Practical Kinetics

Exercise 1:

Introduction to Data Analysis in Python

Objectives:

1. Plotting Kinetic Data
2. Fitting to a Rate Law
3. Simulating Kinetic Scenarios

Introduction

Kinetic Data Analysis

(1) Plot experimental data.

(2) Fit data to rate law and assess fit.

(3) Simulate other plausible scenarios.

How to Use These Tutorials:

Download the IPython Notebook (`.ipynb`) for each exercise and follow along.

The code in each exercise can be adapted to a new set of data. You may treat the code as a black box, but you will find it more rewarding if you follow along.

Every line of code will be explained.

Step 1: The Import Statement

We will start by making some graphs. To do that, we need the following code:

```
import matplotlib
import matplotlib.pyplot as plt

%matplotlib inline
```

The first two lines load the `matplotlib` library. A **library** is a collection of code that has been written by someone else to perform common tasks. `matplotlib` is a set of codes that make graphs.

In English:

```
import matplotlib
```

"We need the `matplotlib` library to make graphs."

Step 1: The Import Statement

```
import matplotlib.pyplot as plt
```

This line sets `plt` as the abbreviation for the plotting library.

Because there are thousands of Python libraries available, it is possible for the same command to have have different meanings in different libraries. This statement allows us to write `plt.plot` (instead of just `plot`) so the reference to `plot` is unambiguous. In general, the period "`.`" means "belong to."

```
%matplotlib inline
```

This tells IPython Notebook (aka. Jupyter) to print out the graphs in the browser window. (This statement does not work in regular Python.)

In the rest of this tutorial, the necessary import statements will be provided to you. They are also summarized at the end.

Step 2: Plot a Straight Line

In a new cell, type the following:

```
import matplotlib
import matplotlib.pyplot as plt

%matplotlib inline

x=[1.0,2.0,3.0,4.0]
y=[2.0,4.0,6.0,8.0]

plt.xlim(0.0,5.0)
plt.ylim(0.0,10.0)
plt.plot(x,y,"ko")
```

(If you are cutting and pasting, you might have to remove the blank lines. Additionally, check that the quotation marks have not been auto-replaced.)

Your window should look like this:

In [1]:
```
import matplotlib
import matplotlib.pyplot as plt

%matplotlib inline

x=[1.0,2.0,3.0,4.0]
y=[2.0,4.0,6.0,8.0]

plt.xlim(0.0,5.0)
plt.ylim(0.0,10.0)
plt.plot(x,y,"ko")
```

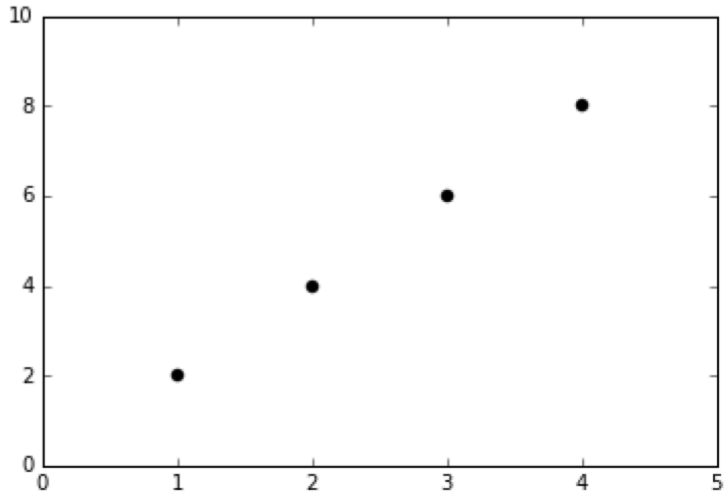
Step 1: Plot a Straight Line

Notice that pressing **enter** goes to the next line and does not execute anything.

To execute the code, press **shift-enter**. A plot will appear underneath:

In [1]:
```
import matplotlib
import matplotlib.pyplot as plt

%matplotlib inline

x=[1.0,2.0,3.0,4.0]
y=[2.0,4.0,6.0,8.0]

plt.xlim(0.0,5.0)
plt.ylim(0.0,10.0)
plt.plot(x,y,"ko")
```

Out[1]:
```
[<matplotlib.lines.Line2D at 0x10cb81b10>]
```



In [ ]:

Step 1: Plot a Straight Line

```
import matplotlib
import matplotlib.pyplot as plt

%matplotlib inline

x=[1.0,2.0,3.0,4.0]
y=[2.0,4.0,6.0,8.0]

plt.xlim(0.0,5.0)
plt.ylim(0.0,10.0)
plt.plot(x,y,"ko")
```

The import statements.

Plot graphs in the browser.

The (x,y) coordinates. **Specify ".0" after any integers.**

The x and y axis limits.

In English, the last line means:

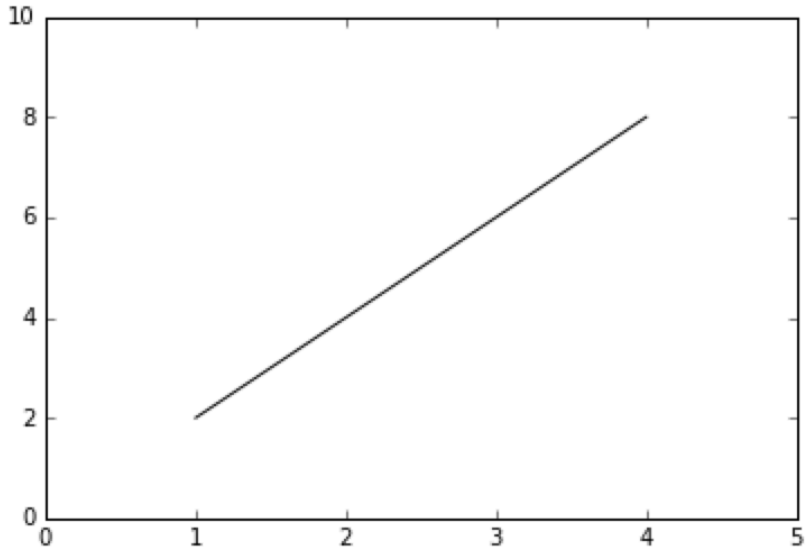
"Plot y vs. x using blac**k** circles (**o**)."

In a new cell, delete the "o" and press **shift-enter** again to re-evaluate the cell. (That's a lowercase o, as in "oak.")

Step 1: Plot a Straight Line

Without the “o,” just the line is plotted:

```
In [2]: plt.xlim(0.0,5.0)
        plt.ylim(0.0,10.0)
        plt.plot(x,y,"k")

Out[2]: [<matplotlib.lines.Line2D at 0x110995ed0>]
```



Notice that the import statements only have to be specified once. Once imported, the libraries stay loaded for the rest of the session.

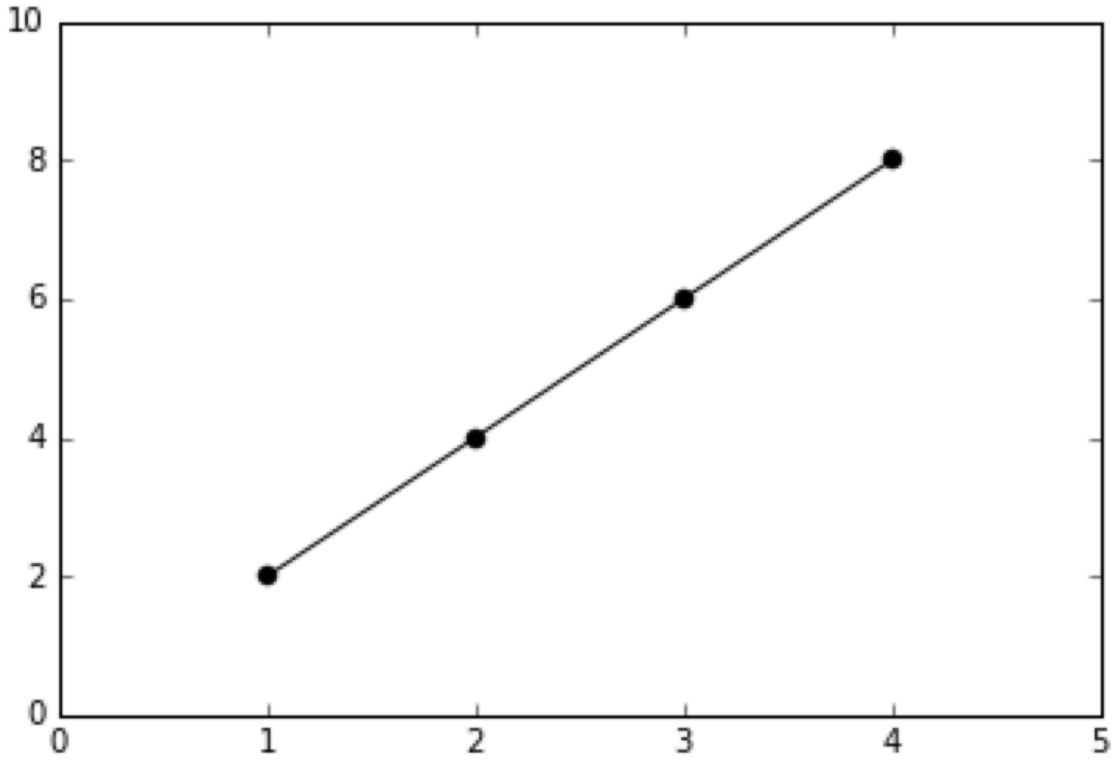
Similarly, `x` and `y` were already defined in the first cell, and are now stored in memory.

