

THERMODYNAMICS STATISTICAL MECHANICS

PH332

①

Feb 6, 2019

Thermodynamics

- macroscopic properties of system P, V, T, etc.
- used w/ systems that are large enough that microscopic fluctuations can be ignored

Stat mech

- individual states of atoms / microscopic states of particles in system + uses statistics to describe macroscopic behavior

This course focuses on systems of large numbers of particles.
 ? → how large?

Large? 1 mole $\rightarrow N_A = 6.022 \times 10^{23}$ particles \rightarrow Avogadro's #

Why need statistics? \rightarrow Ex. Say we want to count # of particles in a mole of water.

$3\text{GHz} \rightarrow 3 \times 10^9 \text{ s}^{-1}$ count rate $\rightarrow 2 \times 10^{14} \text{ s} = 6.4 \times 10^6 \text{ yrs.}$
 \rightarrow needs stats models...

What is a mole? \rightarrow A mole is the amount of matter that contains as matter as 12g of ^{12}C

Molar Mass

M: mass of 1 mole of a substance in grams.

$$\begin{aligned} \text{Ex } M_{^{12}\text{C}} &= 12 \text{ g/mol} & M_{\text{H}_2\text{O}} &\approx 18 \text{ g/mol} \\ M_{^{4}\text{He}} &= 4 \text{ g/mol} \end{aligned}$$

Temperature

\rightarrow always use K. Don't use Fahrenheit.

Fahrenheit scale \rightarrow freezing point of water: 32°F
 Boiling point of water: 212°F

Celsius \rightarrow

$${}^\circ\text{F} = 32 + \frac{9}{5} {}^\circ\text{C}$$

0°C

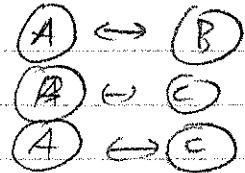
100°C

$$T_{(K)} = T_{(C)} + 273.15$$

What is temperature?

0th law of thermodynamics

- { If A is in thermoequilibrium with B
 - but C is in thermoequilibrium with C
 - then A = C
- "thermoequilibrium" = same T.



Temperature: a measure of how likely it is for a system to give energy to another system. Generally, higher T → more likely to give off energy

\rightarrow

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Ideal Gas Law

$$PV = nRT$$

or

$$PV = Nk_B T$$

n : # of moles R : Gas constant 8.31 J/mole

N : # of particles k_B : Boltzmann Constant $= 1.38 \times 10^{-23} \text{ J/K}$

$$\therefore nR = Nk_B$$

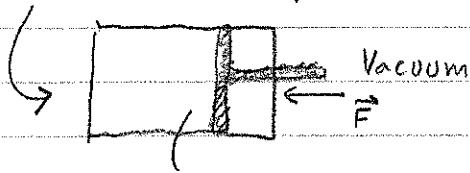
Note $N = nN_A \therefore$

$$R = N_A k_B$$

$$\text{or } k_B = \frac{R}{N_A}$$

Assumptions: point-like particles, don't interact

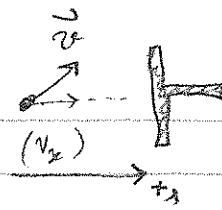
How does Temperature T of ideal gas relate to its KE?



$$\text{Pressure} = \frac{F}{A} = \frac{1}{A} \frac{dp}{dt} = \frac{1}{A} \frac{\Delta p}{\Delta t}$$

* assume perfectly elastic collision

(1) Change in momentum of single particle.

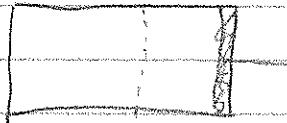


$$\Delta p = mv_f - mv_i$$

$$= -mv_x' + mv_x = -2mv_x$$

So $\Delta p_{\text{piston}} = 2mv_x$

(2) # of collisions?



assume N molecules in volume V

$$\text{density} = \frac{N}{V} = \frac{\text{# molecules}}{\text{volume}}$$

So # of collisions = $\frac{N}{V} \cdot (v_x t)$

so # collision/sec = $\frac{N}{V} (v_x A)$

(3) Force on piston

$$F = \frac{\Delta P}{\Delta t} = (2mv_x) \left(\frac{N v_x A}{V} \right)$$

$$= 2mv_x^2 \frac{NA}{V}$$

So $P = \frac{F}{A} = 2mv_x^2 \frac{N}{V}$

Now, corrections. Not all particles have the same v_x .

$\rightarrow \langle v_x^2 \rangle$ instead of v_x^2 . Also, $1/2$ of particles are moving in the other direction ($-v_x$) \rightarrow divide by 2

So $P = m \langle v_x^2 \rangle \frac{N}{V}$

$$\text{Now } v^2 = v_x^2 + v_y^2 + v_z^2$$

$\Rightarrow PV = m \langle v^2 \rangle N$

\Rightarrow Assume $\langle v^2 \rangle$ equal

$$\Rightarrow \langle v^2 \rangle = \langle v_x^2 \rangle$$

(4)

$$\text{So } PV = NkT = \frac{1}{3}m\langle v^2 \rangle N \blacktriangleleft = \frac{2}{3}\left[\frac{1}{2}m\langle v^2 \rangle\right]N$$

$$\text{So } kT = \frac{2}{3}\langle KE \rangle$$

$$\text{So } \langle KE \rangle = \frac{3kT}{2}$$

Average speed of the particles?

$$\text{Naively } \frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}kT \quad = mN_A$$

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

(g), not $M = m/N_A^{-1}$

↑

But this is NOT

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

$\langle v \rangle$

$$\langle v \rangle = \sqrt{\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle}$$

We will (can) show that

$$\text{But } \langle v^2 \rangle = \sqrt{\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle}$$

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}} < v_{rms}$$

v_{rms}

Ex Find rms v of N_2 molecule at room temp, $\sim 300K$

$$v_{rms} = \sqrt{\frac{3k \cdot 300}{28/N_A}} \approx$$

$$\text{or } v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3nRT}{nM}} = \sqrt{\frac{3RT}{M}} \approx \sqrt{\frac{3 \cdot 8.31 J/mol \cdot K \cdot 300}{28 g/mol}}$$

$$\text{Now } 28 \text{ g/mol} = 28 \times 10^{-3} \text{ kg/mol} \rightarrow v_{rms} \approx 517 \text{ m/s}$$

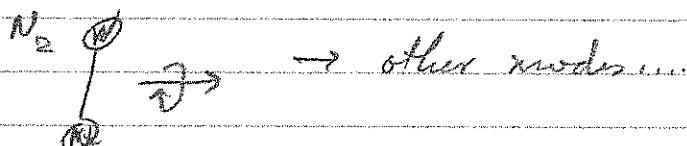
(5)

What's the total thermal energy of a gas?

$$U = \frac{3}{2} kT \cdot N = \langle KE \rangle N \rightarrow \text{but only true for monatomic ideal gas}$$

↳ like noble gas.

why? Degrees of freedom



If translational motion is not the only contributing factor

↳ Equivibration theorem

{ At some temp T, the average energy for energy }
 quadratic degree of freedom = $\frac{1}{2} kT$
 ex. $\frac{1}{2} m(v^2)$

So

$$U_{\text{thermal}} = Nf \frac{1}{2} kT \quad f = \# \text{ of quadratic df}$$

Degrees of freedom?

↗ for a gas

↳ translational : x, y, z (3 df)

• rotational : how many axes of rotations introduce asymmetries?

$$\text{ex. } \textcircled{1} \text{ } \textcircled{2} \text{ } \textcircled{3} \text{ } \rightarrow (2 \text{ df})$$

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Ex $\text{H}_2\text{O} \rightarrow (3 \text{ df})$

• vibrational (O-H-O) \rightarrow classical mech tells us KE

$\langle \text{KE} \rangle = \langle \text{PE} \rangle$ for SHO \rightarrow 2 degrees of freedom,
both quadratic

at normal temp

\rightarrow small effect. Most diatomic molecules only have (5) df at typical room temp, as vibr. df are frozen out.

$$\rightarrow U_{\text{internal } \text{N}_2} \approx N \cdot \left(\frac{3+2+0}{2} \right) kT$$

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Heat = Work

\rightarrow Exchange is energy

last time $U = \frac{f}{2} N kT$

{ Heat (Q) \rightarrow spontaneous flow of energy from one system to another due to a ΔT }

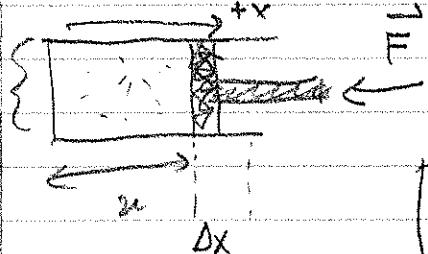
↳ [if $\Delta T \neq 0$, then $Q \neq 0$ (Heat) spontaneously]

{ Work (W) non-spontaneous transfer of energy
 \rightarrow need an "agent" to transfer energy }

Heat & Work are not intrinsic to system. \rightarrow They're processes.

Compression work

A



$$P = \frac{F}{A}$$

positive, since $\Delta x < 0$

[$W_{\text{on gas}} = -F \Delta x = -PA \Delta x = -P \Delta V$]

(7)

So $W_{\text{on gas}} = -P\Delta V$

- Q Ques Should use differentials, but they are not exact diff. because of path-dependence

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

A differential is exact if $\exists f = f(x, y)$ such that

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$$

→ True for conservative vector fields $\vec{v} = \nabla f$

$$A = \frac{\partial f}{\partial x}$$

In other words, $df = Adx + Bdy$ exact diff. if $\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}$

$$\vec{\nabla} \times [A, B] = \begin{vmatrix} \frac{\partial}{\partial x} & \frac{\partial}{\partial y} \\ \frac{\partial f}{\partial x} & \frac{\partial f}{\partial y} \end{vmatrix} = \frac{\partial^2 f}{\partial x \partial y} - \frac{\partial^2 f}{\partial y \partial x} = 0$$

Can use Euler's test to determine if we have an exact diff.

Let $df = Adx + Bdy$

check if $\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}$ → Yes? → Exact

↓ No? → Not exact

Exact differentials are written as $\rightarrow dw$ or ds

→ path-dependence!

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- ◻ Inexact differentials can become exact by multiplying by some integrating factor.

e.g. $\frac{dw}{P} = dV \rightarrow$ volume $dV \rightarrow$ exact diff

$$\left\{ \frac{dT}{T} = \frac{ds}{s} \rightarrow \text{entropy} \quad ds \rightarrow \text{exact diff} \right.$$

- ◻ If Q & W are the only ways energy is transferred, their conservation of energy

$$\boxed{\Delta U = Q + W_{on}} \rightarrow 1^{\text{st}} \text{ law of thermodynamics}$$

Q : heat added to system, W : work done on system

In differential $\rightarrow \boxed{dU = \delta Q + \delta W_{on} = \delta Q - \delta W_{by}}$

Units of energy $\rightarrow 1 \text{ J} \rightarrow 1 \text{ kg m}^2/\text{s}^2$

1 cal $\rightarrow 4.186 \text{ J}$

1 cal \rightarrow heat needed to raise 1g of H₂O by 1°C or 1K

Cloud-like shape containing the text "Compression Work"

$$W_{on} = -Fdx \stackrel{?}{=} -PAV$$

(Let $P \rightarrow P(V)$)

\curvearrowleft
 $x \Delta x$

Refer, we assumed that P is constant over the process \rightarrow assumed piston movement was slow

(9)

Quasi-static process → slow process, allow P to equilibrate

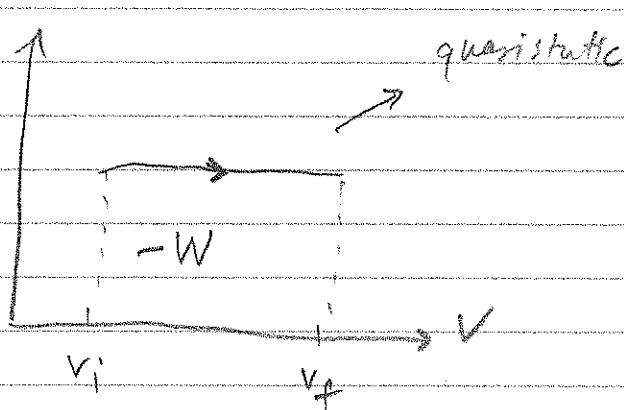
$$\rightarrow W_m = -P\Delta V \quad \text{or} \quad dW_m = PdV$$

Note there is heat flow in quasi-static process

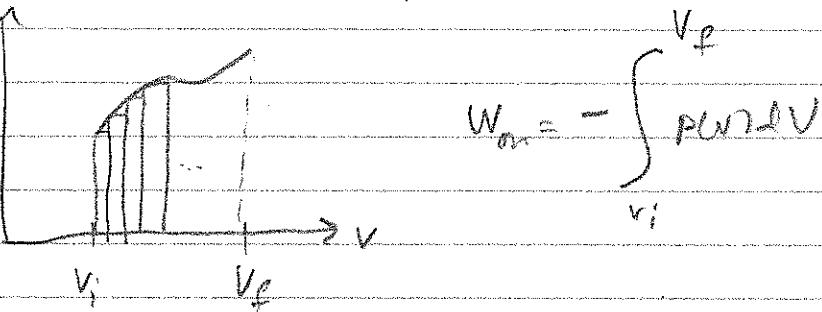
We often consider infinitesimal changes that are each quasistatic
in their neighborhood

$$W_{\text{on}} \approx - \int_{V_1}^{V_2} P(V)dV$$

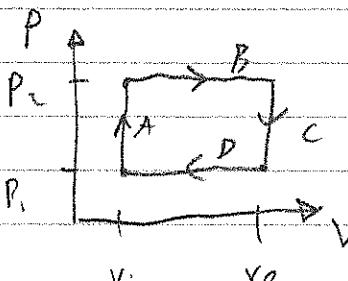
P-V diagrams



Non-quasi-static



Example of PV diagram Interpreting PV diagrams



An ideal diatomic gas (N_e)

For steps A \rightarrow D, we want to determine
 W_m , Q_{add} , ΔU , and W_{total} , Q_{tot}

(10)

	A	B	C	D	E
W_m	0	$P_2(V_1 - V_2)$	0	$P_1(V_2 - V_1)$	< 0
Q	$\sum V_1(P_2 - P_1)$	$\frac{1}{2}P_2(V_2 - V_1)$:	:	> 0
ΔU	$\frac{1}{2}\sum V_1(P_2 - P_1)$	$\frac{1}{2}P_2(V_2 - V_1)$:	:	0

A: $W = 0$, $\Delta U = \frac{f}{2}NkT = \frac{f}{2}Nk \frac{PV}{NkT} = \frac{f}{2}PV$

So $\Delta U_A = \frac{f}{2}V_1 \Delta P$

$$\Delta U = Q + W$$

B $\Delta U = \frac{\sum P \Delta V}{2} = \frac{1}{2}P_2(V_2 - V_1)$

$$Q = \Delta U - W = \frac{1}{2}P_2(V_2 - V_1) - P_2(V_1 - V_2)$$

Note $\left\{ \begin{array}{l} W_{on, total} < 0 \\ Q > 0 \\ \Delta U = 0 \end{array} \right\}$

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Quasistatic process "slow" \rightarrow so that system can equilibriate
 \rightarrow pressure is uniform over system

$$W_{on} = -F\Delta x \rightarrow -P\Delta V$$

Not-quasistatic "fast" \rightarrow pressure depends on position

Compressing of an ideal gas

Isothermal compression

"slow" compression such that
 $T = \text{constant}$

Temp doesn't increase

$$\Delta U = W_m + Q_{add} \rightarrow Q \text{ leaves system} \rightarrow \Delta U = 0$$

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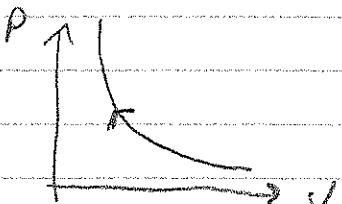
Adiabatic compression \rightarrow "fast" compression. So fast that no heat can escape

$$\partial = 0 \quad \therefore \Delta U = W + Q_{\text{add}} = W_m$$

\rightarrow Temp increases

P-V diagram

Isothermal process \rightarrow Quasistatic



$$W_m = - \int_{V_i}^{V_f} P(V) dV = - \int_{V_i}^{V_f} \frac{NkT}{V} dV \quad \hookrightarrow PV = \text{const}$$

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

$$W_m = - NkT \ln \left(\frac{V_f}{V_i} \right)$$

\rightarrow Work done on system
in isothermal compression.

Since T does not increase, how much heat is lost?

$$\downarrow \Delta U = W_m + Q_{\text{add}} = 0 \quad \text{or} \quad \{ W_m = Q_{\text{out}}$$

$\downarrow \Delta T$

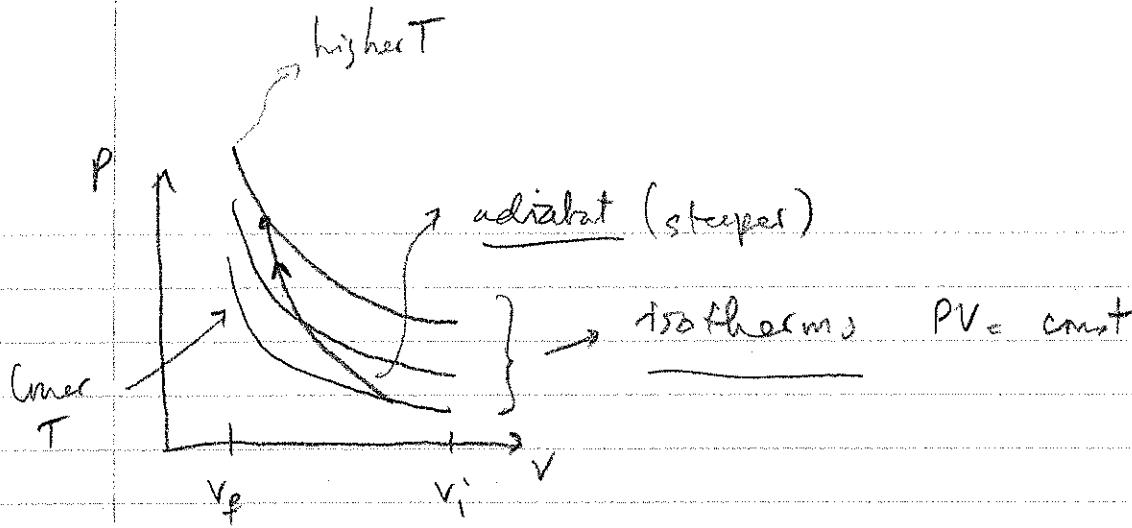
$$\therefore Q_{\text{add}} = - W_m = NkT \ln \left(\frac{V_f}{V_i} \right)$$

Adiabatic process \rightarrow fast

Adiabatic process ... $\Delta U = W_m + Q_{\text{add}}$

By definition of adiabatic $\rightarrow Q = 0$

$\} \rightarrow \Delta U = W_m$



How do different parameters change during adiabatic compression?

For ideal gas $\Delta U = \underline{W} + Q = W$

$$U = \frac{f}{2} NkT \rightarrow dU = \frac{f}{2} Nk dT = dW = -PdV$$

$$\int \frac{f}{2} Nk dT = - \frac{NkT}{V} dV$$

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

$$\text{So } \frac{f}{2} \ln\left(\frac{T_f}{T_i}\right) = - \ln\left(\frac{V_i}{V_f}\right)$$

$$\left(\frac{T_f}{T_i}\right)^{\frac{f}{2}} = \left(\frac{V_i}{V_f}\right)^{-1} \rightarrow V_i T_i^{\frac{f}{2}} = T_f^{\frac{f}{2}} V_f$$

$$\boxed{V T^{\frac{f}{2}}} \rightarrow \text{constant}$$

→ adiabatic compression/expansion

Can write this in volume & pressure of ideal gas

$$T = \frac{PV}{Nk} \rightarrow V \cdot \left(\frac{PV}{Nk}\right)^{\frac{f}{2}} \rightarrow \text{constant} \quad \left\{ \Rightarrow PV^{1+\frac{2}{f}} = \text{constant} \right.$$

$$\left. \rightarrow P^{\frac{f}{2}} V^{1+\frac{f}{2}} \rightarrow \text{constant} \right\} \text{Call } \gamma = 1 + \frac{2}{f} = \frac{f+2}{f}$$

$$\rightarrow P V^{\frac{(1+\gamma)}{f}} \rightarrow \text{constant} \quad \rightarrow \boxed{P V^\gamma = \text{constant}}$$

We call $\gamma \rightarrow$ "adiabatic exponent" $\gamma = \frac{f+2}{f}$

$$\gamma = \frac{f+2}{f} \quad \text{is} \quad PV^\gamma = \text{constant}$$

$$VT^{1/\gamma-1} = \text{constant}$$

Now, pressure & temp.

$$\hookrightarrow V^\gamma P = \text{constant} \quad \downarrow \quad VT^{-\gamma} = \text{constant}$$

$$\therefore (V^\gamma P)(V^{-\gamma} T^{-1/\gamma})$$

$$= PT^{-1/\gamma} \text{ constant}$$

$$\therefore \boxed{PT^{-1/\gamma}} \text{ constant}$$

Ex Diesel engine (no spark plugs...)

atm air is quickly compressed to $1/20$ original volume
 \rightarrow Estimate temp of air in cylinder...

$$\text{well } \frac{V_f}{V_i} = \frac{1}{20} \rightarrow \text{assume ideal gas (diatomic } \Rightarrow f=5)$$

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

$$\hookrightarrow \left(\frac{T_f}{T_i} \right)^{5/2} = \left(\frac{1}{20} \right)^{-1} = 20$$

$$\rightarrow \sqrt[5]{20} \approx 3^3 \rightarrow 300$$

$$\hookrightarrow T_f = \sqrt[5/2]{20 T_i} = \sqrt[5/2]{20} T_i$$

$$\hookrightarrow \boxed{T_f \approx 1000K \Rightarrow 700^\circ C}$$

\rightarrow hot enough to ignite Diesel without spark plug.

Heat capacity

↳ The amount of heat necessary to raise a substance by 1°C

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

$$Q = C\Delta T = mc\Delta T$$

Specific heat capacity

$$c = \frac{C}{m}$$

But recall → $Q = \Delta U - W_m$, limiting case $\rightarrow W=0$
 \rightarrow no change in V
 get heat capacity at constant volume, C_V

not the most physical

$$C_V = \frac{\Delta U - W}{\Delta T} = \frac{\Delta U}{\Delta T} = \left(\frac{\partial U}{\partial T} \right)_{V \text{ constant}}$$

Ex for 1g of H_2O $C_V = 1 \text{ cal/K}$

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Heat Capacity

$$\left. \begin{array}{l} \rightarrow W=0, \Delta V=0 \rightarrow C_V = \frac{\Delta U - W}{\Delta T} = \left(\frac{\partial U}{\partial T} \right)_{V \text{ const}} \\ \text{limiting cases} \quad \left. \begin{array}{l} \text{Constant volume} \\ \text{Constant pressure} \end{array} \right. \end{array} \right.$$



Heat capacity at constant pressure

$$C_P = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T} = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T} \right)_{P \text{ const}}$$

$$C_P = \left(\frac{\partial U}{\partial T} + P \frac{\partial V}{\partial T} \right)_{P \text{ const}}$$

→ heat needed to compensate for expansion

$$\text{Note } \left(\frac{\partial u}{\partial T} \right)_P \approx \left(\frac{\partial U}{\partial T} \right)_{V \text{ const}} \rightarrow$$

(energy loss at work due to expansion)

Suppose we have a system that obeys equipartition theorem

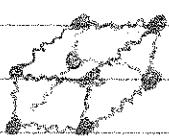
$$U = \frac{f N k T}{2}$$

then

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V, \text{constant}} = \frac{f N k}{2}$$

if we can measure C_V
then we can find f .

Ex



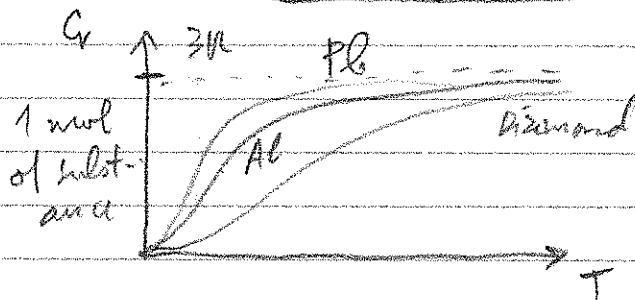
Consider solids/liquids

no rotation/translational

→ only f is rotation.

→ Solid should have 6 d.f.s

$$\therefore C_V = \frac{6 N k}{2} = 3 N k = 3 n R \rightarrow \text{for solids}$$



Heat capacity at constant pressure for ideal gas.

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

↓ above eq. partition.

$$= \frac{f N k}{2} + P \frac{\partial}{\partial T} \left[\frac{N k T}{P} \right]$$

$$+ n R = C_V + N k = C_P = \frac{f N k}{2} + N k$$

$$\text{Real } \gamma = \frac{f+2}{f} + \frac{2}{f}$$

$$= \left(\frac{f}{2} + 1 \right) N k$$

$$\rightarrow \gamma - 1 = \frac{2}{f}$$

$$C_P = \frac{\gamma}{\gamma-1} N k$$

$$\frac{f}{2} + 1 = \frac{1}{\gamma-1} + 1$$

Recall the Adiabatic exponent γ

$$\text{Definition} \rightarrow \gamma = \frac{C_p}{C_V} = \frac{C_V + nR}{C_V} = \frac{f/2 + 1}{f/2} = \frac{g+f}{f}$$

Example of heat capacity

Heat capacity of a star

$$\text{Well } U_{\text{pot}} = -\frac{GMm}{r} \quad KE = \frac{1}{2}mv^2 \quad v = \sqrt{\frac{GM}{r}}$$

S

$$k = \frac{1}{2}m \frac{GM}{r}$$

Virial
Theorem

$$\rightarrow U_{\text{tot}} = U_{\text{pot}} + KE = \frac{1}{2}m \frac{GM}{r} - \frac{GMm}{r} = -\frac{1}{2} \frac{GMm}{r}$$

$$-2KE \rightarrow U_{\text{tot}} = -k = -\frac{1}{2} \frac{GMm}{r}$$

Star $\{$ it goes (3 df) \rightarrow quadratic

$\{$ obeys eq. part. then $k = \frac{1}{2}mv^2 = \frac{f}{2}NkT = \frac{3}{2}NkT$

$$\therefore \boxed{U_{\text{tot}} = -\frac{3}{2}NkT}$$

$$\therefore \boxed{C_V = \left(\frac{\partial u}{\partial T}\right) = -\frac{3}{2}Nk} \rightarrow \text{negative heat capacity}$$

\hookrightarrow so, as a star radiates ε , it gets hotter.

Ex [Latent heat] → useful for phase transitions.

e.g. melting ice Solid \rightarrow liquid \rightarrow vapor

Note temperature stays constant during phase transitions.

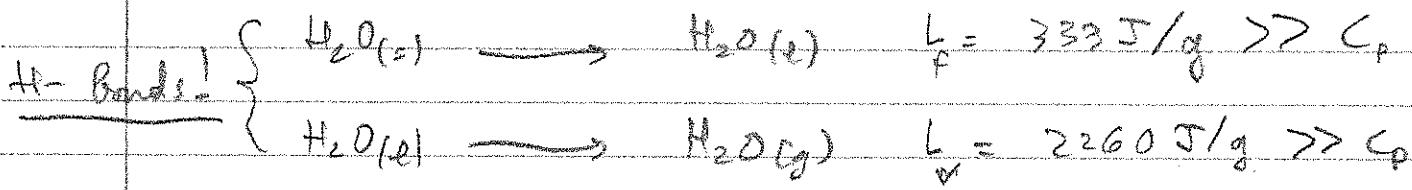
(need to know how much heat is needed to complete phase transitions)

$$\text{Latent heat } (L = \frac{\Delta Q}{m})$$

• Assume that $P = \text{constant}$ over phase transitions

• Assume that no other such bonds expansion/contraction

Ex Latent heat of fusion



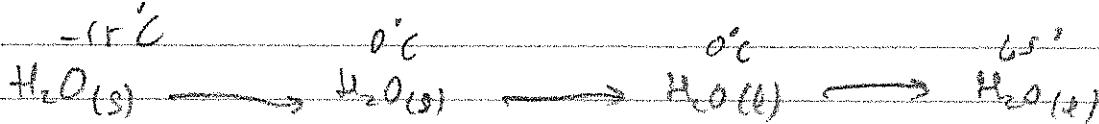
Ex 200g cup of tea that is @ boiling pt (212°F 100°C)

I want to cool down to drink $\sim 150^\circ\text{F} \sim 65^\circ\text{C}$
How much ice do we want?

$$T_{\text{ice}} = -15^\circ\text{C} \quad C_{\text{ice}} = 0.5 \text{ cal/gC}$$

$$C_{\text{H}_2\text{O}_{(l)}} = 1 \text{ cal/gC} \quad L_f = 80 \text{ cal/g}$$

$$\text{Q lost heat} = m_{\text{ice}} \Delta T C_{\text{H}_2\text{O}} = 200 (100 - 65) 1 \text{ cal} \\ = 7000 \text{ cal}$$



$$\frac{7000}{\text{Kcal}} = m C_p \Delta T + L \cdot m + m CDT$$

$$\text{So } m = \frac{7000 \text{ cal}}{C_{\text{p,0}}(0-(-15)) + L + (65-0) C_{\text{H}_2\text{O}(\text{l})}} \approx 46 \text{ g of ice}$$

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Enthalpy

→ total heat content of a system

$$H \equiv U + PV$$

→ useful for constant P processes

H is useful for constant - pressure processes.

Ex Add heat to a system at constant pressure. Then U, V, H change:

$$\text{So } H + \Delta H = U + \Delta U + P(V + \Delta V)$$

$$H + \Delta H = (\underbrace{U + PV}_{H}) + (\underbrace{\Delta U + P\Delta V}_{\Delta H})$$

$$\text{So } \boxed{\Delta H = \Delta U + P\Delta V} \rightarrow @ \text{constant pressure.}$$

First law if $\Delta U = Q + (-P\Delta V)$ → compression work + W_{other}

Then $\Delta H = \Delta U + P\Delta V = Q + W_{\text{other}}$

So

$$\boxed{\Delta H = Q_{\text{add}} + W_{\text{other}}} \rightarrow \text{true for constant P processes.}$$

Heat capacity at constant pressure

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

(19)

Examples ΔH for boiling H_2O (phase transition...)

$\Delta H = 40660 \text{ J/mol}$ at 1 atm, 298K

$$\Delta H = \frac{40660 \text{ J/mol}}{18 \text{ g/mol}} \approx 2260 \text{ J/g} = L_{H_2O}$$

↳ latent heat of vaporization

How much work is needed to create space for H_2O vapor.

$$V_f \approx 0 \quad V_f \approx \frac{nRT}{P} = \frac{RT}{P} \quad (n=1)$$

$$\therefore \Delta V = \frac{RT}{P} \rightarrow W = PDV = RT = 8.314 \text{ J/K} \cdot 298 \text{ K} \\ \approx 3100 \text{ J}$$

Statistics

Random Walk problem



$$\begin{cases} 1 & P(\text{left}) = P(\text{right}) = 1-p = q \\ 2 & P(\text{right}) = p \end{cases}$$

Final position $x = ml$ after N total steps where N_m are integers: $-N \leq m \leq N$

$\therefore P_N(m) = \text{Probability of finding one drunk at } x = ml$
after N steps.

$$\left. \begin{array}{l} \text{let } n_R = \# \text{ steps to R} \\ n_L = \# \text{ steps to L} \end{array} \right\} \quad N = n_R + n_L$$

$$\text{And } m = n_R - n_L = n_R - (N - n_R) = -N + 2n_R$$

Probability of any sequence of steps (ass. independent) is

$$P^{n_R} (1-p)^{n_L} = P^{n_R} (1-p)^{N-n_R} \quad \text{the products}$$

But there are many ways of taking N steps with $n_R = n_L$

The number of ways is called "Multiplicity", & S_2

↳ "of microstates"

$$S_2 = \frac{N!}{n_R! n_L!} = C_{n_R}^N$$

Say there are N objects $\rightarrow N!$ permutations. But this is only true for distinguishable objects, since order matters.

What about the # of ways N objects can be arranged into n_R spaces? where $n_R < N$

$$\hookrightarrow P_{n_R}^N = (N)(N-1) \dots (N-n_R) \frac{N!}{(N-n_R+1) \dots (N-n_R)!}$$

If we have indistinguishable objects, we have all $n_R!$ ways of arranging N into n_R spaces are the same \rightarrow divide them out

$$\rightarrow \frac{N!}{(N-n_R)! n_R!} = \frac{N!}{n_R! n_L!}$$

\rightarrow For indistinguishable objects, we can ignore ... Total multiplicity of outcomes

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

(21)

$$\text{So } P_N(n_R \geq n_L) = \binom{N}{n_R} p^{n_R} (1-p)^{N-n_R}$$

or other material

$$\hookrightarrow W_N(n_R) = \binom{N}{n_R} p^{n_R} (1-p)^{N-n_R} \rightarrow \text{same thing}$$

\hookrightarrow Binomial distribution

$$\text{Q} \sum_{n=0}^N W_N(n) = 1 \quad \text{E}(n) = Np \quad \text{D.V.} = Np(1-p)$$

Feb 18, 2019

Binomial Distribution

$$P_N(n) = \binom{N}{n} p^n q^{N-n}$$

$$\sum_{n=0}^N P_N(n) = 1$$

$$\text{More generally, } \sum_{n=0}^N W_N(n) = (p+q)^N$$

Example Roll 4 dice

$$P(\text{one of 4 is } \square) = \binom{4}{1} \left(\frac{1}{6}\right)^1 \left(\frac{5}{6}\right)^{4-1} = 1 - \left(\frac{5}{6}\right)^4 \approx 39\%$$

Example Roll 2 1's, 4 dice

$$P_4(2) = \binom{4}{2} \left(\frac{1}{6}\right)^2 \left(\frac{5}{6}\right)^{4-2} = \left(\frac{5}{6}\right)^2 \frac{1}{6} \approx 12\%$$

Note high multiplicity, don't rule likely outcome.

Random Walk

$$\begin{array}{c} \uparrow \\ \sum_{n=0}^N \end{array} \quad x = nl$$

What is the probability that we're back at $m=0$ after N steps?

(a) If N is even?

(b) If N is odd?

$$P_N(m) = \frac{N!}{n_R!(N-n_R)!} p^{n_R} (1-p)^{N-n_R}$$

$$N = n_R + n_L$$

$$m = n_R - n_L$$

$$\therefore N = 2n_L - m$$

$$= \frac{(n_R + n_L)!}{n_R! n_L!} p^{n_R} (1-p)^{N-n_R}$$

$$= \frac{N!}{\left(\frac{N+m}{2}\right)! \left(\frac{N-m}{2}\right)!} p^{\frac{N+m}{2}} (1-p)^{\frac{N-m}{2}}$$

Assume that $p = 1-p = \frac{1}{2}$

So

$$P_N(m) = \frac{N!}{\left(\frac{N+m}{2}\right)! \left(\frac{N-m}{2}\right)!} \cdot \left(\frac{1}{2}\right)^N$$

$$\boxed{\therefore P_N(m=0) = \frac{N!}{\left(\frac{N}{2}\right)! \left(\frac{N}{2}\right)!} \left(\frac{1}{2}\right)^N \Rightarrow \text{if } N \text{ even}}$$

if N is odd, then $m \neq 0$ since $N = 2n_L - m$

$$\boxed{\therefore P_N(m=0) = 0}$$

$\uparrow \pi \uparrow$
odd even odd

Determination of mean values

Random walk with $N = 2$ steps. Let's say after 2 steps, don't fish & and pick it up.

$$\text{C } x = -2l \quad \$1$$

$$\text{C } x = 0 \quad \$5$$

$$\text{C } x = 2l \quad \$20$$

Question or average, how much I would you fish up?

$$\text{Well } P_x(-2l) = ? \quad P_x(2l) = ? ; E(W) = ?$$

$$\rightarrow P_x(0) = 1/2$$

$$\left. \begin{array}{l} P_x(-2l) = P_x(2l) = 1/4 \\ \end{array} \right\}$$

"by inspection"

Let $f(m)$ be the amount of f at location m .

$$\text{In general, } \langle x \rangle = E(x) = \sum_{x=0}^{\infty} x \cdot W_N(x)$$

$$\text{or } \bar{x} = \frac{\sum_{i=0}^{\infty} P(x_i) x_i}{\sum_{i=1}^{\infty} P(x_i)}$$

But since we're dealing w probabilities, $\sum P(x_i) = 1$

↳ Mean value of f_n .

$$E[f(u)] = \sum_{n=0}^{\infty} f(u_n) P(u_n)$$

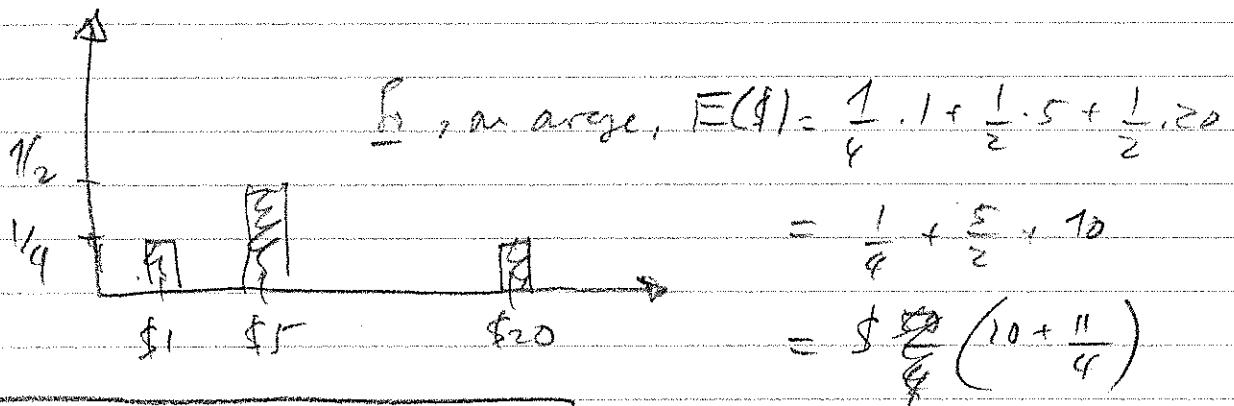
(24)

$$\text{Note } E[f(u) + g(u)] = E(f(u)) + E(g(u))$$

$$\text{If } s \in E(f(u)) = E(sf(u)), \quad s \in \mathbb{R}$$

+/-

So



On average, how far away from the average are we?

$$\rightarrow E(u - E(u)) = ? = E(u) - \overline{E(u)} = 0$$

What about $E((u - E(u))^2)$?

