

Introduction to Thermodynamics and Ideal Gases

Thermodynamics is the physics of heat, what it is and how it is transported. Heat is the kinetic energy associated with the *random motion* of a large number of molecules which constitute a gas, liquid or solid. It is a *statistical theory* i.e. properties such as pressure, temperature and density are averages.

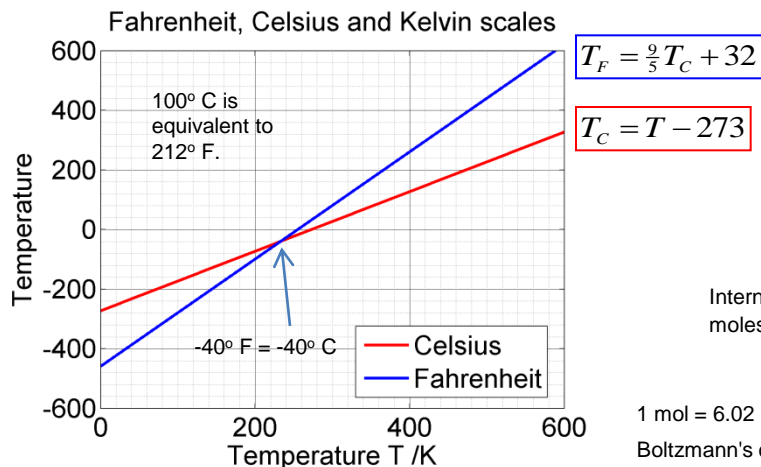
Ideal Gas Equation

$$pV = nRT$$

P	Pressure in Pascals (Pa)	R	Molar gas constant 8.314 Jmol ⁻¹ K ⁻¹
V	Volume / cubic metres		
n	Number of moles of gas	T	Temperature /Kelvin

An ideal gas assumes a *large number of point particles colliding elastically*. It neglects any *short-range intermolecular forces* resulting from *repulsion or attraction due to molecular charges*, and the fact that molecules have a *finite volume* i.e. are not infinitely small! This means a *real gas is not infinitely compressible* whereas an ideal gas has no such limits.

Temperature scales



At **1 atm = 101,325 Pa**, one mole of gas at **20°C = 293K** has volume $V = 2.40 \times 10^{-2} \text{ m}^3 = \mathbf{24 \text{ litres}}$

The **Kelvin** temperature scale (or “absolute” scale) is proportional to the **mean kinetic energy of molecules**.

$$U = \frac{1}{2} \alpha nRT$$

Internal energy of n moles of gas

Number of degrees of freedom of molecular motion (e.g. $\alpha = 3$ for x, y, z translation)

1 mol = 6.02×10^{23} molecules. So energy of a *molecule* is $u = \frac{1}{2} \alpha n k_B T$
Boltzmann's constant $k_B = R / 6.02 \times 10^{23} = 1.38 \times 10^{-23} \text{ JK}^{-1}$

Fahrenheit is a **temperature scale**, where 32° F is the freezing point of water and 212° F is the boiling point of water, defined at sea level at **standard atmospheric pressure** (101,325Pa). It was proposed in 1724 by Daniel Gabriel Fahrenheit. 0° F corresponded to the lowest temperature he could cool brine (salt water) and 100° F was the average human body temperature (37°C).

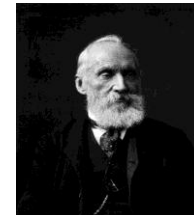
A more popular scale is the **Celsius** scale, with 0° C and 100° C representing the freezing and boiling points of water at standard atmospheric pressure.