Step 2: Overlaying Plots

When multiple plot statements are present, the plots are automatically overlaid:

```
In [3]: plt.xlim(0.0,5.0)
        plt.ylim(0.0,10.0)
        plt.plot(x,y,"ko")
        plt.plot(x,y,"k")
```

```
Out[3]: [<matplotlib.lines.Line2D at 0x110a059d0>]
```



Step 3: Formatting Plots

In each plot command, the third argument is the “format string”:

```
plt.plot(x,y, "ko" )
```

Each format string is a combination of a color abbreviation and a line style abbreviation:

colors: r = red, b = blue, g = green, k = black

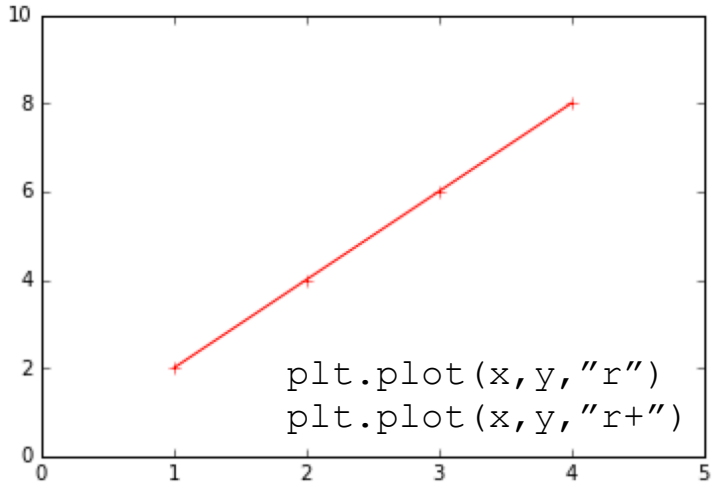
line styles

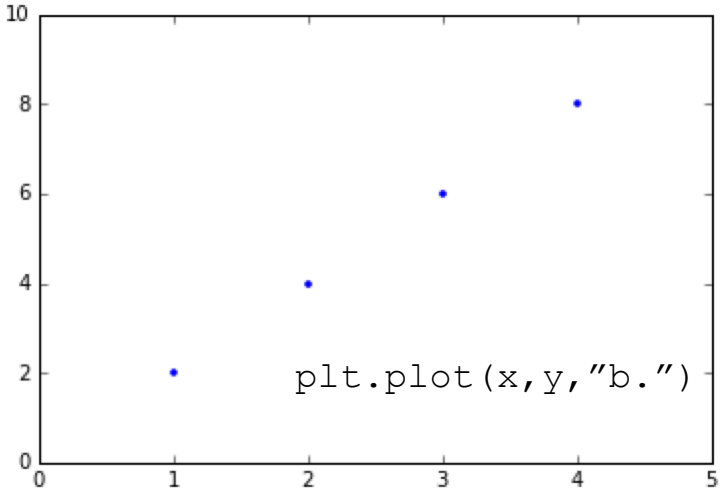
(nothing)	connect points with straight, solid lines
`--`	connect lines with straight, dashed lines

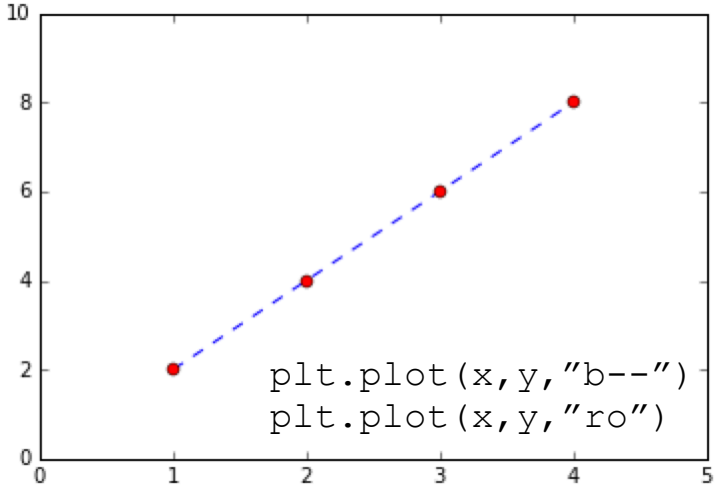
`.` (a period)	mark points with dots
`o`	mark points with circles
`+`	mark points with crosses

Step 3: Formatting Plots

Here are a few examples:





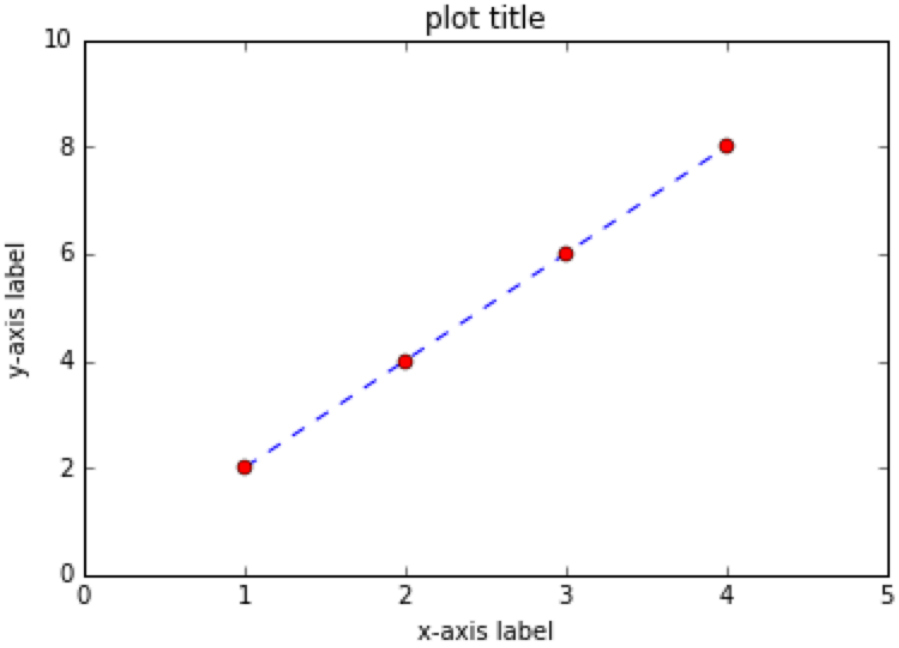


Remember, the color goes first and the line style goes second.

Step 4: Labeling Plots

Try adding the following:

```
plt.xlabel("x-axis label")
plt.ylabel("y-axis label")
plt.title("plot title")
```



Note: Further customization of fonts, legends, line styles, etc. is possible. See: http://matplotlib.org/users/pyplot_tutorial.html

Saving plots: If you want to save your plot to disk, add a line:

```
plt.savefig("my_plot.png")
```

This will save a graphic to the directory you started IPython Notebook in.

You can replace `.png` with `.pdf` to make PDF files.

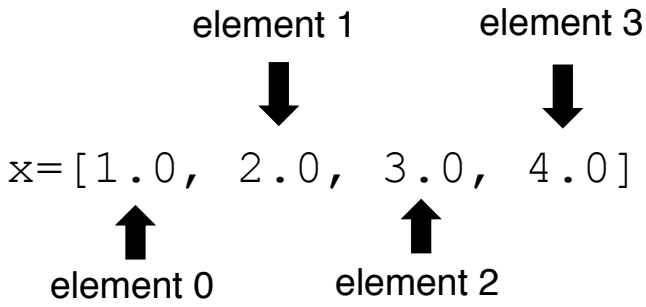
Step 5: Introduction to Lists

Preivously wrote:

```
x=[1.0,2.0,3.0,4.0]
y=[2.0,4.0,6.0,8.0]
```

These are called **lists**: ordered sequences of objects. (We'll deal with lists that contain numbers, but they can contain other things too.)

Each *element* has an *index:*



Notice that the numbering starts at 0, not 1.

Step 5: Introduction to Lists

The symbol `x` is the name of the list:

```
x=[1.0, 2.0, 3.0, 4.0]
```

name of list

To access an element directly:

```
print x[0]
```

result:

```
1.0
```

To change an element of `x`:

```
x[0]=8.0
print x
```

result:

```
[8.0, 2.0, 3.0, 4.0]
```

To find out how many elements `x` contains:

```
print len(x)
```

result:

```
5
```

Step 5: Introduction to Lists

In a new cell, try typing:

```
print x[0]
print y[2]
print len(x)
```

Press **shift-enter** to evaluate again.

```
print x[0]
print y[2]
print len(x)
```

```
1.0
6.0
4
```

Does this make sense given the previous code?

```
x=[1.0,2.0,3.0,4.0]
y=[2.0,4.0,6.0,8.0]
```

In English: the 0th element of `x` is `1.0`. The third element of `y` is `6.0`. There are `4` items in the list `x`.

