Ideal Gases

Experimental results on gases:

Boyle's Law

PV = constant (fixed amount of gas,
constant T)

Charles' Law

V/T = 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,

$$k = 1.38\times10^{-23}\ \mathrm{J/K}$$

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

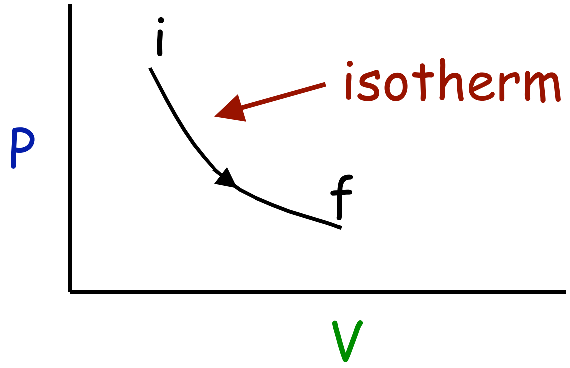
All real gases approach the "ideal gas" in the limit of very low density.

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: $\square W = \int_i^f P\,dV$

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

Note: if $V_f > V_i$ (expansion), then $\square W$ is +

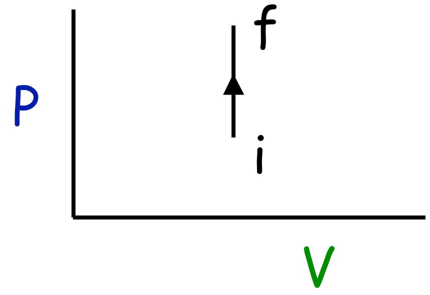
if $V_f < V_i$ (compression), then $\square W$ is -

Work done in other processes

$$\square W = \int_i^f P \, dV$$

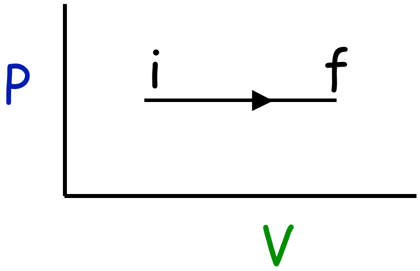
Constant Volume:

$\square W = 0$



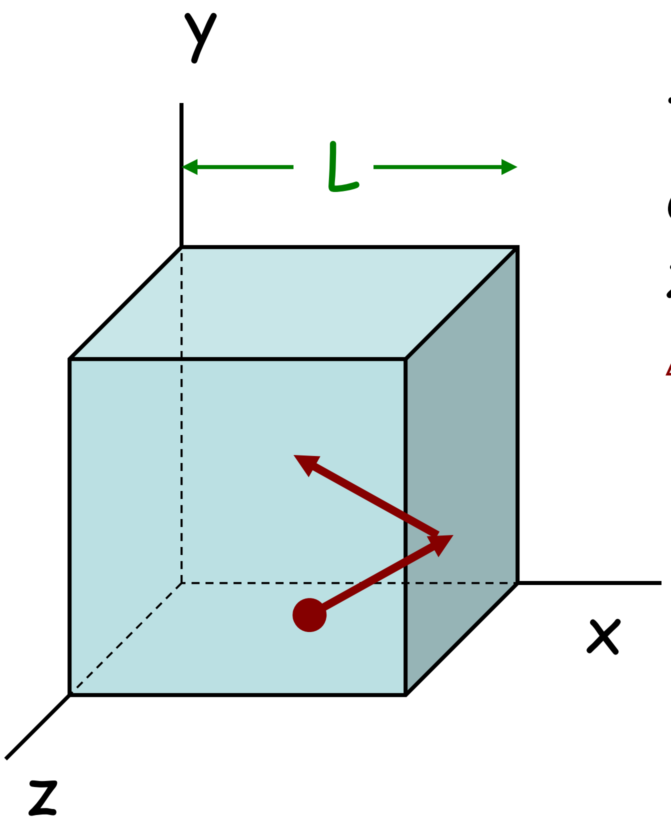
Constant Pressure:

$\square W = P\,(V_f - V_i)$



Kinetic Theory of Gases

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



Change in momentum at the x=L wall is
$\Delta p_x = 2\, m\, v_x$

Time between collisions with the x=L wall is
$\Delta t = 2\, L / v_x$

Average rate of change of momentum in x-direction:

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

This is force exerted by the molecule.

