Lecture 30 - Temperature and ideal gas laws

Atomic Theory of Matter

To introduce the concept of temperature we need to start from the atomic theory, which considers matter to be composed of atoms.

A useful unit when discussing the mass of atoms is the atomic mass unit $[u]$

$$1u = 1.6605 \times 10^{-27} \text{kg}$$

Atoms and molecules are in continual motion, the amount of motion is proportional to the temperature, which we can think of as a measure of energy.

Brownian motion (https://en.wikipedia.org/wiki/Brownian_motion), named after Robert Brown who observed it as random movements of pollen or dust suspended in water (http://www.youtube.com/watch?v=iB7Eu7U73qg&feature=related) was explained by Albert Einstein in 1905 as a product of the thermal motion of molecules or atoms (http://www.youtube.com/watch?v=6VdMp46ZIL8&feature=related).

We can consider temperature (https://en.wikipedia.org/wiki/Temperature) to be a measure of the energy contained in the motion of the microscopic constituents of a material.

Temperature Scales

To be able to measure temperature we need a scale. The temperature scale in common usage in the United States, Fahrenheit (https://en.wikipedia.org/wiki/Fahrenheit), $^\text{o}\text{F}$ is based on what may now seem to be fairly arbitrary reference points.

Most of the world uses the Celsius (https://en.wikipedia.org/wiki/Celsius) scale, $^\text{o}\text{C}$, for everyday measurements. This is based on dividing the difference between the freezing point and boiling point of water in to 100 degrees and fixing 0^oC as the freezing point.

For thermodynamics an absolute temperature scale, in which 0 is the complete absence of thermal energy, is appropriate. This scale is the Kelvin (https://en.wikipedia.org/wiki/Kelvin) Scale. In this scale water freezes at 273.15K. Note that we do not use a degree symbol for temperatures in Kelvin.

To convert between Farenheit and Celsius you can use the fact that water freezes at 32^oF and boils at $212^\text{o}F$ to deduce that:

$$T(^\text{o}\text{C}) = \tfrac{5}{9}(T(^\text{o}\text{F}) - 32)$$

or

$$T(^\text{o}\text{F}) = \tfrac{9}{5}T(^\text{o}\text{C}) + 32$$

Thermal Equilibrium

If two objects with different temperatures are brought in to contact with one another thermal energy will flow from one to another until the temperatures are the same, and we then say that the objects are in thermal equilibrium.

The [zeroth law of thermodynamics (https://en.wikipedia.org/wiki/Zeroth_law_of_thermodynamics)](https://en.wikipedia.org/wiki/Zeroth_law_of_thermodynamics) states that:

"If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other."

This law may seem obvious but this is only because we already have some expectation from our everyday experience that temperature is a general quantity that we can measure with a thermometer. This law allows us to declare this formally, and turns out to be important, in conjunction with the First and Second Laws (we'll talk about these later!), for establishing the true definition of thermal equilibrium.

Thermal Expansion

Most, but not all, materials expand when heated. The change in length of material due to linear thermal expansion is

$$\Delta l = \alpha l_0 \Delta T$$

α is the coefficient of linear expansion of the material, measured in $(^{\mathrm{o}}\mathrm{C})^{-1}$

The length of the object after it's temperature has been changed by ΔT is

$$l = l_0(1 + \alpha \Delta T)$$

A material expands in all directions, and if we are interested in the volume changes of a rectangular object, that is isotropic, meaning it expands in the same way in all directions, then

