Mathcad Chat

1) General Comments

Originally designed for mathematicians, physicists, and engineers. Everything based on matrices (800 x 800 limit).

Atkins' physical chemistry textbook uses Mathcad and has supplemental cd. A supplemental text: M.P. Cady and C.A. Trapp, *A Mathcad Primer for Physical Chemistry*, Freeman 1999 (ISBN 0-7167-3859-7) is a pretty good reference. The Mathcad *User's Guide* is installed and quite an assortment of "E-Books" (featuring "cut and paste") is available. The Help files are quite extensive and are also "cut and paste".

Many worksheets available at www.monmouth.edu/~tzielins/mathcad for all disciplines of chemistry. Also *J Chem Ed* has many articles each year.

Pretty steep learning curve, but that is true of MATLAB and Mathematica also. (With the level of calculations done, spreadsheet calculations also required a considerable amount of instruction.) Each fall about 3/4 of student questions are computer related, 1/4 chemistry related. Two lengthy discussions following short experiments begin the fall semester and all calculations are reviewed by substituting experimental data into instructor templates at the end of each subsequent lab.

There are two types of fields in the workspace. By default, a text region is in Arial font (Insert / Text Region or ") and a math region is in Times New Roman font. There are three types of equal signs: use : which generates := on the screen to define a variable, use = which generates a regular = on the screen to determine a value, and use CTRL = which generates a **=** on the screen to represent a constrained equality.

Many entries are most easily done using the nine Toolbars above the workspace (although there are keystroke equivalents)--particularly those for mathematical operations such as summation, differentiation, integration, and pi. Tables or columns of numbers can be entered using the Insert Table icon (#19 across).

Mathcad reads left to right and top to bottom. Regions can be aligned by selecting and using the align buttons on the tool bar.

An error is normally represented in red and a (many-times meaningless) message as the cursor is held over the offending term.

2) Simple Calculations

What is 2 + 3? Enter 2, +, 3, =.

$$2 + 3 = 5$$

What is -4^2? Enter -, 4, ^, 2, spacebar, =.

$$-4^2 = -16$$

Mathcad can handle units. For example, $F = ma$ using m = 75 kg and a = 100 m s^{-2} would look like mass, :, 75, * kg; acc, :, 100, *, m/s^2; F, :, mass, *, acc; F, =.

$$\text{mass} := 75 \cdot \text{kg}$$

$$\text{acc} := 100 \cdot \frac{\text{m}}{\text{s}^2}$$

$$\text{F} := \text{mass} \cdot \text{acc}$$

$$\text{F} = 7.5 \times 10^3\ \text{N}$$

3) Differential Calculus

To evaluate a derivative be sure to use the derivative operator from the Calculus Toolbar. To evaluate symbolically, use the right arrow from the Evaluation Toolbar.

Let's take the derivative of $x^3 - 2xy$ with respect to x. Enter d/dx from Calculus toolbar, x, (, x^3, spacebar, -, 2, *, x, *, y,), spacebar, right arrow from Evaluation toolbar and then click outside the equation area.

$$\frac{d}{dx}\left(x^3 - 2\cdot x\cdot y\right) \rightarrow 3\cdot x^2 - 2\cdot y$$

Let's take the derivative of $x^3 - 2xy$ with respect to x and evaluate it at $x = 3$ and $y = 4$. Enter x, :, 3; y, :, 4; result, :, d/dx from Calculus toolbar, x, (, x^3, spacebar, -, 2, *, x, *, y,); result, =.

$$x := 3$$

$$y := 4$$

$$result := \frac{d}{dx}\left(x^3 - 2\cdot x\cdot y\right)$$

$$result = 19$$

4) Integral Calculus

To evaluate an integral use the integral operator from the Calculus Toolbar. To evaluate symbolically, use the arrow from the Evaluation Toolbar.

