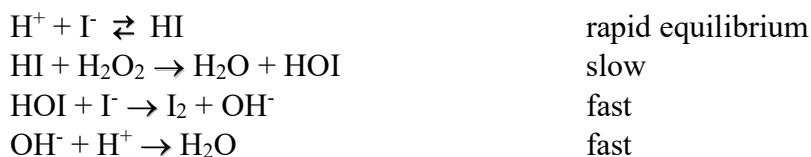
**Plot Variables:**  A  X  P  Better plot quality (requires Java)

**Maximum time:**  **Time steps:**

The “reservoirs” (green rectangles) are shown for  $t = 10 \text{ s}$ , showing a significant concentration of the intermediate. The plot is shown below. The disappearance of A corresponds to the curve in part (a) for  $k_a = 0.2 \text{ s}^{-1}$ , that is, the faster rate constant. However, the appearance of product corresponds to the curve for  $k_a = 0.05 \text{ s}^{-1}$ , that is the slower rate constant. So the appearance of product is given by the slower second step. So, the rate determining step for the appearance of product is the intrinsically slower step. Since  $k_1 \gg k_2$ , this is as we expected and the intermediate is a stable intermediate. The concentration of the intermediate builds to a significant fraction of the initial concentration of A. Note that the steady-state approximation would not be appropriate for this case.



8. Consider the reaction:  $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$ . The following mechanism has been proposed:



Show that this mechanism is consistent with the experimentally determined rate law:

$$v = k [\text{H}^+][\text{I}^-][\text{H}_2\text{O}_2]$$

*Answer:* The rate law for the disappearance of  $\text{H}_2\text{O}_2$  is:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k_2 [\text{HI}][\text{H}_2\text{O}_2]$$

If the first step is a rapid pre-equilibrium, that is  $k_1$  and  $k_{-1} \gg k_2$  then we can obtain the HI concentration from the equilibrium expression:

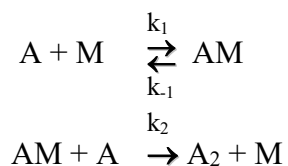
$$K_c = \left( \frac{[\text{HI}]}{[\text{H}^+][\text{I}^-]} \right)_{\text{eq}} \quad \text{giving } [\text{HI}] = K_c [\text{H}^+][\text{I}^-]$$

Substituting this value for [HI] into the rate law for  $\text{H}_2\text{O}_2$  gives:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k_2 K_c [\text{H}^+][\text{I}^-][\text{H}_2\text{O}_2]$$

For the overall reaction,  $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$ :  $v = -\frac{d[\text{H}_2\text{O}_2]}{dt}$ . Fast steps after the rate determining step don't have an effect on the rate law for the disappearance of a reactant in the rate determining step.

9. A possible mechanism for 3<sup>rd</sup> order reactions is:



Show that the rate law can be expressed as:  $\frac{d[A_2]}{dt} = \frac{k_1 k_2 [A]^2 [M]}{k_{-1} + k_2 [A]}$

*Answer:* The plan is to use the steady-state approximation for the concentration of the reactive intermediate AM. Use the steps in the generalized scheme in Section 4.2. Step 1: The rate law for the formation of product is:

$$\frac{d[A_2]}{dt} = k_2 [AM][A]$$

Step 2: The rate law for the formation of the reactive intermediate is equal to zero by the steady-state approximation:

$$\frac{d[AM]}{dt} = k_1 [A][M] - k_{-1} [AM] - k_2 [AM][A] \approx 0 \quad (k_1 \ll k_2)$$

Step 3: Solving for the concentration of the reactive intermediate, AM, gives:

$$k_1 [A][M] = k_{-1} [AM] + k_2 [AM][A] \quad \text{giving} \quad [AM] = \frac{k_1 [A][M]}{k_{-1} + k_2 [A]}$$

Since there is only one reactive intermediate, we can skip step 4.

Step 5: Substituting the concentration of the reactive intermediate into the rate law for the formation of product gives the final desired result:

$$\frac{d[A_2]}{dt} = k_2 \frac{k_1 [A][M]}{k_{-1} + k_2 [A]} [A] = \frac{k_1 k_2 [A]^2 [M]}{k_{-1} + k_2 [A]}$$

Step 6: If  $k_{-1} \gg k_2 [A]$ , then this mechanism is a pre-equilibrium mechanism and is third-order overall. On the other hand, if  $k_2 [A] \gg k_{-1}$ , this overall rate law reverts to a second-order process.

10. Use the steady-state approximation to determine the rate law for the following mechanism:



*Answer:* The plan is to treat B as a reactive intermediate using the steady-state approximation.

Step 1: The rate law for the production of product is:

$$\frac{d[D]}{dt} = k_3 [B][C]$$



Step 2: The rate law for the formation of the reactive intermediate is equal to zero by the steady-state approximation:

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] - k_3[B][C] \approx 0 \quad (k_1 \ll k_3)$$

Step 3: Solving this last equation for the steady-state concentration of B gives:

$$k_1[A] = k_2[B] + k_3[B][C] \text{ giving } [B] = \frac{k_1[A]}{k_2 + k_3[C]}$$

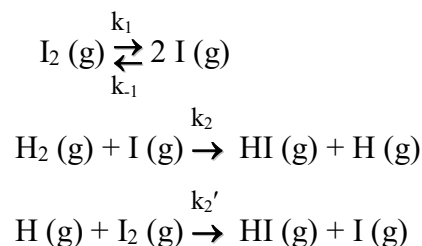
Since there is only one reactive intermediate, we can skip step 4.

Step 5: Substitution into the rate law for the formation of product gives:

$$\frac{d[D]}{dt} = \frac{k_1 k_3 [A][C]}{k_2 + k_3 [C]}$$

Step 6: If  $k_2 \gg k_3[C]$ , is a pre-equilibrium mechanism, with  $K_{eq} = k_1/k_2$ , and then the process is second order overall. If  $k_3[C] \gg k_2$ , then the first step is the rate determining step making the reaction first-order overall.

11. Determine the overall rate law for the proposed  $H_2 + I_2$  mechanism:



*Answer:* The plan is to use the steady-state approximation on both H and I atoms, as reactive intermediates. Step 1 is to write the rate law for the formation of product:

$$\frac{d[HI]}{dt} = k_2 [H_2][I] + k_2' [H][I_2] \quad 1$$

Step 2 for the steady-state mechanistic scheme is to find the rate law for the formation of the reactive intermediates:

$$\frac{d[I]}{dt} = 2 k_1 [I_2] - 2 k_{-1} [I]^2 - k_2 [H_2][I] + k_2' [H][I_2] = 0 \quad 2$$

$$\frac{d[H]}{dt} = k_2 [H_2][I] - k_2' [H][I_2] = 0 \quad 3$$

Step 3: To solve for the concentration of the reactive intermediate, I, add Eqs. 2 and 3:

$$(2 + 3): \quad 2 k_1 [I_2] - 2 k_{-1} [I]^2 = 0 \quad 4$$

and solve for [I]:

$$[I] = \left(\frac{k_1}{k_{-1}}\right)^{1/2} [I_2]^{1/2} \quad 5$$

We have two reactive intermediates in this problem. Note, however, if we add Eq. 3 to Eq. 1 that the rate law for formation of product becomes:

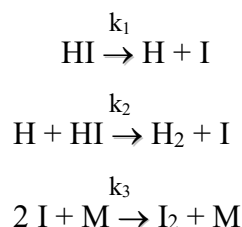
$$(1 + 3): \quad \frac{d[HI]}{dt} = 2 k_2 [H_2][I] \quad 6$$

So only [I] is needed, which eliminates one of the unknowns. We can now proceed to Step 5 and find the overall rate law by substituting the steady-state I concentration from Eq. 5 back into the rate law for the formation of product, Eq. 6:

$$\frac{d[HI]}{dt} = 2 k_2 \left(\frac{k_1}{k_{-1}}\right)^{1/2} [H_2] [I_2]^{1/2} \quad 7$$

This mechanism does not agree with the empirical rate law, and may contribute only at high temperatures.

12. The decomposition of HI is given by the reaction  $2 HI \rightarrow H_2 + I_2$ . One proposed mechanism is:



Use the steady-state approximation to find the rate law for this mechanism. Show that this mechanism does not agree with the experimentally determined rate law:

$$\frac{d[H_2]}{dt} = k [HI]^2$$

*Answer:* The rate law for the production of  $H_2$  from the second elementary step is:

$$\frac{d[H_2]}{dt} = k_2 [H][HI]$$

This rate law is dependent on a reactive intermediate, so it is not in a form that would be typically found from an experimental study. We need to use the steady-state approximation to find the concentration of the reactive intermediate. To do this we need to assume that  $k_1 \ll k_2$ . Step 1 in the general scheme for the steady-state approximation is to write the rate law for the formation of products, which we have already done, above. Step 2 is to write the rate laws for the formation of any reactive intermediates. For the H atom:

$$\frac{d[H]}{dt} = k_1[HI] - k_2 [H][HI] = 0$$

This rate law will allow us to solve for the H atom concentration in terms of the reactant, so we don't need to consider the formation of the other reactive intermediate, which is the I atom. Step 3 is to apply the steady-state approximation to the last equation by setting the rate of formation of H atoms equal to zero. Then solving for [H] gives:

$$[H] = k_1/k_2$$

Step 5 is to substitute this value for the reactive intermediate back into the rate law for the formation of products:

$$\frac{d[H_2]}{dt} = k_2 [H][HI] = k_1 [HI]$$

Notice that to apply the steady-state approximation, we assumed that the first step was slower than the second step. In other words, the slow step is the first step, which is unimolecular in HI. This result does not agree with the experimentally determined rate law.

13. (a) Determine the integrated rate law for the Michaelis-Menten mechanism. Note that during the portion of the reaction where the steady-state approximation applies,  $-d[S]/dt = d[P]/dt$  so that Eq. 4.2.31 becomes:

$$-\frac{d[S]}{dt} = \frac{k_1 [E]_0 [S]}{k_M + [S]}$$

(b) Show that for short times, [S] is a linear function of time:  $[S] - [S]_0 = -\frac{[E]_0([S]_0 + 1) k_1}{k_M} t$

[Hint: you can approximate  $\ln(x) \approx x - 1$ , when x is close to 1.]

