

Thermal Thermodynamics

$$PV = nRT$$

$$U = \frac{3}{2} nRT$$

$$U = \frac{3}{2} PV$$

- particles undergo elastic collisions
- only have KE & ignore intermolecular potentials
- Particles are pt like \Rightarrow don't take up any volume

- Estimating the gas pressure of a moving gas @ temp T

Assume:

1. pt particles in a square box

2. collision with walls will be elastic -

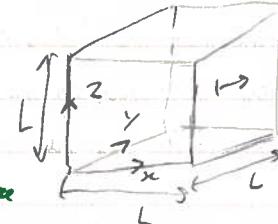
3. particles are pts

4. time of collision w/ wall is much smaller than time between collisions

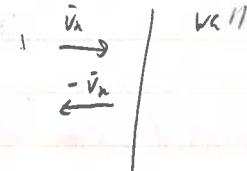
consider collision w/ only one wall

\hookrightarrow component that is orthogonal to the wall
will be considered

\therefore only this component produce an outward force
to produce a pressure on a wall



avg Speed: \bar{v}_n



Change in momentum after

colliding w/ a wall : $\Delta p = m\bar{v}_n - (-m\bar{v}_n)$

$$\Delta p = 2m\bar{v}_n$$

$$\bar{v}_n = \frac{2L}{T} \quad \text{period of collision}$$

$$T = \frac{2L}{\bar{v}_n}$$

where $T = \frac{1}{f}$

$$f = \frac{1}{T}$$

\uparrow collision frequency

Finding pressure $P = \frac{F}{A} = \frac{F}{L^2}$

$$F = \frac{\Delta p}{T} = \frac{2m\bar{v}_n \bar{v}_n}{2L} = \frac{2m\bar{v}_n^2}{2L} = \frac{m\bar{v}_n^2}{L}$$

$$\bar{s} = \sqrt{\bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2}$$

\therefore isotropic $\Rightarrow v_x = v_y = v_z$

$$\bar{s}^2 = 3\bar{v}_x^2$$

$$\text{from } U = \frac{1}{2} Nm\bar{s}^2$$

$$2U = Nm\bar{s}^2$$

$$P = \frac{2}{3} \frac{U}{V}$$

$$PV = \frac{2}{3} U$$

$$U = \frac{3}{2} PV = \frac{3}{2} nRT$$

$$\therefore \text{Force: } F = \frac{m\bar{s}^2}{3L}$$

$$\text{for all particles: } F = \frac{Nm\bar{s}^2}{3L}$$

- Energy of a gas
 during $U = \frac{3}{2} nRT$ $k = 1.38 \times 10^{-23}$ $\bar{S}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2$
 $= 3\bar{v}_n^2 \therefore$ isotropic

$$\therefore = \frac{3}{2} N k T$$

Accepting for the time being:

$$E = \frac{1}{2} N m \bar{v}^2 = \frac{3}{2} N k T$$

Which means the avg energy of the particle in the gas @ thermal eq^{mr} (T)

$$\left. \begin{aligned} \frac{1}{2} M \bar{v}_x^2 &= \frac{1}{2} k T \\ \frac{1}{2} M \bar{v}_y^2 &= \frac{1}{2} k T \\ \frac{1}{2} M \bar{v}_z^2 &= \frac{1}{2} k T \end{aligned} \right\} \text{eqn partition of energy}$$

Probability of energy state

- for any particular system, we would like to have a general way of finding bulk properties / avg properties
- & finding a way of calculating how energy is distributed for a mixture of particles @ defined temperatures

1. We have a mixture or ensemble of particles which importantly can be placed in only 2 states

$$E = \epsilon \text{ or } E = 0$$

$$\epsilon \dots \dots \rightarrow N$$

$$0 \dots \dots \rightarrow N$$

2 states of energy

$$\text{other } E \neq \epsilon \text{ or } E \neq 0$$

2. Put a smaller subset of n atoms into states w/ energy $E = \epsilon$ \therefore total energy $U = n\epsilon$

3. Prob of an atom w/ $E = \epsilon$: $p(E = \epsilon) = \frac{n}{N} \rightarrow$ probability

4. w/o proof 住毛:

$$T = \frac{dU}{dS} = \frac{\Delta U}{\Delta S} \quad \& \quad \Delta U = T \Delta S$$

$$S = k \ln S_2$$

$$S_2 = \frac{N!}{n!(N-n)!}$$

\rightarrow entropy

$$= \frac{N!}{n!(N-n)!} \quad \text{def of } S_2$$

↳ number of n combinations of a set of N states

$$5. S_i = k \ln \frac{N!}{n!(N-n)!}$$

add ϵ more energy in the system $\therefore S_f = k \ln \frac{N!}{(n+1)!(N-n-1)!}$

$$= k \ln \frac{N!}{(n+1)!}$$

\rightarrow diff in entropy

$$6. \Delta S = S_f - S_i$$

$$= k \ln \left[\frac{N^n}{n!} \right]$$

$$7. \text{ wanna use relation } T = \frac{dU}{dS} = \frac{\Delta U}{\Delta S} \quad \left(\frac{n}{N} = p(E = \epsilon) \right)$$

8. w/ energy ϵ & no with another unit of ϵ

$$\Delta U = \epsilon$$

$$9. \text{ Sub } T = \frac{\Delta U}{\Delta S}$$

$$T = \frac{\epsilon}{k \ln \left(\frac{N}{n} \right)}$$

$$T = \frac{\epsilon}{k \ln(\frac{N}{n} - 1)}$$

$$\ln\left(\frac{N}{n} - 1\right) = \frac{\epsilon}{kT}$$

$$\frac{N}{n} = e^{\frac{\epsilon}{kT}} + 1$$

$$P(E=\epsilon) = \frac{1}{N} = \frac{1}{e^{\frac{\epsilon}{kT}} + 1}$$

$$= \frac{e^{-\frac{\epsilon}{kT}}}{(1 + e^{-\frac{\epsilon}{kT}})} e^{-\frac{\epsilon}{kT}} = \frac{e^{-\frac{\epsilon}{kT}}}{e^{-\frac{\epsilon}{kT}} + 1}$$

- probability in terms
of energy

$\epsilon \rightarrow \infty \Rightarrow P(E) \rightarrow 0$
 $\Leftrightarrow \text{prob} \rightarrow 0$

* More generally for many levels : (not just the 2 considered here)

probability for a particle to be in a particular state ; Boltzmann distribution

$$P_i = \frac{e^{-\frac{E_i}{kT}}}{\sum_{j=0}^{N-1} e^{-\frac{E_j}{kT}}} \quad \frac{\epsilon}{kT}$$

↑
summing
from 0 to N

probability of being in the i^{th} state of energy
of many states :

$$P_i \propto e^{-\frac{E_i}{kT}}$$

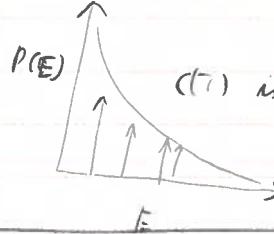
$$P_i = C(T) e^{-\frac{E_i}{kT}}$$

constant dependent of temp

$$\sum P_i = 1$$

$$1 = \sum C(T) e^{-\frac{E_i}{kT}}$$

$$C(T) = \frac{1}{\sum e^{-\frac{E_i}{kT}}}$$



for entropy :

$$dS = \int \frac{dQ_{\text{rev}}}{T}$$

↑ reversible process

$$dS \geq \frac{dQ}{T}$$

$$dS = \frac{dQ}{T}$$

↓

$$dQ = T dS$$

by first law

$$dU = dQ + dW \quad ; \text{ no work done}$$

$dW = 0$

$$dU = dQ$$

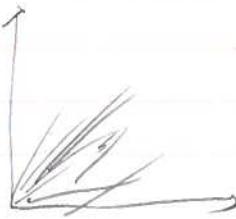
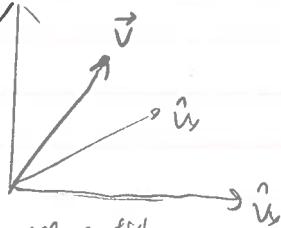
$$dU = T dS$$

$$\Delta U = T \Delta S$$

$$T = \frac{\Delta U}{\Delta S}$$

Consider a gas w/ continuous distribution of energies

$$\vec{v} = \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix}$$



looking @ one particle
w/ a particular velocity (\vec{v})

how are they distributed?

Energy of a particular state

$$E(v_x, v_y, v_z) = \frac{1}{2} m \vec{v}^2$$

Using Boltzmann distribution

$$P(v_x, v_y, v_z) \propto e^{-\frac{m \vec{v}^2}{2kT}}$$

normalization constant

$$= C(T) e^{-\frac{m \vec{v}^2}{2kT}}$$

now determining $C(T)$ to use $P(v_x, v_y, v_z)$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P(v_x, v_y, v_z) dv_x dv_y dv_z = 1$$

$$C(T) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}} dv_x dv_y dv_z = 1$$

Finding $C(T)$

Standard Integrals:

What does it look like?

$$I_n(a) = \int_{-\infty}^{\infty} e^{-ax^2} x^n dx$$

when $n=0$

$$I_0(a) = \sqrt{\frac{\pi}{a}}$$

\nwarrow
 $n < 0$??

when $n > 0$

$$I_n(a) = \frac{(n-1)!!}{2^{n/2} a^{n/2}} \sqrt{\frac{\pi}{a}}$$

$$(n-1)!! = (n-1)(n-3)(n-5)\dots$$

Gaussian integrals. Proof of standard integrals

[Wolfram]

$$I_n(a) = \int_{-\infty}^{\infty} e^{-ax^2} x^n dx$$

$$\text{for } n=0 : I_0(a) = \sqrt{\pi}$$

$$\text{for } n > 0 : I_n(a) = \frac{(n-1)!!}{2^{n/2} a^{n/2}} \int_a^{\infty}$$

when n is even

$$I_n(a) = \frac{(\frac{1}{2}(n-1))!}{2a^{(n+1)/2}}$$

Setting $x = a^{-\frac{1}{2}} y$

$$dx = a^{-\frac{1}{2}} dy$$

$$\Rightarrow I_n(a) = \int_{-\infty}^{\infty} e^{-a\frac{y^2}{a}} (ya^{-\frac{1}{2}})^{n-\frac{1}{2}} dy \quad \text{when } n \text{ is odd.}$$

$$I_n(a) = a^{-\frac{n+1}{2}} \int_{-\infty}^{\infty} e^{-y^2} y^n dy = 2a^{-\frac{n+1}{2}} \int_0^{\infty} e^{-y^2} y^n dy$$

$$I_n(a) = 2a^{-\frac{n+1}{2}} \int_0^{\infty} e^{-y^2} y^n dy$$

[by symmetry]

solving $n=0$:

$$I_0(a) = a^{-\frac{1}{2}} \int_{-\infty}^{\infty} e^{-y^2} dy$$

using cylindrical coordinates:

$$\begin{aligned} r &= 8\cos\phi & dA &= 8d\theta d\phi & \theta \in [0, \infty] \\ y &= 8\sin\phi & \phi &\in [0, \pi] \end{aligned}$$

$$I_0^2 = \int_{-\infty}^{\infty} e^{-y^2} dy \int_{-\infty}^{\infty} e^{-z^2} dz$$

$$I_0^2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(x^2+y^2)} dx dy$$

$$= \int_0^{2\pi} \int_0^{\infty} 8e^{-r^2} dr d\theta$$

$$= 2\pi \left[\frac{-e^{-r^2}}{r} \right]_0^{\infty} = 2\pi \left[-e^{-\infty} - (-e^0) \right]$$

$$I_0^2 = \pi \Rightarrow I_0 = \sqrt{\pi}$$

\Rightarrow

$$I_0(a) = \sqrt{\pi}$$

solving $n=1$:

$$I_1(a) = a^{-\frac{1}{2}} \int_{-\infty}^{\infty} e^{-y^2} y dy$$

$$= \frac{2}{a} \left[-\frac{e^{-y^2}}{2} \right]_0^{\infty}$$

$$= \frac{1}{a} \left[-e^0 + (e^0) \right]$$

$$I_1(a) = \frac{1}{a}$$

Recalling $I_n(a) = a^{\frac{n+1}{2}} \int_0^\infty e^{-y^2} y^n dy = 2a^{\frac{n+1}{2}} \int_0^\infty e^{-y^2} y^n dy$ [by symmetry]

Solving $n > 1$:

for $n > 1$:

Using $L_n(a)$:

$$I_n(a) = \int_0^\infty e^{-ax^2} x^n dx = 2 \int_0^\infty e^{-ax^2} x^{n-2} dx \quad L_n(a)$$

Now

We want to get an expression which is recursive and has a pattern which n goes down to 0 trying:

$$-\frac{d}{da} \int_0^\infty e^{-ax^2} x^n dx = \int_0^\infty x^2 e^{-ax^2} x^n dx = \int_0^\infty e^{ax^2} x^{n+2} dx$$

Now we want to get rid of x^2 as it has a similar / identical form as $L_n(a)$

$$n \Rightarrow n-2$$

We have the relation:

$$-\frac{d}{da} \int_0^\infty e^{-ax^2} x^{n-2} dx = \int_0^\infty e^{-ax^2} x^{n-2} dx = L_{n-2}(a) \quad -\frac{d}{da} L_{n-2}(a) = L_n(a)$$

Suppose: $n = 2s$ so that $n > 1$ and n is even

Subbing in factor $L_n(a)$

$$L_n(a) = -\frac{d}{da} L_{n-2}(a) = \left(-\frac{d}{da}\right)^2 L_{n-4}(a) = \left(-\frac{d}{da}\right)^2 L_{n-6}(a) \dots$$

$$L_n(a) = \frac{\sqrt{\pi}}{2} \frac{(2s-1)!! (-1)^s}{2^s s!!}$$

$$L_{2s}(a) = \left(-\frac{d}{da}\right)^s L_0(a)$$

and so on....

from before:

$$L_0(a) = \underbrace{\frac{d}{da} a^{-\frac{1}{2}}}_{f_1(a)} \frac{\sqrt{a}}{2}$$

as $2s = n$ even

$$= L_n(a) = \frac{1}{2} \sqrt{\frac{\pi}{a}} \frac{(n-1)!! (-1)^{\frac{n}{2}}}{2^{\frac{n}{2}} \left(\frac{n}{2}\right)!!} = \frac{1}{2} \sqrt{\frac{\pi}{a}} \frac{(n-1)!! (-1)^{\frac{n}{2}}}{2^{\frac{n}{2}} \left(\frac{n}{2}\right)!!}$$

$$\text{As } I_n(a) = 2 L_n(a)$$

considering $f_s(a)$: noticing the pattern:

$$s=1 \Rightarrow \frac{d}{da} a^{-\frac{1}{2}} = \left(-\frac{1}{2}\right) a^{-\frac{3}{2}} (-1)^1 \quad \text{Working } s \text{ in descending order: } I_n(a) = \sqrt{\frac{\pi}{a}} \frac{(n-1)!!}{2^{\frac{n}{2}} a^{\frac{n}{2}}} \quad \text{for } n > 1$$

$a: 2 \cdot 2 \cdot 2 \dots$

$$s=2 \Rightarrow \frac{d^2}{da^2} a^{-\frac{1}{2}} = \left(-\frac{1}{2}\right) \left(-\frac{3}{2}\right) a^{-\frac{5}{2}} (-1)^2 \quad = 2^s \text{ depending on } s$$

b: indices of $[a]$ go

$$s=3 \Rightarrow \frac{d^3}{da^3} a^{-\frac{1}{2}} = \left(-\frac{1}{2}\right) \left(-\frac{3}{2}\right) \left(-\frac{5}{2}\right) a^{-\frac{7}{2}} (-1)^3 \quad \text{up by odd numbers}$$

in numerator while

$$s=4 \Rightarrow \frac{d^4}{da^4} a^{-\frac{1}{2}} = \left(-\frac{1}{2}\right) \left(-\frac{3}{2}\right) \left(-\frac{5}{2}\right) \left(-\frac{7}{2}\right) a^{-\frac{9}{2}} (-1)^4 \quad \text{denominator = 2}$$

$\therefore a^{-\frac{s+1}{2}}$

$$s=s \Rightarrow \frac{(-1)^s (s-\frac{1}{2})!}{a^{\frac{s+1}{2}}} \Rightarrow \frac{(2s-1)!! (-1)^s}{2^{\frac{s}{2}} a^{\frac{s}{2}}} \quad \begin{aligned} c: & \text{ goes down by 2} \\ & \text{ have odd numbers} \\ & \text{ multiplied together} \end{aligned}$$

$$\therefore (2s-1)!! (2s-3)!! \dots (1)$$

finding $C(T)$ using standard integrals

$$C(T) \iiint_{-\infty}^{\infty} e^{-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)} dV_x dV_y dV_z = 1$$

$$\Rightarrow I = C(T) \iiint e^{-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)} dV_x dV_y dV_z = C(T) I_x I_y I_z$$

$$I_x = \int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2kT}} dV_x = \int_{-\infty}^{\infty} e^{-\alpha v_x^2} V_x^0 dV_x$$

$\lambda=0$

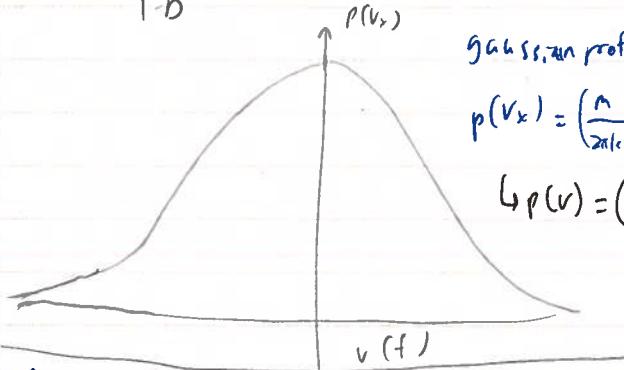
$$I_x = \sqrt{\frac{\pi}{\alpha}} = I_y = I_z$$

$$\alpha = \frac{m}{2kT}$$

$$I = \left(\sqrt{\frac{\pi}{\alpha}} \right)^3 C(T)$$

$$\underline{C(T) = \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}}}$$

1-D



Gaussian profile

$$p(v_x) = \left(\frac{m}{2\pi kT} \right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}} P(v_x, v_y, v_z) dV_x dV_y dV_z$$

$$\hookrightarrow p(v) = \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} \text{ And } v^2 = v_x^2 + v_y^2 + v_z^2$$

- observed in Absorption & Emission line spectra

for n modd $\Rightarrow 2s+1=n$ similarly

$$L_n(a) = \left(-\frac{\partial}{\partial a} \right) L_{n-2}(a) = \left(-\frac{\partial}{\partial a} \right)^2 L_{n-4}(a) \dots$$

$$\Rightarrow \left(-\frac{\partial}{\partial a} \right)^s L_1(a) = \left(\frac{\partial^s}{\partial a^s} \right) \left(\frac{1}{a} \right)$$

$$\Rightarrow L_n(a) = 2 \ln(a)$$

$$\begin{aligned} &= 2 \frac{s!}{2^s a^{s+1}} \\ &= \frac{\left(\frac{1}{2}(n-1)\right)!}{a^{\frac{n-1}{2} + \frac{s}{2}}} = \frac{\left[\frac{1}{2}(n-1)\right]!}{a^{\frac{n-1}{2}}} \end{aligned}$$

for n modd

$$\langle s \rangle_{\text{mean}} = \left(\frac{RT}{T_M} \right)^{\frac{1}{2}}$$

$$S_{\text{avp}} = \left(\frac{2RT}{m} \right)^{\frac{1}{2}}$$

$$\langle s^2 \rangle = \frac{\sqrt{RT}}{m}$$

|

The speed distribution

$$s = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

$$p(s) \propto e^{-\frac{ms^2}{2kT}}$$

diff velocities have same speed

$$(v_x, v_y, v_z) = \pm (-v_x, -v_y, -v_z)$$

Better to think of energy states associated w/ speed

as a shell of particles w/ the same speed

with the shell of radius $s +$ a spread in speed of ds

$$dV = dv_x dv_y dv_z$$

$$= 4\pi s^2 ds$$

volume element in speed ~~units~~ $\text{m}^3 \text{ s}^{-2} \text{ J}^{-1}$

$$dV = 4\pi$$

solving for:

$$\int_0^\infty C' s^2 e^{-\frac{ms^2}{2kT}} ds = 1$$

$$\text{When } n > 0 : I_n(a) = \frac{(n-1)!!}{2^{n/2} a^{n/2}} \sqrt{\frac{\pi}{a}} \quad \text{for function } \int_{-\infty}^\infty e^{-ax^2} x^n dx$$

functions

even

$$\int_0^\infty C' s^2 e^{-\frac{ms^2}{2kT}} ds = \frac{1}{2} \times C' \times \frac{(n-1)!!}{2^{n/2} a^{n/2}} \sqrt{\frac{\pi}{a}} = 1$$

By definition

$$f(-x) = -f(x)$$

$$\text{Let } a = \frac{m}{2kT}$$

$$\frac{1}{2} \times C' \times \frac{(2 \cdot 1)}{2 a} \sqrt{\frac{\pi}{a}} = 1$$

$$C' = 4 a \sqrt{\frac{a}{\pi}}$$

$$C' = \frac{4 m}{2 k T} \left(\frac{m}{2 k T \pi} \right)^{\frac{1}{2}}$$

$$= \frac{4}{\sqrt{\pi}} \times \frac{m}{2 k T} \times \left(\frac{m}{2 k T} \right)^{\frac{1}{2}}$$

$$= \frac{4}{\sqrt{\pi}} \times \left(\frac{m}{2 k T} \right)^{\frac{3}{2}}$$

$$kT = \frac{m}{M} RT$$

Maxwell Boltzmann distribution.

