

As an aside we note that the

"average energy of a gas"

is an important quantity

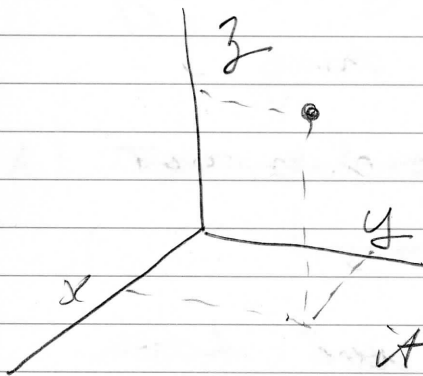
→ It's dependence on T determines the

"HEAT CAPACITY" of the gas.

— this is a measurable macroscopic quantity — how much energy does it take to heat up your lunch?

↳ determined by heat capacity of food.

Defining Degree of Freedom by Example



A point like particle

in 3 dimensions, needs

3 numbers to specify

it's position $\vec{r} = (x, y, z)$

Point like particle has

3 TRANSLATIONAL DEGREES OF FREEDOM

changing x, y, or z TRANSLATES

the position of the particle in space.

If you have two point like particles you need 6 numbers to describe their positions - - - etc - - -

For n - point like particles need $3n$ numbers

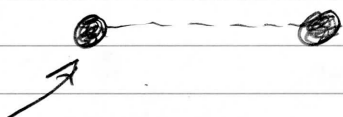
n particles have $3n$ DEGREES OF FREEDOM

↳ note that we assume that the particles have no "connections" with each other → like being connected by springs or being in a molecule (≡ same thing!)

Moving one particle does not affect the others.

Actually, whether we have the particles in molecules is indeed of interest.

DIATOMIC MOLECULE eg: N₂



2 point like particles bound together by an interatomic force — represented here by a rod

A single N₂ molecule still has

6 d.o.f → helps to re-organize them

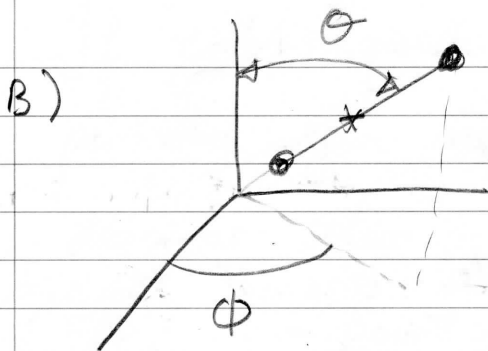
⇒ remember that you can represent a point in space by several different coordinate systems
Cartesian
polar
cylindrical



↳ center of mass of molecule

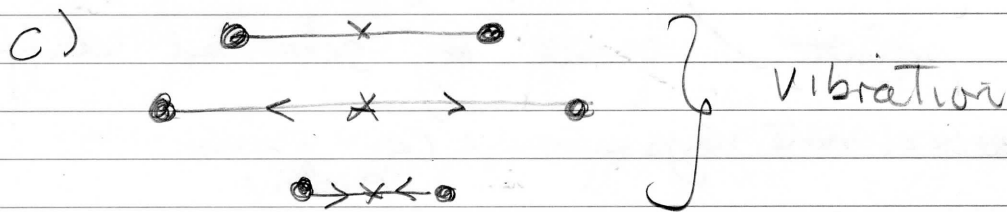
its motion describes the motion of the molecule as a whole.

= 3 translational dof.



ϕ, θ — 2 angles describe the orientation of the molecule in space

— 2 rotational d.o.f.



1 number = 1 vibrational dof.