*Answer:* (a). Separating variables by cross multiplying:

$$\frac{k_M + [S]}{[S]} d[S] = -[E]_0 k_1 dt$$

which simplifies to:

$$\left(\frac{k_M}{[S]} + 1\right) d[S] = -[E]_0 k_1 dt$$

The integration limits start at  $t=0$ ,  $[S] = [S]_0$ :

$$\int_{[S]_0}^{[S]} \left(\frac{k_M}{[S]} + 1\right) d[S] = -\int_0^t [E]_0 k_1 dt$$

The sum in the first integral can be split into two terms:

$$k_M \ln([S]) \Big|_{[S]_0}^{[S]} + [S] \Big|_{[S]_0}^{[S]} = -[E]_0 k_1 t$$

$$k_M \ln \frac{[S]}{[S]_0} + ([S] - [S]_0) = -[E]_0 k_1 t$$

(b). At the beginning of the reaction  $[S] \approx [S]_o$  and  $[S]/[S]_o \approx 1$  in the logarithmic term. Remembering that the Taylor series for  $\ln x \approx x - 1$ , expanded about  $x = 1$ , then:

$$k_M \left( \frac{[S]}{[S]_o} - 1 \right) + ([S] - [S]_o) = -[E]_o k_1 t$$

Factoring  $1/[S]_o$  out of the first term in parentheses gives:

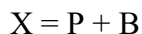
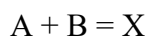
$$\frac{k_M}{[S]_o} ([S] - [S]_o) + ([S] - [S]_o) = \left( \frac{k_M}{[S]_o} + 1 \right) ([S] - [S]_o) = -[E]_o k_1 t$$

Solving for the concentration difference gives:  $[S] - [S]_o = -\frac{[E]_o [S]_o k_1}{k_M + [S]_o} t$

which is a linear function of time.

14. Use the “*Kinetic Mechanism Simulation*” applet to numerically integrate the rate laws for the Michaelis-Menten enzyme mechanism, Eq. 4.2.22. Set  $k_2 = 0.40 \text{ M}^{-1}\text{s}^{-1}$ ,  $k_{-1} = 0.1 \text{ s}^{-1}$ , and  $k_1 = 0.10 \text{ s}^{-1}$ . Use the initial conditions  $[S]_o = 1.0 \text{ M}$  and  $[E]_o = 0.1 \text{ M}$ . Such a large enzyme concentration will make the plot scaling more convenient. (a). Plot  $[S]$ ,  $[ES]$ , and  $[P]$  for a maximum of 300 s to verify the linear time course for short times. (b). To observe the pre-induction lag, using the same conditions, plot  $[ES]$  and  $[P]$  for a maximum time of 15 s.

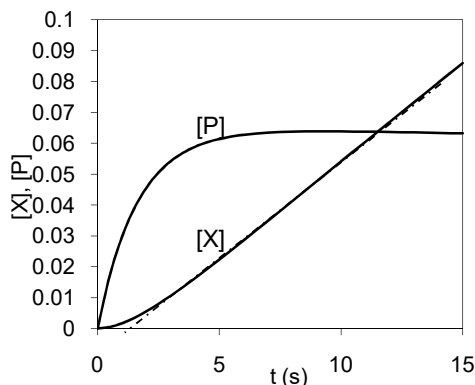
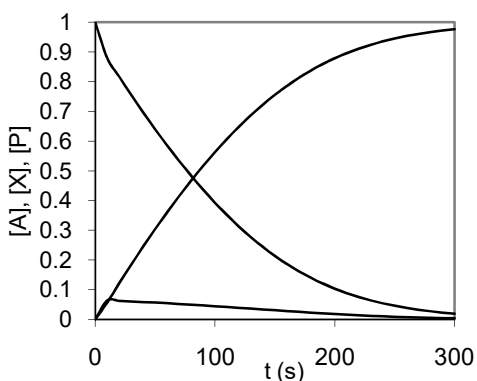
*Answer:* In our Michaelis-Menten simulation, we will use the symbols:



where B is the enzyme, A is the substrate, X is the enzyme substrate complex, and P is the product. The set-up for the “*Kinetic Mechanism Simulation*” applet is:

The screenshot shows the configuration for the "Kinetic Mechanism Simulation" applet. At the top, the reaction scheme is defined as  $A + B = X$  and  $X = P + B$ . The rate constants are set to  $k_1 = 0.1$ ,  $k_2 = 0.4$ , and  $k_{-1} = 0.1$ . Under "Initial Conditions", the concentrations are  $A_0 = 1$ ,  $B_0 = 0.1$ ,  $X_0 = 0$ ,  $Y_0 = 0$ ,  $P_0 = 0$ ,  $Q_0 = 0$ , and  $M = 1$ . The "Plot Variables" section shows  $A$ ,  $X$ , and  $P$  selected. The "Maximum time" is set to 300 and "Time steps" to 750. Buttons for "Initialize", "Run Full", "Step", and "Close" are visible at the bottom.

The requested plots are:



A straight line is included for the shorter time scale plot to show the pre-induction lag. The linear portion of the time course is offset from the origin.

15. Consider the Lindemann-Henshelwood Mechanism for first-order reactions. Compare the net rate of the pre-equilibrium step to the rate of the unimolecular step during the majority of the time course of the reaction. Look at the rate dependence after any induction period.

*Answer:* This portion of the time course is adequately approximated using the steady-state approximation. The rate law for the formation of the activated molecule is:

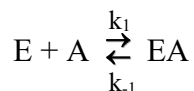
$$\frac{d[A^*]}{dt} = k_2[A]^2 - k_{-2}[A^*][A] - k_1[A^*] = 0$$

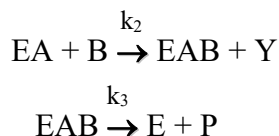
Applying the steady-state approximation corresponds to setting this rate equal to zero. We can rearrange this equation to place the rate terms for the appearance and disappearance of reactant on the left and the rate terms for the appearance of product from the activated molecule on the right:

$$\begin{array}{rcccl} k_2[A]^2 & - & k_{-2}[A^*][A] & = & k_1[A^*] \\ \nu_+ & - & \nu_- & = & \nu_2 \\ \text{forward rate} & & \text{reverse rate} & & \\ \text{first step} & & & & \text{second step} \end{array}$$

In accordance with the results from Eq. 4.2.19, the terms on the left give the net rate of the reversible first step and the term on the right gives the rate of the second step. As expected, these rates are equal during the majority of the time course for the reaction.

16. The following mechanism has been proposed for an enzyme reaction with two substrates, A and B:





where EA and EAB are enzyme substrate complexes. Assuming that  $k_2$  and  $k_3$  are large compared to  $k_1$ , show that the mechanism gives the rate law:

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [E][A][B]}{k_{-1} + k_2 [B]}$$

*Answer:* The plan is to use the steady state approximation for both reactive intermediates EA and EAB. Since the overall rate law is written in terms of the formation of product, we start with the rate law for the formation of products.

The rate law for the formation of products is a function of the reactive intermediate EAB:

$$\frac{dP}{dt} = k_3 [EAB] \quad 1$$

The rate laws for the formation of EA and EAB are equal to zero by the steady state approximation:

$$\frac{d[EA]}{dt} = k_1[E][A] - k_{-1}[EA] - k_2[EA][B] = 0 \quad 2$$

$$\frac{d[EAB]}{dt} = k_2[EA][B] - k_3[EAB] = 0 \quad 3$$

Solving Eq. 2 for [EA] gives:  $[EA] = \frac{k_1[E][A]}{k_{-1} + k_2[B]}$  4

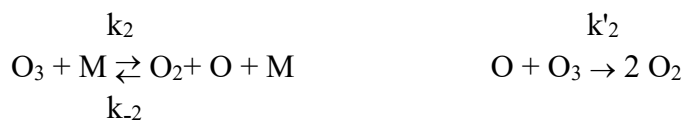
Solving Eq. 3. for [EAB] gives:  $[EAB] = \frac{k_2}{k_3} [EA][B]$  5

Substituting Eq. 4 into EQ. 5 gives:  $[EAB] = \frac{k_1 k_2 [E][A][B]}{k_3 (k_{-1} + k_2[B])}$  6

Substituting the concentration of the reactive intermediate from Eq. 6 into the rate law for the formation of product, Eq. 1, gives the final rate law:

$$\frac{dP}{dt} = \frac{k_1 k_2 [E][A][B]}{(k_{-1} + k_2[B])}$$

17. Consider the following proposed mechanism for the decomposition of ozone. M is an unreactive gas molecule that collides with the ozone to break the ozone apart:



Assume  $k'_2 \gg k_2$ . Show that the rate law that corresponds to this mechanism is:

$$\frac{d[\text{O}_2]}{dt} = \frac{3 k'_2 k_2 [\text{O}_3]^2 [\text{M}]}{k_{-2} [\text{O}_2] [\text{M}] + k'_2 [\text{O}_3]}$$

*Answer:* The plan is to use the steady state approximation for the reactive intermediate O atoms. Since the rate law is written in terms of the formation of the product O<sub>2</sub>, we start with the rate law for the formation of O<sub>2</sub>.