$$\Delta V = \beta V_0 \Delta T$$

$$V_0 = l_0 w_0 h_0 \rightarrow V = l_0(1 + \alpha \Delta T) w_0(1 + \alpha \Delta T) h_0(1 + \alpha \Delta T)$$
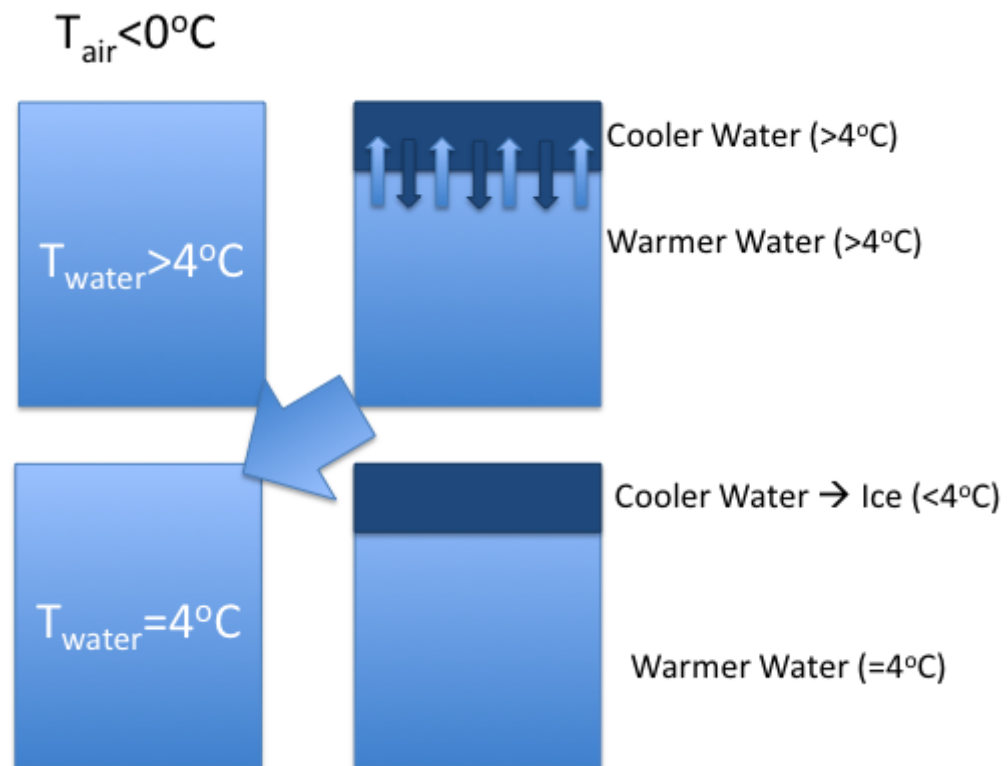
$$\Delta V = V - V_0 = V_0(1 + \alpha \Delta T)^3 - V_0 = V_0[3(\alpha \Delta T) + 3(\alpha \Delta T)^2 + (\alpha \Delta T)^3]$$

If $\alpha \Delta T >> 1$ then $\beta \approx 3\alpha$

Coefficients of thermal expansion can be found [here (http://en.wikipedia.org/wiki/Thermal_expansion)](http://en.wikipedia.org/wiki/Thermal_expansion) or your textbook.

Negative Thermal Expansion

Some materials in certain temperature ranges do not expand with temperature. An example is water, which actually decreases in volume as it's temperature is increased from $0^{\mathrm{o}}\mathrm{C}$ to $4^{\mathrm{o}}\mathrm{C}$. This has an important effect, it explains why the surface of lakes freeze, which helps prevent the flow of heat out of the lake. If the thermal expansion was normal between $0^{\mathrm{o}}\mathrm{C}$ and $4^{\mathrm{o}}\mathrm{C}$ the circulation effect would continue below $4^{\mathrm{o}}\mathrm{C}$ and the whole lake would freeze, starting from the bottom.