Sub C'

$$P(s) = \frac{4}{\pi} \left(\frac{m}{2kT} \right)^{\frac{3}{2}} \times s^2 e^{-\frac{ms^2}{2kT}}$$

$$= 4s^2 \frac{1}{\pi} \times \frac{m}{2kT} \left(\frac{m}{2kT} \right)^{\frac{3}{2}} e^{-\frac{ms^2}{2kT}}$$

$$= 4\pi s^2 \left(\frac{m}{2kT} \right)^{\frac{3}{2}} e^{-\frac{ms^2}{2kT}} \text{ or } 4\pi s^2 \left(\frac{m}{2RT} \right)^{\frac{3}{2}} e^{-\frac{ms^2}{2RT}}$$

most probable speed.

$$\frac{d(P(s))}{ds} = \frac{d}{ds} \left(4\pi \left(\frac{m}{2RT} \right)^{\frac{3}{2}} s^2 e^{-\frac{ms^2}{2RT}} \right)$$

$$\text{Let } 4\pi \left(\frac{m}{2RT} \right)^{\frac{3}{2}} = \alpha \quad b = \frac{m}{2RT}$$

$$P'(s) = \frac{d}{ds} (\alpha \cdot s^2 e^{-bs^2})$$

$$= 2\alpha s e^{-bs^2} + \alpha s^2 \cdot (-2bs) e^{-bs^2}$$

$$= 2\alpha s e^{-bs^2} - 2bs \cdot \alpha s^2 \cdot e^{-bs^2}$$

$$= 2\alpha s e^{-bs^2} (1 - bs^2)$$

Setting: $P'(s) = 0$

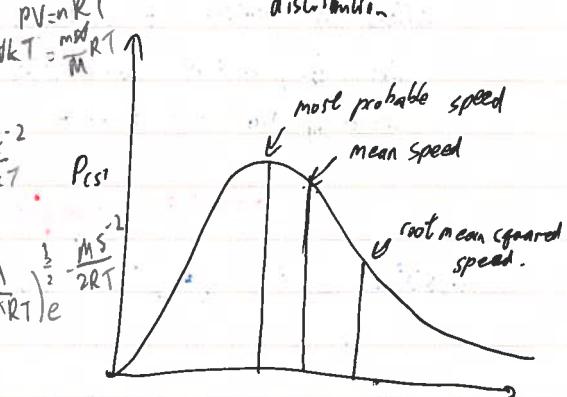
$$1 - bs^2 = 0$$

$$bs^2 = 1$$

$$s^2 = \frac{1}{b}$$

$$s^2 = \frac{2kT}{m}$$

$$s = \sqrt{\frac{2kT}{m}}$$



✓ decaying exponential func.

↳ fraction of molecules w/ v. high speeds will be very small

$\because e^{-x} \Rightarrow$ becomes small for large x

✓ factor of $-\frac{m}{2RT}$ or $-\frac{M}{2RT}$

implies for heavier, more massive molecules, the exponential function factor rapidly goes towards zero

↳ heavy molecule are unlikely to be found.

✓ for the factor of $-\frac{M}{2RT}$

as $T \uparrow$, factor decreases
factor falls slowly as $s \uparrow$

↳ greater fraction of molecules will have higher energy at high T.

✓ s^2 multiplies the exponential

$$s^2 \rightarrow 0, s \rightarrow 0$$

fraction of molecules w/ v. slow speeds will also be very small

↳ $\int_0^\infty f(s) ds = 1$

mean speed mean square speed / not mean squared speed

using distribution to calculate a halfe property

given prob func $p(s)$

mean of func $f(s)$ = $\langle f(s) \rangle$ given by:

$$\langle f(s) \rangle = \int f(s) p(s) ds$$

$$\frac{1}{2} m \langle s^2 \rangle = \int_0^\infty s^2 C' s^2 e^{-\frac{ms^2}{2kT}} ds$$

$$= \int_0^\infty s^4 C' e^{-\frac{ms^2}{2kT}} = C' \int_0^\infty s^4 e^{-\frac{ms^2}{2kT}}$$

$$a = \frac{m}{2kT}$$

$$\langle s^2 \rangle = \frac{1}{2} C' \frac{(4-1)!!}{2^2 a^2} \int_a^\infty s^4 e^{-\frac{3}{8a^2}} \times C'$$

$$= \frac{3}{28} \left(\frac{2kT}{m} \right)^2 \left(\frac{\pi}{m} \right)^{\frac{1}{2}} \times \frac{1}{\sqrt{a}} \times \left(\frac{m}{2kT} \right)^{\frac{3}{2}}$$

$$\langle s^2 \rangle = \frac{3}{2} \frac{\pi}{\sqrt{a}} \times \left(\frac{2kT}{m} \right)^{\frac{5}{2}} \times \left(\frac{2kT}{m} \right)^{-\frac{3}{2}} = \frac{3}{2} \frac{\pi kT}{m}$$

$$= \frac{3kT}{m} \quad \langle s^3 \rangle = \frac{3kT}{m}$$

$$\sqrt{\langle s^2 \rangle} = \sqrt{\frac{3kT}{m}}$$

$$\text{linking to energy: } U = \frac{1}{2} m \langle s^2 \rangle$$

$$= \frac{1}{2} m \frac{3kT}{m}$$

$$\text{all particles: } U = N \frac{1}{2} \frac{m \cdot 3kT}{m} = \frac{3}{2} kT$$

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

mean speed

$$V_{\text{avg}} = \bar{v} = \frac{\int v f(v) dv}{\int f(v) dv}$$

$$\langle v^n \rangle = \int_0^\infty v^n f(v) dv \Rightarrow \bar{s}^n = \int_0^\infty s^n p(s) ds$$

$$\bar{s}_{\text{avg}} = \bar{s} = \int_0^\infty s \cdot p(s) ds = \sqrt{\frac{8RT}{\pi M}}$$

$$\bar{s} = \int_0^\infty s \cdot 4\pi s^2 \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{ms^2}{2kT}} ds$$

$$\text{Setting } C \frac{m}{2kT} = \alpha$$

$$\Rightarrow \bar{s} = \underbrace{4\pi B}_{A} \int_0^\infty s^3 e^{-\alpha s^2} ds \quad \downarrow B$$

$$\begin{aligned} & \sqrt{\frac{2}{\pi}} \left[\frac{1}{2\alpha^2} \right] \left(\frac{m}{kT} \right)^{\frac{3}{2}} \\ &= \sqrt{\frac{2}{\pi}} \frac{k^2 T^2}{2M} \left(\frac{m}{kT} \right)^{\frac{3}{2}} \\ &= \sqrt{\frac{s}{\frac{m}{kT}}} \end{aligned}$$

$$\begin{aligned} A: & 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \\ &= \left(\frac{4^{\frac{3}{2}} \pi^{\frac{2}{3}} m^{\frac{3}{2}}}{4^{\frac{1}{2}} \pi^{\frac{1}{3}} k^{\frac{3}{2}}} \right)^{\frac{3}{2}} = \left(\frac{4^{\frac{4}{6}-\frac{3}{6}} m^{\frac{3}{2}}}{\pi^{\frac{1}{3}} k^{\frac{3}{2}}} \right)^{\frac{3}{2}} \\ &= \left(\frac{4^{\frac{1}{6}} m^{\frac{3}{2}}}{\pi^{\frac{1}{3}} k^{\frac{3}{2}}} \right)^{\frac{3}{2}} = \frac{4^{\frac{3}{4}}}{\pi^{\frac{1}{2}}} \left(\frac{m}{kT} \right)^{\frac{3}{2}} \\ &\equiv \sqrt{\frac{2}{\pi}} \left(\frac{m}{kT} \right)^{\frac{3}{2}} \end{aligned}$$

$$\text{By } PV=nkT$$

$$PV=nRT$$

$$Nk=nR$$

$$k = \frac{nR}{N}$$

$$\begin{aligned} \bar{s} &= \sqrt{\frac{8kT}{\pi M}} \\ &= \sqrt{\frac{8nRT}{\pi Nm}} \\ &= \sqrt{\frac{8kT}{\pi M}} \end{aligned}$$

$$B = \int_0^\infty s^3 e^{-\alpha s^2} ds$$

Using Gaussian integral as proven:

$$\begin{aligned} B &= \frac{1}{2} \int_{-\infty}^{\infty} e^{-\alpha s^2} s^3 ds \quad n=3 \\ &= \frac{1}{2} \left[\frac{\left(\frac{1}{2} \alpha s^2 + 1 \right)!}{-\frac{3}{2} \alpha^2} \right] = \frac{1}{2} \frac{1}{\alpha^2} \end{aligned}$$

mean relative speed: mean speed with which molecule approaches another of the same kind

$$V_{\text{rel}} = \sqrt{2} V_{\text{mean}}$$

$$= \left(\frac{8kT}{\pi \mu} \right)$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

Energy partition:

$$\langle E \rangle = \frac{3}{2}kT \text{ (for a single gas particle @ temp T)}$$

$$\langle E_v \rangle = \langle E_r \rangle = \langle E_t \rangle = \frac{1}{2}kT$$

how is energy partitioned for vibrational motion & rotation for gases?

vibrational molecule \Rightarrow a spring

$$PE = E_p = \frac{1}{2}Kx^2$$

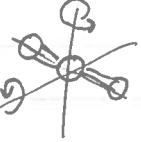
if we assuming the energy \Rightarrow we gas gives that: $\langle E_p \rangle = \frac{1}{2}kT$
 $\langle E_k \rangle = \frac{1}{2}kT$

$$\therefore \langle E_{tot} \rangle = \langle E_p \rangle + \langle E_k \rangle$$

$$\langle E_{tot} \rangle = kT$$

degrees of freedom for linear triatomic molecules:

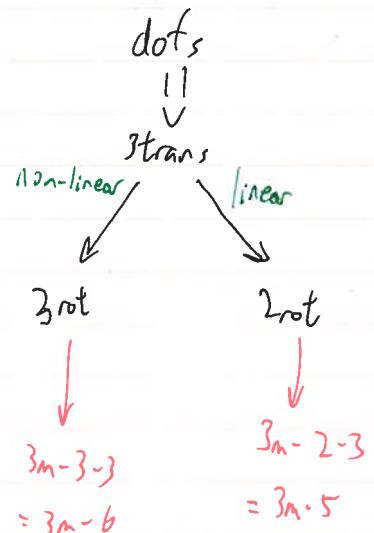
Degrees of freedom

| vibration (x 4) | rotation (x 2) | translation |
|---|--|---------------------|
| $\ddot{\sigma}_O \neq 0$ bending |  | $\sigma = \phi = 0$ |
| $\ddot{\sigma}_O = \ddot{\sigma}_O = 0$ symmetric stretching | | |
| $\ddot{\sigma}_O \neq \ddot{\sigma}_O \neq 0$ asymmetric stretching | | |

| | | |
|--|--|---|
| $\langle E_p \rangle + \langle E_k \rangle$ \therefore for each vibration | For each rotational mode $\langle E_{rot} \rangle = \frac{1}{2}kT$ | $\langle E \rangle = \frac{1}{2}kT$ |
| $\langle E_{vib} \rangle = kT$ | $\langle E_{rot} \rangle = kT$ linear | $\langle E_{trans} \rangle = \frac{3}{2}kT$ |

Equi-partition of energy

| vibration | rotation | translation |
|------------|--|-----------------|
| $(3m-5)kT$ | $2 \times \frac{1}{2}kT = kT$ | $\frac{3}{2}kT$ |
| $(3m-6)kT$ | $3 \times \frac{1}{2}kT = \frac{3}{2}kT$ | $\frac{3}{2}kT$ |



where m is the number of atoms

\hookrightarrow there are $3m$ degrees of freedom

Energy partition:

- classical partition of energy can break down
 - ↳ when discrete nature of motion (e.g. & particularly vibration) is taken into account in microscopic systems
- Velocity is a continuous function
 - ↳ However when confined into a small space / @ low temp \rightarrow becomes discrete
- must consider nuclear & electronic motion when we reach temp $>> 300\text{ K}$ (10000 K)
[quantum effects]
- $V \propto T$
- $V = \frac{3}{2}kT$ only true for ideal gases

eg

Benzene C_6H_6

- Number of d.o.f = # co-ordinates that describes the positions for each atom
 $= 3m$

translation/centre of mass motion

↳ requires 3 d.o.f for each particle

eg water vapour $H_2O_{(g)}$

$$\text{dof} = 3m$$

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

dof in: trans: 3

$$\langle E_{\text{trans}} \rangle = \frac{3}{2}kT \Rightarrow U_{\text{trans}} = \frac{3NkT}{2} = \frac{3}{2}nRT$$

rot: 3

$$\langle E_{\text{rot}} \rangle = \frac{3}{2}kT \Rightarrow U_{\text{rot}} = \frac{3}{2}nRT$$

vib: 3

$$\langle E_{\text{vib}} \rangle = 3kT \Rightarrow U_{\text{vib}} = 3nRT$$

$$U_{\text{total}} = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}}$$

$$= 6nRT$$

water vapour: heat capacity @ constant volume

energy partition is observed when measuring heat capacity

$$C_v = \frac{dQ}{dT} \quad \text{did not take into account of discrete nature of motions (quantum mech)}$$

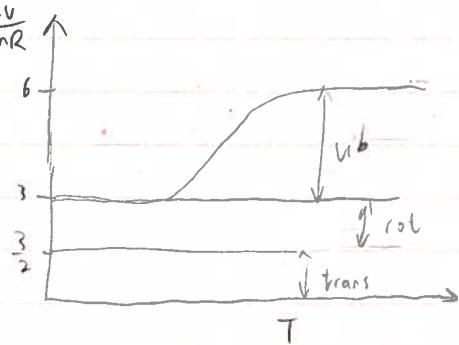
for gas @ const volume: $C_v = \left(\frac{\partial U}{\partial T}\right)_v$

$$\text{trans} \rightarrow C_{v,\text{trans}} = \frac{\partial}{\partial T} \left(\frac{3}{2}nRT \right) = \frac{3}{2}nR$$

$$\text{rot} \rightarrow C_{v,\text{rot}} = \frac{\partial}{\partial T} \left(\frac{3}{2}nRT \right) = \frac{3}{2}nR$$

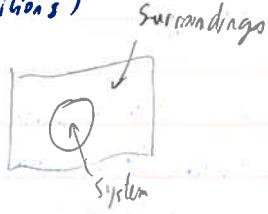
$$\text{vib} \rightarrow C_{v,\text{vib}} = \frac{\partial}{\partial T} (3nRT) = 3nR$$

$$C_{v,\text{total}} = C_{v,\text{trans}} + C_{v,\text{rot}} + C_{v,\text{vib}} = 6nR$$



Thermodynamic systems (mostly definitions)

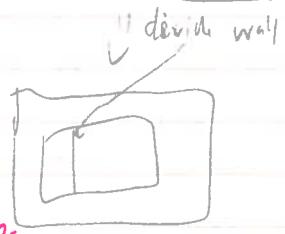
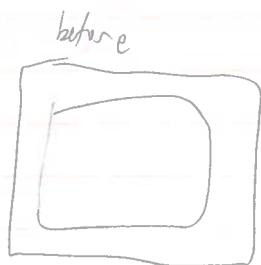
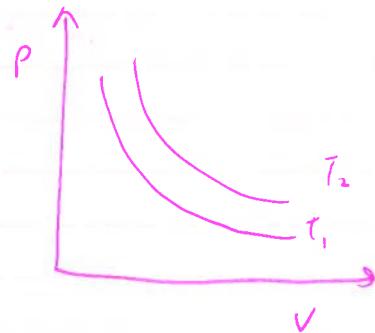
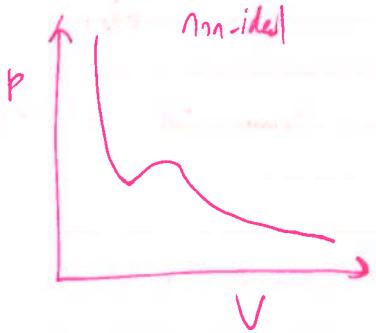
- System : part of the universe in which we are interested
- Surroundings : rest of the universe
- Several systems of interest may be treated as a single composite system
- Isolated system: system which has no interactions (no exchange in energy, matter, momentum) with other systems or surroundings
- Equilibrium: \rightarrow 2 types of properties
 - intensive - property of system which is the same as the whole (Temp, pressure, density)
 - extensive - property that is different to that of the whole system (mole, mass, volume)
- Eqⁿ of state $f(p, V, T) = 0$



ideal gas: $pV - nRT = 0$
 $pV = nRT$

real, non-ideal gas: $(p - \frac{a}{V^2})(V - nb) = nRT / \left(\rho \frac{n^2}{V^2}\right)(V - nb) = nR_T$

$V = \frac{V}{n}$ a & b are constants depending on the gas



Thermal contact \rightarrow 2 system A & B in thermal contact
 $T_A = T_B$ \hookrightarrow @ eq^{rr} their temps are equal
 - allowed : by a diathermal wall
 via conduction, convection, radiation
 - prevented : by an adiabatic wall




0th law of thermodynamics
 if 2 systems are @ thermal eq^{rr} w/ a 3rd system, then they are all in thermal eq^{rr}

Mechanical contact \rightarrow @ eq^{rr}, pressures are equal
 $p_A = p_B$

- Eq^{rr} occurs by movable walls

\hookrightarrow transfer energy in the form of work, $W = Fd$

movable wall

Mass contact \rightarrow @ eq^{rr}, gas densities are equal

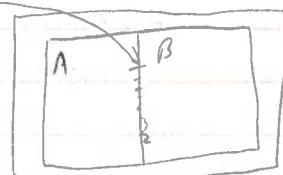
$$\rho_A = \rho_B$$

- A + B are in mass contact \rightarrow mass is exchanged \rightarrow mass eq^{rr}

\hookrightarrow allowed by permeable wall

(have holes in it)

↑ ↑ displacement

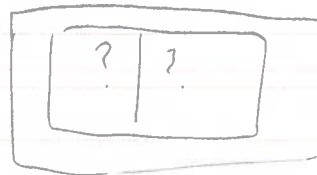


Usually! problems will expressed in the following way:

What is the new eq^{rr} state after the removal of an internal constraint on an isolated system?



adiabatic



diathermal

adiabatic \Rightarrow X heat transfer

diathermic \Rightarrow ✓ heat transfer

heat \Rightarrow transfer of energy as a result of a temp difference

thermal motion \Rightarrow disorderly motion of molecules

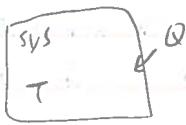
heat \Rightarrow energy transferred to surroundings as heat \Rightarrow transfer stimulates random motion of atoms in surr.

vs

work \Rightarrow system does work \Rightarrow stimulate orderly motion in the surroundings

Defining heat capacity C

consider having an isolated system which @ temp T



we add energy in the form of heat Q

↳ we expect that T changes to T + ΔT

$$C = \lim_{\Delta T \rightarrow 0} \frac{Q}{\Delta T} = \frac{dQ}{dT}$$

specific heat capacity: $c = \frac{C}{m}$

C is weakly dependent on temp

dt bar notation

↳ path dependent

thermodynamic process

Latent heat: L (J/kg)

@ phase change s → l → g or $dQ = L dm$

↳ taking finite heat to melt or boil

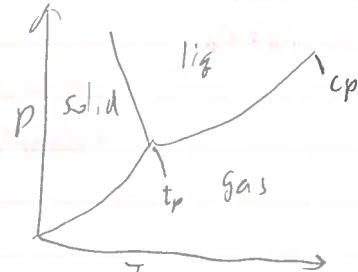
in given mass w/ no change in temp

$$Q = L m$$

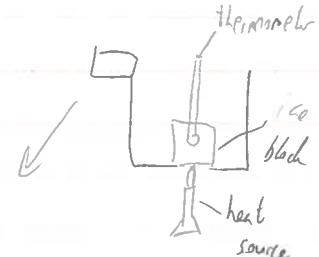
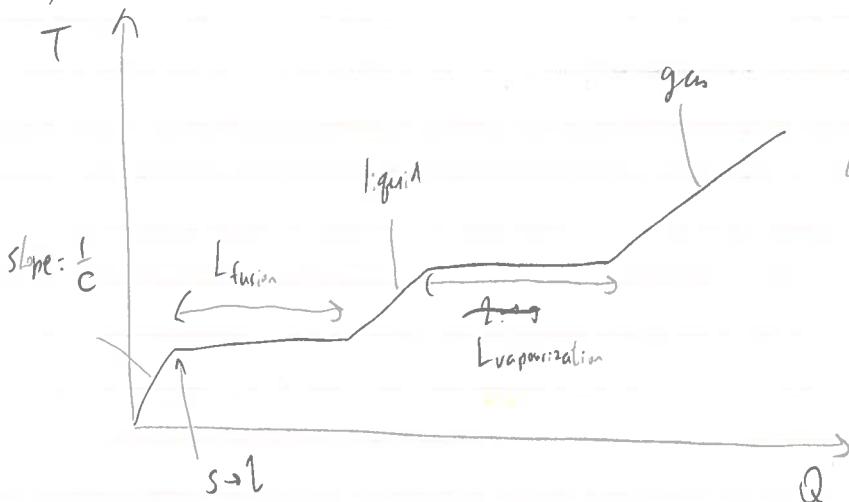
$$dQ = L dm$$

s → l : L_{fusion}

l → g : L_{vaporization}



e.g.



