Exercise 3 (see http://murov.info/chemexpts.htm
for additional experiments)
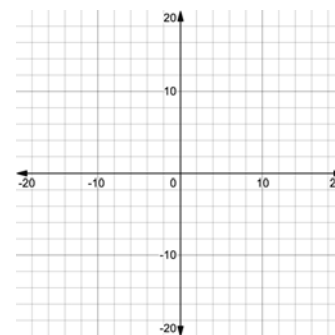
GRAPHING QUANTITATIVE RELATIONSHIPS

Your experience with graphing in mathematics courses has often involved the plotting of a function. In the realm of science experimentation, the reverse of this process is a common procedure. As one variable is changed (while trying to keep all but one other variable constant), another variable is measured. The challenge then becomes the determination of the relationship, if any, between the two sets of variables. One of the variables is plotted versus the other and it is sometimes possible to visually determine the relationship. If the data appear to fall within experimental error of a straight line, the relationship is in the familiar form $y = mx + b$. Other relationships are sometimes discernable visually such as $y = m/x$ but it is best to confirm the relationship by mathematically testing it or converting the data to a form where a straight line should result. A couple of examples that involve the gas laws will be used to demonstrate some of the methodology used to determine an equation that fits the data.

The volume of a gas at several temperatures is reported in the table below. A graph generated using Excel is included for the temperature range -40°C to 100°C. The data appear to be linearly related and fit an equation of the form $V = Mt + b$. A best fit trend-line from Excel results with the equation, $V = 0.0079t + 2.21$. The temperature at which the volume should go to zero is of considerable interest. Setting $V = 0.00$ L in the best fit line results in an extrapolated temperature of -280°C for the zero volume temperature. It is not surprising that this value is about 7°C below the expected value of 0K or -273°C as the data was determined between 1.88 L and 2.98 L and had to be extrapolated to a value substantially below the measured range.   Small errors in the measurements can cause a significant error in the result when extrapolated over such a large range of temperatures (see second graph with extrapolation).

| temp. (°C)	volume (Liters)
100	2.98
80	2.87
60	2.68
40	2.53
20	2.33
0	2.21
-20	2.07
-40	1.88
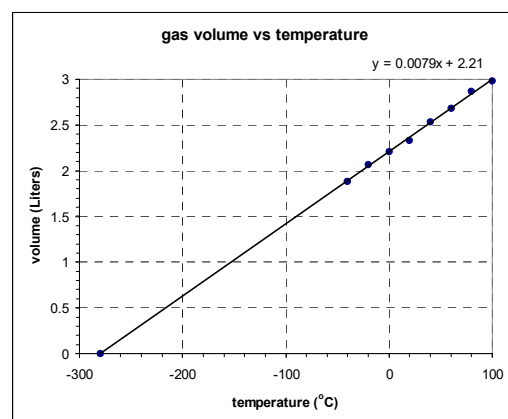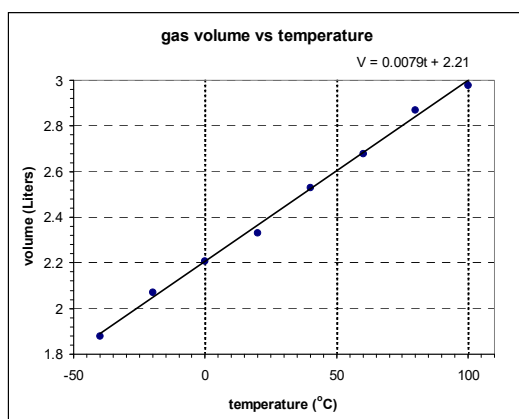
The very good fit of the data to a straight line strongly supports Charles' Law which states that the volume of a gas is proportional to the absolute temperature of the gas when other variables (pressure, amount) are held constant. Using graphs to support Boyle's Law as seen in the next section is somewhat more complex.

