Chapter 6 Problems

1. Qualitatively predict the effect of wind turbulence on the exchange of CO_2 across the air/sea interface.

Answer: Wind caused turbulence increases the mixing rate at the air/sea interface, thus decreasing the thickness of the stagnant boundary layer. Assuming a linear concentration gradient, using Eq. 6.1.29:

$$J_o = -\frac{D_{CO_2}}{\delta}\left([CO_2]^{bulk} - [CO_2]^{w/a}\right)$$

The thinner the boundary layer, the larger the concentration gradient and the larger the flux.

2. Find the second derivative with respect to x of a Gaussian distribution for a non-zero mean. Use explicit differentiation of the general form of the Gaussian distribution in Eq. 6.1.8.

Answer: Starting with Eq. 6.1.8:

$$g(x) = \frac{1}{\sigma\sqrt{2\pi}}\, e^{-(x-\mu)^2/2\sigma^2} \qquad 1$$

Taking the first derivative with respect to x of Eq. 6.1.8 gives:

$$\frac{dg}{dx} = \frac{1}{\sigma\sqrt{2\pi}}\,\frac{d\left(e^{-(x-\mu)^2/2\sigma^2}\right)}{dx} = \frac{1}{\sigma\sqrt{2\pi}}\left(\frac{-2(x-\mu)}{2\sigma^2}\right) e^{-(x-\mu)^2/2\sigma^2} \qquad 2$$

This last equation can be written more simply by substituting back in the definition of g(x):

$$\frac{dg}{dx} = \left(\frac{-(x-\mu)}{\sigma^2}\right) g \qquad 3$$

and then the derivative of this last equation gives the second derivative. Let f equal the first term: $f = (-(x-\mu)/\sigma^2)$. Using the product rule $d(fg)/dx = f\,dg/dx + g\,df/dx$:

$$\frac{d^2g}{dx^2} = \frac{d\left(\frac{-(x-\mu)}{\sigma^2}\, g\right)}{dx} = \left[\left(\frac{-(x-\mu)}{\sigma^2}\right)\left(\frac{dg}{dx}\right) + g\,\frac{d\left(\frac{-(x-\mu)}{\sigma^2}\right)}{dx}\right] \qquad 4$$

Using Eq. 3 for the first derivative of g gives:

$$\frac{d^2g}{dx^2} = \frac{d\left(\frac{-(x-\mu)}{\sigma^2}\, g\right)}{dx} = \left[\left(\frac{-(x-\mu)}{\sigma^2}\right)\left(\frac{-(x-\mu)}{\sigma^2}\right) g + \left(\frac{-1}{\sigma^2}\right) g\right] = \left[\left(\frac{(x-\mu)^2}{\sigma^4}\right) - \left(\frac{1}{\sigma^2}\right)\right] g$$

3. In deriving Eq. 6.1.24, we used Eq. 6.1.19 from *General Pattern* ℘ **5**. Instead, derive Eq. 6.1.24 by explicit differentiation of Eq. 6.1.7.

Answer: Starting with the Gaussian concentration profile from Eq. 6.1.7:

$$c(x,t) = \frac{n_o}{A\sqrt{4\pi Dt}}\, e^{-x^2/4Dt}$$

Taking the first derivative of Eq. 6.1.7 with respect to distance while keeping t constant gives:

$$\left(\frac{\partial c}{\partial x}\right)_t = \frac{n_o}{A\sqrt{4\pi Dt}} \frac{d\left(e^{-x^2/4Dt}\right)}{dx} = \frac{n_o}{A\sqrt{4\pi Dt}} \left(\frac{-2x}{4Dt}\right) e^{-x^2/4Dt}$$

Using the definition of c(x,t) in this last equation gives:

$$\left(\frac{\partial c}{\partial x}\right)_t = \left(\frac{-2x}{4Dt}\right) c$$

and then the derivative of this last equation gives the second derivative. Let f equal the first term: f = (–2x/4Dt). Using the product rule d(fc)/dx = f dc/dx + c df/dx :

$$\left(\frac{\partial^2 c}{\partial x^2}\right)_t = \frac{d\left(\frac{-2x\ c}{4Dt}\right)}{dx} = \left[\left(\frac{-2x}{4Dt}\right)\left(\frac{dc}{dx}\right) + c\left(\frac{-2}{4Dt}\right)\right]$$

Substitution of the first derivative gives:

$$\left(\frac{\partial^2 c}{\partial x^2}\right)_t = \left[\left(\frac{-2x}{4Dt}\right)\left(\frac{-2x}{4Dt}\right) c + \left(\frac{-2}{4Dt}\right) c\right] = \left[\left(\frac{x^2}{4D^2t^2}\right) - \left(\frac{1}{2Dt}\right)\right] c$$

4. Write an Excel spreadsheet that uses the finite difference approximation to solve Eq. 6.1.6 for the one-dimensional planar diffusion problem. The analytical solution is Eq. 6.1.7. To do this, first assume finite differences for Eq. 6.1.6 to give:

$$\Delta c(x) = D\left(\frac{\partial^2 c}{\partial x^2}\right)_t \Delta t$$

where this equation is applied at each point, x, on equally spaced intervals along the x-axis. We also need an approximation for the second derivative. Assume the concentrations along the x-axis are c_0, c_1, c_2, c_3, …., which are evaluated at points x = 0, dx, 2dx, 3dx,… The first derivative from c_0 to c_1 and the first derivative from c_1 to c_2 are:

$$\left(\frac{dc}{dx}\right)_{x=0.5\ dx} = \frac{c_1 - c_0}{dx} \qquad \text{and} \qquad \left(\frac{dc}{dx}\right)_{x=1.5\ dx} = \frac{c_2 - c_1}{dx}$$

The second derivative is the derivative of the first derivatives:

$$\left(\frac{d^2c}{dx^2}\right)_{x=dx} = \frac{\left(\frac{c_2 - c_1}{dx}\right) - \left(\frac{c_1 - c_0}{dx}\right)}{dx} = \frac{c_2 - 2\,c_1 + c_0}{dx^2}$$