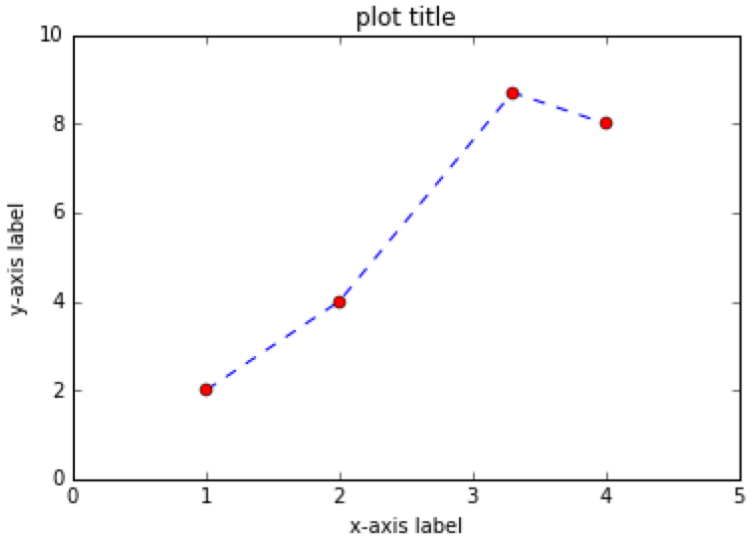
Step 5: Introduction to Lists

In a new cell:

Change the **third** point to (3.3, 8.7). Remember, the third point means index = 2. Re-plot the result.

```
In [8]: x[2]=3.3
        y[2]=8.7
        plt.xlim(0.0,5.0)
        plt.ylim(0.0,10.0)
        plt.plot(x,y,"b--")
        plt.plot(x,y,"ro")

        plt.xlabel("x-axis label")
        plt.ylabel("y-axis label")
        plt.title("plot title")
```

```
Out[8]: <matplotlib.text.Text at 0x10a0d1c10>
```



Note: If you scroll back up in your notebook, you will see that the previous plots have not changed. If you were to re-evaluate them, they would be updated to reflect your changes to `x` and `y`.

Step 6: List Comprehensions

Instead of entering numbers into lists manually, we can use mathematical expressions.

The simplest command is `range`:

```
list1 = range(5)
print list1
print len(list1)
```

Result:

```
[0, 1, 2, 3, 4]
5
```

Typing in `range(n)` returns the numbers from 0 to n-1 as a list:

```
range(n) = [0, 1, ..., n-1]
```

Step 6: List Comprehensions

We can use `range` to generate more complicated lists:

```
list1 = range(5)
list1 = [0, 1, 2, 3, 4]

list2 = [ i*2 for i in list1 ]        Result:
print list2                           [0, 2, 4, 6, 8]
```

Placing an expression in square brackets to define a list is called making a **list comprehension**.

In English:

"Take each item in `list1`, one at a time, and call it `i`. Multiply `i` by 2 and put the result in `list2`."

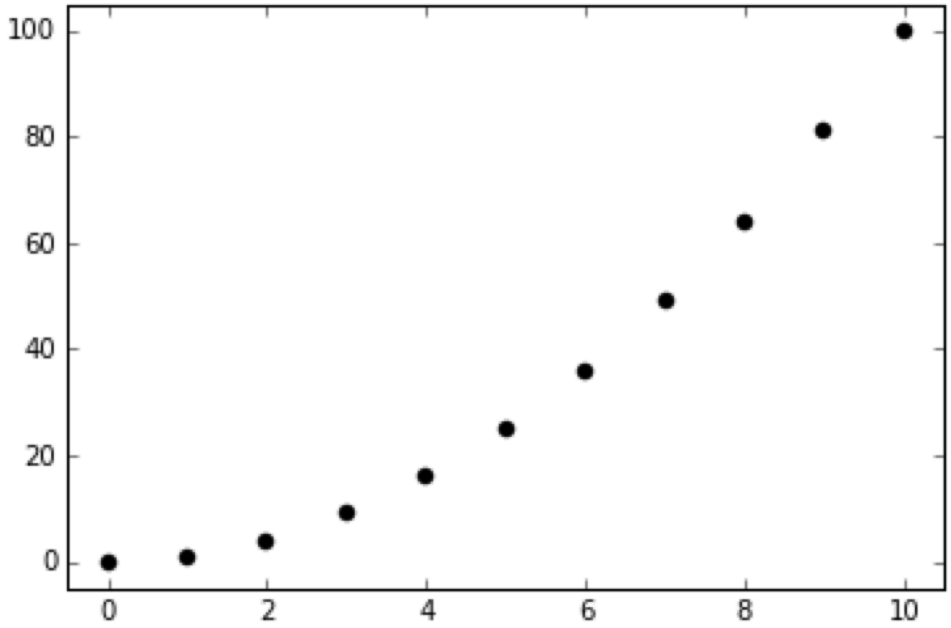
Taking items one at a time from a list is called **iteration**.

Step 6: List Comprehensions

In a new cell, plot the function $y=x^2$ from 0 to 10 using a list comprehension.

In [11]:
```
x2 = range(11)
y2 = [ x**2 for x in x2 ]
plt.xlim(-0.5,10.5)
plt.ylim(-5,105)
plt.plot(x2,y2,"ko")
```

Out[11]:
```
[<matplotlib.lines.Line2D at 0x10a29e550>]
```



Notice that we need `range(11)`, not `range(10)`.

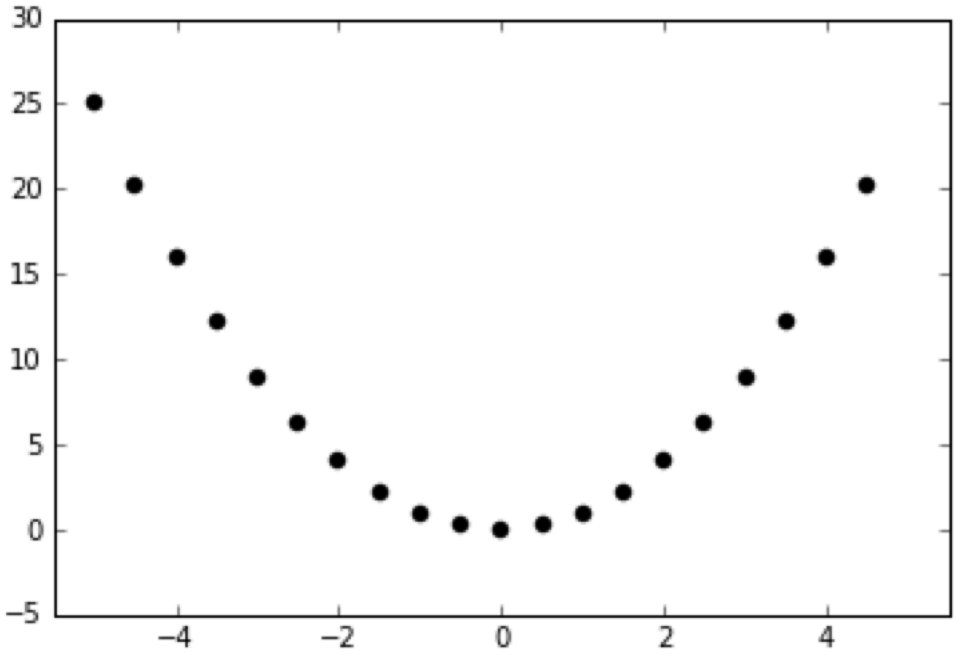
`x**2` means x raised to the power of 2.

Step 7: Using NumPy

What if we wanted to plot from –5 to +5, every 0.5? Instead of `range`, we need a more generalized function called `np.arange`:

In [17]:
```
import numpy as np
x3 = np.arange(-5.0,5.0,0.5)
y3 = [ x**2 for x in x3 ]
plt.xlim(-5.5,5.5)
plt.ylim(-5,30)
plt.plot(x3,y3,"ko")
```

Out[17]:
```
[<matplotlib.lines.Line2D at 0x10a704750>]
```



Step 7: Using NumPy

```
import numpy as np
```

This loads the NumPy (**Num**erical **Py**thon) library. This library contains many routines for doing math with lists.

To refer to a NumPy function instead of a regular Python function, we need to preface the function's name with `np`.

`sqrt` (regular Python)
`np.sqrt` (numpy)

```
np.arange(-5.0, 5.0, 0.5)
```

"Fill a list with the numbers from –5 to +5 every 0.5." Just like with the `range` function, the last point is not included.

The general syntax is:

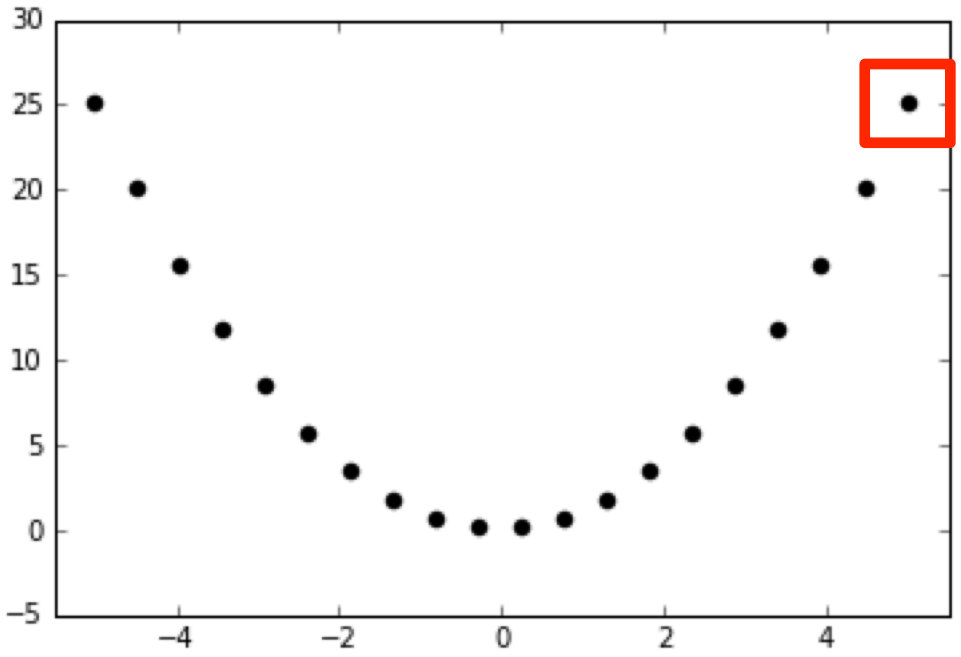
```
np.arange(start, stop, step_size)
```

Step 7: Using NumPy

To fill the range from –5 to +5 evenly with 20 points, you can use `np.linspace`:

In [18]:
```
x4 = np.linspace(-5.0,5.0,20)
y4 = [ x**2 for x in x4 ]
plt.xlim(-5.5,5.5)
plt.ylim(-5,30)
plt.plot(x4,y4,"ko")
```

Out[18]:
```
[<matplotlib.lines.Line2D at 0x10a800390>]
```



With `np.linspace`, the last point *is* included.

