Lecture: Collection and Analysis of Rate Data

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This lecture is coordinated with Chapter 5 of Fogler.

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I. The integral method for k_o, and the activation energy, E_a, with rate law known.

Earlier in the semester, we showed that, if one knew the rate law, one could record concentration vs time data in a batch reactor operated under isothermal conditions for several different temperatures, and from that data, extract the rate constant prefactor, k_o, and the activation energy, E_a.

As a review, the key steps in this process are listed below. We consider a homogeneous reaction with the following stoichiometry,

$$\upsilon_A A + \upsilon_B B \rightarrow \upsilon_C C + \upsilon_D D \tag{1}$$

taking place in an isothermal, jacketed, batch reactor. The rate of reaction, $r(t)$, is of the elementary form:

$$r(t) = k C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} \tag{2}$$

where C_A is the concentration of species A in moles/liter, C_B is the concentration of species B in moles/liter and k is the rate constant, defined as

$$k = k_o e^{\frac{-E_a}{RT}} \tag{3}$$

where k_o is the reaction rate prefactor constant, E_a is the activation energy, R is the gas constant, 8.314 J/mol/K, and T is the temperature in K.

The mole balance on A in a batch reactor is simply, accumulation = generation, or

$$\frac{dC_A}{dt} = \upsilon_A r(t) = \upsilon_A C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} k_o e^{\frac{-E_a}{RT}} \tag{4}$$

In order to integrate this ODE, we must eliminate the concentration of B from the equation. The mole balance on B in a batch reactor is

$$\frac{dC_B}{dt} = \upsilon_B r(t) = \frac{\upsilon_B}{\upsilon_A}\frac{dC_A}{dt} \tag{5}$$

We can solve for C_B in terms of C_A without ever involving time,

$$\int_{C_B(t_o)}^{C_B(t)} dC_B = \frac{\upsilon_B}{\upsilon_A}\int_{C_A(t_o)}^{C_A(t)} dC_A \tag{6}$$

Integration yields

$$C_B(t) - C_B(t_o) = \frac{\upsilon_B}{\upsilon_A}\left[C_A(t) - C_A(t_o)\right] \tag{7}$$

Isolating the concentration of B yields

$$C_B(t) = C_B(t_o) + \frac{\upsilon_B}{\upsilon_A}\left[C_A(t) - C_A(t_o)\right] \tag{8}$$

We substitute the expression for C_B into equation the mole balance for A yields

$$\frac{dC_A}{dt} = \upsilon_A C_A^{|\upsilon_A|}\left\{C_B(t_o) + \frac{\upsilon_B}{\upsilon_A}\left[C_A(t) - C_A(t_o)\right]\right\}^{|\upsilon_B|} k_o e^{\frac{-E_a}{RT}} \tag{9}$$

This equation can be integrated. For elementary rate laws, it can be integrated analytically.

$$\frac{dC_A}{\upsilon_A C_A^{|\upsilon_A|}\left\{C_{B,o}+\frac{\upsilon_B}{\upsilon_A}\left[C_A-C_{A,o}\right]\right\}^{|\upsilon_B|}}=k_o e^{\frac{-E_a}{RT}}dt \tag{10}$$

Integrate over time from t_o to t.

$$\int_{C_{A,o}}^{C_A}\frac{dC_A}{\upsilon_A C_A^{|\upsilon_A|}\left\{C_{B,o}+\frac{\upsilon_B}{\upsilon_A}\left[C_A-C_{A,o}\right]\right\}^{|\upsilon_B|}}=\int_{t_o}^{t}k_o e^{\frac{-E_a}{RT}}dt \tag{11}$$

The integral on the right hand side of equation is trivial to evaluate under isothermal conditions.

$$\int_{t_o}^{t}k_o \exp^{\frac{-E_a}{RT}}\,dt=k_o e^{\frac{-E_a}{RT}}\left(t-t_o\right) \tag{12}$$

The integral on the left hand side is somewhat trickier. Let's massage it into shape. Let $a=\frac{\upsilon_B}{\upsilon_A}$, $b=C_{B,o}-\frac{\upsilon_B}{\upsilon_A}C_{A,o}$, $n=|\upsilon_A|$, $m=|\upsilon_B|$, $x=C_A$. With these substitutions we have

$$\int_{C_{A,o}}^{C_A}\frac{dC_A}{\upsilon_A C_A^{|\upsilon_A|}\left\{C_{B,o}+\frac{\upsilon_B}{\upsilon_A}\left[C_A-C_{A,o}\right]\right\}^{|\upsilon_B|}}=-\frac{1}{n}\int_{x_o}^{x}\frac{dx}{x^n\left(ax+b\right)^m}=I_{n,m}(A)-I_{n,m}(A_o) \tag{13}$$

where

$$I_{n,m}=-\frac{1}{n}\int_{x_o}^{x}\frac{dx}{x^n\left(ax+b\right)^m} \tag{14}$$

Regardless of the particular form of the left-hand-side integral, the analytical function can be obtained. Check the Appendix for some examples of the analytical evaluation of this integral for realistic values of n and m.

After the integration, equation (11) becomes

$$I_{n,m}(C_A)-I_{n,m}(C_{A,o})=k_o e^{\frac{-E_a}{RT}}\left(t-t_o\right) \tag{15}$$

We linearize this so that we can perform a linear least squares regression to obtain k_o and E_a. The linearization involves taking the log of both sides.

$$\ln\left[I_{n,m}(C_A) - I_{n,m}(C_{A,o})\right] = \ln\left[k_o e^{\frac{-E_a}{RT}}\left(t - t_o\right)\right] \tag{16}$$

On the RHS, the log of a product is the sum of the logs.

$$\ln\left[I_{n,m}(C_A) - I_{n,m}(C_{A,o})\right] = \ln\left[k_o\right] + \ln\left[e^{\frac{-E_a}{RT}}\right] + \ln\left[t - t_o\right] \tag{17}$$

The natural log and the exponential are inverse operations.

$$\ln\left[I_{n,m}(C_A) - I_{n,m}(C_{A,o})\right] = \ln\left[k_o\right] + \frac{-E_a}{RT} + \ln\left[t - t_o\right] \tag{18}$$

If we move $\ln\left[t - t_o\right]$ to the LHS, and use the fact that the difference of logs is the log of the quotient, we have,

$$\ln\left[\frac{I_{n,m}(C_A) - I_{n,m}(C_{A,o})}{t - t_o}\right] = \ln\left[k_o\right] + \frac{-E_a}{RT} \tag{19}$$

Let $y = \ln\left[\frac{I_{n,m}(C_A) - I_{n,m}(C_{A,o})}{t - t_o}\right]$, $x = -\frac{1}{RT}$, $m = E_a$, $b = \ln\left[k_o\right]$. With these substitutions, we see that our equation is in the form

$$y = mx + b \tag{20}$$

We can perform a linear least-squares regression to obtain the parameters of best fit for the slope and the intercept. From these we can obtain k_o and E_a. Since *x* is a function of temperature, we need data from several different temperatures. (Two data points is the minimum required to fit our two-parameter model.)

Example 1.

Consider the case of an isomerization reaction where A → B. Equation 11 is

$$\int_{C_{A,o}}^{C_A} \frac{dC_A}{\upsilon_A C_A^{|\upsilon_A|}\left\{C_{B,o} + \frac{\upsilon_B}{\upsilon_A}\left[C_A - C_{A,o}\right]\right\}^{|\upsilon_B|}} = \int_{t_o}^{t} k_o e^{\frac{-E_a}{RT}} dt \tag{11}$$

which when υ_B is zero, simplifies to

$$-\int_{C_{A,o}}^{C_A} \frac{dC_A}{C_A} = \int_{t_o}^{t} k_o e^{\frac{-E_a}{RT}} dt \qquad (21)$$

Integration yields

$$-\ln\left(\frac{C_A}{C_{A,o}}\right) = k_o e^{\frac{-E_a}{RT}} \left(t - t_o\right) \qquad (22)$$

Linearization and simplification yields

$$\ln\left(\frac{\ln\left(\frac{C_{A,o}}{C_A}\right)}{t - t_o}\right) = \ln\left[k_o\right] + \frac{-E_a}{RT} \qquad (23)$$

(As a reminder, we know the analytical solution to this problem,

$$C_A = C_{A,o} \exp\left[-k_o e^{\frac{-E_a}{RT}} \left(t - t_o\right)\right] \qquad (22)$$

Consider a case where $k_o = 0.01$ s^{-1}, $E_a =$ 2000 J/mol and $C_{A,o} = 10.0$ mol/liter. If we run the reactor at two temperatures, 300 K and 400 K, and take only one measurement at a time of 60 s, then we have the following data, assuming perfect adherence to the model.

perfect model data

T (K)	time (s)	k	CA
300	60	0.004485	7.640696658
400	60	0.00548	7.197669005

Of course a regression of this data, will yield exactly the correct values of k_o and E_a.

regression of perfect model data

T	x	y	
300	-0.00040093	-5.40703	
400	-0.0003007	-5.20657	
slope	2000	-4.60517	intercept

The exp of the intercept yields $k_o = 0.01$ s^{-1}.

If we introduce up to 1% uncertainty into the measurements of the concentration, we have for example

model data with 1% uncertainty

T (K)	time (s)	k	CA
300	60	0.004484938	7.701162
400	60	0.005480464	7.213837

A regression of this data yields

regression of 1% uncertainty data

T	x	y	
300	-0.00040093	-5.436760456	
400	-0.0003007	-5.213412367	
slope	2228.299215	-4.5433681	intercept
ko =	0.010637518		
Ea error	0.114149608		
ko error	0.063751793		

So k_o = 0.0106 s^{-1}, E_a = 2228 J/mol for this particular random number used in the calculation, with errors of 6.3% and 11.4% respectively.

If we introduce up to 10% uncertainty into the measurements of the concentration, we have for example

model data with 10% uncertainty

T (K)	time (s)	k	CA
300	60	0.004485	7.29074
400	60	0.00548	7.599657

A regression of this data yields

regression of 10% uncertainty data

T	x	y	
300	-0.0004	-5.24642	
400	-0.0003	-5.38721	
slope	-1404.67	-5.80959	intercept
ko =	0.002999		
Ea error	-1.70233		
ko error	-0.70014		

So k_o = 0.0030 s^{-1}, E_a = -1404 J/mol for this particular random number used in the calculation, with errors of -70% and -170% respectively.

The point of this exercise is to illustrate that relatively small uncertainties in the concentrations can lead to huge errors in the kinetic parameters. How do you fix this? More data. Either you run the reactor at more temperatures or you collect data at more points at each temperature (or both).

Here we repeat the same example with one point at four temperatures.