↳ Second moment about the mean? \rightarrow Variance

$$\Delta u^2 = \sigma^2 = E[(u - E(u))^2]$$

$$= E(u^2) - 2E(u)\overline{E(u)} + E(\overline{E(u)^2})$$

$$\boxed{\text{Var}(u) = E(u^2) - \overline{E(u)^2}}$$

$$\text{Standard deviation} \rightarrow \boxed{\sqrt{\text{Var}(u)} = \sigma_u = \sqrt{E(u^2) - \overline{E(u)^2}}}$$

(25)

Mean values - Random Walk problem

Feb 19,
2019

Recall

$$P_N(n_R) = \frac{N!}{n_R!(N-n_R)!} p^{n_R} q^{N-n_R}$$

$$\mathbb{E}[f(n_R)] = \sum_{n_R=0}^N f(n_R) P_N(n_R)$$

↳

At each step go to the right

$$\mathbb{E}[n_R] = \sum_{n_R=0}^N n_R P(n_R) = \sum_{n_R=0}^N n_R \frac{N!}{n_R!(N-n_R)!} p^{n_R} q^{N-n_R}$$

$$\text{Notice } n_R p^{n_R} = p \frac{\partial}{\partial p} (p^{n_R})$$

$$\mathbb{E}[n_R] = \sum_{n_R=0}^N \frac{N!}{n_R!(N-n_R)!} p \frac{\partial}{\partial p} (p^{n_R}) q^{N-n_R}$$

$$= p \frac{\partial}{\partial p} \sum_{n_R=0}^N \frac{N!}{n_R!(N-n_R)!} p^{n_R} q^{N-n_R}$$

$$= p \frac{\partial}{\partial p} (p+q)^N$$

$$= p \cdot N \frac{\partial}{\partial p} (p+q)^{N-1} \quad \text{But } p+q=1$$

↳ $\boxed{\mathbb{E}[n_R] = pN}$

$$\left. \right\} \mathbb{E}[m] = \mathbb{E}[n_R - n_L]$$

Similarly

$$\boxed{\mathbb{E}[n_L] = qN = N(1-p)}$$

$$= \mathbb{E}[n_R] - \mathbb{E}[n_L]$$

$$= N(p-q)$$

$$\text{So } E(n) = N(p-q)$$

→ If $p=q$, then $E(n) = 0$.

Variance

$$\text{Var}(n_R) = E(n_R^2) - E(n_R)^2$$

$$E(n_R^2) = \sum_{n_R=0}^N n_R^2 P(n_R)$$

$$= \sum_{n_R=0}^N n_R^2 \frac{N!}{n_R!(N-n_R)!} p^{n_R} q^{N-n_R}$$

→ Same trick as before ... $n_R^2 p^{n_R} = n_R p \frac{\partial}{\partial p} p^{n_R} = p \frac{\partial}{\partial p} (n_R p^{n_R})$

$$E(n_R^2) = \sum_{n_R=0}^N \binom{N}{n_R} \left(p \frac{\partial}{\partial p} \right)^2 p^{n_R} q^{N-n_R} = \left(p \frac{\partial}{\partial p} \right)^2 p^{n_R}$$

$$= \sum_{n_R=0}^N \binom{N}{n_R} \left(p \frac{\partial}{\partial p} \right)^2 p^{n_R} q^{N-n_R}$$

$$= \left(p \frac{\partial}{\partial p} \right)^2 \sum_{n_R=0}^N \binom{N}{n_R} p^{n_R} q^{N-n_R}$$

$$= \left(p \frac{\partial}{\partial p} \right)^2 [p + q]^N$$

$$= \left[p \frac{\partial}{\partial p} \right] \left(p + N(p+q)^{N-1} \right)$$

$$= p \left[N(p+q)^{N-1} + pN(N-1)(p+q)^{N-2} \right]$$

$$= pN + p^2 N(N-1) = pN + (pN)^2 - p^2 N$$

$$q+p=1 \rightarrow$$

$$\begin{aligned} \text{So } \text{Var}(n_R) &= pN + (qN)^2 - p^2N - (pqN)^2 \\ &= pN(1-p) \end{aligned}$$

$$\boxed{\text{Var}(n_R) = Npq}$$

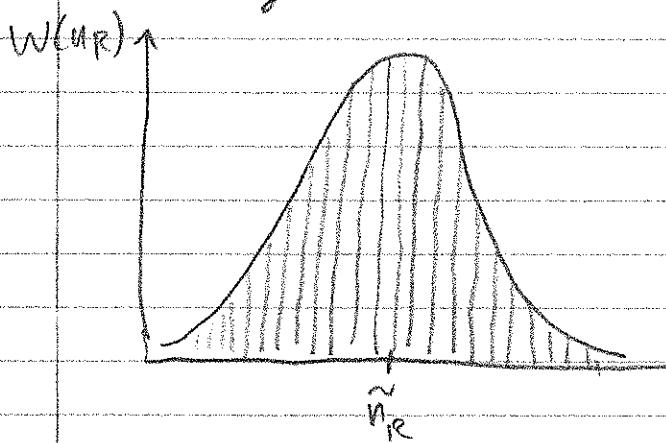
Relative Width of a distribution

$$\boxed{\frac{\sigma_{n_R}}{\bar{n}_R} = \frac{\sigma_{n_R}}{E(n_R)} = \frac{\sqrt{Npq}}{Np} = \frac{\sqrt{q}}{\sqrt{Np}} = \boxed{\frac{\sqrt{q}}{\sqrt{Np}}}}$$

when $p \approx q$, $\boxed{\frac{\sigma_{n_R}}{E(n_R)} = \frac{1}{\sqrt{N}}}$

→ relative width is $\propto \frac{1}{\sqrt{N}}$ ($p \neq q$ in general)

For large N , there's a well defined peak or a well-defined peak in $W_N(n_R) \propto n_R = \tilde{n}_R$, where \tilde{n}_R is the most likely value.



We can treat this as a continuous function as N, n_R get large

To find \tilde{n}_R as a fn of N, p, q , we need to look for
here $\frac{dW(n_R)}{dn_R} = 0$

Instead of evaluating $\frac{dW}{dn_R}$, we'll do

$\frac{d}{dn_R} \ln(W(n_R))$ since it has the same \tilde{n}_R & is a more gradually varying fn of n_R .

$$\frac{dW_m}{dn_p} = 0 = \frac{d\ln(W(n_p))}{dn_p}$$

■ Taylor series expansion around \tilde{n}

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

\rightarrow We want to expand $\ln(W(n_p))$ around \tilde{n} .

$$n_p = \tilde{n} + \varepsilon \quad (\varepsilon \ll \tilde{n}) \quad (\text{let's write } n \Leftarrow n_p)$$

$$\begin{aligned} \ln(W(n)) &= \ln(W(\tilde{n})) + \left. \frac{d}{dn} \ln(W(n)) \right|_{\tilde{n}} \varepsilon + \left. \frac{1}{2} \frac{d^2}{dn^2} \ln(W(n)) \right|_{\tilde{n}} \varepsilon^2 \\ &\quad 0 \text{ since } \tilde{n} \text{ most likely ...} \end{aligned}$$

$$= \ln(W(\tilde{n})) + \left. \frac{1}{2} \frac{d^2}{dn^2} \ln(W(n)) \right|_{\tilde{n}} \varepsilon^2$$

$$\therefore W(n) \approx W(\tilde{n}) \cdot \exp \left[\frac{1}{2} \left. \frac{d^2}{dn^2} \ln W(n) \right|_{\tilde{n}} \varepsilon^2 \right]$$

Next $\frac{d\ln W(n)}{dn} = \frac{d}{dn} \left(\ln \left[\left(\frac{N}{n} \right) p^n q^{N-n} \right] \right)$

$$\begin{aligned} &= \frac{d}{dn} \left[\ln(N!) - \ln(n!) - \ln((N-n)!) \right. \\ &\quad \left. + n \ln p + (N-n) \ln q \right] \end{aligned}$$

- Note that $\boxed{\frac{d}{dx} \ln x! \approx \ln x}$ for large X

$$\therefore \left. \frac{d}{dn} \ln(W(n)) \right|_{\tilde{n}} = -\ln \tilde{n} + \ln(N-\tilde{n}) + \ln p - \ln q$$

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Recall

$$W(n) = W(\tilde{n}) \exp \left[-\frac{1}{2} (n - \tilde{n})^2 \frac{d^2 \ln W}{dn^2} \Big|_{\tilde{n}} \right]$$

$$\frac{d \ln W}{dn} \Big|_{\tilde{n}} = -\ln \tilde{n} + \ln(N-\tilde{n}) + \ln p - \ln q$$

$$e^{d \ln W} = e^{-\ln \tilde{n} + \ln(N-\tilde{n}) + \ln p - \ln q}$$

$$e^{\circ} = e^{\ln \left(\frac{(N-\tilde{n})p}{\tilde{n}q} \right)} = E(n)$$

$$\text{S} \quad 1 = \frac{(N-\tilde{n})p}{\tilde{n}q} \Rightarrow \boxed{\tilde{n} = \frac{Np}{p+q} = Np}$$

Nun, evaluieren $\frac{d^2 \ln W}{dn^2} \Big|_{\tilde{n}}$

$$\frac{d^2 \ln W}{dn^2} = \frac{d}{dn} \left(\frac{d \ln W}{dn} \right) = \frac{d}{dn} \left[-\ln \tilde{n} + \ln(N-\tilde{n}) + \ln p - \ln q \right]$$

$$= -\frac{1}{\tilde{n}} \Big|_{\tilde{n}} = \frac{-N+n-n}{n(N-n)} \Big|_{\tilde{n}}$$

$$\text{S} \quad \frac{d^2 \ln W}{dn^2} \Big|_{\tilde{n}} = \frac{-N}{\tilde{n}(N-\tilde{n})} = \frac{-N}{Np(N-Np)} \frac{-1}{Np(1-p)}$$

$$\boxed{\frac{d^2 \ln W}{dn^2} \Big|_{\tilde{n}} = -\frac{1}{Npq}} \rightarrow 20$$

Finally, we need $W(\tilde{n})$

$$W(\tilde{n}) = \frac{N!}{\tilde{n}!(N-\tilde{n})!} p^{\tilde{n}} q^{N-\tilde{n}} ? \text{ For large } N$$

Use Stirling formula

$$n! \approx \sqrt{2\pi n} n^n e^{-n}$$

for $n \gg 1$

$$W(\tilde{n}) = \frac{\sqrt{2\pi N} N^N e^{-N}}{\sqrt{2\pi N_p} (N_p)^{N_p} e^{N_p} \cdot \sqrt{2\pi (N-N_p)} (N-N_p)^{N-N_p} e^{-(N-N_p)}}$$

$$\rightarrow W(\tilde{n}) = \frac{1}{\sqrt{2\pi N_p q}} \xrightarrow{\text{max of a Gaussian of } \sigma^2 = N_p q}$$

Now

$$W(n) = W(\tilde{n}) \exp \left[\frac{1}{2} (n - \tilde{n})^2 \frac{d^2 \ln W}{dn^2} \Big|_{\tilde{n}} \right]$$

$$W(n) = \frac{1}{\sqrt{2\pi N_p q}} e^{-\frac{(n-N_p)^2}{2N_p q}}$$

Gaussian
Normal

Random walk for large N .

$$W(n) = \frac{1}{\sqrt{2\pi \sigma^2}} e^{-\frac{(n-\bar{E}(n))^2}{2\sigma^2}}$$

Example large N . A penny is tossed 400 times
Find the probability of exactly 215 heads

$$p = q = \frac{1}{2}$$

$$N = 400$$

$$n = 215$$

$$N_p = 200$$

$$W(215) = \frac{1}{\sqrt{2\pi 100}} \cdot \exp \left[-\frac{1}{2} \frac{(215-200)^2}{100} \right]$$

$$= 1.3\% \rightarrow \text{very unlikely? ...}$$

More generally,

$$\int f(x) dx = \frac{1}{\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

→ probability density function - PDF

$$\int_a^b f(x) dx = P(a \leq x \leq b)$$

If probability dist. that depends on more than 1 var

$$P(u_i, v_i) = f(u_i) f(v_i) \rightarrow u_i \text{ by } u, v \text{ independent}$$

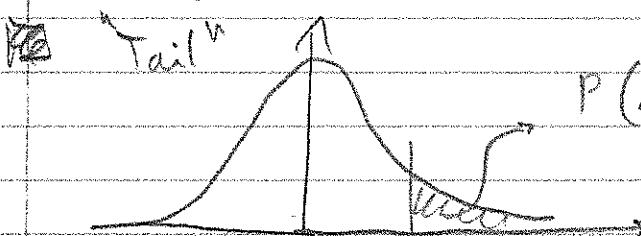
Gaussian Integrals are difficult to evaluate
analytically

But there 2 cases when we can have precise answers.

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

But since it's symmetrical about $x=0$

$$\int_0^{\infty} e^{-x^2} dx = \int_{-\infty}^0 e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$$



$$P(X \geq a) = \text{erf}(x) = \int_a^{\infty} e^{-t^2} dt \cdot \frac{2}{\sqrt{\pi}}$$

$$\Phi(x \geq a) = \Phi(1 - \Phi(a)) = 1 - \int_{-\infty}^a \phi(u) du$$

Ex Town A has 2000 customers and they want to talk to town B. What is the minimum # lines needed such that at most 1% of town A's customers fail to have access to a line during the busiest hour of the day?

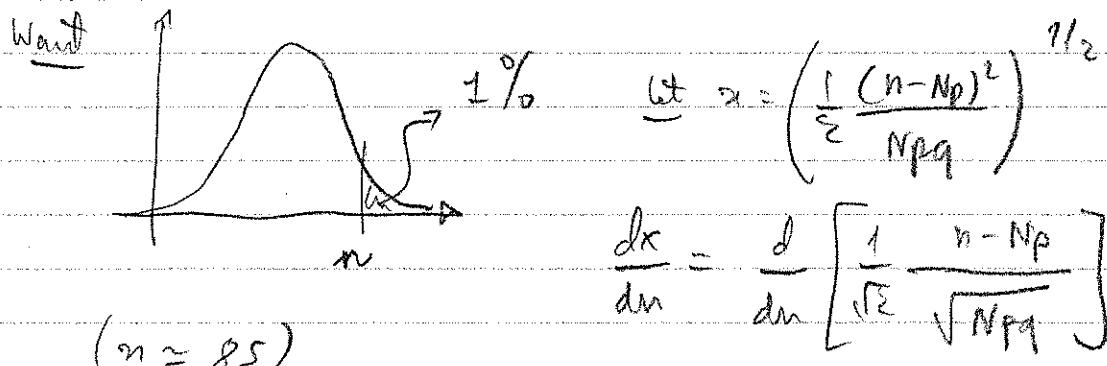
↪ assume each caller is on the line for 2 mins in that hr randomly dist.

$$N = 2000 \quad p = P(\text{line in use}) = \frac{2}{60} = \frac{1}{30}$$

$$n = ?$$

$$q = \frac{29}{30}$$

$$W(n) = \frac{1}{\sqrt{2\pi Npq}} \exp\left[-\frac{1}{2}\frac{(n-Np)^2}{Npq}\right]$$



Feb 22
2019

Back to Schroeder, Chap 2.

Terminology \rightarrow **microstate** \rightarrow any individual outcome

(state of each individual particle in the system (order matters)). $S =$

Macrostate \rightarrow more general description of the system \uparrow
has same multiplicity - some microstates are indistinguishable \uparrow multiplex

\rightarrow [multiplicity Ω] \rightarrow the number of microstates in a macrostate

Ex Example

4 dice rolled \rightarrow outcome 1 3 1 5

microstate

Macrostate could be system where we roll two 1's in 4 dice

$$\text{multiplicity} \rightarrow \Omega = \binom{4}{2} = 6$$

\square Note that small multiplicity implies highly ordered system.

Vv large multiplicity implies disorder

[Second Law of Thermodynamics]

\hookrightarrow Systems tend towards more disorder
because multiplicity is higher

\Rightarrow because these macrostates are more likely... (?)

[Ω is related to entropy]

\square Two physical systems where we can count individual microstate

Ex (1) Two-state paramagnet \rightarrow material in a B field

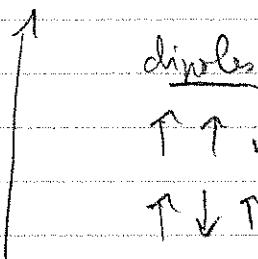
Individual dipoles line up in 1 or 2 states: aligned
or anti-aligned

Microstate \rightarrow Specified by static direction of all
individual dipoles.

macrostate \rightarrow total # of dipoles that point up, N_p

$$N = N_p + N_d$$

\vec{B}



Macrostate $S \downarrow + S \uparrow$

$\mu \rightarrow$ magnetic moment of individual dipole

only 2 allowed energy levels: E_\uparrow and E_\downarrow

Total magnetic dipole moment

$-\mu_B + 1T\uparrow\downarrow\uparrow\downarrow$

$$\hookrightarrow \vec{M} = \vec{\mu} (N_p - N_d)$$

or $\boxed{\vec{M} = \vec{\mu} (N_p - N + N_p) = \vec{\mu} (2N_p - N)}$

energy of single dipole $= -\vec{\mu} \cdot \vec{B} = E_i$ or $\pm \mu B$ for $\vec{\mu} \parallel \vec{B}$

So energy of paramagnet is $\rightarrow \partial(-2N_p + N)$

$$\boxed{U = -\vec{M} \cdot \vec{B} = \mu B (N_p - N_d)}$$

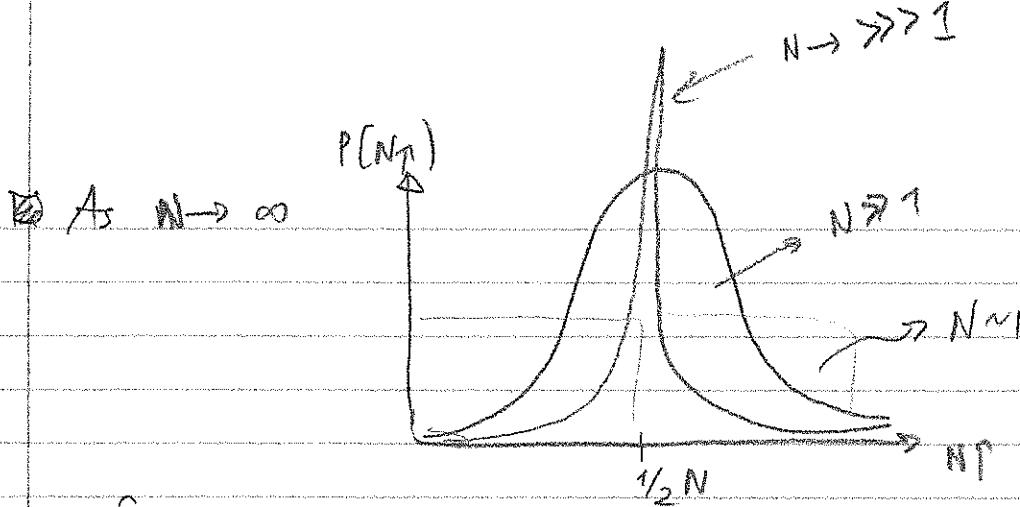
or

$$\boxed{U = \mu B (N - 2N_p)}$$

Calculate most probable energy

$$p = q = \frac{1}{2}$$

$$\boxed{P(N_p) = \binom{N}{N_p} p^{N_p} q^{N-N_p} = \Omega(w)/2^N}$$

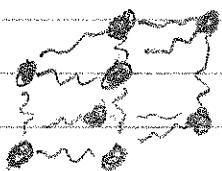


As $N \rightarrow \infty$

So, random orientation of dipoles is not possible
 \rightarrow 2nd law of thermodynamics.

there Ω_1 & Ω_2

(2) Einstein's model of solid / Debye-Hückel model



N atoms which have $3N$ independent harmonic oscillators, which provides 6 degrees of freedom each. (per atom)
 $(1\text{KE} + 1\text{PE})$ per spring

Classical spring

$$U = \frac{1}{2}mv^2 + \frac{1}{2}kx^2 = KE + PE$$

$$= \frac{1}{2}m(x_x^2 + x_y^2 + x_z^2) + \frac{1}{2}k(x_x^2 + x_y^2 + x_z^2)$$

↳ here we have "unlimited energy spectrum", but as quantum oscillator \rightarrow discrete energies that are allowed

$$\epsilon_i = q_i; hf = q_i \hbar \omega = q_i \hbar \nu$$

For $N = 3$ oscillators, the multiplicity of different energy levels

osc	# 1	# 2	# 3	Σ	-2
	0	0	0	0	1
	0	1	0	$h\nu$	2
	1	0	0	$h\nu$	3
	0	0	1	$h\nu$	3

# 1	# 2	# 3	E_U	S_U
2	0	0	$\{$	
0	2	0	$2h\nu$	6
0	0	2	$\}$	
1	1	0		
1	0	1		
0	1	1		
			$3h\nu$	10
			Koker	
				multiplicity of equilibrium

→ General expression for multiplicity:

$$S + \binom{N}{q} \quad \text{Instead}$$

$$S(N, q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!}$$

#_{total} units of oscillators energy

Feb 25, 2019

Heat flow & irreversible processes

Consider 2 Einstein solids that can interact

Solid A

Solid B

single atom {

$$N_A = 3$$

$$N_B = 3$$

$$U = qh\nu$$

$$\left\{ \begin{array}{l} q = \text{total # of energy quanta} = 6 = q_A + q_B \\ 0 \leq q_A \leq 6, \quad 0 \leq q_B \leq 6 \end{array} \right\}$$

Multiplicity

$$\Omega = \binom{q+N-1}{q}$$

For A $\Omega_A = \binom{q_A + N_A - 1}{q_A}$

Since A + B independent

$$\Omega_{\text{tot}} = \Omega_A \Omega_B$$

For B

$$\Omega_B = \binom{q_B + N_B - 1}{q_B}$$

B)

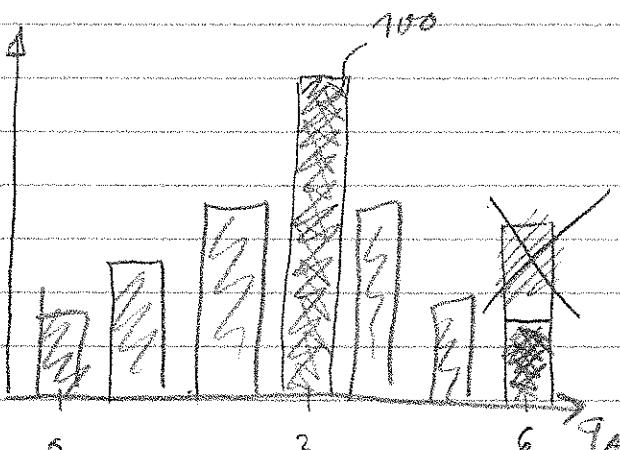
$$\Omega_{\text{tot}} = \Omega_A \Omega_B$$

$$\Omega_{\text{tot}}$$

100

Ex

$$\Omega_A (q_A=3) = \binom{3+3-1}{3} = 10$$



$$\Omega_B (q_B=4) = 10$$

$$\Omega_{\text{tot}} = \Omega_A \Omega_B = 100$$

$$(q_A + q_B = 6)$$

B) Ex $\Omega_A (q_A=6) = \binom{6+3-1}{6} = 28$

$$\Omega_B (q_B=0) = \binom{0+3-1}{0} = 1$$

$$\Omega_{\text{tot}} = \Omega_A \Omega_B = 28 \times 1 = 28$$

Fundamental assumption in stat mech

Any given microstate is equally probable. But some macrostates will be more probable than others because of higher multiplicity Ω

If you start out with a system near most likely macrostate

very unlikely that it will move far away from this distribution.



$$\text{Ex } N_A = 50, N_B = 50, \eta_{tot} = 50$$

$$\frac{\text{Case 1}}{\text{Case 2}} \quad q_A = 50, q_B = 0 \rightarrow S_{tot} = \binom{100-1}{50-50-1} = \binom{99}{50} \binom{49}{0}$$

$$q_A = q_B = 25$$

$$\hookrightarrow S_{tot} = \binom{25+75-1}{25}^2 = 1 \times 10^{39} \approx 5 \times 10^{28}$$

So $q_A = 25 = 1/3 \leftarrow$ macrostate 20 billion times more probable than $q_A = 50, q_B = 0,$

Irreversible processes

↳ energy flows from system A to system B, increasing the total S of the interacting systems.

Rishabh 2nd Law of Therm

↳ {systems in thermal equilibrium will be arranged} with the highest amount of disorder

(or)

{spontaneous flow of energy stops when a system is} at or very near its most likely microstate greatest S

Large System

(S) • Small # $\rightarrow (n < 100)$

(L) • Large # \rightarrow Small # that are exponentially 10^{-3}

(L) • Very large # \rightarrow Large # that are exponentially $10^{10^{23}}$ or large # in Statistical ...

Ex $10^{10^{23}}$

Note some properties

$$(\text{Add}) \cdot 10^{23} + 23 \approx 10^{23}$$

$$(\text{mult.}) \cdot 10^{10^{23}} \times 10^{23} = 10^{10^{23} + 23} \approx 10^{10^{23}}$$

$$(\text{Division}) \cdot \frac{10^{10^{23}} \times 10^{23}}{10^{10^{23}}} = 10^{23}$$

$$\underline{\text{Manipulating large numbers}} \quad e^{10} \rightarrow \ln[e^{10}] = 10^{23}$$

$$\rightarrow e^{10^{23}} \approx 10^{4.34 \times 10^{22}}$$

$$e^{10^{23}} \text{ as } 10^x \rightarrow 10^{23} = \ln 10^x \rightarrow x = 10^{23} \ln(10) \approx 4.34 \times 10^{22}.$$

Multiplicity of Einstein solid (large)

at high $T \Rightarrow q \gg N, \sim N$ large

$$\Omega = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \approx \frac{(q+N)!}{q! N!}$$

Take the log

$$\ln \Omega = \ln \left[\frac{(q+N)!}{q! N!} \right] = \ln(q+N)! - \ln q! - \ln N!$$

Use Stirling's formula: $N! \sim N^N e^{-N} \sqrt{2\pi N}$

$$\rightarrow \boxed{\ln(N!) \approx N \ln N - N}$$

$$\text{So } \ln \Omega = (q+N) \ln(q+N) - (q+N) - [q \ln q - q] - [N \ln N - N]$$

\approx \rightarrow next page

$$\text{So } \ln S = (q+N) \ln (N+q) - N \ln N - q \ln q$$

$$\text{Rewrite } \ln (q+N) = \ln(q(1+\frac{N}{q})) \rightarrow \ll$$

$$= \ln q + \ln(1+N/q)$$

$$\approx \ln q + \frac{N}{q}$$

$$\text{So } \ln S \approx (q+N) \left[\ln q + \frac{N}{q} \right] - N \ln N - q \ln q \quad (q \gg N)$$

$$= N \ln q + \frac{N^2}{q} - N \ln N + N \quad \hookrightarrow \frac{N^2}{q} \approx 0$$

So

$$S = \exp[N \ln q - N \ln N + N]$$

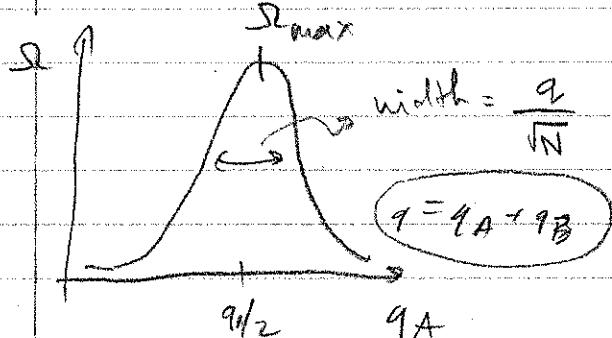
$$= \frac{e^{N \ln q} e^N}{e^{N \ln N}} = \frac{e^{N \cdot q^N}}{N^N} = \left(\frac{eq}{N}\right)^N$$

So $\boxed{S = \left(\frac{eq}{N}\right)^N}$ or total multiplicity of loose Einstein solid in high temp limit, (like room temp)

Feb 26, 2019

$$\rightarrow S_{\text{tot}} = S_A S_B$$

For interacting solids $\rightarrow S = S_{\text{max}} e^{-N(2x/\epsilon)^2}$ ~ Gaussian



At $N \uparrow$, the fluctuations away from the most likely macrostate become increasingly improbable.
 \rightarrow Thermodynamic limit

(41)

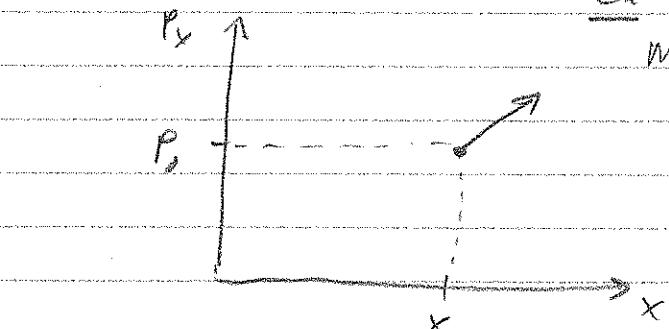
Multiplicity of an ideal gas

- * Specify the state of a system in classical mechanics using phase space.

If an object's position & momentum is known, we can predict it's position & momentum at any other time.

Ex

$$m\ddot{x} = \vec{p} = \vec{c}\vec{x}$$



We can determine
 $x(t) \propto p(t)$ from
initial conditions.

$$m \frac{dx}{dt} = cx \rightarrow \int \frac{dx}{x} = \int c dt$$

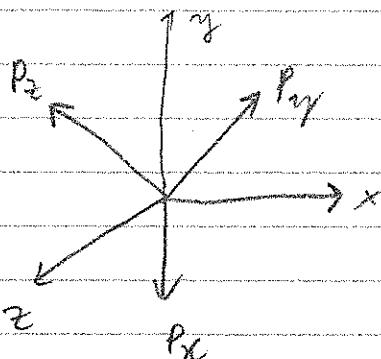
$$\text{So } \ln\left(\frac{x}{x_0}\right) = \frac{ct - t_0}{m}$$

So

$$x(t) = x_0 e^{\frac{ct - t_0}{m}}$$

To get $p(t)$

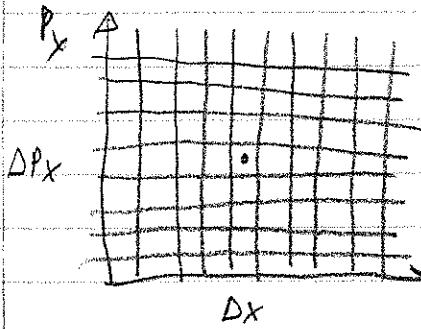
$$\rightarrow p = m\dot{x} = m \cdot \frac{c}{m} x_0 e^{\frac{ct - t_0}{m}} = c x_0 e^{\frac{ct - t_0}{m}}$$

For particle in space

$$(x, y, z, p_x, p_y, p_z)$$

For N objects, we need $6N$ coordinates to describe its phase space.

- ☒ To describe state of system in phase space



particle located between $x \sim x + \Delta x$
and $p_x \sim p_x + \Delta p_x$

☒ Heisenberg Uncertainty principle

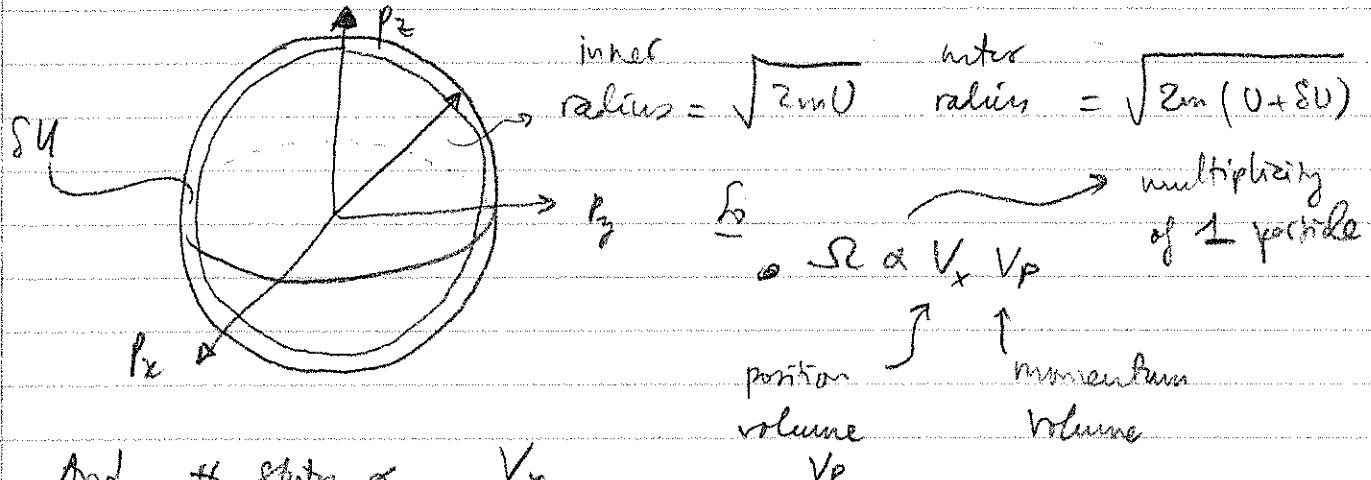
$$\rightarrow \text{let } \Delta x \Delta p = h \quad \Delta p \Delta x \geq \frac{\hbar}{2} (?)$$

- ☒ For a monatomic ideal gas, energy is all kinetic

$$U = \frac{1}{2} m(v_x^2 + v_y^2 + v_z^2) = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$$

$$\therefore p = \sqrt{p_x^2 + p_y^2 + p_z^2} = \sqrt{2mU}$$

☒ In 3-D momentum space



$\frac{S}{d}$

$$S \propto \iiint_{u}^{u+\Delta u} dx dy dz \, dp_x dp_y dp_z$$

$$dp_x dp_y dp_z \quad \text{for 1 particle}$$

→ For N particles

$$S \propto \int_{u}^{u+\Delta u} \int d^3r_1 \dots d^3r_N \, d^3p_1 \dots d^3p_N$$

Volume is independent of

$$S(u) \propto V^N \int_{-\infty}^{u+\delta u} \cdots \int_{-\infty}^{u+\delta u} d^3 p_1 \cdots d^3 p_N$$

$$\propto V^N \int_{-\infty}^{\sqrt{2m(U+\delta U)}} p^{3N-1} \cdot dp$$

Thickness
"Surface area"

$$\underline{S} \quad S(u) \propto V^N (\sqrt{2mU})^{3N-1} \left[\sqrt{2m(U+\delta U)} - \sqrt{2mU} \right]$$

$$= V^N \sqrt{2mU} \left[\sqrt{2mU} \sqrt{1 + \frac{\delta U}{U}} - \sqrt{2mU} \right]$$

Thickness

$$S(u) \propto V^N (\sqrt{2mU})^{3N} \left[\sqrt{1 + \frac{\delta U}{U}} - 1 \right]$$

• Taylor expand $(1+x)^n \approx 1+nx$ ($x \ll 1$)

$$\underline{S} \quad S(u) \propto V^N (\sqrt{2mU})^{3N} \cdot \left(\frac{\delta U}{2m} \right)$$

$$\underline{S} \quad S(u) \propto V^N (\sqrt{2m})^{3N} \cdot \frac{\delta U}{2m}$$

$$S(u) \propto V^N u^{3N/2} \cdot (\delta U) u^{-1}$$

small number

$$\underline{S} \quad S(u) \propto V^N u^{(3N/2)-1} \frac{\delta U}{8U}$$

ignore u^{-1} as well as

$$\boxed{S(u) \propto V^N u^{\frac{3N}{2}}}$$

More careful derivation gives

→ multiplicity of monatomic ideal gas:

$$S(u) \approx \frac{\pi}{N! h^{3N/2}} V^N (\sqrt{2mU})^{3N}$$

$$S \sim u^{(3/2)N}$$

{ For general result $\rightarrow \boxed{\Omega \sim u^{Nf/2}}$, $f = \# \text{ df for single particle}$ }

Feb 27, 2019

Result for monoatomic ideal gas

$$\Omega(u, V, N) \approx \frac{\pi^{3N/2}}{N! h^{3N} (3N/2)!} v^N (\sqrt{2\mu u})^{3N}$$

☒ Interacting ideal gas

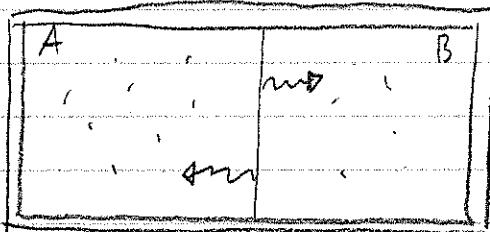
$$\Omega_{\text{tot}} = \Omega_A \Omega_B$$

{ assuming Ω_A and Ω_B }
 $\{ A \neq B \}$

$$= [f(N)]^2 (V_A V_B)^N (u_A u_B)^{\frac{3N}{2}}$$

3 ways to exchange multiplicity

① Exchange energy



$$(\Omega \sim u^{3N/2})$$

☒ Width of peak in the multiplicity function $\Omega_{\text{tot}} = \frac{u_{\text{tot}}}{\sqrt{3N/2}}$
and maximum u_{tot} is at $u_A = \frac{1}{2} u_{\text{tot}}$

② Exchange volume via a movable partition

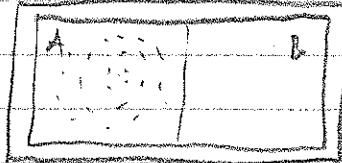
$$\Rightarrow \text{width of peak in } \Omega = \frac{V_{\text{tot}}}{\sqrt{N}} \quad (\Omega \sim V^N)$$

③ Exchange particles in permeable membrane (membrane)



as more complicated overall
beam of $f(N) \approx u(N)$

Consider specific case



here $V_{tot} \sqrt{2} \rightarrow$ this reduces ω_{tot} by 2^n

*

ENTROPY

$$S = k \ln \Omega$$

where k is Boltzmann constant $= 1.38 \times 10^{-23} \text{ J/K}$
 Ω is the multiplicity.

2nd Law of Thermodynamics: $\Delta S \geq 0$

Note For interacting systems $S_{tot} = \Omega_A \Omega_B$

$$S_{tot} = h \ln \Omega_{tot} = h \ln (\Omega_A \Omega_B)$$

$$= h \ln \Omega_A + h \ln \Omega_B$$

$$= S_A + S_B$$

S

$$S_{tot} = S_A + S_B$$

④ Spontaneous process occurs due to a net increase in entropy.

Entropy of an ideal gas

$$S = k \ln \Omega$$

$$\geq k \ln \left[\frac{\pi^{3N/2}}{N! h^{3N} (3N/2)!} V^N (\sqrt{2\pi mV})^{3N} \right]$$

Stirling's formula: $\ln N! \approx N \ln N - N$

$$\begin{aligned} S &= k \left[\frac{3N}{2} \ln \pi + N \ln V + \frac{3N}{2} \ln(2\pi mV) - (N \ln N - N) \right. \\ &\quad \left. - 3N \ln h - \left(\frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2} \right) \right] \\ &= Nk \left[\frac{3}{2} \ln \pi + \ln V + \frac{3}{2} \ln(2\pi mV) - (\ln N - 1) \right. \\ &\quad \left. - 3 \ln h - \left(\frac{3}{2} \ln \frac{3N}{2} - \frac{3}{2} \right) \right] \end{aligned}$$

$$S = Nk \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi mV}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right\} \rightarrow \text{entropy of ideal monatomic gas}$$

↑
Sackur-Tetrode equation

300 K 10^5 Pa

Ex) Calc. S of 1 mole of He gas @ room temp & 1 atm.

