PHAS1000 – THERMAL PHYSICS

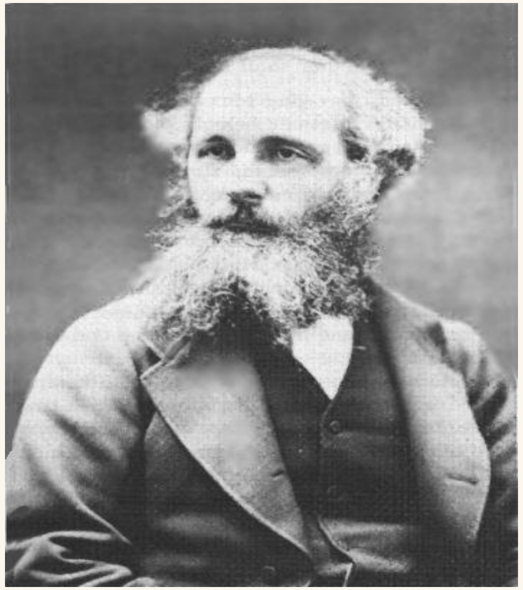
Lecture 8

Maxwell Boltzmann Distribution

Overview

This lecture covers:

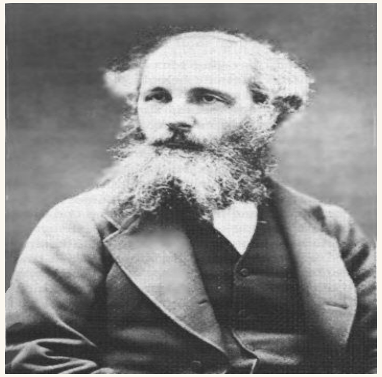
- Maxwell Boltzmann distribution
- Most probable speed
- Atmospheric escape velocity



James Clerk Maxwell
1831-1879

Ludwig Boltzmann
1844-1906

Maxwell and Boltzmann



James Clerk Maxwell
1831-1879

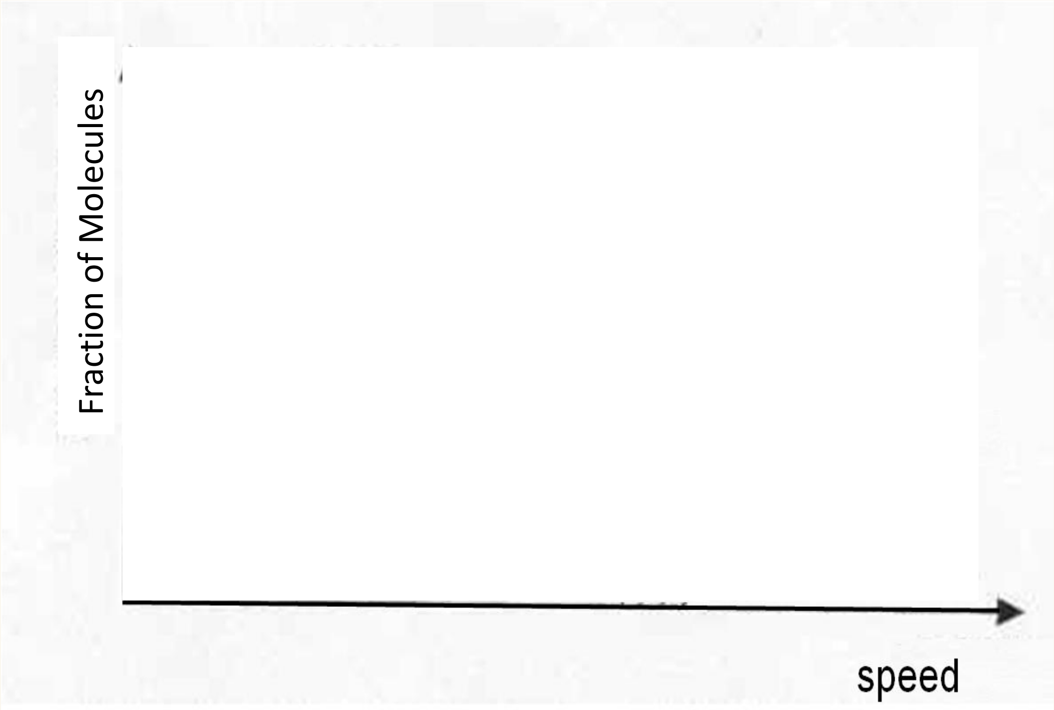
- Born in Edinburgh
- Wrote first scientific paper at age 14
- Major work in thermodynamics; Maxwell's relations, Maxwell's demon
- Put Faraday's ideas about electromagnetism into mathematical form
- Died of cancer, aged 48

Ludwig Boltzmann
1844-1906

- Born in Vienna
- PhD supervised by Josef Stefan
- In awe of Maxwell
- Hanged himself just before his kinetic theories were universally recognise
- Famous entropy equation $S = k \log W$ engraved on his tombstone

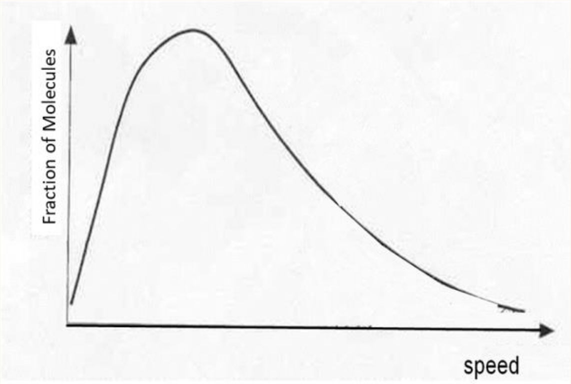
The Distribution of speeds

At any temperature the molecules in a gas have a range of speeds, given by :-



In thermal equilibrium

Equation



Exponential drop off, dominates at high speeds

$$f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{\frac{3}{2}} v^2 e^{\frac{-mv^2}{2kT}}$$