A) Translation = 3

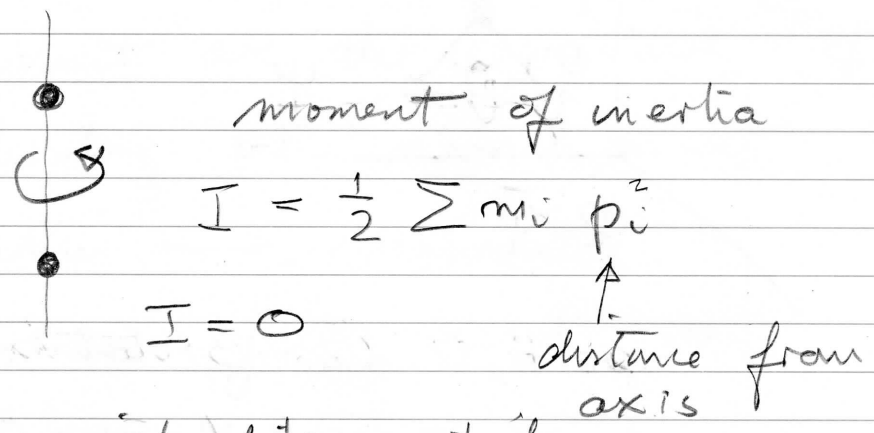
B) rotation = 2

C) vibration = 1

6 dof

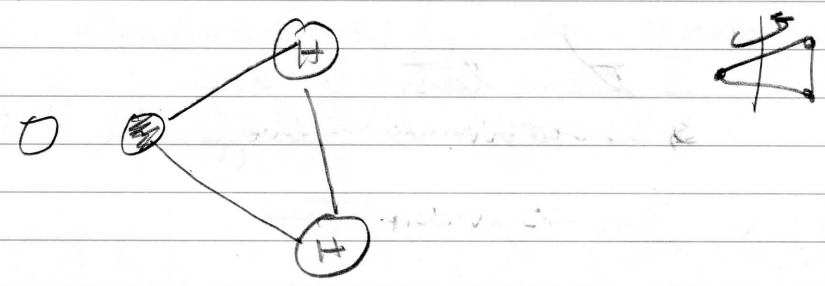
describes the state of the 2 particles in a molecule,

NB Linear molecule



these are point like particles
- they have zero moment of inertia.

If molecule is NON LINEAR

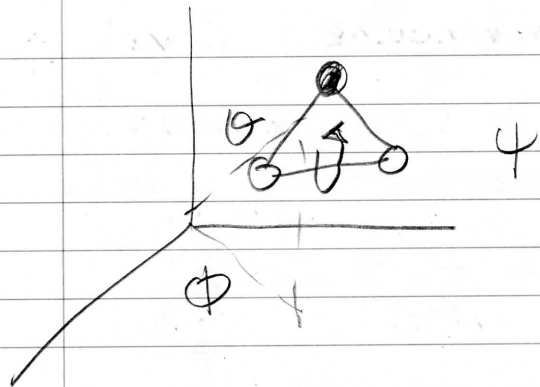


to describe its orientation need 3
not 2 numbers

$\theta, \phi \rightarrow$ overall orientation in space.

ψ rotation about some internal
axis

eg the H - H axis



so H_2O has 3 rotations and 3 translations and 3 vibrations

$$9 = 3 \times 3 \text{ dof}$$

* m -atomic molecule - linear one

3 translational dof.

2 rotational dof.

$3m - 5$ vibrational

↳ Σ must be $3m$

$$3 + 2 + 3m - 5 = 3m$$

For NONLINEAR

3 translational dof

3 rotational dof

$3m - 6$ vibrational

② N m-atomic LINEAR Molecules

$$U = N \times \left(\frac{3}{2} kT + \frac{2}{2} kT + (3m-5) kT \right)$$

3 translational

2 rotational

(3m-5)
vibrational

$$U = N \left(3m - \frac{5}{2} \right) kT \quad m \geq 2$$

LINEAR

Expressions for U useful in
~~that~~ changes in the energy of
a gas are important in physical
(or chemical, etc-----) processes

EQUIPARTITION \rightarrow JUSTIFICATION

Put large number ($\sim 10^{24}$...) of molecules in a box.

- give them some kinetic energy
 \rightarrow could be just given to a few of them — not all

- they start to collide
 \rightarrow many times in a short period of time

\rightarrow each molecule in air collides every 10^{-7} s.

- Collisions lead to redistribution of energy among molecules

\rightarrow leads eventually to thermodynamic equilibrium.