If we introduce up to 1% uncertainty into the measurements of the concentration, we have for example

model data with 1% uncertainty

T (K)	time (s)	k	CA
300	60	0.004485	7.665222
300	60	0.004485	7.521488
300	60	0.004485	7.361643
400	60	0.00548	7.267751

A regression of this data yields

regression of 1% uncertainty data

T	x	y	
300	-0.0004	-5.41901	
333	-0.00036	-5.35024	
367	-0.00033	-5.27753	
400	-0.0003	-5.23648	
slope	1858.737	-4.67464	intercept
ko =	0.009329		
Ea error	-0.07063		
ko error	-0.06711		

So k_o = 0.0093 s^{-1}, E_a = 1858 J/mol for this particular random number used in the calculation, with errors of 6.7% and 7.1% respectively.

If we introduce up to 10% uncertainty into the measurements of the concentration, we have for example

model data with 10% uncertainty

T (K)	time (s)	k	CA
300	60	0.004485	7.141118
300	60	0.004485	6.925675
300	60	0.004485	7.1172
400	60	0.00548	6.804351

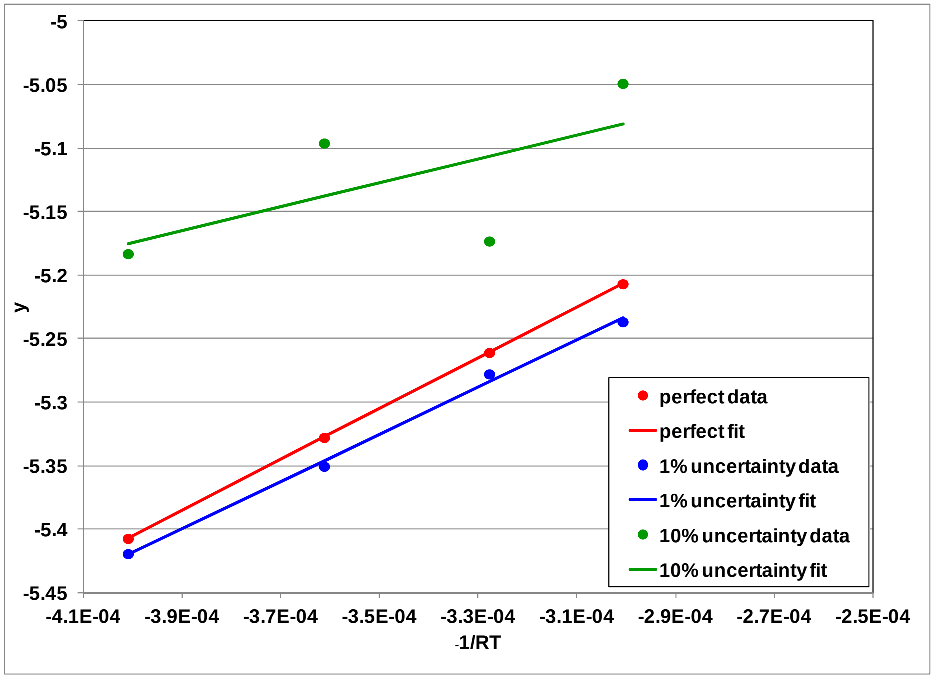
A regression of this data yields

regression of 10% uncertainty data

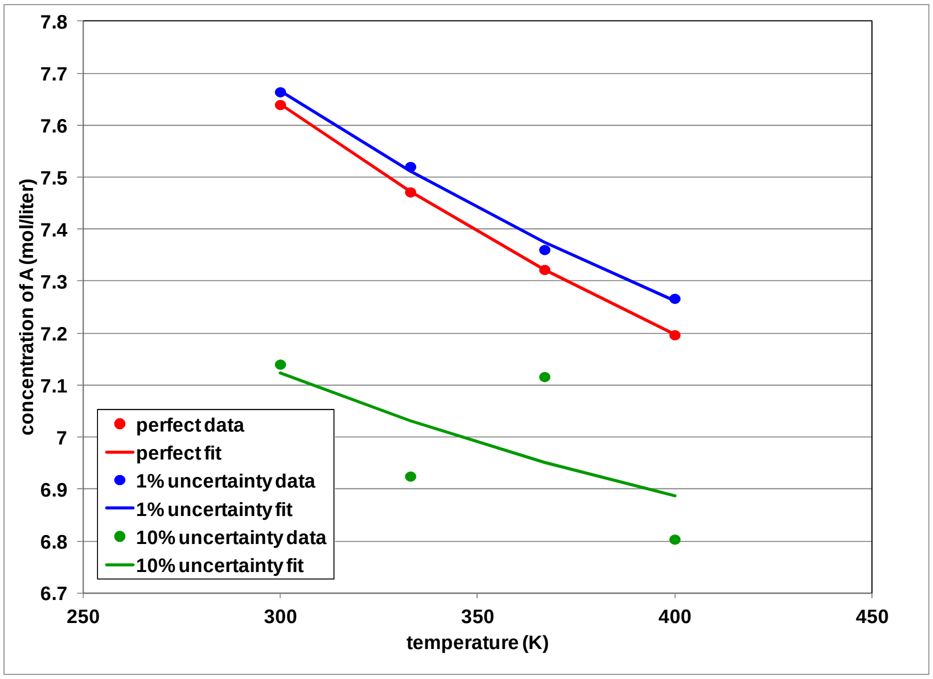
T		x	y	
	300	-0.0004	-5.18286	
	333	-0.00036	-5.09579	
	367	-0.00033	-5.17295	
	400	-0.0003	-5.0488	
slope		944.2857	-4.79683	intercept
ko =		0.008256		
Ea error		-0.52786		
ko error		-0.17441		

So $k_o = 0.00083\ \text{s}^{-1}$, $E_a = 944$ J/mol for this particular random number used in the calculation, with errors of -17% and -52% respectively.

The Arrhenius Plot is shown below



We also show a picture of the concentration of A versus reactor temperature at 60 sec.



concentration of A (mol/liter)
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7
6.9
6.8
6.7
250
300
350
400
450
temperature (K)
perfect data
perfect fit
1% uncertainty data
1% uncertainty fit
10% uncertainty data
10% uncertainty fit

II. The integral method for *k* only (not k_o and E_a individually) with rate law known.

Suppose we only need to know k and not k_o and E_a individually, then we don't need to run the reactor at multiple temperatures, because we don't need E_a. We still have our mole balance for A in the isothermal batch reactor.

$$\frac{dC_A}{dt} = \upsilon_A r(t) = \upsilon_A k C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} \tag{23}$$

We once again eliminate C_B in terms of C_A, which yields a mole balance like

$$\frac{dC_A}{dt} = \upsilon_A k C_A^{|\upsilon_A|} \left\{ C_B(t_o) + \frac{\upsilon_B}{\upsilon_A}\left[C_A(t) - C_A(t_o)\right] \right\}^{|\upsilon_B|} \tag{24}$$

As before, we separate and integrate

$$\int_{C_{A,o}}^{C_A} \frac{dC_A}{\upsilon_A C_A^{|\upsilon_A|} \left\{ C_{B,o} + \frac{\upsilon_B}{\upsilon_A}\left[C_A - C_{A,o}\right] \right\}^{|\upsilon_B|}} = k\left(t - t_o\right) \tag{25}$$

After the integration, we have

$$I_{n,m}(C_A) - I_{n,m}(C_{A,o}) = k\left(t - t_o\right) \tag{26}$$

where

$$I_{n,m} = -\frac{1}{n}\int_{x_o}^{x} \frac{dx}{x^n\left(ax + b\right)^m} \tag{27}$$

Check the Appendix for some examples of the analytical evaluation of this integral for realistic values of n and m.

In this case, the equation is already linear in the unknown, k. So, if we identify $y = I_{n,m}(C_A) - I_{n,m}(C_{A,o}) = k\left(t - t_o\right)$, $x = \left(t - t_o\right)$, and $m = k$, then it is easy to see that our equation is of the form y = mx+b where b = 0. Thus the slope of the curve is the rate constant. For this problem, we require only one run of the reactor with multiple measurements of concentration as a function of time.

Example 2.

Consider the same first order reaction, A → B, worked in the previous example with $k_o = 0.01$ s^{-1}, $E_a = 2000$ J/mol and $C_{A,o} = 10.0$ mol/liter.

The integrated mole balance was derived above,

$$\ln\left(\frac{C_{A,o}}{C_A}\right) = k\left(t - t_o\right) \tag{28}$$

If we run the reactor at only one temperature, 300 K, and measure at several times we have the following data for a perfect model, data with 1% uncertainty and data with 10% uncertainty.

	perfect model data	data with 1% uncertainty	data with 10% uncertainty
time (s)	CA	CA	CA
50	7.991177889	8.044038	8.721793
100	6.385892406	6.328766	6.217796
150	5.103080219	5.148634	5.478777
200	4.077962182	4.11007	3.684187
250	3.258772122	3.273692	3.306552
300	2.604142773	2.627322	2.703003
350	2.081016814	2.076428	1.960632
400	1.662977555	1.656794	1.721018
450	1.328914947	1.329199	1.277423
500	1.061959574	1.060793	1.066324

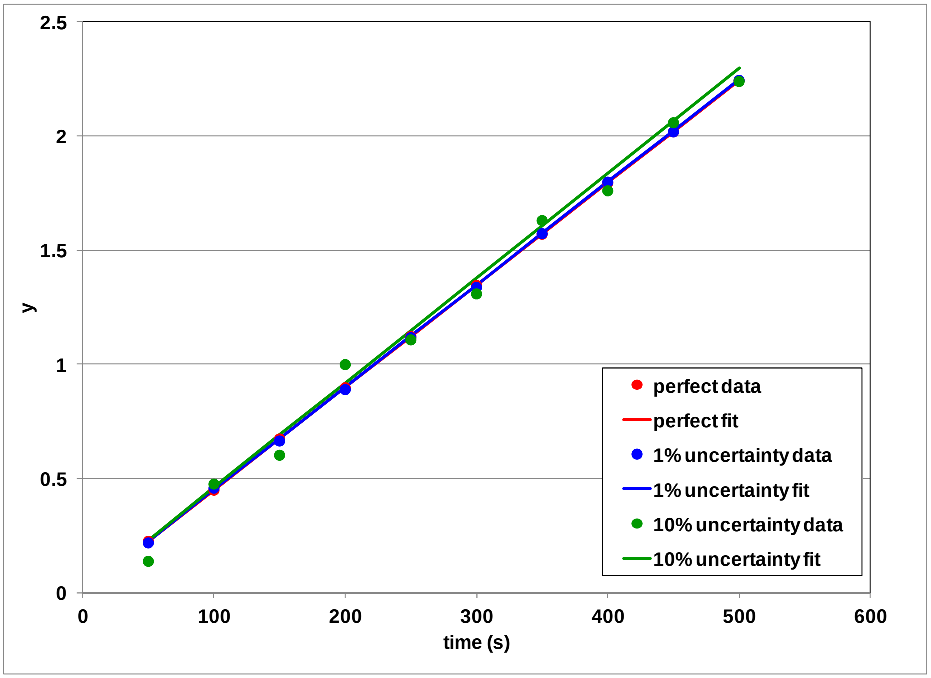
The data can be manipulated in sets of x and y upon which regression can be performed.