Let's evaluate the definite integral of exp(-x^2) from 0 to infinity. Enter the definite integral operator from the Calculus Toolbar; 0, infinity, e^x from the Calculator Toolbar, -x^2, x, spacebar, right arrow from the Evaluation Toolbar and click outside the equation area.

$$\int_0^{\infty} e^{-x^2}\,dx \rightarrow \frac{1}{2}\cdot\pi^{\frac{1}{2}}$$

Let's evaluate the definite integral of 1/x from a to b. Enter the definite integral operator from the Calculus Toolbar; a, b, 1/x, x, spacebar, right arrow from the Evaluation Toolbar and click outside the equation area.

$$\int_a^b \frac{1}{x}\,dx \rightarrow \ln(b) - \ln(a)$$

5) Plotting

Mathcad has fairly powerful graphing capabilities. If desired, data can be copied and pasted to Axum (the MathSoft graphing package) or other graphing packages or to spreadsheets. Illustrated in the examples that follow will only be simply 2-D graphs with minimal enhancements.

Let's plot the fraction of Cu^{2+} ion in the various forms of copper-ammine complexes as a function of the logarithm of the ammonia concentration. To plot more than one variable on an axis, separate the variables with a comma.

Notation used:

β = association constant
pCL = logarithm of the ligand concentration, concentration is 10 raised to the pCL power
L = ligand, in this case NH_3
Cu = copper +2 ion in all forms

$$\beta1 := 2.0\cdot10^{4} \qquad \beta2 := 9.5\cdot10^{7} \qquad \beta3 := 1.0\cdot10^{11} \qquad \beta4 := 2.1\cdot10^{13}$$

$$pCL := -6.0, -5.9 .. 0.0$$

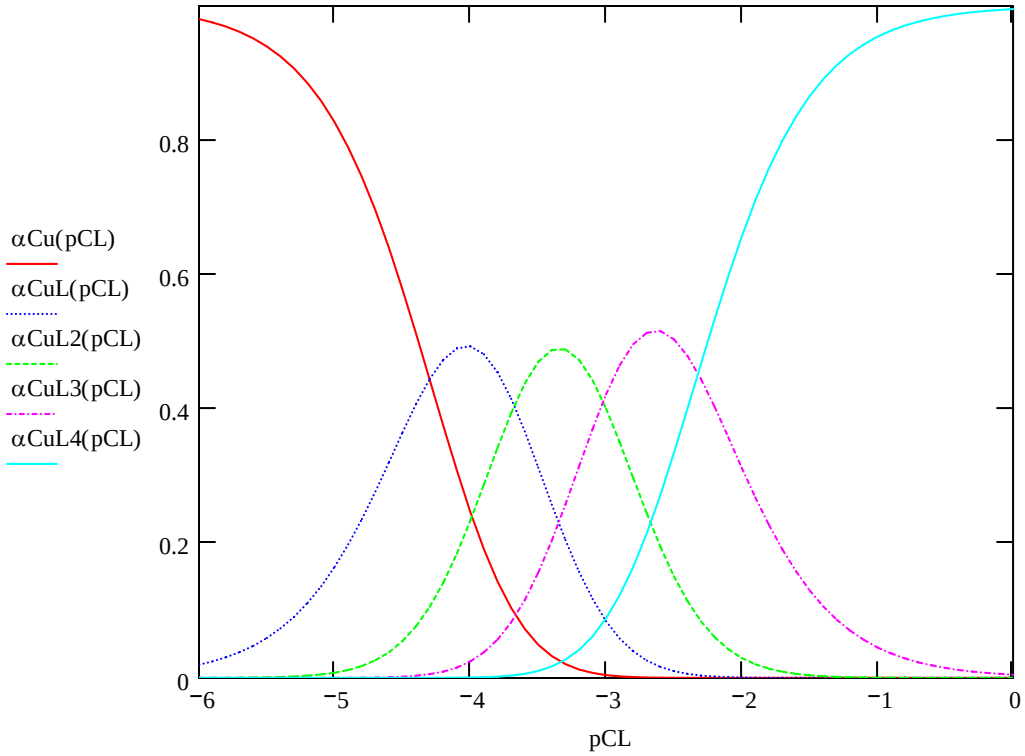
$$\alpha Cu(pCL) := \frac{1}{1 + \beta1\cdot10^{pCL} + \beta2\cdot\left(10^{pCL}\right)^{2} + \beta3\cdot\left(10^{pCL}\right)^{3} + \beta4\cdot\left(10^{pCL}\right)^{4}}$$

