

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:

$$n = \frac{N}{N_A} \leftarrow \text{number of molecules in sample}$$

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

$$N = \frac{m_{\text{sample}}}{m} \leftarrow \begin{array}{l} \text{total mass of sample} \\ \text{mass of one molecule} \end{array}$$

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

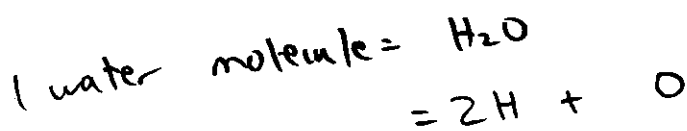
where

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

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:

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

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

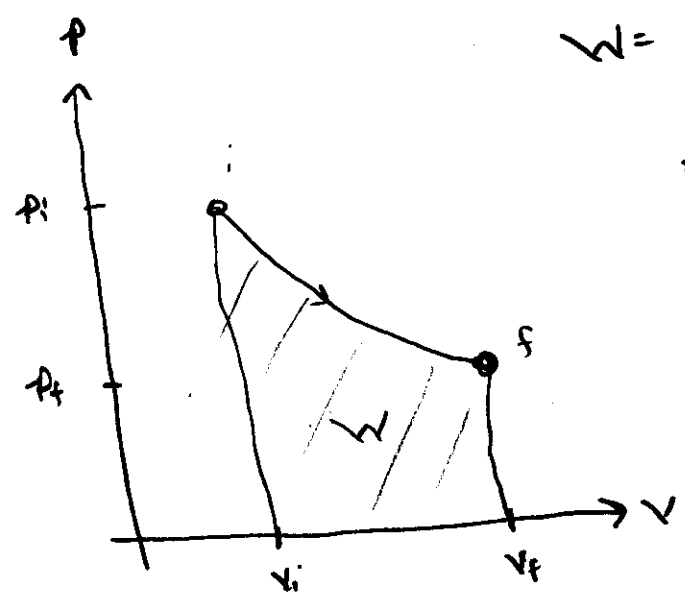
where $N = n N_A = \# \text{ of molecules in sample}$

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

Work by Isothermal Ideal Gas

isothermal \rightarrow gas is held at constant temp

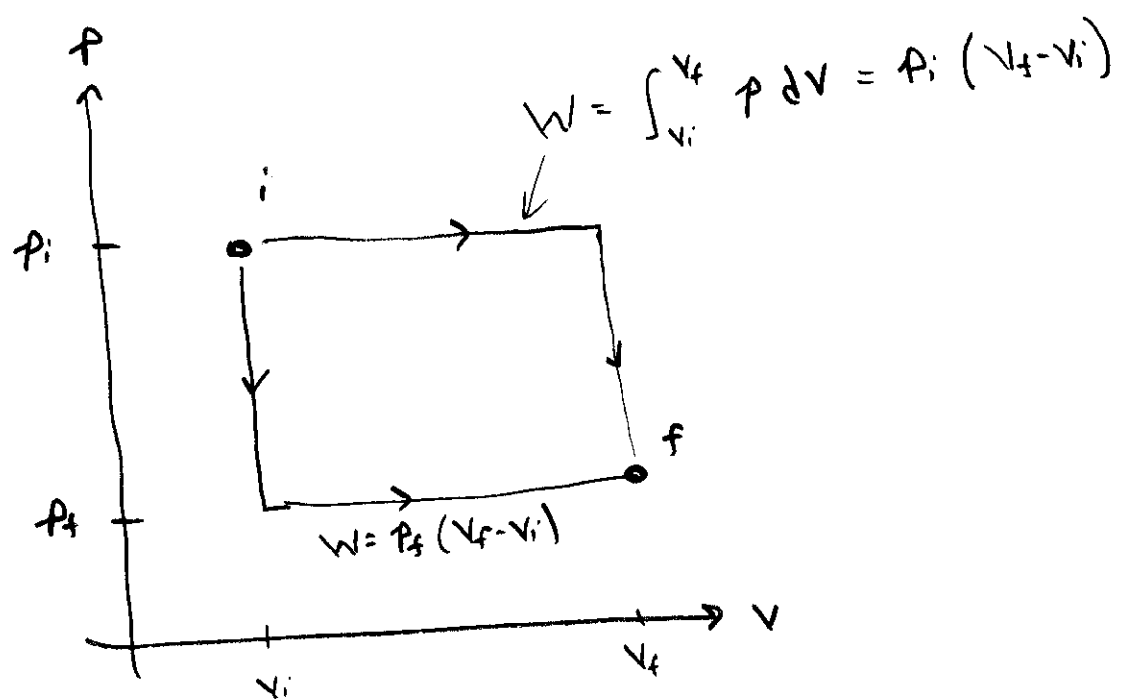
$$\text{so } P = \frac{nRT}{V} \quad \text{and}$$



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

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?

