

## THE MAXWELL-BOLTZMANN DISTRIBUTION FUNCTION

In this exercise you will use Excel to create a spreadsheet for the Maxwell-Boltzmann speed distribution and then plot the speed distribution for particles of two different molecular weights and temperatures. By varying the molecular weight and temperature you can see how these parameters affect the speed distribution. Also, from the plots you can determine the most probable speed for a given molecular weight and temperature and the fraction of molecules with a particular speed at this molecular weight and temperature, and how both are affected by these variables. Next, you will calculate an energy distribution. From the energy distribution, you can determine the fraction of molecules with energies above a given threshold value. This will be used as an indication of the number of molecules possessing enough energy to undergo a reaction. By varying the temperature you can see how temperature affects reactivity.

By now you should be familiar with the commands you will need to execute in Excel for completing this exercise. You will be given a "bare-bones" spreadsheet as a starting point and, using this handout, add to the spreadsheet to create the plots for the speed and energy distributions.

At the end of the session you should hand in a print out of the plots you created (speed and energy distributions) and answers to the questions on both parts.

### DISTRIBUTION OF MOLECULAR SPEEDS:

Molecules at any given temperature do not all have the same speed but in fact a distribution of speeds given by the Maxwell-Boltzmann distribution

$$\frac{dN}{N} = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} c^2 e^{-\frac{Mc^2}{RT}} dc \quad (1)$$

where  $N$  is the total number of molecules in the sample,  $dN/N$  is the fraction of molecules with speed between  $c$  and  $c+dc$ ,  $M$  is the molecular weight in kg/mole,  $T$  the temperature in °K, and  $R$  the gas constant constant (J/K). If we plot  $dN/N$  vs.  $c$  (see figure 1) we can graphically see what this complicated function looks like. As you will find, the function has a fast rising portion at smaller values of  $c$ , reaches a peak, and has a decreasing "tail" as  $c$  increases.

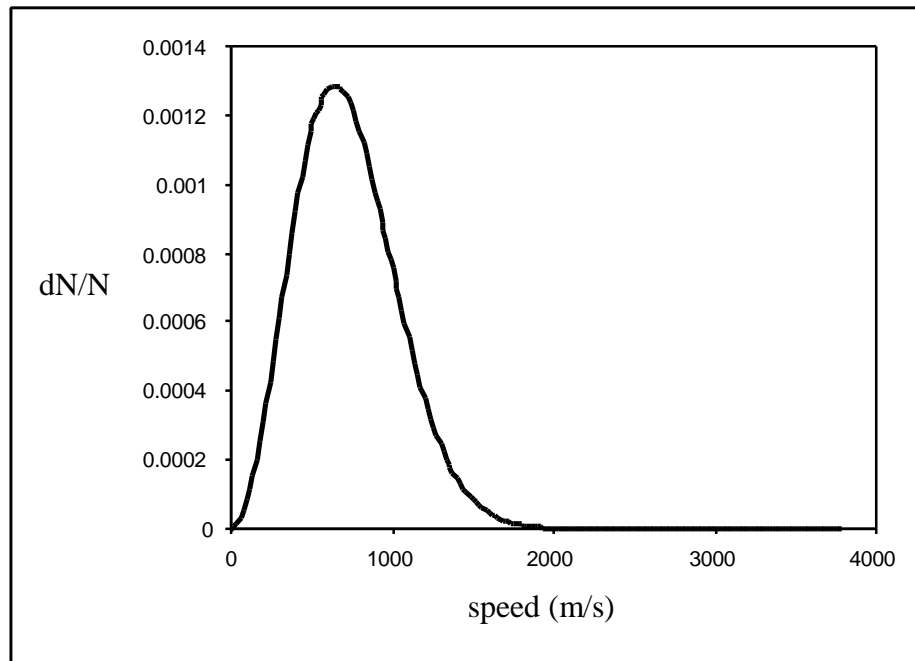


Figure 1

Now in Excel you will create the data points for  $dN/N$  and  $c$  and then plot  $dN/N$  vs.  $c$ . You will create two distribution functions, each with a different temperature and molecular weight. Finally, you will be able to change either molecular weight or temperature (the plots will be updated for each change) – for example, you can fix the temperature and change the molecular weight or vice versa– and see how these variables affect the distribution function. For example, if temperature increases does the distribution get broader or narrower? Similarly, how does molecular weight affect the distribution?

