

Ideal Gases

Experimental results on gases:

Boyle's Law

$PV = \text{constant}$ (fixed amount of gas,
constant T)

Charles' Law

$V/T = \text{constant}$ (fixed amount of gas,
constant P)

(T is in Kelvins)

Combining these two laws:

THE IDEAL GAS LAW

$$PV = nRT$$

where n is the number of moles of gas
and R is the gas constant,
 $R = 8.31 \text{ J}/(\text{mol} \cdot \text{K})$

Alternate form:

$$PV = NkT$$

where N is the number of molecules in the gas

and k is the Boltzmann's constant,

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

(Comparing the two forms gives $R = N_A k$.)

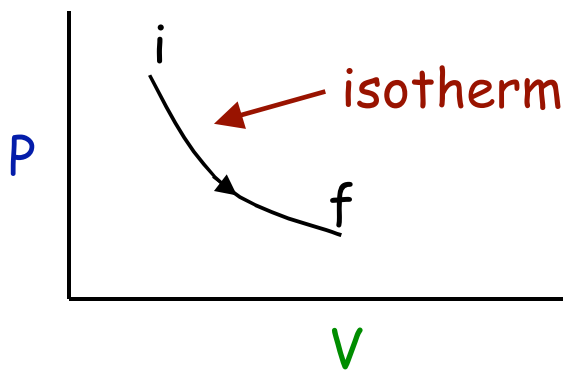
All real gases approach the "ideal gas" in the limit of very low density.

Work done at constant T

(ideal gas)

Isothermal expansion:

$$PV = nRT = \text{constant}$$



$$P = nRT/V$$

• Isotherm: a curve along which T is constant.

Work done by gas: $\Delta W = \int_i^f P dV$

$$\Delta W = \int_i^f (nRT/V) dV = nRT \ln(V_f/V_i)$$

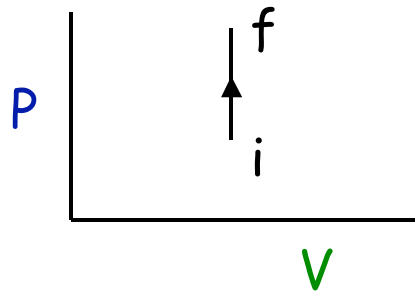
Note: if $V_f > V_i$ (expansion), then ΔW is +
if $V_f < V_i$ (compression), then ΔW is -

Work done in other processes

$$\Delta W = \int_i^f P dV$$

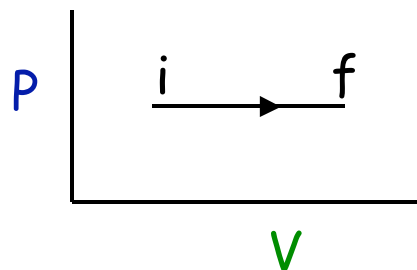
Constant Volume:

$$\Delta W = 0$$



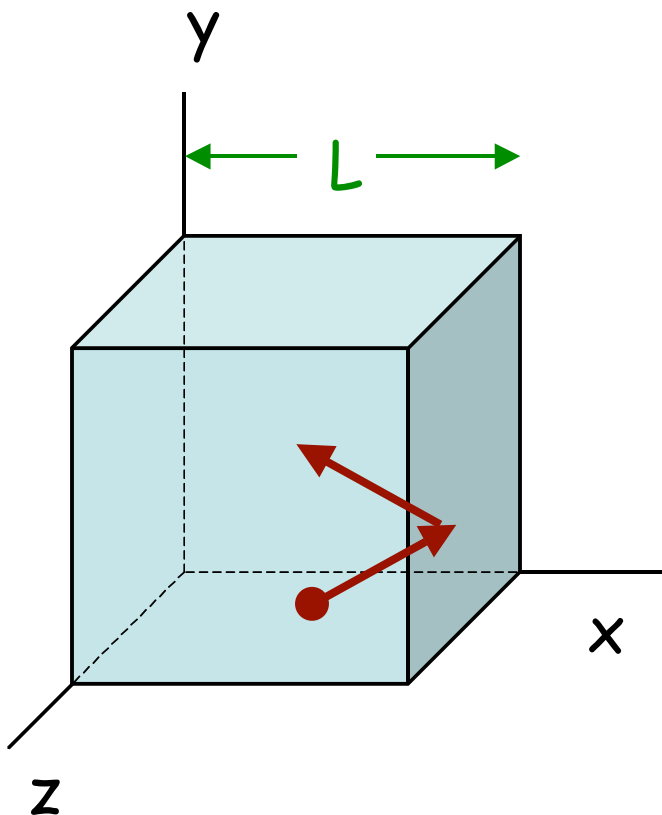
Constant Pressure:

$$\Delta W = P (V_f - V_i)$$



Kinetic Theory of Gases

Consider N molecules (n moles with $n = N/N_A$) in a cubical box of side L , i.e. $\text{Volume} = L^3$.