For the formation of product:

$$\frac{d[\text{O}_2]}{dt} = k_2 [\text{O}_3] [\text{M}] - k_{-2} [\text{O}_2] [\text{O}] [\text{M}] + 2 k'_2 [\text{O}] [\text{O}_3] \quad 1$$

Use the steady-state approximation for the reactive intermediate, [O]:

$$\frac{d[\text{O}]}{dt} = k_2 [\text{O}_3] [\text{M}] - k_{-2} [\text{O}_2] [\text{O}] [\text{M}] - k'_2 [\text{O}] [\text{O}_3] = 0 \quad 2$$

Subtracting Eq. 2 from Eq. 1 cancels terms, eliminating the explicit dependence on [M]:

$$\frac{d[\text{O}_2]}{dt} = 3 k'_2 [\text{O}] [\text{O}_3] \quad 3$$

Solving Eq. 2 for the concentration of the reactive intermediate gives:

$$[\text{O}] = \frac{k_2 [\text{O}_3] [\text{M}]}{k_{-2} [\text{O}_2] [\text{M}] + k'_2 [\text{O}_3]} \quad 4$$

Substitute this result for [O] into Eq. 3:  $\frac{d[\text{O}_2]}{dt} = \frac{3 k'_2 k_2 [\text{O}_3]^2 [\text{M}]}{k_{-2} [\text{O}_2] [\text{M}] + k'_2 [\text{O}_3]}$

18. Report all six of the rate constants for the kinetics of proton exchange in aqueous solution of acetic acid, Figure 4.5.1. The reaction was studied at pH = 4.74 with the acetic acid and acetate concentrations both 0.100 M. The rate constants determined from temperature jump kinetics studies are  $k_{31} = 4.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{23} = 1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>1</sup> Use the data from Example 3.6.1 for the auto-protolysis constants for water. The  $K_a$  for acetic acid is:

$$K_a = \frac{[\text{H}^+][\text{OAc}^-]}{[\text{HOAc}]} = 1.75 \times 10^{-5} \text{ M}$$

*Answer:* Because of the cyclic mechanism, the number of independent rate constants is five. The specification of the acid dissociation constant,  $K_a = k_{13}/k_{31}$ , relates  $k_{13}$  and  $k_{31}$ . The auto-protolysis equilibrium constant for water is  $K_c = k_{21}/k_{12}$ , with water explicitly in the equilibrium expression, Example 3.6.1. The auto-protolysis equilibrium constant for water relates  $k_{12}$  and  $k_{21}$  giving three independent rate constants left to be determined (Example 4.5.1). With the given rate constant for the recombination of the proton and the conjugate base of the weak acid,  $k_{31} = 4.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , and the  $K_a$  we can find the weak acid dissociation rate constant:

$$k_{13} = K_a k_{31} = 1.75 \times 10^{-5} \text{ M} (4.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}) = 7.9 \times 10^5 \text{ s}^{-1} \quad 1$$

At equilibrium, the forward and reverse rates for the hydrolysis of acetate, (2) $\rightleftharpoons$ (3), are equal and given by:

$$k_{32} [\text{OAc}^-][\text{H}_2\text{O}] = k_{23} [\text{OH}^-][\text{HOAc}] \quad 2$$

with the concentration of water explicitly given in the rate law. Since  $\text{pH} = 4.74$ ,  $[\text{H}^+] = 10^{-4.74}$ , giving  $[\text{OH}^-] = 10^{-9.26} = 5.50 \times 10^{-10} \text{ M}$ . With the given rate constant for proton transfer from the weak acid to hydroxide,  $k_{23}$ :

$$\begin{aligned} k_{32} (0.100 \text{ M})(55.33 \text{ M}) &= 1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} (5.50 \times 10^{-10} \text{ M})(0.100 \text{ M}) \\ k_{32} &= 0.181 \text{ M}^{-1} \text{ s}^{-1} \end{aligned} \quad 3$$

with water explicitly in the rate expression. Alternatively, if the concentration of water is combined with the  $k_{32}$  rate constant then Eq. 2 is written:

$$\begin{aligned} k_{32} [\text{OAc}^-] &= k_{23} [\text{OH}^-][\text{HOAc}] \\ k_{32} (0.100 \text{ M}) &= 1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} (5.50 \times 10^{-10} \text{ M})(0.100 \text{ M}) \\ k_{32} &= 9.9 \text{ s}^{-1} \end{aligned} \quad 4$$

Instead of working with the rate laws directly, Eq. 2 and 4, we could have done this problem equivalently using the equilibrium constant for the hydrolysis. Remembering from General Chemistry that:

$$K_b = \frac{K_w}{K_a} = \frac{[\text{OH}^-][\text{HOAc}]}{[\text{OAc}^-]} = 5.76 \times 10^{-10} \text{ M} \quad 5$$

Then  $K_b = k_{32}/k_{23}$  and from the given  $k_{23}$ :

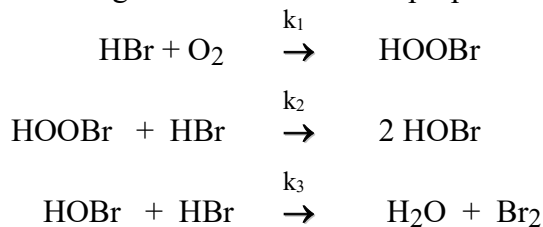
$$k_{32} = 5.76 \times 10^{-10} \text{ M} (1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}) = 10.4 \text{ s}^{-1} \quad 6$$

where Eq. 4 and 6 differ because of round-off error.

Just a note on uncertainty; the relaxation times and rate constants are uncertain to about 30%, so the number of significant figures is really only 1 for each result. The rate constants for the auto-protolysis of water are given in Example 3.6.1:

$$\begin{aligned} k_{21} &= 1.35 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1} \\ k_{12} &= k_{21}/K_c = 2.45 \times 10^{-5} \text{ s}^{-1} \end{aligned}$$

19. The following mechanism has been proposed for the oxidation of HBr to  $\text{Br}_2$ :



To give the proper overall stoichiometry, this last step must be doubled. All the steps are unidirectional. Show that the corresponding rate law can be expressed as:

$$\frac{d[\text{Br}_2]}{dt} = k_1 [\text{HBr}][\text{O}_2]$$



*Answer:* There are two reactive intermediates in this mechanism, HOBr and HOOBr. The way to determine that these are reactive intermediates is to note that neither HOOBr nor HOBr are reactants or products. We will need to apply the steady-state approximation to both. Step 1: The rate law for the production of product is:

$$\frac{d[\text{Br}_2]}{dt} = k_3 [\text{HOBr}][\text{HBr}] \quad 1$$

Step 2: The rate laws for the formation of the reactive intermediates are equal to zero by the steady-state approximation:

$$\frac{d[\text{HOOBr}]}{dt} = k_1 [\text{HBr}][\text{O}_2] - k_2 [\text{HOOBr}][\text{HBr}] \approx 0 \quad 2$$

$$\frac{d[\text{HOBr}]}{dt} = 2 k_2 [\text{HOOBr}][\text{HBr}] - 2 k_3 [\text{HOBr}][\text{HBr}] \approx 0 \quad 3$$

The  $2 k_3$  is required to give the proper overall stoichiometry. Step 3: Multiplying Eq. 2 by two and adding to Eq. 3 gives:

$$2 k_1 [\text{HBr}][\text{O}_2] - 2 k_3 [\text{HOBr}][\text{HBr}] = 0 \quad 4$$

and solving for  $[\text{HOBr}]$ :

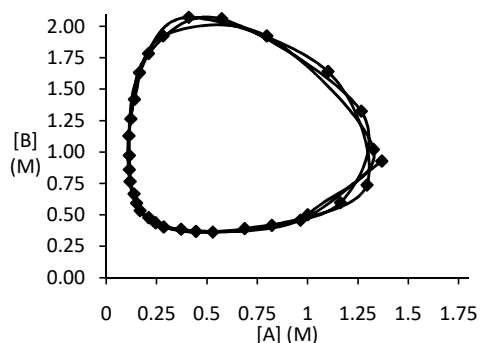
$$[\text{HOBr}] = \frac{k_1 [\text{HBr}][\text{O}_2]}{k_3 [\text{HBr}]} \quad 5$$

Step 5: Substitution of this last equation into the rate law for the production of products, Eq. 1, gives:

$$\frac{d[\text{Br}_2]}{dt} = k_3 \frac{k_1 [\text{HBr}][\text{O}_2]}{k_3 [\text{HBr}]} [\text{HBr}] = k_1 [\text{HBr}][\text{O}_2] \quad 6$$

**20.** For some oscillating mechanisms the same cycle results, after a short initial period, no matter the starting conditions. For such cases the plot of the oscillating concentrations is called a **limit cycle**. Does the Lotka-Volterra mechanism give a limit cycle? [Hint: repeat Example 4.4.1 but with initial conditions  $[\text{A}]_0 = 1 \text{ M}$  and  $[\text{B}]_0 = 0.5 \text{ M}$ . Does the same cycle result as in Figure 4.4.2b?]

*Answer:* The settings specified in Example 4.4.1 were used for the “Kinetics Mechanism Simulation,” except with the new starting conditions. The new starting conditions give the cycle shown below:



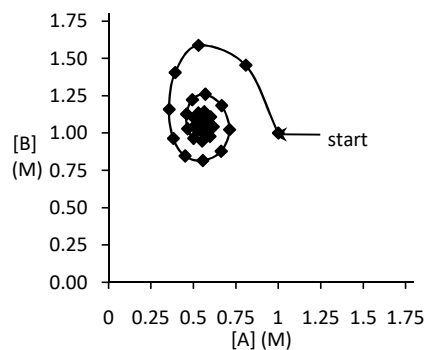
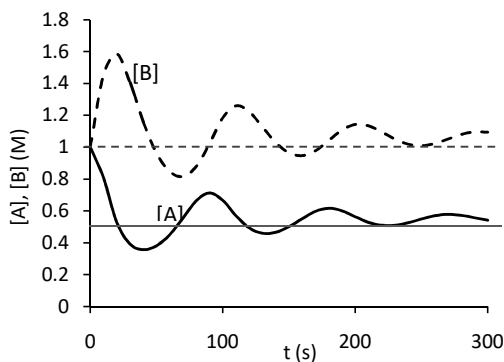
The cycle concentration ranges are larger than Example 4.4.2b. The Lotka-Volterra mechanism does not give a limit cycle. Similarly, Example 4.4.1 showed that no time dependence resulted when the steady state concentrations were used as the initial conditions.

21. The Lotka-Volterra mechanism with all irreversible steps, Eqs. 4.4.6, are unrealistic in several ways. One result is that oscillations occur for too wide a range of rate constants and starting conditions. In addition, the system does not evolve towards a steady state. Modify the mechanism to include reversible reactions for the formation of A and B (steps 1 and 2), but leave the formation of products as irreversible. Run a simulation with the same conditions as in Example 4.4.1, except set the equilibrium constants for the formation of A and of B at 20. Comment on the results.

*Answer:* The “Kinetic Mechanism Simulation” applet was set up as in Example 4.4.1, but with the reverse rate constants for steps 1 and 2 set to 0.005, since  $K_{eq} = k_f/k_r = 0.1/0.005 = 20$ .