\rightarrow each molecule has, on average, energy $\sim kT$

If molecules MONOATOMIC only have translational dof, average $E \sim \frac{3}{2} kT$

If the molecules are MULTIATOMIC, these collisions can lead to ROTATIONS
VIBRATIONS

as well as translational energy

EQUIPARTITION — EVERY DEGREE OF FREEDOM

GET ENERGY $\frac{kT}{2} \rightarrow$ translational
rotational

OR $kT \rightarrow$ vibrational

\Rightarrow the many collisions (conserving energy, momentum & angular momentum) lead, ON AVERAGE, to equal distribution of energy between the various degrees of freedom \rightarrow IN THERMODYNAMIC EQUILIBRIUM.

EVIDENCE FOR EQUIPARTITION?

→ EXPERIMENTAL!

→ follows from Statistical Mechanics

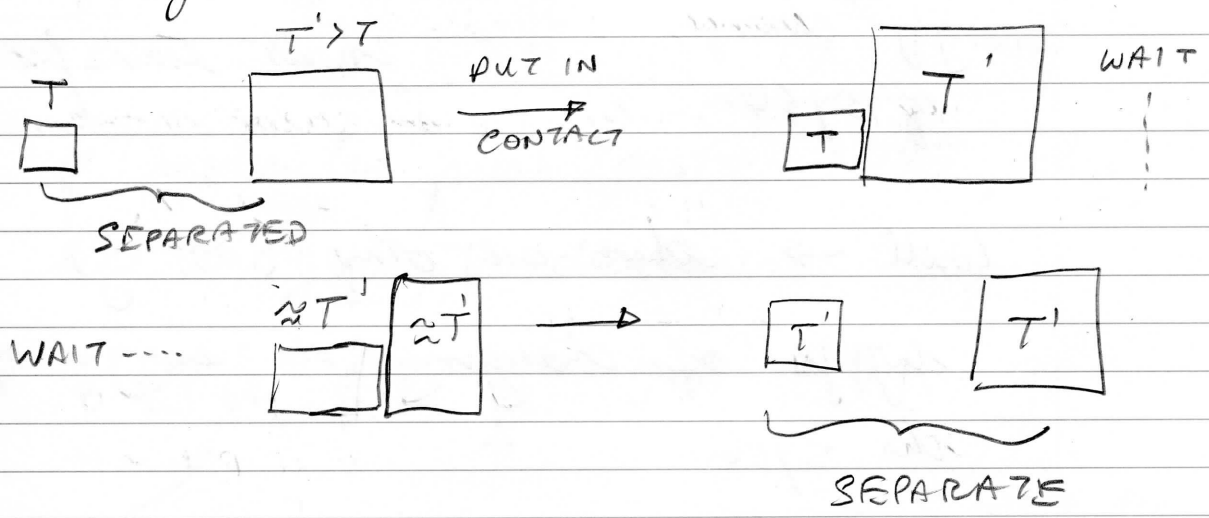
EXPERIMENTAL? — IDEAL GAS LAW

* implies equipartition from simple molecular model

* simple molecular model, does not tell us if gas is monoatomic

→ How do we change ENERGY OF GAS

one way is HEAT EXCHANGE



Spontaneous transfer of energy from hotter → colder system, when in THERMAL CONTACT.

HEAT TRANSFER $T \rightarrow T'$

Energy of (ideal, monoatomic) gas changes

$$\frac{3}{2} NkT \rightarrow \frac{3}{2} NkT'$$

(RECALL $U = \frac{3}{2} kT \times N$ molecules)

$$\begin{aligned} \text{SO } \Delta U &= U(\text{final}) - U(\text{initial}) \\ &= \frac{3}{2} Nk (T' - T) \end{aligned}$$

RESULT OF HEAT TRANSFER

write $\Delta U = Q$

energy change of system \swarrow \nwarrow amount of heat transfer

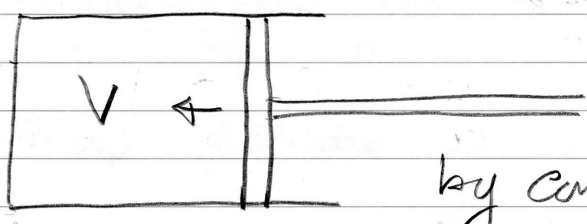
Well \rightarrow there are other (many)