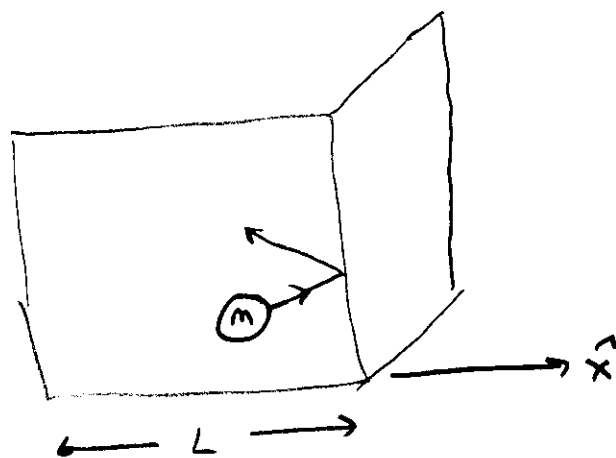


Pressure, Temperature, & Speed

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

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

velocity² 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 velocity² $\left\{ \begin{array}{l} \uparrow \\ \text{since } (v_x^2)_{avg} = (v_y^2)_{avg} \end{array} \right.$

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

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

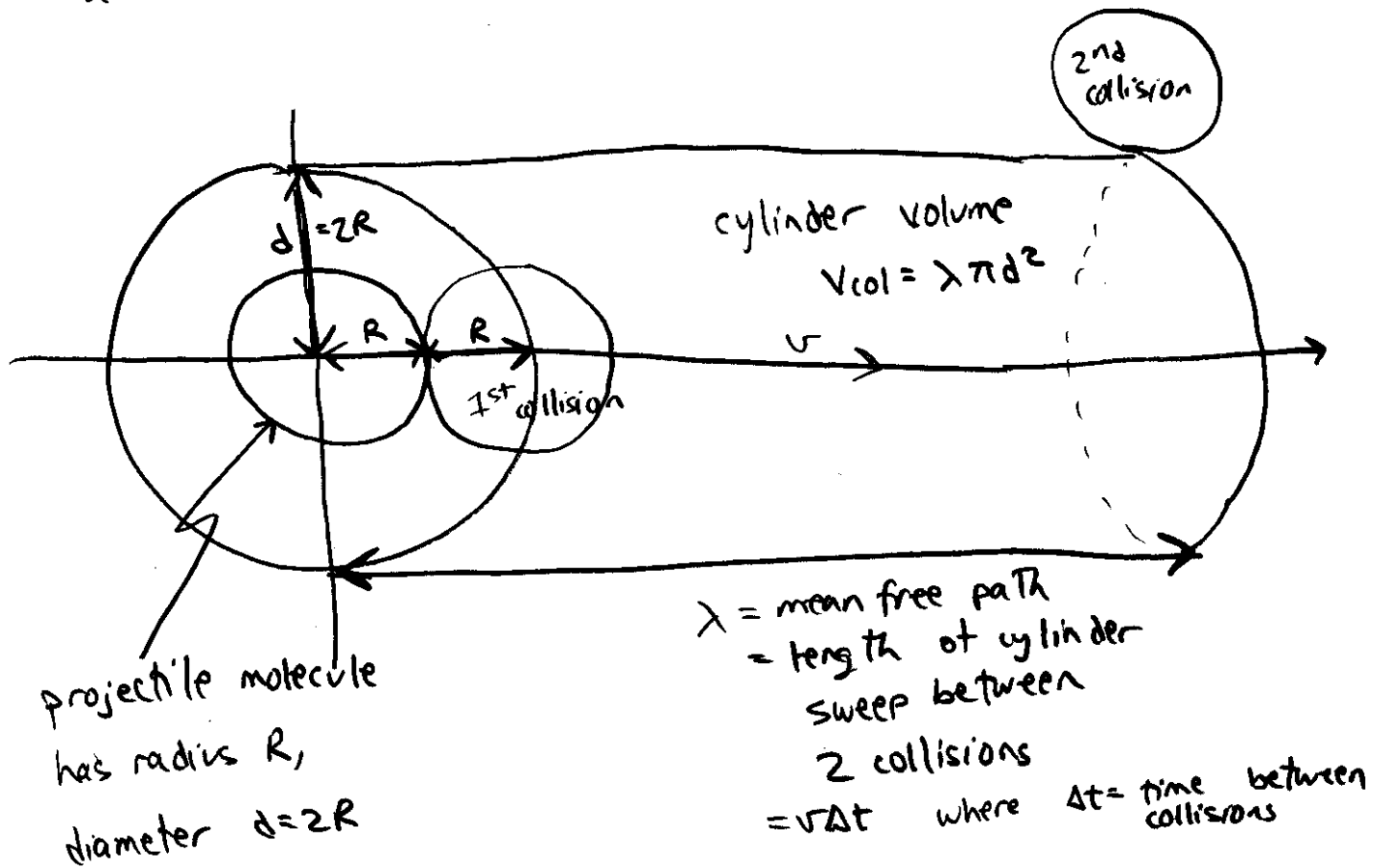
so $K_{avg} = \frac{3}{2} kT$

⇒ 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 ≥ 1 target molecule,

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

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

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

