Week 2

Sections 1.5 - 1.6

1.5 Compression work.

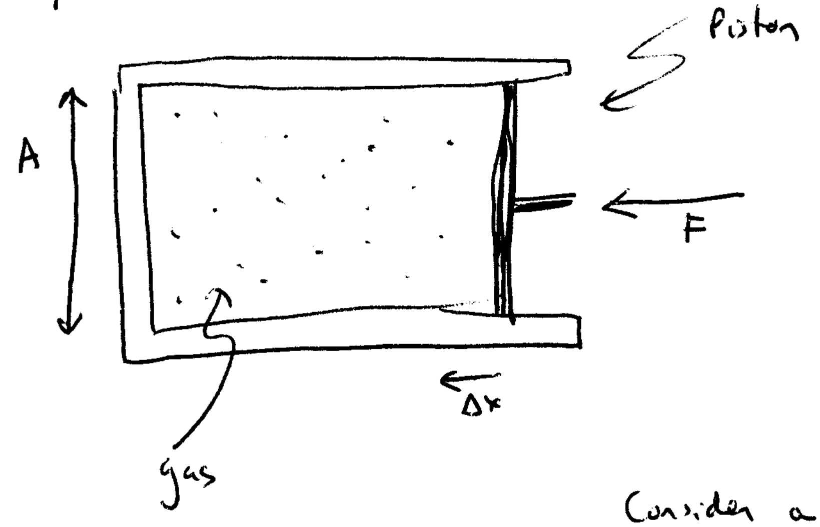
Example of work done on a system $\Rightarrow$ Compressing gas.

force acting over some distance

$$W = \vec{F} \cdot d\vec{r}$$

work done on system.

external force acting on system.



Consider a piston compressing gas. — compress gas ~~so~~ slow enough (quasistatic) so gas always equilibrates.

$$W = F\Delta x$$

$$F = PA$$

$$W = PA\Delta x$$

relate to change in volume $A\Delta x = -\Delta V$

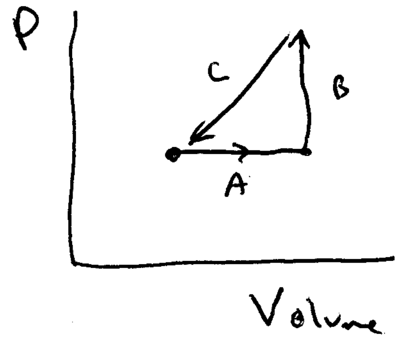
required since $\Delta V < 0$

$$W = -P\Delta V$$

Generalize

$$W = -\int_{V_1}^{V_2} P(V)\, dV$$

~~Examp~~ **Example** Problem 1.33



	A	B	C
work done on gas	$-$	0	$+$
change in Energy content	$+$	$+$	$-$
heat added to gas	$+$	$+$	$-$

to calculate first line, use $W = -\int_{V_1}^{V_2} P(V)\, dV$

for A, volume expands so $W<0$
for B, No volume change so $W=0$
for C, volume contracts so $W>0$

to fill in second Line, use ideal gas law / internal energy equation

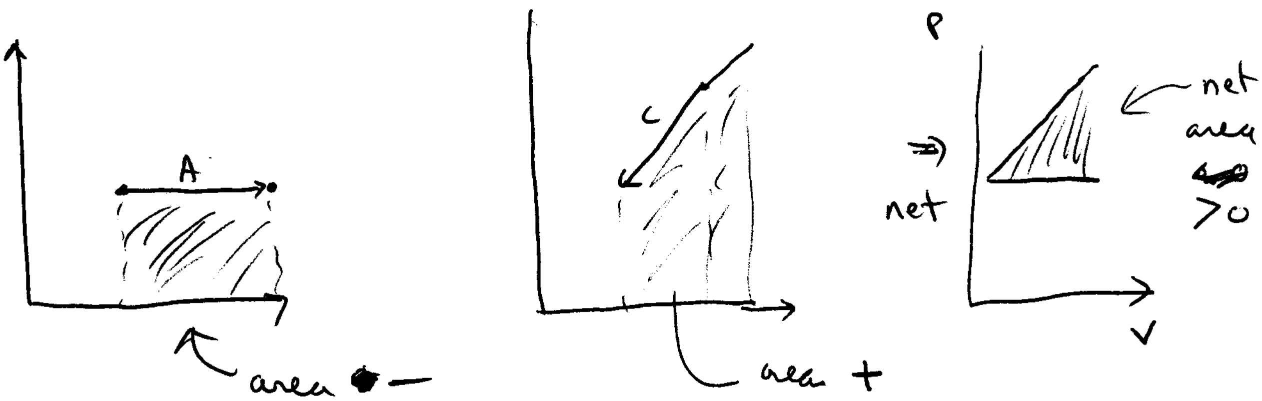
$$U = N \cdot f \cdot \tfrac{1}{2} kT = \tfrac{f}{2} PV$$