Need V, N, U, m_{He}

$$N \approx 10^{23}$$

$$m_{He} =$$

$$V \approx \frac{RT}{P} \approx 25 \text{ L}$$

$$1$$

$$U = \frac{3}{2} NkT = \frac{3}{2} \times 10^2 \times 300 = 3700 \text{ J}$$

Get

$$S_{He} \approx 126 \text{ J/K}$$

(47)

If we hold $N = V$ fixed and allow V to change

$$\rightarrow S \sim Nk_B \ln(V)$$

$$\Delta S = Nk_B \ln\left(\frac{V_f}{V_i}\right)$$

$$\text{So } \Delta S = Nk_B \frac{V_f}{V_i}$$

Quasi-static isoenthalpic expansion/collapse

Note if $\Delta S > 0$

Mar 1, 2019

How entropy is related to the heat input to system A?

Heat in = work done by system
= - work done on system.

$$\Delta u = 0 \text{ (isothermal)} \quad Q_{\text{add}} = W_{\text{by}} = -W_{\text{on}}$$

$$Q_{\text{add}} = -W_{\text{in}} = \int_{V_i}^{V_f} P(V) dV$$

$$= \int_{V_i}^{V_f} \frac{NkT}{V} dV = NkT \ln\left(\frac{V_f}{V_i}\right) = T\Delta S$$

$$\text{So } \Delta S = \frac{Q_{\text{add}}}{T} \Rightarrow \text{quasi-static isothermal}$$

more precisely

$$\Delta S = \frac{\delta Q}{T}$$

Free expansion = non quasi-static



vacuum

$$n, T \text{ constant} \rightarrow \Delta U = 0 \Rightarrow Q_{\text{add}} + W_{\text{in}} = 0$$

$Q_{\text{add}} = 0$ because no heat enters or leaves system. So $W = 0$.

But there's an increase in entropy. Neff can't use

$\Delta S = \partial S / \partial T$ because the eq describes quantity isothermal

Entropy of mixing

Consider

He	Ar
1 1 1 1	0 0 0
1 1 1 1	0 0 0

$$\text{know } S_{\text{tot}} = S_A + S_B$$

He Ar

Now, remove partition & let gases mix - how does S change?

$$\text{Recall to } S-T \text{ eqn: } S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m u}{3Nk^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

For He: N const, u const, $V' = 2V$

For Ar: same thing.

$$\Delta S = Nk \ln(2) \left|_{\text{He}} \right. + Nk \ln(2) \left|_{\text{Ar}} \right.$$

$$\boxed{\Delta S = 2Nk \ln(2)} \quad \text{or entropy of mixing (different gases)}$$

Consider (same gas)



Add Ar to cylinder with same N , u as He
→ expect ST by a factor of 2

If we add He instead (at same energy) → same temperature

$$S = Nk \left[\frac{1}{2} \left(\frac{4\pi m u}{3Nk^2} \right)^{3/2} + \frac{5}{2} \right] \quad \left. \right\}$$

$$V \text{ const } N' = 2N$$

$$U = \frac{3}{2} kNT \rightarrow u' = 2u$$

(44)

$$S' = 2S_{He} + 2Nk \ln\left(\frac{1}{2}\right)$$

$$= 2S_{He} + \underbrace{(-2Nk \ln(2))}_{}$$

$$\boxed{S' = 2S_{He} - 1S_{mix}} \rightarrow \text{don't sum yet } S' = 2S$$

Gibbs Paradox \rightarrow why does distinguishability matter?

Ball

$$\text{particular} \quad S_N \approx \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} (\sqrt{2\pi N})^{3N}$$

$$\hookrightarrow \ln S \approx \ln\left(\frac{V}{h^3}\right) \approx -(Nk \ln h - N)$$

What if we're able to distinguish particles in gas $\rightarrow N! \frac{1}{N!}$
because particles matter

$$\boxed{S = Nk \ln \left[V \left(\frac{4\pi m}{3Nh^3} \right)^{3/2} + \frac{3}{2} \right]} \rightarrow \text{distinguishable}$$

Consider

↑	↑	↑
↓	↓	↓

 consider with indistinguishable particles. Add a partition,

$$N_1 \times 1, N_2 \times 2, N_3 \times 2$$

$$\frac{1}{2} S^{\text{new}} = \frac{1}{2} S_{\text{original}} + \frac{1}{2} Nk \ln(1/2)$$

$$\frac{1}{2} S^{\text{new}} = \frac{1}{2} S_{\text{original}} - \frac{1}{2} Nk \ln(2) \rightarrow \text{decrease in entropy}$$

↓ get decrease in entropy

Reversible vs Irreversible process

- A process is irreversible if $\Delta S > 0$
 - A process is reversible if $\Delta S = 0$
- need to be quasistatic process.

(can be reversible, but can't have to be)

- ☒ All reversible processes are quasistatic. But not all
- ☒ quasistatic processes are reversible

[Reversible \neq Quasistatic]

- ☒ Spontaneous heat flow is always irreversible

$$sT \quad sT$$

~~☒~~ "Reversible heat flow"

System in $T_{\max} \Rightarrow$ thermal equilibrium

$\overline{\partial T} \rightarrow$ infinitesimal change in temperature

$$\frac{d}{dt}$$

Mar 4, 2019

CHAPTER 3: RELATIONSHIP BETWEEN ENTROPY, TEMPERATURE

- ☒ Simple interacting system of 2 Einstein solids

$$N_A = 3 \text{ oscillators}$$

$$N_B = 2$$

$$q = 6$$

$$\Omega = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!}$$

$$S = k \ln \Omega$$

(J1)

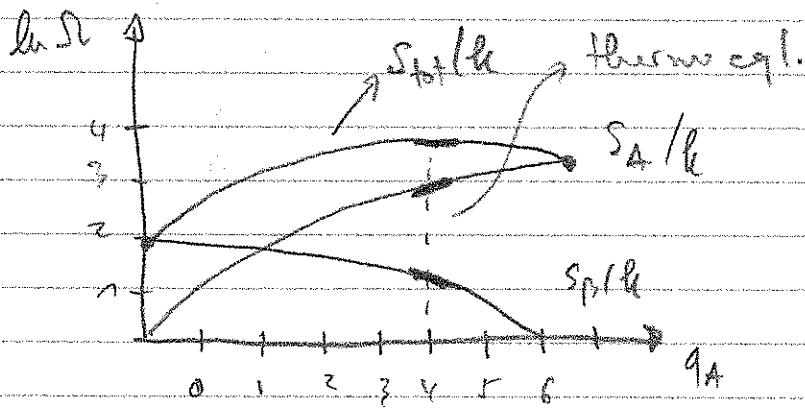
$$\underline{S} = \frac{S}{k} = \underline{E}$$

$$N_A = 3$$

$$N_B = 2$$

	η_A	S_A	S_A/k	η_B	S_B	S_B/k	S_{tot}	S_{tot}/k
0	0	1	0	6	2	1.9	7	1.9
1	3	11	3	5	6	1.8	10	2.9
2	6	18	4	4	15	1.6	26	3.4
3	10	23	3	3	18	1.4	40	3.7
4	15	27	2	2	21	1.1	45	3.9
5	21	30	1	1	22	0.7	42	3.7
6	28	33	0	0	1	0	28	3.3

Plot of $\ln S_I$ versus ϵ .



$\frac{\partial S_{tot}}{\partial \eta_A} = 0$, then we get maximum entropy
 $\frac{\partial S_{tot}}{\partial \eta_B} = 0$

→ condition for thermodynamic equilibrium

Real $V_A = \eta_A$ (constant)

$$\underline{\frac{\partial S_{tot}}{\partial \eta_A}} = 0 \Leftrightarrow \underline{\frac{\partial S_{tot}}{\partial V_A}} = 0 \text{ at eql.}$$

$$\text{Now, } S_{tot} = S_A + S_B \Rightarrow \partial S_{tot} = \partial S_A + \partial S_B$$

$$\underline{\frac{\partial S_{tot}}{\partial V_A}} = \underline{\frac{\partial S_A}{\partial V_A}} + \underline{\frac{\partial S_B}{\partial V_A}} = 0 \Leftrightarrow \underline{\frac{\partial S_A}{\partial V_A}} = \underline{-\frac{\partial S_B}{\partial V_A}} \text{ at eql.}$$

Note $U_{tot} = u_A + u_B$ - U_{tot} is conserved

$$\rightarrow \frac{\partial U_{tot}}{\partial u_A} = 0 = \frac{\partial u_A}{\partial n_A} + \frac{\partial u_B}{\partial n_B} \rightarrow \frac{\partial u_A}{\partial n_A} = - \frac{\partial u_B}{\partial n_B}$$

In next

$$\boxed{\frac{\partial S_A}{\partial n_A} = \frac{\partial S_B}{\partial n_B}}$$

Note when g_A is small $\rightarrow \frac{\partial S_A}{\partial n_A}$ steep. \rightarrow entropy of system A is increasing faster than entropy of B is decreasing

\rightarrow Spontaneous heat flow, energy

Energy flows to object with steeper S vs U slope

The steeper the slope the lower the temperature!

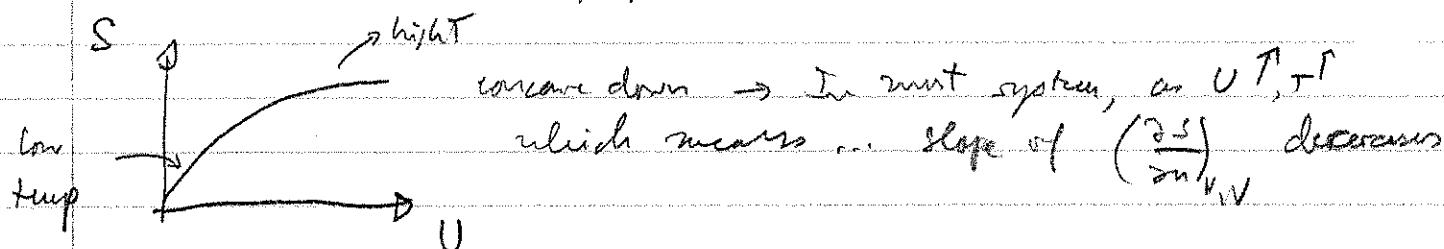
$$\begin{array}{l} \text{Units of } S \rightarrow J/K \\ \text{Units of } U \rightarrow J \end{array} \quad \left. \right\} T = \frac{\partial U}{\partial S} = \frac{\partial U}{\partial S}$$

Definition of temperature

$$\boxed{T = \frac{-1}{\frac{\partial S}{\partial U}}} \rightarrow N, V \text{ constant}$$

-4

Q Patterns in S vs U graphs.

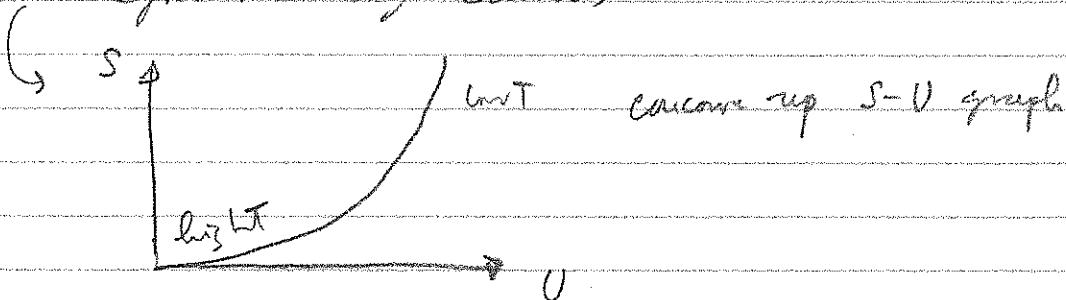


Bell $\Delta U = Q_{\text{add}} + \nabla_{\text{ext}} \cdot \vec{P}$ (assume V constant)

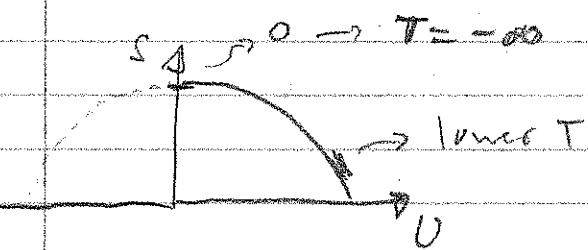
$$Q_{\text{add}} = C \Delta T$$

$$\therefore \Delta U = C \Delta T \rightarrow \text{makes sense}$$

- Q) However, there are systems with negative heat capacity (gravitationally bound)



- Q) Ex Cancer down with negative slope ...



Ex paramagnet: $U = \mu B (N_f - N_i)$

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \text{negative} \rightarrow \boxed{\text{negative temperature}}$$

- Q) Example Relationship between S, U, T

- ① ^{large} Exist in solid & high temp limit $\rightarrow q \gg N \gg 1$

$$S = \left(\frac{q}{N}\right)^N$$

$$\underline{S = k \ln S = Nk \ln \left(\frac{q^q}{N!}\right) = Nk + Nk \ln \left(\frac{q}{N}\right)}$$

$$\text{def } u = \varepsilon \cdot g$$

$$S = Nk \left[\ln \left(\frac{u}{N\varepsilon} \right) + 1 \right]$$

$$= Nk \ln \left(\frac{u}{N\varepsilon} \right) + Nk$$

$$= Nk \ln u - Nk \ln (N\varepsilon) + Nk$$

$$\rightarrow T = \left(\frac{\partial S}{\partial u} \right)_{N, V} = \frac{Nk}{u} = 0 + 0$$

$$T = \frac{u}{Nk}$$

$$\text{Recall } u = \frac{1}{2} NkT$$

or

$$u = NkT$$

$f = 2$ because STO has 2 dofs.

② Ideal gas (monatomic)

$$S = Nk \left(\ln \left[\frac{V}{N} \left(\frac{4\pi m u}{3Nk^2} \right)^{3/2} \right] + \frac{5}{2} \right) \xrightarrow{\text{constant kills by eq(1)}} \text{constant kills}$$

$$T = \left(\frac{\partial S}{\partial u} \right)_{N, V}^{-1} = \left[Nk \cdot \frac{V}{N} \left(\frac{4\pi m}{3Nk^2} \right)^{3/2} \cdot \frac{3}{2} \cdot \frac{1}{u} \right]^{-1}$$

$$T = \left(\frac{3Nk}{2} \frac{1}{u} \right)^{-1} \rightarrow u = \frac{3}{2} NkT$$

[Entropy = Heat Capacity]

Mar 5, 2019

$$\text{Recall: } C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}$$

$$\begin{aligned} \text{1st law } \Delta U &= Q_{\text{add}} + W_m \quad \} \\ \text{if } V \text{ constant} \rightarrow W_m &= 0 \quad \} \Rightarrow \Delta U = Q_{\text{add}} \end{aligned}$$

$$\text{Now } T = \left(\frac{\partial U}{\partial V}\right)^{-1} \Rightarrow dS = \frac{dU}{T} \text{ with constant volume} \\ = \frac{Q}{T} \quad \boxed{dS = \frac{dQ}{T}}$$

$$\text{But recall } dU = C_V dT$$

$$\int dS = C_V \int \frac{dT}{T} \Rightarrow \int dS = \int C_V \frac{dT}{T} / \text{if temp range is small} \rightarrow C_V$$

$$\Rightarrow \boxed{dS = C_V \ln\left(\frac{T_f}{T_i}\right)} \text{ constant}$$

Ex 6 Heat a cup of H₂O from 20°C to 100°C. Calculate (20g) how much entropy increases? $C_V = 1 \text{ cal/gK} = 4.186 \text{ J/K}$

$$\Delta S = 4.186 \frac{\text{J}}{\text{gK}} (20\text{g}) \ln\left(\frac{373}{293}\right)$$

$$\approx 200 \text{ J/K}$$

$$\text{In terms of } \frac{S_2}{S_1} \rightarrow \Delta S = k \ln \frac{S_2}{S_1} \rightarrow S_2 = e^{\frac{S}{k}} S_1$$

$$\approx S_2 = e^{20054 / 1.38 \times 10^{-23} \text{ J/K}} S_1$$

$$\boxed{S_2 = e^{2.5 \times 10^{25}} S_1}$$

Q Total entropy of the system

$$\Delta S = S_f - S_{(T=0)} = \int_0^T \frac{C_v}{T} dT$$

But we need C_v at $T=0$. Guess that $S(0) \rightarrow 0$

Third Law of Thermodynamics

↳ Planck's Formalism: As $T \rightarrow 0$, entropy goes to its minimum value

↳ Note this is only true for crystalline solids

Another way to state 3rd law $[At T \rightarrow 0, C_v \rightarrow 0]$

Ex ideal gas $C_v = \frac{3}{2}Nk \rightarrow 0$ as $T \rightarrow 0$

Q Macroscopic view of Entropy $\Rightarrow dS = \frac{dQ}{T}$

* Example The sun heating the surface of the Earth

$$\sim 1000 \text{ W/m}^2 \quad T_0 = 6000 \text{ K}$$

$$T_\theta = 300 \text{ K}$$

Estimating energy created in 1 year by the flow of heat to the Earth's surface.

$$\Delta S_\theta = \frac{Q}{T} = \frac{(-1000 \text{ J/s})(60^2)(24)(365)}{6000 \text{ K}, 1 \text{ m}^2}$$

$$= -1.75 \times 10^6 \text{ J/K}$$

$$\Delta f_\theta = \frac{Q}{T} = \frac{(-10000 \text{ J/s})(60^2)(124)(765)}{200 \text{ K}, 1 \text{ m}^2}$$

$$= +3.5 \times 10^7 \text{ J/K}$$

(5)

$$\Delta S_{tot} = \Delta S_0 + \Delta S_{\text{env}} = 7.3 \times 10^7 \text{ J/Km}^2$$

B Suppose we plant grass on this 1 m^2 area. Does the decrease in entropy violate the 2nd law?

On $1 \text{ m}^2 \rightarrow$ maybe 10g of grass. Let's say grass is C
 $n = 12 \text{ g/mol}$
 say 1200 g of grass

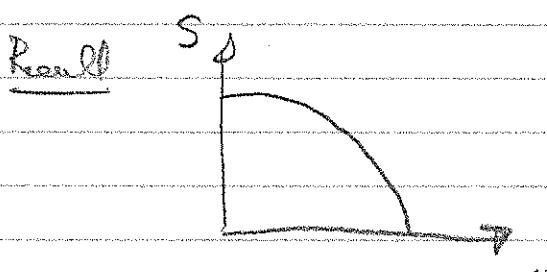
$$\rightarrow N = 1000 N_A \text{ C atoms/m}^2$$

To assemble grass out of smaller molecules.

$$S \sim Nk \sim nR^2 = 1000R = 1000 \cdot 1.31 \frac{\text{J}}{\text{K mol}}$$

$$\rightarrow S \approx 10^4 \text{ J/K} < \Delta S_0$$

Q Paramagnetism 1) S 2) S 3) T 4) U(G) 5) C_v



For paramagnets

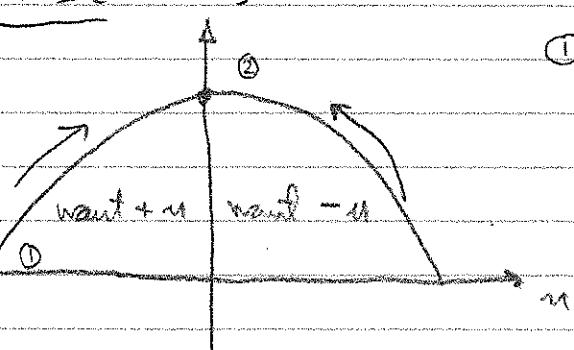
$$\begin{aligned} u &= \mu B(N_f - N_p) \\ &= \mu B(2N_f - N) \end{aligned}$$

Question how do U, M depend on temperature

$$M = \mu (N_f - N_p) = \frac{-U}{B}$$

(*)

(1) Get S



- ① all N are N_f } \rightarrow low T,
 $S \propto U \rightarrow$ steep positive
- \rightarrow wants to absorb u

- ② $N_f = NT = \frac{1}{2}N$. Max entropy
 $u = 0$ - If it absorbs u
 $\rightarrow S \propto U$ less (\rightarrow) slope

Temp of paramagnet ① u is negative but $\frac{\partial U}{\partial n} = \text{positive}$

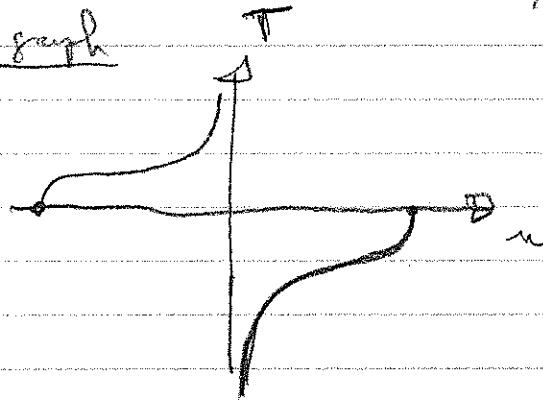
$T \uparrow \text{as } u \uparrow$

② $u = \text{positive}$ but $\frac{\partial U}{\partial n} = \text{negative}$

$T \downarrow \text{as } u \uparrow$

\rightarrow system wants to give off energy

Temp graph

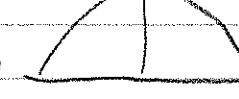


$$\text{Recall } \left(\frac{\partial S}{\partial V}\right)_{n,T} = \frac{1}{T}$$

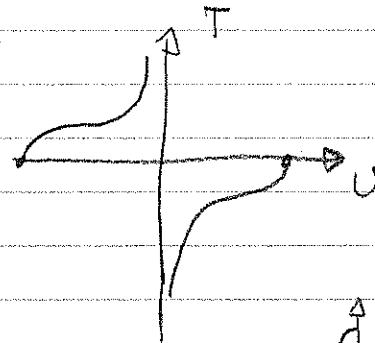
S

Mar 6, 2019

Recall paramagnet has a "normal" S-V graph:



$\therefore T \text{ vs } V$ looks like



u

Flip the axes



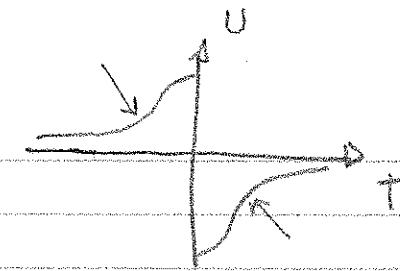
Recall

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{n,V}$$

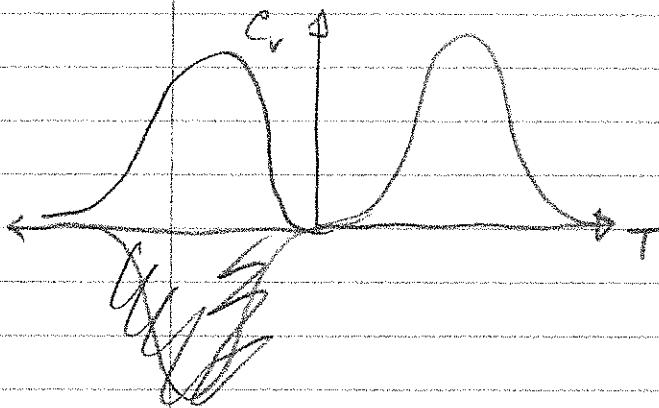
$$\rightarrow \text{and } \left\{ \begin{array}{l} C_V = \left(\frac{\partial U}{\partial T}\right)_{n,V} > 0 \text{ when } T=0 \\ C_V = 0 \text{ when } T \rightarrow \pm \infty \end{array} \right.$$

$$C_V = 0 \text{ when } T \rightarrow \pm \infty$$

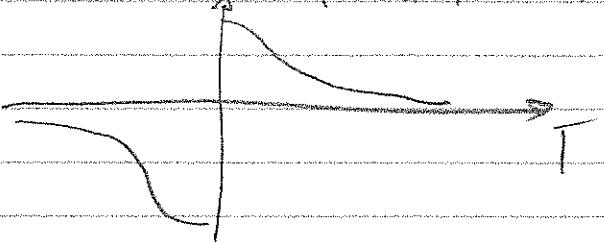
There's also an inflection point



- Consider (positive) temperatures only



\rightarrow magnetism
And recall $M_{\text{ext}} = u$ (reflection of u)
 M about T



Analytic solutions to paramagnets

recall $S = \left(\frac{N!}{N^N} \right) = \frac{N!}{N^N N!} = \frac{N!}{N_p! (N-N_p)!}$ assume $N \gg 1$

$$S = k \ln \Omega = k \ln(N!) - \ln(N_p!) - \ln((N-N_p)!)$$

Stirling's approx $\ln N! \approx N \ln N - N$

$$\begin{aligned} \frac{\partial S}{\partial u} &= (N \ln N - N) + (N_p \ln N_p - N_p) + \frac{(N-N_p) \ln (N-N_p)}{N} \\ &\quad + (N_p - N) \end{aligned}$$

$$= N \ln N - N_p \ln N_p - (N - N_p) \ln (N - N_p)$$

$$\frac{\partial S}{\partial u} \left(\frac{1}{T} \right) = \frac{\partial S}{\partial u} \Big|_{N_p} \quad \text{and} \quad u = \mu B (N - N_p)$$

$$\frac{\partial^2 S}{\partial u^2} \left(\frac{1}{T} \right) = \frac{\partial^2 S}{\partial N_p^2} \left(\frac{\partial N}{\partial u} \right) = (-2\mu B)^2 \frac{\partial S}{\partial N_p} \Big|_{N_p} = \frac{-1}{2\mu B} \frac{\partial^2 S}{\partial N_p^2} \left(\frac{1}{T} \right)$$

$$-\frac{\partial^2 S}{\partial N_p^2} \left(\frac{1}{T} \right) = k \left[-\ln N_p - 1 + \ln(N - N_p) + \frac{N - N_p}{N - N_p} \right]$$

$$N_F = \frac{1}{2} \left(N - \frac{u}{\mu_B} \right)$$

(60)

$$\text{So } \left(\frac{\partial S}{\partial N_F} \right) = k \left[-\ln \left(\frac{1}{2} \left(N - \frac{u}{\mu_B} \right) \right) + \ln \left(N - \frac{1}{2} N + \frac{u}{2\mu_B} \right) \right]$$

$= \dots$

$$\boxed{\frac{\partial S}{\partial N_F} = k \ln \left(\frac{N + u/\mu_B}{N - u/\mu_B} \right)}$$

$$\text{So } \left(\frac{\partial S}{\partial u} \right) = \frac{\partial S}{\partial N_F} \frac{\partial N_F}{\partial u} = \left(\frac{k \ln}{-2\mu_B} \left(\frac{N + u/\mu_B}{N - u/\mu_B} \right) \right) = \frac{1}{T}$$

$$\text{So } \boxed{\frac{1}{T} = \frac{k}{2\mu_B} \ln \left(\frac{N - u/\mu_B}{N + u/\mu_B} \right)} \quad T(u)$$

So we can solve for $u(T)$

$$\frac{2\mu_B}{kT} = \ln \left(\frac{N - u/\mu_B}{N + u/\mu_B} \right)$$

$$e^{\frac{2\mu_B}{kT}} = \frac{N - u/\mu_B}{N + u/\mu_B} = \frac{1 - u/N_{\mu B}}{1 + u/N_{\mu B}}$$

$$\text{So } e^{\frac{2\mu_B}{kT}} + \frac{u}{N_{\mu B}} e^{\frac{2\mu_B}{kT}} = 1 - \frac{u}{N_{\mu B}}$$

$$\text{So } \frac{u}{N_{\mu B}} \left(e^{\frac{2\mu_B}{kT}} + 1 \right) = 1 - e^{\frac{2\mu_B}{kT}}$$

$$\text{So } u(T) = N_{\mu B} \frac{1 - e^{\frac{2\mu_B}{kT}}}{1 + e^{\frac{2\mu_B}{kT}}}$$

Now, simplify \rightarrow use $\sinh(x) = \frac{1}{2}(e^x - e^{-x})$, $\cosh(x) = \frac{1}{2}(e^x + e^{-x})$

$$\text{So } \tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}} = \frac{(1 - e^{-2x})}{(1 + e^{-2x})}$$

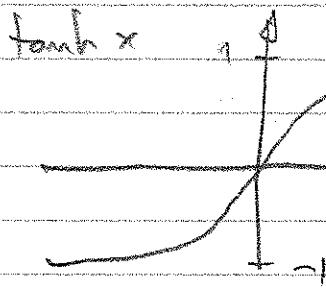
$$\text{So } -\tanh x = \frac{1 - e^{-2x}}{1 + e^{-2x}}$$

If $\mu t \ll x = \left(\frac{\mu B}{kT}\right)$, then

$$u(T) = -\mu B N \tanh\left(\frac{\mu B}{kT}\right)$$

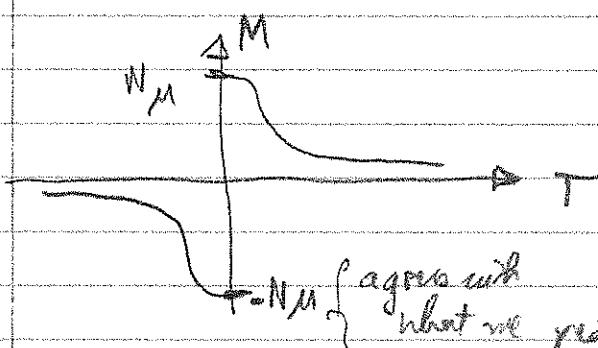
with $M = -\frac{n}{B}$

$$M(T) = \pm N_a \tanh\left(\frac{\mu B}{kT}\right)$$



as $x \rightarrow 0$, $\tanh x \rightarrow 0$

$\square x = \frac{\mu B}{kT}, T \rightarrow \pm \infty$
 $\rightarrow (M, u \rightarrow 0)$



$\square x \rightarrow \infty, \rightarrow T \rightarrow 0_+$
 $\tanh x \rightarrow 1 \rightarrow M = N_a u$

$\square x \rightarrow -\infty, T \rightarrow 0_-$
 $\tanh x \rightarrow -1 \rightarrow M = -N_a u$

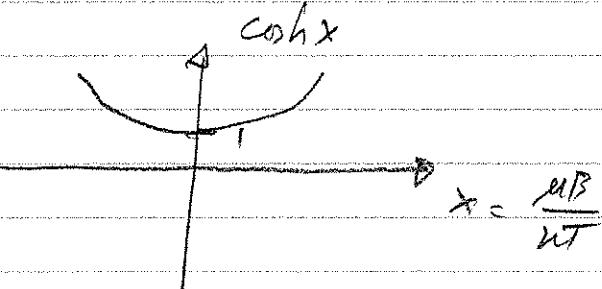
What about heat capacity of paramagnet?

$$C_p = \left(\frac{\partial U}{\partial T}\right)_{N,B} \quad \text{Now, } u = -N_a B \tanh\left(\frac{\mu B}{kT}\right)$$

$$\text{Recall } \frac{d}{dx} \tanh(x) = \operatorname{sech}^2(x) \cdot dx \approx \frac{1}{\cosh^2(u)} du$$

$$\left(\frac{\partial V}{\partial T}\right)_{N,B} = -N_\mu B \cosh^2\left(\frac{\mu B}{kT}\right) \left(\frac{-\mu B}{kT^2}\right) = C_B$$

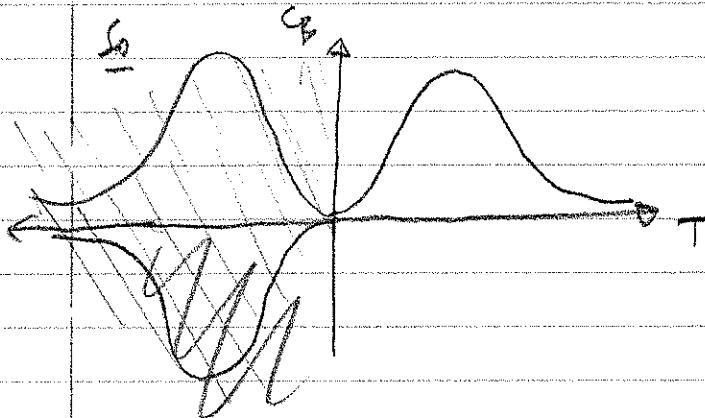
$$\text{So } C_B = N_\mu \left(\frac{\mu B}{kT}\right)^2 \left[\cosh^2\left(\frac{\mu B}{kT}\right) \right]$$



① as $x \rightarrow 0$, $T \rightarrow \pm \infty$ $\cosh(x) \rightarrow 1$
 $\rightarrow [C_B \rightarrow 0 \text{ as } T \rightarrow \pm \infty]$

② as $x \rightarrow \infty$, $T \rightarrow 0_+$, $\cosh(x) \rightarrow +\infty$ (Faster)

$$\text{So } [C_B \rightarrow 0 \text{ as } T \rightarrow 0]$$



Ex Consider two-state paramagnet.

Let $\mu = \mu_B$ Bohr magneton $\mu_B = \frac{e\hbar}{4\pi me} = \frac{e\hbar}{2m_e}$

$$\text{Let } B = 1 \text{ T}$$

$$\begin{aligned} &= 5.788 \text{ eV/T} \\ &\approx 9.274 \times 10^{-21} \text{ J/T} \end{aligned}$$

$$\text{Then } M = ? \quad \mu_B = 5.8 \times 10^{-5} \text{ eV} \quad \left. \begin{array}{l} \\ \end{array} \right\} \rightarrow \frac{\mu_B}{kT} \ll 1$$

$$kT = \frac{1}{40} \text{ eV}$$

Now $\tanh(x) \approx x$ for small x

$$\left(\begin{array}{l} M \approx (N_\mu) \left(\frac{\mu B}{kT}\right) = \frac{N_\mu^2 B}{kT} \end{array} \right) \rightarrow \text{"high-temperature limit.}$$

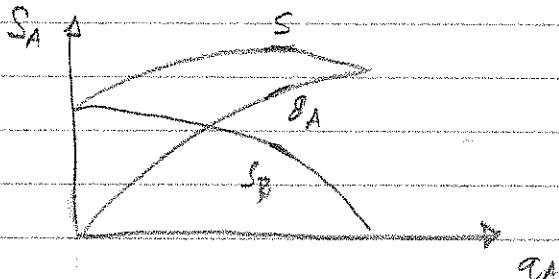
$M \propto \frac{1}{T}$ \rightarrow Curie's Law (Pierre Curie)
 (high temp limit)

$C \propto \frac{1}{T^2}$ \rightarrow (high temp limit)

Mar 9, 2019

MECHANICAL EQUILIBRIUM

we're been discussing dU and dS



So get

constant V

$$\text{at thermal eq} \quad \frac{\delta S_{\text{tot}}}{\delta U} = 0 \Rightarrow \boxed{\frac{\delta A}{\delta U_A} = \frac{\delta B}{\delta U_B}}$$

Consider some interacting system that can exchange volume as well as energy



\rightarrow change in V governed by change in P

\rightarrow change in V governed by change in T

$$\left. \begin{array}{l} \text{as } U, T, \sigma, S \\ \text{or } V, T, \sigma, S \end{array} \right\} \text{Goal: develop a relationship between } \frac{\delta S}{\delta V} \text{ and } P$$

Just like $\delta S_{\text{tot}}/\delta U$ gives thermal equilibrium

($\boxed{\frac{\delta S_{\text{tot}}}{\delta V} = 0}$) \rightarrow mechanical equilibrium

$$\text{if } \frac{\partial S_{\text{ext}}}{\partial V_A} = 0 \Rightarrow \boxed{\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}}$$

↓ ↑

volume is conserved

$$\frac{\partial S_{\text{ext}}}{\partial V_A} + \frac{\partial S_B}{\partial V_B} = 0, \text{ but } \partial V_A = -\partial V_B \rightarrow \text{ mech-equl.}$$

What are these held constant?

$$\left(\frac{\partial S_A}{\partial V_A} \right)_{V_B, N_B} = \left(\frac{\partial S_B}{\partial V_B} \right)_{V_A, N_A}$$

Dimensional analysis.

$$[S] : \frac{J/K}{[m^3]} = \frac{N \cdot m/K}{m^3} = \frac{N}{m^2} \cdot \frac{1}{K} = \frac{[P]}{[T]}$$

Guess

$$\boxed{\left(\frac{\partial S}{\partial V} \right)_{V, N} = \frac{P}{T}}$$

Look at ideal monatomic gas... $n = f(N) V^{N/4} u^{3N/2}$

$$S = k \ln \Omega = k \left[\ln f(N) + \ln V^N + \ln u^{3N/2} \right]$$

$$= k \left[\ln f(N) + N \ln V + \frac{3N}{2} \ln u \right]$$

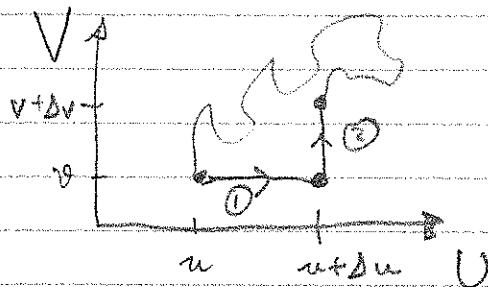
if $P = T \left(\frac{\partial S}{\partial V} \right)_{V, N}$, then

$$? = T k \cdot N \cdot \frac{1}{V}$$

$$\Rightarrow P = \frac{NkT}{V} \quad \text{works...}$$

$$\boxed{PV = NkT} \quad \checkmark$$

We'd like to combine both of these relations for thermal and mechanical equilibria.



Entropy is an exact differential

path independent

$$\Delta S_{\text{tot}} = \Delta S_1 + \Delta S_2$$

① Isochoric process \rightarrow volume constant

② Isothermal process \rightarrow temp constant or energy

$$\Delta S_{\text{tot}} = \left(\frac{\partial S}{\partial u}\right)_{N,T} du + \left(\frac{\partial S}{\partial V}\right)_{N,T} dV$$

$S(u, V, N)$

$$\Delta S_{\text{tot}} = \left(\frac{\partial S}{\partial u}\right)_{V,N} du + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV$$

T vol \neq put.

$$= \frac{1}{T} du + \frac{P}{T} dV$$

So

$$dU = TdS - PdV \rightarrow \text{thermo dynamic identity}$$

T as long as N is constant.

Note this is just the first law of thermo.

$$dU = dW_m + dQ$$

{ For quasi-static processes $\rightarrow W_m = -PdV$

For quasi-static isothermal process $\rightarrow dQ / dS = \frac{Q}{T} \rightarrow dQ = TdS$

$\boxed{Q = TdS}$ → for any quasi-static process.
Not just isothermal

$$dU = TdS - PdV \leftarrow \text{more fundamental.}$$

Now, if $u = u(s, v)$ and dU exact, then

$$\frac{\partial^2 u}{\partial S \partial S} = \frac{\partial^2 u}{\partial V \partial V} \quad \text{order of diff. doesn't matter.}$$

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

$$du = TdS - PdV$$

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

\cancel{u} \cancel{u}
 T $-P$

\therefore

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

from Maxwell's relation

Constant Entropy process?

If we have quasi-static process & adiabatic process (no heat transfer)

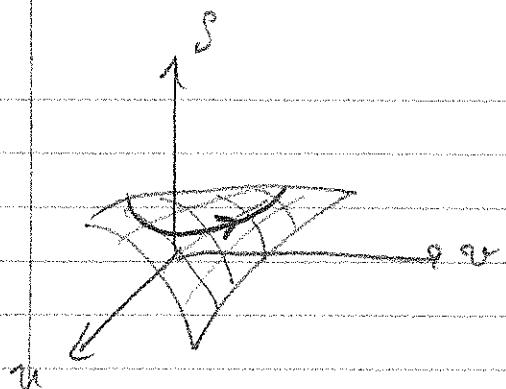
(P equilibrium)

(leave system)

→ no change in Entropy

$$Q = TdS = 0 \quad ? \rightarrow \text{Isentropic} \quad \left\{ \begin{array}{l} \text{quasi static} \\ \text{adiabatic} \end{array} \right.$$

(67)



$$dU = TdS - PdV$$

$$TdS = 0 \Rightarrow dU + PdV$$

$$dS_{\text{tot}} = 0 \text{ but } \frac{\partial S}{\partial U} \neq 0 \neq \frac{\partial S}{\partial V}$$

Recall $C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}$

$$\delta Q = C_V dT = TdS$$

$\Delta S = \int_T^S C_V dT$ But we want to work at constant pressure processes

$$(\Delta S)_P = \int \frac{C_P}{T} dT \rightarrow \text{more useful in many cases...}$$

Example 1L of air ($N_2 + O_2$) at 1 atm. Heat air until it doubles in volume. What is ΔS ?