This result is then used to find the new value for the concentration at c_1 in the next time interval using the finite difference formula. Assume the diffusion coefficient is $1.0\text{x}10^{-9}$ m^2s^{-1}. Assume a time interval of $\Delta t = 0.01$ s and integrate to 0.3 s. Assume an x spacing of $dx = 1.0\text{x}10^{-5}$m from 0 to $1\text{x}10^{-4}$m. (In other words, use a range from 0 to 100 μm.) Assume the initial conditions are a concentration of 1.00 mol m^{-3} in the first x interval and zero at larger distances. One problem arises however. The second derivative can't be calculated at the very first or very last spatial point. For this problem, just set the value of the concentration at the largest value of x at zero. For the value of the concentration at x = 0, that is c_0, we can use conservation of mass. In other words find the sum of the concentrations: $c_1+c_2+c_3+c_4\ldots$ and then subtract from the initial concentration, c_0 at t = 0. Here is a start on how you might lay out the first few rows of your spreadsheet. The concentrations at equally spaced x are arranged across the columns and successive time points correspond to successive rows:

A1	B	C	D	E	F	G	H	I	J	K	L	M	N
2			dt=	0.01	s								
3			dx=	1.E-05	m								
4			D=	1.E-09	$m^2\ s^{-1}$								
5			c(0,0)=	1	mol m^{-3}								
6			x (m):										
7		t (s):	0	1.E-05	2.E-05	3.E-05	4.E-05	5.E-05	6.E-05	7.E-05	8.E-05	9.E-05	1.E-04
8		0	1.00	0	0	0	0	0	0	0	0	0	0
9		0.01											
10		0.02											

:

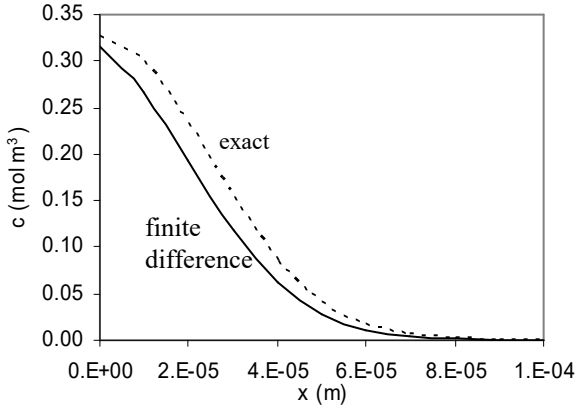
:

Answer: The formula in cell E9 is: "=E8+$E$4*(F8-2*E8+D8)/$E$3^2*$E$2". This formula can then be automatically filled across and down the spreadsheet to provide the formulas for all the other cells, except the first and last concentration points. The formula in the cell D9 is: "=$E$5-SUM(E9:N9)". This formula can then be filled down for all the other c_0 values. The last concentration at $x = 1.0\text{x}10^{-4}$ m is set to zero for each time.

A1	B	C	D	E	F	G	H	I	J	K	L	M	N
2			dt=	0.01	s								
3			dx=	1.E-05	m								
4			D=	1.E-09	$m^2\ s^{-1}$								
5			c(0,0)=	1	mol m^{-3}								
6			x (m):										
7		t (s):	0	1E-05	2E-05	3E-05	4E-05	5E-05	6E-05	7E-05	8E-05	9E-05	1E-04
8		0	1.00	0	0	0	0	0	0	0	0	0	0
9		0.01	0.90	0.100	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10		0.02	0.82	0.170	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
11		0.03	0.76	0.219	0.025	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
12		0.04	0.70	0.253	0.042	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000
13		0.05	0.66	0.277	0.059	0.007	0.000	0.000	0.000	0.000	0.000	0.000	0.000
14		0.06	0.62	0.293	0.076	0.011	0.001	0.000	0.000	0.000	0.000	0.000	0.000
15		0.07	0.59	0.304	0.091	0.017	0.002	0.000	0.000	0.000	0.000	0.000	0.000
16		0.08	0.56	0.311	0.105	0.023	0.003	0.000	0.000	0.000	0.000	0.000	0.000
17		0.09	0.53	0.315	0.117	0.029	0.005	0.001	0.000	0.000	0.000	0.000	0.000
18		0.1	0.51	0.317	0.128	0.035	0.007	0.001	0.000	0.000	0.000	0.000	0.000
19		0.11	0.49	0.318	0.138	0.042	0.009	0.001	0.000	0.000	0.000	0.000	0.000

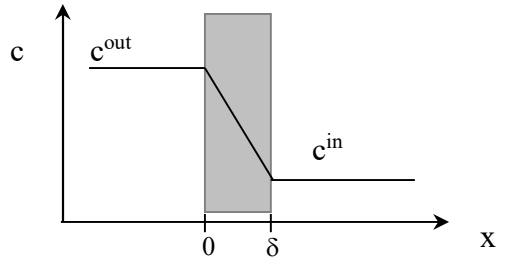
20		0.12	0.47	0.317	0.146	0.048	0.012	0.002	0.000	0.000	0.000	0.000	0.000
21		0.13	0.46	0.316	0.153	0.054	0.014	0.003	0.000	0.000	0.000	0.000	0.000
22		0.14	0.44	0.314	0.160	0.060	0.017	0.004	0.001	0.000	0.000	0.000	0.000
23		0.15	0.43	0.311	0.165	0.066	0.020	0.005	0.001	0.000	0.000	0.000	0.000
24		0.16	0.42	0.309	0.170	0.071	0.023	0.006	0.001	0.000	0.000	0.000	0.000
25		0.17	0.41	0.306	0.174	0.076	0.026	0.007	0.002	0.000	0.000	0.000	0.000
26		0.18	0.40	0.303	0.177	0.081	0.029	0.009	0.002	0.000	0.000	0.000	0.000
27		0.19	0.39	0.300	0.180	0.086	0.032	0.010	0.003	0.001	0.000	0.000	0.000
28		0.2	0.38	0.297	0.183	0.090	0.036	0.011	0.003	0.001	0.000	0.000	0.000
29		0.21	0.37	0.294	0.185	0.094	0.039	0.013	0.004	0.001	0.000	0.000	0.000
30		0.22	0.36	0.291	0.187	0.097	0.042	0.015	0.004	0.001	0.000	0.000	0.000
31		0.23	0.36	0.288	0.188	0.101	0.044	0.016	0.005	0.001	0.000	0.000	0.000
32		0.24	0.35	0.284	0.189	0.104	0.047	0.018	0.006	0.002	0.000	0.000	0.000
33		0.25	0.34	0.281	0.190	0.107	0.050	0.020	0.007	0.002	0.000	0.000	0.000
34		0.26	0.34	0.278	0.191	0.109	0.053	0.021	0.007	0.002	0.001	0.000	0.000
35		0.27	0.33	0.276	0.192	0.112	0.055	0.023	0.008	0.003	0.001	0.000	0.000
36		0.28	0.33	0.273	0.192	0.114	0.058	0.025	0.009	0.003	0.001	0.000	0.000
37		0.29	0.32	0.270	0.192	0.116	0.060	0.027	0.010	0.003	0.001	0.000	0.000
38		0.3	0.32	0.267	0.192	0.118	0.062	0.028	0.011	0.004	0.001	0.000	0.000

The plot of the last row at t = 0.3 s is shown below with the analytical solution from Eq. 6.1.7.



