

# Ch 20: Kinetic Theory of Gases

lecture covers sections 1-6, 8-11

Kinetic theory = study of the motions of individual gas molecules

See "molecular motion..." demo

Most gases obey the ideal gas law:

$$PV = nRT$$

↑ pressure  
 ↑ volume  
 ↑ temp  
 ↑ gas constant

ideal gas = swarm of colliding hard spheres

where the gas constant  $R = 8.31 \text{ J/mol}\cdot\text{K}$

and  $n = \#$  of moles in the gas:

$$n = \frac{N}{N_A}$$

← number of molecules in sample

and  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1} = \text{Avogadro's number}$   
 = # of molecules in 1 mole (mol) of a substance.

Also note that the # of molecules in sample is

$$N = \frac{m_{\text{sample}}}{m}$$

← total mass of sample  
 ← mass of one molecule

$$\text{so } n = \frac{M_{\text{sample}}}{m \cdot N_A} = \frac{M_{\text{sample}}}{M}$$

where

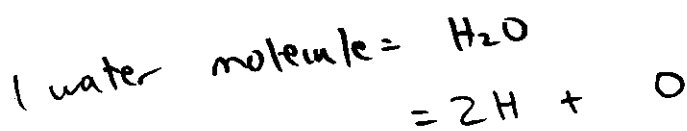
$$M = m \cdot N_A = \frac{\text{molar mass}}{\text{mass of 1 mole}}$$

eg,  $M_{\text{Hydrogen}} = 1 \text{ gm}$

$M_{\text{Carbon}} = 12 \text{ gm}$

$$= (\# \text{ of protons + neutrons in 1 molecule}) \text{ grams}$$

Example: How many moles in  $M_{\text{sample}} = 1 \text{ kg}$  of water?



hydrogen has  $M_{\text{H}} = 1.0 \text{ gm/mole}$

oxygen has  $M_{\text{O}} = 16.0 \text{ gm/mole}$

} Appendix F

$$\text{so } M = 2M_{\text{H}} + M_{\text{O}} = 18 \text{ gm/mole}$$

= "atomic weight"  $\times 1 \text{ gm/mole}$   
 18 protons + neutrons

$$= 0.018 \text{ gm/mole}$$

$$\text{so } n = \frac{M_{\text{sample}}}{M} = 56 \text{ moles of H}_2\text{O}$$

How many molecules are in this sample?

$$N = n N_A = 3.4 \times 10^{25} \text{ molecules}$$

Physicists often put the ideal gas law in a slightly different form:

$$k = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K} = \text{Boltzmann constant}$$

$$\text{so } PV = nRT = n N_A kT$$

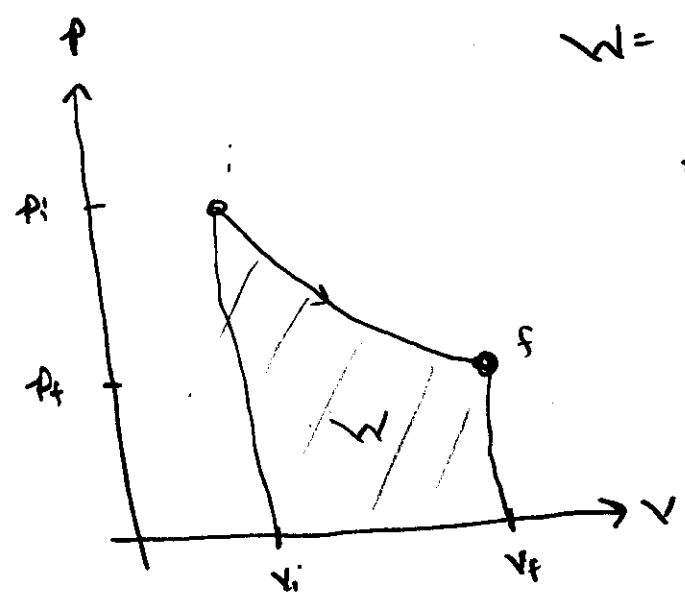
where  $N = n N_A = \#$  of molecules in sample

$$\text{so } PV = NkT$$

### Work by Isothermal Ideal Gas

isothermal  $\rightarrow$  gas is held at constant temp

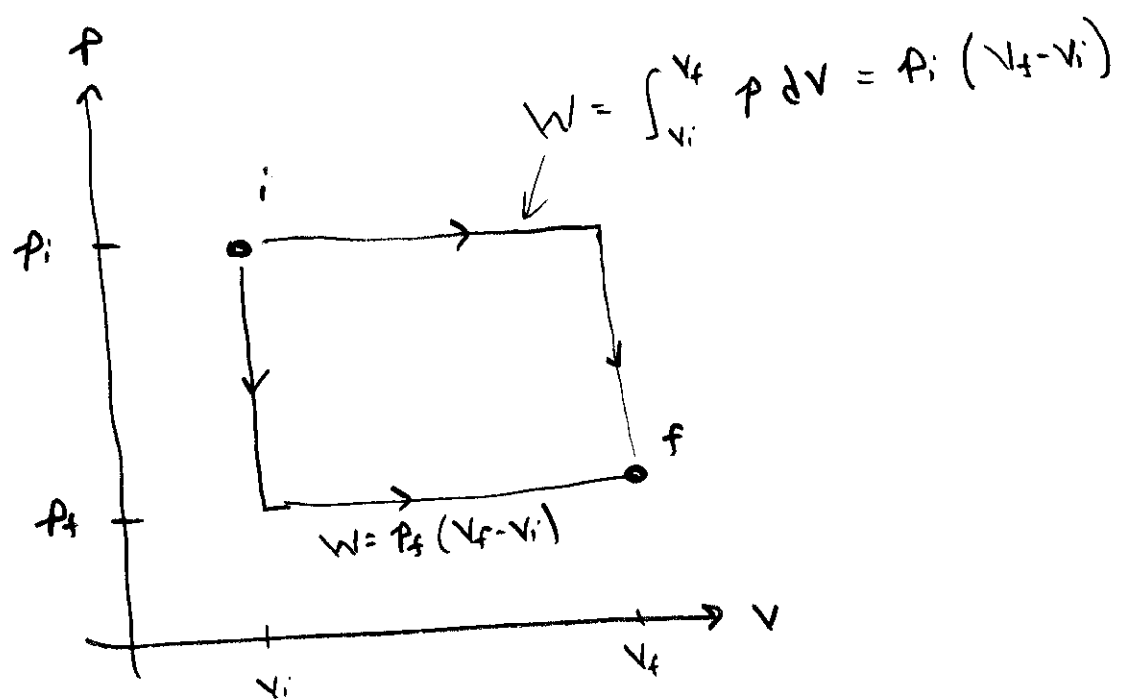
$$\text{so } P = \frac{nRT}{V} \quad \text{and}$$