#### Creating the spreadsheet for the speed distribution function and plotting the function.

Open the spreadsheet titled “speed”. There will be some entries made to this spreadsheet. Save this file to your floppy disk (File -> **SAVE AS**. Give the file a name and save to FLOPPY DISK).

- 1) First note the units which will be used (SI units). So for example, the molecular weight of the molecule is in kg/mole not g/mole, and speed in m/s not cm/s.
- 2) There are two entries for molecular weight, MW1 and MW2, and two for temperature, temp1 and temp2. You will calculate the distribution function for each pair (MW1,temp1) and (MW2,temp2). The term gasconst refers to the gas constant ( $R = 8.314 \text{ J/}^\circ\text{K}$ ).
- 3) The distribution function has been broken up into three terms (i) a term that is independent of speed (called coeff1 for (MW1,temp1) and coeff2 for (MW2,temp2) in the spreadsheet), (ii) the  $c^2$  term and (iii) the exponential term.

Splitting up the function this way, just makes it easier to create a spreadsheet for calculating the distribution function. The distribution function is obtained by multiplying the three terms.

$$\frac{dN/N}{dc} = \underbrace{4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}}_{\text{coeff term}} \underbrace{c^2}_{\text{c}^2 \text{ term}} \underbrace{e^{-\frac{Mc^2}{2RT}}}_{\text{exponential term}} \quad (2)$$

- 4) The term labeled dc is the interval or step size over which the distribution function will be calculated.
- 5) In the column labeled "speed" you will enter the values of the speed over which the distribution function will be calculated, in intervals of dc. For example, if the first point is 0, the next point is 0 + dc, the next 0 + 2 dc, etc. In the spreadsheet dc has been set to be 20 m/s.
- 6) In the column labeled "speed x speed", you will calculate the square of the speed.
- 7) In the column labeled "exp1", you will calculate the exponential term for (MW1,temp1) and in the column "exp2" the exponential term for (MW2,temp2).
- 8) In the column labeled "distribution1" you will calculate the value of the distribution function for (MW1,temp1) for each speed value, and in the column "distribution2" the same for (MW2,temp2).
- 9) Finally the column labeled "speed" (before the columns for distribution1 and distribution2), is a copy of the speed column (see 5 above). It is positioned here to make plotting easier.

Fill in the speed column (column A)

The first entry is 0 in this column, the second 0 + dc which in this example is 20 m/s. Copy cell A27 and paste in cells A28 to A215.

Fill in the speedxspeed column (column B)

Copy cell B27 and paste in cells B28 to B215

Repeat the same for the columns labeled exp1, exp2, speed, distribution1, distribution2 i.e. copy the 27<sup>th</sup> cell of each column and paste into the 28<sup>th</sup> to the 215<sup>th</sup> cell.

You have now created the spreadsheet for plotting the speed distribution. Next you will plot these data points. Select columns H26 to I26 down to H215 and I215. In the Insert -> Chart menu select XY scatter. For the chart sub-type select the top right option (scatter with data points connected by smooth lines). Finish the plot on the same sheet.

Now you should have a plot of the two distribution functions for (MW1,temp1) and (MW2,temp2) that looks like figure 1. Vary the values of MW1, MW2, temp1, and temp2 and see how the distribution changes.

### QUESTIONS

- 1) How does molecular weight affect the distribution – does the distribution get broader or narrower as molecular weight increases? How does temperature affect the distribution?
- 2) The speed corresponding to the peak of the speed distribution curve is called the **most probable speed**, since the largest fraction of molecules move at this speed (hence, it is the most probable speed). From the graph determine the most probable speed for a particle of molecular weight of 0.040 kg/mole and a temperature of 1000° K?
- 3) From the graph determine the fraction of molecules with speed 1040 m/s, molecular weight 0.040 kg/mole and temperature of 1000° K? How does this fraction change as (a) the molecular weight is lowered (temperature kept at 1000° K), (b) the temperature is lowered (molecular weight kept at 0.040 kg/mole)?

