

Handin 3: Kinetics

1. Show that the integrated rate law for a second-order reaction that is first-order in A and first-order in B for the stoichiometry, $2 A + B \rightarrow \text{products}$, is:

$$\frac{1}{2 [B]_0 - [A]_0} \ln \left[\frac{[A]_0([B]_0 - \xi)}{[B]_0([A]_0 - 2\xi)} \right] = k_2 t \quad \text{and} \quad \xi = [B]_0 \frac{(1 - e^{(2[B]_0 - [A]_0) k_2 t})}{\left(1 - \frac{2[B]_0}{[A]_0} e^{(2[B]_0 - [A]_0) k_2 t}\right)}$$

[Try Chapter 3 Problem 19, first. See the integral table on the inside-back cover.]

Answer: The rate law is:

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

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

$$\frac{d\xi}{dt} = k_2 ([A]_0 - 2\xi)([B]_0 - \xi) \quad 2$$

Separating variables:

$$\frac{d\xi}{([A]_0 - 2\xi)([B]_0 - \xi)} = k_2 dt \quad 3$$

The indefinite integrals are:

$$\int \frac{d\xi}{([A]_0 - 2\xi)([B]_0 - \xi)} = \int k_2 dt \quad 4$$

Integral tables give (CRC):

$$\int \frac{d\xi}{(a + bx)(a' + b'x)} = \frac{1}{ab' - a'b} \ln \left(\frac{a' + b'x}{a + bx} \right) \quad 5$$

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

$$\int \frac{d\xi}{([A]_0 - 2\xi)([B]_0 - \xi)} = \frac{1}{2 [B]_0 - [A]_0} \ln \left(\frac{[B]_0 - \xi}{[A]_0 - 2\xi} \right) \quad 6$$

The integrated rate law is:

$$\frac{1}{2 [B]_0 - [A]_0} \ln \left(\frac{[B]_0 - \xi}{[A]_0 - 2\xi} \right) = k_2 t + c \quad 7$$

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

$$c = \frac{1}{2 [B]_0 - [A]_0} \ln \left(\frac{[B]_0}{[A]_0} \right) \quad 8$$

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

$$\frac{1}{2 [B]_o - [A]_o} \ln\left(\frac{[B]_o - \xi}{[A]_o - 2\xi}\right) = k_2 t + \frac{1}{2 [B]_o - [A]_o} \ln\left(\frac{[B]_o}{[A]_o}\right) \quad 9$$

Collecting common terms gives the linearized form commonly found in texts:

$$\frac{1}{2 [B]_o - [A]_o} \ln\left[\frac{[A]_o([B]_o - \xi)}{[B]_o([A]_o - 2\xi)}\right] = k_2 t \quad 10$$

Multiplying both sides of Eq. 9 by $2[B]_o - [A]_o$ and exponentiating gives:

$$\left(\frac{[B]_o - \xi}{[A]_o - 2\xi}\right) = e^{(2[B]_o - [A]_o) k_2 t + \ln([B]_o/[A]_o)} = \frac{[B]_o}{[A]_o} e^{(2[B]_o - [A]_o) k_2 t}$$

Cross multiplying and multiplying out terms:

$$[B]_o - \xi = [B]_o e^{(2[B]_o - [A]_o) k_2 t} - \frac{[B]_o}{[A]_o} 2\xi e^{(2[B]_o - [A]_o) k_2 t}$$

Collecting terms in ξ :

$$\xi - \frac{[B]_o}{[A]_o} 2\xi e^{(2[B]_o - [A]_o) k_2 t} = [B]_o - [B]_o e^{(2[B]_o - [A]_o) k_2 t}$$

Solving for ξ :

$$\xi = [B]_o \frac{(1 - e^{(2[B]_o - [A]_o) k_2 t})}{\left(1 - \frac{2[B]_o}{[A]_o} e^{(2[B]_o - [A]_o) k_2 t}\right)}$$

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

$$\xi = [A]_o \frac{(1 - e^{(2[B]_o - [A]_o) k_2 t})}{\left(\frac{[A]_o}{[B]_o} - 2 e^{(2[B]_o - [A]_o) k_2 t}\right)} \quad (2A + B \rightarrow \text{products})$$

For comparison for $A + B \rightarrow \text{products}$ the integrated rate law is very similar (see Problem 19):

$$\xi = [A]_o \frac{(1 - e^{([B]_o - [A]_o) k_2 t})}{\left(\frac{[A]_o}{[B]_o} - e^{([B]_o - [A]_o) k_2 t}\right)} \quad (A + B \rightarrow \text{products})$$

2. The rate constants of a first order reaction as a function of temperature is given below.

T (°C)	0.0	10.0	20.0	30.0	40.0
k (s ⁻¹)	2.53x10 ⁻⁶	1.11x10 ⁻⁵	4.37x10 ⁻⁵	1.72x10 ⁻⁴	5.54x10 ⁻⁴

- Use linear least squares curve fitting to find the activation energy and pre-exponential factor.
- Use propagation of errors rules to find the uncertainty in the activation energy and pre-exponential factor starting from the uncertainty in the slope and intercept.