	perfect model data	data with 1% uncertainty	data with 10% uncertainty
x	y	y	y
50	0.224247	0.217654	0.13676
100	0.448494	0.45748	0.47517
150	0.672741	0.663854	0.601703
200	0.896988	0.889145	0.998535
250	1.121235	1.116667	1.106679
300	1.345482	1.33662	1.308222
350	1.569728	1.571936	1.629318
400	1.793975	1.797701	1.759669
450	2.018222	2.018009	2.05774
500	2.242469	2.243569	2.238368

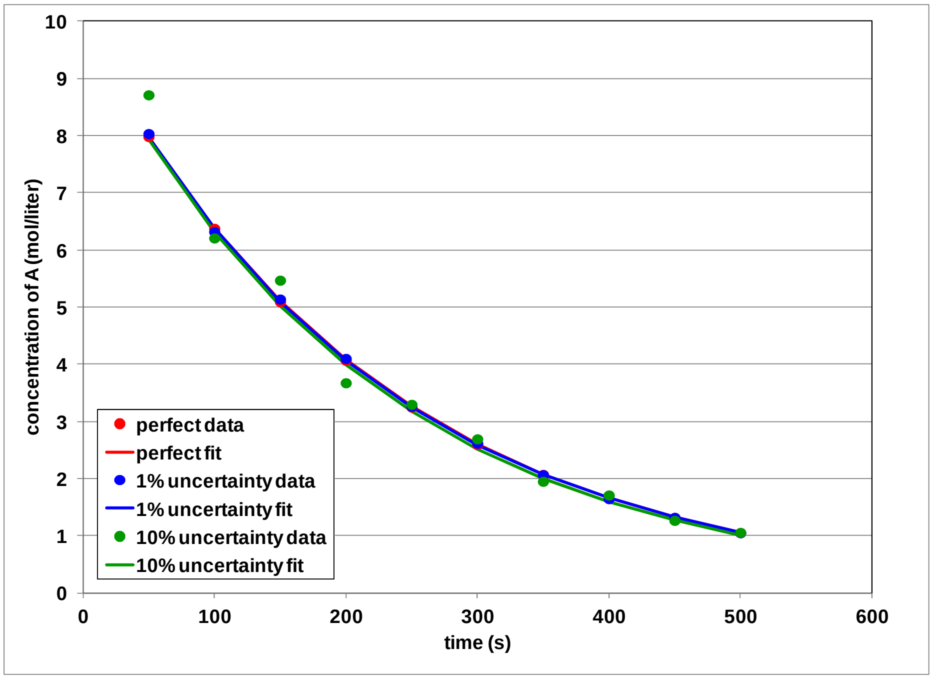
The regressions on these three data sets yields.

	perfect model data	data with 1% uncertainty	data with 10% uncertainty
k (1/s)	0.004484938	0.004496	0.004591
k error	0.0	0.25%	2.4%

We see a couple things in this example. First, with ten data points, the error in the rate constant is smaller. The error in the rate constant is smaller than the error associated with each individual measurement of the concentration. Second, we see that with data from only one temperature, we cannot simultaneously compute k_o and E_a, just their combination in k. Plots of the fits are shown below. In the first figure, we show the actual curve from which the regression was taken.



In the curve below, we plot concentration as a function of time.



10
9
8
7
6
5
4
3
2
1
0
concentration of A (mol/liter)
0
100
200
300
400
500
600
time (s)
perfect data
perfect fit
1% uncertainty data
1% uncertainty fit
10% uncertainty data
10% uncertainty fit

III. The differential method for *k* only (not k_o and E_a individually) with rate law known.

Suppose we only need to know *k* and not k_o and E_a individually, then we don't need to run the reactor at multiple temperatures, because we don't need E_a. We still have our mole balance for A in the isothermal batch reactor.

$$\frac{dC_A}{dt} = \upsilon_A r(t) = \upsilon_A k C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} \tag{23}$$

We either measured C_B or we eliminate C_B in terms of C_A,

$$C_B(t) = C_B(t_o) + \frac{\upsilon_B}{\upsilon_A}\left[C_A(t) - C_A(t_o)\right] \tag{28}$$

If we have data, then we can use a centered finite-difference formula to estimate the rate. Once we have the rate, we simply assign values of $y = \frac{dC_A}{dt}$, $x = \upsilon_A C_A^{|\upsilon_A|} C_B^{|\upsilon_B|}$, and $m = k$. This is of the form y = mx+b with b = 0. We directly regress for the rate constant. Again, since we aren't looking for E_a individually, we only need a run at one temperature. We can use the following centered-finite difference formula for all points in the interior of the data set.

$$\left.\frac{dC_A}{dt}\right|_{t_i} = \frac{C_A(t_{i+1}) - C_A(t_{i-1})}{t_{i+1} - t_{i-1}} \tag{29.a}$$

We either ignore the first point and last point or we use the forward and backward finite difference formulae respectively for them,

$$\left.\frac{dC_A}{dt}\right|_{t_i} = \frac{C_A(t_{i+1}) - C_A(t_i)}{t_{i+1} - t_i} \tag{29.b}$$

$$\left.\frac{dC_A}{dt}\right|_{t_i} = \frac{C_A(t_i) - C_A(t_{i-1})}{t_i - t_{i-1}} \tag{29.c}$$

Example 3.

Consider the same first order reaction, A → B, worked in the previous example with k_o = 0.01 s^{-1}, E_a = 2000 J/mol and $C_{A,o}$ = 10.0 mol/liter. In this case $y = \frac{dC_A}{dt}$ and $x = -C_A$.

If we run the reactor at only one temperature, 300 K, and measure at several times we have the following data for a perfect model, data with 1% uncertainty and data with 10% uncertainty.

	perfect model data	data with 1% uncertainty	data with 10% uncertainty
time (s)	CA	CA	CA
50	7.991177889	7.994621	8.360794
100	6.385892406	6.371816	6.076995
150	5.103080219	5.115098	5.319733
200	4.077962182	4.041021	4.411273
250	3.258772122	3.244587	3.338548
300	2.604142773	2.581941	2.593858
350	2.081016814	2.061444	1.881243
400	1.662977555	1.65551	1.812195
450	1.328914947	1.324587	1.28708
500	1.061959574	1.065157	1.005825

The data can be manipulated in sets of x and y upon which regression can be performed.

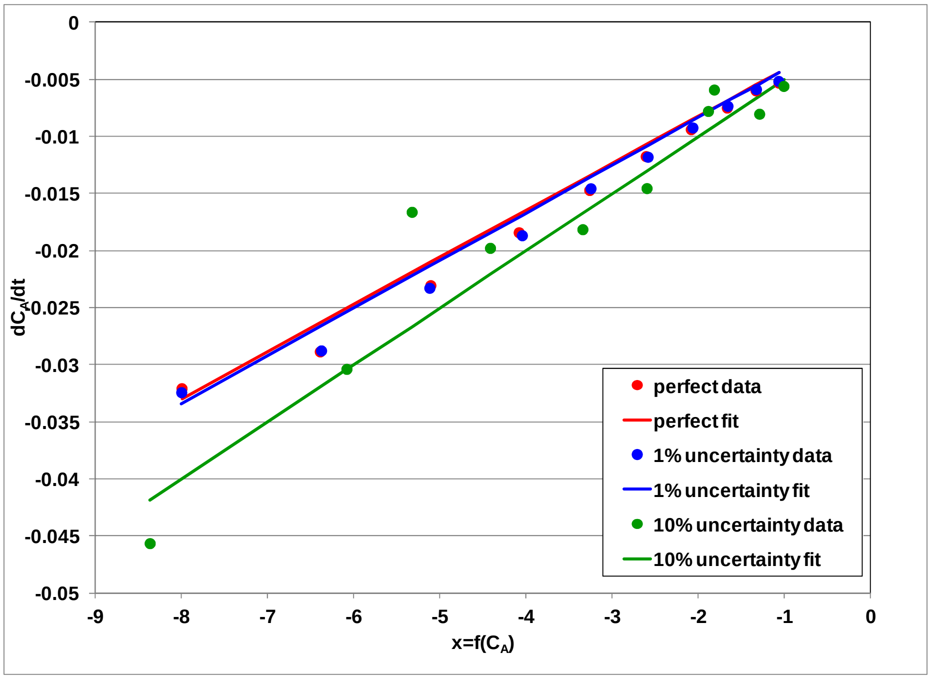
perfect model data		data with 1% uncertainty		data with 10% uncertainty	
x	y	x	y	x	y
-7.991177889	-0.03211	-7.99462	-0.03246	-8.36079	-0.04568
-6.385892406	-0.02888	-6.37182	-0.0288	-6.07699	-0.03041
-5.103080219	-0.02308	-5.1151	-0.02331	-5.31973	-0.01666
-4.077962182	-0.01844	-4.04102	-0.01871	-4.41127	-0.01981
-3.258772122	-0.01474	-3.24459	-0.01459	-3.33855	-0.01817
-2.604142773	-0.01178	-2.58194	-0.01183	-2.59386	-0.01457
-2.081016814	-0.00941	-2.06144	-0.00926	-1.88124	-0.00782
-1.662977555	-0.00752	-1.65551	-0.00737	-1.81219	-0.00594
-1.328914947	-0.00601	-1.32459	-0.0059	-1.28708	-0.00806
-1.061959574	-0.00534	-1.06516	-0.00519	-1.00583	-0.00563

The regressions on these three data sets yields.

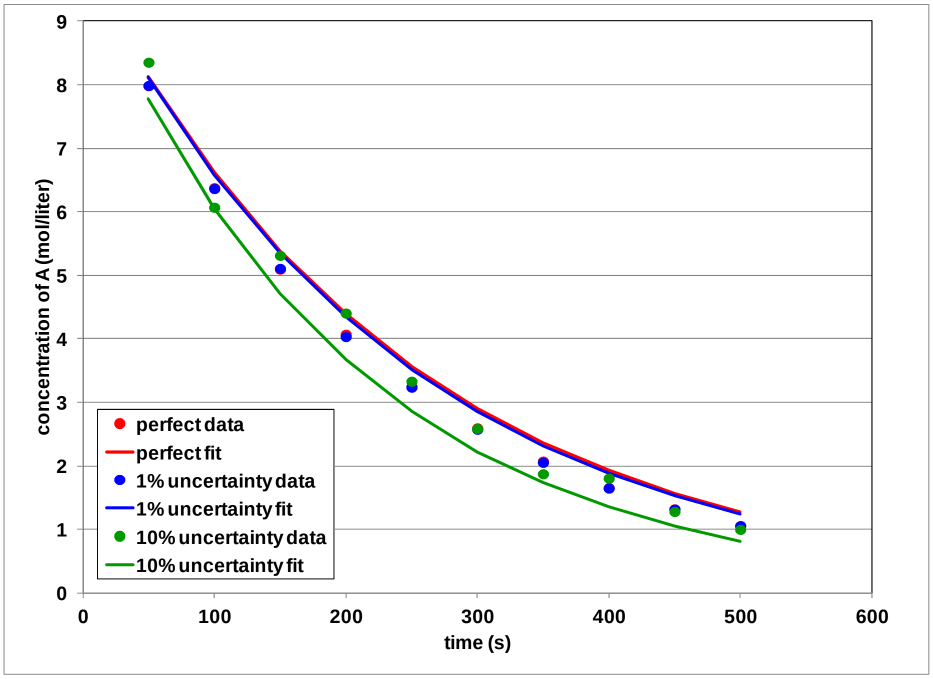
	perfect model data	data with 1% uncertainty	data with 10% uncertainty
k (1/s)	0.004124175	0.004180	0.005012
k error	-8.0%	-6.8%	11.8%

In this example, we see that the differential approach is inferior to the integral approach because even in the perfect model case, there is error? Why? Because the centered finite-difference formula is an approximation. It is an unnecessary approximation since we saw that if we used the integral approach, we could fit the perfect model data without any error.

