

Chapter 5 Problems

1. Show that the units are correct for Eq. 5.1.15 with ϵ in $M^{-1} \text{ cm}^{-1}$, \mathcal{A} in m^2 , and V in liters in Eq. 5.1.6.

Answer: Substituting Eq. 5.1.6 into Eq. 5.1.15 gives:

$$\frac{d[B]}{dt} = 2.303 J_0 \Phi_B \epsilon \ell [A] = \left(\frac{2.303 J_0 \epsilon \ell \Phi_B}{N_A h \nu} \right) \left(\frac{\mathcal{A}}{V} \right) [A]$$

with J_0 in $\text{J m}^{-2} \text{ s}^{-1}$, ϵ in $M^{-1} \text{ cm}^{-1}$, ℓ in cm , \mathcal{A} in m^2 , and V in L . The concentrations are in mol L^{-1} . Substituting in just the units:

$$\text{mol L}^{-1} \text{ s}^{-1} = \left(\frac{\text{J m}^{-2} \text{ s}^{-1} (\text{mol}^{-1} \text{ L cm}^{-1})(\text{cm})}{\text{mol}^{-1} (\text{J s})(\text{s}^{-1})} \right) \left(\frac{\text{m}^2}{\text{L}} \right) [\text{mol L}^{-1}]$$

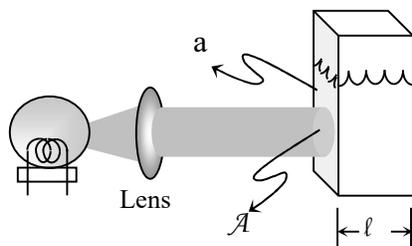
No other unit conversions are necessary.

2. Show that the photochemical rate constant for an optically thin solution is independent of path length for a cell with a uniform cross section. For example, a cell with uniform cross section includes cylindrical cells and rectangular cells where the volume is given by the area of the solution exposed on the face of the cell, a , multiplied by the path length, $V = a\ell$. Determine any unit conversion factors in the final result.

Answer: The photochemical rate constant for the formation of a secondary photoproduct from Eqs. 5.1.6 and 5.1.19 is:

$$j_B = \left(\frac{2.303 J_0 \epsilon \ell \Phi_B}{N_A h \nu} \right) \left(\frac{\mathcal{A}}{V} \right) \quad \text{with } \ell \text{ in cm, } \mathcal{A} \text{ in m}^2, \text{ and } V \text{ in L.}$$

The total volume of the solution is given by $V = a\ell$, where ℓ is the reaction cell path length.



Substituting $V = a\ell$ into Eqs. 5.1.6 and 5.1.19 gives:

$$j_B = \left(\frac{2.303 J_0 \epsilon \ell \Phi_B}{N_A h \nu} \right) \left(\frac{\mathcal{A}}{a\ell} \right) = \left(\frac{2.303 J_0 \epsilon \Phi_B}{N_A h \nu} \right) \left(\frac{\mathcal{A}}{a} \right)$$

which is independent of path length. In other words, as the path length increases, the volume of the solution also increases, keeping the increase in moles per unit volume per unit time constant.

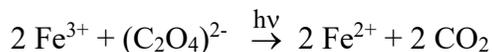
However, now we need to be careful about units. With J_o in $\text{J m}^{-2} \text{s}^{-1}$, ϵ in $\text{M}^{-1} \text{cm}^{-1}$, and j_B in s^{-1} the conversions needed are:

$$j_B = \left(\frac{2.303 J_o \epsilon \Phi_B}{N_A h \nu} \right) (100 \text{ cm/1 m})(1 \text{ m}^3/1000 \text{ L})$$

In other words, putting in just the units:

$$\text{s}^{-1} = \left(\frac{\text{J m}^{-2} \text{s}^{-1} (\text{mol}^{-1} \text{L cm}^{-1})}{\text{mol}^{-1} (\text{J s})(\text{s}^{-1})} \right) (100 \text{ cm/1 m})(1 \text{ m}^3/1000 \text{ L})$$

3. A chemical actinometer is a solution with known quantum yield that can be used to find the incident intensity in photochemical experiments. The ferrioxalate actinometer uses the reaction:



A ferrioxalate concentration of 0.15 M is normally used for actinometry, which is optically thick. A common light source for photochemical reactions is the 366 nm emission line of a mercury lamp. The quantum yield for the ferrioxalate reaction at 366 nm is 1.18.¹ The progress of the reaction is monitored using the visible absorption of the *ortho*-phenanthroline complex of Fe^{2+} at 522 nm. The molar absorption coefficient of the Fe^{2+} complex at 522 nm is $8650 \text{ M}^{-1} \text{cm}^{-1}$. The *ortho*-phenanthroline complex for Fe^{3+} is very weak and transparent at 522 nm. The following experiment was used to determine the incident intensity for a photoreactor. A solution of 0.15 M ferrioxalate was irradiated for 10.0 min. A 1.00 mL aliquot was withdrawn and diluted with water to a total volume of 100.0 mL in a volumetric flask. The absorbance of this solution in a 1.00 cm pathlength cuvette at 522 nm was 0.410. Calculate the incident flux in $\text{mol L}^{-1} \text{s}^{-1}$.

Answer: The plan is to use the Beer-Lambert Law to calculate the concentration of Fe^{2+} in the aliquot. Then the dilution factor is used to calculate the Fe^{2+} concentration in the actinometer solution. Since the solution is optically thick, we assume a zeroth-order reaction and, using Eq. 5.1.14, we calculate the incident intensity.

Using the Beer-Lambert law: $A = \epsilon c \ell$ the concentration of the aliquot is:

$$c = A/\epsilon \ell = 0.410/(8650 \text{ M}^{-1} \text{cm}^{-1} \cdot 1.00 \text{ cm}) = 4.74 \times 10^{-5} \text{ M}$$

The dilution factor for the absorbance sample is 1/100 giving the concentration of Fe^{2+} in the original actinometer as $[\text{Fe}^{2+}] = 4.74 \times 10^{-3} \text{ M}$. Assuming zeroth-order kinetics, Eq. 5.1.14:

$$\frac{d[\text{Fe}^{2+}]}{dt} = \Phi_B J_a = \Phi_B J_o$$

which integrates to $[\text{Fe}^{2+}] = [\text{Fe}^{2+}]_o + \Phi_B J_o t$, where the initial concentration is zero, $[\text{Fe}^{2+}]_o = 0$. Using the known photochemical quantum yield, $\Phi_B = 1.18$, and the Fe^{2+} concentration at 10.0 min gives the incident intensity as:

$$[\text{Fe}^{2+}] = \Phi_B J_o t$$

$$\text{or } J_0 = [\text{Fe}^{2+}]/(\Phi_B t) = \frac{4.74 \times 10^{-3} \text{ M}}{1.18 (10.0 \text{ min})(60 \text{ s/1 min})} = 6.70 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$$

4. A high power mercury lamp produces 219.0 W m^{-2} at 366 nm at the surface of a photochemical reaction cell (see Problem 3). Assume the cross-section of the incident beam is 1.00 cm^2 and the solution volume is 10.0 mL . Calculate the incident flux in $\text{mol L}^{-1} \text{ s}^{-1}$.