$$\begin{aligned}
 W &= \int_{V_i}^{V_f} P \, dV \\
 &= nRT \int_{V_i}^{V_f} \frac{dV}{V} \\
 &= nRT \ln V \Big|_{V_i}^{V_f} \\
 &= nRT \ln \left( \frac{V_f}{V_i} \right) \\
 &\quad \uparrow \\
 &\quad \text{natural logarithm.} \\
 &= \text{work done by gas} \\
 &\quad \text{as } V_i \rightarrow V_f
 \end{aligned}$$

How much work is by the gas as  $P_i \rightarrow P_f$ ,  
via a constant volume process?

What about work done at constant pressure?

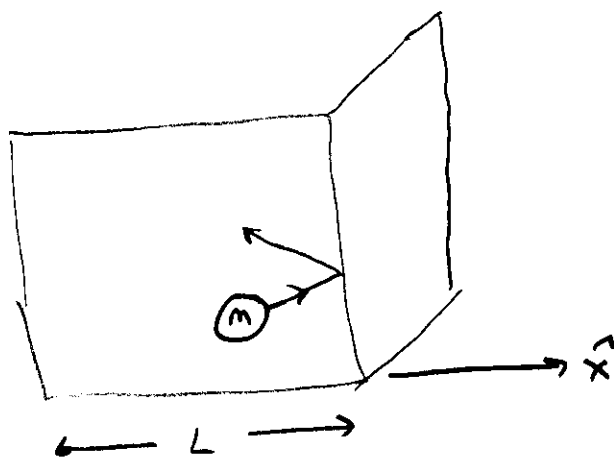


## Pressure, Temperature, & Speed

Use kinetic theory to relate  $p$  &  $T$  to a gas molecule's mean speed.

The gas is contained in a box of size  $L$ .

A single molecule rebounds off a wall.



so its horizontal speed  $v_x \rightarrow -v_x$ .

The molecule's initial momentum along  $\vec{x}$  axis is

$$\vec{p}_{x, \text{init}} = mv_x$$

while  $\vec{p}_{x, \text{final}} = -mv_x$

$$\text{so } \overline{\Delta p_x} = -mv_x - mv_x = -2mv_x$$

= molecule's change in its  $x$ -momentum

20-6  
How much momentum is delivered to the wall after this collision?

The time interval, between collisions with the same wall is  $\Delta t = 2L/v_x$

$F_1 = \frac{\overline{\Delta P_x}}{\Delta t}$  = rate at which this molecule delivers momentum to wall

$$= \frac{2m v_x^2}{2L} = \frac{m v_x^2}{L}$$

average force 1 molecule exerts on wall

$F_{\text{total}} = F_1 + F_2 + \dots + F_N$  = total force exerted by  $N$  molecules

so  $p = \frac{F_{\text{total}}}{\text{Area}}$  = pressure the gas exerts on wall

$$= \frac{m}{L^3} (v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \dots + v_{xN}^2)$$

velocity<sup>2</sup> of molecule 1, 2, 3, ...

which all differ...

Let  $(v_x^2)_{avg} = \text{average of } (v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2)$   
 $= \frac{v_{x1}^2 + \dots + v_{xN}^2}{N}$

so  $p = \frac{Nm (v_x^2)_{avg}}{V}$  since  $L^3 = V = \text{volume}$

Recall also that  $N = n N_A$   $\left\{ \begin{array}{l} \downarrow \text{\# of moles in sample} \\ \uparrow \text{Avogadro's \#} \end{array} \right.$

so  $Nm = n \underbrace{N_A m}_{\text{mass of 1 molecule}}$   
 $= n M$   $\left\{ \begin{array}{l} \uparrow \text{molar mass} \end{array} \right.$

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

Also note that  $v_{rms}^2 = (v_x^2)_{avg} + (v_y^2)_{avg} + (v_z^2)_{avg}$   
 $= 3(v_x^2)_{avg}$   
 "root-mean-square" or avg velocity<sup>2</sup>  $\left\{ \begin{array}{l} \uparrow \\ \text{since } (v_x^2)_{avg} = (v_y^2)_{avg} \end{array} \right.$

so  $p = \frac{nM v_{rms}^2}{3V} = \text{pressure of ideal gas}$

Alternately,  $pV = \frac{1}{3} n M v_{rms}^2 = nRT$

$$\Rightarrow v_{rms} = \sqrt{\frac{3RT}{M}} = \text{rms speed of a gas molecule.}$$