The data (arbitrary units) in the table are reproduced from the data Boyle originally obtained as he searched for the quantitative relationship between the volume of a gas and its pressure (at const. temp.) according to the web site, http://web.lemoyne.edu/%7Egiunta/classicalcs/boyleverify.html..

volume	pressure	volume	pressure
48	29.125	23	61.313
46	30.563	22	64.063
44	31.938	21	67.063
42	33.5	20	70.688
40	35.313	19	74.125
38	37	18	77.875
36	39.313	17	82.75
34	41.625	16	87.875
32	44.188	15	93.063
30	47.063	14	100.44
28	50.313	13	107.81
26	54.313	12	117.56
24	58.813		

Volume vs Pressure (original data of Boyle)

Volume vs 1/Pressure

$y = 1406.3x + 0.037$

lnV vs lnP

$lnV = -1.0015\ lnP + 7.2561$

Intuitively, the volume should be expected to decrease as the pressure is increased. This expectation is realized in practice as indicated in the graph on the upper right but the question of the mathematical relationship between the volume and pressure remains. Clearly, the data do not support a linear relationship. Probably the simplest relationship possible that is qualitatively consistent with the behavior is an inverse proportionality or V = C/P where C is a proportionality constant. This equation does yield a hyperbola when plotted but it is difficult to visually confirm that the experimental line is hyperbolic. A very useful technique to test a relationship is to graph the variables in a way that a straight line should result if the relationship is correct. This is possible for V = C/P if we let P = 1/x and calculate values for x from the values of P. This changes the equation to V = Cx and a straight line should result if the equation is correct. For the second graph, V has been plotted vs x and the straight line that results is strong support for Boyle's Law, V = C/P. Notice also that the intercept is very close to the expected 0.00.

An alternative and more general method involves assuming that the relationship is in the form $V = CP^y$. Taking the logarithm of both sides of the equation yields $lnV = ylnP + ln\ C$. A plot of lnV vs lnP should yield a straight line if $V = CP^y$ is correct with a slope of y. The 3rd graph contains a plot of lnV vs lnP. The straight line supports the equation $V = CP^y$ and the slope of -1.00 indicates the relationship is V = C/P consistent with the 2nd graph.
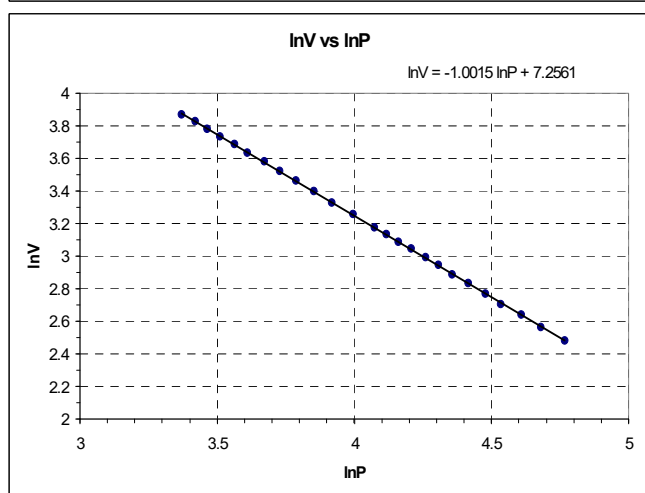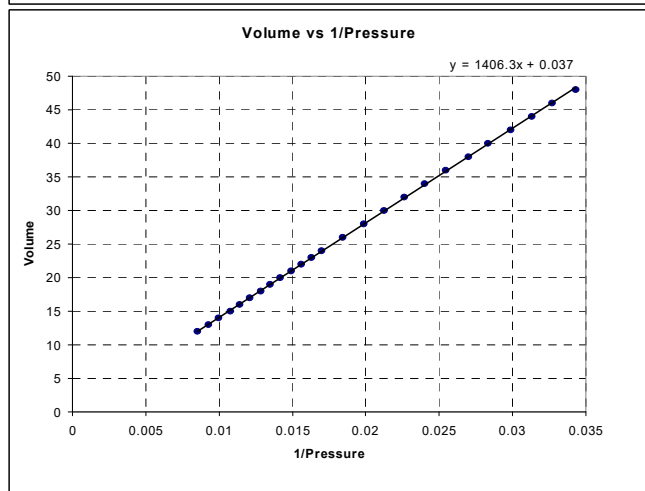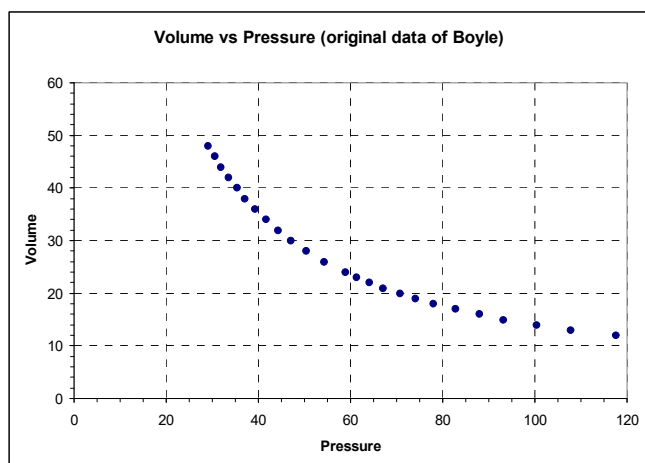
As observed above, it is possible to convert variables to new ones with the result that the equation is in the form y = mx + b. Log log plots are especially useful for determining relationships but not without limitations. One very common relationship in chemistry is $y = Ae^{B/x}$. Taking logarithms of both sides of the equation results in $\ln y = B/x + \ln A$. A plot of lny vs lnx should not yield a straight line. To test the equation, lny should be plotted vs 1/x. Thus it is usually possible to convert the data to variables that should result in linear relationships but there is not a single plot that solves all relationships. For the exercises that follow, your primary goal will be to determine the quantitative relationship if one exists between the two variables given. This will usually involve the conversion of at least one of the variables to a new variable so that the variables are related by an equation in the form y = mx + b.