Anders Celsius
1701-1744



Daniel Fahrenheit
1686-1736



William Thompson
(Lord Kelvin)
1824-1907



Robert Boyle
1627-1691



Jacques Charles
1746-1823

Ideal Gas Equation in practical units

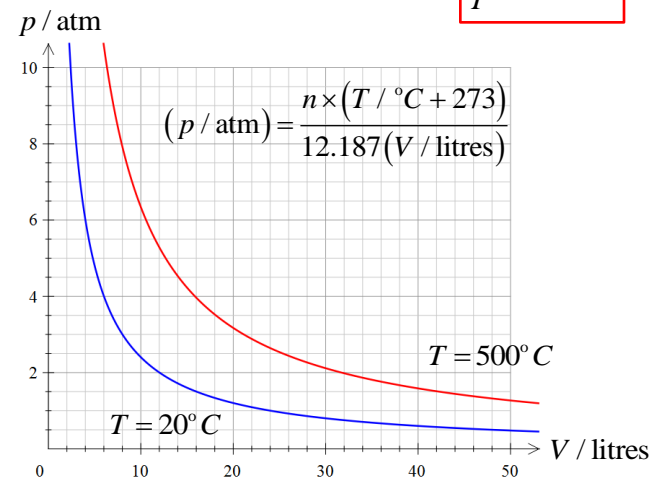
$$\left(\frac{p}{\text{atm}} \times 101325\right) \left(\frac{V}{\text{litres}} \times \frac{1}{1000}\right) = 8.314 \times \left(\frac{T}{\text{K}}\right) \times n$$

$$\left(\frac{p}{\text{atm}}\right) = \frac{n \times (T / ^\circ\text{C} + 273)}{12.187(V / \text{litres})}$$

Special cases of the ideal gas equation:

Boyles' Law. At constant temperature, gas pressure is inversely proportional to volume. $p \propto \frac{1}{V}$
 $\therefore pV = \text{constant}$

Charles' Law. At constant pressure, gas volume is proportional to temperature. $V \propto T$
 $\therefore \frac{V}{T} = \text{constant}$



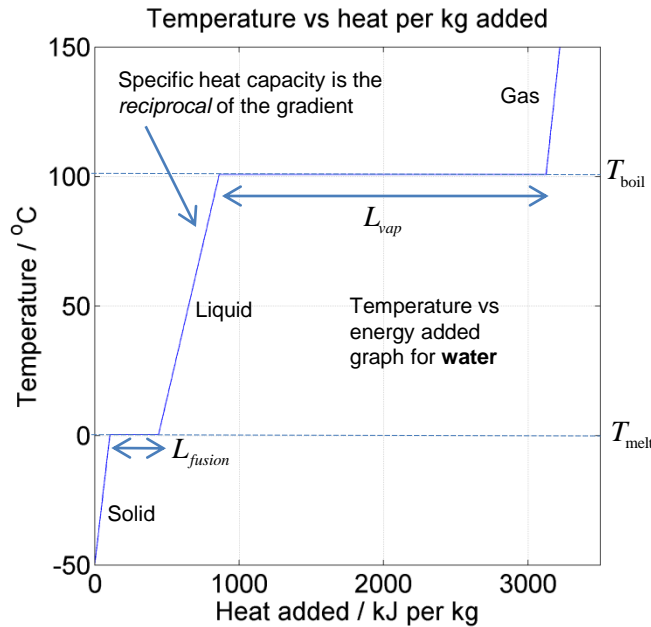
Latent heat is the amount of energy required cause a collection of molecules to **change state**. In practical terms, it is the energy required to overcome the intermolecular forces which bind solids and liquids together.

The **specific latent heat of fusion** is the energy required to convert 1kg of a substance from a **solid** to **liquid** phase.

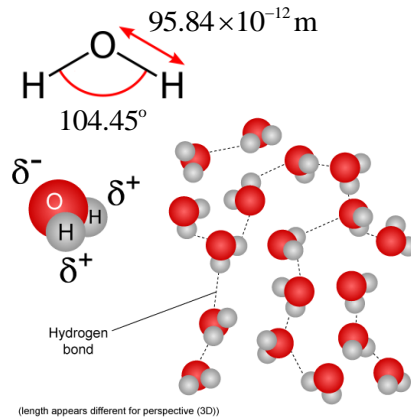
The **specific latent heat of vaporization** is the energy required to convert 1kg of a substance from a **liquid** to **gaseous** phase.

During the phase transition, all energy input is 'spent' breaking the intermolecular bonds rather than increasing the mean kinetic energy of molecules. This means there is *no rise* on a temperature vs energy input graph.