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

the molecules' average speed increases as  $T^{1/2}$ , and decreases as

$m^{-1/2}$   
↑  
mass of one molecule

See "temperature of gas" demo

## Translational Kinetic Energy (KE)

a single molecule's average translational KE is

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

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

$$= \frac{3}{2} \frac{R}{N_A} T$$

but  $M = mN_A$

but  $k = \frac{R}{N_A}$   
= Boltzmann constant

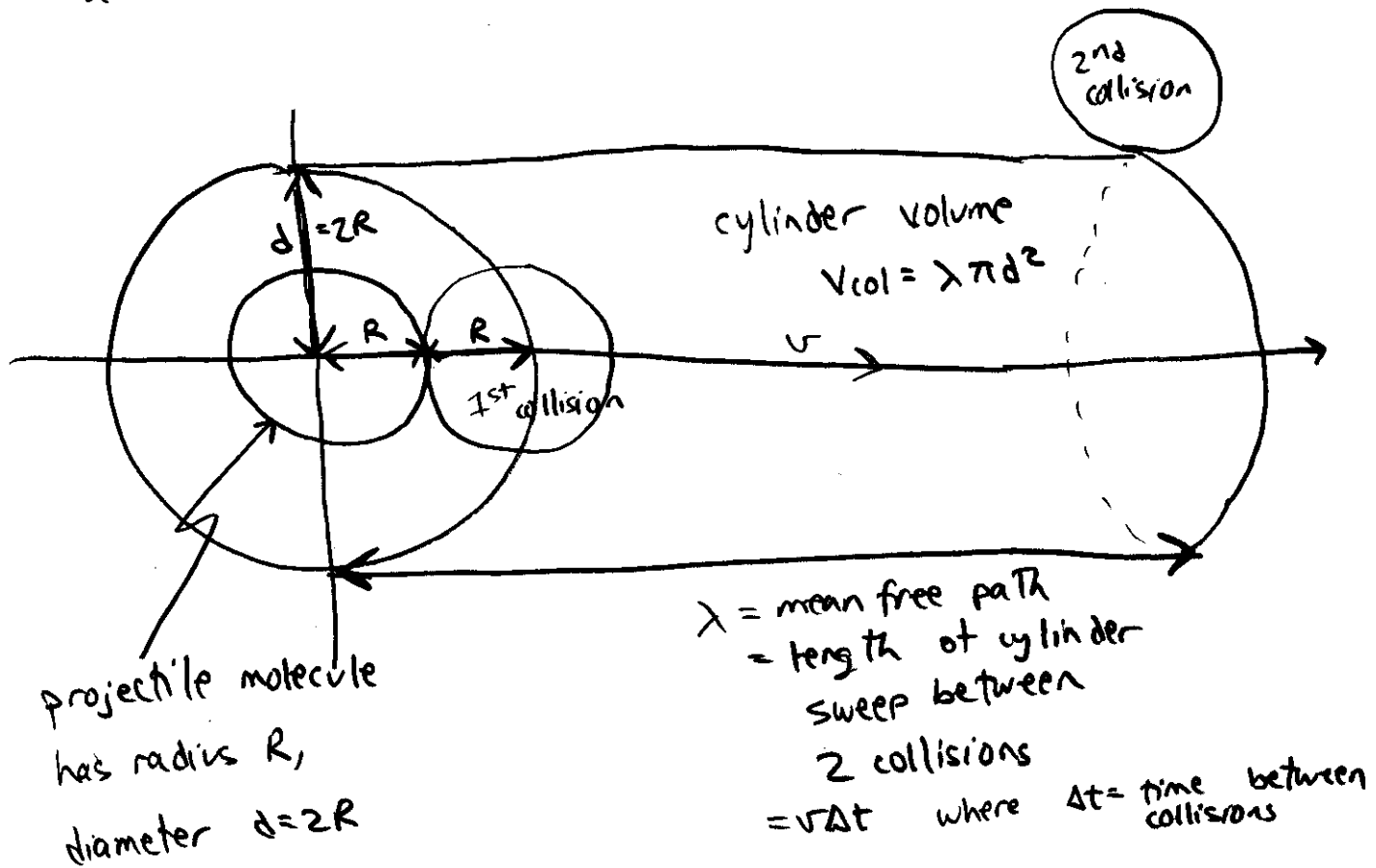
so  $K_{avg} = \frac{3}{2} kT$

⇒ a molecule's average KE depends only on the gas temp  $T$ , and is independent of molecule mass  $m$

⇒ more massive molecules have slower average speeds

Mean Free Path = typical travel distance  
between collisions.

Between 2 subsequent collisions,  
a molecule sweeps out the cylinder



gas number density is  $\rho = \frac{N}{V} = \frac{\text{total \# of molecules}}{\text{total volume}}$

The condition for a collision is that the cylinder contain  $\geq 1$  target molecule,

so 
$$\rho \cdot V_{col} = \# \text{ of target molecules in cylinder} \approx 1 \text{ for a collision}$$

so 
$$\frac{N V_{col}}{V} = \frac{N \lambda \pi d^2}{V} \approx 1$$

$$\Rightarrow \lambda \approx \frac{V}{N \pi d^2} = \begin{array}{l} \text{approximate} \\ \text{mean free path} \\ \text{= typical distance} \\ \text{traveled btwn'} \\ \text{collisions.} \end{array}$$

Actually, this estimate assumed that the target molecules are stationary. If instead we allow them to move, then their relative speed increase by  $\sqrt{2}$ , and  $\lambda$  decreases by  $\sqrt{2}$ , so

$$\lambda \rightarrow \frac{V}{\sqrt{2} N \pi d^2} = \text{exact mean free path.}$$

## Sample Problem 20-4

b) What is  $\lambda$  for  $O_2$  gas at  $T=300\text{K}$  and  $P=1\text{atm}=10^5\text{N/m}^2$ , and the molecular diameter of  $O_2$  is  $d=290\text{pm}=290\times 10^{-12}\text{m}$

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

where  $PV = NkT$  is ideal gas law

so  $\frac{N}{V} = \frac{P}{kT}$  = gas number density

where  $k = 1.4 \times 10^{-23} \text{ J/K}$  - Boltzmann const

$$\text{and } \lambda = \frac{kT}{\sqrt{2} \pi d^2 P} = 1.1 \times 10^{-7} \text{ m}$$

$$= 390 \text{ \AA}$$

b) what is the frequency of collisions?

