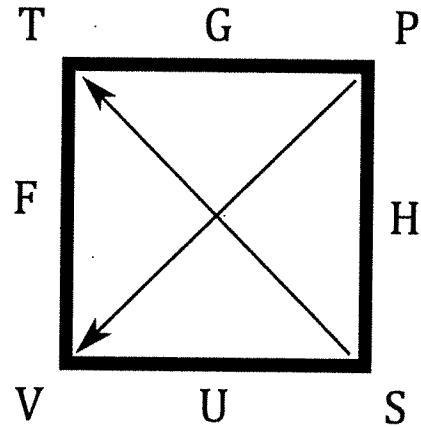


Review of the Thermodynamic Square



Mnemonic: "Good Physicists Have Studied Under Very Fine Teachers"

To get the thermodynamic identities, pick a thermodynamic potential (U , H , F , G). The side of the box that it appears on tells you what it is a function of. For example, $F = F(T, V)$. If you want to know how F changes when you vary either T , or V , the proportionality constants are given by looking at the variables diagonally opposite T and V . The sign of the differentials is given by noticing which way the arrows are pointing. If the arrowhead points towards the differential, it is negative. If the tail of the arrow is located at the differential, then it is positive. For example, $dF = -SdT - PdV$. Finally, you must add a factor μdN to all identities.

Thermodynamic Identities

$$dU = TdS - PdV + \mu dN$$

$$dH = VdP + TdS + \mu dN$$

$$dF = -SdT - PdV + \mu dN$$

$$dG = VdP - SdT + \mu dN$$

Partial Derivative relations

Energy:

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

Enthalpy:

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

Helmholtz Free Energy:

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

Gibbs Free Energy:

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

Maxwell relations

From setting $\left(\frac{\partial^2 U}{\partial S \partial V}\right) = \left(\frac{\partial^2 U}{\partial V \partial S}\right)$:

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

From setting $\left(\frac{\partial^2 H}{\partial S \partial P}\right) = \left(\frac{\partial^2 H}{\partial P \partial S}\right)$:

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

From setting $\left(\frac{\partial^2 F}{\partial T \partial V}\right) = \left(\frac{\partial^2 F}{\partial V \partial T}\right)$:

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

From setting $\left(\frac{\partial^2 G}{\partial T \partial P}\right) = \left(\frac{\partial^2 G}{\partial P \partial T}\right)$:

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

Thermodynamics Cheat Sheet

Various numerical values:

$$k = 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}} \quad \text{Boltzmann's constant}$$

$$N_A = 6.02 \times 10^{23} \frac{\text{particles}}{\text{mole}} \quad \text{Avagadro's number}$$

$$M = mN_A \quad M = \text{Molar mass}$$

$$R = N_A k = 8.31 \frac{\text{J}}{\text{mole K}} \quad \text{gas constant}$$

$$1 \text{ cal} = 4.187 \text{ J} \quad 1 \text{ erg} = 10^{-7} \text{ J}$$

$$1 \text{ liter} = 10^{-3} \text{ m}^3 \quad 1 \text{ Pa} = 1 \frac{\text{N}}{\text{m}^2}$$

$$1 \text{ atm} = 1.01 \times 10^5 \text{ Pa} = 76.0 \text{ cm-Hg}$$

$$c_P = 4186 \frac{\text{J}}{\text{kg-K}} \Rightarrow \text{for water (per kg)}$$

$$L = 3.33 \times 10^5 \frac{\text{J}}{\text{kg}} \Rightarrow \text{H}_2\text{O latent heat of fusion (melt ice at } T = 0^\circ \text{C)}$$

$$L = 2.26 \times 10^6 \frac{\text{J}}{\text{kg}} \Rightarrow \text{H}_2\text{O latent heat of vaporization (boil water at } T = 100^\circ \text{C)}$$

Temperature:

$$T(\text{ }^\circ\text{C}) = T(\text{K}) - 273.15$$

$$0^\circ \text{C} = 273.15 \text{ K} \Rightarrow \text{ice point H}_2\text{O (freezing at 1 atm)}$$

$$T_{\text{triple pt}} = 273.16 \text{ K} \Rightarrow \text{triple point H}_2\text{O (at P = .006 atm)}$$

Ideal gases:

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

$$U = U(T) \Rightarrow \text{only T dependence}$$

$$c_V = c_V(T) \Rightarrow \text{only T dependence (or constant)}$$

$$c_P = c_V + R$$

$$PV^\gamma = \text{const} \Rightarrow \text{adiabatic expansion} \quad \gamma = \frac{c_P}{c_V}$$

Monatomic Ideal gases:

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

$$c_P = \frac{5}{2} R \quad c_V = \frac{3}{2} R \quad \gamma = \frac{c_P}{c_V} = \frac{5}{3}$$



THERMODYNAMICS

PH332

(1)

STATISTICAL MECHANICS

Feb 6, 2019

Thermodynamics

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

Stat mech

- individual states of atoms / microscopic states of particles in system & ways statistics to describe macroscopic behavior.

This course focuses on systems of large numbers of particles.
 ? \rightarrow 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.

3GHz $\rightarrow 3 \times 10^9 \text{ s}^{-1}$ count rate $\Rightarrow 2 \times 10^{14} \text{ s} = 6.4 \times 10^7 \text{ yrs.}$
 \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.

$$\text{Ex } M_{^{12}\text{C}} = 12 \text{ g/mol} \quad M_{\text{H}_2\text{O}} = 18 \text{ g/mol}$$

$$M_{^4\text{He}} = 4 \text{ g/mol}$$

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

 0°C 100°C

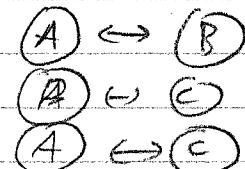
$$^\circ\text{F} = 32 + \frac{9}{5}^\circ\text{C}$$

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

What is temperature?

0th law of thermodynamics

If A is in thermoequilibrium with B
 but C is in thermoequilibrium with C
 then $T_A = T_C$
 "thermoequilibrium" \equiv same T.



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

Feb 8, 2019

Ideal Gas Law

$$PV = nRT$$

vs

$$PV = NkT$$

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

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

$$\therefore nR = Nk_B$$

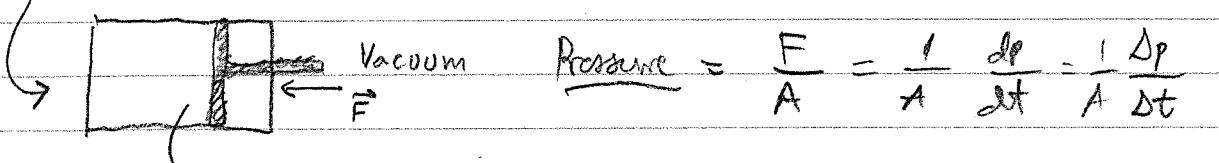
Note $N = nN_A \therefore$

$$R = N_A k_B$$

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

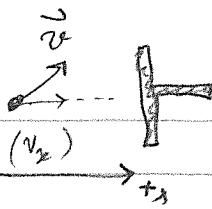
Assumptions: point-like particles, don't interact

How does temperature T of ideal gas relate to its kF?



* assume perfectly elastic collisions

(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

$$\rightarrow \text{density} = \frac{N}{V}$$

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

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

(3) Force on piston

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

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

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

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

$\rightarrow PV = m \langle v_x^2 \rangle N$

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

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

(4)

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

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

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

Average speed of the particles?

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

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

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

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

$\langle v \rangle$

But this is Not

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

We will (can) show that

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

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

v_{rms}

Ex Find rms v of N_2 molecule at room temp. $\sim 300\text{K}$

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

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

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

(5)

or internal

What's the total thermal energy of a gas?

$$U = \frac{3}{2} kT \cdot N = \langle KE \rangle N$$

→ but only true for
monatomic ideal gas

↳ like noble gas.

Why? Degrees of freedom



If translational motion is not the only contributing factor

↳ [Equipartition theorem]

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

So

$$U_{\text{thermal}} = Nf \frac{1}{2} kT$$

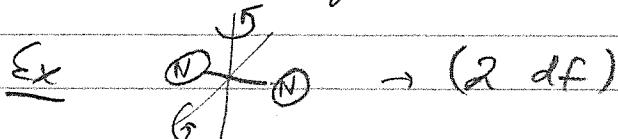
f = # of quadratic df.

Degrees of freedom

↗ for a gas

↳ translational : x, y, z (3 df)

• Rotational : how many axes of rotation introduce asymmetries?





• vibrational $\text{O=O} \rightarrow$ classical mech tells us this

$\langle \text{KE} \rangle = \langle \text{PE} \rangle$ 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.

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

Feb 11, 2019

Heat = Work \rightarrow Exchange is energy

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

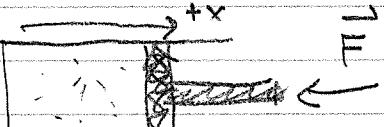
$\left. \begin{array}{l} \text{Heat (Q)} \rightarrow \text{spontaneous flow of} \\ \text{energy from one system to} \\ \text{another due to a } \Delta T \end{array} \right\}$

↳ if $\Delta T \neq 0$, then $Q \neq 0$ (Heat) Spontaneously

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

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

Compression work

A {  F $P = \frac{F}{A}$ positive, since $\Delta x < 0$ }

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

So $\boxed{W_{\text{gross}} = -P\Delta V}$

- ◻ Note Shouldn't use differentials, but they are not exact diff. because of path-dependence

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

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 $\vec{v} = \vec{\nabla}f$

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

- ◻ In other words, $df = Adx + Bdy$ exact diff. if $\begin{cases} B = \frac{\partial f}{\partial y} \\ A = \frac{\partial f}{\partial x} \end{cases}$

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

- ◻ Can we 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

- ◻ Incorrect differentials are written as →

$$\boxed{dW \text{ or } dQ}$$

↳ path-dependence!

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

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

$$\left\{ \frac{dQ}{T} = dS \rightarrow \text{entropy} \quad dS \rightarrow \text{exact diff} \right.$$

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

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

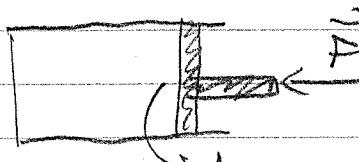
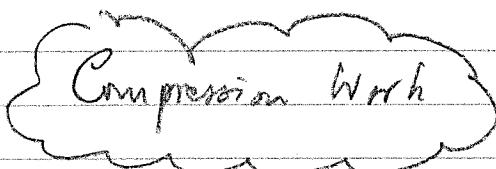
Q : heat added to system, W : work done on system

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

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

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

$1 \text{ cal} \rightarrow$ # heat needed to raise 1g of H_2O by 1C or 1K



$$W_{on} = -F\Delta x \stackrel{?}{=} -PAV$$

(let $P \rightarrow P(V)$)

$\curvearrowleft \Delta x$

Before, 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

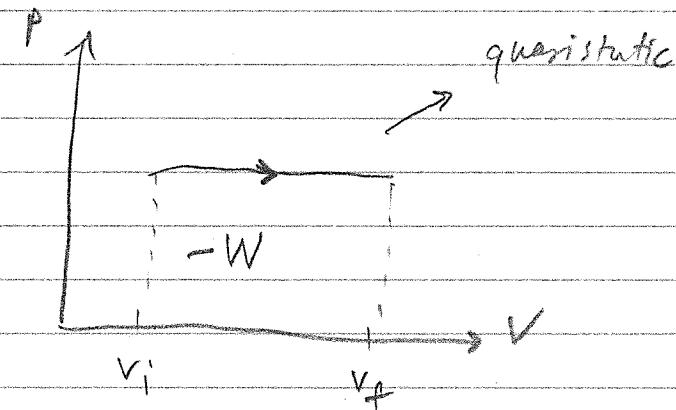
$$\hookrightarrow W_m = -P\Delta V \quad \text{or} \quad dW_m = PdV$$

Note there is heat flow in quasi-static process

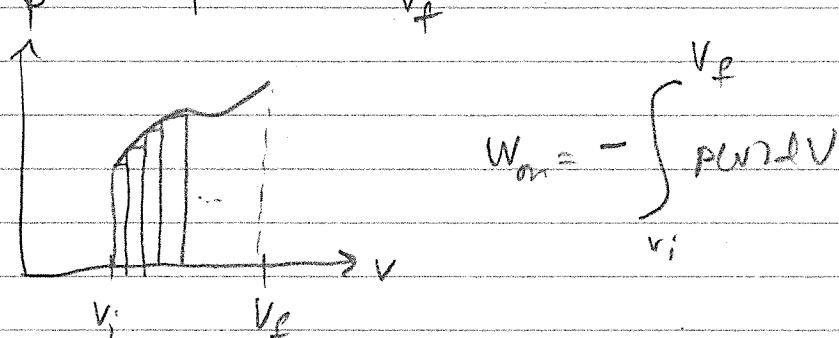
We often consider infinitesimal changes that are each quasi-static
→ then integrate

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

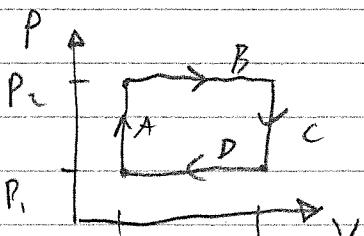
B P-V diagrams



Non quasi-static



Example of PV diagram Interpreting PV diagrams



An ideal diatomic gas (N_e)

For steps A → D, we want + determine
 W_m , Q_{add} , ΔU , and W_{total} , Q_{tot}

(10)

	A	B	C	D	Σ
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	$\frac{1}{2} V_1 (P_2 - P_1)$	$\frac{1}{2} P_2 (V_2 - V_1)$:	:	0

A: $W = 0, \Delta U = \frac{f}{2} N k T = \frac{f}{2} N h \frac{PV}{N k E} = \frac{f}{2} PV$

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

$\Delta U = Q + W$

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

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

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

Feb 12, 2019

Quasistatic review "slow" \rightarrow so that system can equilibrate
 \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 \rightarrow "slow" compression such that $T = \text{constant}$

Temp doesn't increase

$\Delta U = W_m + Q_{add}$

$\rightarrow Q$ leaves system $\rightarrow \Delta U = 0$

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Adiabatic compression → "fast" compression. So fast that no heat can escape

$$Q = 0 \quad \text{so} \quad \Delta U = W_{\text{in}} + Q_{\text{add}} = W_{\text{in}}$$

→ Temp increases

P-V diagram



Isothermal process → Quasistatic

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

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

$$W_{\text{in}} = - NkT \ln \left(\frac{V_f}{V_i} \right)$$

↑ work done on system
in isothermal
compression.