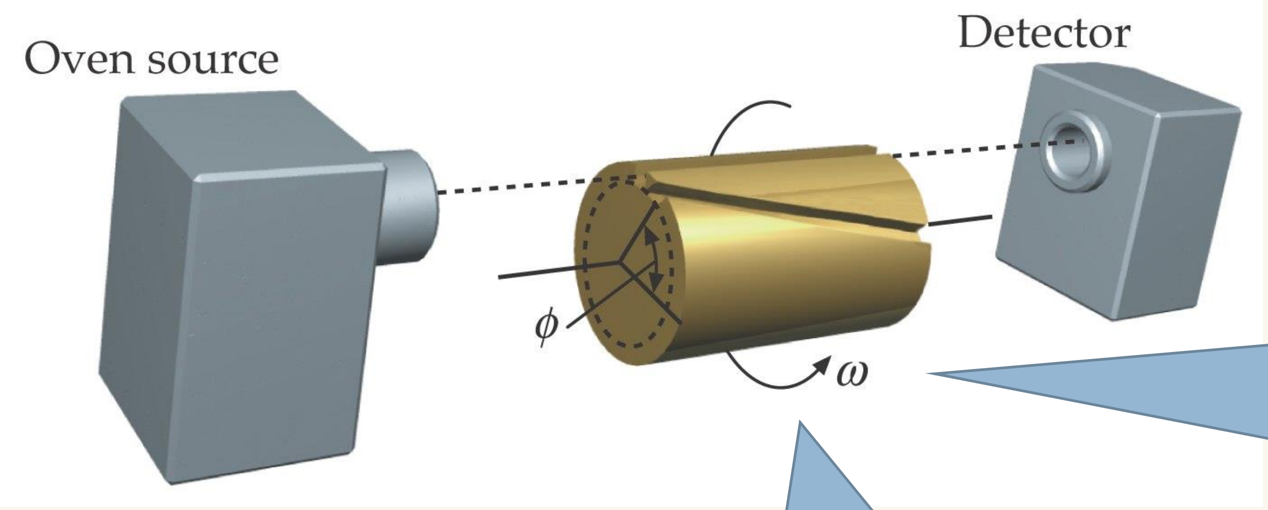
Exponent = $\dfrac{\text{kinetic energy}}{\text{thermal energy}} = \dfrac{\frac{1}{2}mv^2}{kT}$

fraction of molecules with speed v

Prefactor to normalise area under curve to 1

v^2 dependence, dominates at low speeds

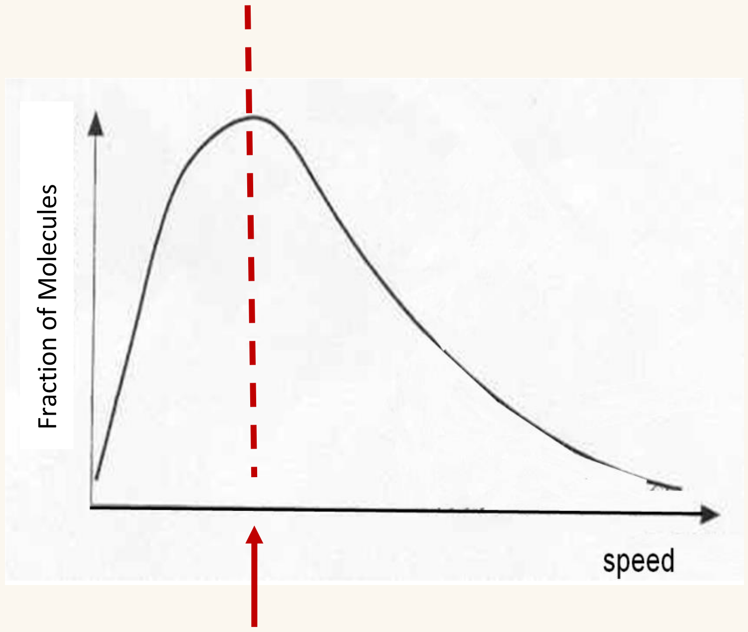
Experimental measurement



Velocity selector. When rotating at angular velocity ω, only molecules travelling at speed v (= r ω) pass through without being absorbed.

Rotate at successive values of ω to map out distribution for given temperature.

Most probable speed $v_{\max}$



$v_{\max}$

At the maximum (turning point) $\frac{d}{dv}f(v) = 0$

lose the constant prefactor

$$\frac{d}{dv}\left(v^2 e^{-\frac{mv^2}{2kT}}\right) = 0$$

$$2\cancel{v}\,\cancel{e^{-\frac{mv^2}{2kT}}} + v^{\cancel{2}}\left(\frac{-\cancel{2}mv}{\cancel{2}kT}\right)\cancel{e^{-\frac{mv^2}{2kT}}} = 0$$

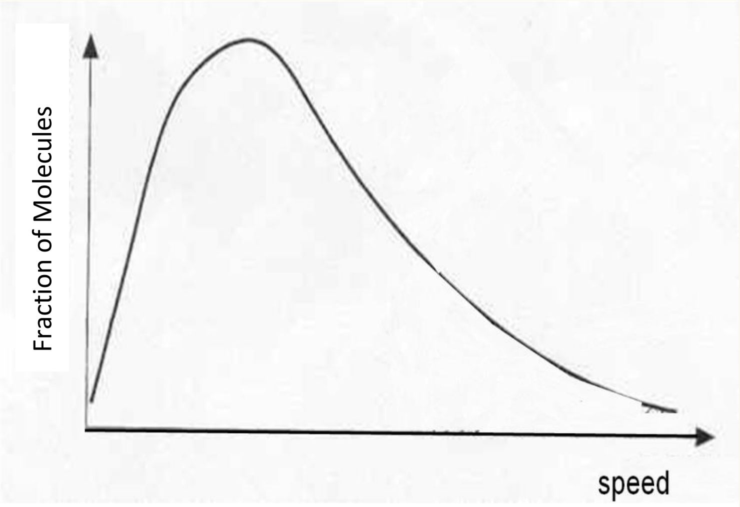
$$2 - \frac{v^2 m}{kT} = 0 \qquad v^2 = \frac{2kT}{m} \qquad v_{max} = \sqrt{\frac{2kT}{m}}$$

$$f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{\frac{3}{2}} v^2 e^{\frac{-mv^2}{2kT}}$$