$$\alpha CuL(pCL) := \frac{\beta1\cdot10^{pCL}}{1 + \beta1\cdot10^{pCL} + \beta2\cdot\left(10^{pCL}\right)^{2} + \beta3\cdot\left(10^{pCL}\right)^{3} + \beta4\cdot\left(10^{pCL}\right)^{4}}$$

$$\alpha CuL2(pCL) := \frac{\beta2\cdot\left(10^{pCL}\right)^{2}}{1 + \beta1\cdot10^{pCL} + \beta2\cdot\left(10^{pCL}\right)^{2} + \beta3\cdot\left(10^{pCL}\right)^{3} + \beta4\cdot\left(10^{pCL}\right)^{4}}$$

$$\alpha CuL3(pCL) := \frac{\beta3\cdot\left(10^{pCL}\right)^{3}}{1 + \beta1\cdot10^{pCL} + \beta2\cdot\left(10^{pCL}\right)^{2} + \beta3\cdot\left(10^{pCL}\right)^{3} + \beta4\cdot\left(10^{pCL}\right)^{4}}$$

$$\alpha CuL4(pCL) := \frac{\beta4\cdot\left(10^{pCL}\right)^{4}}{1 + \beta1\cdot10^{pCL} + \beta2\cdot\left(10^{pCL}\right)^{2} + \beta3\cdot\left(10^{pCL}\right)^{3} + \beta4\cdot\left(10^{pCL}\right)^{4}}$$


αCu(pCL)
αCuL(pCL)
αCuL2(pCL)
αCuL3(pCL)
αCuL4(pCL)
0.8
0.6
0.4
0.2
0
−6
−5
−4
−3
−2
−1
0
pCL

6) Elementary Statistics

A simple example to show calculation of average and confidence limit (interval) for the mean at the 95% probability limit.

To enter data in a table, use Insert Table icon. The table appears like a spreadsheet (if you are familiar with one). Type in the numbers, use arrow keys to move vertically or horizontally. Resize using little black squares. All numbers do not need to appear on the screen.

$\alpha :=$

	0
0	10.07
1	10.04
2	10.08
3	10.06
4	10.03
5	10.03
6	10.08
7	10.06
8	10.04
9	10.05

To determine the number of data you can count the number of values, look at the numbers in the data table, or use the following:

$$N := \text{length}(\alpha) \qquad N = 10$$

Calculate the average (mean) of the data using the "mean" function.

$$\alpha\text{ave} := \text{mean}(\alpha) \qquad \alpha\text{ave} = 10.054$$

Calculate the confidence limit using the "sample estimate of the standard deviation" function.

$$\Delta\alpha := \text{qt}\left(\frac{1 - 0.95}{2}, N - 1\right) \cdot \frac{\text{Stdev}(\alpha)}{N^{0.5}} \qquad \Delta\alpha = -0.014$$

Be sure to use the capital Stddev function because this uses the N-1 term for the limited sample size. The negative sign means nothing--a confidence limit is a measure of random error which is +/-.

7) Random Error Propagation

This is a simple worksheet to illustrate the propagation of random error (estimating error in a calculated result from errors in factors used in the calculation) for experimental heat capacity ratio C_p/C_v data using an irreversible isobaric expansion method. Note that the square brackets are entered just as a set of ( ) and automatically change as new ( ) are added to the expression. To wrap the equation use CTRL and ENTER.

Data

$P1He := 45.2$ $\Delta P1He := 0.5$ $Patm := 764.3$ $\Delta Patm := 0.5$

$P2He := 0.0$ $\Delta P2He := 0.5$ $R := 8.314$

$P3He := 15.3$ $\Delta P3He := 0.5$ $CplitHe := 20.786$

Calculations

$$\gamma(Patm, P1He, P2He, P3He) := \frac{\frac{P1He + Patm}{P2He + Patm} - 1}{\left(\frac{P1He + Patm}{P3He + Patm} - 1\right)}$$