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

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

$\downarrow \quad \Delta T$

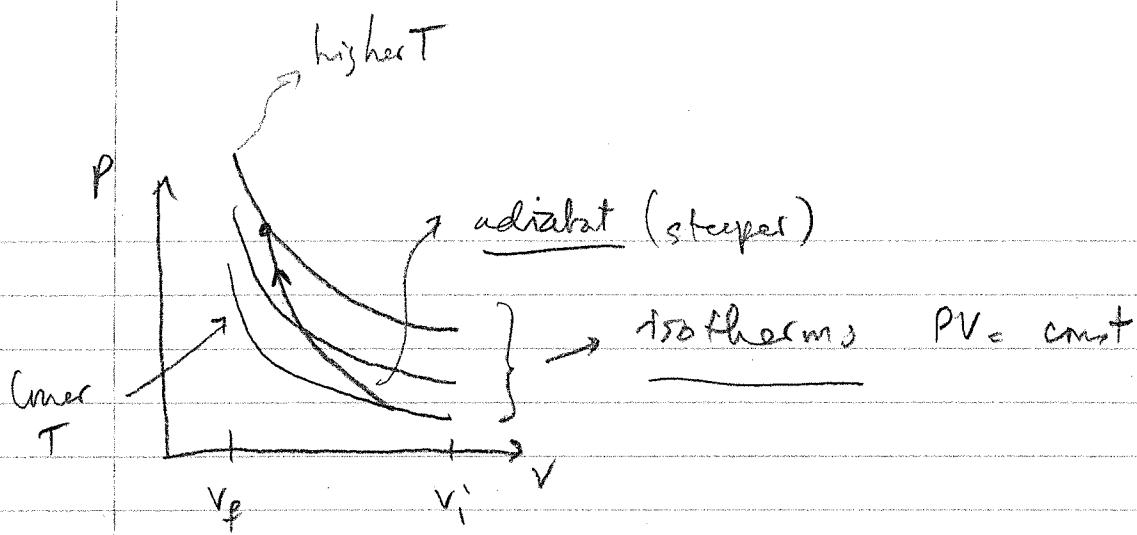
$$\therefore Q_{\text{add}} = - W_{\text{in}} = NkT \ln \left(\frac{V_f}{V_i} \right)$$

Adiabatic process → fast

Assume quasistatic process... $\Delta U = W_{\text{in}} + Q_{\text{add}}$

By definition of adiabatic $\rightarrow Q = 0$

$$\} \rightarrow \Delta U = W_{\text{in}}$$



Q How do different parameters change during adiabatic compression?

↳ Ideal gas $\Delta U = W + Q = W_m$

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

$$\therefore \frac{f}{2} NkT = -\frac{NkT}{V} dV$$

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

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

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

$$\boxed{\underbrace{VT^{\frac{f}{2}}}_{\text{constant}}} \rightarrow \text{adiabatic}$$

compression / expansion
of ideal gas

Can write this in volume & pressure

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

$$\rightarrow P^{\frac{f}{2}} V^{1+\frac{f}{2}} \rightarrow \text{constant}$$

$$\rightarrow PV^{\frac{(1+f)}{f}} \rightarrow \text{constant}$$

$$\text{Call } \gamma = 1 + \frac{2}{f} = \frac{f+2}{f}$$

$$\boxed{PV^\gamma = \text{constant}}$$

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

$$\gamma = \frac{f+2}{f} \quad \left\{ \begin{array}{l} PV^\gamma = \text{constant} \\ VT^{1/\gamma-1} = \text{constant} \end{array} \right\}$$

Now, pressure \approx temp.

$$\left(\rightarrow V^\gamma P = \text{constant} \quad \underbrace{V^{-\gamma} T^{-\gamma/(1-\gamma)} = \text{constant}} \right)$$

$$\underline{\text{so}} \quad (\gamma^\gamma P)(V^{-\gamma} T^{-\gamma/(1-\gamma)})$$

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

$$\underline{\text{so}} \quad \boxed{P^{\gamma/(1-\gamma)} T^\gamma \text{ constant}}$$

Ex Diesel engine (no spark plugs...)

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

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

$$\underline{\text{Ok}} \quad VT^{\gamma/(1-\gamma)} = \text{constant}$$

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

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

$$\underline{\text{so}} \quad \boxed{T_f \approx 1000k > 700^\circ C}$$

\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 → $Q = \Delta U - W_{\text{int}}$. limiting case $\rightarrow W=0$
 → 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 $C_V = 1 \text{ cal/K}$

Feb 13, 2019

Heat Capacity

$$\rightarrow W=0, \Delta V=0 \rightarrow C_V = \frac{\Delta U - W}{\Delta T} = \left(\frac{\partial U}{\partial T} \right)_{V \text{ const}}$$

limiting cases { Constant volume
Constant pressure }



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

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

(energy loss at
work due to

Suppose we have a system that obeys equipartition theorem

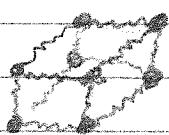
$$U = \frac{f}{2} N k T$$

Then

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

if we can measure C_V
then we can find f .

Ex

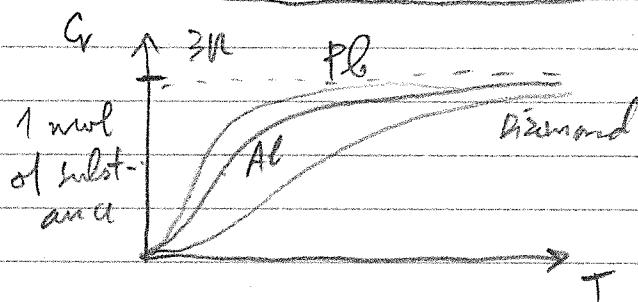


Consider solids / crystal
no rotation / translation

→ only f is rotation.

→ Solid should have 6 d.f.s

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



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.

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

$$\text{Recall } \gamma = \frac{C_P}{C_V} = 1 + \frac{2}{f}$$

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

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

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

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

Recall the Adiabatic exponent γ

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

Example of heat capacity

Heat capacity of a star

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

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

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

Star $\left\{ \begin{array}{l} \text{It goes } (3 \text{ df}) \\ \text{obeys eq. part. then } k = \frac{1}{2}mv^2 = \frac{f}{2}NkT = \frac{3}{2}NkT \end{array} \right.$ quadratic

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

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

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

Latent heat → useful for phase transitions.

e.g. melting ice Solid → liquid → Vapor

Now temperature stays constant during phase transitions.

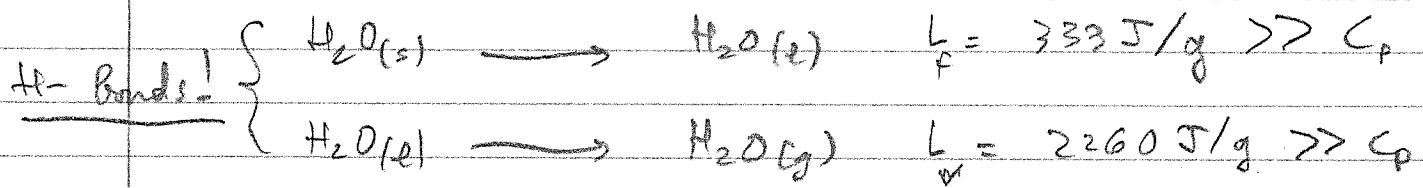
↳ need to know how much heat is needed to complete phase transitions.

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

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

- Assume that no other work besides expansion/compression

Ex latent heat of fusion

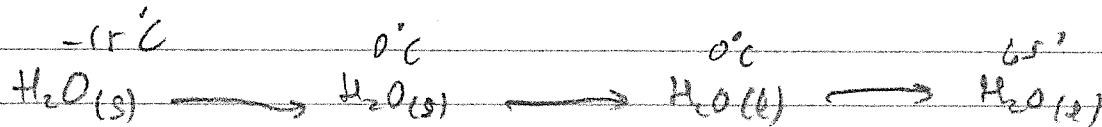


Ex 200g cup of tea that is @ boiling pt (212°F
 100°C)

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

$$T_{\text{ice}} = -15^\circ\text{C} \quad C_{\text{ice}} = 0.5 \text{ cal/g°C} \\ C_{\text{H}_2\text{O}(l)} = 1 \text{ cal/g°C} \quad L_f = 80 \text{ cal/g}$$

$$\text{Q(frost tea)} = m_{\text{tea}} \Delta T C_{\text{H}_2\text{O}} = 200 (100 - 15) 1 \text{ cal} \\ = 7000 \text{ cal}$$



$$\frac{7000}{\text{cal}} = m C_i \Delta T + L \cdot m + m C DT$$

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

Feb 15, 2019

Enthalpy

→ total heat content of a system

$$H = U + PV$$

→ 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:

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

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

So

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

→ @ constant pressure.

First law

$$\text{if } \Delta U = Q + (-P\Delta V)$$

→ compression work

$\rightarrow +W_{\text{other}}$

Then

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

So

$$\Delta H = Q_{\text{add}} + W_{\text{other}}$$

→ true for constant P processes.

Heat capacity at constant pressure

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

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

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

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

↳ Latent heat of vaporization

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

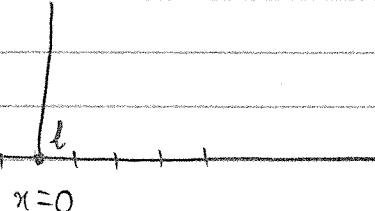
$$V_i \approx 0 \quad V_f \approx \frac{nRT}{P} = \frac{RT}{P} \quad (n=1)$$

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

$$\approx 3100 \text{ J}$$

Statistics

Random Walk problem



$$\underline{1} \quad P(\text{left}) = P(\text{right}) = 1-p = q$$

$$\underline{2} \quad P(\text{right}) = p$$

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

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

Let $n_R = \# \text{ steps to R}$ } $N = n_R + n_L$
 $n_L = \# \text{ steps to L}$ }

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

Probability of any sequence of steps (ass. independence) 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 $n_R < N$

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

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.

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

\rightarrow For indistinguishable objects, use combinations... Total multiplicity of outcomes

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

(21)

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

or other notation

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

\hookrightarrow Binomial distribution

$$\textcircled{B} \quad \sum_{n=0}^N W_N(n) = 1 \quad \textcircled{E} \quad E(n_R) = Np \quad \textcircled{D} \quad \text{Var} = Np(1-p)$$

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 15, 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, least likely outcome.

Random Walk

$$x = nl$$

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

(a) If N is even?

(b) If N is odd?

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

$$N = n_R + n_L$$

$$m = n_R - n_L$$

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

$$\text{So } N = 2n_L - m$$

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

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

So

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

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

If N is odd, then $m \neq 0$ Since $N = 2n_L - m$

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

↑
odd even odd

Determination of mean values

Random walk with $N = 2$ steps. Let's say after 2 steps, drunk finds \$ and picks it up.

- (1) $x = -2l \quad \$1$
- (2) $x = 0 \quad \$5$
- (3) $x = 2l \quad \$20$

Question: on average, how much \$ would you pick up?

Well $P_1(-2l) = ?$, $P_2(2l) = ?$; $P_2(0) = ?$

$$\rightarrow \left\{ \begin{array}{l} P_2(0) = 1/2 \\ P_2(-2l) = P_2(2l) = 1/4 \end{array} \right. \quad \left. \right\} \text{"by inspection"}$$

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

In general, $\langle x \rangle = E(x) = \sum_{x_i=0}^{\infty} x_i P_N(x_i)$

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, ... $\sum_i P(x_i) = 1$

↳ Mean value of f_n .

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

Note $E[f(u) + g(u)] = E(f(u)) + E(g(u))$

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



Ex: an average, $E(f) = \frac{1}{4} \cdot 1 + \frac{1}{2} \cdot 5 + \frac{1}{2} \cdot 20$

$$= \frac{1}{4} + \frac{5}{2} + 10$$

$$= \$ \frac{50}{4} (10 + \frac{11}{4})$$

On average, how far from average are we?

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

What about $\mathbb{E}(f(u) - E(u))^2$?

(Second moment about the mean) \rightarrow Variance

$$\overline{u^2} = \sigma^2 = E[(u - E(u))^2]$$

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

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

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

Mean values - Random Walk problem

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2019

Recall

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

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

↳

After n_R steps to the right

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

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

∴

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

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

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

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

But $p+q=1$

∴

$$\boxed{\mathbb{E}[n_R] = pN}$$

Similarly

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

$$\left. \begin{aligned} \mathbb{E}[m] &= \mathbb{E}[n_R - n_L] \\ &= \mathbb{E}[n_R] - \mathbb{E}[n_L] \\ &= N(p-q) \end{aligned} \right\}$$

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

→ If $p=q$, then $E(n) = 0$.

Variance

$$\xrightarrow{\quad} \xrightarrow{\quad} (pn)^2$$

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

$$E(n_p^2) = \sum_{n_p=0}^N n_p^2 p(n_p)$$

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

$$\rightarrow \text{Same trick as before} \dots n_p^2 p^{n_p} = n_p p \frac{\partial}{\partial p} p^{n_p} = p \frac{\partial}{\partial p} (n_p p^{n_p})$$

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

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

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

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

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

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

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

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

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

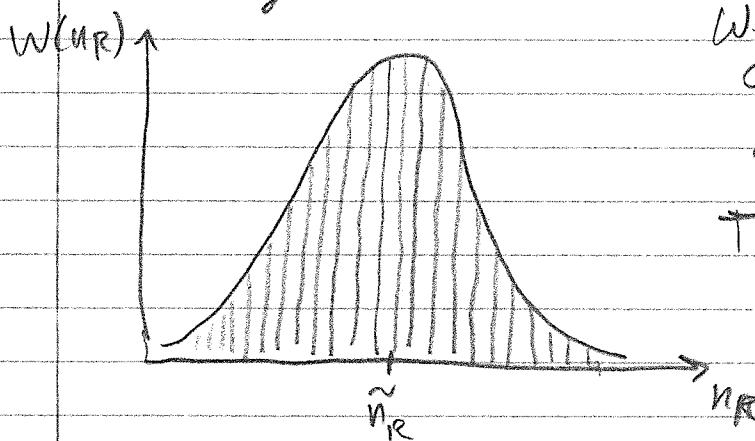
Relative Width of a distribution

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

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

\Rightarrow 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 $W_{nR}(n_R)$ at $n_R = \tilde{n}_R$, where \tilde{n}_R is the most likely value.



We can treat this as a continuous function as $N \cdot n_R$ 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

$$\frac{dW_{nr}}{dn_r} = 0 = \frac{d\ln(W(n_r))}{dn_r}$$

B Taylor series expansion around \tilde{n}

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

\hookrightarrow We want to expand $\ln(W(n_r))$ around \tilde{n}_r .

$$n_r = \tilde{n}_r + \varepsilon \quad (\varepsilon \ll \tilde{n}_r) \quad (\text{let's work with } n \neq n_r)$$

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

0 since \tilde{n} most likely ...

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

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

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

$$= \frac{d}{dn} \left[\ln(N!) - \ln(n!) - \ln((N-n)!) + np \ln p + (N-n) \ln q \right]$$

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

$$\text{So } \left. \frac{d}{dn} \ln(W(n)) \right|_{\tilde{n}} = -\ln \tilde{n} + \ln(N-\tilde{n}) + np - Nq$$

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

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

~~error (R) $\times (R - \tilde{n}) \times \dots \times q$~~

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

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

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

$$\begin{aligned} \frac{d^2 \ln W}{dn^2} &= \frac{d}{dn} \left(\frac{d \ln W}{dn} \right) = \frac{d}{dn} \left[-\ln \tilde{n} + \ln(N-\tilde{n}) + \ln p - \ln q \right] \\ &= -\frac{1}{\tilde{n}} - \frac{1}{N-\tilde{n}} \Big|_{\tilde{n}} = \frac{-N+n-n}{n(N-n)} \Big|_{\tilde{n}} \end{aligned}$$

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

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

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

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

Use Stirling formula

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

for $n \gg 1$

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

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

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 .

