$$\frac{1}{2}mc^2 = \frac{3}{2}(R/N_0)T$$

R/N_0 is the (gas constant) / molecule and is called Boltzmann's constant $k = (R/N_0)$

$$\boxed{\frac{1}{2}mc^2 = \frac{3}{2}kT}$$

Kool result!!

$$N_0(\frac{1}{2}mc^2) = \frac{3}{2}RT$$

$N_0\left(\frac{1}{2}mc^2\right)$ is the kinetic energy of one mole of gas atoms

Since $N_0 m = M$ (molecular weight) → $(1/2)Mc^2 = (3/2)RT$

Units: $\frac{mc^2}{2}$ is a kinetic energy, therefore

$$PV = n\left(\frac{2}{3}\right)N_0\left(\frac{mc^2}{2}\right)$$ must also have units of energy

PV ~ [pressure] [volume]

= [(force / Area)] [(Area) (Length)]

PV ~ force × length

Energy = Force × Distance

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Typical Molecular Speeds

Understand that $c = \sqrt{\overline{c^2}} = c_{rms}$ [Root Mean Square Speed]

[Later we will define c_{rms} more fully.]

$(1/2)mc^2 = (3/2)kT$ $\rightarrow$ $c = (3kT/m)^{1/2}$

Notice: $c = (3N_0kT/N_0m)^{1/2}$ [N_0 is Avagadro's number]

But $N_0k = R$ and $N_0m = M$ (molecular weight)

$c = (3RT/M)^{1/2}$ $\rightarrow$ $c^2 = 3RT/M$

Consider Gas with At wt of 0.001 Kg/mole (H atoms!)

R= 8.314 Joules/mole-deg, T = 300 deg

$c^2 = 3RT/M = 7.47 \times 10^6$ Joules/Kg $= 7.47 \times 10^6$ (m/sec)^2

Typical Molecular Speeds

Understand that $c = \sqrt{\overline{c^2}} = c_{rms}$ [Root Mean Square Speed]

$(1/2)mc^2 = (3/2)kT$ → $c = (3kT/m)^{1/2}$

Consider Gas with At wt of 0.001 Kg/mole (H atoms!)

$m = (0.001 \text{ Kg / mole}) / (6.02 \times 10^{23} \text{ molecule / mole})$
$= 1.66 \times 10^{-27}$ Kg/molecule

$k = 1.38 \times 10^{-23}$ Joules/molecule - deg, $T = 300$ deg

$c^2 = 3kT/m = 7.47 \times 10^6 \text{ Joules/Kg} = 7.47 \times 10^6 \text{ (m/sec)}^2$

$c = 2.73 \times 10^3$ m/sec (Fast Moving Particle)

$c = 1.37 \times 10^3$ m/sec for He = 0.004 Kg/mole

Note $c \sim T^{1/2}$ → $c_{1200} = 2\ c_{300}$,

Note $c \sim 1/m^{1/2}$ → $c_{H_2} = 4c_{O_2}(M_{H_2} = 2, M_{O_2} = 32)$

Why do Light and Heavy Gases Exert Same Pressure at Constant V,T, n (# moles)? (p = nRT/V)

wall collision frequency/unit area =
(1/6) (N/V) (Ac t)/(At) = (1/6) (N/V) c However, since

$$c \sim \frac{1}{\sqrt{m}}$$

Lighter molecules collide with wall more frequently than heavy molecules!