Note: $\frac{1}{2}mv^2 = kT$

$$v_{max} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$

Average Speed



Calculating the average speed v_{av}

Average speed: mean of all values of v, weighted by their probability

$$v_{av} = \int_0^{\infty} v\, f(v) dv$$

$$\boxed{v_{av} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}}$$

Average Speed derivation

$$\begin{aligned} \langle v \rangle &= \int_{-\infty}^{\infty} v\, f(v) dv \\ &= \int_{-\infty}^{\infty} v\, 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} v^2 \exp\left(\frac{-mv^2}{2k_B T}\right)\, dv \\ &= 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \int_{-\infty}^{\infty} v^3 \exp\left(\frac{-mv^2}{2k_B T}\right)\, dv \end{aligned}$$

The following can be found in a table of integrals:

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}$$

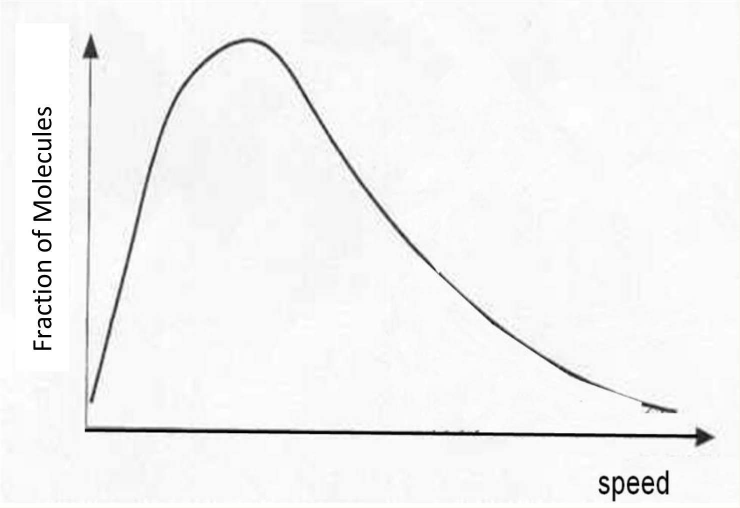
So

$$\langle v \rangle = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \left[\frac{1}{2\left(\frac{m}{2k_B T}\right)^2} \right]$$

Which simplifies to

$$\langle v \rangle = \left(\frac{8k_B T}{\pi m}\right)^{1/2}$$

Root Mean Square Speed



Calculating the root mean square speed v_{rms}

This is the speed of molecules with average kinetic energy

$$(v^2)_{av} = \int_0^{\infty} v^2 f(v) dv$$

$$\boxed{v_{rms} = \sqrt{(v^2)_{av}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}}$$

Root mean square speed derivation

$$\begin{aligned}\langle v^2\rangle &= \int_{-\infty}^{\infty} v^2\, f(v)dv \\ &= \int_{-\infty}^{\infty} v^2\, 4\pi\sqrt{\left(\frac{m}{2\pi k_BT}\right)^3} v^2 \exp\left(\frac{-mv^2}{2k_BT}\right)\, dv \\ &= 4\pi\sqrt{\left(\frac{m}{2\pi k_BT}\right)^3}\int_{-\infty}^{\infty} v^4 \exp\left(\frac{-mv^2}{2k_BT}\right)\, dv\end{aligned}$$

A table of integrals indicates that

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1\cdot 3\cdot 5\ldots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}}$$

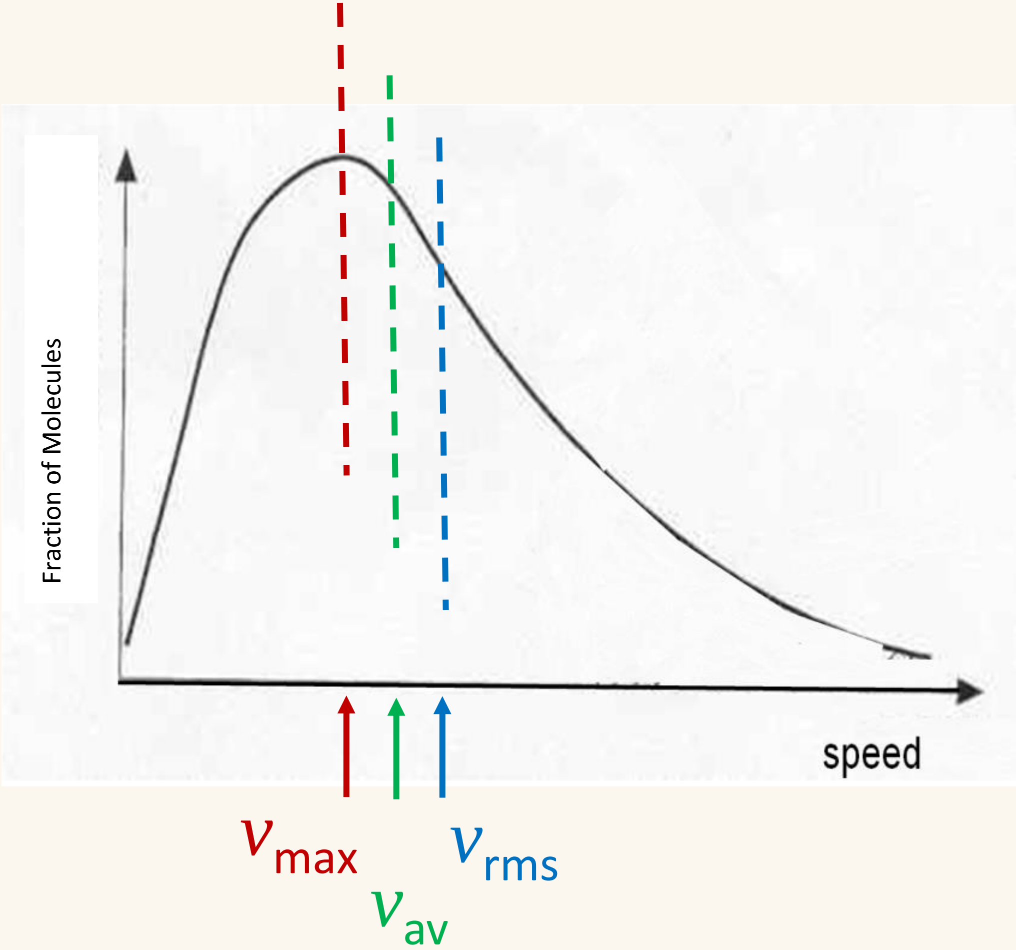
Substitution (noting that $n = 2$) yields