$t = c_p L / Q_p \Rightarrow$ heat added at constant pressure

Molar heat capacities: $C_{p,m}$

$$C_{p,m} = a + bT + \frac{c}{T^2}$$

a, b, c → temperature independent

empirical parameters
obtained by experiment

take variation of heat capacity w/ temp.

is significant if temperature range is large

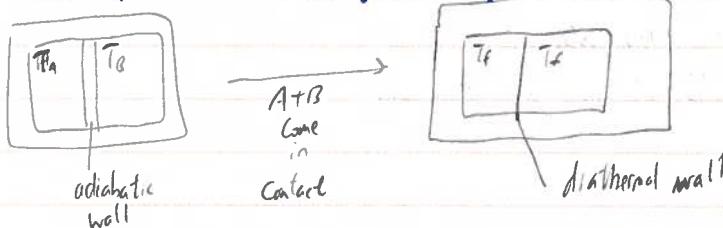
when C_p is not

constant

use the empirical expression

Final temp problem:

object A @ temp T_A placed in thermal contact w/ object B @ temp T_B . What's the final temp of both A+B?



sol sol^r

if $T_A > T_B \Rightarrow$ heat flows from A to B
 $\hookrightarrow Q_B > 0, Q_A < 0$

By conservation of energy: $Q_A = -Q_B$

using: $Q = \Delta T$

$$C_A(T_f - T_A) = -C_B(T_f - T_B)$$

$$(C_A + C_B)T_f = C_B T_B + C_A T_A$$

$$T_f = \frac{C_A T_A + C_B T_B}{C_A + C_B} \quad \text{or} \quad T_f = \frac{m_A C_A T_A + m_B C_B T_B}{m_A C_A + m_B C_B}$$

heat capacity specific heat capacity

if $m_A = m_B, C_A = C_B$

$$T_f = \frac{T_A + T_B}{2} \rightarrow \text{avg of 2 temperatures}$$

Thermal reservoir:

$$\text{Suppose: } \frac{C_n}{C_1} = \frac{C_B m_B}{C_A m_A} = \varepsilon \ll 1$$

✓ as $\varepsilon \rightarrow 0$
 $T_f \rightarrow T_A$

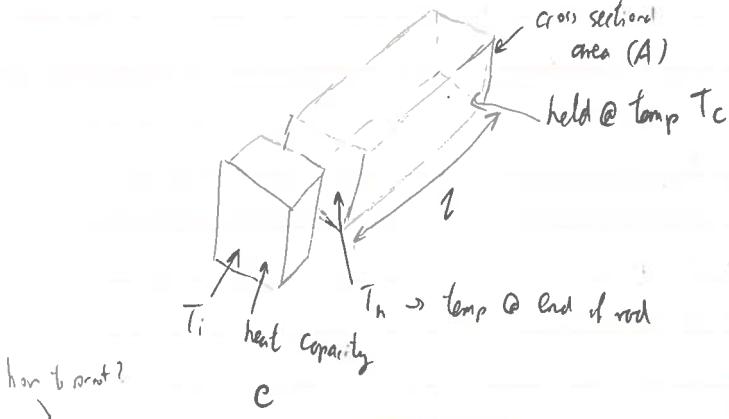
$$T_f = \frac{(C_A m_A T_A + C_B m_B T_B) / C_{A+B}}{(C_A m_A + C_B m_B) / C_{A+B}} = \frac{\frac{C_A m_A}{C_{A+B}} T_A + \frac{C_B m_B}{C_{A+B}} T_B}{1 + \frac{C_B m_B}{C_A m_A}} = \frac{T_A + \varepsilon T_B}{1 + \varepsilon}$$

- A acts as a thermal reservoir for B / a heat bath
 \hookrightarrow object placed in contact w/ it will take on its temp

- thermal surroundings are pictured as a thermal reservoir AND a pressure bath \rightarrow fixed [p,T] for the system

Thermal conduction:

- consider a rectangular rod of cross-sectional area (A) & length (l)
- one end of the rod is attached to a cold reservoir @ T_c
- another end is connected to a hot object initially @ T_i
- hot object has heat capacity C
- wts the temp of the hot end as a function of time



$$\dot{Q} = \frac{dQ}{dt} = -kA \frac{dT}{dx} = -kA \frac{T_n - T_c}{l}$$

heat flux
thermal conductivity
↳ change in heat transfer per unit time
 $(\frac{W}{mK})$

We know

$$\frac{dQ}{dT_h} = C$$

Solving the 1st ODE

$$\frac{dQ}{dt} = C \frac{dT_h}{dt} = -kA \frac{(T_h - T_c)}{l}$$

$$\frac{dT_h}{dt} = -\frac{kA}{C^2} (T_h - T_c)$$

$$T_0 = C_1 e^{-\frac{kA}{C^2} t}$$

$$T_0 = C_1 e^{-\frac{kA}{C^2} t}$$

$$\text{Let } T_0 = T_h - T_c$$

$$\text{at } t=0 \Rightarrow T = T_i - T_c = C_1 e^0$$

$$dT_0 = dT_h \quad (T_c \text{ is a const.})$$

$$T_0 = (T_i - T_c) e^{-\frac{kA}{C^2} t}$$

$$\frac{dT_0}{dt} = -\frac{kA}{C^2} T_0$$

$$T_h - T_c = (T_i - T_c) e^{-\frac{kA}{C^2} t}$$

$$\frac{dT_0}{T_0} = -\frac{kA}{C^2} dt$$

$$T_h = T_c + (T_i - T_c) e^{-\frac{kA}{C^2} t}$$

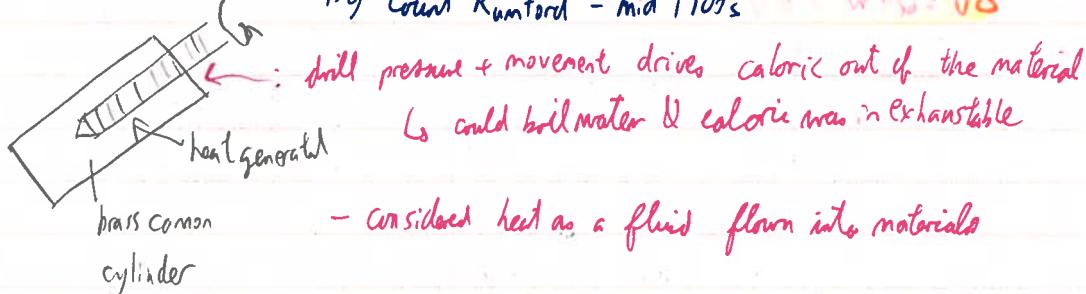
$$\frac{1}{T_0} dT_0 = -\frac{kA}{C^2} dt$$

exponential decay

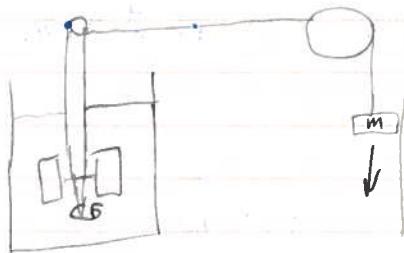
as $t \rightarrow \infty \quad T_h \rightarrow T_c$

Preamble : Caloric

By Count Rumford - mid 1700's $W + \text{heat} = U_0$



Toule's Paddle wheel:



- work done by weight converted to heat in water

heat is simply a type of

$$PE = W = mgh$$

$$mgh = Q$$

$$mgh = COT$$

energy like

mechanical work

Internal Energy & 1st Law:

Thermodynamics predicts the result of the change

between 2 eqst states A & B \Rightarrow passage is called a process

- quasistatic process \Rightarrow process involves very successive of eqst states. \rightarrow slow enough that it remains in eqst

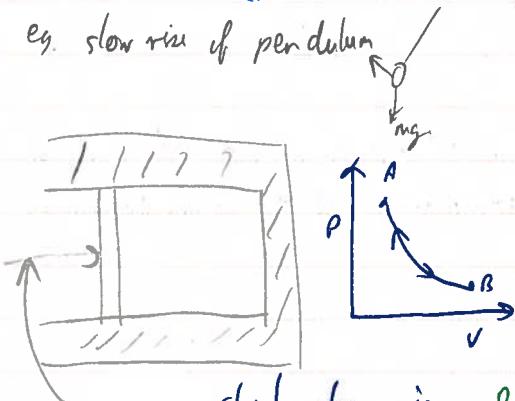
* Reversible process : quasistatic process in which \Rightarrow process that can be reversed

\nwarrow no dissipation forces [friction] act by an infinitesimal modification

* IR Irreversible process is its opposite of a variable

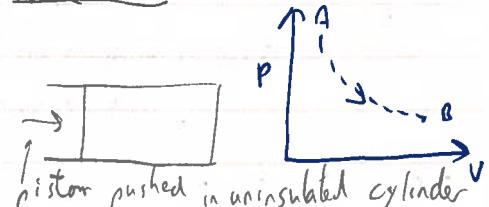
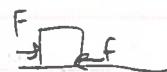
Reversible

e.g. slow rise of pendulum



Irreversible process

e.g. weight pushed along table on surface w/ fricti. (f.)



slowly change in force on piston

- During a process, energy may be transferred between system & surroundings in diff ways \Rightarrow consider HSAI & work

1st Law

\uparrow +ve flow in \rightarrow flow of energy is intensive if $V_m = \frac{U}{n}$
 \downarrow -ve flow out \rightarrow as g/w flow in perspective
 of system

- Statement: $\Delta U = Q + W / dU = dW + dQ$ - for ideal gas: U/n depends ONLY on temp(T)

- U is extensive (depends on amount of substance present)

- a state func, which is a $U = U(p, T, n)$
 func of thermodynamic variables $= nU(p, T)$

↓
 diff 1st differential form:

$$dU = dW + dQ$$

↓
 state variable

d : inexact differential

change in work/heat

2 inexact differential dependent on thermodynamic process

↓ exact differential d

or path it takes

$dU \Rightarrow$ function of the properties that determines
 the current state of the system

pV work: suppose we have a gas compressed by a movable wall [piston]



piston has area A

↓ no friction

↓ adiabatic

in compression

$$dV < 0$$

$dW > 0$: work is done

$dW < 0$: gas is doing work

- applying force F , assume: - quasistatic $F = F'$ at all times

- gas supplies F' , \rightarrow reversible, all W.D. goes

$$dW = -F dn \rightarrow \text{into gas (no friction)}$$

$= -pA dn$ works on expansion as well!

$$= -p dV$$

gas does work on surroundings

$$w = \int_{V_i}^{V_f} p dV$$

Thermochemistry:

exothermic \rightarrow release heat ($\Delta H < 0$)

endothermic \rightarrow absorbs heat ($\Delta H > 0$)

ΔH° FPAR/CRAP

$\Delta H^\circ \rightarrow$ energy change when one mole of substance reacts completely w/ oxygen under standard condition

$\Delta_f H^\circ$ Energy change when one mole of compound is formed from its constituent elements from in their standard states under standard conditions.

Redefining heat capacity:

$C_V \Rightarrow$ heat capacity @ constant volume

$$\Delta U \rightarrow \text{const. } V. \quad \Delta U = q_V$$

$$\Delta H \rightarrow \text{const. } P. \quad \Delta H = q_P$$

$$\underline{\underline{C_V = \frac{dQ_V}{dT}}} \Rightarrow \text{heat added while maintaining constant volume}$$

using 1st law: $\Delta U = \frac{dQ}{dT}V$ eq. engine

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V$$

$$dU = dQ + dW$$

$$= dQ - pdV$$

$$dV = 0 \text{ @ const. } V$$

$$\Delta U = dQ \quad (\text{heat transfer at const } V)$$

$$\therefore C_V = \frac{dQ_V}{dT} = \frac{dU_V}{dT}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$C_P \Rightarrow$ heat capacity @ constant pressure

$$\underline{\underline{C_P = \frac{dQ_P}{dT}}} \Rightarrow \text{heat added at const. pressure}$$

$$\Delta Q_P = C_P dT$$

using 1st law: $dU = dQ + dW$

$$dQ_P = dU + pdV$$

$$dU = dQ_P - pdV$$

(now at const. P)

$$dQ_P = C_P dT$$

Pertaining enthalpy: $\Delta H = q_P$ $\Delta H = \Delta U + \Delta n g RT$ (internal)

$H = U + PV \Rightarrow$ sum of internal mechanical energy in the system @ const. pressure

$$dH = dU + pdV + Vdp$$

for const. P , $dp = 0$

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P$$

$$dH = dU + pdV$$

$$dH = C_P dT = dQ_P$$

$$C_P = \frac{dH_P}{dT}$$

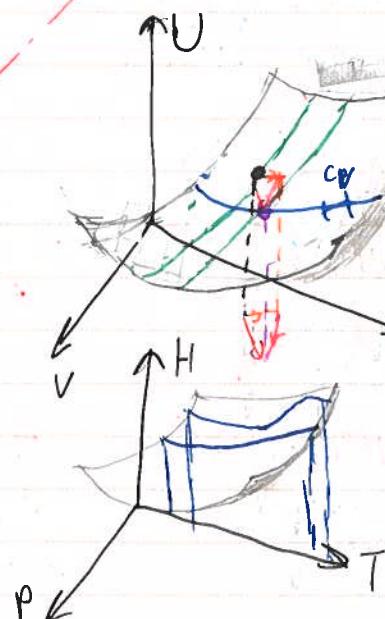
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\Delta H = q_P$$

q is not a state func.

x integral: q depends on path

path is not analytical unless we re-integrate



$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT \rightarrow$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV \quad \downarrow$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \downarrow$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \pi_T$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$dH = \frac{\partial H}{\partial T} dT$$

Case of Ideal gas:

We know:

$$c_v = \left(\frac{\partial U}{\partial T} \right)_v \quad & U = nU(T)$$

$$c_v = n \left(\frac{\partial U}{\partial T} \right)_v$$

using 1st law:

$$dU = dQ + dW$$

$$dW = -pdV \quad \Rightarrow \quad dU = c_p dT$$

$$\therefore c_p dT = dQ - pdV$$

$$dQ = c_p dT + pdV$$

Let take derivative wrt T keeping p const.

$$\frac{dQ_p}{dT} = c_v + p \left(\frac{\partial V}{\partial T} \right)_p$$

$$\frac{dQ_p}{dT} \text{ for ideal gas:}$$

$$pV = nRT$$

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

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{nR}{P}$$

$$c_p = \frac{\text{and}}{\frac{dQ_p}{dT}}$$

$$c_p = c_v + \cancel{x} \frac{nR}{P}$$

$$\underline{-c_p \rightarrow c_v = nR}$$

- true for all gases @ low pressures

For a monoatomic gas: $U = \frac{3}{2} nRT$

$$@ \text{const. } V: \quad c_v = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} nR$$

$$c_p - c_v = nR$$

$$c_p = nR + \frac{3}{2} nR$$

$$c_p = \frac{5}{2} nR$$

$$\Rightarrow c_v = \frac{3}{2} nR$$

Time dependence of U and H by measuring $c_v + c_p$

$$\text{Knowing } c_v = \left(\frac{\partial Q}{\partial T} \right)_V = \frac{dQ_v}{dT}$$

$$\text{measure } U \text{ at diff temps } T_2, T_1$$

$$\Delta U = U(T_2) - U(T_1) = \int_{T_1}^{T_2} c_v dT$$

Similarly

$$c_p = \frac{dQ_p}{dT} = \left(\frac{\partial H}{\partial T} \right)_p$$

$$\Delta H = H(T_2) - H(T_1) = \int_{T_1}^{T_2} c_p dT$$

$$\Delta_r C_p^\circ = \sum_{\text{products}} c_{p,m}^\circ + \sum_{\text{reactants}} v_i c_{p,m}^\circ$$

Find ΔU from measurement of ΔU & ΔV

@ constant, fixed pressure

$$\therefore \Delta H = \Delta U + p \Delta V$$

if phase change \rightarrow include latent heat

$$\Delta U = \int_{T_1}^{T_2} c_v dT + L_m$$

$$\Delta H = \int_{T_1}^{T_2} c_p dT + L_m$$

Kirchoff's laws:

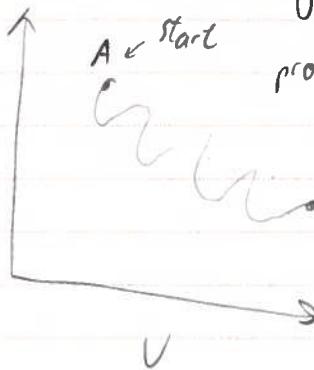
$$\text{Kirchoff's law: } \Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\circ dT$$

State functions:

- consider process where n is constant \Rightarrow fixed no. of gas

• can discuss energy in a system, but not heat/work in a system

• heat/work are forms of energy transfer.



$$U = (p, V)$$

process $A \rightarrow B$

state function - independent of path

$$\Delta U = U(p_B, V_B) - U(p_A, V_A)$$

$$\Delta U = Q + W$$

path dependent
by path functions

gas has internal energy

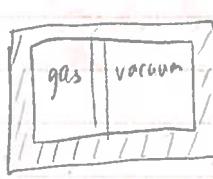
but heat is transferred

&

work is done

Process in ideal gas:

Adiabatic free expansion



remove wall
move to
now eq^W



- irreversible
- p & T are non-uniform during expansion
 \hookrightarrow eventually come in eq^W

1st law: $\Delta U = Q + W$ no heat added $\Rightarrow Q = 0$

no work is done $\Rightarrow W = 0$

$$\hookrightarrow \Delta U = 0$$

$$\therefore U = \frac{3}{2} nRT$$

$$\Delta U = \frac{3}{2} nR \Delta T$$

no ΔU , no ΔT

\hookrightarrow no temp change

State functions:

- value depends on the current state of the system,
- independent of how that state has been prepared or independent of its history

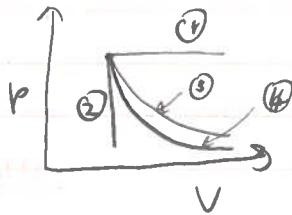
Reversible processes with fixed n

① isobaric - const. p

② isovolumetric - const. v

③ isothermal - const. T

④ Adiabatic



$$P = \left(\frac{nRT}{V} \right)$$

Isobaric

Isovolumetric

Isothermal

fixed no. of n.



