MathCad Basics

What is MathCad?
- Equation-solving software for scientists and engineers
  - Convenient design tool
  - Math problem solver
  - Physical unit converter, advanced calculator, and more
- Can be indispensable for upper division courses in Chemistry

MathCad Features
- Reminiscent of a programming language but much more interactive
- Instantaneous compilation / debugging of input data
- Automatic recalculation of worksheets (it is similar to Excel in this respect)
- Equations displayed in a readable form (just the way people write them)
- Conversion of physical units between SI, MKS, CGS, and other systems
- Symbolic mathematics
- A number of built-in functions, methods, and graphing capabilities
- Good integration with other applications
The MathCad Work Place

**Title Bar**

**Scroll Bars**

**Various Tool Bars**

**Page Margin**

**Sample Calculation**

Normal execution order: left-to-right and top-to-bottom

Radius := 18cm
Enter the value for the radius of a circle

Area := \( \pi \cdot \text{Radius}^2 \)
Enter the formula for calculation of area of a circle

Area = 0.102 m²
Evaluate the result for the area

Area = 1.096 ft²
Evaluate again requesting a conversion from SI units to square feet
MathCad Toolbars

Interface has a standard appearance for a windows application:

- The **math** toolbar gives you access to a number of capabilities:
  - Calculator toolbar
  - Graph toolbar
  - Matrix toolbar
  - Evaluation toolbar
  - Calculus toolbar
  - Boolean toolbar
  - Programming toolbar
  - Greek toolbar
  - Symbolic toolbar

- The **standard** and **formatting** toolbars simplify editing:
Programming vs MathCad

Write the Program Code

Debug the Program Code

Compile the Program Code

Execute the Compiled Code

Identify Problems with the Code

Write MathCad Statements

Edit MathCad Statements

Execute statements "on the Fly"

Identify Problems
Programming, MathCad, or Spreadsheets?

**Fortran-90** code for calculating the volume of a sphere:

```fortran
PROGRAM volume
IMPLICIT NONE
REAL :: radius, volume, pi
OPEN(unit=15, file="out.txt", action = "write")
radius=3.0
pi=3.14159
volume=4.0*pi*radius^3/3.0
WRITE(15,*) radius, volume
CLOSE(15)
END PROGRAM volume
```

**MathCad** version of the same calculation:

- Radius := 3
- Volume := \( \frac{4 \pi \cdot \text{Radius}^3}{3} \)
- Volume = 113.097

**Excel** version of the same calculation:

<table>
<thead>
<tr>
<th>Radius</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>113.097</td>
</tr>
</tbody>
</table>

- Excel is a fine choice for very simple everyday calculations
- MathCad is a better choice for more advanced calculations that benefit from more complicated graphing, unit handling, symbolic math, etc.
- Programming should be used for more complex problems, especially if the calculation needs to be done repetitively and/or on very large data sets
- MathCad/Excel codes require MathCad/Excel applications to execute them, whereas codes created by programming languages are stand-alone applications that can run on (more or less) any machine
Four "Equal" Signs in MathCad

**Assignment (:=)**
- Entered by typing the colon key [:]
- Assign values to variables: \( Volume:=24\, m^2 \)
- Do calculations on variables: \( Volume:=Volume+16\, m^2 \)

**Display result (=)**
- Entered by typing the equal key [=]
- Displays the result of the last calculation \( Volume=40\, m^2 \)

**Symbolic Equality (=)**
- Entered by typing the colon key while holding Control [Ctrl =]
- Establishes functional relationship between variables \( V\cdot P = n\cdot R\cdot T \)

**Global Assignment (≡)**
- Entered by typing the [~] key
- Overrides normal left-to-right, top-to-bottom evaluation order
- Equations with the "≡" sign are evaluated **first**
Defining Variables in MathCad

