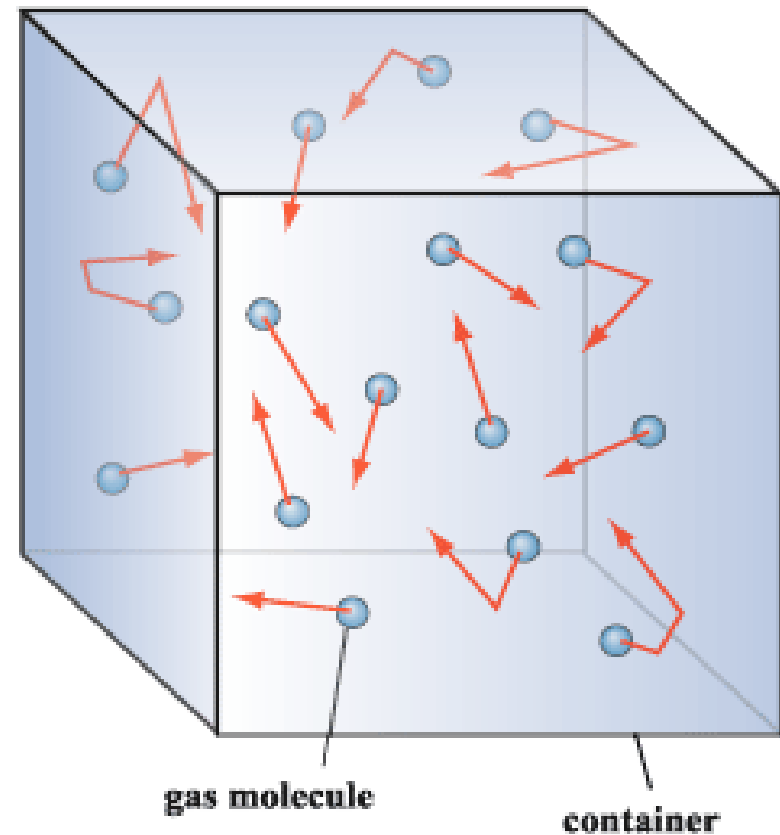


Lecture 14
Chapter 19
Ideal Gas Law and
Kinetic Theory
of Gases

Chapter 20
Entropy and the Second
Law of Thermodynamics

Now we to look at temperature, pressure, and internal energy in terms of the motion of molecules and atoms? Relate to the 1st Law of Thermodynamics



- Thermal expansion cracking the nut. (Strength of electrical forces)
- Jug O' Air (Inflate with bike pump and watch temp. rise)
 $p/T = \text{constant}$
- Boiling by Cooling (Ice on beaker)
- Boiling by Reducing Pressure (Vacuum in Bell jar)
- Dipping Duck Toy
 - wet head cools as water evaporates off it -
 - pressure drops inside head
 - contained pressure pushes water up tube
 - when center of gravity is exceeded head tips
 - exposes bottom of tube then pressure equalized
- Leslie cube and the laser thermometer.

- Pressure reduction due to cooling inside coke can crushing it when placed in water. $pV=nRT$, $p/T=\text{constant}$

Thermal effects using liquid nitrogen again.

For air in the balloon at room temp

At room temp we have $pV=nRT$ and $T=273K$

then dip it liquid nitrogen

$p'V'=nRT$ with $T=78K$,

$p'V'$ should be smaller by a factor of $273/78=3.5$
compared to pV

So why does the balloon get a lot smaller?

Since air boils at 90 K, air is liquid at 78 K and is no longer a gas so the ideal gas law does not apply.)

Avogadro's Number

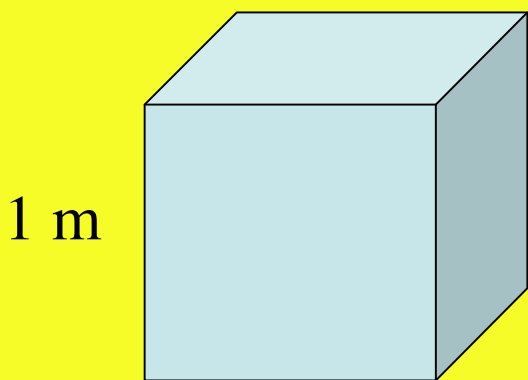
How many molecules are there in a cubic meter of air at STP?

First, find out how much mass there is.

The mass is the density times the volume.

$$m = 1.2 \text{ kg/m}^3 \times 1 \text{ m}^3 = 1.2 \text{ kg. (or 2.5 lbs)}$$

Now find the number of moles in the cubic meter and multiply by Avogadro's number



Avogadro's Number

$N_A = 6.02 \times 10^{23}$ atoms or molecules in one mole of any gas.

One mole is the molecular weight in grams. It is also called the molar mass.

1 mole of air contains 29 gms

Then the number of moles in 1.2 kg is

$$n = 1200 \text{ gm} \times \frac{1}{29 \text{ gm} / 1 \text{ mol}} = 41.3 \text{ mol}$$

Then the number of molecules or atoms is

$$N = 41.3 N_A = 2.49 \times 10^{25}$$

Also $1 / N_A = 1.66 \times 10^{-24}$ gms \approx Mass of the proton $= 1.67 \times 10^{-24}$ gms

Avogadro's number is also related to the Ideal Gas law.

Ideal Gases

Experiment shows that 1 mole of any gas, such as helium, air, hydrogen, etc at the same volume and temperature has almost the same pressure. At low densities the pressures become even closer and obey the Ideal Gas Law:

$$p = nRT / V$$

V = volume in units of m^3

n = number of moles

T = temperature in units of $^\circ\text{K}$

$R = 8.31\text{J}/\text{moles} \cdot ^\circ\text{K}$ ← Called the gas constant

p = pressure(absolute) in units of $\text{Pa}(\text{N}/\text{m}^2)$

Ideal Gas Law in terms of Boltzman Constant

$$p = nRT / V$$

$$R = N_A k$$

$$nR = nN_A k = Nk$$

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

$$pV = NkT$$

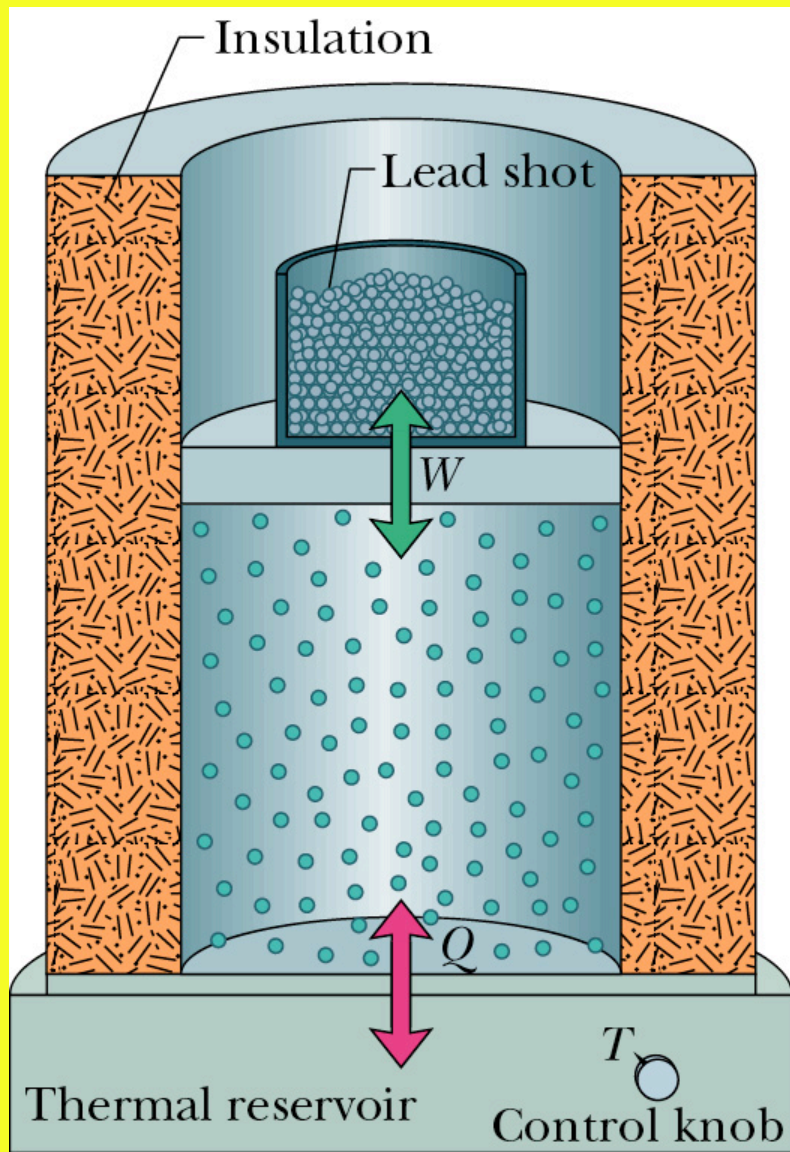
At high gas densities you must add the Van der Waal corrections where a and b are constants.

$$p = \frac{NkT}{V - b} - \left(\frac{a}{V}\right)^2$$

Lets use the ideal gas law to understand the 1st law of Thermodynamics

$$\Delta E_{\text{int}} = Q - W$$

Work done by an ideal gas



Always keep this picture in your head. Memorize it!!

$$W = \int F dx$$

$$W = \int \frac{F}{A} A dx$$

$$W = \int p dv$$

$$\Delta E_{\text{int}} = Q - W$$

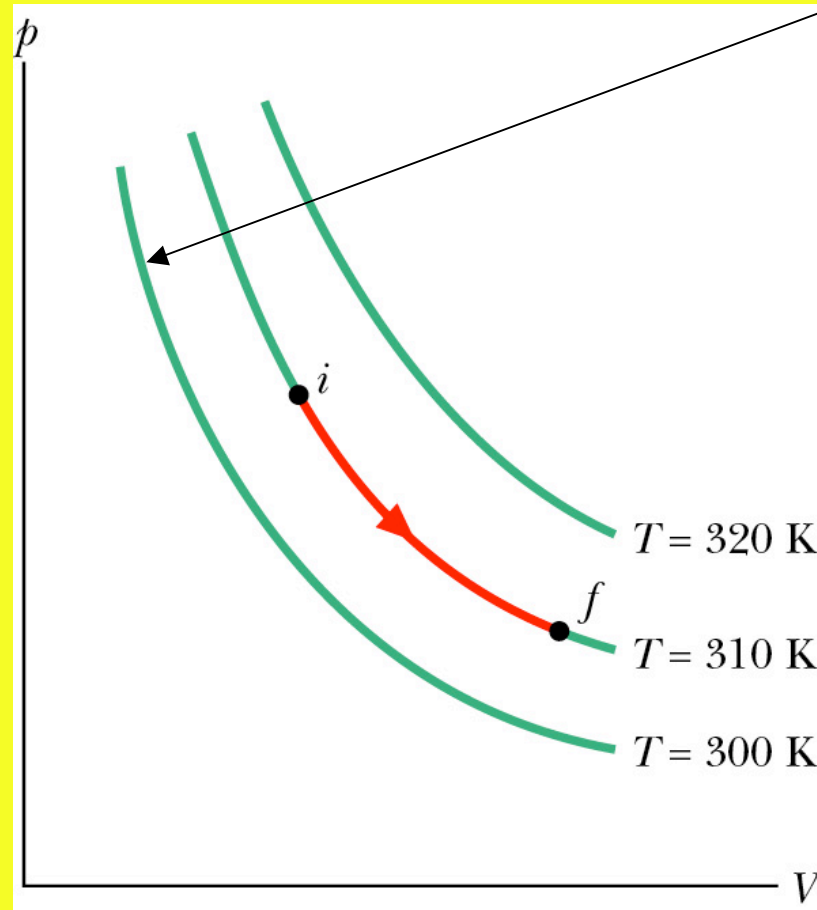
pV diagram

For an isothermal process or constant temperature.