Answer: (a) The energy of 366 nm light in kJ mol^{-1} is:

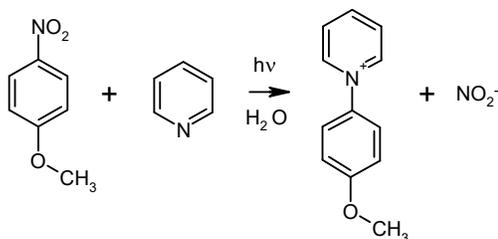
$$E = N_A h\nu = N_A hc/\lambda = 6.022 \times 10^{23} \text{ mol}^{-1} (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})/366 \times 10^{-9} \text{ m} = 3.268 \times 10^5 \text{ J mol}^{-1} = 326.8 \text{ kJ mol}^{-1}$$

Using Eq. 5.1.6 gives the flux in $\text{mol L}^{-1} \text{ s}^{-1}$:

$$J_0 = \frac{J_0}{N_A h\nu} \left(\frac{A}{V} \right) = \frac{219.0 \text{ J m}^{-2} \text{ s}^{-1}}{3.268 \times 10^5 \text{ J mol}^{-1}} \left(\frac{1 \text{ cm}^2 (1 \text{ m}/100 \text{ cm})^2}{0.0100 \text{ L}} \right) = 6.70 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$$

(which, by the way, corresponds to the answer from Problem 3).

5. When *p*-nitroanisole and pyridine are photolyzed in aqueous solution the reaction is:



The quantum yield for a solution containing $1.00 \times 10^{-5} \text{ M}$ *p*-nitroanisole and 0.0100 M pyridine in 1% acetonitrile is 4.65×10^{-3} at 366 nm .² The molar absorption coefficient at 366 nm of *p*-nitroanisole is $1990 \text{ M}^{-1} \text{ cm}^{-1}$. Calculate the photochemical rate constant and write the rate law for an optically thin solution assuming the incident flux is $6.70 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$ for a 10.00 cm path length reaction cell.

Answer: For an optically thin solution, using Eq. 5.1.19:

$$\begin{aligned} j_B &= 2.303 J_0 \Phi_B \varepsilon l \\ &= 2.303 (6.70 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1})(4.65 \times 10^{-3})(1990 \text{ M}^{-1} \text{ cm}^{-1})(10.0 \text{ cm}) \\ &= 1.43 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

The rate constants for environmental problems is often given in days^{-1} :

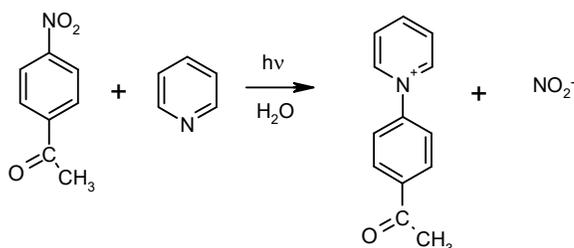
$$j_B = 1.43 \times 10^{-3} \text{ s}^{-1} (60 \text{ s/1 min})(60 \text{ min/1 hr})(24 \text{ hr/1 day}) = 123 \text{ day}^{-1}$$

Using Eq. 5.1.17 gives the rate law:

$$\frac{d[B]}{dt} = j_B [A] = 1.43 \times 10^{-3} \text{ s}^{-1} [\text{PNA}]$$

where [PNA] is the concentration of *p*-nitroanisole. This reaction is commonly used as an actinometer for environmental studies.

6. A solution with a known photochemical quantum yield can be used to calculate the incident light flux during a photolytic reaction. Such solutions are called chemical actinometers (see Problems 3 and 5). Consider the reaction of *p*-nitroacetophenone and pyridine:



A chemical actinometer and a solution of *p*-nitroacetophenone and pyridine were simultaneously photolyzed at 366 nm in reaction cells with identical geometry. The path length of the reaction cell is 1.00 cm. The quantum yield for the actinometer is 4.65×10^{-3} with a molar absorption coefficient $1990 \text{ M}^{-1} \text{ cm}^{-1}$. The photochemical rate constant for the actinometer is determined to be $1.43 \times 10^{-3} \text{ s}^{-1}$. The molar absorption coefficient of *p*-nitroacetophenone is $160. \text{ M}^{-1} \text{ cm}^{-1}$.² The photochemical rate constant for $1.00 \times 10^{-5} \text{ M}$ *p*-nitroacetophenone and 0.100 M pyridine is $4.18 \times 10^{-5} \text{ s}^{-1}$. Calculate the quantum yield for the *p*-nitroacetophenone and pyridine reaction at 366 nm.

Answer: For an optically thin solution, using Eq. 5.1.19:

$$j_B = 2.303 J_o \Phi_B \varepsilon \ell$$

The incident flux calculated from the actinometer is:

$$\begin{aligned} J_o &= \frac{j_{\text{act}}}{2.303 \Phi_{\text{act}} \varepsilon \ell} = \frac{1.43 \times 10^{-3} \text{ s}^{-1}}{2.303 (4.65 \times 10^{-3})(1990 \text{ M}^{-1} \text{ cm}^{-1} 1 \text{ cm})} \\ &= 6.71 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

Then applying Eq. 5.1.19 for the *p*-nitroacetophenone, PNAP, reaction gives:

$$\begin{aligned} \Phi_{\text{PNAP}} &= \frac{j_{\text{PNAP}}}{2.303 J_o \varepsilon \ell} = \frac{4.18 \times 10^{-5} \text{ s}^{-1}}{2.303 (6.71 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1})(160. \text{ M}^{-1} \text{ cm}^{-1} 1 \text{ cm})} \\ &= 1.69 \times 10^{-3} \end{aligned}$$

This reaction is also commonly used as a chemical actinometer. This actinometer is appropriate with slower environmental reactions than are covered by the PNA actinometer in Problem 5.

7. Consider the following reversible first-step mechanism for a first-order photochemical reaction:



where k_D is the combined rate constant for all the non-photochemical deactivation processes, with $k_D = k_f + k_{ISC} + k_{nr}$. Derive Eq. 5.1.24 directly from this mechanism. [Hint: Express the rate law in the form of Eq. 5.1.17 and then use Eq. 5.1.19]

Answer: The plan is to use the steady-state approximation to find the overall rate law for the formation of products in the form of Eq. 5.1.17 and then find the photochemical quantum yield using Eq. 5.1.19. The reactive intermediate is the molecular excited state, A^* . Step 1 is to write the rate law for the formation of product:

$$\frac{d[B]}{dt} = k_R [A^*]$$

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

$$\frac{d[A^*]}{dt} = j_{A^*} [A] - k_D [A^*] - k_R [A^*] = 0$$

Step 3: Solving for the concentration of the reactive intermediate, A^* :

$$[A^*] = \frac{j_{A^*}}{k_D + k_R} [A]$$

With only one unknown we can proceed to Step 5 and find the overall rate law by substituting the steady state A^* concentration back into the rate law for the formation of product:

$$\frac{d[B]}{dt} = k_R \frac{j_{A^*}}{k_D + k_R} [A]$$

Comparing this last equation with Eq. 5.1.17 and 5.1.19, that is $j_B = \Phi_B j_{A^*}$, gives:

$$j_B = k_R \frac{j_{A^*}}{k_D + k_R} = \Phi_B j_{A^*}$$

which is an important equation in its own right. This equation shows the relationship between j_B , which is the rate constant for the overall production of the product while k_R is the rate constant for the formation of product from the molecular excited state. So solving for the photochemical quantum yield and using the definition of $k_D = k_f + k_{ISC} + k_{nr}$ gives:

$$\Phi_B = \frac{k_R}{k_f + k_{ISC} + k_{nr} + k_R}$$

8. Anthracene fluorescence is quenched by halogenated compounds like CCl_4 . A Stern-Volmer quenching study was completed giving the fluorescence intensities, as a function of CCl_4

concentration, in the following table.³ The intensities are in arbitrary units. The fluorescence lifetime in the absence of CCl₄ is 5.03 ns. Calculate the quenching rate constant.