Predefined Variables
- \( \pi = 3.1415926536 \ldots \) (entered as Ctrl-Shift-p)
- \( e = 2.7182818285 \ldots \) (entered as e)
- \( g = 9.80665 \text{ m s}^{-2} \) (entered as g)
- \( \% = 0.01 \) of the variable entered (entered as \% after the variable name)

Your Own Variables
- You can define new variables anytime, e.g., Size:=50 cm

Redefining Variables
- You can redefine the variables that were either predefined or defined by you previously. For example, typing \( e:=42 \) will change the value associated with the predefined variable e from 2.7182818285… into 42.
- MathCad will warn you when you redefine previously defined variables by underlying the variable with a green wavy line and stating:
  - This expression modifies a Mathcad built-in unit.
  - This expression modifies a previously defined variable.
  - Who do you think you are messing around with my constants?
Two Subscripts in MathCad

Text subscripts

– Variable names can contain subscripts for *purely cosmetic* purposes
– Variable names are case sensitive, and so are the text subscripts
– \( V_{\text{empty}} \) is entered in MathCad by typing \( V.\text{empty} \)
– MathCad automatically hides the period

Index subscripts

– Look similar to the text subscript but have a very different purpose!!!
– Used for indexing arrays (e.g., vectors or matrices)
– \( V_2 \) is entered in MathCad by typing \( V[2 \)
– MathCad automatically hides the left square bracket
Units in MathCad

Predefined units
- Predefined units for: mass (kg, gm, lb), length (m, cm, ft), time (s, hr, yr, day), charge, temperature, volume, pressure, luminosity, substance, etc.
- Predefined unit modifiers (n = nano, c = centi, m = milli, etc.)
- Mathcad internally converts all inputs into SI system but can display the results in any units it knows about
- In earlier versions only **multiplicative** unit conversions were possible (e.g., degrees Celsius could not be automatically converted into degrees Kelvin)
- For temperature unit conversions you have to do the following:
  - Insert a postfix operator (Ctrl-Shift-x) after the value to be converted
  - Insert the desired unit from the **Insert → Unit** menu

Defining custom units
- New units can be defined from MathCad built-in units
  - \( nA := 10^{-9} \cdot \text{amp} \)
  - \( \text{kmol} := 10^3 \cdot \text{mole} \)
# Keyboard Entries

<table>
<thead>
<tr>
<th><strong>Space</strong></th>
<th>Starts a new text region (the region does not need to start with space; two words separated by a space will do)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>:</strong></td>
<td>Assignment statement</td>
</tr>
<tr>
<td><strong>=</strong></td>
<td>Result statement</td>
</tr>
<tr>
<td><strong>Ctrl =</strong></td>
<td>Symbolic equality statement (will not use in this course)</td>
</tr>
<tr>
<td><strong>~</strong></td>
<td>Global statement (will not use in this course)</td>
</tr>
<tr>
<td>*<strong>/+-</strong></td>
<td>Multiply, divide, plus, minus operators</td>
</tr>
<tr>
<td><strong>^</strong></td>
<td>Raise to the power of (or press superscript sign)</td>
</tr>
<tr>
<td><strong>.</strong></td>
<td>Starts a text subscript</td>
</tr>
<tr>
<td><strong>[</strong></td>
<td>Starts an index subscript</td>
</tr>
<tr>
<td><strong>cm</strong></td>
<td>Many standard units can be entered after the variable definition</td>
</tr>
<tr>
<td><strong>Ctrl-Shift-p</strong></td>
<td>π</td>
</tr>
<tr>
<td><strong>Insert</strong></td>
<td>Moves the cursor between the front and back of the selection – very handy during editing</td>
</tr>
<tr>
<td><strong>Ctrl-Shift-x</strong></td>
<td>Insert a postfix operator (before inserting the units)</td>
</tr>
</tbody>
</table>
Practice: Solvent Preparation

Calculate the molar concentration and mixing ratio for a solvent obtained by mixing 55 mg of solute with MW of 200 g/mol and 500 mL of solvent with MW of 70 g/mol and density of 0.8 g/mL. The total volume of the solution after mixing is 540 mL.