This is an equation of a hyperbola.

$$pV = nRT$$

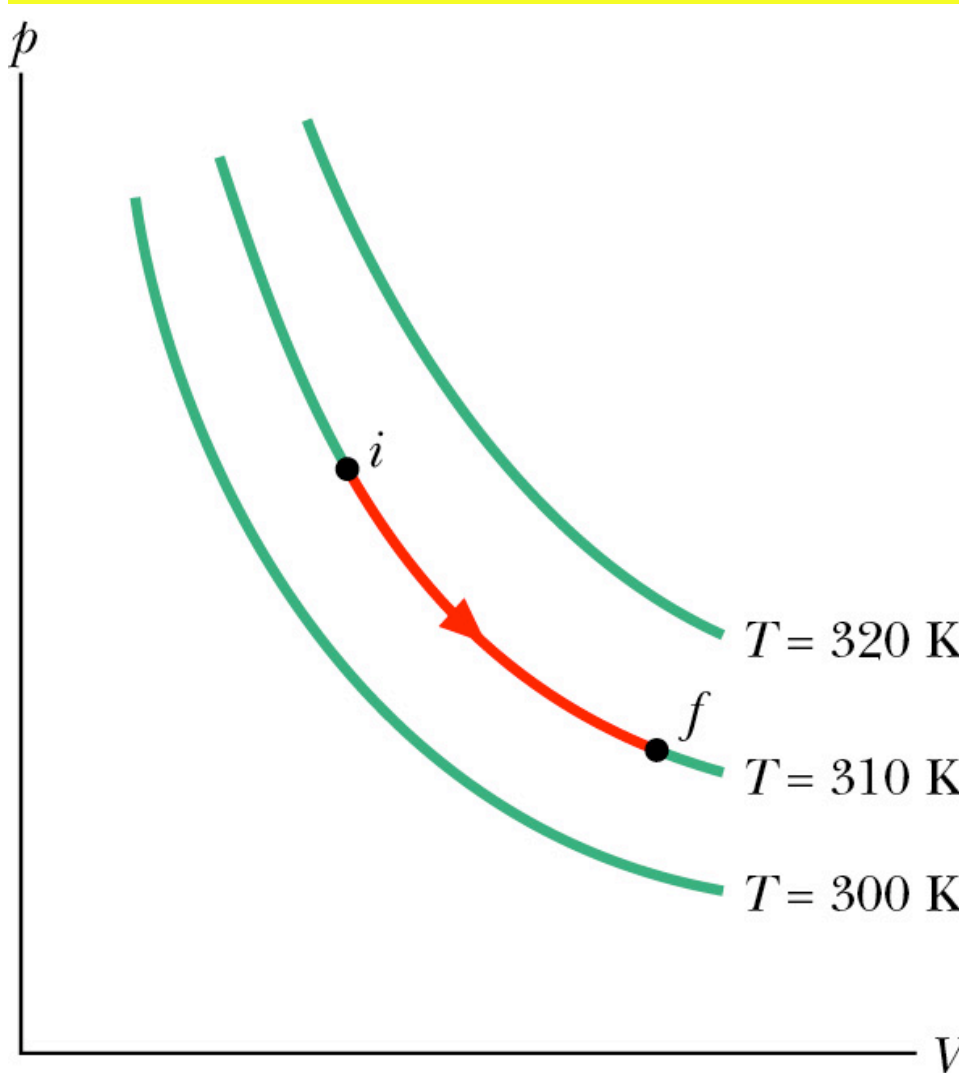
$$p = \frac{nRT}{V} = \frac{\text{constant}}{V}$$



What is the work done by an ideal gas when the temperature is constant?

$$pV = nRT$$

For constant temperature.



$$W = \int_{V_i}^{V_f} p dV$$

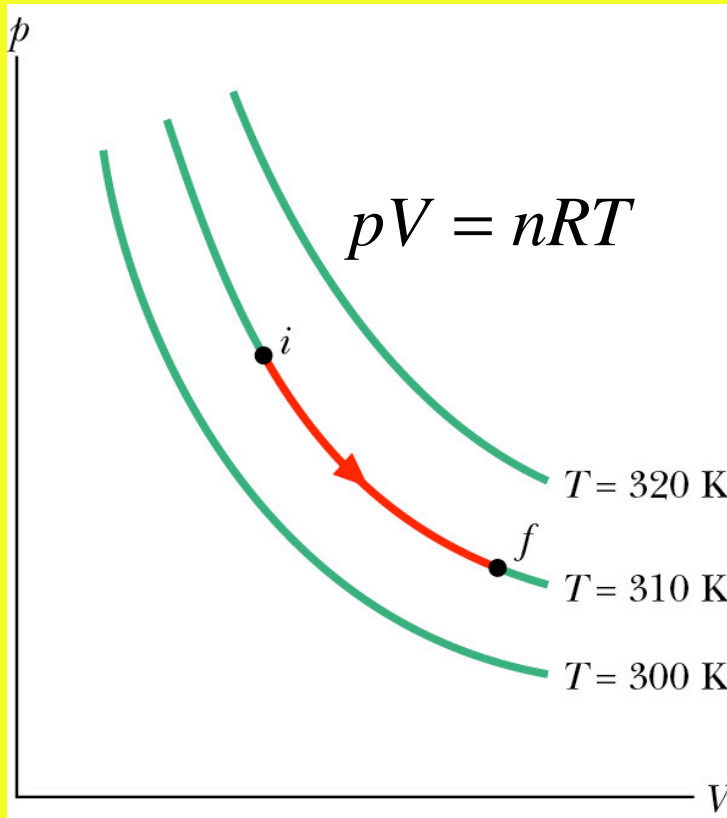
$$W = \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

constant

$$W = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT [\ln V]_{V_i}^{V_f}$$

$$W = nRT \ln \frac{V_f}{V_i}$$

What is the work done by an ideal gas when the temperature is constant?



$$W = nRT \ln \frac{V_f}{V_i}$$

Isothermal expansion

$$V_f > V_i$$

$$W > 0$$

ln is positive

Isothermal compression

$$V_f < V_i$$

$$W < 0$$

ln is negative

Constant volume

$$V_f = V_i$$

$$W = 0$$

$$\ln 1 = 0$$

$$\Delta E_{\text{int}} = Q - W$$

Four situations where the work done by an ideal gas is very clear.

$$W = \int_{V_i}^{V_f} p dV$$

For a constant volume process:

$$W = 0$$

For a constant pressure process

$$W = p(V_f - V_i)$$

For a constant temperature process

$$W = nRT \ln \frac{V_f}{V_i}$$

For an ideal gas undergoing any reversible thermodynamic process.

$$W = nR \int_{V_i}^{V_f} \frac{T}{V} dV$$

Sample problem 19-2

One mole of oxygen expands from 12 to 19 liters at constant temperature of 310 K. What is the work done?

$$W = nRT \ln \frac{V_f}{V_i} \quad (\text{Note volume units cancel})$$

$$n = 1 \text{ mol}$$

$$R = 8.31 \text{ J / mol} \cdot \text{K}$$

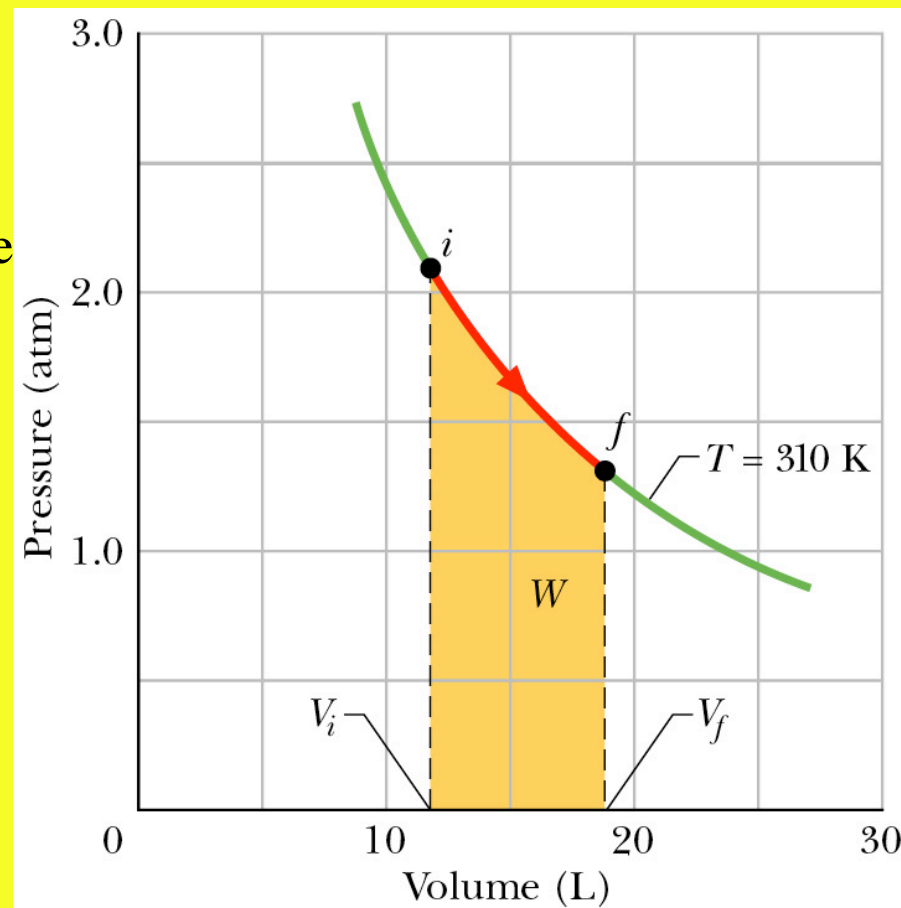
$$T = 310 \text{ K}$$

$$V_i = 12 \text{ l}$$

$$V_f = 19 \text{ l}$$

$$W = (1)(8.31)(310) \ln\left(\frac{19}{12}\right)$$

$$= 1180 \text{ J}$$



W = The area under the curve.

$$\Delta E_{\text{int}} = Q - W$$

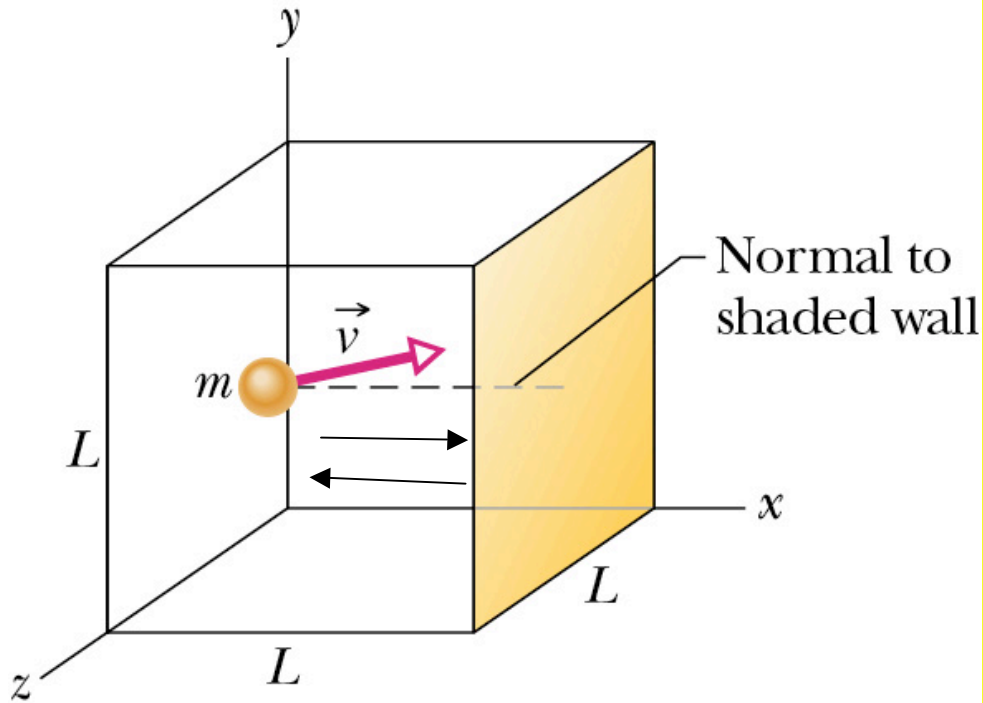
What's Next

$$W = nR \int_{V_i}^{V_f} \frac{T}{V} dV$$

$$\Delta E_{\text{int}} = Q - W$$

We know how to find W . If we can find the change in internal energy, then we know Q . Resort to a microscopic or kinetic theory of a gas.

Kinetic theory model of a gas: Find p due to one molecule first and then sum them up



What is the connection between pressure and speed of molecules?