[CCl ₄] (M)	0	0.02	0.04	0.08	0.12
Intensity	2437	1860	1490	1110	893

Answer: Using Eq. 5.1.31 in the absence of quencher, $k_R = k_q[Q] = 0$ gives:

$$k_f + k_{ISC} + k_{nr} = 1/\tau = 1/5.03 \times 10^{-9} \text{ s} = 1.99 \times 10^8 \text{ s}^{-1}$$

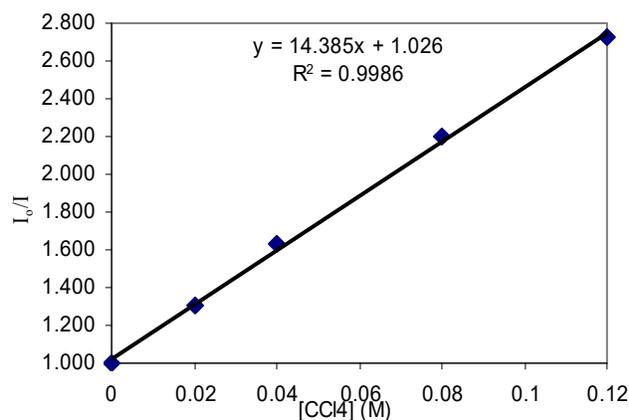
Using Eq. 5.1.28, in terms of the intensity ratio:

$$I_0/I = \Phi_0/\Phi_f = 1 + \frac{k_q[Q]}{k_f + k_{ISC} + k_{nr}}$$

a plot of I_0/I versus [CCl₄] is constructed. The slope is determined by a least squares fit using the spreadsheet and linest():

[CCl ₄]	Intensity	I_0/I
0	2437	1.000
0.02	1860	1.310
0.04	1490	1.636
0.08	1110	2.195
0.12	893	2.729

slope	14.3850	1.0260	intercept
±	0.3139	0.0212	±
r ²	0.9986	0.0302	s(y)
F	2099.9195	3.0000	df
SS _{regression}	1.9203	0.0027	SS _{residual}



From the slope the quenching rate constant is:

$$k_q = \text{slope} (k_f + k_{ISC} + k_{nr}) = 14.38 (1.99 \times 10^8 \text{ s}^{-1}) = 2.86 \times 10^9 \pm 0.06 \times 10^9 \text{ s}^{-1}$$

9. Run a numerical simulation for the Chapman mechanism for the rate constants and concentrations appropriate at an altitude of 25 km. A table of appropriate constants is given below.^{4,5S} Determine the steady-state concentration of ozone using Eq. 5.2.11 and by numerical simulation.

Altitude km	j_1 s^{-1}	k_2 $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	j_3 s^{-1}	k_4 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	[M] molecule cm^{-3}	[O ₂] molecule cm^{-3}
25	3.0×10^{-12}	1.2×10^{-33}	5.5×10^{-4}	6.9×10^{-16}	9×10^{17}	1.8×10^{17}
40	5.7×10^{-10}	9.1×10^{-34}	1.9×10^{-3}	2.2×10^{-15}	8.1×10^{16}	1.7×10^{16}

Answer: We proceed by editing the *MatLab* files listed in Addendum 5.7. A longer maximum time is necessary to achieve a steady state. The changes necessary to the files listed in the Addendum define the rate constants:

```
% Constants for 25 km:
j1=3.0e-12;
k2=1.2e-33;
j3=5.5e-4;
k4=6.9e-16;
M=9.0e17;
```

and the main file is changed to give:

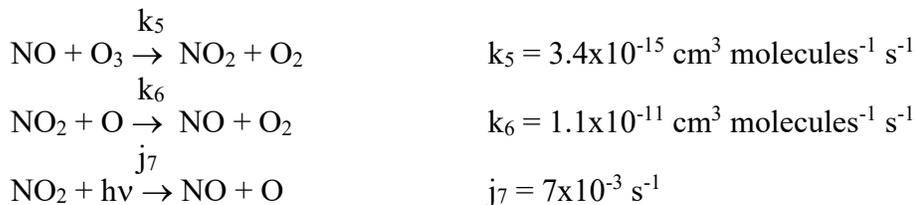
```
% Set the initial values
Xo = [0 1.8e17 0];
% Set the total integration time in seconds
maxTime = 4.0e7;
```

The steady-state concentration of ozone that results is 1.645×10^{13} molecules cm^{-3} . A short Excel spread sheet was written to solve the quadratic equation for the steady-state ozone concentration from Eq. 5.2.11:

j1	3.00E-12	s^{-1}
k2	1.20E-33	$\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$
j3	5.50E-04	s^{-1}
k4	6.90E-16	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
[M]	9.00E+17	molecule cm^{-3}
[O2]	1.80E+17	molecule cm^{-4}
a	7.59E-19	
b	7.45E-10	
c	-2.10E+08	
O3 (+root)	1.66E+13	molecule cm^{-6}
(-root)	-1.66E+13	molecule cm^{-7}

The listed a, b, and c cells are the normal coefficients for $ax^2 + bx + c = 0$. The analytical value, 1.66×10^{13} molecules cm^{-3} , is differs slightly from the limiting numerical value because of numerical error. Stiff methods are usually not as accurate as the much slower 4th order Runge-Kutta algorithm, `ode45()`.

10. Nitrogen oxides catalyze the destruction of ozone and must be taken into account in accurate stratospheric models. The reactions and the rate constants appropriate for 25 km are:



The values for the rate constants j_1 - k_4 and $[M]$ at 25 km are given in Problem 9. Guesses for the starting concentrations for NO and NO_2 that you can use are:

$$[\text{NO}]_0 = 8.0 \times 10^8 \text{ molecules cm}^3 \quad \text{and} \quad [\text{NO}_2] = 1.0 \times 10^9 \text{ molecules cm}^3$$

Add these three reactions to the numerical simulation outlined in Addendum 5.7 to find the change of the ozone concentration with and without catalysis. You can use *MatLab* or *MathCad*, or any numerical routines that employ stiff methods.

Answer: The rate laws are:

$$\frac{d[\text{O}]}{dt} = 2 j_1 [\text{O}_2] - k_2 [\text{O}][\text{O}_2][\text{M}] + j_3 [\text{O}_3] - k_4 [\text{O}][\text{O}_3] - k_6 [\text{NO}_2][\text{O}] + j_7 [\text{NO}_2] \quad 1$$

$$\frac{d[\text{O}_2]}{dt} = -j_1 [\text{O}_2] - k_2 [\text{O}][\text{O}_2][\text{M}] + j_3 [\text{O}_3] + 2 k_4 [\text{O}][\text{O}_3] + k_5 [\text{NO}][\text{O}_3] + k_6 [\text{NO}_2][\text{O}] \quad 2$$

$$\frac{d[\text{O}_3]}{dt} = k_2 [\text{O}][\text{O}_2][\text{M}] - j_3 [\text{O}_3] - k_4 [\text{O}][\text{O}_3] - k_5 [\text{NO}][\text{O}_3] \quad 3$$

$$\frac{d[\text{NO}]}{dt} = -k_5 [\text{NO}][\text{O}_3] + k_6 [\text{NO}_2][\text{O}] + j_7 [\text{NO}_2] \quad 4$$

$$\frac{d[\text{NO}_2]}{dt} = k_5 [\text{NO}][\text{O}_3] - k_6 [\text{NO}_2][\text{O}] - j_7 [\text{NO}_2] \quad 5$$

The rate of formation of odd oxygen species is obtained by adding Eqs. 1 and 3 to give:

$$\frac{d([\text{O}_3] + [\text{O}])}{dt} = 2 j_1 [\text{O}_2] - 2 k_4 [\text{O}][\text{O}_3] - k_5 [\text{NO}][\text{O}_3] - k_6 [\text{NO}_2][\text{O}] + j_7 [\text{NO}_2] \quad 6$$