ways of changing the energy of the system

eg - MECHANICAL = WORK

CAN DO WORK ON SYSTEM
OR SYSTEM CAN DO WORK

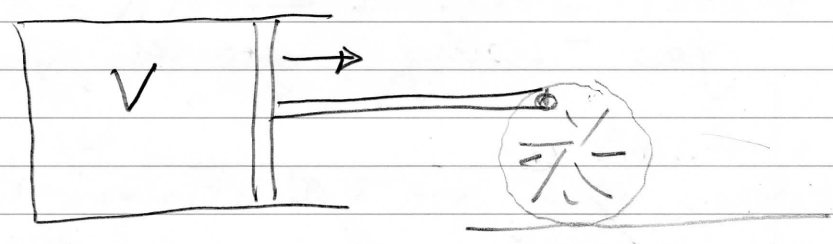
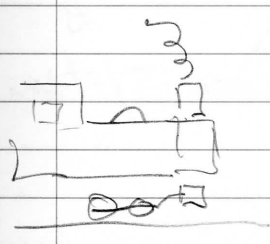
MOVING
PISTON



work done
ON gas
by compressing it

As the piston moves IN, it accelerates molecules that collide with it $F=ma$.

↳ they gain energy, and so
T of the gas INCREASES $U \uparrow$



if molecules push piston OUT, they lose energy, T decreases $U \downarrow$

$$\Delta U = Q + W$$

Change of energy of gas

heat absorbed or lost

work done on or by the gas.

N fixed for N_{mol} .

$$\Delta U = Q + W$$

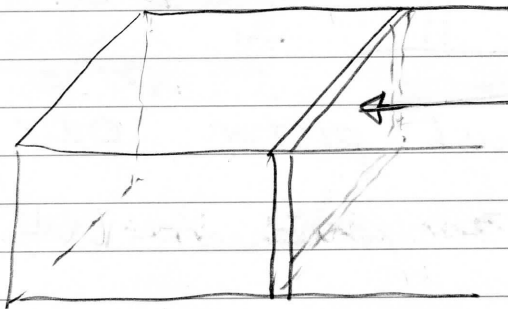
U , the energy of the gas in this case — CAN ONLY CHANGE FOR A REASON

U is CONSERVED QUANTITY

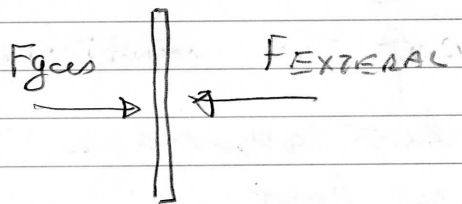
This equation expresses CONSERVATION OF ENERGY, in system in Thermodynamic Equilibrium

1ST LAW OF THERMODYNAMIC $\rightarrow \Delta U = Q + W$

Investigate work done on or by gas — using model of piston system



Piston has area A



$$F_{\text{gas}} = F_{\text{EXT}}$$

if piston does not move

$$F_{\text{gas}} (\text{on piston}) = \text{PRESSURE} \times \text{AREA}$$
$$p \cdot A$$

$$\Delta U = -P \Delta V$$

Now let's say that HEAT is EXCHANGE between gas and external environment

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

for an infinitesimal change ΔV

If we are mathematically inclined we know the Q is small, so

$$\Delta U = \delta Q - P \Delta V$$

If $\Delta V \rightarrow$ large, P will change during process — How to compute ΔU for finite ΔV ?

Hard \rightarrow unless we have a well defined process

\Rightarrow Process is such that gas

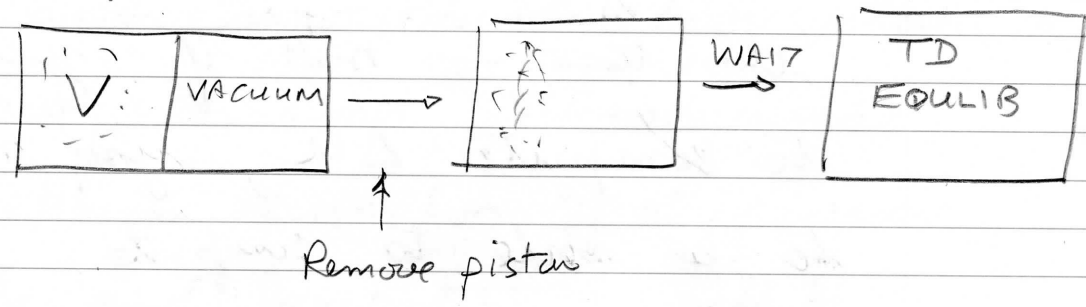
molecules can establish thermodynamic equilibrium at all instants of process

⇒ Expansion / Compression must be slow enough that the molecules' kinetic energy gets "Equipartitioned" at all times.