We want to find the x component of force per unit area

$$F_x = \frac{\Delta P_x}{\Delta t}$$

$$\Delta P = P_f - P_i$$

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

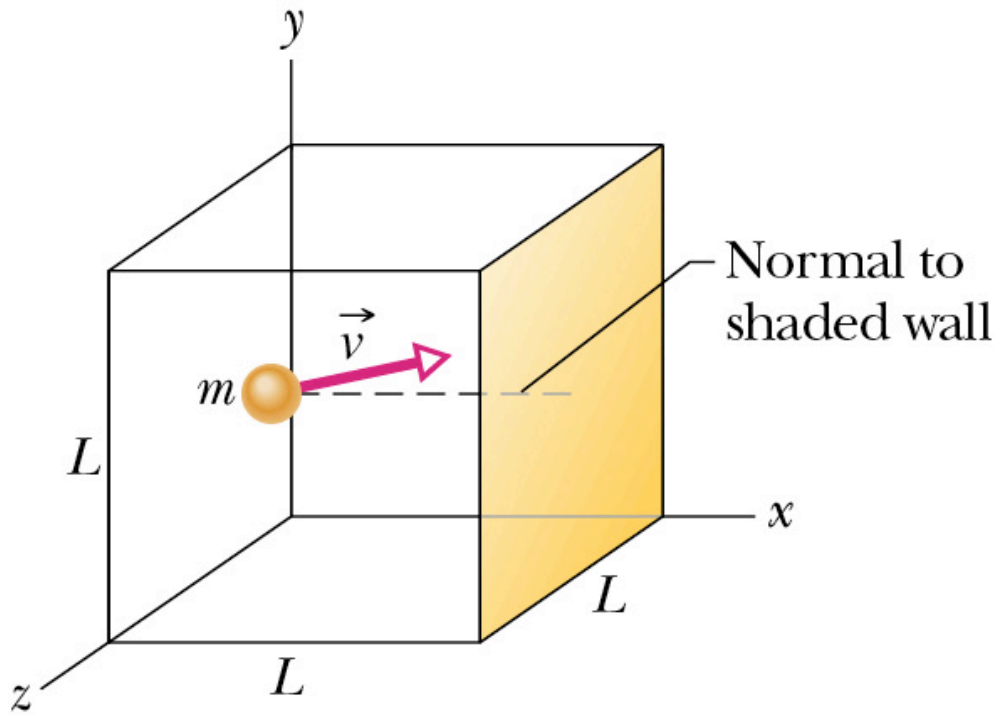
$$\Delta t = 2L / v_x$$

x component of momentum given to wall is $-\Delta P_x$

$$F_x = -\frac{\Delta P_x}{\Delta t} = \frac{2mv_x}{2L / v_x} = \frac{mv_x^2}{L}$$

$$p = \frac{F_x}{L^2} = \frac{mv_x^2 / L}{L^2} = m(v_x^2) / L^3$$

due to one molecule



Find pressure due to all molecules

$$p = \frac{F_x}{L^2} = \frac{mv_x^2 / L}{L^2} = m(v_x^2) / L^3$$

Due to one molecule

$$p = \frac{m(v_{1x}^2 + v_{2x}^2 + \dots)}{L^3} = \frac{mnN_A(v_x^2)_{avg}}{L^3}$$

Due to all molecules

$$p = \frac{nM(v_x^2)_{avg}}{V}$$

where M is the molar mass and V is L^3
Now find the average molecular velocity.

What is the root mean square of the velocity of the Molecules?

$$p = \frac{nM(v_x^2)_{avg}}{V}$$

$$v_{avg}^2 = (v_x^2)_{avg} + (v_y^2)_{avg} + (v_z^2)_{avg} \quad \text{and} \quad (v_x^2)_{avg} = (v_y^2)_{avg} = (v_z^2)_{avg}$$

$$v_{avg}^2 = 3(v_x^2)_{avg} \quad \text{then} \quad (v_x^2)_{avg} = \frac{v_{avg}^2}{3}$$

$$p = \frac{nM(v^2)_{avg}}{3V}$$

Define the root mean square of v

$$v_{rms} = \sqrt{(v^2)_{avg}}$$

$$p = \frac{nMv_{rms}^2}{3V}$$

$$pV = nRT$$

$$v_{rms}^2 = \frac{3pV}{nM} = \frac{3nRT}{nM} = \frac{3RT}{M}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

Average Molecular speeds at 300 K

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

$$R = 8.31 \text{ J / mol}$$

$$T = 300 \text{ K}$$

$$M = 0.002 \text{ kg}$$

Gas	m/s
Hydrogen	1920
Helium	1370
Water vapor	645
Nitrogen	517
Oxygen	483

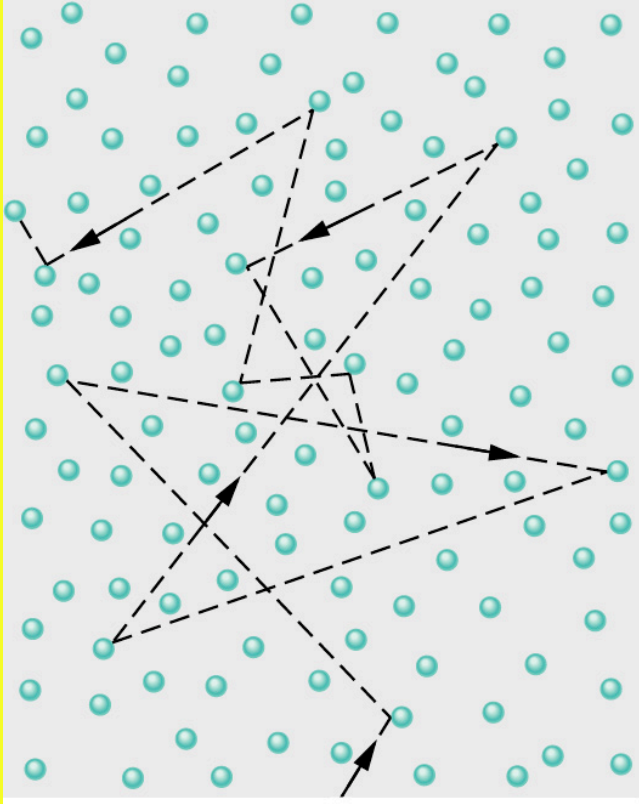
$$v_{rms} = \sqrt{\frac{3(8.31)(300)}{0.002}} = 1933$$

$$v_{rms} = \sqrt{\frac{3(8.31)(300)}{0.032}} = 483$$

Notice that the speed decreases with mass

What is the kinetic energy of the molecules?

Average Kinetic Energy of the Molecule



$$K_{avg} = \frac{1}{2} m v_{avg}^2 = \frac{1}{2} m v_{rms}^2$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

$$K_{avg} = \frac{1}{2} m \frac{3RT}{M} = \frac{3RT}{2N_A}$$

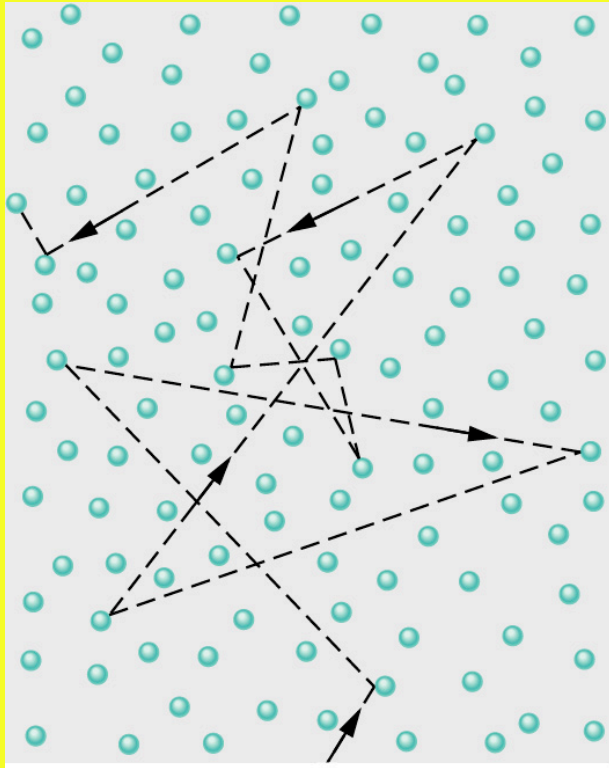
$$K_{avg} = \frac{3}{2} kT$$

$$K_{avg} = (1.5)(1.38 \times 10^{-23} \text{ J / K}) * (293\text{K}) = 6.07 \times 10^{-22} \text{ J}$$

at room temperature.

All ideal gas molecules have the same translational energy at a given T independent of their mass. Remarkable result.

Mean Free Path



mean free path = average distance
molecules travel in between collision

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V}$$

d is the diameter of the molecule

N/V is the density of molecules

Problem. Suppose we have a oxygen molecule at 300 K at $p = 1$ atm with a molecular diameter of $d = 290$ pm. What is λ , v , and f where f is defined as the frequency of collisions in an ideal gas?

$f = \text{speed of the molecule} / \text{mean free path} = v / \lambda$

Find λ

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V}$$

$$pV = NkT$$

$$\frac{N}{V} = \frac{p}{kT}$$

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 p} = \frac{1.38 \times 10^{-23} \text{ J / K } (300 \text{ K})}{1.414(3.14)(290 \times 10^{-12} \text{ m})^2 (1.01 \times 10^5 \text{ Pa})}$$

$$\lambda = 1.1 \times 10^{-7} \text{ m} = 380d$$

What is v , the speed of a molecule in an ideal gas?

Use the rms speed.

$$v_{rms} = \sqrt{\frac{3RT}{M}} \qquad v_{rms} = \sqrt{\frac{3(8.31)(300)}{0.032}} = 483 \text{ m / s}$$

What is f , the frequency of collision?

$$f = v_{rms} / \lambda$$

$$f = \frac{483}{1.1 \times 10^{-7}} = 4.38 \times 10^9 / s$$

What is the time between collisions?

$$t = \frac{1}{f} = \frac{1}{4.38 \times 10^9 / s} = 2.2 \times 10^{-9} = 2.2 \text{ ns}$$

Maxwell's speed distribution law:
Explains boiling.

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

$$\int_0^{\infty} P(v) dv = 1$$

Area under red or green curve = 1

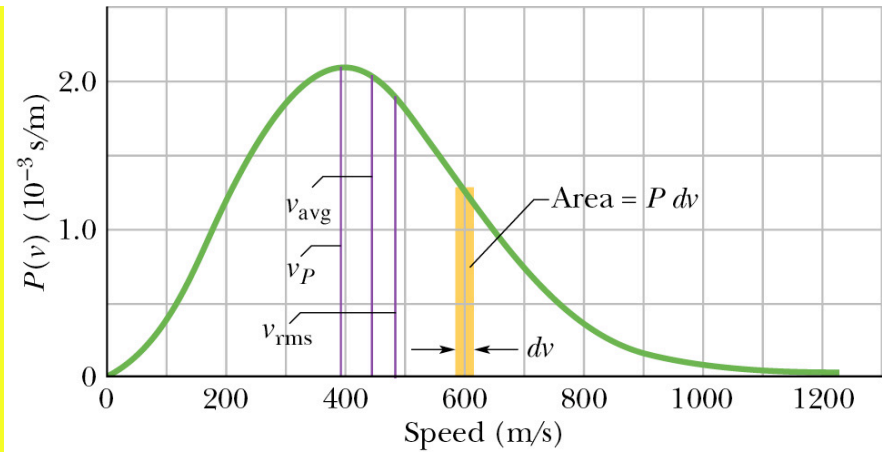
Note there are three velocities

$$v_{avg} = \int_0^{\infty} vP(v) dv$$

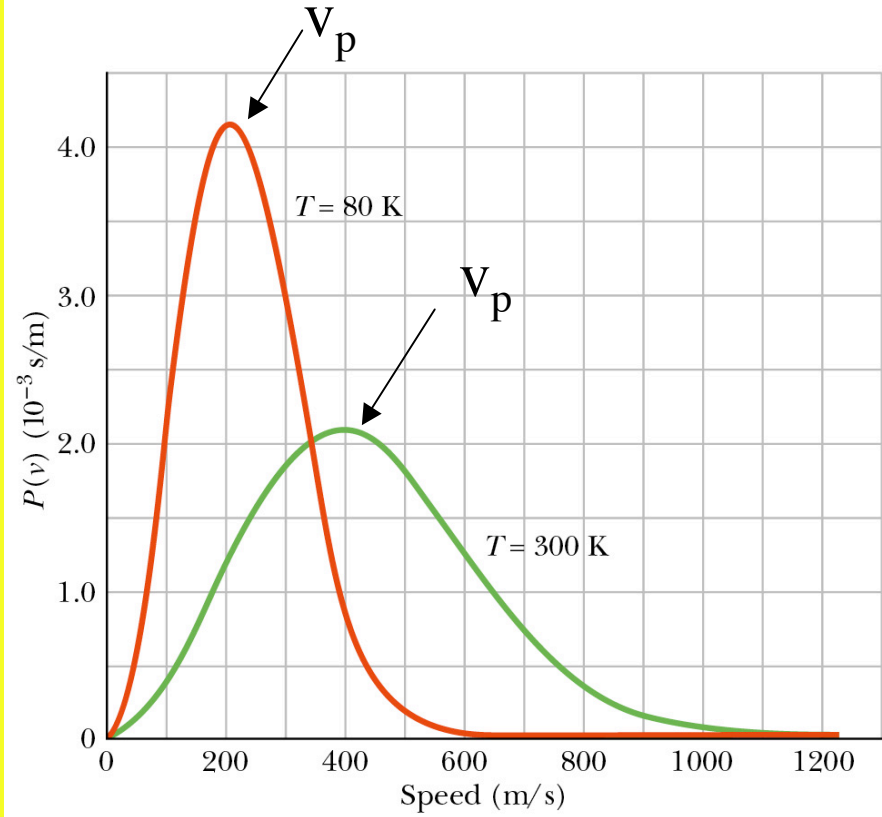
$$v_{rms} = \sqrt{(v^2)_{avg}} = \sqrt{\int_0^{\infty} v^2 P(v) dv}$$

v_p is the most probable speed

It is the faster moving molecules in the tail of the distribution that escape from the surface of a water.



(a)



(b)

Want to relate ΔE_{int} to the kinetic energy of the atoms of the gas.

- Assume we have a monoatomic gas.
- Only have translational energy.
- No rotational energy.
- No vibrational energy.
- Neglect binding energy of electrons.
- No changes in the nucleus.