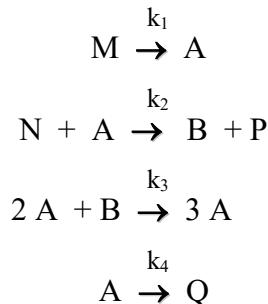
A	+	M	+		=	2A	+		+		$k_f=0.1$	$k_r=0.005$	
A	+	B	+		=		+	2B	+		$k_f=0.1$	$k_r=0.005$	
B	+		+		=	P	+		+		$k_f=0.05$	$k_r=0$	
$A_0:$	1	$B_0:$	1	$X_0:$	0	$Y_0:$	0	$P_0:$	0	$Q_0:$	0	$M:$	1
Plot Variables: <input type="checkbox"/> A <input type="checkbox"/> B <input type="checkbox"/> <input type="checkbox"/> <input checked="" type="checkbox"/> Better plot quality (requires Java)													
Maximum time:		300	Time steps:		1500	Initialize		Run Full		Step		Clear	

The resulting simulation is shown below.



The oscillations now last for a limited time and the system approaches the steady state. Choosing an even smaller equilibrium constant for the first two steps damps out the oscillations. One of the reasons that the reversible processes inhibit oscillations is that the initial conditions are not as far from equilibrium. Notice also that the steady-state shifts slightly for the case with irreversible reactions.

22. The “Brusselator” or “trimolecular” mechanism is a more realistic model for oscillating systems than the Lotka-Volterra mechanism. The Brusselator displays most of the complex phenomena associated with reactions far from equilibrium and is centrally important in the development of non-equilibrium thermodynamics. The mechanism is:<sup>2</sup>



where M and N are held constant by running the reaction in a flowing system. A convenient set of conditions for simulation is to set all the rate constants to 0.10,  $[M]_o = 1.00$  M and  $[N]_o = 3.00$  M. Run kinetics simulations using *MatLab*, *Mathematica*, or the “Kinetic Mechanism Simulation” applet for three sets of initial conditions: (a)  $[A]_o = [B]_o = 1.00$  M; (b)  $[A]_o = 1.00$  M,  $[B]_o = 2.00$  M; and (c)  $[A]_o = 1.00$  M,  $[B]_o = 3.00$  M, which are the steady state concentrations. Run the simulation for 300 s. Because the concentrations change rapidly over the time interval, you will need to choose a large number of time steps to ensure numerical accuracy, choose 15000 time steps. Plot the concentrations of A and B.

*Answer:* The set-up for the “Kinetics Mechanism Simulation” applet is shown below. Notice the large number of time steps to insure better accuracy for the numerical integration.

<input type="text" value=""/>	+	<input type="text" value=""/>	+	M	=	A	+	<input type="text" value=""/>	+	<input type="text" value=""/>	$k_f=0.1$	$k_r=0$
A	+	<input type="text" value=""/>	+	N	=	<input type="text" value=""/>	+	B	+	P	$k_f=0.1$	$k_r=0$
2A	+	B	+	<input type="text" value=""/>	=	3A	+	<input type="text" value=""/>	+	<input type="text" value=""/>	$k_f=0.1$	$k_r=0$
A	+	<input type="text" value=""/>	+	<input type="text" value=""/>	=	<input type="text" value=""/>	+	Q	+	<input type="text" value=""/>	$k_f=0.1$	$k_r=0$

**Initial Conditions:**  
 $A_0:$    $B_0:$    $C_0:$    $X_0:$    $Y_0:$    $P_0:$    $Q_0:$    $M:$    $N:$

**Plot Variables:**     Better plot quality (requires Java)

**Maximum time:**  **Time steps:**

The output for the three runs is shown below:

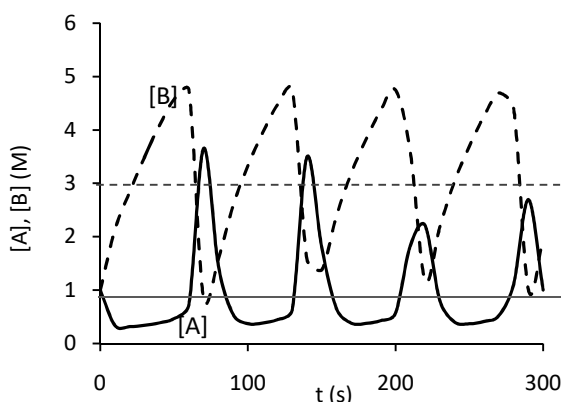


Figure P22.1:  $[A]_0 = [B]_0 = 1.00$  M

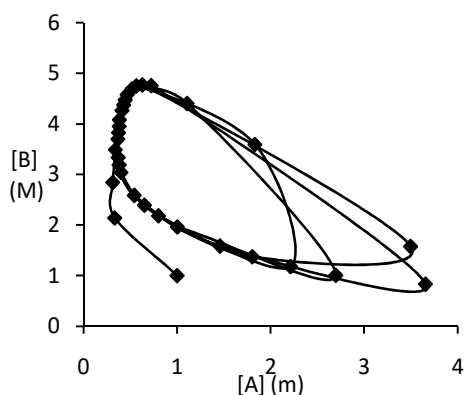


Figure P22.2:  $[A]_0 = [B]_0 = 1.00$  M

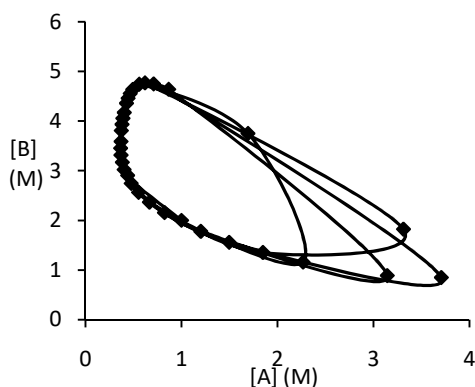


Figure P22.3:  $[A]_0 = 1.00$ ,  $[B]_0 = 2.00$  M

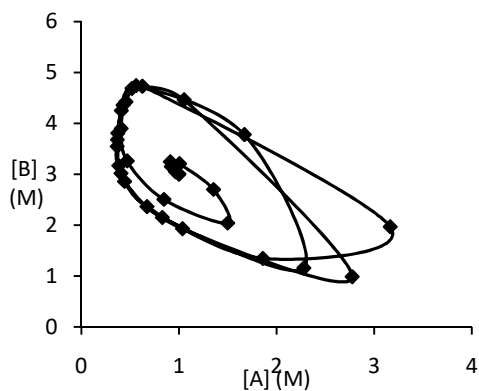


Figure P22.4:  $[A]_0 = 1.00$ ,  $[B]_0 = 3.00$  M

In Figure P22.1, the concentration maximum at 220 s should be comparable to the previous maxima; the appearance of the time course is distorted by the large time interval used for plotting. Notice the similarity between Figures P22.2 and P22.3 at long times. Notice also that when the reaction is started with the steady state conditions,  $[A]_0 = 1.00$  M,  $[B]_0 = 3.00$  M, the reactions also oscillate, Figure P22.4. When run for longer time intervals, all initial conditions result in the same cycle; the Brusselator gives a **limit cycle** (see Problem 20). See the next problem for the derivation of the steady-state conditions.

23. The Brusselator mechanism is given in the previous problem. (a). Find relationships for the steady state concentrations of A and B in terms of the rate constants. (b). Find the steady state concentrations for the conditions given in the previous problem: that is, all the rate constants equal to 0.10,  $[M]_0 = 1.00 \text{ M}$ , and  $[N]_0 = 3.00 \text{ M}$ .

*Answer:* The plan is to use the steady-state approximation for the intermediates A and B.

The rate laws for the appearance of A and B are set to zero, according to the steady-state approximation. For intermediate B:

$$\frac{d[B]}{dt} = k_2[N][A] - k_3[A]^2[B] = 0 \quad 1$$

$$\text{Solving for } [B]_{ss} \text{ gives: } [B]_{ss} = \frac{k_2[N][A]_{ss}}{k_3[A]_{ss}^2} \quad 2$$

The rate law for the appearance of [A] is:

$$\frac{d[A]}{dt} = k_1[M] - k_2[N][A] - 2k_3[A]^2[B] + 3k_3[A]^2[B] - k_4[A] = 0 \quad 3$$

$$= k_1[M] - k_2[N][A] + k_3[A]^2[B] - k_4[A] = 0 \quad 4$$

Substituting the equation for  $[B]_{ss}$  into this last equation gives:

$$k_1[M] - k_2[N][A] + k_2[N][A] - k_4[A] = k_1[M] - k_4[A] = 0 \quad 5$$

$$\text{Solving for } [A]_{ss} \text{ gives: } [A]_{ss} = \frac{k_1}{k_4} [M] \quad 6$$

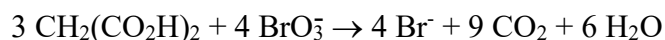
$$\text{Substitution of Eq. 6 into Eq. 2 gives: } [B]_{ss} = \frac{k_2 k_4 [N]}{k_1 k_3 [M]} \quad 7$$

(b). Eqs. 6 and 7 give the steady-state conditions as:

$$[A]_{ss} = \frac{0.1}{0.1} [1.00 \text{ M}] = 1.00 \text{ M} \quad \text{and} \quad [B]_{ss} = \frac{(0.1)(0.1)[3.00 \text{ M}]}{(0.1)(0.1)[1.00 \text{ M}]} = 3.00 \text{ M}$$

as given in the previous problem.