Step 8: First-Order Kinetics

Recall that for a first-order reaction:

$$A \xrightarrow{k_1} B$$

$$\frac{d[A]}{dt} = -k_1[A]$$

$$[A] = [A]_0 \exp\left(-k_1 t\right)$$

$$\log[A] = \log[A]_0 - k_1 t$$

To simulate the timecourse of a reaction, enter the following *in a new cell:*

```
from math import exp
import numpy as np

time = np.arange(0.0,10.0,0.1)
initial_concentration = 1.0
rate_constant = 1.0
concentration = [ initial_concentration *
exp(-rate_constant*t) for t in time ]
plt.plot(time, concentration, "k.")
```

Place this on one line.

Technical Note: Strictly speaking, we don't have to include the NumPy import again.

Step 8: First-Order Kinetics

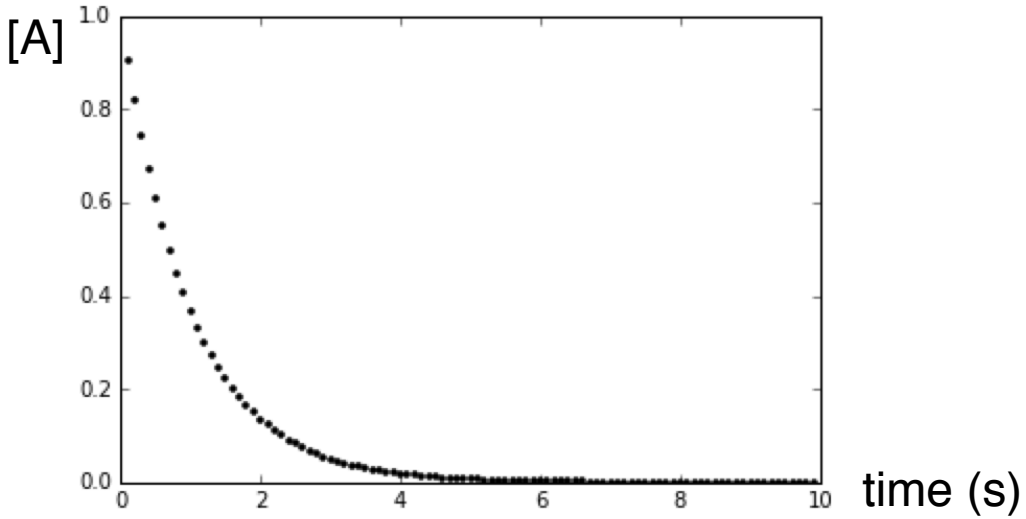
```
from math import exp
```

"From now on, whenever I type `exp`, interpret that to mean the `exp` function from the `math` library."

```
In [36]: from math import exp
         import numpy as np

         time = np.arange(0.0,10.0,0.1)
         initial_concentration = 1.0
         rate_constant = 1.0
         concentration = [ initial_concentration * exp(-rate_constant*t) for t in time ]
         plt.plot(time, concentration, "k.")

Out[36]: [<matplotlib.lines.Line2D at 0x105f48b10>]
```

0 to 10 seconds in 0.1 s steps

the integrated rate law as a list comprehension



Step 9: Make a Log Plot

Recall that a log plot will show a straight line:

$$A \xrightarrow{k_1} B$$

$$\frac{d[A]}{dt} = -k_1[A]$$

$$[A] = [A]_0 \exp\left(-k_1 t\right)$$

$$\log[A] = \log[A]_0 - k_1 t$$

You can perform log calculations with:

```
from math import log

log_concentration = [ log(conc) for conc in concentration ]
plt.plot(time, log_concentration, "k.")
```

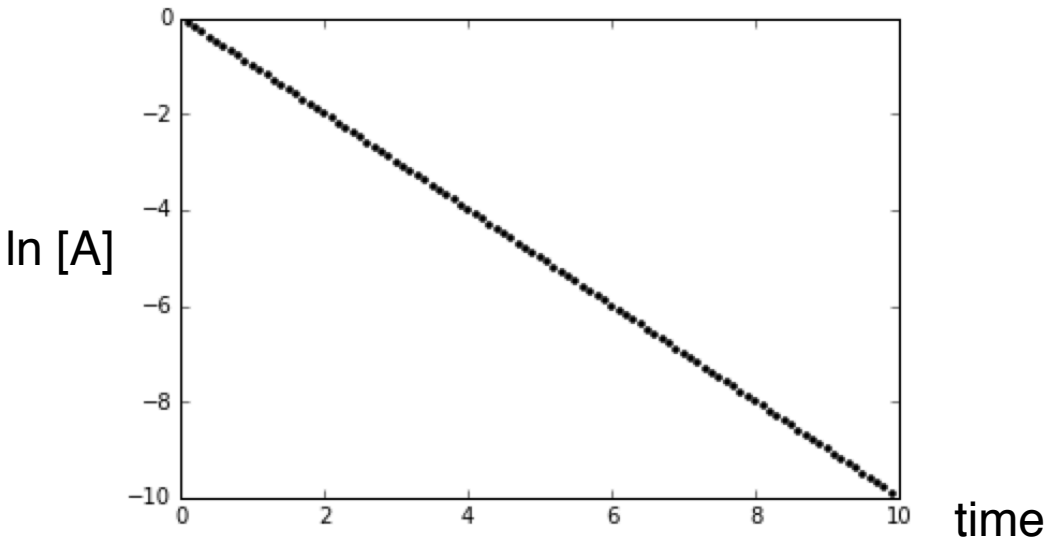
Try this out *in a new cell*.

Step 9: Make a Log Plot

This is a straight line with unit negative slope.

```
In [38]: from math import log

         log_concentration = [ log(conc) for conc in concentration ]
         plt.plot(time, log_concentration, "k.")
```

```
Out[38]: [<matplotlib.lines.Line2D at 0x1060735d0>]
```



The list comprehension “iterates” over `concentration` to produce a new list:

“Take each value in the `concentration` list, one at a time, take the logarithm and add it to a new list called `log_concentration`.”

Note that `log` means the natural logarithm (ln). You can use `log10` for base 10.

Step 10: Fit a Straight Line

What if you wanted to fit a straight line to get the slope and intercept?

In a new cell, try this:

```
from scipy.optimize import curve_fit

def f(x, m, b):
    return m*x + b

optimized_parameters, covariance_matrix = curve_fit(f, time, log_concentration)
slope = optimized_parameters[0]
intercept = optimized_parameters[1]

print ”optimized_parameters:", optimized_parameters
print ”covariance_matrix:", covariance_matrix
print
print "slope: ", slope
print "intercept: ", intercept
```

Step 10: Fit a Straight Line

```
In [26]: from scipy.optimize import curve_fit

         def f(x, m, b):
             return m*x + b
```

```
from scipy.optimize import curve_fit
```

SciPy (**Sci**entific **Py**thon) is a standard Python library that contains many routines scientific computing. In this case, we are importing the `curve_fit` function from the SciPy optimization library.

```
def f(x, m, b):
    return m*x + b
```

"Define a function `f` that takes three parameters: `x`, `m`, and `b`. Return `m` **x** `x` **+** `b` whenever `f` is called."

Step 10: Fit a Straight Line

```
def f(x, m, b):
    return m*x + b

optimized_parameters, covariance_matrix = curve_fit(f, time, log_concentration)
slope = optimized_parameters[0]
intercept = optimized_parameters[1]
```

`curve_fit` is a function in `scipy.optimize`.

The information we pass to `curve_fit` is in the parentheses.

```
curve_fit(f, time, log_concentration)
```

`f`, the functional form of the curve we want to fit
`time`, the x values
`log_concentration`, the y values

`curve_fit` adjusts `m` and `b` in `f` to minimize the sum of squares between `f(time, m, b)` and `log_concentration`.

Step 10: Fit a Straight Line

```
def f(x, m, b):
    return m*x + b

optimized_parameters, covariance_matrix = curve_fit(f, time, log_concentration)
slope = optimized_parameters[0]
intercept = optimized_parameters[1]
```

When `curve_fit` is finished, the result is stored in `optimized_parameters` and `covariance_matrix`.