The concentrations are set to $X(4) = [\text{NO}]$ and $X(5) = [\text{NO}_2]$. The revised “chapman.m” method file for *MatLab* is called “chapmanNOx.m”:

```
function dX = chapmanNOx(t,X);
% Differential equations for the Chapman Mechanism.
% Based on work by Farhan Akhtar, School of Earth and Atmospheric Sciences
% Georgia Institute of Technology:
% http://www.prism.gatech.edu/~gte618p/chapman.html
% Constants for 25 km:
j1=3.0e-12;
k2=1.2e-33;
j3=5.5e-4;
k4=6.9e-16;
k5=3.4e-15;
k6=1.1e-11;
j7=7.0e-3;
M=9.0e17;
%Calculations
dX = zeros(5,1) ;
dX(1) = 2*j1*X(2)-k2*X(1)*X(2)*M+j3*X(3)-k4*X(1)*X(3)-k6*X(5)*X(1)+j7*X(5) ;
dX(2) = -j1*X(2)-k2*X(1)*X(2)*M+j3*X(3)+2*k4*X(1)*X(3)+k5*X(5)*X(3)+k6*X(5)*X(1) ;
dX(3) = k2*X(1)*X(2)*M-j3*X(3)-k4*X(1)*X(3)-k5*X(4)*X(3) ;
dX(4) = -k5*X(4)*X(3)+k6*X(5)*X(1)+j7*X(5) ;
dX(5) = -dX(4) ;
```

And the revised main program is:

```
% The differential equations are defined in the -m file: 'chapmanNOx.m'
%
clear
% Set the initial values
```

```

Xo = [0 1.8e17 0 8e8 1e9];
% Set the total integration time in seconds
maxTime = 4.0e7;
trange = [0 maxTime];

% solve the differential equations
[T,X] = ode15s(@chapmanNOx,trange,Xo);

```

These calculations give a steady-state ozone concentration of 8.74×10^{12} molecules cm^3 , which is a factor of 0.53 smaller than the case without NO and NO_2 . However, the exact change in ozone concentration is very dependent of the values of the rate constants and the total NO and NO_2 concentration. Hopefully, you noticed that the graph of $[\text{O}_2]$ shows a slow, constant increase for long times. This increase is from numerical errors that are caused by the use of the less accurate stiff differential equations solver. However, using the more accurate `ode45()`, a 4th order Runge-Kutta solver, requires many hours of computation time.

11. Problem 10 lists the three reactions that supplement the Chapman mechanism to account for the catalytic destruction of ozone caused by NO and NO_2 . (a) At steady state, show that the rate law for odd oxygen species can be expressed as:

$$\frac{d([\text{O}_3] + [\text{O}])}{dt} = 2 j_1 [\text{O}_2] - 2 k_4 [\text{O}_3][\text{O}] \left(1 + \frac{k_6 [\text{NO}_2]}{k_4 [\text{O}_3]} \right)$$

The term in parentheses is called the enhancement factor, ρ :

$$\rho = \left(1 + \frac{k_6 [\text{NO}_2]}{k_4 [\text{O}_3]} \right)$$

which determines the extent of the catalysis of the destruction of ozone by NO and NO_2 . Use the rate constants given in Problems 9 and 10 along with the following rough estimates for the steady-state concentrations to estimate the enhancement factor at 25 km. These concentrations are from the results of Problem 10 at 25 km:

$$[\text{O}_3] = 8.74 \times 10^{12} \text{ molecules cm}^{-3} \quad [\text{NO}_2] = 1.45 \times 10^9 \text{ molecules cm}^{-3}$$

Answer: The rate laws are:

$$\frac{d[\text{O}]}{dt} = 2 j_1 [\text{O}_2] - k_2 [\text{O}][\text{O}_2][\text{M}] + j_3 [\text{O}_3] - k_4 [\text{O}][\text{O}_3] - k_6 [\text{NO}_2][\text{O}] + j_7 [\text{NO}_2] \quad 1$$

$$\frac{d[\text{O}_2]}{dt} = -j_1 [\text{O}_2] - k_2 [\text{O}][\text{O}_2][\text{M}] + j_3 [\text{O}_3] + 2 k_4 [\text{O}][\text{O}_3] + k_5 [\text{NO}][\text{O}_3] + k_6 [\text{NO}_2][\text{O}] \quad 2$$

$$\frac{d[\text{O}_3]}{dt} = k_2 [\text{O}][\text{O}_2][\text{M}] - j_3 [\text{O}_3] - k_4 [\text{O}][\text{O}_3] - k_5 [\text{NO}][\text{O}_3] \quad 3$$

$$\frac{d[\text{NO}]}{dt} = -k_5 [\text{NO}][\text{O}_3] + k_6 [\text{NO}_2][\text{O}] + j_7 [\text{NO}_2] \quad 4$$

$$\frac{d[\text{NO}_2]}{dt} = k_5 [\text{NO}][\text{O}_3] - k_6 [\text{NO}_2][\text{O}] - j_7 [\text{NO}_2] \quad 5$$

The rate of formation of odd oxygen species is obtained by adding Eqs. 1 and 3 to give:

$$\frac{d([\text{O}_3] + [\text{O}])}{dt} = 2 j_1 [\text{O}_2] - 2 k_4 [\text{O}][\text{O}_3] - k_5 [\text{NO}][\text{O}_3] - k_6 [\text{NO}_2][\text{O}] + j_7 [\text{NO}_2] \quad 6$$

Eq. 6 involves both the NO and O atom concentrations. One of these intermediate concentrations can be eliminated using the steady-state approximation. Assume that the reactions are at steady state. The rate law for reaction 5 can then be set equal to zero. Adding Eqs. 5 and 6 eliminates [NO] as a variable and gives an additional destruction term:

$$\frac{d([\text{O}_3] + [\text{O}])}{dt} = \underbrace{2 j_1 [\text{O}_2]}_{\text{production}} - \underbrace{2 k_4 [\text{O}_3] [\text{O}]}_{\text{destruction}} - \underbrace{2 k_6 [\text{NO}_2][\text{O}]}_{\text{destruction}} \quad 7$$

which can be rearranged to give:

$$\frac{d([\text{O}_3] + [\text{O}])}{dt} = \underbrace{2 j_1 [\text{O}_2]}_{\text{production}} - \underbrace{2 k_4 [\text{O}_3] [\text{O}]}_{\text{destruction}} \left(1 + \frac{k_6 [\text{NO}_2]}{k_4 [\text{O}_3]} \right) \quad 8$$

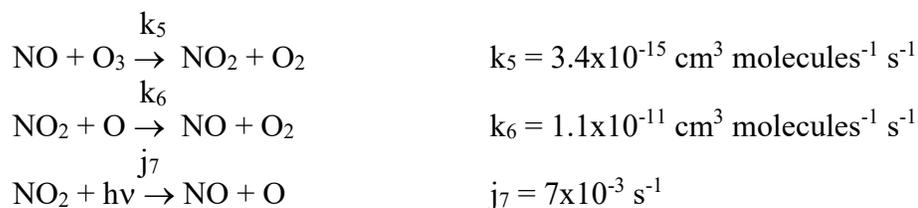
$$\text{with } \rho = \left(1 + \frac{k_6 [\text{NO}_2]}{k_4 [\text{O}_3]} \right) \quad 9$$

Substituting in the values of the constants from Problems 9 and 10 and the steady-state concentrations of O₃ and NO₂ gives:

$$\begin{aligned} \rho &= \left(1 + \frac{k_6 [\text{NO}_2]}{k_4 [\text{O}_3]} \right) = \left(1 + \frac{1.1 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} (1.45 \times 10^9 \text{ molecules cm}^{-3})}{6.9 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (8.74 \times 10^{12} \text{ molecules cm}^{-3})} \right) \\ &= 3.6 \end{aligned}$$

The ozone destruction processes are accelerated by a factor of 3.6 by NO and NO₂ catalysis. This value is very sensitive to the values of the rate constants, especially the photolytic rate constant j_7 , as shown in the next problem.

