2. Thermodynamics, 3

lecture 10, September 20, 2017

housekeeping

exam 1 is in about 1.5 weeks

- Friday, 29 September
- Relativity and Thermodynamics…through Monday's content

Some changes:

- you saw that I deleted a problem that I didn't think was useful in chapter 18
- we will skip sections 19.6 and 19.7 as they will be dealt with in a more grown-up way in Thornton and Rex later

Shameless plug:

- ISP220

Honors option

- someone show me what you've got to submit

Gripes

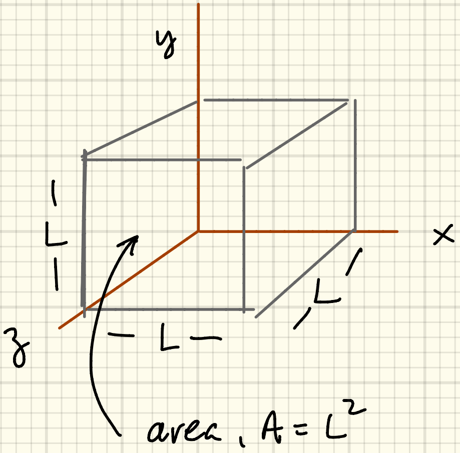
"Kinetic Theory"

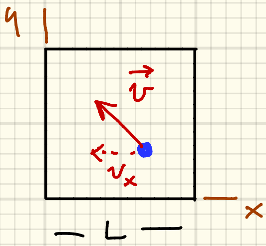
very old & very cool

Imagine a volume filled with molecules

- Identical, m
- no size
- no interactions
- numerous $\Rightarrow$ ignore fluctuations $\sim \frac{1}{\sqrt{N}}$

Sounds like?





collides elastically from wall

$\overleftarrow{\quad}$ v_x

$\overrightarrow{\quad}$ v_x'

Δt = average time between collisions at $x=0$ & $x=L$, round trip

$$\Delta t = \frac{2L}{|v_x|}$$

momentum transfered to wall

$$\Delta p_x = 2m|v_x|$$

<u>rate</u> at which momentum is transfered

"average"

$$\frac{\Delta p_x}{\Delta t} = \frac{2m|v_x|}{2L/|v_x|} = \frac{mv_x^2}{L} = \langle F_x \rangle$$

by one molecule

total force applied to $x=0$ or $x=L$ walls:

$$\langle F \rangle = \frac{Nmv_x^2}{L}$$

pressure:

$$P = \frac{\langle F \rangle}{A} = \frac{Nmv_x^2}{L^2 L} = \frac{Nmv_x^2}{V}$$

use averages: $v_x^2 \rightarrow \langle v_x^2 \rangle$

$$P = \frac{Nm\langle v_x^2 \rangle}{V}$$

$$P = \frac{Nm\langle v_x^2\rangle}{V}$$

nothing special about x .. on average

$$\langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle \equiv \langle v^2\rangle$$

so $\langle v_x^2\rangle = \frac{1}{3}\langle v^2\rangle$

$$P = \frac{Nm\langle v^2\rangle}{3V}$$

$$PV = \frac{1}{3}Nm\langle v^2\rangle \quad = \text{Constant} \;...\; \text{Boyle's Law}$$

Now remember ideal gas law: $PV = NkT$

THE MAGIC!

$$PV = \frac{1}{3}Nm\langle v^2\rangle = NkT \qquad \text{for an ideal gas}$$

$$kT = \frac{1}{3}m\langle v^2\rangle = \frac{2}{3}\cdot\frac{1}{2}m\langle v^2\rangle = \frac{2}{3}K$$

WHOA.

$$PV = \frac{1}{3} N m \langle v^2 \rangle = NkT$$ for an ideal gas

$$kT = \frac{1}{3} m \langle v^2 \rangle = \frac{2}{3} \cdot \frac{1}{2} m \langle v^2 \rangle = \frac{2}{3} K \quad \ldots \text{ really } \frac{2}{3} \langle K \rangle$$