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

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,

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

probability density function - PDF

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

If probability dist. that depends on more than 1 var

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

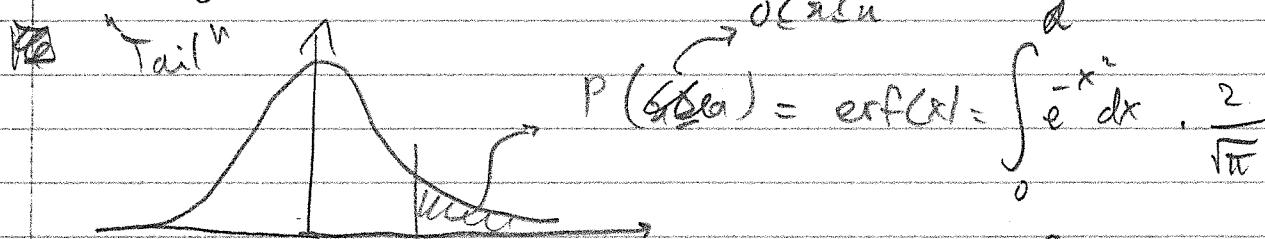
Gaussian integrals are difficult to evaluate analytically

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 $x=0$

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



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

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?

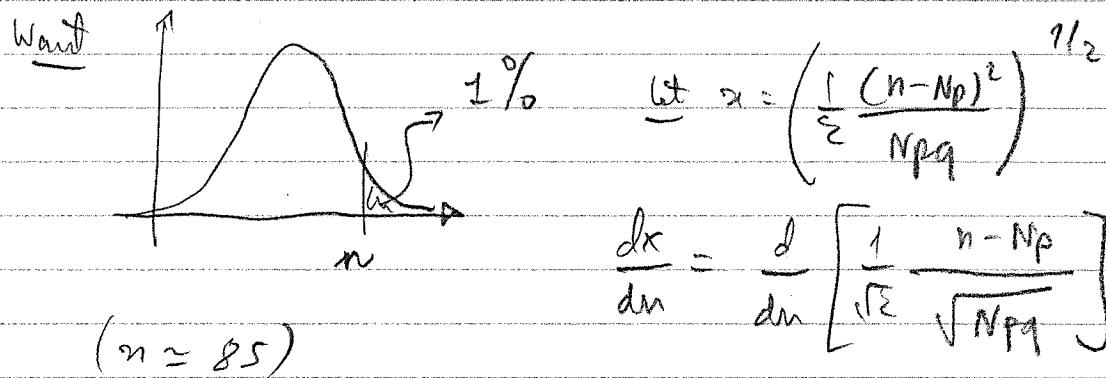
→ Assume each call is on the line for 2 mins in that hr randomly dist.

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

$$n = ?$$

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

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



$$\frac{dx}{dn} = \frac{d}{dn} \left[\frac{1}{\sqrt{2\pi}} \frac{n-Np}{\sqrt{Npq}} \right]$$

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2019

Back to Schroeder, Chap 2.

Terminology \rightarrow microstate \rightarrow any individual outcome

(state of each individual particle in the system (order matters)). $S = 1$

Macrostate \rightarrow more general description of the system \uparrow
has same multiplicity. Some microstates are multipli-

→ multiplicity Ω → the number of microstates in a macrostate

Example

4 dice rolled \Rightarrow outcome 1 3 1 5
microstate

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

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

Note that small multiplicity implies highly ordered system

or large multiplicity implies disorder.

Second Law of Thermodynamics

Systems tend towards more disorder
because multiplicity is higher

Because these macrostates are more likely... (?)

Ω is related to entropy

Two physical systems where we can't count individual microstate

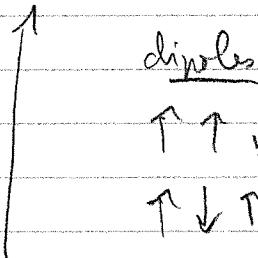
ex (1) Two-state paramagnet \rightarrow material in a B field

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

Microstate \rightarrow specified by stating direction of all
individual dipoles.

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

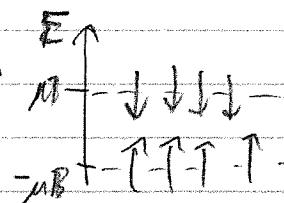
$$\vec{B} \quad N = N_p + N_\downarrow$$



Macrostate $5\downarrow + 5\uparrow$

$\mu \rightarrow$ magnetic moment of individual dipole

only 2 allowed energy levels:



Total magnetic dipole moment

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

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

$$\text{energy of single dipole} = -\vec{\mu} \cdot \vec{B} = \epsilon_i \approx \pm \mu B \text{ for } \mu \ll B$$

So energy of paramagnet is $\rightarrow \propto -2N_p + N$

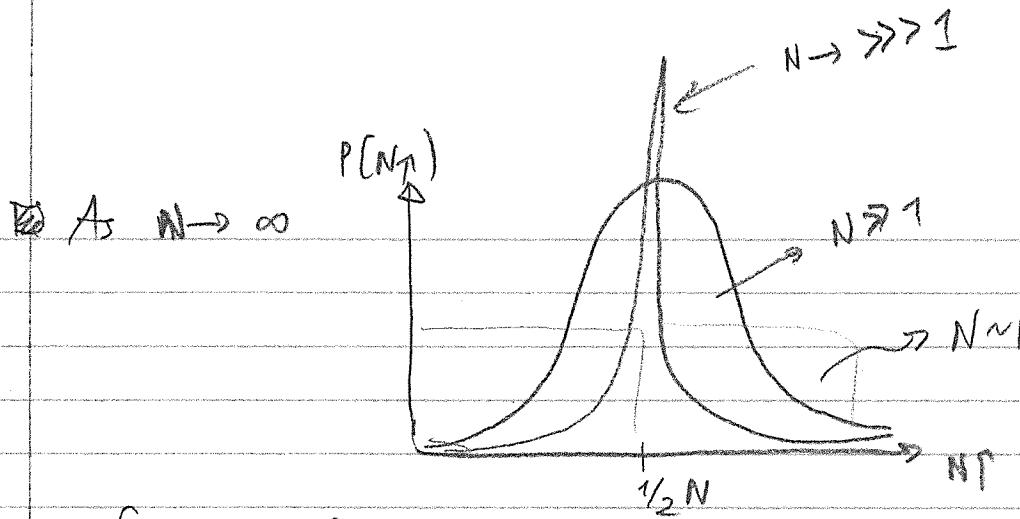
$$\boxed{U = -\vec{M} \cdot \vec{B} = \mu B (N_\downarrow - N_p)}$$

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

Calculate most probable energy

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

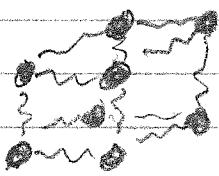
$$\boxed{P(N_p) = \binom{N}{N_p} p^{N_p} q^{N-N_p} = S(N_p) / \sum_n S(n)}$$



So, random orientation of dipoles is most probable
→ 2nd law of thermodynamics.

Here $P \propto S^2$

(2) Einstein's model of solid / bed spring model



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

Classical spring

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

$$= \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) + \frac{1}{2}k(x^2 + y^2 + z^2)$$

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

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

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

Osc	# 1	# 2	# 3	Σ	S
0	0	0	0	0	1
0	0	1	0	$h\nu$	2
1	0	0	0	$h\nu$	3
-	-	-	-	LJ	

# 1	# 2	# 3	Σv	s
2	0	0		
0	2	0	{ 2hv	6
0	0	2		
1	1	0		
1	0	1		
0	1	1		
			3hv	10
			Kokes	

→ General expression for multiplicity:

$$s = \binom{N}{q} \quad \text{Instead}$$

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

↑ ↑ ↓ ↓
states units of energy # oscillators

multiplicity of
solid

Feb 25, 2019

Heat flow & Irreversible processes

Consider 2 Einstein solids that can interact

Solid A

Solid B

single atom {

$$N_A = 3$$

$$N_B = 3$$

$$U = qhv$$

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

Multiplicity

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

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

Since A ~ B independent

For B

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

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

B

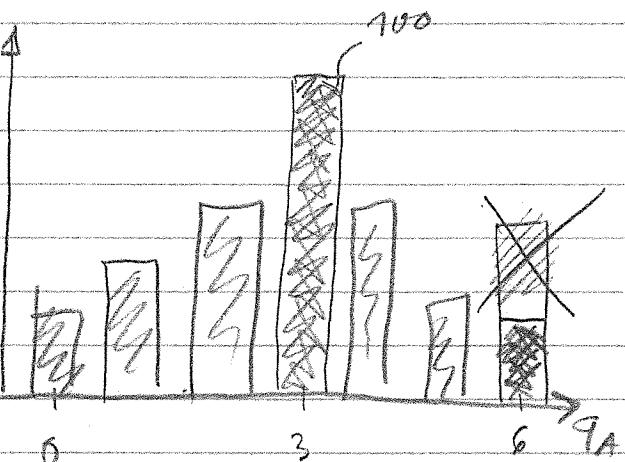
$$\Omega_{tot} = \Omega_A \Omega_B$$

$$\Omega_{tot}$$

Ex

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

$$\Omega_B (q_B = 3) = 10$$



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

$$(q_A = q_B = 3)$$

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

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

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

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 }

B If you start out with a system near most likely macrostate

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

 Ex $N_A = 50, N_B = 50, q_{tot} = 50$

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

$$q_A = q_B = 25$$

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

$$= \binom{49}{50} \binom{49}{0}$$

$$\approx 5 \times 10^{22}$$

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.

Rustek's 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 }

irreversible

not spontaneous

Large System

- (i) • Small # $\rightarrow (n < 100)$
- Large # \rightarrow Small # that we expectable 10^3

- (ii) • Very large # \rightarrow Large # that are expected or large # in statistical. :-

$\therefore 10^{23}$

Note some properties

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

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

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

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

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

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

Multiplicity of Einstein solid (large)

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

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

Take the log

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

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

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

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

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

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

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

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

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

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

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

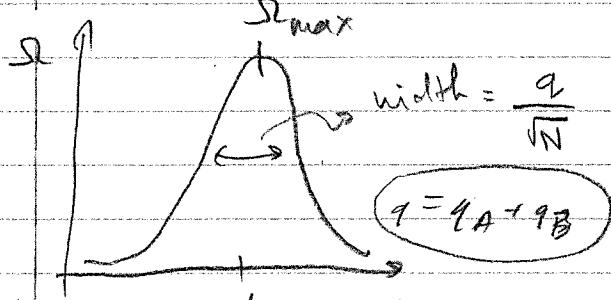
$$= \frac{e^{N \ln q - N}}{e^{N \ln N}} = \frac{e^N \cdot q^N}{N^N} = \left(\frac{eq}{N}\right)^N$$

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

Feb 26, 2019

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

For interacting solids \rightarrow $\boxed{\Omega = \Omega_{\text{max}} e^{-N(2\pi/\lambda)^2}}$ \hookrightarrow Gaussian



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

Multiplicity of an ideal gas

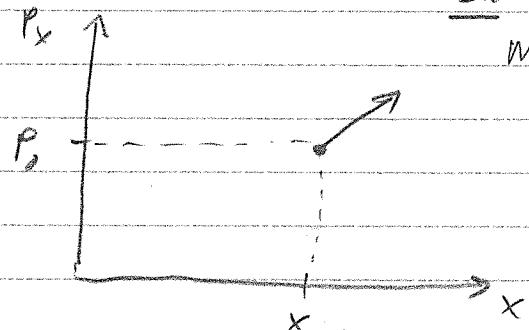
* Specify the state of a system in classical mechanics using phase space.

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

Ex

$$m\dot{x} = \vec{p} = \hat{c}\vec{x}$$

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



$$m \frac{dx}{dt} = cx \rightarrow \int_{x_0}^{x_1} m dx = \int_{t_0}^{t_1} c dt$$

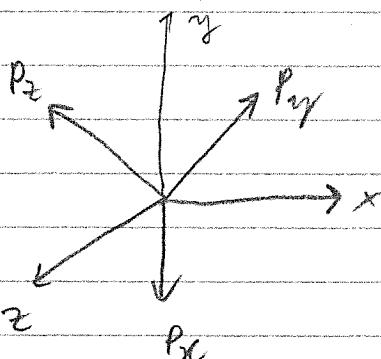
$$\text{So } \ln\left(\frac{x}{x_0}\right) = \frac{c(t-t_0)}{m}$$

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

To get $p(t)$

$$\text{So } p = m\dot{x} = m \cdot \frac{c}{m} x_0 e^{\frac{cm}{m}(t-t_0)} = c x_0 e^{\frac{cm}{m}(t-t_0)}$$

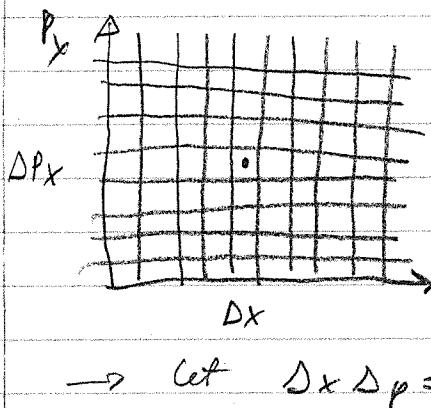
For particle in space



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

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

To describe state of system in phase space



particle located between $x_2 \dots x_2 + \Delta x$
and $p_2 = p_x + \Delta p_x$

Heisenberg Uncertainty principle

$$\Delta p \Delta x \geq \frac{\hbar}{2} (?)$$

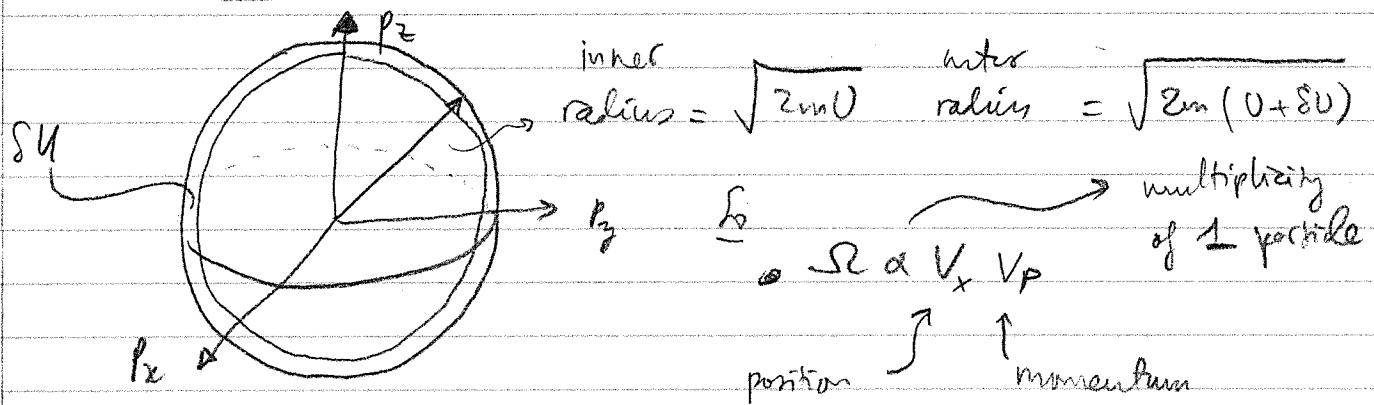
→ Let $\Delta x \Delta p = h$

For a monatomic ideal gas, energy is all kinetic

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

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

In 3-D momentum space



• And # states $\propto \frac{V_x}{\Delta x \Delta y \Delta z} \cdot \frac{V_p}{\Delta p_x \Delta p_y \Delta p_z}$

$$\underline{\Omega} = \int_{u}^{u+\Delta u} \int_{u}^{u+\Delta u} \int_{u}^{u+\Delta u} dx dy dz \int_{p_x}^{p_x+\Delta p_x} dp_x \int_{p_y}^{p_y+\Delta p_y} dp_y \int_{p_z}^{p_z+\Delta p_z} dp_z$$