We show the plot that was used for the regression:



We also show the plot with concentration as a function of time.



IV. The differential method for *k_o*, and the activation energy, *E_a*, with rate law known.

Suppose we need both k_o and E_a individually, then we must run the isothermal reactor at multiple temperatures. We still have our mole balance for A in the isothermal batch reactor.

$$\frac{dC_A}{dt} = \upsilon_A r(t) = \upsilon_A k C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} = \upsilon_A k_o \exp\left(-\frac{E_a}{RT}\right) C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} \tag{23}$$

We either measured C_B or we eliminate C_B in terms of C_A,

$$C_B(t) = C_B(t_o) + \frac{\upsilon_B}{\upsilon_A}\left[C_A(t) - C_A(t_o)\right] \tag{28}$$

As in the previous example, we use finite-difference formula to estimate the rate, $\frac{dC_A}{dt}$. We then linearize the equation, as follows,

$$\frac{\frac{dC_A}{dt}}{\upsilon_A C_A^{|\upsilon_A|} C_B^{|\upsilon_B|}} = k_o \exp\left(-\frac{E_a}{RT}\right) \tag{30}$$

$$\ln\left(\frac{\frac{dC_A}{dt}}{\upsilon_A C_A^{|\upsilon_A|} C_B^{|\upsilon_B|}}\right) = \ln(k_o) - \frac{E_a}{RT} \tag{31}$$

We assign values of $y = \ln\left(\frac{\frac{dC_A}{dt}}{\upsilon_A C_A^{|\upsilon_A|} C_B^{|\upsilon_B|}}\right)$, $x = -\frac{1}{RT}$, $m = E_a$ and $b = \ln(k_o)$. This is of the form y = mx+b. We directly regress for k_o and E_a.

Example 4.

Consider the same first order reaction, A → B, worked in the previous example with $k_o = 0.01\ \mathrm{s}^{-1}$, $E_a =$ 2000 J/mol and $C_{A,o} = 10.0$ mol/liter. In this case $y = \frac{dC_A}{dt}$ and $x = -C_A$.

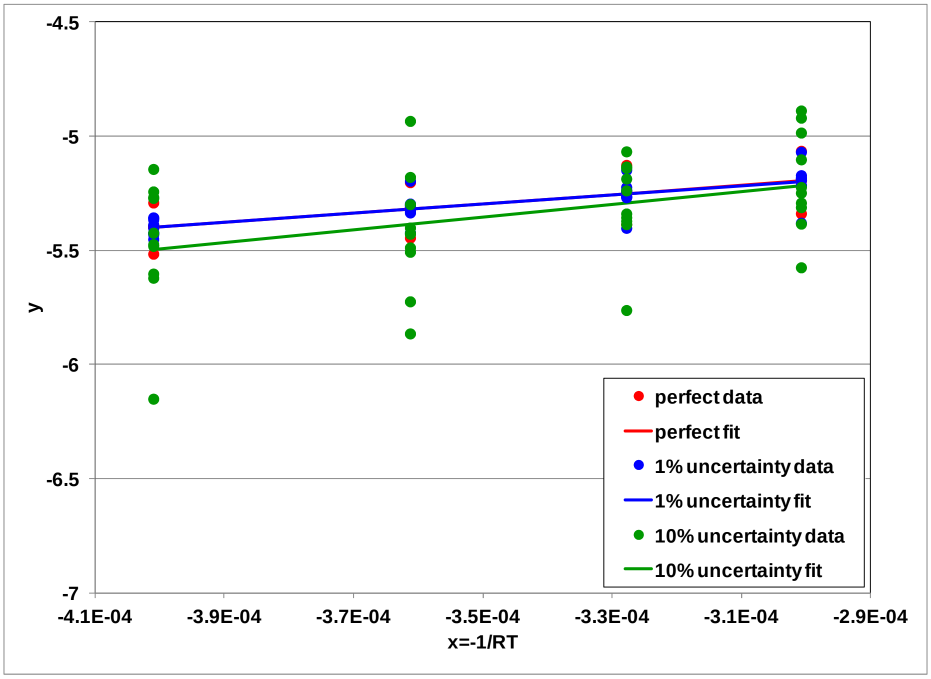
If we run the reactor at several temperatures and measure at several times we have the following data for a perfect model, data with 1% uncertainty and data with 10% uncertainty. In the same table, the regression variables x and y are also given.

raw data					**regression variables**			
		perfect model data	data with 1% uncertainty	data with 10% uncertainty		perfect model data	data with 1% uncertainty	data with 10% uncertainty
T (K)	time (s)	CA (mol/l)	CA	CA	x	y	y	y
300	50	7.991177889	8.055904	7.277559	-0.00040093	-5.51706	-5.45295	-6.15217
300	100	6.385892406	6.330473	6.502918	-0.00040093	-5.39866	-5.35825	-5.62265
300	150	5.103080219	5.074785	4.926715	-0.00040093	-5.39866	-5.40395	-5.48287
300	200	4.077962182	4.047438	4.454689	-0.00040093	-5.39866	-5.38949	-5.60424
300	250	3.258772122	3.227406	3.286399	-0.00040093	-5.39866	-5.42546	-5.24434
300	300	2.604142773	2.626394	2.720364	-0.00040093	-5.39866	-5.43206	-5.27295
300	350	2.081016814	2.078598	1.891275	-0.00040093	-5.39866	-5.36704	-5.14574
300	400	1.662977555	1.656122	1.61885	-0.00040093	-5.39866	-5.39214	-5.47532
300	450	1.328914947	1.324694	1.213155	-0.00040093	-5.39866	-5.42453	-5.26898
300	500	1.061959574	1.072308	0.994214	-0.00040093	-5.29281	-5.35863	-5.42517
333	50	7.844334579	7.905152	7.143151	-0.000361198	-5.44651	-5.42392	-5.48957
333	100	6.153358498	6.162138	5.668229	-0.000361198	-5.31776	-5.30179	-5.42655
333	150	4.826900285	4.834768	4.650127	-0.000361198	-5.31776	-5.30654	-5.72572
333	200	3.786382081	3.764551	4.151821	-0.000361198	-5.31776	-5.29751	-5.42958
333	250	2.970164789	2.950978	2.829581	-0.000361198	-5.31776	-5.31106	-4.93536
333	300	2.329896636	2.307741	2.117958	-0.000361198	-5.31776	-5.33048	-5.29985
333	350	1.827648874	1.833631	1.772226	-0.000361198	-5.31776	-5.3365	-5.40262
333	400	1.433668926	1.425274	1.319609	-0.000361198	-5.31776	-5.3008	-5.18072
333	450	1.124617873	1.122764	1.030085	-0.000361198	-5.31776	-5.3266	-5.50867
333	500	0.882187887	0.879546	0.902269	-0.000361198	-5.20372	-5.19747	-5.86634
367	50	7.713611763	7.646181	7.374697	-0.000327736	-5.38763	-5.40399	-5.76371
367	100	5.949980644	5.926323	6.21707	-0.000327736	-5.24944	-5.26979	-5.38762
367	150	4.589584069	4.597285	4.531723	-0.000327736	-5.24944	-5.26766	-5.18808
367	200	3.540226966	3.556127	3.68713	-0.000327736	-5.24944	-5.2642	-5.35751
367	250	2.730793637	2.757508	2.794113	-0.000327736	-5.24944	-5.24813	-5.23979
367	300	2.106428192	2.106405	2.205867	-0.000327736	-5.24944	-5.2247	-5.13522
367	350	1.624816928	1.623846	1.495799	-0.000327736	-5.24944	-5.24293	-5.06887
367	400	1.253320697	1.248243	1.265082	-0.000327736	-5.24944	-5.23663	-5.37307
367	450	0.966762927	0.96001	0.908818	-0.000327736	-5.24944	-5.24945	-5.14087
367	500	0.745723389	0.744199	0.733189	-0.000327736	-5.12804	-5.14993	-5.34105
400	50	7.603144176	7.578544	8.107917	-0.000300698	-5.34045	-5.38146	-5.29361
400	100	5.780780136	5.835071	6.071383	-0.000300698	-5.19408	-5.21673	-4.98645
400	150	4.395210483	4.413003	3.96125	-0.000300698	-5.19408	-5.17301	-4.88975
400	200	3.341741898	3.334005	3.091223	-0.000300698	-5.19408	-5.19338	-5.31319
400	250	2.540774545	2.561554	2.43845	-0.000300698	-5.19408	-5.21655	-5.225
400	300	1.931787519	1.944108	1.779248	-0.000300698	-5.19408	-5.18582	-5.10379
400	350	1.468765902	1.473759	1.357788	-0.000300698	-5.19408	-5.19073	-5.38533
400	400	1.116723892	1.123525	1.156926	-0.000300698	-5.19408	-5.19337	-5.57661
400	450	0.849061275	0.849834	0.919849	-0.000300698	-5.19408	-5.18334	-5.24978
400	500	0.645553529	0.646835	0.674126	-0.000300698	-5.06643	-5.07091	-4.92123