ΔE_{int} = sum of the average translational energies of all the atoms.

$\Delta E_{\text{int}} = K_{\text{avg}}$ and $K_{\text{avg}} = \frac{3}{2} n N_A k T$ from kinetic theory.

Therefore,

$$\Delta E_{\text{int}} = \frac{3}{2} n N_A k T = \frac{3}{2} n R T$$

- We know ΔE_{int}
- We know W
- We have $\Delta E_{\text{int}} = Q - W$
- We now can get the heat Q

From the heat we can calculate the specific heat for various processes. For example,

Lets calculate the specific heat, C_V of an ideal gas at constant volume

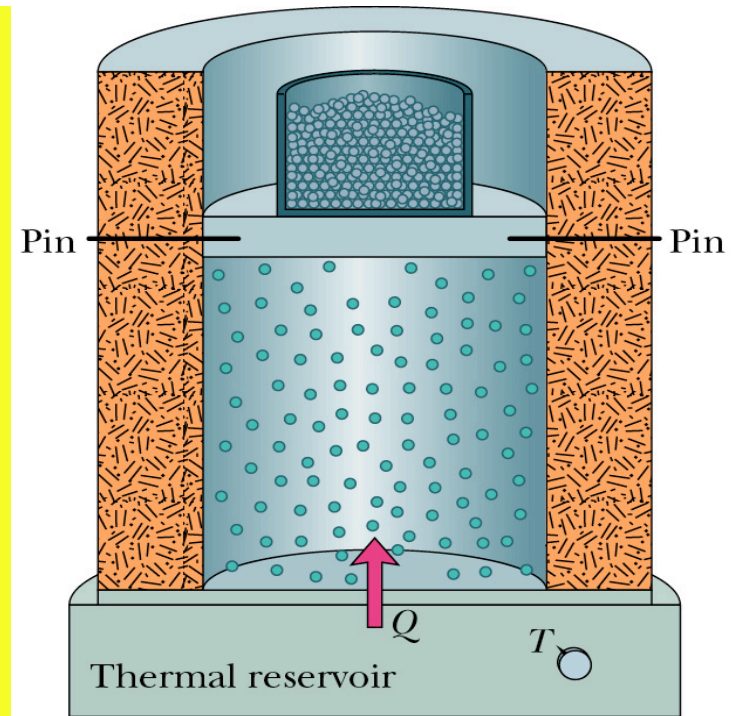
The internal energy of an ideal monatomic gas like helium and neon is given by the kinetic energy

$$E_{\text{int}} = \left(\frac{3}{2}\right)nRT$$

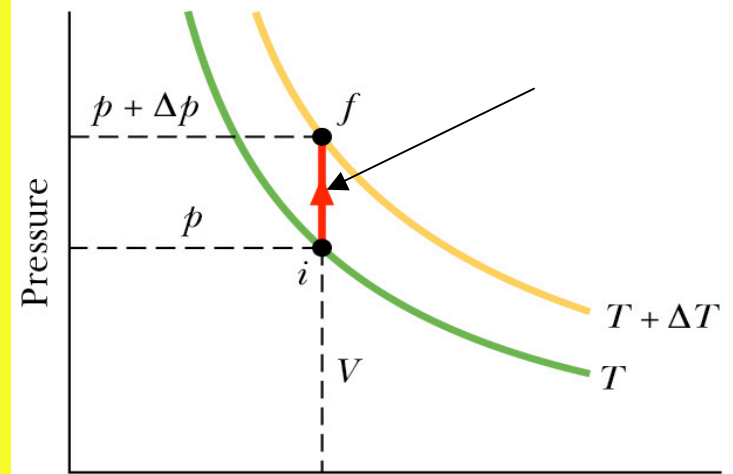
and only depends on temperature.

We know from experiment in the figure at the right that $Q = n C_V \Delta T$, where C_V is called the molar specific heat at constant volume

The first law of thermo: $\Delta E_{\text{int}} = Q - W$
at constant volume gives $\Delta E_{\text{int}} = Q$ since $W=0$



(a)



(b)

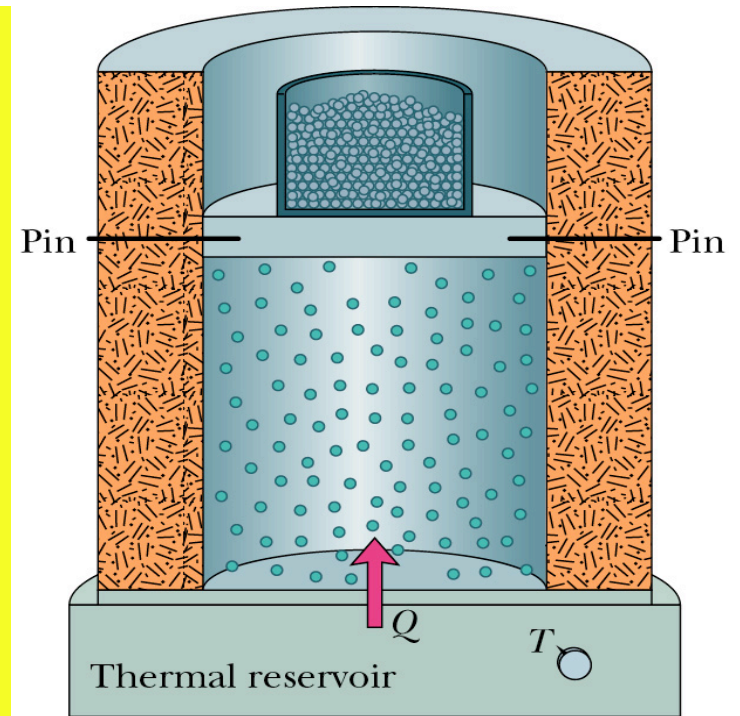
Calculate C_V

But $\Delta E_{\text{int}} = \left(\frac{3}{2}\right)nR\Delta T$ from above

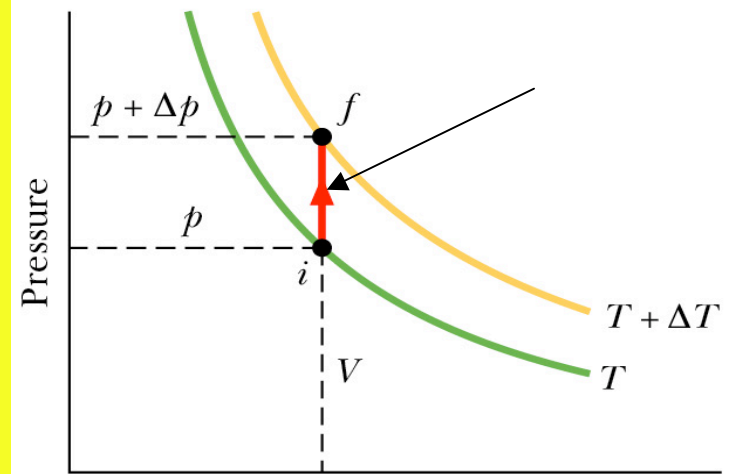
Using $Q = \Delta E_{\text{int}}$

$$nC_V\Delta T = \frac{3}{2}nR\Delta T$$

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



(a)



(b)

C_V for different gases

The internal energy for any ideal gas can be written as long as the correct C_V is used.

$$E_{\text{int}} = nC_V T$$

The internal energy and change in internal energy only depends on the temperature change. That is it only depends on the endpoints and not the path. This confirms what we said earlier about the first law. Also note that Q and W depend on the path but the difference $Q-W$ is path independent. See Fig 19-9 in text.

$3/2R$	12.5 J/mole.K
Helium gas	12.5 exp
Argon	12.6 exp

Specific Heat at Constant Pressure

Now C_p will be greater because the energy must now do work as well as raise the temperature.

$$Q = nC_p \Delta T$$

$$\Delta E_{\text{int}} = Q - W$$

$$W = p\Delta V$$

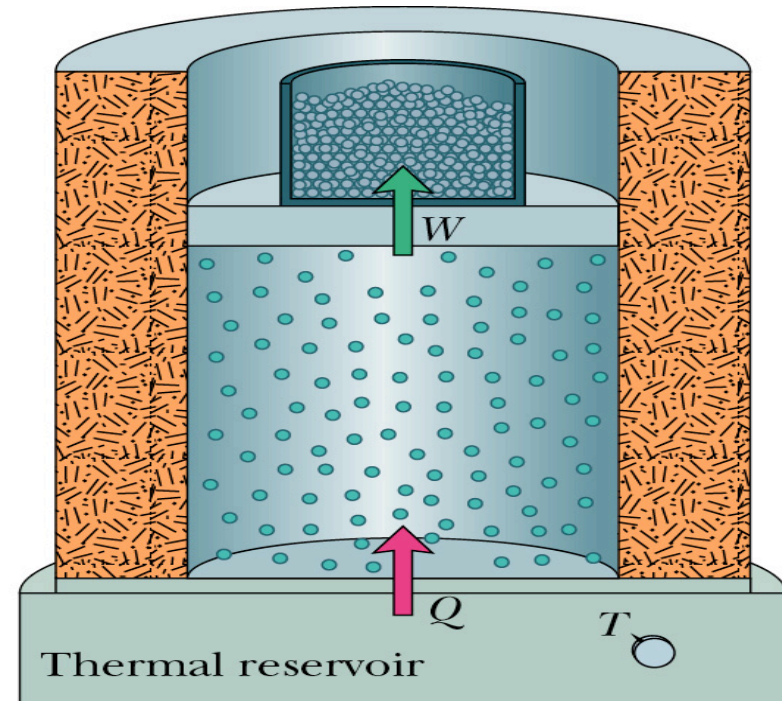
$$pV = nRT$$

$$\Delta E_{\text{int}} = nC_v \Delta T$$

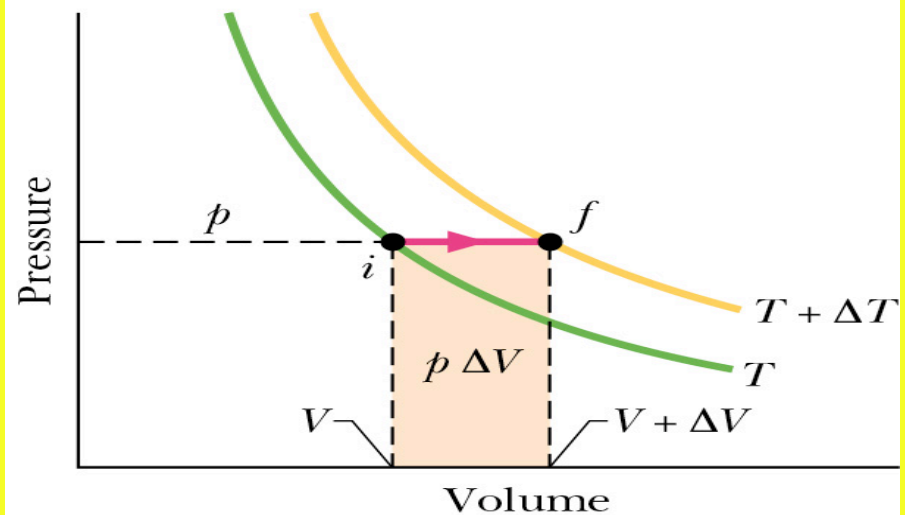
$$nC_v \Delta T = nC_p \Delta T - nR\Delta T$$

$$C_v = C_p - R$$

Another fantastic relation

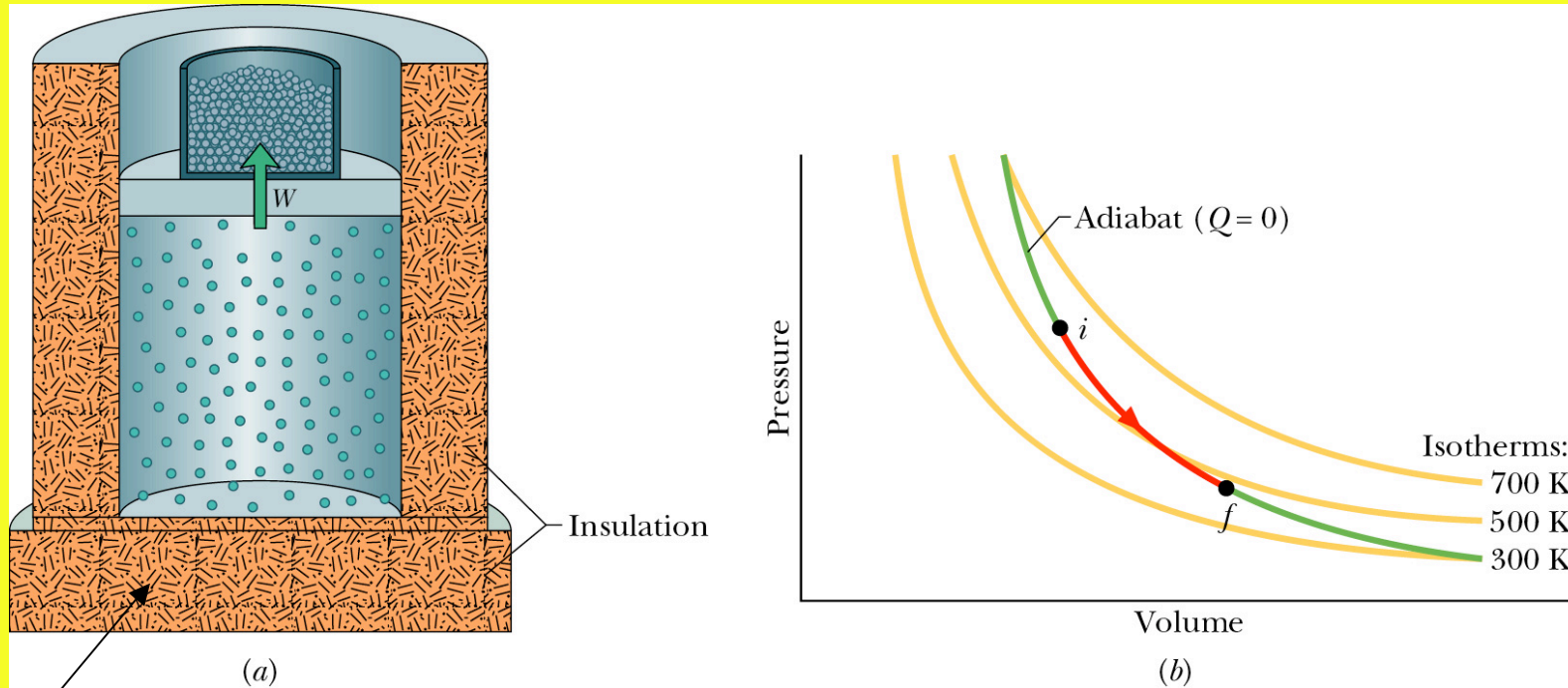


(a)