→ For N particles $\underline{\Omega} \propto \int_u^{\infty} \int_{r_1}^{\infty} \int_{r_2}^{\infty} \dots \int_{r_N}^{\infty} d^3 r_1 \dots d^3 r_N d^3 p_1 \dots d^3 p_N$

Volume is independent, so

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

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

\downarrow thickness

"surface area"

$$\text{So } S(u) \propto V^N (\sqrt{2mu})^{3N-1} \left[\sqrt{2m(u+\delta u)} - \sqrt{2mu} \right]$$

$$= V^N \frac{\text{Art tan area}}{\sqrt{2mu}} \frac{\text{Thickness}}{\left[\sqrt{2mu} \sqrt{1 + \frac{\delta u}{u}} - \sqrt{2mu} \right]}$$

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

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

$$\text{So } S(u) \propto V^N (\sqrt{2mu})^{3N} \cdot \left(\frac{\delta u}{2mu} \right)$$

$$\text{So } S(u) \propto V^N (\sqrt{2u})^{3N} \cdot \frac{\delta u}{u}$$

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

$$\text{So } S(u) \propto V^N u^{(3N/2)-1} \delta u \quad \begin{matrix} \xrightarrow{\text{small number}} \\ \text{- ignore } u^{-1} \text{ as well as} \end{matrix}$$

$$\boxed{\text{So } S(u) \propto V^N u^{\frac{3N}{2}-1}}$$

More careful derivation goes

→ multiplicity of monatomic ideal gas

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

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

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

Feb 27, 2019

Result for monatomic ideal gas

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

\blacksquare Interacting ideal gas

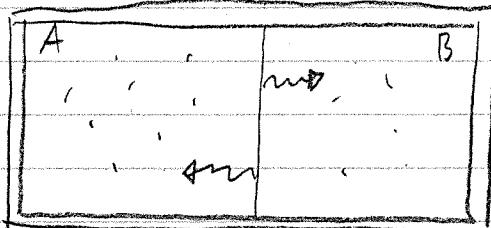
{ assuming } \rightarrow
 $\{ A \neq B \}$

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

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

3 ways to exchange multiplicity

① Exchange energy



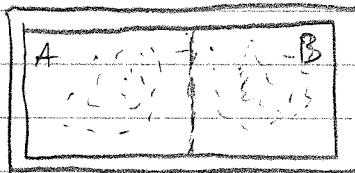
$$(\Omega \sim u^{3N/2})$$

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

② Exchange volume via a movable partition

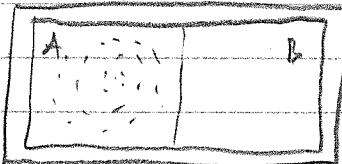
Width of peak in $\Omega = \frac{V_{\text{tot}}}{\sqrt{N}} \quad (\Omega \sim V^N)$

③ Exchange particles in permeable membrane (membrane)



\rightarrow more complicated overall
because of $f(N) \approx u(N)$

Consider specific case



Hence $V_{tot} \propto 2^n \rightarrow$ this reduces S_{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 $S_{tot} = \Omega_A \Omega_B$

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

$$= k \ln \Omega_A + k \ln \Omega_B$$

$$= S_A + S_B$$

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

◻ Spontaneous processes occur due to a net increase in entropy.

Entropy of an ideal gas

$$S = k \ln \Omega$$

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

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

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

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

→ entropy of ideal monatomic gas

↑ Sackur-Tetrode equation

300 K 10^5 Pa
J

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

Need V, N, U, m_{He}

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

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

$$m_{He} =$$

$$\int_1$$

$$U = \frac{3}{2} NkT = \frac{3}{2} N \bar{U} R = 3700 \text{ J}$$

Get

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

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

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

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

$$\delta \boxed{\Delta S = Nk \ln \frac{V_f}{V_i}}$$

so ΔS quasi-static iso-thermal expansion/capacity

Note if $\Delta S > 0$, then $\Delta S > 0$

Mar 1, 2019

How entropy is related to the heat input to system $\textcircled{2}$?

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

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

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

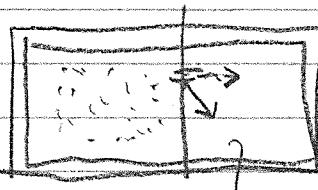
$$= \int_{V_i}^{V_f} \frac{NkT}{V} dV = NkT \ln\left(\frac{V_f}{V_i}\right) = T\Delta S$$

$$\delta \boxed{\Delta S = \frac{Q_{\text{add}}}{T}} \Rightarrow \text{quasi-static iso-thermal}$$

more precisely

$$\boxed{\Delta S = \frac{\partial Q}{T}}$$

Free expansion - non quasi-static



T, V constant $\rightarrow \Delta U = 0 = Q_{\text{add}} + W_{\text{on}}$

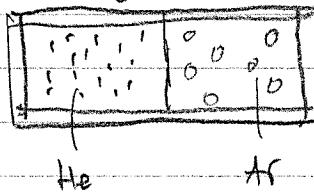
$Q_{\text{add}} = 0$ because no heat enters or leaves system. So $W = 0$.

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

$\Delta S = \partial Q / T$ because the eq describes quasi-static isothermal

Entropy of mixing

Consider



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

Now, reverse partition & let gases mix. How do S change?

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

He: N const, U const, $V' = 2V$

Ar: same thing.

$$\Delta S = N_{\text{He}} \ln(2) / \text{He} + N_{\text{Ar}} \ln(2) / \text{Ar}$$

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

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

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

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

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

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

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

$$\boxed{S' = 2S_{He} - 2S_{mixing}} \rightarrow \text{don't ignore } S' \in 25$$

Gibbs' Paradox

→ why does distinguishability matter?

Recall

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

$$\hookrightarrow \ln S_N \approx \ln\left(\frac{1}{N!}\right) \approx -(N \ln N - N)$$

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

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

Consider $\begin{array}{|c|c|c|} \hline & \vdots & \vdots \\ \hline \vdots & \vdots & \vdots \\ \hline \end{array}$ container with indistinguishable particles. Add a partition,

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

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

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

↓ get decrease in entropy

Reversible vs Irreversible process

- so 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 don't have to be

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

[Reversible \subsetneq 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)

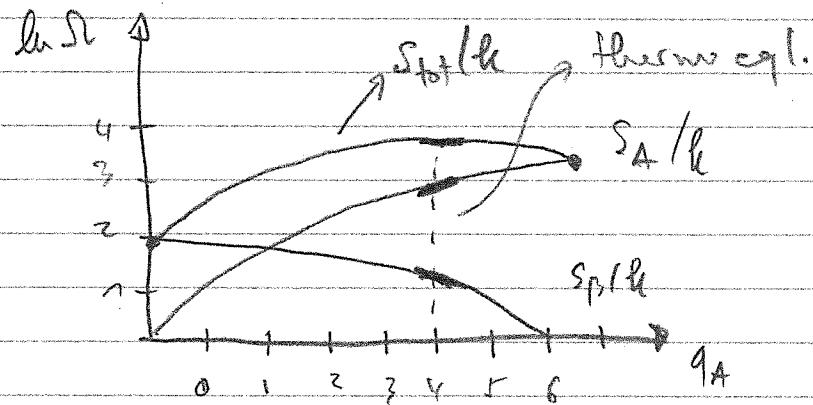
$$\underline{S} = \frac{S}{k} = \ln 2$$

$$N_A = 3$$

$$N_B = 2$$

	Ω_A	S_A/k	Ω_B	S_B/k	S_{tot}/k	S_{th}/k
1	0	1	0	6	1.9	1.9
1	3	1.1	5	6	1.8	1.8
2	6	1.8	4	9.5	1.6	3.6
3	10	2.3	3	14	1.4	4.0
4	15	2.7	2	18	1.1	4.5
5	21	3.0	1	22	0.7	4.2
6	28	3.3	0	1	0	2.8

Plot of $\ln S$ versus ϵ .



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

→ condition for thermodynamic equilibrium

Recall $V_A = \epsilon_A$ (constant)

$$\underline{\ln} \frac{\partial S_{tot}}{\partial \epsilon_A} = 0 \rightarrow \frac{\partial S_{tot}}{\partial V_A} = 0 \text{ at eql.}$$

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

$$\underline{\ln} \frac{\partial S_{tot}}{\partial V_A} = \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = 0 \quad \underline{\ln} \left[\frac{\partial S_A}{\partial V_A} = -\frac{\partial S_B}{\partial V_A} \text{ at eql.} \right]$$

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

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

So, we get

$$\boxed{\frac{\partial S_A}{\partial u_A} = -\frac{\partial S_B}{\partial u_B}}$$

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

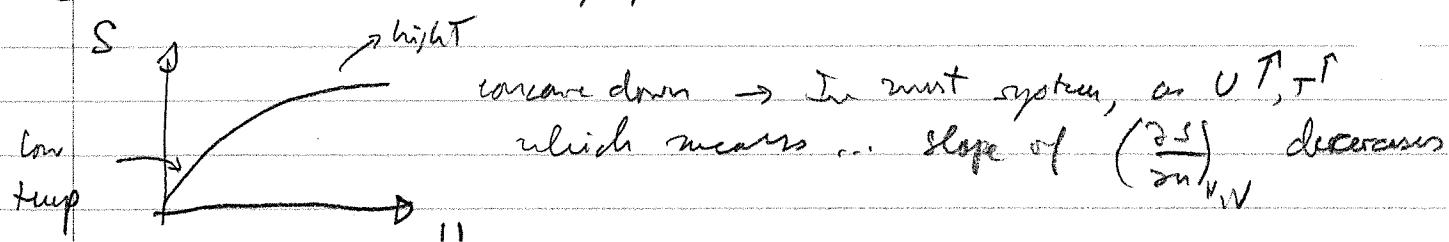
$$\begin{array}{l} \text{Units of } S \rightarrow J/K \\ \text{Units of } U \rightarrow J \end{array} \quad \left. \right\} T = \frac{\Delta U}{\Delta S} = \frac{\Delta U}{\Delta S}$$

Definition of temperature

$$\boxed{T = -\frac{\partial S}{\partial U}}$$

↑ N,V content

To Patterns in S vs U graphs.

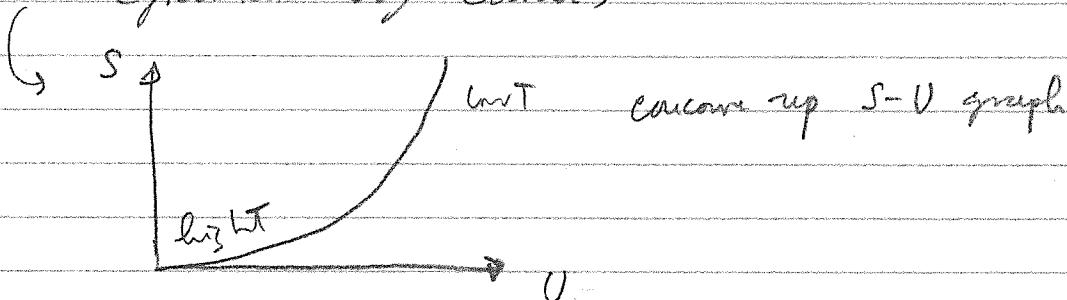


Result $\Delta U = Q_{\text{add}} + \cancel{W}_{\text{ext}}$ (assume V constant)

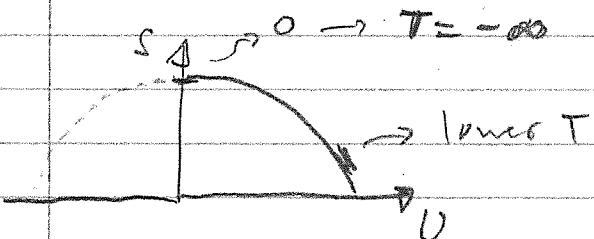
$$Q_{\text{add}} = C\Delta T$$

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

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



B Ex Concave down with negative slope ...



Ex paramagnet. $V = \mu B (N_f - N_i)$

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

B Example Relationship between S, V, T

(1) ^{large} Crystal solid at high temp limit $\rightarrow q \gg N \gg 1$

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

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

$$\text{def } U = \varepsilon \cdot q$$

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

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

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

$$\rightarrow \frac{1}{T} = \left(\frac{\partial S}{\partial u} \right)_{N, V} = \frac{Nk}{u} - 0 + 0$$

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

$$\text{Recall } u = \frac{E}{z} NkT$$

or

$$u = NkT$$

$f = 2$ brane SHO has 2 d.o.f.