↳ QUASISTATIC PROCESS

EXAMPLES of NON QUASISTATIC PROCESSES

1) FAST Expansion



If piston is removed quickly

↳ depletion of molecules near piston

↳ Pressure is lower than equilibrium
∴ work is less

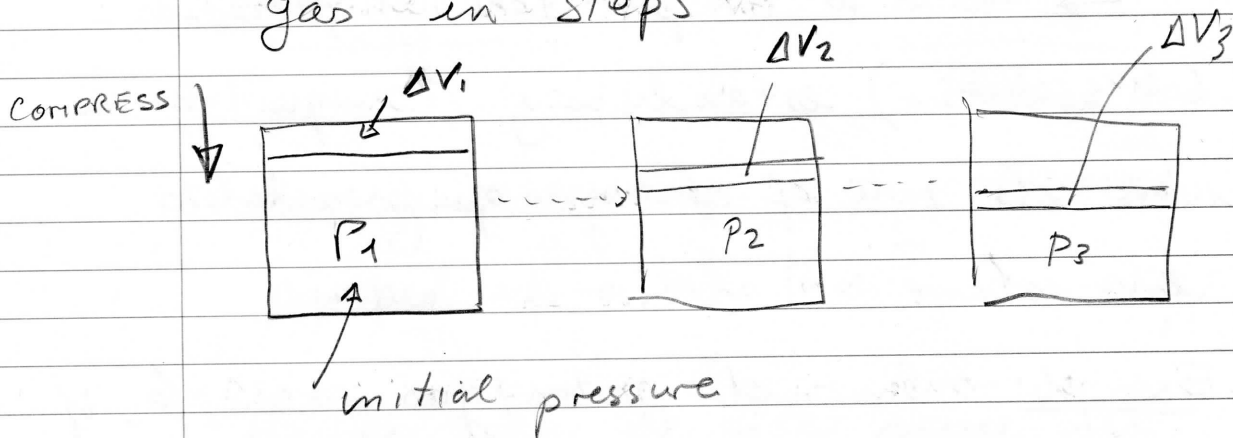
In reality many processes are only APPROXIMATELY QUASISTATIC

↳ have to compare rate of processes (like collisions) establishing TD equilibrium with the rate of change of parameters like volume.

Example In the piston/gas example, if the piston moves much slower than the VELOCITY OF SOUND, ^{1003 m/s} Thermodynamic Equilibrium (uniformity of pressure density and equipartition) will be maintained through out the process.

↳ so a slow expansion like this is QUASI (QUASI?) STATIC

For a quasi static process, one can compute the work done on the gas in steps



Work done on gas is given by:

$$W = -p_1 \Delta V_1 - p_2 \Delta V_2 - p_3 \Delta V_3 \dots - p_n \Delta V_n$$

↑
work done
ON gas

Again if we are mathematically inclined, this is just integration

$$W = - \int_{V_{init}}^{V_{final}} p dV \equiv - \int_{V_{in}}^{V_{if}} p(V) dV$$

↑
pressure varies
with volume.

Actually $p \equiv p(V, T)$

(27)

$$p = p(V, T)$$

the pressure in this integral is the equilibrium, for instantaneous values of V, T ← How can we know this?

↳ need to make more assumptions about the physical situation.

If the compression occurs at FIXED T

→ call it ISOTHERMAL

? How could we physically realize an ISOTHERMAL PROCESS?

