NY Times 11/25/03

"This is an enormous opportunity for farmers," said Richard Sandor, "It's estimated that American agriculture can offset about 20 percent ... these conservation projects, you'd be able to clean up the environment." ... soil, and keeping it trapped there by ... bat global warming.

South Florida Freezes Are Linked to Draining of Wetlands

By ANAHAD O'CONNOR

Draining the lush wetlands that once dominated South Florida's landscape was supposed to make the region more suitable for agriculture than the state's cooler areas up north.

But the transformation from wetland to farmland may have actually spurred a number of crop freezes in recent decades, ruining harvests and costing Florida's farmers hundreds of millions of dollars, according to the results of a new study.

The researchers based their findings on computer models that re-created weather conditions on several days when temperatures below freezing swept across several fields of sugarcane and winter vegetables. In some cases, they found, the areas would not have been as susceptible to freezing if they had been natural wetlands.

"What we saw is that the wetlands act as a buffer against these colder temperatures," said Dr. Roger A. Pielke Sr., a professor of atmospheric science at Colorado State University and one of the study's authors. "The natural land cover holds more heat than the agricultural areas, making the freezes less frequent and their durations shorter."

Around the beginning of the 20th century, large swaths of trees were chopped down and hundreds of miles of drainage canals were installed in the wetlands, partly so that Florida's farmers could move south and avoid winter freezes further north.

But farmers in South Florida who have awakened to find their crops covered in frost have repeatedly learned that the southern fields of sugar cane, tomatoes, bell peppers and lettuce can still freeze over with little or no warning. One cold spell, on Jan. 19, 1997, caused such widespread damage to crops and trees that farmers lost more than $300 million.

Land is cleared and a natural buffer to the cold is removed too.

Using data from that freeze and ... during the 1980's, Dr. Pielke and his colleagues looked at what happened and compared it with computer simulations of what might have unfolded if the areas had been wetlands.

"The wetlands would not have frozen over as often because the water holds more heat," Dr. Pielke said.

"In this condition," added Curtis Marshall, the lead author of the study and a colleague of Dr. Pielke's at Colorado State, "there's also more water vapor released into the atmosphere; putting more humidity in the atmosphere allows it to stay warmer at night."

That process, when factored into the computer models, brought about an increase in temperature of about two degrees Celsius in key agricultural areas. Though it may sound insignificant, Mr. Marshall said, an extra two degrees could keep light freeze conditions from creating havoc with fragile fruits and vegetables.

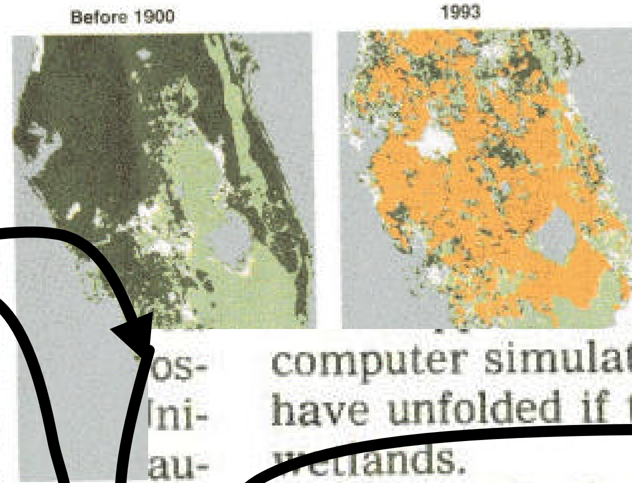
The scientists also noted that when temperatures sank low enough to damage crops, the agricultural lands experienced freezing for several hours longer. The wetlands, it appeared, were able to bounce back faster from freezing temperatures.

Their research was published Nov. 5 in the journal Nature.

Crop freezing, said David Zierden, the assistant state climatologist, is one of the biggest weather threats to Florida's agricultural industry. "How the land-use change is affecting the local climate is nothing new, ...

Crops and Cold Move South

Conversion of Florida wetlands into farmland over the past century may have led to more freezing in those areas. While farmers moved south to protect crops from the cold, clearing the water from the land appears to have reduced its heat-retaining properties.



Source: U.S. Geolog...

computer simulations of what might have unfolded if the areas had been wetlands.

"The wetlands would not have frozen over as often because the water holds more heat," Dr. Pielke said.

"In this condition," added Curtis Marshall, the lead author of the study and a colleague of Dr. Pielke's

Thermodynamics and Gases

Last Time

- specific heats
- phase transitions
- Heat and Work
- 1st law of thermodynamics
- heat transfer
  - conduction
  - convection
  - radiation

Today

- Kinetic Theory of Gases

review

Empirical Behavior of Ideal Gases in *P, T, V*

- **17 – 18th Centuries … Experiments giving empirical behavior of gases in terms of volume, pressure, temperature, and mass of gas**
- **Keep other quantities fixed … and …**

$V \mu \frac{1}{P}$	**Boyle's Law**
$V \mu T$	**Charles Law**
$P \mu T$	**Gay-Lussac Law**
$V \mu m$	**where *m* = mass of gas**

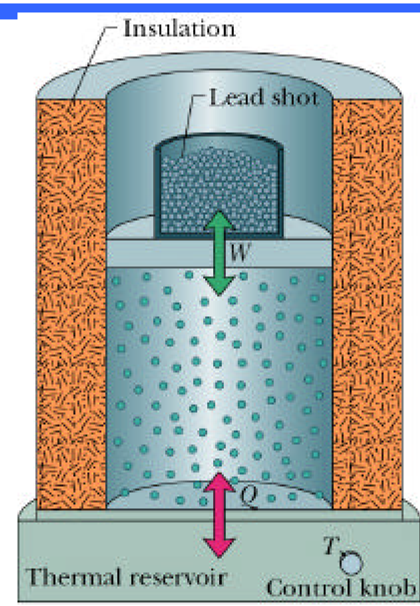
- **We put them together and express as the *Ideal Gas Law***
  - n=#of moles
  - R= gas constant

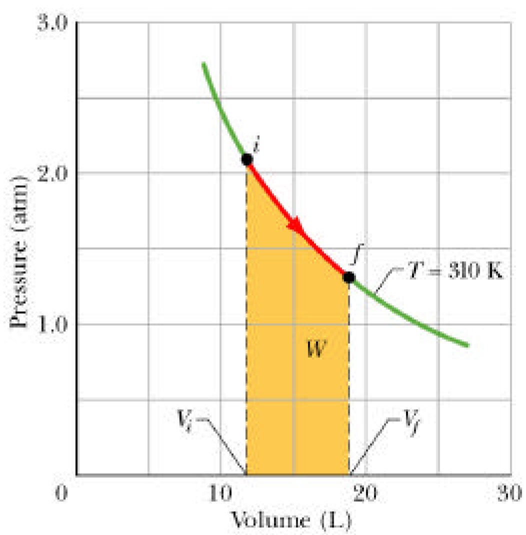
$$pV = nRT$$

Isothermal Expansion and Compression

Note

- in general, the following can vary
  - V=volume
  - p=pressure
  - n=number of moles (amount) of gas
  - T=temperature
- Isothermal = 'T is constant'
- Essential, to predict general behavior, to know what varies, what is constant, and more rules
  - recall possible processes