First note that  $\lambda = v \Delta t$  where  $\Delta t$  = time between collisions,

$$\text{so } f = \frac{1}{\Delta t} = \frac{v}{\lambda} = \text{frequency of collisions.}$$

Get  $v$  from

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \text{rms, or average molecular speed}$$

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

$$M = \text{molar mass of } O_2 \text{ molecule}$$

$$= 32 \text{ gm/mole (Appendix F)}$$

$$= 0.032 \text{ kg/mole}$$

so  $v_{rms} = 480 \text{ m/sec} = \text{average molecular speed}$

(about 40% faster than the sound speed)

and  $f = \frac{v}{\lambda} = 4.4 \times 10^9 \text{ sec}^{-1}$

= # of collisions per second experienced by a gas molecule

Also  $Q = c M_{\text{sample}} \Delta T =$  heat needed to raise sample temp by  $\Delta T$

↑  
specific heat of sample

since  $K_{\text{avg}} = \frac{3RT}{2N_A}$

The gas' total internal energy is

$$E_{\text{int}} = N K_{\text{avg}} = \frac{3}{2} \frac{N}{N_A} RT = \frac{3}{2} nRT$$

Likewise, if you change the gas temp by  $\Delta T$ ,

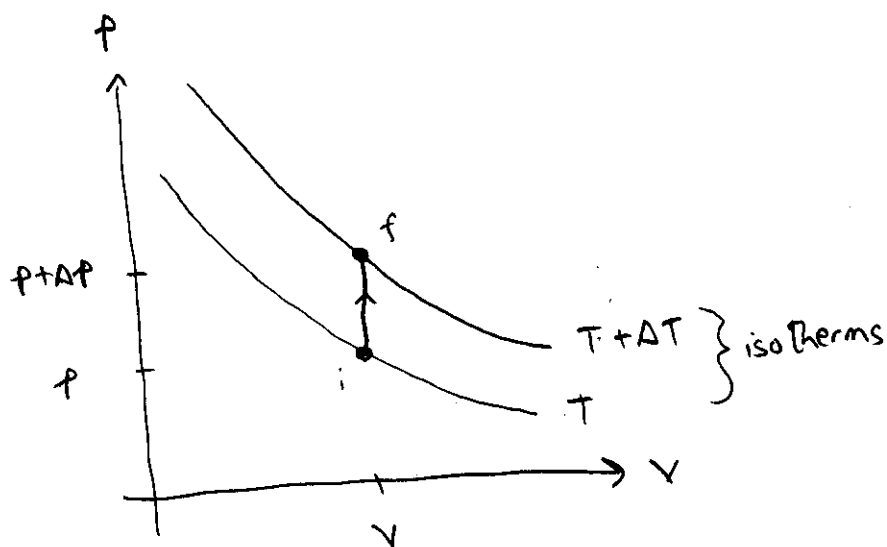
$$\Delta E_{\text{int}} = \frac{3}{2} nR \Delta T$$

⇒ The internal energy of an ideal gas depends only on T

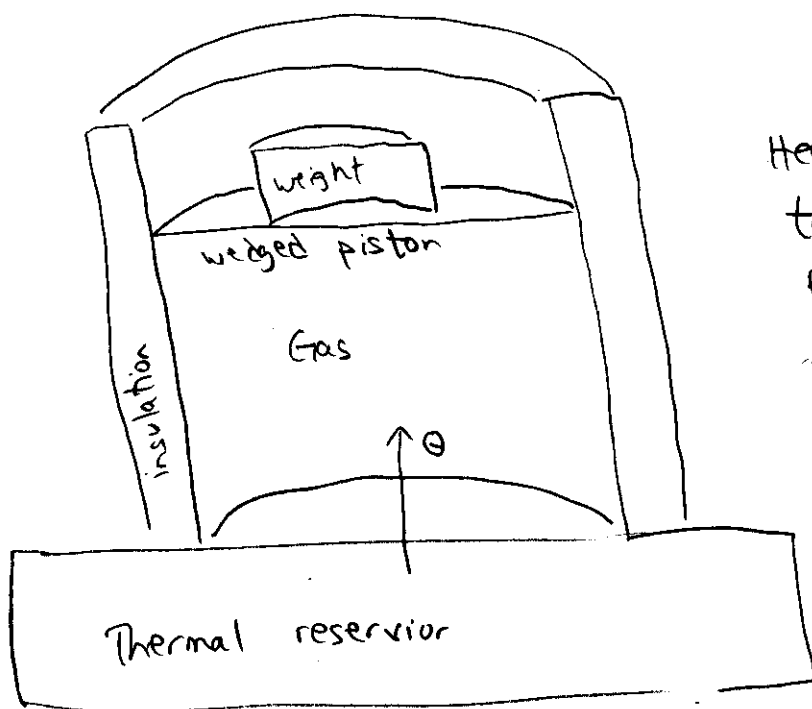
(will use this result later)

## Specific Heat of an Ideal Gas

First, let's consider a constant volume process:



Piston



Heat  $Q$  is supplied to gas while piston is wedged, so  $P$  &  $T$  increase while  $V = \text{constant}$

Heat supplied to gas  $Q = c M_{\text{sample}} \Delta T$   
 $= c n M \Delta T$

$M = \text{mass of 1 mole}$

$$\equiv n C_V \Delta T$$

where  $C_V \equiv c M =$  specific heat at constant volume

Substitute  $Q$  into 1<sup>st</sup> Law of Thermo:

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

where  $W = \int_{V_i}^{V_f} P dV$

What is  $W$ ?

$$\Delta E_{\text{int}} = Q = n C_V \Delta T = \frac{3}{2} n R \Delta T$$

so  $C_V = \frac{\Delta E_{\text{int}}}{n \Delta T} = \frac{3}{2} R = 12.5 \text{ J/mol} \cdot \text{K}$

