

Chapter 3 Problems

1. In Example 3.3.1 we discussed denitrification of contaminated ground water. The literature assumes a half-order reaction with respect to NO_3^- , but the differential method for the particular data set gives $3/4$ order. The best fit values for the corresponding rate constants are $k_{1/2} = 26.71$ and $k_{3/4} = 7.12$. Give the units for the rate constants with the concentration expressed in mg L^{-1} .

Answer: For a half-order reaction the rate law is in the form: $-\frac{d[A]}{dt} = k_{1/2} [A]^{1/2}$

The units of the rate, based on the data, are $\text{mg L}^{-1} \text{ hr}^{-1}$. The units of $[A]^{1/2}$ are $\text{mg}^{1/2} \text{ L}^{-1/2}$, giving the rate constant as: $k_{1/2} = 26.71 \text{ mg}^{1/2} \text{ L}^{-1/2} \text{ hr}^{-1}$

For a $3/4$ -order reaction the rate law is in the form: $-\frac{d[A]}{dt} = k_{3/4} [A]^{3/4}$

The units of the rate are $\text{mg L}^{-1} \text{ hr}^{-1}$ and $k_{3/4} = 7.12 \text{ mg}^{1/4} \text{ L}^{-1/4} \text{ hr}^{-1}$.

2. The half-life of the pesticide aldicarb (trade name Temik) is 30.0 days. The decomposition of aldicarb is first-order. Calculate the time necessary for the amount of adicarb in a soil sample to drop to 10.0% of its initial value.

Answer: First we calculate the rate constant and from the integrated rate law, Eq. 3.2.5, solve for the time to achieve $[A] = 0.100 [A]_0$. Solving, Eq. 3.2.11:

$$t_{1/2} = \frac{\ln 2}{k_1} = \frac{0.6931}{k_1} \quad \text{rearranges to} \quad k_1 = \frac{0.6931}{30.0 \text{ days}} = 0.0231 \text{ days}^{-1}$$

Then from Eq. 3.2.5, when $[A] = 0.100 [A]_0$:

$$\ln \left(\frac{0.100 [A]_0}{[A]_0} \right) = -0.0231 \text{ days}^{-1} t$$

$$t = 99.7 \text{ days.}$$

3. Organisms require iron for survival. Reduced iron in the form of Fe^{2+} is readily available for acquisition by living systems. However, Fe^{2+} is oxidized by O_2 from the air to produce Fe^{3+} , which precipitates from solution as mixed hydrated oxides and hydroxides. Iron(II) stability is strongly pH dependent. The oxidation of Fe^{2+} in aqueous 0.5 M HClO_4 solution at 35°C follows the rate law:

$$-\frac{d[\text{Fe}^{2+}]}{dt} = k [\text{Fe}^{2+}]^2 P_{\text{O}_2}$$

where P_{O_2} is the partial pressure of O_2 above the solution and $k = 3.65 \times 10^{-3} \text{ mol}^{-1} \text{ L atm}^{-1} \text{ hr}^{-1}$. Assume that the air above the solution is at constant $P_{\text{O}_2} = 0.200 \text{ atm}$. (a) Calculate the half-time of the reaction in days for an initial concentration of 0.100 M Fe^{2+} . (b) How long would it take for the concentration of Fe^{2+} to drop to 0.0100 M?

Answer: For a constant P_{O_2} the reaction is pseudo-second order with effective rate constant, $k_{\text{eff}} = k P_{O_2} = 7.30 \times 10^{-4} \text{ mol}^{-1} \text{ L hr}^{-1}$.

(a) The half-time is given by Eq. 3.2.30:

$$t_{1/2} = \frac{1}{[A]_0 k_{\text{eff}}} = \frac{1}{0.100 \text{ M}(7.30 \times 10^{-4} \text{ mol}^{-1} \text{ L hr}^{-1})} = 1.370 \times 10^4 \text{ hr} = 571 \text{ days}$$

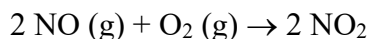
(b) The integrated rate law is given by Eq. 3.2.27 with $[A] = 0.0100 \text{ M}$:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k_{\text{eff}} t$$

or
$$\frac{1}{0.0100 \text{ M}} - \frac{1}{0.100 \text{ M}} = (7.30 \times 10^{-4} \text{ mol}^{-1} \text{ L hr}^{-1}) t$$

Solving for t : $t = 1.233 \times 10^5 \text{ hr} = 5.14 \times 10^3 \text{ days}$. Unfortunately for living organisms, the half-life of Fe^{2+} at neutral pH is many orders of magnitude shorter.

4. The concentration of ozone, O_3 , in the stratosphere is dependent on interactions with the odd electron reactive nitrogen species, NO. The concentration of NO in the atmosphere is determined in part by the rate of oxidation by O_2 :



An initial rate study at 25°C was completed with the following results. Determine the rate law and the rate constant. The initial rate is the slope of the time course for very short times, $t \approx 0$:

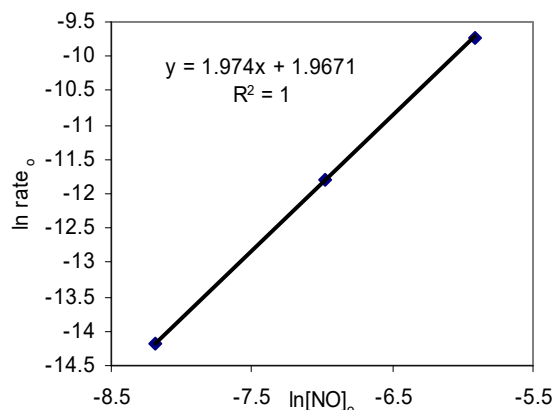
initial rate = $v_o = -\left(\frac{d[\text{O}_2]}{dt}\right)_0$	Exp	$[\text{O}_2]_0 \text{ (mol L}^{-1}\text{)}$	$[\text{NO}]_0 \text{ (mol L}^{-1}\text{)}$	$v_o \text{ (mol L}^{-1} \text{ s}^{-1}\text{)}$
	1	1.44×10^{-3}	0.28×10^{-3}	6.90×10^{-7}
	2	1.44×10^{-3}	0.93×10^{-3}	7.50×10^{-6}
	3	1.44×10^{-3}	2.69×10^{-3}	6.00×10^{-5}
	4	6.60×10^{-5}	2.69×10^{-3}	3.00×10^{-6}

Answer: The order with respect to O_2 can be calculated from experiments 3 and 4. Just looking at the ratios, since they are about equal, first-order behavior is indicated. To be more precise, using Eq. 3.3.4 gives:

$$\begin{aligned} \ln\left(\frac{v_{o2}}{v_{o1}}\right) &= n \ln\left(\frac{[A]_{o2}}{[A]_{o1}}\right) \\ \ln\left(\frac{3.00 \times 10^{-6}}{6.00 \times 10^{-5}}\right) &= n \ln\left(\frac{6.60 \times 10^{-5}}{1.44 \times 10^{-3}}\right) \\ -2.996 &= n(-3.083) \quad \text{or } n = 0.972 \end{aligned}$$

To determine the order with respect to NO we could just do the same. In fact with just three data points, using Eq. 3.3.4 is the best approach. But, if we did have more data points a curve fitting approach would make better use of the experimental uncertainties. So as an example, a spreadsheet was constructed based on the left and right-hand sides of Eq. 3.3.4:

[NO] _o	rate _o	ln[NO] _o	ln rate _o
2.80E-04	6.90E-07	-8.1807	-14.187
9.30E-04	7.50E-06	-6.9803	-11.801
2.69E-03	6.00E-05	-5.9182	-9.7212

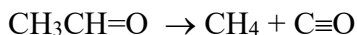


The order with respect to NO is then 1.97, which rounds to 2. It would be silly to do any serious error analysis using `linest()` with only three data points. So we won't bother, other than using significant figure rules. The ln values are good to 2-3 significant figures, so the final order is good to about 2-3 significant figures. The rate law is then: $v = k_3 [\text{O}_2][\text{NO}]^2$. The rate constant can be calculated from each run and then the averaged result can be calculated. Using run 1:

$$v = k_3 [\text{O}_2][\text{NO}]^2$$

gives $6.90 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} = k_3 (1.44 \times 10^{-3} \text{ mol L}^{-1})(0.28 \times 10^{-3} \text{ mol L}^{-1})^2$
solving for k_3 : $k_3 = 6.11 \times 10^3 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$

5. The decomposition of acetaldehyde:



at 518°C and at an initial pressure of 363 mm Hg can be monitored by measuring the total pressure of the reaction at constant volume.¹ What is the order of the reaction and the rate constant? Use non-linear curve fitting. [Hint: you need to solve for the partial pressure of acetaldehyde from the total pressure.]

t (s)	42	73	105	190	242	310
P (mm Hg)	397	417	437	477	497	517
t (s)	384	480	665	840	1070	1440
P (mm Hg)	537	557	587	607	627	647

Answer: The total pressure during the reaction is the sum for the reactants and products:

$$P = P_{\text{CH}_3\text{CHO}} + P_{\text{CH}_4} + P_{\text{CO}} \quad 1$$

The stoichiometric relationships for the initial pressure, P_o , give:

$$\begin{array}{l} \text{CH}_3\text{CH}=\text{O} \rightarrow \text{CH}_4 + \text{C}\equiv\text{O} \\ P_i : \quad P_o - \xi \quad \quad \xi \quad \quad \xi \end{array} \quad 2$$

Substituting these values into the total pressure gives:

$$P = P_o - \xi + \xi + \xi = P_o + \xi \quad 3$$

solving for ξ gives:

$$\xi = P - P_o \text{ and then } P_{\text{CH}_3\text{CHO}} = P_o - \xi = 2 P_o - P \quad 4$$

The transformation from Eq. 4 was used in an Excel spreadsheet to calculate the acetaldehyde partial pressures:

t (s)	P (mm Hg)	2P _o -P (mm Hg)
0	363	363
42	397	329
73	417	309
105	437	289
190	477	249
242	497	229
310	517	209
384	537	189
480	557	169
665	587	139
840	607	119
1070	627	99
1440	647	79

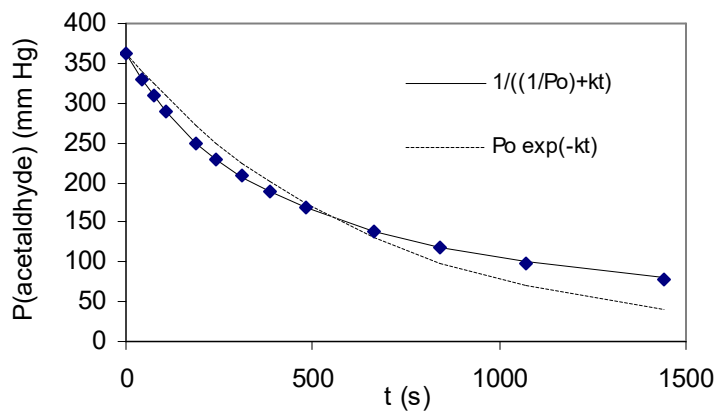
Using the “Nonlinear Least Squares Curve Fit” applet on the text book Web site and on the companion CD with the “a exp(–bx)” fitting function for a first-order fit gives:

```
===== Results =====
a= 337.6 +- 8.8
b= 0.00133 +- 0.000091
-----
sum of squared residuals= 2912
stand. dev. y values= 16.27
correlation between a & b= 0.6541
```

Using the “1/((1/a)+bx)” fitting function for a second-order fit gives:

```
===== Results =====
a= 363.24 +- 0.76
b= 0.000006674 +- 3.5e-8
-----
sum of squared residuals= 13.9
stand. dev. y values= 1.124
correlation between a & b= 0.5758
```

The corresponding plots are:



The second-order fit is much better, giving the rate constant as:

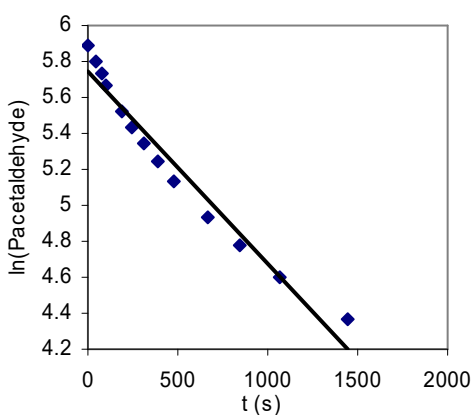
$$k = 6.674 \times 10^{-6} \pm 0.035 \times 10^{-6} \text{ mm Hg}^{-1} \text{ s}^{-1}.$$