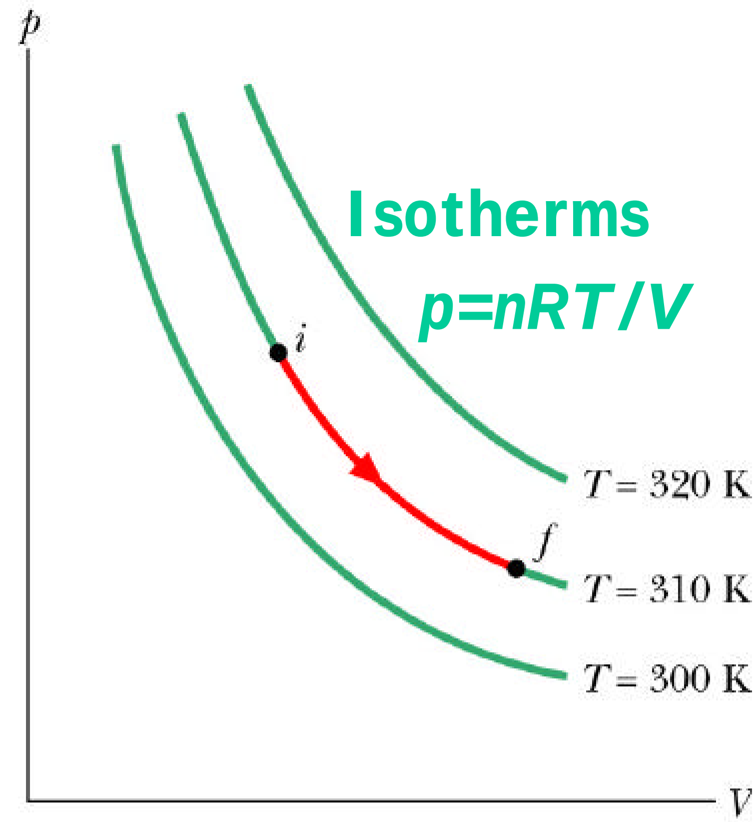




Expansion at Constant Temperature

$$pV = nRT$$

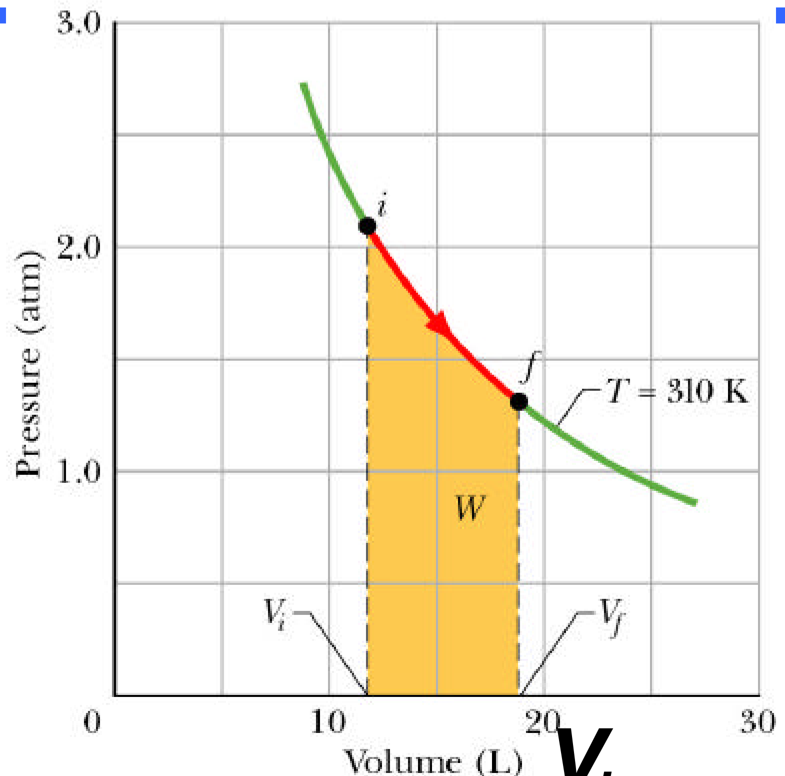
- **Units**
  - $R = 8.31\ J/(mol\text{-}K) = kN_A$
- **Work (constant temperature) done obtained from integral in p-V (see sample prob 20-1)**
- **Expansion (or compression) at constant T follows "isothermal contours" with $p = constant/V$**



$$W = \int_{V_i}^{V_f} p\, dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \ln\left[\frac{V_f}{V_i}\right]$$

Sample Problem 20-2

- **Isothermal (T=310K) expansion of 1 mole (with *p*=2 atm) of oxygen from 12 liters to 19 liters**
- **How much work done?**
- **Final pressure?**



$$W = nRT\ \ln(V_f / V_i)$$
$$= (1)(8.31)(310)\ \ln(19 / 12)$$
$$= 1180 \text{ Joules}$$