(2) Ideal gas (monatomic)

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

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

$$T = \left(\frac{7}{2} Nk \frac{1}{u} \right)^{-1} \rightarrow u = \frac{3}{\varepsilon} NkT$$

Entropy = Heat Capacity

Mon 5, 2019

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

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

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

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

$$\int dS = \boxed{C_V \frac{dT}{T}} \rightarrow \int dS = \int C_V \frac{dT}{T} \quad \begin{array}{l} \text{if temp range} \\ \text{is small} \\ \rightarrow C_V \end{array} \\ \Rightarrow \boxed{\Delta S = C_V \ln \left(\frac{T_f}{T_i} \right)} \quad \text{constant}$$

Ex 6 Heat a cup of H₂O from 20°C to 100°C. Calculate (200g) how much entropy increases? $C_V = 1 \text{ cal/gK} = 4.186 \text{ J/gK}$

$$\Delta S = 4.186 \frac{J}{gK} \cdot (200g) \ln \left(\frac{373}{293} \right)$$

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

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

$$\rightarrow S_2 = e^{200 \text{ J/K} / 1.38 \times 10^{-23} \text{ J/K}} S_1$$

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

Q Total entropy of the system

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

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 Microscopic view of entropy $\Rightarrow ds = \frac{dq}{T}$

* Example The sun heating the surface of the Earth
 $\sim 1000 \text{ W/m}^2$. $T_0 = 6000 \text{ K}$
 $T_\oplus = 300 \text{ K}$

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

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

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

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

$$= +2.5 \times 10^7 \text{ J/K}$$

(5)

$$\Delta S_{tot} = \Delta S_0 + \Delta S_{\oplus} = 7.3 \times 10^3 \text{ J/Km}^2$$

Q 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 = C
 $M = 12 \text{ g/mol}$

Say 1200g of grass

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

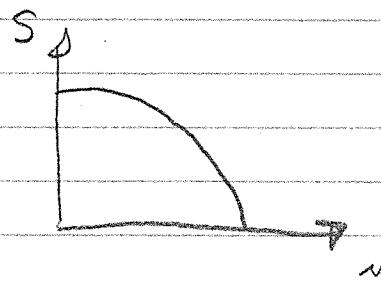
To assemble grass out of smaller molecules.

$$S \sim Nk \sim nR^2 = 1000R = 1000 \cdot 1.31 \text{ J/molK}$$

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

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

Result



For paramagnets

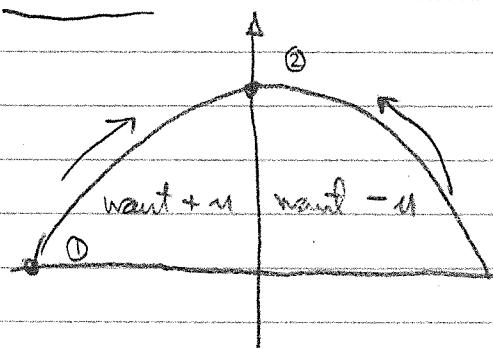
$$\begin{aligned} u &= \mu B(N_f - N_p) \\ &= \mu B(2N_f - N) \end{aligned}$$

Question how do U, M
depend on temperature

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

(*)

(1) Get S



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

② $N_f = N_f = \frac{1}{2}N$. Max entropy
 $n = 0$. If it absorbs n
 $\rightarrow S \propto U$ low \rightarrow slope

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

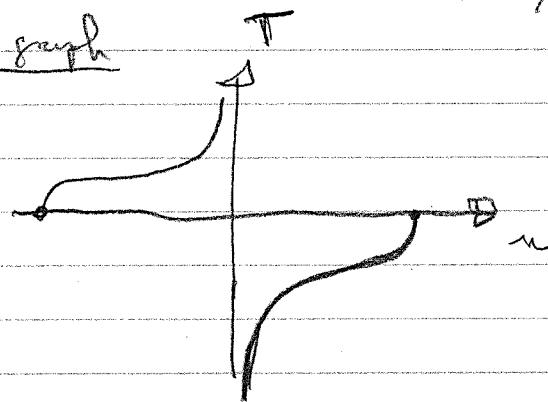
$T \uparrow \text{as } u \uparrow$

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

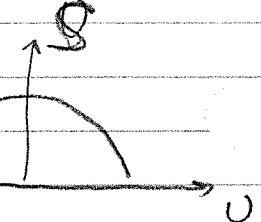
$T \downarrow \text{as } u \uparrow$

\rightarrow system wants to give off energy

Temp graph



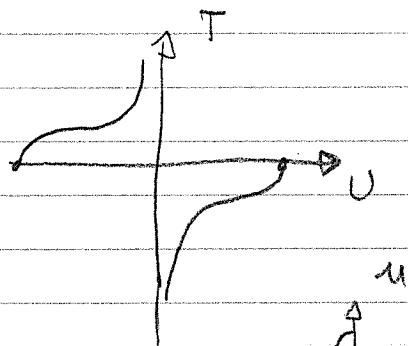
$$\text{Recall } \left(\frac{\partial S}{\partial T}\right)_{N,V} = \frac{1}{T}$$



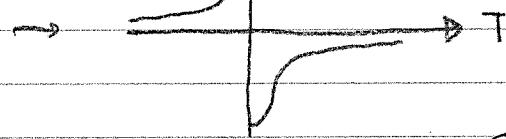
Mar 6, 2019

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

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



Flip the axes



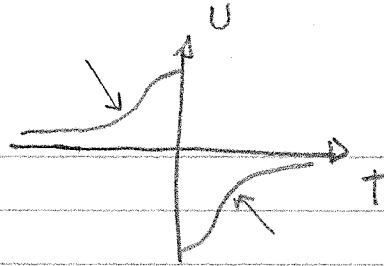
Recall

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

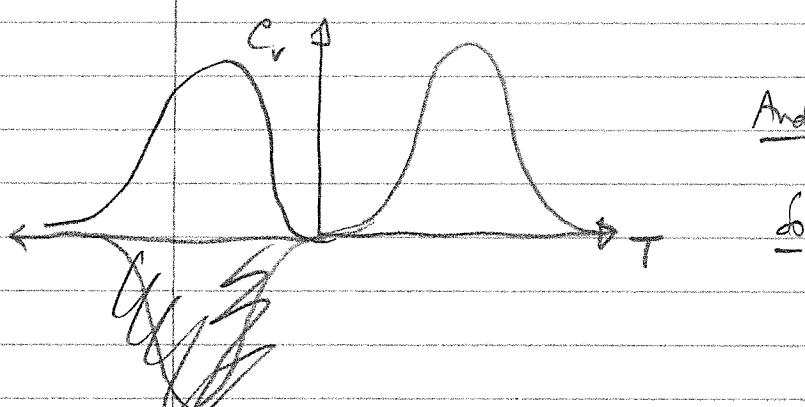
$$\rightarrow \text{and } \left\{ C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = 0 \text{ when } T=0 \right.$$

$$\left. C_V = 0 \text{ when } T = \pm \infty \right.$$

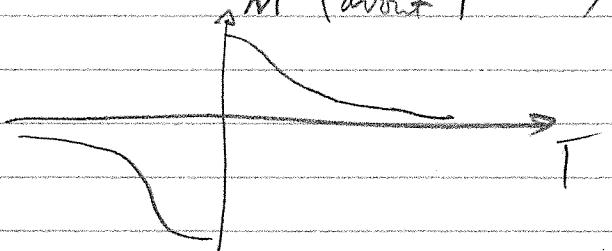
There's also an inflection point



- Consider (positive) temperatures only



\rightarrow magnetism
And recall $M_{\text{tot}} = u$ (fraction of n)
 M about T



Analytic solutions to paramagnets

Recall $S_2 = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} = \frac{N!}{N_\uparrow! (N-N_\uparrow)!}$ assume $N \gg 1$

$$S = k \ln S_2 = k \ln \left(\frac{N!}{N_\uparrow! (N-N_\uparrow)!} \right) = \ln(N_\uparrow!) + \ln((N-N_\uparrow)!)$$

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

$$\begin{aligned} \frac{S}{k} &= (N \ln N - N) - (N_\uparrow \ln N_\uparrow - N_\uparrow) + (\partial_{N_\uparrow} \ln(N-N_\uparrow)) \\ &= N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow) \end{aligned}$$

$$\frac{\partial S}{\partial T} = \frac{(2S)}{2u} \quad \text{and} \quad u = \mu B (N - 2N_\uparrow)$$

$$\frac{\partial}{\partial u} \left(\frac{\partial S}{\partial T} \right) = \left(\frac{\partial S}{\partial N_\uparrow} \right) \left(\frac{\partial N_\uparrow}{\partial u} \right) = (-2\mu B) \left(\frac{\partial S}{\partial N_\uparrow} \right) = \frac{-1}{2\mu B} \left(\frac{\partial S}{\partial N_\uparrow} \right)$$

$$\frac{\partial}{\partial u} \left(\frac{\partial S}{\partial T} \right) = k \left[-\ln N_\uparrow - \frac{1}{u} + \ln(N - N_\uparrow) + \frac{N - N_\uparrow}{N - N_\uparrow} \right]$$

$$N_p = \frac{1}{2} \left(N - \frac{u}{\mu B} \right)$$

(60)

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

$= \dots$

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

So

$$\left(\frac{\partial S}{\partial u} \right) = \frac{\partial S}{\partial N_p} \frac{\partial N_p}{\partial u} = \frac{k \ln \left(\frac{N + u/\mu B}{N - u/\mu B} \right)}{-2\mu B} = \frac{1}{T}$$

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 $u(T)$

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

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

So

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

So

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

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

$$\text{Now, simplifying} \rightarrow \underline{\underline{u(T)}} \quad \sinh(x) = \frac{1}{2} (e^x - e^{-x}), \cosh(x) = \frac{1}{2} (e^x + e^{-x})$$

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

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

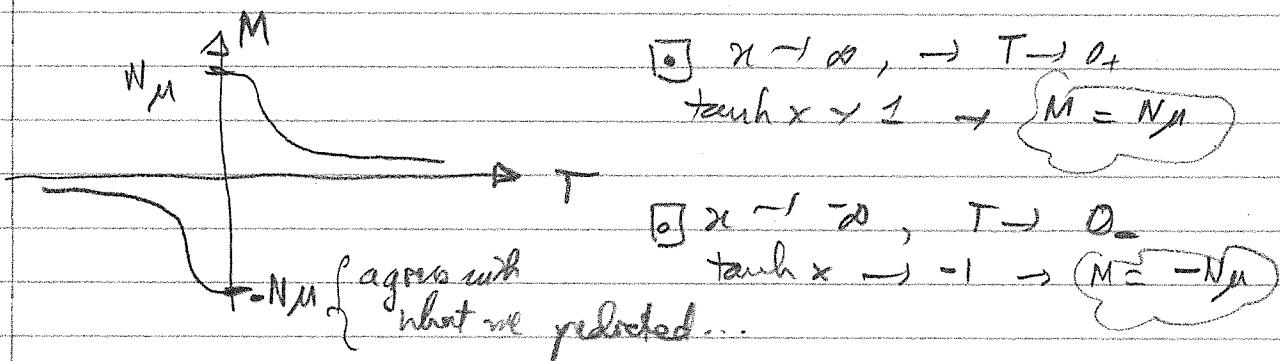
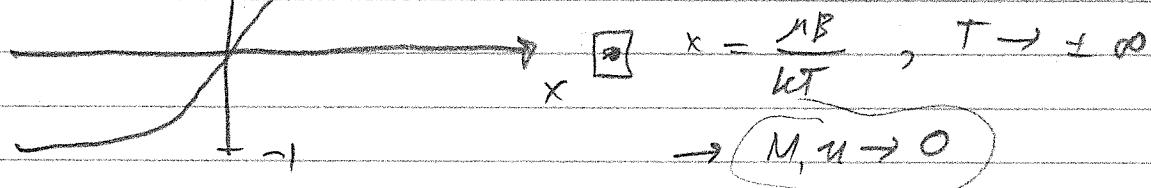
Let $x = \left(\frac{\mu B}{kT}\right)$, then

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

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

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

$\tanh x \rightarrow 1$ as $x \rightarrow 0$, $\tanh x \rightarrow 0$



What about heat capacity of paramagnet?

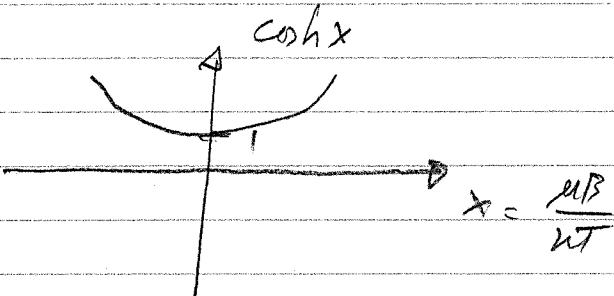
$$C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B} \quad \text{Now, } u = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

Recall $\frac{d}{dx} \tanh(x) = \operatorname{sech}^2(x) \cdot \frac{du}{dx} = \frac{1}{1 + e^{2x}} \frac{du}{dx}$

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

So

$$C_B = \frac{Nk \left(\frac{\mu B}{kT}\right)^2}{\cosh^2\left(\frac{\mu B}{kT}\right)}$$

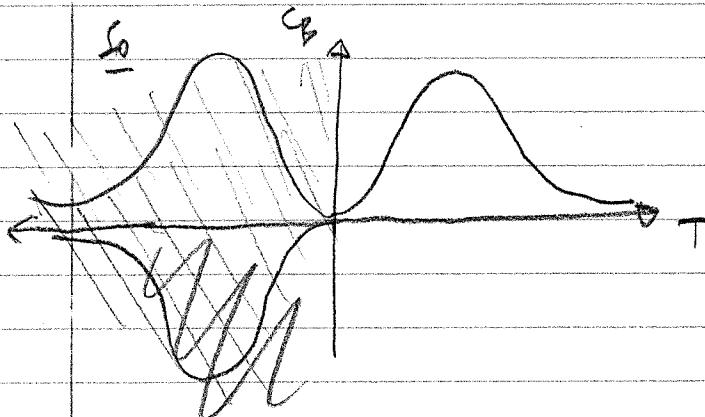


① as $x \rightarrow 0$, $T \rightarrow \pm \infty$ $\cosh(x) = 1$
 $\rightarrow [C_B \rightarrow 0 \text{ as } T \rightarrow \pm \infty]$

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

So

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



Ex

Consider two-state paramagnet.

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

Let $B = 1 T$

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

Then $M = ?$ $\mu_B = 5.8 \times 10^{-3} \text{ eV}$
 $kT = \frac{1}{40} \text{ eV}$ } $\rightarrow \frac{\mu_B}{kT} \ll 1$

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

$\hookrightarrow M \approx (N_\mu) \left(\frac{\mu B}{kT}\right) = \frac{N\mu^2 B}{kT}$ \rightarrow true in "high-temperature" limit.

(63)

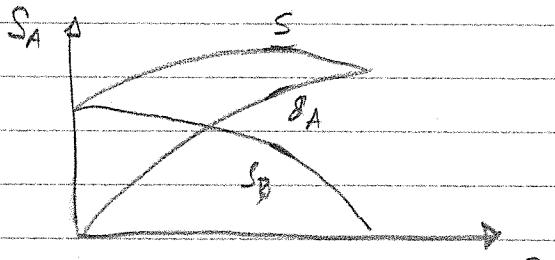
Get $M \propto \frac{1}{T}$ \rightarrow Curie's law (Pierre Curie)
 (high temp limit)

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

Mar 8, 2019

MECHANICAL EQUILIBRIUM

we've been discussing dV and dS

 S_A get

at thermal eq $\frac{\partial S_{tot}}{\partial V} = 0 \Rightarrow \boxed{\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}}$

constant V

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



\rightarrow changes in V governed by changes in P

\rightarrow changes in V governed by change in T

$$\left. \begin{array}{l} \text{as } V^T, \sigma^T, S^T \\ V^P, \sigma^P, S^P \end{array} \right\}$$

Goal develop a relationship between $\frac{\partial S}{\partial V}$ and P

Just like dS_{tot}/dV gives thermal equilibrium

6 $\boxed{\frac{\partial S_{tot}}{\partial V} = 0} \rightarrow$ mechanical equilibrium

$$\text{So } \frac{\delta S_{A+B}}{\delta V_A} = 0 \Rightarrow \boxed{\frac{\delta S_A}{\delta V_A} = \frac{\delta S_B}{\delta V_B}}$$

↓ ↑

$$\frac{\delta S_{A+B}}{\delta V_A} + \frac{\delta S_B}{\delta V_B} = 0, \text{ but } \delta V_A = -\delta V_B$$

} volume is conserved
mech-equl.

What are these hold constant \Rightarrow

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

Dimensional analysis.

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

Gross

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

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

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

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

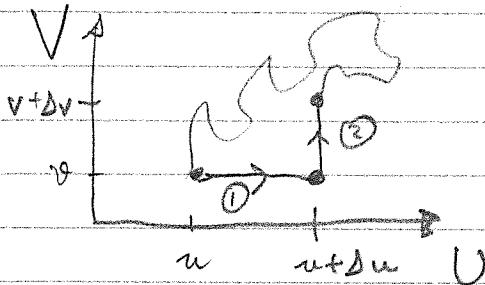
if $P = T \left(\frac{\delta S}{\delta V} \right)_{N}$, then

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

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

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

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 → volume constant

② Isothermal process → temp constant or energy

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

$\underline{s}(u, v, N)$

$\uparrow \uparrow \uparrow$
T vol #pos.