Change in momentum at the x-wall is

$$\Delta p_x = 2 m v_x$$

Time between collisions with the x-wall is

$$\Delta t = 2 L / v_x$$

Average rate of change of momentum in x-direction:

$$\Delta p_x / \Delta t = (2mv_x) / (2L/v_x) = m v_x^2 / L$$

This is force exerted by the molecule.

$$\text{Total Force} = \sum_{i=1}^N (m v_x^2)_i / L$$

$$\begin{aligned} \text{Pressure } P &= \text{Force/Area} = F/L^2 \\ &= (m/L^3) \sum (v_x^2)_i \end{aligned}$$

$$\square \quad P = (m/L^3) N \langle v_x^2 \rangle$$

average

$mN = nM$ is the total mass.

where $n = \#$ of moles
 $M =$ molar mass

$$\square \quad P = (nM/V) \langle v_x^2 \rangle$$

For any molecule: $v^2 = v_x^2 + v_y^2 + v_z^2$

$$\square \langle v_x^2 \rangle = (1/3) \langle v^2 \rangle$$

$$\square P = (nM/3V) \langle v^2 \rangle$$

Define **root-mean-square speed** v_{rms} :

$$v_{rms} = \sqrt{\langle v^2 \rangle}$$

$$\square PV = (nM/3) v_{rms}^2$$

From ideal gas law: $PV = nRT$

$$\square (nM/3) v_{rms}^2 = nRT$$

$$\square v_{rms} = \sqrt{3RT/M}$$

microscopic v_{rms} \square macroscopic T

Kinetic Energy

Average (translational) kinetic energy per molecule

$$= (1/2) m \langle v^2 \rangle = (1/2) m (3RT/M)$$

Using $M/m = N_A$,

$$\langle K \rangle = 3RT/(2N_A) = (3/2) k T$$

$$\square \quad \langle K \rangle = (3/2) k T$$

A measurement of the Temperature of a gas is equivalent to a measure of the average kinetic energy of its molecules.

Molecular Speeds at Room Temp (T=300 K)

<u>Gas</u>	<u>molar mass(g)</u>	<u>v_{rms}(m/s)</u>
Hydrogen, H ₂	2	1920
Helium, He	4	1370
Water vapor, H ₂ O	18	645
Nitrogen, N ₂	28	517
Oxygen, O ₂	32	483
Carbon Dioxide, CO ₂	44	412
Sulfer Dioxide, SO ₂	64	342