= specific heat for monatomic gas  
 (eg, noble gases like He, Ar, etc)

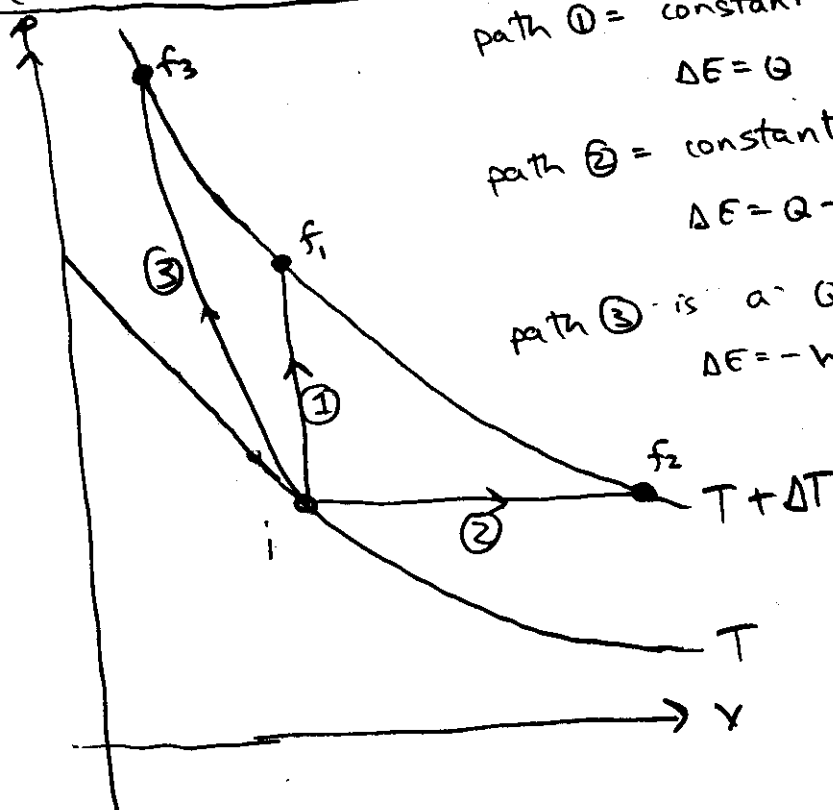
Later we will show that

diatomic molecules ( $O_2, N_2, \text{etc}$ ) have  $C_v = \frac{5}{2} R$

polyatomic molecules ( $CH_4, CO_2, \text{etc}$ ) have  $C_v = 3R$

Note that  $E_{int}$  and  $\Delta E_{int}$  depend only on  $T, \Delta T$ , which implies that these energy changes are independent of the thermodynamic process, i.e.,

the path thru a p-v diagram:



path ① = constant  $v$  process (isochore)  
 $\Delta E = 0$  since  $\Delta v$  &  $w = 0$

path ② = constant  $p$  process (isobaric)  
 $\Delta E = Q - W$  where  $Q \text{ \& } W > 0$

path ③ is a  $Q = 0$  process (adiabatic)  
 $\Delta E = -W > 0$   
 discussed later

isotherms  
 $(T = \text{const curves})$

Although each process is distinct, the change in internal energy,  $\Delta E_{int} = \frac{3}{2}nR\Delta T$  is the same among paths 1-3  
 $= nC_v\Delta T$

$\Rightarrow$  We can always use ~~the~~ constant-V process ① to easily calculate  $\Delta E_{int}$  that results from any process

Specific heat of a constant pressure process

this time  $Q = nC_p\Delta T =$  heat exchanged during a constant p-process

1<sup>st</sup> Law:  $\Delta E_{int} = Q - W = nC_v\Delta T$  since  $\Delta E_{int}$  depends only on  $\Delta T$

where work  $W = \int_{V_i}^{V_f} p\Delta V = p(V_f - V_i) = p\Delta V$   
 $\uparrow$  constant

The ideal gas law is  $pV = nRT$   
so  $p\Delta V = nR\Delta T$

so  $\Delta E_{int} = nC_v\Delta T = nC_p\Delta T - nR\Delta T$

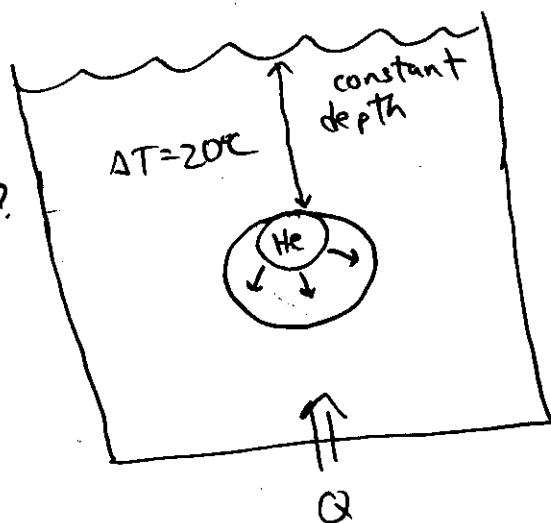
$\Rightarrow C_p = C_v + R =$  specific heat @ constant p.

## Sample Problem 20-7

A balloon containing  $n=5$  moles of He is submerged in a tub of water. The water & balloon have  $T$  raised by  $\Delta T=20^\circ\text{C}$ , causing the bubble to expand.

a.) how much heat  $Q$  does this process add to the He?

Does  $p$  change during this process?  
Why?



Use  $Q = n C_p \Delta T$

where  $C_p = C_v + R$

What is  $C_v$  for this gas?