The agreement between the finite difference approach and the analytical solution is much better than you might expect from the coarse grid of x points and the large Δt that we used. Better agreement would be obtained for smaller Δt.

5. In this problem we will use Fick's Second Law to model diffusion through a membrane. Consider a membrane of thickness δ separating two well mixed solutions of concentration c^{out} and c^{in}. The origin of the x-axis is chosen to be at the interface between the membrane and the solution at concentration c^{out} as shown below:



(a.) Show that the concentration profile:

$$c(x) = \left(\frac{c^{in} - c^{out}}{\delta}\right) x + c^{out}$$

has the correct behavior at the surfaces of the membrane.
(b). Assume Fick's Second Law holds for diffusion within the membrane. Show that this linear concentration profile is a valid solution to Fick's Second Law at steady-state.
(c). Find the relationship for the flux across the membrane.

Answer: (a) At $x = 0$, $c(0) = c^{out}$ and at $x = \delta$:

$$c(\delta) = \left(\frac{c^{in} - c^{out}}{\delta}\right) \delta + c^{out} = c^{in} \qquad 1$$

This linear concentration profile has the correct concentrations at the edges of the membrane. In other words, it obeys the proper boundary conditions.
(b). At steady state, Eq. 6.1.6 is equal to zero and we no longer need to worry about time dependence:

$$D\frac{d^2c}{dx^2} = 0 \qquad 2$$

We need to show that the second derivative of the proposed solution is equal to zero. Starting with the first derivative gives the gradient:

$$\frac{dc}{dx} = \frac{d\,[(c^{in} - c^{out})\, x/\delta + c^{out}]}{dx} = \left(\frac{c^{in} - c^{out}}{\delta}\right) \qquad 3$$

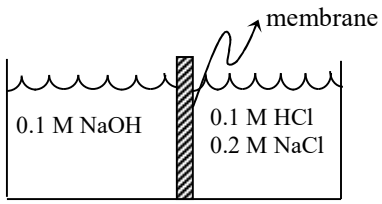
The second derivative is equal to zero, because the first derivative is a constant, as required by Eq. 2. Therefore, the proposed solution is a valid solution for $0 < x < \delta$.
(c). Fick's First Law of diffusion, Eq. 2.3.4, relates the molar flux of a substance to the concentration gradient, $J_m = -D\, dc/dx$. Eq. 3 is the gradient so that:

$$J_m = -D\left(\frac{c^{in} - c^{out}}{\delta}\right) \qquad 4$$

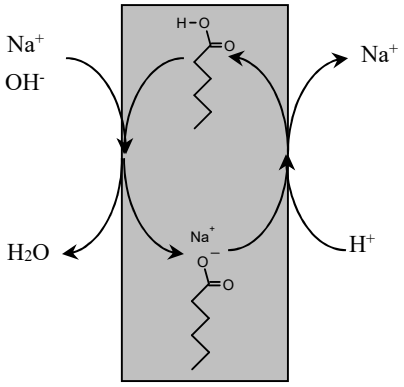
This final result is the same as for diffusion across an interface, Eq. 6.1.29, and also the general form from Eqs. 2.3.3 and 2.3.4. Therefore, all of the theory that we have developed for gas exchange across an interface is applicable to membrane diffusion.

6. A very simple model for active transport of Na^+ ions across a membrane is shown below, where the driving force for the transfer results from a H^+ gradient.[9] The key is the membrane soluble fatty acid that shuttles Na^+ and H^+ ions across the membrane in opposite directions. The

fatty acid is only soluble in the membrane. The reactions at the membrane surfaces are shown at right.



low $[Na^+]$ $\rightarrow$ high $[Na^+]$
low $[H^+]$ $\leftarrow$ high $[H^+]$



The two forms of the fatty acid are HR and NaR. The reactions at the surfaces of the membrane are:

$$\text{Left:} \quad HR + Na^+(\text{left}) + OH^-(\text{left}) \xrightarrow{k_L} NaR + H_2O$$

$$\text{Right:} \quad NaR + H^+(\text{right}) \xrightarrow{k_R} HR + Na^+(\text{right})$$

$$\text{Net:} \quad Na^+(\text{left}) + OH^-(\text{left}) + H^+(\text{right}) \rightarrow Na^+(\text{right}) + H_2O$$

The reactions don't occur within the membrane, so Eq. 6.1.26 applies just at each interface as a surface reaction. For the purposes of this problem, you can assume that the reactions are unidirectional. Assume that the solutions on the left and right are well mixed. Use Fick's Second Law to write the differential equations for the transport within the membrane. Indicate how you would find the steady-state for the fluxes. You don't need to solve the differential equations, but linear concentration gradients would be applicable at steady state if you did.

Answer: The rate of the reactions on the left-hand side are:

$$\upsilon_L = -\frac{d[HR]}{dt} = \frac{d[NaR]}{dt} = k_L\,[HR][Na^+(\text{left})][OH^-(\text{left})] \qquad (x = 0)$$

and for the right-hand side:

$$\upsilon_R = = -\frac{d[NaR]}{dt} = \frac{d[HR]}{dt} = k_R\,[NaR][H^+(\text{right})] \qquad (x = \delta)$$

at the left-hand interface using Eq. 6.1.26:

$$\left(\frac{\partial[HR]}{\partial t}\right)_x = D\left(\frac{\partial^2[HR]}{\partial x^2}\right)_t - k_L\,[HR][Na^+(\text{left})][OH^-] \qquad (x = 0)$$

$$\left(\frac{\partial[NaR]}{\partial t}\right)_x = D\left(\frac{\partial^2[NaR]}{\partial x^2}\right)_t + k_L\,[HR][Na^+(\text{left})][OH^-] \qquad (x = 0)$$

and at the right-hand interface:

$$\left(\frac{\partial[HR]}{\partial t}\right)_x = D\left(\frac{\partial^2[HR]}{\partial x^2}\right)_t + k_R\,[NaR][H^+(right)] \qquad (x = \delta)$$

$$\left(\frac{\partial[NaR]}{\partial t}\right)_x = D\left(\frac{\partial^2[NaR]}{\partial x^2}\right)_t - k_R\,[NaR][H^+(right)] \qquad (x = \delta)$$

and within the membrane with no chemical reactions:

$$\left(\frac{\partial[HR]}{\partial t}\right)_x = D\left(\frac{\partial^2[HR]}{\partial x^2}\right)_t \quad \text{and} \quad \left(\frac{\partial[NaR]}{\partial t}\right)_x = D\left(\frac{\partial^2[NaR]}{\partial x^2}\right)_t \qquad (0 < x < \delta)$$

For steady-state fluxes, the time derivatives in the six above equations would be set to zero.