1.   Percent transmission and absorption of light values were measured for a series of five concentrations of iron(III) salicylate solutions at 530 nm in a 1.00 cm pathlength cell. The results are given in the table below along with the percent transmission and absorption for an iron(III) salicylate solution of unknown concentration. Prepare two graphs, the first with the percent transmission on the vertical axis and concentration on the horizontal axis and the second with absorption on the vertical axis and concentration on the horizontal axis.

solution #	Concentration (mol/L)	Transmittance	Absorption
1	9.88×10^{-5}	68%	0.17
2	1.98×10^{-4}	47%	0.33
3	2.96×10^{-4}	31%	0.51
4	3.95×10^{-4}	21%	0.68
5	4.94×10^{-4}	14%	0.86
unknown		24%	0.62

   a.   Give an equation that relates either the % transmission or the absorption to the concentration. Explain how you arrived at your equation.

   b.   What is the relationship between the percent transmission and the absorption?

   c.   Determine the concentration of the iron(III) salicylate in the unknown directly from the graph and from the best fit trend-line (least squares analysis) of the graph that yielded a straight line.

2.   The energy and wavelengths for several colors of light are given in the table below. Graph energy vs. wavelength, energy vs the inverse of the wavelength and the logarithm of the energy vs the logarithm of the wavelength.

description	near uv	violet	blue	green	yellow	orange	red	near ir
wavelength (nm)	350	420	470	530	580	620	700	750
energy (kJ/mol)	341.8	284.8	254.5	225.7	206.3	192.9	170.9	159.5

   a.   Give an equation that relates the energy to the wavelength. Explain how you arrived at your equation.

   b.   The very approximate energies of carbon - carbon single bonds and carbon - hydrogen bonds are 347 and 413 kJ/mol respectively. Is light in the visible range energetic enough to break these bonds? Explain your answer.