The first element of `optimized_parameters` is the slope (`m`). The second is the intercept (`b`).

The order is determined by the ordering of parameters for `f`. The independent variable (`x`) must always come first. Any subsequent parameters will be adjusted to minimize the sum of squares and returned in `optimized_parameters`, in the same order.

Had we defined `f(x, b, m)`, the ordering would be reversed.

Step 10: Fit a Straight Line

```
print "optimized_parameters:", optimized_parameters
print "covariance_matrix:", covariance_matrix
print
print "slope: ", slope
print "intercept: ", intercept
```

```
optimized_parameters: [ -9.99999998e-01  -1.02301068e-08]
covariance_matrix: [[  1.06308464e-20  -1.17417750e-20]
 [ -1.17417750e-20   5.82440087e-20]]

slope:  -0.99999999849
intercept:  -1.0230106755e-08
```

This is a line with unit negative slope and zero intercept (to within numerical precision). `-1.02E-08` means -1.02×10^{-8}.

Technical Note:

`covariance_matrix` contains the (symmetric) covariance matrix for the parameter estimates. The nested square brackets mean that this is really a 2x2 matrix. The diagonal entries `covariance_matrix[0][0]` and `covariance_matrix[1][1]` represent the uncertainties of the slope and intercept, respectively. The off-diagonal entries indicate how the uncertainty in slope and intercept are related. In this case, the uncertainties are very small and meaningless because no error bars were passed to `curve_fit`.

Step 10: Fit a Straight Line

Let's plot the result. *In a new cell:*

```
best_fit = [ f(x, slope, intercept) for x in time ]
plt.plot(time[::5], log_concentration[::5], "k+", label="data")
plt.plot(time, best_fit, "b", label="fit")
plt.legend()
```

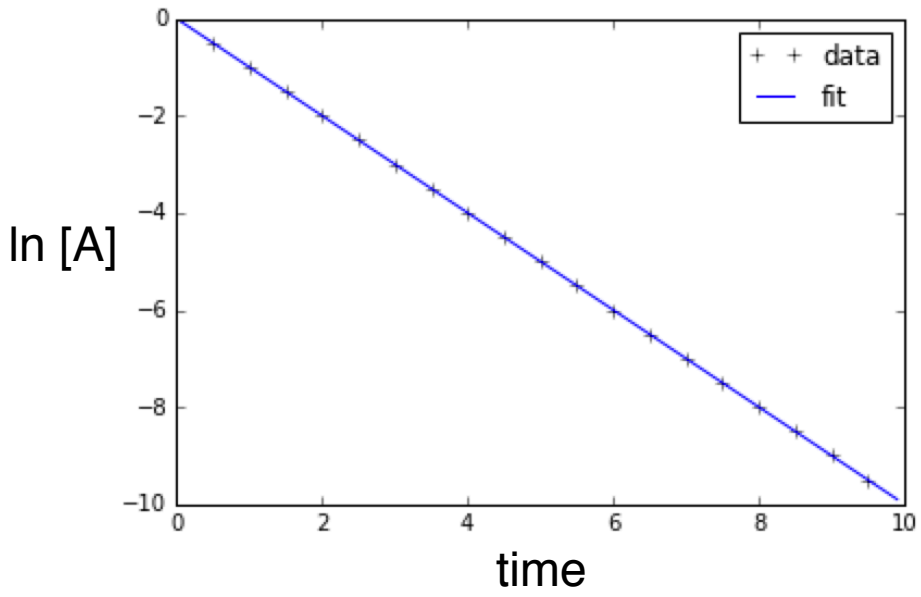
The `time[::5]` notation tells Python to take every fifth point in the `time` list and create a new list. I did that so the points aren't jammed together.

The `plt.legend()` command requests that a legend be added to the plot.

Step 10: Fit a Straight Line

In [28]:
```
best_fit = [ f(x, slope, intercept) for x in time ]
plt.plot(time[::5], log_concentration[::5], "k+", label="data")
plt.plot(time, best_fit, "b", label="fit")
plt.legend()
```

Out[28]: <matplotlib.legend.Legend at 0x10c36add0>



The fit is perfect because this the data are synthetically generated.

Step 11: Non-Linear Curve Fitting

There is no reason that `f` must be linear! Instead of fitting log(concentration) vs. time, let's fit concentration vs. time directly.

In a new cell, type this:

```
def f2(t, initial_concentration, k):
    return initial_concentration*np.exp(-k*t)

popt, pcov = curve_fit(f2, time, concentration)
fitted_initial_concentration = popt[0]
fitted_k = popt[1]
print "fitted initial concentration:", fitted_initial_concentration
print "fitted rate constant:", fitted_k
best_fit2 = [ f2(t, fitted_initial_concentration, fitted_k) for t in time ]
plt.plot(time[::5], concentration[::5], "k+", label="data")
plt.plot(time, best_fit2, "b", label="fit")
plt.legend()
```

Technical Notes:

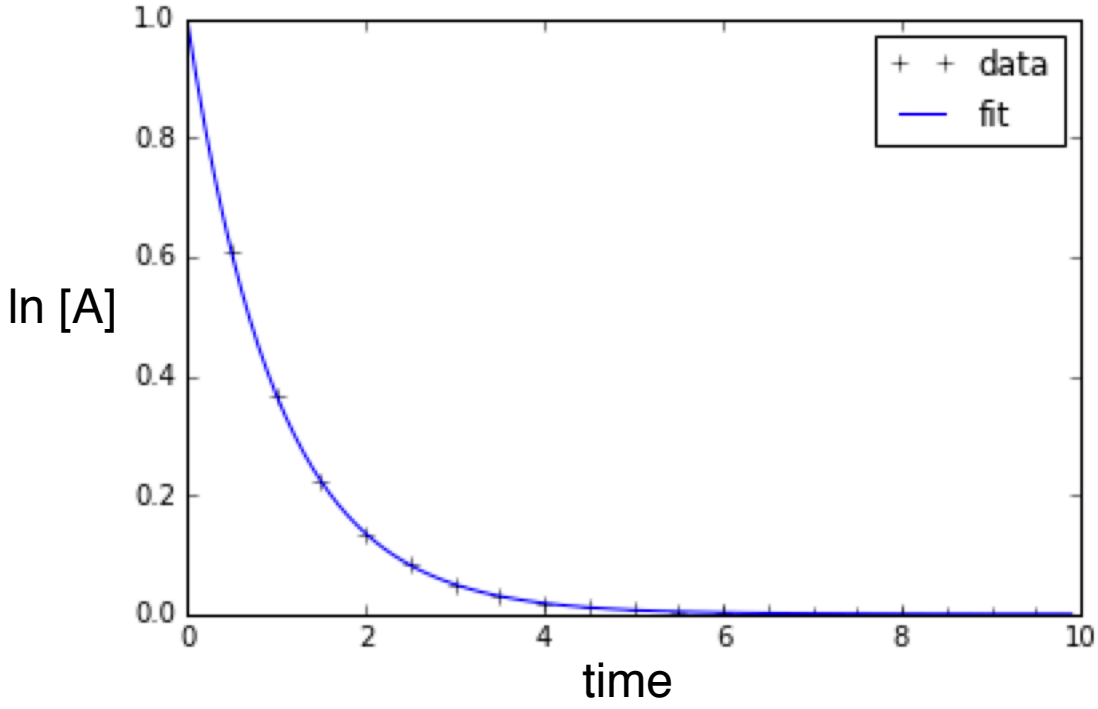
I changed `optimized_parameters, covariance_matrix` to their conventional short forms, `popt, pcov`. (They are short for: parameters, optimal and parameters, covariance.)

We need `np.exp` instead of `exp` because the latter does not work on arrays.

Step 11: Non-Linear Curve Fitting

The parameters are exactly recovered:

```
fitted initial concentration: 1.0
fitted rate constant: 1.0

Out[29]: <matplotlib.legend.Legend at 0x10c4b4050>
```



Technical Notes: The `initial_concentration` variable inside `f2` is *shadowed*, meaning that its value is local to the scope of the function. It is not the same as the `initial_concentration` variable defined in previous cells. You can think of it as a dummy variable that disappears as soon as the `f2` evaluates.

Step 12: The Two Step System

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

There are three ways to treat this system:

1. Pre-Equilibrium Approximation

Assume that the ratio K = [B]/[A] is maintained at its thermodynamic value, k_1/k_{-1}. This is valid if the subsequent rate constant, k_2, is relatively slow.

2. Steady State Approximation

Alternatively, we could assume that d[B]/dt ≈ 0 ([B] changes much more slowly than [C]). This means that [B]/[A] would be held at its kinetic value of $k_1/(k_{-1}+k_2)$. This is valid of k_2 is fast.

3. Differential Equations

If we solve the differential equations exactly, we can see when the pre-equilibrium and steady state approximations are valid. We will do that here.

Step 12: The Two Step System

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

The integrated rate laws for this system are:

$$p = k_1 + k_{-1} + k_2, \quad q = \sqrt{p^2 - 4k_1k_2}$$

$$\lambda_2 = \frac{p+q}{2.0}, \quad \lambda_3 = \frac{p-q}{2.0}$$

$$[A] = \frac{k_1[A]_0}{\lambda_2 - \lambda_3}\left(\frac{\lambda_2 - k_2}{\lambda_2}e^{-\lambda_2 t} - \frac{\lambda_3 - k_2}{\lambda_3}e^{-\lambda_3 t}\right)$$

$$[B] = \frac{k_1[A]_0}{\lambda_2 - \lambda_3}\left(e^{-\lambda_3 t} - e^{-\lambda_2 t}\right)$$

The derivation uses the Laplace Transform (*J. Chem. Educ.* **1999**, *76*, 1578).
I have presented the solution into a more convenient form (Chemical Kinetics and Catalysis Notes 2011, Professor Clark Landis, University of Wisconsin-Madison).