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

$$\text{Pressure } P = \text{Force/Area} = F/L^2$$

$$= (m/L^3) \sum (v_x^2)_i$$

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

average

mN = nM is the total mass.

where n = # of moles
M = molar mass

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

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

$\Rightarrow \quad \langle v_x^2 \rangle = (1/3) \; \langle v^2 \rangle$

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

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

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

$\Rightarrow \quad PV = (nM/3)\, v^2_{rms}$

From <u>ideal gas law</u>: $PV = nRT$

$\Rightarrow \quad (nM/3)\, v^2_{rms} = nRT$

$$\Rightarrow \quad \boxed{v_{rms} = \sqrt{3RT/M}}$$

microscopic $v_{rms} \Leftrightarrow$ macroscopic T

Kinetic Energy

Average (translational) kinetic energy per molecule

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

Using $M/m = N_A$,

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

□ $$\boxed{\langle K \rangle = (3/2)\, k\, T}$$

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)

Gas	molar mass(g)	v_{rms}(m/s)
Hydrogen, H_2	2	1920
Helium, He	4	1370
Water vapor, H_2O	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

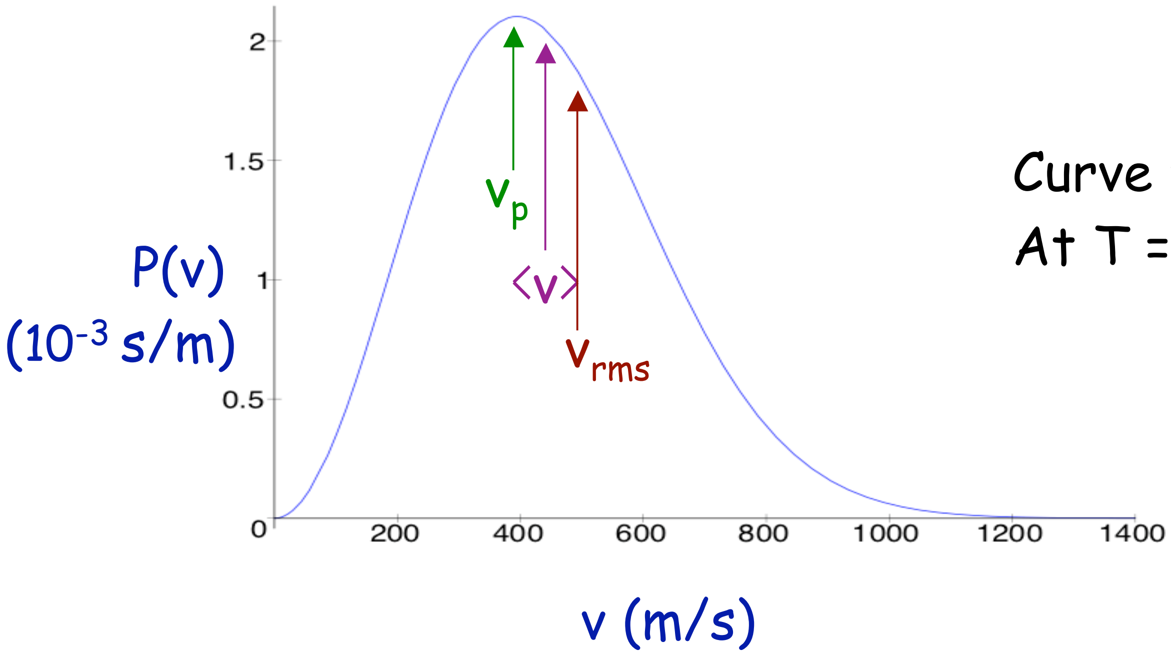
Maxwell's Speed Distribution

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

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

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

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



Curve for O_2
At T = 300 K

Average speed:

$$\langle v \rangle = \int_0 v\, P(v)\, dv = \sqrt{8RT/(\square M)}$$

Root-mean-square speed:

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

Most probable speed (maximum of distribution curve):

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

The velocity function is known as the Maxwell-Boltzmann distribution

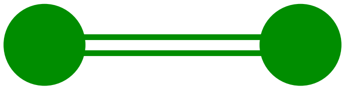
Internal Energy

(due only to kinetic energy of atoms)

- Monatomic gas - Single atoms:

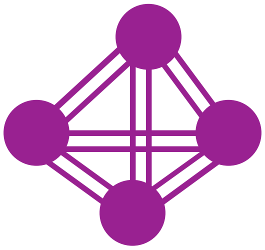
$U = N\,(3/2)\,kT = (3/2)\,nN_A kT = (3/2)\,nRT$

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.