**TASK:**
- Define unit
  - amu := 0.001 kg/mol
  - mg := 10^{-3} gm
- Assign molecular weight of solute in {amu}
  - MW\(_{\text{solute}}\) := 200 amu
- Assign mass of solute in {mg}
  - m\(_{\text{solute}}\) := 55 mg
- Assign volume of added solvent in {mL}
  - V\(_{\text{added}}\) := 500 mL
- Assign volume of resulting solution in {mL}
  - V\(_{\text{solution}}\) := 540 mL
- Assign density of solvent in {kg/cm\(^3\)}
  - \(\rho_{\text{solvent}}\) := 0.8 g/cm\(^3\)
- Assign molecular weight of solvent in {amu}
  - MW\(_{\text{solvent}}\) := 70 amu

**VALUE:**
- C\(_{\text{molar}}\) = (moles of solute) / (volume of solution)
- WeightFraction = (weight of solute) / (weight of solution)
- Molality = (moles of solute) / (weight of solvent)
Solution: Solvent Preparation

**Define new units**

\[ amu := 0.001 \frac{kg}{mol} \]
\[ mg := 10^{-3} \text{ gm} \]

**Solute properties**

\[ MW_{solute} := 200 \text{ amu} \]
\[ m_{solute} := 55 \text{ mg} \]

**Solvent properties**

\[ V_{solvent} := 500 \text{ mL} \]
\[ \rho_{solvent} := 0.8 \frac{\text{ gm}}{\text{ cm}^3} \]
\[ MW_{solvent} := 70 \text{ amu} \]

**Solution properties**

\[ V_{solution} := 540 \text{ mL} \]

**RESULTS:**

\[ C_{molar} := \frac{m_{solute}}{MW_{solute}} \cdot \frac{1}{V_{solution}} = 5.093 \times 10^{-4} \text{ mol/L} \]

\[ \text{WeightFraction} := \frac{m_{solute}}{\rho_{solvent} \cdot V_{solvent} + m_{solute}} = 1.375 \times 10^{-4} \]

\[ \text{Molality} := \frac{m_{solute}}{MW_{solute}} \cdot \frac{1}{\rho_{solvent} \cdot V_{solvent}} = 6.875 \times 10^{-4} \text{ mol/kg} \]

**Things to watch out for:** In MathCad, the default meaning of \( g \) is gravitational constant (9.807 m/s\(^2\)) not 1 gram!!! Gram is entered as \( \text{gm} \). Interchanging the two may cause all kinds of mistakes in calculations (try it out for this calculation). It is always better to check the unit definitions when in doubt.
Example of Redefining Units

Here is what happens if we use "g" for gram:

\[ \text{MW} := \frac{200 \text{ g}}{\text{mol}} \]

\[ \text{MW} = 1.961 \times 10^3 \frac{\text{m}}{\text{mol} \cdot \text{s}^2} \]

\[ g = 9.807 \frac{\text{m}}{\text{s}^2} \]

Notice how the program displays the molecular weight incorrectly because of our initial assumption that "g"=gram

We can insist that "g" is "gram" by redefining it:

\[ g := 0.001 \text{ kg} \]

\[ \text{MW} := \frac{200 \text{ g}}{\text{mol}} \]

\[ \text{MW} = 0.2 \frac{\text{kg}}{\text{mol}} \]

\[ g = 1 \times 10^{-3} \text{ kg} \]
Intro: Energy Levels of Molecules

Classification of energy levels of a diatomic molecule:

- Electronic (spaced by \( \approx 10^3-10^5 \) cm\(^{-1}\))
- Vibrational (spaced by \( \approx 10^1-10^3 \) cm\(^{-1}\))
  
