Chapter 1: *Mathematica* Basics

Basic Math

Mathematica can perform basic math. Start by typing in an operation and hit *shift+enter* to execute; for example:

```
2 * 4
8
```

Mathematica follows the computational order of PEMDAS (parentheses, exponents, multiplication, division, addition and subtraction):

```
(2 * 4 ^ 2) + 2 - (3 * 2)
28
```

Brackets

You've seen that the parenthesis brackets ( ) are used to dictate order of operations. Curly brackets { } are used to make lists (see Chapter 2 for more details on lists). There are other brackets that *Mathematica* recognize, the most important are the square brackets [ ]. Square brackets are used for *Mathematica* defined commands. All defined commands are capitalized and the argument always goes inside square brackets. For example, the command *Sin* will evaluate the sine of any argument:

```
Sin[Pi / 2]
1
```

The Style Menu

Exponents can be written with the carrot ^ symbol or using the palettes. To open a basic typesetting palette, go to *File/Palettes/BasicInput*. Select the first option of the palette, which shows a box with an exponential box. Click on each box to input your values. Rewrite the previous equation:

$(2 * 4^2) + 2 - (3 * 2)$

28

The palettes are good for symbols and to make your equations look nice. It is advisable to learn the meanings of the palette symbols before making extreme use of them.

Formatting

To type text in a *Mathematica* notebook, go to *Format/Show Toolbar*. The menu on the far left of the toolbar should say "*Input*." Input is the text style that *Mathematica* executes in. If you want to write something but not have it executed, pull down the style menu and select "*text*." You may also want to try other style options to format your notebook.

Keep in mind that only one style option may exist per cell. It is best to start a new cell, by clicking below any cell to display a horizontal line, before selecting the text style. If you forget you can always select the cell bracket, after you have typed the text, to change the text style.

Spaces

Spaces are really important in *Mathematica* because spaces between numbers act the same as the multiplication symbol (*). Do not put any spaces into your input unless you mean to multiply. Start by typing in two numbers that you want to add:

```
42 + 36
78
```

But with spaces between the numbers, the argument is executed as 4 x 2 + 3 x 6:

```
4 2 + 3 6
26
```

Spaces between mathematical symbols are ok. Put spaces before and after the + sign:

```
42 + 36
78
```

Symbols

There are a lot of symbols in Chemistry and it would be useful to define and use them. For example, start with the ideal gas law: P = n R T / V and find the pressure of 1.0 mole of a perfect gas at 298 K and 1.0 L volume.

Start by defining the given variables with a symbol. *Mathematica* capitalizes all its commands so it's convenient to use lowercase letters to avoid a conflict with a built-in command.

```
n = 1.0
r = 0.0821
t = 298
v = 1.0
```

```
1.
0.0821
298
1.
```

Mathematica will repeat any definition that you give. To prevent this, put a semicolon (;) after each definition. The semicolon suppresses the output.

```
n = 1.0;
r = 0.0821;
t = 298;
v = 1.0;
```

Now define and solve for the pressure using your defined variables:

```
p = n * r * t / v
24.4658
```

Print

However, physical quantities have units. To give units to the pressure evaluated above, use the *Print* command. Square brackets are used for all commands. Separate text from numerical values using commas. Make sure that all the text that you want printed are enclosed in quotation marks. Blank spaces can be printed if they are within the quote marks. Note that the value is represented as *p*, which was what was previously defined.

```
Print["The pressure of 1.0 mole of ideal gas at 25°C
   and 1.0 L is ", p, " atm."]
```

```
The pressure of 1.0 mole of ideal gas at 25°C and 1.0 L is
 24.4658 atm.
```