$U = (5/2)\,nRT$



- Polyatomic molecule:
  Rotates in all 3 planes
  □ 6 degrees of freedom.
  (3 translational + 3 rotational).

$U = (6/2)\,nRT = 3\,nRT$

"Equipartion 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, $\Delta W = 0$.

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

Comparing with definition of C_V gives:

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

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: $P\, \Delta V = nR\, \Delta T$

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

$\Rightarrow \quad C_p = (5/2)\, R$ (again, for monatomic gas)

In General:

$$\boxed{C_P = C_V + R}$$

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. 19-11 of Fishbane)

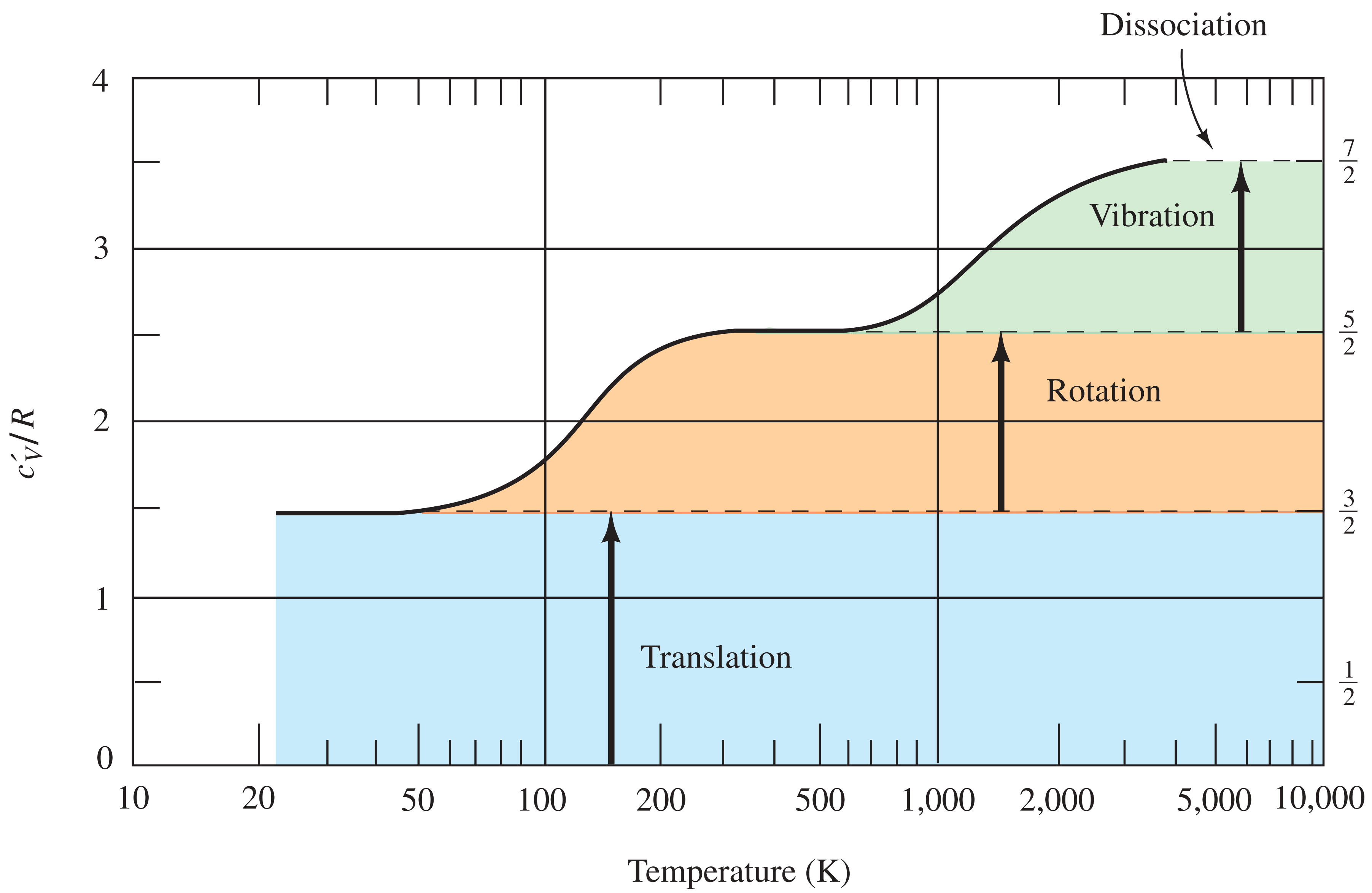


Figure Number: 19 11
Fishbane/Gasiorowicz/Thornton
Physics for Scientists and Engineers, with
Modern Physics 3E