$T_{air} < 0°C$

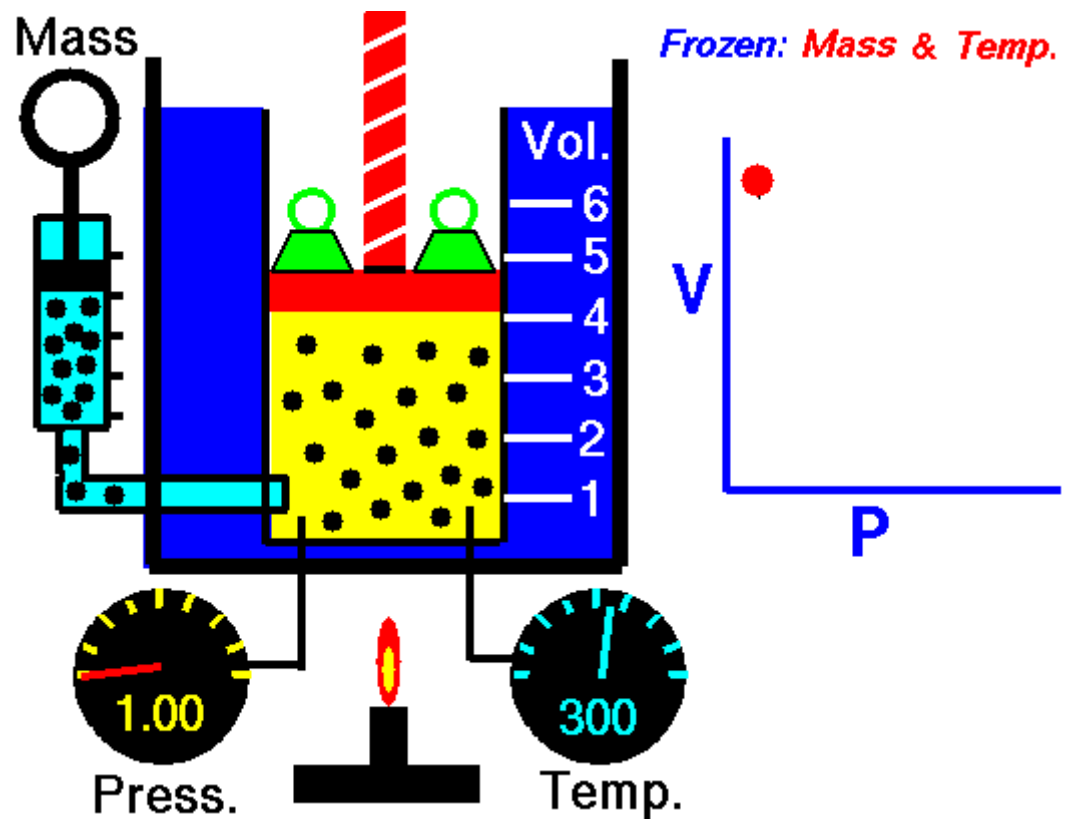
Boyle's Law

At constant temperature, it is found that the product of the pressure and volume of an ideal gas are constant

$$PV = \text{constant}$$

This is named Boyle's Law (https://en.wikipedia.org/wiki/Boyle%2527s_law), after Robert Boyle who formulated it in 1662.
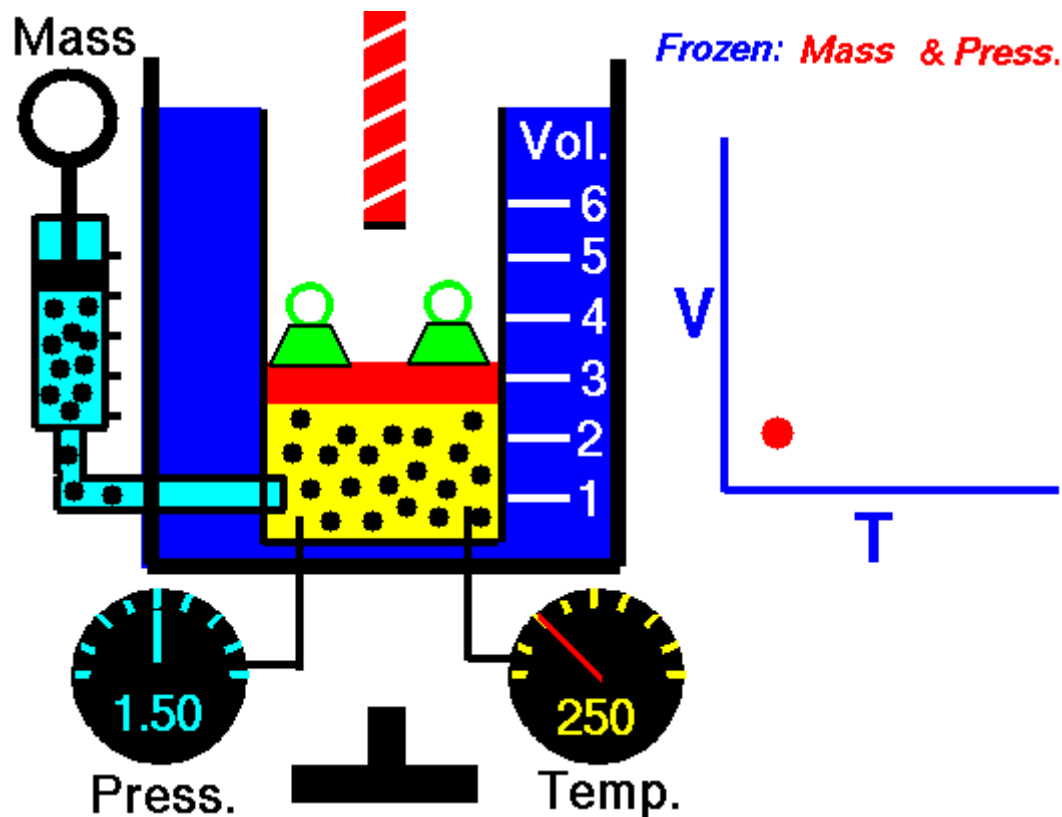
Charles' Laws