Diatomeric gas $C_V = \frac{f}{2} Nk$

$$C_P = C_V + Nk$$

Fix diatomic gas at room temp. $T = 300K$

So $C_P = \frac{7}{2} Nk$

Ideal gas law $\rightarrow PV = NkT \rightarrow Nk = \frac{PV}{T} = \frac{(10^5 \text{ Pa})(1 \times 10^{-3} \text{ m}^3)}{120 \text{ K}}$

$$N = nRT$$

So $T^2 = 2T$

$$= \frac{1}{3} J/K$$

(68)

$$\text{So } (\Delta S)_p = \int \frac{C_p}{T} dT = C_p \ln \frac{T_f}{T_i} = C_p \ln(2)$$

$$\text{So } (\Delta S)_p = C_p \ln(2) = \left(\frac{7}{2} Nk\right) \ln(2) \approx 0.81 \text{ J/K}$$

Another way to do this

$$\rightarrow dQ = TdS - PdV$$



$$\sum \frac{kN}{2} dT = TdS - \frac{Nh}{V} dV$$

$$\sum \frac{kN}{2} dT = T \sum dS - \sum Nh$$

$$\sum \frac{kN}{2} \frac{dT}{T} = dS - \frac{Nh}{V} dV$$

b

$$\Delta S = \sum \frac{kN}{2} \ln \frac{T_f}{T_i} + Nh \ln \left(\frac{V_f}{V_i} \right)$$

$$(\Delta S)_p = \frac{7}{2} kN \ln(2)$$

→

Mr 11, 2019

recall $dQ = TdS - PdV$ → can be used for non-quasi-static processes

① Fast compression

$dV \approx 0$. We have done work but work is greater than $-PdV$



$$dQ = TdS - PdV = Q + W$$

$$\text{So } Q < TdS \rightarrow \left| \frac{ds}{T} \right| > \left| \frac{Q}{T} \right| \rightarrow \text{added entropy}$$

② Free-expansion



vacuum \rightarrow allows gas expand into vacuum

$$W=0, \delta=0 \text{ so } d\delta=0 \quad \text{no work static}$$

$$\text{But } dU = TdS - PdV = 0 \Rightarrow TdS = PdV > 0 \quad (W \neq PdV)$$

↳ we added entropy

Example

Fast compression of air at $P = 1 \text{ atm}$, $T = 300K$
 $= 10^5 \text{ Pa}$



$$F = 2000 \text{ N}$$

$$n = \frac{1}{25} \text{ mol}$$

$$A = 0.01 \text{ m}^2 \quad V_i = 1 \text{ L}$$

Say piston moves 1 mm before it stops.

If this is quasi-static $W = \int PdV = \int \frac{nRT}{V} dV = nR \ln \frac{V_f}{V_i}$

$$W = nR \ln \frac{V_f}{V_i}$$

$$V_i = \frac{1.00 \text{ L}}{1000}, \quad V_f = \frac{1.00 - (0.001)(0.01)}{1000}$$

Work actually done

$$W = F \cdot d = (2000 \text{ N}) (0.001 \text{ m}) = 2 \text{ J}$$

$$> -PdV$$

Fast compression Adiabatic $\Rightarrow \delta=0$

$$\Rightarrow \Delta U = Q + W = 0 + W = 2 \text{ J}$$

How does S change?

$$dU = TdS - PdV$$

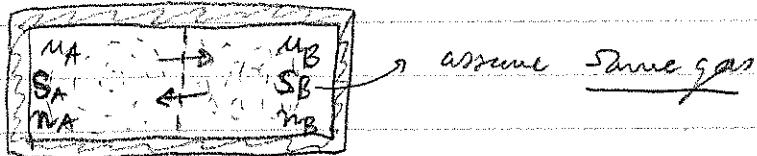
$$\delta S = dS = \frac{dU + PdV}{T} = \frac{2 \text{ J} + (10^5 \text{ Pa})(-0.01 \text{ m}^2)(0.001 \text{ m})}{300 \text{ K}} \approx \frac{1}{3} \text{ J/K}$$

Diffusion Equilibrium

Thermal equil \rightarrow T same

Mech equil \rightarrow P same

Diffusion equil \rightarrow N same (μ)



Assume V constant. Assume that gases can exchange energy and particles. Assume same gas in both sides - - -

$$n_{\text{tot}} = N_{\text{tot}} = \text{const}$$

$$S_{\text{tot}} = S(\mu_A, N_A)$$

Before • $\left(\frac{\partial S_{\text{tot}}}{\partial \mu_A} \right)_{N,V} = \left(\frac{\partial S_{\text{tot}}}{\partial \mu_B} \right)_{N,V} = 0$ at equilibrium.

• $\left(\frac{\partial S_{\text{tot}}}{\partial N_A} \right)_{V,V} = \left(\frac{\partial S_{\text{tot}}}{\partial N_B} \right)_{V,V} = 0$ at diffusion eq.

• $\left(\frac{\partial S_A}{\partial N_A} \right)_{V,V} = \left(\frac{\partial S_B}{\partial N_B} \right)_{V,V} = 0$ at equilibrium.

Rather not N, but μ

$\rightarrow \mu$: chemical potential (μ) has units of energy [J]

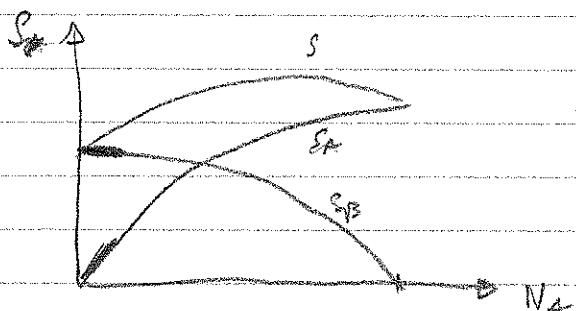
Relating $\frac{\partial S}{\partial N}$ to μ & $\frac{\partial S}{\partial N} = \left(\frac{\partial S}{\partial n} \right)$ multiply by temperature + set $n = 1$

$$\frac{J/K}{#}$$

$$\mu = -T \left(\frac{\partial S}{\partial n} \right)_{V,V}$$

(71)

At equilibrium $\mu_A = \mu_B$. Consider S vs. N



→ particles will flow from system with lower $\frac{\partial S}{\partial N}$ to high $\frac{\partial S}{\partial N}$

Since, larger $\left(\frac{\partial S}{\partial N}\right)$ → smaller μ

→ particles flow from system with high to low μ

$\mu \rightarrow$ concentration / density of gas...

Generalized Thermodynamic identity

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial V}\right)_{N,T} dV + \left(\frac{\partial S}{\partial N}\right)_{V,T} dN + \left(\frac{\partial S}{\partial T}\right)_{V,N} dT \\ &= \frac{1}{T} dV + \frac{-\mu}{T} dN + \frac{P}{T} dT \end{aligned}$$

δ $TdS = dV - \mu dN + PdT$

$$dV = TdS + \mu dN - PdT$$

if quin. \rightarrow "heat" "diss work" "mech work"
- static -

When V, T const $\rightarrow \mu = -T \left(\frac{\partial S}{\partial N}\right)$ } see due to change in N
When, S, V const $\rightarrow \mu = \left(\frac{\partial V}{\partial N}\right)_{S,T}$

Normally, to keep $\Delta S = 0$, if we TN, need to fix S

e.g. Einstein solid $n = N = 3, q = 3$

$$S = \binom{3+2-1}{3} = 10$$

Then

$S = k \ln S$. If we TN by 1, $N = 4$

$$\text{then } S' = \binom{4+3-1}{3} = 20 \quad S' = k \ln 20 > S.$$

to keep S constant \rightarrow need to decrease $q \rightarrow q = 2$

$$S'' = \binom{4+2-1}{2} = 10 \text{ so that } S'' = S$$

$$\left. \begin{array}{l} \Delta U = q\varepsilon = q \cdot \varepsilon = 2\varepsilon_1 - 3\varepsilon_1 = -\varepsilon \\ \Delta N = 1 \end{array} \right\} \frac{\partial \mu}{\partial N} = -1$$

$$\underline{\mu} = -\left(\frac{\partial S}{\partial N}\right)_{V,T} = \frac{1}{2}\varepsilon = -\varepsilon$$

Nov 1st, 2019 | Chemical potential of ideal gas | (nonatomic)

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{V,T}$$

$$S = Nk \left[\ln \left(\sqrt{\frac{4\pi mU}{3h^2}} \right)^{3/2} - \ln N + \frac{5}{2} \right]$$

$$\begin{aligned} \mu &= -T \left\{ k \left[\ln \left(\sqrt{\frac{4\pi mU}{3h^2}} \right)^{3/2} \right] - \ln N + \frac{5}{2} \right\} \\ &\quad + Nk \left[0 - \frac{5}{2} \frac{1}{N} \right] \end{aligned}$$

$$\boxed{\mu = -T k \ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3h^2} \right)^{3/2} \right]}$$

$$\text{But } n = \frac{3NkT}{2}$$

Q

$$\underline{\mu} = -T k \ln \left[\frac{v}{N} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right]$$

$\frac{kT}{P}$

Ex for He at room temp ~ 1 atm. $\rightarrow \mu = -0.32 \text{ eV}$

higher $\mu \rightarrow$ higher concentration \rightarrow more likely to give off particles

[What about for a mixture of gases?]

$$\mu_1 = -T \left(\frac{\partial S}{\partial N_1} \right)_{\text{Total}, \text{O}_2, \text{N}_2}^{\text{Total}}$$

$$\mu_2 = -T \left(\frac{\partial S}{\partial N_2} \right)_{\text{Total}, \text{O}_2, \text{N}_2}$$

Theano identity $\rightarrow dD = TdS - PdV + \sum_i \mu_i dN_i$

In diffusive equilibrium $\rightarrow \mu_A = \mu_{A1} + \mu_{A2} + \dots$
 where $\{ A, B, \dots \} \rightarrow$ systems
 $1, 2, \dots \rightarrow$ species of atoms / molecules

Note Chemists $\mu_i = -T \left(\frac{\partial S}{\partial N_i} \right)_{\text{Total}} \rightarrow \# \text{ moles}$ $n = N / N_A$



In a mixture of ideal gases, each μ_i behaves as if the other species weren't present. At constant partial pressure

$$P_i = x_i P$$

Defn mole $\rightarrow x_i = \frac{N_i}{N_{\text{tot}}}$

$$\text{Now } P_i = x_i P = \frac{x_i}{V} N_{\text{tot}} kT = \frac{N_i}{N_{\text{tot}}} \frac{N_{\text{tot}} kT}{V} = \boxed{\frac{N_i kT}{V} = P_i}$$

~~Now consider 2 gases A + B → mixture occupying the same volume V~~

$$S_{\text{tot}} = S_A + S_B = S(V, V, N_A) \approx S(V, V, N_B)$$

if we hold n constant at equilibrium, then this is the same as holding x_A & x_B constant.

$$\boxed{M_A = -T \left(\frac{\partial S_{\text{tot}}}{\partial N_A} \right)_{V, V, N_B} = -T \left(\frac{\partial S_A}{\partial N_A} \right)_{V, V}} \quad (\text{since } \partial S_B = 0)$$

~~same as if B not present~~

Classical Statistical of A Large Crystalline Solid

$$(1) \quad \Omega = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} = \frac{(q+N)!}{(q+N)N!q!}$$

$$\text{note } (N-1)! = \frac{N!}{N}$$

Fermi's approximation $\rightarrow N! \approx N^N e^{-N} \sqrt{2\pi N}$

$$\Omega \approx \frac{(q+N)^{q+N} e^{-q-N} \sqrt{2\pi(q+N)}}{(q+N)} \cdot \frac{N}{q^q e^{-q} \sqrt{2\pi q} N^N e^{-N} \sqrt{2\pi N}}$$

$$\approx \frac{(q+N)^{q+N}}{q^q N^N} \sqrt{\frac{N}{2\pi q(1+N)}} \approx 1$$

$$\approx \left(\frac{q+N}{q} \right)^q \left(\frac{q+N}{N} \right)^N \sqrt{\frac{N}{2\pi q(1+N)}} \approx \boxed{\left(\frac{q+N}{q} \right)^q \left(\frac{q+N}{N} \right)^N}$$

25

$$S = k \ln \Omega = q \ln \frac{1}{N} + N k \ln \left(\frac{q+N}{N} \right)$$

$$S = k \ln \left(\frac{1+N}{N} \right) + N k \ln \left(\frac{q}{N} + 1 \right)$$

$$\text{So } \frac{\partial S}{\partial N} = k \ln \frac{1}{1+N} \cdot \frac{1}{N} + k \ln \left(\frac{q}{N} + 1 \right) + N k \frac{1}{1+\frac{q}{N}} \cdot \left(-\frac{q}{N^2} \right)$$

$$\boxed{\frac{\partial S}{\partial N} = k \ln \left(\frac{1+N}{N} \right)} \rightarrow \text{chemical potential of a large } \begin{cases} \text{Einstein solid} \end{cases}$$

Now

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{V,T} = -k T \ln \left(\frac{1+N}{N} \right)$$

-ET

Ch-4 HEAT ENGINE & REFRIGERATOR

Concept → absorb Q. Convert to mechanical W.

Combiner



Design consideration

- ① Want to start & end at the same macrostate (energy)
 → cyclic in PV diagram
 engine → W_{eq}

$$\text{So } \Delta U = 0$$

- ② Must obey 1st law of Thermodynamics

$$\boxed{\Delta U = Q_{\text{absorb}} - W_{\text{eq}}}$$

- ③ Must obey 2nd law of thermodynamics $\boxed{\Delta S \geq 0}$

- If turns out that it is impossible to convert 100% of absorb & into usable work because we have heat flow.

→ Look at entropy of system

{ For reversible engine, want $\Delta S_{\text{engine}} = 0$

$$\Delta S_{\text{reservoir}} = -\frac{Q_h}{T_h} \geq 0$$

1st law

$$\Delta U = Q_{\text{abs}} - W_{\text{sys}} \rightarrow Q_{\text{abs}} = W_{\text{sys}}$$

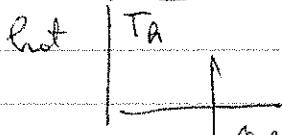
$$\therefore \Delta S_{\text{system}} = \Delta S_{\text{engine}} + \Delta S_{\text{reservoir}} = -\frac{Q_h}{T_h} = -\frac{W_{\text{sys}}}{T_h} \geq 0$$

But then W_{sys} has to be negative

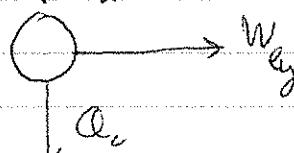
Result: cannot build an engine with a single reservoir that converts heat into work

To fix this

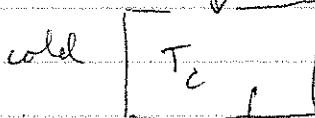
Assume cyclic engine $\Delta U = 0$



$$\text{Then } \Delta S_h - \Delta S_c = 0$$



$$Q_h - Q_c - W_{\text{sys}} = 0$$



$$\therefore W_{\text{sys}} = Q_h - Q_c$$

work done by the engine

$Q_h = Q$ absorbed by the cold engine

$W_{\text{sys}} = W$ done by engine.

$Q_c = Q$ expelled by the engine

Efficiency

$$\epsilon = \frac{\text{Heat Work}}{\text{Q_{abs}}} = \frac{W_{th}}{Q_h}$$

Rd

$$\epsilon = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

$$\Delta S_{\text{hot}} = -\frac{Q_h}{T_h}, \quad \Delta S_{\text{cold}} = \frac{Q_c}{T_c}$$

so $\frac{Q_c}{T_c} \geq -\frac{Q_h}{T_h}$ for $\Delta S \geq 0$

∴

$$\epsilon \leq 1 - \frac{T_c}{T_h}$$

Example

$$T_h = 100^\circ C$$

$$Q_h = 150 J$$

Assume $\Delta n = 0$

$$W = 150 J - 125 J = 25 J$$

$$Q_{abs} = Q_h - Q_c$$

$$Q_c = 125 J$$

$$T_c = 20^\circ C$$

$$\epsilon = \frac{W_{th}}{Q_h} = \frac{25}{150} = \frac{1}{6}$$

Does this engine reach maximum eff?

$$\text{Max } \epsilon = 1 - \frac{T_c}{T_h} = 1 - \frac{20 + 273}{100 + 273} = 21.4\%$$

B

No, doesn't reach maximum efficiency.

Carnot Cycle

→ towards a more efficient engine.

- To avoid creating excess entropy in an engine.

$$T_{\text{engine}} = T_h \rightarrow \text{not possible.}$$

Instead, we want T_{engine} just slightly below T_h

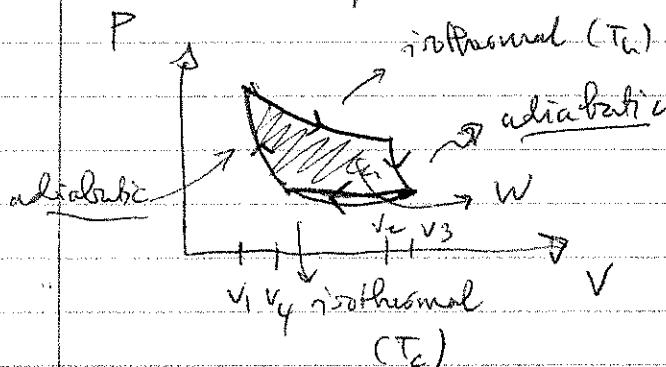
→ let it expand isothermally to keep $T_{\text{engine}} \approx$ constant

* after isothermal expansion → bring temp of engine down

$$\text{to } T_c \rightarrow (T_{\text{engine}} > T_c \text{ slightly})$$

→ Want [adiabatic expansion] (to avoid additional heat flow)

→ expel waste heat during an isothermal compression.



Carnot Cycle

(1) Isothermal @ T_h

(2) Adiabatic expansion to get T_c

(3) Isothermal compression @ T_c (Waste heat drop)

(4) Adiabatic compression to bring engine

back to T_h .

$$(i) Q_h = W_{cy} = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{NkT_h}{V} dV = NkT_h \ln \frac{V_2}{V_1}$$

$$(V_3 > V_4) Q_c = - \int_{V_3}^{V_4} P dV = - NkT_c \ln \left(\frac{V_4}{V_3} \right) = NkT_c \ln \left(\frac{V_2}{V_4} \right)$$

$$\eta = 1 - \frac{Q_c}{Q_h} = 1 - \frac{\ln(V_3/V_4)}{\ln(V_2/V_1)} \cdot \frac{T_c}{T_h}$$

Now, for adiabatic processes

$$\rightarrow VT^{\gamma-1} = \text{constant}$$

$$\therefore V_3 T_c^{\gamma-1} = V_2 T_h^{\gamma-1} \Rightarrow V_4 T_c^{\gamma-1} = V_1 T_h^{\gamma-1}$$

$$\therefore \frac{V_3 T_c^{\gamma-1}}{V_4 T_c^{\gamma-1}} = \frac{V_2 T_h^{\gamma-1}}{V_1 T_h^{\gamma-1}} \Rightarrow \frac{V_3}{V_4} = \frac{V_2}{V_1} \Rightarrow \frac{\ln(V_3/V_4)}{\ln(V_2/V_1)}$$

So

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

\rightarrow assuming adiabatic.

\rightarrow Carnot cycle produces near efficiency.

et

Mr 18, 2018

Hence engines

Recall



Cyclic process $\rightarrow \Delta U = 0$

$\rightarrow W_{cy}$



$$W_{cy} = Q_{in} - Q_{out}$$

$$\eta = \frac{Q_{in} - Q_{out}}{Q_{in}} = \frac{W_{cy}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

Since $\Delta S \geq 0$, $\frac{\delta}{T_h} \leq 1 - \frac{T_c}{T_h}$ equality holds when
Carnot engine

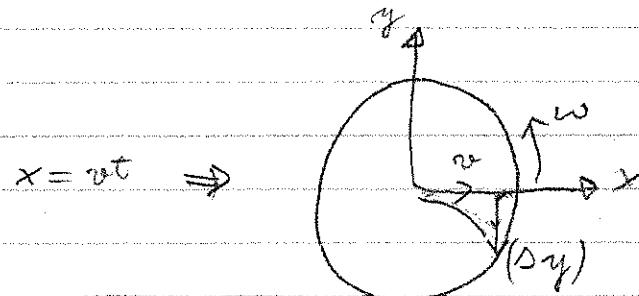
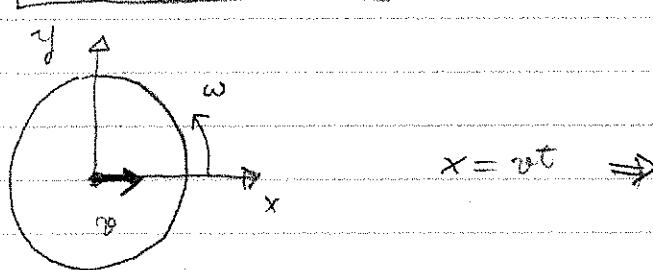
Hurricanes as Heat Engines

Hot reservoir \rightarrow ocean surface

Cold reservoir \rightarrow atmosphere.

$\odot \rightarrow$ Low pressure system w/ circulation due to Coriolis effect

$$F_c = 2\pi r v \times w$$



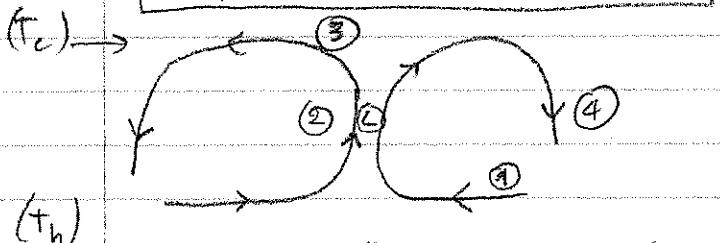
if $v \perp w$, Then

$$\Delta y = (wt)x$$

Coriolis acceleration

$$\text{Rearrange } x = vt \rightarrow \Delta y = cvt^2 = \frac{1}{2} (2cv)^t^2 = \frac{1}{2} a_{\text{act}}^2 t^2$$

Steps of Hurricane engine \rightarrow same as Carnot's



(1) Isothermal expansion of air over hot ocean ($T \approx 300K$)

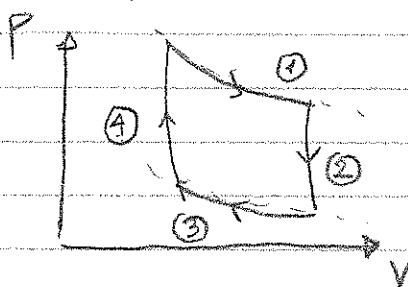
(2) Adiabatic expansion

\rightarrow air moves rapidly up eye wall into tropopause

(3) Isothermal compression in tropopause ($T \approx 200K$)

(4) Adiabatic compression of dry air

On PV diagram



Work produced by turbines dissipated by friction
 $\rightarrow \alpha v^2$ (turbulent flow)

$$W = F_{\text{drag}} \cdot x$$

$$\text{So } \frac{dW}{dt} = (\alpha v^2) v \approx \alpha v^3$$

heat transfer from the ocean by forced convection. $Q_h \propto v$

$$\text{So Total: } Q_h = \alpha v^3 + bv \rightsquigarrow Q_{\text{ocean}}$$

\downarrow
Q due to friction

So

$$\epsilon = \frac{W_{\text{net}}}{Q_{\text{heat}}} = \frac{\alpha v^3}{\alpha v^3 + bv} = 1 - \frac{b}{T_h} \rightsquigarrow \text{Const engine}$$

\Rightarrow Can solve for v .

$$\frac{\alpha v^3}{\alpha v^3 + bv} = 1 - \frac{T_c}{T_h} \Rightarrow \alpha v^3 \left(\frac{\alpha v^3 + b}{\alpha v^3} \right) \left(1 - \frac{T_c}{T_h} \right) = \alpha v^3 \left(1 - \frac{T_c}{T_h} \right) + b \left(1 - \frac{T_c}{T_h} \right)$$

$$\text{So } \alpha v^3 \left(\frac{T_c}{T_h} \right) = b \left(1 - \frac{T_c}{T_h} \right)$$

$$v = \sqrt[3]{\frac{b}{\alpha} \left(\frac{T_h}{T_c} - 1 \right)}$$

Refrigerator



Work done on substance to pull heat out cold reservoir

W_{on}

\Rightarrow useful work heat to heat reservoir.

$$\text{Now, } \Delta m = 0 \Rightarrow Q_c + W_m = Q_h$$

↓ compression work -

Coefficient of Performance

$$\text{COP} = \frac{Q_c}{W_m}$$

replace $W_m = Q_h - Q_c$

$$\therefore \boxed{\text{COP} = \frac{Q_c}{Q_h - Q_c} = \frac{1}{\frac{Q_h}{Q_c} - 1} \geq 1}$$

By 2nd law, $\Delta S \geq 0 \Rightarrow \frac{Q_h}{T_h} - \frac{Q_c}{T_c} \geq 0 \therefore \frac{Q_h}{Q_c} \geq \frac{T_h}{T_c}$

$$\therefore \boxed{\text{COP} = \frac{1}{\frac{Q_h}{Q_c} - 1} \leq \frac{1}{\frac{T_h}{T_c} - 1}}$$

Carrot cycle once again creates the most efficient refrigerator

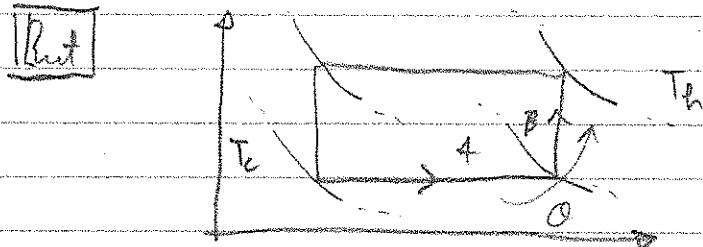
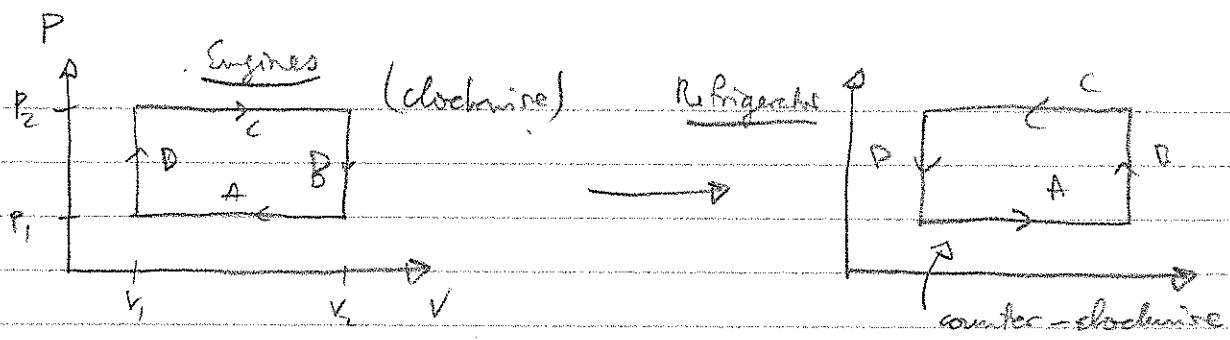
Need $T \geq T_h$ during heat rejection

$T \leq T_c$ during heat absorption

Example what is the max possible COP for a standard AC unit?

$$\text{Let } t_{in} = 22^\circ C \quad \text{Then} \quad \text{COP}_{\max} = \frac{1}{\frac{30+273}{22+273} + 1} \approx 36.9$$

PV diagram

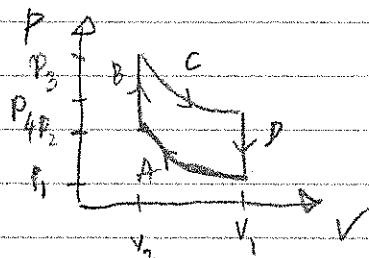


Need $T_c > T_h$ for heat flow A, B
and $T_h < T_c$ for heat flow C, D

\Rightarrow Need adiabatic processes

Nov 19, 2019 Real Heat Engine

Example Internal Combustion Engine (Otto cycle)



A, C \rightarrow adiabats.

- A : adiabatic compression of air + fuel
- B : spark plug ignites the mixture, increasing T, P, holding V constant
- C : adiabatic expansion inside cylinder due to high pressure
- D : hot exhaust is expelled and replaced by new mixture at lower temperature

Efficiency of this engine?

$$\epsilon = 1 - \frac{Q_c}{Q_h} \quad \text{Steps A \& C are adiabatic} \rightarrow Q = 0$$

B $\rightarrow Q_h$
D $\rightarrow Q_c$

Step B $\Delta U_B = Q + \dot{W}^0 \Rightarrow Q = \frac{f}{2} N k T = \frac{f}{2} P V = \frac{f}{2} V_2 (P_3 - P_2)$

Step D $\Delta U_D = Q_c + \dot{W}^0 = -\frac{f}{2} N k T \Rightarrow Q_c = \frac{f}{2} V_2 (P_4 - P_1)$

So,
$$\boxed{\epsilon = 1 - \frac{Q_c}{Q_h} = 1 - \frac{V_1 (P_4 - P_1)}{V_2 (P_3 - P_2)}}$$

But more convenient with temperatures

Adiabatic $\Rightarrow P_1 V_1^\gamma = P_2 V_2^\gamma \Rightarrow P_1 V_1^\gamma = P_2 V_2^\gamma$

So $(P_4 - P_1) V_1^\gamma = (P_3 - P_2) V_2^\gamma$

So $\frac{P_4 - P_1}{P_3 - P_2} = \frac{V_2^\gamma}{V_1^\gamma} = \left(\frac{V_2}{V_1}\right)^\gamma$

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

So
$$\boxed{\epsilon = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}}$$

Compared to Carnot engine: $\boxed{\epsilon = 1 - \frac{T_c}{T_h} = \epsilon = 1 - \frac{T_1}{T_3}}$

Remember that $T V^{\gamma-1}$ = constant for an adiabat $\Rightarrow \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$

$\rightarrow \boxed{\epsilon = 1 - \frac{T_1}{T_2}}$

or, another adiabat $\Rightarrow T_2 V_2^{\gamma-1} = T_4 V_4^{\gamma-1}$

$$\therefore \frac{T_4}{T_2} = \left(\frac{V_2}{V_4}\right)^{\gamma-1} \Rightarrow \eta = 1 - \frac{T_4}{T_2}$$

Note $\frac{T_1}{T_3} < \frac{T_1}{T_2}$ and $\frac{T_1}{T_3} < \frac{T_4}{T_2}$

$\therefore \eta_{Otto} < \eta_{Carnot}$

$\hookrightarrow \left\{ \begin{array}{l} \text{Otto cycle will always be less efficient than Carnot engine} \\ \text{for the same T} \end{array} \right.$

[Revising 3rd Law]

\hookrightarrow "Planck's statement - "as $T \rightarrow 0$, $S \rightarrow S_{min}$, $S_{min} = 0$
for pure crystalline solids."

Einstein statement

\hookrightarrow "As $T \rightarrow 0$, S remains finite"

$$\therefore S = \int_0^{T_f} \frac{C_V dT}{T} \text{ if } C_V \neq 0 \text{ then } S \rightarrow S_{min} = -\infty$$

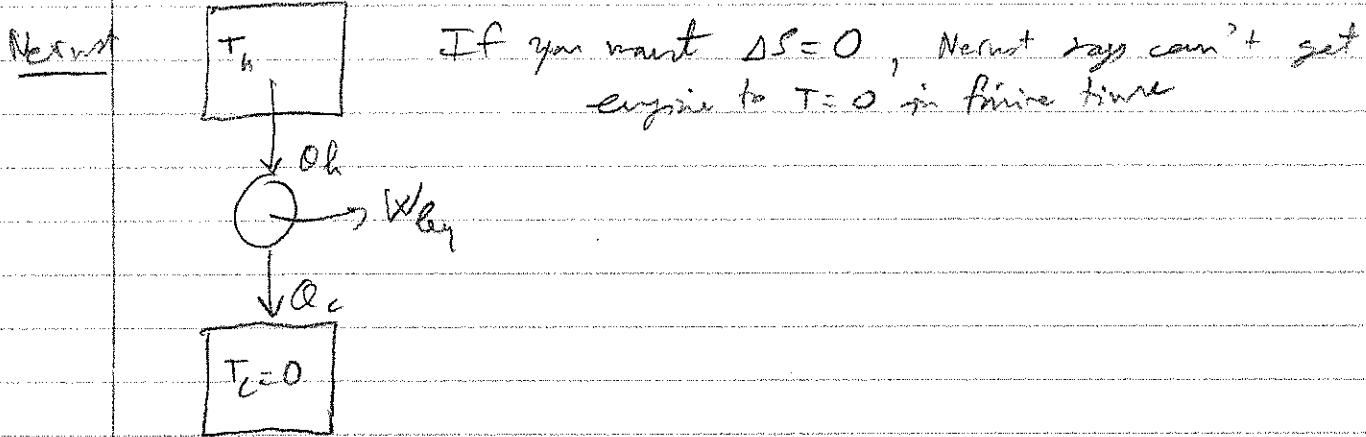
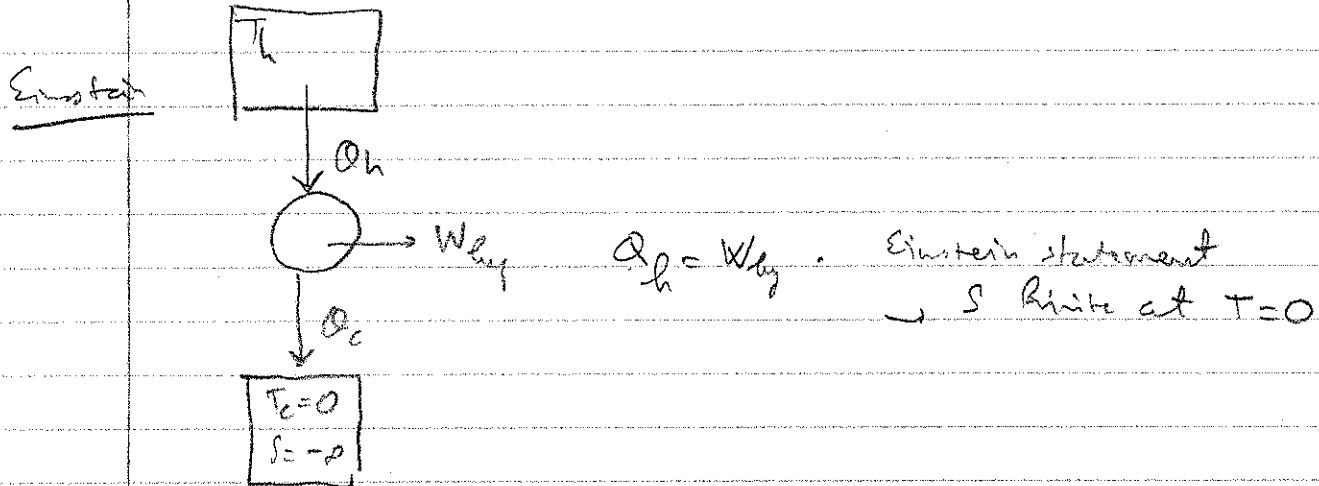
Nernst unattainability principle

\hookrightarrow "Any thermodynamic process cannot reach absolute zero in a finite number of steps in a finite amount of time"

1st law tells us we can't get work for free

2nd law tells us we can't build a mono-thermal heat engine

3rd law tells us we can't get 100% conversion of heat to work even if $\Delta S = 0$



→

Ch. 5 → FREE ENERGY

◻ Enthalpy → useful at constant P

$$H = U + PV \Rightarrow dH = dU + PdV$$

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

\downarrow

$Q + W_{on}$

$\hookrightarrow -P\Delta V + W_{other}$

∴ $\Delta H = Q + W_{other}$

Helmholtz free energy (F)

↳ useful for constant T processes.

$$F \equiv U - TS \quad \begin{matrix} \text{create system} \\ \text{out of nothing} \end{matrix}$$

$$Q = T\Delta S, \text{ quasi-static}$$

Gibbs free energy (G)

↳ useful for constant T, P

$$G \equiv U - TS + PV = H - TS$$

$$\int S_{\text{final}} - S_{\text{initial}} = 0$$

Real Thermodynamic Potential U, H, F, G

link at changes in these: $F \equiv U - TS \Rightarrow dF = dU - SdT - TdS$

For F , T constant $\Rightarrow \boxed{\Delta F = \Delta U - T\Delta S}$ can raise...

$$\boxed{\Delta F = Q_{in} + W_{out} - T\Delta S} \quad \text{Now } Q_{in} < T\Delta S \text{ (in general)}$$

$$\rightarrow \boxed{\Delta F \leq W_{out}} \quad (\text{constant } T, \text{ equality where quasi-static})$$

can be expansion/compression work = $\int PdV + \text{other}$

$$\boxed{\text{Gibbs free energy} \Rightarrow G \equiv U - TS + PV \Rightarrow dG = dU - TdS - SdT + PDV + PVdP}$$

$$\text{↳ constant } T, P \Rightarrow dG = dU - TdS + PDV$$

$$Q_{in} + W_{out}, Q_{in} \leq TdS, W_{out} = -PDV + W_{\text{other}}$$

So

$$\boxed{\Delta G \leq W_{\text{other}}}$$

$$\text{Also } \Delta R = \underbrace{\Delta U}_{\substack{\downarrow \\ Q_{in} + W_{out}}} + PDV = Q_{in} + W_{\text{other}} \Rightarrow \boxed{\Delta G = \Delta R - T\Delta S}$$

$$Q_{in} + W_{out}$$

Ex of using ΔG



$$\Delta H_f = -286.8 \text{ kJ/mol}$$

How much work do we need to apply to get reaction to proceed?