3.   The dissociation constant (K_w) for water [$H_2O_{(l)}$ = H^+ + OH^-] has been measured at several temperatures as reported. Graph K_w vs temperature and then graph again with $\log K_w$ on the y axis and the inverse of the absolute temperature on the x axis. Use Excel to determine the equation for the trend-line from the second graph.
[http://www.chembuddy.com/?left=pH-calculation&right=water-ion-product]

temp. (°C)	K_w (x10^{14})
0	0.11
5	0.18
10	0.29
15	0.45
20	0.68
25	1.00
30	1.47
35	2.08
40	2.91
45	4.07
50	5.47
55	7.24
60	9.55
65	12.58
70	15.85

a. K_w is dependent on temperature according to the equation, $\log K_w = -\Delta H°/2.303RT$ + constant.   From your trendline, calculate the value of $\Delta H°$ for the dissociation of water in kJ/mol.

b.   The heats of formation of liquid water, H^+ and OH^- are 285.84, 0.00 and 229.95 kJ/mol. Use Hess's law to calculate the ΔH for the dissociation of water. Does the value agree with the value obtained from your graph? Explain any significant discrepancies.

c. $1x10^{-14}$ is commonly used as the dissociation constant for water without consideration of the temperature. Does the use of $1x10^{-14}$ cause significant error when used at 0°C? Calculate the pH of neutral water at 0°C.

4.   Data for the vapor pressure of water as a function of the temperature are included in the chart below.
[extracted from http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/watvap.html]

temp. (°C)	-10	0	5	10	15	20	25	30	40	60	80	95	100	110	120
press. (mm$_{Hg}$)	2.15	4.58	6.54	9.21	12.79	17.54	23.76	31.8	55.3	149.4	355.1	634	760	1075	1489

Prepare two graphs, the first with the pressure on the y axis and the temperature on the x axis and the second with logP on the y axis and the inverse of the absolute temperature on the x axis.

a.   Determine the trend-line and the best fit equation for the trend-line of the 2nd graph. Show that the slope of the trend-line should be equal to $-\Delta H_v/2.303R$ where ΔH_v is the heat of vaporization of water. From the slope, determine the value of ΔH_v in kJ/mol.

b.   Using the Internet or an appropriate reference book, find a literature value for ΔH_v and compare the value to the value determined in *a* above.

c.   A plot logP vs 1/T should be linear if the energy change for the process is independent of temperature. While this is often a good approximation over small temperature ranges, the assumption does introduce some error. In both problems 3 and 4, the graphs of $\log K_w$ and logP vs 1/T have been performed assuming the energy change is independent of temperature. For problem #4, comment on the legitimacy of making this assumption. You might want to refer to the site below for information on the dependence of the heat of vaporization of water on temperature. Could this issue be related to any difference you observed between your value of ΔH_v and the literature value?
http://www2.bren.ucsb.edu/~dturney/WebResources_13/WaterSteamIceProperties/EnthalpyOfVaporizationH2O.pdf

5.   The specific heats and atomic masses of 20 of the elements are given in the table below. Use a graphical method to determine if there is a relationship between specific heat and the atomic mass.

a.   If your graphs revealed a mathematical relationship between specific heat and atomic mass, write down an equation for the relationship.

b.   Comment on the usefulness of the determination of specific heat as a method for identifying an element. Would specific heat alone give you much confidence with regard to the identity of the element? If you think measurement of another property would be needed to support an identification, what property would you measure and why?

c.   The elements listed in the table are all selected metals. The values for nitrogen, oxygen, fluorine and neon are 1.040, 0.918, 0.824 and 1.030 J/g K respectively. Do these elements fit your equation?

d.   A theoretical treatment results in the conclusion that the product $(C_p)(M)$ should equal 3R. Is this consistent with your findings?

e.   Compare the temperature change of 1 g of water to that of 1 g of lead if 10 joules of energy are added (starting at 25°C).

element	atomic mass (g/mol)	specific heat (J/g K)
magnesium	24.305	1.023
aluminum	26.982	0.897
calcium	40.078	0.647
titanium	47.867	0.523
chromium	51.996	0.449
manganese	54.938	0.479
iron	55.845	0.449
cobalt	58.933	0.421
nickel	58.693	0.444
copper	63.546	0.385
zinc	65.39	0.388
zirconium	91.224	0.278
silver	107.868	0.235
cadmium	112.411	0.232
tin	118.710	0.228
tungsten	183.84	0.132
platinum	195.078	0.133
gold	196.967	0.129
lead	207.2	0.129
uranium	238.029	0.116

