An Introduction to Mathcad ©

by

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Why use MATHCAD?

MATHCAD is a software program that uses a unique method to manipulate formulas, numbers, text, and graphs. Unlike programming languages, the equations are written as they would appear in a mathematics reference book, against a background screen in which descriptive text may be placed arbitrarily. The equations may be solved analytically or numerically by using functions from a pull-down menu bar. Descriptive text may be placed anywhere inside the document. MATHCAD also produces one-, two-, or three-dimensional plots which may be embedded anywhere in the document. There is also on on-line reference system to assist users. Any document on the screen can be printed out in its entirety on any windows compatible printer. The combination of equations, text, and diagrams in an open-screen environment makes application development easy. Students in particular would benefit from the interactive development of MATHCAD documents for studying various topics in physical chemistry.

What version of Mathcad should you use?

This depends on the type of computer you have and what you have available. This document was written and saved as a Mathcad 6.0+ document. You can open it with any higher version of Mathcad. Higher versions may have some differences in how higher powered features are performed. For simple applications encountered by students version 6.0 is adequate. However, if you have a choice you should use the highest version you have available. Macintosh computer users only have Mathcad 6.0+ available for their use.

Note to users of this document. The methods and procedures of this document may be different in you version of Mathcad. This may be an obstacle if you let it be one. However, instances of version incompatibility should be few. Every effort has been made to keep the exercises here in a form that crosses most levels of Mathcad. You may need to refer to your Mathcad manual for details for performance of certain operations on your particular version of Mathcad.

Part I - Preliminary Exercises

1. Begin your MATHCAD session by opening the MathSoft Apps Group in Windows and double clicking on the MATHCAD icon. You may wish to work through the Mathcad Tutorial before you start the set of exercises in this document. Exit the tutorial session before doing this set of exercises.

2. Simple keyboard practice. Notice the structure of a Mathcad page. It is like a white piece of paper. Sample the various pull down menus. Notice how groups of possible actions are grouped together.

Entering simple equations onto the MATHCAD page.

Enter **16-8/2=**

Note how the division sign behaves. Pressing = produces the numerical result of the operation.
To produce (16-8)/2, one should either type the entry with the parentheses included, or type 16-8 and then highlight the entire operation, and then press the division button. What ever is highlighted, i.e. in the blue box, will appear in the numerator. Try this step now.

The hierarchy of operator evaluation follows the commonly used standards. Powers are followed by multiplication and division, followed by addition and subtraction.

Pressing the = evaluates the mathematical sequence and returns the numerical value to the right of the equal sign.

To take the power of a function use the carat symbol (Shift-6). Evaluate 4 squared. Practice now with other squares. You can make your practice exercises right here in this document or print this document and create your own collection of answers to the exercises. Save your file periodically in case of a computer glitch. You can also annotate your document with text regions. This will give you a personalized tutorial document that you can refer to if you forget something you learned here. You can also add sample exercises to your personal document as the semester proceeds. This is important because you may need to refer to techniques from one exercise to the next and you don't want to waste time recreating a technique that was already constructed in your practice file.

Most users of Mathcad have a file of techniques that they can refer to for new work. Start you file of techniques today.

3. **Variables**

Variables are easily defined in MATHCAD. If you wish to set x to 10 type **x:10**.
The colon acts as the PASCAL operator **:=** , which is what you see on the screen.
This operation assigns the values 10 to the variable x.

Now enter **y:= 2*x^2 +15**.

This defines y in terms of x. Next evaluate y by typing **y=** ; the answer 215 should appear on the screen.
Each entry that you typed should lie below the previous one to form a column of expressions.

MATHCAD evaluates expressions from top to bottom and left to right on the screen.
Sequential entries of equations and data must follow the order for MATHCAD to give the result that you desire. Syntactically incorrect entries will result in various types of MATHCAD error messages.

If you want a function y which changes as x is changed, one must use a **function** definition. The following examples are functions, and you can see that as the variable changes the value of the function changes. Try the following functions and evaluate them at different values of x.

y(x):=6+x (Remember that typing the colon button gives **:=** on the screen)

z(x,y):= 3*x + 9*y -5 (What is z(1,1)?)

Note that x and y above act as dummy variables.