Step 12: The Two Step System

Taking approach 3, let's compute the timecourse of the following reaction:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

$$p = k_1 + k_{-1} + k_2, \quad q = \sqrt{p^2 - 4k_1k_2}$$

$$\lambda_2 = \frac{p+q}{2.0}, \quad \lambda_3 = \frac{p-q}{2.0}$$

$$[A] = \frac{k_1[A]_0}{\lambda_2 - \lambda_3}\left(\frac{\lambda_2 - k_2}{\lambda_2}e^{-\lambda_2 t} - \frac{\lambda_3 - k_2}{\lambda_3}e^{-\lambda_3 t}\right)$$

$$[B] = \frac{k_1[A]_0}{\lambda_2 - \lambda_3}\left(e^{-\lambda_3 t} - e^{-\lambda_2 t}\right)$$

Simulation Parameters:

```
k_1         = 10.0
k_minus1    = 100.0
k_2         = 0.1
A_initial   = 1.0
```

Plot from 0.0 to 5.0 seconds.

We'll do this step by step.

Step 12: The Two Step System

In a new cell:

```
k_1 = 10.0
k_minus1 = 100.0
k_2 = 0.1
A_initial = 1.0

from math import sqrt

p = k_1 + k_minus1 + k_2
q = sqrt(p**2 - 4*k_1*k_2)
lambda_2=(p+q)/2.0
lambda_3=(p-q)/2.0

c_1 = (k_1*A_initial)/(lambda_2-lambda_3)
c_2 = (lambda_2-k_2)/lambda_2
c_3 = (lambda_3-k_2)/lambda_3
```

Step 12: The Two Step System

First, setup some variables:

In [36]:
```
k_1 = 10.0
k_minus1 = 100.0
k_2 = 0.1
A_initial = 1.0
```

We can reevaluate this cell later when we want to change the rate constants.

Next, calculate:

$$p = k_1 + k_{-1} + k_2, \quad q = \sqrt{p^2 - 4k_1k_2}$$

$$\lambda_2 = \frac{p+q}{2.0}, \quad \lambda_3 = \frac{p-q}{2.0}$$

None of these variables depends on time, so it makes sense to calculate them ahead of time.

Step 12: The Two Step System

$$p = k_1 + k_{-1} + k_2, \quad q = \sqrt{p^2 - 4k_1k_2}$$

$$\lambda_2 = \frac{p+q}{2.0}, \quad \lambda_3 = \frac{p-q}{2.0}$$

In [31]:
```
from math import sqrt

p = k_1 + k_minus1 + k_2
q = sqrt(p**2 - 4*k_1*k_2)
lambda_2=(p+q)/2.0
lambda_3=(p-q)/2.0
```

Again, we need an import statement to perform square roots.

Step 12: The Two Step System

$$[A] = \frac{k_1[A]_0}{\lambda_2 - \lambda_3}\left(\frac{\lambda_2 - k_2}{\lambda_2}e^{-\lambda_2 t} - \frac{\lambda_3 - k_2}{\lambda_3}e^{-\lambda_3 t}\right) = c_1\left(c_2 e^{-\lambda_2 t} - c_3 e^{-\lambda_3 t}\right)$$

$$[B] = \frac{k_1[A]_0}{\lambda_2 - \lambda_3}\left(e^{-\lambda_3 t} - e^{-\lambda_2 t}\right) = c_1\left(e^{-\lambda_2 t} - e^{-\lambda_3 t}\right)$$

Examining the expressions for [A] and [B], we find that there are constants that also do not depend on time. I highlighted one of them.

Let's define those, too:

In [32]:
```
c_1 = (k_1*A_initial)/(lambda_2-lambda_3)
c_2 = (lambda_2-k_2)/lambda_2
c_3 = (lambda_3-k_2)/lambda_3
```

Remember, if we change the rate constants later, we'll have to re-evaluate all of these cells to update everything.

Step 12: The Two Step System

In a new cell:

```
def A(t):
    return c_1 * (c_2 * exp(-lambda_2*t) - c_3 * exp(-lambda_3*t))

def B(t):
    return c_1 * (exp(-lambda_3*t)-exp(-lambda_2*t))

time = np.arange(0.0,5.0,0.01)
conc_A = [ A(t) for t in time ]
conc_B = [ B(t) for t in time ]
conc_C = [ A_initial - conc_A[i] - conc_B[i] for i in range(len(time)) ]

plt.plot(time, conc_A, "r", label="[A]")
plt.plot(time, conc_B, "g", label="[B]")
plt.plot(time, conc_C, "b", label="[C]")
plt.legend()
```

Step 12: The Two Step System

$$[A] = \frac{k_1[A]_0}{\lambda_2 - \lambda_3}\left(\frac{\lambda_2 - k_2}{\lambda_2}e^{-\lambda_2 t} - \frac{\lambda_3 - k_2}{\lambda_3}e^{-\lambda_3 t}\right) = c_1\left(c_2 e^{-\lambda_2 t} - c_3 e^{-\lambda_3 t}\right)$$

$$[B] = \frac{k_1[A]_0}{\lambda_2 - \lambda_3}\left(e^{-\lambda_3 t} - e^{-\lambda_2 t}\right) = c_1\left(e^{-\lambda_2 t} - e^{-\lambda_3 t}\right)$$

Now, let's create functions for [A] and [B]. We will calculate [C] by mass balance later.

In [33]:
```
def A(t):
    return c_1 * (c_2 * exp(-lambda_2*t) - c_3 * exp(-lambda_3*t))

def B(t):
    return c_1 * (exp(-lambda_3*t)-exp(-lambda_2*t))
```

Technical Note: These functions depend on variables that are outside their scope. For example, `c_1` appears inside `A(t)` even though it is not defined there. This is perfectly acceptable in Python.

Step 12: The Two Step System

Now we need to run the simulation.

```
time = np.arange(0.0,5.0,0.01)
conc_A = [ A(t) for t in time ]
conc_B = [ B(t) for t in time ]
conc_C = [ A_initial - conc_A[i] - conc_B[i] for i in range(len(time)) ]
```

First, we fill up the `time` list with values from 0.0 to 5.0 in steps of 0.01.

Then, we iterate over `time`. For each value `t` in `time`, we call the function `A` to get the value `A(t)`. These values are placed, one at a time, in `conc_A`.

We do the same thing for [B]. For [C], we use mass balance:

“The total concentration minus [A] minus [B] for every point in time.”

Step 12: The Two Step System

```
time = np.arange(0.0,5.0,0.01)
conc_A = [ A(t) for t in time ]
conc_B = [ B(t) for t in time ]
conc_C = [ A_initial - conc_A[i] - conc_B[i] for i in range(len(time)) ]
```

Step by step:

`len(time)` returns the number of time points (i.e., the number of elements in `time`)

`range(len(time))` returns a list `[0, 1, ..., len(time)-1]`. We can use this to iterate over each list in parallel, since each list has the same number of elements.

Finally,
```
conc_C = [ A_initial - conc_A[0]   - conc_B[0],
           A_initial - conc_A[1]   - conc_B[1],
           ...,
           A_initial - conc_A[n-1] - conc_B[n-1] ]
```

where n = len(time).

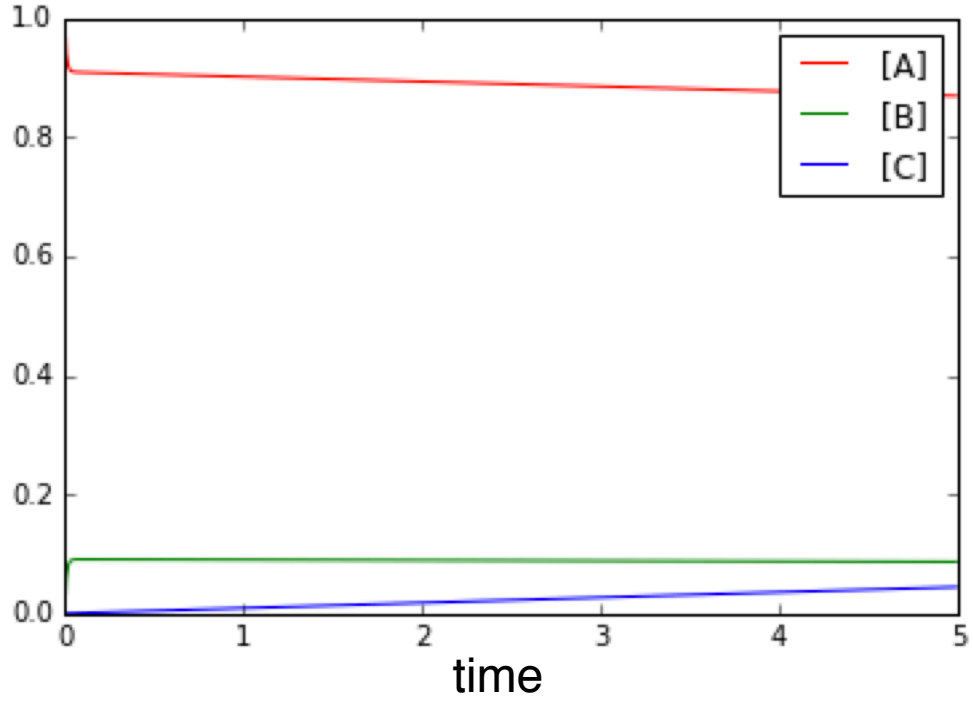
In English, this is the total concentration minus [A] minus [B] for every point in time.