$$\langle v^2\rangle = 4\pi\sqrt{\left(\frac{m}{2\pi k_BT}\right)^3}\left[\frac{1\cdot 3}{2^3\left(\frac{m}{2k_BT}\right)^2}\sqrt{\frac{\pi}{\left(\frac{m}{2k_BT}\right)}}\right]$$

which simplifies to

$$\langle v^2\rangle = \frac{3k_BT}{m}$$

Comparing the different measures of speed



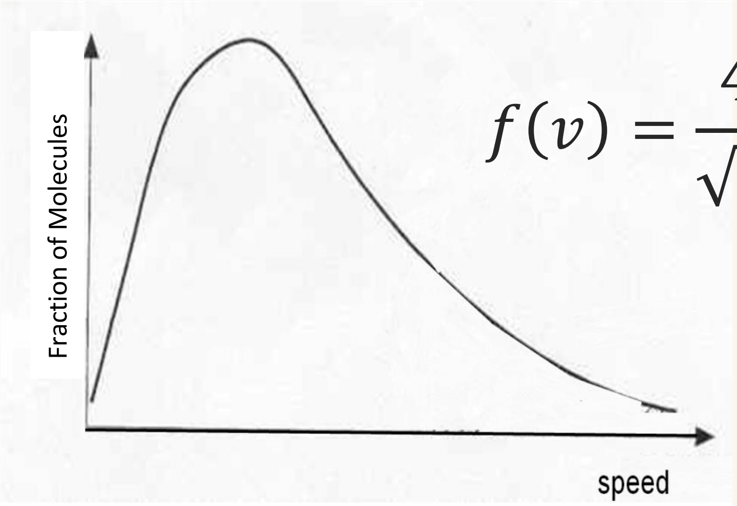
$$v_{max} = \sqrt{\frac{2kT}{m}} = \sqrt{2} \times \sqrt{\frac{kT}{m}}$$ ~1.4

$$v_{av} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8}{\pi}} \times \sqrt{\frac{kT}{m}}$$ ~1.6

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{3} \times \sqrt{\frac{kT}{m}}$$ ~1.7

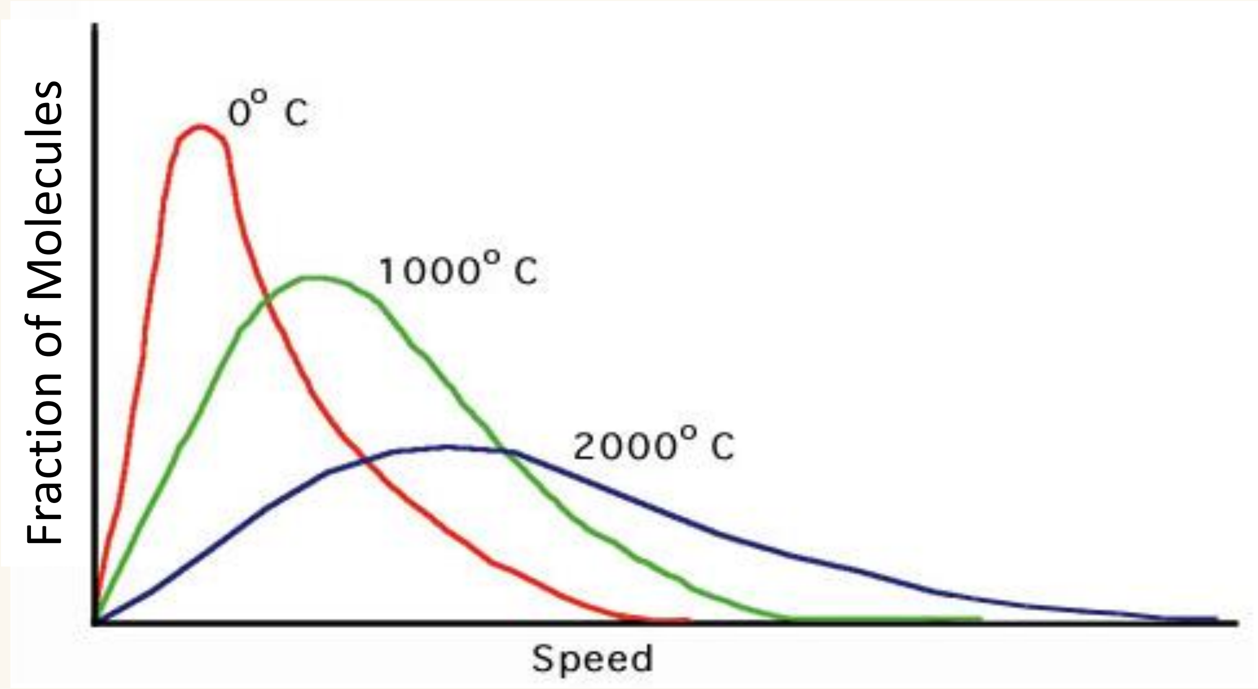
In describing the curve, use v_{max}. In calculations asking for 'average speed' use v_{rms}. We almost never use the strict average speed.