  \( \nu \) – harmonic frequency
  
  \( x_e \) – anharmonic correction
  
  \( v \) – vibrational quantum number (\( v = 0,1,2,… \))

- Rotational (spaced by \( 10^{-1}-10^2 \) cm\(^{-1}\))
  
  \( B \) – rotational constant
  
  \( I \) – moment of inertia
  
  \( J_{\text{rot}} \) – rotational quantum number (\( J = 0,1,2,… \))

\[
E_{\text{vib}} = h\nu \left( \nu + \frac{1}{2} \right) - h\nu x_e \left( \nu + \frac{1}{2} \right)^2 + \ldots
\]

\[
E_{\text{rot}} = BJ_{\text{rot}}(J_{\text{rot}} + 1)
\]

\[
B = \frac{\hbar^2}{8\pi^2 I} \quad \text{where} \quad I = \frac{m_1 m_2}{m_1 + m_2} R^2
\]
Practice: Energy Levels of Molecules

Hint: Without selecting anything, go to Format → Result menu and set "Zero threshold" to 40 or so. This is necessary to display small numbers correctly.

Define: Plank's constant
Define: nanometer
Define: Avogadro's number
Define: atomic unit of weight
Input: vibrational quantum number
Input: rotational quantum number
Input: vibrational frequency
Input: anharmonic correction
Input: masses of atoms in {au}
Input: Interatomic distance in {nm}
Output: Vibrational energy in {J}
Output: Rotational constant {J}
Output: Rotational energy in {J}
Output: Total energy in {J}

\[ h := 6.62608 \times 10^{-34} \text{ J s} \]
\[ \text{nm} := 10^{-9} \text{ m} \]
\[ N_a := 6.02214 \times 10^{23} \]
\[ \text{au} := 0.001 \text{ kg}/N_a \]
\[ v := 1 \]
\[ J_{\text{rot}} := 20 \]
\[ v := 10^{14} \text{ s}^{-1} \]
\[ x_e := 0.005 \]
\[ m_1 := 14 \text{ au} \quad m_2 := 16 \text{ au} \]
\[ R := 0.12 \text{ nm} \]
\[ E_{\text{vib}} \text{ (see previous page)} \]
\[ B \text{ (see previous page)} \]
\[ E_{\text{rot}} \text{ (see previous page)} \]
\[ E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} \]
Solution: Energy Levels of Molecules

**Energy Levels of Molecules**

**Definitions**

\[ h := 6.62608 \times 10^{-34} \text{ J s} \quad N_a := 6.02214 \times 10^{23} \quad \text{nm} := 10^{-9} \text{ m} \quad \text{au} := \frac{0.001}{N_a} \text{ kg} \]

**Inputs**

\[ v := 1 \quad J_{rot} := 20 \quad v := 10^{14} \text{ s}^{-1} \quad \varepsilon_c := 0.005 \]

\[ m_1 := 14 \text{ au} \quad m_2 := 16 \text{ au} \quad R := 0.12 \text{ nm} \]

**RESULTS:**

\[ B := \frac{h^2}{8 \cdot \pi^2 \cdot R^2} \cdot \frac{m_1 + m_2}{m_1 \cdot m_2} \quad B = 3.114 \times 10^{-23} \text{ J} \]

\[ E_{rot} := B \cdot J_{rot} \cdot (J_{rot} + 1) \quad E_{rot} = 1.308 \times 10^{-20} \text{ J} \]

\[ E_{vib} := h \cdot \nu \left( \nu + \frac{1}{2} \right) - h \cdot \nu \cdot \varepsilon_c \left( \nu + \frac{1}{2} \right)^2 \quad E_{vib} = 9.865 \times 10^{-20} \text{ J} \]

\[ E_{total} := E_{vib} + E_{rot} \quad E_{total} = 1.117 \times 10^{-19} \text{ J} \]