$$\Delta U = \tfrac{f}{2}\left(\Delta P\, V + P \Delta V\right) = \tfrac{f}{2}\, \Delta(PV)$$

For Heat added, use 1^{st} Law of thermo

$$\Delta U = Q + W \quad \Rightarrow \quad Q = \Delta U - W$$

For Net W, over whole cycle, its the area under curves



Net for cycle $W > 0$

If begining point is same as final point, $P_i V_i = P_f V_f$

$\Rightarrow$ so $T_i = T_f \Rightarrow \Delta U = 0$

Since $Q = \cancel{\Delta U}^{0} - W \Rightarrow$ ~~$Q \leq 0$~~ ~~$Q > 0$ since $W < 0$~~

$Q < 0$ since $W > 0$

Cycle acts as a refrigorator (not efficient)

work is done to remove heat.

Compression of Ideal gas

- isothermal – compression slow enough so that heat enters/leaves system so that T is constant. [redacted] $\Delta T = \Delta U = 0$

- adiabatic – so fast that no heat is exchanged with environment. [redacted]$= 0$

Work done for isothermal.

$$W = -\int_{V_i}^{V_f} P\,dV = -NkT\int_{V_i}^{V_f}\frac{dV}{V}$$

$$= -NkT\ln\frac{V_f}{V_i}$$

$$W = +NkT\ln\left(\frac{V_i}{V_f}\right) \qquad \text{(Isothermal)}$$

$U = \frac{1}{2}N f kT$ $\qquad Q = \cancel{\Delta U}^{\,0} - W \qquad \Rightarrow \quad Q = -W = NkT\left(\frac{V_f}{V_i}\right)$

$Q < 0$ when volume is compressed

$\Rightarrow$ heat leaves gas, goes into outside environment

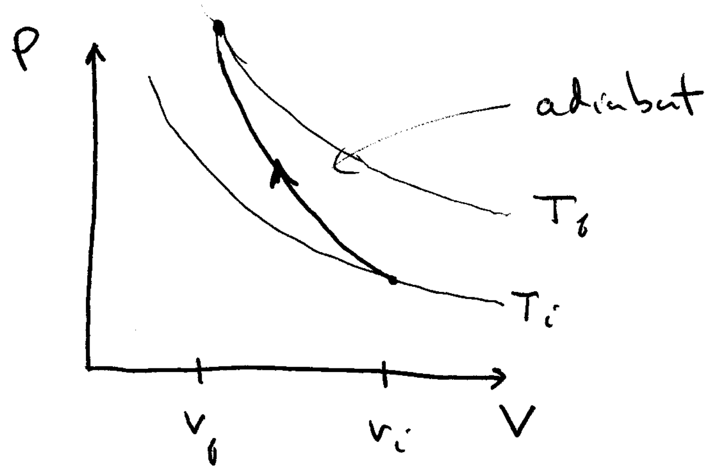
$Q > 0$ when volume is decompressed

$\rightarrow$ heat enters gas from outside environment.

Adiabatic compression $\Rightarrow$ $Q = 0$

$$\Delta U = \cancel{Q}^{\,0} + W$$

$$\Delta U = W$$



<u>Derive shape of curve:</u>

$$\Delta U = W$$

$$U = \frac{f}{2} NkT$$

$$\frac{f}{2} Nk\,\Delta T = -P\,\Delta V$$

→ generalize to differential.