$$p_f = p_i \frac{V_i}{V_f}$$
$$= (2.0)\frac{12}{19}$$
$$= 1.26 \text{ atm}$$

review

Gas Law from Atomic Perspective

$$pV = nRT$$

equivalent

$$pV = nRT = nN_A \left(\frac{R}{N_A} \right) T$$

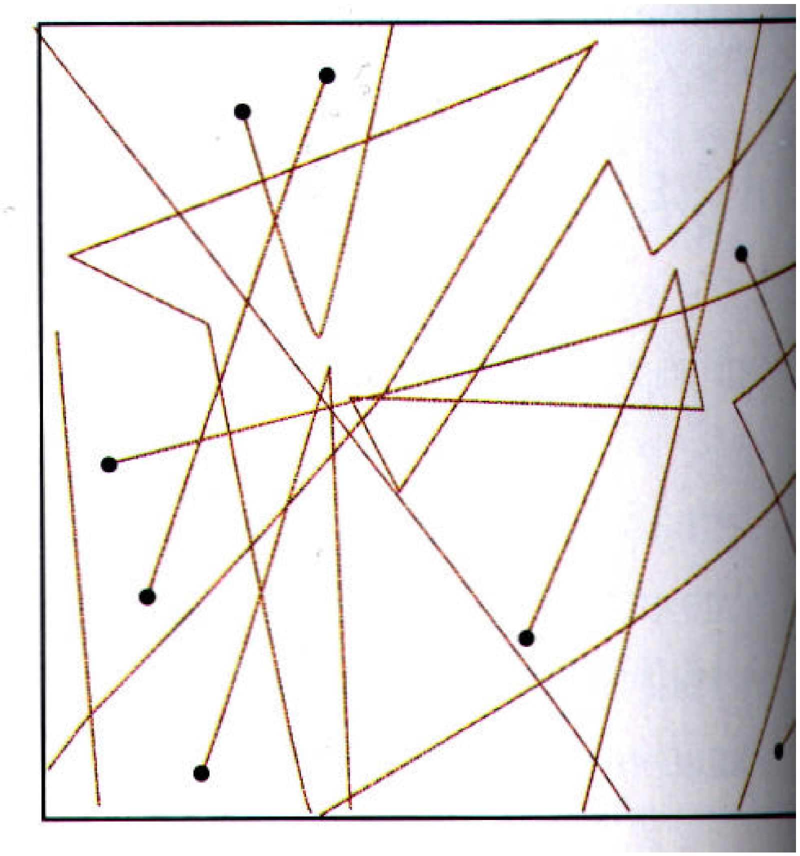
$$pV = NkT$$

N = # molecules

k = Boltzmann constant

- **Units**
  - $R = 8.31\ J/(mol\text{-}K) = kN_A$
  - $k = 1.38\ 10^{-23}\ J/K$ (Boltzmann constant)

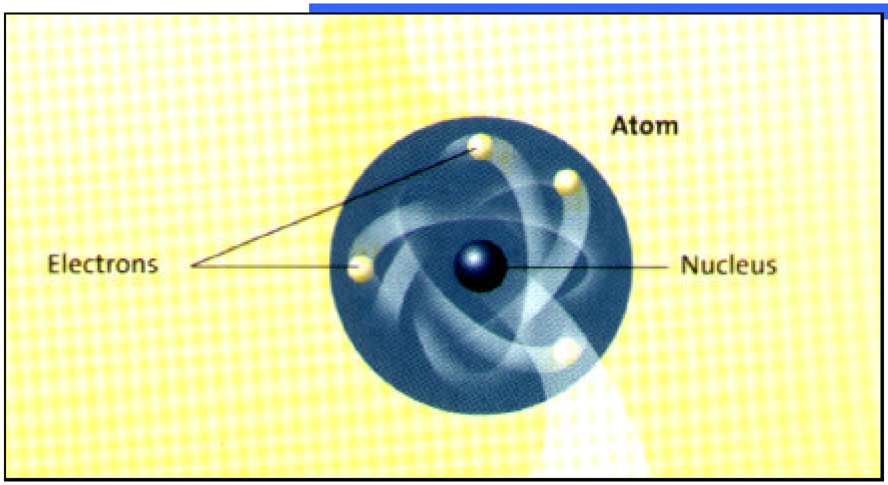
Gases and Atoms (molecules)



We will soon evaluate "mean free path", l, between collisions!

- We recognize now that gases consist of free (from each other) atoms or molecules
- "Ideal Gas": interactions between atoms are elastic
  - ◆ Interatomic forces can be neglected except at the instant of collision
  - ◆ Most gases behave in a nearly "ideal" manner
    - ☐ Interatomic forces (Van der Waal forces) make only small modifications to the "Ideal Gas Laws"
- Monatomic Gas … simple … behaves like a billiard ball
  - ◆ We consider this first and generalize

Kinetic Theory … Atoms in Gases



- mass proton ~ mass neutron
  - m_N ~ 1.7 10^{-24} grams
- A = # protons + # neutrons

- From whence Avogadro's Number (N_A)?
- Atom contains nucleus and electrons
  - ◆ nucleus has neutrons (no charge) and protons (+e charge)
- <u>Essentially all mass</u> is in the nucleus
  - ◆ atomic wt. A
  - ◆ Molecule: use molecular weight = $A_1 + A_2 + \ldots$

Derive Avogadro's Number (from the nucleon mass)

1) Define $M_{mole} = A$ (grams)

2) But we hypothesize that the mole contains

a fixed number of molecules (N_A)

3) Mass of a single molecule is $m_{1molecule} = m_N A$

4) Follows: $M_{mole} = N_A m_{1molecule} = N_A m_N A$

5) For (1) and (4) be consistent requires

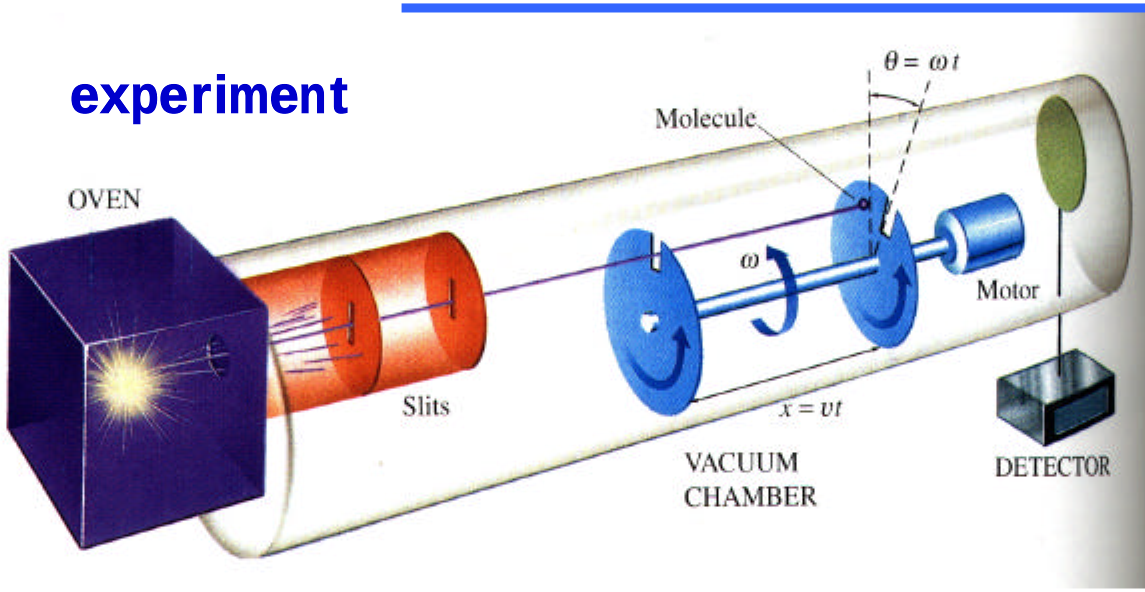
$N_A m_N = 1$ or $N_A = 1 / m_N$

6) $N_A = \dfrac{1}{1.7 \times 10^{-24}}$ or $N_A = 6.02 \times 10^{23}$ atoms

Can also do experiments to measure atomic velocities!!