12. Nitrogen oxides catalyze the destruction of ozone and must be taken into account in accurate stratospheric models. The reactions and the rate constants appropriate for 25 km are:



Show that the ratio of the NO₂ and NO concentrations at steady-state are given by the relationship:

$$\frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_5 [\text{O}_3]}{k_6 [\text{O}] + j_7}$$

Calculate the steady-state ratio assuming that the O atom concentration is small enough that $k_6[\text{O}] \ll j_7$. Assume $[\text{O}_3] = 8.74 \times 10^{12} \text{ molecules cm}^{-3}$ (as in Problem 11).

Answer: The rate laws are:

$$\frac{d[\text{NO}]}{dt} = -k_5 [\text{NO}][\text{O}_3] + k_6 [\text{NO}_2][\text{O}] + j_7 [\text{NO}_2] = 0 \quad 1$$

$$\frac{d[\text{NO}_2]}{dt} = k_5 [\text{NO}][\text{O}_3] - k_6 [\text{NO}_2][\text{O}] - j_7 [\text{NO}_2] = 0 \quad 2$$

At steady-state both are equal to zero. Either Eq. 1 or 2 can be solved for the NO₂ to NO ratio:

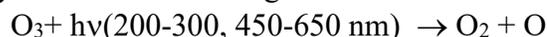
$$k_5 [\text{NO}][\text{O}_3] = k_6 [\text{NO}_2][\text{O}] + j_7 [\text{NO}_2] \quad 3$$

$$\frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_5 [\text{O}_3]}{k_6 [\text{O}] + j_7} \quad 4$$

This relationship can also be used to find the enhancement factor in Problem 11 in terms of the NO and O atom concentrations. Assuming $k_6[\text{O}] \ll j_7$ and substitution of the constants gives:

$$\begin{aligned} \frac{[\text{NO}_2]}{[\text{NO}]} &= \frac{k_5 [\text{O}_3]}{j_7} = \frac{3.4 \times 10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} (8.74 \times 10^{12} \text{ molecules cm}^{-3})}{7 \times 10^{-3} \text{ s}^{-1}} \\ &= 4.2 \end{aligned}$$

This relationship shows that the ratio of NO₂ and NO and the O atom concentrations are sensitive to the rate constant for the photolytic decomposition of NO₂. Photolytic rate constants are dependent on time of day, time of year, and altitude and so are highly variable. The range of photolytically active wave lengths for the decomposition of NO₂ is 300-400 nm. Direct O₃ photolysis occurs in the ranges of 200-300 and 450-650 nm.



The UV-A range is 320–400 nm and the UV-B range is 280–320 nm.

13. The combustion of carbon sources, such as coal or charcoal, in limited amounts of oxygen produces carbon monoxide. Carbon monoxide is a commonly used reducing agent, especially in metallurgy. The reaction of carbon with high temperature steam produces carbon monoxide and hydrogen gas. Carbon monoxide and hydrogen are the feed stocks for industrial processes like the Fischer-Tropsch process, which can be used to produce transportation fuels from coal or biomass. Carbon monoxide readily adsorbs onto charcoal surfaces. The equilibrium surface loading of CO on charcoal at 0°C is given in the following table. Determine the Langmuir coefficient for this system.

P_{CO} (bar)	0.0973	0.240	0.412	0.720	1.176
Γ (mmol g ⁻¹)	0.113	0.248	0.378	0.573	0.787

Answer: Based on Eq. 5.3.11 or 5.3.18, using the general form “ $abx/(1+bx)$ ” in the “Nonlinear Least Squares Curve Fitting” applet gives the following results and corresponding curve-fit plot.

===== Results =====

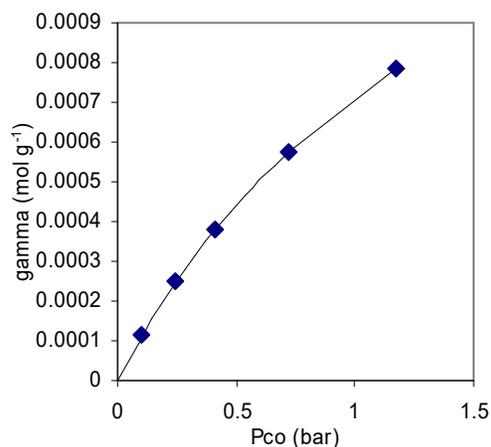
$$a = 0.001823 \pm 0.000061$$

$$b = 0.643 \pm 0.033$$

sum of squared residuals = 8.473e-11

stand. dev. y values = 0.000005315

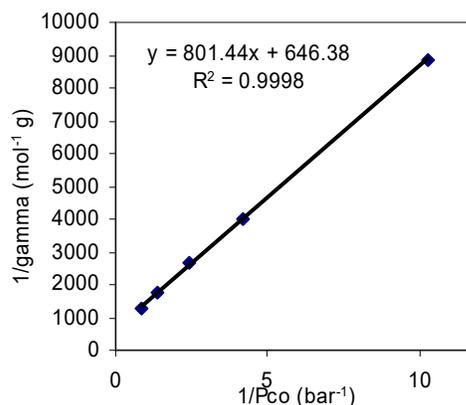
correlation between a & b = -0.989



The fit gives $b = 0.643 \pm 0.033 \text{ bar}^{-1}$. A double reciprocal plot also works well, but again the nonlinear fit parameters are better because the uncertainties are handled better. Inverting Eq. 5.3.18:

$$\Gamma_{A\sigma} = \Gamma_{\max\sigma} \frac{b P_A}{1 + b P_A} \quad \text{gives} \quad \frac{1}{\Gamma_{A\sigma}} = \frac{1}{\Gamma_{\max\sigma} b P_A} + \frac{1}{\Gamma_{\max\sigma}}$$

Pco (bar)	Γ (mol g ⁻¹)	1/Pco (bar ⁻¹)	1/ Γ (mol ⁻¹ g)
0.0973	0.000113	10.27671	8859.907
0.240	0.000248	4.167778	4027.23
0.412	0.000378	2.427832	2647.382
0.720	0.000573	1.389259	1744.076
1.176	0.000787	0.850567	1270.541



The linear fit gives $b = 0.81 \text{ bar}^{-1}$, which is outside the error bounds from the non-linear fit.

However, the double reciprocal plot does help verify Langmuir behavior. Notice the very high correlation coefficient between fit parameters in the non-linear fit, -0.989. The values of the maximum binding capacity and the Langmuir coefficient are highly correlated. To resolve this issue, to generate results that can be published, experimental points at higher P_{CO} are necessary.

14. Antibody-antigen interactions are very strong and very specific. The interaction between a protein, bovine serum albumin, and anti-BSA immunoglobulin G (IgG) was determined using SPR. BSA was attached to a gold surface and the IgG was flowed over the surface at constant concentration. The results for the observed association rate constant are given in the table below. The dissociation rate constants, from nonlinear curve fitting from the time courses, were averaged over each run and found to be $5.94 \times 10^{-5} \text{ s}^{-1}$. Find k_a , the association equilibrium

constant, K_A , and the dissociation equilibrium constant, K_D . Convert K_D to picomolar units, pM, which is typical of the conventional choice of units in the medicinal chemistry literature.

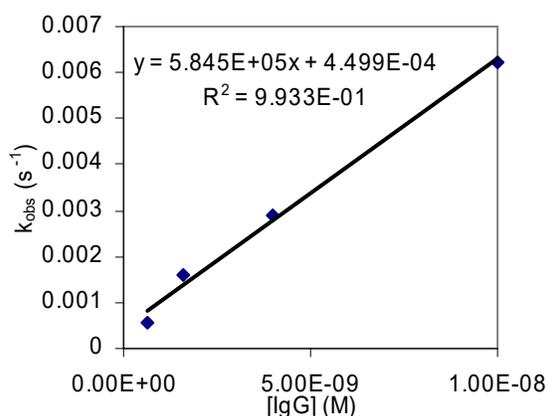
[IgG] (nM)	10.0	4.00	1.60	0.640
k_{obs} (s^{-1})	0.00623	0.002914	0.001578	0.00057

Answer: From Eq. 5.4.10, $k_{\text{obs}} = k_a [A]_o + k_d$, a plot of k_{obs} versus the concentration of IgG flowing over the surface, $[A]_o$, should yield a straight line. The `linest()` fit is for k_{obs} vs. [IgG] in units of nM, so the final slope must be multiplied by 1×10^9 to convert to $\text{M}^{-1} \text{s}^{-1}$.