Units

It is also possible to include units in the definitions if you separate the numerical value from the units with a space. For multiple units, separate each unit with a space. For example:

```
n = 1.0 mol;
r = 0.0821 L atm K^-1 mol^-1;
t = 298 K;
v = 1.0 L;

p = n * r * t / v
```

```
24.4658 atm
```

```
Print["The pressure of 1.0 mole of ideal gas at 25°C
   and 1.0 L is ", p]
```

```
The pressure of 1.0 mole of ideal gas at 25°C and 1.0 L is
 24.4658 atm
```

Clear

All variables that you define with a value, either numerical or symbolic, will remain in the *Mathematica* kernel. For example, execute the variable *p* that you defined above:

```
p
24.4658 atm
```

To remove a variable from the kernel, use the *Clear* command and execute *p* again:

```
Clear[p]
p
p
```

There will be times in which your argument will not execute as expected. In that case, clear all the variables and try again. Of course, you can quit the kernel by going to *Kernel/Quit Kernel/Local*. Quitting the kernel should remove all the defined variables.

Substitution

If you plan on defining a set of variables but with different values each time, you may want to consider the substitution command symbolized with a slanted bar and a period.

Calculate the pressure of 1.0 mol of ideal gas at 298 K and 1.0 L volume using substitution. The advantage of substitution is that none of the variables will be placed in the kernel. This means that you can use the variables later without conflict. Make sure to clear all the variables first. You'll need to make a list of substitutions after the /. command, with each substitution defined using an arrow.

```
Clear[p, n, r, t, v];
p = n * r * t / v /. {n → 1.0 mol, r → 0.0821 L atm K^-1 mol^-1,
   t → 298 K, v → 1.0 L}
24.4658 atm
```

The *p* variable is now in the kernel, but none of the other variable are. Make a list of all the variables used and check to see if that statement holds true:

```
variables = {p, n, r, t, v}
{24.4658 atm, n, r, t, v}
```

Substitution is also useful to convert one unit into another. For example, convert the pressure executed above into pascals. Recall that 1 atm = 1.013 x 10^5 Pa.

```
pressurePa = p /. atm → 1.013 * 10^5 Pa
2.47839 × 10^6 Pa
```

1 Pa is otherwise known as 1 N m^{-2}. Convert the pressure in Pa into N m^{-2}:

```
pressureN = pressurePa /. Pa → N m^-2
2.47839 × 10^6 N
----------------
       m^2
```

Mathematica Commands

You can evaluate the square root of a number using the palette, but you can also use the command *Sqrt*:

```
Sqrt[4]
2
```

Natural logarithms (base *e*) are evaluated using the *Log* command.

```
Log[13.1]
2.57261
```

To find the antilog of a value with base *e*, use the *Exp* command:

```
Exp[2.57261]
13.1
```

Logs using other bases must include two arguments, the base and the number:

```
Log[10, 1000]
3
```

Sometimes you'll find that *Mathematica* will not evaluate your command beyond the input. The reason is usually because *Mathematica* will not give an inexact value (something with decimals) if you put in an exact value (no decimals):

```
Log[12]
Log[12]
```

To get around this, put a decimal after your value:

```
Log[12.]
2.48491
```

Numerical Values

Rather than typing decimals, you can use the *N* command:

```
N[Log[12]]
2.48491
```

Another way to use the *N* command is at the end of your input. The advantage is that there's less editing.

```
Log[12] // N
2.48491
```

```
Sqrt[15] // N
3.87298
```

Writing Functions

Going back to the ideal gas law, you can define a function that will evaluate the pressure of any gas given n, r, t, and v. Functions are defined using square brackets where the variables inside all have underscores. You must put a colon before the equal sign to define your function. Make sure to clear your variables before writing any function.

```
Clear[n, r, t, v];
pressure[n_, r_, t_, v_] := n * r * t / v
```

Once your function is defined, simply put the values and units corresponding to the variables inside the brackets:

```
pressure[1.0 mol, 0.0821 L atm K^-1 mol^-1, 298 K, 1.0 L];
Print["pressure = ", %]
pressure  = 24.4658 atm
```

The *%* sign can be used if the Print command is in the same cell as the output you want printed. The *%* sign symbolizes the output of the line directly above it. This is useful if you didn't define your outputs with a variable name.