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 λ 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 λ 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 Δt = time between collisions,

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

Get v from

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

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

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

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

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

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

(about 40% faster than the sound speed)

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

= # of collisions per second experienced by a gas molecule

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

↑
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 ΔT ,

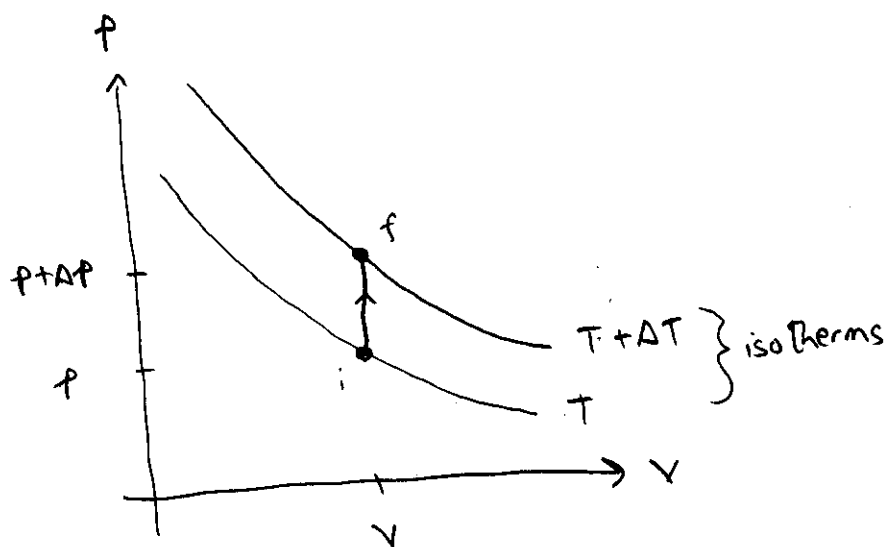
$$\Delta E_{\text{int}} = \frac{3}{2} nR \Delta T$$