Molecule	Melting temp. / °C	Boiling temp. / °C	Latent heat of fusion / $\times 10^4 \text{ Jkg}^{-1}$	Latent heat of vaporization / $\times 10^5 \text{ Jkg}^{-1}$	Specific heat capacity (solid) / $\text{Jkg}^{-1}\text{K}^{-1}$	Specific heat capacity (liquid) / $\text{Jkg}^{-1}\text{K}^{-1}$	Specific heat capacity (gas) / $\text{Jkg}^{-1}\text{K}^{-1}$
Ammonia	-77.8	-33.4	33.3	13.7	1,465	4,700	2,060
Benzene	5.5	80.1	12.6	3.94	1,516	2,100	1,090
Copper	1,083	2,566	20.7	47.3	385	386	380
Ethyl alcohol	-114.4	78.3	10.8	8.55	970	2,440	1,900
Gold	1,063	2,808	6.28	17.2	128.9	?	?
Lead	327.3	1,750	2.32	8.59	136	117.6	?
Mercury	-38.9	356.6	1.14	2.96	124	140	?
Nitrogen	-210	-195.8	2.57	2.00	890	2,042	1,040
Oxygen	-218.8	-183.0	1.39	2.13	779	1,669	919
Water	0	100	33.5	22.6	2,090	4,186	1,930

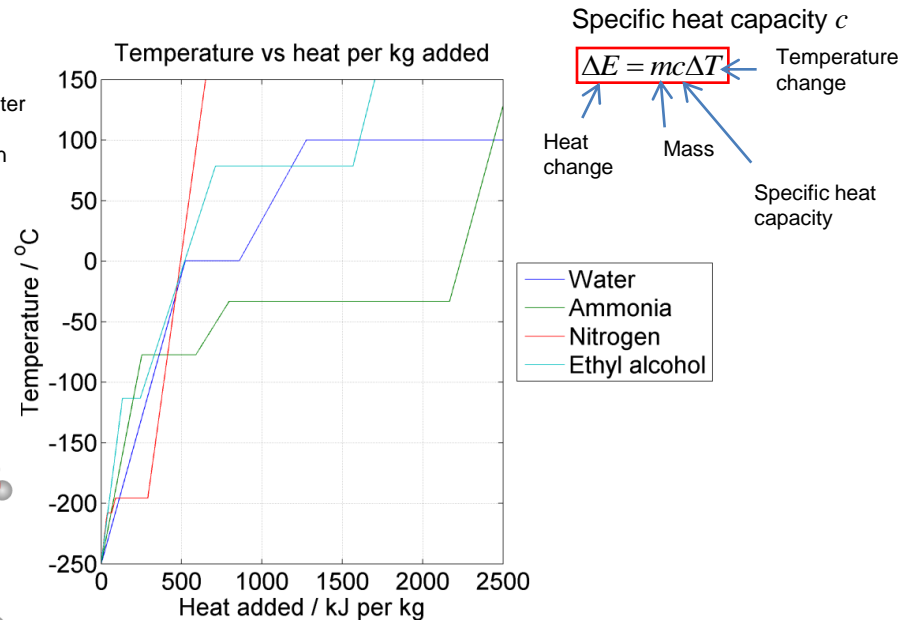


Water has a fairly high latent heat of vaporization due to the strength of the **hydrogen bond** intermolecular forces. This, and the angled geometry of the water molecule, also explains why ice is less dense than liquid water. Solid water is an open structure with holes rather than a densely packed molecular lattice.



(length appears different for perspective (3D))

Dept. Biol. Penn State ©2002



Specific heat capacity c

$$\Delta E = mc\Delta T$$

Heat change Mass Specific heat capacity Temperature change

Outside phase transitions, the temperature will typically rise linearly* with energy input i.e. we assume a *constant* heat capacity.

*The heat capacity will change as different modes of molecular vibration are excited. For a solid, three translational (x, y, z) modes are typical.

