Note on Atkins' Example 1.6 and Self-Test 1.6 (in 6th edition) and Example 24.1 and Self-Test 24.1 (in Atkins 7th edition)

The whole point of these problems is to calculate an *expectation value* for velocity (*mean velocity*), $\bar{c}$ or $\langle v \rangle$) or the *root mean square* (rms) *velocity*, $\langle v^2 \rangle^{1/2}$.

Generally speaking, the expectation value of some variable, *x*, whose variation can be described by a function *f*(*x*), is calculated from the equation:

$$\langle x \rangle = \int_0^\infty x f(x)\, dx$$

where $f(x)\,dx$ represents the "fraction" of molecules with the property *x*. So, the "expected velocity" or mean velocity of a collection of atoms or molecules, can be calculated as

$$\bar{c} = \langle v \rangle = \int_0^\infty v f(v)\, dv$$

where $f(v)\,dv$ is the fraction of atoms or molecules with the mean speed $\bar{c}$.

If the case of the Maxwell distribution of velocities, where

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

the integral above becomes:

$$\bar{c} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \int_0^\infty v^3 e^{-Mv^2/2RT} dv \ .$$

The integral must be evaluated from a table of standard integrals (these can be found in any calculus textbook, the CRC Handbook or in Barrante's "*Applied Mathematics for Physical Chemistry*").

If we are interested in evaluating the rms velocity (self-test), then we must consider:

$$c = \langle v^2 \rangle^{1/2} = \left[4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \int_0^\infty v^4 e^{-Mv^2/2RT} dv \right]^{1/2} .$$

Unfortunately, the form of the indefinite integral in Atkins 6th edition is incorrect (p. 28), but it is corrected in the 7th edition. The real form of the integral should be:

$$\int_0^\infty x^4 e^{-ax^2} dx = \frac{3}{8} \left(\frac{\pi}{a^5} \right)^{1/2} .$$

If this integral is applied for the self-test, then *c* will be correctly evaluated as $(3RT/M)^{1/2}$.