[IgG] nM	[IgG] (M)	k_{obs} (s^{-1})
10	1.00E-08	0.00623
4	4.00E-09	0.002914
1.6	1.60E-09	0.001578
0.64	6.40E-10	0.00057

In nM concentration units:

slope	0.00058452	0.00045	intercept
\pm	3.3891E-05	0.000185	\pm
r^2	0.9933	0.000247	$s(y)$
F	297.467	2	df
SS _{regression}	1.812E-05	1.22E-07	SS _{residual}



The resulting $k_a = 5.85 \times 10^5 \pm 0.34 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, giving $K_A = 5.85 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} / 5.94 \times 10^{-5} \text{ s}^{-1} = 9.84 \times 10^9 \text{ M}^{-1}$ and $K_D = 1/K_A = 1.02 \times 10^{-10} \text{ M}$. In picomolar units:

$$K_D = 1.02 \times 10^{-10} \text{ M} (1 \text{ pM} / 1.0 \times 10^{-12} \text{ M}) = 102. \text{ pM} = 1. \times 10^2 \text{ pM}$$

15. SPR is a commonly used technique in immunology. The interaction between a protein, porcine serum albumin, PSA, and anti-PSA immunoglobulin G (IgG) was determined using SPR. The anti-PSA IgG was attached to a gold surface and PSA was flowed over the surface at constant concentration. The results for the observed association rate constant are given in the table below.⁶ The dissociation rate constants, from nonlinear curve fitting from the time courses, were averaged over each run and found to be $1.02 \times 10^{-3} \text{ s}^{-1}$. Find k_a , the association equilibrium constant, K_A , and the dissociation equilibrium constant, K_D . Convert K_D to nanomolar units, nM, which is typical of the conventional choice of units in the medicinal chemistry literature.

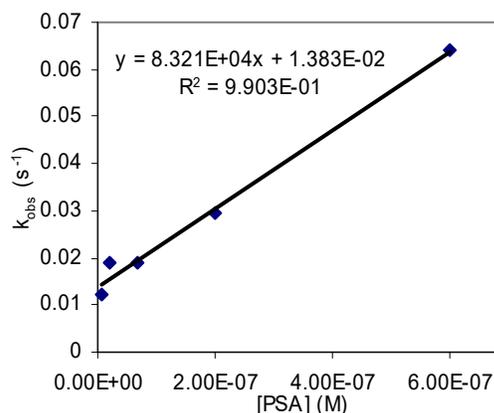
[PSA] (nM)	7.18	21.5	66.4	201.	601.
k_{obs} (s^{-1})	0.0122	0.00189	0.00189	0.0297	0.0641

Answer: From Eq. 5.4.10, $k_{\text{obs}} = k_a [A]_o + k_d$, a plot of k_{obs} versus the concentration of PSA flowing over the surface, $[A]_o$, should yield a straight line. The `linest()` fit is for k_{obs} vs. [PSA] in units of nM, so the final slope must be multiplied by 1×10^9 to convert to $\text{M}^{-1} \text{ s}^{-1}$.

[PSA] nM	[PSA] (M)	k_{obs} (s^{-1})
7.18E+00	7.18E-09	0.0122
2.15E+01	2.15E-08	0.0189
6.64E+01	6.64E-08	0.0189
2.01E+02	2.01E-07	0.0297

In nM concentration units:

slope	8.3207E-05	0.013825	intercept
\pm	4.7595E-06	0.001358	\pm
r^2	0.99028	0.00235969	$s(y)$
F	305.627	3	df
SS _{regression}	0.0017018	1.6704E-05	SS _{residual}



The resulting $k_a = 8.32 \times 10^4 \pm 0.48 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, giving $K_A = 8.32 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} / 1.02 \times 10^{-3} \text{ s}^{-1} = 8.16 \times 10^7 \text{ M}^{-1}$ and $K_D = 1/K_A = 1.23 \times 10^{-8} \text{ M}$. In nanomolar units:

$$K_D = 1.23 \times 10^{-8} \text{ M} (1 \text{ nM} / 1.0 \times 10^{-9} \text{ M}) = 12.3 \text{ nM} = 1. \times 10^1 \text{ nM}$$

16. It is not necessary in dynamic SPR measurements to wait for the surface adsorption to reach equilibrium. However, if the time course for the association does essentially reach equilibrium, the equilibrium values can be fit to the Langmuir adsorption isotherm. Such equilibrium SPR experiments provide an alternative method to determine the equilibrium dissociation constant that is complementary to dynamic measurements. Comparison between equilibrium and dynamic results helps to determine experimental uncertainties. The limiting refractive index values from the time course measurements for the system in Problem 15 are given below.⁶ By fitting the results to a Langmuir adsorption isotherm, determine the equilibrium dissociation constant in nanomolar units. The units typical for SPR instrument output are micro-refractive index units, or μRIU .

[PSA] (nM)	0	7.18	7.18	19.7	59.2	181.3	538.5
R (μRIU)	0	23.6	26.5	38	55.6	57.6	58.8

Answer: Based on Eq. 5.3.11 or 5.3.18, using the general form “ $abx/(1+bx)$ ” in the “Nonlinear Least Squares Curve Fitting” applet gives the following results and corresponding curve-fit plot, below. The non-linear fit value for $K_A = 9.52 \times 10^7 \pm 1.0 \times 10^7 \text{ M}^{-1}$. Then $K_D = 1/K_A = 1.05 \times 10^{-8} \text{ M} = 10.5 \text{ nM}$. The value from Problem 16 was $\approx 12 \text{ nM}$, which agrees within experimental uncertainty.

===== Results =====

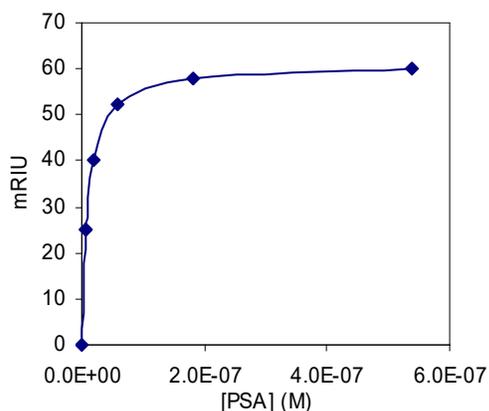
$$a = 61.36 \pm 1.55$$

$$b = 95200000 \pm 10000000$$

sum of squared residuals = 22.66

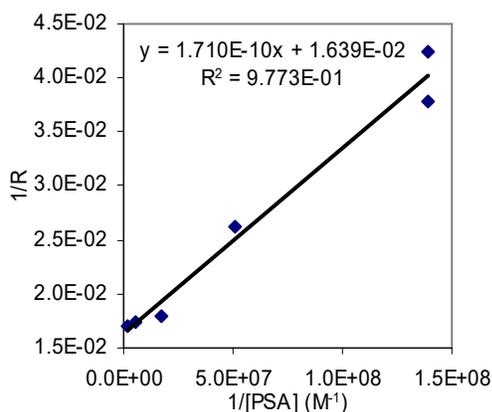
stand. dev. y values = 2.129

correlation between a & b = -0.6582



A double reciprocal plot also works well, but again the nonlinear fit parameters are better because the uncertainties are handled better:

[PSA] (M)	R (μ RIU)	1/[PSA] (M^{-1})	1/R
0	0		
7.18E-09	23.6	1.39E+08	4.24E-02
7.18E-09	26.5	1.39E+08	3.77E-02
1.97E-08	38.0	5.06E+07	2.63E-02
5.92E-08	55.6	1.69E+07	1.80E-02
1.81E-07	57.6	5.52E+06	1.74E-02
5.38E-07	58.8	1.86E+06	1.70E-02



17. The rate of decomposition of NH_3 was determined as a function of the initial partial pressure of H_2 and is inhibited by product formation:⁷

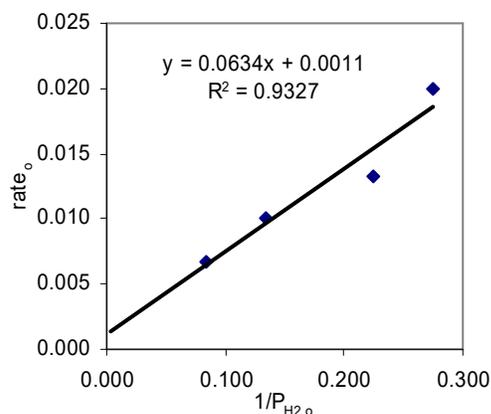


The initial pressure of NH_3 in each run was 100 mm Hg, and varying amounts of H_2 gas were added to the reaction vessel at the beginning of the reaction. The catalyst was platinum and the reaction was run at 1138°C . The results are given below. Show that the dependence on the product, H_2 , partial pressure is described by Eq. 5.5.17.

ΔP_{NH_3} in 120 s	P_{H_2} initially added
33	50
27	75
16	100
10	150

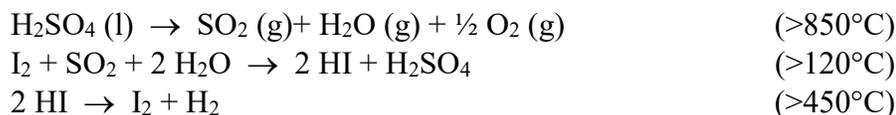
Answer: First we approximate the initial rate as $v_o = \Delta P_{\text{NH}_3}/120 \text{ s}$. Then a plot of the initial rate as a function of $1/P_{\text{H}_2}$ should give a straight line in accordance with Eq. 5.5.17. A spreadsheet was set up and the plot was constructed:

ΔP_{NH_3}	$P_{\text{H}_2,0}$	$v_o \text{ (mm Hg s}^{-1}\text{)}$	$1/P_{\text{H}_2,0}$
33	50	0.275	0.020
27	75	0.225	0.013
16	100	0.133	0.010
10	150	0.083	0.007

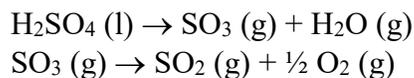


The inverse dependence on P_{H_2} is verified by the linear plot, to within experimental error.

18. Hydrogen is a clean burning substance that is being suggested as a transportation fuel. However, hydrogen is costly to produce. One proposal is to use solar thermal energy to provide the energy necessary to convert water into hydrogen gas. The Sulfur-Iodine cycle consists of three coupled reactions, which add to give the dissociation of water:



The first step is the most unfavorable thermodynamically and kinetically. The reaction occurs in two steps:



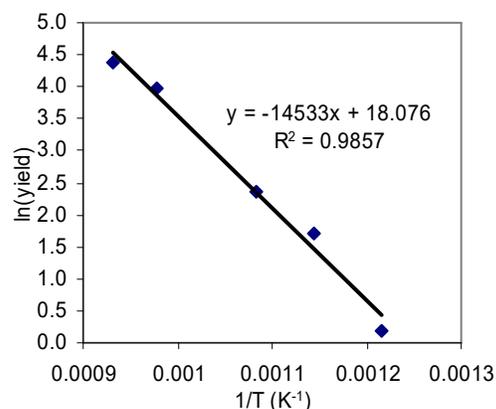
The decomposition of SO_3 has a negligible rate at 800°C without a catalyst. Mixed chromium-iron oxide catalysts have been proposed for the gas phase decomposition of SO_3 .⁸ The heterogeneous decomposition of SO_3 on $\text{Fe}_{1.6}\text{Cr}_{0.4}\text{O}_3$ in a constant flow reactor has been studied as a function of temperature. The percent yields at several temperatures are given in the table, below. The residence time of the reactant in a constant flow reactor is constant with temperature, so the percent yield is directly proportional to the reaction rate. Verify Arrhenius behavior and determine the activation energy.

T ($^\circ\text{C}$)	550	600	650	750	800
SO_2 yield %	1.2	5.5	10.7	52.7	79.3

Answer: The $\ln(\text{rate})$ and $\ln(\text{yield})$ can be used interchangeably for this constant flow reactor data. A plot of $\ln(\text{yield})$ versus $1/T$ will verify Arrhenius behavior with the slope $= -E_a/R$. A spreadsheet was set up, the plot was constructed, and the slope determined using `linest()`:

T (°C)	SO ₂ yield	T (K)	1/T (K ⁻¹)	ln(yield)
550	1.2	823.2	0.001215	0.182
600	5.5	873.2	0.001145	1.705
650	10.7	923.2	0.001083	2.370
750	62.7	1023.2	0.000977	4.138
800	79.3	1073.2	0.000932	4.373

slope	-14532.895	18.076	intercept
±	1011.114	1.087	±
r ²	0.986	0.236	st.dev. Y
F	206.588	3.000	df
SS _{reg}	11.506	0.167	SS _{resid}

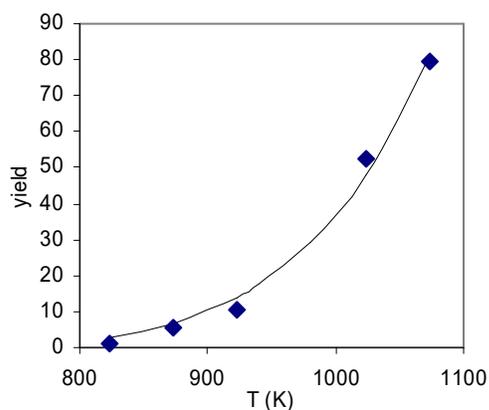


Given the experimental uncertainty, Arrhenius behavior may be justified. The lowest temperature point, which is the point with the largest absolute and relative uncertainty, deviates significantly from the line. Several additional data points at low temperatures would be necessary to judge if systematic curvature exists for the plot. Given Arrhenius behavior, the activation energy is:

$$E_a = -\text{slope } R = 148 \pm 23 \text{ kJ mol}^{-1}$$

The nonlinear fit using the “Nonlinear Least Squares Curve Fitting” applet, however, provides a very important lesson:

```
===== Results =====
a= 4130000 +- 4750000
b= -11630 +- 1200
-----
sum of squared residuals= 43.02
stand. dev. y values= 3.787
correlation between a & b= -0.9994
```



The activation energy from the non-linear fit is $97 \pm 10 \text{ kJ mol}^{-1}$, which is outside the range of the experimental uncertainties. Why the large difference? The correlation coefficient between the fit values is very large at -0.9994 , showing a very strong correlation between the fit values of A and E_A . You wouldn't have noticed this problem without the non-linear fit and you would have underestimated the uncertainty in the activation energy. In fact, using the linearized form of the data in the “Nonlinear Least Squares Curve Fitting” applet using the simple line option, “ $ax + b$ ”, also gives a very large correlation coefficient between the slope and the intercept of -0.9953 . The

results from this experiment are best given as $1 \times 10^2 \text{ kJ mol}^{-1}$ to avoid over-representing the uncertainty.

19. Derive the rate law for a bimolecular heterogeneous reaction with stoichiometry: $A + C \rightarrow P$. Assume that reactant C is strongly adsorbed to the catalytic surface and A is weakly adsorbed.