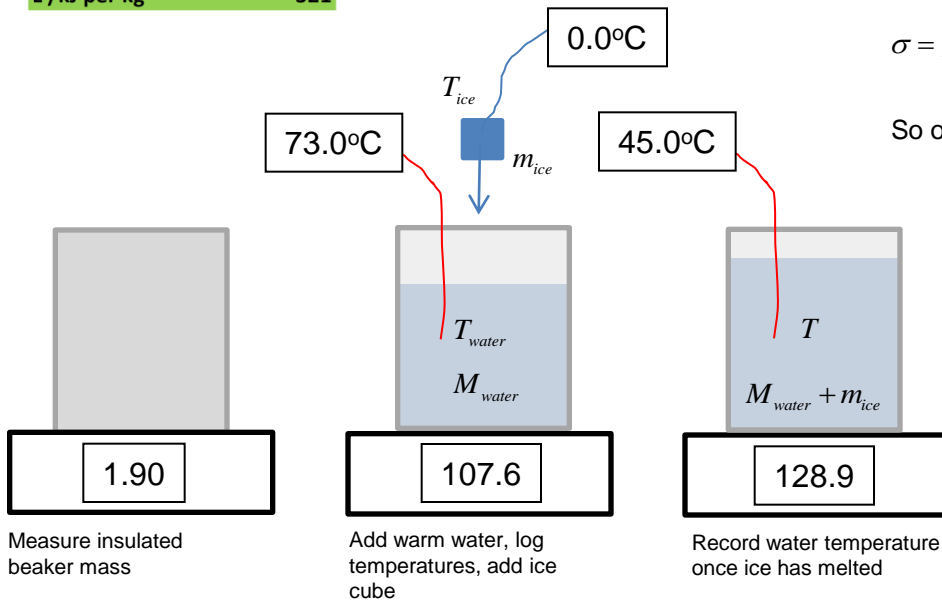
Measuring the specific latent heat of fusion L of water

The idea is to log the temperature of a small insulated beaker of warm water, before and after an ice cube is added. The beaker is mounted on a mass balance to enable the mass of (i) the beaker (ii) the beaker + warm water and (iii) the beaker + water + ice cube to be measured. A thermocouple or 'culinary spike' digital thermometer can be used to measure the ice cube temperature before it is added to the water. The idea is to use a datalogger to record the temperature of the water in the beaker from prior to adding the ice cube, till just after it has melted. The water temperature change following the addition of the ice cube can be used to determine the **latent heat of fusion**. Clearly heat will be lost continuously from the beaker, so insulating it is important. Using a datalogger with thermocouples will give a good idea of the time history of the system, and perhaps a better idea of what to take as the temperature change due to the addition of the ice cube. i.e. the step change should be in the context of a general cooling trend..

Worked (albeit somewhat crude) example, with three repeats.

	1	2	3
Cup mass in g	1.9	1.9	1.9
Cup + water	110	107.6	100.6
M /g	108.1	105.7	98.7
Cup + water + ice	130.6	128.9	114.6
m /kg	22.5	23.2	15.9
T0 /degC	64.5	73	72
T1 /degC	45.5	45	48
L (kJ/kg)	192	347	424

L /kJ per kg **321**



Calculation is based upon an energy balance, and assuming no loss of heat to the surroundings. The idea is that the energy to enable state change from solid to liquid of the ice, and then a rise of temperature from T_{ice} to T , is accounted for by the loss of heat of the water, which cools from T_{water} to T . The **specific heat capacity** of liquid water is assumed to be $c = 4200 \text{ Jkg}^{-1}\text{K}^{-1}$.

$$m_{ice} L + cm_{ice} (T - T_{ice}) = cM_{water} (T_{water} - T)$$

$$\therefore L = \frac{cM_{water} (T_{water} - T) - cm_{ice} (T - T_{ice})}{m_{ice}}$$

In our case the mean L is:

$$\bar{L} = \frac{1}{3}(192 + 347 + 424) \text{ kJkg}^{-1} = 321 \text{ kJkg}^{-1}$$

and the *unbiased estimator** of the standard deviation in L is:

$$\sigma = \sqrt{\frac{1}{3-1} \sum_{i=1}^3 (L_i - \bar{L})^2} = \sqrt{\frac{1}{2} \times ((192 - 321)^2 + (347 - 321)^2 + (424 - 321)^2)} = 118 \text{ kJkg}^{-1}$$