4. **Range Variables**

Some variables act as indices for identifying the elements of arrays of numbers. These are called **range variables**. They have the form $\mathbf{x_i}$ where x is the name of a variable and i is an index, also called a step variable. Typically, i ranges from 0 up to any positive integer. For example 0 and 1 in x_0 and x_1 would be two values in the range of the step variable that identifies each element in the array x. x_0 and x_1 are the first two elements in the x array.

To define a range variable, one can use the colon and define each member independently. Alternatively, one may use a **step variable**. The following procedure will define a range of a step variable for an array xx containing the first ten even numbers.

Step 1 for the range	**i:= 0...9**	**type**	**i:0;9**
Step 2 for the array	$\mathbf{xx_i := 2(i+1)}$	**type**	**xx [i := 2 * (i + 1)**

Notice how the colon acts as the assignment operator, and the semicolon sets the end of the range, so that i ranges from 0 to 9. If one wanted to have a range such as 0, 2, 4, 6, 8, 10, one would type i:=0,2;10 . Here the initial value is 0; the 2 tells the program to change the values of i by increments of 2 by telling Mathcad the next integer in the series ending at 10. Range values can also go in descending order by making the second number smaller than the first as in I:=0, -2;-20. We can also use range variables for a noninteger series of numbers.

Type xx = to see how xx is defined at this point.

Now extend the definition by typing **xx [10 :=20**

The left bracket [is used as a subscript operation key for range variables.

Type xx = see that the range variable has been extended to include the new value of xx.

Type k:1,1.1;2 What do you see? **Type k=**
What are the values for k? How might this be useful?

Next try

Type xx[12:=24

Type xx[11=

Not only has x_{12} been defined, but so has x_{11} (which has been set to zero.).
In this way, range variables may be defined from 0 to the highest index.

Do not confuse range variables with subscripts on variable names. Subscripts that are part of a variable name are typed by using a period immediately to the right of the variable name.

For example, enter the following: **A.ini**

the result A_{ini} appears on the screen. This is an example of a literal subscript. These are part of the of the variable name. On the other hand an array subscript represents a reference to an array element in a vector or matrix. This distinction is important for work in quantum chemistry.

5. **Graphics**

MATHCAD has a strong graphics program, which plots range variables against each other or against an index. Suppose we wish to graph x_2 from -2 to +2 by increments of 0.04. This involves 101 points. Set up the range variables for t going from -2 to +2 and define a range variable xsq in which each element is equal to t2 .

Enter: **j shift: 0;100**
t[j shift: - 2 + j / 25
xsq[j shift: t[j^2

note: enclose the t[j in a blue selection box before typing ^2

Now use the graphics pull-down Menu bar and choose XY plot. A square appears on the screen.
Click on the black dot at the middle of the vertical axis and enter xsq[j
Click on the dot at the middle of the horizontal axis and enter t[j

(Other dots are used for manually entering upper and lower limits for the ordinate and abscissa of the graph). It is possible to graph two- and three-dimensional functions. Some of the sample exercises obtained from the WWW show this feature. You will see more of these later.

6. **Multiple line graphs**.

MATHCAD can also be used to prepare multiple line graphs. As an example of this you can prepare two representations of typical potential functions.

Enter **r.e : 1.0** **D:100** **a: 6/r.e** **and** **r:0.5,0.53;3.0**

Note what appears on your screen.

In the space on the right here type in the following equations. Be very careful. The two equations are the Morse potential and the Leonard Jones 6-12 potential. You can find graphs of these two functions in many physical chemistry texts.

V.M(r):D*(1-e^-a*(r-r.e))^2

and

V.LJ(r):D*((r.e/r)^12 - 2*(r.e/r)^6) +D

This equation has two parts. Enclose the first part (between the : and the -) in a blue box before typing the negative sign.

These equations make use of the literal subscript concepts. Be careful how you type these onto the MATHCAD page.

This time start the graph by pressing the @ symbol below the equations.

Enter r in the place holder on the x axis.

Enter **V.M (r), V.LJ(r)** into the y axis place holder. (Yes, use a comma. It is the comma that lets you put two functions on the same graph)

The graph will not look very informative as the upper limit on the y axis is too large. Click on the place holder for the upper value of the y axis. The number should become highlighted. Press delete once. Then enter 200 as the new upper limit into the blank place holder. The resulting graph should look familiar.