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

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

So

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

Case by case N is constant.

Note this is just the first law of thermo.

$$dU = dW_{\text{int}} + dQ$$

{ For quasi-static processes → $W_{\text{int}} = -PdV$

For quasi-static isothermal process → $dU = \frac{\partial U}{\partial T} dT = TdS$

Q = TdS → for any quasi-static process.
Not just isothermal

$dU = TdS - PdV$ ← more fundamental.

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

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

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

$$du = TdS - PdV$$

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

\approx \approx
T -P

$\left(\frac{\partial}{\partial V}\right)_S T = -\left(\frac{\partial}{\partial S}\right)_V P$ ← Maxwell's relation

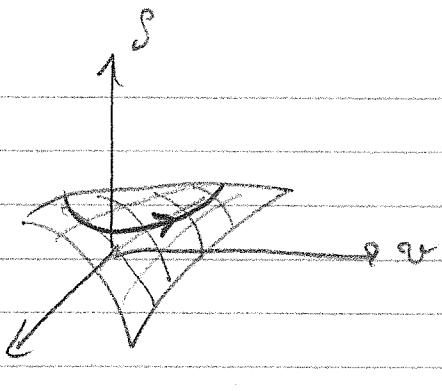
Constant Entropy process?

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

→ no change in Entropy

$$Q = TdS = 0 \quad ? \rightarrow \begin{cases} \text{a} \\ \text{I} \end{cases} \text{entropic} \quad \begin{cases} \text{u} \\ \text{p} \end{cases} \text{ quasi static} \quad \begin{cases} \text{a} \\ \text{p} \end{cases} \text{ adiabatic}$$

(67)



$$dU = TdS - PdV$$

$$TdS = 0 = dU + PdV$$

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

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

$$\varnothing = C_V DT = TdS$$

so $dS = \int_T C_V dT$ But we want to look at constant pressure processes

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

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

Diatomeric gas $C_V = \frac{7}{2} Nk$

$$C_P = C_V + Nk$$

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

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

Ideal gas law $\rightarrow PV = NkT \rightarrow Nk = \frac{PV}{T} = \frac{(10^5 \text{ Pa})(1 \times 10^{-3} \text{ m}^3)}{100 \text{ K}}$

$$N = nRT$$

so $T^2 = 2T$

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

$$\underline{\underline{S}} \quad (AS)_p = \int \frac{C_p}{T} dT = C_p \ln \frac{T_f}{T_i} = C_p \ln(2)$$

$$\underline{\underline{S}} \quad (AS)_p = C_p \ln(2) = \left(\frac{7}{2} Nk\right) \ln(2) \approx 0.81 J/K$$

Another way to do this

$$\hookrightarrow dU = TdS - PdV$$

↓

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

$$\cancel{\sum kN} = T \cancel{\frac{dS}{dT}} - \cancel{\sum NkT}$$

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

B

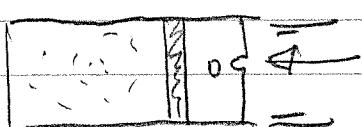
$$AS = \sum \ln \frac{T_f}{T_i} + Nk \ln \left(\frac{V_f}{V_i} \right)$$

$$\boxed{(AS)_p = \frac{7}{2} Nk \ln(2)}$$

Mar 11, 2019

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

① Fast compression



$dU \approx TdS - PdV$. We have done work but work is greater than $-PdV$

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

$$\underline{\underline{S}} \quad Q < TdS \rightarrow \boxed{dS > \frac{Q}{T}} \rightarrow \text{added entropy}$$

② free-expansion



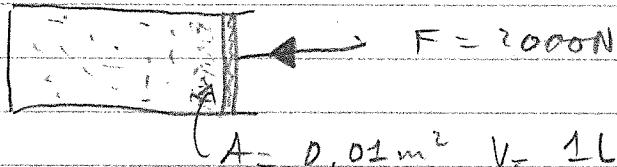
\rightarrow vacuum \rightarrow allow gas expand into vacuum

$$W=0, \Delta Q=0 \rightarrow \Delta U=0 \quad \text{with quasi-static}$$

but $dU = TdS - PdV = 0 \Rightarrow TdS = PdV > 0$ ($W \neq PdV$)

\hookrightarrow we added entropy

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



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

Say piston moves 1mm before it stops.

- If this is quasi-static $W = \int F dV = \int \frac{NkT}{V} dV = NkT \ln \frac{V_f}{V_i}$

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

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

Work actually done

$$W = Fd = (2000 \text{ N}) (0.001 \text{ m}) = 2 \text{ J}$$

$$> -PdV$$

Fast compression Adiabatic $\rightarrow \Delta Q = 0$

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

How does S change?

$$dU = TdS - PdV$$

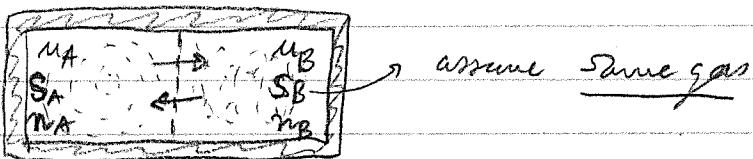
$$\Delta S = dS = \frac{dU + PdV}{T} = \frac{2 \text{ J} + (10^5 \text{ Pa})(-0.01 \text{ m}^2)(0.001 \text{ m})}{300 \text{ K}} \approx \frac{1}{5} \text{ J/K}$$

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 on both sides - - -

$$n_{\text{tot}} \equiv N_{\text{tot}} = \text{Const}$$

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

$$\text{Because } \left(\frac{\partial S_{\text{tot}}}{\partial \theta_A} \right)_{N, V} = \left(\frac{\partial S_{\text{tot}}}{\partial \theta_B} \right)_{N, V} = 0 \text{ at equilibrium.}$$

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

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

Rather not N , but μ

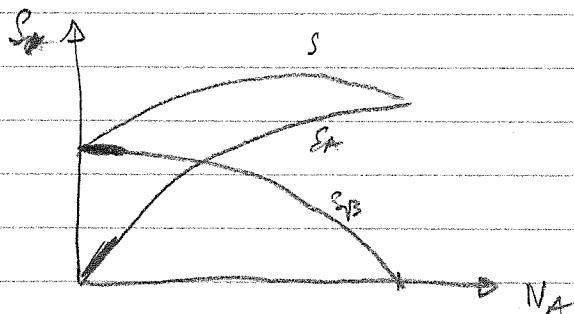
$\rightarrow \boxed{\mu: \text{Chemical potential } (\mu) \text{ has units of energy } [J]}$

Relating $\frac{\partial S}{\partial N}$ to μ $\frac{\partial S}{\partial N} = \frac{\partial S}{\partial n} \times n = \frac{\partial S}{\partial n} \times \text{constant} = \frac{\partial S}{\partial n} \times T = \frac{\partial F}{\partial n}$ multiply by temperature + set μ

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

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

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

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

$$\delta TdS = dV - \mu dN + PdV$$

$$\boxed{\delta V = TdS + \mu dN - PdV}$$

↑ ↑ ↑ "heat" "driv. work" "mech. work"

if quasi-static \rightarrow "heat" "driv. work"

- static ...

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

Normally, to keep $\Delta S = 0$, if we $\uparrow N$, need to $\downarrow s$

e.g. Einstein solid w/ $N=3$, $q=3$

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

Then

$s = k \ln \Omega$. If we $\uparrow N$ by 1, $N=4$

$$\text{Then } s' = \binom{4+2-1}{3} = 20 \quad s'' = k \ln 20 > s.$$

To keep s constant \rightarrow need to decrease $q \rightarrow q=2$

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

$$\left. \begin{array}{l} \Delta U = q\varepsilon - q:\varepsilon = 2\varepsilon_i - 3\varepsilon_f = -\varepsilon \\ \Delta N = 1 \end{array} \right\} \frac{\partial U}{\partial N} = -1$$

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

Mar 12, 2019 [Chemical potential of ideal gas] (nonatomic)

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

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

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

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

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

So

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

$$\frac{h^2}{P}$$

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?

$$\mu_i = -T \left(\frac{\partial S}{\partial N_i} \right)_{U, V, N_j}^{\text{Total}}$$

$$\mu_2 = -T \left(\frac{\partial S}{\partial N_2} \right)_{U, V, N_1}$$

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

In diffusive equilibrium $\rightarrow \mu_A = \mu_{1A}, \mu_{2A} = \mu_{2B}, \dots$
 where $\begin{cases} A, B = \text{systems} \\ 1, 2, \dots = \text{species of atoms/molecules} \end{cases}$

Notes Chemist are $\mu_i = -T \left(\frac{\partial S}{\partial n} \right)_{V, T} \rightarrow \# \text{ moles}$ $n = N / N_A$

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

$$P_i = x_i P$$

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

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

~~(a)~~ Now, consider 2 gases A + B \rightarrow mixture occupying the same volume V

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

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

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

↑ same as if B not present

Chemical Potential of A Large Finited Solid

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

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

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

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

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

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

75

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

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

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

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

chemical potential of a large
Einstein solid

Now

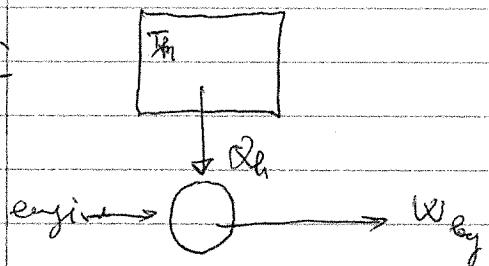
$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{V,T} = -kT \ln \left(1 + \frac{q}{N} \right)$$

-4-

Ch. 4 HEAT ENGINE, REFRIGERATOR

Concept → absorb heat. Convert to mechanical W

Consider



Design considerations

①

Want to start & end at the same macrostate (energy)
→ Cyclic in PV diagram

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

② Must obey 1st law of Thermodynamics

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

③ Must obey 2nd law of Thermodynamics $\Delta S \geq 0$

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

→ Look at entropy of system

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

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

1st law

$$\Delta U = \Omega_{\text{abs}} - W_{\text{egy}} \Rightarrow \Omega_{\text{abs}} = W_{\text{egy}}$$

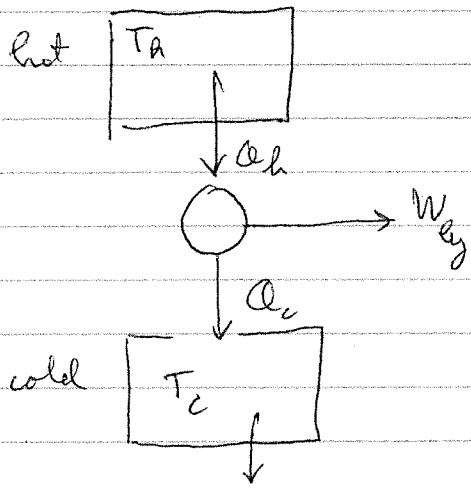
$$\therefore \Delta S_{\text{system}} = \Delta S_{\text{engine}} + \Delta S_{\text{reservoir}} = -\frac{\Omega_h}{T_h} = -\frac{W_{\text{egy}}}{T_h} \geq 0$$

But then W_{egy} has to be negative...

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

To fix this

Assume cyclic engine $\Delta u = 0$



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

$$\Omega_h - \Omega_c - W_{\text{egy}} = 0$$

$$\therefore W_{\text{egy}} = \Omega_h - \Omega_c$$

work done by the engine.

Ω_h = Ω absorbed by the cold engine

W_{egy} = W done by engine.

Ω_c = Ω expelled by the engine

Efficiency

$$\epsilon = \frac{W_{\text{net}}}{Q_{\text{abs}}} = \frac{W_{\text{net}}}{Q_h}$$

Rd

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

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

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

So

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

Example

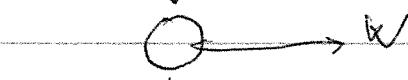
$$T_h = 100^\circ C$$

$$Q_h = 150 J$$

Assume $\Delta n = 0$

$$W = \underbrace{150 J - 125 J}_{= 25 J} = 25 J$$

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



$$Q_c = 125 J$$

$$T_c = 20^\circ C$$

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

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.

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

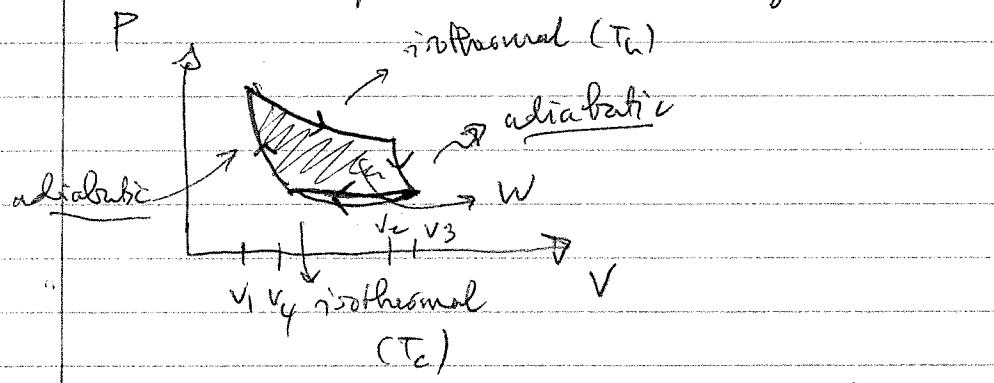
Instead, we want T_{engine} just slightly below T_h

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

- after isothermal expansion → bring temp of engine down to T_c → ($T_{\text{engine}} > T_c$ 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 dump)
- (4) Adiabatic compression to bring engine back to T_h .

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

$$(V_3 > V_4) Q_c = - \int_{V_3}^{V_4} P dV = - NkT_c \ln \left(\frac{V_4}{V_3} \right) = NkT_c \ln \left(\frac{V_3}{V_4} \right)$$

$$\therefore e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{\ln(V_3/V_4)}{\ln(V_2/V_1)} \cdot \frac{T_c}{T_h}$$

Now, for adiabatic processes

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

$$\therefore V_3 T_c^{\gamma-1} = V_2 T_h^{\gamma-1} \quad \& \quad V_4 T_c^{\gamma-1} = V_1 T_h^{\gamma-1}$$

$$\therefore \frac{V_3 T_c^{\gamma-1}}{V_4 T_c^{\gamma-1}} = \frac{V_2 T_h^{\gamma-1}}{V_1 T_h^{\gamma-1}} \Rightarrow \frac{V_3}{V_4} = \frac{V_2}{V_1} \Rightarrow \frac{\ln(V_3/V_4)}{\ln(V_2/V_1)}$$

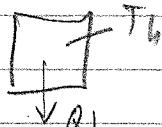
$$\therefore e = 1 - \frac{T_c}{T_h}$$

\rightarrow assuming adiabatic.

\rightarrow Carnot cycle produces max efficiency.