Velocity Distribution

experiment

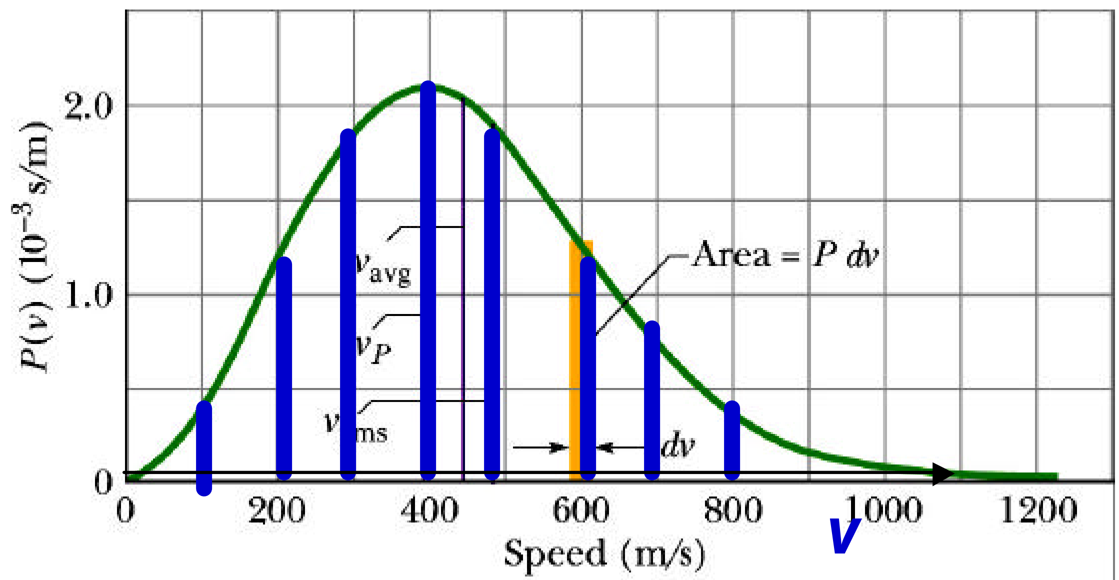


$$q = wt \qquad x = vt$$

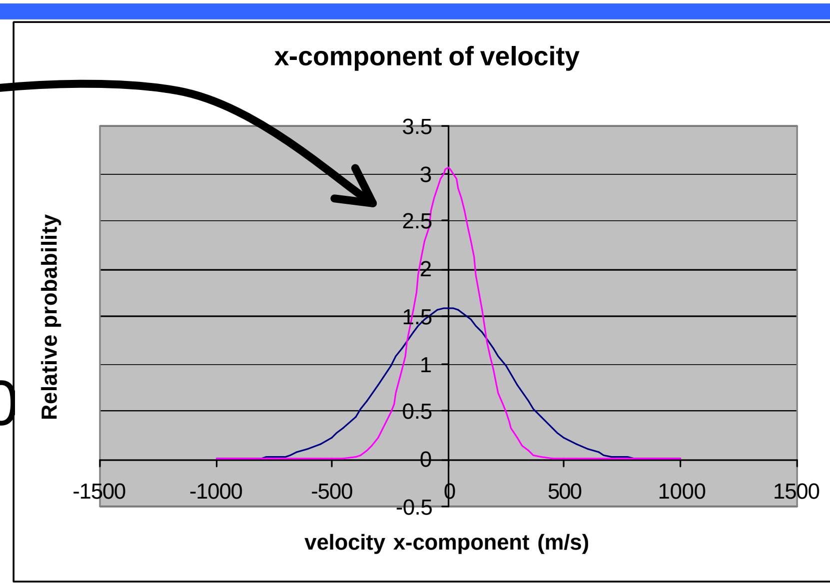
$$v = w\frac{x}{q}$$

Number molecules in fixed time interval.

- Measure and plot number vs speed
  - this is velocity distribution or spectrum
  - Peak of distribution moves higher if oven temperature is increased



Probability (frequency) distributions



probability to have v_x in dv_x

$$\langle v_x \rangle = \frac{1}{N}\sum_1^N v_x = \int v_x P(v_x)\,dv_x = 0$$

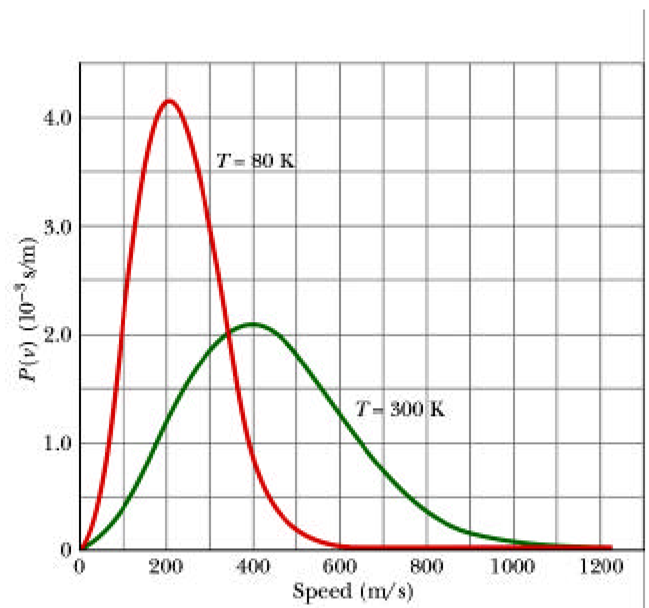
$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle = 0$$