Note that for a more realistic model, the chemical reactions at each interface should be reversible, which would add additional terms to the rate laws. At steady state for the fluxes, the reaction rate at both interfaces would be equal, $\upsilon_L = \upsilon_R$, which would help simplify the problem. Also note that H^+ gradients across membranes are used to drive many processes, including the primary events in photosynthesis.

7. Find the eigenvalue-eigenvector solution to the set of linear equations:

$$\begin{aligned} x + y &= 0 \\ x + y + z &= 0 \\ y + z &= 0 \end{aligned} \qquad \text{which give the coefficient matrix } \underset{\approx}{M} = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 1 \\ 0 & 1 & 1 \end{pmatrix}$$

Calculate the eigenvalues by hand and the eigenvectors using *MatLab*, *MathCad*, *Maple*, or *Mathematica*. (For symmetric matrices, you can also use the "Matrix Diagonalization" applet on the textbook Web site and on the companion CD.) The *MatLab* command to use is [X,L] = eig(M), where X is the matrix of eigenvectors and L is the diagonal matrix of eigenvalues of the input matrix M.

Answer: Using the given coefficient matrix, the characteristic equation is:

$$(\underset{\approx}{M} - \lambda_i \underset{\approx}{I})\underset{\sim}{X}_i = \begin{pmatrix} 1-\lambda_i & 1 & 0 \\ 1 & 1-\lambda_i & 1 \\ 0 & 1 & 1-\lambda_i \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

This characteristic equation has the characteristic determinate $(\lambda - 1)(\lambda^2 - 2\lambda - 1) = 0$. The factor $(\lambda - 1) = 0$ gives the eigenvalue $\lambda = 1$. Solving the quadratic factor $(\lambda^2 - 2\lambda - 1) = 0$ gives the additional eigenvalues: $\lambda = -0.4142$ and 2.4142.

Here is the *MatLab* input (after the >>) and output:

```
>> M=[1,1,0;1,1,1;0,1,1]

  M =
       1     1     0
       1     1     1
       0     1     1

>> [X,L] =eig(M)
```

```
X =
    0.5000   -0.7071    0.5000
   -0.7071    0.0000    0.7071
    0.5000    0.7071    0.5000

L =
   -0.4142         0         0
         0    1.0000         0
         0         0    2.4142
```

Note that the L matrix lists the three eigenvalues along the diagonal. The X matrix lists the eigenvector as columns. The three sets of eigenvalues and eigenvectors are:

$\lambda_1 = -0.4142$ $\lambda_2 = 1$ $\lambda_3 = 2.4142$

$$\underset{\sim}{X}_1 = \begin{pmatrix} 0.5000 \\ -0.7071 \\ 0.5000 \end{pmatrix} \quad \underset{\sim}{X}_2 = \begin{pmatrix} -0.7071 \\ 0 \\ 0.7071 \end{pmatrix} \quad \underset{\sim}{X}_3 = \begin{pmatrix} 0.5000 \\ 0.7071 \\ 0.5000 \end{pmatrix}$$

To help you get used to eigenvectors, we can verify that $\underset{\sim}{X}_1$ is a valid solution. We need to prove that $\underset{\approx}{M}\underset{\sim}{X}_i = \lambda_i \underset{\sim}{X}_i$, for eigenvector 1:

$$\underset{\approx}{M}\underset{\sim}{X}_1 = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 1 \\ 0 & 1 & 1 \end{pmatrix} \begin{pmatrix} 0.5000 \\ -0.7071 \\ 0.5000 \end{pmatrix} = \begin{pmatrix} 1(0.5)+1(-0.7071)+0(0.5) \\ 1(0.5)+1(-0.7071)+1(0.5) \\ 0(0.5)+1(-0.7071)+1(0.5) \end{pmatrix} = \begin{pmatrix} -0.2071 \\ 0.2929 \\ -0.2071 \end{pmatrix} = -0.4142\ \underset{\sim}{X}_1$$

Notice that any constant multiple of the listed eigenvectors is also a solution, including the case where all the signs are reversed. Matrix techniques allow the solution of problems that would otherwise be exceedingly time consuming to solve.

8. A bi-exponential process is given by the form:

$$[A] = c_1 e^{-k_1 t} + c_2 e^{-k_2 t}$$

The logarithmic plot of a bi-exponential process produces two straight line segments and a transition region between. Bi-exponential decay curves are fit in two segments. First the long time behavior of the logarithmic plot is fit to a straight line to determine the slope, k_2, and intercept $\ln(c_2)$. The non-linear transition region is avoided when points are selected for this plot. Then, the long time behavior is "stripped" from the time course:

$$\ln[A]_{short} = \ln([A] - c_2 e^{-k_2 t})$$

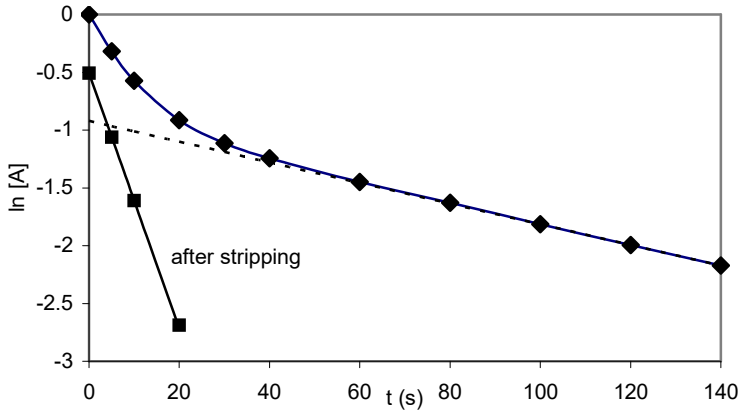
and a second logarithmic plot of the stripped data produces the short time k_1 and $\ln(c_1)$. These estimated constants are then used as guesses for non-linear curve fitting. Fit the following data to a bi-exponential function. For the non-linear fit, use the four-parameter version of the "Nonlinear Least Squares Curve Fit" applet on the textbook Web site and on the companion CD.