(b)

Adiabatic Expansion of an Ideal Gas: $Q = 0$



Note we do not let any heat get exchanged between system and environment

We want to show

$$pV^\gamma = \text{constant}$$
$$\gamma = \frac{C_p}{C_v}$$

for $Q = 0$ thermodynamic processes

Adiabatic Expansion of an Ideal Gas: $Q = 0$

$$\Delta E_{\text{int}} = Q - W$$

$$Q = 0$$

$$dE_{\text{int}} = -W = -pdV$$

$$dE_{\text{int}} = nC_V dT$$

$$-pdV = nC_V dT$$

$$ndT = -pdV / C_V$$

From the ideal gas law $pV = nRT$

$$pdV + Vdp = nRdT = n(C_P - C_V)dT$$

$$pdV + Vdp = (C_P - C_V)ndT = -(C_P - C_V)pdV / C_V$$

$$pdV + Vdp = -\left(\frac{C_P}{C_V} - 1\right)pdV$$

$$\frac{dP}{P} + \frac{C_P}{C_V} \frac{dV}{V} = 0$$

Adiabatic Expansion of an Ideal Gas: $Q = 0$

$$\int \frac{dP}{P} + \gamma \int \frac{dV}{V} = 0$$

$$\ln P + \gamma \ln V = \text{constant}$$

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

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

$$\gamma = \frac{C_p}{C_v}$$

PROBLEM 20-58E

Show that the speed of sound in a ideal gas for an adiabatic process is $v_s = \sqrt{\frac{\gamma RT}{M}}$

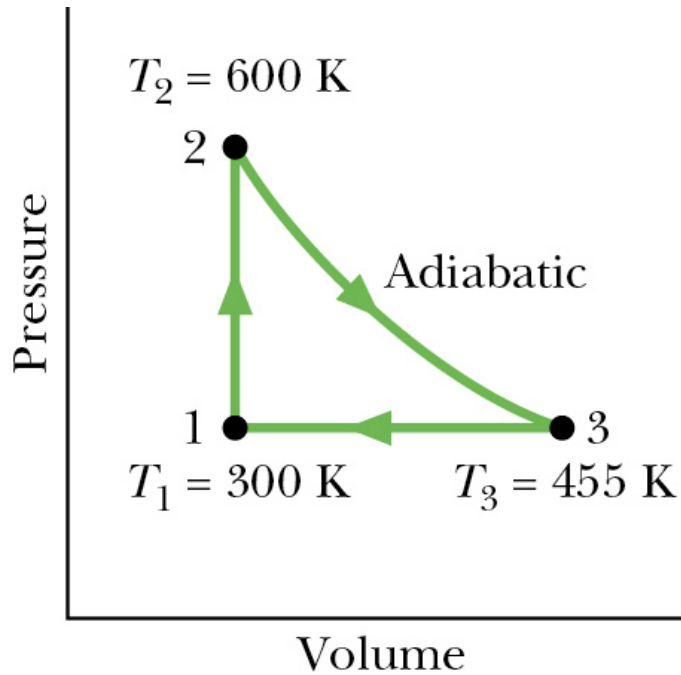
Recall $v_s = \sqrt{\frac{B}{\rho}}$ $B = -V \frac{dp}{dV}$ $\frac{dp}{dV} = -\gamma \frac{p}{V}$ $B = \gamma p$

$$v_s = \sqrt{\frac{\gamma p}{\rho}} = \sqrt{\frac{\gamma nRT / V}{\rho}} = \sqrt{\frac{\gamma RT}{M}}$$

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

Also $v_s = \sqrt{\frac{\gamma RT}{M}} = \sqrt{\frac{\gamma}{3}} \sqrt{\frac{3RT}{M}} = \sqrt{\frac{\gamma}{3}} v_{rms}$ $\gamma = \frac{C_p}{C_v} = \frac{5}{3}$

For helium at 300 K, the molecular speed is $v_{rms} = 1370$ m/s and. Then the predicted speed of sound in helium is 1021 m/s. The measured value is 965m/s



Problem 20-61P

One mole of an ideal monatomic gas traverses the cycle shown in the figure.

(a) Find Q , ΔE_{int} , and W for each process.

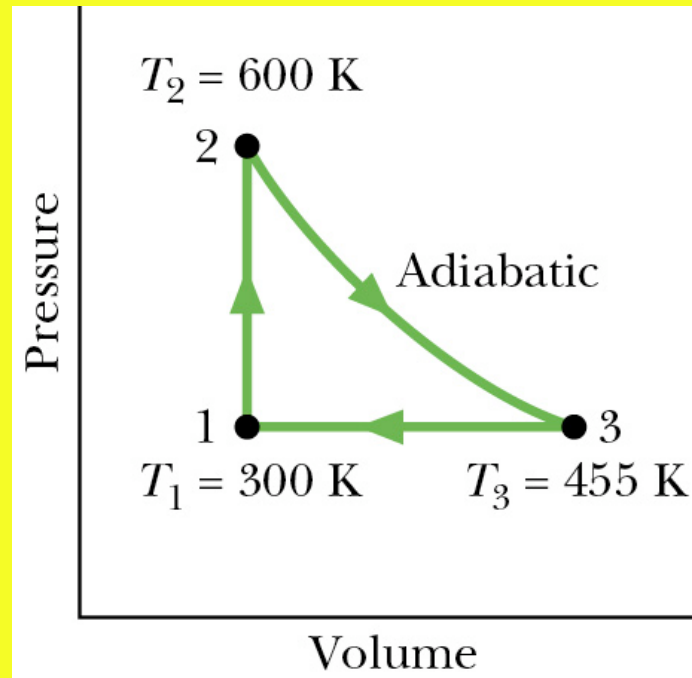
1 \rightarrow 2 constant volume

$$\boxed{W = 0}$$

$$\Delta E_{\text{int}} = Q$$

$$\Delta E_{\text{int}} = nC_v\Delta T = n\frac{3}{2}R\Delta T = (1\text{mol})(1.5)(8.314\text{J} / \text{mol} \cdot \text{K})(600 - 300)\text{K}$$

$$\boxed{\Delta E_{\text{int}} = Q = 3.74 \times 10^3 \text{ J}}$$

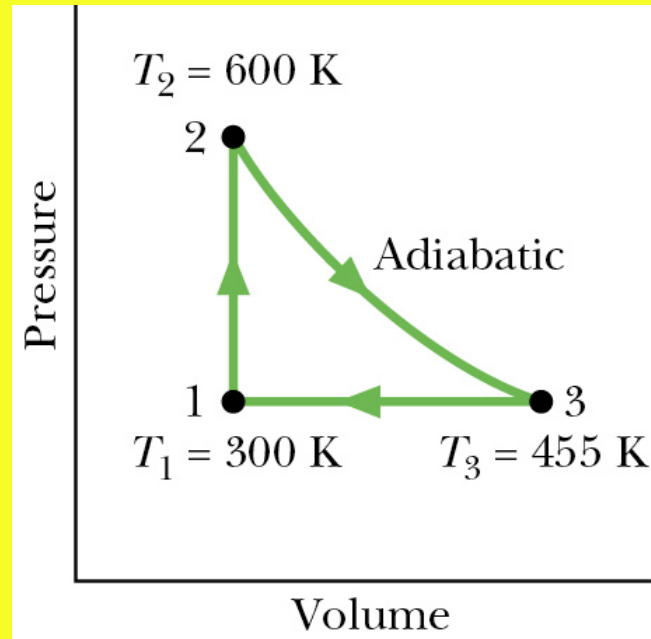


$$2 \rightarrow 3 \quad Q = 0$$

$$\Delta E_{\text{int}} = nC_V\Delta T = n\frac{3}{2}R\Delta T = (1\text{ mol})(1.5)(8.314\text{ J / mol} \cdot \text{K})(455 - 600)\text{ K}$$

$$\Delta E_{\text{int}} = -1.81 \times 10^3 \text{ J}$$

$$W = Q - \Delta E_{\text{int}} = 1.81 \times 10^3 \text{ J}$$



3 \longrightarrow 1 constant pressure

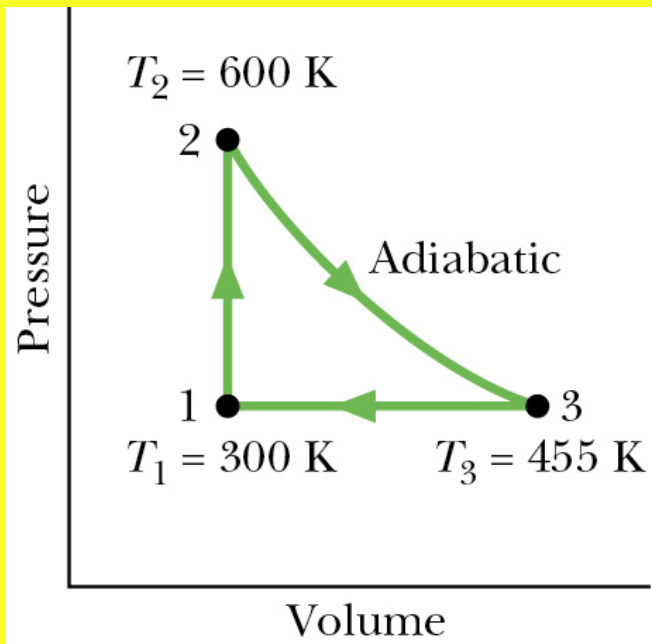
$$C_p = C_v + R = \frac{3}{2}R + R = \frac{5}{2}R$$

$$Q = nC_p \Delta T = n \frac{5}{2} R \Delta T = (1 \text{ mol})(2.5)(8.314 \text{ J / mol} \cdot \text{K})(300 - 455) \text{ K}$$

$$Q = -3.22 \times 10^3 \text{ J}$$

$$\Delta E_{\text{int}} = nC_v \Delta T = n \frac{3}{2} R \Delta T = (1.5)(8.314)(300 - 455) = -1.93 \times 10^3 \text{ J}$$

$$W = Q - E_{\text{int}} = [(-3.22) - (-1.93)] \times 10^3 \text{ J} = -1.29 \times 10^3 \text{ J}$$



(b) Find the pressure and volume at points 2 and 3.

The pressure at point 1 is
 $1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$.