$$\langle v_x^2 \rangle = \frac{1}{N}\sum_1^N v_x^2 = \int v_x^2 P(v_x)\,dv_x$$

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle \neq 0$$

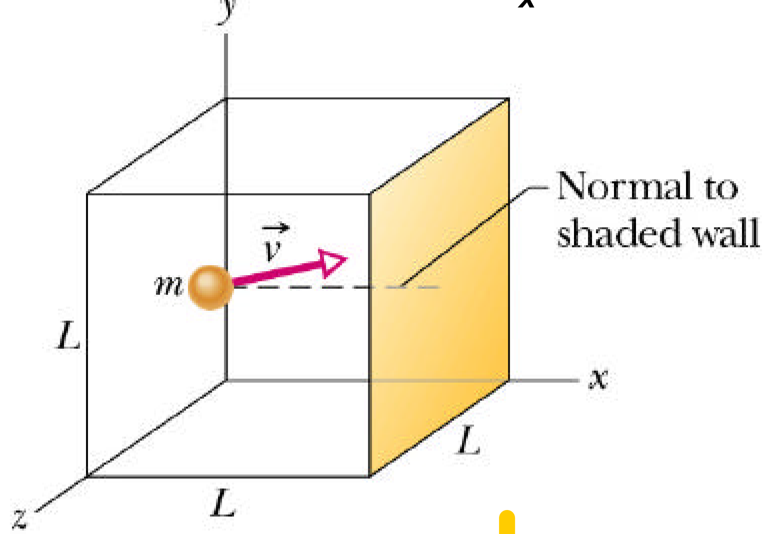
$$v^2 = v_x^2 + v_y^2 + v_z^2$$

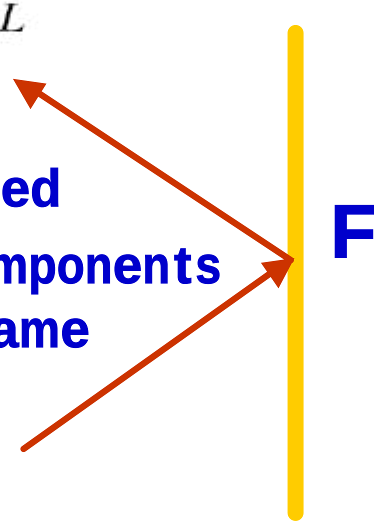
$$\langle v^2 \rangle = 3\langle v_x^2 \rangle$$



Ideal Gas Law … Derived from atoms!

Average time between collisions on shaded wall is $\Delta t = 2L/v_x$





v_x reversed

other components the same

- Consider dilute system of *N* moving, <u>marble-like atoms</u> in a (cubic) box
  - pressure comes from impacts of atoms on walls
  - Equal and opposite forces on atoms
  - Calculate <u>average</u> force by wall on atom
  - Infer pressure (F/A) on the wall

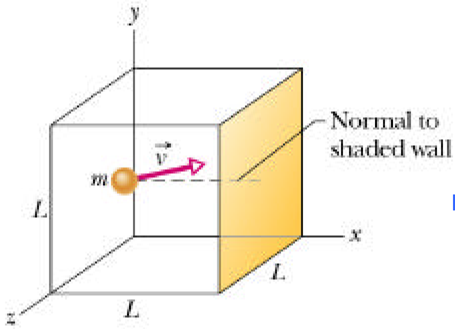
$$F_x^{1\ \mathrm{atom}} = \frac{m\Delta v_x}{\Delta t} = \frac{m(2v_x)}{2L/v_x} = \frac{mv_x^2}{L}$$

$$p = \frac{\sum F_x}{A} = \frac{\sum \frac{mv_x^2}{L}}{L^2}$$

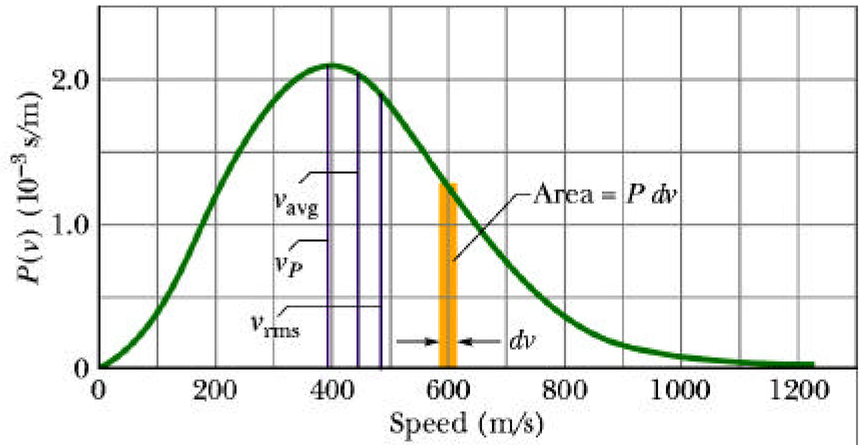
$$p = \left(\frac{m}{L^3}\right)\sum_1^N v_x^2 \qquad \text{with } V = L^3$$

$$pV = m\sum_1^N v_x^2$$

Ideal Gas



$$pV = m\sum_{1}^{N} v_x^2$$



$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle = 0$$

$$\langle v_x^2 \rangle \equiv \frac{1}{N}\sum_{1}^{N} v_x^2 = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$v_{rms}^2 \equiv \langle v^2 \rangle = 3\langle v_x^2 \rangle$$