- piston moves to
mainly $\Delta p = 0$
 $\rightarrow \text{ATP}$
Heat added



piston fixed
 $\Delta V = 0$
 $P \uparrow$



$P \cdot V \text{ change}$
but $\Delta T = 0$
 $T = \frac{PV}{nR}$

Changes:

change in V

$$V = \frac{3}{2} nRT \Rightarrow \Delta V = \frac{3}{2} nR\Delta T$$

$$\Delta U = PV = nRT$$

$$\Delta T = \frac{PV}{nR} \Rightarrow \Delta T = \frac{P_2V_2 - P_1V_1}{nR}$$

$$\Delta U = \frac{3}{2} nR \frac{P_2V_2 - P_1V_1}{nR}$$

$$\Delta U = \frac{3}{2} (P_2V_2 - P_1V_1)$$

$$\text{W.D.}$$

$$W = \int_{V_1}^{V_2} -pdV = - \int_{V_1}^{V_2} pdV$$

$$\text{if } p \text{ is const.}$$

$$W = -p(V_2 - V_1)$$

$$\text{if } dV = 0$$

$$W = 0$$

$$\text{if } T \text{ is const.}$$

$$W = - \int_{V_1}^{V_2} pdV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$W = -nRT \left[\ln V \right]_{V_1}^{V_2} = -nRT \left[\ln \frac{V_2}{V_1} \right]$$

Heat added

using 1st Law:

diff approach

$H = U + PV$

$$\Delta H = \Delta U + PV + V\Delta P$$

$$\Delta P = 0$$

$$\Delta H = \Delta U + P\Delta V = Q_p$$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p, \Delta H = C_p \Delta T$$

$$C_p = \frac{5}{2} nR$$

$$Q_p = \Delta H$$

$$Q_p = C_p \Delta T$$

$$Q_p = \frac{5}{2} nR \Delta T$$

$$\therefore \Delta H / Q_p$$

$$\Delta U = Q + W$$

$$\Delta U = Q_p + W$$

$$Q_p = \Delta U - W$$

$$Q_p = \Delta U - (-p\Delta V) = \Delta U + PV$$

on
from P4!

$$V = \frac{nRT}{P}, \Delta U = \frac{3}{2} nR\Delta T$$

$\therefore p, n, R \text{ const.}$

$$\therefore \Delta V = \frac{nR}{P} \Delta T$$

$$Q_p = \frac{3}{2} nR\Delta T + \sigma \frac{nR\Delta T}{P}$$

$$Q_p = \left(\frac{3}{2} nR + \sigma R \right) \Delta T$$

$$Q_p = \frac{5}{2} nR \Delta T$$

$$Q_p = C_p \Delta T$$

$$\therefore C_p = \frac{5}{2} nR$$

$$C_p = \frac{dQ_p}{dT}$$

$$\Delta U = Q + W$$

$$Q = \Delta U - W$$

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

$$\Delta V = 0$$

$$Q = \Delta U$$

$$\therefore \Delta U = C_v \Delta T$$

$$(C_v = \left(\frac{\partial U}{\partial T} \right)_V)$$

$$(C_v = \frac{dU}{dT})$$

$$Q = C_v \Delta T$$

$$Q = \frac{3}{2} nR \Delta T$$

↓ same

$$dQ =$$

$$\Delta U = Q + W$$

$$dQ = dW$$

$$Q = -W$$

$$Q = nRT \left[\ln V \right]_{V_1}^{V_2}$$

① Reversible adiabatic processes:

$Q=0 \Rightarrow$ no heat is taken or added & corresponds to an insulated container
 1st law: $\Delta U = Q + W \therefore Q=0$ that can expand or contract
 $\Delta U = W$

Work done in adiabatic process:

$$\Delta U = W$$

$$\Delta U = \frac{3}{2} nR \Delta T \\ = \frac{3}{2} nR (T_f - T_i)$$

$$pV = nRT$$

$$T = \frac{pV}{nR}$$

$$\Delta T = \frac{p_f V_f - p_i V_i}{nR}$$

$$\Delta U = \frac{3}{2} (p_f V_f - p_i V_i)$$

$$\Rightarrow$$

Relation between p & V for adiabatic processes

$$dU = dQ + dW$$

$dQ=0$ for adiabatic process

$$dU = dW$$

$$dU = C_v dT$$

$$dW = -pdV$$

$$C_v dT = -pdV$$

$$\text{for ideal gas: } pV = nRT$$

$$p = \frac{nRT}{V}$$

$$C_v dT = -\frac{nRT}{V} dV$$

divide by T

$$\int \frac{C_v dT}{T} = - \int \frac{nR dV}{V}$$

$$C_v \ln T = -nR \ln V + C_1$$

$$\text{let } \gamma = \frac{C_p}{C_v} \text{ (ratio of heat capacities)}$$

$$C_p = \frac{5}{3} nR$$

$$C_v = \frac{3}{3} nR$$

$$\underline{\underline{C_p - C_v = nR}}$$

$$pV^\gamma = \text{Const} = C_2 \quad TV^{\gamma-1} = \text{Const.} 2 = C_3$$

$$C_v \ln T = -(C_p - C_v) \ln V + C_1$$

divide by C_v

$$\ln T = -(\gamma-1) \ln V + C_2$$

$$\ln T + \ln V^{\gamma-1} = C_2$$

$$TV^{\gamma-1} = e^{C_2}$$

$$TV^{\gamma-1} = C_3 \rightarrow$$

$$\text{Sub } T: \frac{pV}{nR}$$

$$\frac{pV V^{\gamma-1}}{nR} = C_3$$

$$pV^\gamma = C_3 \cdot nR$$

$$pV^\gamma = C_4$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$

$$T_2 = \left(\frac{V_1}{V_2} \right)^{\gamma-1} \cdot T_1$$

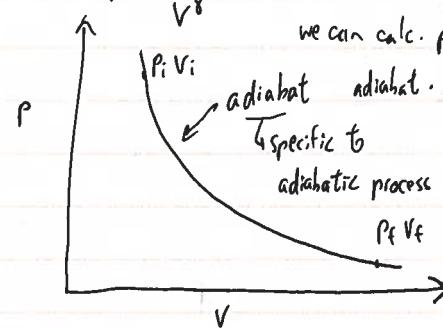
if $V_1 > V_2$

$$T_2 < T_1$$

if we have some initial

$$p = \frac{C_4}{V^\gamma} \quad p, V \text{ or } T \text{ on an adiabat,}$$

we can calc. p, V, T along



Calculating work in an adiabatic process: $W = \frac{\gamma}{\gamma - 1} P_1 V_1 - P_2 V_2$

$\Delta U = Q + W, Q = 0 \rightarrow \text{heat added}$
 $\Delta U = W$

$$W = \frac{1}{2} (P_2 V_2 - P_1 V_1)$$

for expansion, $\Delta V > 0, W = -P\Delta V < 0$

for compression, $\Delta V < 0, W = -P\Delta V > 0$

Work $\Rightarrow W = - \int_{V_1}^{V_2} P dV \quad P V^\gamma = \text{const}$

$$P = \frac{\text{const}}{V^\gamma}$$

$$W = - \int_{V_1}^{V_2} \frac{\text{const}}{V^\gamma} dV$$

$$\int_A^B x^n dx = \left[\frac{x^{n+1}}{n+1} \right]_A^B$$

$$W = \text{const} \left[\frac{V_2^{-\gamma+1}}{-\gamma+1} - \frac{V_1^{-\gamma+1}}{-\gamma+1} \right]$$

$$= \frac{-\text{const}}{-\gamma+1} (V_2^{-\gamma+1} - V_1^{-\gamma+1}) \quad P_1 V_1^\gamma = P_2 V_2^\gamma = \text{const}$$

$$W = \frac{\text{const}}{\gamma-1} \left(\frac{V_2}{V_2^\gamma} - \frac{V_1}{V_1^\gamma} \right) = \frac{\text{const}}{\gamma-1} \left(\frac{P_2 V_2}{\text{const}} - \frac{P_1 V_1}{\text{const}} \right) \quad V_2 = \frac{\text{const}}{P_2}$$

$$W = \frac{1}{\gamma-1} (P_2 V_2 - P_1 V_1)$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2} n R}{\frac{3}{2} n R} = \frac{5}{3}$$

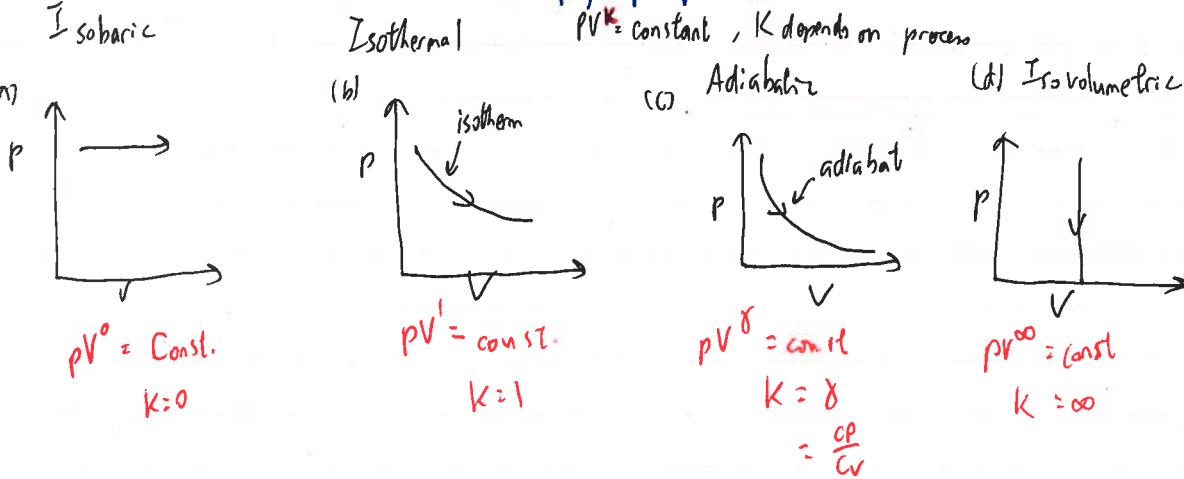
$$W = \frac{1}{\gamma-1} (P_2 V_2 - P_1 V_1)$$

for ideal monoatomic gas

$$\Rightarrow W = \frac{1}{2} (P_2 V_2 - P_1 V_1)$$

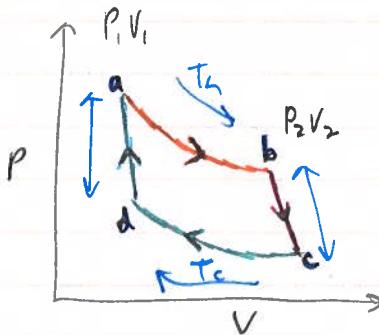
Polytropic process

$PV^K = \text{constant}$, K depends on process



Carnot Engine!

pV diagram:



- connected to hot reservoir

- $Q_h \rightarrow W$

- doing work

- internal energy is converted

- b work done by gas

- connected to cold reservoir

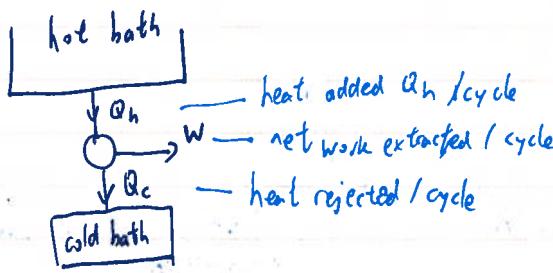
- external work on gas turned into heat

- ↳ going which goes into the cold reservoir

- adiabatic compression ↗

- d → a : - work done on gas, $\Delta U \uparrow T$

- $W \rightarrow \Delta U$



Heat flows from a hot reservoir to a cold reservoir

Work is extracted / cycle

- operates between 2 heat reservoirs

- operates in a cycle w/ a working substance

- reversible

- best / most efficient engine possible

- fundamental limit in efficiency of any engine

- all Carnot engines

isothermal process:

$$\frac{\Delta U + Q}{\Delta U} = 0$$

$$\Delta U = Q$$

$$\Delta U = 0$$

$$Q = -W$$

$$Q_h = -nRT \ln\left(\frac{V_b}{V_a}\right)$$

$$Q_c = nRT \ln\left(\frac{V_b}{V_a}\right)$$

$$\frac{T_c}{T_h} = \left(\frac{V_b}{V_c}\right)^{\gamma-1} = \left(\frac{V_a}{V_d}\right)^{\gamma-1}$$

$$\frac{V_b}{V_a} = \frac{V_c}{V_d} = \left(\frac{V_d}{V_a}\right)^{-1}$$

$$n = 1 - \frac{\ln \frac{T_c}{T_h} \ln \left(\frac{V_d}{V_a}\right)}{\ln \frac{T_c}{T_h} \ln \left(\frac{V_b}{V_a}\right)}$$

$$n = 1 - \frac{T_c}{T_h}$$

Efficiency :

Using 1st law:

$$\Delta U = Q + W$$

$$= Q_h - Q_c - W = 0$$

$$W = Q_h - Q_c$$

$$n = \frac{W}{Q_h}$$

$$n = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

$$\Delta TV^{\gamma-1} = \text{const}$$

$$T_h V_b^{\gamma-1} = T_c V_c^{\gamma-1}$$

$$T_c V_d^{\gamma-1} = T_h V_a^{\gamma-1}$$

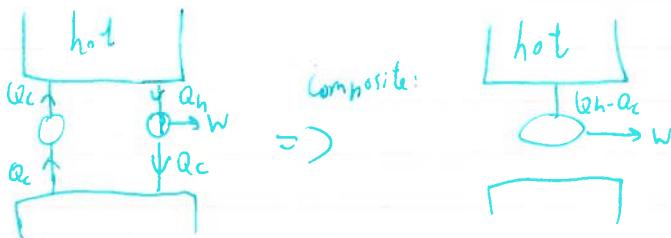
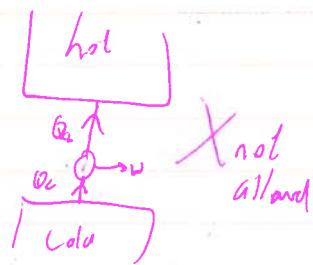
2nd law of thermodynamics based on limits of heat transfer in engines:

- Clausius:

impossible to transfer heat spontaneously from cold reservoir to hot reservoir in a single cycle providing no work drives the process

assume statement is false:

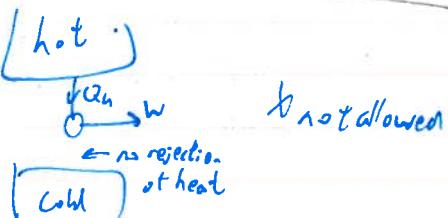
↳ add another, additional engine which produces work/cycle



- violates planck / kelvin statement

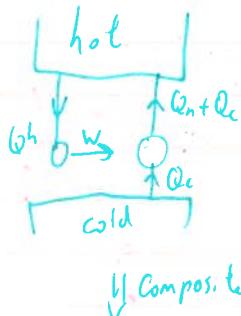
- Planck / Kelvin statement:

A cyclic process whose only effect is the conversion from heat to work is impossible

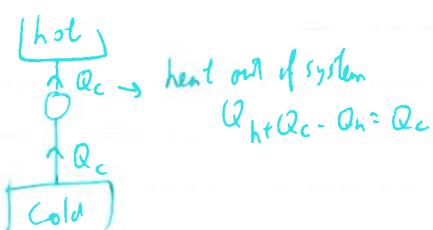


assume statement is false

↳ make a composite engine where process drives the a Carnot engine in reverse



- heat comes in from work done by hypothetical process that defies Planck's statement
- use the work to drive another Carnot engine
- heat comes from the cold reservoir
- + put $Q_h + Q_c$ into hot reservoir using W

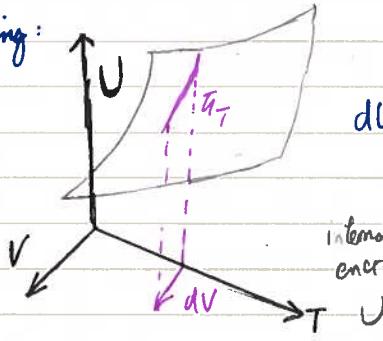


- violate clausian statement

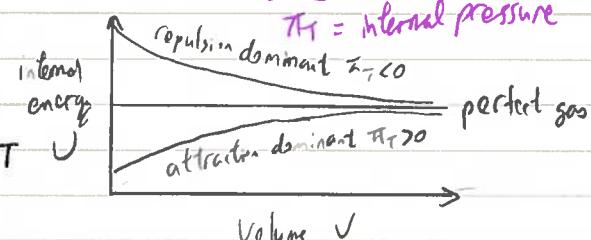
$$Q_h + Q_c - Q_h = Q_c$$

More on changes in internal energy: internal pressure, expansion coefficient, isothermal compressibility, relations to C_V , C_p , Joule - Thomson effect

Recalling:



$$dU = \left(\frac{\partial U}{\partial T}\right) dT + \left(\frac{\partial U}{\partial V}\right) dV \quad dU = C_V dT + \pi_i dV$$



using $dU = C_V dT + \pi_i dV \quad U(C, P, T, V)$ Proving Euler chain relation:

$$\Rightarrow \frac{du}{dT} = C_V + \pi_i \frac{du}{dT}$$

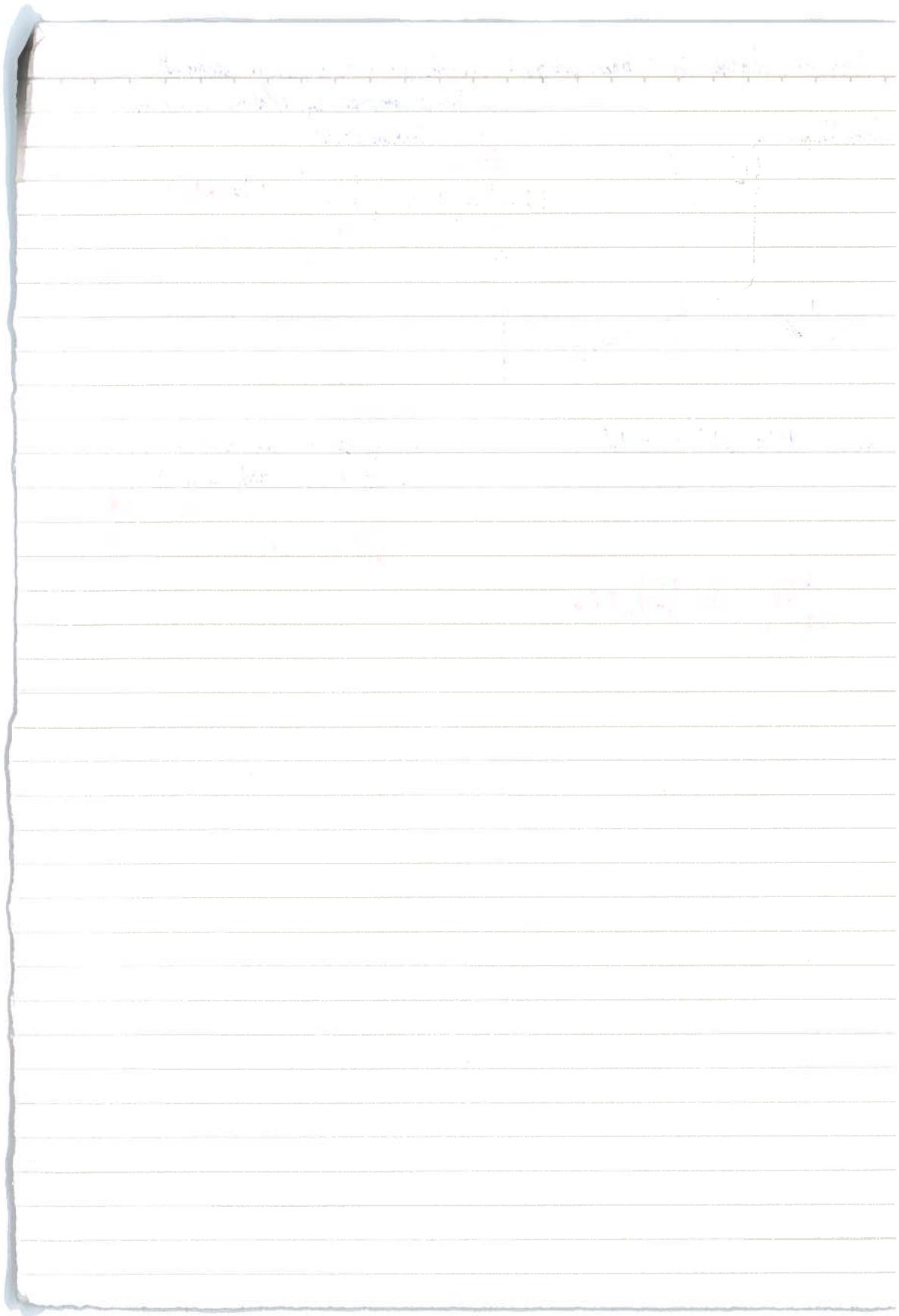
imposing const. pressure $\Rightarrow U(P, T, V)$

$$\left(\frac{\partial U}{\partial T}\right)_P = \pi_i \left(\frac{\partial V}{\partial T}\right)_P + C_V \quad \text{Proving Euler chain relation:}$$

let $f(x, y, z)$ and $z(x, y)$

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x_y}\right)_z + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z - \dots$$

$$\left(\frac{\partial U}{\partial T}\right)_P = \pi_i \left(\frac{\partial V}{\partial T}\right)_P + C_V$$