24. The Belousov-Zhabotinsky reaction is an oscillating reaction based on the oxidation of malonic acid with  $\text{KBrO}_3$ , which is catalyzed by  $\text{Ce(IV)}$ :



The BZ reaction played a central role in the development of techniques to study oscillating reactions and in the theory of non-equilibrium thermodynamics.<sup>2,3</sup> The initiation step is the generation of  $\text{HBrO}_2$ , the key reactive intermediate, from  $\text{BrO}_3^-$ :



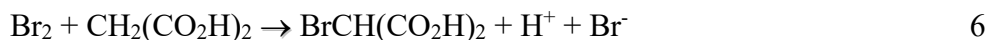
The bulk of the  $\text{HBrO}_2$  is produced auto-catalytically:



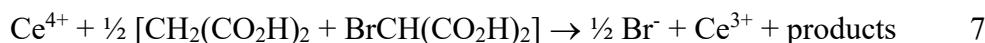
The intermediate  $\text{HBrO}_2$  is consumed in the reactions:



The oxidation of malonic acid is complex, but a simplified version includes first the bromination of malonic acid:



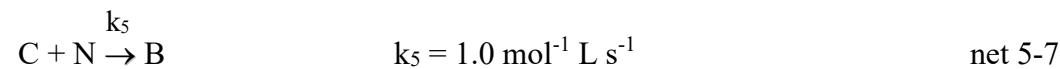
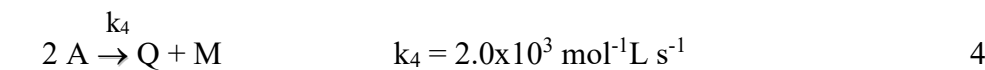
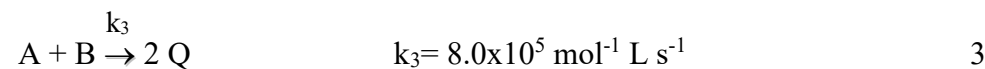
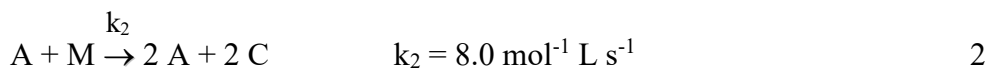
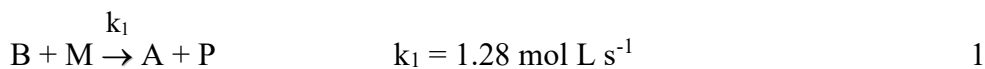
and the oxidation of malonic acid and bromomalonic acid by  $\text{Ce}^{4+}$ :



The products include  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and a mixture of organic acids. For modeling purposes, the oxidation of the malonic acid by  $\text{Ce}(\text{IV})$  is represented by the net  $\text{Ce}(\text{IV})$  to  $\text{Br}^-$  stoichiometry using:



Field, Körös, and Noyes have developed a mechanism for the reaction that displays oscillations. With steps numbered according to the mechanistic steps listed above, the FKN mechanism is:<sup>2,3</sup>



with  $\text{A} = \text{HBrO}_2$ ,  $\text{B} = \text{Br}^-$ ,  $\text{C} = \text{Ce}^{4+}$ ,  $\text{M} = \text{BrO}_3^-$ ,  $\text{N} = \text{malonic acid}$ ,  $\text{Q} = \text{HOBr}$

The  $\text{H}^+$  and  $\text{Ce}^{3+}$  concentrations are roughly constant and are included through pseudo-rate constants.  $\text{M}$  and  $\text{N}$  are held constant by a flowing reactor. This mechanism is also called the “Oregonator.”

Do a numerical simulation of the FKN mechanism using *MatLab*, *Mathematica*, or the “Kinetics Mechanism Simulation” applet on the companion CD or the textbook Web site with the following conditions:

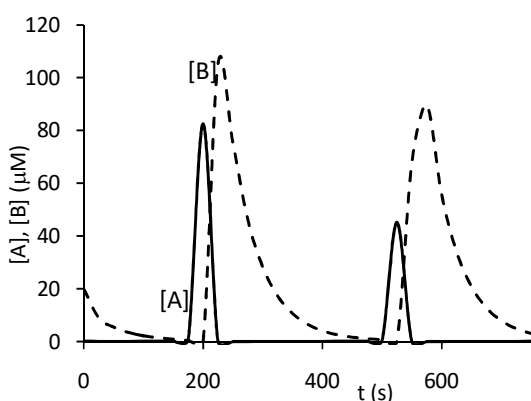
$$[\text{M}] = [\text{BrO}_3^-] = 0.06 \text{ M}, \quad [\text{N}] = [\text{malonic acid}] = 0.02 \text{ M}$$

$$[\text{A}]_0 = [\text{HBrO}_2] = 2.0 \times 10^{-7} \text{ M}, \quad [\text{B}]_0 = [\text{Br}^-] = 2.0 \times 10^{-5} \text{ M}, \quad [\text{C}]_0 = [\text{Ce}^{4+}] = 1.0 \times 10^{-4} \text{ M}.$$

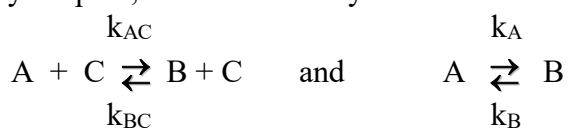
Run the simulation for 750 s. Because the rate constants span almost six orders of magnitude, you will need to choose a large number of time steps to ensure numerical accuracy, choose 7500 or more total time steps. Plot the concentrations of  $\text{A}$  and  $\text{B}$ .

*Answer:* The set-up for the “Kinetics Mechanism Simulation” applet is shown below. Notice the large number of time steps which insure better accuracy for the numerical integration.

<input type="text" value=""/>	+	<input type="text" value="B"/>	+	<input type="text" value="M"/>	=	<input type="text" value="A"/>	+	<input type="text" value=""/>	+	<input type="text" value="P"/>	$k_f=$	<input type="text" value="1.28"/>	$k_r=$	<input type="text" value="0"/>			
<input type="text" value="A"/>	+	<input type="text" value=""/>	+	<input type="text" value="M"/>	=	<input type="text" value="2A"/>	+	<input type="text" value="2C"/>	+	<input type="text" value=""/>	$k_f=$	<input type="text" value="8"/>	$k_r=$	<input type="text" value="0"/>			
<input type="text" value="A"/>	+	<input type="text" value="B"/>	+	<input type="text" value=""/>	=	<input type="text" value=""/>	+	<input type="text" value="2Q"/>	+	<input type="text" value=""/>	$k_f=$	<input type="text" value="8e5"/>	$k_r=$	<input type="text" value="0"/>			
<input type="text" value="2A"/>	+	<input type="text" value=""/>	+	<input type="text" value=""/>	=	<input type="text" value="Q"/>	+	<input type="text" value="M"/>	+	<input type="text" value=""/>	$k_f=$	<input type="text" value="2000"/>	$k_r=$	<input type="text" value="0"/>			
<input type="text" value=""/>	+	<input type="text" value="C"/>	+	<input type="text" value="N"/>	=	<input type="text" value=""/>	+	<input type="text" value="B"/>	+	<input type="text" value="P"/>	$k_f=$	<input type="text" value="1"/>	$k_r=$	<input type="text" value="0"/>			
$A_0:$	<input type="text" value="2e-7"/>	$B_0:$	<input type="text" value="2e-5"/>	$C_0:$	<input type="text" value="1e-4"/>	$X_0:$	<input type="text" value="0"/>	$Y_0:$	<input type="text" value="0"/>	$P_0:$	<input type="text" value="0"/>	$Q_0:$	<input type="text" value="0"/>	$M:$	<input type="text" value="0.06"/>	$N:$	<input type="text" value="0.02"/>
Plot Variables: <input type="text" value="A"/> <input type="text" value="B"/> <input type="text" value=""/>																	
<input checked="" type="checkbox"/> Better plot quality (requires Java)																	
Maximum time:		<input type="text" value="750"/>	Time steps:		<input type="text" value="15000"/>	Initialize		Run Full		Step		Clear					



25. Consider a reaction  $A \rightleftharpoons B$  at equilibrium that can occur via a catalyzed path and an uncatalyzed path, with C the catalyst:



Show that if 10% of the forward process at equilibrium occurs by the uncatalyzed path that 10% of the reverse process will also occur by the uncatalyzed path.

*Answer:* The overall rate law is given by:

$$v = \frac{d[A]}{dt} = -k_{AC}[A][C] - k_A[A] + k_{BC}[B][C] + k_B[B] \quad 1$$

At equilibrium the rate with respect to A is zero and then the overall forward rate is equal to the overall reverse rate,  $v_+ = v_-$ :

$$k_{AC}[A][C] + k_A[A] = k_{BC}[B][C] + k_B[B] \quad 2$$

By detailed balance, the forward rate must be equal to the reverse rate for each elementary step and then for the uncatalyzed path:

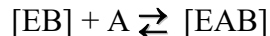
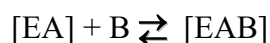
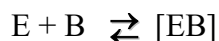
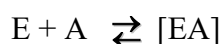
$$k_A [A] = k_B [B] \quad 3$$

Dividing Eq. 3 by Eq. 2 gives the ratio of the uncatalyzed to the overall rate:

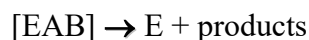
$$\frac{k_A [A]}{k_{AC} [A][C] + k_A [A]} = \frac{k_B [B]}{k_{BC} [B][C] + k_B [B]} \quad 4$$

The term on the left of the equality is the fraction of the forward reaction that proceeds by the uncatalyzed path. The term on the right is the fraction of the reverse reaction that proceeds by the uncatalyzed path. The fractions are then shown to be equal.

26. A random bi-substrate enzyme mechanism requires two substrates, but the substrates can bind to the enzyme in either order. One example is an enzyme that phosphorylates a protein using ATP as the phosphate source; ATP and the protein target are the two substrates. The mechanistic steps are:

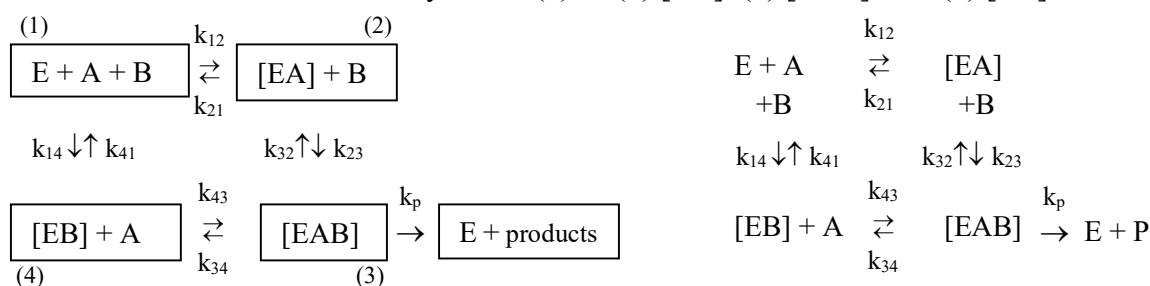


all of which are assumed to be in quasi-equilibrium (in the same sense as the pre-equilibrium mechanism). The production of product is assumed to be essentially irreversible:



Draw the quasi-equilibrium mechanistic steps as a four-state cyclic process, and give the relationship among the corresponding rate constants.