$$v_{rms}^2 \equiv \frac{1}{N}\sum_{1}^{N} v^2 = \frac{3}{N}\sum_{1}^{N} v_x^2$$

It follows that

$$pV = \frac{Nm}{3} v_{rms}^2$$

Compare with

$$pV = NkT$$

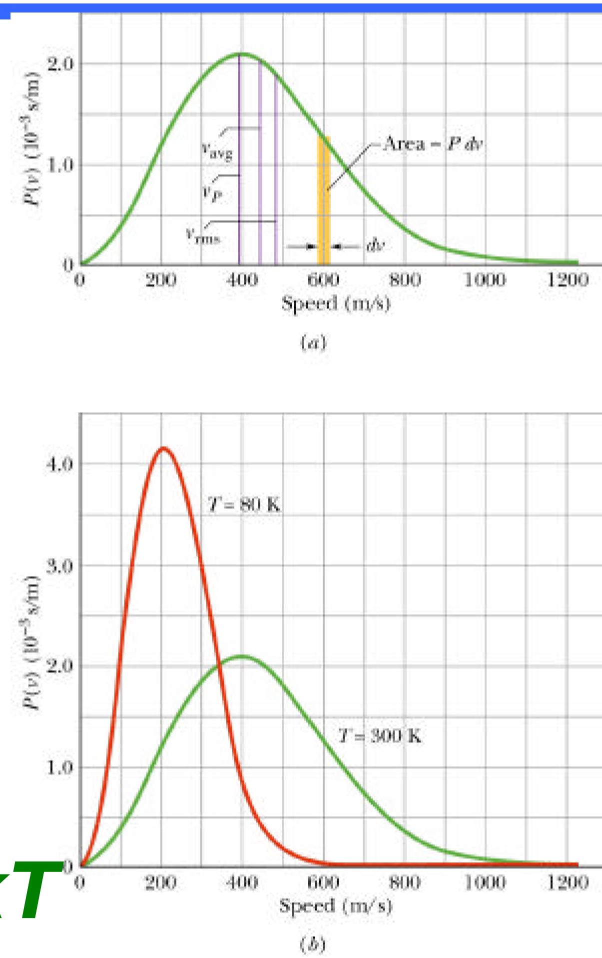
Molecules in Motion

$$pV = \frac{Nm}{3} v_{rms}^2$$

$$pV = NkT$$

$$kT = \tfrac{1}{3} m v_{rms}^2$$

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$



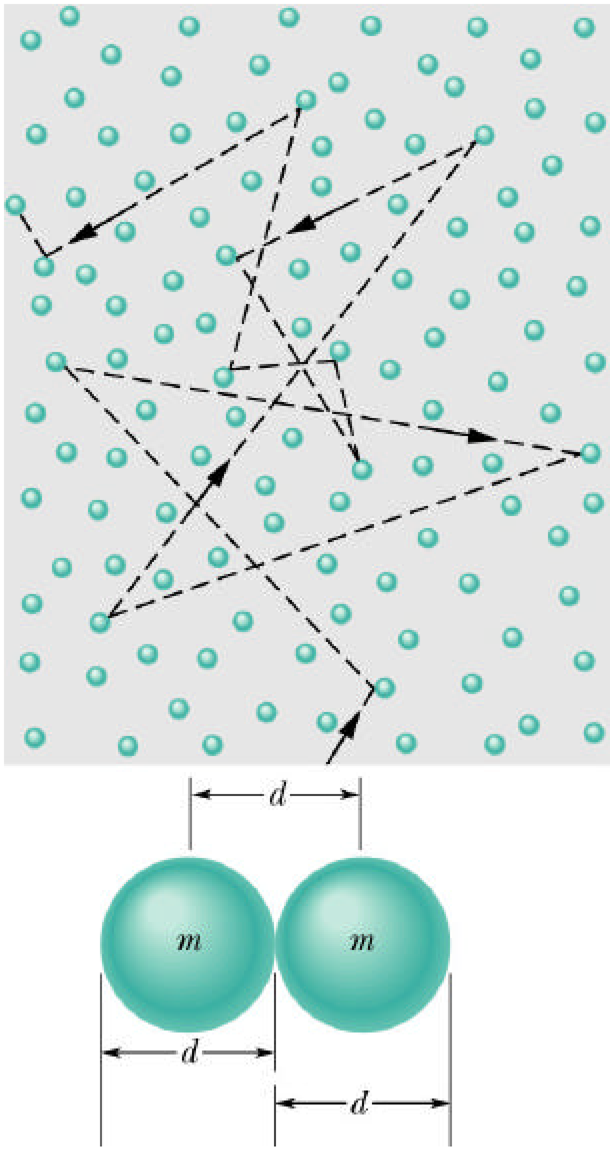
Check table 20-1 for typical molecular speeds

- eg, oxygen at room temp has v ~ 483m/s

$$\langle K_{atom} \rangle = \tfrac{1}{2} m v_{rms}^2 = \tfrac{3}{2} kT$$

$$E_{int} = N \langle K_{atom} \rangle = \tfrac{3}{2} NkT$$ for gas of "billiard ball" atoms

Collisions between Gas Molecules

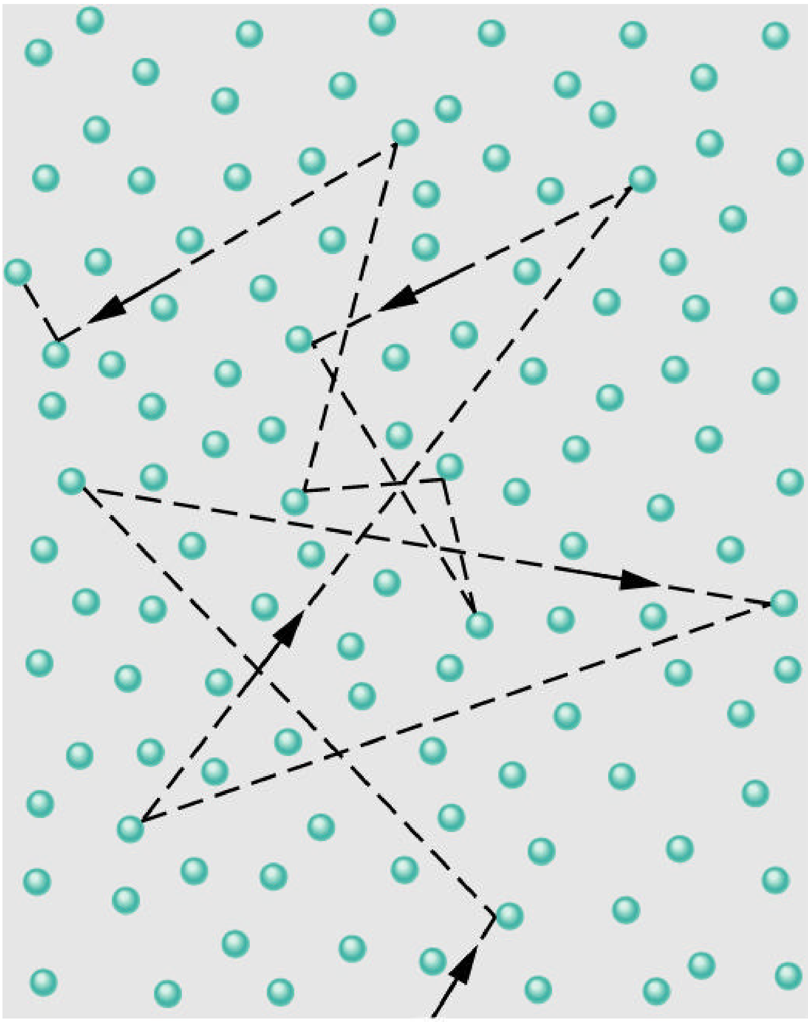


Mean Free Path

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

- λ = average distance “free” before collision
- Rough derivation in text (section 20-6)
  - Should depend on atomic density (N/V) and cross sectional area of atom
  - Note dimensional analysis and intuition give above dependence up to factor 1.4
- Sample problem 20-4: gas evaluated at STP (standard temp = 300K and pressure = 1 atmosphere)
  - $d \sim 3 \times 10^{-10}$ m
  - $\lambda \sim 10^{-7}$ m ~ 10^{-4} mm ~ 300 d
  - $t \sim \lambda / v_{rms} \sim .24 \times 10^{-9}$ sec is average time between collisions (for $v_{rms} \sim 450 m/s$)

Bouncing Molecules



- l ~ 10^{-7} m ~ 400 d means they collide 10^7 times per meter traveled (at STP)
- Forces between atoms (Van der Waals) are very weak until they are essentially in contact
- Then they bounce
  - energy of collisions much smaller than excitation energies of insides
  - makes collisions elastic
- Small deviations ideal gas law due to Van der Waals forces

Specific Heat Measures the Internal Energy of a Gas

- Useful: Also tells us how the heat may be transformed to useful (mechanical) energy
  - Does this happen?
  - Sure … lots of examples …