7. **Evaluating mathematical expressions**: Mathcad can be used to evaluate expressions. Here we see a calculation of pressure as a function of volume using the van der Waals equation. Notice how the index i is used below to compute a series of volumes. There are two types of subscripts in Mathcad. One is a real index as shown here. It is called a vector subscript and is created by using the [key followed by the number or the varying index. The other is an index that is part of the name of a variable. This is called a literal subscript and it is created by using the period '.' followed by the letter or number that is to be part of the variable name. We saw this before in previous exercises in this worksheet.

Here we will study the PV behavior of a gas with the van der Waals equation.

$R := 82.05 \qquad T := 4.2$

$b := 23.7 \qquad a := 3.41 \cdot 10^4$

First we define the parameters that we will use in the calculation. Notice that Mathcad uses the := to associate a number with a variable name. The same := is used to define functional relationships as shown here for P(V).

Next we write the van der Waals equation. Notice how we write the equation with P as a function of V.

$$P(V) := \frac{R \cdot T}{V - b} - \frac{a}{V^2}$$

Notice how the equation looks like what you would write on a page in your notebook. This is one of the advantages of using Mathcad.

$i := 0 .. 100$

Here we define the range for the calculation of the volumes.

$$V_i := 35 + (200 - 35) \cdot \frac{i}{100}$$

$$P_i := P\left(V_i\right)$$

Notice how we must be sure to specify each variable and its range of values. View the array V_i and examine its contents. Notice how you don't need to type in all these values if you can find a way to calculate them. Once the V_i are defined it is an easy step to define P_i.

We already saw how easy it is to prepare graphs with Mathcad. Practice this in the space to the left. Fill in the place holders with P_i and V_i. Be careful about which type of subscript you use here. Remember that most of the time you will need only to place the x and y variable names in the place markers for them. Mathcad will generate the scale of the graph for you. However if you want to adjust the formatting of the graph then you can use the Graph pull down menu or double click on the graph itself. Try this and see what happens.

Exercise: Prepare a graph for the variation of pressure as a function of volume with the Redlich-Kwong equation of state for the same data range used in the van der Waals sample given above. Practice changing the range of the calculation and the range shown in the plot for the x and y axis. What units of volume do you have here?

Note to students: By now you have the rudimentary skills to do many homework problems in physical chemistry. Most of these require a function and values for the variables. You can also prepare graphs of data and annotate a worksheet like this one using Mathcad's text feature. This means that you can write lab reports using this software.

8. **Units**: Units are easy to use in Mathcad. You will need to look in the Mathcad manual to see the correct spelling of the many units you will use in physical chemistry. It is important to note that the mole unit is not supported in Mathcad 6.0+ so all calculations should be done for one mole and then adjusted later to account for the number of moles you need for the answer to a problem. Higher versions of Mathcad support the mole. To see the correct spelling of the unit names you can pull down the menu for units and select insert units (check your manual for the location of the Units menu). This opens a window in which the current system of units is identified and a scroll of types of units available. Find the energy entry. In the square brackets you will see that Joules are written as joule when included as a unit in a calculation. More information about units is given in the Mathcad manual in Chapter 8 or use the Help menu. Here we review only a few of the basics.

$mass := 25 \cdot kg$

$acc := 9.81 \cdot \frac{m}{sec^2}$

$F := mass \cdot acc$

$F = 245.25 \cdot kg \cdot m \cdot sec^{-2}$

Here the mass is defined for a problem. The unit kg is added to the definition by multiplication. The same procedure is used for the acceleration. Then we define the force as F. Typing F = where the ordinary equal sign is used yields the result of the calculation including units. Whenever units are used to define a variable then units are produced in the answer.

The calculation is now extended to include momentum. Notice the time unit.

$time := 5 \cdot sec$

$momentum := \frac{F}{time}$

$momentum = 49.05 \cdot kg \cdot m \cdot sec^{-3}$

Units are important for checking equations to be sure a derivation is correct. If units are incompatible then Mathcad will give you an error message.

$wrong := mass + acc$

incompatible units

Exercise: Calculate the pressure when 200 grams of CO_2 are confined to a volume of 2 liters at 400 ºC. Include all required units. repeat the exercise using the van der Waals equation.