6. Redo the kinetic analysis for the data from Problem 5 using the linearized forms of the integrated rate laws.

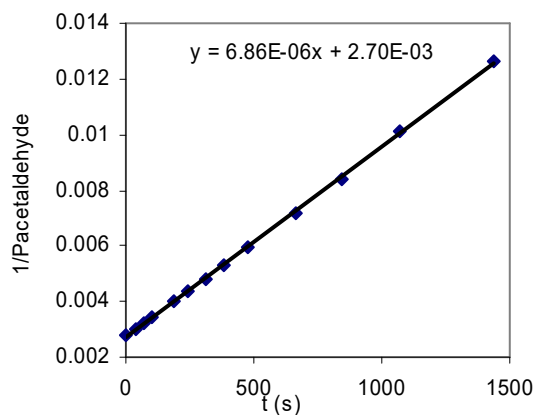
Answer: The data transformations using Eqs. 3.2.18 and 3.2.25 are given below as an Excel spreadsheet:

t (s)	P (mm Hg)	2P _o -P (mm Hg)	ln(P _{CH₃CHO})	1/P _{CH₃CHO}
0	363	363	5.894	0.0027548
42	397	329	5.796	0.0030395
73	417	309	5.733	0.0032362
105	437	289	5.666	0.0034602
190	477	249	5.517	0.0040161
242	497	229	5.434	0.0043668
310	517	209	5.342	0.0047847
384	537	189	5.242	0.005291
480	557	169	5.13	0.0059172
665	587	139	4.934	0.0071942
840	607	119	4.779	0.0084034
1070	627	99	4.595	0.010101
1440	647	79	4.369	0.0126582

The corresponding plots are:



(a) First-order plot



(b) Second-order plot

The output from the linest() spreadsheet linear fit for the second-order plot is:

slope	6.864E-06	2.703E-03	intercept
±	3.745E-08	2.312E-05	±
r ²	0.99967	5.715E-05	st.dev. y
F	33585.36	11	df
SS _{reg}	1.097E-04	3.593E-08	SS _{resid}

The reaction is second order with a rate constant of $6.864 \times 10^{-6} \pm 0.037 \times 10^{-6} \text{ mm Hg}^{-1} \text{ s}^{-1}$. Notice that the difference between the non-linear fit rate constant and this current value is greater than

the estimated uncertainty. This underestimate of the uncertainty from the linearized forms is another reason to rely on non-linear curve fitting, which has a firmer statistical basis. The reason for the better statistical treatment is that the random errors are evaluated directly and not in the transformed $1/P$ form.

7. Use the differential method during the time course for the data in Problem 5.

Answer: First note that $v = -dP_{\text{CH}_3\text{CHO}}/dt$. We next need to calculate the average rate for each time interval. For example, for the first interval:

$$\bar{v} = -\frac{P_i(t_2) - P_i(t_1)}{t_2 - t_1} = -\frac{329 - 363}{42 - 0} = 0.8095 \text{ mm Hg s}^{-1}$$

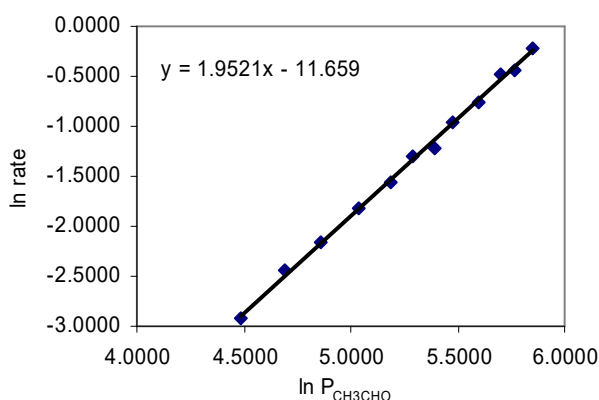
and the partial pressure in the middle of this first time interval is:

$$\bar{P}_{\text{CH}_3\text{CHO}} = \frac{P_i(t_1) + P_i(t_2)}{2} = \frac{329 + 363}{2} = 346 \text{ mm Hg}$$

A spreadsheet was constructed with rates and average acetaldehyde partial pressures, as shown below. The \ln of the average partial pressure and the \ln of the rate are also included.

t (s)	$2P_o - P$ (mm Hg)	average rate	average $P_{\text{CH}_3\text{CHO}}$	$\ln P_{\text{CH}_3\text{CHO}}$	$\ln \text{rate}$
0	363				
42	329	0.8095	346	5.8464	-0.2113
73	309	0.6452	319	5.7652	-0.4383
105	289	0.6250	299	5.7004	-0.4700
190	249	0.4706	269	5.5947	-0.7538
242	229	0.3846	239	5.4765	-0.9555
310	209	0.2941	219	5.3891	-1.2238
384	189	0.2703	199	5.2933	-1.3083
480	169	0.2083	179	5.1874	-1.5686
665	139	0.1622	154	5.0370	-1.8192
840	119	0.1143	129	4.8598	-2.1691
1070	99	0.0870	109	4.6913	-2.4423
1440	79	0.0541	89	4.4886	-2.9178

The plot of $\ln(\text{rate})$ versus $\ln P$ is given below:



The output from the `linest()` spreadsheet linear fit is:

slope	1.9521	-11.659	intercept
\pm	0.0303	0.1603	\pm
r^2	0.9976	0.0439	st.dev. y
F	4159	10	df
SS _{reg}	8.0012	0.0192	SS _{resid}

The reaction order is 1.95 ± 0.03 , which is close enough to the integer 2.

You'll probably agree that the non-linear curve fitting method is easiest, followed by the linearized equation fitting. However, the differential method is somewhat less susceptible to problems arising from offsets than the linearized methods.

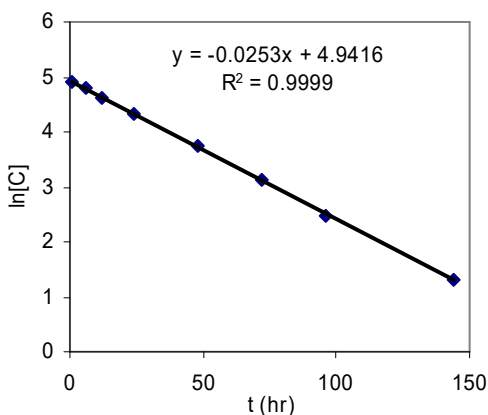
8. Pharmacokinetics is the study of the absorption, disposition, metabolism, and excretion (ADME) of drugs in living organisms. Pharmacokinetics uses chemical kinetics as a tool to predict drug levels in the body and anticipate drug distribution problems that might arise. Your study of chemical kinetics puts you in a good position to understand ADME properties of drug substances. In the terminology of pharmacology, a bolus dose is a drug given in a short period of time, for example by intravenous injection or oral tablet administration. The table, below, gives the plasma concentration as a function of time for the administration of a 184-mg bolus dose of ceftriaxone to a newborn infant.^{2,3} Ceftriaxone is an antibiotic. Find the effective kinetic order for the time course of the drug concentration, the rate constant, and half-life of the drug in the body.

t (hr)	1.0	6.0	12.	24.	48.	72.	96.	144.
Concentration (mg L ⁻¹)	137.	120.	103.	76.	42.	23.	12.	3.7

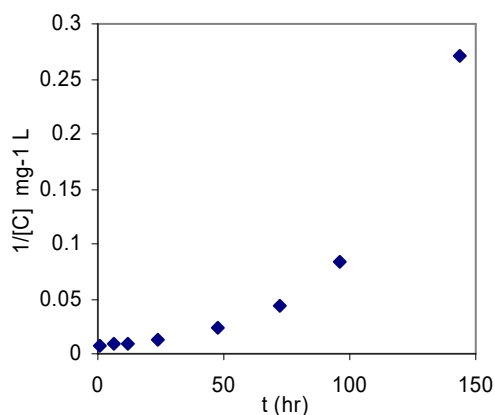
Answer: To construct kinetic plots based on the linear forms of the integrated rate laws, Eq. 3.2.18 for first-order and Eq. 3.2.27 for second-order, the following spreadsheet was constructed:

t (hr)	[C] (mg L ⁻¹)	ln [C]	1/[C]
1	137	4.919981	0.007299
6	120	4.787492	0.008333
12	103	4.634729	0.009709
24	76	4.330733	0.013158
48	42	3.73767	0.02381
72	23	3.135494	0.043478
96	12	2.484907	0.083333
144	3.7	1.308333	0.27027

The corresponding plots are given below:



(a) first-order plot



(b) second-order plot

The output from the `linest()` linear least squares curve fitting function in Excel for the first-order plot is:

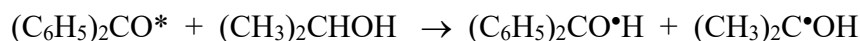
slope	-0.02529	4.941594	intercept
±	0.000109	0.007509	±
r ²	0.999889	0.014537	st. dev. Y
F	54177.75	6	df
SS _{reg}	11.44938	0.001268	SS _{residuals}

The plasma concentrations clearly decrease by first-order kinetics. The slope of the $\ln[C]$ versus t curve gives the rate constant: slope = $-k_1$. The half-time for a first-order reaction is given by $t_{1/2} = \ln(2)/k_1$. The final results are then:

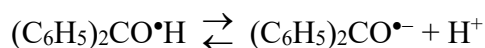
$$k_1 = 0.02529 \pm 0.00011 \text{ hr}^{-1} \quad \text{and} \quad t_{1/2} = \ln(2)/k_1 = 0.6931/0.02529 = 27.4 \pm 0.1 \text{ hr}$$

The uncertainty in the half-time was calculated from the relative standard deviation in the slope, which is 0.43 %. In other words the relative uncertainty in $1/x$ is the relative uncertainty in x , since multiplication and division are involved.

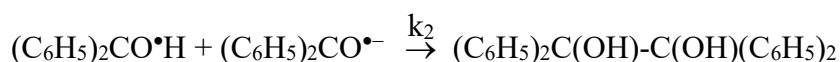
9. The absorption of UV light by benzophenone creates a long-lived excited state. When isopropanol-water mixtures are used as the solvent, the excited state of benzophenone rapidly reacts with isopropanol to produce protonated benzophenone ketyl ($(\text{C}_6\text{H}_5)_2\text{CO}^*\text{H}$), which is a free radical:



The “*” indicates an electronic excited state. In basic solution protonated benzophenone ketyl rapidly loses a proton to produce the benzophenone ketyl radical anion:

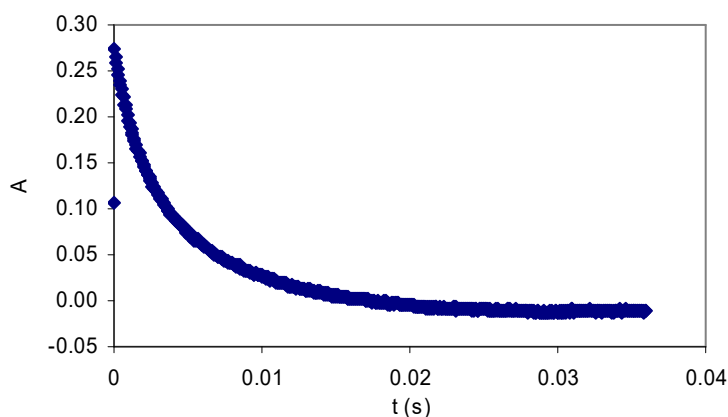


The benzophenone ketyl radical anion then reacts with the protonated form to produce benzpinacol:

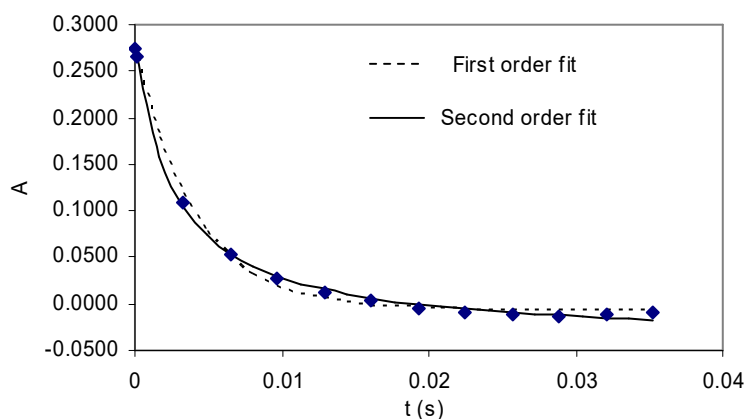


The benzophenone ketyl radical anion has an absorption maximum at 630 nm, which allows the disappearance of the radical anion to be followed as a function of time in a laser flash photolysis instrument. The absorbance time course for the reaction is given below. The data table is extracted from the much larger data file from the instrument, which is plotted at right. Find the order of the reaction and the rate constant with respect to benzophenone ketyl radical anion using non-linear least squares curve fitting.

t (ms)	A
0.064	0.2736
0.128	0.2660
3.264	0.1080
6.464	0.0540
9.664	0.0282
12.864	0.0129
16.064	0.0029
19.264	-0.0039
22.464	-0.0084
25.664	-0.0109
28.864	-0.0125
32.064	-0.0111
35.264	-0.0102



Answer: The long-time portion of the absorbance time course is negative, which shows that the data has a constant offset. That is, A_{∞} in Eq. 3.2.38 is negative. The long-time behavior of the time course has some low frequency noise, such that the time course has a minimum before the end of the time course. This level of noise is common for real world kinetics runs. The noise makes the determination of A_{∞} in Eq. 3.2.38 very difficult. Therefore, the curve fit equations chosen included a constant offset as a fit parameter. The data table was pasted into the “Nonlinear Least Squares Curve Fitting” applet, which is available on the textbook companion Web site and the and on the companion CD. For first-order fitting, Eq. 3.2.6 with a constant offset, is the “ $a \exp(-bx) + c$ ” option. For second-order curve fitting, Eq. 3.2.26 with a constant offset, is the “ $1/((1/a)+bx) + c$ ” option. The results are plotted below.



The first-order fit results are:

```

===== Results =====
a= 0.2821 +- 0.0051
b= 242 +- 12
c= -0.0076 +- 0.0025
-----
sum of squared residuals= 0.0003994
stand. dev. y values= 0.00632
correlation between a & b= 0.05997
correlation between b & c= 0.5454
correlation between a & c= -0.4078

```

The second-order fit results are:

```

===== Results =====
a= 0.3208 +- 0.0031
b= 1180 +- 6.3
c= -0.0395 +- 0.0023
-----
sum of squared residuals= 0.0001139
stand. dev. y values= 0.003375
correlation between a & b= -0.4096
correlation between b & c= 0.8893
correlation between a & c= -0.5629

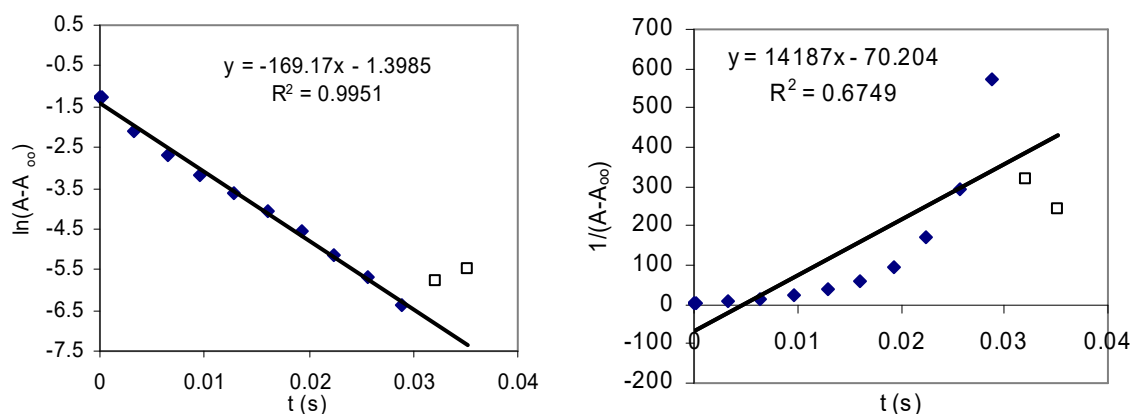
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The second-order fit appears to reproduce the time-course better. In addition, in agreement with our visual inspection, the standard deviation of the y values for the second-order plot, 0.003375, is about half that for the first-order plot. The effective second-order rate constant is $1180 \pm 6 \text{ s}^{-1}$. Note that a second-order rate constant should have units $\text{M}^{-1} \text{ s}^{-1}$. Because the absorbance is plotted instead of the actual concentration, an effective rate constant using Eq. 3.2.37 is the result, $k_{\text{eff}} = k_2/\epsilon b$, which has units of s^{-1} . Absorbance is unitless. To distinguish this result from a first-order rate constant you might give the result as $1180 \pm 6 \text{ au}^{-1} \text{ s}^{-1}$, where “au” stands for absorbance units (which are officially unitless). The fit parameter correlation coefficients are acceptable. However, notice that the “correlation between b & c= 0.8893” value shows that final rate constant is very dependent on the choice of the offset constant, A_∞ .

10. Use the data in the last problem with linear curve fitting to determine the order of the reaction and the rate constant.

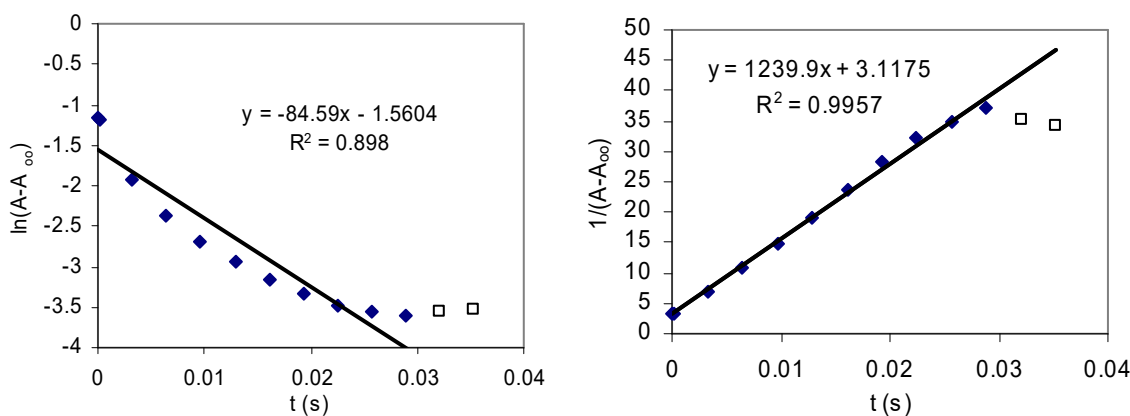
Answer: In the last problem, the long-time portion of the absorbance time course is negative, which shows that the data has a constant offset. The difficulty in using the linear integrated rate law forms, Eq. 3.2.18 for first-order and Eq. 3.2.27 for second-order, is that the constant offset must be handled explicitly. As a first approach, choose the minimum value for the offset, $A_\infty = -0.0125$. Then the corresponding data point can't be used in the fit, since $\ln 0$ is undefined. A spreadsheet that is set up to do the transformations is given below with the resulting curve fits:

t (s)	A	A - A_∞	$\ln[A]$	$1/[A]$
0.000064	0.2736	0.2861	-1.251	3.4956
0.000128	0.2660	0.2785	-1.278	3.5910
0.003264	0.1080	0.1205	-2.116	8.3002
0.006464	0.0540	0.0665	-2.710	15.031
0.009664	0.0282	0.0407	-3.202	24.600
0.012864	0.0129	0.0254	-3.672	39.337
0.016064	0.0029	0.0154	-4.173	64.968
0.019264	-0.0039	0.0086	-4.761	116.897
0.022464	-0.0084	0.0041	-5.508	246.592
0.025664	-0.0109	0.0016	-6.445	629.445



The last two data points are included in the plot to show the effect of noise, but they weren't used in the curve fitting. Notice that these plots predict a first-order reaction in contradiction to Problem 5. If instead of the minimum value from the time course, the A_{∞} value from the non-linear curve fits is used, $A_{\infty} = -0.0395$, then the following plots are obtained:

t (s)	A	A - A_{∞}	$\ln[A]$	$1/[A]$
0.000064	0.2736	0.3131	-1.161	3.1941
0.000128	0.2660	0.3055	-1.185	3.2736
0.003264	0.1080	0.1475	-1.914	6.7806
0.006464	0.0540	0.0935	-2.369	10.691
0.009664	0.0282	0.0677	-2.693	14.780
0.012864	0.0129	0.0524	-2.948	19.076
0.016064	0.0029	0.0424	-3.160	23.589
0.019264	-0.0039	0.0356	-3.336	28.125
0.022464	-0.0084	0.0311	-3.471	32.200



In which case the reaction appears to be second-order with a rate constant of 1240 s^{-1} (please see the answer to the last problem concerning units). This problem shows that non-linear curve fitting is often the best method. If you choose an incorrect value for the long time value, the resulting kinetic plots can be so distorted that you determine the incorrect order. Non-linear curve fitting provides a non-biased method to determine the long time value because A_{∞} can be treated as an adjustable parameter.

11. Determine the fluorescence lifetime for anthracene using the following fluorescence intensity measurements.

t (ns)	0	2	4	6	8	10
Intensity	62620	41250	27218	17708	11352	7560

Answer: First convert the times from nano-seconds to seconds. Using the “Nonlinear Least Squares Curve Fit” applet on the text book Web site and on the companion CD with the “a exp(–bx)” fitting function for a first-order fit gives:

```

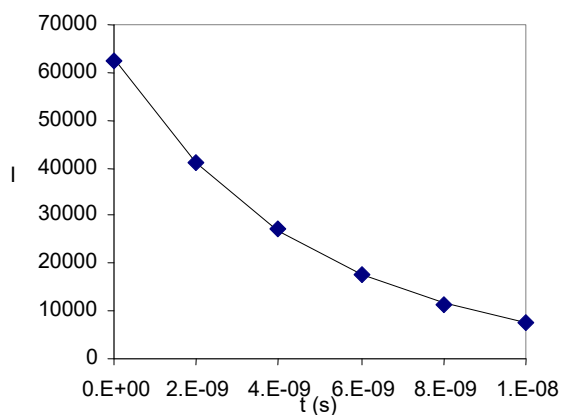
===== Results =====
a= 62720 +- 170
b= 210700000.0 +- 1100000
-----
sum of squared residuals= 145100
stand. dev. y values= 190.5
correlation between a & b= 0.5655

```

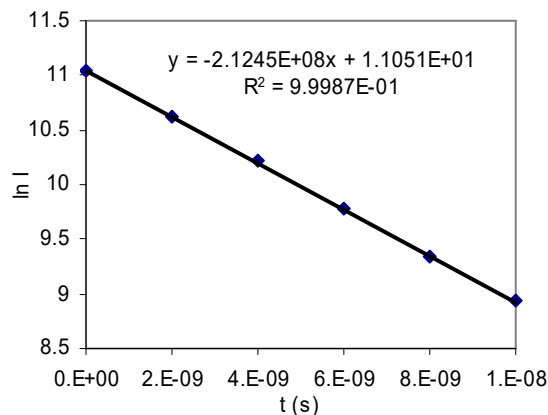
with the fluorescence lifetime τ from the slope: $\tau = 2.11 \times 10^8 \pm 0.011 \times 10^8 \text{ s}^{-1}$. You could also do the linear fit as $\ln I$ versus t using the following spreadsheet.

t (s)	Intensity	ln I
0.00E+00	62620	11.04483999
2.00E-09	41250	10.62740639
4.00E-09	27218	10.2116338
6.00E-09	17708	9.781771794
8.00E-09	11352	9.337149219
1.00E-08	7560	8.930626469

The plot from the non-linear fit and the linear version are shown below:



(a) Non-linear fit



(b) First-order plot

12. Determine the integrated rate law for a zeroth-order reaction with stoichiometry $2 A \rightarrow P$. Use definite integrals. Zeroth-order reactions are common with reactions involving surfaces. Find the half-time for a zeroth-order reaction with this stoichiometry.

Answer: The rate law is $-\frac{1}{2} \frac{d[A]}{dt} = k_o$.

The rate of the reaction is independent of the amount of reactant. Separation of variables to isolate all concentration dependent terms on the left side of the equality and all the time dependent terms on the right side gives:

$$d[A] = -2k_o dt$$

The integral limits are at $t = 0$, $[A] = [A]_o$, and at time t the concentration is $[A]$. The definite integrals are:

$$\int_{[A]_o}^{[A]} d[A] = - \int_0^t 2k_o dt$$

The integrals are:

$$[A] \Big|_{[A]_o}^{[A]} = -2k_o t \Big|_0^t$$

Evaluating the integrals at the limits gives:

$$[A] - [A]_o = -2k_o t$$

This equation can be rearranged into the linear form by adding $[A]_o$ to both sides:

$$[A] = [A]_o - 2k_o t$$

which has slope $= -2k_o$ and intercept $[A]_o$. The half-time is when $[A] = [A]_o/2$:

$$[A]_o/2 - [A]_o = -2k_o t_{1/2}$$

Solving for the half-time:

$$t_{1/2} = \frac{[A]_o}{4k_o} \quad (\text{for } 2 A \rightarrow P)$$

The half-time is greater when you start with more material, since the rate of the reaction is independent of the starting amount.

13. The half-time for a chemical reaction is the time when $\frac{1}{2}$ the original amount of reactant remains. However, the choice of the half-time point as a measure of the reaction rate is not unique. We can also determine the time when $\frac{1}{4}$ of the original amount remains, or when $1/p$ of the original amount remains. Find the formula that relates the time to reach the $1/p$ point to the rate constant, for a first-order and a second-order reaction.

Answer: For a first order reaction, starting with the integrated rate law in the form, Eq. 3.2.5:

$$\ln \left(\frac{[A]}{[A]_o} \right) = -k_1 t$$

The $1/p$ time corresponds to the concentration of a dropping to $[A] = [A]_o/p$. Substituting into the integrated rate law gives:

$$\ln \left(\frac{[A]_0/p}{[A]_0} \right) = -k_1 t_{1/p}$$

Simplifying the ln term:

$$\ln \left(\frac{[A]_0/p}{[A]_0} \right) = \ln(1/p) = -\ln p$$

Then solving for $t_{1/p}$ gives:

$$t_{1/p} = \frac{\ln p}{k_1}$$

which for $p = 2$ reduces to Eq. 3.2.11. As an example, assume that the half-time for a first order reaction is $t_{1/2} = 10$ s, or $k_1 = 0.0693 \text{ s}^{-1}$. The $1/4$ time would occur at 20 s, which is $2 t_{1/2}$, and the $1/8$ time at 30 s, which is $3 t_{1/2}$.

For a second-order reaction, from Eq. 3.2.27:

$$\frac{1}{[A]_0/p} - \frac{1}{[A]_0} = k_2 t_{1/p}$$

Simplifying the left-hand side gives:

$$\frac{1}{[A]_0/p} - \frac{1}{[A]_0} = \frac{p}{[A]_0} - \frac{1}{[A]_0} = \frac{p-1}{[A]_0} = k_2 t_{1/p}$$

Solving for the $1/p$ time gives:

$$t_{1/p} = \frac{p-1}{[A]_0 k_2}$$

which reduces to Eq. 3.2.30 when $p = 2$. As an example, assume that the half-time for a second order reaction is $t_{1/2} = 10$ s. The $1/4$ time would occur at 30 s and the $1/8$ time at 70 s.

14. Determine the integrated rate law and the half-time for a third-order reaction with the stoichiometry $A \rightarrow P$.

Answer: The rate law is:

$$-\frac{d[A]}{dt} = k_3 [A]^3$$

Separation of variables to isolate all concentration dependent terms on the left side of the equality and all the time dependent terms on the right side gives:

$$-\frac{d[A]}{[A]^3} = k_3 dt$$

The indefinite integrals are:

$$-\int \frac{1}{[A]^3} d[A] = \int k_3 dt$$

Note that $-\int \frac{1}{x^3} dx = \frac{1}{2x^2}$

Combining the integration constants:

$$\frac{1}{2[A]^2} = k_3 t + c$$

The boundary condition is at $t = 0$, $[A] = [A]_0$, the initial concentration:

$$c = \frac{1}{2[A]_0^2}$$

Substituting the integration constant back in to the integrated rate law gives the linear form:

$$\frac{1}{2[A]^2} = k_3 t + \frac{1}{2[A]_0^2}$$

Rearranging gives the standard form often seen in texts:

$$\frac{1}{2[A]^2} - \frac{1}{2[A]_0^2} = k_3 t$$

Or solving for the time course gives:

$$[A] = \frac{1}{\left(\frac{1}{[A]_0^2} + 2k_3 t\right)^{1/2}}$$

For the half-time:

$$\frac{1}{2([A]_0/2)^2} - \frac{1}{2[A]_0^2} = \frac{2}{[A]_0^2} - \frac{1}{2[A]_0^2} = \frac{3}{2[A]_0^2} = k_3 t_{1/2}$$

Solving for the half-time gives:

$$t_{1/2} = \frac{3}{2[A]_0^2 k_3}$$

15. Determine the integrated rate law for a half-order reaction with the stoichiometry $A \rightarrow P$.

Answer: The rate law is:

$$-\frac{d[A]}{dt} = k_{1/2} [A]^{1/2}$$

Separation of variables to isolate all concentration dependent terms on the left side of the equality and all the time dependent terms on the right side gives:

$$-\frac{d[A]}{[A]^{1/2}} = k_{1/2} dt$$

The indefinite integrals are:

$$\int \frac{1}{[A]^{1/2}} d[A] = -\int k_{1/2} dt$$

Note that $\int \frac{1}{x^{1/2}} dx = 2 x^{1/2}$ or conversely in proof: $\frac{d(2 x^{1/2})}{dx} = x^{-1/2}$

Combining the integration constants:

$$2 [A]^{1/2} = -k_{1/2}t + c$$

The boundary condition is at $t = 0$, $[A] = [A]_0$, the initial concentration:

$$c = 2 [A]_0^{1/2}$$

Substituting the integration constant back in to the integrated rate law gives the linear form:

$$2 [A]^{1/2} = -k_{1/2}t + 2 [A]_0^{1/2} \quad \text{and} \quad [A]^{1/2} = -\frac{k_{1/2}}{2} t + [A]_0^{1/2}$$

Solving for the time course gives:

$$[A] = \left([A]_0^{1/2} - \frac{k_{1/2}}{2} t \right)^2$$

16. In biology, exponential population growth arises from the rate law:

$$\frac{d[P]}{dt} = k [P]$$

where $[P]$ is the population of a given organism and $d[P]/dt$ is the birth rate. In short, the greater the number of individuals the greater the birth rate. Find the integrated rate law for the population.

Answer: Separation of variables to isolate all concentration dependent terms on the left side of the equality and all the time dependent terms on the right side gives:

$$\frac{1}{[P]} d[P] = k dt$$

The indefinite integrals are:

$$\int \frac{1}{[P]} d[P] = \int k dt$$

Integrating and combining the integration constants gives:

$$\ln [P] = kt + c$$

The boundary condition is at $t = 0$, $[P] = [P]_0$; if you don't start with at least a few individuals, there can be no population growth. Evaluating the integration constant:

$$c = \ln [P]_0$$

Substituting the integration constant back into the integrated rate law gives:

$$\ln [P] = kt + \ln [P]_0$$

Combining the \ln terms gives:

$$\ln [P] - \ln [P]_0 = kt \quad \text{or} \quad \ln \frac{[P]}{[P]_0} = kt$$

Solving for the population gives:

$$[P] = [P]_0 e^{kt}$$

which is Malthusian exponential population growth.

17. Determine the integrated rate law for a $3/4$ -order reaction with the stoichiometry $A \rightarrow P$.

Answer: The rate law is:

$$-\frac{d[A]}{dt} = k_{3/4} [A]^{3/4}$$

Separation of variables to isolate all concentration dependent terms on the left side of the equality and all the time dependent terms on the right side gives:

$$-\frac{d[A]}{[A]^{3/4}} = k_{3/4} dt$$

The indefinite integrals are:

$$\int \frac{1}{[A]^{3/4}} d[A] = -\int k_{3/4} dt$$

Note that $\int \frac{1}{x^{3/4}} dx = 4 x^{1/4}$ or conversely in proof: $\frac{d(4 x^{1/4})}{dx} = x^{-3/4}$

Combining the integration constants:

$$4 [A]^{1/4} = -k_{3/4}t + c$$

The boundary condition is at $t = 0$, $[A] = [A]_0$, the initial concentration:

$$c = 4 [A]_0^{1/4}$$

Substituting the integration constant back in to the integrated rate law gives the linear form:

$$4 [A]^{1/4} = -k_{3/4}t + 4 [A]_0^{1/4} \quad \text{and} \quad [A]^{1/4} = -\frac{k_{3/4}}{4}t + [A]_0^{1/4}$$

Solving for the time course gives:

$$[A] = \left([A]_0^{1/4} - \frac{k_{3/4}}{4}t \right)^4$$

18. In Example 3.3.1 we discussed denitrification of contaminated ground water. The literature assumes a half-order reaction with respect to NO_3^- , but the differential method for the data set gives $3/4$ order. Plot the time course for a $1/2$ -order and a $3/4$ -order reaction using $[\text{NO}_3^-]_0 = 409 \text{ mg L}^{-1}$ for 0 hr to 1.7 hr. Include the data points from Example 3.3.1. The best fit values for the rate constants are $k_{1/2} = 26.71 \text{ mg}^{-1/2} \text{ L}^{1/2} \text{ hr}^{-1}$ and $k_{3/4} = 7.12 \text{ mg}^{-3/4} \text{ L}^{3/4} \text{ hr}^{-1}$. [Hint: restrict the time interval for the half-order plot so that $([A]_0^{1/2} - k_{1/2}t/2) \geq 0$ or for the $3/4$ -order plot, $([A]_0^{1/4} - k_{3/4}t/4) \geq 0$]

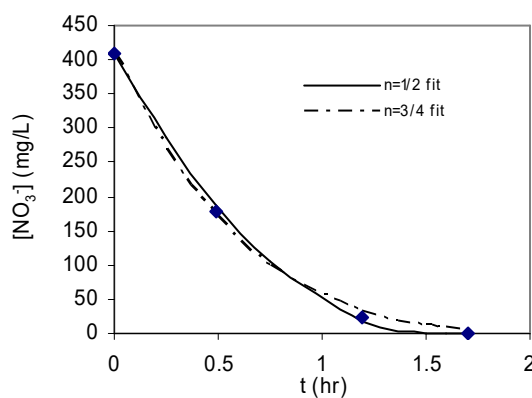
Answer: The following spreadsheet was set up using the equations from Problems 15 and 17, or alternatively from the Chapter Summary Table:

$$\text{For } 1/2\text{-order: } [A] = \left([A]_0^{1/2} - \frac{k_{1/2}}{2}t \right)^2$$

$$\text{For } 3/4\text{-order: } [A] = \left([A]_0^{1/4} - \frac{k_{3/4}}{4}t \right)^4$$