Hero's engine

steam engine

Internal Energy from Atomic Nature

- *pV=nRT* understood from atomic nature of matter
  - *pV=NkT* is equivalent form
  - Both are generally applicable (up to small van der Waals corrections) for all gases … $pV \propto$ kinetic energy of atoms
- Internal energy of the gas is a sum of all the energy forms (including kinetic energy) of the molecules
  - simplest is monatomic gas (one atom in the molecule, rotationally symmetric) -> energy all translational
  - real world: coefficient, 3/2, only applies to "noble gases"

monatomic gas

$$pV = NkT = nRT$$

$$\langle K_{atom} \rangle = \tfrac{3}{2} kT$$

$$E_{\text{int}} = N \langle K_{atom} \rangle = \tfrac{3}{2} NkT$$

$$E_{\text{int}} = \tfrac{3}{2} nRT$$

ANY gas (prove soon!)

$$pV = NkT = nRT$$

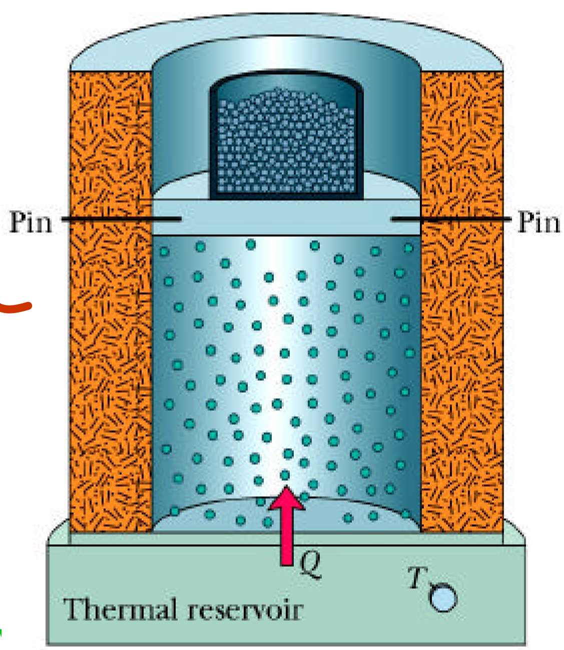
$$\langle E_{atom} \rangle = \frac{C_V}{R} kT$$

$$E_{\text{int}} = N \langle E_{atom} \rangle = N \frac{C_V}{R} kT$$

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

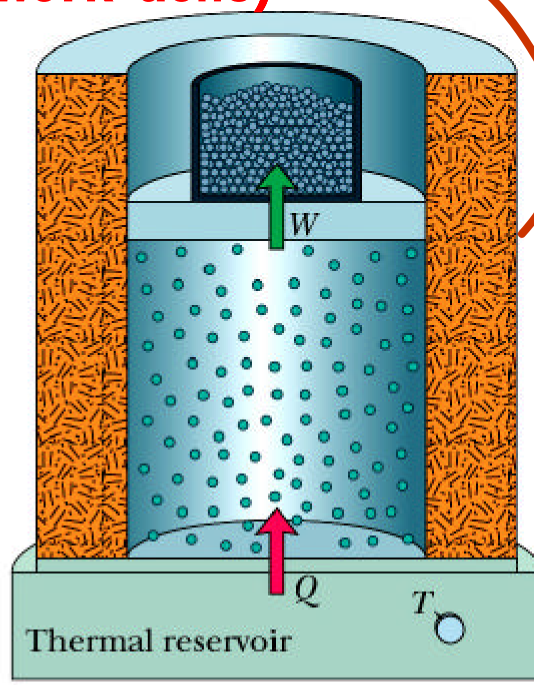
Specific Heats of Gas

- For simplicity of notation, we will use <u>molar specific heats</u> [instead of specific heat in J/(kg K)]
  - $Q \equiv n C \Delta T$ defines C in J/(mol K)
- Two ways of adding heat with different answers:
  - Keep <u>volume</u> of system fixed (no work done), so that the pressure must change
  - Keep <u>pressure</u> fixed, vary volume (work done)

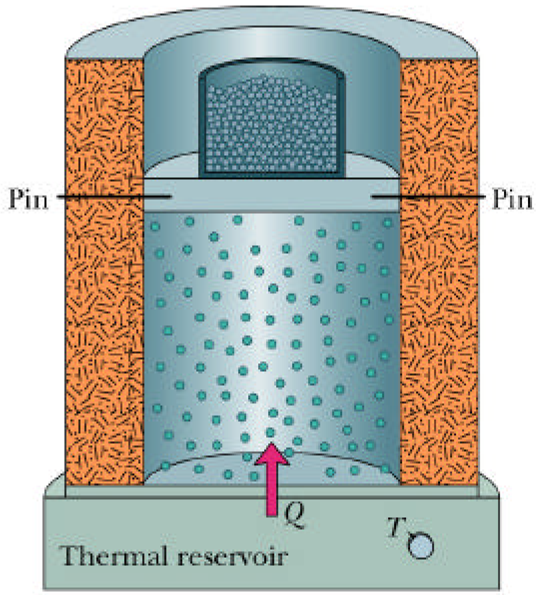


C_V

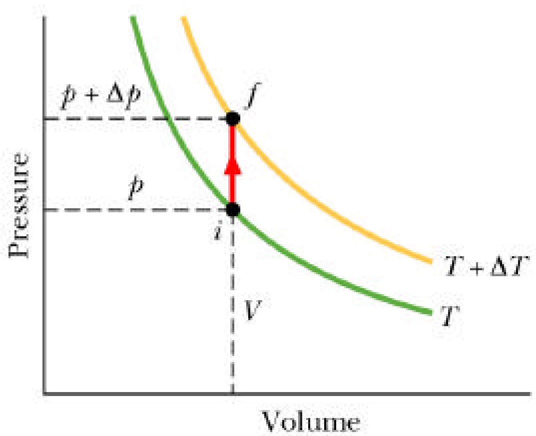
C_P



Specific Heat at Constant Volume (isochoric)



(a)



(b)

1st Law of Therm.