$$\frac{f}{2} Nk\,dT = -P\,dV$$

let $P = \dfrac{NkT}{V}$

$$\frac{f}{2}\cancel{N}k\,dT = -\frac{\cancel{N}kT}{V}\,dV$$

$$\frac{f}{2}\frac{dT}{T} = -\frac{dV}{V}$$

Integrate both sides:

$$\frac{f}{2}\int_{T_i}^{T_f}\frac{dT}{T} = -\int_{V_i}^{V_f}\frac{dV}{V}$$

$$\frac{f}{2}\ln\frac{T_f}{T_i} = -\ln\frac{V_f}{V_i}$$

take exponential

$$\left(\frac{T_f}{T_i}\right)^{f/2} = +\frac{V_i}{V_f}$$

or

$$V_i T_i^{f/2} = V_f T_f^{f/2}$$

or

$$\boxed{VT^{f/2} = \text{constant}}$$

If substitute $T = \frac{PV}{Nk}$, can show

$$V^{\gamma}P = \text{constant}$$

$$\gamma = \frac{f+2}{f} \quad \Leftarrow \text{adiabatic constant}$$

Example: Problem 1-37

Diesel engine — compresses air Quickly (adiabatically) to 1/20 its volume. Estimate T after Compression.

Eq. 1.38 $$V_f T_f^{f/2} = V_i T_i^{f/2}$$

$$\frac{V_f}{V_i} = \left(\frac{T_i}{T_f}\right)^{f/2}$$

$$T_f = T_i \left(\frac{V_i}{V_f}\right)^{2/f}$$

take $T_i = 300\text{ K}$ $\quad \frac{V_i}{V_f} = 20$ assuming N_2 for air.

$f = 5$ degrees of freedom $\Rightarrow$ 3 translational, 2 rotational.

$$T_f = 300(20)^{2/5} \sim 1000\text{ K}$$

should be hot enough to ignite fuel.

Section 1.7 Heat Capacities

$$C \equiv \frac{Q}{\Delta T}$$

specific heat capacity $\quad c \equiv \frac{C}{m}$ ← normalize out effect of different amount of material

By itself, C not well-defined

$$C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}$$ ← C depends on work done

Need to specify some other parameter.

$$C_v = \left(\frac{\Delta U}{\Delta T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v$$ ← volume constant so $W = 0$

Another case is if the Pressure is constant.... For example heating a block of metal in ambient atmosphere.

$$C_p = \left(\frac{\Delta U - W}{\Delta T}\right)_p$$ ← constant pressure

$$= \left(\frac{\Delta U}{\Delta T}\right)_p - \left(\frac{-P\Delta V}{\Delta T}\right)_p$$

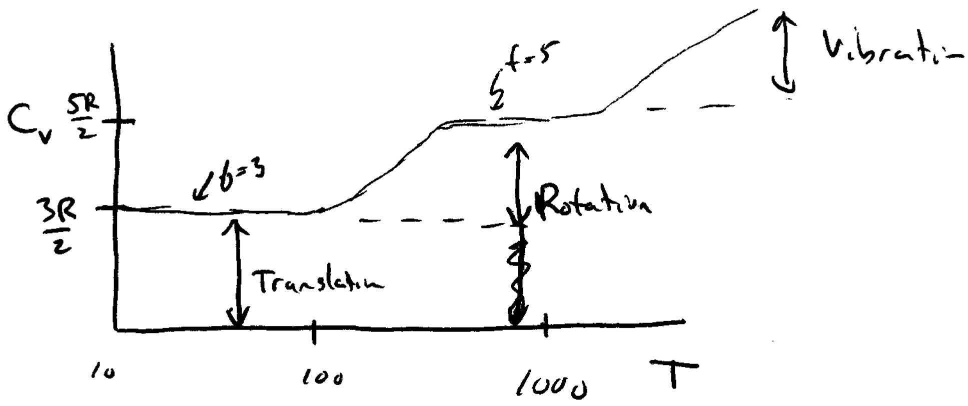
$$= \left(\frac{\Delta U}{\Delta T}\right)_p + P\left(\frac{\Delta V}{\Delta T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p$$

By Equipartion Theorom, $U = \frac{1}{2} N f k T$

so $C_v = \frac{1}{2} N f k = \frac{1}{2} f R n$

← can be used to measure # of degrees of freedom.

Note that rotational and vibrational degrees of motion can "freeze out" at low temp.