At point 1 the volume is determined from

$$V_1 = \frac{nRT}{P_1} = \frac{(1)(8.314)(300)}{1.013 \times 10^5} = 2.46 \times 10^{-2} \text{ m}^3$$

$$\text{At point 2, } V_2 = V_1 = 2.46 \times 10^{-2} \text{ m}^3$$

$$p_2 = \frac{nRT_2}{V_2} = \frac{(1)(8.314)(600)}{2.46 \times 10^{-2}} = 2.02 \times 10^5 \text{ Pa}$$

$$\text{At point 3, } P_3 = P_1 = 1.013 \times 10^5 \text{ Pa}$$

$$V_3 = \frac{nRT_3}{P_3} = \frac{(1)(8.314)(455)}{1.013 \times 10^5} = 3.73 \times 10^{-2} \text{ m}^3$$

Equipartition Theorem

Equipartition Theorem: Each molecule has $1/2kT$ of energy associated with each independent degree of freedom

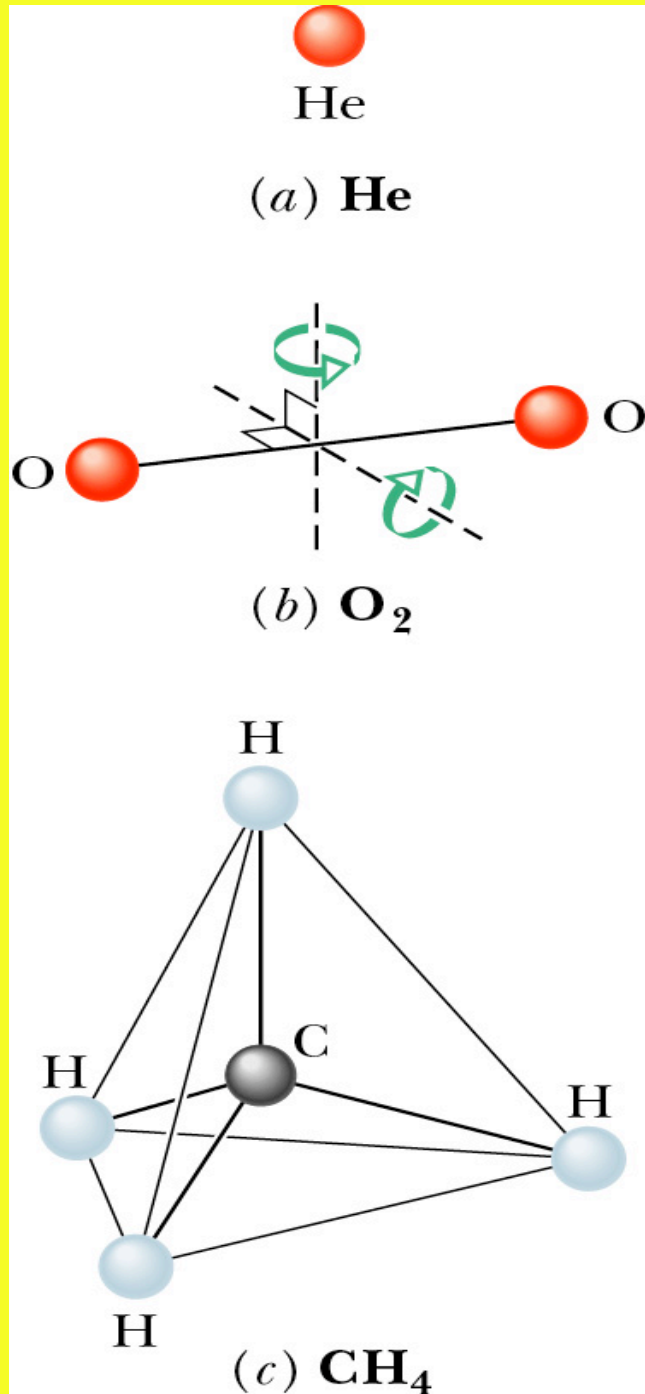
All molecules have three ways to move in translation v_x, v_y, v_z

Diatomic molecules also have two rotational degrees of freedom as well

Polyatomic molecules have three rotational degrees of freedom as well.

Monatomic molecules have 0 rotational degrees of freedom

How does this effect the specific heats?



Specific heats including rotational motion

Let f be the number of degrees of freedom

$$E_{\text{int}} = \frac{f}{2} kt = \frac{f}{2} nRT$$

$$C_V = (3/2) R \quad \text{for monatomic gas} \quad (f=3)$$

$$C_V = (5/2) R \quad \text{for diatomic gas} \quad (f=5)$$

$$C_V = (3) R \quad \text{for polyatomic gas} \quad (f=6)$$

$$C_P = C_V + R$$

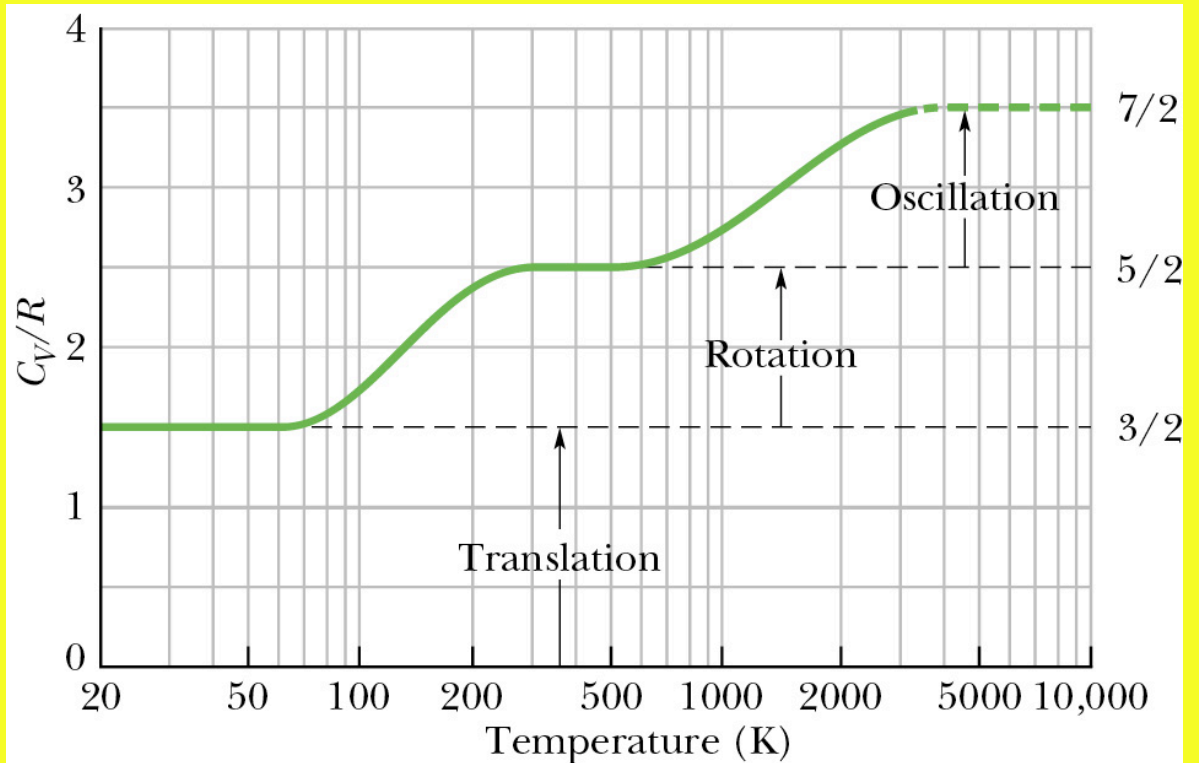
C_V for a diatomic gas as a function of T

Below 80 K only translational modes can be excited

Above 80 K rotational modes begin to get excited

Above 1000 oscillatory modes begin to get excited.

At 3200 K the molecule breaks up into two atoms



Quantum mechanics is required to explain why the rotational and oscillatory modes are frozen out at lower temperatures. Oscillatory or vibrational modes give 2 more degrees of freedom.

What is Entropy S? Two equivalent definitions

- It is a measure of a system's energy gained or lost as heat per unit temperature.

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

- It is also a measure of the ways the atoms can be arranged to make up the system. It is said to be a measure of the disorder of a system.

$$S = k \ln W$$

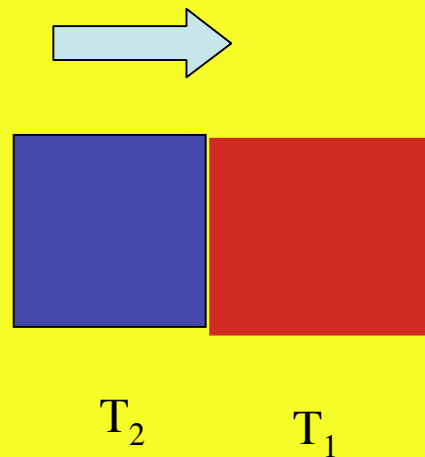
$$\Delta S = k \ln W_f / W_i$$

A system tends to move in the direction where entropy increases

- For an irreversible process the entropy always increases. $\Delta S > 0$
- For a reversible process it can be 0 or increase. $\Delta S \geq 0$

Heat Flow Direction

- Why does heat flow from hot to cold instead of vice versa? Because the entropy increases.
- What is this property that controls direction?



$$T_2 > T_1$$

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

The statistical nature of entropy

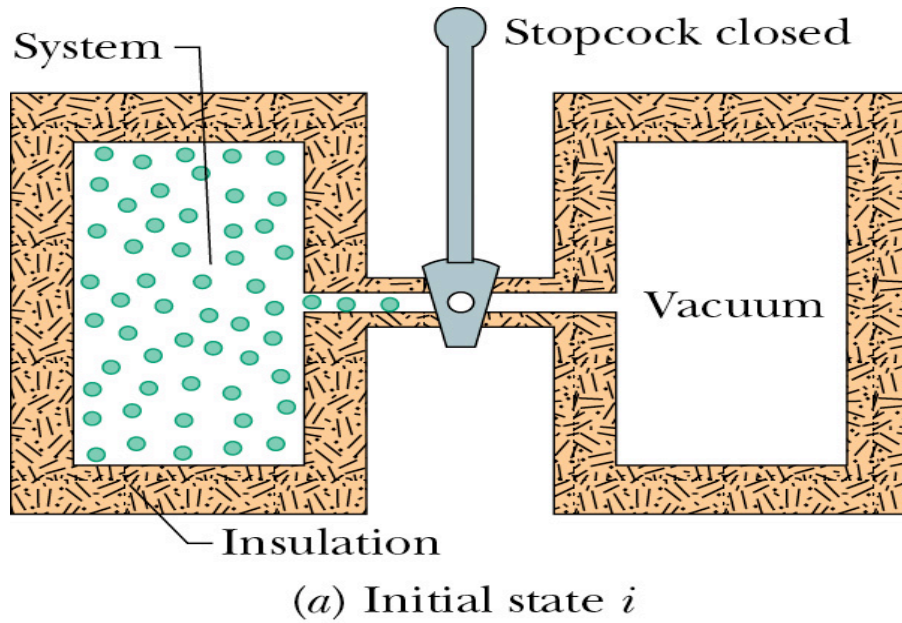
- Black beans on the right
- White beans on the left
- Add some energy by shaking them up and they mix
- They never will go back together even though energy of conservation is not violated.
- Again what controls the direction?

- Assume that entropy is a state property like pressure and volume and only depends on the initial and final state, but not on how it got there . Then the change in entropy is defined as:

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

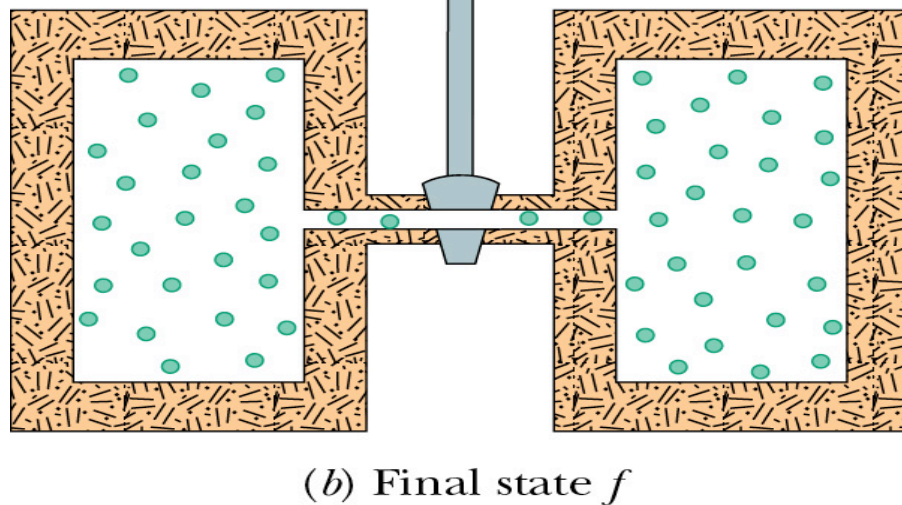
Note that units are Joule per kelvin and the sign is the same as Q since $T > 0$

- However, the above formula can only be used to calculate the entropy change if the process is reversible..
- To find the entropy for an irreversible process and since state functions only depend on the end points, the trick is to replace the irreversible one with a reversible one that has the same end points. Consider the isothermal free expansion of an ideal gas.

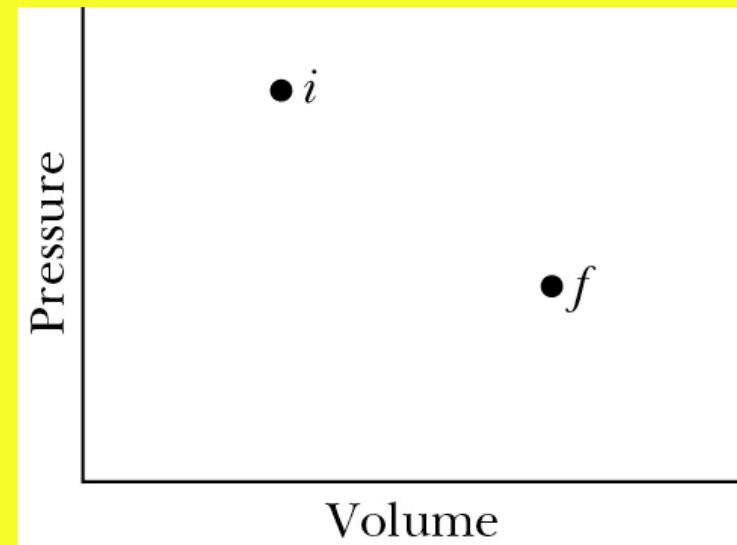


Irreversible process

Stopcock open



Calculate the Change in Entropy for an Isothermal Irreversible Free Expansion of an Ideal Gas. No change in temperature.