Joesph Louis Gay-Lussac published [Charles' Law
(https://en.wikipedia.org/wiki/Charles%2527s_law)](https://en.wikipedia.org/wiki/Charles%2527s_law) in 1802, attributing it to unpublished work of
Jacques Charles in the 1780's (Gay-Lussac has his own law..though it's not clear he should!).

Charles' Law states that at constant pressure the volume of a gas is proportional to the
temperature.

$$V \propto T$$

Gay-Lussac's law

[Gay Lussac's Law (https://en.wikipedia.org/wiki/Gay-Lussac%2527s_Law)](https://en.wikipedia.org/wiki/Gay-Lussac%2527s_Law) states that for a fixed volume the pressure is proportional to the temperature

$$P \propto T$$

Ideal Gas Law

The combination of the previous 3 laws implies that

$$PV \propto T$$

Our previous laws were for systems of constant mass, but we can see that the amount of mass should effect the volume (at a given pressure) or the pressure (at a given volume).

$$PV \propto mT$$

Measuring the amount of mass in moles will allow us to write the ideal gas law in terms of a universal constant. A mole of gas is a given number of molecules, Avagadro's number, $N_A = 6.02 \times 10^{23}$. If we have a certain mass m of a gas which has a certain [molecular mass (https://en.wikipedia.org/wiki/Molecular_mass)](https://en.wikipedia.org/wiki/Molecular_mass) (measured in atomic mass units, u, which are also the number of grams per mole.), the the number of moles n is given by

$$n = \frac{m[\text{g}]}{\text{molecular mass}[\text{g/mol}]}$$

and

$PV = nRT$ where $R = 8.314\text{J}/(\text{mol. K})$

This equation is the [ideal gas law (https://en.wikipedia.org/wiki/Ideal_gas_law)](https://en.wikipedia.org/wiki/Ideal_gas_law)

Ideal Gas Law for a number of molecules

The ideal gas law can also be written in terms of the number of molecules N

$$PV = nRT = \frac{N}{N_A}RT = NkT$$

where $k = \frac{R}{N_A} = \frac{8.314\text{J}/(\text{mol.K})}{6.02 \times 10^{23}} = 1.38 \times 10^{-23}\text{J/K}$ is the [Boltzmann Constant (https://en.wikipedia.org/wiki/Boltzmann_constant)](https://en.wikipedia.org/wiki/Boltzmann_constant).