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

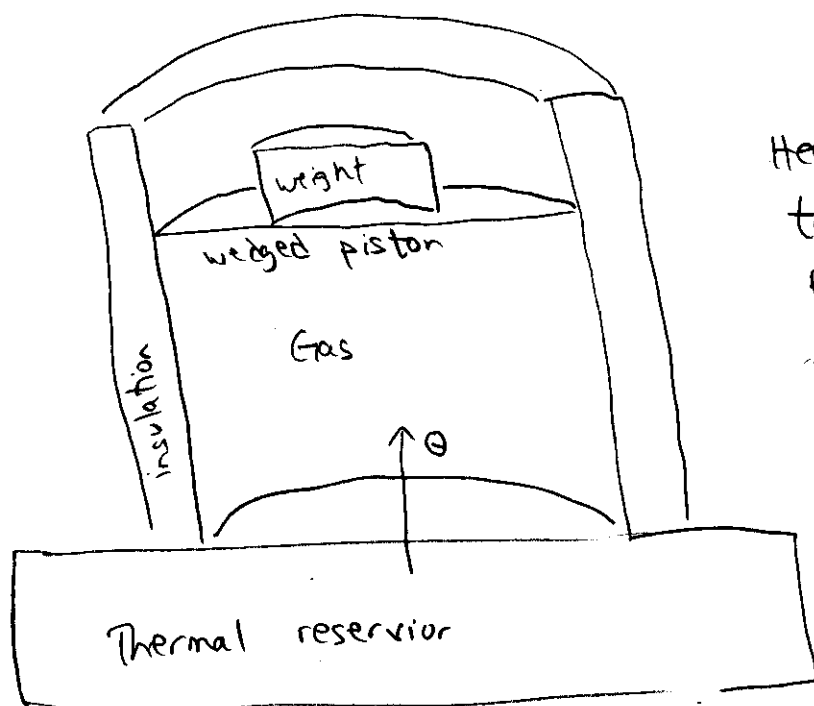
(will use this result later)

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 1st 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)

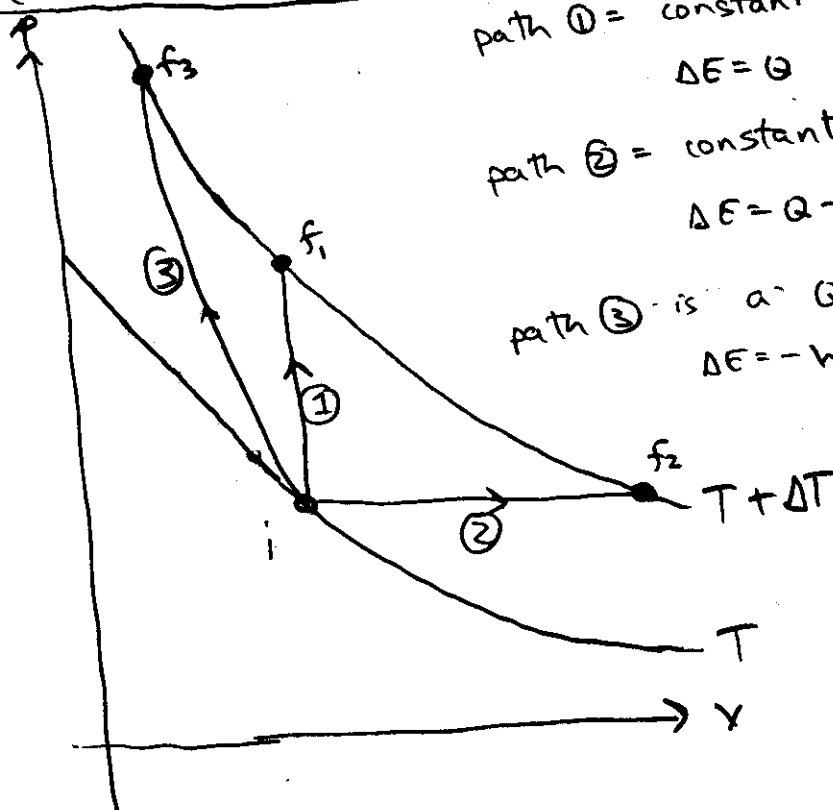
Later we will show that

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

polyatomic molecules (CH_4, CO_2, etc) have $C_v = 3R$

Note that E_{int} and ΔE_{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 (isochoric)
 $\Delta E = Q$ since $\Delta v \& W = 0$

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

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 ΔE_{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

1st Law: $\Delta E_{int} = Q - W = nC_v\Delta T$ since ΔE_{int} depends only on ΔT

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

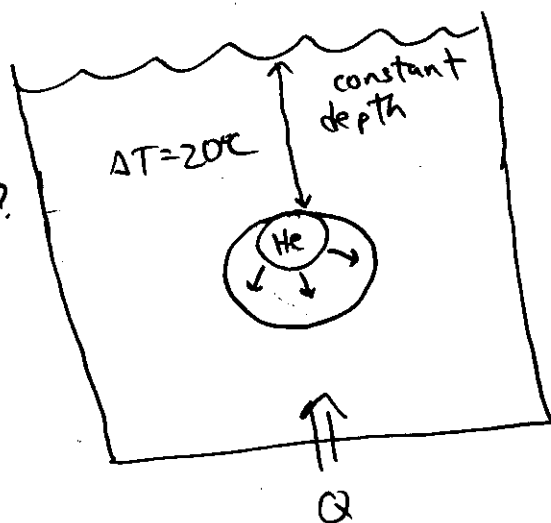
$\Rightarrow C_p = C_v + R =$ specific heat @ constant p .