Adiabatic Expansion ($\Delta Q = 0$)

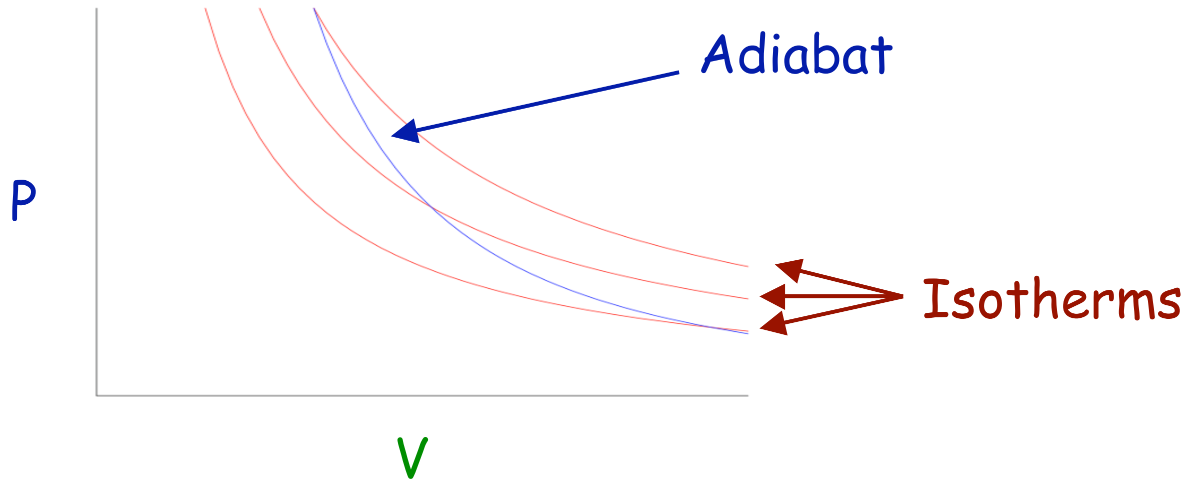
Occurs if:

- change is made sufficiently quickly
- and/or with good thermal isolation.

Governing formula:

$$PV^{\gamma} = \text{constant}$$

where $\gamma = C_P/C_V$



Because PV/T is constant (ideal gas):

$V^{\gamma-1}T = \text{constant}$ (for adiabatic)

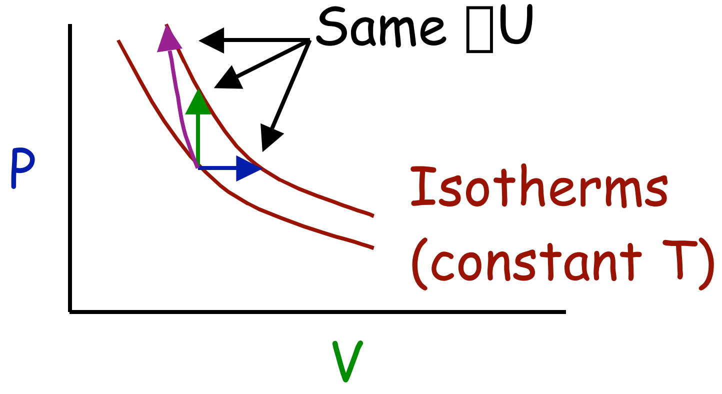
Proof of $PV^{\square}$=constant

(for adiabatic process)

1) Adiabatic: $dQ = 0 = dU + dW$

$= dU + PdV$

2) U only depends on T:



$dU = n\,C_V\,dT$ (derived for constant volume, but true in general)

3) Ideal gas: $T = PV/(nR)$

$dT = [(dP)V + P(dV)]/(nR)$

Plug into 2): $dU = (C_V/R)[VdP + PdV]$

Plug into 1): $0 = (C_V/R)[VdP + PdV] + PdV$

Rearrange:

$$
\begin{aligned}
(dP/P) &= -\,(C_V+R)/C_V\,(dV/V) \\
&= -\,\gamma\,(dV/V)
\end{aligned}
$$

where $\gamma = (C_V+R)/C_V = C_P/C_V$

Integrate both sides:

$\ln(P) = -\,\gamma\ln(V) + \text{constant}$

or

$\ln(PV^{\gamma}) = \text{constant}$

or

$PV^{\gamma} = \text{constant}$

<u>QED</u>