time	0	5	10	20	30	40	60	80	100	120	140
[A]	1	0.727	0.564	0.401	0.328	0.288	0.235	0.196	0.163	0.136	0.114

Answer: The spreadsheet to implement the stripping procedure is:

time	[A]	original ln [A]	original ln [A]	stripped ln([A]- $c_2\exp(k_2t)$)
0	1	0		-0.50777
5	0.727	-0.3188		-1.06062
10	0.564	-0.5727		-1.61001
20	0.401	-0.9138		-2.68794
30	0.328	-1.1147		
40	0.288	-1.2448		
60	0.235	-1.4482		
80	0.196	-1.6296		
100	0.163		-1.8140	
120	0.136		-1.995	
140	0.114		-2.1716	

The last few points are moved into a separate column so the curve fit can be done from the chart, directly. The stripped data is in the last column. The plot showing the stripped data is:



The linest() output for the long curve fit and the stripped, short-time curve fit are given below:

Long time fit				Short time fit after stripping			
slope	-0.00894	-0.9209	intercept	slope	-0.11022	-0.50834	intercept
±	6.7E-05	0.008109	±	±	0.000199	0.001288	±
r2	0.999944	0.001894	st.dev. y	r2	0.999997	0.001411	st.dev. y
F	17822.69	1	df	F	305307.4	1	df
SS_{reg}	0.063922	3.59E-06	SS_{resid}	SS_{reg}	0.607473	1.99E-06	SS_{resid}

The corresponding values for the constants are

$c_2 = e^{-0.9209} = 0.3982$ $\qquad$ $k_2 = 0.00894\ s^{-1}$

$c_1 = e^{-0.5083} = 0.6015$ $\qquad$ $k_1 = 0.1102\ s^{-1}$

www Using these fit values as guesses in the "Nonlinear Least Squares Curve Fit" applet with the "a exp(–bx) + c exp(–dx)" option and the above guesses gives:

```
===========   Results   ============
 a= 0.596731 +- 0.000631
 b= 0.111514 +- 0.00022
 c= 0.403231 +- 0.0006
 d= 0.0090422 +- 0.0000204
-----------------------------------
 sum of squared residuals= 7.226e-7
 stand. dev. y values= 0.0003213
 correlation between a & b= -0.5727
```

```
correlation between b & c= 0.8166
correlation between a & c= -0.8726
correlation between c & d= 0.907
correlation between b & d= 0.6811
correlation between a & d= -0.8034
```

Notice that the correlation coefficient between c and d is high, but acceptible. If the long-time behavior were extended, the linear version of the fit could give good uncorrelated results for these parameters. Fitting bi-exponential curves is a difficult issue, and the corresponding fit coefficients are difficult to estimate accurately.

9. Draw the Chapman ozone mechanism, Section 5.2, as a box model.

Answer: The Chapman mechanism from Section 5.2 is comprised of four steps:

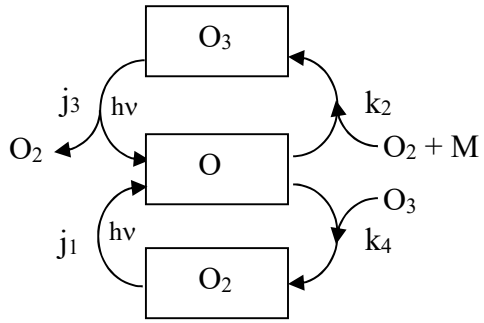
$$O_2 + h\nu \xrightarrow{j_1} 2\,{\bullet}O{\bullet}$$

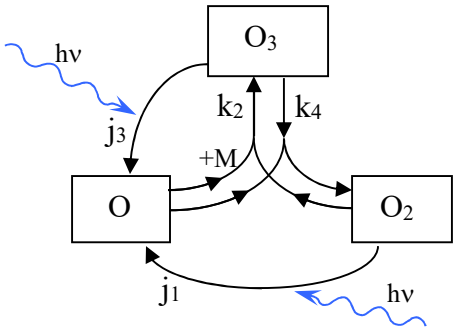
$${\bullet}O{\bullet} + O_2 + M \xrightarrow{k_2} O_3 + M$$

$$O_3 + h\nu \xrightarrow{j_3} {\bullet}O{\bullet} + O_2$$

$${\bullet}O{\bullet} + O_3 \xrightarrow{k_4} 2\,O_2$$

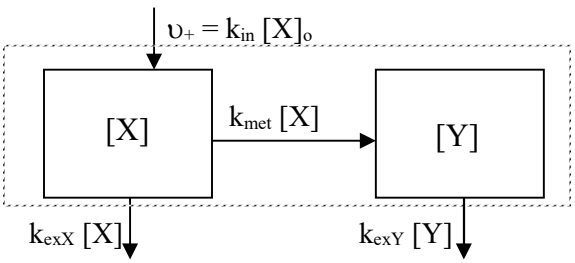
Common depictions of the Chapman model are:





Since steps 2 and 4 aren't first order, the additional reactants must be shown with additional arrows, unlike purely first-order processes. There are many other possibilities, but all would have three boxes and at least four arrows that relate to the four elementary steps.

10. Would the residence time in the body for X be altered if an excretion pathway for Y was added to the model in Section 6.2, Figure 6.2.2? The added pathway is shown below.



Answer: The residence time for X would not be altered, because the new differential equation for X still does not involve the concentration for Y; Eq. 6.2.8 still holds:

$$\frac{d[X]}{dt} = k_{in}\,[X]_o - k_{ex}\,[X] - k_{met}\,[X]$$

Just as for any chemical reaction, the concentration of X does not depend on any unconnected "downstream" processes, if the mechanistic steps are uni-directional. However, if the metabolic process were reversible, then the concentration of X would depend on Y and the residence time would change (the effective rate of the metabolic removal would decrease).