BUT momentum change per collision ~ mc, with

$$mc \sim \frac{m}{\sqrt{m}} \sim \sqrt{m}$$

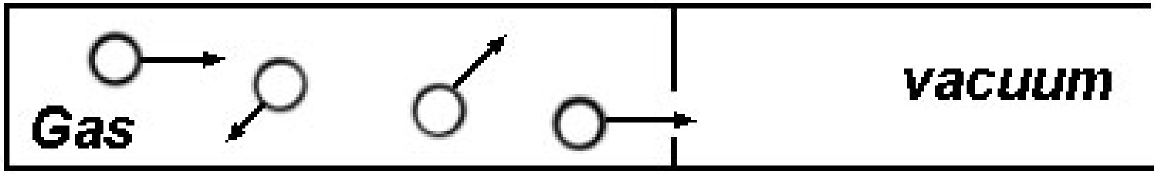
Thus, heavier molecules transfer more momentum per impact

Two effects cancel since $(1/m^{1/2}) \times (m^{1/2})$ is independent of m

Result is that p scales like n, the number of moles or the number of particles! $pV = nRT$

Experimental Evidence for Kinetic Theory: Effusion

Put very small hole in box and measure # of molecules coming through. If hole is really small , molecules won't know it's there and will collide with hole at same rate as they collide with the wall.

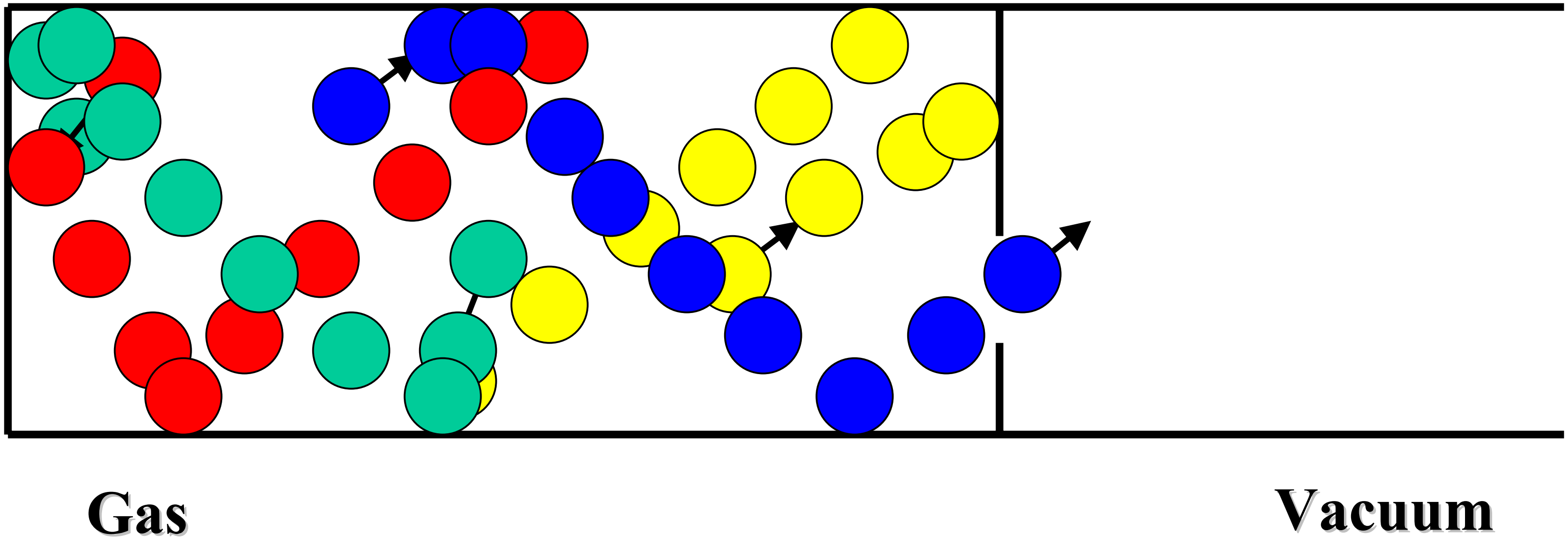


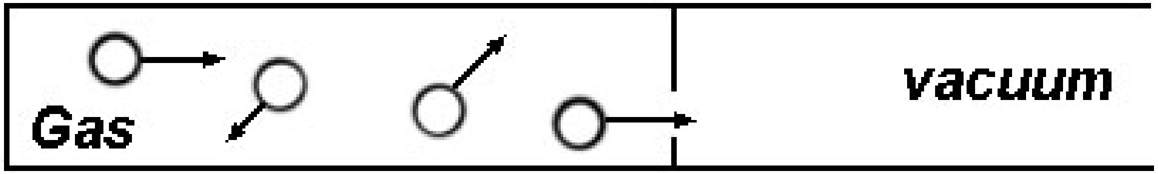
Effusion of Gases: The Movie

QuickTime™ and a
Video decompressor
are needed to see this picture.

