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

Edit Cursor

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 := π · Radius²
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
- Boolean toolbar
- Graph toolbar
- Programming toolbar
- Matrix toolbar
- Greek toolbar
- Evaluation toolbar
- Symbolic toolbar
- Calculus 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

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

Excel version of the same calculation

<table>
<thead>
<tr>
<th>Radius=</th>
<th>Volume = 4/3*pi()*B1^3</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:=24m²
- Do calculations on variables: Volume:=Volume+16m²

Display result (=)
- Entered by typing the equal key [=]
- Displays the result of the last calculation Volume=40m²

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

- $\pi = 3.1415926536…$ (entered as Ctrl-Shift-p)
- $e = 2.7182818285…$ (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 normally 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 $V\.empty$
– 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
- Limitations: only **multiplicative** unit conversions are possible (e.g., degrees Celsius cannot be automatically converted into degrees Kelvin)

Defining a unit

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

**Space**
- Starts a new text region (the region does not need to start with space; two words separated by a space will do)

**:**
- Assignment statement

**=**
- Result statement

**Ctrl =**
- Symbolic equality statement (will not use in this course)

**~**
- Global statement (will not use in this course)

***/+-**
- Multiply, divide, plus, minus operators

**^**
- Raise to the power of (or press superscript sign)

**.**
- Starts a text subscript

**[**
- Starts an index subscript

**cm**
- Many standard units can be entered after the variable definition

**Ctrl Shift p**
- \(\pi\)

**Insert**
- Moves the cursor between the front and back of the selection – very handy during editing
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 solution of 540 mL.

**TASK:**
- Define unit
- Define unit
- Assign molecular weight of solute in \{amu\}
- Assign mass of solute in \{mg\}
- Assign volume of added solvent in \{mL\}
- Assign volume of resulting solution in \{mL\}
- Assign density of solvent in \{kg/cm^3\}
- Assign molecular weight of solvent in \{amu\}
- Output 1: molar concentration of the resulting solution in \{mol/L\}
  \[ C_{\text{molar}} = \frac{\text{moles of solute}}{\text{volume of solution}} \]
- Output 2: weight mixing ratio of the resulting solution \{dimensionless\}
  \[ \text{Mixing}_{\text{weight}} = \frac{\text{weight of solute}}{\text{weight of solvent}} \]
- Output 3: molar mixing ratio of the resulting solution \{dimensionless\}
  \[ \text{Mixing}_{\text{molar}} = \frac{\text{moles of solute}}{\text{moles of solvent}} \]
**Solution: Solvent Preparation**

**Solvent Preparation**

Define new units

\[ \text{amu} := 0.001 \frac{\text{kg}}{\text{mol}} \quad \text{mg} := 10^{-6} \text{kg} \]

Solute properties

\[ \text{MW}_{\text{solute}} := 200 \text{amu} \quad m_{\text{solute}} := 55 \text{mg} \]

Solvent properties

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

Solution properties

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

**RESULTS:**

\[ C_{\text{molar}} := \frac{m_{\text{solute}}}{\text{MW}_{\text{solute}}} \cdot \frac{1}{V_{\text{solution}}} \]

\[ C_{\text{molar}} = 5.093 \times 10^{-4} \frac{\text{mol}}{\text{L}} \]

\[ \text{Mixing weight} := \frac{m_{\text{solute}}}{\rho_{\text{solvent}} \cdot V_{\text{solvent}}} \]

\[ \text{Mixing weight} = 1.375 \times 10^{-4} \]

\[ \text{Mixing molar} := \frac{m_{\text{solute}} \cdot \text{MW}_{\text{solvent}}}{\text{MW}_{\text{solute}} \cdot \rho_{\text{solvent}} \cdot V_{\text{solvent}}} \]

\[ \text{Mixing molar} = 4.812 \times 10^{-5} \]

**Things to watch out for:** In MathCad, the default meaning of \( g \) is gravitational constant (9.807 \( \text{m/s}^2 \)) not 1 gram!!! Gram is entered as \text{gm}. Interchanging the two may cause all kinds of mistakes in calculations involving masses. 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:

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

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

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

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:

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

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

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

\[
g = 1 \times 10^{-3} \text{kg}
\]
Defining Your Own Units

Hmmm… I need to know my stomach volume and volume of an average college student:

\[ N \approx \frac{V_{\text{stomach}}}{V_{\text{student}}} \]

*From Whale’s encyclopedia:*

Average volume of a sperm whale stomach:

\[ V_{\text{stomach}} = 2 \text{ oooye}^3 \]

Average density of a college student

\[ \rho_{\text{student}} = 2.2 \text{ auuu/zumm}^3 \]

Average mass of a college student

\[ m_{\text{student}} = 85,000 \text{ auuu} \]

Relationship to human units:

\[ 1 \text{ oooye} = 1.25 \text{ m} \]

\[ 1 \text{ auuu} = 0.95 \text{ g} \]

\[ 1 \text{ zumm} = 1.333 \text{ cm} \]
Solution

Define all units

\[ \text{oooye} := 1.25 \text{m} \quad \text{auuu} := 0.95 \text{gm} \quad \text{zumm} := 1.333 \text{cm} \]