Charge in S: $S_{H_2O(l)} = 70 \text{ J/K}$

$$S_{H_2(g)} = 131 \text{ J/K}$$

$$S_{O_2(g)} = 205 \text{ J/K}$$

$$\Delta S = (131 \text{ J/K} + \frac{1}{2} \cdot 205 \text{ J/K}) - 70 \text{ J/K} = 163 \text{ J/K}$$

Max amount of heat that can enter system: $TDS = 49 \text{ kJ}$

$$\Delta G = \Delta H - T\Delta S = 286 \text{ kJ} - 49 \text{ kJ} = \boxed{\Delta G = 237 \text{ kJ}}$$

Thermodynamic identities

$$dU = TdS - PdV + u(N) \Rightarrow u(S, V)$$

$$\therefore dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV$$

$$\therefore \frac{\frac{\partial^2 u}{\partial v \partial s}}{\frac{\partial^2 u}{\partial s \partial v}} \Rightarrow \frac{\partial}{\partial v} \left[\left(\frac{\partial U}{\partial S}\right)_{V,N} \right]_{S,N} = \frac{\partial}{\partial s} \left[\left(\frac{\partial U}{\partial V}\right)_{S,N} \right]_{V,N}$$

$$\textcircled{1} \quad \boxed{\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}} \rightsquigarrow \text{independent variables } S, V \quad \text{Maxwell's relation \#1}$$

$$\textcircled{2} \quad dU = TdS - PdV = TdS - d(PV) + VdP \Rightarrow d(V+PV) = TdS + VdP$$

$$\therefore \boxed{dH = TdS + VdP} \rightsquigarrow \text{how to set } \Delta H \text{ at non-standard P, T...} \\ + n \Delta N$$

$$\text{S} \quad H = H(s, p)$$

$$\text{S} \quad dH = \left(\frac{\partial H}{\partial s}\right)_{p,N} ds + \left(\frac{\partial H}{\partial p}\right)_{s,N} dp$$

$\underbrace{}_T \qquad \underbrace{}_V$

$$\text{S} \quad T = \left(\frac{\partial H}{\partial s}\right)_{p,N} ; \quad V = \left(\frac{\partial H}{\partial p}\right)_{s,N}$$

$$\text{Nav} \quad \frac{\partial}{\partial p} \left(\frac{\partial H}{\partial s}\right)_{p,N} + \frac{\partial}{\partial s} \left(\frac{\partial H}{\partial p}\right)_{s,N}$$

$$\text{S} \quad \boxed{\left(\frac{\partial T}{\partial p}\right)_{s,N} = \left(\frac{\partial V}{\partial s}\right)_{p,N}} \rightarrow \underline{\text{Maxwell's relation th 2}}$$

③ Independent variables T, V

$$dU = Tds - Pdv$$

$$= d(Ts) - sdT - Pdv$$

$$\text{S} \quad d(U - TS) = - sdT - Pdv$$

$$\boxed{dF = - sdT - Pdv}$$

Func F(T,V)

$$\text{S} \quad dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV$$

$\underbrace{}_S \qquad \underbrace{}_P$

$$\text{S} \quad \boxed{S = - \left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = - \left(\frac{\partial F}{\partial V}\right)_{T,N}}$$

$$\text{C} \quad \frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right) = \frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right)$$

$$\text{D} \quad - \left(\frac{\partial S}{\partial V} \right)_{T,N} = - \left(\frac{\partial P}{\partial T} \right)_{V,N}$$

$$\text{E} \quad \boxed{\left(\frac{\partial S}{\partial V} \right)_{T,N} = \left(\frac{\partial P}{\partial T} \right)_{V,N}}$$

(4) Independent variables : $T \neq P$

$$dU = TdS - PdV = d(TS) - SdT - d(PV) + VdP$$

$$\text{F} \quad d(U - TS + PV) = - SdT + VdP$$

$$\boxed{dG = - SdT + VdP}$$

$$\text{G} \quad \boxed{V = \left(\frac{\partial G}{\partial P} \right)_{T,N}, \quad S = - \left(\frac{\partial G}{\partial T} \right)_{P,N}}$$

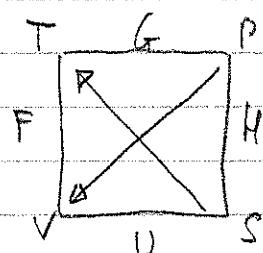
and

$$\boxed{\left(\frac{\partial V}{\partial T} \right)_{P,N} = \left(\frac{\partial S}{\partial P} \right)_{T,N}}$$

Mar 23, 2019

Thermodynamics potentials $U, H, F, G \rightarrow$ "good physicists have studied under very fine teachers"

Use square



$$dH = VdP + TdS + \mu dN$$

$$dU = TdS - PdV + \mu dN$$

Write potentials as fn of vars on front side of square { signs + amnt pt to (-) diff. } cols diagno

Maxwell's Relation

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

← arrow point to minus signs for the constant variable.

Definition of Potentials From squares

$$H = U + PV$$

○, against arrow $\rightarrow (+)$

$$G = H - TS$$

$$= U + PV - TS$$

Usefulness of Maxwell's Relations

→ can derive a relationship between C_p , C_v for any substance

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

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

① Start by writing S in terms of T, V

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

↔

$$= \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

Express $V = V(T, P)$ ← consider constant pressure

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

$$\therefore (dS)_P = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial V} \right)_T dV = \left(\frac{\partial V}{\partial T} \right)_P dT$$

[5]

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

For C_p , use identity for enthalpy - $dH = TdS + VdP$

At constant pressure $\Rightarrow dH = (TdS)_p$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \underset{dH}{=} \left(\frac{\partial H}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p$$

So

$$T \left(\frac{\partial S}{\partial T}\right)_p = C_V + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

$$\text{So } C_p = C_V + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

Q Use Maxwell's relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

So

$$C_p = C_V + T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

- Let $B \equiv \left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial T}\right)_p$ \rightarrow "Thermal volume coefficient of expansion"

- Let $K_T \equiv \left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial P}\right)_T$ \rightarrow "isothermal compressibility"

Q

To write $C_p = C_V$ in terms of B & K_T , more partial derivatives manipulation is required.

$$z = z(x, y), \text{ then } \left(\frac{\partial z}{\partial y}\right)_x = \frac{-(\partial z / \partial x)x}{(\partial z / \partial x)_y}$$

$$\text{Ansatz } dz = \left(\frac{\partial z}{\partial y}\right) dy + \left(\frac{\partial z}{\partial x}\right) dx$$

when z constant $\rightarrow dz = 0$

$$\therefore \left(\frac{\partial z}{\partial x}\right) dx = - \left(\frac{\partial z}{\partial y}\right) dy \quad (dz = 0)$$

$$\therefore \left(\frac{dx}{dy}\right)_z = - \frac{(\partial z / \partial y)_x}{(\partial z / \partial x)_y}$$

$$\therefore \left(\frac{dx}{dy}\right)_z = - \frac{(\partial z / \partial y)_x}{(\partial z / \partial x)_y}$$

↳ Back to derive

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

$$\begin{aligned} \downarrow (C_P - C_V) &= T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = -T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T^{-1} \left(\frac{\partial V}{\partial T}\right)_P \\ &= -T (V_B)^2 \frac{-1}{k_T V} \end{aligned}$$

$$\boxed{C_P - C_V = \frac{T B^2 V}{k_T}} \quad \text{and true for any substance}$$

Ex For ideal gas $\rightarrow C_P - C_V = nR = NR$

$$B = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P, \quad k_T = \frac{-1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$= \frac{1}{V} \left(\frac{Nk}{P}\right), \quad = \frac{-1}{V} \left(\frac{-NkT}{P^2}\right) = \frac{NkT}{PV^2} = \frac{1}{P}$$

$$B = \frac{1}{T} \quad \text{So} \quad \boxed{C_P - C_V = \frac{T(1 - \frac{2}{P})^2 V}{P^2} = \frac{PV}{T} = NR} \quad \checkmark$$

April 1, 2019

Extensive vs. Intensive parameters

1 2

Say we have a homogeneous system

- ① if $y_1 + y_2 = y$ then y is an extensive parameter,
- ② if $y_1 = y_2 = y$ then y is an intensive parameter.

<u>Extensive</u>	{ volume, mass, # particles, internal energy, entropy (V) (m) (N) (U) (S) enthalpy (H), (F), (G)}
<u>Intensive</u>	{ Temp, pressure, density, chemical potential (T) (P) (ρ) (μ) }

Rules of multiplication & addition:

① $(Ext) \cdot (Int) = (Ext)$ ex $v \times p = m$

② $\frac{[Ext]}{[Ext]} = [Int]$ ex $\frac{m}{v} = \rho$
or $\frac{c_v}{mass} = c_v$

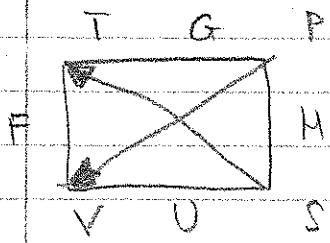
③ $(Ext, Ext) \Rightarrow$ neither (extensive) nor (intensive)

④ $[Ext] + [Ext] = [Ext]$

⑤ Not allowed $\cancel{[Ext] + [Int]}$

Ex G has units of J But $G \cdot \mu$ does not make sense
 μ has units of J

Gibbs free energy & chemical potential



$$dG = VdP - SdT + \mu dN$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V, \quad \left(\frac{\partial G}{\partial T}\right)_{P,N} = -S, \quad \left(\frac{\partial G}{\partial N}\right)_{P,T} = \mu$$

Now $\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$ ^{ext} intensive
 int ext

At constant PT $\rightarrow G = \mu N$ $\propto N^1$, G proportional

for a system involving 1 type of particles.

$$\mu = G/N$$

Helmholtz free energy & chemical potential

$$dF = -\delta F - SdT - PDV + \mu dN$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \rightarrow F = N\mu(V)$$

↑ ext
int

Derivation of chemical potential of ideal gas

$$\text{Before, } \mu = -T \left(\frac{\partial S}{\partial N}\right)_{U,V}$$

Now,

$$G = \mu N \text{ or } \mu = \frac{G}{N}$$

Consider a fixed amount of gas (N) at const (T) and allow P to vary

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,N} = \frac{1}{P} \left(\frac{\partial G}{\partial N}\right)_{T,N} = \frac{1}{N} \left(\frac{\partial G}{\partial P}\right)_{T,N} = \frac{V}{N}$$

$$\underline{\text{Ex}} \quad \int_{T,N} d\mu = \int_{T,N} \left(\frac{V}{N}\right) dP \Rightarrow d\mu = \int_{P_i}^{P_f} \frac{kT}{P} dP = kT \ln \left(\frac{P_f}{P_i}\right)$$

So

$$\boxed{\mu(T, P_f) - \mu(T, P_i) = kT \ln \left(\frac{P_f}{P_i}\right)}$$

write $\mu(T, P_i) = \mu^\circ(T) \Rightarrow \boxed{\mu(T, P) = \mu^\circ + kT \ln \left(\frac{P}{P_0}\right)}$

1 atm

(typically, 1 atm)

• P is the partial pressure

Ex $\boxed{\text{He, H}}$ $\mu_{\text{He}}(T, P) = \mu_{\text{He}}^\circ + \cancel{kT \ln \left(\frac{P}{P_0}\right)} + kT \ln \left(\frac{P_{\text{He}}}{P_0}\right)$

B Test vs μ derived for a monatomic ideal gas

$$\mu = -T \left(\frac{\partial S}{\partial N}\right)_{V,T} \pi$$

$$\mu = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \right]$$

$$= -kT \ln \left[\frac{P^\circ kT}{P^0 P} \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \right]$$

$$= -kT \ln \left[\frac{kT}{P^0} \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \right] + kT \ln \left(\frac{P}{P^0} \right)$$

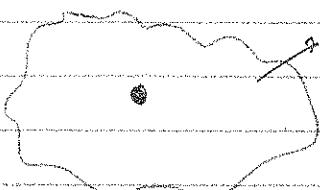
$$\boxed{\mu = -kT \ln \left[\frac{kT}{P^0} \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \right] + kT \ln \left(\frac{P}{P^0} \right)}$$

 $\mu^\circ(T)$

Free Energy as a Force Towards Equilibrium

- For isolated system $\rightarrow S^\ddagger$
- For interacting system $\rightarrow S_{\text{tot}}^\ddagger$

Assume environment is a reservoir of constant T, V, N



$$S_{\text{tot}}^\ddagger = S_{\text{System}} + S_{\text{Reservoir}}$$

$$dS_{\text{tot}}^\ddagger = dS_{\text{sys}} + dS_{\text{res}}$$

For reservoir, $TdS = dU + PdV - \mu dN$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

if T, N, V constant, then $dS_{\text{res}} = \frac{1}{T}dU_{\text{res}}$

$dS_{\text{tot}}^\ddagger = dS_{\text{sys}} + \frac{1}{T}dU_{\text{res}}$

In eqs, $T_{\text{sys}} > T_{\text{res}}$, $dU_{\text{sys}} = -dU_{\text{res}}$

$dS_{\text{tot}}^\ddagger = dS_{\text{sys}} - \frac{1}{T_{\text{sys}}}dU_{\text{sys}}$

$dS_{\text{tot}}^\ddagger = -\frac{1}{T}(dU - TS) \rightsquigarrow$ dropping sys. subscript
 dF

b

$$dS_{\text{tot}}^\ddagger = -\frac{dF}{T}$$

If $dF < 0 \rightarrow$ spontaneous flow towards equilibrium



Now, let T vary, holding $P, T, (\pm N)$ constant

$$dS_{\text{tot}}^\ddagger = dS_{\text{sys}} + \frac{1}{T_{\text{res}}}dU_{\text{res}} + \frac{P_{\text{res}}}{T_{\text{res}}}dV_{\text{res}} - \frac{\mu_{\text{res}}}{T_{\text{res}}}dN_{\text{res}}$$

At equilibrium, $P_{\text{res}} = P_{\text{sys}}$, $T_{\text{res}} = T_{\text{sys}}$, $dV_{\text{res}} = -dV_{\text{sys}}$
 $dV_{\text{res}} = -dV_{\text{sys}}$

↳

$$dS_{\text{tot}} = dS - \frac{1}{T} dV - \frac{P}{T} dV$$

$$\underline{\text{L}} \quad dS_{\text{tot}} = -\frac{1}{T} (dV - TdS + PdV)$$

 dG

↳

$$\boxed{dS_{\text{tot}} = -\frac{dG}{T}} \rightarrow dG = dG_{\text{sys}}, T = \text{equilibrium } T$$

↳

For fixed $P, T, N \Rightarrow G$ tends to decrease

(if $\Delta G < 0 \rightarrow$ spontaneous process)

Example use of free energy to calculate whether a reaction is spontaneous or not

Crystallized ammonium nitrate NH_4NO_3



look up $\Delta_f H$, $\Delta_f S$

	$\Delta_f H$	$\Delta_f S$	@ eq, $\Delta G = 0$
$\text{NH}_4\text{NO}_3(\text{s})$	-365.56	151.08	
$\text{NH}_4^+(\text{aq})$	-132.51	113.4	
$\text{NO}_3^-(\text{aq})$	-205.0	146.4	

$$\Delta G = \Delta H - T\Delta S = -4.4 \text{ kJ} < 0 \rightarrow \text{spontaneous}$$

@ constant T

In general, $H = U + PV$ for constant P processes, $\Delta H = \Delta U + P\Delta V$

$$\Delta H = \Delta U + P\Delta V = Q_{\text{abs}}$$

$\Delta H < 0 \Rightarrow$ exothermic rxn
$\Delta H > 0 \Rightarrow$ endothermic rxn

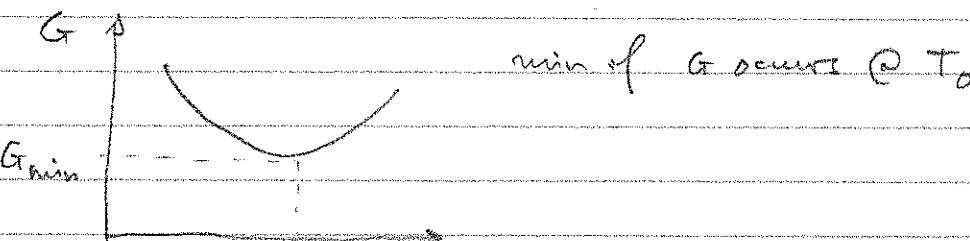
If $\Delta H < 0, \Delta S > 0 \Rightarrow \Delta G < 0$ spontaneous
 $\Delta H > 0, \Delta S < 0 \Rightarrow \Delta G > 0$ not spontaneous rxn.

<input checked="" type="checkbox"/> Summary	<u>Reservoir</u>	<u>System</u>
• At const	U, V	$S \uparrow$
• At const	T, V	$F \downarrow$
• At const	T, P	$G \downarrow$

Stability against Temperature Fluctuations

Consider a system. Let T, V be independent parameters that describe system.

1st, hold V fixed & allow T to vary
 Interacting with respect to constant T, P, N



• Expand G around eq. value T_0 $\Delta G = G - G_{\text{min}} = \left(\frac{\partial G}{\partial T}\right)_{T_0} \Delta T + \frac{1}{2} \left(\frac{\partial^2 G}{\partial T^2}\right)_{T_0} (\Delta T)^2$

where $\Delta T = T - T_0$

~~evaluate~~ derive at $T = T_0$

$$\left(\frac{\partial G}{\partial T}\right)_V = 0, \quad \left(\frac{\partial^2 G}{\partial T^2}\right)_V > 0$$

T_0 ~~sec~~ T_0

• $G = U - TS + PV \quad G_0 @ T_0, P_0$

• $G_0 = U_0 - T_0 S + P_0 V$

~~b~~ $\left(\frac{\partial G_0}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V - T_0 \left(\frac{\partial S}{\partial T}\right)_V = 0 \quad @ T = T_0$

$$dU = T dS - P dV \quad \& \quad \left(\frac{dU}{dT}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

$$\left(\frac{\partial G}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V - T_0 \left[\frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V \right]$$

$$\boxed{\left(\frac{\partial G_0}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left[1 - \frac{T_0}{T} \right]}$$

• ~~evaluate~~ $\left(\frac{\partial^2 G_0}{\partial T^2}\right)_V = \left(\frac{\partial}{\partial T}\right) \left(\frac{\partial G_0}{\partial T}\right)_V = \frac{T_0}{T^2} \left(\frac{\partial U}{\partial T}\right)_V + \left(1 - \frac{T_0}{T}\right) \left(\frac{\partial^2 U}{\partial T^2}\right)_V > 0$

at $T = T_0$

~~b~~ $\frac{T_0}{T^2} \left(\frac{\partial U}{\partial T}\right)_V > 0$

~~b~~ $\boxed{\left(\frac{\partial U}{\partial T}\right)_V > 0}$

$c_v > 0$

if heat cap
 > 0 , then

stable
around
 δT

Le Chatelier's Principle

Jan 3, 2019

If a system in eq. is disturbed, it will respond in a (stable) way to restore itself back to equilibrium.

Result for V Changes

$$\text{Gibbs free energy } G = G_0 + RT \ln \frac{V}{V_0} \quad \left(\frac{\partial G}{\partial V} \right)_{T=70} = - \left(\frac{\partial P}{\partial V} \right)_T > 0$$

$$K_T = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$\frac{1}{K_T} > 0 \text{ or simply } K_T > 0$$

Chemical Equilibrium

Can we Gibbs to determine equilibrium conditions?

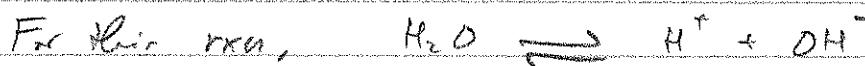


Mixture of H_2O - ions is most stable state (lower G)

$$G = U - TS$$

e.g. $\Delta G = 0$. Ions have a higher entropy. But additional entropy of mixing makes the mixture more stable.

$$\text{e.g., } dG = \delta H - T\delta S = \mu\delta N_i = \sum_i \mu_i dN_i = \sum_i \mu_i dN_i$$



$$dN_{\text{H}_2\text{O}} = -1, \quad dN_{\text{H}^+} = +1, \quad dN_{\text{OH}^-} = +1 \quad \& \quad \text{e.g., } dG = 0 = \sum_i \mu_i dN_i$$

$$\text{Eq 1} \quad -\mu_{H_2O}^{\circ} \mu_{OH^-} + \mu_H^{\circ} = 0$$

$$\text{Eq 2} \quad \boxed{\mu_{OH^-} + \mu_H^{\circ} = \mu_{H_2O}}$$

More generally, $v_1 X_1 + v_2 X_2 + \dots \rightleftharpoons v_3 X_3 + v_4 X_4 + \dots$

$v_i \rightarrow$ stoichiometric coefficient of species i

In eq, $\boxed{v_1 \mu_1 + v_2 \mu_2 + \dots = v_3 \mu_3 + v_4 \mu_4 + \dots}$

The rxn $H_2O \rightleftharpoons H^+ + OH^-$ produces a solute, which is a mixture of a solvent (primary component) + solute (secondary comp)

Dilute solution { # of solute molecules \ll # of solvent molecules
 { const solute molecules don't interact
 with each other
 → can treat them as an ideal gas!

Q Need to calculate μ for solvent & solute in order to predict eq.

Suppose we have pure water... 100% H_2O ... solvent A $\xrightarrow{\text{"pure"}}$

$$G = N_A \mu_A = N_A \mu_A^{\circ} (T, P) \quad \mu_A^{\circ}: \text{chem. pot. of pure solvent}$$

Add a single B molecule (solute), holding T, P fixed

$$\begin{aligned} dG &= \underbrace{dU}_{\downarrow \text{indep. of } N_A} + \underbrace{PdV}_{\text{indep. of } N_A} - TdS \\ &\quad \xrightarrow{\text{dep. on } N_A} (R \sim N_A) \\ &\quad \text{only dep. on } N_B \end{aligned}$$

$dS = k_B \ln N_A \rightarrow$ additional terms indep. of N_A

$$\text{Eq 3} \quad \boxed{dG = -k_B \ln N_A + f(T, P)} \quad \text{for adding 1 mol.} \quad \text{indep. of } N_A$$

Holding 2 B molecules...

$$\text{Gross} \rightarrow dG' = 2dG = 2 \left[f(T, P) - kT \ln N_A \right] \quad (\times)$$

But B molecules are indistinguishable.

→ 2 needs to be divided by $2!$ → indistinguishable
So...

$$\begin{aligned} dG' &= 2f(T, P) - T \left[2k \ln N_A - k \ln 2 \right] \\ &= 2f(T, P) - 2kT \ln N_A + kT \ln 2 \end{aligned}$$

Generalizing (for N_B molecules)

$$kT N_B \ln N_B = kT N_B$$

$$dG = N_B f(T, P) - N_B kT \ln N_A + kT \ln(N_B!)$$

pure Solvent

$$G = N_A \mu^0(T, P)$$

Dilute solution $G + dG$

Solution

$$\begin{aligned} G &= N_A \mu^0(T, P) + N_B f(T, P) - N_B kT \ln N_A \\ &\quad + N_B kT \ln N_B - N_B kT \end{aligned}$$

valid if $N_B \ll N_A$ (dilute solution.)

Since, $\mu = \left(\frac{\partial G}{\partial N} \right)_{T, P}$ we can solve for μ_A & μ_B

$$\boxed{\mu_A = \left(\frac{\partial G}{\partial N_A} \right)_{T, P, N_B} = \mu^0(T, P) - N_B kT / N_A} \quad \begin{array}{l} \rightarrow \text{chem. pt.} \\ \text{of solvent} \end{array}$$

$$\boxed{\mu_B = \left(\frac{\partial G}{\partial N_B} \right)_{T, P, N_A} = f(T, P) - kT \ln N_A - kT + kT + kT \ln \frac{N_B}{N_A}} \quad \begin{array}{l} \rightarrow \text{chem. pt.} \\ \text{of solute} \end{array}$$

April 5, 2019

Recall ① Started with G for pure solvent (A)

$$G = \mu^\circ(T, P) N_A$$

② Add solute particles (B) to this

$$dG = \underbrace{dU + PdV - TdS}_{\text{some terms dep. on } N_A}$$

time index of N_A

$f(T, P)$ independent of N_A

$$\underline{\Delta S} = \frac{N_A!}{N_B!(N_A-N_B)!}, \text{ and since } N_A \gg N_B \Rightarrow \underline{\Delta S} \approx \frac{N_A^{N_B}}{N_B!}$$

$$\begin{aligned} \underline{\Delta S} &= k \ln \underline{\Delta S} = k \ln \left[\frac{N_A^{N_B}}{N_B!} \right] = k \ln (N_A^{N_B}) - k \ln (N_B!) \\ &\approx N_B k \ln (N_A) - N_B k \ln N_B + N_B k \end{aligned}$$

Now, $G = G_A + dG$

$$\underline{\Delta S} \quad \underline{dG} = N_B f(T, P) - N_B k T \ln N_A + k T \ln N_B - N_B k T$$

$$\underline{\Delta S} \quad \boxed{G = \mu^\circ(T, P) N_A + N_B f(T, P) + N_B k T \ln \left(\frac{N_B}{N_A} \right) - N_B k T}$$

Now,

$$\begin{aligned} \mu &= \left(\frac{\partial G}{\partial N} \right)_{T, P} \Rightarrow \left\{ \begin{array}{l} \mu_A = \left(\frac{\partial G}{\partial N_A} \right)_{T, P} = \mu^\circ(T, P) - \frac{N_B k T}{N_A} \\ \mu_B = \left(\frac{\partial G}{\partial N_B} \right)_{T, P} = f(T, P) + k T \ln \frac{N_B}{N_A} \end{array} \right. \\ &\quad \left. \begin{array}{l} \text{(solvent)} \\ \text{(solute)} \end{array} \right\} \end{aligned}$$

Definition

"Molarity" \rightarrow # moles of solute per kg of solvent.

$$m = \frac{\text{moles solute}}{\text{kg solvent}} \propto \frac{N_B}{N_A}$$

Re-writing μ_B in terms of m : \rightarrow absorbed ... extra term ...

$$\star \mu_B = f(T, P) + kT \ln(m_B) \quad (1)$$

$\star \mu_B^\circ(T, P) \rightsquigarrow$ standard condition for molality = 1 = m_B

$$\text{So when } m_B = 1 \rightarrow \boxed{\mu_B = \mu_B^\circ(T, P) + kT \ln(m_B)}$$

Example Dissociation of water



Treat as dilute solution + solvent H_2O

$$\star \mu_{\text{H}_2\text{O}} = \mu_{\text{H}_2\text{O}}^\circ(T, P) - \frac{N_{\text{H}}kT}{N_{\text{H}_2\text{O}}} - \frac{N_{\text{OH}}kT}{N_{\text{H}_2\text{O}}} \quad \left. \begin{array}{l} \text{H}^+ \\ \text{OH}^- \end{array} \right\}$$

$$\star \mu_{\text{H}^+} = \mu_{\text{H}^+}^\circ(T, P) + kT \ln m_{\text{H}^+}$$

$$\star \mu_{\text{OH}^-} = \mu_{\text{OH}^-}^\circ(T, P) + kT \ln m_{\text{OH}^-}$$

at room temp, $kT \approx 4 \times 10^{-21} \text{ J}$

$$\therefore \mu_{\text{H}_2\text{O}} = \mu_{\text{H}^+} + \mu_{\text{OH}^-} \Rightarrow \mu_{\text{H}_2\text{O}} - \mu_{\text{H}^+} - \mu_{\text{OH}^-} = 0$$

$$\Rightarrow \mu_{\text{H}_2\text{O}}^\circ - \mu_{\text{H}^+}^\circ - \mu_{\text{OH}^-}^\circ = kT \ln(m_{\text{H}^+}) + kT \ln(m_{\text{OH}^-}) \\ = kT \ln(m_{\text{H}^+} \cdot m_{\text{OH}^-})$$

$$\therefore -N_A \left[\mu_{\text{H}^+}^\circ + \mu_{\text{OH}^-}^\circ - \mu_{\text{H}_2\text{O}}^\circ \right] = RT \ln(m_{\text{H}^+} \cdot m_{\text{OH}^-})$$

$$\boxed{-\Delta G^\circ = RT \ln(m_{\text{H}^+} \cdot m_{\text{OH}^-})}$$

Ex ΔG° dissociation of water = -74.9 kJ/mol

Now

$$\Rightarrow m_{H^+} \cdot m_{OH^-} = e^{-\Delta G^\circ / RT}$$

K equilibrium constant

for same temp & standard P ,

$$K_{H_2O} = 10^{-14}$$

$$\therefore m_{H^+} \cdot m_{OH^-} = 10^{-14} = (m_{OH^-})^2 = (m_{H^+})^2$$

$$\therefore m_{H^+} = m_{OH^-} = 10^{-7} \text{ moles/liter H}_2O$$

$$pH = -\log_{10}(m_{H^+}) \Rightarrow pH = 7 \text{ for "pure" H}_2O$$

{ if fewer H^+ conc. then basic, $pH \uparrow$
 { if more H^+ conc. then acidic, $pH \downarrow$

partial pressure



Treat as ideal gas : $\mu(T, P) = \mu^\circ(T) + RT \ln\left(\frac{P}{P_0}\right)$

std. atm. pressure

$$(\mu_{p^+}^\circ + \mu_{e^-}^\circ - \mu_H^\circ) = RT \ln\left(\frac{P_H}{P_0}\right) - RT \ln\left(\frac{P_e^-}{P_0}\right) - RT \ln\left(\frac{P_{p^+}}{P_0}\right)$$

$$\Rightarrow -\Delta G^\circ = N_A RT \ln \left[\frac{P_H P_0}{P_{p^+} P_{e^-}} \right] \quad \left. \frac{RT}{P_0} \right]$$

$$\therefore \text{Recall, for ideal gas } \mu^\circ = -RT \ln \left[\frac{V}{N} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right]$$

But μ for H should be less than -13.6 eV when at rest ($kE=0$)

$$\therefore \boxed{\mu_H^0 = -kT \ln \left[\frac{kT}{p_0} \left(\frac{2\pi m_H kT}{h^2} \right)^{3/2} \right] - 13.6\text{ eV}}$$

Assume p^+ , e^- unbound \Rightarrow

$$\mu_{p^+}^0 = -kT \ln \left[\frac{kT}{p_0} \left(\frac{2\pi m_p kT}{h^2} \right)^{3/2} \right]$$

$$\mu_{e^-}^0 = -kT \ln \left[\frac{kT}{p_0} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \right]$$

Now, $m_H \approx m_e$

$$\therefore \mu_{p^+}^0 + \mu_{e^-}^0 - \mu_{H,0}^0 = -kT \ln \left(\frac{kT}{p_0} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \right) + 13.6\text{ eV}$$

Therefore,

$$-\ln \left(\frac{p_H p^0}{p_p + p_{e^-}} \right) = \ln \left(\frac{kT}{p_0} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \right) - 13.6\text{ eV} / kT$$

$$\therefore \frac{(p_H p^0)^{-1}}{p_p + p_{e^-}} = \frac{kT}{p_0} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \cdot e^{-13.6\text{ eV} / kT}$$

$$\therefore \frac{p_H + p_{e^-}}{p_H} = \frac{kT}{p_0} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \cdot e^{-13.6\text{ eV} / kT}$$

$$\therefore \boxed{\frac{p_H^+}{p_H} = \frac{kT}{p_0} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \cdot e^{-13.6\text{ eV} / kT}} \quad \text{Saha's Eqn}$$

$$\frac{N_{p^+}}{N_H}$$

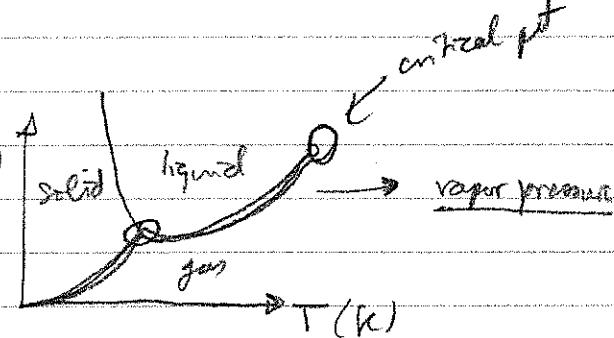
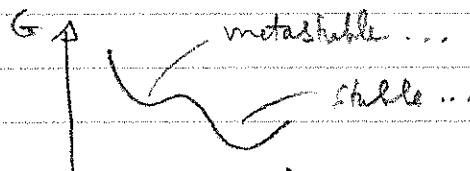
PHASE TRANSFORMATION

def { A continuous change in properties of matter as its environment changes infinitesimally.

Phases { different states of matter - or unique structural arrangement of atoms within matter.

Can depend on many variables : e.g. P, T, B, ...

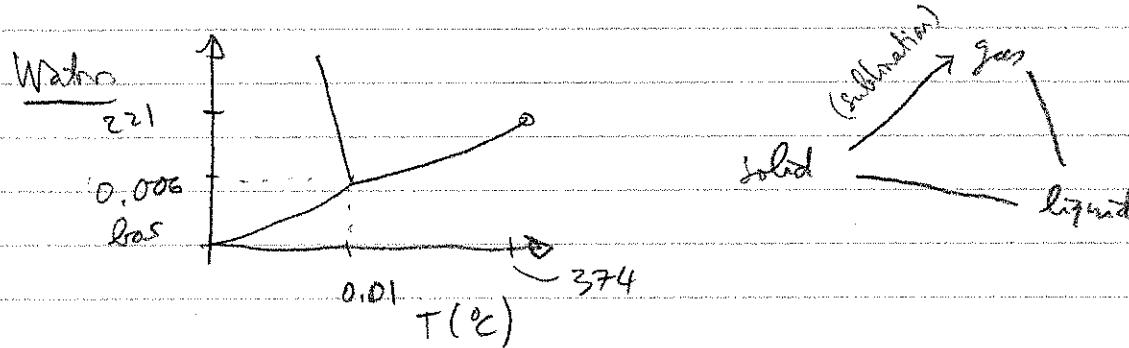
↳ Gibbs free energy is key to understanding these...



Phase diagram for water

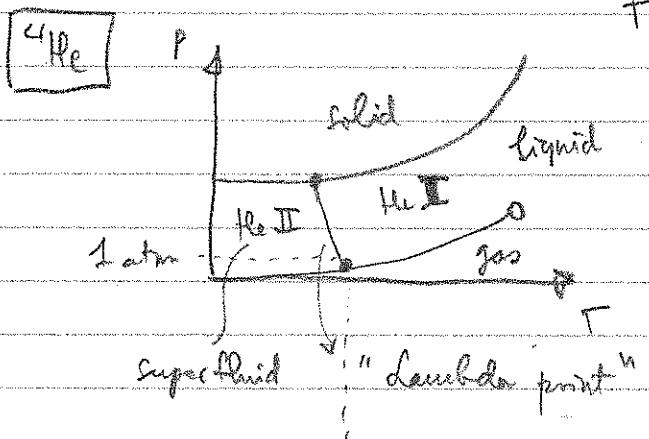
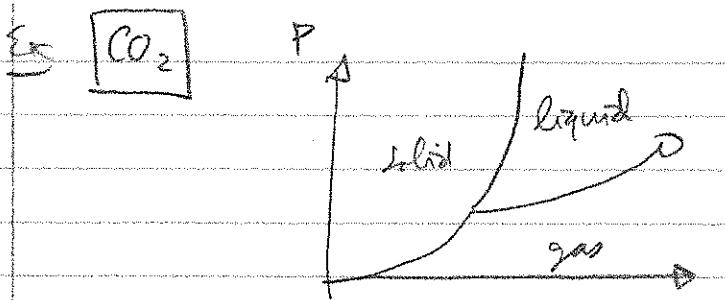
Vapor pressure → pressure at which liquid or solid phase can coexist with gas

• Triple point → precise T, P at which all 3 phases (liquid, gas, solid) can coexist...



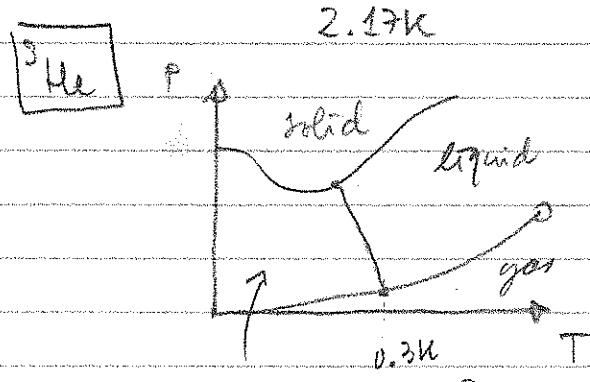
• Critical point As P or T increases, we reach a point where liquid & gaseous phases are indistinguishable.

Ex plasma --



"He is a superfluid below the lambda point (@1 atm, 2.17 K)

Superfluid → $\begin{cases} \text{zero viscosity} \\ \text{zero entropy} \\ \text{high conductivity} \end{cases}$



2 superfluid phases

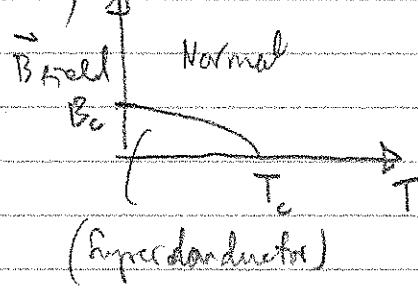
Other variables that can cause phase change:

- chemical composition:

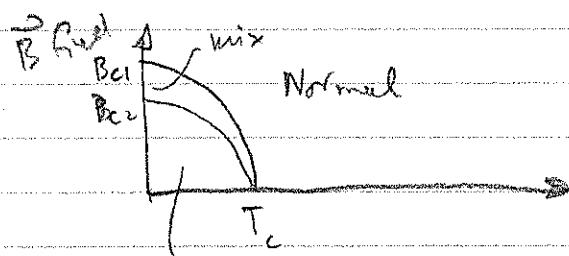
- external B field strength → (Type I superconductor)
(0 resistivity)

(Type I superconductor)

Typical $B_c \sim 0.01 - 0.1 \text{ T}$
 $T_c \sim 10 \text{ K}$



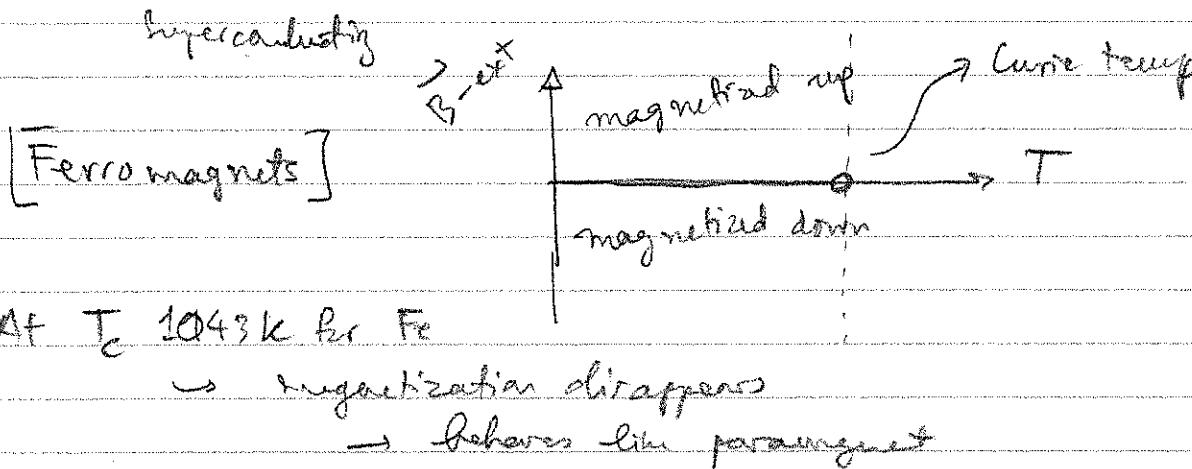
Axide Type II - Superconductor



$$B_{C_2} \gg B_{C_1}$$

$$T_c \sim 10K \sim 90K$$

25T



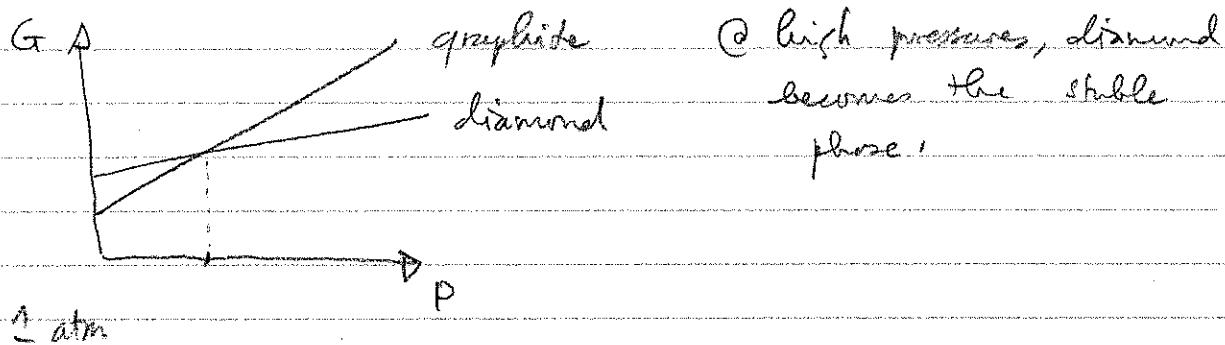
Using Gibbs free energy to evaluate stable phase for substances

$$\delta G = -SdT + VdP + \mu dN$$

$$\text{Ex } \left(\frac{\partial G}{\partial T} \right)_{P,N} = -S ; \quad \left(\frac{\partial G}{\partial P} \right)_{T,N} = V$$

Ex Diamond vs Graphite, look up $\Delta_f G$ for both @ $T = 1\text{ atm}$

$\Delta_f G_{\text{graphite}}$ is 29.00 J less than $\Delta_f G_{\text{diamond}}$ @ 298K, 1 atm



(111)

New topic at T dependence

$$\left(\frac{\partial G}{\partial T}\right) = -S \text{ as } T \uparrow, G \downarrow$$

Entropy of diamond vs graphite.