Distribution change with temperature



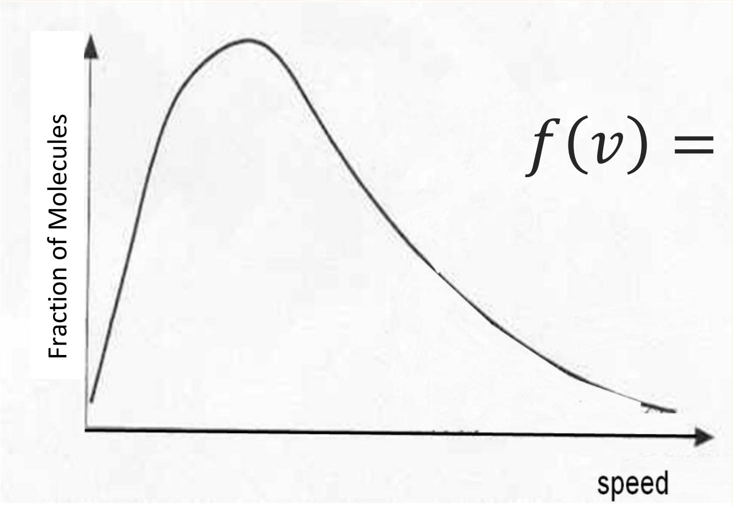
$$f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{\frac{3}{2}} v^2 e^{\frac{-mv^2}{2kT}}$$

$$v_{max} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$

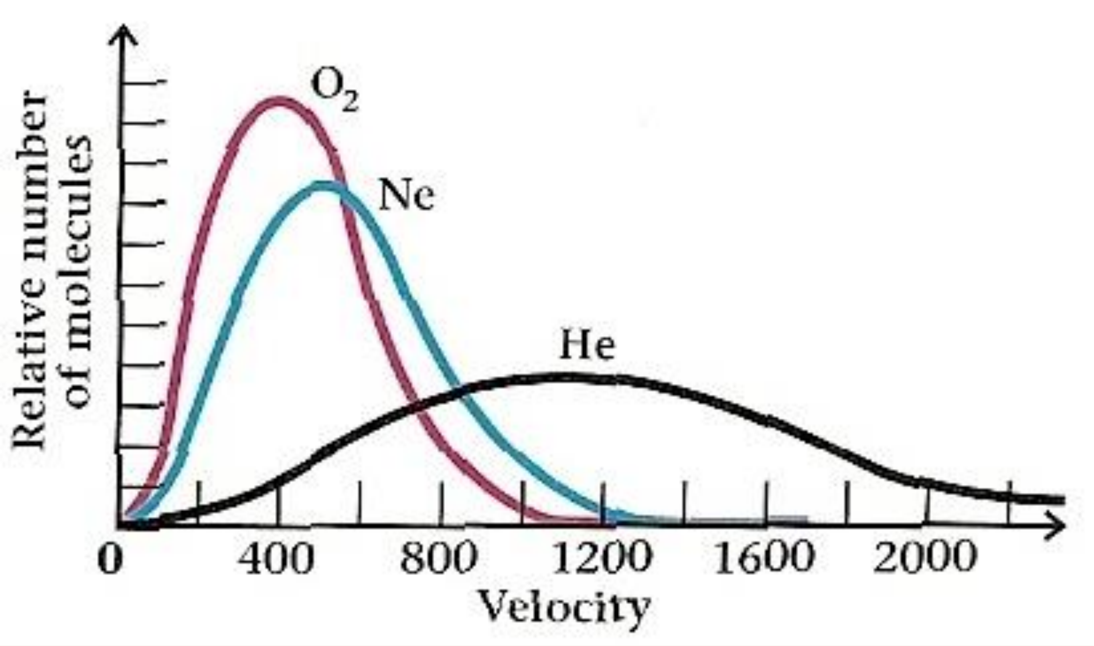


- v_{max} increases with temperature
- Area under curve remains constant, so peak is lower

Distribution change with molar mass



$$f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{\frac{3}{2}} v^2 e^{\frac{-mv^2}{2kT}}$$



$$v_{max} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$

- v_{max} reduces with increasing molar mass
- Area under curve remains constant, so peak is higher

One cylinder contains helium at 500 K. Another cylinder contains oxygen. At what temperature should the oxygen be to have the same v_{max} as the helium molecules?

Molar mass helium = 4g Molar mass oxygen = 32 g

A 62.5 K

B 63.2 K

C 1414 K

D 4000 K

0

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Showing Results

One cylinder contains helium at 500 K. Another cylinder contains oxygen. At what temperature should the oxygen be to have the same vmax as the helium molecules?
Molar mass helium = 4g Molar mass oxygen = 32 g

A 62.5 K

0%

B 63.2 K

0%

C 1414 K

0%

D 4000 K

0%

Question

One cylinder contains helium at 500 K. Another cylinder contains oxygen. At what temperature should the oxygen be to have the same v_{max} as the helium molecules?

Molar mass helium = 4g

Molar mass oxygen = 32 g

A 62.5 K

B 63.2 K

C 1414 K

D 4000 K

$$v_{max} = \sqrt{\frac{2RT}{M}} \propto \sqrt{\frac{T}{M}}$$

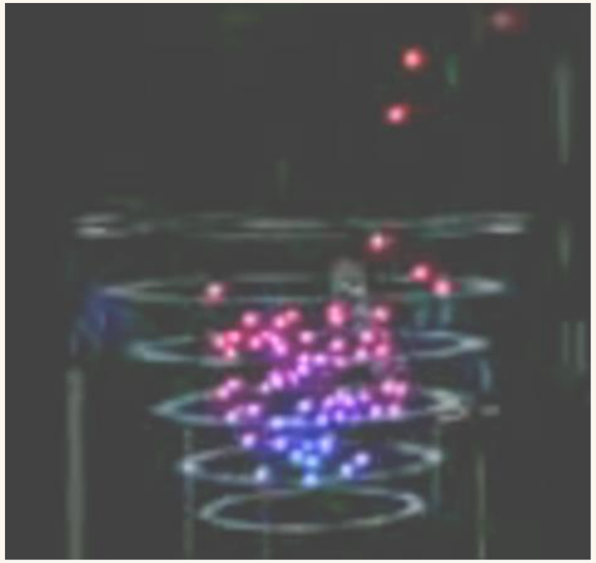
$$\sqrt{\frac{T_{O_2}}{M_{O_2}}} = \sqrt{\frac{T_{He}}{M_{He}}}$$

