

# MAXWELL DISTRIBUTION OF GAS MOLECULE VELOCITIES ©

by

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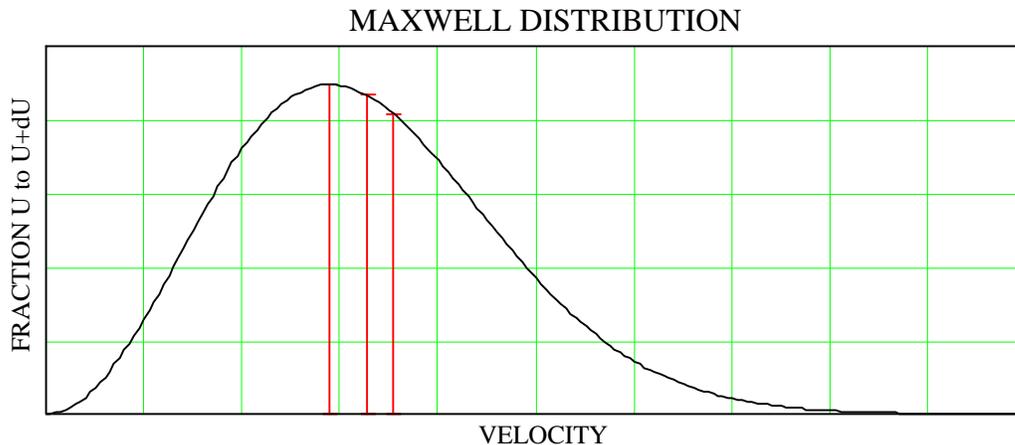
## Objectives:

At the end of this lesson you will be able to:

1. describe the distribution of molecular velocities for a sample of gas;
2. explain how the distribution changes with the temperature or molecular weight of a sample of gas;
3. compute the most probable, average and root mean square speeds of a gas sample and locate these on the Maxwell distribution curve;
4. determine the fraction of molecules that have a kinetic energy that exceeds a specified value and then relate this to the probability of a successful chemical reaction due to a sufficiently energetic collision.

## Student Instructions

This document concerns the Maxwell distribution of gas velocities which is shown below:



### EXERCISE 1

In the above figure, do all the molecules in a sample of gas have the same velocity? Is this curve symmetric about the maximum?

The three vertical lines in the figure represent special velocities which we will consider in greater detail later. The left-hand one is  $U_{mpv}$ , the most probable velocity corresponding to the maximum of the curve. The next one is  $U_{ave}$ , the average velocity, and the right-hand one is  $U_{rms}$ , the root mean square velocity.

The formula for the Maxwell distribution is:

$$P(u) := 4 \cdot \pi \cdot \left( \frac{M}{2 \cdot \pi \cdot R \cdot T} \right)^{\frac{3}{2}} \cdot \exp\left( \frac{-M \cdot u^2}{2 \cdot R \cdot T} \right) \cdot u^2 \cdot du$$

where  $u$  is the velocity,  $M$  the molecular weight in kg/mole,  $R$  in joules/(°K mole) and  $T$  in °K.

## EXERCISE 2

The first part of the computational document contains distributions for three different temperatures. Which graph corresponds to which temperature?

Switching to the next page of the computational document we see the effect of varying the molecular weight of the gases at the same temperature.

## EXERCISE 3

Which gas corresponds to which curve?

## EXERCISE 4

Now determine the speed corresponding to the maxima of the three curves. See instructions in the next paragraph.

MATHCAD offers a convenient and accurate way to do this. First move the cursor anywhere on the graph and click on it. Among other things a blue line should surround the graph meaning that it is 'selected.' Now click on 'x-y plot', then 'trace' and a dialog box should appear. Make sure that the 'track points' is checked. Now move the cursor somewhere near the maximum of one of the peaks and click on it. A dashed crosshair should appear. It can be moved along the curve using the right and left arrow keys. Locate the speed giving the maximum y value. Repeat for the other curves.

Now calculate (calculator or MATHCAD) the kinetic energy of each molecule at the speed corresponding to its maximum. How do the energies compare? What general conclusion can you reach?

Next we integrate the Maxwell function. Since the function is a probability, what value should we get integrating over all accessible speeds?

In our studies in chemical kinetics later on we will find that only the most energetic molecules will react. Lower-speed molecules will simply collide and bounce apart without reaction. We can use integrals of the Maxwell relationship to find the fraction of molecules with speeds greater than 2500 m/sec.

### EXERCISE 5

Change the integration limits to calculate the fraction of molecules having speeds between 3000 and 5000 m/sec at 300°K. Repeat for 310 and 320°K. Does this explain how modest increases in temperature affect reaction rates?

If we know the speed distribution, we can use it to calculate other quantities such as the average speed, average squared speed, etc. The average speed can be calculated from the formula

$$v_{\text{ave}} := \frac{\int_0^{\infty} v \cdot P(v) \, dv}{\int_0^{\infty} P(v) \, dv} \quad \text{where} \quad P(v) := 4 \cdot \pi \cdot \left( \frac{m}{2 \cdot \pi \cdot R \cdot T} \right)^{\frac{3}{2}} \cdot \exp\left( \frac{-m \cdot v^2}{2 \cdot R \cdot T} \right) \cdot v^2$$

Think carefully what we are doing here. For each speed we are first computing the fraction of molecules having that speed ( $P(v)$ ) and multiplying it by the speed  $v$ . Then by integration we are adding up the contributions of all the different speeds. Note also that you have already shown in the computational document that the denominator of this expression is 1.

### EXERCISE 6

Fix up the expression for  $\text{Int} :=$  on page 3 of the computational document to calculate the average velocity  $v_{\text{ave}}$ . Be sure to fix the limits of integration. Compare with the result for  $v_{\text{ave}}$  for the same  $M$  and  $T$ .

$$v_{\text{ave}} := \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M}}$$

### EXERCISE 7

Fix up the expression for  $\text{Int} :=$  on page 3 to calculate the average of  $v_2$ . The square root of this quantity is called the root mean square speed  $v_{\text{rms}}$ . Compare with the result

$$v_{\text{rms}} := \sqrt{\frac{3 \cdot R \cdot T}{m}}$$

### EXERCISE 8

Outline the procedure for finding the maximum of a function like the Maxwell distribution. Let MATHCAD help you do it. Although doing the operations by hand is not too difficult there are many places where error can occur. A modern tool like MATHCAD helps you to do things like this more accurately and efficiently.

### EXERCISE 9

An expression for the Maxwell distribution is shown on page 4 of the computational document. Click on a 'u' (independent variable) in the expression and press the 'up arrow' key. If all goes well you should have a u with a little blue box around it. Next click on 'symbolic,' then 'differentiate on variable.' Hopefully a complicated expression for the derivative should appear. Again select a u from this derivative expression and click on 'symbolic' then 'solve for variable.' What did you obtain from the solve for variable operation? Write an expression for the most probable velocity. Justify what you wrote as an answer.