A spreadsheet based on these equations and the corresponding plot is:

t (hr)	$[\text{NO}_3^-]$	n=1/2 fit	n=3/4 fit
0	409	409	409
0.25		285.11	269.53
0.49	178.2	187.14	172.56
0.75		104.20	99.88
1.19	23.8	18.76	31.96
1.5		0.04	11.11
1.6		0	7.37
1.7	0	0	4.66



The values for the half-order fit for 1.6 and 1.7 hr were just manually set to zero since $([A]_0^{1/2} - k_{1/2}t/2)$ was negative for these times. The plots show that both orders fit fairly well. The key time range for determining the correct order is the long-time region where the concentrations get close to zero. More data points in the 1.25-1.5 hr range would be helpful.

19. Find the integrated rate law for a third-order reaction that is second-order in A and first-order in B for the stoichiometry: $2 A + B \rightarrow \text{products}$. In actual examples, B is often called a “third body” and is often an inert gas, an N_2 molecule from the air, a particle, or the walls of the container. If the third body were not present, the collision of two A molecules would not be stable and would dissociate back to form two A molecules. The third body is necessary to carry away the excess energy of the collision.

Answer: The rate law would be given as:

$$v = -\frac{1}{2} \frac{d[A]}{dt} = k_3 [A]^2[B]$$

Given the stoichiometric relationships, $[A] = ([A]_0 - 2\xi)$ and $[B] = ([B]_0 - \xi)$:

$$\frac{d\xi}{dt} = k_3 ([A]_0 - 2\xi)^2 ([B]_0 - \xi)$$

Separating variables: $\frac{d\xi}{([A]_0 - 2\xi)^2 ([B]_0 - \xi)} = k_3 dt$

The indefinite integrals are: $\int \frac{d\xi}{([A]_0 - 2\xi)^2 ([B]_0 - \xi)} = \int k_3 dt$

Integral tables give:

$$\int \frac{dx}{(a + bx)^2 (a' + b'x)} = \frac{1}{ab' - a'b} \left(\frac{1}{a + bx} + \frac{b'}{ab' - a'b} \ln \frac{(a' + b'x)}{(a + bx)} \right)$$

With $b = -2$ and $b' = -1$:

$$\int \frac{d\xi}{([A]_0 - 2\xi)^2 ([B]_0 - \xi)} = \frac{1}{2[B]_0 - [A]_0} \left(\frac{1}{[A]_0 - 2\xi} - \frac{1}{2[B]_0 - [A]_0} \ln \left(\frac{[B]_0 - \xi}{[A]_0 - 2\xi} \right) \right)$$

The integrated rate law is:

$$\frac{1}{2[B]_0 - [A]_0} \left(\frac{1}{[A]_0 - 2\xi} - \frac{1}{2[B]_0 - [A]_0} \ln \left(\frac{[B]_0 - \xi}{[A]_0 - 2\xi} \right) \right) = k_3 t + c$$

The boundary condition is at $t = 0$, $\xi = 0$, and the integration constant is:

$$c = \frac{1}{2[B]_0 - [A]_0} \left(\frac{1}{[A]_0} - \frac{1}{2[B]_0 - [A]_0} \ln \left(\frac{[B]_0}{[A]_0} \right) \right)$$

Substituting the integration constant back into the integrated rate law and collecting common terms gives:

$$\frac{1}{2[B]_0 - [A]_0} \left(\frac{1}{[A]_0 - 2\xi} - \frac{1}{[A]_0} - \frac{1}{2[B]_0 - [A]_0} \ln \left(\frac{[A]_0([B]_0 - \xi)}{[B]_0([A]_0 - 2\xi)} \right) \right) = k_3 t$$

This equation is often rearranged by taking a common denominator for the terms:

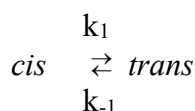
$$\frac{1}{[A]_o - 2\xi} - \frac{1}{[A]_o} = \frac{2\xi}{[A]_o([A]_o - 2\xi)}$$

Substitution back into the integrated rate law gives:

$$\frac{1}{2[B]_o - [A]_o} \left[\frac{2\xi}{[A]_o([A]_o - 2\xi)} - \frac{1}{2[B]_o - [A]_o} \ln \left(\frac{[A]_o([B]_o - \xi)}{[B]_o([A]_o - 2\xi)} \right) \right] = k_3 t$$

In the next chapter we will discuss a method of calculating numerical approximations to rate laws that avoids having to do complicated integrals. However, this rate law arises often enough that it is handy to have a closed-form solution.

20. The *cis-trans* isomerization of 1-ethyl-2-methylcyclopropane is first order in the forward and reverse directions:^{4,5}



The reaction, starting with only *cis* isomer has the following time course. The long-time value for the *cis*-isomer concentration is 0.00443 M. Determine k_1 and k_{-1} .

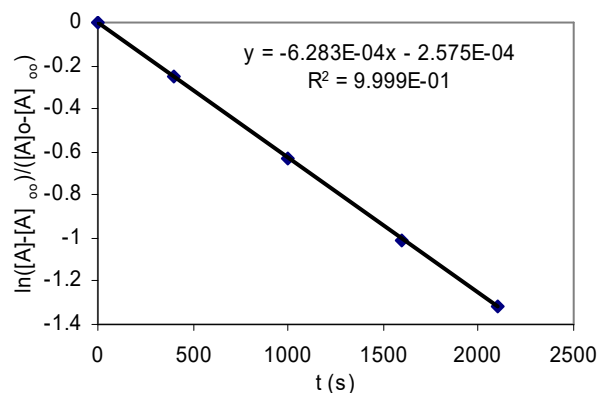
t (s)	0	400	1000	1600	2100
[<i>cis</i>] (M)	0.01679	0.01406	0.01102	0.00892	0.00775

Answer: Using Eq. 3.4.23 with $A_o = 0.01679$ M and $A_\infty = 0.00443$ M, the follow spreadsheet was constructed:

t (s)	[<i>cis</i>] (M)	$\frac{([A] - [A]_\infty)}{([A]_o - [A]_\infty)}$	$\ln \frac{([A] - [A]_\infty)}{([A]_o - [A]_\infty)}$
0	0.01679	1	0
400	0.01406	0.7791	-0.2496
1000	0.01102	0.5332	-0.6289
1600	0.00892	0.3633	-1.0126
2100	0.00775	0.2686	-1.3145

The corresponding plot and linest() output is:

slope	-0.0006283	-0.000258	intercept
±	3.039E-06	0.003875	±
r ²	0.999929	0.00520	st. dev. y
F	42737.8	3	df
SS _{reg}	1.15585	8.114E-05	SS _{res}



The slope gives the sum of the rate constants: slope = $-(k_1 + k_{-1}) = -0.0006283$, or:

$$(k_1 + k_{-1}) = 0.0006283 \quad 1$$

To calculate the rate constants separately, we can use the equilibrium constant. The long-time, equilibrium concentration of the *cis* isomer is $[cis]_{\infty} = 0.00443 \text{ M}$, and from the 1:1 stoichiometry:

$$[trans]_{\infty} = [cis]_0 - [cis]_{\infty} = 0.01679 - 0.00443 \text{ M} = 0.01236 \quad 2$$

The ratio gives the equilibrium constant:

$$K_c = \frac{k_1}{k_{-1}} = \frac{0.01236}{0.00443} = 2.79 \quad 3$$

We now have two equations in two unknowns, Eq. 1 and 3. Solving Eq. 3 for k_{-1} gives $k_{-1} = k_1/K_c$ and substitution into Eq. 1 gives:

$$(k_1 + k_1/K_c) = 6.283 \times 10^{-4} \text{ s}^{-1} \quad 4$$

Solving for k_1 :

$$k_1 = \frac{6.283 \times 10^{-4}}{1 + 1/K_c} = \frac{6.283 \times 10^{-4}}{1 + 1/2.79} = 4.625 \times 10^{-4} \text{ s}^{-1}$$

and then $k_{-1} = k_1/K_c = 4.625 \times 10^{-4} \text{ s}^{-1}/2.79 = 1.658 \times 10^{-4} \text{ s}^{-1}$

21. The rate of decomposition of acetaldehyde has been studied as a function of temperature. The table below gives the rate constant for the reaction as a function of temperature. Determine the activation energy and the pre-exponential factor.

T (K)	703	733	759	791	811	836
$k_2 \text{ (M}^{-1} \text{ s}^{-1}\text{)}$	0.011	0.035	0.105	0.343	0.79	2.14

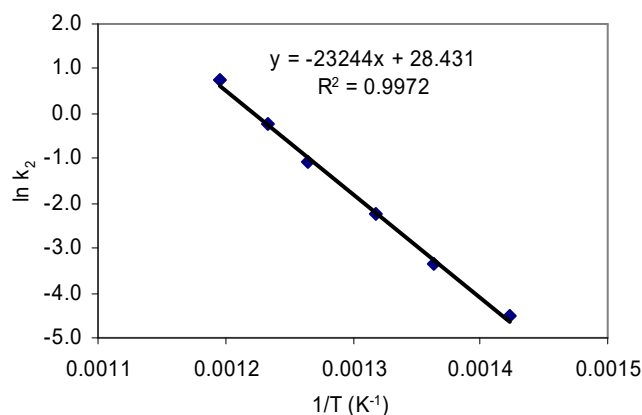
Answer: We will first do the common Arrhenius plot and then compare the results with a non-linear curve fit in the next problem. The non-linear fit gives a more realistic view of the experimental errors.

The following spreadsheet was developed to fit the linear form of the Arrhenius equation, Eq. 3.5.3.

T (K)	$k_2 \text{ (M}^{-1} \text{ s}^{-1}\text{)}$	$1/T \text{ (K}^{-1}\text{)}$	$\ln k_2$
703	0.011	0.001422	-4.5099
733	0.035	0.001364	-3.3524
759	0.105	0.001318	-2.2538
791	0.343	0.001264	-1.0700
811	0.79	0.001233	-0.2357
836	2.14	0.001196	0.7608

The `linest()` output and plot are:

slope	-23243.86	28.4312	intercept
\pm	619.84	0.8069	\pm
r2	0.9972	0.1176	st.dev.y
F	1406.2193	4.0000	df
SS _{reg}	19.4383	0.0553	SS _{resid}



The activation energy is given by: slope = $-E_a/R$ or $E_a = -\text{slope}(R) = 193.2 \pm 5.1 \text{ kJ mol}^{-1}$.
The pre-exponential factor is given by intercept = $\ln A$ or:

$$A = e^{28.43} = 2.2 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}.$$

See the next problem for more on error analysis.

22. This problem concerns the error analysis of the results from the last problem. (a) Using the results from the last problem, determine the error in the activation energy and the pre-exponential factor. (b) Often a better approach is to use a non-linear fit. Do a non-linear fit to the original data in the last problem and compare the fit values and the uncertainties with the linearized fit.

Answer: From the last problem, the relative uncertainty in the slope is 2.7% giving the activation energy as uncertain to 2.7% or $193.2 \pm 5.1 \text{ kJ mol}^{-1}$. The error for the pre-exponential factor is a bit harder. The intercept is quite uncertain: 28.43 ± 0.81 . The significant figure rule is Significant Figure Rule 4 from Appendix 1:

“The number of significant figures in 10^x is the number of significant figures in the mantissa of x . Use the same rule for e^x .”

Using significant figure rules, the uncertainty is in the order of magnitude; there are no significant figures in the mantissa. Using the “Uncertainty Calculator” applet on the textbook Web site and on the text companion CD:

Equation = $\exp(b)$

Variable	Value	Uncertainty
b	28.4312	0.8069

Calculate Reset Constants

Variable	Resultant
Uncertainty	Uncertainty
b	0.8069 +-1870563311743.0417

Result = 2200000000000 +- 1900000000000
 uncorrelated
 +- 1900000000000 correlated

The pre-exponential factor and uncertainty are $2.2 \times 10^{12} \pm 1.9 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$, which is a bit smaller than expected by the significant figure rules.

The full propagation of errors rule is: the relative variance in e^x is equal to the variance in x (Rule 4, Appendix 1). In this case there is only one error term so we can work with standard deviations directly (Rule 5, Appendix 1). The standard deviation in x is 0.8069 so the relative standard deviation in $e^{28.43}$ is 0.8069, or in other words 81%. The final result is the same as given by the “Uncertainty Calculator.”

A better approach is to do non-linear curve fitting, which is also quicker and easier. However, for non-linear curve fitting you need to specify initial guesses for the fit parameters. Sometimes these guesses can be far from the final value. For this particular function the guesses need to be pretty close to the final results. To get guesses for the fit parameters, we can use the results from the linear fit that we obtained in the last problem. The fit function is set up as:

Fit function: $a \exp(b/x) + c$

Parameter guesses:

a = 2.23e13

b = -23200

c = 0 ☒ Fixed

Convergence Mode: ☒ Fast ☐ Damped ☐ Strongly Damped

The results of the non-linear fit are significantly different from the linear form for the pre-exponential factor:

```
===== Results =====
a= 171000000000000 +- 75000000000000
b= -26760 +- 360
-----
sum of squared residuals= 0.0007028
stand. dev. y values= 0.01326
correlation between a & b= -0.9999
```

This fit gives $E_a = 222.5 \pm 3.0 \text{ kJ mol}^{-1}$ and $A = 1.71 \times 10^{14} \pm 0.75 \times 10^{14} \text{ M}^{-1} \text{ s}^{-1}$. The correlation between the fit values shows why the uncertainties are so large. This very large correlation between the fit values suggests that the value would be best reported as $\log A \approx 14$ to avoid over-representing the precision.

A Note on Convergence: If you start with a guess that results in the error message “Not Converged,” try clicking on one of the damping options. Choosing “Damped” or “Strongly Damped” allows a much larger range of input guesses to converge on the final result for this particular function. Unfortunately, damping is not always helpful for other fitting functions.

23. Calculate the activation energy and pre-exponential factor for the decomposition of N_2O_5 from the following temperature dependence.⁶

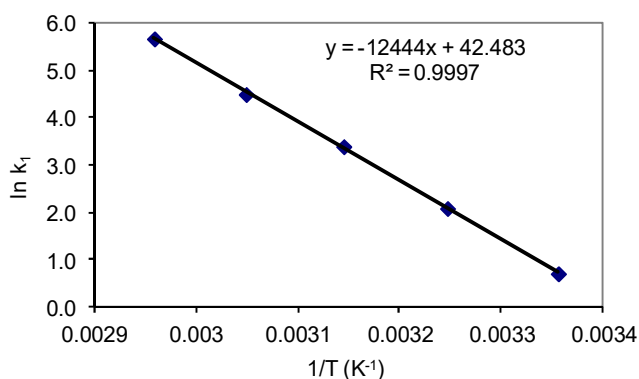
T (K)	298.0	308.0	318.0	328.0	338.0
k_1 (min^{-1})	2.03	8.09	29.9	90.1	291.5

Answer: The plan is to use the linearized form of the Arrhenius temperature dependence, Eq. 3.5.8, and linear least squares curve fitting.

The linearized form of the Arrhenius equation is $\ln k = -E_a/R + \ln A$. A fit of the $\ln k_1$ versus $1/T$ is done using `linest()` in the following spreadsheet and plot.

T (K)	k_1 (min^{-1})	$1/T$ (K^{-1})	$\ln k_1$
298.0	2.03	0.003356	0.7080
308.0	8.09	0.003247	2.0906
318.0	29.9	0.003145	3.3979
328.0	90.1	0.003049	4.5009
338.0	291.5	0.002959	5.6750

slope	-12443.7	42.483	intercept
\pm	123.38	0.389	\pm
r^2	0.9997	0.0387	st.dev.y
F	10171.6	3.00	df
ssreg	15.2657	0.0045	ssresid



The straight-line behavior verifies Arrhenius temperature dependence. The slope is $-E_a/R$, giving: $E_a = -(-12443.7)8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ ($1 \text{ kJ}/1000 \text{ J}$) = $103.46 \text{ kJ mol}^{-1}$. Relative errors propagate upon multiplication and division, giving the uncertainty of 1.0% or $E_a = 103.5 \pm 1.0 \text{ kJ mol}^{-1}$.

The pre-exponential factor is determined from the intercept, $\ln A = 42.48 \pm 0.39$, giving:

$$A = e^{42.48} = 2.81 \times 10^{18} \text{ min}^{-1}$$

The relative uncertainty of e^x is the absolute uncertainty in x . The absolute uncertainty in the pre-exponential factor is ± 0.39 or equivalently 39% of the final result:

$$A = 2.8 \times 10^{18} \pm 1.1 \times 10^{18} \text{ min}^{-1}$$

The pre-exponential factor always has the same units as the rate constant.

24. The rate constant for the disappearance of chlorine in the reaction of NO with Cl_2 to form NOCl is $4.52 \text{ M}^{-2} \text{ s}^{-1}$ at 0.0°C and $8.03 \text{ M}^{-2} \text{ s}^{-1}$ at 22.0°C . What are the activation energy and pre-exponential factor for this reaction?

Answer: The plan is to follow Example 3.5.1. The linearized form of the Arrhenius relationship for two data points is Eq. 3.5.7:

$$\ln k_{T_2}/k_{T_1} = -E_a/R (1/T_2 - 1/T_1) \quad (3.5.7)$$

$$\ln (8.03/4.52) = -\frac{E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} (1/295.15 \text{ K} - 1/273.15 \text{ K})$$

$$0.5747 = -\frac{E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} (-2.7288 \times 10^{-4} \text{ K}^{-1})$$

$$E_a = 17.51 \text{ kJ mol}^{-1}$$

Then $k = A e^{-E_a/RT}$ using the lower temperature data point:

$$4.52 \text{ M}^{-2} \text{ s}^{-1} = A e^{(-17.51 \times 10^3 \text{ J mol}^{-1} / 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} / 273.15 \text{ K})} = A e^{-7.710} = A (4.484 \times 10^{-4})$$

$$A = 1.01 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$$

The number of significant figures in e^x is the number of significant figures in the mantissa of x . The mantissa of the argument of the exponential is the “.710” part, or two significant figures. Either original data point gives the same pre-exponential factor. The units of the pre-exponential factor are always the same as the rate constant.

25. The decomposition of urea is $\text{NH}_2\text{CONH}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{NH}_4^+ + \text{CO}_3^-$. The activation energy for the reaction is $128.0 \text{ kJ mol}^{-1}$. The rate constant 71.2°C is $2.77 \times 10^{-5} \text{ min}^{-1}$. Calculate the rate constants at 40.0°C .

Answer: The plan is to use the linearized form of the Arrhenius temperature dependence, Eq. 3.5.7. The temperatures must be converted to absolute temperatures.

At 71.2°C the absolute temperature is 344.4 K . The linearized form of the Arrhenius relationship for two data points is Eq. 3.5.7:

$$\ln k_{T_2}/k_{T_1} = -E_a/R (1/T_2 - 1/T_1) \quad (3.5.7)$$

$$\ln (k_{T_2}/2.77 \times 10^{-5} \text{ min}^{-1}) = -\frac{128.0 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} (1/313.2 \text{ K} - 1/344.4 \text{ K})$$

$$\ln (k_{T_2}/2.77 \times 10^{-5} \text{ min}^{-1}) = -1.5394 \times 10^4 (2.892 \times 10^{-4} \text{ K}^{-1}) = -4.452$$

$$k_{T_2} = 2.77 \times 10^{-5} \text{ min}^{-1} e^{-4.452} = 3.228 \times 10^{-7} \text{ min}^{-1} = 3.2 \times 10^{-7} \text{ min}^{-1}$$

There are only three significant figures in the inverse temperature difference:

$$(1/313.2 \text{ K} - 1/344.4 \text{ K}) = \underbrace{3.19285 \times 10^{-3}}_{3 \text{ SFpdpt}} - \underbrace{2.90360 \times 10^{-3}}_{3 \text{ SFpdpt}} = \underbrace{0.28925 \times 10^{-3}}_{3 \text{ SFpdpt}} \text{ K}^{-1}$$

where “3 SF pdpt” is short for three significant figures past the decimal point. The number of significant figures in e^x is the number of significant figures in the mantissa of x . The mantissa of the argument of the exponential is the “.452” part, or two significant figures.

26. The rate constant for the decomposition of N_2O_5 is 8.09 min^{-1} at 308.0 K and 90.1 min^{-1} at 328.0 K .⁶ Calculate the rate constant at 298.2 K .

Answer: The plan is to calculate the activation energy using Arrhenius temperature dependence and then use the same equation and one of the data points to calculate the new rate constant.

The linearized form of the Arrhenius relationship for two data points is Eq. 3.5.7:

$$\ln k_{T_2}/k_{T_1} = -E_a/R (1/T_2 - 1/T_1) \quad (3.5.7)$$

$$\ln (90.1/8.09) = -\frac{E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} (1/328.0 \text{ K} - 1/308.0 \text{ K})$$

$$2.4103 = -\frac{E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} (-1.9797 \times 10^{-4} \text{ K}^{-1})$$

$$E_a = 101.23 \text{ kJ mol}^{-1}$$

There are four significant figures in the \ln because the number of significant figures in the mantissa of $\ln x$ is the number of significant figures in x ; the mantissa is the “.4103” portion. There are only three significant figures in the inverse temperature difference:

$$(1/328.0 \text{ K} - 1/308.0 \text{ K}) = \underbrace{3.048}_{3 \text{ SFdpdt}} \times 10^{-3} - \underbrace{3.246}_{3 \text{ SFdpdt}} \times 10^{-3} = \underbrace{0.197}_{3 \text{ SFdpdt}} \times 10^{-3} \text{ K}$$

where “3 SFdpdt” is short for three significant figures past the decimal point.


Then using the lower temperature data point and Eq. 3.5.7 gives the rate constant at 298.2 K:

$$\ln k_{T_2}/k_{T_1} = -E_a/R (1/T_2 - 1/T_1) \quad (3.5.7)$$

$$\ln (k_{T_2}/8.09 \text{ min}^{-1}) = -\frac{101.23 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} (1/298.2 \text{ K} - 1/308.0 \text{ K})$$

$$\ln (k_{T_2}/8.09 \text{ min}^{-1}) = -1.2175 \times 10^4 (-1.0670 \times 10^{-4} \text{ K}^{-1}) = 1.2991$$

$$k_{T_2} = 8.09 \text{ min}^{-1} e^{-1.2991} = 2.207 \text{ min}^{-1} = 2.2 \text{ min}^{-1}$$

 We can verify the significant figure propagation using the “Uncertainty Calculator,” from the text Web site. The activation energy calculation propagation is given by the following input.

Equation:

Equation = -LNe(k2/k1)/(1/T2-1/T1)*R

Variable	Value	Uncertainty
k2	90.1	0.1
k1	8.09	0.01
T2	328.0	0.1
T1	308.0	0.1
R	8.3144621	7.5e-6

Variable	Resultant
Uncertainty	Uncertainty
k2	0.1
k1	0.01
T2	0.1
T1	0.1
R	0.00001

Result = 101230 +- 720 uncorrelated
+- 1100 correlated

The propagation for the Arrhenius temperature dependence of the rate constant gives:

Equation:

$k_1 \exp(-E_a/R \cdot (1/T_2 - 1/T_1))$

calculate

Equation = $k_1 \exp(-E_a/R \cdot (1/T_2 - 1/T_1))$

Variable	Value	Uncertainty
k1	8.09	0.01
Ea	101.23e3	0.72e3
R	8.3144621	7.5e-6
T2	298.2	0.1
T1	308.0	0.1

Calculate

Reset

Constants

	Variable	Resultant
	Uncertainty	Uncertainty
k1	0.01	+ - 0.00273
Ea	720.0	+ - 0.02038
R	0.00001	+ - 0.0
T2	0.1	+ - 0.03023
T1	0.1	+ - 0.0283

Result = 2.207 + - 0.046 uncorrelated

+ - 0.082 correlated

Significant figure rules and careful error propagation both give two significant figures in the final result: $2.207 \pm 0.046 \text{ min}^{-1} = 2.2 \text{ min}^{-1}$. For publication, the result is best expressed as $2.207 \pm 0.046 \text{ min}^{-1}$. Significant figure rules are a poor substitute for careful error analysis, used only as a time saving convenience.

[Alternately, the pre-exponential factor can be determined by solving for A from $k_2 = A e^{-E_a/RT}$, and then the rate constant at the new temperature is determined using A and E_a . However, this approach is much more difficult to determine the proper number of significant figures in the final result. While algebraically equivalent, using Eq. 3.5.7 is the preferable approach.]