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:

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

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

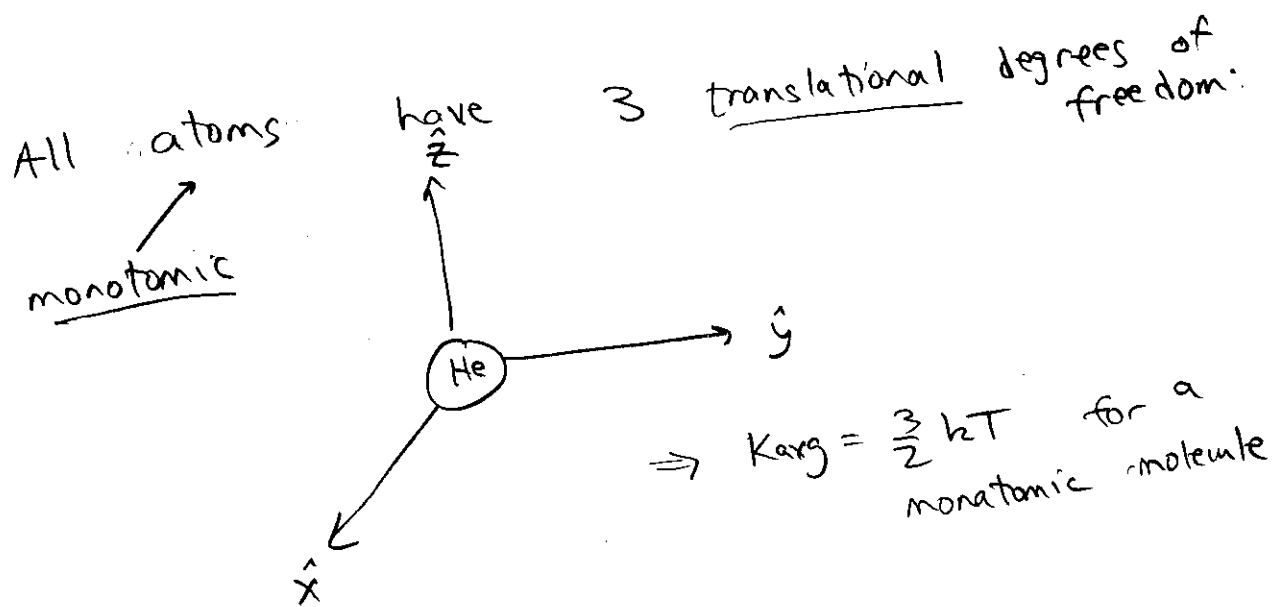
$$\text{so } P \Delta V = n R \Delta T$$