### **ENERGY DISTRIBUTION**

Now you will calculate an energy distribution for a given temperature. The kinetic energy of a particle of molecular weight M is given by

$$E = \frac{1}{2} M c^2 \quad (3)$$

If we substitute

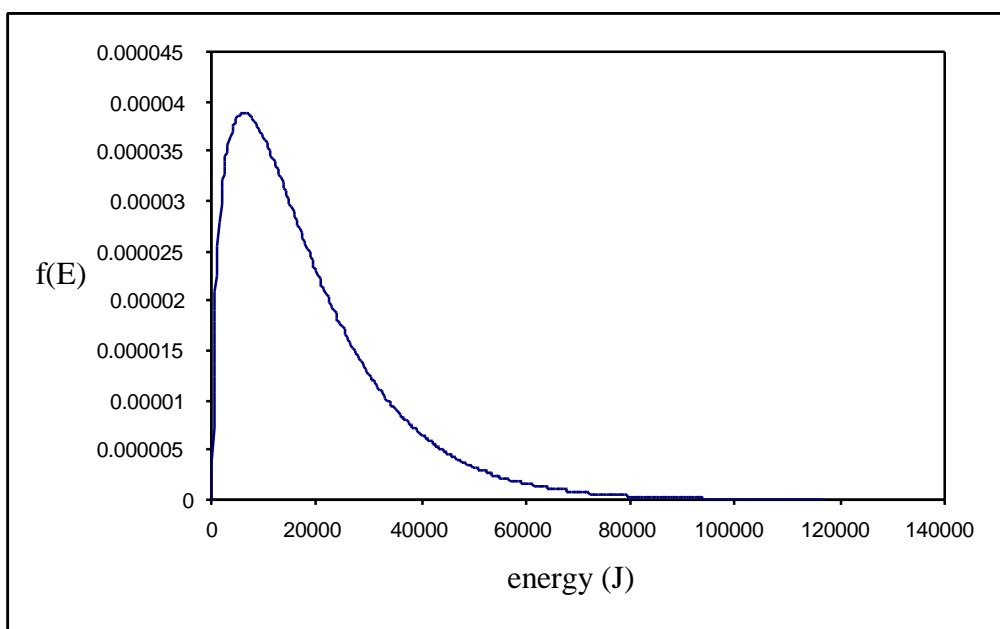
$$c = \sqrt{\frac{2E}{M}} \quad (4)$$

in the equation for the Maxwell – Boltzmann distribution it can be shown that that the fraction of molecules with energies between E and E+dE (f(E)) is given by:

$$f(E) = \frac{dN_E/N}{dE} = 2\pi \left(\frac{1}{\pi RT}\right)^{3/2} \sqrt{E} e^{-\frac{E}{RT}} \quad (5)$$

Figure 2 shows a plot of the energy distribution ( $\frac{dN_E/N}{dE}$  vs. E) at a given temperature. The energy distribution has a sharply rising component at low energies, peaks and then decreases rapidly at larger energies. The width of the distribution is affected by the temperature of the molecules.

Figure 2



We can use this energy distribution to determine the number of molecules that have energies above a certain threshold energy, where this threshold energy is the minimum amount of energy that a molecule must have to undergo a reaction. Also, by plotting the energy distribution we can see how temperature affects this fraction of molecules above the threshold energy and hence how temperature can affect the yield of a reaction (i.e. the number of molecules that successfully go from reactant to product).

#### Creating a spreadsheet for the energy distribution.

Open the spreadsheet titled "energy". Note that there are some entries made in this spreadsheet. Save this file to your floppy disk (File -> **SAVE AS**. Give the file a name and save to FLOPPY DISK).

1) Units are SI units. Energy in Joules (J).