Calculate C_p $\Rightarrow$ $C_p = C_v + P\left(\frac{\partial V}{\partial t}\right)_P$

Ideal gas. $PV = NkT$

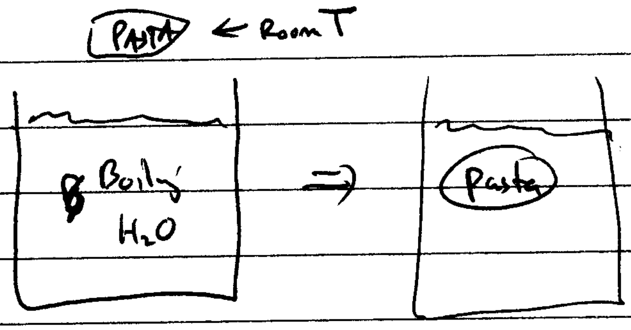
$$\frac{\partial}{\partial T}(PV) = \frac{\partial}{\partial T}(NkT)$$

$$P\left(\frac{\partial V}{\partial T}\right)_P = Nk$$

So $C_p = C_v + P\left(\frac{Nk}{P}\right)$

$C_p = C_v + Nk = C_v + nR$ due to change of volume of gas.

Example Prob. 142



Before After.

Right when pasta added, T goes down.

Heat energy exchanged between pasta / water.

Energy conserved ⇒ NO work done.

$$m_{H_2O} C_{H_2O} T_{H_2O} + m_p C_p T_p = \text{constant}.$$

$$m_{H_2O} C_{H_2O} T_f + m_p C_p T_f = m_{H_2O} C_{H_2O} T_{373} + m_p C_p T_{298}$$

$$T_f = \frac{\left(m_{H_2O} C_{H_2O} T_{373} + m_p C_p T_{298}\right)}{m_{H_2O} C_{H_2O} + m_p C_p}$$

$1.5\,l$ H_2O = 1500 gm H_2O $\qquad C_{H_2O} = 4.186\ J/g\,°C$

$\qquad C_p = 1.8\ \frac{J}{g\,°C}$

$$T_f = \frac{1500(4.186)\,373 + (340)(1.8)\,298}{1500(4.186) + (340)(1.8)} \sim 93.3° \quad \sim 366.3\,K$$

~7° temp. drop.

Example on $\left(\frac{\partial U}{\partial T}\right)_V \neq \left(\frac{\partial U}{\partial T}\right)_P$

Problem 1.45

$w = xy \qquad x = yz$

(a) $w = xy \Rightarrow w = x\left(\frac{\cancel{x}}{z}\right) = \frac{x^2}{z}$

$w = xy \Rightarrow w = (yz)\,y = y^2 z$

(b) $\left(\frac{\partial w}{\partial x}\right)_y = y \qquad \left(\frac{\partial w}{\partial x}\right)_z = \frac{2x}{z}$

$\left(\frac{\partial w}{\partial x}\right)_z = \frac{2y\cancel{z}}{\cancel{z}} = 2y$

so $\left(\frac{\partial w}{\partial x}\right)_y \neq \left(\frac{\partial w}{\partial x}\right)_z$

(c) $\left(\frac{\partial w}{\partial y}\right)_x \overset{?}{=} \left(\frac{\partial w}{\partial y}\right)_z$

$\boxed{\left(\frac{\partial w}{\partial y}\right)_x = x \qquad \left(\frac{\partial w}{\partial y}\right)_z = 2yz = 2x}$

$\boxed{\left(\frac{\partial w}{\partial z}\right)_x = -\frac{x^2}{z^2} \qquad \left(\frac{\partial w}{\partial z}\right)_y = y^2 = \frac{x^2}{z^2}}$

More of Phase transition and Heat capacity

At a phase transition, $\Delta T = 0$ so C is undefined

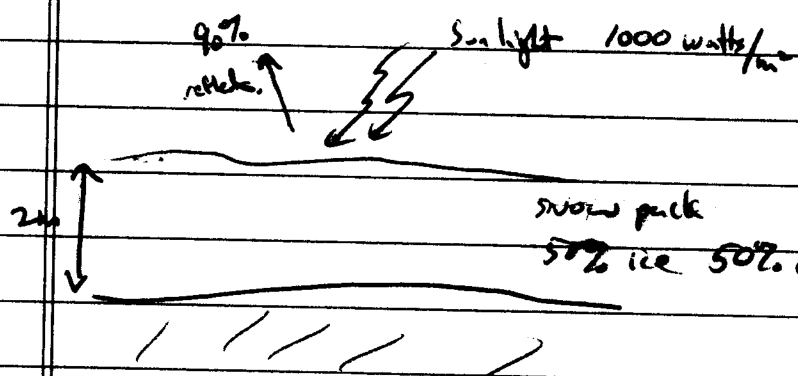
$$C = \frac{\Delta Q}{\Delta T} = \frac{\Delta Q}{0} = \infty$$

