

Problem 12E (Chapter 20) Calculate work done by  
external agent during an isothermal compression of  
 1 mol of  $O_2$  from  $V = 22.4 \text{ L}$  @  $0^\circ\text{C}$  and pressure  
 of 1 atm to  $V = 16.8 \text{ L}$

$$W = nRT \ln \frac{V_f}{V_i} \quad \leftarrow \text{work done by gas}$$

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

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

$$T = 0^\circ\text{C} = 273 \text{ K}$$

$$W = (1)(8.31) \ln \left( \frac{16.8}{22.4} \right)$$

$$W = -653 \text{ J}$$

↑ work done "on" gas "by" "external agent"

$$W = +653 \text{ J by agent.}$$

ideal

Problem 9E. A quantity of  $n$  gas at  $10^\circ\text{C}$  and pressure  $100\text{ kPa}$  occupies a volume of  $2.5\text{ m}^3$ .

- a) How many moles of the gas are there?  
 b) If pressure raised to  $300\text{ kPa}$  and temperature raised to  $30^\circ\text{C}$ ... what is the new volume?

Pressure getting to me! UNIT REVIEW:

pressure at sea level of the weight of the atmosphere:

$$\begin{aligned}
 1\text{ atm} &= 1.013 \times 10^5 \text{ N/m}^2 = 14.7 \text{ lb/in}^2 \\
 &= 1.013 \times 10^5 \text{ Pa} \quad \text{"Pascals"} \quad \text{SI units} \\
 &= 1013 \text{ millibars} \\
 &= 76.0 \text{ cm Hg}
 \end{aligned}$$

\* Whew \*

so, here  $100\text{ kPa} = 10^5 \text{ Pa} \sim \text{about } 1\text{ atm.}$

a) moles.

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{(10^5)(2.5)}{(8.31)(273+10)}$$

$$n = 106 \text{ mol}$$

= (mol)



not necessarily right -- not obviously wrong!

**GOOD SKILL TO DEVELOP!**

$$(mol)(m) \left( \frac{N}{m^2} \right) \left( \frac{s^2}{kg} \right) \left( \frac{kg \cdot m^2 / s^2}{N} \right)$$

is it right? -- probably.

I know how to find out quickly if it's WRONG.

DIMENSIONAL ANALYSIS:

$$n = \frac{PV}{RT}$$

units:  $[n] = \frac{[P][V]}{[R][T]}$

$$\text{mol} = \frac{(\text{Pa})(\text{m}^3)}{(\text{J/mol}\cdot\text{K})(\text{K})} \left[ \frac{(\text{N/m}^2)}{(1 \text{ Pa})} \right] \frac{1 \text{ J}}{\text{kg m}^2/\text{s}^2}$$

$$=$$

$$b) \quad \begin{array}{l} P \rightarrow 300 \text{ kPa} \\ T \rightarrow 30^\circ \text{C} \end{array} \quad \left\{ \begin{array}{l} \text{what's } V? \end{array} \right.$$

$$P_1 V_1 = n_1 R T_1$$

$$P_2 V_2 = n_2 R T_2$$

any molecules of gas added (lost)? NO.

$$\text{so } n_1 = n_2 = n$$

$$P_1 V_1 = n R T_1$$

$$P_2 V_2 = n R T_2$$

$$\frac{P_1 V_1}{T_1} = n R$$

$$n R = \frac{P_2 V_2}{T_2}$$

so,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1 V_1}{T_1} \frac{T_2}{P_2} = \left( \frac{P_1}{P_2} \right) \left( \frac{T_2}{T_1} \right) V_1$$

$$= \frac{(100)}{(300)} \frac{(303)}{(283)} 2.5$$

$$V_2 = 0.892 \text{ m}^3$$

pressure goes up

temperature goes up less... ✓



# "DEGREES OF FREEDOM"

For a monatomic gas --  
there is no "structure"



He, etc.

Suggested that the Internal Energy was all

KINETIC

$$U = N \frac{3}{2} kT = \frac{3}{2} n N_A kT = \frac{3}{2} nRT$$

MAXWELL invented the notion of "degrees of freedom" -- ~~literally~~ literally, how many different ways can you contribute to energy --

For just KINETIC ENERGY of a structureless object (not just a gas molecule) --

THERE ARE 3:  $v_x, v_y, v_z$

THAT'S THE "3" IN

$$U = N \frac{3}{2} kT$$

each "dof" adds  $\frac{1}{2} kT \cdot N$  to  $U$

Suppose it's a DIATOMIC molecule --  $O_2$  etc.



a dumbbell -- ☺

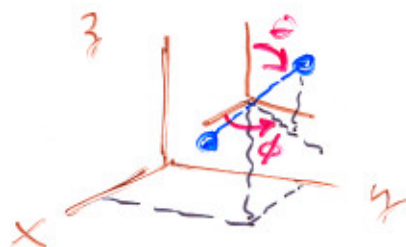
now, it can translate in all 3 directions