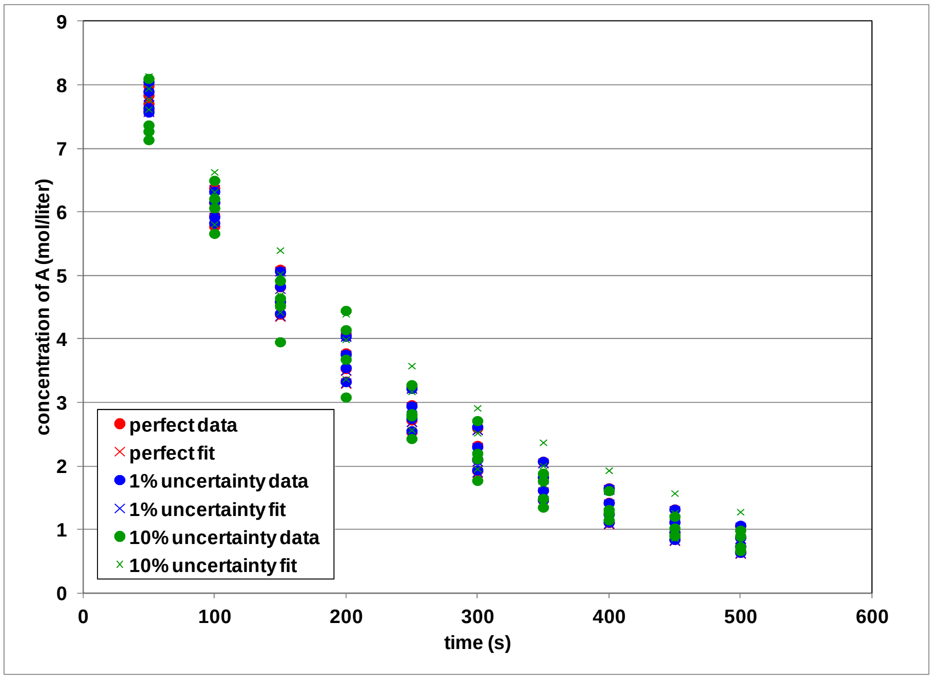
The results of the regression are provided in the table below.

	perfect model data	data with 1% uncertainty	data with 10% uncertainty
Ea	2034.811048	1970.8816	2793.073
ko	0.010212205	0.0099783	0.012569
Ea error	1.74%	-1.46%	39.65%
k error	2.12%	-0.22%	25.69%

We observe again that using the differential method introduces error even when presented with perfect model data. We also observe in this example, where we had 40 data points, (10 measurements at different times at each of the four temperatures) that the data with 1% variation was well described. The errors in the data for the 10% variations are much larger. The plot on which the regression was based is shown below.



The plot of concentration as a function of time, shown once for each temperature (four times for each of the three data sets is also shown below) although now there is too much data to make much sense of it.



concentration of A (mol/liter)
9
8
7
6
5
4
3
2
1
0
0
100
200
300
400
500
600
time (s)
● perfect data
× perfect fit
● 1% uncertainty data
× 1% uncertainty fit
● 10% uncertainty data
× 10% uncertainty fit

V. Determining the rate law – elementary rate laws via fitting the exponents

In the four sections described above, we assumed that we knew the rate law and we were tasked with finding *k* or k_o and E_a. We used our knowledge of the rate law in the mole balance. If we don't know the rate law, our task is to find the rate law and the parameters simultaneously.

In general, the procedure is as follows. First, we postulate a rate law. Then we perform some check against the data to determine if our guess was a good one. If it wasn't we perform postulate a different rate law until we find one that fits well or we give up. As illustrated above, we need good data to do this kind of determination. We will split the examples up into elementary rate laws and non-elementary rate laws.

If we assume the rate law is elementary, then we know in an isothermal batch reactor, the mole balance is of the form:

$$\frac{dC_A}{dt} = \upsilon_A r(t) = \upsilon_A k C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} \qquad (23)$$

The complication is now we do not know the stoichiometric coefficients. They are also unknowns. If we use the differential method, then we can estimate the rate of loss of concentration of A from the concentration data using the finite difference formulae. So, we linearize the equation by taking the log.

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln\left(|\upsilon_A| k\right) + |\nu_A| \ln\left(C_A\right) + |\nu_B| \ln\left(C_B\right) \qquad (32)$$

where we rewrote $\upsilon_A = -|\upsilon_A|$ since we know A is a reactant and its coefficient is negative. Grouping the negative sign with the rate (also negative) allows us to take the log of a positive number.

This equation is a multivariate linear equation of the form,

$$y = b + m_1 x_1 + m_2 x_2 \qquad (33)$$

where $y = \ln\left(-\frac{dC_A}{dt}\right)$, $b = \ln\left(|\upsilon_A| k\right)$, $m_1 = |\nu_A|$, $x_1 = \ln\left(C_A\right)$, $m_2 = |\nu_B|$ and $x_2 = \ln\left(C_B\right)$.

Multivariate linear regression is the same process as single variable linear regression except applied to more variables. The equation is linear in the unknowns, m_1, m_2 and *b*.

Example 5.

We will work two examples here. A simple example first and a more complicated example next. In the first example, we model a first order reaction, A → B in an isothermal batch reactor. In this case, there is only reactant, so the mole balance becomes

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln\left(|\upsilon_A| k\right) + |\nu_A| \ln\left(C_A\right) \qquad (34)$$

The slope of this is the order of the reaction in A and the intercept will yield the rate constant. Consider the same first order reaction, A → B, worked in the previous example with $k_o = 0.01$ s^{-1}, E_a = 2000 J/mol and $C_{A,o}$ = 10.0 mol/liter. If we run the reactor at only one temperature, 300 K, and measure at several times we have the following data for a perfect model, data with 1% uncertainty and data with 10% uncertainty.

	perfect model data	data with 1% uncertainty	data with 10% uncertainty
time (s)	CA	CA	CA
50	7.991177889	8.015368	7.635204
100	6.385892406	6.42855	6.037697
150	5.103080219	5.062454	5.196529
200	4.077962182	4.100368	3.757393
250	3.258772122	3.254426	3.315543
300	2.604142773	2.592243	2.419732
350	2.081016814	2.069532	1.892247
400	1.662977555	1.652325	1.768125
450	1.328914947	1.341064	1.296133
500	1.061959574	1.066879	1.136096

The data can be manipulated in sets of x and y upon which regression can be performed.

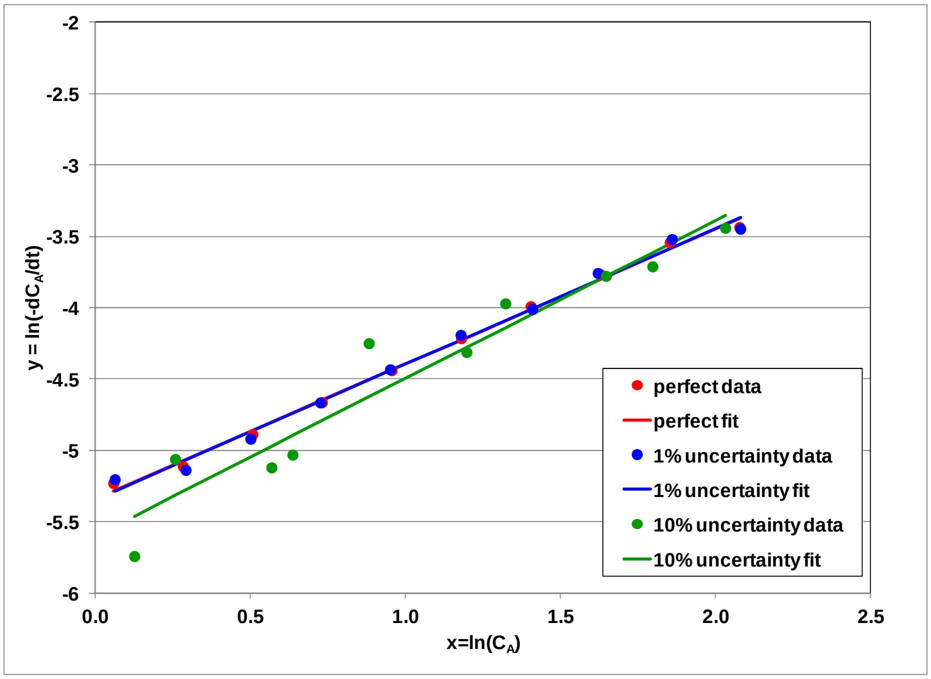
perfect model data		data with 1% uncertainty		data with 10% uncertainty	
x	y	x	y	x	y
2.078338169	-3.43872	2.0813607	-3.45029	2.03277	-3.44358
1.854091246	-3.54457	1.8607491	-3.52238	1.798023	-3.71372
1.629844322	-3.76882	1.6218514	-3.76008	1.647991	-3.78086
1.405597398	-3.99307	1.4110766	-4.01293	1.323725	-3.97337
1.181350475	-4.21731	1.1800159	-4.1943	1.198621	-4.31425
0.957103551	-4.44156	0.9525236	-4.43552	0.883657	-4.2522
0.732856627	-4.66581	0.7273224	-4.66713	0.637765	-5.03348
0.508609704	-4.89005	0.5021833	-4.92198	0.569919	-5.12249
0.28436278	-5.1143	0.2934632	-5.14055	0.259385	-5.06399
0.060115856	-5.2327	0.0647375	-5.20598	0.127598	-5.74437

The regressions on these three data sets yields.

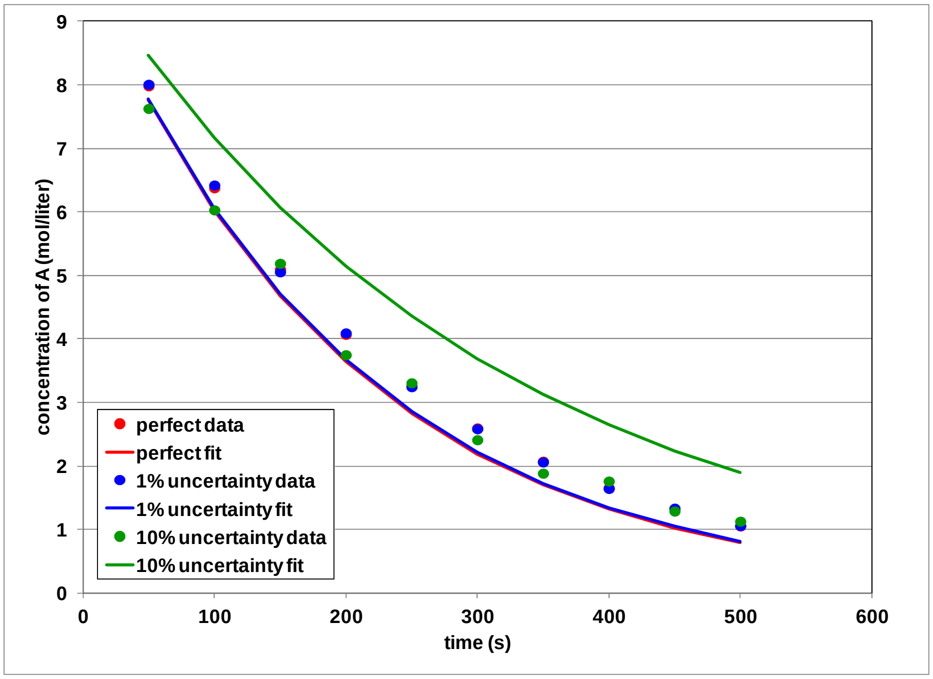
	perfect model data	data with 1% uncertainty	data with 10% uncertainty
$\lvert\nu_A\rvert$	0.945	0.948	1.107
$\lvert\nu_A\rvert$ error	-5.5%	-5.0%	10.7%
k (1/s)	0.00506	0.00501	0.00332
k error	12.9%	11.8%	-25.9%

In all cases, the stoichiometric coefficient is close to unity. Therefore, we can confirm that this reaction is first order in A. The rate constant is also reproduced relatively well.