11. Use *Maple* or *Mathematica* to solve for $X_1$and X_2 for the reversible two-box problem starting from the rate matrix, Eq. 6.3.3. Find the concentrations symbolically first. Then substitute in the specific constants: $k_1 = 0.3\ s^{-1}$, $k_{-1} = 0.15\ s^{-1}$, and $k_{ex} = 0.1\ s^{-1}$, with initial conditions $[X_1]_o = 1.0$ M and $[X_2]_o = 0$. Solve for the concentrations at t = 1 s. Note that in general Eqs. 6.3.8, 6.3.9, and 6.3.28 can be combined into:

$$\underset{\sim}{[X]} = \underset{\sim}{C}\,(\exp\,\underset{\sim}{\Lambda t})\,\underset{\sim}{C}^{-1}\underset{\sim}{[X]}_o$$

where $\exp\,\underset{\sim}{\Lambda t}$ is the matrix with the exponential terms along the diagonal:

$$\exp\,\underset{\sim}{\Lambda t} = \begin{bmatrix} e^{\lambda_1 t} & 0 & 0 & \ldots \\ 0 & e^{\lambda_2 t} & 0 & \ldots \\ 0 & 0 & e^{\lambda_3 t} & \ldots \\ \ldots & \ldots & \ldots & \end{bmatrix}$$

Let K be the rate matrix, L be the vector of eigenvalues, C be the matrix of eigenvectors, and E be the diagonal matrix, $\exp\,\underset{\sim}{\Lambda t}$. The set of initial conditions is given by the vector X_o. After defining the rate matrix, K, and initial values vector, X_o, the Maple commands to do these calculations symbolically are:

```
(L,C) := Eigenvectors(K) ;
E := DiagonalMatrix(Map(exp,L*t)) ;
X := C.E.MatrixInverse(C).Xo ;
```

Answer: The *Maple* input is:

```
with(LinearAlgebra) ;
K := Matrix([[ –kex–k1 , k-1 ], [ k1 ,–k-1 ]]) ;
Xo := Vector([1,0]) ;
(L,C) := Eigenvectors(K) ;
E := DiagonalMatrix(Map(exp,L*t)) ;
X := C.E.MatrixInverse(C).Xo ;
```

$k_{ex} := 0.1$;
$k_1 := 0.3$;
$k_{-1} := 0.15$;
$t := 1.0$;
eval(X) ;

which gives:

$$\begin{bmatrix} 0.68597 \\ 0.21308 \end{bmatrix}$$

The advantage of determining the result symbolically is that the concentrations can easily be calculated at any time. A finite difference numerical solution would need to start at t = 0 and integrate up to the desired time. The symbolic result is also exact.

12. Use *MatLab* to solve the two-box model in Figure 6.3.1 and Eq. 6.3.3. Plot $[X_1]$ and $[X_2]$ for t = 0 – 30 s. See Problem 11 for a hint on how to compactly write the solution. The corresponding *MatLab* commands are in the form:

```
[C,L] = eig(K) ;
```

to determine the eigenvalues, L, and eigenvectors, C. Then at time t, the vector of concentrations is given by:

```
E = diag(exp(diag(L)*t)) ;
X = C*E*inv(C)*X0 ;
```

[Note: You can create a matrix with concentrations as the rows and the time points indexed along the columns by using:

```
X(:,t+1) = C*E*inv(C)*X0 ;
```

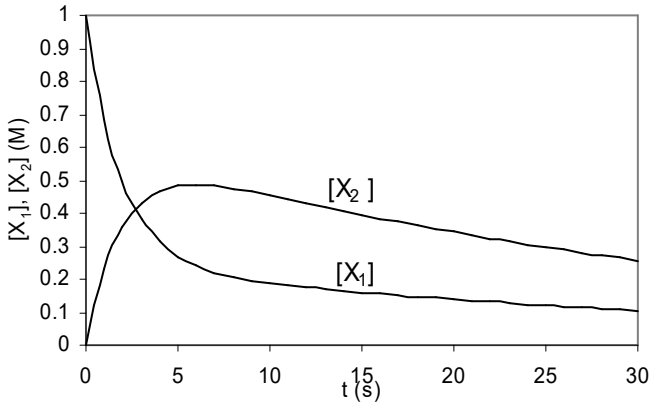
which makes plotting easier. The t values would be successive integers, so they can be used as array indices. The t+1 is necessary because we want to evaluate the concentrations at t = 0, but *MatLab* indexes vectors and matrices starting at 1.]

Answer: The MatLab –m file is:

```
kex = 0.1 ;
kf1 = 0.3 ;
kr1 = 0.15 ;
X0 = [1;0] ;
tmax = 30 ;

K(1,1) = -kex-kf1 ;
K(1,2) = kr1 ;
K(2,1) = kf1 ;
K(2,2) = -kr1 ;

[C,L] = eig(K) ;
```

```
for t = 0:1:tmax
    T(t+1) = t ;
    E = diag(exp(diag(L)*t)) ;
    X(:,t+1) = C*E*inv(C)*X0 ;
end

% Plot data
figure(1)
plot(T,X)
xlabel('Time (s)')
ylabel('[X1],[X2] (M)')
```

The plot is given below:



13. Use *Maple* or *Mathematica* to symbolically verify the solution to the reversible two-box problem, Eqs. 6.3.24-6.3.26, and also find the time course for X_2.

Answer: Refer to Example 6.3.3. Let K be the rate matrix, L be the vector of eigenvalues, and C be the matrix of eigenvectors with each eigenvector corresponding to a column. The set of initial conditions is given by the vector X_o and A is the vector of the α values. The *Maple* input is:

with(LinearAlgebra) ;
K := Matrix([[–k_{ex}–k₁,k₋₁], [k₁,–k₋₁]]) ;
X_o := Vector([1,0]) ;
(L,C) := Eigenvectors(K) ;
A := MatrixInverse(C).X_o ;
A[1] ·C[1..2,1] ;
A[2] ·C[1..2,2] ;

The eigenvectors are listed as:

$$\begin{bmatrix} -\tfrac{1}{2}\,k_{-1}-\tfrac{1}{2}\,k_{ex}-\tfrac{1}{2}\,k_1+\tfrac{1}{2}\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2} \\ -\tfrac{1}{2}\,k_{-1}-\tfrac{1}{2}\,k_{ex}-\tfrac{1}{2}\,k_1-\tfrac{1}{2}\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2} \end{bmatrix} = \begin{bmatrix} \lambda_1 \\ \lambda_2 \end{bmatrix} \qquad 1$$

The results for *A[1] ·C[1..2,1]* corresponding to the first eigenvalue, λ_1 :

$$\left(\frac{(-k_{-1}+k_{ex}+k_1+\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2})\,(k_{-1}-k_{ex}-k_1+\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2})X_o}{k_1\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2}}\right).$$

$$\begin{bmatrix} \frac{-1}{4}\,\frac{k_1}{-\frac{1}{2}k_{-1}+\frac{1}{2}k_{ex}+\frac{1}{2}k_1+\frac{1}{2}\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2}} \\ \frac{-1}{4} \end{bmatrix} \qquad 2$$