27. The half-time for the first-order denaturation of yeast invertase at 55.0°C and pH 3 is 26.7 min. The activation energy is 308. kJ mol⁻¹.⁷ Calculate the time for the denaturation of the protein to be 75% complete at 60.0°C.

Answer: The plan is to calculate the rate constant at 55°C from the half-time and use the linearized form of the Arrhenius temperature dependence, Eq. 3.5.7, to calculate the rate constant at 60°C. Next the time for 75% completion is calculated using $[A]/[A]_0 = 0.75$. The temperatures must be converted to absolute temperatures.

At 55.0°C the absolute temperature is 328.2 K and at 60.0 C the temperature is 333.15 K. The rate constant at 55°C is calculated from the half-time using Eq. 3.2.11, $t_{1/2} = \ln 2/k_2$:

$$k_{2.328\text{K}} = 0.6932/26.7 \text{ min} = 0.02596 \text{ min}^{-1}$$

The linearized form of the Arrhenius relationship for two data points is Eq. 3.5.7:

$$\ln k_{T_2}/k_{T_1} = -E_a/R (1/T_2 - 1/T_1) \quad (3.5.7)$$

$$\ln(k_{T_2}/0.02596 \text{ min}^{-1}) = -\frac{308. \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} (1/333.2 \text{ K} - 1/328.2 \text{ K})$$

$$\ln(k_{T_2}/0.02596 \text{ min}^{-1}) = -3.704 \times 10^4 (-4.5722 \times 10^{-5} \text{ K}^{-1}) = 1.6937$$

$$k_{T2} = 0.02596 \text{ min}^{-1} e^{1.6937} = 1.412 \times 10^{-7} \text{ min}^{-1} = 0.1412 \text{ min}^{-1}$$

The final result is $2.037 \pm 0.098 \text{ min}^{-1}$, which is significantly more precise than the uncertainty based on significant figure rules, namely $2. \text{ min}^{-1}$. For publication, the result is best expressed as $2.037 \pm 0.098 \text{ min}^{-1}$. Significant figure rules are a poor substitute for careful error analysis, used only as a time saving convenience.

28. The development of biological complexity and the emergence of life have important time constraints. These time constraints in turn give a corresponding range of reaction rate constants for the production of the building blocks of life. All reactions are reversible, and the ratio of the forward and reverse rate constants is given by the equilibrium constant, $K_{\text{eq}} = k_f/k_r$. Favorable equilibrium is required to allow the significant build-up of products. A careful balancing of rate and equilibrium constants is necessary for the persistence necessary to build molecular and organizational complexity. If reactions are too fast, complexity can't be established because the lifetimes of the molecules are too short. If reactions are too slow, interdependent sets of complex reaction sequences can't develop. The range of reaction half-times that are amenable for the building of complexity is estimated to be in the 1 s to 100 yr range, which still spans more than 9 orders of magnitude.⁸ Assume a range of pseudo-first order half-times of 1 s to 100 yr to calculate the range of amenable activation energies for reactions that build complexity at 298 K. Typical pre-exponential factors are in the range of $1.0 \times 10^{10} \text{ s}^{-1}$ to $1.0 \times 10^{11} \text{ s}^{-1}$.

Answer: The plan is to use $k = A e^{-E_a/RT}$ to calculate a range of corresponding activation energies, where the range of rate constants is determined from the half-times, $t_{1/2} = \ln(2)/k$.

The range of half-times, 1 s to 100 years, corresponds to a range of pseudo-first order rate constants from 0.693 s^{-1} to $2.20 \times 10^{-10} \text{ s}^{-1}$, respectively. The following table then gives the values of the activation energies, depending on the chosen value of the pre-exponential factor and half-time, using $E_a = -RT \ln(k/A)$:

Table: Activation Energies for Specific Pre-exponential Factors and Rate Constants

A	$k = 0.693 \text{ s}^{-1}$	$k = 2.20 \times 10^{-10} \text{ s}^{-1}$
$1.0 \times 10^{10} \text{ s}^{-1}$	58 kJ mol ⁻¹	112 kJ mol ⁻¹
$1.0 \times 10^{11} \text{ s}^{-1}$	64 kJ mol ⁻¹	118 kJ mol ⁻¹

Notice that significant activation energies are required. The activation energies are sizable fractions of typical covalent bond energies. The conclusion is that the development of complexity must be mediated through covalent bonding.⁸ Non-covalent interactions, such as hydrogen bonding and π - π interactions, are insufficient to provide the persistence necessary for building complexity. However, after significant complexity is established, networks of cooperative non-covalent interactions are sufficient. For example, protein denaturation typically has high activation energies (see the previous problem). Even though the range of half-times covers nine-orders of magnitude, the corresponding activation energies vary only by a factor of two. Molecules involved in cell signaling, such as NO and acetylcholine, typically have short half-times. Structural scaffold polymers, such as cellulose and collagen, have long half-times. Both extremes are necessary to maintain complex systems.

29. In this problem we compare the integrated rate law for $A + B \rightarrow P$ with $A \rightarrow P$ for a simple first-order and second-order reaction. (a) For a second-order reaction that is first order in A and first order in B, solve Eq. 3.2.52 for ξ . Then plot $[A] = [A]_0 - \xi$ using the initial conditions $[A]_0 = 0.5 \text{ M}$, $[B]_0 = 1.0 \text{ M}$ and $k_2 = 0.1 \text{ M}^{-1} \text{ s}^{-1}$. Let t range from 0 to 20 s. (b) On the same axis, plot the corresponding time course for a first-order reaction, $A \rightarrow P$, with $[A]_0 = 0.5 \text{ M}$ and $k_1 = 0.1 \text{ s}^{-1}$. (c) On the same axis, plot the corresponding time course for a simple second-order reaction of the form and stoichiometry $A \rightarrow P$. For this last plot, use a rate constant of $k_2 = 0.2 \text{ M}^{-1} \text{ s}^{-1}$ so that the initial rates for all three types of reactions are equal, to make a fair comparison. (d) Rationalize the differences in the plots.

Answer: The integrated rate law for $A + B \rightarrow P$ that is first-order in both reactants is given in Eq. 3.2.52:

$$\frac{1}{([B]_0 - [A]_0)} \ln \left(\frac{[B]_0 - \xi}{[A]_0 - \xi} \right) = k_2 t + \frac{1}{([B]_0 - [A]_0)} \ln \left(\frac{[B]_0}{[A]_0} \right)$$

Multiplying both sides of the equation by $[B]_0 - [A]_0$ and exponentiating gives:

$$\left(\frac{[B]_0 - \xi}{[A]_0 - \xi} \right) = e^{([B]_0 - [A]_0) k_2 t + \ln([B]_0/[A]_0)} = \frac{[B]_0}{[A]_0} e^{([B]_0 - [A]_0) k_2 t}$$

Cross multiplying and multiplying out terms:

$$[B]_0 - \xi = [B]_0 e^{([B]_0 - [A]_0) k_2 t} - \frac{[B]_0}{[A]_0} \xi e^{([B]_0 - [A]_0) k_2 t}$$

Collecting terms in ξ :

$$\xi - \frac{[B]_0}{[A]_0} \xi e^{([B]_0 - [A]_0) k_2 t} = [B]_0 - [B]_0 e^{([B]_0 - [A]_0) k_2 t}$$

Solving for ξ :

$$\xi = [B]_0 \frac{(1 - e^{([B]_0 - [A]_0) k_2 t})}{\left(1 - \frac{[B]_0}{[A]_0} e^{([B]_0 - [A]_0) k_2 t}\right)}$$

Alternatively, multiplying numerator and denominator by $[A]_0/[B]_0$ gives:

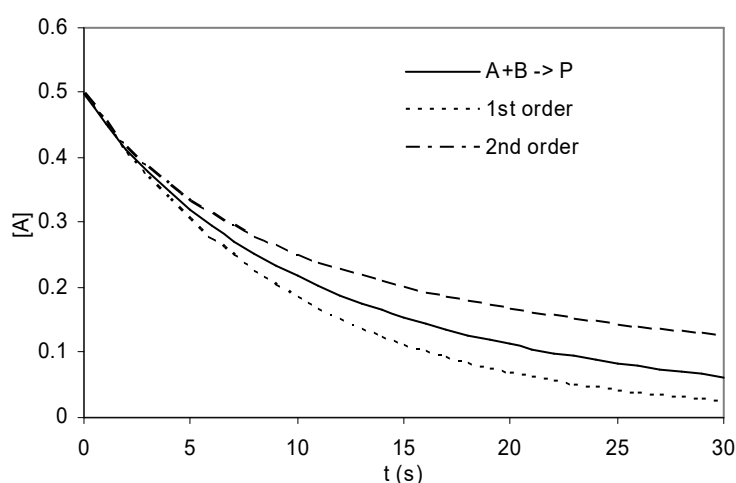
$$\xi = [A]_0 \frac{(1 - e^{([B]_0 - [A]_0) k_2 t})}{\left(\frac{[A]_0}{[B]_0} - e^{([B]_0 - [A]_0) k_2 t}\right)}$$

A spreadsheet was set up to calculate $e^{([B]_0 - [A]_0) k_2 t}$, ξ , and $[A]_0 - \xi$. Additional columns were added for the first-order function, $[A] = [A]_0 e^{-k_1 t}$, and the simple second-order function:

$$[A] = \frac{1}{\left(\frac{1}{[A]_0} + k_2 t\right)}$$

			$[A]_0 - \xi$	$[A]$	$[A]$
t (s)	$\exp((b-a)kt)$	ξ	A+B \rightarrow P	1st order	2nd order
0	1	0	0.5	0.5	0.5
2	1.105	0.087	0.413	0.409	0.417
4	1.221	0.153	0.347	0.335	0.357
6	1.350	0.206	0.294	0.274	0.313
8	1.492	0.248	0.252	0.225	0.278
10	1.649	0.282	0.218	0.184	0.250
12	1.822	0.311	0.189	0.151	0.227
14	2.014	0.335	0.165	0.123	0.208
16	2.226	0.355	0.145	0.101	0.192
18	2.460	0.372	0.128	0.083	0.179
20	2.718	0.387	0.113	0.068	0.167

The corresponding plot is:



(d) To rationalize the differences, we write the rate laws at 10 s as an example. At 10 s, from the table, for the $A + B \rightarrow P$ case, $[A] = 0.218$ M and $[B] = [B]_0 - \xi = 0.718$ M. Substituting the actual concentrations:

$$\text{2nd order overall} \quad A + B \rightarrow P \quad -\frac{d[A]}{dt} = k_2 [A] [B] = k_2 [A] (0.718) \quad 1$$

For the first-order rate law:

$$\text{1st order} \quad A \rightarrow P \quad -\frac{d[A]}{dt} = k_1 [A] \quad 2$$

and for the simple second-order rate law, $[A] = 0.250$ at $t = 10$ s giving:

$$\text{2nd order} \quad A \rightarrow P \quad -\frac{d[A]}{dt} = k_2 [A] [A] = k_2 [A] (0.250) \quad 3$$

In Eq. 1, $[A]$ is multiplied by (0.718) thus decreasing the rate of disappearance. In Eq. 2, $[A]$ stands alone, so the rate of disappearance of $[A]$ is faster than Eq. 1. In Eq. 3, $[A]^2$ is effectively $[A] (0.250)$ which is the smallest product of all three and therefore the slowest.

30. Show that Eq. 3.4.22 reduces to simple first-order behavior, with a rate constant of just k_1 , for a reaction that runs to completion.

Answer: Eq. 3.4.22 involves the sum of the rate constants:

$$\frac{d([A] - [A]_{eq})}{dt} = -(k_1 + k_{-1})([A] - [A]_{eq})$$

which doesn't look like it will reduce to a form that only depends on k_1 . However, note that from the equilibrium constant:

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[B]_{eq}}{[A]_{eq}}$$

or solving for k_{-1} gives:

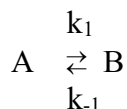
$$k_{-1} = k_1/K_{eq}$$

giving:

$$\frac{d([A] - [A]_{eq})}{dt} = -k_1(1 + 1/K_{eq})([A] - [A]_{eq})$$

In addition, $[A]_{eq} = [B]_{eq}/K_{eq}$. For a reaction that runs to completion, $K_{eq} \rightarrow \infty$, $k_{-1} \rightarrow 0$, and $[A]_{eq} \rightarrow 0$, which gives Eq. 3.2.2.

31. Find the lifetime and half-time for a reversible first-order/first-order reaction from Eq. 3.4.23:



Answer: The lifetime, τ , is the $1/e$ time for the course of the reaction. Since the reaction doesn't run to completion, the $1/e$ point is when the displacement is $1/e$ of the way to equilibrium:

$$\left(\frac{[A] - [A]_{eq}}{[A]_o - [A]_{eq}} \right) = 1/e$$

Then Eq. 3.4.23 reduces to:

$$\ln \left(\frac{[A] - [A]_{eq}}{[A]_o - [A]_{eq}} \right) = \ln(1/e) = -\ln e = -1 = -(k_1 + k_{-1}) \tau$$

Solving for the lifetime gives:

$$\tau = \frac{1}{(k_1 + k_{-1})}$$

This equation should be compared to the temperature-jump relaxation time for the same reaction order and stoichiometry, Eq. 3.6.14. These two equations are the same.

Now for the half-time:

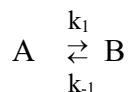
$$\left(\frac{[A] - [A]_{eq}}{[A]_o - [A]_{eq}} \right) = 1/2$$

Then Eq. 3.4.23 reduces to:

$$\ln\left(\frac{[A] - [A]_{eq}}{[A]_o - [A]_{eq}}\right) = \ln(1/2) = -\ln 2 = -0.6931 = -(k_1 + k_{-1}) \tau$$

and the half-time is $t_{1/2} = \frac{\ln 2}{(k_1 + k_{-1})} = \frac{0.6931}{(k_1 + k_{-1})}$

32. For a reversible first-order/first-order reaction:



(a) Show that the displacement for A after n half-times is given by:

$$[A] - [A]_{eq} = ([A]_o - [A]_{eq}) \left(\frac{1}{2}\right)^n$$

(b) What percentage of the initial displacement for A remains after five half-times?

Answer: The half-time for a reversible first-order/first-order reaction with 1:1 stoichiometry is the time when:

$$\left(\frac{[A] - [A]_{eq}}{[A]_o - [A]_{eq}}\right) = 1/2 \quad \text{or} \quad t_{1/2} = \frac{\ln 2}{(k_1 + k_{-1})}$$

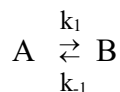
For n half-times, substituting $t = n t_{1/2}$ into Eq. 3.4.24 gives:

$$\begin{aligned} [A] - [A]_{eq} &= ([A]_o - [A]_{eq}) e^{-(k_1 + k_{-1})n t_{1/2}} = ([A]_o - [A]_{eq}) e^{-n \ln 2} = ([A]_o - [A]_{eq}) e^{\ln 2^{-n}} \\ &= ([A]_o - [A]_{eq}) 2^{-n} = ([A]_o - [A]_{eq}) \left(\frac{1}{2}\right)^n \end{aligned}$$

(b) After five half-times the displacement is $[A] - [A]_{eq} = ([A]_o - [A]_{eq}) \left(\frac{1}{2}\right)^5$

and $\left(\frac{1}{2}\right)^5 = 0.0312$ or 3.1% remains compared to its equilibrium value.

33. For a reversible first-order/first-order reaction:



(a) Show that the displacement for A after n lifetimes is given by:

$$[A] - [A]_{eq} = ([A]_o - [A]_{eq}) \left(\frac{1}{e}\right)^n$$

A commonly quoted rule is that a reaction or process has essentially returned to equilibrium after five lifetimes. (b) What percentage of the initial displacement for A remains after five lifetimes?

Answer: The lifetime for a reversible first-order/first-order reaction with 1:1 stoichiometry is the time when:

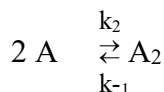
$$\left(\frac{[A] - [A]_{eq}}{[A]_o - [A]_{eq}}\right) = 1/e \quad \text{or} \quad \tau = \frac{1}{(k_1 + k_{-1})}$$

For n lifetimes, substituting $t = n \tau$ into Eq. 3.4.24 gives:

$$\begin{aligned} [A] - [A]_{eq} &= ([A]_o - [A]_{eq}) e^{-(k_1 + k_{-1})n\tau} = ([A]_o - [A]_{eq}) e^{-n} \\ &= ([A]_o - [A]_{eq}) \left(\frac{1}{e}\right)^n \end{aligned}$$

(b) After five lifetimes the displacement is $[A] - [A]_{eq} = ([A]_o - [A]_{eq}) \left(\frac{1}{e}\right)^5$ and $(1/e)^5 = 6.74 \times 10^{-3}$ or 0.67% remains compared to its equilibrium value.

34. Show that the relaxation time for a dimerization:



$$\text{is } \tau = \frac{1}{(4k_2[A]_{eq} + k_{-1})}$$

Assume that the reaction is second order in the forward direction and first order in the reverse direction.

Answer: The rate law is given by:

$$v = \frac{d[A_2]}{dt} = k_2 [A]^2 - k_{-1}[A_2] \quad 1$$

Equilibrium is established when the forward and reverse rates are equal:

$$K_{eq} = \frac{k_2}{k_{-1}} = \frac{[A_2]_{eq}}{[A]_{eq}^2} \quad \text{or} \quad k_2[A]_{eq}^2 - k_{-1}[A_2]_{eq} = 0 \quad 2$$

Subtracting Eq. 2 from Eq. 1 references the concentrations to the equilibrium values:

$$\frac{d[A_2]}{dt} = k_2 [A]^2 - k_2[A]_{eq}^2 - k_{-1}[A_2] + k_{-1}[A_2]_{eq} \quad 3$$

Factoring out the rate constants gives:

$$\frac{d[A_2]}{dt} = k_2([A]^2 - [A]_{eq}^2) - k_{-1}([A_2] - [A_2]_{eq}) \quad 4$$

Eq. 3.1.2 gives the relationship of the concentration changes, $d[A] = -2 d[A_2]$. The displacement in the product concentration is $x = [A_2] - [A_2]_{eq}$ and then for the reactant $[A] - [A]_{eq} = -2x$ or solving for $[A]$:

$$[A] = [A]_{eq} - 2x \quad 5$$

The $[A]^2$ in terms of the displacement is the square of eq. 5:

$$[A]^2 = [A]_{eq}^2 - 4[A]_{eq} x + 4x^2 \approx [A]_{eq}^2 - 4[A]_{eq} x \quad 6$$

However for the last inequality, we assume the displacement is small so that the $4x^2$ is negligible (as we assumed for Eq. 3.6.7). Substituting Eq. 6 into Eq. 4 and using $x = [A_2] - [A_2]_{eq}$, the rate law in terms of the displacements is:

$$\frac{dx}{dt} = -4k_2[A]_{eq} x - k_{-1} x \quad 7$$

Distributing out the factor of x gives:

$$\frac{dx}{dt} = -(4k_2[A]_{eq} + k_{-1}) x \quad 8$$

Setting the relaxation time to:

$$\tau = \frac{1}{(4k_2[A]_{eq} + k_{-1})} \quad 9$$

Substituting this definition for the relaxation time gives: $\frac{dx}{dt} = -\frac{x}{\tau}$ which integrates to:

$$x = x_0 e^{-t/\tau} \quad 10$$

as in Eq. 3.6.13. Once again, neglecting the term in x^2 in Eq. 6 guarantees the relaxation is simple-exponential.

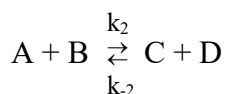
35. Consider the reaction: $A + B \rightleftharpoons C + D$

Show that the displacement for each product is x and for each reactant is $-x$, independent of the initial concentrations used to prepare the reaction mixture.

Answer: Set up the following reaction table to show the stoichiometric relationships based on the extent of the reaction:

	A	+	B	\rightleftharpoons	C	+	D
Initial	$[A]_0$		$[B]_0$		$[C]_0$		$[D]_0$
During	$[A] = [A]_0 - \xi$		$[B] = [B]_0 - \xi$		$[C] = [C]_0 + \xi$		$[D] = [D]_0 + \xi$
Equilibrium	$[A]_{eq} = [A]_0 - \xi_{eq}$		$[B]_{eq} = [B]_0 - \xi_{eq}$		$[C]_{eq} = [C]_0 + \xi_{eq}$		$[D]_{eq} = [D]_0 + \xi_{eq}$
Displacement	$[A] - [A]_{eq} =$ $([A]_0 - \xi) - ([A]_0 - \xi_{eq})$ $= \xi_{eq} - \xi = -x$		$[B] - [B]_{eq} =$ $([B]_0 - \xi) - ([B]_0 - \xi_{eq})$ $= \xi_{eq} - \xi = -x$		$[C] - [C]_{eq} =$ $([C]_0 + \xi) - ([C]_0 + \xi_{eq})$ $= \xi - \xi_{eq} = x$		$[D] - [D]_{eq} =$ $([D]_0 + \xi) - ([D]_0 + \xi_{eq})$ $= \xi - \xi_{eq} = x$

36. Consider a temperature jump perturbation for a reaction that is second order in the forwards and second order in the reverse direction:



Show the relaxation time is: $\tau \equiv \frac{1}{k_2([A]_{eq} + [B]_{eq}) + k_{-2}([C]_{eq} + [D]_{eq})}$

Answer: For the displacement away from equilibrium $x \equiv [C] - [C]_{eq} = [D] - [D]_{eq}$. Since the stoichiometry is 1:1 the displacement in A is $[A] - [A]_{eq} = [B] - [B]_{eq} = -x$. The stoichiometric relationships are summarized in Table P30.1.

Table P30.1: Concentrations for an opposed second-order/second-order reaction.

Progress	[A]	[B]	[C]	[D]
initial, new T	$[A]_o$	$[B]_o$	$[C]_o$	$[D]_o$
middle	$[A]_{eq} - x$	$[B]_{eq} - x$	$[C]_{eq} + x$	$[D]_{eq} + x$
equilibrium	$[A]_{eq}$	$[B]_{eq}$	$[C]_{eq}$	$[D]_{eq}$
displacement	$[A] - [A]_{eq} = -x$	$[B] - [B]_{eq} = -x$	$x \equiv [C] - [C]_{eq}$	$x \equiv [D] - [D]_{eq}$

The rate law is:

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

At equilibrium, the forward rate is equal to the reverse rate, $k_2[A]_{eq}[B]_{eq} = k_{-2}[C]_{eq}[D]_{eq}$, since at equilibrium the time derivative is zero:

$$k_2[A]_{eq}[B]_{eq} - k_{-2}[C]_{eq}[D]_{eq} = 0 \quad 2$$

Using Eq. 3.6.5

$$\frac{d[C]}{dt} = \frac{d([C]_{eq} + x)}{dt} = \frac{dx}{dt} \quad 3$$

Substituting the values from Table P30.1 and Eq. 3 into Eq. 1 gives:

$$\frac{dx}{dt} = k_2([A]_{eq} - x)([B]_{eq} - x) - k_{-2}([C]_{eq} + x)([D]_{eq} + x) \quad 4$$

Multiplying out each term gives:

$$\frac{dx}{dt} = k_2[A]_{eq}[B]_{eq} - k_2[A]_{eq}x - k_2[B]_{eq}x + k_2x^2 - k_{-2}[C]_{eq}[D]_{eq} - k_{-2}[C]_{eq}x - k_{-2}[D]_{eq}x - k_{-2}x^2 \quad 5$$

Since the perturbation is small, the displacement away from equilibrium, x , must be small. The term in x^2 is then negligible. Neglecting the terms in x^2 and subtracting Eq. 2 from Eq. 5 gives:

$$\frac{dx}{dt} = -k_2[A]_{eq}x - k_2[B]_{eq}x - k_{-2}[C]_{eq}x - k_{-2}[D]_{eq}x \quad 6$$

Distributing out the common factor of $-x$ gives:

$$\frac{dx}{dt} = - \{k_2([A]_{eq} + [B]_{eq}) + k_{-2}([C]_{eq} + [D]_{eq})\} x \quad 7$$

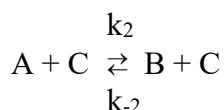
All the terms in the braces are constants. We define the relaxation time:

$$\tau \equiv \frac{1}{k_2([A]_{eq} + [B]_{eq}) + k_{-2}([C]_{eq} + [D]_{eq})} \quad 8$$

The rate law in terms of the displacement again reduces to

$$\frac{dx}{dt} = - \frac{x}{\tau} \quad 9$$

37. Consider a temperature jump perturbation for a reaction that is second order in the forwards and second order in the reverse direction and catalyzed by C:⁹



Given the catalyst concentration is $[C]_o$, show that the relaxation time is: $\tau = \frac{1}{(k_2 + k_{-2})[C]_o}$

Answer: Assuming that the reaction as written is complete and no other mechanistic steps are involved, the concentration of the catalyst is constant. The rate law is:

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

This reaction is pseudo-first order in both directions with effective rate constants that combine the original rate constants with the catalyst concentration:

$$\frac{d[B]}{dt} = (k_2[C]_o) [A] - (k_{-2}[C]_o) [B]$$

The reaction is then pseudo-first order in both directions, with relaxation time given by Eq. 3.6.14:

$$\tau = \frac{1}{(k_2[C]_o) + (k_{-2}[C]_o)}$$

which simplifies to: $\tau = \frac{1}{(k_2 + k_{-2})[C]_o}$

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