*Answer:* The four states for the cycle are (1) E, (2) [EA], (3) [EAB], and (4) [EB]:



(a) Box model style

(b) Conventional depiction



The relationship of the rate constants around the cycle is the product of all the forward rate constants divided by the product of all the reverse rate constants:

$$\frac{k_{12} k_{23} k_{34} k_{41}}{k_{21} k_{32} k_{43} k_{14}} = 1$$

27. Consider the bidirectional reaction:



The initial rate law for the reaction, starting with A only, is experimentally determined to be:

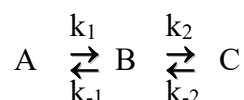
$$\frac{d[A]}{dt} = -k_{\text{obs},f} [A]_0$$

If the reverse reaction is run starting with C only, the initial rate law is determined to be:

$$\frac{d[C]}{dt} = -k_{\text{obs},r} [C]_0$$

Why isn't the equilibrium constant for the overall reaction given by the ratio of the initial forward to the initial reverse rate constants,  $k_{\text{obs},f}/k_{\text{obs},r}$ ?

*Answer:* The given experimentally determined rate laws are for the system away from equilibrium. Detailed balance only applies to reactions at equilibrium. For the reaction at equilibrium, applying detailed balance:

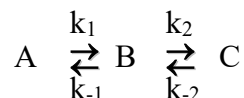


Comparing to the given experimental initial rate laws we find that  $k_{\text{obs},f} = k_1$  and  $k_{\text{obs},r} = k_{-2}$ . Rather, at equilibrium detailed balance gives:

$$K_c = \frac{k_1 k_2}{k_{-1} k_{-2}}$$

See the next problem for a detailed analysis of the rate laws for the complete mechanism.

28. This problem is an example of finding the relationship among the rate constants in a mechanism and the overall equilibrium constant, based on detailed balance. For the mechanism:



determine the rate law for the overall forward process,  $v_+$ , and the rate law for the overall reverse process,  $v_-$ , at equilibrium. Show that the ratio of the resulting rate constants gives the overall equilibrium constant.

*Answer:* The plan is to note that this problem is essentially like a steady-state approximation derivation, but the steady state approximation is exact at equilibrium. The flow of the problem is to formulate the overall rate law for A and then determine the portion that applies for the forward reaction and the portion that applies for the reverse reaction.

The rate laws with respect to A, B, and C are:

$$\frac{d[A]}{dt} = -k_1 [A] + k_{-1}[B] \quad 1$$

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[B] + k_{-2}[C] \quad 2$$

$$\frac{d[C]}{dt} = k_2[B] - k_{-2}[C] \quad 3$$

At equilibrium, the change of the concentration of B with time is zero and the second rate law equals zero:

$$k_1[A] - k_{-1}[B] - k_2[B] + k_{-2}[C] = 0 \quad 4$$

Solving for [B] gives:

$$[B] = \frac{k_1[A] + k_{-2}[C]}{k_{-1} + k_2} \quad 5$$

Substitution into the rate law for A and taking a common denominator gives:

$$\frac{d[A]}{dt} = -k_1 [A] + k_{-1} \left( \frac{k_1[A] + k_{-2}[C]}{k_{-1} + k_2} \right) = - \left( \frac{k_1 k_{-1} + k_1 k_2}{k_{-1} + k_2} \right) [A] + \left( \frac{k_{-1} k_{-1} [A] + k_{-1} k_{-2} [C]}{k_{-1} + k_2} \right) \quad 6$$

Cancelling terms gives:

$$\frac{d[A]}{dt} = - \frac{k_1 k_2}{k_{-1} + k_2} [A] + \frac{k_{-1} k_{-2}}{k_{-1} + k_2} [C] \quad 7$$

The overall rate is given by:

$$v = \frac{1}{V} \frac{d\xi}{dt} = - \frac{d[A]}{dt} \quad 8$$

In terms of the overall process  $A \rightarrow C$ , near equilibrium we would write the overall rate law in terms of the initial reactant and the final product:

$$v = - \frac{d[A]}{dt} = k_f [A] - k_r [C] \quad \text{with } K_{eq} = k_f/k_r \quad \text{(overall)} \quad 9$$

Comparing Eqs. 7 and 9, the first term in Eq. 7 is the rate law for the overall forward process and the second term is the rate law for the overall reverse process at equilibrium:

$$v_+ = \frac{k_1 k_2}{k_{-1} + k_2} [A] \quad v_- = \frac{k_{-1} k_{-2}}{k_{-1} + k_2} [C] \quad 10$$

The effective rate constants for the forward and reverse processes are:

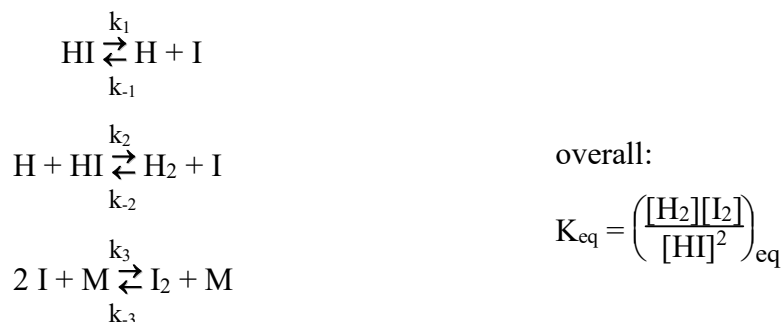
$$k_f = \frac{k_1 k_2}{k_{-1} + k_2} \quad \text{and} \quad k_r = \frac{k_{-1} k_{-2}}{k_{-1} + k_2} \quad 11$$

and the ratio should give the overall equilibrium constant:

$$K_c = \frac{k_f}{k_r} = \frac{k_1 k_2}{k_{-1} k_{-2}} \quad 12$$

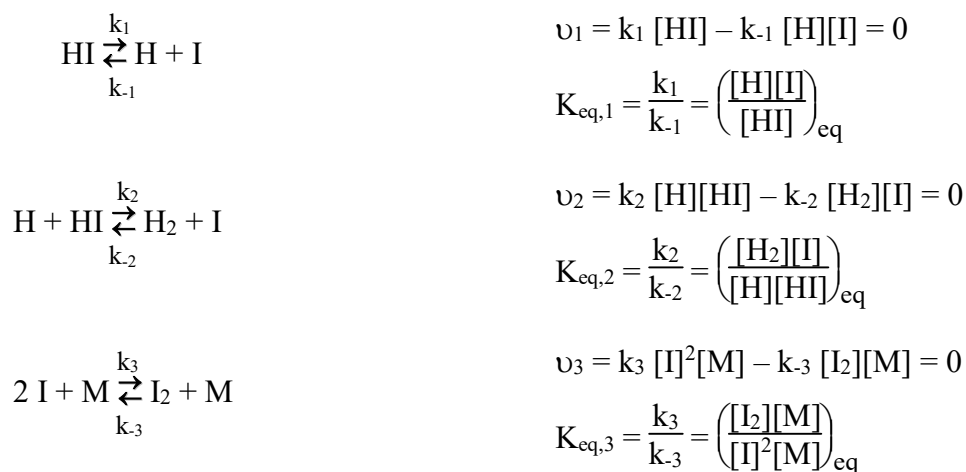
This result agrees with Eq. 4.5.12, which is required by detailed balance.

29. Using the Principle of Detailed Balance, show that the following mechanism generates the expected overall equilibrium ratio when the reaction is at equilibrium:



Derive the relationship between the rate constants and the overall equilibrium constant, starting from the rate laws for each mechanistic step.

*Answer:* Detailed balance requires that each mechanistic step and its exact reverse must be at equilibrium:



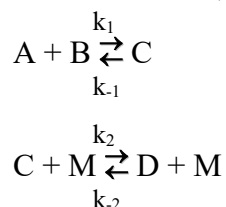
The overall equilibrium constant is then

$$K_{\text{eq}} = K_{\text{eq},1} K_{\text{eq},2} K_{\text{eq},3} = \left( \frac{[\text{H}][\text{I}]}{[\text{HI}]} \right)_{\text{eq}} \left( \frac{[\text{H}_2][\text{I}]}{[\text{H}][\text{HI}]} \right)_{\text{eq}} \left( \frac{[\text{I}_2][\text{M}]}{[\text{I}]^2[\text{M}]} \right)_{\text{eq}} = \left( \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} \right)_{\text{eq}}$$

and the relationship to the rate constants give the ratio of the forward rate constants to the reverse rate constants:

$$K_{eq} = K_{eq,1} K_{eq,2} K_{eq,3} = \frac{k_1 k_2 k_3}{k_{-1} k_{-2} k_{-3}}$$

30. The reaction  $A + B \rightleftharpoons D$  is proposed to have the following mechanism:



where C is a reactive intermediate and M is an inert gas in large concentration. (a). Show that with appropriate approximations that the rate law is:

$$\frac{d[D]}{dt} = \left( \frac{k_1 k_2 [A][B][M] - k_{-1} k_{-2} [D][M]}{k_{-1} + k_2 [M]} \right)$$

(b). In terms of the overall process,  $A + B \rightarrow D$ , near equilibrium, the overall rate law in terms of the initial reactant and the final product is:

$$v = \frac{d[D]}{dt} = k_f [A][B] - k_r [D]$$

Show that the equation in part (a) reduces to this last overall equation and find the relationship between the overall equilibrium constant and the four rate constants for the mechanistic steps from this equation. Discuss any approximations that you make for parts (a) and (b).