Mar 18, 2019
[heat engines]

Recall



cyclic process $\rightarrow \Delta U = 0$

$\therefore W_{\text{cy}}$

$$W_{\text{cy}} = Q_{\text{in}} - Q_{\text{out}}$$

$$\frac{Q_c}{T_c}$$

$$\varepsilon = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} = \frac{W_{\text{cy}}}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}}$$

Since $\Delta S \geq 0$, $\delta \leq 1 - \frac{T_c}{T_h}$ equality holds when
Carnot engine

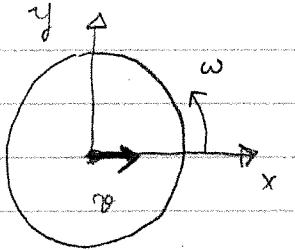
Hurricanes as Heat Engines

Hot reservoir \rightarrow Ocean surface

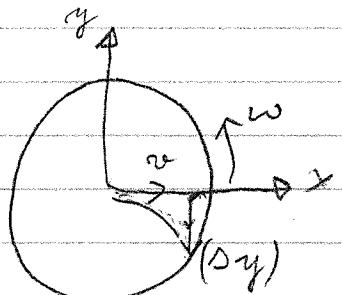
Cold reservoir \rightarrow atmosphere.

 \rightarrow Low pressure system with circulation due to Coriolis effect

$$F_c = 2\pi r \times w$$



$$x = vt \Rightarrow$$



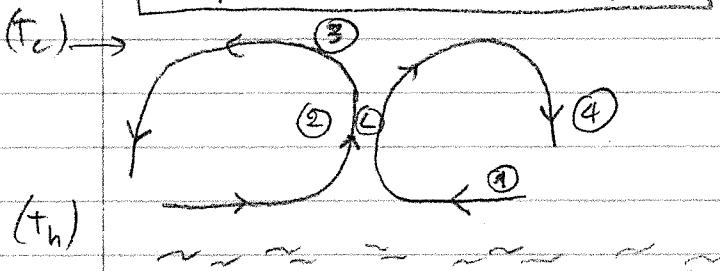
| if $v \perp w$, then

$$\Delta y = (wt)x$$

Coriolis acceleration

But since $x = vt \Rightarrow \Delta y = cvt^2 = \frac{1}{2} (2\omega r)t^2 = \frac{1}{2} a_c t^2$

[Steps of Hurricane engine] \rightarrow same as Carnot's



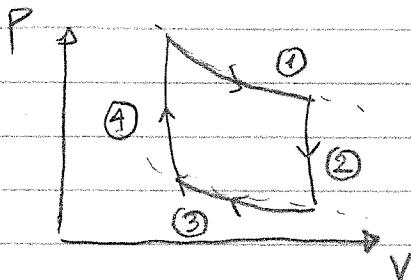
(1) Isothermal expansion of air over hot ocean ($T \approx 300K$)

(2) Adiabatic expansion
 \rightarrow air moves rapidly up 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)

$$W = F_{\text{drag}} \cdot x$$

$$\therefore \frac{dW}{dt} = (\alpha v^2) v \approx \alpha v^3$$

Heat transfer from the ocean by forced convection. $Q_h \propto v$

$$\therefore \text{Total : } Q_h = \alpha v^3 + bv \rightsquigarrow Q_{\text{ocean}}$$

\downarrow

Q due to friction

So

$$e = \frac{W_{\text{cy}}}{Q_{\text{abs}}} = \frac{\alpha v^3}{\alpha v^3 + bv} = \frac{1 - T_c}{T_h} \rightsquigarrow \text{Carot engine}$$

\Rightarrow Can solve for v .

$$\frac{\alpha v^2}{\alpha^2 + b} = 1 - \frac{T_c}{T_h} \Rightarrow \alpha v^2 = (\alpha v^2 + b)(1 - \frac{T_c}{T_h}) = \alpha v^2 \left(1 - \frac{T_c}{T_h}\right) + b \left(1 - \frac{T_c}{T_h}\right)$$

$$\therefore \alpha v^2 \left(\frac{T_c}{T_h}\right) = b \left(1 - \frac{T_c}{T_h}\right)$$

$$v = \sqrt{\frac{b}{\alpha} \left(\frac{T_h}{T_c} - 1\right)}$$

Refrigerator



Work done on substance, to pull heat out cold reservoir

W_{on}

\rightarrow expel waste heat to heat

$$\text{Now, } \Delta h = 0 \Rightarrow Q_c + W_{an} = Q_h$$

↓ compression work.

Coefficient of Performance

$$\text{COP} = \frac{Q_c}{W_{an}}$$

replace $W_{an} = Q_h - Q_c$

$$\therefore \boxed{\text{COP} = \frac{Q_c}{\frac{Q_h - Q_c}{Q_h/Q_c - 1}} = \frac{1}{Q_h/Q_c - 1} \geq 1}$$

By 2nd law, $\Delta S \geq 0 \Rightarrow \frac{Q_h}{T_h} - \frac{Q_c}{T_c} \geq 0 \therefore \frac{Q_h}{Q_c} \geq \frac{T_h}{T_c}$

$$\therefore \boxed{\text{COP} = \frac{1}{\frac{Q_h/Q_c - 1}{T_h/T_c - 1}} \leq \frac{1}{T_h/T_c - 1}}$$

→ Carnot cycle once again creates the most efficient refrigerator

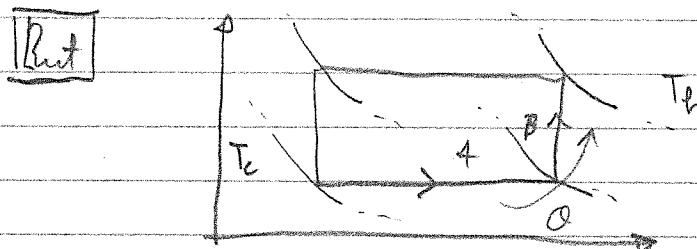
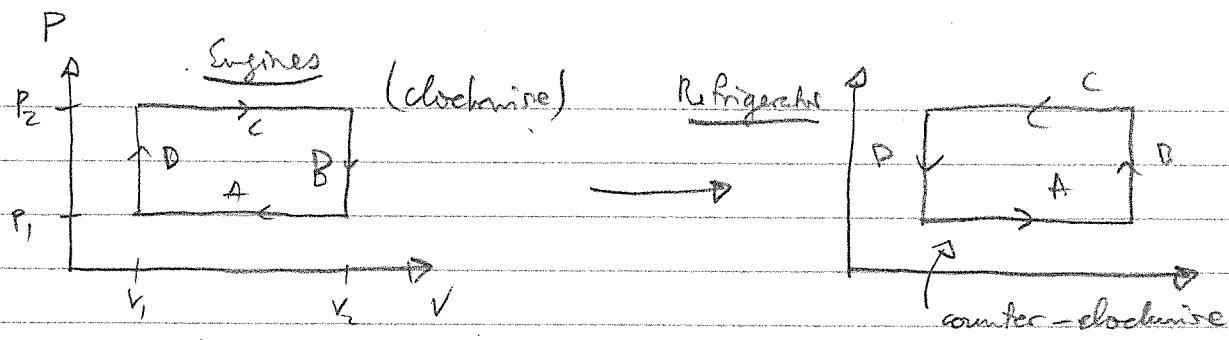
Need $T \geq T_h$ during heat expulsion

$T \leq T_c$ during heat absorption

Example what is the max possible COP for a standard AC unit?

$$\text{let } t_{in} = 22^\circ\text{C} \quad \text{then} \quad \text{COP}_{\max} = \frac{1}{\frac{30+273}{22+273} + 1} \approx 36.9$$

PV diagram



Need $T_c > T_h$ for heat flow A,B ? not going to work
and $T_h < T_c$ for heat flow C,D ?

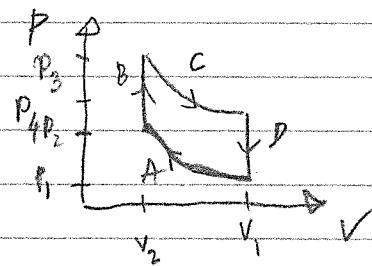
→ Need adiabatic processes -

↔

Mar 19, 2019

Real Heat Engines

Example Internal Combustion Engine (Otto cycle)



A,C → 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
D

$\rightarrow Q_h$
 $\rightarrow Q_c$

Step B $\Delta U_B = Q + \cancel{W^0} \Rightarrow Q = \frac{f}{2} N k T = \frac{f}{2} P V = \frac{f}{2} V_2 (P_3 - P_2)$

Step D $\Delta U_D = Q_c + \cancel{W^0} = -\frac{f}{2} N k T \Rightarrow Q_c = \frac{f}{2} V_2 (P_4 - P_1)$

So,
$$\boxed{\epsilon = 1 - \frac{Q_c}{Q_h} = 1 - \frac{V_2 (P_4 - P_1)}{V_2 (P_3 - P_2)}}$$

But more convenient with Carnot theorem

Adiabatic $\Rightarrow P_4 V_1^\gamma = P_3 V_2^\gamma \Rightarrow P_1 V_1^\gamma = P_2 V_2^\gamma$

$\Rightarrow (P_4 - P_1) V_1^\gamma = (P_3 - P_2) V_2^\gamma$

$\therefore \frac{P_4 - P_1}{P_3 - P_2} = \frac{V_2^\gamma}{V_1^\gamma} = \left(\frac{V_2}{V_1}\right)^\gamma$

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 $\rightarrow T_2 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$

$$\therefore \frac{T_4}{T_3} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} \Rightarrow \eta = 1 - \frac{T_4}{T_3}$$

Note $\frac{T_1}{T_3} < \frac{T_1}{T_2}$ and $\frac{T_1}{T_3} < \frac{T_4}{T_3}$

$$\therefore \eta_{Otto} < \eta_{Carnot}$$

$\therefore \left\{ \begin{array}{l} \text{Otto cycle will always be less efficient than Carnot engine} \\ \text{over the same T} \end{array} \right.$

Revisiting 3rd Law

\hookrightarrow "Planck's statement = "as $T \rightarrow 0$, $S \rightarrow S_{min}$, $S_{min} = 0$
for pure crystalline solids."

Einstein statement

"As $T \rightarrow 0$, S remains finite"

$$\therefore S = \int_0^T \frac{C_V}{T} dT \quad \text{if } C_V \rightarrow 0 \text{ then } S \rightarrow S_{min} = -\infty$$

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

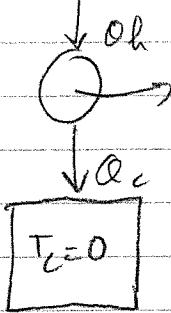
3rd Law tells us we can't get 100% conversion of heat to work even if

Einstein

$$Q_h = W_h \quad \text{Einstein statement} \quad \rightarrow S \text{ finite at } T=0$$

Nernst

If you want $\Delta S = 0$, Nernst says can't get easier to $T=0$ in finite time



~~if~~

ch. 5 \rightarrow FREE ENERGY



Enthalpy \rightarrow useful at constant P

$$H = U + PV \Rightarrow dH = dU + PdV$$

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

$Q + W_{\text{on}}$

$-P\Delta V + W_{\text{others}}$

∴
$$\Delta H = Q + W_{\text{others}}$$

Helmholtz free energy (F)

useful for constant T processes.

$$F \equiv U - TS \quad \begin{array}{l} \text{create system} \\ \text{out of nothing} \end{array}$$

$$Q = T\Delta S, \text{ quasi-static}$$

Gibbs free energy (G)

useful for constant $T \& P$

$$G \equiv U - TS + PV = H - TS$$

$$\downarrow \\ S_{\text{final}} = 0$$

Mar 10, 2019 Recall Thermodynamic Potential U, H, F, G

Look at changes in these: $F \equiv U - TS \Rightarrow dF = dU - SdT - TdS$

For F , T constant $\Rightarrow \boxed{dF = \Delta U - T\Delta S}$ can rewrite...

$$\boxed{dF = Q_{in} + W_{on} - T\Delta S} \quad \text{Now } Q_{in} \leq T\Delta S \text{ (in general)}$$

$$\hookrightarrow \boxed{dF \leq W_{on}} \quad (\text{constant } T, \text{ equality when quasi static})$$

can be expansion/compression work = $\int PdV + \text{others}$.

Gibbs free energy $\Rightarrow G \equiv U - TS + PV = dG = dU - TdS - SdT + PDV + VdP$

constant $T, P \Rightarrow dG = dU - TdS + PDV$

$$Q_{in} + W_{on}, Q_{in} \leq TdS, W_{on} = -P\Delta V + W_{\text{others}}$$

b

$$\boxed{\Delta G \leq W_{\text{others}}}$$

$$\underline{\Delta F = \Delta U + PV} = Q_{in} + W_{\text{others}} \Rightarrow$$

$$Q_{in} + W_{on}$$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

Ex of using ΔG



$$\Delta H_f = -286 \text{ kJ/mol}$$

How much work do we need to supply to get reaction to proceed?

Charge in S: $S_{\text{H}_2\text{O}(l)} = 70 \text{ J/K}$

$$S_{\text{H}_2(g)} = 131 \text{ J/K}$$

$$S_{\text{O}_2(g)} = 205 \text{ J/K}$$

$$\Delta S = (131 \text{ J/K} + \frac{1}{2} \cdot 205 \text{ J/K}) - 70 \text{ J/K} = 163 \text{ J/K}$$

Max amount of heat that can enter system = $T\Delta S = 49 \text{ kJ}$

$$\Delta G = \Delta H - T\Delta S = 286 \text{ kJ} - 49 \text{ kJ} = \boxed{\Delta G = 237 \text{ kJ}}$$

Thermodynamic identities

$$dU = TdS - PdV \quad (\text{f}, \mu, N) \Rightarrow u(s, v)$$

$$\text{So } dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV$$

$$\text{So } \frac{\frac{\partial^2 u}{\partial S \partial S}}{\frac{\partial^2 u}{\partial S \partial V}} = \frac{\frac{\partial^2 u}{\partial V \partial S}}{\frac{\partial^2 u}{\partial V \partial V}} \Rightarrow \frac{\partial}{\partial V} \left[\left(\frac{\partial U}{\partial S}\right)_{V,N} \right]_{S,N} = \frac{\partial}{\partial S} \left[\left(\frac{\partial U}{\partial V}\right)_{S,N} \right]_{V,N}$$

$$\textcircled{1} \quad \left(\frac{\partial T}{\partial V}\right)_{S,N} = - \left(\frac{\partial P}{\partial S}\right)_{V,N} \quad \begin{array}{l} \rightarrow \text{independent variables } s, v \\ \text{Maxwell's relation \#1} \end{array}$$

$$\textcircled{2} \quad dU = TdS - PdV = TdS - d(PV) + VdP \Rightarrow d(VdP) = TdS + Vd$$

$$\text{So } \boxed{dH = TdS + VdP} \quad \rightarrow \text{how to set } \Delta H \text{ at non-standard } P, T \dots$$

$$\text{H} = H(S, P)$$

2
$$dH = \underbrace{\left(\frac{\partial H}{\partial S} \right)_{P,N} dS}_{T} + \underbrace{\left(\frac{\partial H}{\partial P} \right)_{S,N} dP}_{V}$$

3
$$T = \left(\frac{\partial H}{\partial S} \right)_{P,N} ; V = \left(\frac{\partial H}{\partial P} \right)_{S,N}$$

Now $\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial S} \right)_{P,N} = \frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P} \right)_{S,N}$

4
$$\frac{\partial}{\partial P} \left(\frac{\partial T}{\partial S} \right)_{P,N} = \left(\frac{\partial V}{\partial S} \right)_{P,N} \rightarrow \text{Maxwell's relation #2}$$

(3) Independent variables T, V

$$dU = TdS - PdV$$

$$= d(TS) - SdT - PdV$$

5
$$d(U - TS) = - SdT - PdV$$

$dF = - SdT - PdV$

Have $F(T, V)$

6
$$dF = \underbrace{\left(\frac{\partial F}{\partial T} \right)_{V,N} dT}_{-S} + \underbrace{\left(\frac{\partial F}{\partial V} \right)_{T,N} dV}_{-P}$$

7
$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N}, P = - \left(\frac{\partial F}{\partial V} \right)_{T,N}$$

$$\text{Eq} \quad \frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right) = \frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right)$$

$$\text{So} \quad - \left(\frac{\partial S}{\partial V} \right)_{T,N} = - \left(\frac{\partial P}{\partial T} \right)_{V,N}$$

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

(4) Independent variables : $T \neq P$

$$dU = TdS - PdV = d(TS) - SdT - d(PV) + VdP$$

$$\text{So} \quad d(U - TS + PV) = - SdT + VdP$$

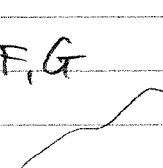
$$\boxed{dG = - SdT + VdP}$$

$$\text{Eq} \quad V = \left(\frac{\partial G}{\partial P} \right)_{T,N}, \quad S = - \left(\frac{\partial G}{\partial T} \right)_{P,N}$$

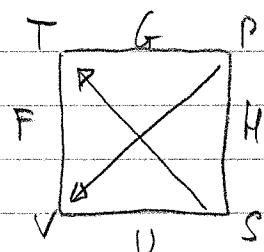
and

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

Mar 22, 2019

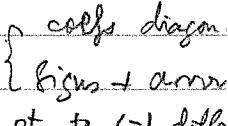
Thermodynamics potentials U, H, F, G  "good physicists have studied under very fine teachers"

Ufe square



$$dH = VdP + TdS + mdN$$

$$dU = TdS - PdV + mdN$$

Write potentials as fn of vars on that side of square 

Maxwell's Relations

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

arrow point to minus signs for the constant variable.