We show the plot that was used for the regression:



We also show the plot with concentration as a function of time.



Example 6.

Let's also examine a case with more than one reactant, so we can perform the multivariate regression. Consider the reaction A + B → C performed in an isothermal batch reactor. In order to generate our perfect model data, we first solve the model analytically. From the analytical solution we can randomize concentrations and generate data with varying degrees of uncertainty, as we have done in the previous examples.

We begin with our mole balance for A in the isothermal batch reactor.

$$\frac{dC_A}{dt} = \upsilon_A r(t) = \upsilon_A k C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} \tag{23}$$

We once again eliminate C_B in terms of C_A, which yields a mole balance like

$$\frac{dC_A}{dt} = \upsilon_A k C_A^{|\upsilon_A|} \left\{ C_B(t_o) + \frac{\upsilon_B}{\upsilon_A}\left[C_A(t) - C_A(t_o)\right] \right\}^{|\upsilon_B|} \tag{24}$$

As before, we separate and integrate

$$\int_{C_{A,o}}^{C_A} \frac{dC_A}{\upsilon_A C_A^{|\upsilon_A|} \left\{ C_{B,o} + \frac{\upsilon_B}{\upsilon_A}\left[C_A - C_{A,o}\right] \right\}^{|\upsilon_B|}} = k(t - t_o) \tag{25}$$

After the integration, we have

$$I_{n,m}(C_A) - I_{n,m}(C_{A,o}) = k(t - t_o) \tag{26}$$

where

$$I_{n,m} = -\frac{1}{n}\int_{x_o}^{x} \frac{dx}{x^n (ax+b)^m} \tag{27}$$

where $a = \frac{\upsilon_B}{\upsilon_A}$, $b = C_{B,o} - \frac{\upsilon_B}{\upsilon_A} C_{A,o}$, $n = |\upsilon_A|$, $m = |\upsilon_B|$, $x = C_A$. In this example *n* = 1 and *m* = 1,

$$\begin{aligned} I_{1,1} &= -\int_{x_o}^{x} \frac{dx}{x(ax+b)} = -\frac{1}{b}\ln\left(\frac{x}{ax+b}\right)\Bigg|_{x_o}^{x} = -\frac{1}{b}\ln\left(\frac{x}{ax+b}\right) + \frac{1}{b}\ln\left(\frac{x_o}{ax_o+b}\right) \\ &= \frac{1}{b}\ln\left(\frac{x_o(ax+b)}{x(ax_o+b)}\right) \end{aligned} \tag{35}$$

Evaluating the integral in terms of the variables of interest yields

$$\frac{1}{C_{B,o} - C_{A,o}} \ln\left(\frac{C_{A,o}(C_A + C_{B,o} - C_{A,o})}{C_A(C_{A,o} + C_{B,o} - C_{A,o})}\right) = k(t - t_o) \tag{36}$$

This is the analytical solution for the concentration of A as a function of time. For our numerical example, we specify k_o = 0.01 liter/mol/s, E_a = 2000 J/mol and $C_{A,o}$ = 2.0 mol/liter and $C_{B,o}$ = 3.0 mol/liter. We use this model to generate values of C_A and C_B as a function of time. (Actually, it is easiest to pick values of C_A and then compute the corresponding values of C_B and time.) Then we can use the differential method to estimate the rate of loss of A and multivariate regression on the linearized expression.

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln(|\upsilon_A|k) + |\nu_A|\ln(C_A) + |\nu_B|\ln(C_B) \tag{32}$$

We can use this equation to generate data. We show the perfect model data below.

perfect model data

T (K)	time (s)	k	CA	CB
300	3.87781077	0.004485	1.9	2.9
300	8.108839037	0.004485	1.8	2.8
300	12.74452575	0.004485	1.7	2.7
300	17.8470024	0.004485	1.6	2.6
300	23.49207604	0.004485	1.5	2.5

300	29.7732942	0.004485	1.4	2.4
300	36.80758417	0.004485	1.3	2.3
300	44.74324378	0.004485	1.2	2.2
300	53.77154185	0.004485	1.1	2.1
300	64.14403992	0.004485	1	2

We use the centered finite difference formula to estimate dCA/dt.

regression of perfect model data

x1	x2	y
0.641853886	1.064711	-3.70239262
0.587786665	1.029619	-3.79174229
0.530628251	0.993252	-3.88549045
0.470003629	0.955511	-3.98411576
0.405465108	0.916291	-4.08818327
0.336472237	0.875469	-4.19836729
0.262364264	0.832909	-4.31548274
0.182321557	0.788457	-4.44052887
0.09531018	0.741937	-4.57475202
-7.77156E-16	0.693147	-4.64174298

The regression yields

	m_2	m_1	b
	4.022410041	-0.81456	-7.45263508
abs(nuA)	-0.814564271		
abs(nuB)	4.022410041		
k	-0.000711928		
abs(nuA) error	-181.46%		
abs(nuB) error	302.24%		
k error	-115.87%		

The results should have both stoichiometric coefficients equal to unity. Thus this method completely failed. It can be rigorously shown that the reason for the failure was very small error introduced by the centered finite-difference formula. If the data itself has even small uncertainties, the results are even worse. Therefore, the sensitivity of this method to small errors in the rate renders it practically useless.

VI. Determining the rate law – elementary rate laws via postulating the rate law

We have shown in the previous example that we cannot simply regress for the stoichiometric coefficients based on available experimental data because small uncertainties result in huge errors. The alternative is to guess the rate law and solve for the rate constant, determining which model provides the best fit.

Example 7.

We examine the same problem given in example 6. Consider the reaction A + B → C performed in an isothermal batch reactor. We begin with our mole balance for A in the isothermal batch reactor.

$$\frac{dC_A}{dt} = \upsilon_A r(t) = \upsilon_A k C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} \tag{23}$$

This is linear with $y = \frac{dC_A}{dt}$, $x = \upsilon_A C_A^{|\upsilon_A|} C_B^{|\upsilon_B|}$, and $m = k$.

We will assume values of υ_A and υ_B. Then we simply follow the procedure to regress the rate constant, assuming the rate law is known.

Table of Measure of Fit on the Linear Regression

perfect model data

	$\upsilon_B = 0$	$\upsilon_B = 1$	$\upsilon_B = 2$
$\upsilon_A = 1$	0.996	0.997	0.983
$\upsilon_A = 2$	0.994	0.991	0.976

model with 1% uncertainty

	$\upsilon_B = 0$	$\upsilon_B = 1$	$\upsilon_B = 2$
$\upsilon_A = 1$	0.960	0.965	0.962
$\upsilon_A = 2$	0.952	0.950	0.932

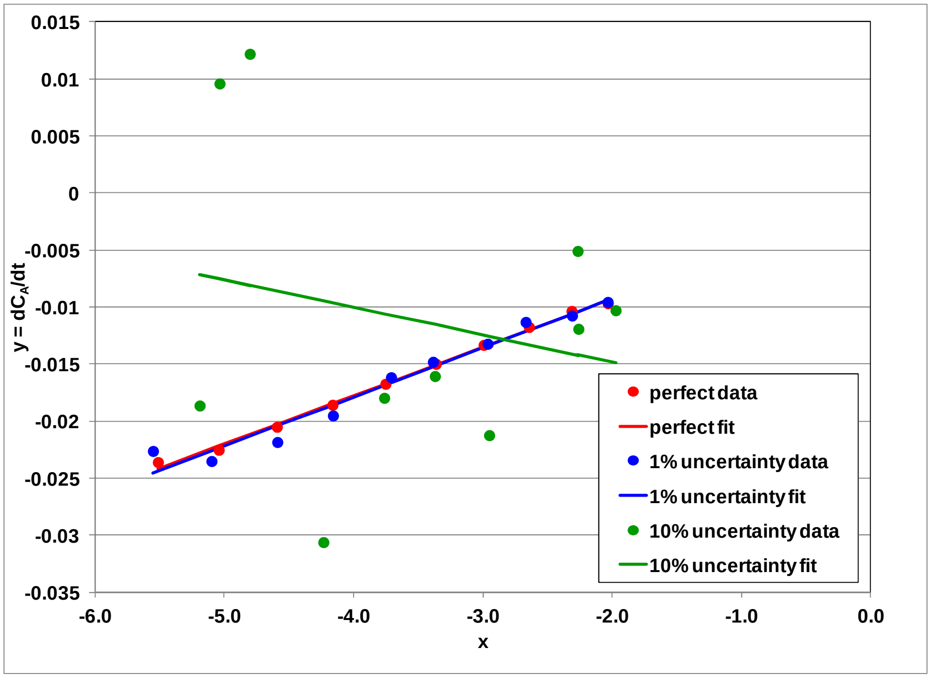
model with 10% uncertainty

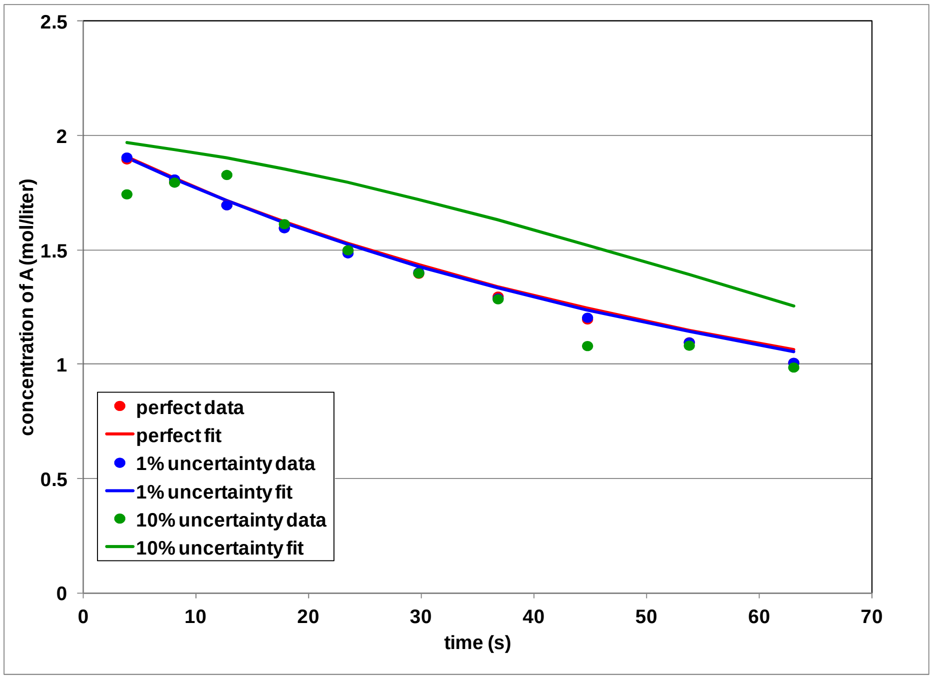
	$\upsilon_B = 0$	$\upsilon_B = 1$	$\upsilon_B = 2$
$\upsilon_A = 1$	0.049	0.047	0.002
$\upsilon_A = 2$	0.065	0.066	0.072

We see from these results that for the perfect model data and for the data with 1% uncertainty, the best fit is with $\upsilon_A = 1$ and $\upsilon_B = 1$. When the data is bad, all the fits are bad.