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

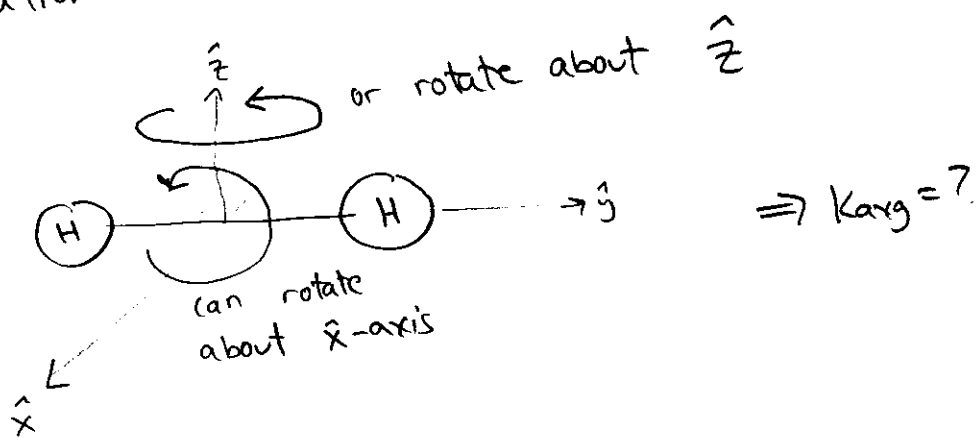
Specific Heat & Degrees of Freedom

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

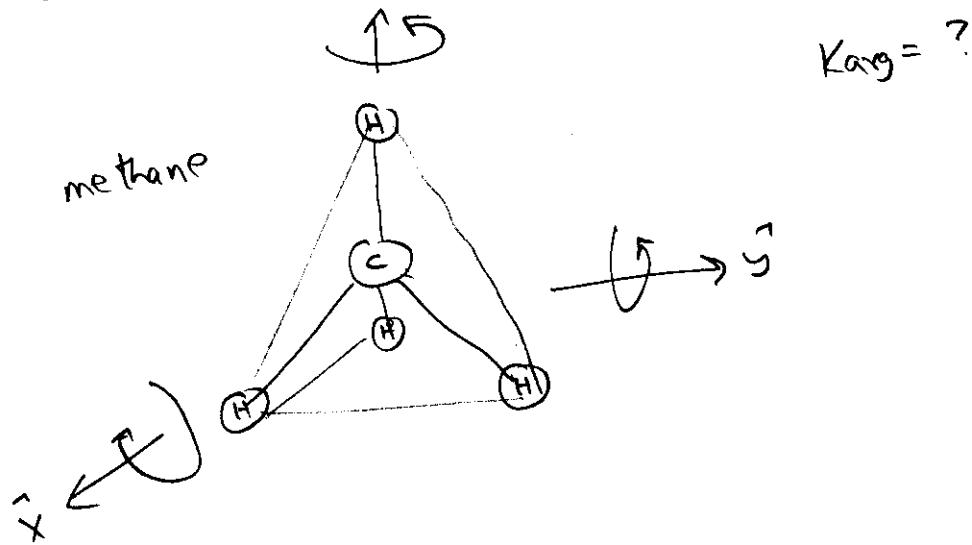
"degree of freedom" contributes $\frac{1}{2}kT$ to its average KE.



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 ΔT change

$$= n C_V \Delta T$$

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

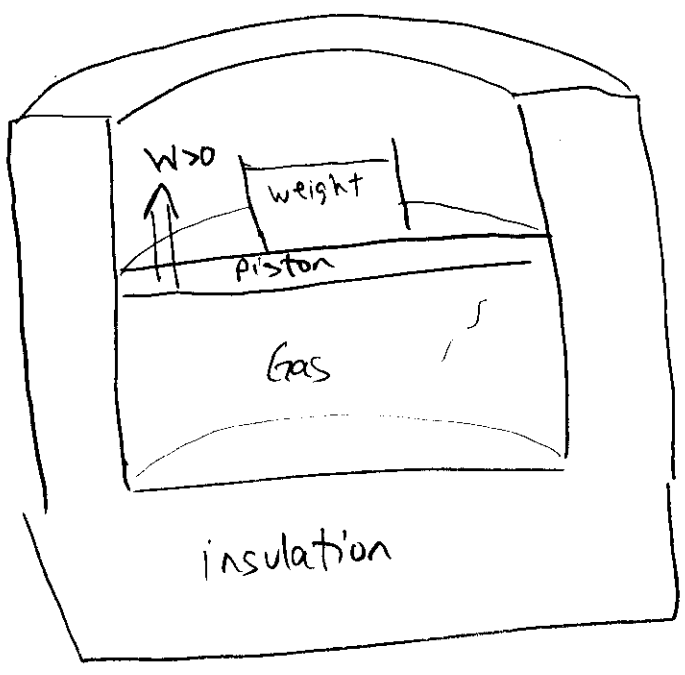
$$C_V = \begin{cases} \frac{3}{2} R & \text{for monatomic molecules } (f=3) \\ \frac{5}{2} R & \text{for diatomic } (f=5) \\ 3R & \text{for polyatomic } (f=6) \end{cases}$$