- 2) The term temp refers to the temperature of the molecules (in °K) and the term gasconst, the gas constant (R, units J/K)
- 3) The equation for the energy distribution has been split into three parts (i) a constant term called coeff in the spreadsheet, (ii)  $\sqrt{E}$  term and (iii) the exponential term.

$$\frac{dN_E / N}{dE} = 2\pi \underbrace{\left(\frac{1}{\pi RT}\right)^{3/2}}_{\text{coeff term}} \underbrace{\sqrt{E}}_{\text{square root term}} \underbrace{e^{-\frac{E}{RT}}}_{\text{exponential term}} \quad (6)$$

- 4) In the column titled "energy" (in column A) you will calculate the energy points over which the energy distribution will be determined (in intervals of dE J). Enter the equation =A11+dE into cell A12. Now copy cell A12 and paste into cells A13 to A400.
- 5) In the column titled "sqrt(energy)" you will calculate the square root of each energy point. Copy cell C11 and paste into cells C12 to C400.
- 6) In the column titled "exp" you will calculate the exponential term. Copy cell E12 and paste into cells E13 to E400.
- 7) Column H (Energy (J)) is a copy of column A. Enter into cell H11 the equation = A11. Copy cell H11 and paste into cells H12 to H400.
- 8) In the column titled "f(E)" you will calculate the fraction of molecules in the range E to E+dE. Copy cell I11 and paste into cells I12 to I400.

Now you are ready to plot the energy distribution (f(E) vs E). Select cells H11-I11 down to H400 –I400. Create an XY scatter plot with a smooth line joining points as you did for the speed distribution. You should see a plot similar to that shown in figure 2. This is the energy distribution. Vary temperature to see how it affects the distribution.

Determining the fraction of molecules with energies above a threshold value.

The function  $f(E)$  is a normalized function; i.e. if we were to multiply each point  $f(E)$  by the energy interval  $d(E)$  (equivalently,  $f(E)*dE$ ) and then sum all these points, we should get 1. What we are doing is summing up the fraction of molecules with all possible energies (for a given temperature) and this number should be one. By doing this we are effectively integrating the area under the distribution curve (the shaded area in figure 3).

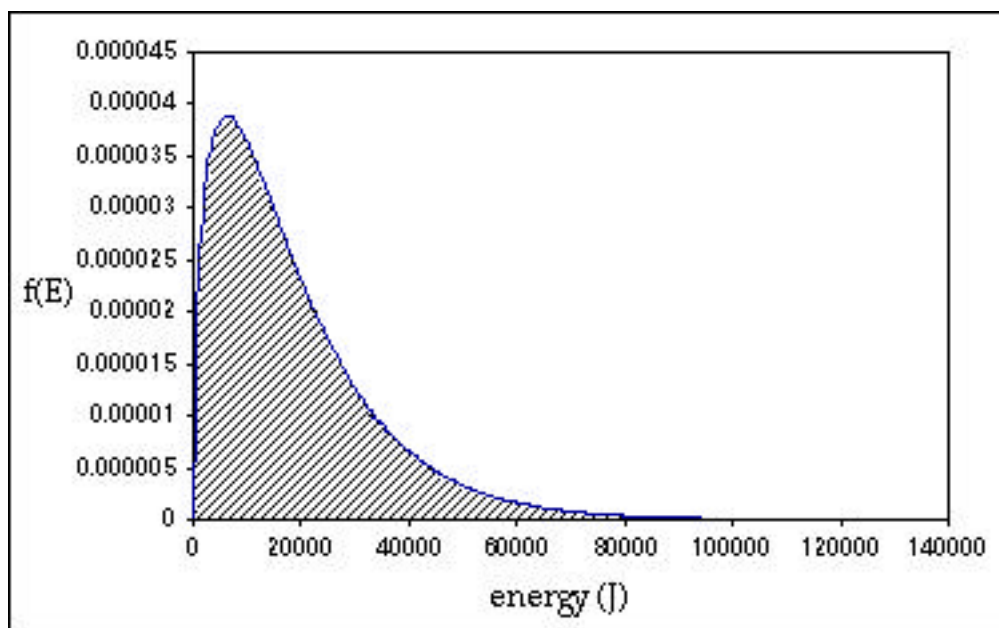


Figure 3

You can check to see if this is true. In column K create a list of  $f(E)*dE$ . This will correspond to multiplying points in the  $f(E)$  column by  $dE$  (for example, the first entry in K11 will be I11\*dE. Copy cell K11 and paste into cells K12 to K400). Next we will sum values in column K. So in cell M11 input the equation