6.   According to a table in Barrow, G. M., *Physical Chemistry*, 3rd ed., McGraw-Hill, **1973**, p.7, a model atmosphere exhibits the properties as a function of altitude given in the table to the right.

a.   By executing the appropriate graphs, try to find linear relationships between altitude and each of the parameters temperature, pressure and density. It is possible that altitude is not related linearly to one or more of the parameters.

altitude (km)	Temp. (K)	Pressure (atm)	Density (kg/m³)
0	288	1.00	1.22
20	217	5.4×10^{-2}	8.9×10^{-2}
40	261	3.0×10^{-3}	4.0×10^{-3}
60	254	2.5×10^{-4}	3.5×10^{-4}
80	166	9.9×10^{-6}	2.1×10^{-5}
100	199	2.1×10^{-7}	3.7×10^{-7}

b.   Mt. Everest has a height of 8848 m. What are the pressure and atmospheric density on the top of Mt. Everest? Considering the oxygen requirements for a human, should humans be able to survive on the top of Mt. Everest without an oxygen tank? For more information, see: https://wildsafe.org/resources/ask/altitude-safety/oxygen-levels/
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1114067/
https://hypoxico.com/pages/altitude-to-oxygen-chart

7.   One of the simplest types of nuclear or chemical reaction involves the decay of an element or decomposition of a molecule without a collision with another reaction center. For these first order unimolecular processes, the initial rate of the process should be proportional to the concentration of the reacting species, rate = kc (in the language of calculus, $-dc/dt = kc$). One method for providing support for the first order reaction is to measure initial rates of reaction and determine if the rates are proportional to the starting concentration. Another method of checking a proposed mechanism involves integration of the equation. A first order reaction results in $\ln(c/c_o) = -kt$ or $\ln c = -kt + \ln c_o$ where c_o is the original concentration of the reacting species. A graph of $\ln c$ vs t should give a straight line if the reaction is first order. More complex reactions can also be tested by the measurement of initial rates to determine concentration dependence or by integration of the proposed mathematical relationship. The latter method requires support by a graphical test such as a straight line.

Technetium is the first element in the periodic chart that does not have any stable isotopes. Technetium-99m is an especially interesting and valuable isotope as it emits a gamma ray with a half life ideally suited for medical tests. It would seem that the decay of technetium should fit the treatment above with the result $\ln(c/c_o) = -kt$. The table below includes data from the site:
http://www.druginformation.com/RxDrugs/T/Technetium%20Tc%2099m%20Albumin%20Aggregated%20Injection%20Kit.html

a.   Graph the fraction (c/c_o) on the vertical axis versus the time on the horizontal axis. Also graph $\ln(c/c_o)$ on the vertical axis versus time on the horizontal axis.

b.   When half of the original amount of starting material has disappeared, $c/c_o = \frac{1}{2}$ and the equation $\ln(c/c_o) = -kt$ becomes
$\ln(0.5) = -kt_{1/2}$ where $t_{1/2}$ is the half life (the time for half of the material to decay away). Determine the slope of your $\ln(c/c_o)$ vs t graph and calculate the half life of technetium-99m. Compare your value to a literature or Internet value for the half life.

c.   Name some of the medical tests that utilize technetium-99m. Explain why technetium-99m is used for these applications.

hours	fraction remaining
0	1.000
1	0.891
2	0.794
3	0.708
4	0.631
5	0.562
6	0.501
7	0.447
8	0.398
9	0.355
10	0.316
11	0.282
12	0.251
18	0.13

8.   The dropping of a 200 g weight resulted in the time and distance data in the table. Graph distance on the y axis vs time on the x axis, distance on the y axis vs the square of the time on the x axis and ln(distance) on the y axis vs ln(time) on the x axis (ignore the 0,0 points for this graph).

time (sec.)	distance(cm.)
0	0.0
0.1	5.1
0.2	19.6
0.3	43.4
0.4	77.2

a.   From the graphs, determine a mathematical relationship between distance and time.

b.   Explain how the relationship is consistent with the equation and the three graphs. Report the slopes of any straight lines that result and give the meaning of the slopes.