$C_v = \frac{3}{2} R$  for a monatomic gas

so  $Q = n \frac{5}{2} R \Delta T = \frac{5}{2} (5 \text{ mol}) (8.31 \text{ J/mol}\cdot\text{K}) (20 \text{ K})$   
 $= 2080 \text{ J} = \text{heat energy acquired by He gas.}$

b.) What is the He's change in energy?

$$\Delta E_{\text{int}} = \frac{3}{2} n R \Delta T = 1250 \text{ J}$$

c.) how much work is done by the He gas during this expansion?

$$1^{\text{st}} \text{ Law: } \Delta E_{\text{int}} = Q - W$$

$$\Rightarrow W = Q - \Delta E_{\text{int}} = 830 \text{ J}$$

Alternate solution:

$$W = \int_{V_i}^{V_f} P dV = P(V_f - V_i) = P \Delta V \quad \text{since } p = \text{constant}$$

$$\text{ideal gas law: } PV = nRT$$

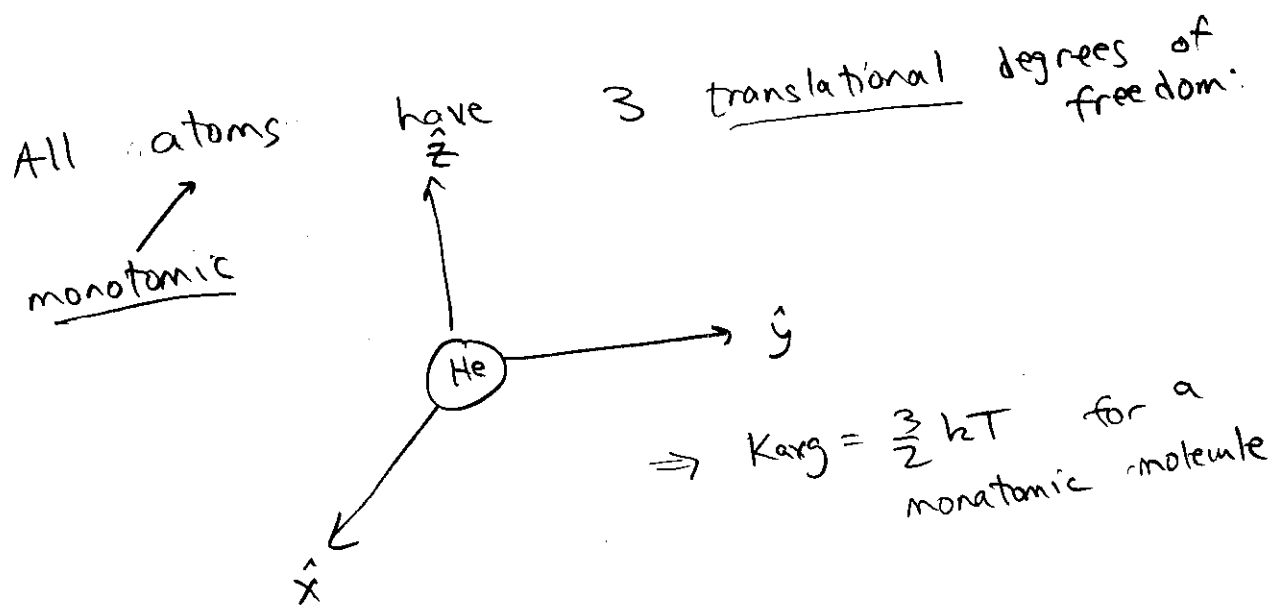
$$\text{so } P \Delta V = n R \Delta T$$