$$\frac{T_{O_2}}{M_{O_2}} = \frac{T_{He}}{M_{He}}$$

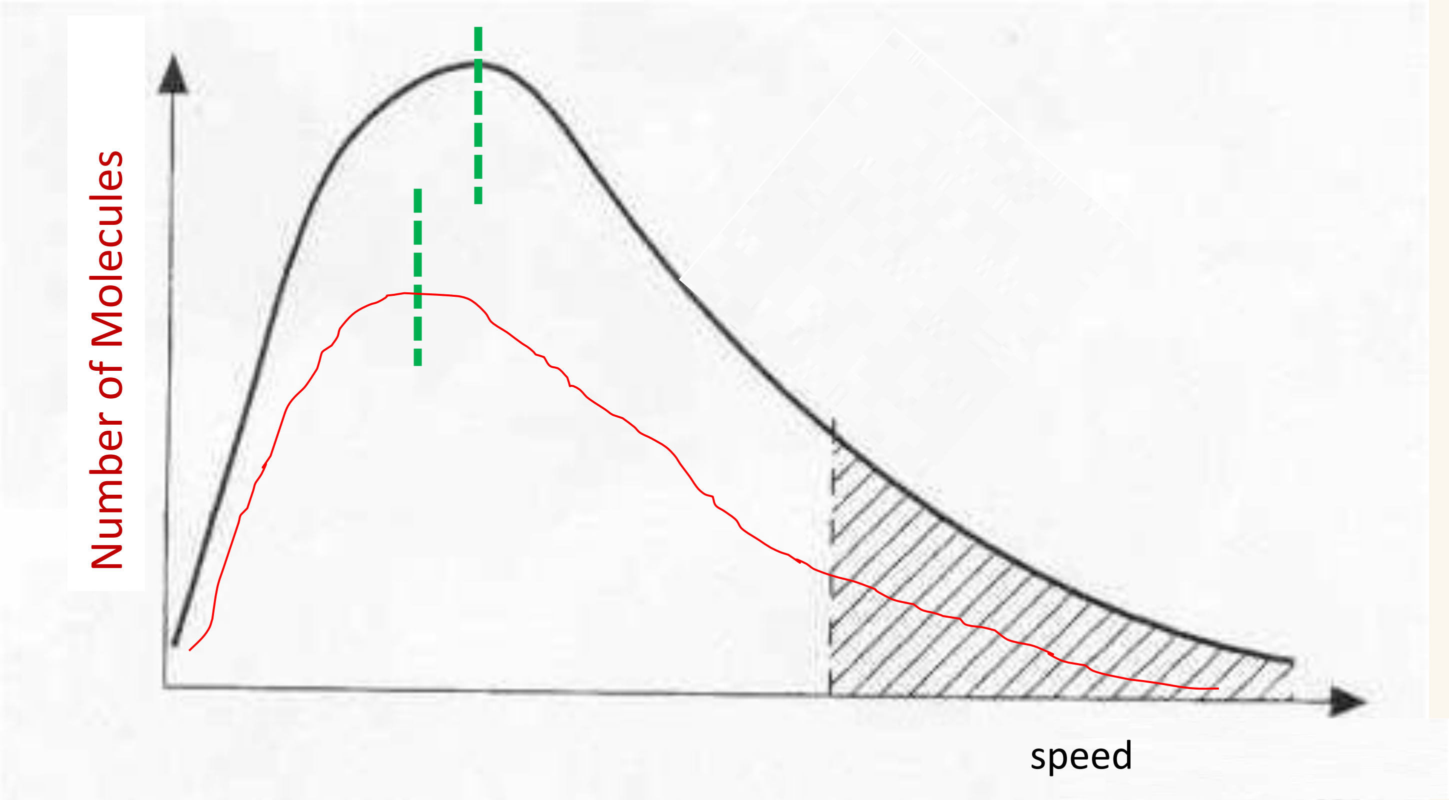
$$T_{O_2} = T_{He}\frac{M_{O_2}}{M_{He}} = 500 \times \frac{32}{4} = \underline{\underline{4000\ K}}$$

Evaporation

Evaporation loses the fastest molecules



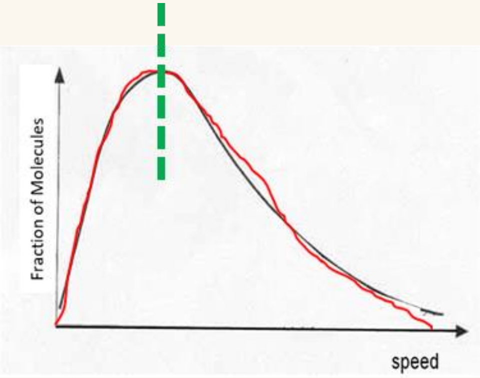
Distribution change with evaporation



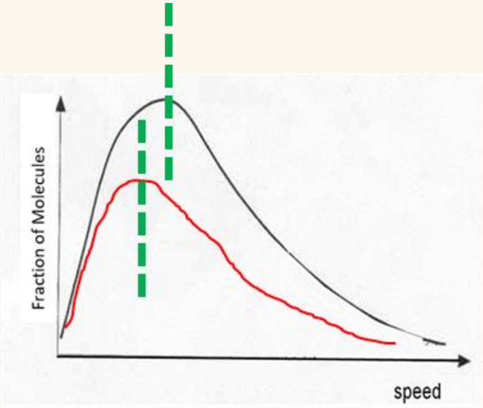
$$v_{max} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$

- ❑ Shape re-establishes itself (in thermal equilibrium)
- ❑ v_{max} reduced with reduced temperature
- ❑ Area under curve reduced as some molecules lost (graph is number not fraction)

