Problem 12E (Chapter 20) Calculate work done by 
external agent during an isothermal compression of 
1 mol of O₂ from \( V = 22.4 \text{ L} \) @ 0°C and pressure 
of 1 atm to \( V = 16.8 \text{ L} \)

\[
W = nRT \ln \frac{V_f}{V_i}
\]

\( R = 8.31 \text{ J/mol·K} \)
\( n = 1 \text{ mol} \)
\( T = 0°C = 273 K \)

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

\( W = -653 \text{ J} \)

Work done “on” gas “by” “external agent”

\( W = +653 \text{ J by agent} \).
Problem 9E. A quantity of gas at 10°C and pressure 100 hPa occupies a volume of 2.5 m³.

a) How many moles of the gas are there?

b) If pressure raised to 300 hPa and temperature raised to 30°C, what is the new volume?

Pressure getting to me! UNIT REVIEW:

Pressure at sea level of the weight of the atmosphere:

$$1 \text{ atm} = 1.013 \times 10^5 \text{ N/m}^2 = 14.7 \text{ lb/in}^2$$

$$= 1.013 \times 10^5 \text{ Pa} \quad \text{"Pascals" SI units}$$

$$= 1013 \text{ millibars}$$

$$= 76.0 \text{ cm Hg}$$

*when*

So, here

$$100 \text{ hPa} = 10^5 \text{ Pa} \approx \text{ about 1 atm.}$$

a) moles.

$$PV = nRT$$

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

$$n = 106 \text{ mol}$$
not necessarily right -- not obviously wrong!

GOOD SKILL TO DEVELOP!
\[
\left( \frac{N}{10^7} \right) \left( \frac{b_y}{\sigma} \right) \left( \frac{\sigma_y}{\sigma} \right) \left( \frac{m}{10^7} \right)
\]
is it right? -- probably.

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

**DIMENSIONAL ANALYSIS:**

\[ n = \frac{PV}{RT} \]

**Units:**

\[ [n] = \frac{[P][V]}{[L][T]} \]

\[ \text{mol} = \frac{(Pa)(m^3)}{(J/mol \cdot K)(K)} \left[ \frac{(N/m^2)}{(1 \text{ Pa})} \right] \frac{1 J}{kg \text{ m}^2 \text{s}^2} \]
b) \( P \rightarrow 300 \, kPa \)  
\( T \rightarrow 30^\circ C \)  
\( \text{what's } V_2 \)

\[ P_1 V_1 = n_1 RT_1 \quad P_2 V_2 = n_2 RT_2 \]

any molecules of gas added/lost? NO.

so  \( n_1 = n_2 = n \)

\[ P_1 V_1 = nRT_1 \quad P_2 V_2 = nRT_2 \]

\[ \frac{P_1 V_1}{T_1} = nR \quad nR = \frac{P_2 V_2}{T_2} \]

so...

\[ \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \]

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

\[ = \left( \frac{100}{300} \right) \left( \frac{303}{283} \right) 2.5 \]

\[ = \frac{1}{3} \left( \frac{303}{283} \right) \]

\[ V_2 = 0.892 \, m^3 \]

pressure goes up

temperature goes up less... ✔
"DEGREES OF FREEDOM"

For a monoatomic gas -- He, etc.
there is no "structure"

Suggested that the internal energy was an kinetic

\[ U = N \frac{3}{2} kT = \frac{3}{2} nN_A kT = \frac{3}{2} nRT \]

MAXWELL invented the notion of "degrees of freedom" -- better 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 "dot" adds \( \frac{1}{2} kT \cdot N \) to \( U \)
Suppose it's a DIATOMIC molecule -- \( \text{O}_2 \) 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

\[
U_l = \frac{5}{2} uR T
\]
Suppose it's a vibrating dumbbell—

\[ E = \frac{1}{2} MV_x^2 + \frac{1}{2} MV_y^2 + \frac{1}{2} MV_z^2 + \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2 + \frac{1}{2} u x^2 + \frac{1}{2} u y^2 \]

\[ U = \frac{1}{2} \mu u^2 \quad 7 \text{ dof.} \]

In general for a system with \( N \) molecules

<table>
<thead>
<tr>
<th>structure</th>
<th># dof</th>
<th>( U )</th>
</tr>
</thead>
<tbody>
<tr>
<td>monotonic</td>
<td>( N \cdot 3 )</td>
<td>( \frac{3N \mu u^2}{2} )</td>
</tr>
<tr>
<td>+ diatomic</td>
<td>( N \cdot 5 )</td>
<td>( \frac{5N \mu u^2}{2} )</td>
</tr>
<tr>
<td>+ vibrating dumbbell</td>
<td>( N \cdot 7 )</td>
<td>( \frac{7N \mu u^2}{2} )</td>
</tr>
</tbody>
</table>
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 us in 1960.
MOLAR SPECIFIC HEATS