You can also put variables into your function and substitute for their numeric values:

```
Clear[n, r, t, v];
pressure[n, r, t, v] /.
  {n → 1.0 mol, r → 0.0821 L atm K^-1 mol^-1, t → 298 K, v → 1.0 L};
Print["pressure = ", %]
pressure  = 24.4658 atm
```

As you can see, *Mathematica* is very efficient with “plug and chug” questions.

From Physical Chemistry, 6th Edition by Peter Atkins:

Exercise 12.1
Calculate the energy separation in joules, kilojoules per mole of electrons, electronvolts and wavenumbers of an electron in a box of length 1.0nm between the levels
a) n = 2 and n = 1
b) n = 6 and n = 5

Energy of a particle in a box: $E_n = \frac{n^2 h^2}{8 m L^2}$

Change in energy: E_{n+1} - E_n

h = 6.62608 x 10^{-34} J s

m = 9.10939 x 10^{-31} kg (mass of an electron)

L = length of box (in meters)

1 nm = 1 x 10^{-9}m

Avogadro = 6.022 x 10^{23} electrons / mole

1 eV = 1.60218 x 10^{-19}J

Wavenumber = cm^{-1}

1 cm^{-1} = 1.9864 x 10^{-23}J

J = kg m^2 s^{-2}

For constants in joules, use kg m^2 s^{-2} instead or the units will not cancel out. You can use the **/.** command to get J

Answers: Exercise 12.1

For n = 2 and n = 1:

Since *h*, *mass* and *l* are held constant, we can define them using variables. Otherwise substitution would be preferable:

```
h = 6.62608 * 10^-34 kg m^2 s^-2 s;
mass = 9.10939 * 10^-31 kg;
l = 1.0 * 10^-9 m;
energy = (2^2 - 1^2) (h^2 / (8 mass l^2))
```

$$\frac{1.8074\times10^{-19}\ \text{kg m}^2}{\text{s}^2}$$

Substitute for joules:

```
energyJa = energy /. kg m^2 s^-2 → J;
Print["Energy = ", energyJa]
```

Energy = 1.8074×10^{-19} J

Convert J to kJ/mol:

```
avo = 6.022 * 10^23 mol^-1;
energykJa = energyJa * avo /. J → 10^-3 kJ;
Print["Energy = ", energykJa]
```

Energy = $\frac{108.842\ \text{kJ}}{\text{mol}}$

Convert J to eV:

```
energyeVa = energyJa /. J → eV / (1.60218 * 10^-19);
Print["Energy = ", energyeVa]
```

Energy = 1.12809 eV

Convert J to cm^{-1}:

```
energycma = energyJa /. J → cm^-1 / (1.9864 * 10^-23) ;
Print["Energy = ", energycma]
```

Energy = $\frac{9098.89}{\text{cm}}$

For n = 6 and n = 5:

```
energyJb = (6^2 - 5^2) (h^2 / (8 mass l^2)) /. kg m^2 s^-2 → J;
Print["Energy = ", energyJb]
```

Energy = 6.62715×10^{-19} J

Convert J to kJ/mol:

```
avo = 6.022 * 10^23 mol^-1;
energykJb = energyJb * avo /. J → 10^-3 kJ;
Print["Energy = ", energykJb]
```

Energy = $\frac{399.087\ \text{kJ}}{\text{mol}}$

Convert J to eV:

```
energyeVb = energyJb /. J → eV / (1.60218 * 10^-19);
Print["Energy = ", energyeVb]
```

Energy = 4.13633 eV

Convert J to cm^{-1}:

```
energycmb = energyJb /. J → cm^-1 / (1.9864 * 10^-23) ;
Print["Energy = ", energycmb]
```

Energy = $\frac{33362.6}{\text{cm}}$