Step 12: The Two Step System

Here is the plot of the result:

In [41]:
```
plt.plot(time, conc_A, "r", label="[A]")
plt.plot(time, conc_B, "g", label="[B]")
plt.plot(time, conc_C, "b", label="[C]")
plt.legend()
```

Out[41]: <matplotlib.legend.Legend at 0x10c700190>



Would you call this pre-equilibrium, steady state, or neither?
To find out, let's plot [B]/[A].

Step 13: Pre-Equilibrium or Steady State?

In a new cell:

```
conc_ratio = [ conc_B[i] / conc_A[i] for i in range(len(time)) ]
plt.ylim(0.08,0.12)
plt.plot(time, conc_ratio, "k", label="[B]/[A]")
plt.legend()
```

This divides [B]/[A] for each point in time.

The “foreach” expression

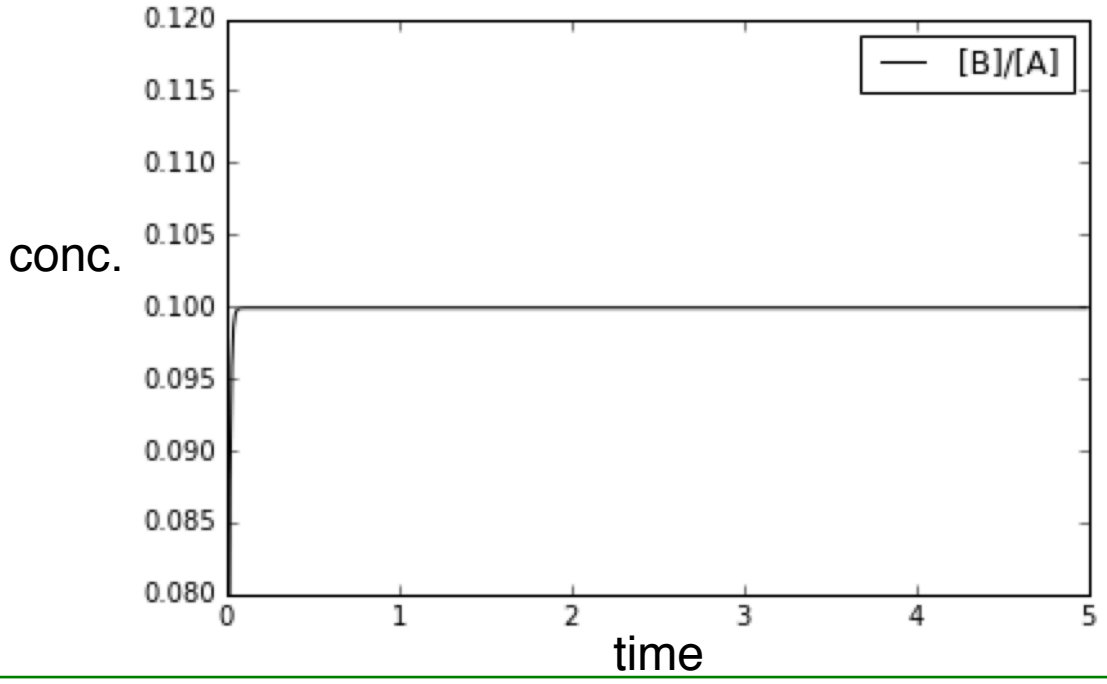
```
for i in range(len(time))
```

iterates over `[0, 1, ..., len(time)-1]`, the indices of `conc_A` and `conc_B`.

Step 13: Pre-Equilibrium or Steady State?

In [38]:
```
conc_ratio = [ conc_B[i] / conc_A[i] for i in range(len(time)) ]
plt.ylim(0.08,0.12)
plt.plot(time, conc_ratio, "k", label="[B]/[A]")
plt.legend()
```

Out[38]: <matplotlib.legend.Legend at 0x1134f38d0>

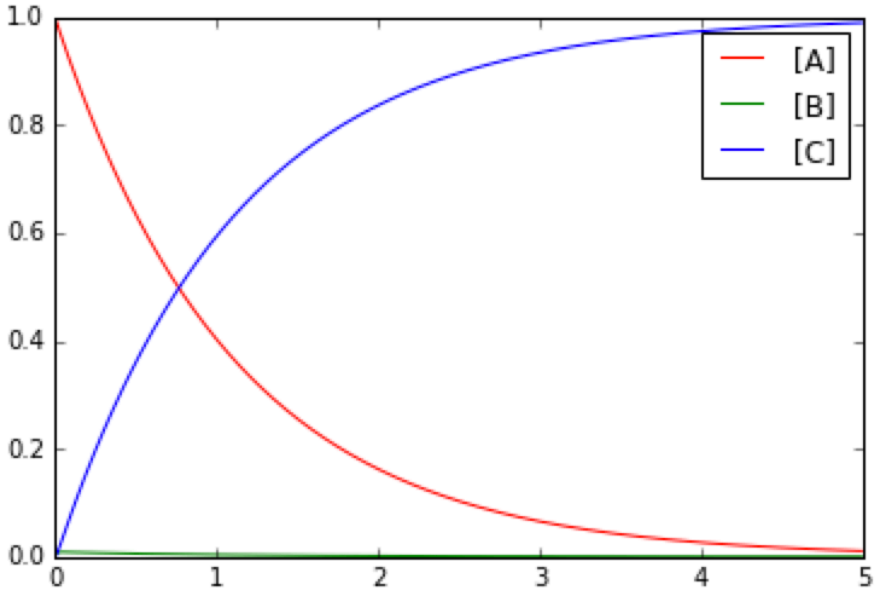


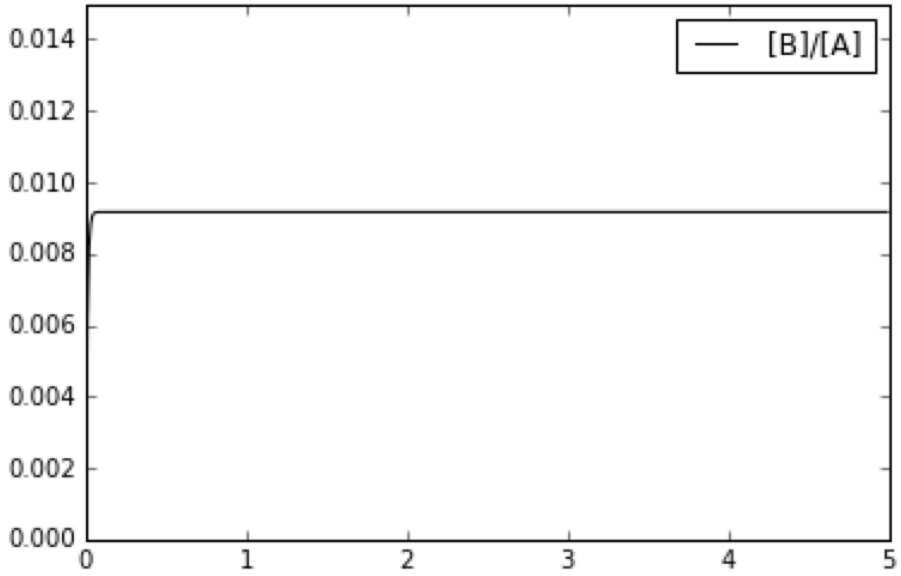
The ratio is 1:10 for most of the reaction. Recall, `k_1 = 10.0, k_minus1 = 100.0, k_2 = 0.1`. The thermodynamic ratio is $k_1/k_{-1} = 0.1$, so this is pre-equilibrium. This happens when k_2 is slow relative to k_1 and k_{-1}.

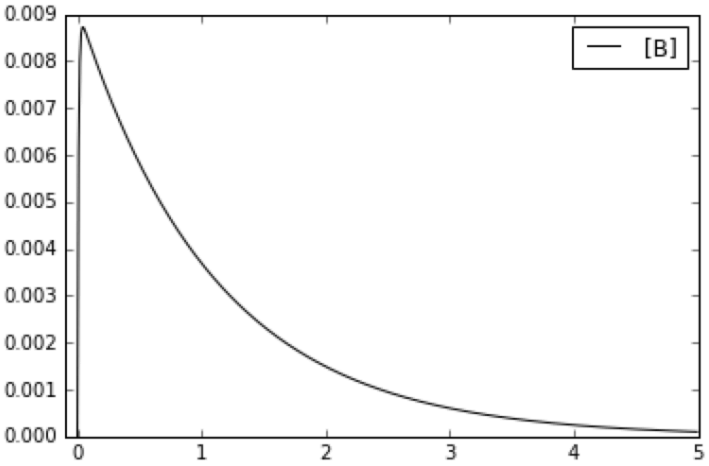
Step 13: Pre-Equilibrium or Steady State?