TWO KINDS OF SPECIFIC HEAT FOR GASES

- CONSTANT VOLUME
- CONSTANT PRESSURE

CONSTANT V:

\[ \Delta Q = nC_v \Delta T \]

"specific heat at constant volume"

REMEMBER:

[Diagram]

\[ P \] \quad \text{constant volume}

\[ \Delta W = 0 \]

1st LAW:

\[ \Delta Q = \Delta U + \Delta W \]

\[ \Delta U = \Delta W \]

\[ \Delta Q = \Delta U = \frac{3}{2} nR \Delta T \] (monotonic)

also:

\[ \Delta Q = nC_v \Delta T \]

\[ nC_v \Delta T = \frac{3}{2} nR \Delta T \]

\[ C_v = \frac{3}{2} R \] for monotonic gas

\[ C_v = 12.5 \text{ J/mole.K} \]
**CONSTANT P:**

\[ \Delta Q = nC_p \Delta T \]

\[ P \]

\[ \Delta W = P \Delta V \]

**1st Law:**

\[ \Delta Q = \Delta U + \Delta W \]

\[ \Delta Q = \Delta U + P \Delta V \]

(\( P \Delta V + n \Delta p = nR \Delta T \))

**IDEAL GAS LAW:**

\[ P \Delta V = nR \Delta T \]

\[ \Delta Q = \frac{3}{2} nRT + nR \Delta T \] (monotonic)

\[ \Delta Q = \frac{5}{2} nRT \] (monotonic)

**also:** \[ \Delta Q = nC_p \Delta T \]

\[ \frac{5}{2} nRT = nC_p \Delta T \]

\[ C_p = \frac{5}{2} R = 20.78 \text{ J/mol.K} \]

**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

\[ \Delta Q = 0 = \Delta U + \Delta W \]

\[ \text{"adiabatic" steeper than isotherms} \]

\[ \text{isotherms} \]

\[ T \]

\[ V \]

to go adiabatically from one \( V_i \) to \( V_f \)

\( \Delta U \) decreases \( \Rightarrow \) internal energy all goes to work to increase \( V \)

\( T \) decreases

\[- \Delta U = \Delta W \]

A tricky point:

\[ nC_v = \left[ \frac{\Delta Q}{\Delta T} \right]_V = \left[ \frac{\Delta U}{\Delta T} \right]_V \]

\( \Rightarrow \) 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
so
\[ nC_v = \frac{du}{dT} \bigg|_v \rightarrow \frac{du}{dT} \text{ period} \]

So, back to the 1st law... differentially:

\[ \delta W + \delta Q = \delta U + \delta W \]

\[ \delta W = nC_v \delta T + P \delta V \]

Also, from equation of state

\[ PV = nRT \]

\( \text{take differential} \)

\[ \frac{VdP + PdV}{PdV} = nRdT \]

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

\[ dT = \frac{PdV}{nR} \]

and

\[ dT = -\frac{PdV}{nC_v} \]
rearranging...

\[ PdV \left( 1 + \frac{R}{C_v} \right) = -VdP \]

Remember: \[ R = C_v + C_p \]

\[ PdV \left( 1 + \frac{C_p - C_v}{C_v} \right) = -VdP \]

\[ PdV \left( 1 + \frac{C_p - C_v}{C_v} \right) = -VdP \]

called \[ \gamma \]

\[ PdV \gamma = -VdP \]

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

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 \[ PV^\gamma = \text{constant} \] in Ideal Gas.
\[
\frac{P_i V_i^i}{V_i^f} = \frac{P_f V_f^i}{V_f^i} = \text{constant} = k
\]

\[
P = \frac{k}{V_f^i}
\]

\[
W = \int_{V_i^i}^{V_f^i} P dV = \int_{T_i^i}^{T_f^i} -nC_V dT
\]

\[
W = K \int \frac{dV}{V_f^i}
\]

\[
= \frac{1}{1-\gamma} \left( K V_f^{1-\gamma} - K V_i^{1-\gamma} \right)
\]

\[
W = \frac{P_f V_f^i - P_i V_i^i}{1-\gamma}
\]

Adiabatic transitions are special.

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**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 not to lose heat to surroundings.
Gasoline and diesel engines are adiabatic.

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

\( \delta > 1 \), no get a boost in changing pressure...

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

\[
P_i V_i^\delta = P_f V_f^\delta
\]

\( \delta = 1.4 \) for air

\[
P_f = P_i \left( \frac{V_i}{V_f} \right)^\delta
\]

\[
P_f = P_i \left( \frac{15}{V_f} \right)^{1.4} \approx 44. P_i \rightarrow 44 \text{ atm}
\]

if \( P_i = 1 \text{ Pa} \)

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

...just like above derivation \( TV^{\delta-1} = \text{constant} \)

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