So our result is: $L = (321 \pm 118) \text{ kJkg}^{-1}$

The 'official' answer is **335 kJkg⁻¹**

*Assumes that each measurement is **independent** and subject to **random error**. The idea is repeat measurements form a **sample**, and from that sample we would like to estimate the mean and standard deviation of the **population** that we are sampling.

$$L = \frac{cM_{water} (T_{water} - T) - cm_{ice} (T - T_{ice})}{m_{ice}}$$

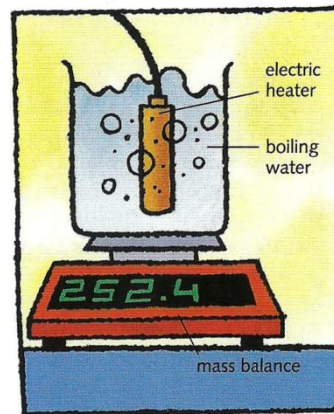
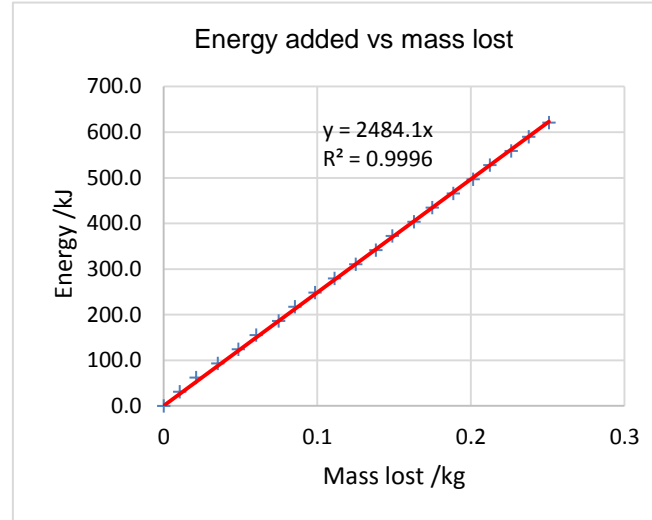
Measuring the specific latent heat of vaporization L_{vap} of water

The idea is to place a (half filled) electric kettle with the lid open on a mass balance, and record the mass lost after the water has started boiling vs time. An electrical meter is used to determine the power input to the system, and therefore a graph of energy input vs mass lost can be plotted. The gradient of this graph (which is particularly linear) yields the latent heat of vaporization of water.

The problem with this method is that the efficiency of conversion of electrical energy to the kettle heating element to the energy used in vaporizing the (boiling) water may not be 100%. There will certainly be heating of the kettle. The data below (measured at Winchester College in 2018) predicts a specific latent heat of vaporization of about **2480 kJkg⁻¹**. The 'official' value is **2260 kJkg⁻¹**. The fact that we overestimate the true result is consistent with the hypothesis that the process of electrical to thermal energy conversion is less than 100%.