$\gamma He := \gamma(Patm, P1He, P2He, P3He)$ $\gamma He = 1.542$

$$\Delta\gamma He := \left[\begin{array}{l} \left(\frac{d}{dPatm}\gamma(Patm, P1He, P2He, P3He)\right)^2 \cdot \Delta Patm^2 \ldots \\ +\left(\frac{d}{dP1He}\gamma(Patm, P1He, P2He, P3He)\right)^2 \cdot \Delta P1He^2 \ldots \\ +\left(\frac{d}{dP2He}\gamma(Patm, P1He, P2He, P3He)\right)^2 \cdot \Delta P2He^2 \ldots \\ +\left(\frac{d}{dP3He}\gamma(Patm, P1He, P2He, P3He)\right)^2 \cdot \Delta P3He^2 \end{array}\right]^{0.5} \qquad \Delta\gamma He = 0.033$$

% Difference

$$\gamma litHe := \frac{CplitHe}{CplitHe - R} \qquad \gamma litHe = 1.667$$

$$\%difflitHe := \frac{\gamma He - \gamma litHe}{\gamma litHe} \cdot 100 \qquad \%difflitHe = -7.479$$

8) Linear Regression

A linear regression (least squares) for experimental viscosity data for methanol, ethanol, *n*-propanol, and *n*-butanol. Note that everything is done in terms of *x* and *y* which means that it is recyclable.

Data

x = number of C atoms y = coefficient of viscosity = η

$x :=$

	0
0	1
1	2
2	3
3	4

$y :=$

	0
0	0.554
1	1.071
2	1.941
3	2.687

$N := \text{length}(x)$

$N = 4$

Calculations

Determine the intercept and slope of the straight line (*y* = *mx* + *b*) using Mathcad functions.

$m := \text{slope}(x, y)$ $b := \text{intercept}(x, y)$

$m = 0.727$ $b = -0.254$

The "goodness of fit" is often represented by "R squared".

$R2 := \text{corr}(x, y)^2$ $R2 = 0.991$

The value of η can be calculated from the defined linear equation.

$$\eta(x) := m \cdot x + b$$

The calculations of the 95% confidence limits for the slope and intercept are a little complicated, but need to be done so that the random error can be propagated in error analysis. The range for *i* is created by typing 0, **;**, and N-1. Note that the default setting for a running index in Mathcad is 0 to a maximum value.

$$i := 0 .. N - 1$$

The operator for the summation over *i* can be found on the Calculus toolbar. The array subscript and vectorize can be found on the Matrix toolbar.

$$SSE := \sum_i \left(y_i - \eta\left(x_i\right)\right)^2 \qquad SSX := \sum_i \left(x_i - \text{mean}(x)\right)^2 \qquad SYX := \left(\frac{SSE}{N-2}\right)^{0.5}$$

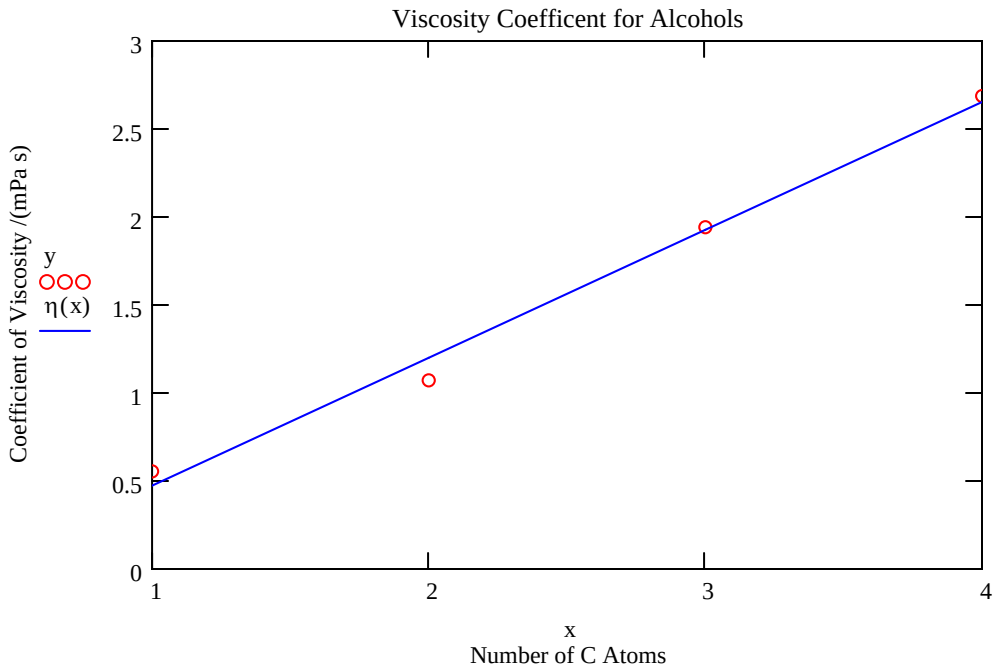
$$mstddev := SYX \cdot \left(\frac{1}{SSX}\right)^{0.5} \qquad \Delta m := qt\left[\frac{(1-0.95)}{2}, N-2\right] \cdot mstddev$$