↑ ↑
lower S higher S

G

diamond
graphite

graphite is always more stable.

298K



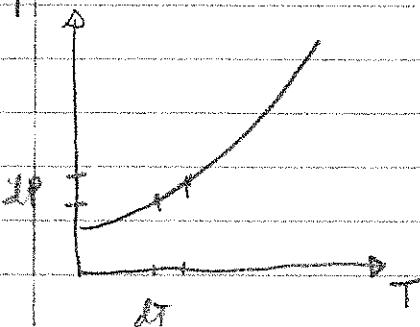
Clausius - Clapeyron relation

Since $\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S$, $\left(\frac{\partial G}{\partial P}\right)_{T,N} = +V$ then slope of the phase boundary line on P.v.T diagram is related to $S \& V$ of the two phases...

assume 1 mole of substance

On the boundary $\Delta G_1 = \Delta G_2$

P



increase P & T at 2 places remain in eq.
 $\Delta G = -SdT + VdP + \mu dN$

$$\therefore SdT = VdP$$

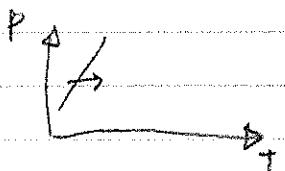
$$\Delta G_2 = -S_2dT + V_2dP$$

$$\Delta G_1 = -S_1dT + V_1dP \quad \text{equal}$$

$$\text{So } (V_g - V_e) dP = (S_g - S_e) dT$$

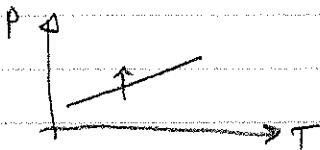
$$\boxed{\frac{dP}{dT} = \frac{S_g - S_e}{V_g - V_e}}$$

- if we have a large entropy difference between phases
→ steep slope...



$\frac{dP}{dT}$ steep: small T changes will change the phase...

- if large volume difference



$\frac{dP}{dT}$ shallow: small P change will change phase.

Reminder $\Delta G = \frac{\partial \mathcal{Q}}{\partial T} = \frac{L}{T}$

$$\boxed{\frac{dP}{dT} = \frac{L}{T\Delta V}}$$

L: total latent heat of vaporization
 $\Delta V = V_g - V_e$

↗ Clausius - Clapeyron Eqn.

$L = \text{l.m.} \rightarrow \text{extensive}$ } \Rightarrow ratio $\frac{L}{\Delta V} = \text{intensive}$,
 $\Delta V = \text{extensive}$

Example Use Clausius - Clapeyron to explain why H₂O has negative $\frac{dP}{dT}$ between solid - liquid phases.

$$\frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{\Delta S}{\Delta V}$$

$$\rho_{sl} = 917 \text{ kg/m}^3, \rho_{liq} = 1000 \text{ kg/m}^3 \rightarrow \text{one 1 mol of H}_2\text{O}$$

$$V_e = m/p = \frac{1 \text{ mol}}{1000 \text{ kg/m}^3} = 1 \text{ m}^3 \quad V_{l,e} = \frac{1000 \text{ kg}}{917 \text{ kg/m}^3} = 1.09 \text{ m}^3$$

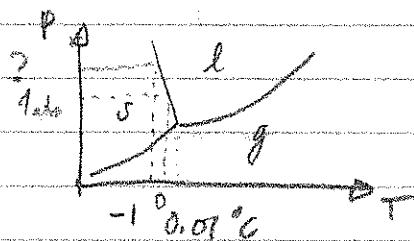
$$(V_e - V_l) = -0.09 \text{ m}^3$$

As we go from ice to water, $V \downarrow, ST$

So $\frac{dP}{dT}$ is negative

$$\text{Assume } L \text{ is constant with } P, T : \frac{dP}{dT} = \frac{333 \text{ J/g} \times 10^6}{(273 \text{ K})(-0.09 \text{ m}^3)} \\ = -1.35 \times 10^9 \text{ Pa/K}$$

How much pressure is required to melt ice at -1°C ?

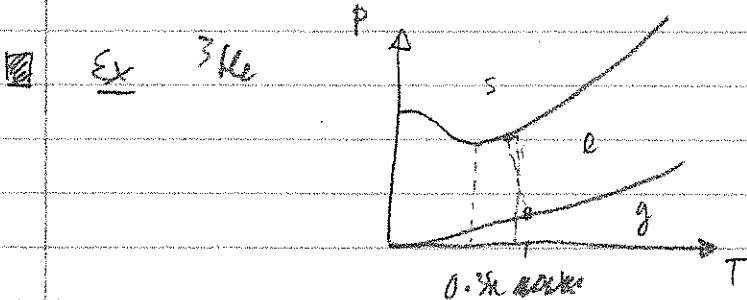


$$\frac{dP}{dT} = -1.35 \times 10^9 \text{ Pa/K}$$

$$dP = (-1.35 \times 10^9 \text{ Pa/K})(-1 \text{ K})$$

$$dP = 1.35 \times 10^9 \text{ Pa} \approx 135 \text{ atm}$$

$$\approx 135 \text{ bars}$$



- At $T < 1.3 \text{ K}$, slope between solid - liquid is negative

- Which phase is more dense? Remember that $(\frac{\partial G}{\partial T})_{P,N} = V$

liquid ^3He is stable phase at high P , so it must have smaller V . Therefore dV/dP
→ liquid is more dense.

Q: Which phase has more entropy?

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} < 0 \text{ @ } T < 0.3K$$

If V increases as we go $l \rightarrow s$, ΔT as we go from $l \rightarrow s$

So solid 3He has more entropy.

Q: What is the slope of the phase boundary at $T = 0$?

3rd law: As $T \rightarrow 0K$, $S \rightarrow$ minimum value.

$\therefore \Delta S = 0$ between the phases @ $T = 0$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \rightarrow \frac{dP}{dT} = 0 \rightarrow \text{slope of phase boundary goes away}$$

April 10, 2019

The van der Waals Model

Ideal gas: $PV = nRT = NkT \rightarrow$ want to correct for finite volumes of molecules & attractive forces between particles

$$\left(P + \frac{\alpha N^2}{V^2} \right) (V - Nb) = NkT \quad \text{van der Waals equation.}$$

Two modifications: ① $V \rightarrow V - V_0 \rightarrow$ can't compress gas to $V = 0$
 "b" represents volume per particle
 min volume = Nb @ $P = \infty$

② $P \rightarrow 1 + \frac{\alpha N^2}{V^2}$ accounts for short range attractive forces between molecules

$$P = \frac{NkT}{V - Nb} - \frac{\alpha N^2}{V^2}$$

Imagine being at $T=0$, frozen thermal motion. \rightarrow no KE, but still has potential energy.

$$PE_{\text{single particle}} \propto N/V \Rightarrow PE_{\Sigma} \propto \frac{N}{V} \cdot N$$

$$\Rightarrow PE_{\text{eff}} = -\frac{\alpha N^2}{V}, \text{ negative since it works against KE}$$

• "a" constant depending on type of molecules $\propto r_0 \cdot e^{-r_0}$

$$\bullet \text{To calculate } P, \quad dV = TdS - PdV \Rightarrow P = -\left(\frac{\partial V}{\partial T}\right)_{S,N}$$

• Contribution to P from PE

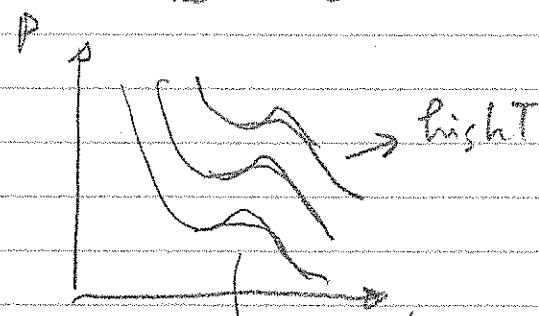
$$\hookrightarrow P = -\left(\frac{\partial}{\partial T}\left(\frac{-\alpha N^2}{V}\right)\right)_{S,N} \Rightarrow \boxed{P = \frac{NkT}{V-Nb} - \frac{\alpha N^2}{V^2}}$$

$$\underline{\text{Ex Molecular Interaction}} \quad H_2O : b \approx 6 \times 10^{-24} \text{ m}^3 \sim (4\text{\AA})^3 \\ N_2 \text{ similar}$$

$$a \text{ varies between molecules} \dots N_2 : a \sim 2.5 \text{ eV A}^3$$

$$H_2O \sim a_{N_2} \text{ due to dipole interaction} \\ He : a_{He} < a_{N_2} \text{ (aromaticity)}$$

Consequences of vdW model



For a given T , plot P vs. V .

\Rightarrow Multiple possible V 's for a given P, T

Use G to find which volume is stable

$$\delta G = -SdT + VdP + \mu dN, \text{ for } T=N \Rightarrow \left(\frac{\partial G}{\partial V}\right)_{T,N} = V\left(\frac{\partial P}{\partial V}\right)_{T,N}$$

$$P = \frac{NkT}{V-Nb} - \frac{\alpha N^2}{V^2} \quad \text{so,}$$

$$V \left(\frac{\partial P}{\partial V} \right)_{T,N} = V \frac{\partial}{\partial V} \left[\frac{NkT}{V-Nb} - \frac{aN^2}{V^2} \right]$$

$$= V \left[\frac{-NkT}{(V-Nb)^2} + \frac{2aN^2}{V^3} \right]$$

$$\Rightarrow \left(\frac{\partial G}{\partial V} \right)_{T,N} = \frac{-NkTV}{(V-Nb)^2} + \frac{2aN^2}{V^2}$$

$$\therefore dG = \int [] dV$$

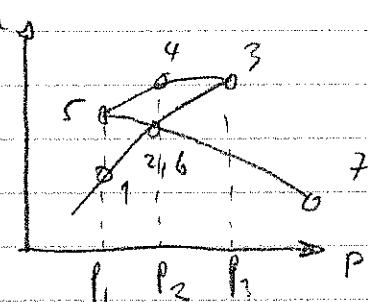
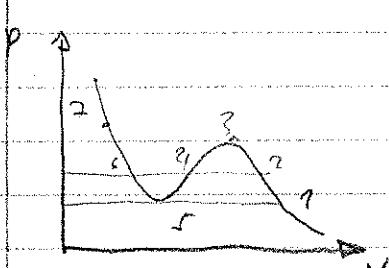
$$= \int \frac{-NkT(V-Nb+Nb)}{(V-Nb)^2} + \frac{2aN^2}{V^2} dV$$

$$= \int \frac{-NkT(V-Nb)}{(V-Nb)^2} - \frac{NkT}{(V-Nb)^2} + \frac{2aN^2}{V^2} dV$$

constant
∫ of int

$$\rightarrow G = -NkT \ln(V-Nb) + \frac{NkT(Nb)}{(V-Nb)} - \frac{2aN^2}{V} + c(T)$$

B Want to know $G \propto P$

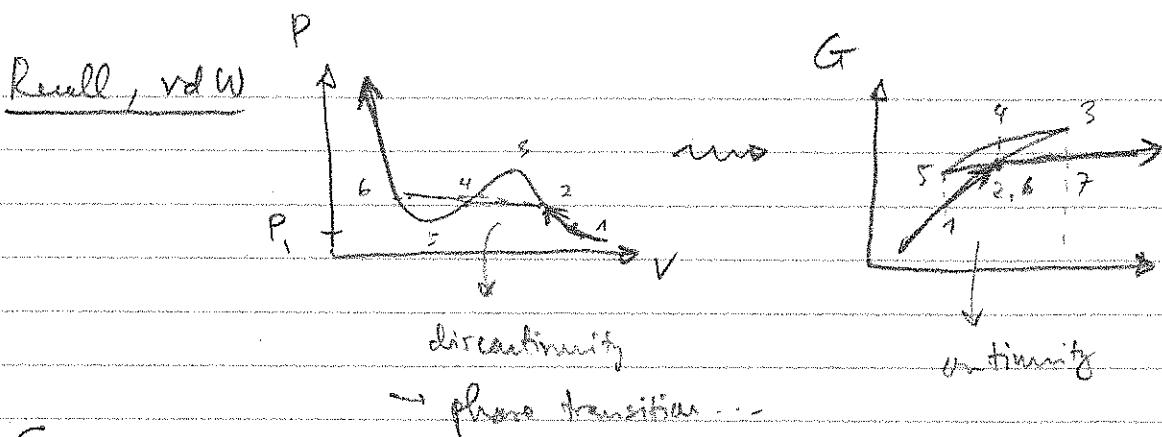


- J2 + J6 are reversible.

- Substance will go directly from vol @ 2 → vol @ 6 as it's compressed
- Discontinuity = phase change

$$\Delta G \text{ around loop} = 0 \quad \int_{\text{loop}} dG = 0, \quad \left(\frac{\partial G}{\partial P} \right)_T = V \Rightarrow \int \left(\frac{\partial G}{\partial P} \right) dP = 0$$

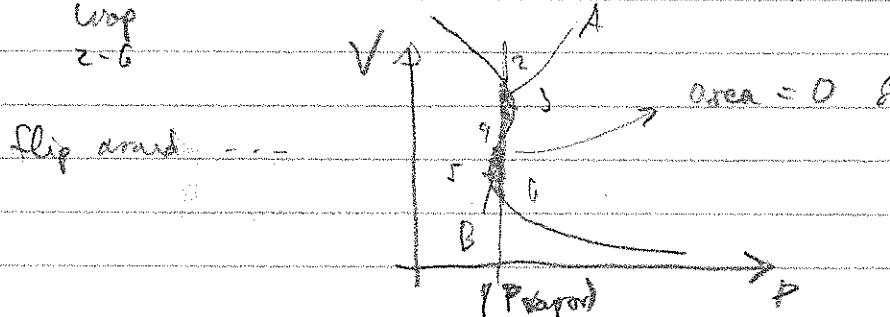
$$\therefore \boxed{0 = \int_{\text{loop}} V dP}$$



$$\int_{\text{loop } 2-6} dG = 0 = \int_{\text{loop } 2-6} dG_{\text{ext}} \quad \text{where } dG_{\text{ext}} = -SdT + PVdV$$

$$\hookrightarrow \left(\frac{\partial G}{\partial P}\right)_{T,N} = V$$

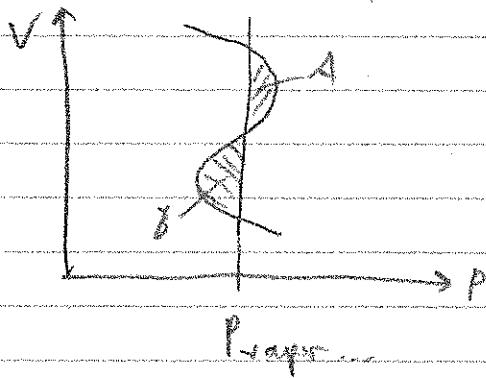
$$\underline{\underline{B}} \int_{\text{loop } 2-6} VdP_T = 0$$



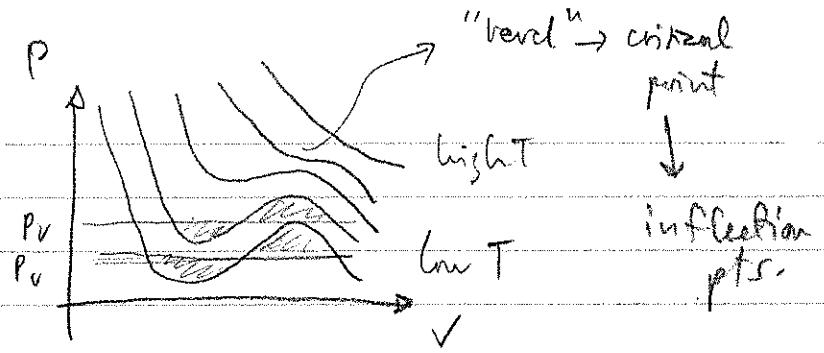
$$\rightarrow \underline{\underline{\text{area}(A) = \text{area}(B)}} \text{ for } \int VdP_T = 0$$

\hookrightarrow "Maxwell's construction"

\Rightarrow P of phase transition occurs where vertical P divides the area in equal halves

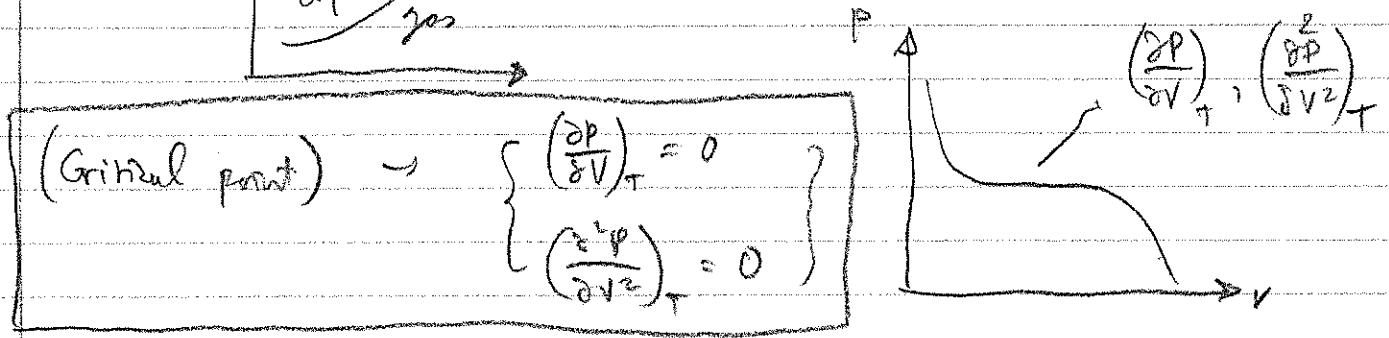


Isotherms @ different T



↳ By finding P_{cav} based on Isotherms...

↳ ↑ liquid & critical point.



$\left\{ T_c = \text{critical temp} \right. \text{ is where 1st \& 2nd derive of } \frac{\partial P}{\partial V} \text{ wrt } V \left. \text{ are zero.} \right\}$

PHASE TRANSFORMATION OF MIXTURES

(§ 5.4)

Start with G $G = U - TS + PV$

Consider a mixture of 2 substances A : B

A	B
---	---

in thermal + mech. equilibrium

$$\rightarrow T_A = T_B \approx P_A = P_B$$

Then $G_{\text{tot}} = G_A + G_B$. Let $x = \frac{\# B}{\Sigma} \rightarrow 1-x = \frac{\# A}{\Sigma}$

Can write $G_A^\circ = \text{Gibbs free energy of pure A}$ ($x=0$)
 $G_B^\circ = \text{Gibbs free energy of pure B}$ ($x=1$)

Remove partition & let A + B mix in U, V

$$G = U - TS + PV, \text{ Assume these changes are small}$$

$$\Delta G = \Delta U - T\Delta S + P\Delta V$$

Initially, $G_{tot}^\circ = (1-x)G_A^\circ + xG_B^\circ$

Recall, $\Delta S_{mixing} = -Nk[x\ln x + (1-x)\ln(1-x)]$

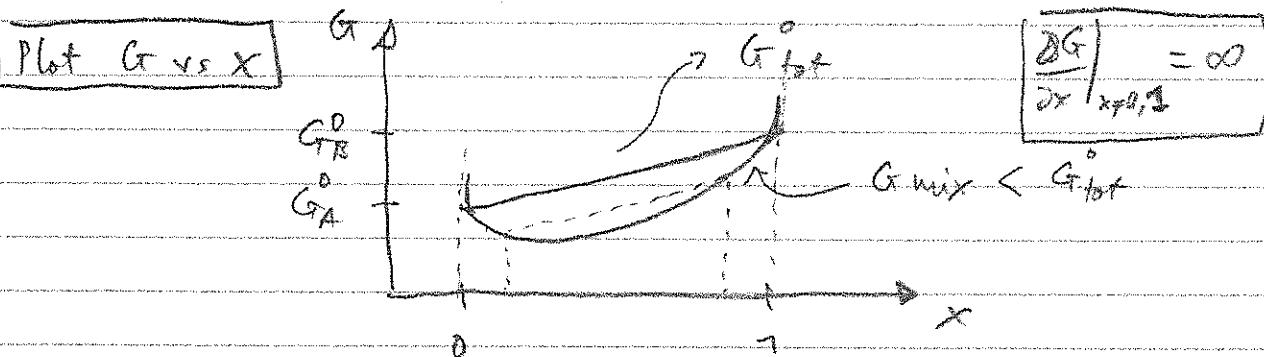
assuming $\Delta U = 0, \Delta V = 0$, then,

$$G_{mixed} = G_{tot}^\circ - T\Delta S$$

$$= G_{tot}^\circ + NkT[x\ln x + (1-x)\ln(1-x)]$$

∴ $G_{mixed} = (1-x)G_A^\circ + xG_B^\circ + nRT[x\ln x + (1-x)\ln(1-x)]$

→ we call this an ideal mixture → derived from ideal gas...



- slope of G vs. x at $x=0, 1$ is ∞

- in fact (mixed) is always more stable bc of entropy of mixing...

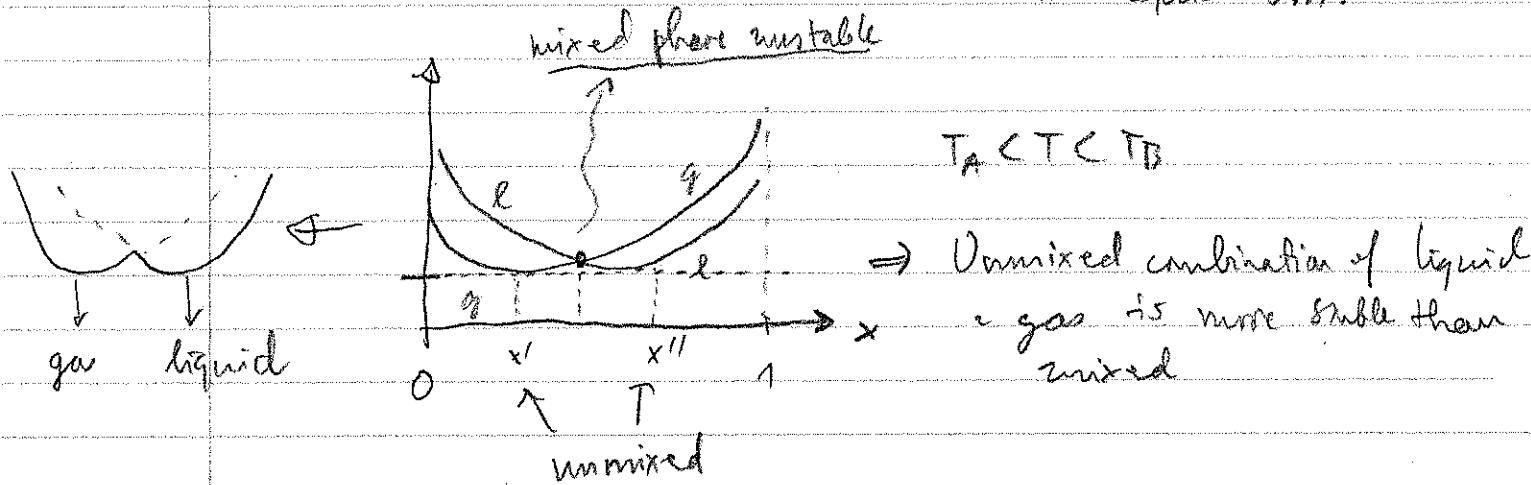
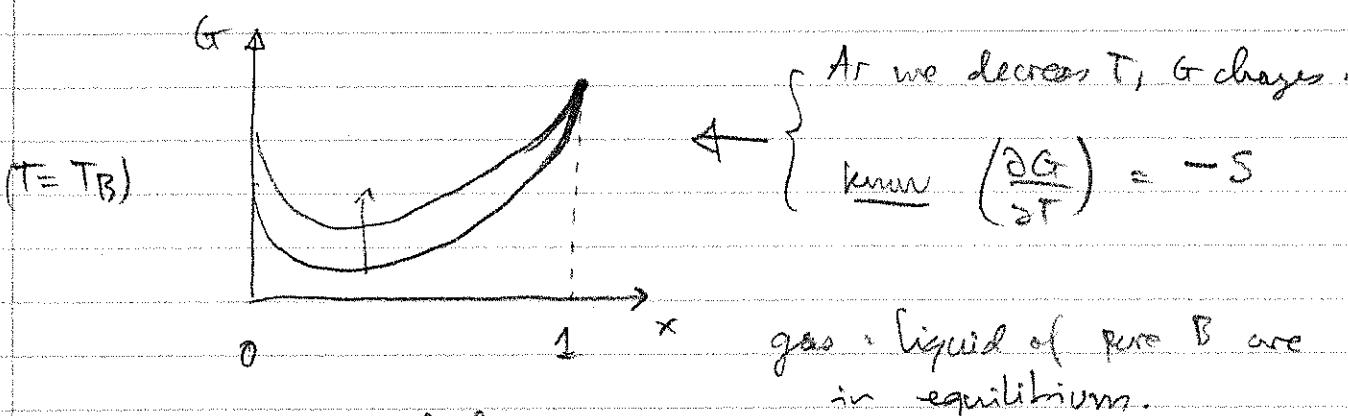
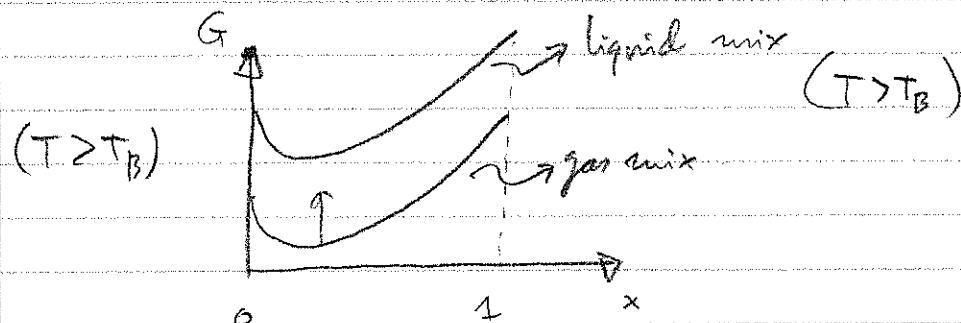
Phase changes of mixtures

e.g. $N_2 + O_2$

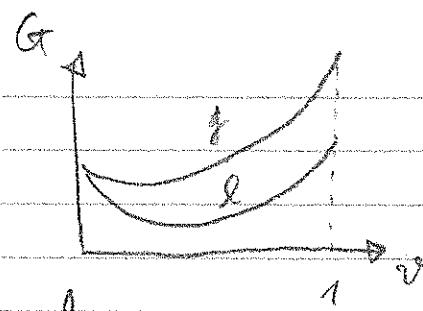
Let T_A = boiling point of pure substance A

T_B = boiling point of pure substance B

Let $T_B \gg T_A$. Then at high temp. $T > T_B > T_A$
 \rightarrow stable phase is a gas regardless of composition ...

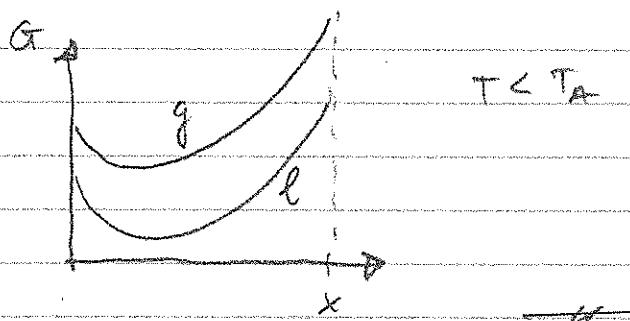


Decrease T for $A \dots$



(crossed)

$T \leq T_A \Rightarrow$ liquid stable
for pure A

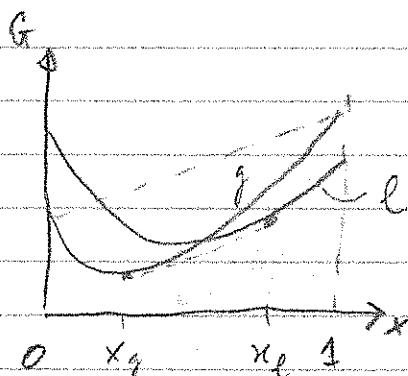


$T < T_A$ and liquid mixed is stable

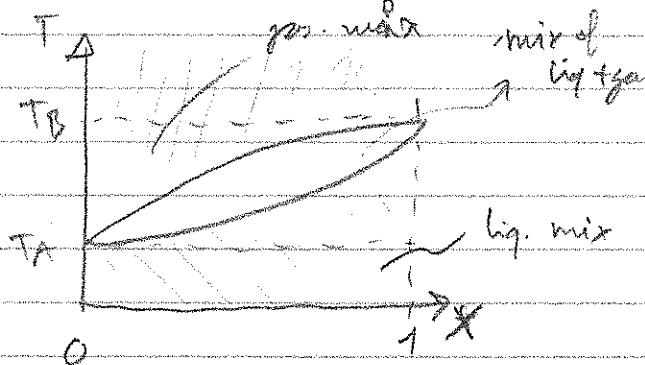
Feb 13, 2019

Gas mix

Gas mix

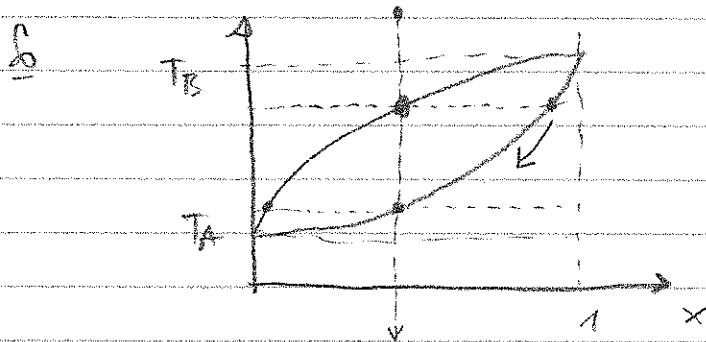


gas mix



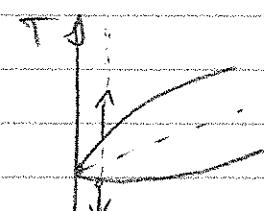
gas mix

liq. mix



as we go down
in temp

For dilute solutions, x is small. Thus solvent does not evaporate \rightarrow gas is pure solvent



\rightarrow only need equilibrium condition for solvent

$A = \text{solvent}, B = \text{solute}$

Q8 $\mu_{A, \text{eq}}(T, P) = \mu_{A, \text{gas}}(T, P) \Rightarrow A \text{ is in equili.}$

Solvent, $\mu_{A, \text{eq}}(T, P) = \mu_0(T, P) - \frac{N_B k T}{N_A}$

And so,

$$\mu_0(T, P) - \frac{N_B k T}{N_A} = \mu_{A, \text{gas}}(T, P)$$

Let T_0 be boiling point of pure solvent (A). Hold pressure steady, vary temperature around T_0 to see how μ changes.

$$\mu_0(T_0, P) + (T-T_0) \left(\frac{\partial \mu_0}{\partial T} \right) = \frac{N_B k T}{N_A} = \mu_{\text{gas}}(T_0, P) + (T-T_0) \left(\frac{\partial \mu_{\text{gas}}}{\partial T} \right)$$

at $T = T_0$, by assumption $\mu_{A, \text{gas}}(T_0, P) = \mu_{\text{gas}}(T_0, P)$ (e.g., assuming gas is pure solvent)

4 $(T-T_0) \left(\frac{\partial \mu_0}{\partial T} \right) = \frac{N_B k T}{N_A} = (T-T_0) \left(\frac{\partial \mu_{\text{gas}}}{\partial T} \right)$

Also,

$$\mu = \frac{G}{N} \Rightarrow \frac{\partial \mu}{\partial T} = \frac{1}{N} \left(\frac{\partial G}{\partial T} \right)_{V, N} = \frac{-S}{N}$$

5 $(T-T_0) \left(\frac{-S_{\text{sol}}}{N_A} \right) = \frac{N_B k T}{N_A} = (T-T_0) \left(\frac{-S_{\text{gas}}}{N_A} \right)$

6 $(T-T_0) \left[\frac{S_{\text{gas}}}{N_A} - \frac{S_{\text{sol}}}{N_A} \right] = \frac{N_B k T}{N_A}$

7 $(T-T_0) = \frac{N_B k T}{S_{\text{gas}} - S_{\text{sol}}} = \frac{N_B k T}{\Delta S} = \frac{N_B k T}{\frac{Q}{L}} = \frac{N_B k T T_0}{L}$

$Q = L = \text{Latent heat}$

Assuming $T_0 \approx T$

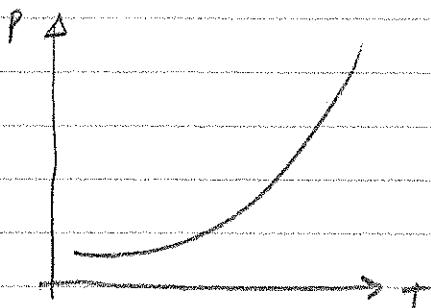
$\rightarrow T - T_0 = \frac{N_B k T_0^2}{L}$

8 $T - T_0 = \frac{N_B R T_0^2}{L}$

shift in boiling point of solvent due to NB solute

Shift in vapor pressure

\rightarrow (derivation in book)



Result? (as

$$\frac{P}{P_0} = 1 - \frac{N_B}{N_A}$$

only for dilute solutions ..

Ch. 6 Boltzmann Statistics

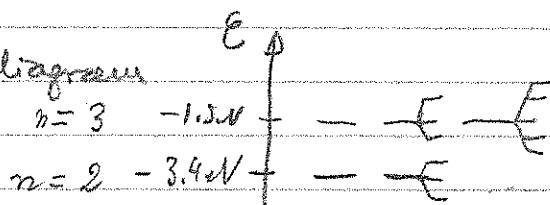
Goal: Get multiplicity for more complicated systems

Defn: "System" of a single atom is a reservoir of other atoms at some temperature T

o Macrostate = energy level. These energy levels are degenerate.
 → multiple microstates.

Ex hydrogen atom: n, l, m_l, m_s

o Energy level diagram



principal quantum number n : $n=1 - 13.6\text{eV}$

$l=0, l=1$

n is # ≥ 1

l : orbital angular momentum. l is $0, 1, \dots (n-1)$

m_l : z-component of orbital angular momentum
 $-l \leq m_l \leq l$

m_s : z-component of spin angular momentum

$m_s = \pm \frac{1}{2}$

Q: In general, for H, degeneracy is $[2n]^2$ for H

- Single atom exchanges energy with reservoir at temp T .
- Assumption \rightarrow all microstates within a given macrostate are equally probable.
- Macrostate of the atom + reservoir system with highest multiplicity should be most probable.

Remember : $P(A) = \frac{\# A}{\# \text{S}_m} \rightarrow \Sigma$

- Use ratios instead of avoid $\#$. Take 2 possible states of atom s_1 & s_2 .

$E(s_1)$ = Energy of atom in s_1 ,

$E(s_2)$ = Energy of atom in s_2

$P(s_1)$ = prob. in s_1 ,

$P(s_2)$ = prob. in s_2

Want state with highest multiplicity in combined atom + reservoir system \rightarrow most probable.

$S_R(s_i)$ \rightarrow multiplicity of reservoir when atom is in state s_i

$$P_R(s_i) \propto S_R(s_i) \Rightarrow \frac{P(s_2)}{P(s_1)} = \frac{S_R(s_2)}{S_R(s_1)} \quad S = k \ln \Sigma$$

$$S = k \ln \Sigma \rightarrow \boxed{\frac{P(s_2)}{P(s_1)} = \frac{e^{S_R(s_2)/k}}{e^{S_R(s_1)/k}} = e^{\underbrace{(S_R(s_2) - S_R(s_1))}_{\text{infinite sum}}/k}}$$

$$\frac{dS}{T} = \frac{1}{k} \left[\underbrace{dW}_{\text{equal & opposite}} + P dV_R - \nu dN_R \right]$$

to the atoms ...

infinite sum
change in energy of reservoir

$$\rightarrow PdV_K \sim (1\text{ Å})^3 \text{ at 1 atm} \rightarrow (10^5 \text{ Pa})(10^{-11}\text{ m})^3 \approx 10^{-25} \text{ J}$$

$$dV_K \sim k_B T \ln z \approx 10^{-11} \text{ J}$$

$\therefore PdV_K \ll dV_K \rightarrow$ ignore. $\rightarrow dV_K \approx 0$

Also, $dN_A \approx 0$

reservoir ...

$$\therefore [S_E(s_2) - S_E(s_1)] = \frac{1}{T_K} [U_K(s_2) - U_K(s_1)] \xrightarrow{\text{atom ...}}$$

$$[S_K(s_2) - S_K(s_1)] = -\frac{1}{T_K} [E(s_2) - E(s_1)]$$

And so,

$$P(s_2) = e^{-[E(s_2) - E(s_1)]/kT}$$

$$\frac{P(s_1)}{P(s_2)} = e^{-E(s_2)/kT}$$

\Rightarrow Boltzmann factor...

$$\frac{P(s_1)}{P(s_2)} = \frac{e^{-E(s_1)/kT}}{e^{-E(s_2)/kT}}$$

$$e^{-E(s)/kT}$$

$$\therefore \frac{P(s_2)}{e^{-E(s_2)/kT}} = \frac{P(s_1)}{e^{-E(s_1)/kT}} \Rightarrow \text{must be constant.}$$

P

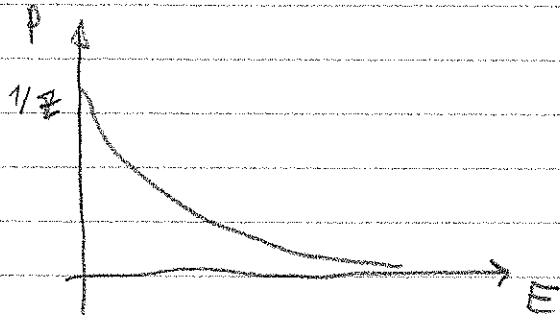
T

index of s_1 index of s_2

$$\underline{\underline{\frac{P(s_2)}{e^{-E(s_2)/kT}}}} \quad \underline{\underline{\frac{P(s_1)}{e^{-E(s_1)/kT}}}} \quad \text{constant} = \frac{1}{z}$$

$$\boxed{P(s) = \frac{1}{z} e^{-E(s)/kT}}$$

\Rightarrow Boltzmann distribution
(canonical distribution)



Z: The Partition Function

Total probability of finding an atom in some state or another = 1

$$1 = \sum_s P(s) = \sum_s \frac{1}{Z} e^{-E(s)/kT} = \frac{1}{Z} \sum_s e^{-E(s)/kT}$$

So $Z = \sum_s e^{-E(s)/kT}$ \rightarrow partition function...