I /A	4.5
V /volts	230
Power /kW	1.04

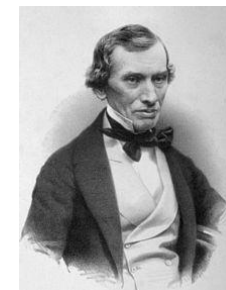
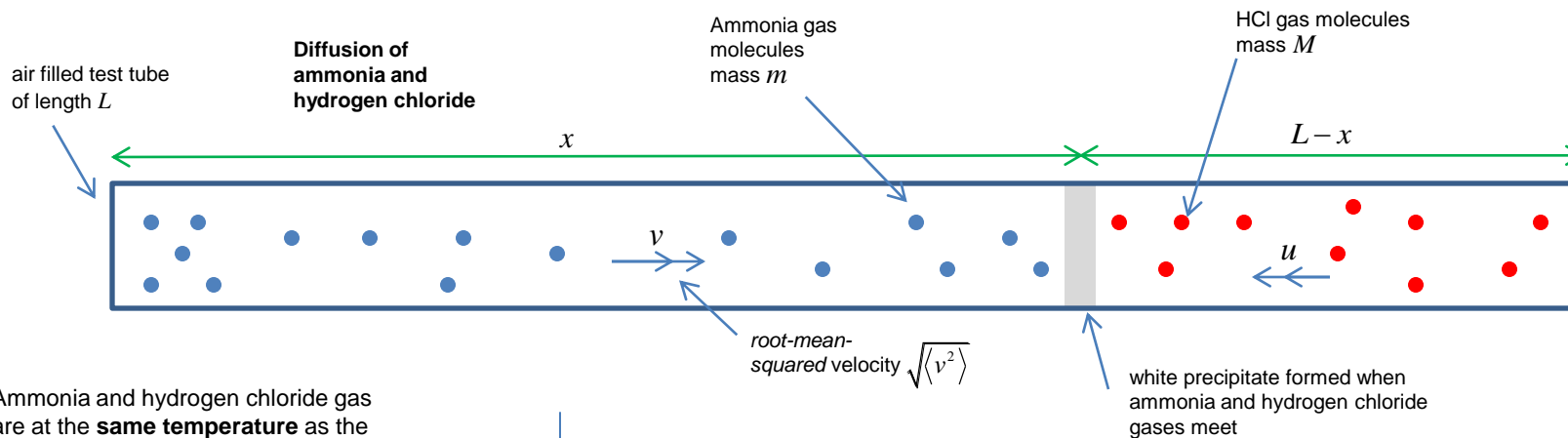
t /s	Energy added /kJ	mass lost /g	mass lost in kg
0	0.0	0	0
30	31.1	10.4	0.0104
60	62.1	21.1	0.0211
90	93.2	35.2	0.0352
120	124.2	48.6	0.0486
150	155.3	60.2	0.0602
180	186.3	74.8	0.0748
210	217.4	85.4	0.0854
240	248.4	98.5	0.0985
270	279.5	111.2	0.1112
300	310.5	125	0.125
330	341.6	138.1	0.1381
360	372.6	148.8	0.1488
390	403.7	162.9	0.1629
420	434.7	174.8	0.1748
450	465.8	188.5	0.1885
480	496.8	201.4	0.2014
510	527.9	212.3	0.2123
540	558.9	226.2	0.2262
570	590.0	237.6	0.2376
600	621.0	250.8	0.2508



Graham's law of molecular diffusion

Kinetic theory shows us the diffusion distance of molecules in thermal equilibrium varies inversely to the square root of their molecular weight.

To explain, consider an air filled tube with Ammonia gas introduced at one end, and Hydrogen Chloride gas introduced at the other.



Thomas Graham
1805-1869

Ammonia and hydrogen chloride gas are at the **same temperature** as the air molecules in the tube. **This means their average kinetic energy is the same**

$$\frac{1}{2}mv^2 = \frac{1}{2}Mu^2$$

$$\therefore \frac{v}{u} = \sqrt{\frac{M}{m}}$$

The precipitate is formed after t seconds at a distance x from the ammonia end of the tube

$$v = \frac{x}{t}, \quad u = \frac{L-x}{t}$$

$$\therefore \frac{x}{L-x} = \frac{v}{u}$$

$$\therefore \frac{x}{L-x} = \sqrt{\frac{M}{m}}$$

So diffusion distance $x \propto \frac{1}{\sqrt{m}}$

Molecular masses

NH ₃	17
HCl	36.5

Therefore expect:

$$\frac{x}{L-x} = \sqrt{\frac{36.5}{17}} \approx 1.47$$

i.e. about 3:2



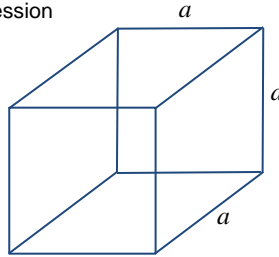
Pressure from kinetic theory – a simplified derivation that gives the correct more general result!