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

monatomic gas

$$E_{int} = \frac{3}{2} nRT$$

- **No change in volume implies no work done:**
  - $dW = 0$
- **Heat introduced proportional to temperature change when no work**
  - $Q \propto n\, C_V\, \Delta T$
- **Since $dW=0$, then the heat added must equal the change in internal energy**
  - $\Delta E_{int} = Q = n\, C_V\, \Delta T$

And we predict: Monatomic (billiard ball) gases have $C_V=3R/2$

any gas

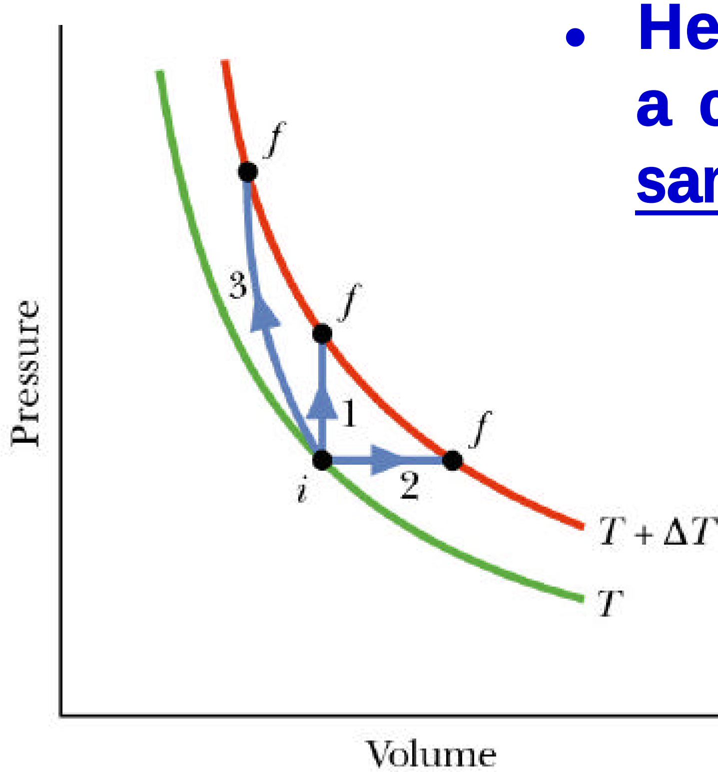
$$\Delta E_{int} = nC_V \Delta T$$

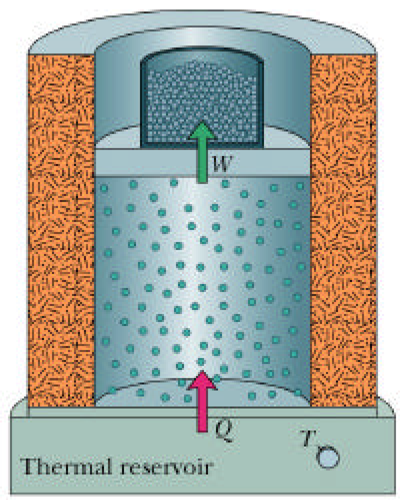
Change in Internal Energy for <u>Any</u> Ideal Gas in Any Process

***any* gas**

$$E_{int} = nC_V T$$

- **Internal energy <u>only</u> a consequence of temperature (and mass) of system.**
- **E_{int} depends on T only, not how it got there**
- **Hence <u>any</u> process ($i \rightarrow f$) resulting in a change in temperature produces the <u>same</u> change in internal energy**



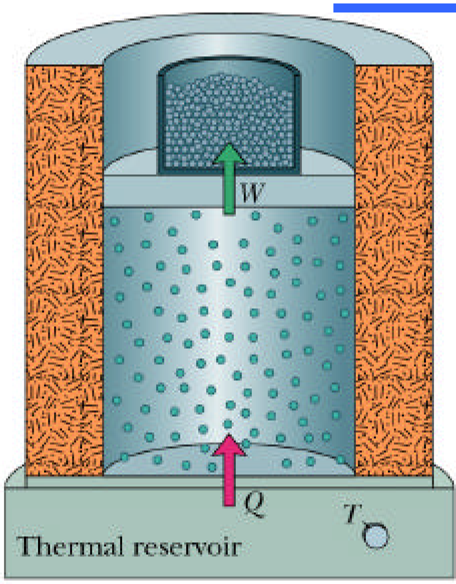


***any* ideal gas**

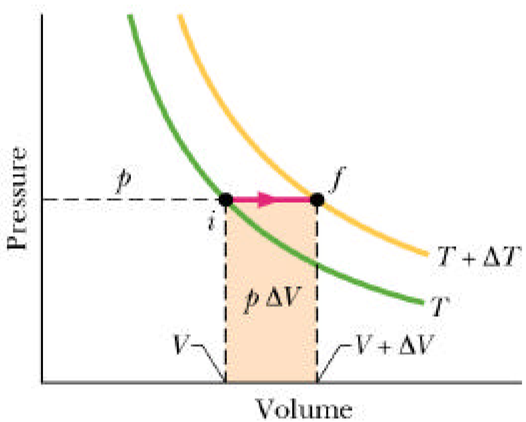
and any process

$$\Delta E_{int} = n\, C_V\, \Delta T$$

Specific Heat at Constant Pressure (isobaric process)



(a)



(b)

Here, as expansion occurs with p constant,

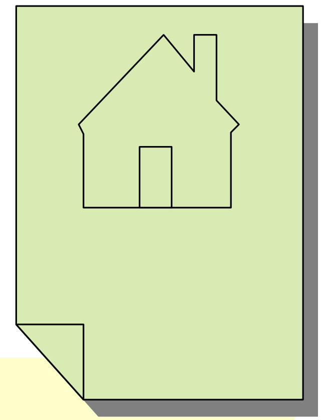
- work is done <u>and</u>
- internal energy increases

For process (*n* fixed)

- $Q \equiv n\, C_P\, \Delta T$
- And $W = p\Delta V = nR\Delta T$

$$Q = \Delta E_{\text{int}} + W$$
$$= nC_V \Delta T + p\,\Delta V$$
$$= nC_V \Delta T + nR\,\Delta T$$
$$Q = n\left(C_V + R\right)\Delta T$$
$$C_P = C_V + R$$

Sample Prob 20-8



- **Warm up cold cabin by turning on the heat (T_i ® T_f, say 270K ® 300K)**
- **What happens to gas (air) in cabin?**

Temperature in cabin increases.

Volume of cabin is fixed.

$$pV = nRT$$

What changes? If *n* were fixed,

then pressure must change

from normal 1 atm (10^5 Pa).

$$\frac{Dp}{p} = \frac{DT}{T} \sim 0.1$$

Force on (eg, picture window)

of 1m ´ 1m area $\sim (0.1)(10^5)(1)$

$\sim 10^4 N \sim 2300 lbs$ **NO WAY!!**

Answer:

p fixed at 1 atm.,

n changes by 10%.

(Air exits through cracks.)

This implies that

for this case

$$E_{int} = nC_V T$$

also stays fixed!

Thermodynamics and Gases

Today

- Kinetic Theory of Gases for simple gases
  - Atomic nature of matter
  - Demonstrate ideal gas law
  - Atomic kinetic energy = internal energy
  - Mean free path and velocity distributions
- From formula for E_{int}, can get specific heats

Next Time

- Discuss further the specific heats of Simplest Gases
  - Constant Volume
  - Constant Pressure
- Specific Heats for more complex gases
- Adiabatic Expansion → Entropy