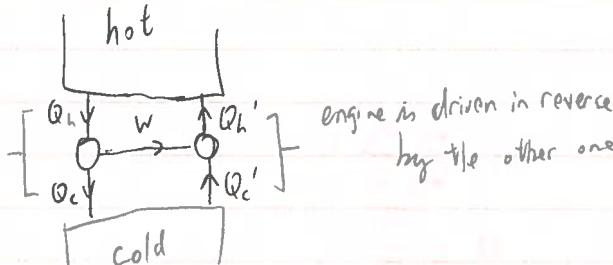
No engine is more effective than a Carnot engine

- suppose having 2 Carnot engines; one drives another

- for ideal Carnot engine:

$$|Q_h| = |Q_h'| ; |Q_c| = |Q_c'|$$

- Engine produces work to drive the other engine

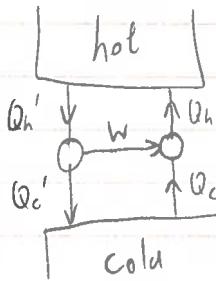


engine is driven in reverse by the other one

- Suppose we have an engine that is more effective

↓ implying a new composite engine

Say one is more eff than the other:



$$\eta' = \frac{W}{Q_h'} \quad \& \quad \eta = \frac{W}{Q_h}$$

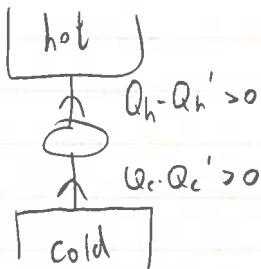
$$\text{if } \eta' > \eta \Rightarrow \frac{W}{Q_h'} > \frac{W}{Q_h}$$

$$Q_h > Q_h'$$

$$Q_c > Q_c' \rightarrow \text{from first law}$$

↓ imply another composite engine

- violates Clavius statement

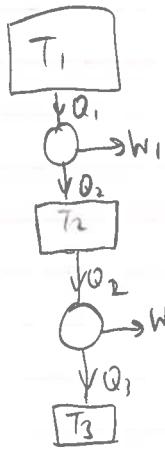


↳ no engine is more efficient than the Carnot engine

Refining temp w/ a carnot engine

$$\eta = 1 - \frac{T_c}{T_h} = 1 - \frac{Q_c}{Q_h}$$

consider a string of Carnot engines



$$\frac{T_1}{T_2} = \frac{Q_1}{Q_2}$$

$$T_3 = \frac{Q_3 / Q_2}{Q_2 / Q_1} T_1$$

$$\frac{T_2}{T_3} = \frac{Q_2}{Q_3}$$

$$T_3 = \frac{Q_3}{Q_1} T_1$$

$$T_3 = T_2 \frac{Q_1}{Q_2}$$

$$T_2 = T_1 \frac{Q_2}{Q_1}$$

- many Carnot engines define any range of temp between many reservoirs
- for ideal gas this is consistent w/ $T_{\text{gas}} = \frac{nR}{pV}$
- useful since ability to define temp is independent of substance (\pm prove)

At Otto cycle: [Internal Engine]

1. Fuel & Air are drawn into the cylinder \rightarrow const. Volume

2. Mixture is compressed

2. Mixture is compressed \rightarrow adiabatic process
(a \rightarrow b)

$$T_a V_1^{\gamma-1} = T_b V_2^{\gamma-1}$$

3. Heat addition \rightarrow heat is added (ignition occurs)

3. Cylinder is maximally compressed \rightarrow isovolumetric

\hookrightarrow heat is added (ignition occurs)

$$V = C_v \Delta T = Q_v$$

$$Q_h = C_v (T_c - T_b)$$

4. Higher temp. now pushes the cylinder \rightarrow adiabatic expansion

$$T_d V_1^{\gamma-1} = T_c V_2^{\gamma-1}$$

5. Heat is transferred to the cylinder \rightarrow isovolumetric

$$Q_c = ?$$

$$Q_c = C_v (T_d - T_a) \quad [\text{just interested in magnitude}]$$

6. Burnt gas is expelled \rightarrow const. volume

\times include fuel \Rightarrow

Efficiency:

$$\eta = 1 - \frac{Q_c}{Q_h} = 1 - \frac{C_v (T_d - T_a)}{C_v (T_c - T_b)} = 1 - \frac{T_d - T_a}{T_c - T_b} \Rightarrow 1 - \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$

$\overline{V_2} \gg V_1$
now: $V_2 < V_1$
 $V_2 \ll V_1$

using adiabatic relations to find Temp diff

$$T_c V_2^{\gamma-1} = T_d V_1^{\gamma-1}$$

$$\therefore T_b V_2^{\gamma-1} = T_a V_1^{\gamma-1}$$

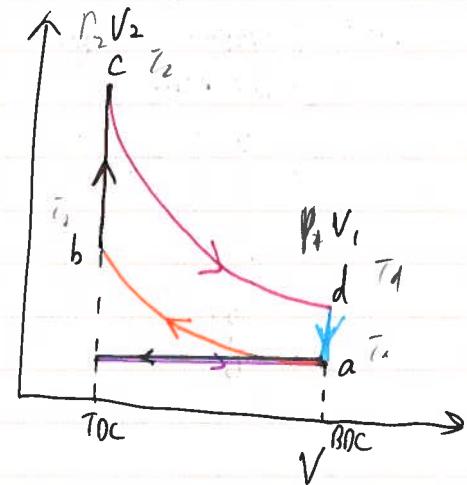
$$(T_c - T_b) V_2^{\gamma-1} = (T_d - T_a) V_1^{\gamma-1}$$

$$\frac{T_d - T_a}{T_c - T_b} = \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$

$\eta = 1 - \left(\frac{V_2}{V_1} \right)^{\gamma-1}$
gas has to be compressed as much as possible to max η
typical effec = $25 \sim 30\%$

for best efficiency \rightarrow this term $\rightarrow 0$

$$V_1 \gg V_2$$



Clausius Inequality:

$$\eta = 1 - \frac{T_c}{T_h} = 1 - \frac{Q_c}{Q_h}$$

For this reversible process

$$\frac{Q_c}{Q_h} : \frac{T_c}{T_h} \Rightarrow \frac{Q_h}{T_h} = \frac{Q_c}{T_c} \Rightarrow \frac{Q_h}{T_h} - \frac{Q_c}{T_c} = 0$$

Consider irreversible process:

$$1 - \frac{Q_c}{Q_h} > \eta_{irrev}$$

$$\frac{Q_c}{Q_h} < \frac{Q_c'}{Q_h'}$$

$$\frac{T_c}{T_h} < \frac{Q_c'}{Q_h'}$$

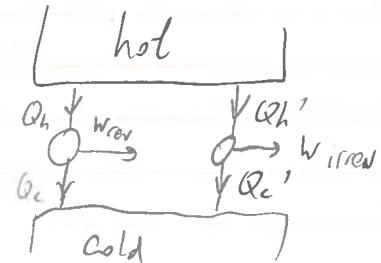
$$\frac{Q_h'}{T_h} < \frac{Q_c'}{T_c}$$

$$\frac{Q_h'}{T_h} - \frac{Q_c'}{T_c} < 0$$

$$\sum_i \frac{Q_i}{T_i} \leq 0 \quad (\text{general})$$

$= 0 \Rightarrow \text{reversible}$

$< 0 \Rightarrow \text{irreversible}$



if we have a continuous process in a closed path:

$$\oint \frac{dQ}{T} \leq 0 \quad (\text{general})$$

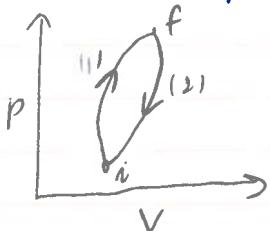
$= 0 \Rightarrow \text{reversible}$

$< 0 \Rightarrow \text{irreversible}$

$$\frac{dQ_{rev}}{T} = dS \quad (\text{ratio entropy}) \quad \text{by Clausius}$$

For rev $\oint \frac{dQ_{rev}}{T} = 0$

consider a closed path on a pV diagram



$$\int_i^f \frac{dQ_{rev,i}}{T} + \int_f^i \frac{dQ_{rev,f}}{T} = 0$$

$$\int_i^f \frac{dQ_{rev,i}}{T} = \int_i^f \frac{dQ_{rev,f}}{T}$$

Entropy / integral is path dependent

like internal energy U \Rightarrow it's a state func.

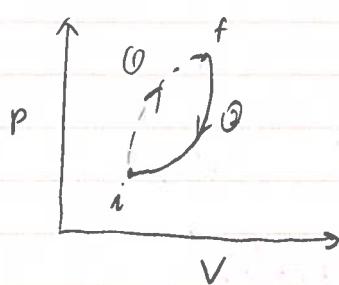
Entropy:

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ_{rev}}{T} \leq 0$$

(state func.)

The principle of increasing entropy:

Closed path on pV diagram, but one path is irreversible



$$\oint \frac{dQ}{T} \leq 0$$

$$\int_i^f \frac{dQ_{irrev}}{T} + \int_f^i \frac{dQ_{rev}}{T} \leq 0$$

$$\int_i^f \frac{dQ_{irrev}}{T} < \int_i^f \frac{dQ_{rev}}{T} = \Delta S$$

What does $\frac{dQ}{T} < dS$ mean?

$dS > \int_i^f \frac{dQ_{irrev}}{T}$ for irrev process

In an infinitesimal irrev process between a pair of eq^{NY} states

↳ there is a large change in entropy dS

↳ which is larger than the ratio of heat transferred

to the temp of the external reservoir.

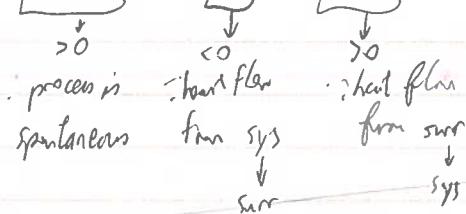
- entropy in a thermally isolated system ∇T

INCREASES in any irrev process AND not altered by a rev. process

(if isolated, $dQ=0$, $dS \geq 0$)

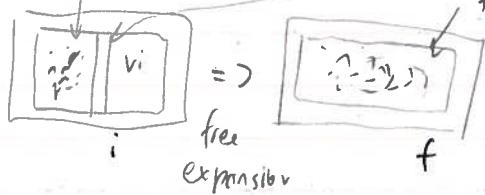
↳ entropy either stays the same or
more likely to increase.

* $dS_{total} = dS + dS_{surround}$ [thermal contact w/ hot & cold block]



Entropy change in a free expansion

Consider an adiabatic free expansion



$$\Delta S = \int_i^f \frac{dQ_{\text{rev}}}{T} \quad \text{equivalent reversible process}$$

$$V_f = 2V_i$$

finding ΔS for $V_f = 2V_i$

$$dU = dQ + dW \quad \text{adiabatic: no heat transfer}$$

$$dQ = dU - dW \quad dU = 0$$

$$2V_i: dQ = -dW = pdV$$

$$\Delta S = \int_{V_i}^{2V_i} \frac{pdV}{T}$$

$$= \int_{V_i}^{2V_i} \frac{nRT \frac{dV}{V}}{T} \quad (pV = nRT)$$

$$= nR \ln 2^{\left(\frac{V_f}{V_i}\right)}$$

$$\Delta S = nR \ln 2$$

Same result

Also

$$pV = nRT \quad PV = NkT$$

$$\underline{nR = Nk}$$

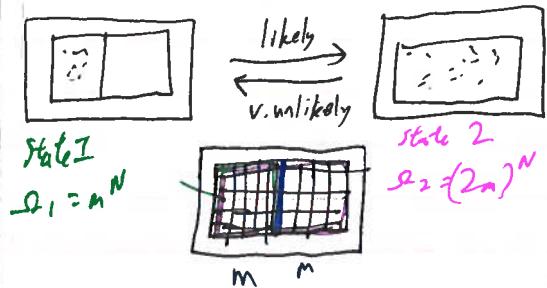
It suggests entropy relates to the number of ways of arranging the inside such that the outside remains the same.

Statistical interpretation of entropy

$$\Delta S = nR \ln 2$$

get same answer using $\Delta S = k \ln S_2$

Boltzmann associated entropy ΔS w/ transitions from a less to more probable state



if we divide box into $2m$ cells
let S_2 be number of ways we can arrange N particles
into those cells

$$\begin{aligned} \Delta S &= k \ln S_2 - k \ln S_1 \\ &= k \ln (2m)^N - k \ln m^N \\ &= kN [\ln 2 + \ln(m/N)] \end{aligned}$$

$$\Delta S = kN \ln 2$$

Centre eq² of thermodynamics
combining the 1st & 2nd law.

$$dU = \underbrace{dQ + dW}_{\delta Q_r = Tds} - pV$$

$$dU = TdS - pdV$$

- true for all processes, reversible or irreversible
- all quantities are state functions

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV$$

$$U = U(S, V); S, S(U, V)$$

$$dU = Tds - pdv$$

$$dQ = dU + pdV$$

$$TdS = dU + pdV$$

$$dS = \frac{dU}{T} + \frac{p}{T} dV$$

$$U = \frac{3}{2} nRT \quad \nabla pV = nRT$$

$$T = \frac{2U}{3nR} \quad T = \frac{PV}{nR}$$

$$dS = \frac{3}{2} nR \frac{dU}{U} + nR \frac{dV}{V}$$

$$S = \frac{3}{2} nR \int \frac{dU}{U} + nR \int \frac{dV}{V}$$

$$S = \frac{3}{2} nR \ln|U| + nR \ln|V| + \text{const.}$$

$$V_0, V_0 \Rightarrow V_0 S_0$$

$$\therefore S_0 = \frac{3}{2} nR \ln|V_0| + nR \ln|V_0| + \text{const.}$$

$$\text{const.} = S_0 - \frac{3}{2} nR \ln|V_0| - nR \ln|V_0|$$

$$S = \frac{3}{2} nR \ln|V| + nR \ln|V| + S_0 - \frac{3}{2} nR \ln|V_0| - nR \ln|V_0|$$

$$S - S_0 = GS = \frac{3}{2} nR \ln \frac{U}{U_0} + nR \ln \frac{V}{V_0}$$

$$\frac{U}{U_0} = \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} e^{\frac{2}{3nR}(S-S_0)}$$

$$U = U_0 \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} e^{\frac{2}{3nR}(S-S_0)}$$

Checking

$$(1). \left(\frac{\partial U}{\partial S} \right)_V = T = \frac{\partial}{\partial S} \left[U_0 \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} e^{\frac{2}{3nR}(S-S_0)} \right]_V$$

$$T = \frac{2}{3nR} U_0 \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} e^{\frac{2}{3nR}(S-S_0)}$$

$$T = \frac{2}{3nR} U$$

$$(2) \left(\frac{\partial U}{\partial V} \right)_S = -p = \frac{\partial}{\partial V} \left[U_0 \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} e^{\frac{2}{3nR}(S-S_0)} \right]$$

$$-p = -\frac{2}{3V} \left(U_0 \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} e^{\frac{2}{3nR}(S-S_0)} \right)$$

$$-p = -\frac{2}{3V} U$$

$$\underline{\underline{U = \frac{3}{2} PV}}$$

Helmholtz free energy

- consider having a process w/ system that is in thermal contact w/ a thermal reservoir [system & reservoir @ same temp]
- T is fixed

Using 2nd law:

$$\Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} \geq 0$$

Using 1st law: fixed V , (no work)

$$\Delta U_{\text{sys}} = Q_{\text{sys}} = -Q_{\text{sur}}$$

- surroundings are a reservoir (heat)

- $T = T_{\text{surroundings}}$ (fixed)

- addition of heat is reversible

$$\Delta S_{\text{sur}} = \int \frac{dQ_{\text{real}}}{T} = \frac{Q_{\text{sur}}}{T}$$

$$\Delta S_{\text{sur}} = \frac{-\Delta U_{\text{sys}}}{T}$$

$$\Delta S_{\text{sys}} - \frac{\Delta U_{\text{sys}}}{T} \geq 0$$

$$-\bar{T}\Delta S_{\text{sys}} + \Delta U_{\text{sys}} \leq 0$$

$$\Delta U_{\text{sys}} - \bar{T}\Delta S_{\text{sys}} \leq 0$$

$$@ \text{fixed } T \Rightarrow \Delta(U_{\text{sys}} - TS_{\text{sys}}) \leq 0$$

$$\Delta F \leq 0$$

Helmholtz free energy

$$\boxed{F = U - TS}$$

$$\Delta F \leq 0$$

Helmholtz free energy is the energy available once the spontaneous energy transfer from reservoir is accounted for.

Gibbs' free energy

- now suppose P & T are fixed

$$\Delta H = C_p dT = Q$$

$$\Delta H_{\text{sys}} = Q_{\text{sys}} = -Q_{\text{sur}}$$

$$\Delta S_{\text{sur}} = \frac{Q_{\text{sur}}}{T} = \frac{-\Delta H_{\text{sys}}}{T}$$

2nd law: $\Delta S_{\text{sys}} + \Delta S_{\text{sur}} \geq 0$

$$\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} \geq 0$$

$$\Delta H_{\text{sys}} - T \Delta S_{\text{sys}} \leq 0$$

(fixed T)

$$\boxed{\Delta(H_{\text{sys}} - TS_{\text{sys}}) \leq 0}$$

$$\Delta G \leq 0$$

$$G = H - TS$$

Gibbs' free energy is the energy available in process of fixed p when spontaneous energy transfer from reservoir is accounted for.

$$\Delta S \geq 0 \Rightarrow \text{isolated sys.}$$

P, T held const applies to non-isolated sys connected to P, T bath
 $\Delta S \geq 0$ expressed in ΔS_{sys} & S_{sur} .

$\Delta G \leq 0$ - replacing max entropy of universe w/ minimizing Gibbs free energy of the sys.