A GAS TEMPERATURE = AVERAGE KINETIC ENERGY OF MOLECULES

$$\langle K \rangle = \frac{3}{2} kT \quad \& \quad U = N \langle K \rangle \text{ so } \quad PV = \frac{2}{3} U$$

N = # molecules

k = Boltzmann's Constant = 1.38066×10^{-23} J/K

n = # moles

R = Universal Gas Constant = 8.3145×10^{23} / mol

$PV = NkT$ & $PV = nRT$ => Ideal gas Law has a basis in a physical model

$$\langle K \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT$$

$$\langle v^2 \rangle = \frac{3kT}{m} \quad \text{or} \quad \langle v_x^2 \rangle = \frac{kT}{m}$$

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}}$$

give me the temperature

I'll tell you how fast the molecules are going.

Air @ 20°C?

$$m \text{ of } N_2 = 28 \text{ amu}^{*} = 28 \times 1.66 \times 10^{-27} \text{ kg}$$

$$= 4.648 \times 10^{-26} \text{ kg.}$$

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{(3)(1.38 \times 10^{-23} \text{ J/K})(293 \text{K})}{4.65 \times 10^{-26} \text{ kg}}}$$

$$= 510 \text{ m/s}$$

$*$ $\frac{1}{12} \times$ mass of Carbon 12

Degrees of Freedom

monotonic gas – Ideal Gas – no structure

The temperature – internal energy, after all → kinetic

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

Maxwell invented: "dof" → how many ways can you contribute to energy

For our Ideal Gas: 3 v_x, v_y, v_z the 3 $U = N \frac{3}{2} kT$

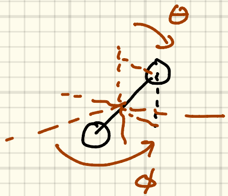
Each dof adds $\frac{1}{2} kT \cdot N$ to U

Suppose a DIATOMIC molecule? $O_2, N_2 \ldots$

physical model

It can translate in 3 directions

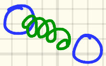
It can rotate in 2 planes independently



So $$E = \frac{1}{2}Mv_x^2 + \frac{1}{2}Mv_y^2 + \frac{1}{2}Mv_z^2 + \frac{1}{2}I_\theta\,\omega_\theta^2 + \frac{1}{2}I_\phi\,\omega_\phi^2$$

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

Suppose it's a VIBRATING dumbbell



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

$$+ \tfrac{1}{2} \mu v_{x'}^2 + \tfrac{1}{2} k x'^2 \quad \Rightarrow 7 \text{ dof}$$

reduced mass of system

distance between atoms

So... $U = \frac{7}{2} nRT$

Equipartition of Energy

An average energy of $\frac{1}{2}nRT$ or $\frac{1}{2}kT$ is associated with each of the variables of a system of particles

and the energy is shared equally among all degrees of freedom.

This will haunt physics in 1900.

Molar Specific Heats

For gases, two kinds of specific heat

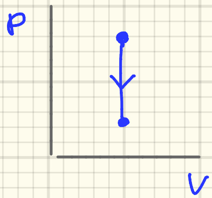
- Constant volume
- Constant pressure

Constant V :

$$\Delta Q = n c_V \Delta T$$

"specific heat at constant volume

Remember:



$\Delta W = 0$

1st Law: $\Delta Q = \Delta U + \Delta W$

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

(monotonic)

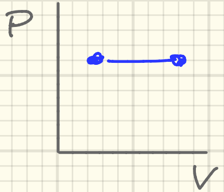
& $\Delta Q = n c_V \Delta T$

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

$$\boxed{c_V = \frac{3}{2} R} = 12.5 \ \mathrm{J/mol \cdot K}$$

Constant P:

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



$\Delta W = P\Delta V$

1st Law: $\Delta Q = \Delta U + \Delta W$

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

For an ideal gas: $PV = nRT$

$\underbrace{\Delta P}_{=0} V + P\Delta V = nR\Delta T$ in general

$$P\Delta V = nR\Delta T$$

also $\Delta U = \frac{3}{2} nRT$ (monatomic)

so $\Delta Q = \frac{3}{2} nRT + nR\Delta T = \frac{5}{2} nRT$

and $nC_p\Delta T = \frac{5}{2} nRT$

$\boxed{C_p = \frac{5}{2} R} = 20{,}78$ J/mol·K

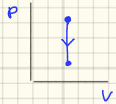
Notice: $c_p = \frac{5}{2}R = 20.78$ J/mol·K

$c_v = \frac{3}{2}R = 12.5$ J/mol·K

so $c_p - c_v = \frac{5}{2}R - \frac{3}{2}R = R$

$c_p = c_v + R$

A HINT



$\Delta W = 0$

1st Law: $\Delta Q = \Delta U + \Delta W$

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

& $\Delta Q = n c_v \Delta T$

$n c_v \Delta T = \frac{3}{2} nR\Delta T$

$\boxed{c_v = \frac{3}{2} R} = 12.5\ \mathrm{J/mol \cdot K}$

$\Delta Q = \Delta U = n C_v \Delta T$

$\frac{dU}{dt} = n C_v$

from equipartion:

$U = \frac{3}{2} RT$ for monotonic ideal gas.

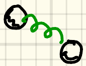
$\frac{1}{n} \frac{dU}{dT} = \frac{3}{2} \frac{RT}{n} = C_v$ ... for 1 mole

$C_v = \frac{3}{2} RT$

C_v

3 dof  $\frac{3}{2} RT$

5 dof  $\frac{5}{2} RT$

7 dof  $\frac{7}{2} RT$

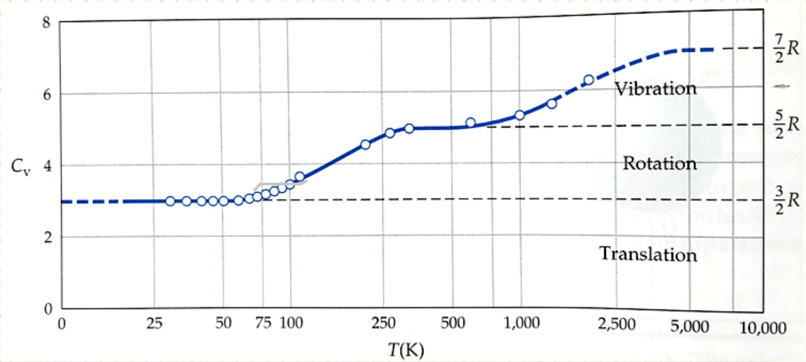
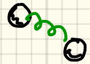
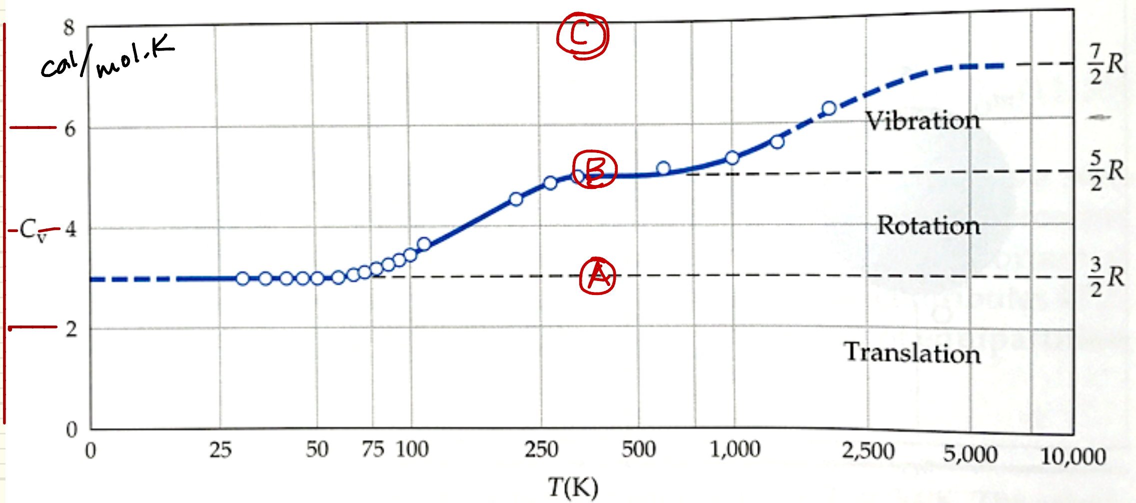