9. Integrals: Numerical integrals are easily performed using MATHCAD. To evaluate an integral open the calculus palette and choose the definite integral symbol. Clicking this produces an integral sign with place holders for the upper and lower limits, the function and variable. Fill in this so that you evaluate the integral of $\exp(-x^2)$ from 0 to 2. When you enter this expression be sure to remember that exp means e . Notice how the power in a power is handled by MATHCAD.

$$\int_0^2 e^{-x^2}\,dx = 0.882$$

Exercise: Evaluate the work that an ideal gas would do if it expanded reversibly and isothermally from 1.0 liters to 5.0 liters at 27 ^oC. Check your text for the requisite integral to evaluate.

More extensive exercises with integrals will wait for a future tutorial worksheet. Many of the Mathcad documents on the Mathcad web page give examples of integrals and differentials that you can add to your collection of examples of techniques.

10. Iterations: Sometimes we want to do a whole of set of steps in a single calculation. In this case you must create a vector in order to get a sequential set of iteration steps. You already examined examples of using an index in previous sections of this set of notes. Here we extend that idea.

$F_0 := 1 \qquad F_1 := 1$

Here we define the first two elements of the vector F. F is a vector of a set of numbers such that the next number is the sum of two previous numbers. We would like to generate the remaining values without typing them in one by one. We can use an index and vary the index systematically. The subscript here is created using the [key.

$i := 0 .. 10$

$F_{i+2} := F_{i+1} + F_i$

First define the range for the set of numbers you wish to calculate. Then define the function that creates each element in the vector. Typing F = immediately below the definition of F_{i+2} produces the desired vector. Mathcad repeats the calculation until all i are exhausted.

Exercise: Change i to 30 and see what happens. Click on the vector array and determine the number of entries it contains. How long did the calculation take?

One thing you must always remember. Mathcad processes the equations and data you provide in a sequential manner. Your exercises must have equations in the right order in order to function. By way of example move the equation here for F1+2 to a region below the matrix array. You do this by creating a selection box around the equation with the mouse In version Mathcad 6.0 you click near the equation to get the red + there. then press the right mouse key and move the mouse in such a way as to enclose the equation with the selection box. Release the mouse key and move the mouse so that a very large + is seen in the selection box. Now depress the left mouse key again and while holding it in the depressed position drag the mouse and move the equation. In higher versions a hand appears to indicate that the move feature is active. Use the mouse button as usual to move the equation. Try using the same technique to change the size of one of the graphs above in this document.

11. Solving equations. In physical chemistry we are often asked to solve equations by finding the roots that satisfy the equation. Here we see some simple examples of solving equations. Mathcad will even let you solve differential equations but that is a story for later.

When solving an equation with Mathcad we must help the software get started. We do this by providing an initial guess for the root in which we are interested.

$f(x) := x^2 - 4 \cdot x + 3$

Here we have a quadratic equation. We will use the root function of Mathcad to find the roots.

Prepare a graph of f(x) as a function of x. You might consider using a range for x of -3 to +10. Can you detect the two roots in this graph? Adjust the range and visually determine the roots.

Now use your guesses to find what Mathcad says the roots are. Here to the right I have typed in 3.5 and 0.5. Replace these with your roots and try several other initial guesses. Get Mathcad's answer by typing **ans=** to the right of the root expression. ans is the variable name that holds the values of the roots.

$x := 3.5$ $\quad ans := root(f(x), x)$

$x := 0.5$ $\quad ans := root(f(x), x)$

$x^2 - 4\cdot x + 3 = 0$

$\begin{pmatrix} 3 \\ 1 \end{pmatrix}$

Here we rewrite the quadratic expression as a symbolic expression. The bold = sign is created by typing **ctrl=**.

Now we will use symbolic menu to find the roots in a more direct way. Place the blue cursor next to the x and highlight the x with a blue selection box r editing lines. From the Symbolic dropdown menu choose solve for variable. The answer should immediately appear.

$g(x) := x\cdot e^x - 1$

$x := .5$

$ans := root(g(x), x)$

$ans = 0.567$

Consider the function to the left.
Provide an estimate for the the point at which g(x) is zero.
Use the root function as shown and then type ans=

Check that the answer actually does give a value for g(x) that is zero or close to zero.

$0 = x\cdot e^x - 1$

$W(1) =$

Here we try the symbolic approach. High light the x with a blue selection box and choose solve for variable. You should observe what is shown here to the left.