**Things to watch out for:** (1) MathCad will display numbers that are smaller than a certain threshold as zeros. This is why we had to change the ways results are formatted before starting. (2) Adding additional operators to your equations can be tricky. However, practice makes perfect.
Intro: Beer-Lambert Law

Defines transmission of radiation through solutions and/or gases

**Definitions:**
- \( A = \ln \left( \frac{I_0}{I} \right) = \text{Absorbance} = \sigma \times L \times n \)
- \( \sigma \equiv \text{absorption cross section} \ [\text{cm}^2/\text{molecule}] \)
- \( L \equiv \text{absorption path length} \ [\text{cm}] \)
- \( n \equiv \text{density of the absorber} \ [\text{molecule/cm}^3] \)

**Pitfalls:**
- Other units are frequently used to express absorbance:
  \( A = \ln \left( \frac{I_0}{I} \right) = \varepsilon \times L \times C \)
  - \( \varepsilon \equiv \text{extinction coefficient} \ [\text{L mol}^{-1} \text{ cm}^{-1}] \)
  - \( C \equiv \text{density of the absorber} \ [\text{mol L}^{-1}] \)
- Base-10 is used in most commercial spectrometers instead of the natural base:
  \( A_{\text{base 10}} = \log \left( \frac{I_0}{I} \right) = A_{\text{base e}} / \ln(10) \)
Practice: Beer-Lambert Law

Input: Initial light intensity  \( I_0 := 0.1 \) W
Input: Final light intensity  \( I := 0.075 \) W
Input: Absorption cell length  \( L_{cell} := 10 \text{ cm} \)
Input: Absorption cross section  \( \sigma := 10^{-18} \text{ cm}^2 \)

Output: % Transmission through  \( T = \frac{I}{I_0} \times 100\% \)
Output: Base-e absorbance  \( A_{be} = \ln\left(\frac{I_0}{I}\right) \)
Output: Base-10 absorbance  \( A_{b10} = \log\left(\frac{I_0}{I}\right) \)
Output: Concentration in \( \text{\{1/cm}^3\} \)  \( C = \frac{A_{be}}{(\sigma L)} \)

Additional calculations:
1. Recalculate the concentration from \( \text{\{1/cm}^3\} \) to \( \text{\{mol/L\}} \). To do so define the Avogadro number in \( \text{\{mol}^{-1}\} \) and define \( L \) as 0.001 m\(^3\).
2. Calculate the extinction coefficient  \( \varepsilon = \frac{A_{b10}}{(C_{\text{molar}} L)} \)
The usual units for extinction coefficient are \( \text{\{L cm mol}^{-1}\} \)
Solution: Beer-Lambert Law

**Beer-Lambert Law**

**Inputs:**

\[ I_0 := 0.1 \text{W} \quad I := 0.075 \text{W} \quad L_{\text{cell}} := 10 \text{cm} \quad \sigma := 10^{-18} \text{cm}^2 \]

**RESULTS:**

\[
T := \frac{I}{I_0} \times 100 \quad T = 75
\]

\[
\text{Abs } e := \ln \left( \frac{I_0}{I} \right) = 0.288 \quad \text{Abs } 10 := \log \left( \frac{I_0}{I} \right) = 0.125
\]

\[
C := \frac{\text{Abs } e}{\sigma \cdot L_{\text{cell}}} = 2.877 \times 10^{16} \frac{1}{\text{cm}^3}
\]

**Additional:**

\[
N_a := 6.02214 \times 10^{23} \text{mol}^{-1} \quad L := 0.001 \text{m}^3
\]

\[
C := \frac{C}{N_a} = 4.777 \times 10^{-5} \text{ mol} \quad L
\]

\[
\varepsilon := \frac{\text{Abs } 10}{C_{\text{molar}} \cdot L_{\text{cell}}} = 26.154 \frac{\text{m}^2}{\text{mol}} \quad \varepsilon = 261.538 \frac{\text{L}}{\text{cm} \cdot \text{mol}}
\]