April 17, 2019

$Z \rightarrow$ normalization factor that converts Boltzmann factor into a prob

Temp. dependence of Z

① Low T, @ room T, $kT \approx 0.0257 \text{ eV}$

ground state energy = 0 eV

\rightarrow dominates partition function.

Ex Excited state $e^{-10.2 \text{ eV}/kT}$ while $e^0 = 1$

\rightarrow @ low T, $Z=1$ \rightarrow 1 possible state available...

② At high T $E \ll kT$

$$Z = e^{-0/kT} + e^{-E_1/kT} + \dots$$

$$= 1 + (\text{order of unity}) + \dots$$

So $Z \gg 1$

* At high temp, there are many states available...

5/9
greetings

Applications of Boltzmann factors

Thermal excitations of atoms in stellar atmospheres.

Consider H atom in atm of sun ($T \approx 5800\text{K}$).

What is the prob. of finding e^- in one of the first excited states compared to probability of finding e^- in ground state.

$$\frac{P(S_2)}{P(S_1)} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}} = e^{-(E_2 - E_1)/kT} \quad \text{Eq}$$

$$\text{For H, } E_2 - E_1 = \Delta E \approx -3.4\text{eV} = 7(-13.6\text{eV}) = 10.2\text{eV}$$

$$\text{At } kT = (8.62 \times 10^{-5} \text{eV/K})(5800\text{K}) = 0.50\text{eV}$$

$$\frac{P(S_2)}{P(S_1)} = e^{-10.2\text{eV}/0.5\text{eV}} = 1.4 \times 10^{-9}$$

But we need to add "statistical weights" to account for degeneracy of energy levels ...

$$\begin{aligned} g_2 &= 8 \quad (2n^2) \quad \therefore P(S_2)/P(S_1) = \frac{g_2}{g_1} e^{-\Delta E/kT} \\ g_1 &= 2 \\ &= 4 [1.4 \times 10^{-9}] \\ &= 5.6 \times 10^{-9} \end{aligned}$$

Care!

At some temp T , we start ionizing atoms.

→ No more e^- for upwards transitions.

→ Boltzmann dist is only part of the story ...



Excitation → need to add Saha equation to account for

ionization. Salin eqn:

$$\frac{P_{\text{H ionized}}}{P_{\text{H neutral}}} = \frac{1}{ne} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-E_I/kT}$$

Average values

Eq 5.2.

$$P(s) = \frac{1}{Z} e^{-E(s)/kT} = \frac{1}{Z} e^{-\beta E(s)}$$

$$\text{where } \beta = 1/kT$$

$$\text{And so } Z = \sum_s e^{-E(s)/kT} = \sum_s e^{-\beta E(s)}$$

Imagine we have an atom with 3 discrete energy levels...
0eV, 4eV, 7eV

Say we have 5 such atoms, 2 in ground, 2 in 1st state,
1, in 2nd state.

Average energy of all 5 atoms is:

$$\bar{E} = \frac{0 \cdot 2 + 4 \cdot 2 + 7 \cdot 1}{5} = \frac{12}{5} = 2.4 \text{ eV} \dots$$

or

$$E = \left(\frac{2}{5} \cdot 0 \text{ eV} \right) + \left(\frac{2}{5} \cdot 4 \text{ eV} \right) + \left(\frac{1}{5} \cdot 7 \text{ eV} \right)$$

$$= P(0s) \cdot 0 \text{ eV} + P(1s) \cdot \dots$$

Generalize

$$E = \frac{\sum_s E(s) N(s)}{N} = \sum_s E(s) \frac{N(s)}{N} = \sum_s E(s) P(s)$$

$$\therefore \bar{E} = \frac{1}{Z} \sum_s E(s) e^{-\beta E(s)}$$

Can do this for avg value of any property

$$\bar{X} = \sum x_i p(s) = \frac{1}{Z} \sum s x(s) e^{-\beta E(s)}$$

Also note that average values are additive.

If \bar{E} is avg value of single atom, so in general,

$$\langle n \rangle = N \bar{E} \rightarrow \text{avg energy of ensemble of } N \text{ particles}$$

* Calculate deviation about the mean

For our 5 atoms @ 3 energy levels $E = 3 \text{ eV}$... then the difference from the mean

$$2 \text{ atoms @ } 0 \text{ eV: } \Delta E = E - \bar{E} = 0 - 3 \text{ eV} = -3 \text{ eV}$$

$$2 \text{ atoms @ } 4 \text{ eV: } \Delta E = E - \bar{E} = 4 \text{ eV} - 3 \text{ eV} = 1 \text{ eV}$$

$$= 4 \text{ eV}$$

$(\Delta E)^2 \rightarrow$ change of the square deviation

$$\sigma^2 = (-3)^2 \cdot 2 + (1)^2 \cdot 2 + 4^2 \cdot 1 = 7.2 \text{ eV}^2$$

Then, $\sqrt{(\Delta E)^2} = \text{rms/ std dev} \dots = \sigma_E = \sqrt{7.2 \text{ eV}^2} = 2.7 \text{ eV}$

But we also learned that

$$\sigma_E^2 = \bar{E}^2 - \bar{E}^2$$

For any systems in thermal equilibrium with reservoir at Temp T, average value of the energy, \bar{E} :

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \quad \text{where } \beta = \frac{1}{kT}$$

or equivalently

$$\bar{E} = -\frac{\partial \ln(Z)}{\partial \beta}$$

Proof

$$\frac{\partial Z}{\partial \beta} = \frac{\partial}{\partial \beta} \left[\sum_s e^{-\beta E(s)} \right] = \sum_s \frac{\partial}{\partial \beta} e^{-\beta E(s)} \approx \sum_s -E(s) e^{-\beta E(s)}$$

So

$$-\frac{1}{Z} \frac{\partial Z}{\partial \beta} = +\frac{1}{Z} \sum_s +E(s) e^{-\beta E(s)} = \sum_s \left(\frac{1}{Z} E(s) e^{-\beta E(s)} \right) = \sum_s E(s) P(s)$$

$$\therefore -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \bar{E}$$

Can also show that

$$\bar{E}^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

How is work related to Z ?

→ suppose we have a system characterized by a single param, x .

→ Quasi-static change in x , $x \rightarrow x + dx$

• Energy of state (s) changes by some small amount

$$\Delta E_s = \frac{\partial E_s}{\partial x} dx$$

• Work done on the system $\Rightarrow W = \int F \cdot dx \approx \sum F_i dx$
 where $F_i \rightarrow$ ith change in Energy w.r.t x .

$$F_i = \frac{\partial E_i}{\partial x}$$

$$\sum_i \frac{\partial E_i}{\partial x} e^{-\beta E(s)} dx$$

$$\therefore \text{Work done on system } W = \frac{\sum_i \frac{\partial E_i}{\partial x} e^{-\beta E(s)} dx}{\sum_s e^{-\beta E(s)}}$$

Re-write numerator

$$\sum_i e^{-\beta E(i)} \frac{\partial E(i)}{\partial x} = -\frac{1}{\beta} \frac{\partial}{\partial x} \left(\sum_i e^{-\beta E(i)} \right)$$

So ~~\sum_i~~ $\sum_i e^{-\beta E(i)} \frac{\partial E(i)}{\partial x} = -\frac{1}{\beta} \frac{\partial}{\partial x} \left(\sum_i e^{-\beta E(i)} \right)$

$= -\frac{1}{\beta} \frac{\partial z}{\partial x}$

So,

$$W = -\frac{1}{\beta} \frac{\partial z}{\partial x} dx / z$$

So $W = -\frac{1}{\beta} \frac{\partial z}{z} = -\frac{1}{\beta z} \frac{\partial z}{\partial x} dx = -\frac{1}{\beta} \frac{\partial \ln z}{\partial x} dx$

So $W_{on} = -\frac{1}{\beta} \frac{\partial \ln z}{\partial x}$

For example, $x = V$ (volume)

$$W_{on} = -P dV = -\frac{1}{\beta} \frac{\partial \ln z}{\partial V} dV$$

So $P = \frac{1}{\beta} \frac{\partial \ln z}{\partial V}$

How is z related to S ?

$$z = z(\beta, S) + \text{For small changes in } z,$$

$$d \ln z = \underbrace{\frac{\partial \ln z}{\partial x}}_{\text{ }} dx + \underbrace{\frac{\partial \ln z}{\partial \beta}}_{\text{ }} d\beta$$

So $d \ln(z) = -\beta W_{on} + -E d\beta$

\uparrow
 dW_{on}

Re-writing $d \ln Z = -\beta dW - d(\bar{E}_B) + \beta d\bar{E}$

So $d(\ln Z + \bar{E}_B) = \beta (\underbrace{d\bar{E} - dW}_{dQ \text{ (First law)}}) = \beta dQ = \frac{dQ}{kT} = \frac{1}{k} dS$

So $d(\ln Z + \bar{E}_B) = \frac{dS}{k}$

Now, $S = k \ln Z$

So $S = k(\ln Z + \beta \bar{E})$

So $\ln Z + \beta \bar{E} = \ln Z$

So $\ln Z = \ln Z - \beta \bar{E}$

Example of paramagnetism

\hookrightarrow Before: ① $Z(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!}$

② $S = k \ln Z$ (free sterling approximation)

③ $\frac{1}{T} = \left(\frac{\partial S}{\partial T} \right)_B$

④ $U = 0(T) \rightarrow u = -N_\uparrow B \tanh\left(\frac{\mu B}{kT}\right)$

⑤ $M = -\frac{u}{B}$

⑥ $C_B = \left(\frac{\partial U}{\partial T} \right)_B$

Now, we'll redo this with Boltzmann statistics. Two possible energy states --

"up" $\mu = -\mu B$ "down" $\mu' = \mu B$ $\{ \text{from } Z = \sum_i e^{-\beta E(i)} = e^{-\beta(-\mu B)} + e^{-\beta(\mu B)}$

$$= e^{\mu B} + e^{-\mu B}$$

So $Z = 2 \cosh(\mu B)$

Q) Probability of finding in up / down direction.

$$P_{\uparrow} = \frac{e^{-\beta \mu B}}{2 \cosh(\mu B)} \quad P_{\downarrow} = \frac{e^{-\beta \mu B}}{2 \cosh(\mu B)}, \quad P_{\uparrow} + P_{\downarrow} = 1$$

Average energy of a dipole

$$\begin{aligned} \bar{E} &= \sum_i E(i) P(i) = (-\mu B) \frac{e^{\beta \mu B}}{2 \cosh(\mu B)} + (\mu B) \frac{e^{-\beta \mu B}}{2 \cosh(\mu B)} \\ &= (\mu B) \frac{2 \sinh(\mu B)}{2 \cosh(\mu B)} \\ &= -\mu B \tanh(\beta \mu B) \end{aligned}$$

$\therefore \bar{E} = -\mu B \tanh(\beta \mu B)$

$\therefore E_{\text{ext}} = -N \mu B \tanh(\beta \mu B) = -N \mu B \tanh\left(\frac{\mu B}{kT}\right)$

Alternate approach

$$\begin{aligned} \bar{E} &= -\frac{1}{2} \frac{\partial}{\partial \beta} \\ &= -\frac{1}{2} \frac{\partial}{\partial \beta} \left[2 \cosh(\beta \mu B) \right] \\ &= -\frac{1}{2} \cdot 2 \left(\mu B \sinh(\beta \mu B) \right) \\ &= (2 \mu B) \frac{1}{2 \cosh(\beta \mu B)} \tanh(\beta \mu B) \\ &= -\mu B \tanh(\beta \mu B) \end{aligned}$$

$\therefore E_{\text{ext}} = -N \mu B \tanh(\beta \mu B)$

Magnetization $\Rightarrow M = N \bar{\mu}_x + \bar{\mu}_z = \sum \mu_s P(s) \dots$

$$= \mu P_{\uparrow} + (-\mu) P_{\downarrow}$$

April 22, 2019

The Equipartition Theorem

G applies to systems with quadratic degrees of freedom.

$$\rightarrow E = \frac{1}{2}mv^2$$

$E = \frac{1}{2}mv^2$ where $v = \text{position or momentum coordinate}$

- $Z = \sum_q e^{-\beta C q^2}$, and assuming that the spacing Δq is constant and small...

$$\therefore Z = \frac{1}{\Delta q} \sum_q e^{-\beta C q^2} \Delta q$$

$$= \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta C q^2} dq$$

Change of variable: Let $x = \sqrt{BC} \cdot q \rightarrow x^2 = BCq^2$

$$dq = \frac{dx}{\sqrt{BC}}$$

$$\therefore Z = \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-x^2} dx \cdot \frac{1}{\sqrt{BC}} = \frac{1}{\Delta q} \frac{1}{\sqrt{BC}} \int_{-\infty}^{\infty} e^{-x^2} dx \quad \begin{matrix} \rightarrow \\ \text{assumption} \end{matrix}$$

$$Z = \frac{\sqrt{\pi}}{\Delta q \sqrt{BC}}$$

(*) As long as $\Delta q \ll kT$, then equipartition holds (high temp)

$$\boxed{Z = \frac{1}{\Delta q} \sqrt{\frac{\pi}{BC}}}$$

or equivalently,

$$\boxed{Z = C \beta^{-1/2}}$$

$\rightarrow C$ is some constant

$$\therefore E = \frac{1}{2} \frac{\partial Z}{\partial \beta} = \frac{-1}{C \beta^{1/2}} \left(\frac{-1}{2} C \beta^{-3/2} \right) \Rightarrow E = \frac{1}{2} \bar{P}^{-1}$$

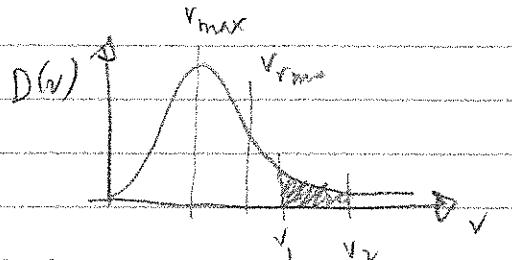
$$\therefore \boxed{E = \frac{1}{2} kT} \rightarrow \text{eq. partition theorem for 1/2 df.}$$

Note Conditions

Equipartition doesn't hold for quantum mechanical system,
since it requires a continuous of ΔE .

Equipartition holds if $E \gg kT$ (high temp)

The Maxwell's Speed Distribution



From equipartition, can imagine:

$$\frac{1}{2}mv^2 = \frac{3}{2}kT, \text{ then } v_{rms} = \sqrt{\frac{3kT}{m}}$$

$$P(v_1 \leq v \leq v_2) = \int_{v_1}^{v_2} D(v) dv, \text{ where } D(v) \text{ is the dist. function.}$$

↓ pdf.

What is $D(v)$? $\rightarrow D(v) \propto$ prob. that a molecule will have
velocity v - \propto # of states \propto correspondingly to speed v .

$$D(v) \propto (\text{prob. of molecule}) \times (\# \text{ of states})$$

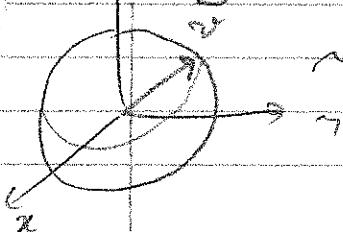
w/ velocity v corresponding to speed v

? ??

know, ? \propto Boltzmann factor $E = \frac{1}{2}mv^2 \propto e^{-mv^2/2kT}$

$$\boxed{?} \propto 4\pi v^2$$

\rightarrow larger v , more surface area, higher $D(v) \propto v^2$.



Q

$$D(v) = C (4\pi v^2) e^{-mv^2/2kT}$$

$$1 = \int_0^\infty D(v) dv = 4\pi C \int_0^\infty v^2 e^{-mv^2/2kT} dv$$

Change of vars. $x = v \sqrt{\frac{m}{2kT}}$, then

$$1 = 4\pi C \int_0^\infty x^2 e^{-x^2} dx \cdot \left(\sqrt{\frac{2kT}{m}}\right)^3$$

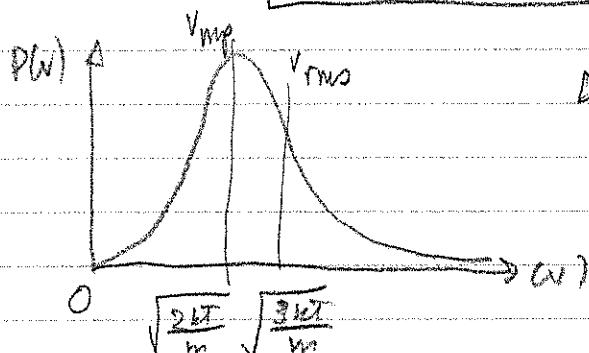
$$= 4\pi C \cdot \left(\frac{2kT}{m}\right)^{3/2} \int_0^\infty x^2 e^{-x^2} dx$$

$\sqrt{\pi/4}$

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

Maxwell's speed distribution

Thus, $D(v) = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}$



$$D(v) = 0 \text{ @ } v=0 - v \rightarrow \infty$$

Q Calculate v_{mp} (most probable)

$$0 = \frac{d}{dv} D(v) = 0 \rightarrow 0 = \frac{d}{dv} \left[v^2 e^{-mv^2/2kT} \right]$$

$$\therefore 0 = 2v e^{-mv^2/2kT} + v^2 \cdot \left(\frac{-mv}{kT}\right) e^{-mv^2/2kT}$$

$$= 2v + \frac{-mv^2}{kT} \Rightarrow 0 = 2 - \frac{mv^2}{kT} \Rightarrow$$

$$v_{mp} = \sqrt{\frac{2kT}{m}}$$

③ Calculate \bar{v}

$$\bar{v} = \bar{E}(v) = \int_0^\infty v D(v) dv = \int_0^\infty 4\pi v^3 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} dv$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^3 e^{-\frac{mv^2}{2kT}} dv$$

$$\bar{v} = \left(\frac{m}{2\pi kT}\right)^{3/2} (4\pi) \cdot \frac{1}{2} \left(\frac{2kT}{m}\right)^{1/2}$$

$$\therefore \bar{v} = \left(\frac{2kT}{m}\right)^{1/2} \cdot \frac{2}{\sqrt{\pi}}$$

$$\boxed{\bar{v} = \left(\frac{8kT}{m\sqrt{\pi}}\right)^{1/2}}$$

$$M = m N_A$$

Ex N_2 in air @ room temp ... $T \approx 298K$, $m_N = 14 \text{ g/mol}$
 $m_{N_2} = 28 \text{ g/mol}$

$$\bar{v}_{N_2} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2(1.38 \times 10^{-23})(298K)}{28 \times 10^{-3} \text{ kg/mol} / (6.02 \times 10^{23})}} \approx [420.5 \text{ m/s}]$$

April 23, 2019 | PARTITION FUNCTION = FREE ENERGY

$S = k \ln \Omega$ @ const $N \Rightarrow S \propto k \ln f(T)$, $S = k \ln \Omega$

$Z(T) \leftrightarrow F @ \text{constant } T$

Recall $F = U - TS \rightarrow \frac{F-U}{T} = -S$

$$dF = -PdV - SdT + \mu dN \rightarrow \left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$$

$$\therefore \left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{F-U}{T} \quad (1)$$

$$\text{Given } \tilde{F} = -kT \ln Z \Rightarrow Z = e^{-\tilde{F}/kT}$$

$$\text{Check deriv w.r.t } T: \frac{\partial \tilde{F}}{\partial T} = \frac{\partial}{\partial T} (-kT \ln Z)$$

$$= -k \ln Z - kT \frac{\partial}{\partial T} \ln Z$$

$$= -k \ln Z - kT \underbrace{\frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \ln Z}_{-1 \cdot \frac{1}{kT^2} \frac{\partial Z}{\partial \beta}}$$

$$\frac{\partial \tilde{F}}{\partial T} = -k \ln Z - \frac{U}{T}$$

$$\frac{\partial \tilde{F}}{\partial T} = \frac{\tilde{E}}{T} - \frac{U}{T} = \frac{\tilde{E}-U}{T}, \text{ same as (1), so } -U$$

\gg we know given

were correct, except there might be a constant

Check initial condition (to determine constant)

$$F = U - TS \quad \text{Let's use } T=0 \rightarrow \text{then } F(T=0) = U_0.$$

$$Z(0) = Z_0 \sum e^{-E_i/kT}$$

T
lowest possible
energy.

$$= e^{-U_0/kT} + \text{high order terms, negligible because } U \gg kT$$

$$\text{So } \tilde{F}(T=0) = -kT \ln Z = -kT(U_0/kT) = -U_0$$

$$\text{So } \tilde{F}(T=0) = U_0 \text{ no constant!}$$

$$\boxed{F = -kT \ln Z}$$

$$dF = -PdV - SdT + \mu dN$$

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = -P, \left(\frac{\partial F}{\partial T}\right)_{V,N} = -S, \left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu$$

Example

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S \quad F = -kT \ln Z, S = \frac{\partial}{\partial T} (-kT \ln Z)$$

$$S = -\frac{\partial}{\partial T} (-k \ln Z) = k \ln Z + \frac{\partial P}{\partial T} \frac{\partial}{\partial P} \ln Z$$

$$= k \ln Z + \frac{E}{T}$$

∴ $\boxed{S = k(\ln Z + \beta E)}$ ✓ same as before

$$\text{or } \ln Z = \frac{S}{k} - \beta E$$

Partition Function for Composite System

Goal: write an expression for Z for an ideal gas

1st: Determine how Z_{tot} depends on Z for each individual particle.

Start w/ system off 2 particles. If they do not interact, total energy:

$$E_{\text{tot}} = E_1 + E_2$$

$$Z_{\text{tot}} = \sum_c e^{-\beta [E_1(c) + E_2(c)]} = \sum_c e^{-\beta E_1(c)} e^{-\beta E_2(c)}$$

If we also assume that states of individual particles are independent of each other:

$$Z_{\text{tot}} = \underbrace{\sum_{s_1} e^{-\beta E_1(s_1)}}_{Z_1} \underbrace{\sum_{s_2} e^{-\beta E_2(s_2)}}_{Z_2} \Rightarrow \boxed{Z_{\text{tot}} = Z_1 Z_2}$$

(non-interacting distinguishable system particles)

If particles are indistinguishable, we have double counted states.

$$\text{∴ } Z_{\text{tot}} \approx \frac{1}{2} Z_1 Z_2$$

$$\text{or } Z_{\text{tot}} = Z_1^N$$

Generalize this to N particles $\rightarrow Z_{\text{tot}} = Z_1 Z_2 \dots Z_N$ distinguishable

For distinguishable $\boxed{Z_{\text{tot}} = \frac{1}{N!} Z^N}$

April 26, 2019

Working towards Z for ideal gas.

$$Z_{\text{tot}} = \frac{1}{N!} Z^N$$

$$E_{\text{tot}} = E_{\text{tr}} + E_{\text{int}}$$

↓
 (translation) internal E
 (KE) modes (rotation/vibration)

or thermal

energy

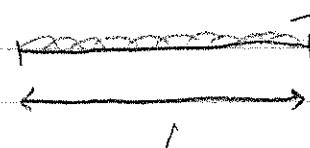
$$\boxed{\text{Boltzmann factor}} \rightarrow e^{-E_{\text{tot}}(s)/kT} = e^{-(E_{\text{tr}})/kT} \cdot e^{-(E_{\text{int}})/kT}$$

$$\therefore Z_i = Z_{\text{tr}} Z_{\text{int}}$$

ignore this one
for now ←

$$Z_{\text{tr}} = \sum_{\text{tr}} e^{-E_{\text{tr}}(s)/kT} \quad \& \quad Z_{\text{int}} = \sum_{\text{int}} e^{-E_{\text{int}}(s)/kT}$$

② When we counted states before:

1D:  $\# \text{Position states} = \frac{L}{dx}$

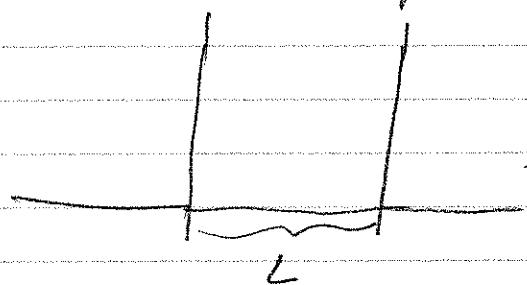
$$\# \text{Momentum states} = \frac{4p}{Ap}$$

Total # of states

$$\frac{L}{dx} \cdot \frac{4p}{Ap} \approx \frac{4p}{\hbar}$$

More formally,

↳ Count all independent, definite energy states or wave functions



Infinite square well

Potential energy $\left\{ \begin{array}{l} 0 \text{ inside box} \\ \text{as outside} \\ 0, \text{ outside the box} \end{array} \right.$

$\rightarrow KE = \left\{ \begin{array}{l} \text{something, finite} \end{array} \right.$

(141)

$$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2}{2mL^2}$$

\Rightarrow only certain wavelengths are allowed

$$\therefore p = \frac{\hbar}{\lambda} = \frac{\hbar n}{2L}$$

$$\rightarrow \lambda_n = \frac{2L}{n}, n=1, 2, 3, \dots$$

allowed momenta

$$\therefore E_n = \frac{p^2}{2m} = \left(\frac{\hbar n}{2L}\right)^2 \frac{1}{2m} = \frac{\hbar^2 n^2}{8mL^2}$$

or allowed independent energies.

$$\text{So, } Z_{1D} = \sum_{(1-D)} e^{-E_n kT}$$

$$= \sum_n \frac{1}{n!} \exp \left[-\frac{\hbar^2 n^2}{8mL^2 kT} \cdot \beta \right]$$

$$\text{assume large } TL \rightarrow \approx \int_0^\infty \exp \left[-\frac{\hbar^2 n^2}{8mL^2 kT} \right] dn$$

$$\Delta n = 1$$

$$\text{let } x = \frac{\hbar n}{\sqrt{8mL^2 kT}} \rightarrow dx = \frac{\hbar}{\sqrt{8mL^2 kT}}$$

$$\text{So, } Z_{1D} = \frac{\sqrt{8mL^2 kT}}{\hbar} \cdot \int_0^\infty e^{-x^2} dx$$

$$= \sqrt{\frac{8mL^2 kT}{\hbar^2}} \cdot \sqrt{\frac{\pi}{2}}$$

$$Z_{1D} = \frac{\sqrt{2\pi m kT}}{h} L = \frac{L}{\lambda_a} \quad \rightarrow \lambda_a = \text{"quantum length"}$$

length

- The quantum length, λ_a is roughly the de Broglie λ of a particle of mass m at energy kT .

$$= \frac{\hbar}{\sqrt{2\pi m kT}} \lambda_a \sqrt{kT}$$

!!

$$\lambda = \frac{\hbar}{p}, E = \hbar\omega = \frac{p^2}{2m} \rightarrow p = \sqrt{2mkT}, \text{ then } \lambda = \frac{\hbar}{\sqrt{2mkT}}$$

↳ $\ell_a \approx$ why the size of a particle... ~~for NC~~

Q) Ex For N_2 @ $T = 290K$, $\ell_a \approx 1.0 \times 10^{-10} m$

$\Rightarrow \frac{L}{\ell_a}$ is large

[In three dimensions]

$$E_T = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

$$\text{each } p_{i,n} = \frac{h n_i}{2L}$$

$$S) E_T = \sum_i e^{-E_i(kT)} = \sum_{n_x n_y n_z} e^{-\frac{h^2 n_x^2}{8m L_x^2 kT}} e^{-\frac{h^2 n_y^2}{8m L_y^2 kT}} e^{-\frac{h^2 n_z^2}{8m L_z^2 kT}}$$

$$= \frac{L_x}{\ell_a} \cdot \frac{L_y}{\ell_a} \cdot \frac{L_z}{\ell_a}$$

$$S) \boxed{\sum_{i,r} = \frac{V}{\ell_a^3} = \frac{V}{v_\alpha}} \rightarrow \text{quantum volume}^4$$

$$S) \boxed{v_\alpha = \ell_a^3 = \left(\frac{h}{\sqrt{2m kT}} \right)^3}$$

$$S) Z_{tot} = \frac{1}{N!} Z_{int}^N \cdot \frac{1}{N!} \left(\sum_{i,r} \cdot Z_{int} \right)^N$$

$$\boxed{Z_{tot} = \frac{1}{N!} \left(\frac{V}{v_\alpha} \cdot Z_{int} \right)^N}$$

Sometimes, log of Z is more useful...

Stirling's approx

$$\ln Z_{\text{tot}} = \frac{N}{k_B} \left(\ln V + \ln Z_{\text{int}} - \ln V_a \right) - Nk_B T + N$$

$$\text{S, } \ln Z_{\text{tot}} = N \left[\ln V + \ln Z_{\text{int}} - \ln V_a - \ln N + 1 \right]$$

(log of partition function for ideal gas)

Now we can predict the thermodynamic properties of ideal gas

• Average energy of ideal gas \rightarrow expect $E = \frac{3k_B T}{2}$

$$\hookrightarrow \ln Z_{\text{tot}} = N \left[\ln V + \ln Z_{\text{int}} - \ln V_a - \ln N + 1 \right]$$

$$E = - \frac{1}{2} \frac{\partial}{\partial \beta} \left(-2 \ln Z \right)$$

Note: V is independent of T, β

N is also independent of T, β

Z_{int}, V_a depend on β .

$$\begin{aligned} \text{S, } \bar{E} &= -N \left[\frac{\partial}{\partial \beta} (\ln Z_{\text{int}}) - \frac{1}{V_a} \frac{\partial V_a}{\partial \beta} \right] \\ &= -N \left[-\bar{E}_{\text{int}} + \frac{1}{V_a} \frac{\partial}{\partial \beta} \left(\frac{\hbar^2}{2\pi m k T} \right)^{3/2} \right] \\ &= N \bar{E}_{\text{int}} + \frac{1}{V_a} \left(\frac{\hbar^2}{2\pi m} \right)^{3/2} \frac{\partial}{\partial \beta} \left(\beta^{3/2} \right) \\ &= N \bar{E}_{\text{int}} + \frac{1}{V_a} \left(\frac{\hbar}{\sqrt{2\pi m}} \right)^3 \frac{3}{2} \beta^{1/2} \end{aligned}$$

$$= N \bar{E}_{\text{int}} + N \left(\frac{\sqrt{2\pi m k T}}{\hbar} \right)^3 \left(\frac{\hbar}{\sqrt{2\pi m}} \right)^3 \cdot \frac{3}{2} \sqrt{\beta}$$

$$= N \bar{E}_{\text{int}} + \frac{3}{2} N p^{-1} \xrightarrow{\text{to}} \boxed{\bar{E} = N \bar{E}_{\text{int}} + \frac{3}{2} N k T}$$

→ if assume no internal energy, $E \rightarrow \frac{3}{2}NkT$
 → Ent depends on Eq. Partition Func.

Heat Cap

$$C_V = \left(\frac{\partial U}{\partial T} \right) = \left(\frac{\partial U_{int}}{\partial T} \right) + \frac{3}{2}Nk$$

April 21, 2011

Ch 7: QUANTUM STATISTICS

↳ we'll use Gibbs factors instead of Boltzmann factor...

↳ think about system that can exchange energy w/ particles...

↳ look at ratio of probabilities $\frac{P(s_2)}{P(s_1)} = \sigma_p(s_2)/\sigma_p(s_1) = \frac{e^{S_p(s_2)/k}}{e^{S_p(s_1)/k}}$

↳, $\frac{P(s_2)}{P(s_1)} = e^{(S_p(s_2) - S_p(s_1))/k}$

$$dS_p = \frac{1}{T} [dU_R + PdV_R - \mu dN_R]$$

↳ Assume that $dV_R = 0$

↳ keep μN term fixed b/c dU_{sys}

↳, $S_p(s_2) - S_p(s_1) = -\frac{1}{T} [(E(s_2) - E(s_1)) - (\mu dN(s_2) - \mu dN(s_1))]$

$$= -\Delta S_R$$

↳ $\frac{P(s_2)}{P(s_1)} = \frac{e^{-[(E(s_2) - \mu N(s_2))]/kT}}{e^{-[E(s_1) - \mu N(s_1)]/kT}}$

↳ instead of Boltzmann factor, we set this factor \rightarrow Gibbs

$$\frac{1}{e^{-(E(s) - \mu N)/kT}}$$

- ② To get absolute probability \rightarrow need constant at front

$$P(s) = \frac{1}{Z} e^{-(E(s) - \mu N(s))/kT}$$

Z \rightarrow "grand partition function" or "Gibbs sum"

constant $\sum_s P(s) = 1 \Rightarrow Z = \sum_s e^{-(E(s) - \mu N(s))/kT}$

sum over all Gibbs factors.

If you have more than 1 type of particles, then sum over all species n, m, N_i :

Ex 2 particles... Gibbs factor: $e^{-\frac{(E_1 - \mu_1 N_1 - \mu_2 N_2)/kT}{2}}$

BOSONS \rightarrow FERMIONS

- ③ Quantum statistics \rightarrow important for high density + low temp systems..

- ④ In this case, derivation of

$$Z_{\text{tot}} = \frac{1}{N!} Z^N \quad \text{weakly true @ high density, low temperature.}$$

so $\frac{1}{N!}$ is not quite correct here.

- ⑤ Ex 2 interacting particles, each with 5 available states in the ground state energy, $E=0$.

$$\square \square \square \square \square E = 0$$

$$\text{Boltzmann factor} = e^{-\frac{E}{kT}} - 1 \Rightarrow Z = 5 \xrightarrow{\text{so}} Z = 5!$$

Rule • If distinguishable $\Rightarrow Z_{\text{tot}} = 5^N$

• If indistinguishable $\Rightarrow Z = \binom{5}{2} = 10$

so $Z = 10$

Premise assumption for indistinguishable particles

$$Z_{\text{tot}} = \frac{1}{N!} Z^N = \frac{25}{2!} = 12.5 \rightarrow \text{does not make sense...}$$

(Fermions) # states for indistinguishable particles $\Rightarrow 10^2$, no² particles are occupying the same state.

(Bosons) • But if we allow them to be in the same state $\Rightarrow 15$ for indistinguishable particles that can be in the same state.
 \rightarrow boson.

\Rightarrow And so $12.5 \rightarrow$ average between bosons + Fermions

$$\boxed{\frac{1}{N!} Z^N}$$

correctly cuts down 20 states for distinguishable particles to 10 for indistinguishable particles. But also cuts down 5 $\rightarrow 2.5$ incorrectly.

Bosons → can share the same (quantum) states (Ex; photons, pions, ${}^4\text{He}$ nuclei) integer spin: 0, 1, 2, ...

Fermions → cannot occupy the same (q) states ($e, \bar{e}, p, \bar{p}, n, \bar{n}, \dots$)
 ↑
 ↳ half-integer spin $\frac{1}{2}, \frac{3}{2}, \dots$

Pauli exclusion principle

↳ $Z_{\text{tot}} = \frac{1}{N!} \gamma^N$ interpolates between exact value for indistinguishable bosons, fermions.

⊗ Bosons → governed by Boltzmann statistics.

⊗ Fermions → governed by Fermi-Dirac statistics.

When do we need to use B-E + F-D stats rather than Boltzmann stats?

↳ when # of single particle states \gg # of particles, then it doesn't matter if we have bosons or fermions, use Boltzmann statistics

→ if $Z \gg N$

⊗ Think back to Ideal gas: $Z_i = \frac{V}{V_0} Z_{\text{tot}}$, where

$$V_0 = \left(\frac{\hbar}{\sqrt{2\pi mkT}} \right)^3, \text{ for } Z \gg N$$

$\frac{V}{V_0} \gg N$, and so, $\frac{V}{N} \gg V_0 \rightarrow$ average distance between particles is \gg de Broglie wavelength.

★ when $\frac{V}{N} \approx V_0$, then it matters whether we have Bosons or Fermions. \rightarrow use Quantum Statistics

either D-E or F-D,

At high temperature, $Z \gg N \rightarrow$ Boltzmann Statistics.

Single-particle state of a system

- System \rightarrow particular state of particle
- "Reservoir" \rightarrow all the possible states.