Note:
← Hole
Must be
very small!

Effusion of a Gas through a Small Hole





If hole area = A, rate at which molecules leave = (1/6) (N / V) Ac = R

For two different molecular speeds c_1, c_2 and concentrations N_1/V, N_2/V:

$$\frac{R_1}{R_2} = \left[\left(\frac{N_1}{V}\right) / \left(\frac{N_2}{V}\right)\right]\left(\frac{c_1}{c_2}\right)$$

If $N_1 = N_2$ (equal initial concentrations)

$$\frac{R_1}{R_2} = \left(\frac{c_1}{c_2}\right) = \frac{\sqrt{\frac{3kT}{m_1}}}{\sqrt{\frac{3kT}{m_2}}} \rightarrow (R_1/R_2) = (m_2/m_1)^{1/2}$$

For m_1 being H_2 and m_2 being O_2 → $\frac{R_1}{R_2} = \sqrt{\frac{32}{2}} = 4$

Find experimentally that light gases escape more quickly than heavy ones!

Experimental Evidence for Kinetic Theory:Heat Capacities

Definition: Heat in calories needed to raise temperature of 1 mole of a substance 1° centigrade.

Two kinds: C_p (add heat at constant pressure)
C_v (add heat at constant volume)

Adding heat means adding energy. Energy goes two places:

(1) Increases kinetic energy of molecules:

KE = (1/2) mc^2, $c^2 \sim T$

(2) Perform work.

As we shall see shortly, no work is done at constant volume.

C_v: volume constant. All heat goes to KE. Compute as follows:

$$\text{KE [1 mole gas]} = \frac{1}{2}mc^2 \times N_0 = \frac{3}{2}kTN_0 = \frac{3}{2}RT$$

Increase T from T_1 to T_2 : KE_1=(3/2)RT_1 & KE_2=(3/2)RT_2

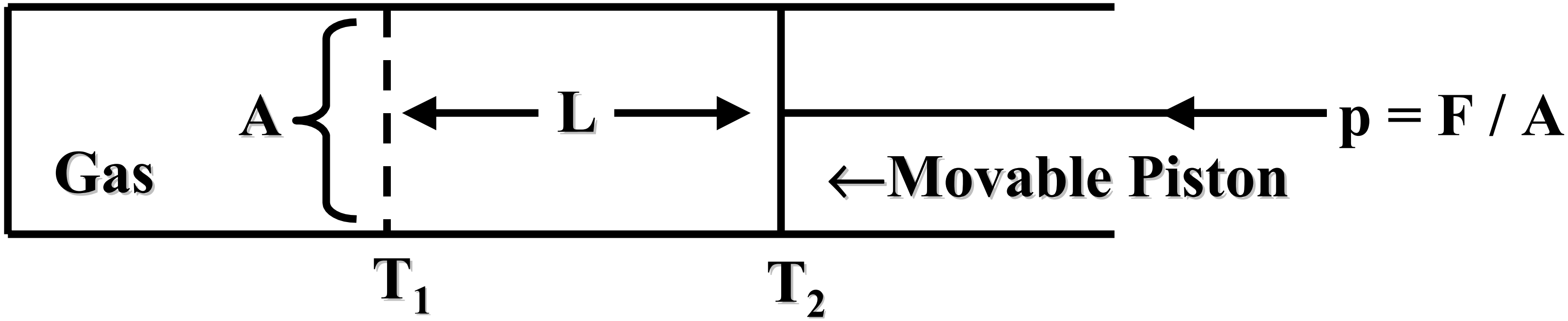
$$KE_2 - KE_1 = \frac{3}{2}R(T_2 - T_1) = \text{energy to increase T form } T_1 \text{ to } T_2$$