IF gas is ISOLATED the process cannot be ISOTHERMAL

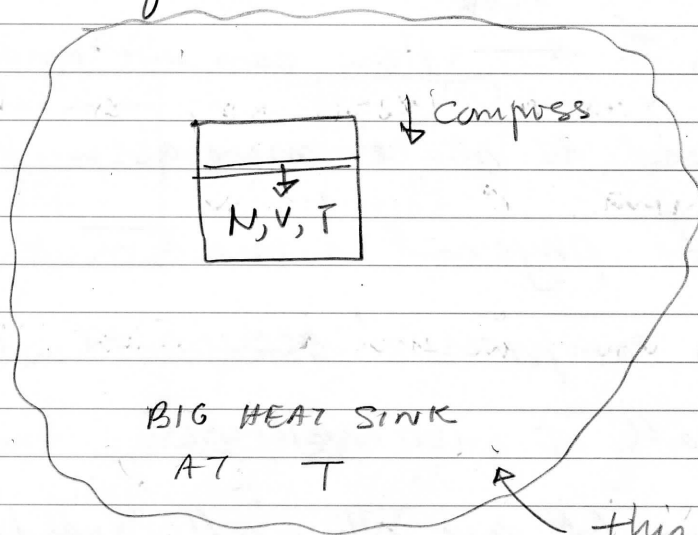
↳ for compression energy will increase and Temp will increase

↳ you are putting energy in & system is ISOLATED.

↳ Energy Conservation.

If want ISOTHERMAL process, need
somewhere for energy to go (compression)

[as come from \rightarrow Expansion]



this is in
thermodynamic
Equilibrium

During isothermal expansion/compression
at every instant will have

$$PV = NkT$$

Fixed

Fixed by
HEAT SINK

so

$$p = \frac{NkT}{V} \leftarrow \text{const.}$$

$$W = - \int_{V_{in}}^{V_{fin}} P(V) dV = -NkT \int_{V_{in}}^{V_{fin}} \frac{dV}{V}$$

$$= -NkT \ln \left(\frac{V_{fin}}{V_{in}} \right)$$

work done on ideal gas during
 Iso thermal compression

→ Change sign and it is EXPANSION

$$W(V_{in} - V_{fin}) = -NkT \ln \left(\frac{V_{fin}}{V_{in}} \right)$$

$W > 0$ COMPRESSION

$W < 0$ EXPANSION

Notice that for this IDEAL GAS

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

So for an ideal gas → it's energy
 does not
 change.

$$W = -NkT \ln \left(\frac{V_{\text{fin}}}{V_{\text{in}}} \right)$$

$$\uparrow$$
$$pV = NkT = \text{constant}$$

T is fixed, Equipartition tells us that all energy is kinetic, and it is determined by temp T

Now since work is done ON n

By the gas, to keep $\Delta U = 0$, heat must be EXCHANGED with heat sinks

$$\text{i.e. } \Delta U = Q + W = 0 \Rightarrow Q = -W$$

ISOTHERMAL

* if gas is compressed heat flows into the heat sink

* if gas expands, heat flows from the heat sink into the gas

So, that's what ISOTHERMAL processes are.

However it can be that the system is either truly isolated — or is isolated pretty well.

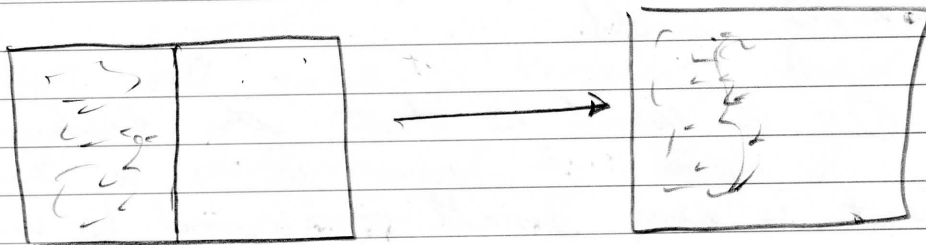
Or it could be that the exchange of heat is very small compared to work done
 $|Q| \ll |W|$

In such a case $Q \Rightarrow 0$

this is an ADIABATIC PROCESS

↳ no heat exchanged with environment

An ADIABATIC process may or may not be QUASISTATIC (Always in Thermodynamic Equilibrium \Rightarrow Equi-partitioned)



ISOLATED SYSTEM

Sudden expansion

no energy exchanged with environment

\hookrightarrow that means it is ADIABATIC

\hookrightarrow clearly not QUASISTATIC

\nearrow
Because piston does not move slowly.