Assume particles collide *elastically* with the walls of a container. Since in an elastic collision the speed of wall approach = speed of recession the impulse exerted on the walls in each x,y,z direction per collision is:

$$\Delta p_{x,y,z} = 2mv_{x,y,z}$$

If we assume particles are contained within a cube of side a , the time between collisions with a given wall is:

$$\Delta t_{x,y,z} = \frac{2a}{v_{x,y,z}}$$



The factor of two is there because in any or the x,y,z directions, a particle must collide with the opposite wall before rebounding to make a second collision with a given wall.

The total average force exerted on a given wall of area a^2 is the average rate of change of momentum times the number of particles N in the cube

$$f_{x,y,z} = \frac{\Delta p_{x,y,z}}{\Delta t_{x,y,z}} = \frac{2mv_{x,y,z}}{2a/v_{x,y,z}} = \frac{mv_{x,y,z}^2}{a}$$

force due to one collision

$$\therefore \overline{F}_{x,y,z} = \frac{Nm\overline{v_{x,y,z}^2}}{a}$$

Total average force on one wall

Define the particle density $\rho = \frac{Nm}{a^3} \therefore \frac{Nm}{a} = \rho a^2 \therefore \overline{F}_{x,y,z} = \rho a^2 \overline{v_{x,y,z}^2}$

Now particle speed is given by $v^2 = v_x^2 + v_y^2 + v_z^2$

Hence since all velocities are deemed to be random, the mean squared speed is

$$\overline{v^2} = 3\overline{v_{x,y,z}^2}$$

Therefore average pressure on each wall is: $P = \frac{\overline{F}_{x,y,z}}{a^2}$

Hence: $P = \frac{1}{3}\rho\overline{v^2}$

Evaporative cooling, and the Maxwell-Boltzmann distribution of molecular speeds

Evaporation is the removal of liquid (e.g. water) from a body to the surrounding air, which is then convected away from the body. The idea is that some of the liquid molecules will be moving fast enough to break free from the inter-molecular bonds which hold the liquid together. They become gaseous and then escape. Since these molecules will represent those with the higher energies (and therefore molecular speeds), removal of them from the liquid will lower the average kinetic energy of the liquid molecules. i.e. as the liquid evaporates, it should cool. This is the principle employed in most air conditioning systems.

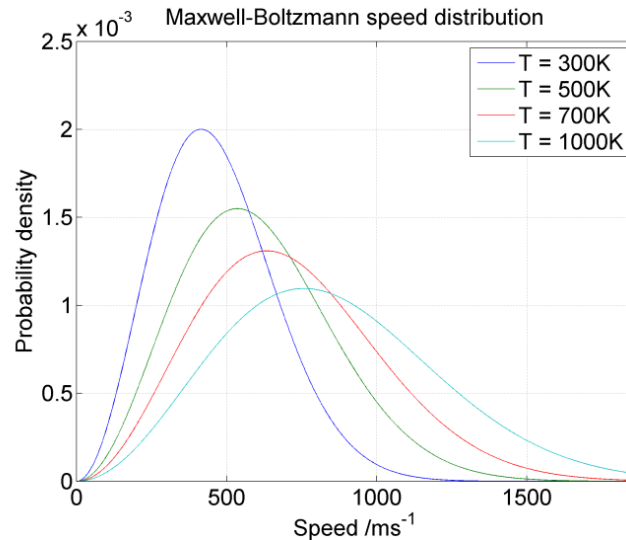
The probability density of molecular speeds follows the **Maxwell-Boltzmann distribution** As temperature reduces, the distribution becomes more narrow.

$$p(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{\frac{1}{2}mv^2}{k_B T}}$$

$$\overline{v^2} = E[v^2] = \frac{3k_B T}{m} \therefore v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}$$

$$E\left[\frac{1}{2}mv^2\right] = \frac{3}{2}k_B T \quad k_B = 1.381 \times 10^{-23} \text{ m}^2 \text{ kgs}^{-2} \text{ K}^{-1}$$

The probability distribution is consistent with the idea that temperature (in K) is **proportional to the mean KE of molecules.**



- Factors which effect the rate of evaporation**
- (1) Temperature
 - (2) Humidity
 - (3) Surface area of liquid body
 - (4) Wind speed