$$\Rightarrow W = n R \Delta T = 830 \text{ J}$$

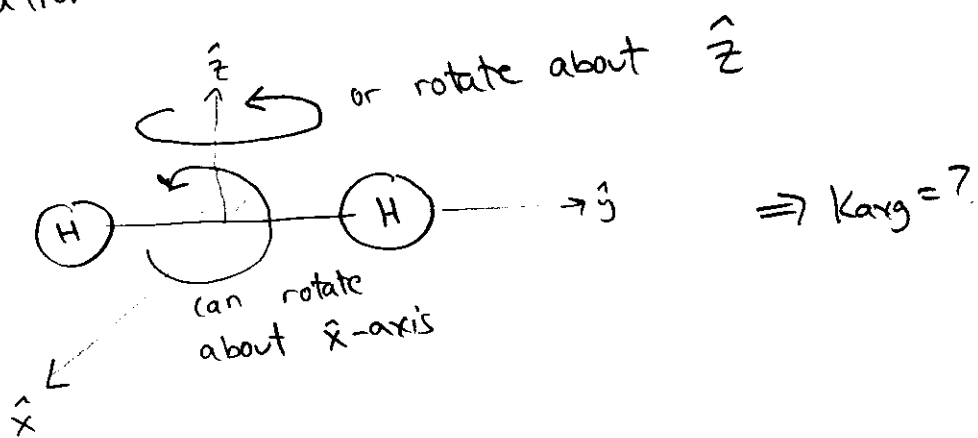
## Specific Heat & Degrees of Freedom

Every molecule in an ideal gas obeys an equipartition of energy: each molecule

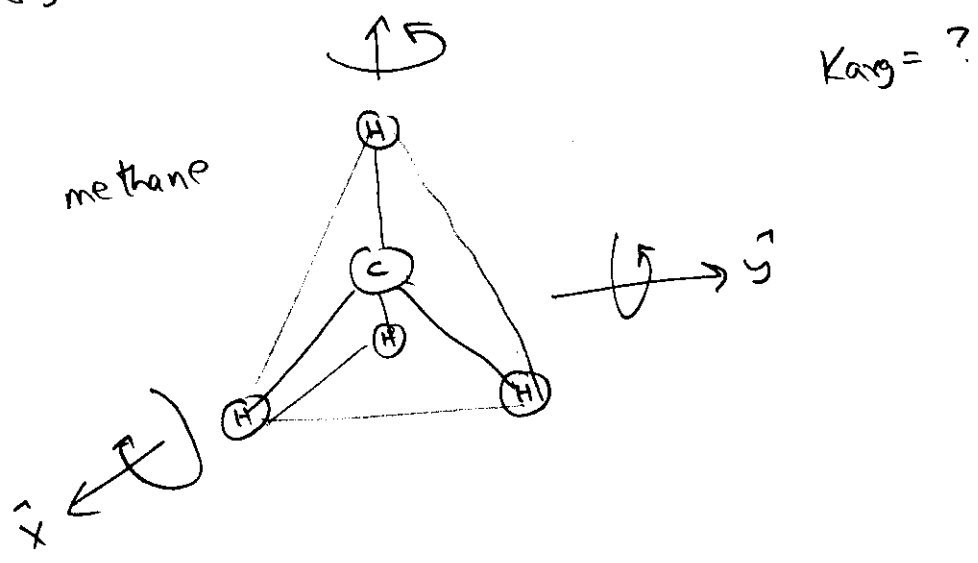
"degree of freedom" contributes  $\frac{1}{2}kT$  to its average KE.



However rotational diatomic molecules have 2 additional degrees of freedom:



While poly atomic molecules have 3 rotational degrees of freedom



Let  $f =$  degrees of freedom available to a molecule

$$E_{int} = \frac{1}{2} f n R T$$

so  $\Delta E_{int} = \frac{1}{2} f n R \Delta T =$  change in internal energy due to  $\Delta T$  change

$$= n C_v \Delta T$$

$$\Rightarrow C_v = \frac{f}{2} R = \text{specific heat at constant volume}$$

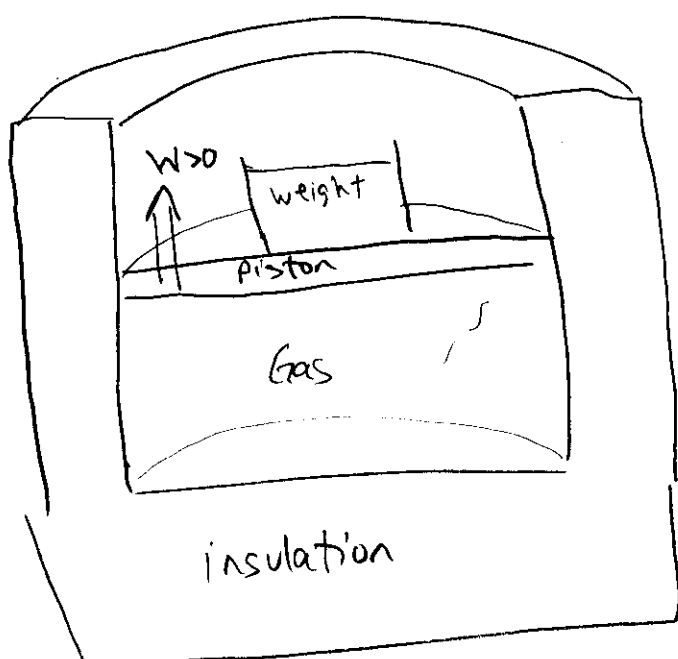
- $C_v = \left\{ \begin{array}{l} \frac{3}{2} R \text{ for monatomic molecules } (f=3) \\ \frac{5}{2} R \text{ for diatomic } (f=5) \\ 3R \text{ for polyatomic } (f=6) \end{array} \right.$

Similarly,  $C_p = C_v + R = \left(\frac{f}{2} + 1\right)R$

= specific heat at constant  $p$

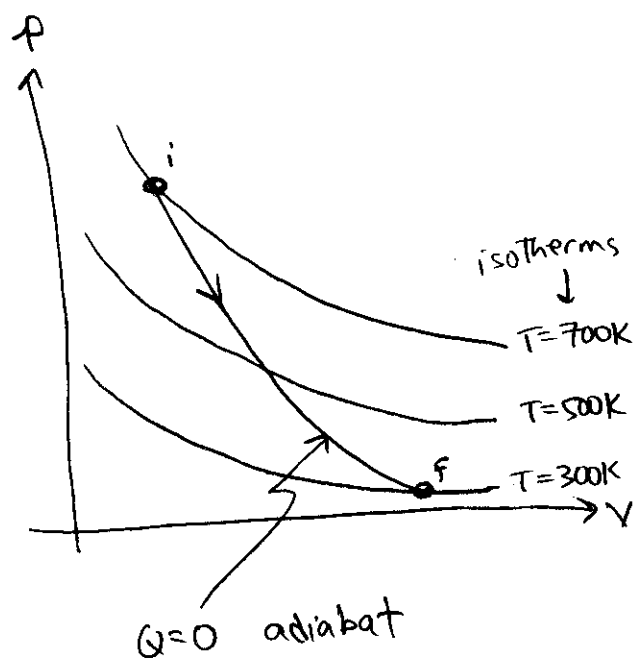
## Adiabatic Expansion of an Ideal Gas

An adiabatic process has  $Q=0$  (no heat exchange)



Remove weight from insulated cylinder.

$V$  increases as  $T, p$  decrease



The differential form of

20-25

The 1<sup>st</sup> Law of Thermo' says:

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

↑  
zero

↑  
 $p dV$

Note that  $p$  is assumed unchanged as  $V$  changes a small amount  $dV$

recall that  $\Delta E_{int} = n C_v \Delta T$  for any process  
(eg, constant  $p$  & constant  $v$  processes)

$$\text{so } dE_{int} = n C_v dT = -p dV$$

$$\text{so } n dT = -\frac{p}{C_v} dV$$

Next, differentiate the ideal gas law  $pV = nRT$ :

$$p dV + V dp = nR dT$$

And recall  $C_p = C_v + R$  so  $R = C_p - C_v$

$$\text{so } n dT = \frac{p dV + V dp}{C_p - C_v} = -\frac{p}{C_v} dV$$

$$\text{or } \left( \frac{1}{C_p - C_v} + \frac{1}{C_v} \right) p dV + \frac{V dp}{C_p - C_v} = 0$$

$$\frac{C_v + C_p - C_v}{C_v (C_p - C_v)} = \frac{C_p}{C_v (C_p - C_v)}$$

multiply by  $\frac{C_p - C_v}{P V}$  :

$$\frac{C_p}{C_v} \frac{dV}{V} + \frac{dP}{P} = 0$$

Set  $\gamma = \frac{C_p}{C_v} = \text{constant}$ , and integrate

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

$$\text{so } \ln V^\gamma + \ln P = A$$

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

$$\Rightarrow PV^\gamma = e^A = B = \text{constant, say } P_i V_i^\gamma$$

$$\Rightarrow P_i V_i^\gamma = P_f V_f^\gamma \quad \text{where } \gamma = \frac{C_p}{C_v}$$

for monatomic gas,  $\gamma = \frac{C_p}{C_v} = \frac{5/2}{3/2} = \frac{5}{3}$

for diatomic gas,  $\gamma = \frac{7/2}{5/2} = \frac{7}{5}$

polyatomic  $\gamma = \frac{4}{3}$

### Sample Problem 20-9

$n=1$  mole of  $O_2$  expands adiabatically from  $V_i=12L$  to  $V_f=19L$ . The initial temp' is  $T_i=310K$ .

a.) what is  $T_f$ ?

Note that  $PV^\gamma = \text{constant } B$

$$\text{so } (PV)V^{\gamma-1} = B$$

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

$$\text{so } nRTV^{\gamma-1} = B$$

$$\text{or } TV^{\gamma-1} = \frac{B}{nR} = \text{another constant}$$

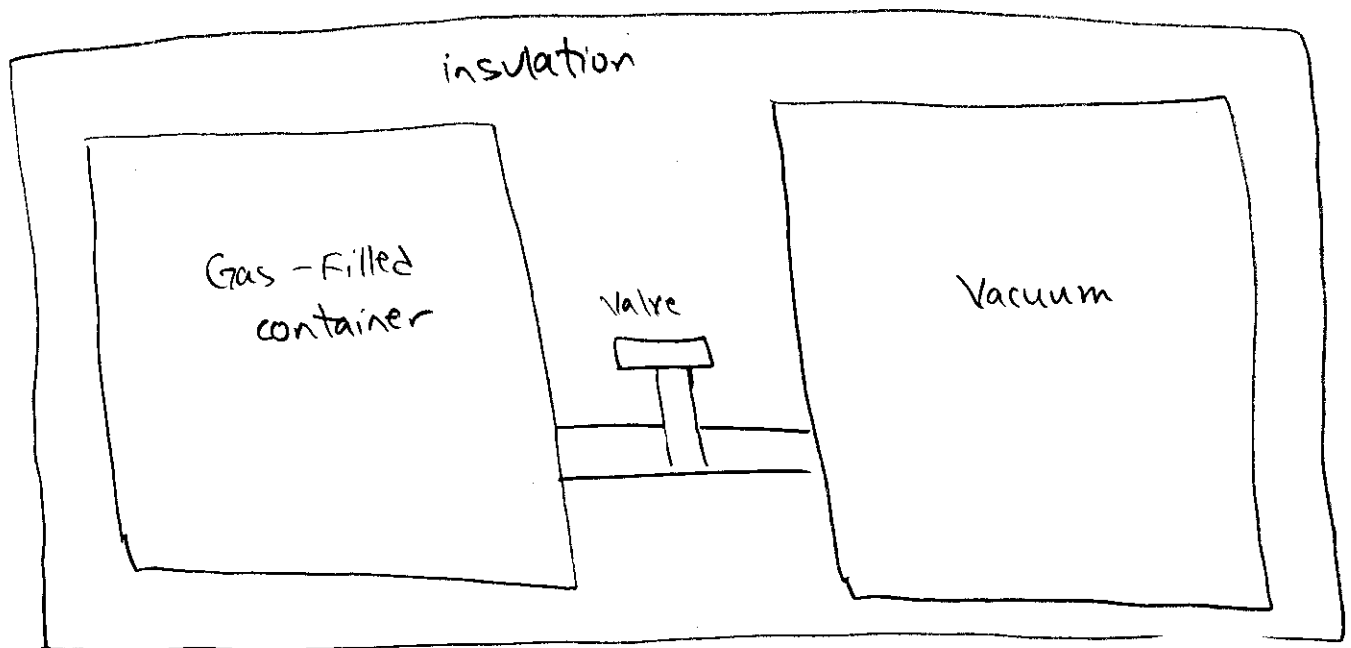
$$\Rightarrow T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \quad \text{What is } \gamma \text{ for } O_2?$$

where  $\gamma = \frac{7}{5}$  for diatomic  $O_2$

$$\Rightarrow T_f = \left( \frac{V_i}{V_f} \right)^{\frac{2}{5}} T_i = 258K = -15^\circ C$$

↑  
must be  
in K,  
NOT  $^\circ C$

## Free Expansion of an ideal gas



Consider a gas that is suddenly allowed to flow from one gas-filled canister to another evacuated canister.

Recall the 1<sup>st</sup> Law of thermo:  $\Delta E_{int} = Q - |W|$

How much heat was supplied during its very quick free expansion?

And how much work did the gas do while 'pushing back' on the environment (ie, the atmosphere?)

$$\Rightarrow \Delta E_{int} = Q = W = 0$$

Is this an adiabatic process?

Has the gas temp. changed? Why?

No - since  $\Delta E_{int} = n C_v \Delta T$  for any process  
 (not just a constant- $V$  process...)

$$\Rightarrow \Delta T = 0$$

so  $T_f = T_i$  during free expansion

What does the ideal gas law,  $PV = nRT$ ,  
 tell us about the system's  $PV$ ?

$P_i V_i = P_f V_f$  during free expansion