$\Delta G \leq 0$ is expressed in

system variables

const T ,
 $\Delta H \neq 0$
 $\Delta S \neq 0$

Temp dependence of entropy @ fixed pressure

in any single phase:

$$dS = \frac{dQ_{rev}}{T} = C_p \frac{dT}{T} = \frac{dH}{T}$$

now consider a phase transition

$$\Delta S = \frac{Q_{res}}{T} = \frac{L}{T}$$

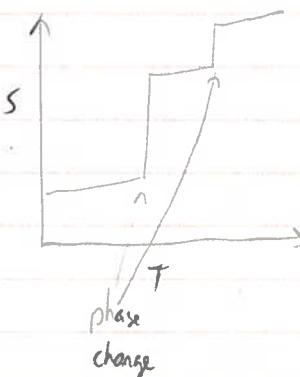
Using Gibbs free energy:

$$\Delta G = \Delta(H - TS)$$

$$\Delta G = L - T \frac{L}{T} = 0$$

generally:

$$\Delta S = \int \frac{C_p dT}{T} + \sum L \quad T_i$$



- remember $\Delta H = \int C_p dT + \sum L$

- evidence that $T=0$, $S(T)=0$

- molar entropy $S = \frac{S}{n}$

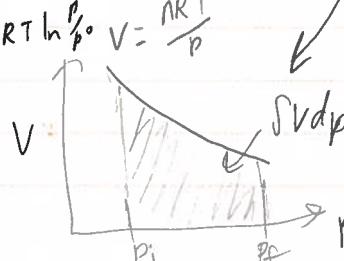
pressure dependence of G_f for ideal gas

$$dG_f = Vdp - SdT \quad dT = 0$$

$$dG_f = Vdp \quad V = \frac{nRT}{P}$$

$$G_f(p) - G_f^{\circ} = ART \ln \frac{P}{P^{\circ}}$$

$$G_f(p) = G_f^{\circ} + nRT \ln \frac{P}{P^{\circ}} \quad V = \frac{nRT}{P}$$



Natural variables:

when calculating work:

- $dW = -pdV$ we need p in terms of V

- Sometimes easier to measure PdT or VdT

($dU = TdS - pdV$, S & V are natural variables)

Legendre transforms:

$$F = U - TS$$

$$dF = dU - SDT - TdS \quad (\text{Helmholtz})$$

$$dU = TdS - pdV$$

$$\hookrightarrow dF = TdS - pdV - SdT - TdS$$

$$\hookrightarrow dF = -pdV - SdT \quad (V \propto T)$$

$$AND$$

$$G = H - TS$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$dG = dH - SDT - TdS$$

$$H = U + PV$$

$$dH = dU + Vdp + pdV$$

$$dG = dU + Vdp + pdV - SdT - TdS$$

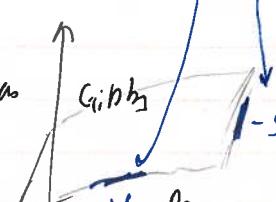
$$= TdS - pdV + Vdp + pdV - SdT - TdS$$

$$dG = Vdp - SdT \quad (p \propto T)$$

$$\left(\frac{\partial V}{\partial S}\right)_p = - \left(\frac{\partial T}{\partial p}\right)_S$$

$$Vdp = \left(\frac{\partial G}{\partial p}\right)_T dp$$

$$-SdT = \left(\frac{\partial G}{\partial T}\right)_p dT$$



Maxwell Relations

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$$

A B

$$dG_{LO}$$

$$\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) = \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \quad \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)$$

$$= \frac{\delta B}{\delta n} \qquad \qquad \qquad = \frac{\delta A}{\delta y}$$

dF_{LO} for spontaneous Rx

$$\frac{\delta A}{\delta y} = \frac{\delta B}{\delta n}$$

~~ΔF~~ \leftarrow
 $\Delta F = -pdV - SdT$

$$dU = TdS - pdV$$

$$dU = TdS - pdV$$

$$G_1 = H - TS$$

$$\left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V$$

$$T = \left(\frac{\partial U}{\partial S} \right)_V, \quad \left(\frac{\partial T}{\partial V} \right)_S = \left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_V \right]_S$$

$$= \left[\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_S \right]_V$$

$$\Delta H = c_p dT = Q$$

$$\Delta S_{Surr} = - \frac{Q_{Surr}}{T} = - \frac{\Delta H}{T}$$

$$\Delta S_{Surr} = \int \frac{Q_{Surr}}{T}$$

$$\Delta S = \frac{\Delta H_{Surr}}{T}$$

$$dU = dQ + dW$$

$$\leftarrow \Delta U = -dQ_{Surr}$$

$$-p = \left(\frac{\partial U}{\partial V} \right)_S$$

$$= - \left(\frac{\partial p}{\partial S} \right)_V$$

$$T\Delta S_{Surr} - \Delta H \geq 0$$

$$\Delta H - T\Delta S \leq 0$$

$$\Delta(H - TS) \leq 0$$

$$\Delta S = \frac{\Delta U}{T} \quad \Delta S_{Surr} = - \frac{\Delta U}{T}$$

$$dU = TdS - pdV$$

$$H = U + PV \quad G_1 = H - TS$$

$$dH = dU + pdV + Vdp \quad dG_1 = dH - dTS - TdS$$

$$= dU + pdV + Vdp - dTS - TdS$$

$$= TdS - pdV + pdV + Vdp - dTS - TdS$$

$$dG_1 = Vdp - SdT$$

$$\Delta U - T\Delta S \leq 0$$

$$\Delta (U - TS) \leq 0$$

$$\Delta F \leq 0$$

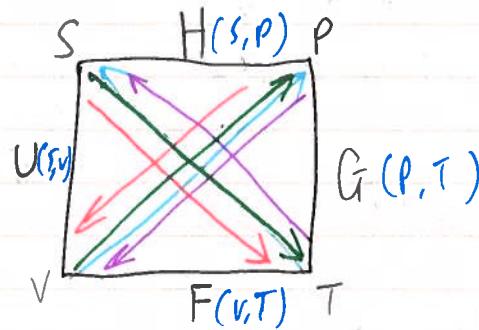
$$\bar{F} = U - TS$$

$$dF = dU - SdT - TdS$$

$$dF = pAV - SdT$$

Mnemonic Device for Thermodynamic Potentials & Maxwell's Relations

| | |
|------------|-----------------------------|
| Good | $G : G_i \text{; bh's}$ |
| Physicists | $P : Pressure$ |
| Have | $A : Enthalpy$ |
| Studied | $S : Entropy$ |
| Under | $U : Internal Energy$ |
| Very | $V : Volume$ |
| Fine | $F : Helmholtz free energy$ |
| Teachers | $T : Temperature$ |



- $\uparrow \downarrow / \uparrow \downarrow \rightarrow$ determine which variables
expressed in terms of

Thermodynamic potentials

in terms of natural variables:

1. $dG = -SdT + VdP$
2. $dH = TdS + VdP$
3. $dU = TdS - PdV$
4. $dF = -pdV - SdT$

Maxwell relations

$$1. \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial S}{\partial P} \right)_T$$

$$2. \left(\frac{\partial V}{\partial S} \right)_P = \left(\frac{\partial T}{\partial P} \right)_S$$

$$3. - \left(\frac{\partial P}{\partial S} \right)_V = \left(\frac{\partial T}{\partial V} \right)_S$$

$$4. \left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

Fig 11.10 \rightarrow diagonal tells you what constant term is
point up: +ve, down: -ve

- 1st arrow start: what am I diffing?
w.r.t. other arrow end w/
while holding first arrow end constant.

Standard reactions entropies

$$\Delta R H^\circ = \sum_{\text{products}} v_i \Delta_f H^\circ - \sum_{\text{reactants}} v_i \Delta_f H^\circ$$

$$\Delta R S^\circ = \sum_{\text{products}} v_i S^\circ - \sum_{\text{reactants}} v_i S^\circ$$

at diff temp T_2 :

$$\Delta R S^\circ(T_2) = \Delta R S^\circ(T_1) + \int_{T_1}^{T_2} \frac{\Delta R C_P^\circ}{T} dT$$

$$\Delta R G^\circ = \sum_{\text{products}} v_i G^\circ - \sum_{\text{reactants}} v_i G^\circ$$

Properties of Matter

Synopsis: Real gases obey perfect gas law when $p \rightarrow 0$

~~and~~ Deviations from the law are important for high P & low T

van der Waal's Eqⁿ of state \Rightarrow thermodynamic eqⁿ relating

state variables which describe
the state of matter

See also physical
chemistry notes

Modifications:

1. Attraction between molecules

rel effect:

reduction in pressure compared
to IG

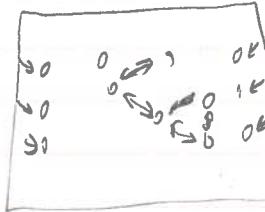
$$\Rightarrow P_{\text{real}} < P_{\text{ideal}}$$

$$P_r = P_i - a \left(\frac{n}{V} \right) \left(\frac{n}{V} \right)$$

$$P_r = P_i - a \left(\frac{n}{V} \right)^2$$

↑ multiply every
molecule in the box

Strength of interactions between gas molecules.



$$P = \frac{NRT}{V-nb} - \frac{n^2 a}{V^2} / P_c = \frac{8Tr}{3Vr-1} - \frac{3}{Vr^2}$$

k_F : effect of attraction.

principle features:

- high T \rightarrow Perfect gas
high M \rightarrow isotherms

when $T \uparrow \uparrow \& V \uparrow \uparrow \Rightarrow V_m \approx nb$

\hookrightarrow 1st term ↑↑ faster than 2nd term

\hookrightarrow reduces to $PV = nRT$

- liquid & gas coexist when
attractive & repulsive effects
are in balance

\hookrightarrow oscillations or V.d.w. loops

-
occur when 1st term \approx 2nd term
1st term k_F
2nd term attractive interactions

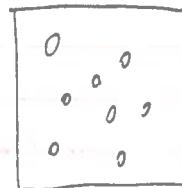
- critical constants are
related to v.d.w constants
in derivations

2. Gas molecules have a volume:

$$V_r > V_i$$

$$V_r = V_i + bn$$

↑ related to
size of the
molecule



Adding in modification in I.G. Eqⁿ

$$(P + a \left(\frac{n}{V} \right)^2) (V - nb) = nRT \quad (\text{v.d.w eqn of state})$$

Define $V_m = \frac{V}{n} = \text{volume per mole}$

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

a, b are v.d.w. coefficients

Extensive vs In extensive variables:

Extensive variable: - depends on System size (mass or vol) depend on amount of substance

Intensive variable: - does not depend on system size (T, P, E, V_m) independent of amount of substance

Maxwell's area construction: (ideally not realistic)

\curvearrowleft V_m vs loops

$V_m(g) \Rightarrow mol^{-1}$

- suggests that under some condition $V_m(l/s) \Rightarrow kg^{-1}$

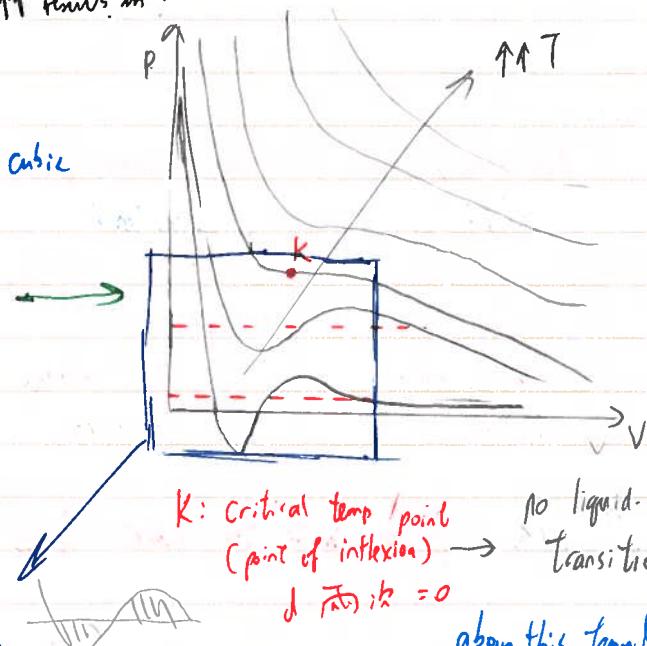
$$pV_m - pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT \quad \hookrightarrow p \uparrow \text{ results in } V \uparrow$$

$$pV_m^3 - pbV_m^2 + aV_m - ab = RTV_m^2$$

$$pV_m^3 - (pb + RT)V_m^2 + aV_m - ab = 0 \rightarrow \text{cubic}$$

- at high $T \Rightarrow pV_m = RT$ (IG)

- low $P \& V \Rightarrow$ difficult to press
atoms close together



K: Critical temp / point
(point of inflection) \rightarrow no liquid-gas transition
 $\int \frac{dP}{dT} dk = 0$

above this temp & p,
gas & liquid
indistinguishable

Maxwell construction \hookrightarrow occurs @ one value of p per temp pair
Liquids & gases can co-exist

Liquids & gases co-exist

\hookrightarrow Liquid Phase Co-existing

- for each temp \Rightarrow there's a pressure where (l) and (g) co-exist

$\#$ Saturated vapour pressure: $(p_{vp}(T))$

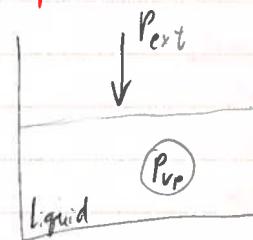
Pressure of gas in Eq^M w/ its liquid phase
or w/ its solid phase

Boiling \Rightarrow in an open container

- for given pressure, if $T \uparrow$

Liquid boils when $p_{vp} > p_{ext}$

- gas forms in bubbles



Phase definition

Phase: Homogeneous portion of matter w/ uniform properties & composition

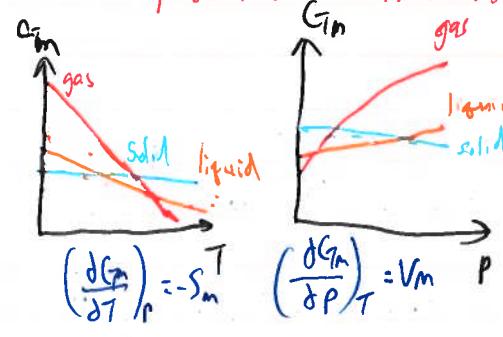
Liquid: - close contact \Rightarrow hard to compress
 - disordered avg. structure
 - described using PDFs

Solids:

- dimensionally stable (i.e. has a volume of its own)
 - ordered (crystals)
 - regular arrangement of atoms
 - long-range order
 - crystalline
- Disordered (glass)
 - random arrangement of atoms
 - short-range order
 - amorphous

Phase transition: discontinuous change in the properties of a substance, as its environment is changed only infinitesimally

Phase diagrams: 'map' of the eq^{MR} phases plotted for 2 (or more) variables



$E_{\text{eq}}^{\text{MR}}$ phase: phase with the lowest Gibbs free energy

$$G = U + PV - TS$$

$$G = H - TS$$

note balance of entropy & enthalpy & V/P
 @ diff values of $p, T \& V$

variables determine Gibbs free energy $\Rightarrow E_{\text{eq}}^{\text{MR}}$ phase

$$G = U + PV - TS$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

G for $s \neq g$

| | U | $-TS$ | PV |
|--------|--|--|-------------------------|
| Solid | atoms close tgt $\therefore U$ is <u>large</u> & <u>-ve</u> | \hookrightarrow highly ordered $\hookrightarrow S$ is low | $V \rightarrow$ minimum |
| gas | atoms far apart $\therefore U$ is <u>small</u> & <u>-ve</u> | very disordered $\hookrightarrow S$ is v. high | high V |
| liquid | similar to cs but less -ve | S is slightly higher than solid | $V \propto$ solid |



Gibbs phase rule

$$F = C - P + 2$$

for one component phase diagrams

F: variance, degrees of freedom

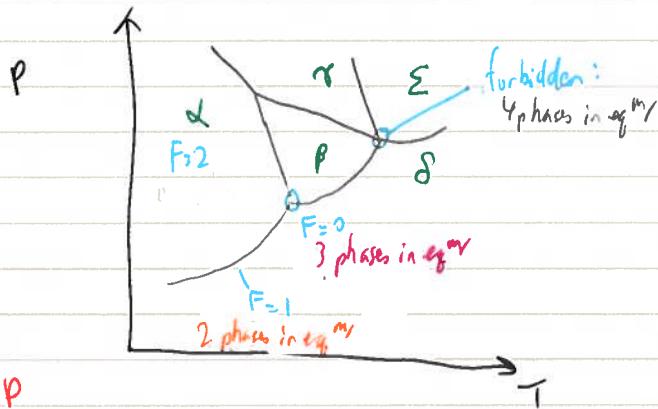
C: number of components

$$C=1$$

$$\Rightarrow F = 1 + 2 - P$$

$$F = 3 - P$$

P: number of phases in eq^{MR}



$$F = 3 - P$$

3 cases:

$$F=0$$

$$P=3$$

- triple point

↳ cannot vary anything

↳ 3 phases in eq^{MR}

$$F=1$$

$$P=2$$

$$F=2$$

$$P=1$$

- phase boundaries: - region of stability (α)

↳ can vary p/T ↳ vary p & T independently

↳ remain at the phase boundary

↳ 2 phases in eq^{MR}

② phase eq^{MR}: n of a component in the same for all phases present in a sample

2012-06-13

1. 2. 3. 4.

1. 2. 3. 4.

1. 2. 3. 4.

1. 2. 3. 4.

1. 2. 3. 4.

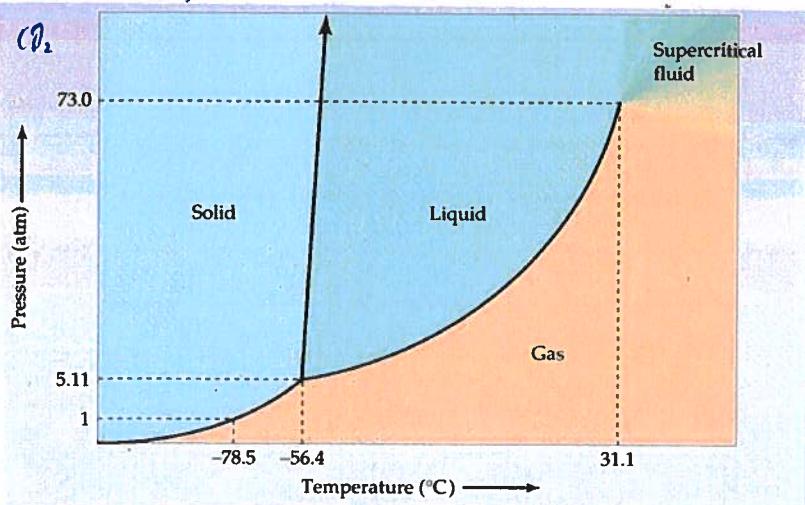
1. 2. 3. 4.

1. 2. 3. 4.

1. 2. 3. 4.

4.