$$mstddev = 0.049 \qquad \Delta m = -0.213$$

$$bstddev := SYX \cdot \left(\frac{\text{mean}\left(\overrightarrow{\left(x^2\right)}\right)}{SSX}\right)^{0.5} \qquad \Delta b := qt\left[\frac{(1-0.95)}{2}, N-2\right] \cdot bstddev$$

$$bstddev = 0.136 \qquad \Delta b = -0.583$$

It is always a good thing to check the math results graphically by plotting the experimental data (as points) and the least squares line (as a line).



Let's use the least squares equation to predict η for n-pentanol.

$$\eta pent := m \cdot 05 + b \qquad \eta pent = 3.38$$

$$\Delta\eta pent := qt\left[\frac{(1 - 0.95)}{2}, N - 2\right] \cdot SYX \cdot \left[\frac{1}{N} + \frac{(5 - mean(x))^2}{SSX}\right]^{0.5}$$

$$\Delta\eta pent = -0.583$$

9) Root of Equation

Let's look at finding the root of an equation (in this case one that I cannot solve algebraically) using a numerical method beginning with a "seed" value. The value of *fratio* below is defined in terms of the partial presssures of the gases for the diffusion of He into CO_2 by measuring partial pressures of the gases. The time of the diffusion is *t* and the length of the diffusion cell is *L*.

$$fratio := 0.812 \qquad t := 600 \qquad L := 30$$

The equation being solved must be rearranged so that it is equal to zero and Mathcad will find the root such that the function *y*(*D*), in this case, is zero.

$$y(D) := \frac{8}{\pi^2} \cdot \left(e^{\frac{-\pi^2 \cdot D \cdot t}{4 \cdot L^2}} + \frac{1}{9} \cdot e^{\frac{-9 \cdot \pi^2 \cdot D \cdot t}{4 \cdot L^2}} + \frac{1}{25} \cdot e^{\frac{-25 \cdot \pi^2 \cdot D \cdot t}{4 \cdot L^2}} \right) - fratio$$

A trial guess for *D* is based on a typical value for gaseous diffusion.

$$D := 0.6$$

The solution for *D* is found using the "root" function. The last two numbers are the lower and upper bounds for *D*.

$$Dvalue := root(y(D), D, 0, 5) \qquad Dvalue = 0.041$$

Let's look at another example of finding roots of equations and plotting functions. These data represent freezing points of various naphthalene/diphenylamine mixtures.

Data

mN :=

	0
0	5
1	5
2	5
3	5
4	5
5	1.67
6	1
7	0

mD :=

	0
0	0
1	1
2	2.5
3	5
4	10
5	5
6	5
7	5

T :=

	0
0	80.8
1	73
2	62.8
3	50.6
4	34.8
5	38.5
6	43.8
7	54.2

$MN := 128.19$

$MD := 169.23$

$N := \text{length}(mN)$

$N = 8$

$i := 0 .. N - 1$

Tplat :=

	0
0	30.8
1	29
2	32.3
3	31
4	

xNplat :=

	0
0	0.57
1	0.4
2	0.31
3	0.21
4	

$R := 8.314 \cdot 10^{-3}$

4	
5	

4	
5	

Calculations

The mole fractions can be calculated. If the values of the mole fraction are requested to be displayed, they will appear in matrix form.

$$xN_i := \frac{\frac{mN_i}{MN}}{\frac{mN_i}{MN} + \frac{mD_i}{MD}} \qquad xN = \begin{pmatrix} 1 \\ 0.868 \\ 0.725 \\ 0.569 \\ 0.398 \\ 0.306 \\ 0.209 \\ 0 \end{pmatrix}$$