April 30, 2011

DISTRIBUTION FUNCTIONS

- System \Rightarrow single-particle quantum state
- Reservoir \Rightarrow all other possible states

~ If state is occupied, it has energy E
 If unoccupied, energy 0

If state can be occupied by N particles \rightarrow Energy NE

Probability of being occupied by N particles

$$P(N) = \frac{1}{Z} e^{-N(E-\mu)/kT}$$

$$S P(N) = \frac{1}{Z} e^{-N(E-\mu)/kT}$$

For Fermions, $n=0 \text{ or } 1$

$$Z_F = e^0 \left(\dots \right) / kT + e^{-1(E-\mu)/kT} = 1 + e^{-(E-\mu)/kT}$$

S Fermions: $Z_F = 1 + e^{-(E-\mu)/kT}$

determine the average # of particles in a state, or the occupancy of the state

$$\bar{n} = \sum_n n P(n) = 0 \cdot P(0) + 1 \cdot P(1)$$

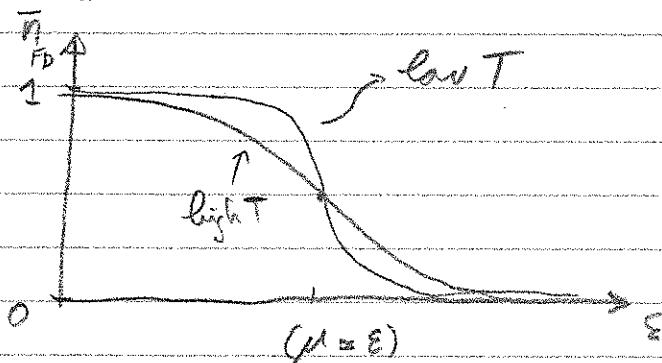
$$= \frac{e^{-(E-\mu)/kT}}{1 + e^{-(E-\mu)/kT}}$$

b) $\bar{n} = \frac{1}{e^{(E-\mu)/kT} + 1}$ \rightarrow Fermi-Dirac distribution

i) If $E \gg \mu$ $\bar{n} \rightarrow 0$

ii) If $E \ll \mu$ $\bar{n} \rightarrow 1$

iii) If $E = \mu$ $\bar{n} \rightarrow 1/2$ $\rightarrow 50\%$ chance of being occupied



$[Results] \rightarrow n \in \mathbb{N} \quad 0, 1, 2, \dots$

Then $Z = 1 + e^{-(E_1 - \mu)/kT} + e^{-(E_2 - \mu)/kT} + \dots$

Use $\frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots$ (geometric series)

b) $Z = \frac{1}{1 - e^{-(E_1 - \mu)/kT}}$

S. partition functions for bosons,

$$Z_B = \frac{1}{1 - e^{-(\varepsilon_m)/kT}}$$

E Average occupancy: $\bar{n} = \sum_n n P(n)$. Let $x = \frac{\varepsilon_m}{kT}$

$$\text{Then } \bar{n} = \sum_n n \frac{e^{-nx}}{Z} = -\frac{1}{Z} \sum_n \frac{d}{dx} e^{-nx}$$

$$= -\frac{1}{Z} \frac{d}{dx} \sum_n e^{-nx}$$

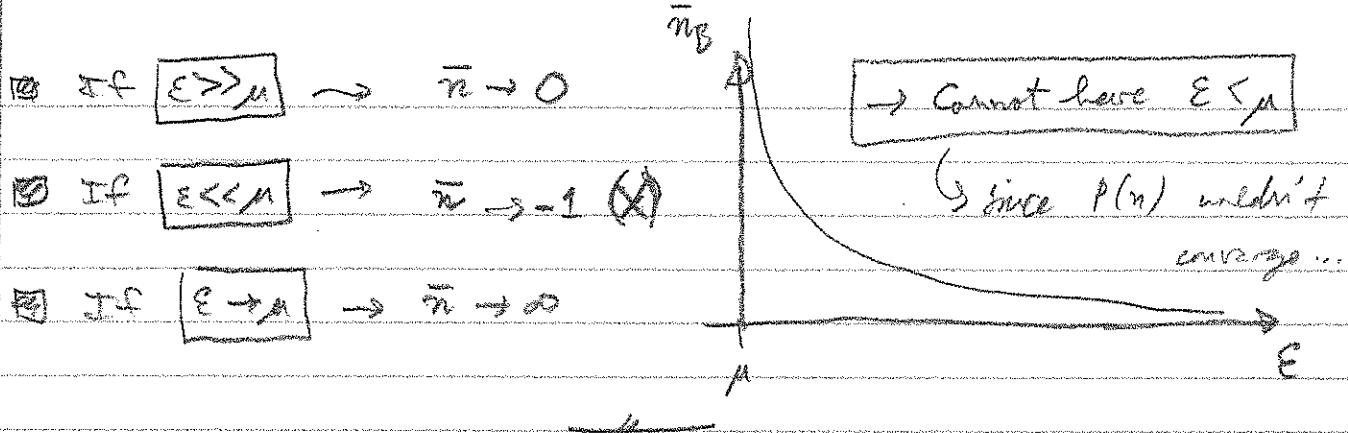
$$\bar{n}_B = \frac{-1}{Z} \frac{d}{dx} Z$$

$$\begin{aligned} \text{or } \bar{n}_B &= -(1 - e^{-x}) \cdot \frac{d}{dx} (1 - e^{-x})^{-1} \\ &= \frac{1 - e^{-x}}{(1 - e^{-x})^2} \cdot (e^{-x}) \\ &= \frac{e^{-x}}{1 - e^{-x}} \end{aligned}$$

$$\bar{n}_B = \frac{1}{e^x - 1}$$

Bose-Einstein dist.

$$\bar{n}_{BE} = \frac{1}{e^{+(\varepsilon_m)/kT} - 1}$$



⑦ Consider particles obeying Boltzmann statistics

$$P(\epsilon) = \frac{1}{Z_1} e^{-E(\epsilon)/kT} . \text{ If we have } N \text{ particles, then}$$

$$\boxed{\bar{n}_p = \frac{N}{Z_1} e^{-E(\epsilon)/kT} = \frac{N}{Z_1} e^{-\epsilon/kT}} \quad \begin{matrix} \text{Boltzmann} \\ \text{distribution.} \end{matrix}$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} \quad \& \quad F = -kT \ln Z$$

So,

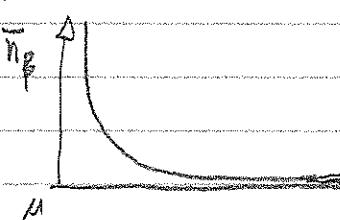
$$\mu = -kT \ln \left(\frac{Z}{N} \right)$$

By

$$e^{-\epsilon/kT} = \frac{Z_1}{N} \quad \& \quad \bar{n}_{\text{Boltz}} = e^{NkT} e^{-\epsilon/kT} = e^{-(\epsilon-\mu)/kT}$$

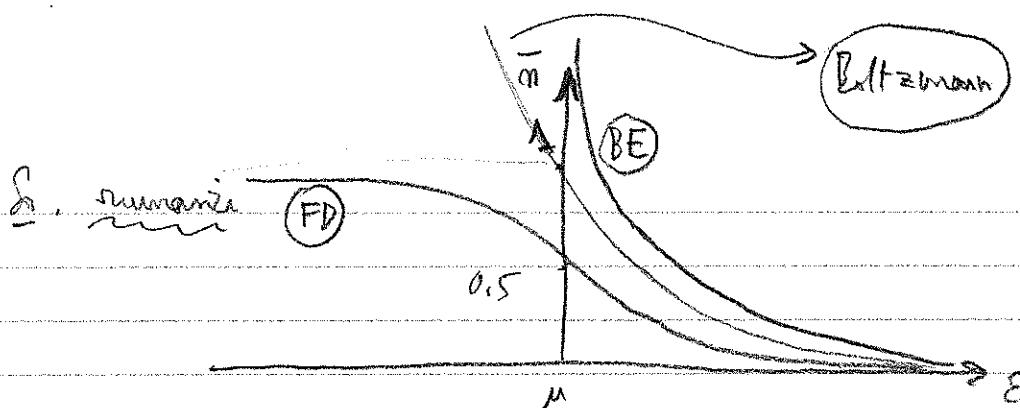
So

$$\bar{n}_F = \frac{1}{e^{(\epsilon-\mu)/kT}}$$



So

$$\bar{n}_F = \frac{1}{e^x + 1}, \quad \bar{n}_B = \frac{1}{e^x - 1}, \quad \bar{n}_F = \frac{1}{e^x}$$



NE
DEGENERATE FERMI GASES

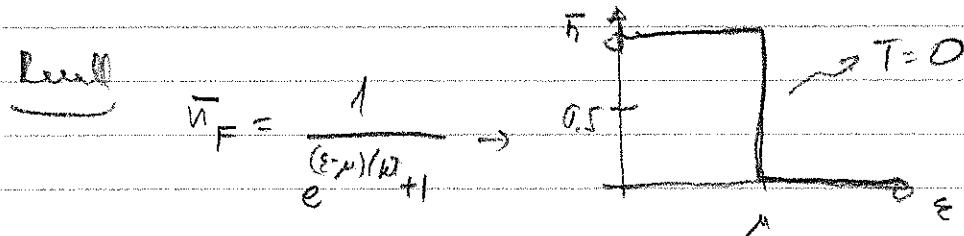
Consider a gas of Fermions at low T, or $\frac{V}{N} \gg V_A$

Ex: for an electron at room temp:

$$V_A = \left(\frac{\hbar}{\sqrt{2\pi m k T}} \right)^3 = (4.3 \text{ nm})^3$$

Typical conductor supplies 1 free e^- for every atom

$$\rightarrow 1 e^- \text{ per atom} \rightarrow V \sim (\text{size of atom})^3 \sim (0.2 \text{ nm})^3$$



At $T=0$ all $\epsilon < \mu$ will be occupied. All $\epsilon > \mu$ unoccupied

→ "Degenerate Fermi gas"

At $T=0$ at $E_F(T=0) = \epsilon_F$ or Fermi Energy

Goal Calculate \rightarrow total, average energy of Fermions

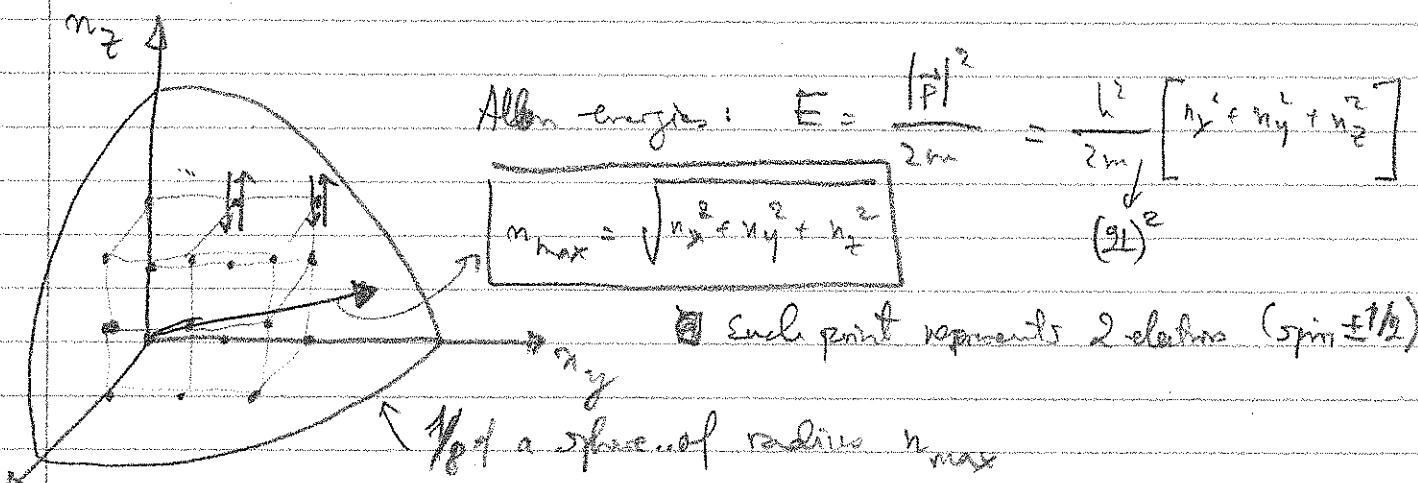
↳ degeneracy pressure. (whereas there's degeneracy for n_F)

Q Consider packing electrons into some 3D volume (infinite square well)

$$\text{Allowed wavefunctions give } \lambda_x = \frac{2L}{n} \quad \text{and} \quad p_x = \frac{\hbar n}{\lambda_x} = \frac{\hbar n}{2L}$$

$$p_x = \frac{\hbar n_x}{2L}, \quad p_y = \frac{\hbar n_y}{2L}, \quad p_z = \frac{\hbar n_z}{2L}$$

n_x, n_y, n_z are integers... independent of each other...



n_x

Q Want to calculate $E_F = \text{max energy}$

$$E_F = \frac{\hbar^2}{2m} \cdot \frac{1}{4L^2} = \frac{\hbar^2 n_{\max}^2}{8m L^2} \quad \left\{ \begin{array}{l} \text{Total # of electrons} = 2 \cdot \text{Volume of} \\ \text{1/8 sphere} \end{array} \right.$$

$$N = 2 \cdot \left[\frac{4}{3} \pi \cdot \frac{n_{\max}^3}{8} \right]$$

$$N = \frac{1}{3} \pi \left[\sqrt{n_x^2 + n_y^2 + n_z^2} \right]^3$$

Solve for n_{\max}

$$\rightarrow n_{\max} = \left(\frac{3N}{\pi} \right)^{1/3}$$

$$E_F = \frac{\hbar^2}{2m} (n_{\max})^2 \cdot \frac{1}{4L^2}$$

$$\rightarrow E_F = \frac{\hbar^2}{8m L^2} \left(\frac{3N}{\pi} \right)^{2/3} \quad \leftarrow \text{Fermi energy.}$$

$$\text{Since } V = L^3 \Rightarrow L^2 = V^{2/3}$$

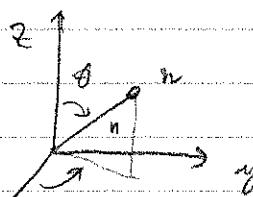
So $\boxed{\epsilon_F = \frac{\hbar^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3}}$ or Fermi energy

number density... intensive property...

Total energy of degenerate Fermi gas

$$U_{\text{tot}} = 2 \iiint_0^\infty \epsilon(n) dx dy dz \rightarrow \text{assuming large \# states...}$$

Convert to spherical coordinates...



$$dV = dx dy dz = r^2 \sin\theta dr d\theta d\phi$$

So $U_{\text{tot}} = 2 \iiint_0^{n_{\max} r^{1/2} t^{1/2}} \epsilon(n) r^2 \sin\theta dr d\theta d\phi$

$$= 2 \frac{(4\pi)}{8} \int_0^{n_{\max}} \epsilon(n) n^2 dn$$

$$= \pi \int_0^{n_{\max}} \epsilon(n) n^2 dn$$

$$= \pi \int_0^{n_{\max}} \frac{\hbar^2 n^2}{8m L^2} n^2 dn$$

$$= \frac{\hbar^2 \pi}{8m L^2} \int_0^{n_{\max}} n^4 dn$$

$$= \frac{\hbar^2 \pi}{8m L^2} \cdot \frac{1}{5} n_{\max}^5 \Rightarrow \boxed{U_{\text{tot}} = \frac{\hbar^2 \pi}{40m L^2} \cdot n_{\max}^5}$$

$$\text{In terms of } \epsilon_F = \frac{\hbar^2}{8\pi l^2} n_{\max}^2, n_{\max} = \left(\frac{3N}{\pi}\right)^{1/3}$$

$$U_{tot} = \frac{\pi(\epsilon_F n_{\max}^3)}{5}$$

temp - inv.

average energy as expected,

$$U_{tot} = \frac{3}{5} N \epsilon_F \text{ at } T=0$$

a little fit $> \frac{1}{2} \epsilon_F$



\Rightarrow average energy per particle ...

$$\bar{U} = U_{tot}/N = \frac{3}{5} \epsilon_F$$

If $\epsilon_F \gg kT \approx \text{degenerate gas}$

Fermi Temperature \rightarrow temp. at which characteristic thermal energy = Fermi energy

$$kT = \epsilon_F \Rightarrow T_F = \frac{\epsilon_F}{k} \rightarrow \text{and } T_F \text{ to get degenerate gas over there}$$

Pressure of degenerate gas (due to Pauli's exclusion principle)

Fermi

$$dU = TdS - PdV + \epsilon_F dN$$

$$P = \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P \Rightarrow P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

$$P_F = -\frac{\partial}{\partial V} \left[\frac{3}{5} N \frac{\hbar^2}{8m} \left(\frac{3N}{\pi}\right)^{2/3} V^{-2/3} \right]$$

$$= \frac{3}{5} N \frac{\hbar^2}{8m} \left(\frac{3N}{\pi}\right)^{2/3} \cdot \left(\frac{2}{3}\right) V^{-5/3} \quad \text{so} \quad P_F = \frac{2}{5} N \frac{\hbar^2}{V} \epsilon_F$$

In terms of $V_{tot} \Rightarrow$

$$P = \frac{2}{3} \frac{V_{tot}}{\sqrt{V}}$$

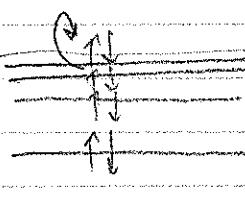
$\frac{2}{3}$ of energy density
of degenerate Fermi gas

$P > 0 \Rightarrow$ pushing outwards

temperature - independent

\rightarrow ex white dwarf star prevents collapse due to gravity

Consider small, non-zero temp

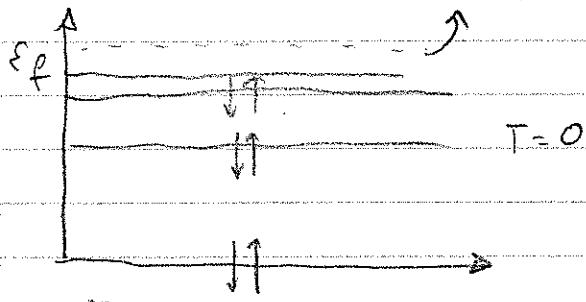
ϵ_f  ϵ_f \Rightarrow total energy gained by degenerate gas
is proportional to $(\# \text{ of } e^-) \cdot (\text{Energy per electron})$

$\propto N_{\text{tot}} \cdot kT$

$\delta \{ U_{\text{gained}} \propto N(kT)^2 \}$

May 6, 2019

Degenerate Fermi gas at small non-zero temp



if $\Delta T > 0$, small, $\epsilon \rightarrow \Delta E = kT$

Energy gained by degenerate
Fermi-gas

$\propto N(kT)^2$

$(\# \text{ of } e^-) \times (\text{Energy per jump})^2$

66

$$U_{\text{gained}} \sim N(kT)^2$$

\rightarrow when $\Delta T > 0$, small

$(NkT) \sim (kT)$

b, since $U_{\text{gained}} \propto N(kT)^2$

$$\text{units of constants} = \left(\frac{1}{\text{energy}} \right)$$

$$\text{Guess} \Rightarrow \frac{1}{E_F}$$

Additional constant of proportionality $\Rightarrow \frac{\pi^2}{4}$

$$\text{So } U_{\text{gained}} = \frac{\pi^2}{4 E_F} N(kT)^2$$

c

$$U_{\text{tot}} = U(T=0) + U(\Delta T)$$

$$U_{\text{tot}} = \frac{3}{5} N E_F + \frac{\pi^2}{4} \frac{N}{E_F} (kT)^2$$

→ energy of
degenerate
gas

this true for any temperature ...

$kT \ll E_F$

Heat capacity

$$\hookrightarrow \text{at constant volume} \rightarrow C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$\text{So } C_V = \frac{\partial}{\partial T} \left(\frac{\pi^2}{4} \frac{N}{E_F} (kT)^2 \right)$$

$$\Rightarrow C_V = \frac{\pi^2 N k^2 T}{2 E_F}$$

$\hookrightarrow \text{as } T \rightarrow 0, C_V \rightarrow 0, \text{ as expected.}$

$C_V \propto T$ (linearly in temp.)

Density of States

$$U = 2 \int_0^{n_{\max}} n^2 \epsilon(n) dn \int_0^{\pi/2} d\phi \int_0^{\pi/2} \sin \theta d\theta$$

$(\downarrow \uparrow)$ $(\pi/2)$

$$U = \pi \int_0^{n_{\max}} n^2 \epsilon(n) dn \rightarrow \text{integrating over all states}$$

What about integrating over all energies...

$$\epsilon = \frac{\hbar^2}{8mL^2} n^2 \rightarrow n = \sqrt{\frac{8mL^2}{\hbar^2} \sqrt{\epsilon}}$$

$$\int_0^{\infty} dn = \sqrt{\frac{8mL^2}{\hbar^2}} \frac{1}{2\sqrt{\epsilon}} d\epsilon \quad (n_{\max} \approx \infty)$$

~~$$\int_0^{\infty} \theta = \pi \int_0^{\infty} \epsilon \int_0^{\pi/2} \frac{8mL^2}{\hbar^2} \frac{1}{2\sqrt{\epsilon}} d\theta d\epsilon$$~~

~~$$U = \pi \int_0^{\infty} \epsilon \left[\left(\frac{8mL^2}{\hbar^2} \right) \epsilon \left(\frac{8mL^2}{\hbar^2} \right)^{1/2} \frac{1}{2\sqrt{\epsilon}} \right] d\epsilon$$~~

Call {Density of States}

$$g(\epsilon) = \pi \left(\frac{8mL^2}{\hbar^2} \right)^{3/2} \cdot \frac{\sqrt{\epsilon}}{2} = \pi (8m) \cdot \frac{\sqrt{\epsilon}}{2\hbar^3}$$

◻ $g(\epsilon) \rightarrow$ probability density, or total # of states with energy ϵ

* Now,

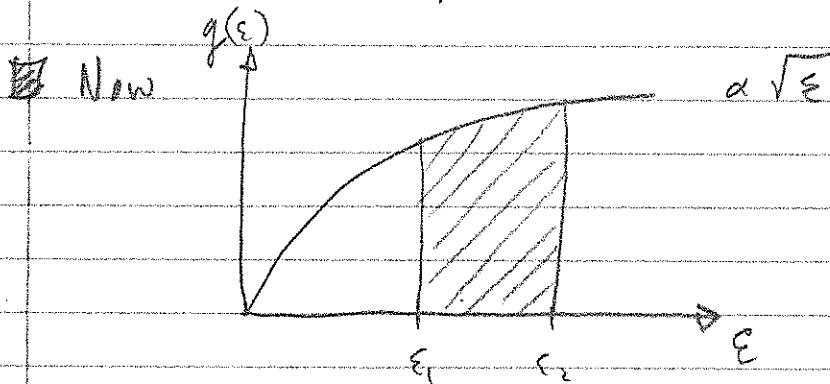
$$\epsilon_F = \frac{\hbar^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3}$$

$$g(\epsilon) = \frac{\pi (8m)^{1/4}}{2\hbar^3} V \sqrt{\epsilon}$$

So

$$g(\epsilon) = \frac{3N}{2\epsilon_F^{3/2}} \sqrt{\epsilon}$$

◻ Note: $g(\epsilon) \propto V$, independent of N
 $\propto \sqrt{\epsilon}$



◻ At $T=0$, then, all ϵ are below ϵ_F , then

$$\left. \begin{cases} P(\text{occupied} \mid \epsilon < \epsilon_F) = 1 \\ P(\text{occupied} \mid \epsilon > \epsilon_F) = 0 \end{cases} \right\}$$

◻ So

$$N(T=0) = \int_0^{\epsilon_F} g(\epsilon) d\epsilon$$

$e^{-\epsilon/kT}$ zero
Termi-

◻ For non-zero temperature ...

$$N(T=t) = \int_0^{\infty} g(\epsilon) \cdot P(\epsilon) d\epsilon$$

Dirac dist

$$N = \int_0^{\infty} g(\epsilon) P(\epsilon) d\epsilon$$

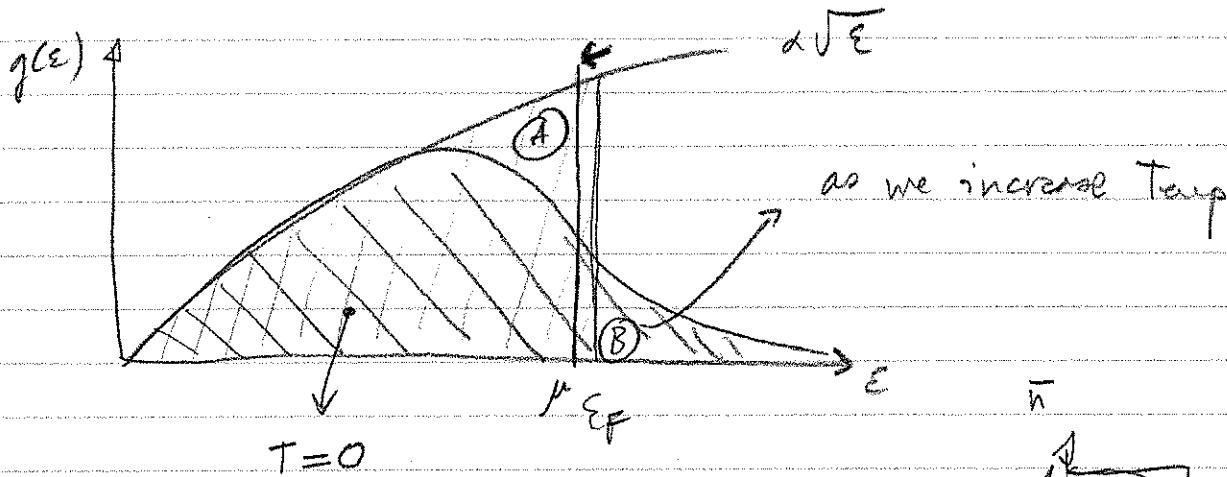
$\bar{n}_{FP} = \frac{1}{e^{(\epsilon - \mu)/kT} + 1}$

b

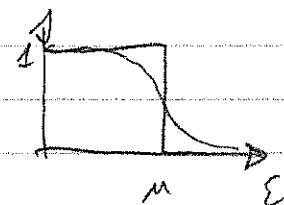
$$N = \int_0^{\infty} g(\epsilon) \frac{1}{e^{(\epsilon - \mu)/kT} + 1} d\epsilon \quad (\text{stuff})$$

So, total energy =

$$U_{\text{tot}} = \int_0^{\infty} \epsilon g(\epsilon) \frac{1}{e^{(\epsilon - \mu)/kT} + 1} d\epsilon$$



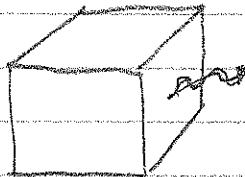
(Area A) = (Area B) At $T=0$, $\epsilon_F = \mu$



At $T > 0$, n decreases.

(concentration drops)

Black-body radiation



Inside box... definite energy wavefunctions

$$\lambda = \frac{c}{\nu}$$

Each wave has frequency $\nu = \frac{c}{\lambda}$

Each wave has 2 d.f.

Average thermal energy = $2 \cdot \left(\frac{1}{2}kT\right) = kT$

Ultraviolet Catastrophe → too much radiation is predicted at short λ ...

Solution comes from QM → energy is quantized.

$$E_n = 0, \hbar\nu, 2\hbar\nu, 3\hbar\nu, \dots$$

$$\text{Then } Z = \sum_n e^{-E_n/kT} = 1 + e^{-\hbar\nu/kT} + (e^{-\hbar\nu/kT})^2 + \dots$$

$$= \frac{1}{1 - e^{-\hbar\nu/kT}}$$

$$\text{Q: } Z = \frac{1}{1 - e^{-\hbar\nu/kT}} = \frac{e^{\hbar\nu/kT}}{e^{\hbar\nu/kT} - 1}$$

L:

$$E = -\frac{1}{z} \frac{\partial z}{\partial \beta} = \frac{\hbar\nu}{e^{\hbar\nu/kT} - 1}$$

Energy comes in units of $\hbar\nu = \hbar\omega$.

Then average # of units = $\frac{\text{Avg. Energy}}{\hbar\nu}$

$$\text{So } \bar{n}_{PL} = \frac{E}{\hbar\nu} = \frac{1}{e^{\frac{h\nu/kT}{1}} - 1}$$

Planck's distribution --

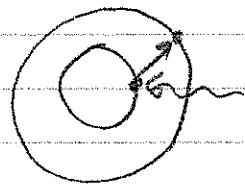
Planck Note Not the same as Bose-Einstein dist where

$$(\bar{n}_{BE} = \frac{1}{e^{\frac{(E-\nu)/kT}{1}} - 1})$$

So $\mu = 0$ for photons

γ not unpaired

photons created & destroyed all the time



$$\mu_e^- + \mu_\gamma = \mu_{e^-} \xrightarrow{y} \mu_\gamma = 0$$

May 7, 2019

→ [Blackbody Radiation]



→ what is the total energy inside the box

Reminder Planck's distribution gives the average "occupancy" of an energy mode

$$\bar{n}_{PL} = \frac{1}{e^{\frac{h\nu/kT}{1}} - 1}$$

Allowed wfn → $\lambda = \frac{2L}{n}$, $\rho = \frac{\hbar}{2L} \rightarrow$ allowed energies?

Allowed energies $\rightarrow E = pc$, not $p^2/c^2 \Rightarrow [E_n = \frac{hc n}{2L}]$

$$\text{In 3D, } E = cp = c/\sqrt{p_x^2 + p_y^2 + p_z^2}$$

$$= \frac{hc}{2L} \sqrt{n_x^2 + n_y^2 + n_z^2}$$

Average energy per mode, \bar{n}_{PC}

$$= E \cdot (\text{frequency of mode}) =$$

Planck's distribution, \bar{n}_{PC}

So,

$$\text{total energy} \rightarrow \left[U = 2 \sum_{n_x} 2 \sum_{n_y} 2 \sum_{n_z} E_{\text{mode}} \cdot \bar{n}_{PC}(E) \right]$$

2 independent

polarization states for photons.

So,

$$U = \sum_{n_x, n_y, n_z} \frac{hc n}{L} \cdot \frac{1}{e^{hc n / 2kT} - 1}$$

Convert this to an integral in spherical coordinates.

$$U = \int_0^\infty n^2 \frac{hc n}{L} \frac{1}{e^{hc n / 2kT} - 1} dn \int_0^{\pi/2} d\phi \int_0^{\pi/2} \sin\theta d\theta$$

$$= \left(\frac{\pi}{2}\right) \cdot [\text{change of variables}] \quad \varepsilon = \frac{hc n}{2kT} \Rightarrow n^2 = \frac{4\varepsilon^2 L^2}{h^2 c^2}$$

$$dE = \frac{hc}{2c} dn$$

$$= \frac{\pi}{2} \int_0^\infty \frac{4\varepsilon^2 L^2 \cdot 2\left(\frac{\varepsilon}{2}\right)}{h^2 c^2} \cdot \frac{1}{e^{\varepsilon / kT} - 1} \left(\frac{2L}{hc}\right) dE$$

$$\text{So, } U = \frac{8\pi L^3}{(hc)^3} \int_0^\infty \frac{\epsilon^3}{e^{\epsilon/kT} - 1} d\epsilon \quad \text{Call } L^3 = V$$

then

$$\frac{U}{V} = \int_0^\infty \frac{8\pi}{(hc)^3} \frac{\epsilon^3}{e^{\epsilon/kT} - 1} d\epsilon$$

\rightarrow total energy density
(per unit volume)

\leftarrow energy density per unit photon energy.

\hookrightarrow spectrum of photons \rightarrow called $u(\epsilon)$

Spectrum

$$u(\epsilon) = \frac{8\pi}{(hc)^3} \frac{\epsilon^3}{e^{\epsilon/kT} - 1}$$

\rightarrow PLANCK'S SPECTRUM

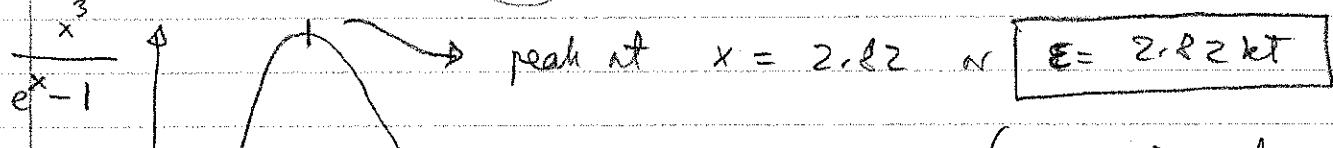
(cancel when convert to $d\sigma$
since $dE \propto d\sigma \dots$)

Next, evaluate the integral..

$$x = \epsilon/kT, \Rightarrow dx = \frac{1}{kT} d\epsilon$$

peak energy of
spectrum of γ

$$\frac{U}{V} = \frac{8\pi}{(hc)^3} \cdot (kT)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx$$



(one version of
Wien's law)

$$\lambda = 3.9 \times 10^{-3} [\text{mK}] / [\text{T}(\text{K})]$$

$$x = \epsilon/kT$$

Q $\int_{0}^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$ (Appendix B)

S $\frac{U}{V} = \frac{8\pi^5 (hc)^4}{15 (hc)^3}$

→ electromagnetic energy density

Energy of Photon gas

Q First calculate heat capacity, C_V

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 4aT^3 \text{ where } a = \frac{8\pi^5 k^4 v}{15 (hc)^3}$$

Q Entropy

$$S = \int_0^T \frac{C_V}{T'} dT' = \int_0^T 4a \frac{(T')^3}{T'} dT' = \int_0^T (4aT')^2 dT' = \frac{4}{3} a T^3$$

S $S = \frac{32\pi^5}{45} V \left(\frac{hc}{kT} \right)^3$

→ entropy of photon gas...

Q Pressure of a photon gas:

$$dU = TdS - PdV + \mu dN$$

$$\Rightarrow P = - \left(\frac{\partial U}{\partial V} \right)_{S, N} \rightarrow \text{med } U = U(V, S) \quad \text{if } S \text{ constant, } N = \text{constant ...}$$

$$\frac{U}{V} = \frac{8\pi^5}{15 (hc)^3} (hc)^4 \approx S = \frac{32\pi^5}{45} \left(\frac{hc}{kT} \right)^3 k \cdot V$$

S want to eliminate temperature ...

Q Let $\alpha = \frac{8\pi^5 k^4}{15(hc)^2}$, then $U = \alpha V \cdot T^4$, $S = \frac{4}{3} \alpha V T^3$

\Rightarrow Solve for temperature... $T = \left(\frac{3S}{4}\right)^{1/3} \cdot (\alpha V)^{-1/3}$

S $U = (\alpha V) \left(\frac{3S}{4}\right)^{4/3} \cdot (\alpha V)^{-4/3}$

$U = \left(\frac{3S}{4}\right)^{4/3} (\alpha V)^{-1/3}$

P, $P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = -\frac{\partial}{\partial V} \left[\left(\frac{3S}{4}\right)^{4/3} (\alpha V)^{-1/3} \right]_{S,N}$

$$= \left(\frac{3S}{4}\right)^{4/3} \cdot \frac{1}{3} \alpha^{-1/3} V^{-4/3}$$

$$= \frac{1}{3} \left(\frac{3}{4} \left[\frac{4}{3} \alpha V T^3 \right] \right)^{4/3} \alpha^{-1/3} V^{-4/3}$$

D $P = \frac{1}{3} \alpha T^4$

or In terms of U/V ... $\Rightarrow P = \frac{1}{3} \frac{U}{V}$

Compare this pressure of Ideal gas ...

Maintaining

$$PV = NkT \Rightarrow U = \frac{f}{2} NkT = \frac{3}{2} NkT$$

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

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

Ex

CMB - Cosmic Microwave Background radiation..

$$T = 2.73 \text{ K} . \quad \text{Peak } \lambda = \frac{2.93 \times 10^{-3}}{2.73} \approx 1 \text{ mm}$$

Total energy density in CMB ..

$$\frac{U}{V} = \frac{8\pi^5 (h\nu)^3}{15(hc)^2} = [0.26 \text{ MeV/m}^3]$$

Ordinary matter $1 \text{ proton/m}^3 \rightarrow [1 \text{ GeV/m}^3]$

→ photon density energy per unit...

$$\text{Energy of CMB} \Rightarrow S = \frac{22\pi^5}{45} V \cdot (h\nu)^2 \cdot k \approx$$

$$\Rightarrow \frac{S}{V} \approx 2.89 \times 10^9 \text{ K} \quad \text{much higher}$$

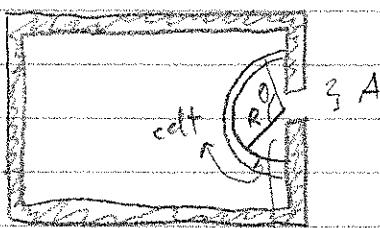
ordinary matter $S/V \sim Nk \sim k$

May 8, 2019

Radiation emitted by a Blackbody

Spectrum of the emitted radiation \approx the Planck spectrum.

How much energy escape from hole?



Volume of chunk of radiation that could escape

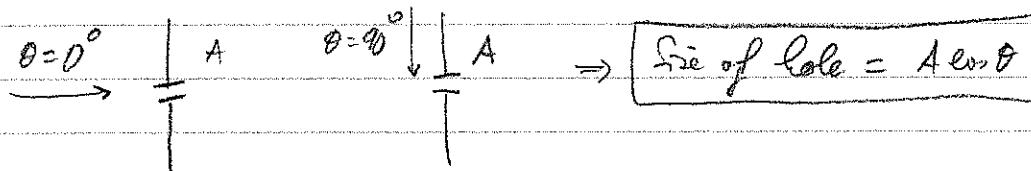
$$= (Rd\theta)(R\sin\theta d\phi)(cdt)$$

3D - chunk
of radiation

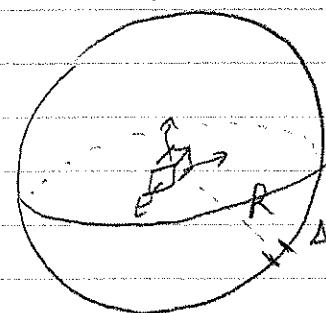
$$\text{Energy density} = \frac{U}{V} = \frac{8\pi^5 (h\nu)^4}{15 (hc)^3}$$

$$\text{Total energy} = \frac{8\pi^5 (c\tau)^4}{15 (hc)^3} R^2 c \sin \theta d\theta d\phi dt$$

Project hole size depend on angle of photon wrt hole ...



Now



$$\left. \begin{array}{l} \text{probability of photon } \\ \text{existing hole} \end{array} \right\} \Rightarrow \frac{A \cos \theta}{4\pi R^2} = \frac{\text{hole size}}{\text{tow area}}$$

Energy that escapes hole

$$U = \frac{U}{V} \times R^2 c \sin \theta d\theta d\phi dt \cdot \frac{A \cos \theta}{4\pi R^2}$$

$$\begin{aligned} U_{\text{tot}} &= \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \sin \theta \cos \theta \cdot \left(\frac{A}{4\pi}\right) \cdot c \left(\frac{U}{V}\right) dt \\ &= 2\pi \cdot \frac{A}{4\pi} \frac{U}{V} dt \int_0^{\pi/2} \cos \theta \sin \theta d\theta \\ &\quad \underbrace{\qquad\qquad\qquad}_{1/2} \end{aligned}$$

$$U_{\text{tot}} = \frac{A}{4} \left(\frac{U}{V}\right) dt$$

\Rightarrow "luminosity"

Energy per unit time gives power

$$P = \frac{U_{\text{tot}}}{dt} \rightarrow \text{Flux} = \frac{\text{Power}}{\text{Area}} = \frac{UC}{4V}$$

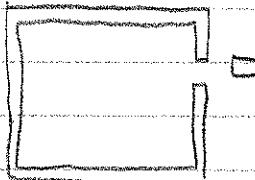
$$\text{Flux} = \frac{c}{4} \left(\frac{u}{v} \right) = \frac{c}{4} \left(\frac{2\pi^5}{15} \right) \frac{(kT)^4}{(\hbar c)^3} = \frac{2\pi^5}{15} \frac{(kT)^4}{h^3 c^2} = \sigma T^4$$

$$\sigma = \frac{2\pi^5 h^4}{15 k^3 c^2} = 5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4$$

Stefan-Boltzmann Constant

{ Stefan-Boltzmann
Law }

Why is this blackbody radiation?



What if our object is not black?

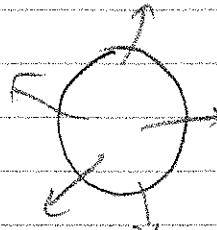
Some λ are reflected rather than absorbedDefine Emissivity, ϵ ϵ = amount of radiation absorbedIf $\epsilon = 1 \rightarrow$ blackbodyIf $\epsilon = 0 \rightarrow$ perfect reflectorNote ϵ is λ -dependent.

$$\text{Power} = \frac{\text{Flux}}{\text{Area}} = \epsilon \sigma T^4$$

$$\text{Power} = \epsilon \sigma A T^4 \rightarrow \text{luminosity}$$

Example Sun assume $\epsilon = 1$

$$\text{Solar luminosity} = \frac{\text{Power}}{4} \Rightarrow L_0 = 3.2 \times 10^{26} \text{ W}$$



$$A = 4\pi R_\odot^2, \quad F_{\text{at surface}} = \frac{L}{A} = \frac{L}{4\pi R_\odot^2} \propto F_\odot = e \sigma T^4$$

$$\text{So } T = \sqrt[4]{\frac{L}{4\pi R_\odot^2 e \sigma}} = \sqrt[4]{\frac{L}{4\pi R_\odot^2 \sigma}} \approx 5800 \text{ K}$$

◻ Can do we Wien's law

$$\lambda_{\text{peak}} = \frac{2.9 \times 10^{-3}}{T} \rightarrow \text{set } T \rightarrow \text{set } R \dots$$

◻ Can do the same thing for the Earth...