Phase Diagrams!



coexisting phases

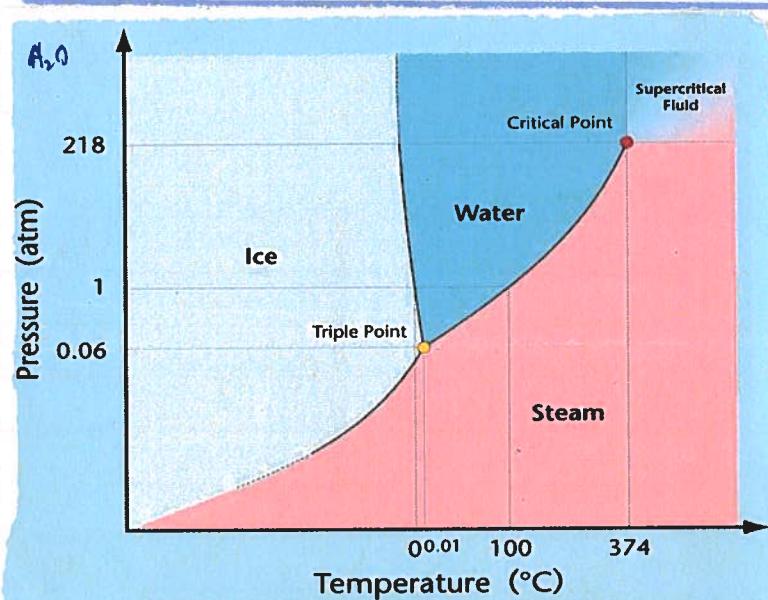
Co-existing phases :

- lines on 2D phase diagram

Co-exist @ p & T on those lines

- 2 phases co-exist
in eq^W

(same Gibbs free energy) $[G_1 = G_2]$



Triple pt:

- pt on phase diagram where 3 lines meet

- 3 phases coexist in Eq^W

Same Gibbs free energy $[G_1 = G_2 = G_3]$

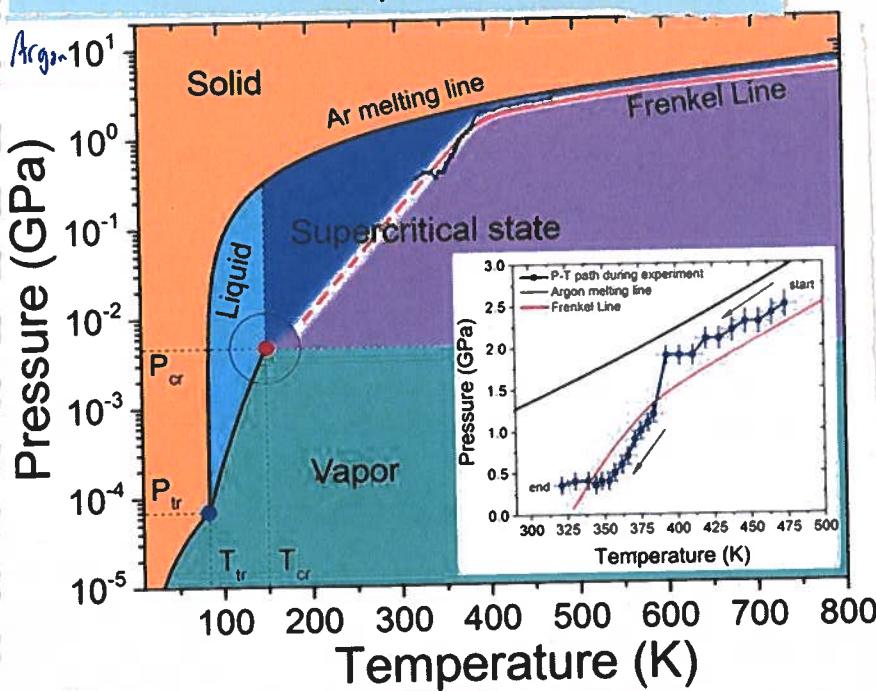
Critical point:

pt on the phase diagram

above which the liquid & gas phases have same density/indistinguishable

Gibbs Phase Rule

See attachment



- Critical Temp / Pressure from v.d.W eqn of state

reduced form:

$$\left(p + \left(\frac{a}{V_m^2} \right) \right) (V_m - b) = RT$$

turning pt @ $\left(\frac{\partial p}{\partial V} \right)_T = 0$

pt of inflection @ $\left(\frac{\partial^2 p}{\partial V^2} \right)_T = 0$

$$p_{inf} \left(\frac{RT}{V_m - b} \right) = \frac{a}{V_m^2}$$

$$\left(\frac{\partial p}{\partial V} \right)_T = \frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0 \quad \text{Dieterici}$$

$$\left(\frac{\partial^2 p}{\partial V^2} \right)_T = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4} = 0$$

$$RT = \frac{3a}{V_m^4} (V_m - b)$$

$$\frac{2a}{RT} = \frac{3a}{V_m^4} (V_m - b)^3$$

$$2V_m = 3V_m - 3b$$

$$V_m = 3b$$

comparing property of V, P, T
and pick a fundamental property
(T_c, P_c, V_c, T_c), and set that as a relative scale as the basis

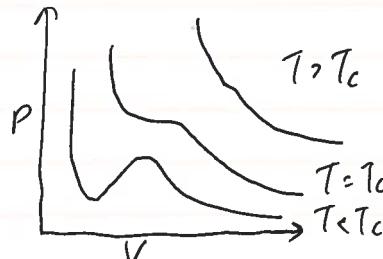
$$RT = \frac{2a}{V_m^3} (V_m - b)^2$$

$$= \frac{2a}{V_c^3} (V_c - b)^2$$

$$RT = \frac{2a}{(3b)^3} (3b - b)^2$$

$$RT = \frac{2a \cdot 4b}{27b^3}$$

$$T_c = \frac{8a}{27bR}$$



see also other eqns of state when v.d.w fails

Berthelot

$$p = \frac{RT}{V-nb} - \frac{n^2 a}{V^2} \quad \text{or} \quad p_r = \frac{8Tr}{3V_r - 1} - \frac{3}{T_r V_r^2}$$

$$p = \frac{nRT e^{-aRTV/n}}{V-nb} \quad \text{or} \quad p_r = \frac{Tr e^{a(1-T_r/V_r)}}{2V_r - 1}$$

$$p = \frac{nRT}{V} \left(1 + n \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots \right)$$

reduce forms

introducing dimensionless and principle of Corresponding states

Reduced variables

By def:

$$V_r = \frac{V_m}{V_c}$$

$$P_r = \frac{P}{P_c}$$

$$T_r = \frac{T}{T_c}$$

Observation: real gases at the same

reduced V & reduced T exert

the same reduced pressure

- approximation

- best for gases as spherical, fails badly when molecules are non-spherical or polar

$$P_c = 27ab \quad V_c = 3b \quad T_c$$

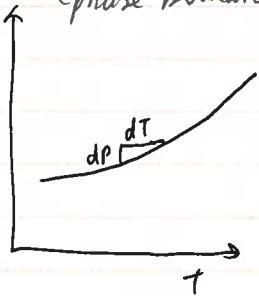
$$V_c = 3b$$

$$P_c = \frac{a}{27b^3}$$

$$T_c = \frac{8a}{27bR}$$

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{T_c}$$

The Claperyon Eq^Y
(phase boundaries)



consider an infinitesimal change in $d\text{temp} \rightarrow dT$

$$\ln p \rightarrow dp$$

so that we stay on the phase boundary

$$dG_i = vdp - SdT$$

both phases in Eq^Y $\Rightarrow dG_1 = dG_2$

$$V_1 dp - S_1 dT = V_2 dp - S_2 dT$$

$$(V_1 - V_2) dp = (S_1 - S_2) dT$$

$$\frac{dp}{dT} = \frac{S_1 - S_2}{V_1 - V_2} = \frac{\Delta S}{\Delta V}$$

- recalling $\Delta S = \frac{Q_L}{T}$ ($S = \frac{Q_{rev}}{T}$)

$$\Delta S = \frac{L_m}{T}$$

- $V_s = \frac{V}{m} \Rightarrow$ reciprocal of density

(volume per unit mass)

$$\Delta V_s = \frac{\Delta V}{m}$$

$$\frac{dp}{dT} = \frac{L_m}{T \Delta V_s}$$

$$\frac{dp}{dT} = \frac{L}{T \Delta V_s}$$

The Clausius - Claperyon Eq^Y

for liquid/solid phase
transition to gas

[liquid-vapour]
boundary

$$\frac{dp}{dT} = \frac{L}{T \Delta V_s}$$

$$dp = \frac{L}{T \Delta V_s} dT$$

Assume: 1. $\Delta V_s = V_{gas} - V_{liquid} \approx V_{gas}$

2. Ideal gas

$$pV_m = RT \Rightarrow V_m = \frac{RT}{p} = V_s$$

$$dp = \frac{L}{R T^2} dT$$

3. L has no temp dependence

$$\int_{P_1}^{P_2} \frac{1}{p} dp = \frac{L}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT$$

$$\ln \left[\frac{P_2}{P_1} \right] = \frac{L}{R} \left[\frac{1}{T_1} \right]_{T_2}$$

$$\ln \frac{P_2}{P_1} = \frac{L}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln \frac{P_2}{P_1} = \frac{L}{R} \left[\frac{\Delta T}{T_1 T_2} \right]$$

$$\ln \left[\frac{P_2}{P_1} \right] = \frac{L}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

④ Electronegativity (Pauling)

- a measure of an atom's tendency to attract electrons towards itself

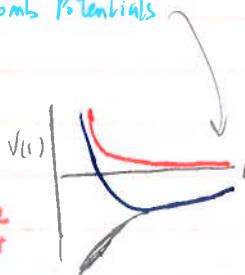
- ionic bonding :

- big diff in electronegativity
- hard, brittle, insulators, high M.P.
- attractions \rightarrow Coulomb Potentials

$$V(r) = \frac{B}{r^2} + \frac{q_1 q_2}{4\pi \epsilon_0 r}$$

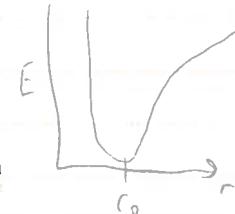
Metallic bonding :

- low electronegativity
- delocalised e⁻s & M⁺
- Cu, Al
- ductile, moderate melting temp., electrical / thermal conductors \rightarrow opaque
- attraction \rightarrow described by model in which Coulombic potential of nucleus + valence of e⁻s (ΘM)



- covalent bonding :

- similar electronegativity
- Si, C (diamond)
- Very hard, brittle, insulators semi conductors, high M.P.
- attractions \rightarrow Morse potential

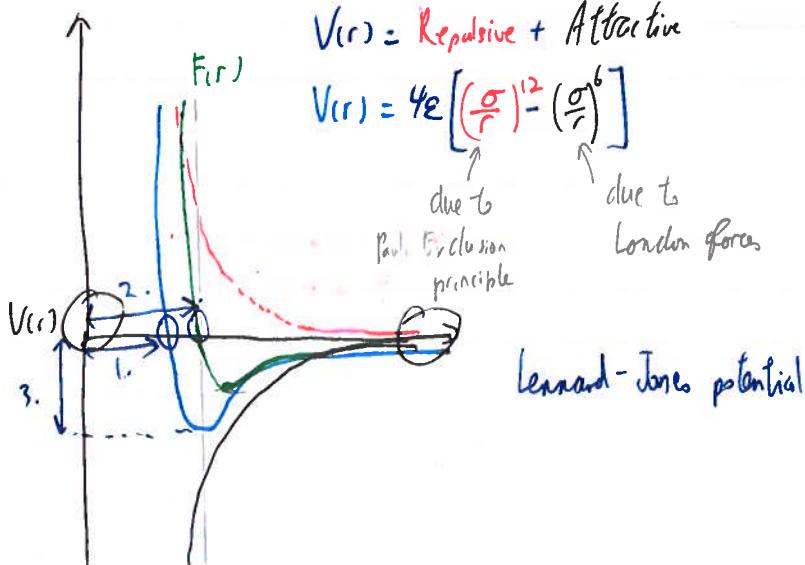


Van der Waals :

- soft, weak, low MP, electrical insulators
- Noble gas, wov, O₂
- charge-density fluctuations lead to attraction of neutral atom/molecule
- London / dispersion forces

Interatomic potentials:

Mathematical function for calculating the potential energy, V(r), of one atom as a function of distance from another



Force:

short r \Rightarrow strong repulsive
large r \Rightarrow attractive

$F(r) = 0$ at eq^m separation

Lennard-Jones potential

for Lennard-Jones potential

$$1. V(r) = 0$$

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] = 0$$

$$\left(\frac{\sigma}{r} \right)^{12} = \left(\frac{\sigma}{r} \right)^6$$

$$\sigma = r_{\text{eq}} = 0$$

$$2. \frac{dV(r)}{dr} = F(r) = 0 \quad [\text{Eq } \text{ separation}]$$

$$\frac{d}{dr} \left[4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right) \right] = 0$$

$$-\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} = 0$$

r_0 where atoms want to sit in eq^{rr}

$$2 \frac{\sigma^{12}}{r^{13}} = \frac{\sigma^6}{r^7}$$

$$2\sigma^6 = r^6$$

$$r_0 = 2^{\frac{1}{6}}\sigma$$

$$3. \text{ well depth} : U$$

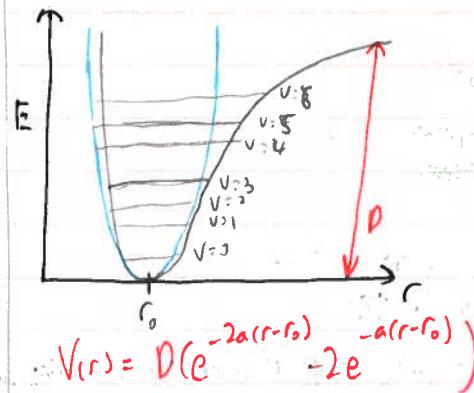
$$V(r_0) = 4\epsilon \left[\left(\frac{\sigma}{2^{\frac{1}{6}}\sigma} \right)^{12} - \left(\frac{\sigma}{2^{\frac{1}{6}}\sigma} \right)^6 \right]$$

$$= 4\epsilon \left[\frac{1}{2^2} - \frac{1}{2} \right]$$

$$= 4\epsilon \left[\frac{1}{4} - \frac{1}{4} \right]$$

$$V_{r_0} = -\epsilon$$

Morse potential for covalent bonding



a: constant relative to width of potential
(different for diff atoms)

D: well depth
(diff for diff atoms)

i: eq^{rr} separation

Cohesive energy:

defined as the energy required to separate all the atoms to infinity

- value is true

- ve of potential energy : U

- higher cohesive energy

↳ higher melting/boiling temp

Thermal expansion

$$\frac{\Delta l}{l} = \alpha \Delta T$$

thermal expansion coefficient

non-directional (unless stated)

↳ we can calculate volume change by calculating length change in D=3 & multiplying

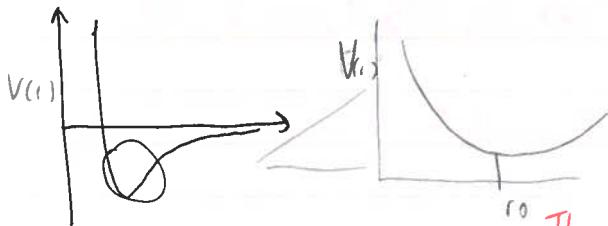
↳ fractional change in length ($\frac{\Delta l}{l}$) of a solid divided by the temp change (ΔT)

- from interatomic potentials

- as we $\uparrow\uparrow T$

↳ giving energy to atoms \Rightarrow vibrating about eqth positions

Using Lennard-Jones potential



- actual shape of potential is not symmetric

or anharmonic

- w/ $\uparrow\uparrow$ KE, atoms move apart from one another more than they move towards each other \therefore shape of $V(r)$

Thermal expansion thus due to the 'anharmonicity' of the well

Revision for mechanical forces: tensile force:

$$\text{stress: } \sigma = F/A \quad (\text{end of rod})$$

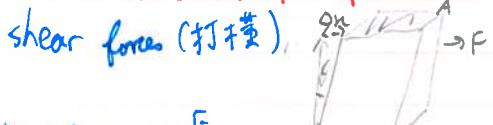
$$\text{strain: } \epsilon = \Delta L/L \quad (\text{pulling apart})$$

$$\text{Young's modulus } E = \sigma/\epsilon$$

\Rightarrow measure of ability of a material

to withstand changes in length

under tension / compression



$$\text{shear stress: } \tau = F/A$$

$$\text{shear strain: } \gamma = \frac{\Delta x}{x}$$

$$\text{shear modulus: } G = \tau/\gamma$$

compressive stress

$$p = -K \left(\frac{\Delta V}{V} \right)$$

↳ bulk modulus

(may change chemistry/physics @ high Pa)

stress-strain curves

- gradient = E

- linear relationship in low stress regime

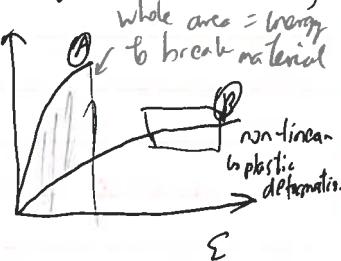
- A: covalent, large E

\rightarrow stiff material but brittle

- B: metallic, small E,

initially linear then shape changes

- area under the curve
= elastic energy



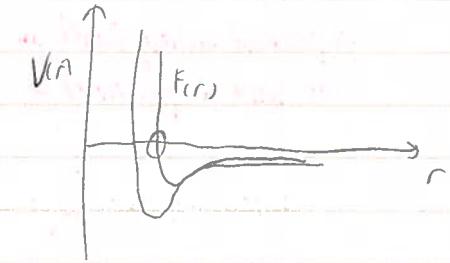
↳ plastic deformation

(E) Young's Modulus from the interatomic potential /

- measure of the ability of a material to withstand changes in length under tension
- steeper the gradient of $F(r)$

↳ more force required to deform atoms from their eq^{rr} positions (r_0)

↳ higher E



→ close to r_0 : gradient of $F(r)$
is approx. linear

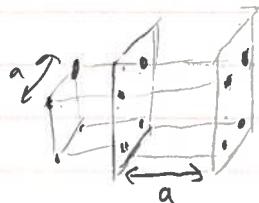
$$E \propto \frac{d^2V}{dr^2} \text{ at } r_0$$

→ proportional to 2nd derivative (curvature) of the interatomic potential curve at eq^{rr} separation

→ strongly curved well \Rightarrow stiff material

→ flat well \Rightarrow material is easily deformed

Derivation of Young's Modulus from interatomic potential for a cubic lattice



→ F_A (Apply a tensile force)

- extend lattice by δr (until eq^{rr}) until force balanced

$$F_A = -F_R(a + \delta r)$$

- relating E & V(r)

using Taylor Series:

if $f(r)$ can be differentiated at a , we can write it as:

$$f(x) = f(a) + \frac{f'(a)}{1!}(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \dots$$

where $f'(a)$ denotes $\left.\frac{df}{dx}\right|_a$ & $x = a + \delta r$ is a differentiable pt.

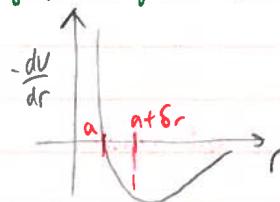
$$F_R(a + \delta r) = F_R(a) + \left.\frac{dF_R}{dr}\right|_a (a + \delta r - a) + \dots$$

$$\hookrightarrow F_R(a + \delta r) = \left.\frac{dF_R}{dr}\right|_a \delta r = F_A$$

$$\sigma = \frac{F_A}{A} = \frac{F_R}{a^2} \quad (\text{area of one bond} = a^2)$$

$$\sigma = \frac{dF_R}{dr} \left.\right|_a \delta r \times \frac{1}{a^2} = -\frac{1}{a} \left.\right|_a \frac{dF_R}{dr} \left.\right|_a$$

$$\sigma = -\frac{1}{a} \varepsilon \left.\right|_a \frac{dF_R}{dr} \quad (F_R = -\frac{dV}{dr})$$



$$\boxed{E = \frac{\sigma}{\varepsilon} = -\frac{1}{a} \left.\right|_a \frac{dF_R}{dr}}$$

$$\boxed{E = \frac{1}{a} \left.\right|_a \frac{d^2V}{dr^2}}$$

Elastic energy

↳ potential energy stored in a material
as work is performed to distort its shape

elastic energy stored per unit volume

→ apply a force \Rightarrow stretching bonds does work on material
[tensile stress]

$$W = Fdl$$

$$\text{volume} = Al$$

$$W = \frac{Fdl}{V} \times V$$

$$= \frac{F}{A} \frac{dl}{l} \times V$$

$$d\varepsilon = \frac{dl}{l}$$

$$\sigma = \frac{F}{A}$$

$$\int \rightarrow W = V \sigma d\varepsilon$$

using $dU = Q + W$ (assume all work goes into internal energy, $Q=0$)

$$dU = V \sigma d\varepsilon$$

deforming a material from strain = 0 to strain = ε

$$\frac{V}{V} = \int_0^\varepsilon \sigma d\varepsilon \approx E \int_0^\varepsilon \varepsilon d\varepsilon \quad \begin{matrix} E = \frac{\sigma}{\varepsilon} \\ \sigma = E\varepsilon \end{matrix}$$

$$\frac{V}{V} = \frac{1}{2} E \varepsilon^2 = \frac{1}{2} \sigma \varepsilon$$

elastic energy stored per unit volume

- Solids:

dimensionally stable \Rightarrow has volume of its own

- crystal: solid in which the comprising atoms/ion/molecules form a periodic arrangement

- 3 important definitions to describe a crystal

- lattice: an infinite set of identical pts within the crystal (grid of pts)

- unit cell: repeat unit (lego brick)

- basis: content of the unit cell

2D Lattices

- need to tile space seamlessly (no gaps)

- need to tile space by translation only

• squares • rectangles • triangles

- note • diff symmetries

• need 2 vectors & one angle

to describe shape

Lattice: an infinite set of identical pts within the crystal

- array of pts (entire grid)

- mathematical abstraction

- describes underlying periodic structure
but NOT the crystal itself

Basis: content of the unit cell

- may contain one atom or many atoms

- constituent of basis described by 'fractional coordinates' \rightarrow
of unit cell

Crystal structure: defined as a convolution of basis & lattice

Lattice pts: points of the lattice

if one lattice pt @ the origin, then:

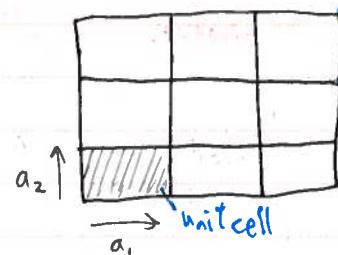
$$r = l_1 \underline{a}_1 + m_2 \underline{a}_2, (2D) ; r = l_1 \underline{a}_1 + m_2 \underline{a}_2 + n_3 \underline{a}_3, (3D)$$

Lattice vector: vector joining any two lattice points

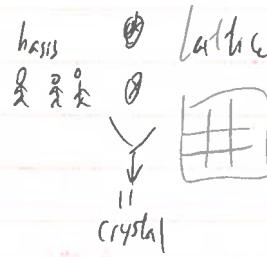
\rightarrow can be written as a linear combination of unit cell vectors

$$\text{eg } \underline{t} = V\underline{a}_1 + V\underline{a}_2 + W\underline{a}_3 \quad \underline{t} \Rightarrow \text{can be written as } [V \ V \ W]$$

vectors specified along diff directions in unit cell



lattice pts:
vertices of
unit cell

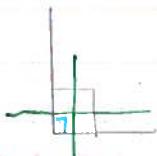


Bravais Lattice:

an infinite periodic lattice that displays translational invariance

[looks like the same from every lattice pt.]