The regression and the plots for this result are shown below.

	perfect model data	data with 1% uncertainty	data with 10% uncertainty
k (liter/mole/s)	0.00424	0.00431	-0.00241
k error	-5.5%	-3.9%	-153.8%





VII. The integral method for ΔH_R.

The rate law and rate constant parameters, k_o and E_a, can be determined from mass balances independently of the heat of reaction as demonstrated in the examples above. Therefore, in this section we assume that we already know the rate law and k_o and E_a.

An adiabatic batch reactor is operated. We previously derived the energy balance for a jacketed batch reactor

$$\frac{dT}{dt} = \frac{-\Delta H_R r}{C_T C_{p,mix}} \tag{37}$$

Assuming we know the rate law, we can integrate and regress this equation for the unknown, ΔH_R, knowing only the concentrations of the reactions and the outlet temperature of the jacket as a function of time. For this example, we assume the rate has an elementary form,

$$r(t) = kC_A^{|\upsilon_A|} C_B^{|\upsilon_B|} = k_o \exp\left(-\frac{E_a}{RT}\right) C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} \tag{38}$$

We integrate from t_o to t.

$$\int_{t_o}^{t} dT = \int_{t_o}^{t} \frac{-\Delta H_R k_o \exp\left(-\frac{E_a}{RT}\right) C_A^{|\upsilon_A|} C_B^{|\upsilon_B|}}{C_T C_{p,mix}} dt \tag{39}$$

Pull the constants out of the integrals.

$$T - T_o = \frac{-\Delta H_R k_o}{C_T C_{p,mix}} \int_{t_o}^{t} \exp\left(-\frac{E_a}{RT}\right) C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} dt \tag{40}$$

We can write this as y = mx + b where $y = T - T_o$, $x = \frac{-k_o}{C_T C_{p,mix}} \int_{t_o}^{t} \exp\left(-\frac{E_a}{RT}\right) C_A^{|\upsilon_A|} C_B^{|\upsilon_B|} dt$, $m = \Delta H_R$, and $b = 0$. Thus a linear regression will yield the heat of reaction as the slope. In order to perform this linear regression, we must evaluate the two integrals for every data point. This requires numerical integration.

Let's work example 8.

Example 8.

Example 8 is working the same problem as example 1. Consider the case of an isomerization reaction where A → B. We already know the rate law. We also have already determined k_o and E_a. In example 1, $k_o = 0.01$ s^{-1}, $E_a = 2000$ J/mol and $C_{A,o} = 10.0$ mol/liter. The heat capacity of A, B and the solvent are all 75.312 J/mol/K. There is 40.0 mol/liter of solvent in the reactor. We run the reactor one run under adiabatic conditions. and take many measurements as a function of time. We generate the data using sysode.m.

```
function dydt = sysodeinput(x,y,nvec);
%
% one reaction in solvent, S
% A --> B
%
% sample usage:
% [y,x]=sysode(2,1000,0,10,[10,0,40,300]);
%
CA = y(1); % mol/liter
CB = y(2);
CS = y(3);
T = y(4); % K
%
% stoichiometry
%
nuA = -1;
nuB = +1;
nuS = 0;
%
% rate law
%
ko = 0.01; % 1/sec
Ea = 2000; % J/mol
R = 8.314; %J/mol/K
DUR = -250000.0; %J/mol
k = ko*exp(-Ea/(R*T)); % liters/mole/sec
r = k*CA; % mole/liter/sec
%
% pure component heat capacities
%
CvA = 4.184*18.0; %J/mol/K
CvB = CvA; %J/mol/K
CvS = CvA; %J/mol/K
%
% mole fractions
%
CT = CA + CB + CS;
xA = CA/CT;
xB = CB/CT;
xS = CS/CT;
%
% mixture heat capacity
%
Cvmix = xA*CvA + xB*CvB + xS*CvS;
%
% mole and energy balances
%
dydt(1) = nuA*r;
dydt(2) = nuB*r;
dydt(3) = nuS*r;
dydt(4) = -DUR*r/(CT*Cvmix);
We run the command:

» [y,x]=sysode(2,100,0,60,[10,0,40,300]);

The output data from the simulation therefore looks like:
```

```
time             CA               CB               CS               Temp
0.0000000e+000 1.0000000e+001 0.0000000e+000 4.0000000e+001 3.0000000e+002
```

```
6.0000000e-001 9.7320229e+000 2.6797714e-001 4.0000000e+001 3.1779113e+002
1.2000000e+000 9.4673841e+000 5.3261587e-001 4.0000000e+001 3.3536062e+002
1.8000000e+000 9.2074904e+000 7.9250956e-001 4.0000000e+001 3.5261509e+002
2.4000000e+000 8.9534429e+000 1.0465571e+000 4.0000000e+001 3.6948143e+002
3.0000000e+000 8.7060690e+000 1.2939310e+000 4.0000000e+001 3.8590470e+002
…
5.7000000e+001 2.0231453e+000 7.9768547e+000 4.0000000e+001 8.2958723e+002
5.7600000e+001 2.0049300e+000 7.9950700e+000 4.0000000e+001 8.3079655e+002
5.8200000e+001 1.9870324e+000 8.0129676e+000 4.0000000e+001 8.3198478e+002
5.8800000e+001 1.9694443e+000 8.0305557e+000 4.0000000e+001 8.3315246e+002
5.9400000e+001 1.9521581e+000 8.0478419e+000 4.0000000e+001 8.3430011e+002
6.0000000e+001 1.9351660e+000 8.0648340e+000 4.0000000e+001 8.3542822e+002
```

We generate the regression variables, x and y. We use the trapezoidal rule to evaluate the integral. We show only the first few rows of the table here. This data is for the perfect fit model.

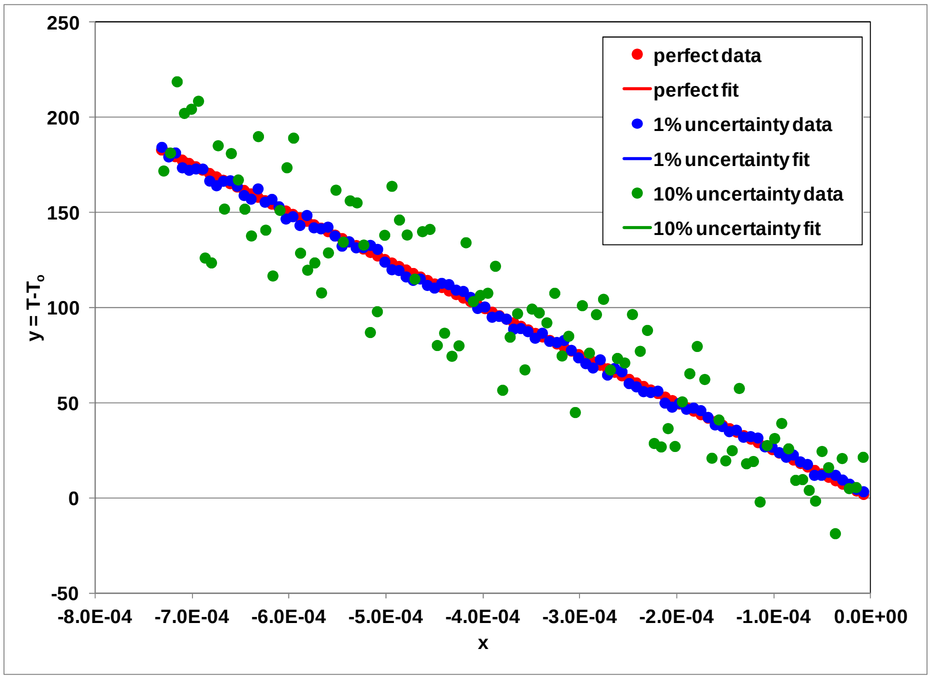
time	CA	CB	CS	temp	RHS integrand	RHS area	RHS integral	LHS
0.0000E+00	1.0000E+01	0.0000E+00	4.0000E+01	3.0000E+02	4.4849E+00		x	y
6.0000E-01	9.9731E+00	2.6937E-02	4.0000E+01	3.0179E+02	4.4942E+00	2.6937E+00	-7.1535E-06	1.7884E+00
1.2000E+00	9.9461E+00	5.3929E-02	4.0000E+01	3.0358E+02	4.5031E+00	2.6992E+00	-1.4322E-05	3.5804E+00
1.8000E+00	9.9190E+00	8.0975E-02	4.0000E+01	3.0538E+02	4.5119E+00	2.7045E+00	-2.1504E-05	5.3759E+00
2.4000E+00	9.8919E+00	1.0807E-01	4.0000E+01	3.0717E+02	4.5203E+00	2.7097E+00	-2.8699E-05	7.1749E+00
3.0000E+00	9.8648E+00	1.3522E-01	4.0000E+01	3.0898E+02	4.5286E+00	2.7147E+00	-3.5909E-05	8.9772E+00
3.6000E+00	9.8376E+00	1.6241E-01	4.0000E+01	3.1078E+02	4.5366E+00	2.7195E+00	-4.3131E-05	1.0783E+01

The regression on this data yields the following slopes.

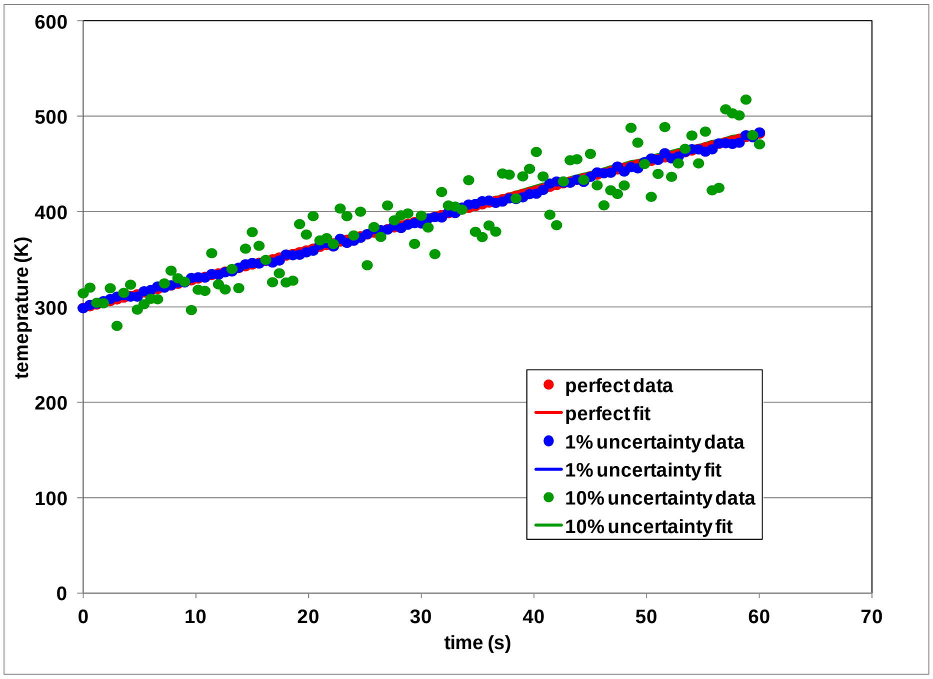
	perfect model data	data with 1% uncertainty	data with 10% uncertainty
ΔH_R (J/mol)	-250001	-250600	-253153

The value used to generate the data was -250,000 J/mol.