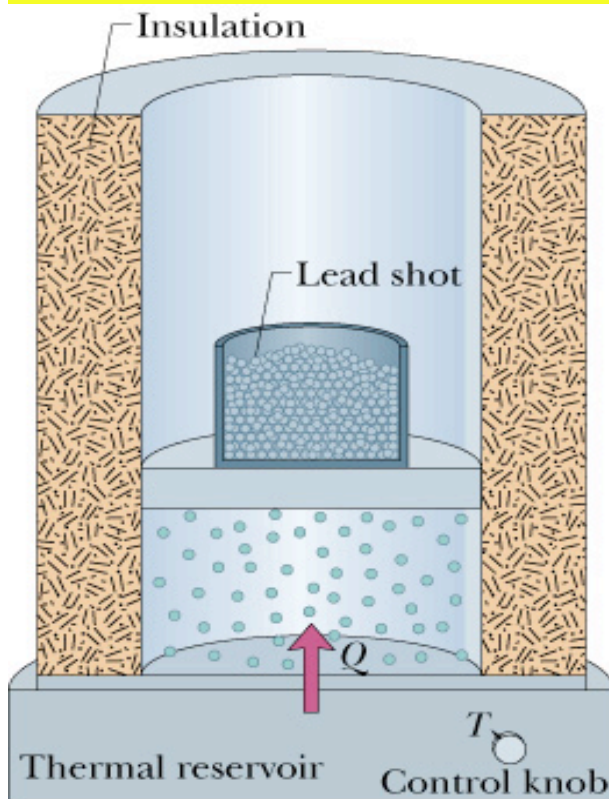
Example: Isothermal Reversible Expansion

How do we evaluate S or the change in S?

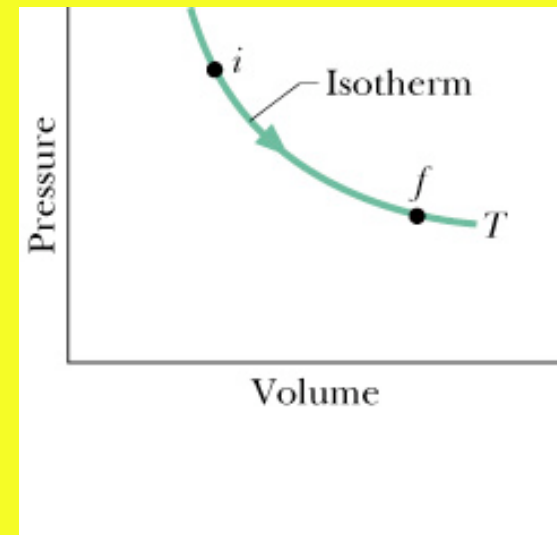
$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} = \frac{1}{T} \int_i^f dQ \quad \Delta S = \frac{Q}{T}$$

To keep the temperature of the gas constant, heat had to be added to the gas while the volume was expanding or else it would have cooled. Since heat was added, Q is +, Hence, the entropy change was + or $\Delta S > 0$

The change in entropy for a free expansion is also given by the above formula since the temperature doesn't change as well.



(a) Initial state *i*



Isothermal expansion of a gas

$$\Delta S = \frac{Q}{T}$$

$$\Delta E_{\text{int}} = nC_V\Delta T = 0 \quad \text{Isothermal process}$$

$$Q = W \quad \text{From the 1st law}$$

$$\Delta S = \frac{W}{T}$$

$$W = \int_i^f p dV$$

$$pV = nRT$$

$$W = \int_i^f nRT \frac{dV}{V}$$

$$W = nRT \ln \frac{V_f}{V_i}$$

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

Example: Four moles of an ideal gas undergo a reversible isothermal expansion from volume V_1 to volume $V_2 = 2V_1$ at temperature $T = 400\text{K}$.

- a) Find the work done by the gas.
- b) Find the entropy change of the gas?
- c) Find the entropy change if the process is adiabatic instead of isothermal

a) Find the work done.

$$W = \int_{V_1}^{V_2} p dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1}$$

$$W = nRT \ln \frac{2V_1}{V_1} = nRT \ln 2 = (4\text{mol})(8.31\text{J} / \text{molK})(400\text{K}) \ln 2 = 9.22 \times 10^3 \text{ J}$$

b) Find the entropy change of the gas.

We just showed that

$$\Delta S = \frac{W}{T}$$

$$\Delta S = \frac{W}{T} = \frac{9.22 \times 10^3 \text{ J}}{400 \text{ K}} = 23.1 \text{ J / K}$$

c) If the expansion is reversible and adiabatic instead of isothermal, find the entropy change of the gas.

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

$$\Delta Q = 0$$



$$\Delta S = 0$$

For an ideal gas in any reversible process where the temperature and volume may change, the entropy change is given by the following:

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

$$dE_{\text{int}} = dQ - dW$$

$$dQ = dE_{\text{int}} + dW = nC_v dT + pdV$$

$$\frac{dQ}{T} = nR \frac{dV}{V} + nC_v \frac{dT}{T}$$

$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_i}$$

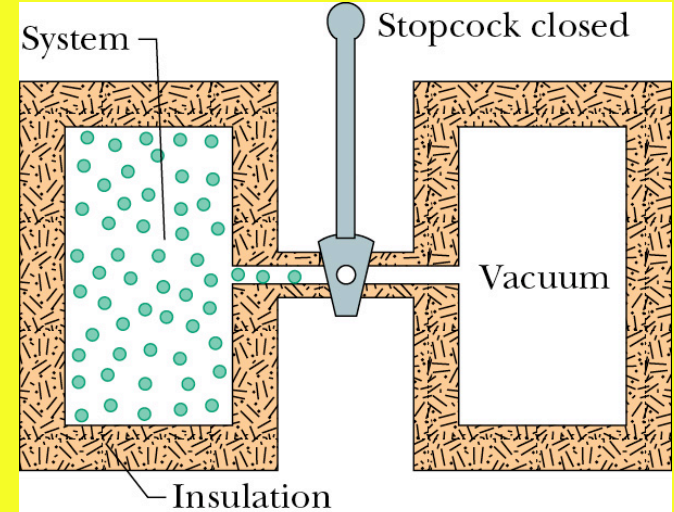
This holds for all reversible processes for an ideal gas.

Summary

For isothermal expansion of a gas where the final volume doubles the initial volume, we have the change entropy equal to:

$$\Delta S = \int_i^f \frac{dQ}{T}$$

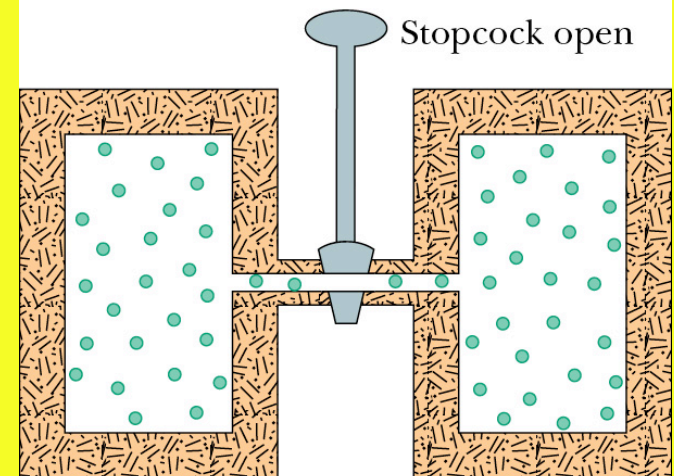
$$\Delta S = nR \ln \frac{V_f}{V_i} = nR \ln 2 = k \ln 2$$



(a) Initial state *i*



Irreversible process



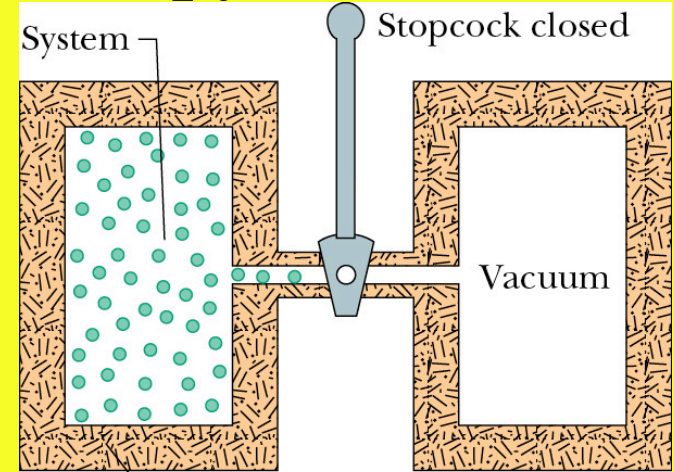
(b) Final state *f*

Statistical View of Entropy

Boltzmann Entropy Equation

$$S = k \ln W$$

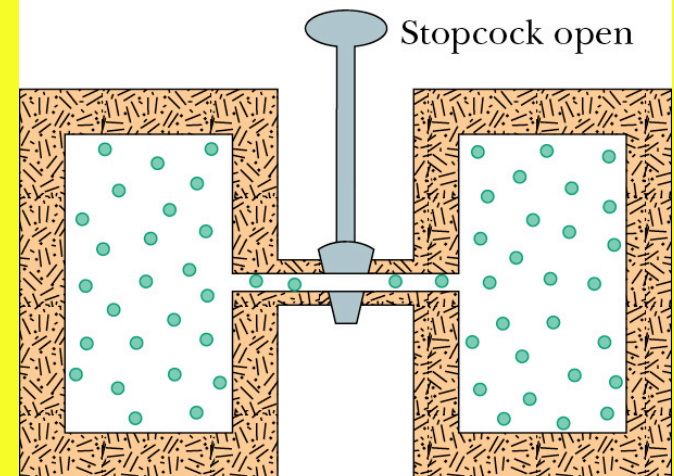
Now find the change in entropy from
The above equation



(a) Initial state *i*



Irreversible
process

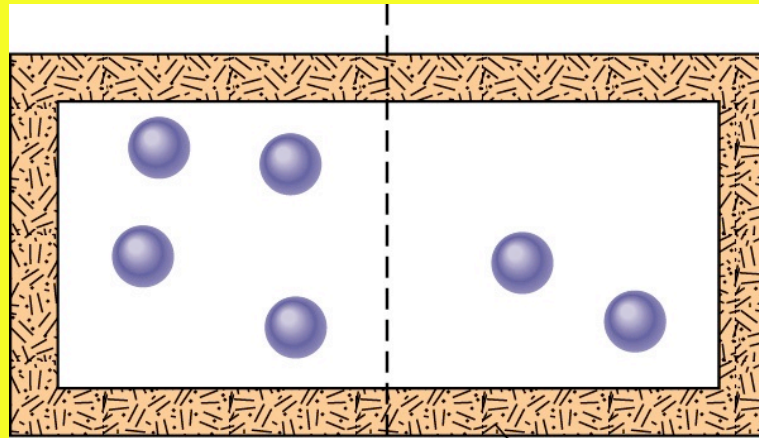


(b) Final state *f*

An insulated box containing 6 molecules

$$n_1=4$$

$$n_2=2$$

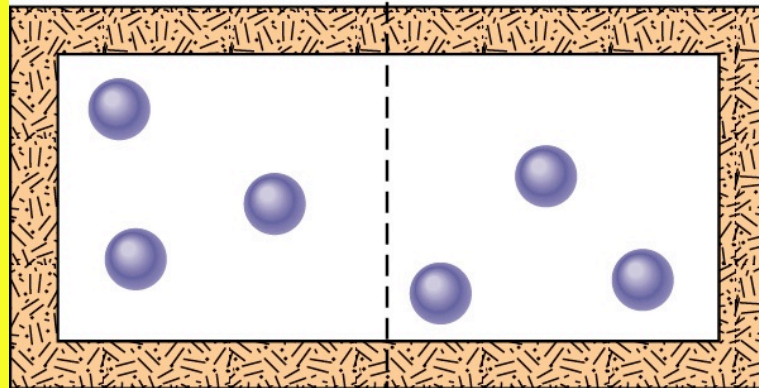


(a)

$$n_1=3$$

Insulation

$$n_1=3$$



(b)

$$N=6$$

Label	Percent age	n_1	n_2	W	S 10^{-23}J/K
I	100	6	0	1	0
II	83	5	1	6	2.47
III	67	4	2	15	3.74
IV	50	3	3	20	4.13
V	33	2	4	15	3.74
VI	17	1	5	6	2.47
VII	0	0	6	1	0