Using the Ideal Gas Law to determine Absolute Zero

If $PV = nRT$ the absolute zero temperature occurs when $P = 0$. In practice most gases will liquefy before this point, but we can measure the pressure of fixed volume of gas at a couple of reference points and extrapolate down to zero pressure to get an estimate for [absolute zero (https://en.wikipedia.org/wiki/Absolute_zero)](https://en.wikipedia.org/wiki/Absolute_zero).
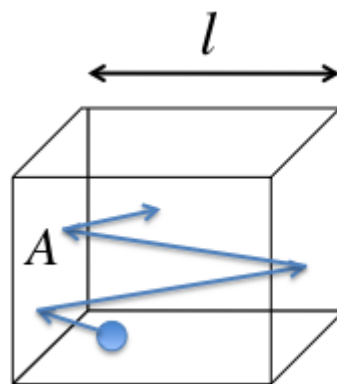
What makes a gas ideal?

There are a number of conditions which must be satisfied for a gas to be considered ideal

- There must be a large number of molecules and they should move in random directions with a range of different speeds.
- The spacing between molecules should be much greater than the size of the molecules.
- Molecules are assumed to interact only through collisions.
- The collisions are assumed to be elastic.

Ideal gas law from a molecular perspective

We can work out the pressure exerted by an ideal gas on it's container by starting from the change in momentum of a molecule when it strikes the container wall

Change in momentum on left wall

$$\Delta(mv) = mv_x - (-mv_x) = 2mv_x$$

Time between collisions on left wall

$$\Delta t = \frac{2l}{v_x}$$

The average force due to one molecule is then

$$F_{molecule} = \frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{2l/v_x} = \frac{mv_x^2}{l}$$

The net force on the wall will be the sum of the forces from all N molecules

$$F_{net} = \frac{m}{l}\Sigma_{i=1..N}v_{xi}^2$$

$$\frac{\Sigma_{i=1..N}v_{xi}^2}{N} = \bar{v_x^2} \rightarrow F_{net} = \frac{m}{l}N\bar{v_x^2}$$

$$v^2 = v_x^2 + v_y^2 + v_z^2 \rightarrow \bar{v^2} = \bar{v_x^2} + \bar{v_y^2} + \bar{v_z^2} = 3\bar{v_x^2}$$

$$F_{net} = \frac{m}{l}N\frac{\bar{v^2}}{3}$$

$$P = \frac{F}{A} = \frac{1}{3}\frac{Nm\bar{v^2}}{Al} = \frac{1}{3}\frac{Nm\bar{v^2}}{V}$$

$$PV = \frac{2}{3}N(\frac{1}{2}m\bar{v^2}) = NkT$$

$$\bar{KE} = \frac{1}{2}m\bar{v^2} = \frac{3}{2}kT$$

Maxwell Boltzmann Distribution

If we look at a simulation (https://www.falstad.com/gas/) of particles moving according to the kinetic theory we can get some idea of the distribution of the speeds of the particles.

The Maxwell-Boltzmann Distribution (https://en.wikipedia.org/wiki/Maxwell%E2%80%93Boltzmann_distribution) gives the probability $f(v)$ that a particular particle in an ideal gas has a given speed v.

$$f(v) = 4\pi(\frac{m}{2\pi kT})^{\frac{3}{2}}v^2e^{-\frac{1}{2}\frac{mv^2}{kT}}$$