By definition when T_2 -T_1 = 1° KE_2 - KE_1 = C_v

C_v = (3/2) R

(Independent of T for an ideal gas)
($C_v \cong 3$ cal / mole - deg)

C_p: Pressure constant so volume increases with increase in T. As we see below, work is done in this case:



$$\text{work} = F \times L = (Ap) \times L = p \text{ x } (AL)$$

But, $AL = V_2 - V_1 = \Delta V$ (volume change)

$$\text{work} = p \text{ x } (AL) = p(V_2 - V_1) = nR(T_2 - T_1) = nR\Delta T$$

$w = p\Delta V = nR\Delta T$ → **For $n=1$ mole, $\Delta T=1°$, $w = R$**

To raise temperature of one mole of gas by one degree must do R units of work.

Heat Capacity at constant pressure has two terms:

C_p = heat added to increase KE + heat added to do work

For $n = 1$ mole and $T_2 - T_1 = \Delta T = 1$ degree:

KE change = $\Delta(KE) = (3/2)\, R\, \Delta T = (3/2)\, R$, (same as for C_v)

Work = $w = R\, \Delta T = R$

$C_p = \Delta(KE) + w = (3/2)\, R + R$

Predict $C_p = (5/2)\, R$ for an ideal gas.

Remember that $C_v = (3/2)\, R$

Heat Capacity Summary for Ideal Gases:

$C_v = (3/2)\,R$, KE change only. Note, C_v independent of T.

$C_p = (3/2)\,R + R$, KE change + work. Also Independent of T

$C_p/C_v = [(5/2)R]/[(3/2)R] = 5/3$

$C_p/C_v = 1.67$

Find for monatomic ideal gases such as He, Xe, Ar, Kr, Ne

$C_p/C_v = 1.67$

For diatomics and polyatomics find $C_p/C_v < 1.67$!

Since work argument above

$P(V_2 - V_1) = RT$ is simple and holds for all gases,

This suggests $KE > (3/2)RT$ for diatomics,

This would make $C_p/C_v < 1.67$

A possible solution:

Equipartition Theorem: This is a very general law which states that for a molecule or atom:

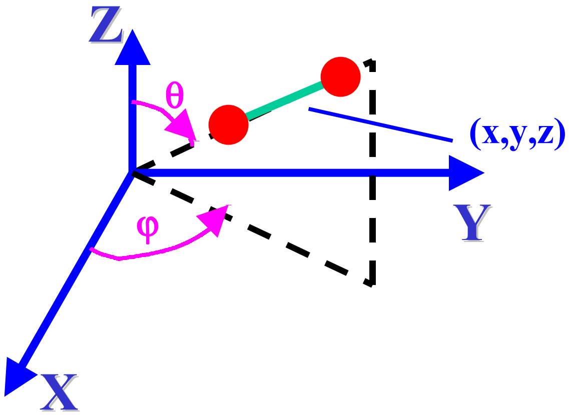
$KE = (1/2)kT$ (or 1/2 RT on a mole basis) per degree of freedom.

A degree of freedom is a coordinate needed to describe position of a molecule in space.

Example: A point has 3 degrees of freedom because it requires three coordinates to describe its position: (x, y, z).

Thus $\text{KE} = 3\left(\frac{1}{2}\text{kT}\right) = \frac{3}{2}\text{kT}$ as for a monatomic gas

A diatomic molecule is a line (2 points connected by a chemical bond). It requires 5 coordinates to describe its position: x, y, z, θ, φ



$$\text{KE} = 5\left(\frac{1}{2}\text{kT}\right) = \frac{5}{2}\text{kT}$$

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