Answer: The reaction mechanism can be approximated by:



where the surface concentration of C is determined by the rapid pre-equilibrium:



The rate law for the formation of products is constructed similarly to Eq. 5.5.2:

$$\frac{1}{\sigma} \frac{d\xi}{dt} = k_{\sigma} [A]_{\sigma} [C]_{\sigma} \quad 3$$

with the pre-equilibrium concentration of free binding sites dominated by the fractional coverage for C, in analogy with Eq. 5.5.15 :

$$[C]_{\sigma} \approx [B]_{\sigma} \quad 4$$

$$\text{and } [B]_{\sigma} \approx \frac{[B]_{\sigma\sigma}}{b_C P_C} \quad 5$$

with $b_C = k_{Ca}/k_{Cd}$ which is the equilibrium constant for the surface adsorption of C, and P_C the partial pressure for C. The rate law for the formation of A bound on the surface from Eq. 1 is:

$$\frac{d[A]_{\sigma}}{dt} = k_{Aa} [B]_{\sigma} P_A - k_{Ad} [A]_{\sigma} - k_{\sigma} [A]_{\sigma} [C]_{\sigma} = 0 \quad (\text{steady-state}) \quad 6$$

where $[B]_{\sigma}$ is given by Eq. 5. Solving for $[A]_{\sigma}$ using the steady-state approximation and substituting Eq. 5 gives:

$$[A]_{\sigma} = \frac{k_{Aa}}{k_{Ad} - k_{\sigma} [C]_{\sigma}} \frac{[B]_{\sigma\sigma}}{b_C P_C} P_A \quad 7$$

Substitution of Eq. 7 for the surface concentration for A into Eq. 3 and using Eq. 4 for the surface concentration of C gives:

$$\frac{1}{\sigma} \frac{d\xi}{dt} = k_{\sigma} \frac{k_{Aa}}{k_{Ad} - k_{\sigma} [B]_{\sigma\sigma}} \frac{[B]_{\sigma\sigma}}{b_C P_C} P_A [B]_{\sigma\sigma} \quad 8$$

For the rate law with respect to the disappearance of A, using Eq. 5.5.5:

$$-\frac{dP_A}{dt} = k_{\sigma}(RT) \frac{k_{Aa}}{k_{Ad} - k_{\sigma}[B]_{o\sigma}} \frac{\sigma/V [B]_{o\sigma}}{b_C P_C} P_A [B]_{o\sigma} \quad 9$$

Gathering together all of the constants defines the observed rate constant:

$$k_{obs} = k_{\sigma}(RT) \frac{k_{Aa}}{k_{Ad} - k_{\sigma}[B]_{o\sigma}} \frac{\sigma/V [B]_{o\sigma}}{b_C} [B]_{o\sigma} \quad 10$$

and then the final rate law is:

$$-\frac{dP_A}{dt} = k_{obs} \frac{P_A}{P_C} \quad 11$$

In some cases the rate constant for the surface reaction, k_{σ} , is assumed to be very small so that the observed rate constant can be written:

$$k_{obs} = k_{\sigma}(RT) \frac{b_A}{b_C} \sigma/V [B]_{o\sigma}^2 \quad 12$$

where $b_A = k_{Aa}/k_{Ad}$, which is the equilibrium constant for the surface adsorption of A.

20. Determine the integrated rate law for surface catalysis from an adsorbed monolayer using Eq. 5.5.7.

Answer: Starting with Eq. 5.5.7 and separating variables:

$$\frac{1 + b_A P_A}{b_A P_A} dP_A = \left(\frac{1}{b_A P_A} + 1 \right) dP_A = -k dt$$

The integration limits start at $t=0$, $P_A = P_{A0}$:

$$\int_{P_{A0}}^{P_A} \left(\frac{1}{b_A P_A} + 1 \right) dP_A = - \int_0^t k dt$$

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

$$\begin{aligned} \frac{1}{b_A} \ln(P_A|_{P_{A0}}^{P_A} + P_A|_{P_{A0}}^{P_A} &= -kt \\ \frac{1}{b_A} \ln \frac{P_A}{P_{A0}} + (P_A - P_{A0}) &= -kt \end{aligned}$$

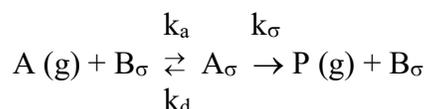
If A is weakly adsorbed, then b_A is small. Notice that if b_A is small, then the $(P_A - P_{A0})$ is negligible compared to the logarithmic term and this last equation reduces to a simple first-order reaction, Eq. 5.5.8:

$$\frac{1}{b_A} \ln \frac{P_A}{P_{A0}} \approx -kt \quad \text{and} \quad \ln \frac{P_A}{P_{A0}} \approx -b_A kt$$

On the other hand, if b_A is large, the logarithmic term is negligible and the reaction is zeroth order, as expected from Eq. 5.5.9:

$$(P_A - P_{A0}) \approx -kt$$

21. We assumed a pre-equilibrium mechanism to determine the rate for a heterogeneously catalyzed reaction according to Eq. 5.5.1:



The rate law for the reaction, in terms of the products is then given by:

$$\frac{d[P]}{dt} = k_\sigma(RT) (\sigma/V) [A]_\sigma$$

To give a better approximation, use the steady-state approximation to determine the rate law. Then show that the more exact rate law reduces to Eq. 5.5.6 using a suitable approximation.

Answer: Eq. 5.5.1 is equivalent to the Michaelis-Menten mechanism, so the derivation for this rate law should be parallel to our previous derivation. The plan is to use the steady-state approximation on $[A]_\sigma$ and then use the mass balance for the total concentration of surface adsorption sites, $[B]_{0\sigma} = [B]_\sigma + [A]_\sigma$, Eq. 5.3.1.

The rate law for the appearance of surface bound A for this mechanism is identical to Eq. 5.5.11:

$$\frac{d[A]_\sigma}{dt} = k_{Aa} [B]_\sigma P_A - k_{Ad} [A]_\sigma - k_\sigma [A]_\sigma \quad 1$$

In steady state, for $[A]_\sigma$ as the reactive intermediate:

$$k_a [B]_\sigma P_A - k_d [A]_\sigma - k_\sigma [A]_\sigma \approx 0 \quad \text{or} \quad [A]_\sigma = \frac{k_a [B]_\sigma P_A}{k_d + k_\sigma} \quad 2$$

Solving the mass balance equation, Eq. 5.3.1, for the concentration of free surface sites gives:

$$[B]_\sigma = [B]_{0\sigma} - [A]_\sigma \quad 3$$

and substitution into Eq. 2 gives:

$$(k_d + k_\sigma)[A]_\sigma = k_a P_A ([B]_{0\sigma} - [A]_\sigma) \quad \text{or} \quad (k_d + k_\sigma + k_a P_A)[A]_\sigma = k_a P_A [B]_{0\sigma} \quad 4$$

Solving for $[A]_\sigma$ gives:

$$[A]_\sigma = \frac{k_a P_A [B]_{0\sigma}}{k_d + k_\sigma + k_a P_A} \quad 5$$

Dividing both numerator and denominator by k_d and using the definition of the Langmuir coefficient, $b_A = k_a/k_d$ gives:

$$[A]_{\sigma} = \frac{b_A P_A [B]_{o\sigma}}{1 + k_{\sigma}/k_d + b_A P_A} \quad 6$$

Substitution of Eq. 6 into the rate law for appearance of product gives the final result:

$$\frac{d[P]}{dt} = k_{\sigma}(RT) (\sigma/V) [A]_{\sigma} = k_{\sigma}(RT) (\sigma/V) \frac{b_A P_A [B]_{o\sigma}}{1 + k_{\sigma}/k_d + b_A P_A} \quad 7$$

If we assume that $k_d \gg k_{\sigma}$ then the k_{σ}/k_d term is negligible and this last equation reduces to the pre-equilibrium mechanism result, Eq. 5.5.6.

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