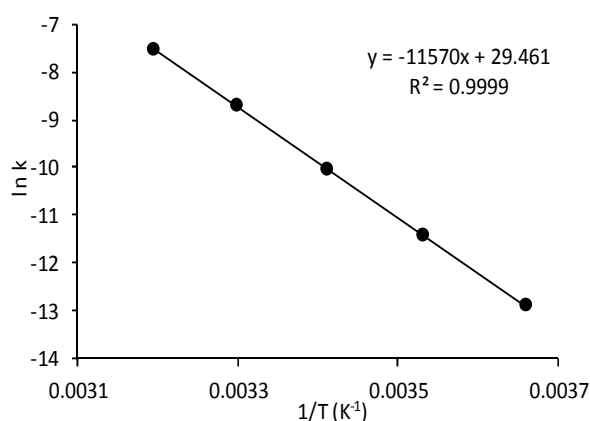
(c). Use non-linear curve fitting to the Arrhenius form, $k = A e^{-E_a/RT}$, to find the activation energy, pre-exponential factor, and corresponding uncertainties. Use the “Non-linear Least Squares Curve Fitting” applet on the course home page:

www.colby.edu/chemistry/PChem/scripts/lffitpl.html.

To make the presentation of the data easier in the applet, multiply the rate constants by 1×10^4 . However, remember to divide the resulting pre-exponential factor by 1×10^4 to get the proper order of magnitude. Comment on the meaning of the between-fit-parameters correlation coefficient from the non-linear fit. [Try Chapter 3 Problems 21 and 22, first.

Answer: Linearized Arrhenius form is: $\ln k = -E_a/RT + \ln A$. A plot of $\ln k$ versus $1/T$ is prepared using Excel as shown below. The activation energy is given by $E_a = -\text{slope} R = -11570.4(8.31447 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ mol}) = 96.20 \text{ kJ mol}^{-1}$. The pre-exponential factor is determined from the intercept as $A = e^{-b} = e^{-29.46} = 6.24 \times 10^{12} \text{ s}^{-1}$.

A1	B	C	D	E	F
2					
3		T (K)	T ⁻¹ (K ⁻¹)	k (s ⁻¹)	ln k
4		273.15	0.0036610	2.53E-06	-12.887
5		283.15	0.0035317	1.11E-05	-11.409
6		293.15	0.0034112	4.37E-05	-10.038
7		303.15	0.0032987	1.72E-04	-8.6680
8		313.15	0.0031934	5.54E-04	-7.4984
9					
10		slope	-11570.40	29.4614	intercept
11		±	80.168011	0.274430	±
12		r ²	0.999856	0.029641	s(y)
13		F	20830.251	3	df
14		SS _{reg}	18.301706	0.00264	SS _{resid}
15					
16		E _a	96.20174	kJ mol ⁻¹	
17		A	6.236E+12	s ⁻¹	



(b). The relative uncertainty in the slope is $80.2/11570$ (100%) = 0.69 % giving the activation energy as uncertain to 0.69 % or $96.20 \pm 0.67 \text{ kJ mol}^{-1}$. The intercept is 29.461 ± 0.274 . 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 the intercept is 0.274 so the relative standard deviation in $e^{29.461}$ is 0.274, or in other words 27%. As a result: $A = 6.2 \times 10^{12} \pm 1.7 \times 10^{12} \text{ s}^{-1}$

(c). The fit function that is closest to $k = A e^{-E_a/RT}$ is “a exp(b/x) + c” with the off-set constant fixed at zero. Scaling the rate constants by 1×10^4 is not necessary, but the presentation in the output listing is more useful. Guesses for the initial values of a and b are taken from the linear fitting. This particular functional form requires guesses fairly close to the final values; other functional forms are more tolerant. The input is shown below along with the final results.