*Answer:* (a). The rate law for the formation of D is given as:

$$\frac{d[D]}{dt} = k_2 [C][M] - k_{-2} [D][M] \tag{1}$$

The rate law for the intermediate is:

$$\frac{d[C]}{dt} = k_1 [A][B] - k_{-1} [C] - k_2 [C][M] + k_{-2} [D][M] = 0 \tag{2}$$

We apply the steady-state approximation to find the steady-state concentration of C. Note that this approximation holds before the system reaches equilibrium, if C is a reactive intermediate:

$$[C] = \frac{k_1 [A][B] + k_{-2} [D][M]}{k_{-1} + k_2 [M]} \tag{3}$$

Substitution into Eq. 1 to gives:

$$\frac{d[D]}{dt} = \frac{k_1 k_2 [A][B][M] + k_2 k_{-2} [D][M]^2}{k_{-1} + k_2 [M]} - k_{-2} [D][M] \tag{4}$$

Taking a common denominator:

$$\frac{d[D]}{dt} = \frac{k_1 k_2 [A][B][M] + k_2 k_{-2} [D][M]^2 - k_{-1} k_{-2} [D][M] - k_2 k_{-2} [D][M]^2}{k_{-1} + k_2[M]} \quad 5$$

Canceling common terms:

$$\frac{d[D]}{dt} = \frac{k_1 k_2 [A][B][M] - k_{-1} k_{-2} [D][M]}{k_{-1} + k_2[M]} \quad 6$$

(b). If M is a buffer gas in large concentration, then  $k_2[M] \gg k_{-1}$  is reasonable in the denominator, which gives:

$$\frac{d[D]}{dt} = \frac{k_1 k_2}{k_2} [A][B] - \frac{k_{-1} k_{-2}}{k_2} [D] \quad 7$$

which is in the form:

$$v = \frac{d[D]}{dt} = k_f [A][B] - k_r [D] \quad 8$$

*forward rate*      *reverse rate*

At equilibrium, Eq. 7 is equal to zero giving:

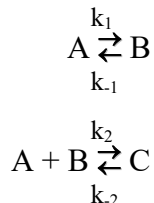
$$\frac{k_1 k_2}{k_2} [A][B] - \frac{k_{-1} k_{-2}}{k_2} [D] = 0 \quad \text{(equilibrium)} \quad 9$$

and solving for the equilibrium concentration ratio gives:

$$K_{eq} = \left( \frac{[D]}{[A][B]} \right)_{eq} = \frac{k_1 k_2}{k_{-1} k_{-2}} \quad 10$$

as expected from detailed balance.

31. The reaction  $2A \rightleftharpoons C$  is proposed to have the following mechanism:



(a). Show that near equilibrium:

$$-\frac{1}{2} \frac{d[A]}{dt} = \frac{d[C]}{dt} = k_1[A] - \left( \frac{k_1 k_{-1} [A] + k_{-1} k_2 [C]}{k_{-1} + k_2[A]} \right)$$

(b). In terms of the overall process,  $2A \rightarrow C$ , at equilibrium we would write the overall rate law in terms of the initial reactant and the final product:

$$v = -\frac{1}{2} \frac{d[A]}{dt} = k_f [A]^2 - k_r [C]$$

Show that the equation in part (a) reduces to this last overall equation and find the relationship between the overall equilibrium constant and the four rate constants for the mechanistic steps.

*Answer:* This problem can be done in several ways. For this answer, we will make the least restrictive assumptions at each step to give the most general interpretation of the final result and to give intermediate results that are as broadly applicable as possible.

(a). The rate law for the formation of A is given as:

$$\frac{d[A]}{dt} = -k_1 [A] + k_{-1} [B] - k_2 [A][B] + k_{-2} [C] \quad 1$$

The rate law for the intermediate is:

$$\frac{d[B]}{dt} = k_1 [A] - k_{-1} [B] - k_2 [A][B] + k_{-2} [C] = 0 \quad 2$$

We will apply the steady-state approximation to find the steady-state concentration of B. Note that this approximation holds before the system reaches equilibrium. The steady-state approximation becomes exact when the system reaches equilibrium. Applying the steady-state approximation gives for [B]:

$$[B] = \frac{k_1 [A] + k_{-2} [C]}{k_{-1} + k_2 [A]} \quad 3$$

At steady state we can simplify Eq. 1 by subtracting Eq. 2 from Eq. 1 to give:

$$\frac{d[A]}{dt} = -2 k_1 [A] + 2 k_{-1} [B] \quad 4$$

which holds away from equilibrium, as long as the steady-state approximation is valid. Substituting in the concentration of the reactive intermediate then gives:

$$\frac{d[A]}{dt} = -2 k_1 [A] + 2 k_{-1} \frac{k_1 [A] + k_{-2} [C]}{k_{-1} + k_2 [A]} \quad 5$$

rearrangement gives:

$$-\frac{1}{2} \frac{d[A]}{dt} = k_1 [A] - \left( \frac{k_1 k_{-1} [A] + k_{-1} k_{-2} [C]}{k_{-1} + k_2 [A]} \right) \quad 6$$

(b). Taking a common denominator gives:

$$-\frac{1}{2} \frac{d[A]}{dt} = \left( \frac{k_1 k_{-1} [A] + k_1 k_2 [A]^2 - k_1 k_{-1} [A] - k_{-1} k_{-2} [C]}{k_{-1} + k_2 [A]} \right) \quad 7$$

or cancelling terms:

$$-\frac{1}{2} \frac{d[A]}{dt} = \left( \frac{k_1 k_2}{k_{-1} + k_2 [A]} \right) [A]^2 - \left( \frac{k_{-1} k_{-2}}{k_{-1} + k_2 [A]} \right) [C] \quad 8$$

If B is a reactive intermediate, the equilibrium between A and B must favor A, such that  $k_1 \ll k_{-1}$ . In other words, the reverse reaction for step one is rapid, with  $k_{-1}$  a large number

compared to  $k_1$ . As the reaction proceeds, the concentration of A drops. When  $k_{-1} \gg k_2[A]$  this last equation reduces to:

$$-\frac{1}{2} \frac{d[A]}{dt} = \left( \frac{k_1 k_2}{k_{-1}} \right) [A]^2 - \left( \frac{k_{-1} k_{-2}}{k_{-1}} \right) [C] \quad 9$$

which is in the form:

$$v = -\frac{1}{2} \frac{d[A]}{dt} = k_f [A]^2 - k_r [C] \quad 10$$

*forward rate*      *reverse rate*

At equilibrium, Eq. 9 is equal to zero giving:

$$\left( \frac{k_1 k_2 [A]^2}{k_{-1}} \right) [A]^2 - \left( \frac{k_{-1} k_{-2}}{k_{-1}} \right) [C] = 0 \quad (\text{equilibrium}) \quad 11$$

and solving for the equilibrium concentration ratio gives:

$$K_{eq} = \left( \frac{[C]}{[A]^2} \right)_{eq} = \frac{k_1 k_2}{k_{-1} k_{-2}} \quad 12$$

as expected from detailed balance.

Notice also, that at equilibrium Eq. 8 would also be equal to zero giving the same equilibrium constant. In other words, the assumption that  $k_{-1} \gg k_2[A]$  is not necessary to find the thermodynamic equilibrium constant.

32. For the reaction:



find the relationship of the experimentally determined, overall activation energy to the activation energies for the individual mechanistic steps. Assume the rate law is:

$$\frac{d[HI]}{dt} = \frac{k_1 k_3}{k_{-1}} [H_2][I_2]$$

*Answer:* The plan is to follow Example 4.4.2. However, we can also consider another method based directly on the Arrhenius Law in the form  $k = A e^{-E_a/RT}$ .

*Method 1 (based on Eq. 4.5.25):* Taking the logarithm of the effective rate constant  $k = k_1 k_3 / k_{-1}$  gives:

$$\ln k = \ln k_1 + \ln k_3 - \ln k_{-1}$$

The terms in the derivatives, at constant volume, are given by the corresponding activation energies for each mechanistic step:

$$\frac{d \ln k}{dT} = \frac{d \ln k_1}{dT} + \frac{d \ln k_3}{dT} - \frac{d \ln k_{-1}}{dT} = \frac{E_{a1}}{RT} + \frac{E_{a3}}{RT} - \frac{E_{a-1}}{RT} = \frac{E_a}{RT}$$

Comparison with the overall activation energy gives:  $E_a = E_{a1} + E_{a3} - E_{a-1}$

*Method 2 (based on  $k = A e^{-E_a/RT}$ ):* The overall reaction rate constant with activation energy  $E_a$  is  $k = A e^{-E_a/RT}$ . This form of the Arrhenius equation can also be applied to each individual elementary step. For the individual elementary steps, for step 1:  $k_1 = A_1 e^{-E_{a1}/RT}$ , for the reverse of step 1:  $k_{-1} = A_{-1} e^{-E_{a-1}/RT}$ , and for the formation of product:  $k_3 = A_3 e^{-E_{a3}/RT}$ . Finding the ratio of the individual rate constants in Arrhenius form gives:

$$k = \frac{k_1 k_3}{k_{-1}} = \frac{A_1 e^{-E_{a1}/RT} A_3 e^{-E_{a3}/RT}}{A_{-1} e^{-E_{a-1}/RT}} = \frac{A_1 A_3}{A_{-1}} e^{-(E_{a1} + E_{a3} - E_{a-1})/RT}$$

The overall activation energy is again  $E_a = E_{a1} + E_{a3} - E_{a-1}$ . The method based on Eq. 4.5.25 is less susceptible to errors for complex rate laws if there are non-integer rate exponents.

33. Consider the  $S_N1$  mechanism as a typical multi-step mechanism. For the case given in Eq. 4.2.17, the rate law has the form:

$$\frac{d[P]}{dt} = k \frac{[RX][Nuc:^-]}{[X^-]} \quad (k_{-1} [X^-] \gg k_2 [Nuc:^-])$$

with the effective rate constant,  $k = k_2 k_1/k_{-1}$ . From Eq. 3.5.1, for the overall reaction with activation energy  $E_a$ :  $k = A e^{-E_a/RT}$ . This form of the Arrhenius equation can also be applied to each individual elementary step. For the individual elementary steps, for step 1:  $k_1 = A_1 e^{-E_{a1}/RT}$ , for the reverse of step 1:  $k_{-1} = A_{-1} e^{-E_{a-1}/RT}$ , and for the formation of product:  $k_2 = A_2 e^{-E_{a2}/RT}$ . Using these Arrhenius expressions, find the relationship between the overall pre-exponential factor and activation energy and the pre-exponential factors and activation energies for the individual elementary steps.