The freezing point change is related to concentration by the Clapeyron equation. Using data points 1 and 2 and data points 7 and 8, the two enthalpies of fusion can be determined. The "seed" guess of x = 20 is just a typical value for organic solids.

$$x := 20$$

$$\Delta HN := \text{root}\left[T_0 - T_1 + \frac{R \cdot \left(T_0 + 273.15\right)^2}{x} \cdot \ln\left(xN_1\right), x\right] \qquad \Delta HN = 18.837$$

$$\%err\Delta HN := \frac{\Delta HN - 19.1}{19.1} \cdot 100 \qquad \%err\Delta HN = -1.376$$

$$\Delta HD := \text{root}\left[T_7 - T_6 + \frac{R \cdot \left(T_7 + 273.15\right)^2}{x} \cdot \ln\left(1 - xN_6\right), x\right] \qquad \Delta HD = 20.071$$

$$\%err\Delta HD := \frac{\Delta HD - 17.8}{17.8} \cdot 100 \qquad \%err\Delta HD = 12.761$$

At the eutectic point, the mole fraction and temperature from both Clapeyron equations will be equal. The guess of the mole fraction of 0.5 is just a value somewhere in the middle. The limits of 0 and 1 represent the minimum and maximum mole fractions, respectively.

$$x := 0.5$$

$$xNeutec := root\left[T_0 + \frac{R\cdot\left(T_0 + 273.15\right)^2}{\Delta HN}\cdot\ln(x) - \left[T_7 + \frac{R\cdot\left(T_7 + 273.15\right)^2}{\Delta HD}\cdot\ln(1 - x)\right], x, 0.1, 0.9\right]$$

$$xNeutec = 0.407$$

The corresponding temperature for this mole fraction is

$$Teutec := T_0 + \frac{R\cdot\left(T_0 + 273.15\right)^2}{\Delta HN}\cdot\ln(xNeutec)$$

$$Teutec = 31.037$$

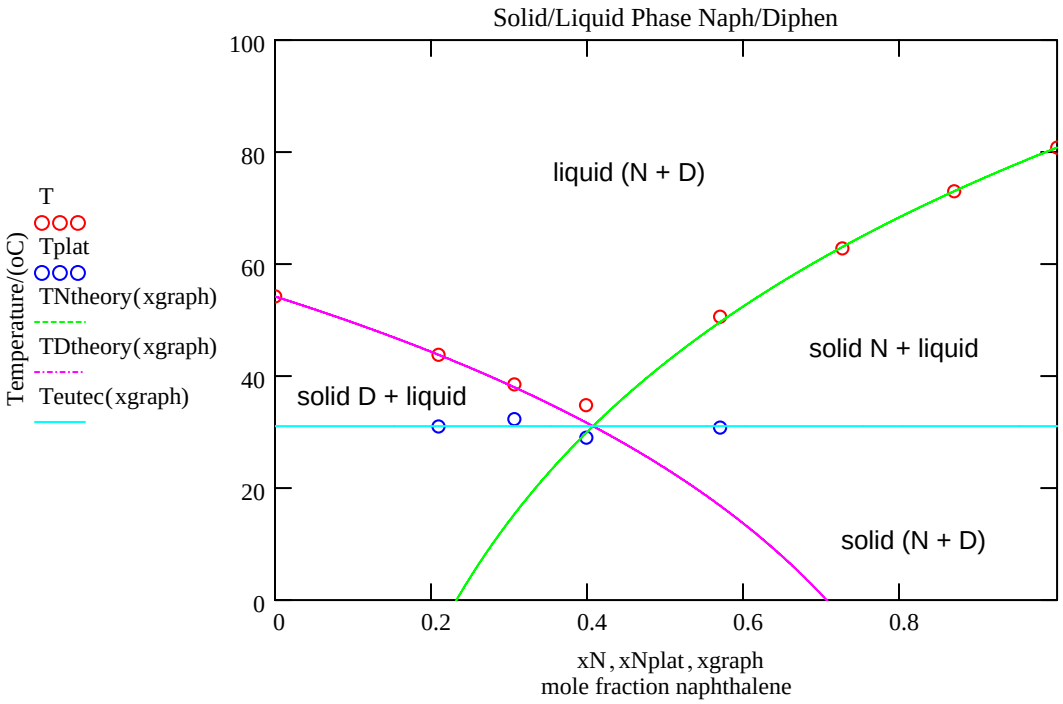
At this point "theoretical" functions can be defined based on the Clapeyron equations and the constants determined above.