The following plots were generated for the linear regression.



We also generated a plot of temperature as a function of time.



VIII. The differential method for ΔH_R.

It is also possible to use a differential method for determining ΔH_R. We will work the same problem as in the previous section. We write the energy balance.

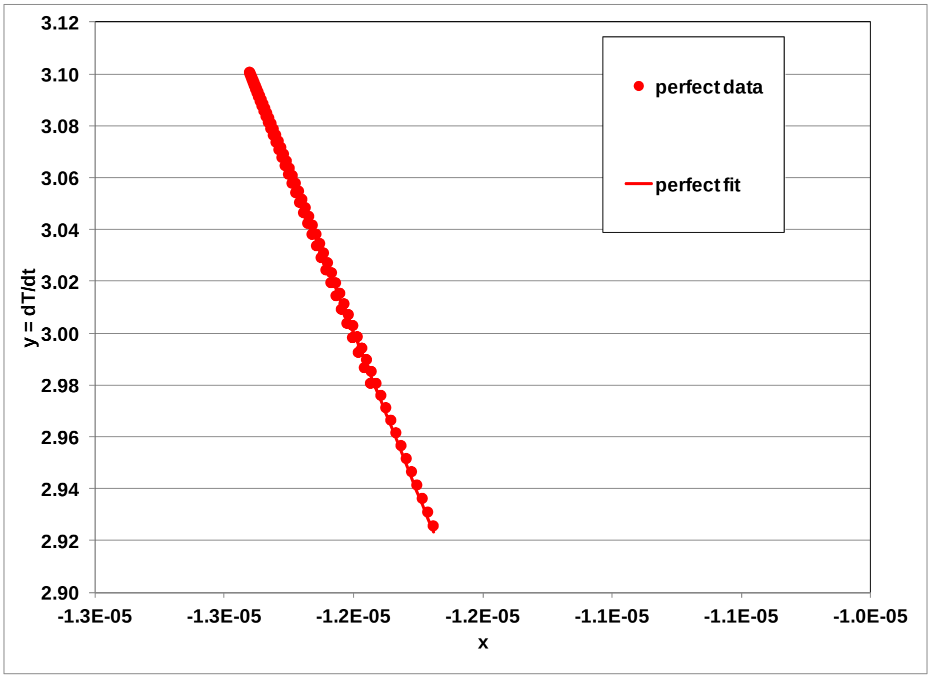
$$\frac{dT}{dt} = \frac{-\Delta H_R r}{C_T C_{p,mix}} \tag{37}$$

We estimate the temperature derivatives using centered-finite difference formulae. The equation is of the form y = mx + b where $y = \frac{dT}{dt}$, $x = \frac{-r}{C_T C_{p,mix}}$, $m = \Delta H_R$, and $b = 0$. Thus a linear regression will yield the heat of reaction as the slope.

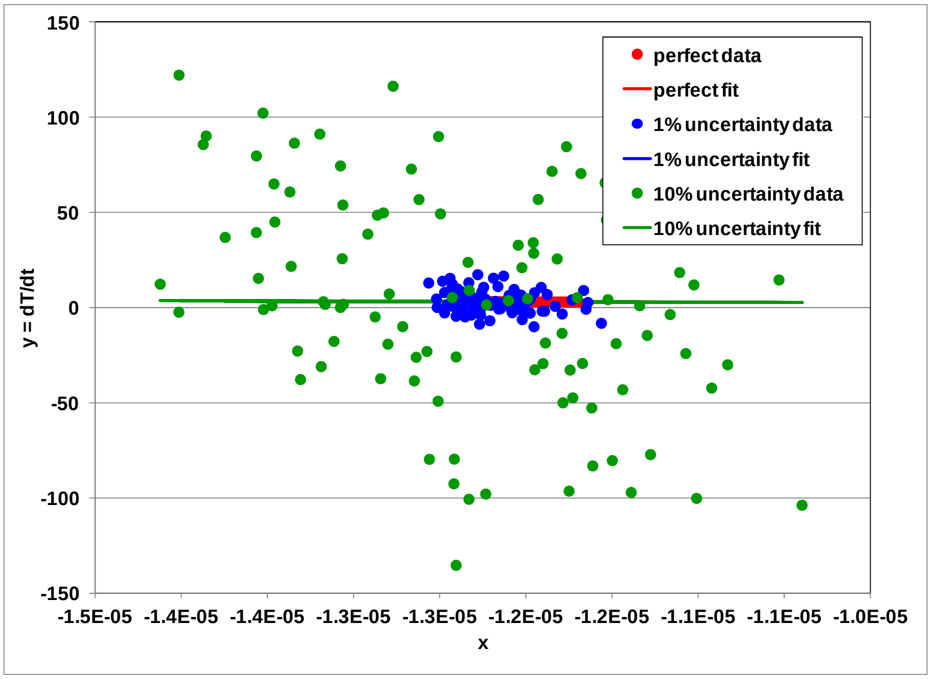
Example 9.
We use the same data as was generated for the previous section using the integral method. The regressions yield the following results.

	perfect model data	data with 1% uncertainty	data with 10% uncertainty
ΔH_R (J/mol)	-250022	-251003	-345942

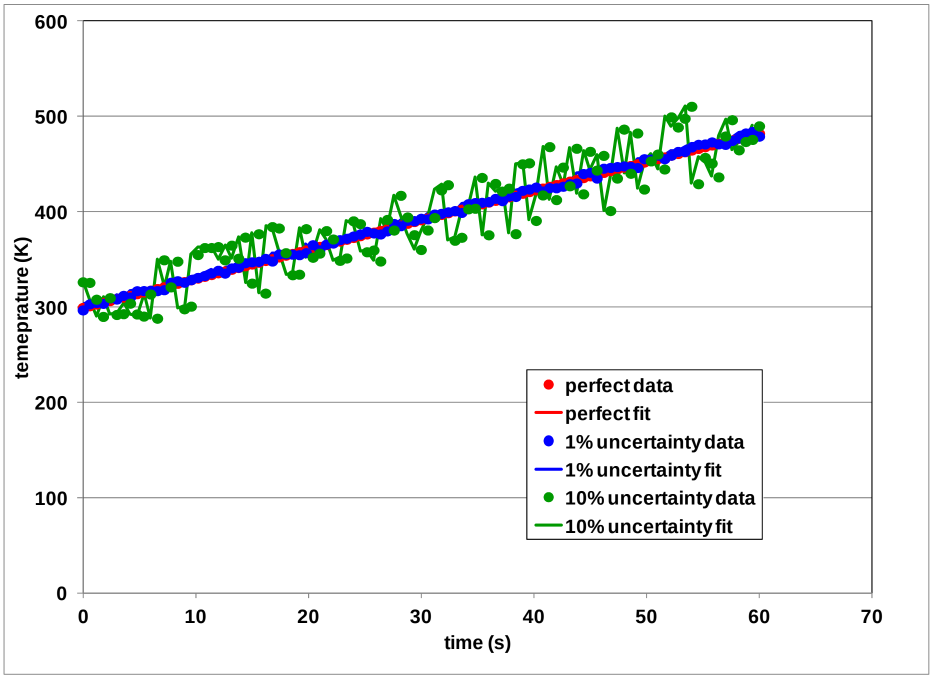
The regression plot for the perfect data is shown below.



The same plot is shown again below for all three data sets. As can be seen the data with uncertainty wreaks havoc on the slopes. The integral method is again superior here, even using a numerical integration technique.



We also show a plot of reactor temperature vs. time.



Appendix I. Table of Relevant Integrals

Examples of analytical evaluations of integrals of the form: $\int \frac{dx}{x^n\left(ax+b\right)^m}$. These can be evaluated using the technique of partial fraction expansions.

n=1, m=1
$$\int \frac{dx}{x^n\left(ax+b\right)^m} = \frac{1}{b}\ln\left(\frac{x}{ax+b}\right) \tag{I.1}$$

n=2, m=1
$$\int \frac{dx}{x^n\left(ax+b\right)^m} = -\frac{1}{bx} + \frac{a}{b^2}\ln\left(\frac{ax+b}{x}\right) \tag{I.2}$$

n=3, m=1
$$\int \frac{dx}{x^n\left(ax+b\right)^m} = \frac{2ax-b}{2b^2x^2} + \frac{a^2}{b^3}\ln\left(\frac{x}{ax+b}\right) \tag{I.3}$$

n=1, m=2
$$\int \frac{dx}{x^n\left(ax+b\right)^m} = \frac{1}{b(ax+b)} + \frac{1}{b^2}\ln\left(\frac{x}{ax+b}\right) \tag{I.4}$$

n=2, m=2
$$\int \frac{dx}{x^n\left(ax+b\right)^m} = \frac{-a}{b^2(ax+b)} + -\frac{1}{b^2x} + \frac{2a}{b^3}\ln\left(\frac{ax+b}{x}\right) \tag{I.5}$$

n=3, m=1
$$\int \frac{dx}{x^n\left(ax+b\right)^m} = -\frac{(ax+b)^2}{2b^4x^2} + \frac{3a(ax+b)}{b^4x} - \frac{a^3x}{b^4(ax+b)} - \frac{3a^2}{b^4}\ln\left(\frac{ax+b}{x}\right) \tag{I.6}$$

n=1, m=3
$$\int \frac{dx}{x^n\left(ax+b\right)^m} = \frac{a^2x^2}{2b^3(ax+b)^2} - \frac{2ax}{b^3(ax+b)} - \frac{1}{b^3}\ln\left(\frac{ax+b}{x}\right) \tag{I.7}$$

n=2, m=3
$$\int \frac{dx}{x^n\left(ax+b\right)^m} = \frac{-a}{2b^2(ax+b)^2} - \frac{2a}{b^3(ax+b)} - \frac{1}{b^3x} + \frac{3a}{b^4}\ln\left(\frac{ax+b}{x}\right) \tag{I.8}$$

n=3, m=3
$$\int \frac{dx}{x^n\left(ax+b\right)^m} = \frac{a^4x^2}{2b^5(ax+b)^2} - \frac{4a^3x}{b^5(ax+b)} - \frac{(ax+b)^2}{2b^5x^2} - \frac{6a^2}{b^5}\ln\left(\frac{ax+b}{x}\right) \tag{I.9}$$