AND

rotate in 2 planes independently.

can specify, say,  $\theta, \phi$  to

uniquely determine its rotations



The energy:

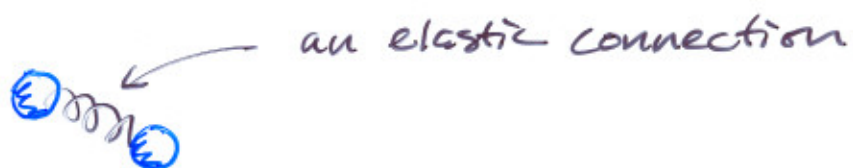
$$E = \frac{1}{2} M v_x^2 + \frac{1}{2} M v_y^2 + \frac{1}{2} M v_z^2 + \frac{1}{2} I_\theta \omega_\theta^2 + \frac{1}{2} I_\phi \omega_\phi^2$$

5 DEGREES OF FREEDOM

$$U = \frac{5}{2} nRT$$



Suppose it's a VIBRATING dumbbell...



$$E = \frac{1}{2} M v_x^2 + \frac{1}{2} M v_y^2 + \frac{1}{2} M v_z^2 + \frac{1}{2} I_G \omega_G^2 + \frac{1}{2} I_P \omega_P^2$$

$$+ \frac{1}{2} \mu v_{x'}^2 + \frac{1}{2} k x'^2$$

↑
↑  
 reduced mass of system      distance between atoms

$$U = \frac{7}{2} N k T \quad 7 \text{ dof.}$$

In general for a system with  
N molecules

structure	# dof	U
monatomic	N · 3	$\frac{3N}{2} kT$
+ diatomic	N · 5	$\frac{5N}{2} kT$
+ vibrating dumbbell	N · 7	$\frac{7}{2} N kT$

## EQUIPARTITION OF ENERGY...

An average energy of  $\frac{1}{2}kT$  is associated with each of the variables to specify the total energy of a system of particles.

→ The energy is shared equally among all of the degrees of freedom.

THIS WILL COME BACK TO HAUNT IN 1900.

# MOLAR SPECIFIC HEATS

TWO KINDS OF SPECIFIC HEAT FOR GASES

- CONSTANT VOLUME
- CONSTANT PRESSURE

CONSTANT V:

$$\Delta Q = n C_V \Delta T$$

↑ "specific heat at constant volume"

REMEMBER:



1<sup>st</sup> LAW:

$$\Delta Q = \Delta U + \Delta W$$

$$0 = \Delta W$$

$$\Delta Q = \Delta U = \frac{3}{2} n R \Delta T$$

(monatomic)

also:  $\Delta Q = n C_V \Delta T$

$$n C_V \Delta T = \frac{3}{2} n R \Delta T$$

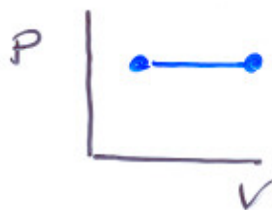
$$C_V = \frac{3}{2} R$$

for monatomic gas

$$C_V = 12.5 \text{ J/mol}\cdot\text{K}$$

CONSTANT P:

$$\Delta Q = n C_p \Delta T$$



$$\Delta W = P \Delta V$$

$$1^{st} \text{ LAW: } \Delta Q = \Delta U + \Delta W$$

$$\Delta Q = \Delta U + P \Delta V$$

also

$$(P \Delta V + V \Delta P = n R \Delta T)$$

$$\text{IDEAL GAS LAW: } P \Delta V = n R \Delta T$$

monotonic

$$\Delta Q = \frac{3}{2} n R T + n R \Delta T$$

$$\Delta Q = \frac{5}{2} n R T$$

(monotonic)

$$\text{also: } \Delta Q = n C_p \Delta T$$

$$\frac{5}{2} n R T = n C_p \Delta T$$

$$C_p = \frac{5}{2} R = 20.78 \text{ J/mol} \cdot \text{K}$$

NOTICE:

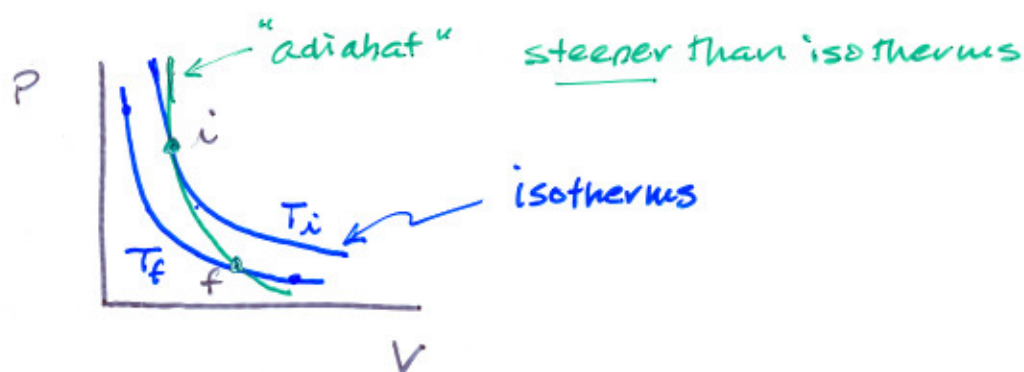
$$C_p = C_v + R$$

# ADIABATIC EXPANSIONS

make a change in a system quickly  
or in a well insulated system

- so that heat neither enters nor leaves

$$\Delta Q = 0 = \Delta U + \Delta W$$



to go adiabatically from one  $V_i$  to  $V_f$

$\Delta U$  decreases  
T decreases } internal energy all goes  
to work to increase  $V$

$$-\Delta U = \Delta W$$

a tricky point:

$$nC_V = \left. \frac{\Delta Q}{\Delta T} \right|_V = \left. \frac{\Delta U}{\Delta T} \right|_V$$

means "at constant volume"

or, for infinitesimal changes  $nC_V = \left. \frac{dU}{dT} \right|_V$



But... for an Ideal gas  $u = u(T)$  only

$$\text{so } nC_V = \left. \frac{du}{dT} \right|_V \rightarrow \frac{du}{dT} \text{ period}$$

So, back to the 1<sup>st</sup> Law... differentially:

~~$0 = dU + dW$~~

$$0 = dU + dW$$

$$\textcircled{A} \quad 0 = nC_V dT + PdV$$

~~$0 = nC_V dT + \frac{nRTdV}{V}$~~

for Ideal gas  
equation of state

also, from equation of state

$$PV = nRT \quad \text{take differential}$$

$$\textcircled{B} \quad VdP + \cancel{VdP} = nRdT$$

$PdV$

(mathematicians... think about the Tigers for  
20 seconds!)

$$\text{and } \left. \begin{array}{l} \textcircled{B} \quad dT = \frac{VdP + \cancel{VdP} + PdV}{nR} \\ \textcircled{A} \quad dT = -\frac{PdV}{nC_V} \end{array} \right\} \frac{VdP + \cancel{VdP} + PdV}{nR} = -\frac{PdV}{nC_V}$$



rearranging...

$$P dV \left( 1 + \frac{R}{C_V} \right) = -V dP$$

remember:

$$R = C_V + C_P$$

$$P dV \left( 1 + \frac{C_P - C_V}{C_V} \right) = -V dP$$

$$P dV \left( 1 + \frac{C_P}{C_V} - 1 \right) = -V dP$$

↑  
called " $\gamma$ "

$$P dV \gamma = -V dP$$

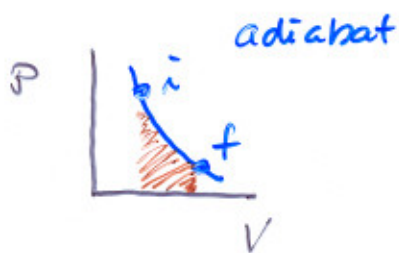
$$\frac{dV}{V} \gamma + \frac{dP}{P} = 0$$

For a finite thermodynamic change -- integrate.

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

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

or  $PV^\gamma = \text{constant}$  for Ideal Gas.



$$P_i V_i^\gamma = P_f V_f^\gamma = \text{constant} = K$$

$$P = \frac{K}{V^\gamma}$$

$$W = \int_{V_i}^{V_f} P dV = \int_{T_i}^{T_f} -n C_V dT$$

$$W = K \int \frac{dV}{V^\gamma}$$

$$= \frac{1}{1-\gamma} (K V_f^{1-\gamma} - K V_i^{1-\gamma})$$

$$W = \frac{P_f V_f - P_i V_i}{1-\gamma}$$

Adiabatic transitions are special.



on the one hand: transitions have to preserve the ideal gas equation of state  
... slowly enough to be uniform throughout

on the other hand: transitions have to be fast enough to not lose heat to surroundings

gasoline and diesel engines <sup>strokes</sup> are adiabatic --



Compression stroke is fast... before heat can leave, no good approximation to adiabatic

$\gamma > 1$ , so get a boost in changing pressure --

Take a diesel engine -- the compression ratio is 15/1 or so.

$$P_i V_i^\gamma = P_f V_f^\gamma \quad \gamma = 1.4 \text{ for air}$$

$$P_f = P_i \left( \frac{V_i}{V_f} \right)^\gamma$$

$$P_f = P_i (15)^{1.4} \approx 44 \cdot P_i \rightarrow 44 \text{ atm}$$

if  $P_i = 1 \text{ Pa}$

that's enough to ignite diesel fuel without a spark plug.

... just like above derivation  $TV^{\gamma-1} = \text{constant}$

$$T_f = T_i \left( \frac{V_i}{V_f} \right)^{\gamma-1} = T_i \cdot 3, \text{ so from } 300 \text{ K to } 900 \text{ K}$$