Input data pairs:

273.15	0.0253
283.15	0.111
293.15	0.437
303.15	1.72
313.15	5.54

Fit function:

Parameter guesses:

a =

b =

c = Fixed

Convergence Mode: Fast Damped Strongly Damped

```

===== Results =====
a= 22800000000000000 +- 10400000000000000
b= -11258 +- 140
-----
Output Data
-----
      x          y          y(fit)    residual
273.15    0.0253    0.02867    -0.00337
283.15    0.111     0.12291    -0.01191
293.15    0.437     0.47712    -0.04012
303.15    1.72      1.69359     0.02641
313.15    5.54      5.54433    -0.00433
-----
sum of squared residuals= 0.002479
stand. dev. y values= 0.02875
correlation between a & b= -0.9999

```

The pre-exponential factor and uncertainty are given from the a-fit parameter, $a = 2.28 \times 10^{16}$, after reversing the scaling by 1×10^4 :

$$A = 2.28 \times 10^{12} \pm 1.0 \times 10^{12} \text{ s}^{-1}$$

The final activation energy is:

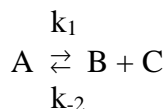
$$E_a = -b R = -(-11258)(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ} / 1000 \text{ J}) = 93.6 \pm 1.2 \text{ kJ mol}^{-1}$$

These results are outside the expected range of uncertainties as compared to the results from the linear fit. The results from the non-linear fit are generally recognized as more reliable and give a better representation of the experimental uncertainties as compared to the results from linearized fits.

The large differences between the linearized and non-linear fit results is explained by the correlation coefficient between a and b. Fit parameters a and b are essentially completely inversely correlated. The large correlation between a and b is greatly unfortunate, which increases the uncertainty in both fit parameters. In other words, a small change in one of the original data points, caused by random error, produces a large correlated change in both a and b. Redoing the linearized fit using the non-linear applet with function “ax+b” (instead of Excel) shows that even in the linearized fit, the correlation between the slope and intercept is equally large, -0.998. The reason for this correlation is that the intercept is far from the range of the data points. So doing the non-linear fit provides a useful lesson. Non-linear fitting programs give the fit parameter correlation, which linear least squares programs do not. Doing the linear fit using Excel hides this important statistic, which shows the linearized fit has significant problems that greatly increase the uncertainties in the fit parameters. The moral of the story is that non-linear fitting is generally the best method to explore the quality of your results. A good way of the final

uncertainty in the pre-exponential factor is to use the difference between the non-linear and linear fit results as a guess for the true uncertainty: $A = 2 \times 10^{12} \pm 4 \times 10^{12} \text{ s}^{-1}$.

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



Starting with A only, show the relaxation time is: $\tau \equiv \frac{1}{k_1 + k_{-2}([\text{B}]_{\text{eq}} + [\text{C}]_{\text{eq}})}$

[Try Chapter 3 Problems 34-37, first]

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

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

The rate law is for the production of B is:

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

At equilibrium, the forward rate is equal to the reverse rate, $k_1[\text{A}]_{\text{eq}} = k_{-2}[\text{B}]_{\text{eq}}[\text{C}]_{\text{eq}}$, since at equilibrium the time derivative is zero:

$$k_1[\text{A}]_{\text{eq}} - k_{-2}[\text{B}]_{\text{eq}}[\text{C}]_{\text{eq}} = 0 \quad 2$$

Using Eq. 3.6.5

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

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

$$\frac{dx}{dt} = k_1([\text{A}]_{\text{eq}} - x) - k_{-2}([\text{B}]_{\text{eq}} + x)([\text{C}]_{\text{eq}} + x) \quad 4$$

Multiplying out each term gives:

$$\frac{dx}{dt} = k_1[\text{A}]_{\text{eq}} - k_1 x - k_{-2}[\text{B}]_{\text{eq}}[\text{C}]_{\text{eq}} - k_{-2}[\text{B}]_{\text{eq}} x - k_{-2}[\text{C}]_{\text{eq}} x - k_{-2}x^2 \quad 5$$

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:

$$\frac{dx}{dt} = -k_1 x - k_{-2}[B]_{eq} x - k_{-2}[C]_{eq} x \quad 6$$

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

$$\frac{dx}{dt} = -\{k_1 + k_{-2}([B]_{eq} + [C]_{eq})\} x \quad 7$$

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

$$\tau \equiv \frac{1}{k_1 + k_{-2}([B]_{eq} + [C]_{eq})} \quad 8$$

The rate law in terms of the displacement again reduces to

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

which is a simple first-order exponential decay to equilibrium with time constant τ , the relaxation time.