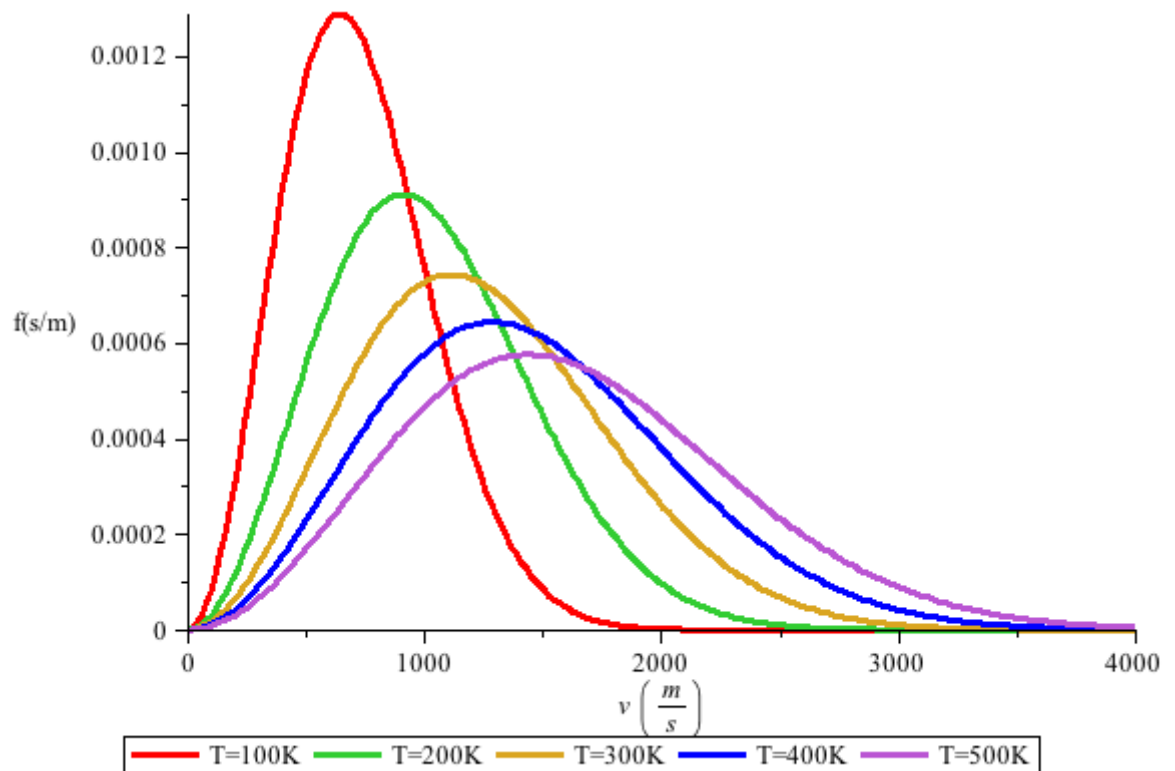It was originally derived by James Clerk Maxwell (https://en.wikipedia.org/wiki/James_Clerk_Maxwell) based on symmetry arguments, later Ludwig Boltzmann (https://en.wikipedia.org/wiki/Ludwig_Boltzmann) derived it on a more general basis.
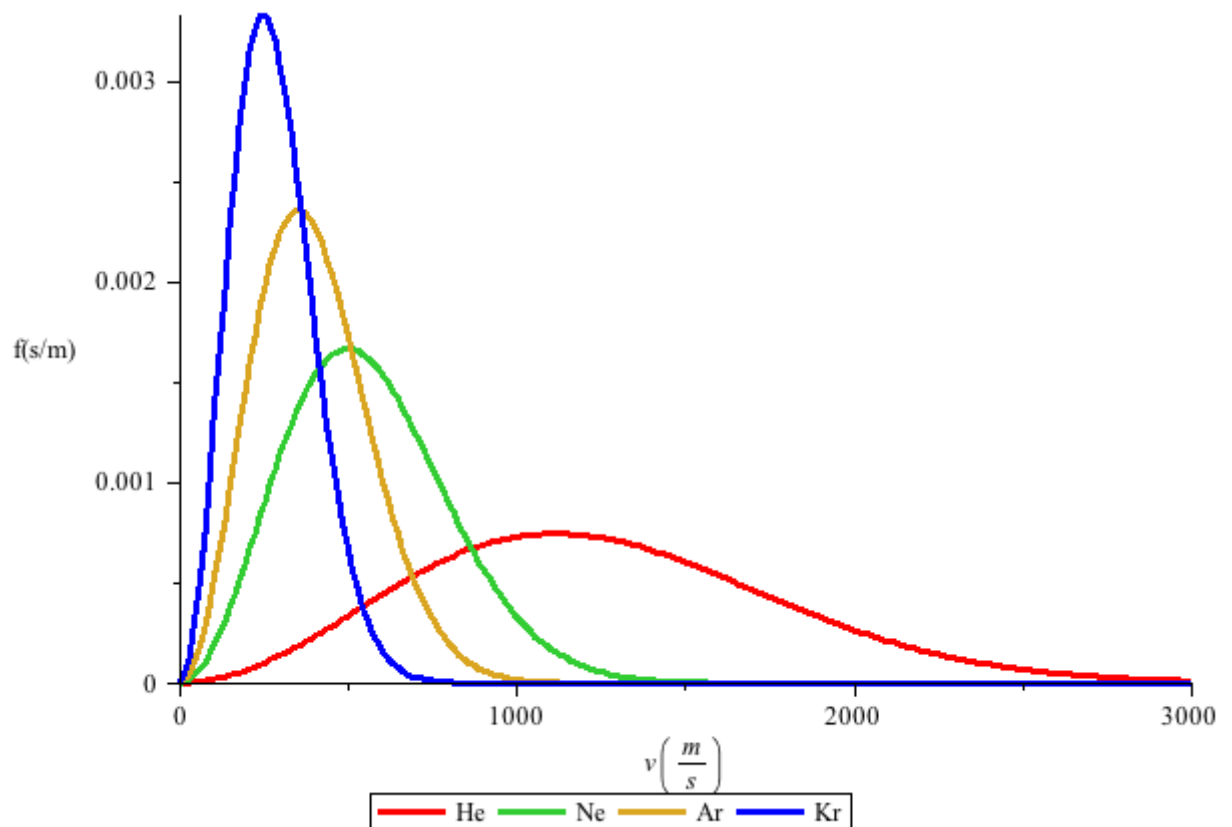
Temperature dependence