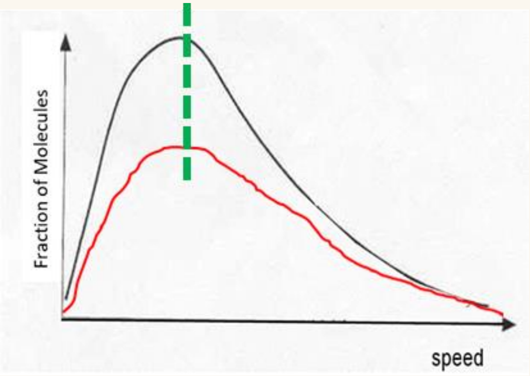
If the graph for effect of evaporation (red curve) was plotted as ‘fraction of molecules’ remaining rather than ‘number of molecules’ remaining, what would it look like?



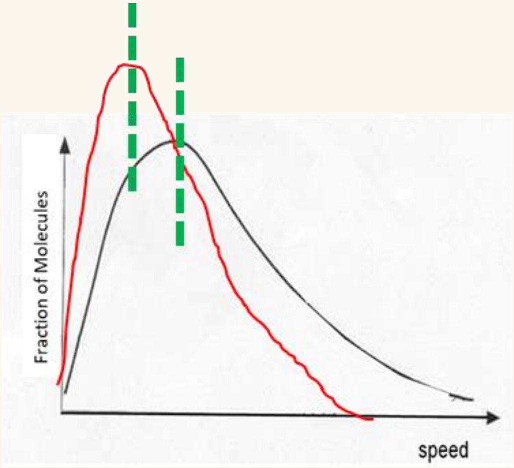
A



B

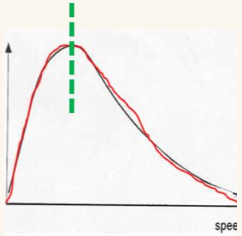


C



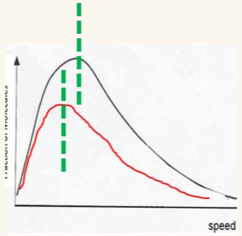
D

If the graph for effect of evaporation (red curve) was plotted as ‘fraction of molecules’ remaining rather than ‘number of molecules’ remaining, what would it look like?



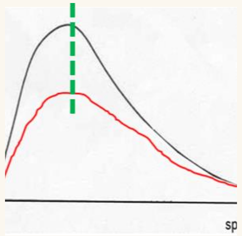
A

0%



B

0%



C

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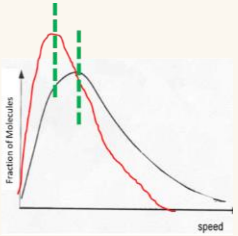


D

0%

Sketching the graph

A sample of oxygen gas is at 400K, and a sample of hydrogen gas is at 800K. Sketch their Maxwell-Boltzmann distributions of speeds (on the same axes)….

(a) by rough sketch

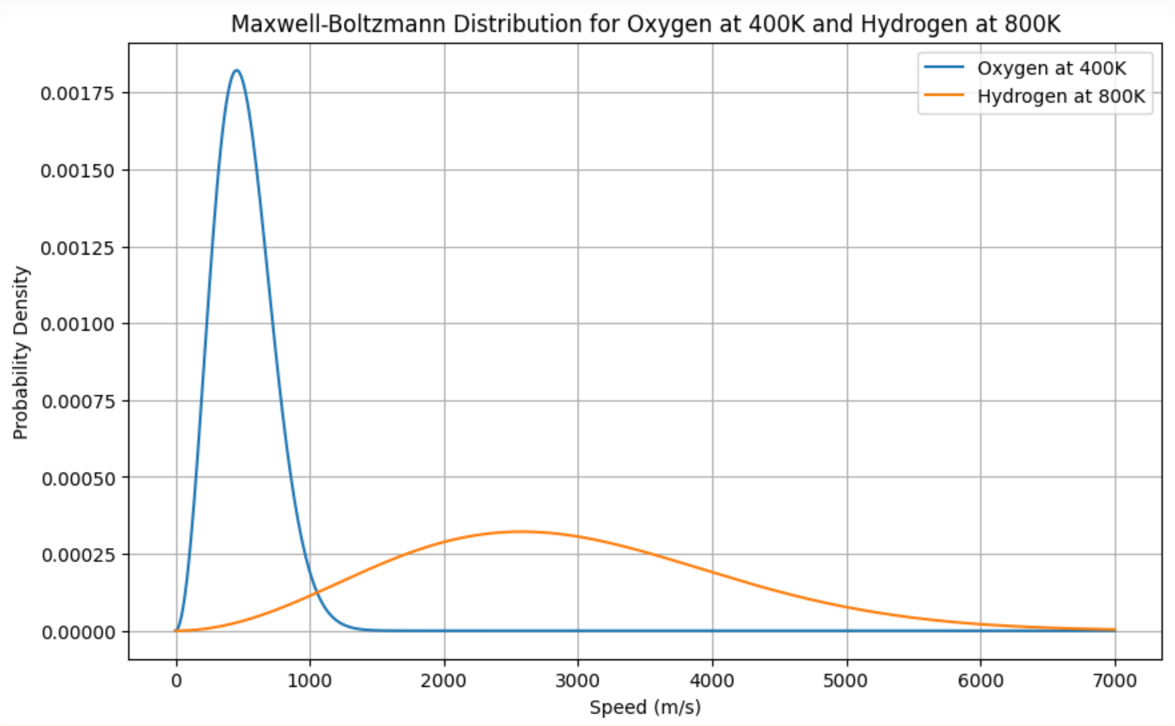
(b) by calculating the coordinates of the peak of each distribution