*Answer:* Finding the ratio of the individual rate constants in Arrhenius form gives:

$$k = \frac{k_2 k_1}{k_{-1}} = \frac{A_2 e^{-E_{a2}/RT} A_1 e^{-E_{a1}/RT}}{A_{-1} e^{-E_{a-1}/RT}} = \frac{A_2 A_1}{A_{-1}} e^{-(E_{a2} + E_{a1} - E_{a-1})/RT}$$

We could also use the method in Example 4.5.2, based on Eq. 4.5.25, but we wouldn't have gotten the expression for the overall pre-exponential factor. The method based on Eq. 4.5.25 is easier for complex rate laws.

34. The connection between detailed balance and forward and reverse reaction rates for a multi-step mechanism is illustrated in Eqs. 4.5.3-4.5.10. The rate laws are written for each individual step in the mechanism, rather than the rate of appearance or disappearance of a particular species. Symbolize the net rates of the individual mechanistic steps as  $v_1$ ,  $v_2$ , and  $v_3$ :

$$v_1 = \frac{1}{V} \frac{d\xi_1}{dt} \quad v_2 = \frac{1}{V} \frac{d\xi_2}{dt} \quad \text{and} \quad v_3 = \frac{1}{V} \frac{d\xi_3}{dt}$$



- (a). Write the rate law for the appearance of intermediate  $A_2$ , the rate law for the appearance of intermediate  $X$ , and the rate law for the appearance of product  $D$  in terms of  $v_1$ ,  $v_2$ , and  $v_3$ . The purpose is to show the relationship between the species specific and step specific methods of writing rate laws.
- (b). For a multi-step mechanism at steady state, the rates of the individual steps are equal, Sec. 4.2. Use the results of part (a) for intermediates  $A_2$  and  $X$  to prove this statement for this example mechanism. [Hint: apply the steady-state approximation].

*Answer:* (a). The rates of appearance for  $A_2$ ,  $X$ , and  $D$  written in the conventional manner is:

$$\frac{d[A_2]}{dt} = k_{AM}[A]^2[M] - k_{MA}[A_2][M] - k_{AB}[A_2][B] + k_{XA}[A][X]$$

$$\frac{d[X]}{dt} = k_{AB}[A_2][B] - k_{XA}[A][X] - k_X[X] + k_{DC}[C][D]$$

$$\frac{d[D]}{dt} = k_X[X] - k_{DC}[C][D]$$

Comparing these conventional rate laws to Eqs. 4.5.7-4.5.9 gives:

$$\frac{d[A_2]}{dt} = v_1 - v_2 \quad \frac{d[X]}{dt} = v_2 - v_3 \quad \text{and} \quad \frac{d[D]}{dt} = v_3$$

- (b). At steady-state, the rate of formation of the reactive intermediates is zero:

$$\frac{d[A_2]}{dt} = v_1 - v_2 = 0 \quad \frac{d[X]}{dt} = v_2 - v_3 = 0$$

Solving for the rates of the individual steps gives  $v_1 = v_2 = v_3$ . At steady-state the net rate of each mechanistic step is identical. There is no “slow” or “fast” step.

**35.** Consider the  $S_N1$  mechanism, Eqs. 4.2.6-4.2.7. The first mechanistic step is reversible and the second is uni-directional. Symbolize the net rates of the two mechanistic steps as  $v_1$  and  $v_2$ :

$$v_1 = \frac{1}{V} \frac{d\xi_1}{dt} \quad \text{and} \quad v_2 = \frac{1}{V} \frac{d\xi_2}{dt}$$

- (a). Write the rate law for the appearance of intermediate  $R^+$  and the rate law for the appearance of product  $R\text{-Nuc}$  in terms of  $v_1$  and  $v_2$ . The purpose is to show the relationship between the species specific and step specific methods of writing rate laws.

- (b). For a multi-step mechanism at steady state, the rates of the individual steps are equal. Use the result of part (a) for intermediate  $R^+$  to prove this statement for this example mechanism. [Hint: apply the steady-state approximation].

*Answer:* The plan is to use Eqs. 4.5.3-4.5.9 as a template for writing the step-specific rate laws.

- (a). The rates of appearance for  $R^+$  and product  $R\text{-Nuc}$  written in the conventional manner is:

$$\frac{d[R^+]}{dt} = k_1[RX] - k_{-1}[R^+][X^-] - k_2[R^+][Nuc:^-]$$

$$\frac{d[P]}{dt} = k_2[R^+][\text{Nuc}^-] \quad 2$$

The step-specific rate laws are:

$$v_1 = \frac{1}{V} \frac{d\xi_1}{dt} = k_1[RX] - k_{-1}[R^+][X^-] \quad 3$$

$$v_2 = \frac{1}{V} \frac{d\xi_2}{dt} = k_2[R^+][\text{Nuc}^-] \quad 4$$

Comparing the conventional rate laws, Eqs. 1-2, to the step specific rate laws, Eqs. 3-4, gives:

$$\frac{d[R^+]}{dt} = v_1 - v_2 \quad \text{and} \quad \frac{d[P]}{dt} = v_2$$

(b). At steady-state, the rate of formation of the reactive intermediate is zero:

$$\frac{d[R^+]}{dt} = v_1 - v_2 = 0 \quad \text{or} \quad v_1 = v_2$$

At steady-state the net rate of each mechanistic step is equal. There is no “slow” or “fast” step. See also Eq. 4.2.19 for an alternate proof.

**36.** After a perturbation, the three unidirectional reactions in Eq. 4.5.1 approach a steady state very differently than a reversible process approaches equilibrium; the approach of the unidirectional steps to a steady state shows oscillatory behavior, but a reversible system approaches equilibrium in an exponential process.<sup>4,5</sup> (a) Use the Web based “*Kinetic Mechanism Simulation*” applet or *MatLab*, *Maple*, or *Mathematica* to numerically integrate the rate laws for the mechanism in Eq. 4.5.1. Set  $k_{AB} = 0.1$ ,  $k_{BC} = k_{CA} = 0.05$ , and  $[A]_o = 1$  while  $[B]_o = [C]_o = 0$ . Plot the approach to the steady state and verify the appearance of oscillations. (b) Change the rate law to match Eq. 4.5.2. Set the forward rate constants as in part (a) and the reverse rate constants to give the equilibrium constant for  $A \rightleftharpoons B$  as 2 and for  $B \rightleftharpoons C$  as 2. Compare the approach to equilibrium with part (a).

*Answer:* (a) Using the “*Kinetics Mechanism Simulation*,” and [X] for [C], the model is set up as:

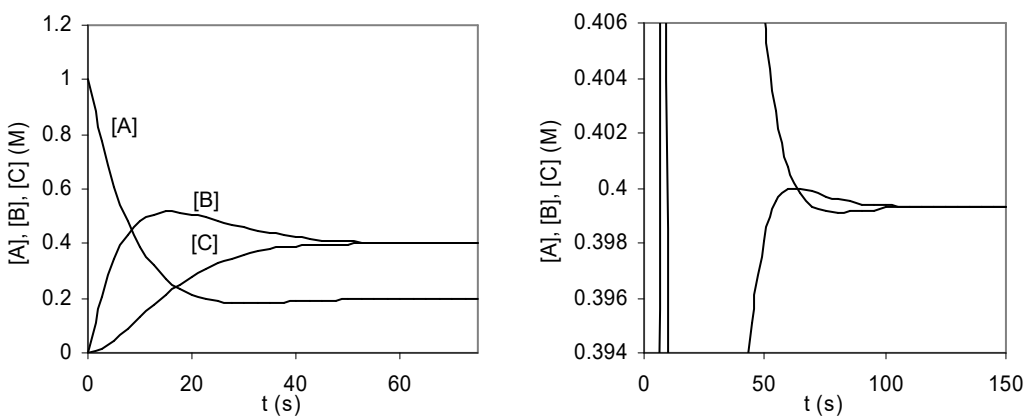
A ⇌ B     $k_f = 0.1$      $k_r = 0$   
 B ⇌ X     $k_f = 0.05$      $k_r = 0$   
 X ⇌ A     $k_f = 0.05$      $k_r = 0$

**Initial Conditions:**  
 $A_0: 1$      $B_0: 0$      $X_0: 0$      $Y_0: 0$      $P_0: 0$      $Q_0: 0$      $M: 1$   
(M and N are constant concentration reservoirs, such as a background gas, the vessel walls, or a constant f

**Plot Variables:** A B X     Better plot quality (requires Java)

**Maximum time:** 150    **Time steps:** 750    Initialize    Run Full    Step    Close

The resulting plot and a plot with the scale expanded in the vertical direction to show the oscillations at longer times better are:



(b) For  $A \rightleftharpoons B$ , given  $K_{AB} = k_f/k_r = 2$ , then  $k_r = 0.05$ . For  $B \rightleftharpoons C$ , given  $K_{BC} = k_f/k_r = 2$ , then  $k_r = 0.025$ . Since this is a cyclic mechanism, from Eq. 4.5.16, with  $k_{CA} = 0.05$ , then  $k_{AC} = 0.2$ . The setup with reversible steps is:

+  +  =  +  +   $k_f=0.1$   $k_r=0.05$   
 +  +  =  +  +   $k_f=0.05$   $k_r=0.025$   
 +  +  =  +  +   $k_f=0.05$   $k_r=0.2$

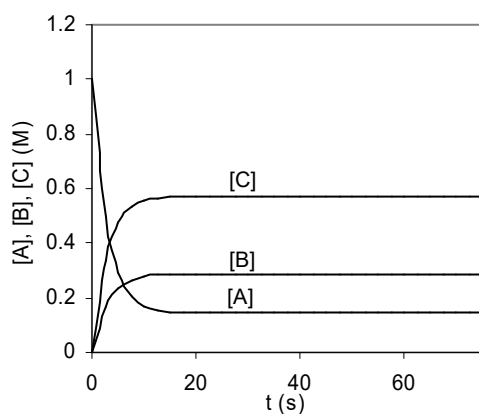
**Initial Conditions:**  
 $A_0:$    $B_0:$    $X_0:$    $Y_0:$    $P_0:$    $Q_0:$    $M:$

(M and N are constant concentration reservoirs, such as a background gas, the vessel walls, or a constant pressure reservoir.)

**Plot Variables:**     Better plot quality (requires Java)

**Maximum time:**  **Time steps:**

The concentrations approach equilibrium smoothly, unlike the unphysical unidirectional case:



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