Insert initial data

\[ V_{\text{stomach}} := 2\cdot \text{oooye}^3 \quad \rho_{\text{student}} := \frac{2.2 \text{auuu}}{\text{zumm}^3} \quad m_{\text{student}} := 8500 \text{auuu} \]

Do the actual calculation

\[ V_{\text{student}} := \frac{m_{\text{student}}}{\rho_{\text{student}}} \quad V_{\text{stomach}} = 3.906 \times 10^3 \text{ L} \]
\[ \rho_{\text{student}} = 882.38 \frac{\text{kg}}{\text{m}^3} \quad m_{\text{student}} = 80.75 \text{ kg} \]
\[ V_{\text{student}} = 91.514 \text{ L} \quad N_{\text{student}} = 42.685 \]

Answer: about 43 college students (i.e., the entire Chem 5 class)

In real life, sperm whales do not normally eat college students. The reverse is unfortunately true; whales are still heavily hunted around the world.
Practice: 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
  
  $J_{rot}$ – rotational quantum number ($J = 0,1,2,...$)

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

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

\[
B = \frac{\hbar^2}{8\pi^2 I} \quad \text{where} \quad I = \frac{m_1 m_2}{m_1 + m_2} R^2
\]
Important: Without selecting anything, go to Format → Result menu and set "Zero threshold" to 40 or so

Define: Plank's constant \( h := 6.62608 \times 10^{-34} \text{ J s} \)
Define: nanometer \( \text{nm} := 10^{-9} \text{ m} \)
Define: Avogadro's number \( N_a := 6.02214 \times 10^{23} \)
Define: atomic unit of weight \( \text{au} := 0.001 \text{ kg}/N_a \)
Input: vibrational quantum number \( v := 1 \)
Input: rotational quantum number \( J_{\text{rot}} := 20 \)
Input: vibrational frequency \( v := 10^{14} \text{ s}^{-1} \)
Input: anharmonic correction \( x_e := 0.005 \)
Input: masses of atoms in \{au\} \( m_1 := 14 \text{ au} \quad m_2 := 16 \text{ au} \)
Input: Interatomic distance in \{nm\} \( R := 0.12 \text{ nm} \)
Output: Vibrational energy in \{J\} \( E_{\text{vib}} \) (see previous page)
Output: Rotational constant \{J\} \( B \) (see previous page)
Output: Rotational energy in \{J\} \( E_{\text{rot}} \) (see previous page)
Output: Total energy in \{J\} \( E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} \)
Solution: Energy Levels of Molecules

Energy Levels of Molecules

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

Inputs
\[ v := 1 \]
\[ J_{\text{rot}} := 20 \]
\[ \nu := 10^{14} \text{ s}^{-1} \]
\[ x_e := 0.005 \]
\[ m_1 := 14 \text{au} \]
\[ m_2 := 16 \text{au} \]
\[ R := 0.12 \text{nm} \]

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

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

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

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

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**

Describes transmission of radiation through solutions and/or gases

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

**Pitfalls:**
- Other units are frequently used to express absorbance:
  \( A = \ln(I_0/I) = \varepsilon \times L \times C \)
  \( \varepsilon \equiv \text{extinction coefficient} \) [L mol\(^{-1}\) cm\(^{-1}\)]
  \( C \equiv \text{density of the absorber} \) [mol L\(^{-1}\)]
- Base-10 is used in most commercial spectrometers instead of the natural base:
  \( A_{\text{base 10}} = \log(I_0/I) = A_{\text{base e}} / \ln(10) \)
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 \( L_{\text{cell}} := 10 \) cm
Input: Absorption cross section \( \sigma := 10^{-18} \) cm\(^2\)

Output: \% Transmission through \( T = \frac{I}{I_0} \times 100\% \)
Output: Base-e absorbance \( A_{\text{base}} = \ln \left( \frac{I_0}{I} \right) \)
Output: Base-10 absorbance \( A_{\text{base10}} = \log \left( \frac{I_0}{I} \right) \)
Output: Concentration in \( \{1/\text{cm}^3\} \) \( C = \frac{A_{\text{base}}}{(\sigma L)} \)

Additional calculations:
1. Recalculate the concentration from \( \{1/\text{cm}^3\} \) 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 \( \varepsilon = \frac{A_{\text{base10}}}{(C_{\text{molar}} L)} \)
The usual units for extinction coefficient are \( \{L \text{ cm mol}^{-1}\} \)
**Solution: Beer-Lambert Law**

**Beer-Lambert Law**

**Inputs**

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

**RESULTS:**

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

\[ \text{Abs}_e := \ln \left( \frac{I_0}{I} \right) \]
\[ \text{Abs}_e = 0.288 \]

\[ \text{Abs}_{10} := \log \left( \frac{I_0}{I} \right) \]
\[ \text{Abs}_{10} = 0.125 \]

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

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

**Additional:**

\[ C_{\text{molar}} := \frac{C}{N_A} \]
\[ C_{\text{molar}} = 4.777 \times 10^{-5} \text{mol L}^{-1} \]

\[ \varepsilon := \frac{\text{Abs}_{10}}{C_{\text{molar}} \cdot L_{\text{cell}}} \]
\[ \varepsilon = 261.538 \frac{\text{L}}{\text{cm} \cdot \text{mol}} \]