What if k_2 is fast? Re-run the simulation (re-evaluate cells) with:

```
k_1 = 1.0        k_minus1 = 10.0      k_2 = 100.0
```







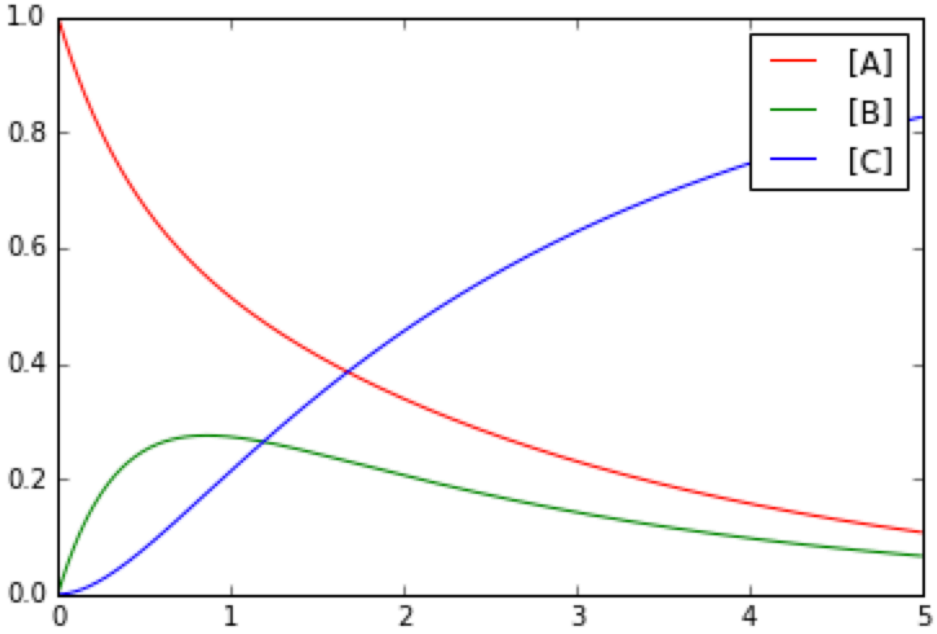
This is steady-state: $\frac{\partial[B]}{\partial t} = 0 = k_1[A] - k_{-1}[B] - k_2[B]$

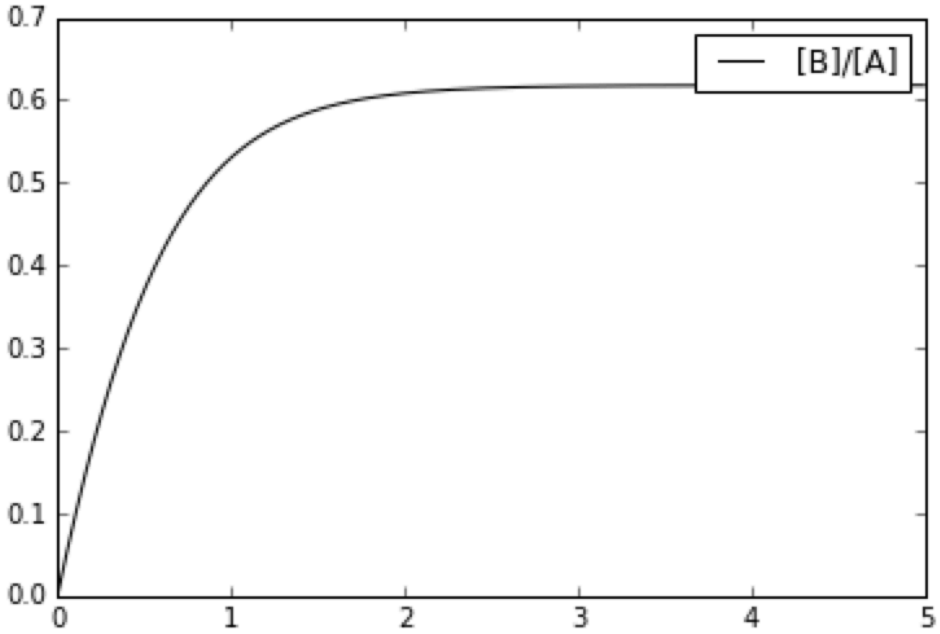
$$\frac{[B]_{SS}}{[A]} = \frac{k_1}{k_{-1} + k_2}$$

In this case, [B]/[A] = 1/(10+100) = 0.009, matching the figure above. This is the "kinetic equilibrium" value.

Step 13: Competitive Rates

To conclude this exercise, let's examine the case where all the rate constants are set to 1.0:





The plot on the right shows that *neither* the pre-equilibrium nor steady state conditions apply until late in the reaction. This scenario represents the "perfect catalysis" scenario where all barriers are equal in height.

Summary: Import Statements

As you learned in this exercise, import statements are often needed to perform common tasks. Here are the imports we used:

Plotting

```
%matplotlib inline
import matplotlib
import matplotlib.pyplot as plt
```

Curve Fitting

```
from scipy.optimize import curve_fit
```

Math

```
from math import sqrt, exp, log, log10
import numpy as np
```

For more functions and imports, see:

https://docs.python.org/2/library/math.html

http://docs.scipy.org/doc/numpy/reference/routines.math.html

http://docs.scipy.org/doc/scipy/reference/tutorial/basic.html

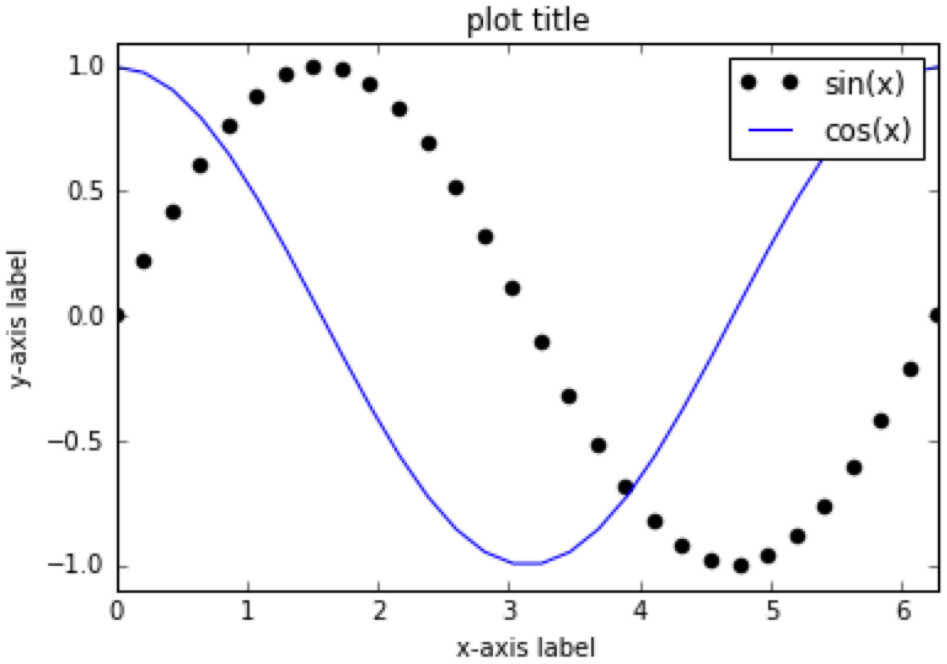
Stack Overflow (http://stackoverflow.com/) is also a good source of situation-specific imports.

Summary: Code Fragments

Here are short code fragments that illustrate some of the things we learned. They can be pasted into your notebook directly.

Plotting

```
# comments start with a hashtag
import matplotlib
import matplotlib.pyplot as plt
%matplotlib inline
import numpy as np

# make some data
x = np.linspace(0.0, 2*np.pi, 30)

# multiple plot statements will automatically overlay
plt.plot(x,np.sin(x),"ko",label="sin(x)")
plt.plot(x,np.cos(x),"b",label="cos(x)")

# set plot boundaries
plt.xlim(0.0,2*np.pi)
plt.ylim(-1.1,1.1)

# add a legend
plt.legend()

# add plot labels
plt.xlabel("x-axis label")
plt.ylabel("y-axis label")
plt.title("plot title")

# save the plot in the current directory
plt.savefig("my_plot.png")
```



Summary: Code Fragments

Lists

```
# basic list operations
list1 = [1.0, 3.0, 7.0]
list1[0] = 1.0
list1[1] = 3.0
list1[2] = 7.0
len(list1) = 3

# range(n) gives 0, 1, ..., n-1
list2 = [ i for i in range(5) ]
list2 = = [0, 1, 2, 3, 4]

# to take every n-th item
list3 = [ i for i in range(10) ]
list3[::5] = [0, 2, 4, 6, 8]
```

Math

```
# use ".0" after integers
from math import sqrt, exp, log, log10
import numpy as np

# addition, subtraction
1.0+2.0, 4.0-2.0

# multiplication, division
2.0*3.0, -4.0/5.0

# exponents
x ** y  # x raised to the y

# square roots
sqrt(x)

# exponentials
exp(x) or np.exp(x)

# natural logarithms (ln)
log(x) or np.log(x)

# base 10 logarithms
log(x) or np.log10(x)

# linearly spaced values
np.arange(start,stop,stepsize)
np.linspace(start,stop,number_of_steps)
```

Further Reading

Congratulations! You now know how to perform simple kinetic analyses in Python!

Python:

https://www.codecademy.com/learn/python

http://learnpythonthehardway.org/book/index.html

NumPy and SciPy:

http://cs231n.github.io/python-numpy-tutorial/

http://www.engr.ucsb.edu/~shell/che210d/numpy.pdf

http://docs.scipy.org/doc/scipy/reference/tutorial/