MATHCAD gives no solution to this problem symbolically!

$x^3 = 4$

Here is another symbolic expression. Highlight the x with a blue selection box and choose solve for variable from the Symbolic menu. What do you get from this. Not very useful is it. This approach to solving equations with Mathcad is limited and when it fails you must use alternative methods.

$x := .5$

$gg(x) := x^3 - 4$

$ans := root(gg(x), x)$

$ans = 1.587$

Like all good scientists we must have multiple approaches for solving problems. Here we describe an alternative to that cubic expression to the upper right.

We define a new function and ask for the root. Don't forget to give a new initial guess or else Mathcad will use what ever was left over from calculations done above.

Vary the initial value for x to see what latitude you have in your initial guess in this case. Try small, large, negative and decimal values.

12. An Equation with two variables. Using a solve block to find the values of x and y that satisfy a set of equations in x nd y. A solve block is a group of commands and equations in which the instructions for solving a system of equations is contained. Within the solve block you provide the initial guess for the solution, the the word **given**, the constraints (equalities and inequalities etc. the function to be operated upon, and the method of operation to be applied to the function. The procedure is outlined here below for the system of simultaneous equations shown below.

$x := 2 \qquad y := 2$ — Provide initial guesses for x and y.

Given

The word 'Given' marks the start of a solve block.

$x^2 + y^2 = 10 \qquad x - y = 1$

Since there are two unknowns Mathcad requires two symbolic equalities. These are the two simultaneous equations we want to solve.

$$\begin{pmatrix} xval \\ yval \end{pmatrix} := \mathrm{Find}(x, y)$$

To the left we see the correct form of using the Find Mathcad function. The Find function ends the solve block.

$$\begin{pmatrix} xval \\ yval \end{pmatrix} = \begin{pmatrix} 2.679 \\ 1.679 \end{pmatrix}$$

Here are the results. To display them I typed the matrix followed by an ordinary = sign. Try this your self for practice. the matrix can be added to the page by cutting and pasting.

Given

$x^2 + y^2 = 10 \qquad x - y = 5$

$$\begin{pmatrix} xval \\ yval \end{pmatrix} := \mathrm{Find}(x, y)$$

did not find solution

Another example. In this case I chose a different second equation. Here we see that you get notice, either a message or red version of the expression, if the software can't solve the equations. I wonder why this happens. What do you think?

13. Preliminary remarks on symbolic manipulation

Differentiation

$x \cdot e^{-x^2}$

Highlight the variable x with a blue selection box and choose differentiate on variable from the Symbolic pull down menu.

This yields: $\exp\left(-x^2\right) - 2 \cdot x^2 \cdot \exp\left(-x^2\right)$

Try this for your self in the space to the left.

Integration

$x \cdot e^{-x^2}$

This time highlight the variable and then choose integrate on variable from the Symbolic menu.

You should obtain $\frac{-1}{2} \cdot \exp\left(-x^2\right)$

Substitution

$u^2 + 1$

Highlight this and copy.

$x \cdot e^{-x^2}$

Highlight the x variable and then choose Substitute for variable from the Symbolic menu. You should obtain:

$$\left(u^2 + 1\right) \cdot \exp\left[-\left(u^2 + 1\right)^2\right]$$

Try this for yourself in the space to the left.

14. Some preliminary remarks on matrices. Matrices are powerful mathematical tools. One primary use is to solve simultaneous equations. You may learn more about this later in your physical chemistry course.

$$AA := \begin{bmatrix} 1 & 2 & 4 & 1 \\ 2 & 0 & 1 & 0 \\ 1 & 0 & 1 & 1 \\ 2 & 1 & 0 & 2 \end{bmatrix} \qquad BB := \begin{bmatrix} 1 \\ 4 \\ 2 \\ 1 \end{bmatrix}$$

Matrices are created using the Matrices symbol from the math palette or by choosing Matrices from the Math menu.

Here we have matrices AA and BB. We can form the product of these two matrices using the normal rules of matrix algebra.

$$xx := AA^{-1} \cdot BB \qquad xx = \begin{bmatrix} 1.643 \\ -1.571 \\ 0.714 \\ -0.357 \end{bmatrix}$$

Notice the names of the variables and the use of mathematical symbols to do the multiplication.

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