Table 9.1 Molar Heat Capacities for Selected Gases at 15°C and 1 Atmosphere

Gas	c_V (J/K)	c_V/R	
Ar	12.5	1.50	A
He	12.5	1.50	
CO	20.7	2.49	
H_2	20.4	2.45	
HCl	21.4	2.57	B
N_2	20.6	2.49	
NO	20.9	2.51	
O_2	21.1	2.54	
Cl_2	24.8	2.98	
CO_2	28.2	3.40	C
CS_2	40.9	4.92	
H_2S	25.4	3.06	
N_2O	28.5	3.42	
SO_2	31.3	3.76	

		C_V
3 dof		$\frac{3}{2}RT$
5 dof		$\frac{5}{2}RT$
7 dof		$\frac{7}{2}RT$

J/mol·K
- 25.1
~20 -
- 16.7
~12 -
- 8.4

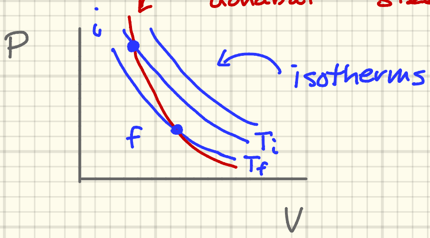


Adiabatic Expansion of an Ideal Gas

high P,
suddenly released

a change that's QUICK or WELL INSULATED → Q neither leaves nor enters
"Adiabatic"

'adiabat" steeper than isotherms



T decreases

U? <u>decreases</u> since T↓

Since $\Delta Q = 0$

$-\Delta U = \Delta W$

a tricky general point: $\Delta Q = n C_v \Delta T \Rightarrow nC_v = \underbrace{\left.\frac{\Delta Q}{\Delta T}\right|_V}_{\text{means "at constant volume"}} = \left.\frac{\Delta U}{\Delta T}\right|_V$

or for infinitesimal changes

$$nC_v = \left.\frac{dU}{dT}\right|_V$$

for Ideal Gases $U = U(T)$ only. & $nC_v = \frac{dU}{dT}$ <u>period</u>

Back to 1st Law: $\Delta Q = \Delta U + \Delta W \rightarrow dQ = dU + dW$

$\uparrow$

ϕ

adiabatic

(A) $0 = dU + dW = nC_v\,dT + P\,dV$

for Ideal Gas: $PV = nRT$

(B) $V\,dP + P\,dV = nR\,dT$

(B) $dT = \dfrac{V\,dP + P\,dV}{nR}$

(A) $dT = -\dfrac{P\,dV}{nC_v}$

$$\frac{V\,dP + P\,dV}{nR} = -\frac{P\,dV}{nC_v}$$

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

but $C_v + C_p = R$

so $P\,dV\left(1 + \dfrac{C_p - C_v}{C_v}\right) = -V\,dP$

$$P\,dV\left(1 + \underbrace{\frac{C_p}{C_v}}_{\text{called } ``\gamma"} - 1\right) = -V\,dP$$

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

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

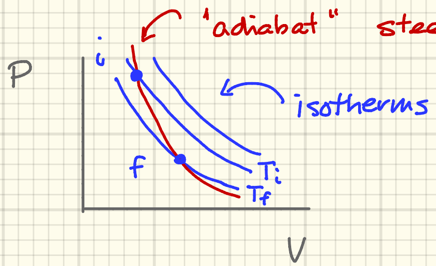
for a finite thermodynamic change $\rightarrow$ integrate