Measure amount of heat need to accomplish

Phase transition by Latent Heat

$$L = \frac{Q}{m}$$

Example: Problem 1.48



~~For~~ For simplicity, ignore heat capacity of air and assume snow pack only melting from sunlight.

remove air

Calculate amount of Heat required to melt $1m^2 \times 1m$ of snow pack: $Q = Lm = L\rho V$ ↙ density of ice

$$= \left(333 \frac{J}{\cancel{g}}\right)\left(\frac{1000\,\cancel{kg}}{m^3}\right) 1m^3 \; \frac{1000\,g}{1\,\cancel{kg}}$$

$$Q = 333 \times 10^6\ J$$

Sunlight: Power $= 1000\ W = 1000 \frac{J}{s}$

$$\text{time} = \frac{333 \times 10^6}{1000 \cdot (.1)} \quad \cancel{333} \quad = \cancel{333 \times 10^6}$$

↑ 90% reflect.

$$\text{time} = 3.33 \times 10^6 \text{ seconds}$$

In spring, ~ 8 hrs of direct sunshine per day.

$$8 \text{ hours} = 8 \cdot 60 \cdot 60 = 28{,}800 \text{ sec.}$$

$$\frac{3.33 \times 10^6}{28{,}800} = 115 \text{ days} \Rightarrow \sim 16.5 \text{ weeks.} \sim 4 \text{ months.}$$

Long time for snow to melt only from sunlight — heating by air also speeds up snow melt.

Enthalpy: Constant Pressure processes are very prevalent in the lab and nature. → Keeping track of compression / decompression work to maintain constant pressure is sometimes not obvious.

Define new quantity:

$$H \equiv U + PV$$

Total energy required to create system out of nothing and put it in environment. PV represents the work required to move ambient air out of the way to make room for your system.

For constant pressure

$$\Delta H \equiv \Delta U + P\Delta V$$

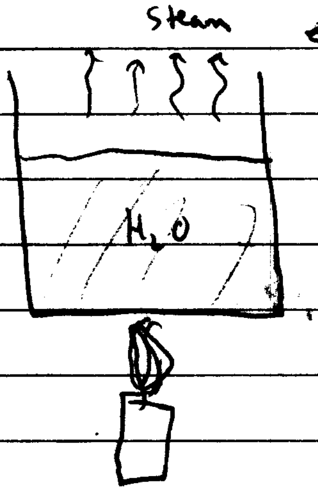
combine with first law: $\Delta U = Q - \underbrace{P\Delta V}_{\text{compression}} + W_{other}$

gel. $\Delta H = Q + W_{other}$ (constant P)

Enthalpy only increases due to heat added or due to work other than compression/decompression

Example of where this is useful:

Boiling water



← steam must push atmosphere out of the way.

⇒ Heat goes into phase transition, and pushing atmosphere out of the way.

$Q \Rightarrow$ liquid → gas ~~#~~ plus expansion of gas

Enthalpy eliminates need to account for expansion of water vapor.

Example ~~1-51~~ Problem: Calculate ΔH for glucose

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

Step 1: "convert" glucose to elemental substances $\Rightarrow$ graphite, H_2, O_2

from table on page 404 $\Delta_f H = -1273$ kJ

formation of glucose from graphite, H_2, O_2

Since breaking glucose up (rather than forming)

$\Delta H_{\text{deconstruct glucose}} = 1273$ kJ $\Leftarrow$ 1 mole

Now form 6 moles each of CO_2 and H_2O from graphite, O_2, and H_2

$\Delta H_f\ H_2O = -285.83$ kJ (Liquid H_2O)

$\Delta H_f\ CO_2 = -393.51$ kJ

Form 6 moles : $\Delta H_{6\text{ moles}} = 6(-285.8 + -393.5)$

$= -4076$ kJ

Net Enthalpy $= 1273 - 4076 = -2803$ kJ

$\Rightarrow$ 2803 kJ generated by "burning" glucose.