This result can be simplified by noticing that:

$$\lambda_1-\lambda_2=\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2} \qquad 3$$

$$k_{-1}+\lambda_1=\tfrac{1}{2}k_{-1}-\tfrac{1}{2}k_{ex}-\tfrac{1}{2}k_1+\tfrac{1}{2}\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2} \qquad 4$$

$$k_{-1}+\lambda_2=\tfrac{1}{2}k_{-1}-\tfrac{1}{2}k_{ex}-\tfrac{1}{2}k_1-\tfrac{1}{2}\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2} \qquad 5$$

Substitution of Eqs. 3-5 into Eq. 2 gives:

$$\begin{bmatrix} \frac{-(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)\,k_{-1}}{-(k_{-1}+\lambda_2)\,k_{-1}\,(\lambda_1-\lambda_2)}X_o \\ \frac{-(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o \end{bmatrix}=\begin{bmatrix} \frac{(k_{-1}+\lambda_1)}{(\lambda_1-\lambda_2)}X_o \\ \frac{-(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o \end{bmatrix}$$

Similarly for *A[2] ·C[1..2,2]* corresponding to the second eigenvalue, λ_2 :

$$\begin{bmatrix} \frac{(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)\,k_{-1}}{-(k_{-1}+\lambda_1)\,k_{-1}\,(\lambda_1-\lambda_2)}X_o \\ \frac{(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o \end{bmatrix}=\begin{bmatrix} -\frac{(k_{-1}+\lambda_2)}{(\lambda_1-\lambda_2)}X_o \\ \frac{(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o \end{bmatrix}$$

The final time profiles are:

coefficients for1st eigenvalue

A[1] ·C[1..2,1] =

$$\begin{bmatrix} \frac{(k_{-1}+\lambda_1)}{(\lambda_1-\lambda_2)}X_o \\ \frac{-(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o \end{bmatrix}$$

coefficients for2nd eigenvalue

A[2] ·C[1..2,2] =

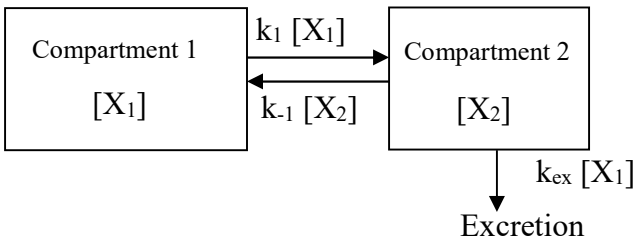
$$\begin{bmatrix} -\frac{(k_{-1}+\lambda_2)}{(\lambda_1-\lambda_2)}X_o \\ \frac{(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o \end{bmatrix}$$

$$\downarrow \qquad\qquad \downarrow$$

$$[X_1]=\frac{(k_{-1}+\lambda_1)}{(\lambda_1-\lambda_2)}X_o\;e^{-\lambda_1 t}\;-\;\frac{(k_{-1}+\lambda_2)}{(\lambda_1-\lambda_2)}X_o\;e^{-\lambda_2 t}$$

$$[X_2]=\frac{-(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o\,e^{-\lambda_1 t}\;+\frac{(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o\,e^{-\lambda_2 t}$$

14. The box model below corresponds to a reversible first-step mechanism, as in Section 4.1, with all first-order processes. Determine the eigenvalues and time constants. Compare the results with the model in Figure 6.3.1 and Eq. 6.3.3.



Answer: The rate laws for this model are:

$$\upsilon_1 = \frac{d[X_1]}{dt} = -k_1 [X_1] + k_{-1} [X_2] \qquad 1$$

$$\upsilon_2 = \frac{d[X_2]}{dt} = k_1 [X_1] - k_{-1} [X_2] - k_{ex} [X_1] \qquad 2$$

The rate matrix is:

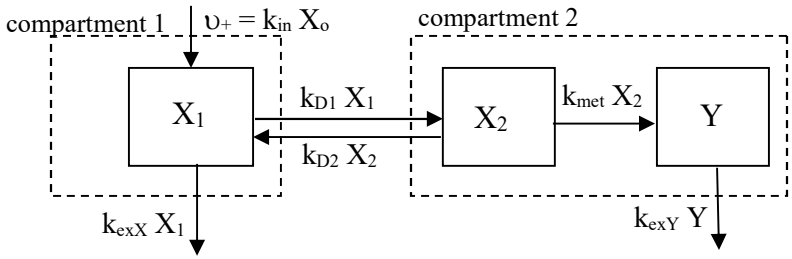
$$\underset{\approx}{K} = \begin{pmatrix} -k_1 & k_{-1} \\ k_1 & -(k_{-1} + k_{ex}) \end{pmatrix} \qquad 3$$

Using Eq. 6.3.23 gives the eigenvalues as:

$$\lambda_i = \frac{-(k_1 + k_{-1} + k_{ex}) \pm \sqrt{(-k_1 + k_{-1} + k_{ex})^2 + 4\, k_1\, k_{-1}}}{2} \qquad 4$$

The result is similar to, but not identical to, Eq. 6.3.24. For the same constant values as Example 6.3.1, the eigenvalues in this case are: λ_i = -0.4886, -0.0614.

15. The model in Section 6.2, Figure 6.2.2, considers the metabolic elimination of a drug in parallel with excretion. Since the liver is often the site for metabolic processes, this model would be more realistic if the drug is first transported by the blood plasma (bulk flow) to the liver where the drug is metabolized and excreted. (Compounds can be excreted from the liver in the bile.) The added pathways are shown below, including a constant flow input.



(a). Set up the differential equations for this model and write the rate matrix. (b). Find the relationship between k_{D1} and k_{D2}. The typical plasma volume of a 70 kg person is 3 L, and the volume of extracellular fluids, excluding plasma, is 12 L. The total body water is about 42 L, so most of the water volume is in the cellular cytoplasm, which is about 80% water. Assume compartment 1 is the blood plasma and compartment 2 is the liver. Assume the effective volume for this process in the liver is 0.5 L.