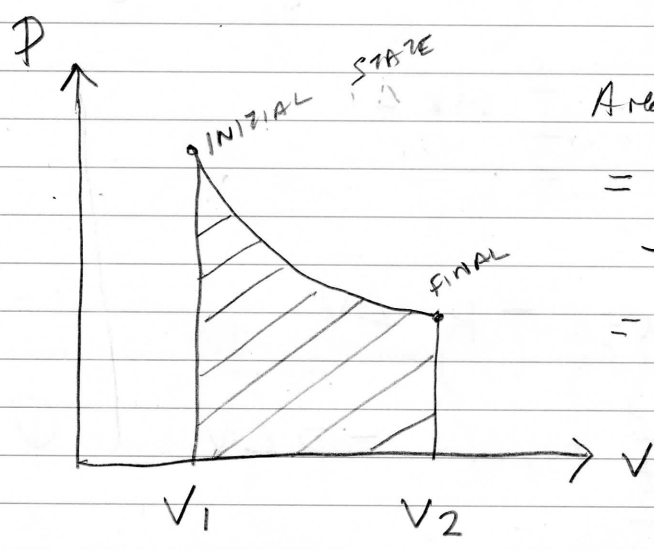
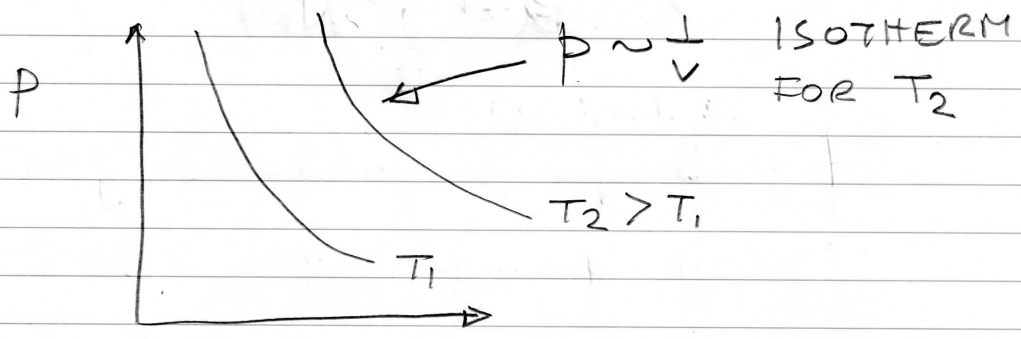
For QUASISTATIC process, since it is always in thermodynamic Equilibrium, the state of the gas can be characterized at every instant by P and V

↳ Can make a PV diagram

$$PV = NkT \quad (\text{ideal gas})$$

P, V → determines T → P, V completely determines MACROSCOPIC STATE

Ⓐ ISOTHERMAL PROCES



Area under curve
 $= \int_{V_1}^{V_2} P dV \quad (T \text{ const})$
 = work done BY gas $V_2 > V_1$
 EXPANSIONS.

ADIABATIC PROCESS \rightarrow more complex

from 1st LAW $\rightarrow \Delta U = Q - p \Delta V$

for adiabatic process $Q = 0$ defn.

$$\text{so } \Delta U = -p \Delta V$$

to understand how P, V change
for $Q = 0 \rightarrow$ need U

But for an ideal gas we
know that

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

$f = 3$ for monoatomic gas

$f = 7$ for diatomic $3 + 2 + 1$
 $t \quad r \quad v$

$$\text{so } \Delta U = \frac{f}{2} Nk \Delta T$$

AND

$$\Delta U = -p \Delta V$$

$$\text{so } \frac{f}{2} Nk \Delta T = -p \Delta V \quad \textcircled{1}$$

$$\frac{f}{2} NK \Delta T = -p \Delta V \quad (1)$$

But $PV = NK T$

$$\hookrightarrow NK \Delta T = p \Delta V + V \Delta p \quad (2)$$

$$\hookrightarrow \Delta(xy) = x \Delta y + y \Delta x$$

$$(1) + (2) \rightarrow -p \Delta V = \frac{f}{2} (p \Delta V + V \Delta p)$$

$$-p \Delta V - \frac{f}{2} p \Delta V = \frac{f}{2} V \Delta p$$

$$-p \frac{\Delta V}{V} - \frac{f}{2} p \frac{\Delta V}{V} = \frac{f}{2} \Delta p$$