$$=SUM(K11:K400)$$

You should get a number very close to 1 (maybe 0.998). If you do, then you know that the function  $f(E)$  that you plotted is normalized.

We can use this sum function in another way. Let's say we want to determine the fraction of molecules with energies above a threshold energy. The threshold energy could correspond to the minimum energy a molecule must have in order for it to undergo a reaction.

So, for example, say we want to determine the fraction of molecules with energies equal to and greater than 34,500 J. We then sum the values of  $f(E)*dE$  for all molecules with energies equal to and greater than 34,500 J. To determine this, enter the equation

$$=SUM(K126:K400)$$

in cell N11 (since cell A126 corresponds to an energy value of 34,500J).

So, for example, if a reaction had a threshold energy of 34,500 J, then from the distribution curve we can deduce that, at a temperature of 1500 °K, the fraction of molecules that have enough energy to undergo this reaction is 0.137 (or if we convert to percentage 13.7% of the molecules). You can get a feeling for the portion of the distribution curve this sum corresponds to by finding the point (34,500,9.46E-6) on the curve. (the shaded area in figure 4).

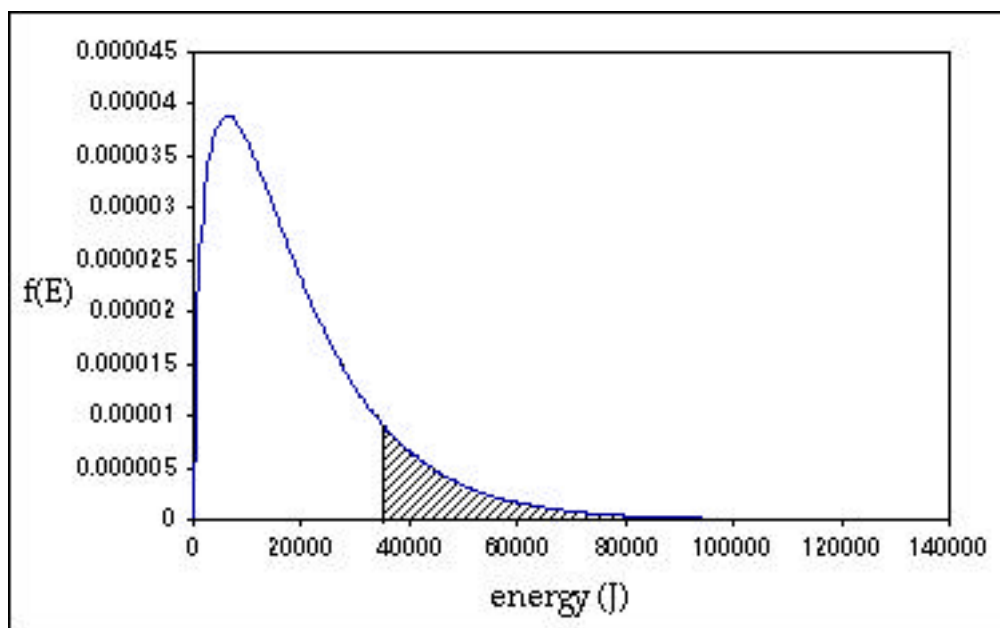


Figure 4

### QUESTIONS

- 1) How does temperature affect the energy distribution – does the distribution get broader or narrower as temperature is lowered?
- 2) What fraction of molecules have energies greater than or equal to 16,800 J. If the temperature is lowered to 1000K or raised to 2000 K how does it affect this fraction?
- 3) Based on your observations for question 2, if you want to increase the number of molecules that undergo a reaction, should you raise or lower the temperature?