Answer: (a). Because this model uses more than one spatial compartment and mass transfer is occurring, the differential equations should be written in terms of moles instead of concentrations, for each process for consistency.
The rate laws are:

$$\frac{dX_o}{dt} = 0 \qquad (X_o \text{ is a constant flow input})$$

$$\frac{dX_1}{dt} = k_{in}X_o - k_{exX}\,X_1 - k_{D1}\,X_1 + k_{D2}\,X_2$$

$$\frac{dX_2}{dt} = k_{D1}\,X_1 - k_{D2}\,X_2 - k_{met}\,X_2$$

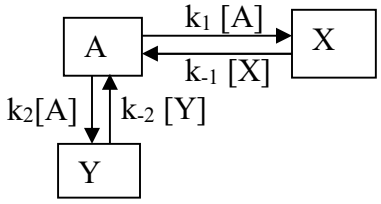
$$\frac{dY}{dt} = k_{met}\,X_2 - k_{exY}\,Y$$

The rate matrix is given below with the rows and columns labeled to help you see the relationships:

$$\underset{\approx}{K} = \begin{array}{c} \begin{matrix} X_o & X_1 & X_2 & Y \\ \downarrow & \downarrow & \downarrow & \downarrow \end{matrix} \\ \begin{pmatrix} 0 & 0 & 0 & 0 \\ k_{in} & -k_{exX} - k_{D1} & k_{D2} & 0 \\ 0 & k_{D1} & -k_{D2} - k_{met} & 0 \\ 0 & 0 & k_{met} & -k_{exY} \end{pmatrix} \end{array} \begin{matrix} \\ \leftarrow dX_o/dt \\ \leftarrow dX_1/dt \\ \leftarrow dX_2/dt \\ \leftarrow dY/dt \end{matrix}$$

The time course for this problem would be determined by numerical simulation.
(b). The ratio of the mass transport coefficients is given by Eq. 6.1.46: $k_{D2}/k_{D1} = V_1/V_2 = 3/0.5$.
This general model has many applications. For example, in atmospheric environmental chemistry, compartment 1 could be the gaseous atmosphere and compartment 2 an aerosol droplet where a reaction occurs. One specific example is the conversion of NaCl particles to $NaHSO_4$ (aq) by reaction with sulfuric acid. Another example is the reaction of dimethyl sulfide produced by bacteria in the ocean with ozone or hydroxyl radical in cloud droplets or on particle surfaces.

16. Show that the kinetic versus thermodynamic control mechanism in Example 4.1.2 gives two exponential time constants. Calculate the time constants using the rate constants given in Example 4.1.2, namely: $k_1 = 0.020\ s^{-1}$, $k_{-1} = 0.00050\ s^{-1}$, $k_2 = 0.50\ s^{-1}$, and $k_{-2} = 1.50\ s^{-1}$. The corresponding box model is shown below.



Answer: The rate matrix is:

$$\underset{\approx}{K} = \begin{pmatrix} -k_{-1}-k_{-2} & k_{-1} & k_{-2} \\ k_1 & -k_{-1} & 0 \\ k_2 & 0 & -k_{-2} \end{pmatrix}$$

The secular equation is:

$$(\underset{\approx}{M} - \lambda_i \underset{\approx}{I})\underset{\sim}{X}_i = 0 = \begin{pmatrix} -k_{-1}-k_{-2}-\lambda_i & k_{-1} & k_{-2} \\ k_1 & -k_{-1}-\lambda_i & 0 \\ k_2 & 0 & -k_{-2}-\lambda_i \end{pmatrix})$$

Expanding the determinant in terms of the first column gives:

$$(-k_{-1}-k_{-2}-\lambda_i)(-k_{-1}-\lambda_i)(-k_{-2}-\lambda_i) - k_1 k_{-1}(-k_{-2}-\lambda_i) - k_2 k_{-2}(-k_{-1}-\lambda_i) = 0$$

The multiplications give:

$$-\lambda_i^3 - \lambda_i^2(k_1 + k_2 + k_{-1} + k_{-2}) - \lambda_i (k_1k_{-2} + k_{-1}k_2 + k_{-1}k_{-2}) = 0$$

Since there is a common factor of λ_i, one of the eigenvalues is zero. A zero eigenvalue is expected because all the processes are reversible (*℘ 7* point 14). Dividing the characteristic polynomial by $-\lambda_i$ gives:

$$\lambda_i^2 + \lambda_i(k_1 + k_2 + k_{-1} + k_{-2}) + (k_1k_{-2} + k_{-1}k_2 + k_{-1}k_{-2}) = 0$$

This equation can then be solved using the quadratic equation using Excel:

k_{f1}	0.02	s^{-1}
k_{r1}	0.0005	s^{-1}
k_{f2}	0.5	s^{-1}
k_{r2}	1.5	s^{-1}
a=	1	
b=	2.0205	
c=	0.031	
lamda(+)=	-0.015461	s^{-1}
lamda(-)=	-2.005039	s^{-1}
$\tau_1 = 1/\lambda 1$	64.6786759	s
$\tau_2 = 1/\lambda 2$	0.49874343	s

The listed a, b, and c cells are the normal coefficients for $ax^2 + bx + c = 0$. Notice that the two time constants differ by over two-orders of magnitude. That is the reason for the very quick rise and comparatively slow decay in Figure 4.1.2.

Literature Cited

1. A. Leifer, *The Kinetics of Environmental Aquatic Photochemistry*, American Chemical Society, Washington, DC, 1988. pp. 149-50.
2. A. Leifer, *The Kinetics of Environmental Aquatic Photochemistry*, American Chemical Society, Washington, DC, 1988. pp. 106-10.
3. W. Legenza, C. J. Morzzacco, "The Rate Constant for Fluorescence Quenching, An undergraduate experiment using the Spectronic 20," *J. Chem. Ed.*, **1977**, *54*, 183-184.
4. F. Akhtar, "The Chapman Reactions: A model of the Production and Destruction of Stratospheric Ozone," School of Earth and Atmospheric Sciences, Georgia Institute of Technology:
   http://www.prism.gatech.edu/~gte618p/chapman.html
5. E. Harvey, R. Sweeney, "Modeling Stratospheric Ozone Kinetics, Part I The Chapman Cycle," *J. Chem. Ed.*, **1999**, *76*, 1309.
6. T. Ryan, Reichert Analytical Instruments, Depew, NY, private communication.
7. C. N. Hinshelwood, R. E. Burk, "," *J. Chem. Soc*., *Transactions*, **1925**, *127*, 1105-17.
8. A. M. Banerjee, M. R. Pai, K. Bhattacharya, A. K. Tripathi, V. S. Kamble, S. R. Bharadwaj, S. K. Kulshreshtha, "Catalytic decomposition of sulfuric acid on mixed Cr/Fe oxide samples and its application in sulfur–iodine cycle for hydrogen production," *International Journal of Hydrogen Energy*, **2008**, *33(1)*, 319-326.
9. I. D. Watson, A. G. Williamson, "The concept of the generalized thermodynamic engine applied to chemical and biochemical processes," *J. Chem. Ed*., **1979**, *56(11)*, 723-26.