$$S = k \ln W$$

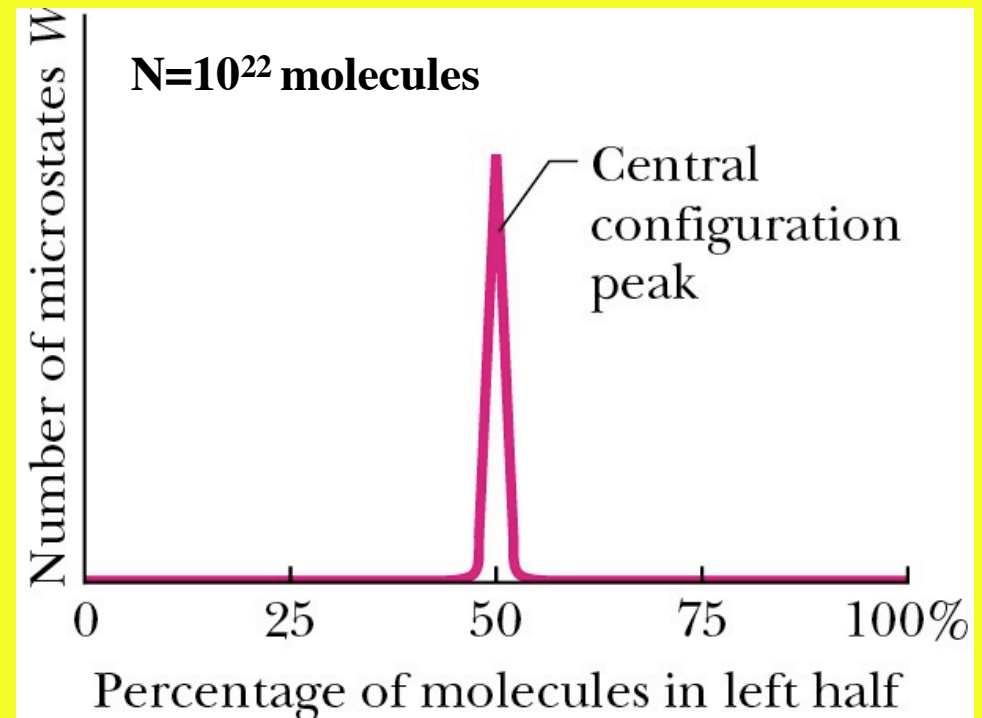
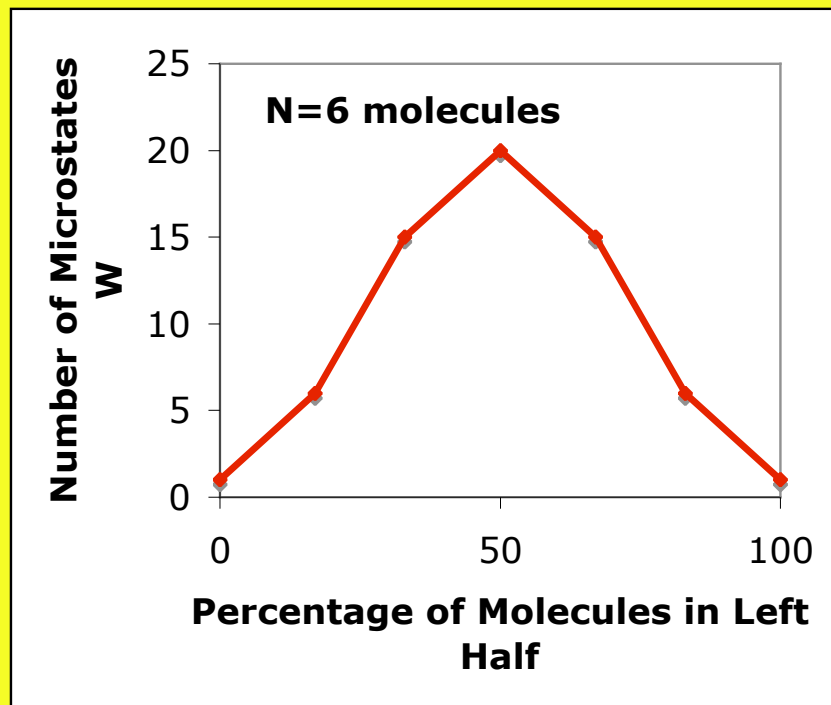
$$W = \frac{N!}{n_1!n_2!}$$

$$N!=6 \times 5 \times 4 \times 3 \times 2 \times 1$$

$$W = \frac{N!}{n_1!n_2!}$$

$$W = \frac{6!}{4!2!} = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{4 \times 3 \times 2 \times 1 \times 2 \times 1} = \frac{6 \times 5}{2} = 15$$

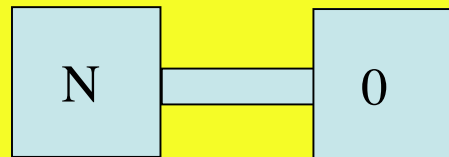
This shows the number of microstates available for each configuration



Statistical View of Entropy

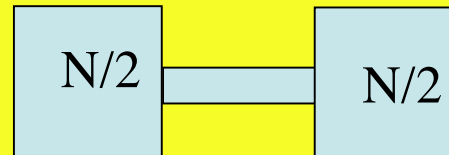
Starting from the Boltzmann equation $S = k \ln W$
show the same result.

$$W_i = \frac{N!}{N!0!} = 1$$



Initial system

$$W_f = \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}$$



Final system

$$\Delta S = k \ln W_f - k \ln \overset{0}{\cancel{W_i}}$$

$$\Delta S = k \ln W_f = k \ln \left(\frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \right) \approx k \ln 2$$

Same result as that obtained
from the gas law.

Use Stirling formula

$$\ln N! \approx N \ln(N) - N$$

For very large N

$$\Delta S = k \ln W_f = k \ln\left(\frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}\right)$$

$$\ln\left(\frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}\right) = \ln(N!) - 2 \ln\left(\left(\frac{N}{2}\right)!\right) = \ln 2$$

$$\Delta S = k \ln 2 = nR \ln 2$$

2nd Law of Thermodynamics

$$\Delta S \geq 0$$

If a process occurs in a closed system, the entropy of the system increases for irreversible processes and is constant for reversible processes.

Entropy is important in the discussion of Engines and efficiency and Refrigerators, etc.

Stop here.

Grading for Phys 631

Homework (100 problems)	30%
Quizzes (3)	35%
Final (1)	29%
Spreadsheet	1%

Four homework assignments scheduled

Fall Homework 1 11:59 PM	Sunday August 12
Fall Homework 2 11:59 PM	Sunday August 26
Fall Homework 3 11:59 PM	Sunday September 9
Fall Homework 4 11:50 PM	Sunday September 23

Final Exam 9:00 AM Sept 24 - Sept 26 7:00 PM
All Multiple Choice 60 Questions
Proctored

Classes 2007-2008

Fall Registration Aug 15

- Phys 605W How things Work I
- Phys 609W Galileo & Einstein

Spring

- Phys 606W How Things Work II
- Phys 641W Physics pedagogy

Summer 2008

- Phys 632 E/M Lecture
- Phys 635 E/M Lab
- Phys 633W Modern Physics Online

Reminders

- Check-out on August 2 11:00 AM
- Turn keys into Conference Services at check-out or you will pay a fine.
- Return any books to the Library
- Return Quiz 3
- Thank the DEMO techs fo a job well done -Roger and Nicolai

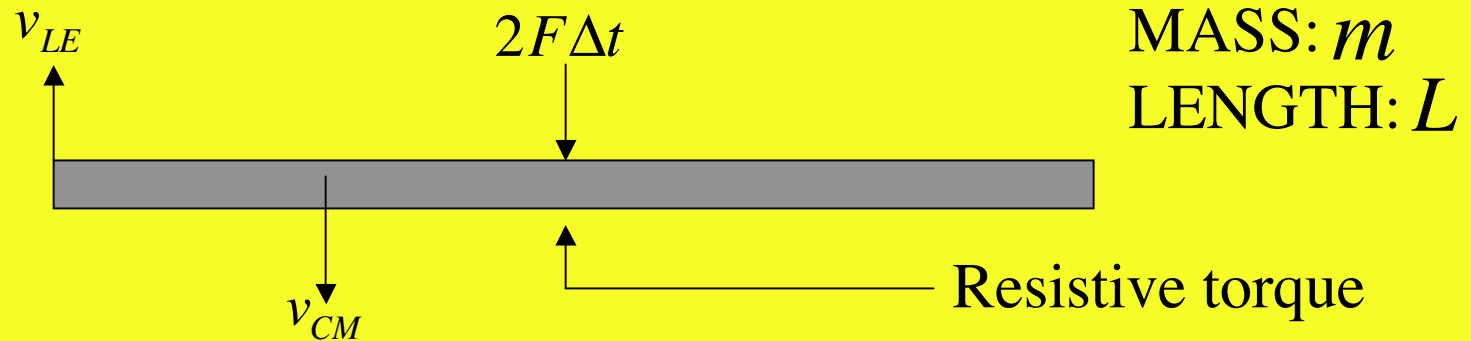
The Breaking Broomstick Demo

“Experiment to demonstrate Inertia”

First published in 1881

Dramatic-Why does the stick break so violently and leave the glass intact?

Breaking Broomstick Demo



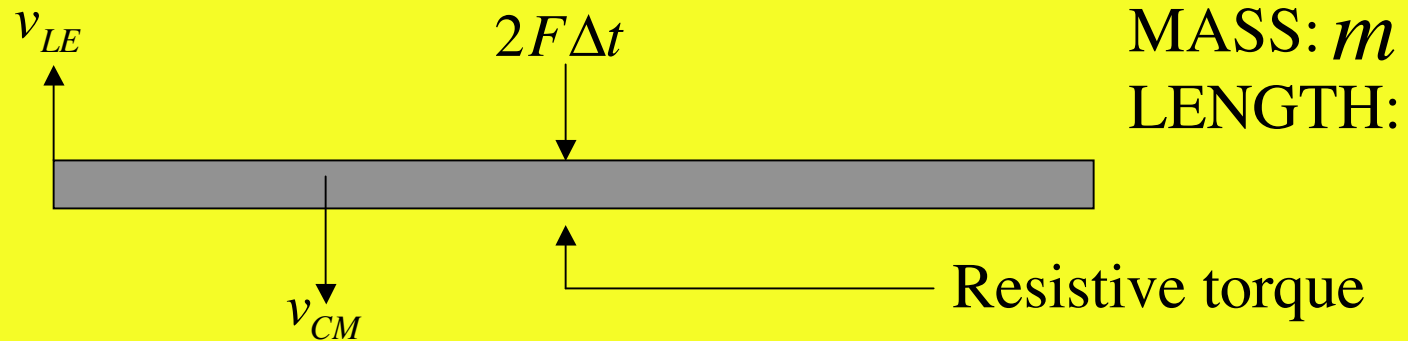
$$(1) \quad v_{CM} = \frac{F\Delta t}{m}$$

$$(2) \quad I\omega = \frac{L}{2}(F\Delta t) - [\tau\Delta t]$$

$$I\omega = \frac{L}{2}mv_{CM} - [\tau\Delta t]$$

$$(3) \quad v_{LE} = v_{CM} - \frac{L}{2}\omega$$

Broomstick Breaking Cont.



LEFT SIDE

$$v_{LE} = v_{CM} - \frac{L}{2} \left(\frac{L}{2} \frac{mv_{CM}}{\frac{1}{12}mL^2} \right) - \left[-\frac{\tau\Delta t}{\frac{1}{12}mL^2} \right]$$

$$v_{LE} = v_{CM} - 3v_{CM} + \frac{6\tau\Delta t}{mL}$$

$$v_{LE} = -2v_{CM}$$

$$v_{LE} = -2v_{CM} + \frac{6\tau\Delta t}{mL}$$

RIGHT SIDE

$$v_{RE} = v_{CM} + \frac{L}{2} \omega$$

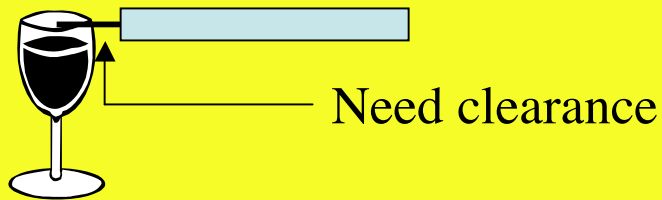
$$v_{RE} = v_{CM} + 3v_{CM}$$

$$v_{RE} = 4v_{CM}$$

$$v_{RE} = 4v_{CM} - \frac{6\tau\Delta t}{mL}$$

Apparatus

- 4 ft long, 7/8in diameter white pine, cedar, or hickory dowel rod or broomstick
- Stick pins in each end; cut off heads
- Support each pin with a wine glass, coke can, block of wood, etc.



- Striking stick: Steel 1/2" in diameter and 2ft long
- Mark the halfway point of stick so you know where to strike it
- Use a hacksaw to etch it around the circumference; avoid stick fracturing due to other weakness.
- Raise striking stick and hit the center as hard as you can; follow through