The distribution of speeds is highly temperature dependent and is predicted by the Maxwell distribution.

The plot below is for He atoms at various temperatures.

Mass dependence

The speed distribution is also a function of the mass of the molecules, the plot below is for the first 4 noble gasses at room temperature.

In [6]:
```python
import numpy as np
import matplotlib.pyplot as plt

k_B = 1.380648e-23   # boltzmann contant (J/K)
uma = 1.66054e-27 # kg/uma
def pmod(v, T, m):
    """
        Maxwell-Boltzmann's distribuion of probability
        for the length of the velocity vector v at temprature T
        for a particle of mass m
    """
    return 4 * np.pi * v**2 * np.power(m / (2 * np.pi * k_B * T), 3 / 2) *

v = np.arange(0,3000,0.1) # velocity range in m/s
#T =  np.arange(0,3000,0.1)
T = 300 #K
m = 18*uma # u, mass of Ar

p_v= pmod(v,T,m)

plt.plot(v,p_v, label='Ar')
plt.xlabel("speed (m/s)")
plt.ylabel("P(v) (m)")

m = 54*uma # u, mass of Xe

p_v= pmod(v,T,m)

plt.plot(v,p_v, label='Xe')
plt.xlabel("speed (m/s)")
plt.ylabel("P(v) (m)")

plt.legend(loc="upper right")
plt.show()
```
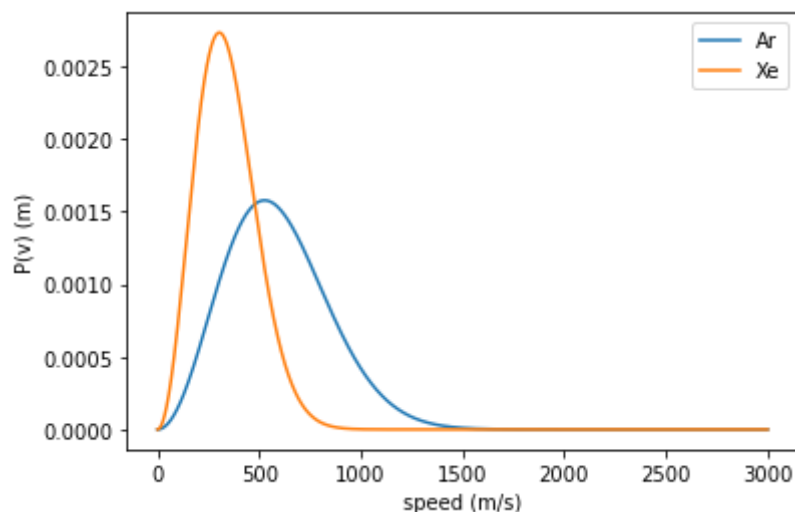

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