$$TNtheory(xgraph) := T_0 + \frac{R\cdot\left(T_0 + 273.15\right)^2}{\Delta HN}\cdot\ln(xgraph)$$

$$TDtheory(xgraph) := T_7 + \frac{R\cdot\left(T_7 + 273.15\right)^2}{\Delta HD}\cdot\ln(1 - xgraph)$$

$$Teutec(xgraph) := Teutec$$

Then, finally, the plot is generated. The extra labels are just text fields dropped on the graph. Some adjustments in the ranges of the axes need to be done by hand.



10) Solving Simultaneous Equations

Mathcad is capable of handling 600 simultaneous equations (linear and nonlinear). Solving these three simultaneous equations by hand took a colleague of mine several hours and more than one try. We will use a "Solve Block" to solve these three equations dealing with the vibrational frequencies and bond force constants in the Raman spectra of benzene and deuterated benzene. A solve block consists of 1) "seed" guesses, 2) the word "Given" (not as a text field), 3) the equations (using the CRTL and =), and 4) asking for the solution. The "factor" is just a bunch of constants lumped together and the "seed" guesses are typical force constants for double bonds.

Data

$$\nu H_0 := 3062 \qquad \nu H_1 := 992 \qquad \nu D_0 := 2293 \qquad \nu D_1 := 943$$

Calculations

$$mH := 1.00 \qquad mD := 2.00 \qquad mC := 12.00 \qquad factor := 5.8918 \cdot 10^{-5}$$

$$ks := 1000 \qquad kt := 1000 \qquad kst := 100$$

Given

$$factor \cdot (\nu H_0)^2 + factor \cdot (\nu H_1)^2 = ks \cdot \left(\frac{1}{mH} + \frac{1}{mC} \right) - \frac{2 \cdot kst}{mC} + \frac{kt}{mC}$$

$$factor \cdot (\nu D_0)^2 + factor \cdot (\nu D_1)^2 = ks \cdot \left(\frac{1}{mD} + \frac{1}{mC} \right) - \frac{2 \cdot kst}{mC} + \frac{kt}{mC}$$

$$\left[factor \cdot (\nu H_0)^2 \right] \cdot \left[factor \cdot (\nu H_1)^2 \right] = \frac{ks \cdot kt - kst^2}{mH \cdot mC}$$

$$soln := Find(ks, kt, kst)$$

$$soln = \begin{pmatrix} 496.421 \\ 778.534 \\ -46.309 \end{pmatrix}$$

11) Solving Differential Equations

Mathcad can solve differential equations (including "stiff" ones) using various approaches. In this example we will look solving the simultaneous differential equations describing the kinetics of three consecutive first order reactions: A --> B --> C. Note the "extra" *t* = 0 to 100 is needed because *t* was used as a variable a couple of times before in this worksheet and no plots will appear in the graph if we don't do this.

$k1 := 1 \qquad k2 := 1 \qquad T := 10 \qquad t := 0 .. 1000$

$a := 1000 \qquad b := 0 \qquad c := 0$

Given

$\frac{d}{dt}A(t) = -k1 \cdot A(t) \qquad A(0) = a$

$\frac{d}{dt}B(t) = k1 \cdot A(t) - k2 \cdot B(t) \qquad B(0) = b$

$\frac{d}{dt}C(t) = k2 \cdot B(t) \qquad C(0) = c$

$\begin{pmatrix} NA \\ NB \\ NC \end{pmatrix} := \text{Odesolve}\left[\begin{pmatrix} A \\ B \\ C \end{pmatrix}, t, T\right]$

To see if the equations have been solved, let's calculate the number of atoms at *t* = 1 and at *t* = 2.

$NA(1) = 367.88 \qquad NB(1) = 367.878 \qquad NC(1) = 264.242$

$NA(2) = 135.336 \qquad NB(2) = 270.67 \qquad NC(2) = 593.995$