$2D \Rightarrow 5$ Bravais Lattice



square

$$a=b$$

$$\gamma=90^\circ$$

$\sqrt{2}$ fold axis

2 mirror planes

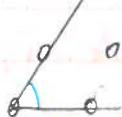


hexagonal

$$a=b, \gamma=120^\circ$$

3-fold

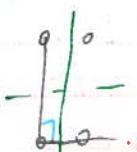
axis



oblique

$$a \neq b, \gamma \neq 90^\circ$$

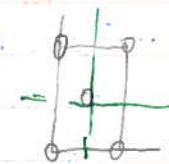
no symmetry



rectangular primitive

$$a \neq b, \gamma=90^\circ$$

two mirror planes



rectangular centred

$a \neq b, \gamma \neq 90^\circ$
(more than one lattice site)

- ⇒ rectangular primitive & centred \Rightarrow symmetry revealed by drawing a larger unit cell
- ⇒ lattice 'looks identical' from each lattice site
- ⇒ allowed lattices must be able to 'tile 2d space' by translation only

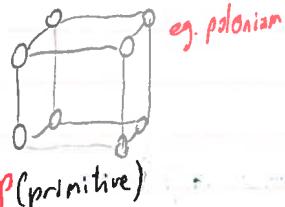
14 Diff Bravais Lattices in 3D

7 close: (see inorg note for others)

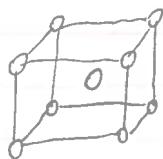
Cubic!

$$a=b=c$$

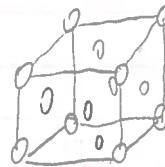
$$\alpha=\beta=\gamma=90^\circ$$



e.g. polonium



I (body-centred)



e.g. NaCl
diamond

tetragonal, orthorhombic

monoclinic, hexagonal, triclinic

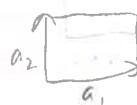
trigonal = rhombohedral

Conventional lattice unit cell:

smallest building block chosen to

reflect the underlying symmetry of the lattice

a) primitive



b) non-primitive



c) non-conventional



Primitive unit cell: minimum area/volume that when translated

by all Bravais lattice vectors just fills space

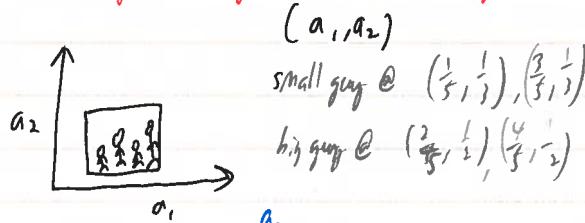
Not uniquely defined and primitive unit cell contains one & only one lattice site

do not always reflect symmetry of lattice each primitive unit cell has the same area

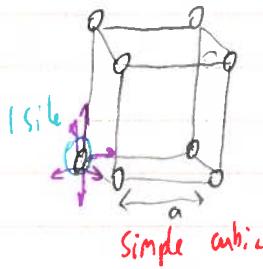
Describing a crystal structure in 2D

- rectangular unit cell, cell vectors a_1, a_2

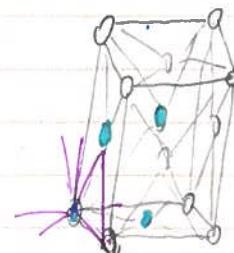
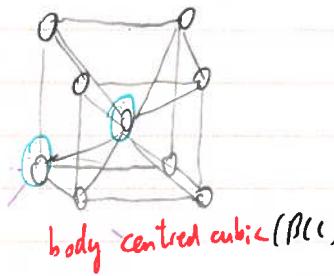
- basis defined as: fractional coordinates of unit cell



Cubic structures!



$$|a_1| = 15 \text{ fm} = 19 \text{ Å}$$



number of
lattice sites
in cubic cell

coordination no.

number of nearest neighbour
of atoms/ions

Important: cohesive energy which is
related to free energy (most stable form)
is dominated by nearest neighbours contributions

6

8

12

linear

triangular

trigonal (4-fold)

octahedral

(4 fold)

(4 fold 8)

(6-fold)

cubic (8-fold)

12 fold

Packing fraction: 0.52

0.68

0.74

ratio of total volume of object
packed into a space to the volume
of that space

Atomic Packing Fraction: $\frac{\text{no. of atoms in unit cell}}{\text{volume of one atom}}$

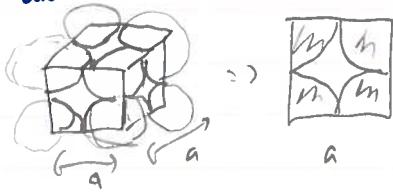
$$\text{APPF} = \frac{\frac{N_a \cdot V_a}{V_u}}{V_u}$$

$N_a \cdot V_a$ volume of one atom
 V_u volume of unit cell

Packing fractions:

$$APF = \frac{N_a V_a}{V_u}$$

simple cubic



$$\text{Radius of one sphere} = \frac{a}{2} = r$$

1 atom in unit cell for simple cubic

$$APF = \frac{1 \times \frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = \frac{\frac{4}{3}\pi\frac{a^3}{8}}{a^3} = \frac{\pi}{6} = 0.52$$

FCC



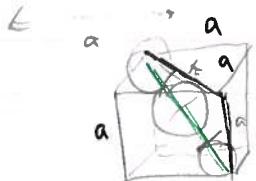
$$r = \frac{a}{4}; 4 \text{ atoms in unit cell}$$

$$APF = \frac{4 \times 4 \pi \times \left(\frac{a}{4}\right)^3}{a^3} = 0.74$$

BCC



~~$$APF = \frac{2 \times \left(\frac{\sqrt{3}a}{4}\right)^3 / 6\pi}{a^3} = 0.68$$~~



$$d = (\sqrt{2}a)^2 + a^2 \\ = \sqrt{3}a$$

$$\text{radius of one sphere} = \frac{\sqrt{3}a}{4}$$

Metals : Maximize no. of neighbours to minimize energy

- fa, hcp, bcc

Cubic \downarrow ABABA

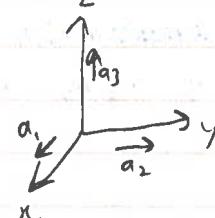
Crystal planes

- surfaces - cuts along diff. planes
- diff. arrangement of atoms
- diff. functionality (e.g. catalysis)

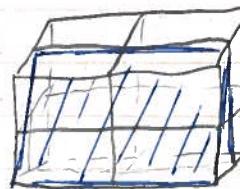
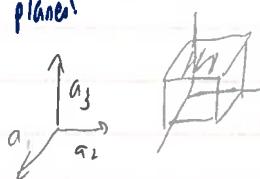
Miller indices: defined such that the plane closest to the origin has the intercepts a_1/h , a_2/k , a_3/l

- describing planes in crystals

- aim is to define a plane in a crystal
- lattice vector: $\vec{t} = u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3$



planes



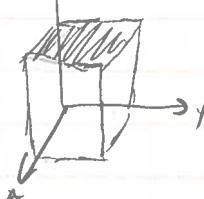
defining any plane in the crystal (not just for unit cells)

Miller indices method in general $x(h) \ y(k) \ z(l)$



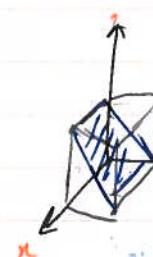
| $u\vec{a}_1$ | $v\vec{a}_2$ | $w\vec{a}_3$ |
|----------------|---------------|---------------|
| intercept | 2 | 2 |
| reciprocal | $\frac{1}{2}$ | $\frac{1}{2}$ |
| Miller indices | 3 | 3 |

Miller index (332) - no commas
- normal bracket



| $u\vec{a}_1$ | $v\vec{a}_2$ | $w\vec{a}_3$ |
|----------------|--------------|--------------|
| intercept | ∞ | ∞ |
| reciprocal | 0 | 0 |
| Miller indices | 0 | 0 |

(001)



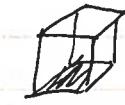
| $u\vec{a}_1$ | $v\vec{a}_2$ | $w\vec{a}_3$ |
|----------------|--------------|--------------|
| intercept | 00 | 1 |
| reciprocal | 0 | 1 |
| Miller indices | 0 | 1 |

(011)



| $u\vec{a}_1$ | $v\vec{a}_2$ | $w\vec{a}_3$ |
|----------------|--------------|--------------|
| intercept | 00 | 1 |
| reciprocal | 0 | 1 |
| Miller indices | 0 | 1 |

(001)



curly bracket
{110} for a family

1. write down intercepts with the axis

2. take reciprocal

3. reduce fractions
eg. multiply lowest common denominator



(100)



(110)



(111)

| $u\vec{a}_1$ | $v\vec{a}_2$ | $w\vec{a}_3$ |
|----------------|--------------|--------------|
| intercept | 00 | 1 |
| reciprocal | 0 | 1 |
| Miller indices | 0 | 1 |

(111)

Know diffraction & EM spectrum

$$\lambda = d \sin\theta$$

X-ray by Röntgen

Thermal emission of e/s from cathode

- accelerate w/ voltage to anode target

- emission of EM radiation (energy $\sim eV = h\nu = hc/\lambda$)

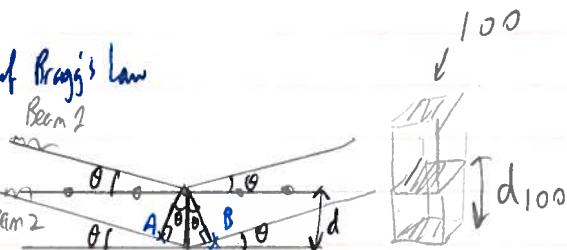
- 1000V acceleration gives an estimation $\lambda \sim 10^{-10}$ m

Law: diffraction of X-ray by atoms in zinc blende ZnS

- d-spacing of planes:

- each plane has an associate d-spacing

↳ distance between that particular set of planes



beams are monochromatic

coherent (in-phase)

X-rays

assuming reflection of X-ray from crystal planes

(actually X-rays elastically)

Scattered from e/s

Beam 1 scatters/reflects on top plane

Beam 2 scatters/reflects on bottom plane

Beam 2 travels AO to OB extra than beam 1

$$\sin\theta = \frac{AO}{d}$$

$$AO = d \sin\theta$$

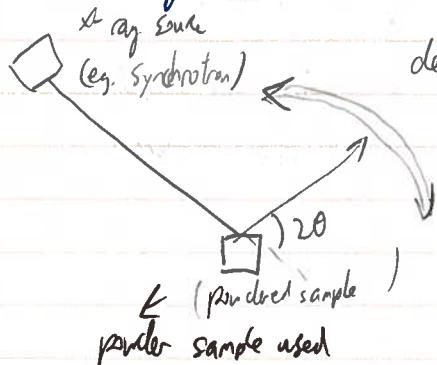
Beam 2 travels $2 \times AO = 2 d \sin\theta$ more than beam 1

* constructive interference, distance must be an integer number of λs.

$$\lambda = 2 d \sin\theta \rightarrow \text{Bragg's Law}$$

↑ separation of planes

Powder X-ray diffraction experiment



- crystal containing many different crystallites in all orientations
- θ to ensure Bragg condition met for all planes in this geometry

Neutrons vs. X-ray scattering

neutrons

- scatter strongly from light elements

X ray

- scatter strongly from heavy elements

rings easier
to measure the lab

e/s

- excellent for nanosized objects

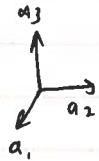
- can do imaging & diffraction
in same experiment

if using single crystal:

gives us a complementary
picture compared to that
from X-rays

spots which depend on alignment of crystal wrt the beam
i.e. \rightarrow more information about the structure

Calculation of the d_{hkl} distance for cubic lattices.



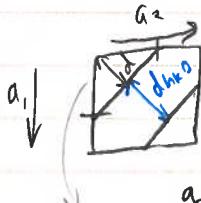
$$d_{100} = a$$

consider d_{hkl}

- Miller indices are defined
such that the plane closest
to the origin has intercepts $\frac{a_1}{h}, \frac{a_2}{k}, \frac{a_3}{l}$



$$d_{110} = \frac{\sqrt{2}a}{2}$$



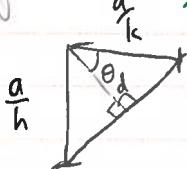
$$\cos \theta = \frac{d}{a/a} = d \frac{k}{a}$$

$$\cos(90^\circ - \theta) = \sin \theta = \frac{d}{a/k} = d \left(\frac{l}{a}\right)$$

$$\cos^2 \theta + \sin^2 \theta = 1$$

$$d^2 \left(\frac{h}{a^2}\right) + d^2 \left(\frac{k}{a^2}\right) = 1$$

$$\frac{h^2 + k^2}{a^2} = \frac{1}{d_{hkl}^2}$$



$$\rightarrow \text{enlarging to 3d } (hkl): \frac{h^2 + k^2 + l^2}{a^2} = \frac{1}{d_{hkl}^2}$$

} only for
orthogonal
axes

$$d_{hkl} = \sqrt{\frac{a^2}{h^2 + k^2 + l^2}}$$

- for cubic
lattice

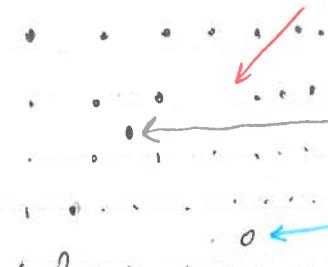
Defects

- 0 point defects
 - 1D line defects (dislocations)
 - 2D defects (grain boundaries)
- Can be good or bad
- ☺ defects are present in every material

Point Defects / 0D defects.

- a 0-dimensional defect as crystal is disrupted as a pt

Several types:



vacancy - an atom is missing from lattice site

self-interstitial - an atom is sitting in a crystal that is not a lattice site

interstitial impurity - an impurity atom is sitting between the lattice site

of a crystal

Interstitial Impurities

e.g. carbon in iron \rightarrow steel
→ carbon atom stop
dislocation movement \rightarrow less brittle

e.g. hydrogen storage of fuel cells

Materials that can store
high density of H₂ for fuel cells

BUT hydrogen interstitials

weakens iron/steel

- need new pipe

infrastructure

Substitutional Impurity:

e.g. in Cu, Al replaced w/ Mg

→ avoid dislocation \rightarrow enhance ductility
corrosion ^{or} resistant

e.g. - creating single spins for quantum computing
(e.g. ³P in Si (quantum info))

Hope diamond

Rubies (Al₂O₃ w/ Cr \leftrightarrow Al)

Sapphire (Al₂O₃ w/ Fe/Ti \leftrightarrow Al)

Amethyst (SiO₂ w/ Fe \leftrightarrow Si_i)

1D defects \rightarrow dislocations

deformation by moving dislocation

\rightarrow dislocation moves thru the crystal lattice

(see caterpillars, rugs & bubblerafts)

\hookrightarrow since one plane is slipping at a time,

only small fraction of bonds broken @ one time

Face centred cubic

* diff planes have diff packing densities



(111) is close packed

metals close packed structures

- metals have close packed planes (fcc is (111))

- bonding is strongest within close packed planes

- bonding is weakest normal to close packed planes

- dislocations move in close packed directions \rightarrow called slip planes

2D defects \rightarrow grain boundaries / planar defects

- most crystals are polycrystalline

\hookrightarrow grain boundaries (crystallites) are 2D join of diff crystallites

\hookrightarrow which form upon crystallisation

X-ray trap impurities \rightarrow structural weakness

- scatter e/s \rightarrow \downarrow conductivity

✓ - arrest dislocation

\hookrightarrow need fine grains to stop dislocations moving

with hardening

\rightarrow dislocation move through material & meet @ grain boundaries / diff. directions

\hookrightarrow they pile up & get stuck \rightarrow material is work hardened.

- can harden certain metals @ low T (e.g. Al, Cu, Steel)

More on thermodynamics!

100% A A ⇌ B

100% B

$$dG = VdP - SdT$$

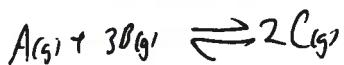
for pressure dependence & const $T \Rightarrow dT=0$

$$\int dG = VdP$$

$$\int_{G_0}^{G} dG = \int_{P_0}^P \frac{RT}{P} dP$$

$$G(P) = G_0 + nRT \ln \frac{P}{P_0}$$

consider :



$$2G_C - G_A - 3G_B = 2\left[G_C^\circ + RT \ln \frac{P_C}{P_0}\right] - G_A - RT \ln \frac{P_A}{P_0} - 3\left[G_B^\circ + RT \ln \frac{P_B}{P_0}\right]$$

$$\Delta_R G - \Delta_R G^\circ = RT \ln \frac{\left(\frac{P_C}{P_0}\right)^2}{\left(\frac{P_A}{P_0}\right)\left(\frac{P_B}{P_0}\right)} = RT \ln Q$$

at standard conditions

$$P.P. \text{ for all species} = 1 \text{ bar } (P_0) \Rightarrow Q = K^\circ$$

$$\Rightarrow RT \ln K^\circ = 0$$

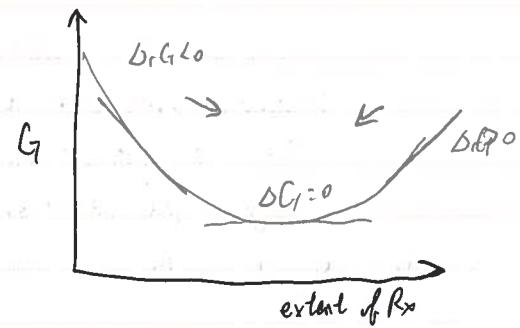
$$\Rightarrow \Delta_Q G = \Delta_R G^\circ$$

for any Ra mixture

$$\Delta_R G = \Delta_R G^\circ + RT \ln Q$$

$$\Delta_R G = 0$$

$$\Rightarrow \Delta_R G^\circ = RT \ln K^\circ$$



State functions & exact differentials: (some tricky definitions)

Def:

State function: property that depends only on the current state of the system

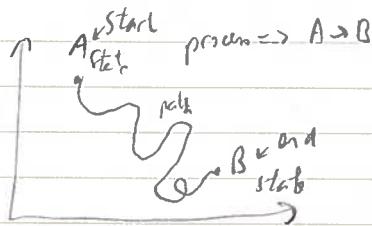
[account holder's] AND independent of its history eg. U, H
Me & Alka's money

Path functions: Path dependent physical quantities

[transaction process] eg. Q, W

eg deposit, buy etc. [do not speak of a system actions spending/earning in a particular state as possessing work or heat]

↳ energy transferred as $W/Q \Rightarrow$ relates to the path taken between states, not the current state itself



Exact differential: infinitesimal quantity, when integrated, gives a result which is independent of the path between initial & final states

$$dU = \int_i^f dU$$

Inexact differential: infinitesimal quantity, when integrated, give a result which depends on the path between initial & final states

↳ recalling line integrals:

$$\oint C(r) \cdot dr = \int_{t_1}^{t_2} C(r(t)) \cdot r'(t) dt$$

Extensive property: property which depends on the amount of substance in the sample eg mass, volume.

Intensive property: property which are independent of the amount of substance in the sample eg. temp., mass density, pressure, partial molar quantities

die Reaktionen an der Aue mit Wasser und Säure
abzuschätzen.

Was kann ich tun?

Um die Reaktionen zu verstehen, muss man
die Reaktionen im Wasser untersuchen.

Was kann man tun, um die Reaktionen im Wasser
zu verstehen?

Was kann man tun, um die Reaktionen im Wasser
zu verstehen?