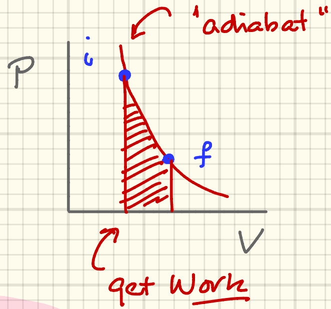
$$\gamma \int \frac{dV}{V} + \int \frac{dP}{P} = 0$$

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

$$PV^{\gamma} = (\text{constant})$$ for an ideal gas

"adiabat" steeper than isotherms





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

Ⓐ $dT = -\frac{P\,dV}{n c_V}$

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

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

$$W = \int_{V_i}^{V_f} \frac{K}{V^{\gamma}}\,dV = \frac{1}{1-\gamma}\left(K V_f^{1-\gamma} - K V_i^{1-\gamma}\right)$$

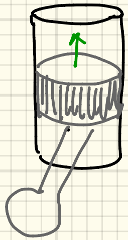
Adiabatic transitions are special... like Goldilocks

Be fast enough to not lose heat

Be slow enough to uniform throughout

just right

Gasoline & Diesel engine strokes are ~adiabatic



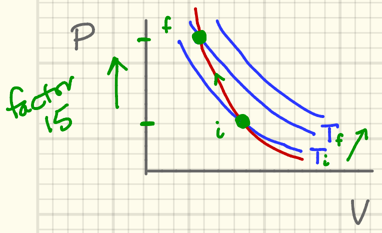
compression stroke is fast — no heat leaves

$\gamma > 1$ so a boost in changing pressure

Compression ratio .. 15/1 or so

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

$$P_f = P_i \left(\frac{V_i}{V_f}\right)^{\gamma} = P_i (15)^{1.4} \sim 44\, P_i \Rightarrow 44 \text{ atm. if } P_i = \text{air}$$



If no molecules escape?

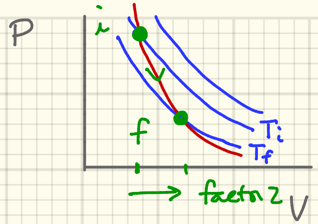
From the Ideal gas law you can show: $T_f = T_i \left(\frac{V_i}{V_f}\right)^{\gamma - 1}$

in fact, do that next time D3

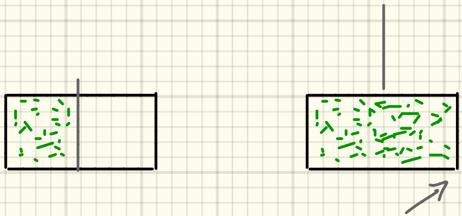
$$T_f = T_i \left(\frac{V_i}{V_f}\right)^{\gamma-1} = 3 T_i \quad \left\{ \begin{array}{c} T \cong 300\text{K} \\ \downarrow \\ T = 900\text{K} \end{array} \right.$$

ignite diesel fuel

standard physical example:



adiabatic
not isothermal



work against wall

air: $\gamma = 1.4$

$V_0 = 2L$ $\qquad$ $V_f = 4L$

$T_0 = 20°C$ $\qquad$ $T_f = ?$

$P_0 = 1\,\text{atm}$ $\qquad$ $P_f = ?$

first pressure ... ignore T

$$P_0 V_0^\gamma = P V^\gamma$$

$$P = P_0 \left(\frac{V_0}{V}\right)^\gamma$$

$$P = 1\,\text{atm} \left(\frac{2}{4}\right)^{1.4}$$

$$P = 0.38\,\text{atm}$$

temperature ... ignore P

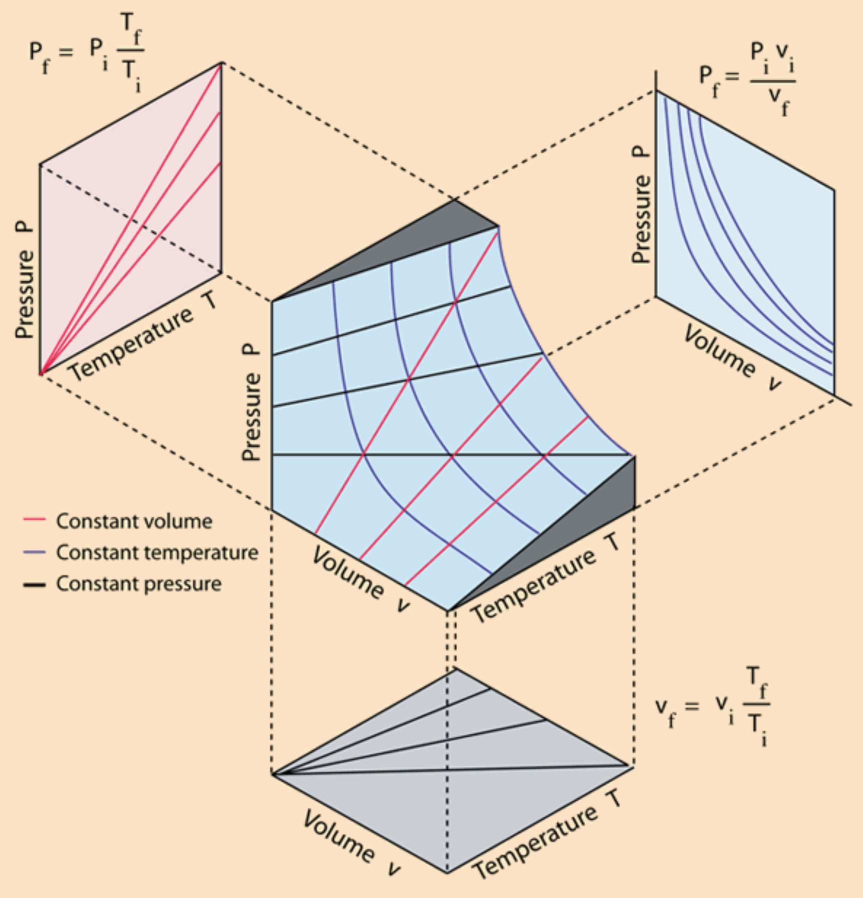
$$T_0 V_0^{\gamma-1} = T V^{\gamma-1}$$

$$T = T_0 \left(\frac{V_0}{V}\right)^{\gamma-1}$$

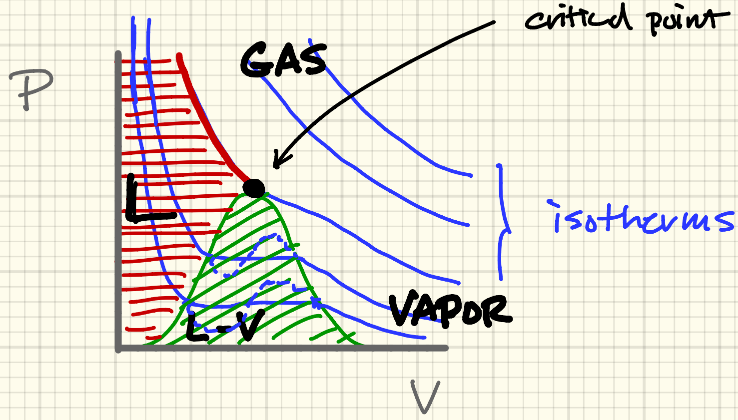
$$= 293 \left(\frac{2}{4}\right)^{0.4}$$

$$T = 222\,K = -51°C$$

from hyperphysics.



For actual materials, phase transitions complicate this



Making it real:

finite size:

b – volume of molecules $\quad V \to V - b$

short-distance attraction:

$P \to P + a/V^2$

$$\left(P + \frac{a}{V^2}\right)(V-b) = nRT$$

Van der Waals Equation

a, b measured.

OBTW: phase diagrams (different year!)