Sketching the graph - answer

Coordinates

Oxygen: 456 ms^{-1}, 1.8×10^{-3}

Hydrogen: 2578 ms^{-1}, 3.2×10^{-4}



$v_{max} = \sqrt{\frac{2RT}{M}}$ $\quad M_{O_2} = 32g \quad M_{H_2} = 2g$

oxygen : $v_{max} = \sqrt{\frac{2\times8.31\times400}{32\times10^{-3}}} = \boxed{456\ m/s}$

hydrogen $v_{max} = \sqrt{\frac{2\times8.31\times800}{2\times10^{-3}}} = \boxed{2578\ m/s}$

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

oxygen : $f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{32\times10^{-3}}{2\times8.31\times400}\right)^{3/2} \times 456^2 \times e^{-\frac{32\times10^{-3}\times456^2}{2\times8.31\times400}}$

$= \boxed{1.8\times10^{-3}}$

hydrogen : $f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{2\times10^{-3}}{2\times8.31\times800}\right)^{3/2} \times 2578^2 \times e^{-\frac{2\times10^{-3}\times2578^2}{2\times8.31\times800}}$

$= \boxed{3.2\times10^{-4}}$

Creating an atmosphere

If the rms speed of a gas is greater than about 15 to 20 percent of the escape velocity of a planet, virtually all the molecules of that gas will escape the atmosphere of the planet.

Taking the formula for escape velocity to be $v_e = \sqrt{2gR_p}$ where R_p is the radius of planet and g is the acceleration due to gravity on the planet, investigate the following:-

(a) Find the temperature at which v_{rms} for O_2 is equal to 15% of the escape velocity for the earth.

(b) Find the temperature at which v_{rms} for H_2 is equal to 15% of the escape velocity for the earth.

(c) Temperatures in the upper atmosphere reach 1000 K. What can you say about the likelihood of finding O_2 and H_2 in the earth's atmosphere?

(d) Suppose an astronomer claims to have found oxygen (O_2) in the atmosphere of the asteroid Ceres, how likely is this? Ceres has a gravity acceleration 0.032 times that on the earth and a surface temperature of about 200K.

Radius of earth = 6400 km. Radius of Ceres = 469 km

Creating an atmosphere - answer

(a) $V_{rms} = \sqrt{\frac{3RT}{M}} = \left(\frac{15}{100}\right)\sqrt{2gR_p}$

$$\frac{3RT}{M} = \left(\frac{15}{100}\right)^2 2gR_p$$

temp needed for escape $\boxed{T = \left(\frac{15}{100}\right)^2 \times \frac{2}{3}\frac{gMR_p}{R}}$

for O_2 $M = 32g$

for earth $g = 9.8\ m/s^2$ $R_p = 6400\ km$

$$T = \left(\frac{15}{100}\right)^2 \times \frac{2}{3} \times \frac{9.8 \times 32\times10^{-3} \times 6400\times10^3}{8.31} = \boxed{3623\ K}$$

(b) for H_2 $M = 2g$

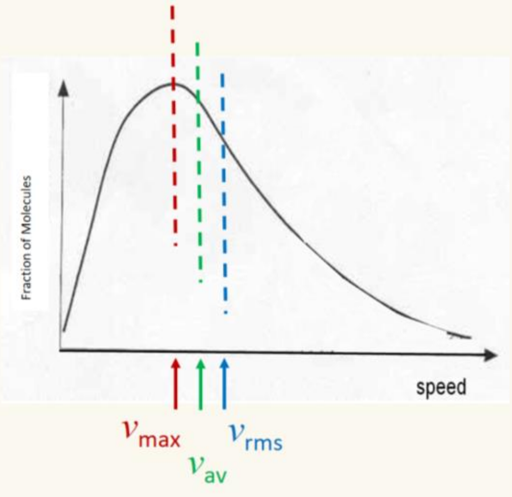
$$T = \left(\frac{15}{100}\right)^2 \times \frac{2}{3} \times \frac{9.8 \times 2\times10^{-3} \times 6400\times10^3}{8.31} = \boxed{226\ K}$$

(c) At 1000 K we are above the temp for H_2 molecules to escape but well below the O_2 threshold.

(d) $T = \left(\frac{15}{100}\right)^2 \times \frac{2}{3} \times \frac{0.032\times 9.8 \times 32\times10^{-3} \times 469\times10^3}{8.31}$

$T = \boxed{8\ K}$ So for surface temp of 200 K I do not think any oxygen will remain.

Summary



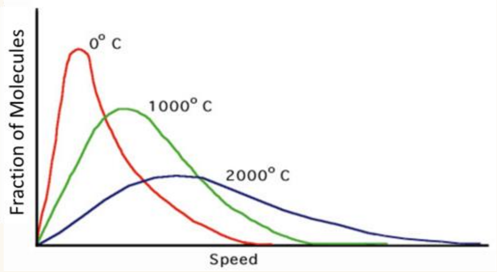
Maxwell Boltzmann distribution of molecular speeds (in thermal equilibrium)

$$f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{\frac{3}{2}} v^2 e^{\frac{-mv^2}{2kT}}$$

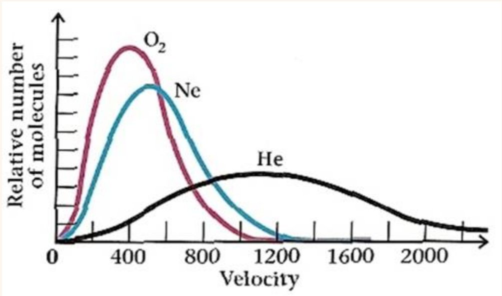
$$v_{max} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$

$$v_{av} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

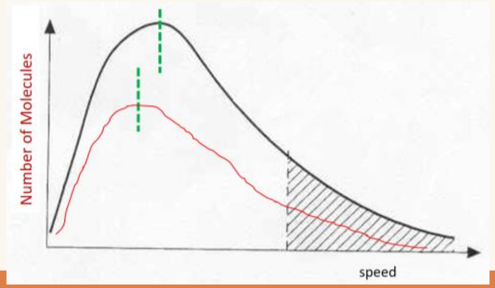
$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$



With temperature



With molar mass



Evaporation