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

= specific heat at constant p

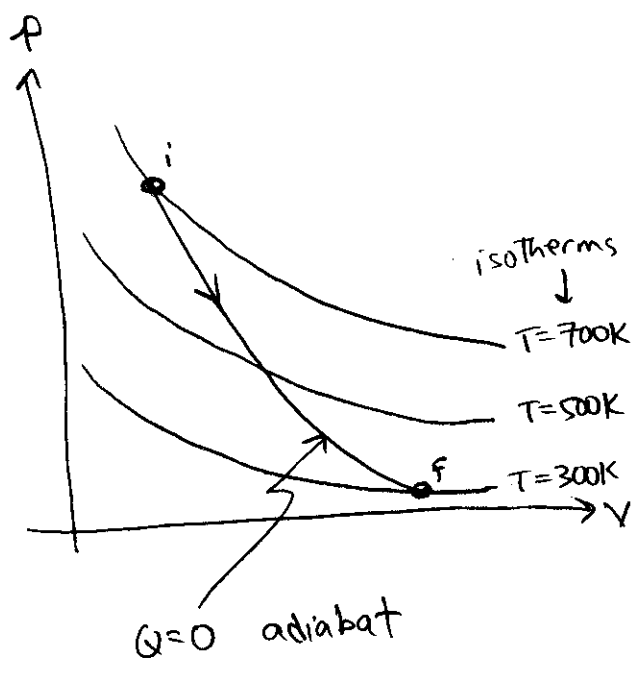
Adiabatic Expansion of an Ideal Gas

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 1st 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

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

a.) what is T_f ?

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

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

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

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

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

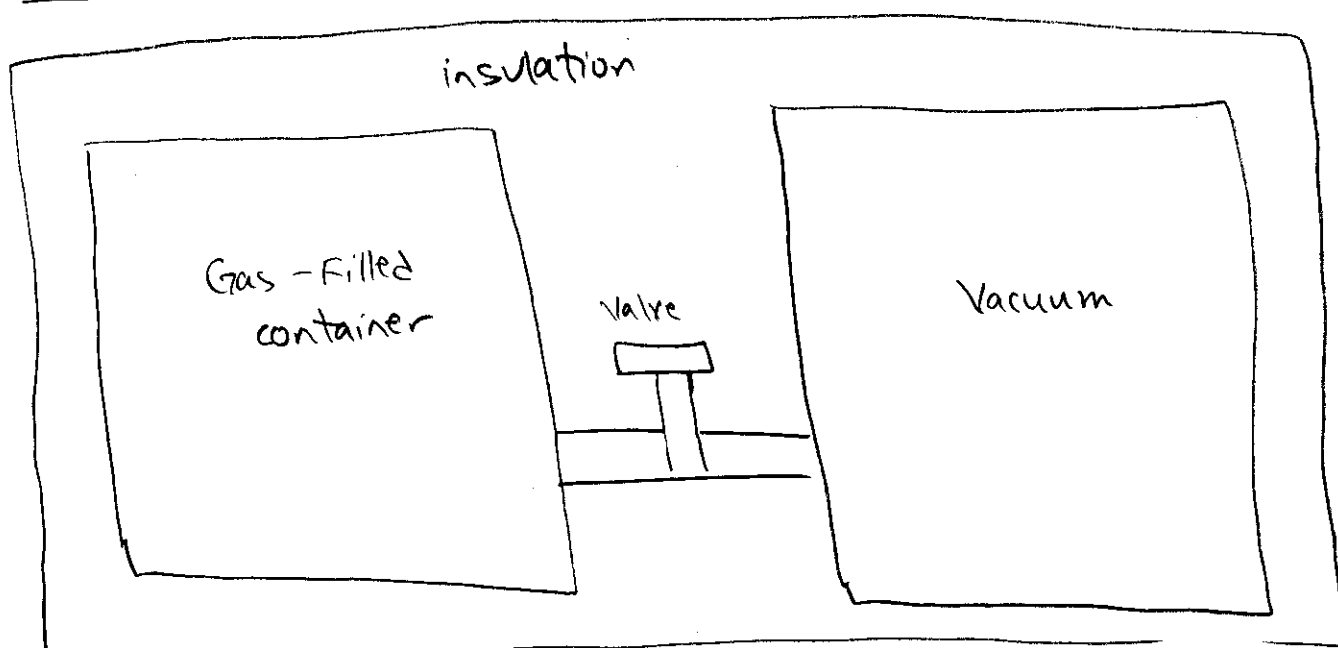
$$\Rightarrow T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \quad \text{What is } \gamma \text{ for } O_2?$$

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

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

↑
must be
in K,
NOT °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 1st 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