Table 20.1

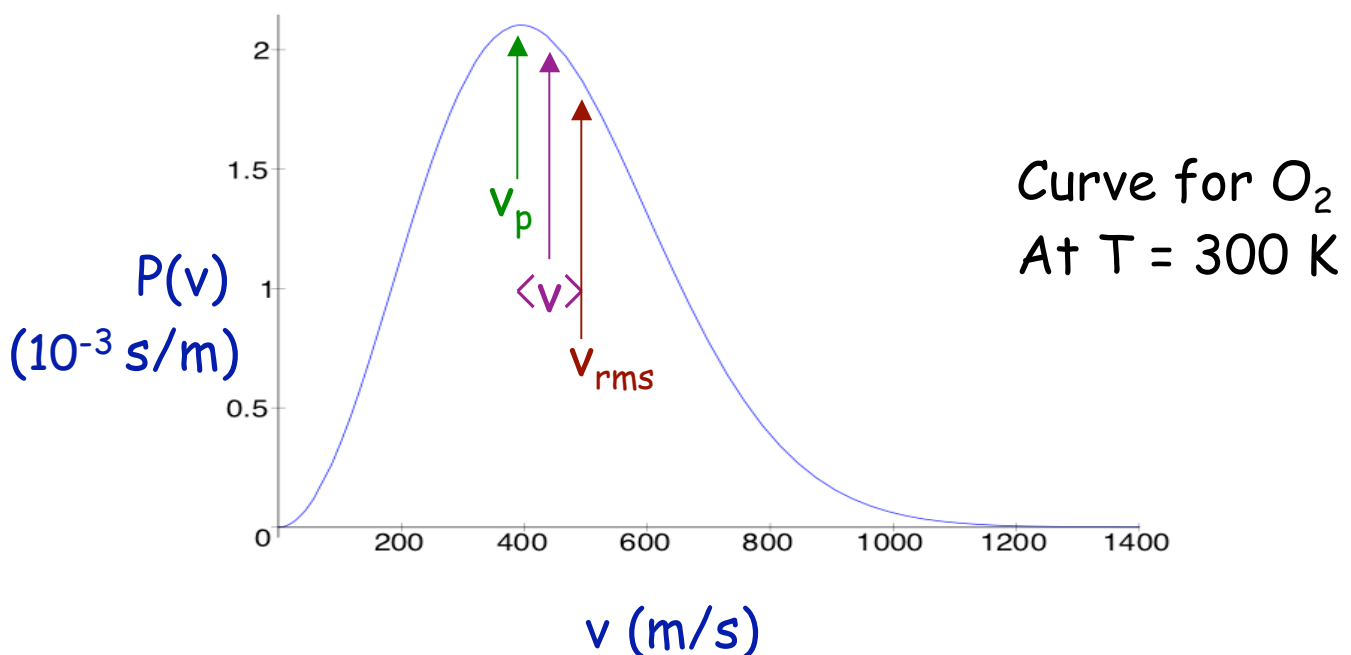
Maxwell's Speed Distribution

The distribution of molecular speeds was first written down by Maxwell (1852):

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

$P(v) dv$ is the probability that a molecule has speed between v and $v + dv$.

It is normalized to 1. $\int_0^\infty P(v) dv = 1$.



Average speed:

$$\langle v \rangle = \int_0^{\infty} v P(v) dv = \sqrt{8RT/(\pi M)}$$

Root-mean-square speed:

$$\langle v^2 \rangle = v_{\text{rms}}^2 = \int_0^{\infty} v^2 P(v) dv = 3RT/M$$

Most probable speed (maximum of distribution curve):

$$v_p = \sqrt{2RT/M}$$

Internal Energy

(due only to **kinetic energy** of atoms)

- Monatomic gas - Single atoms:

$$U = N \left(\frac{3}{2}\right) kT = \left(\frac{3}{2}\right) nN_A kT = \left(\frac{3}{2}\right) nRT$$

Each atom has **3 Degrees of Freedom**.
(K. E. in x, y, or z directions).

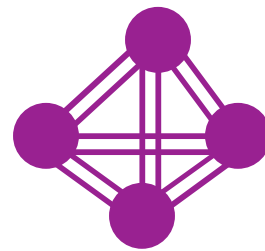
- Diatomic molecule:



Rotates (in two planes)

□ **5 degrees of freedom.**

$$U = \left(\frac{5}{2}\right) nRT$$



- Polyatomic molecule:

Rotates in all 3 planes

□ **6 degrees of freedom.**

(3 translational + 3 rotational).

$$U = \left(\frac{6}{2}\right) nRT = 3 nRT$$

"Equipartition of Energy"

Molar Specific Heats

(of ideal gas)

Recall: Specific heat tells how T changes as Q is added.

This depends on the conditions:
Constant V or Constant P .

Constant Volume: $\Delta Q = n C_V \Delta T$
where C_V is specific heat at constant V .

1st Law of TD: $\Delta Q = \Delta U + \Delta W$

At constant V , $\Delta W = 0$.

$\Delta Q = \Delta U = (3/2) nR \Delta T$ (monatomic gas)

Comparing with definition of C_V gives:

$$C_V = (3/2) R = 12.5 \text{ J}/(\text{mol} \cdot \text{K})$$

Constant Pressure: $\Delta Q = n C_p \Delta T$

where C_p is specific heat at constant P.

1st Law of TD: $\Delta Q = \Delta U + \Delta W$

At constant P, $\Delta W = P \Delta V$.

Ideal gas law: $P \Delta V = nR \Delta T$

$$\Delta Q = (3/2) nR \Delta T + nR \Delta T = (5/2) nR \Delta T$$

$$C_p = (5/2) R \text{ (again, for monatomic gas)}$$

In General:

$$C_p = C_v + R$$

Quantum Mechanics and Equipartition of Energy

Quantum Theory predicts:

rotational energies are quantized
(only have certain discrete values).

- Rotational degrees of freedom only “turn on” above some minimum temperature (roughly when kT is larger than the lowest rotational energy level of the molecule).

(Fig. 20-12 of HRW)