$$-\left(\frac{\Delta V}{V} + \frac{f}{2} \frac{\Delta V}{V}\right) = \frac{f}{2} \frac{\Delta p}{p}$$

$$-\frac{\Delta V}{V} \left(\frac{2+f}{2}\right) = \frac{f}{2} \frac{\Delta p}{p}$$

$$\frac{\Delta p}{p} = -\frac{\Delta V}{V} \cdot \left(\frac{2+f}{f}\right)$$

$$\frac{\Delta p}{p} = -\left(1 + \frac{2}{f}\right) \frac{\Delta V}{V}$$

$$\frac{\Delta p}{p} = - \left(1 + \frac{2}{f}\right) \frac{\Delta V}{V}$$

$$\rightarrow \frac{d}{dp} (\ln p) = \frac{1}{p}$$

$$\Delta(\ln p) = - \left(1 + \frac{2}{f}\right) \Delta(\ln V)$$

$$= - \Delta \left(\ln V^{1 + \frac{2}{f}} \right)$$

$$\text{so } \Delta \left(\ln p + \ln V^{1 + \frac{2}{f}} \right) = 0$$

$\sum \ln \rightarrow \ln(\text{product})$

$$\Delta \ln \left(p V^{1 + \frac{2}{f}} \right) = 0$$

This means that $\ln \left(p V^{1 + \frac{2}{f}} \right)$

is CONSTANT in an ADIABATIC

process

IF $\ln(x) = \text{constant} \rightarrow x$ is constant

$p V^{1 + \frac{2}{f}}$ is constant, same

at beginning and end of

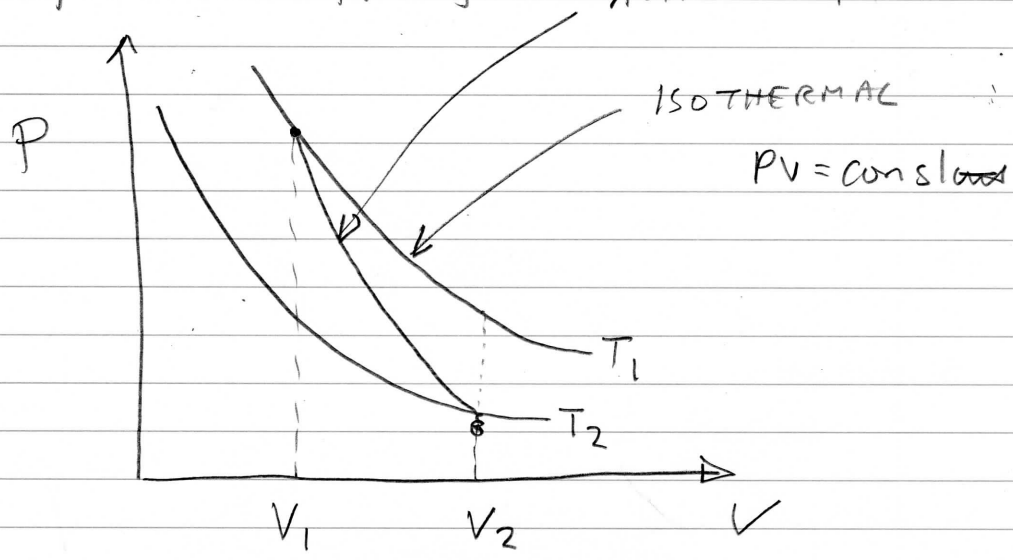
ADIABATIC PROCESS

$\frac{f+2}{f} \equiv \gamma = \text{adiabatic constant of an ideal gas } \gamma > 1$

$\hookrightarrow pV^\gamma = \text{constant}$

$P_{in} V_{in}^\gamma = P_{fin} V_{fin}^\gamma$

ADIABATE $PV^\gamma = \text{const}$



Note that ADIABATE is steeper than ISOTHERM

Actually could use any TWO COORDINATES

- (P, V)
- (P, T)
- (V, T)