Definitions 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

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

~~~~~

$$= \left( \frac{C_V}{T} \right) dT + \left( \frac{\partial S}{\partial V} \right)_T dV$$

Express  $V = V(T, P)$  @ consider constant pressure

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

$$\therefore (dS)_P = \left( \frac{C_V}{T} \right) (dT)_P + \left( \frac{\partial S}{\partial V} \right)_T \text{ and } \left( \frac{\partial S}{\partial T} \right)_P (dT)_P$$

[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  $\Rightarrow (dH)_p = (TdS)_p$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \stackrel{so}{=} \left(\frac{\partial H}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p$$

So

$$T \left(\frac{\partial S}{\partial T}\right)_p = C_V + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

$$\underline{\text{So}} \quad C_p = C_V + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

Q Use Maxwell's relation  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

So

$$\boxed{C_p = C_V + T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p}$$

• Let  $\beta = \left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial T}\right)_p \rightsquigarrow$  "thermal volume coefficient of expansion"

• Let  $\kappa_T = \left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial P}\right)_T \rightsquigarrow$  "isothermal compressibility"

Q To write  $C_p = C_V$  in terms of  $\beta$  &  $\kappa_T$ , more partial derivative manipulation is required.

$$\boxed{z = z(x, y), \text{ then } \left(\frac{\partial x}{\partial y}\right)_z = -\frac{(\partial z / \partial y)x}{(\partial z / \partial x)y}}$$

$$\text{Now } dz = \left(\frac{\partial z}{\partial y}\right) dy + \left(\frac{\partial z}{\partial x}\right) dx$$

when  $z$  constant  $\rightarrow dz = 0$

$$\underline{\text{So}} \quad \left(\frac{\partial z}{\partial x}\right) dx = - \left(\frac{\partial z}{\partial y}\right) dy \quad (dz = 0)$$

$$\underline{\text{So}} \quad \left(\frac{dx}{dy}\right)_z = - \frac{(\partial z / \partial y)_x}{(\partial z / \partial x)_y}$$

$$\underline{\text{So}} \quad \left(\frac{dx}{dy}\right)_z = - \frac{(\partial z / \partial y)_x}{(\partial z / \partial x)_y}$$

Do back to derive.

$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_V &= - \frac{(\partial V / \partial T)_P}{(\partial V / \partial P)_T} \\ \downarrow (C_p - C_V) &= T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = -T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T^{-1} \left(\frac{\partial V}{\partial T}\right)_P \\ &= -T(V_B)^2 \frac{-1}{K_T V} \end{aligned}$$

$$\underline{\text{So}} \quad \boxed{C_p - C_V = \frac{T B^2 V}{K_T}} \quad \rightarrow \text{true for any substance}$$

Ex For ideal gas  $\rightarrow C_p - C_V = nR = Nk$

$$B = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P, \quad K_T = \frac{-1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$= \frac{1}{V} \left(\frac{Nk}{P}\right), \quad = \frac{-1}{V} \left(-\frac{NkT}{P^2}\right) = \frac{NkT}{P^2} = \frac{1}{P}$$

$$\underline{\text{So}} \quad \boxed{C_p - C_V = \frac{T(T)^{-2} V}{P^2} = \frac{PV}{T} = Nk = nR} \quad \checkmark$$

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.

- ③ Extensive { volume, mass, # particles, internal energy, entropy  
 (V) (m) (N) (U) (S)  
 Enthalpy (H), (F), (G)
- ④ Intensive { 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)

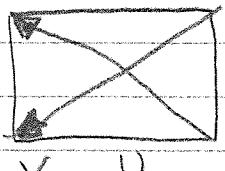
④  $[Ext] + [Ext] = [Ext]$

⑤ Not allowed  $\cancel{[Ext] + [Int]}$

Ex  $G$  has units of J But  $G^{\text{in}}$  does not make sense  
 $\mu$  has units of J

## Gibbs free energy & chemical potential

T G P



$$dG = VdP - SdT + \mu dN$$

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

Now,  $\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$  <sup>ext</sup> intensive  
 int ext

↳  $\boxed{\text{at constant } PT \rightarrow G = \mu N \propto N^1}$ , G  $\propto$  proportionally

for a system with only 1 type of particles.

$$\boxed{\mu = G/N}$$

## Helmholtz free energy & chemical potential

$$dF = -\delta E - SdT - PdV + \mu dN$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \rightarrow \boxed{F = N\mu(V)}$$

↑ ext  
int

## Derivation of chemical potential of ideal gas

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

Now,

$$G = \mu N \rightarrow \mu = \frac{G}{N}$$

Consider ... fixed amount of gas (N) at const (T) and allow P to vary.

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,N} = \frac{1}{P} \left(\frac{\partial G}{\partial N}\right)_{T,N} = \frac{1}{N} \left(\frac{\partial G}{\partial P}\right)_{T,N} = \frac{V}{N}$$

So  $\int d\mu = \int \left(\frac{V}{N}\right) dP \Rightarrow d\mu = \int_{P_i}^{P_f} \frac{kT}{P} dP = kT \ln\left(\frac{P_f}{P_i}\right)$

So

$$\boxed{\mu(T, P_f) - \mu(T, P_i) = kT \ln\left(\frac{P_f}{P_i}\right)}$$

write  $\mu(T, P_i) = \mu^\circ(T) \underset{1 \text{ atm}}{\uparrow} \boxed{\mu(T, P) = \mu^\circ + kT \ln\left(\frac{P}{P_0}\right)}$

(typically 1 atm)

- P is the partial pressure

Ex  $\boxed{\text{He, H}}$   $\mu_{\text{He}}(T, P) = \mu_{\text{He}}^\circ + \cancel{kT \ln\left(\frac{P}{P_0}\right)} + kT \ln\left(\frac{P_{\text{He}}}{P_0}\right)$

Q Test vs  $\mu$  derived for a monoatomic ideal gas

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

$$\mu = -kT \ln \left[ \frac{V}{N} \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \right]$$

$$= -kT \ln \left[ \frac{P^0}{P} \frac{kT}{P^0} \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \right]$$

$$= -kT \ln \left[ \frac{kT}{P^0} \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \right] + kT \ln \left( \frac{P}{P^0} \right)$$

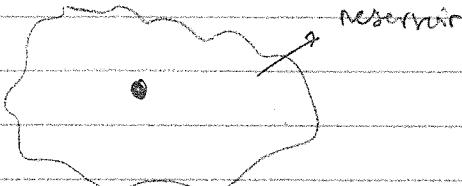
$$\boxed{\mu = -kT \ln \left[ \frac{kT}{P^0} \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \right] + kT \ln \left( \frac{P}{P^0} \right)}$$

 $\mu^\circ(T)$

## Free Energy as a Force Towards Equilibrium

- For isolated system  $\rightarrow S \uparrow$
- For interacting system  $\rightarrow S_{\text{tot}} \uparrow$

Assume environment is a reservoir of constant  $T, V, N$



$$S_{\text{tot}} = S_{\text{system}} + S_{\text{reservoir}}$$

$$dS_{\text{tot}} = dS_{\text{sys}} + dS_{\text{res}}$$

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  $dS_{\text{res}} = \frac{1}{T}dU_{\text{res}}$

$$\therefore dS_{\text{tot}} = dS_{\text{sys}} + \frac{1}{T_{\text{res}}}dU_{\text{res}}$$

In eq,  $T_{\text{sys}} = T_{\text{res}}$ ,  $dU_{\text{sys}} = -dU_{\text{res}}$

$$\therefore dS_{\text{tot}} = dS_{\text{sys}} - \frac{1}{T_{\text{sys}}}dU_{\text{sys}}$$

$$\therefore dS_{\text{tot}} = -\frac{1}{T}(dU - TdS) \quad \xrightarrow{\text{dropping sys. subscript}} dF$$

b

$$dS_{\text{tot}} = -\frac{dF}{T}$$

{ if  $dF < 0 \rightarrow$  spontaneous flow towards equilibrium



Now, let  $V$  vary, holding  $P, T, (\pm N)$  constant

$$dS_{\text{tot}} = dS_{\text{sys}} + \frac{1}{T_{\text{res}}}dU_{\text{res}} + \frac{P_{\text{res}}}{T_{\text{res}}}dV_{\text{res}} - \frac{\mu_{\text{res}}}{T_{\text{res}}}dN_{\text{res}}$$

At equilibrium,  $P_{\text{res}} = P_{\text{sys}}$ ,  $T_{\text{res}} = T_{\text{sys}}$ ,  $dV_{\text{res}} = -dV_{\text{sys}}$   
 $dV_{\text{res}} = -dV_{\text{sys}}$

So

$$dS_{\text{tot}} = dS - \frac{1}{T} dV - \frac{P}{T} dV$$

So  $dS_{\text{tot}} = -\frac{1}{T} (dV - TdS + PdV)$

 $dG$ 

So  $dS_{\text{tot}} = -\frac{dG}{T}$   $dG = dG_{\text{ext}}$ ,  $T = \text{equilibrium } T$

So

For fixed  $P, T, N \Rightarrow G \text{ tends to decrease}$

(if  $\Delta G < 0 \rightarrow \text{spontaneous process}$ )

**Example** use of free energy to calculate whether a reaction is spontaneous or not

Crytstallized ammonium nitrate  $\text{NH}_4\text{NO}_3$



look up  $\Delta_f H$ ,  $\Delta_f S$

|                             | $\Delta_f H$ | $\Delta_f S$ | @ eq, $\Delta G = 0$ |
|-----------------------------|--------------|--------------|----------------------|
| $\text{NH}_4\text{NO}_3(s)$ | -365.56      | 151.08       |                      |
| $\text{NH}_4^+(aq)$         | -132.51      | 113.4        |                      |
| $\text{NO}_3^-(aq)$         | -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,  $\Delta H = \Delta U + P\Delta V$

$$\Delta H = \Delta U + P\Delta V = Q_{\text{abs}}$$

|                |                 |
|----------------|-----------------|
| $\Delta H < 0$ | exothermic rxn  |
| $\Delta H > 0$ | endothermic rxn |

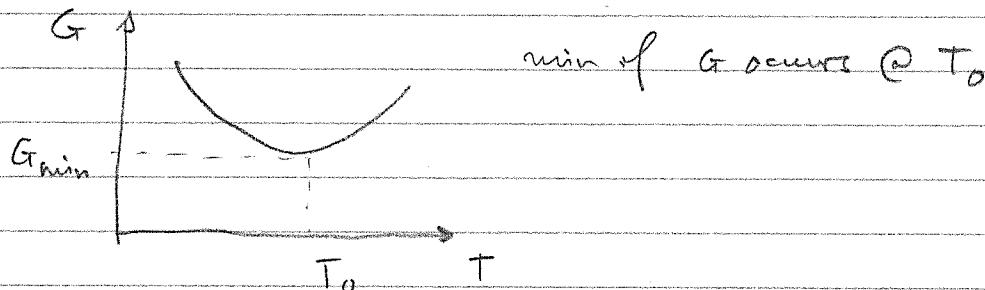
if  $\Delta H < 0, \Delta S > 0 \Rightarrow \Delta G < 0$  spontaneous  
 $\Delta H > 0, \Delta S < 0 \Rightarrow \Delta G > 0$  not spontaneous rxn.

| <input checked="" type="checkbox"/> Summary | <u>Reservoir</u> | <u>System</u>  |
|---------------------------------------------|------------------|----------------|
| • At constant                               |                  | $S \uparrow$   |
| $U, V$                                      |                  |                |
| • At const                                  |                  | $F \downarrow$ |
| $T, V$                                      |                  |                |
| • At const                                  |                  | $G \downarrow$ |
| $T, P$                                      |                  |                |

### Stability against Temperature Fluctuations

Consider a system. Let  $T, V$  be independent parameters that describe system.

1<sup>st</sup>, hold  $V$  fixed & allow  $T$  to vary  
 Interacting with respect to constant  $T, P, N$



• Expand  $G$  around eq. value  $\Delta G = G - G_{\text{min}} = \left(\frac{\partial G}{\partial T}\right)_{V,P} \Delta T + \frac{1}{2} \left(\frac{\partial^2 G}{\partial T^2}\right)_{V,P} (\Delta T)^2$

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~~

•  $G = U - TS + PV \quad G_0 @ T_0, P_0$

•  $G_0 = U_0 - T_0 S + P_0 V$

~~So~~  $\left(\frac{\partial G_0}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V - T_0 \left(\frac{\partial S}{\partial T}\right)_V = 0 \quad @ T = T_0$

$$dU = T dS - P dV \quad \underline{\underline{d}} \quad \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

$$\left(\frac{\partial G}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V - T_0 \left[ \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V \right]$$

$$\boxed{\left(\frac{\partial G_0}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left[ 1 - \frac{T_0}{T} \right]}$$

• ~~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  $T = T_0$

~~So~~  $\frac{T_0}{T^2} \left(\frac{\partial U}{\partial T}\right)_V > 0$

~~So~~  $\boxed{\left(\frac{\partial U}{\partial T}\right)_V > 0}$

$\boxed{C_V > 0}$

if heat cap  $> 0$ , then  
stable around ST

## Le Chatelier's Principle

April 3, 2019

When a system in eq. is disturbed, it will respond in a (stable) way to restore itself back to equilibrium.

### Result for V fluctuations

$$\left(\frac{\partial^2 G}{\partial V^2}\right)_{T=T_0} = -\left(\frac{\partial P}{\partial V}\right)_T > 0$$

$$K_T = \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\frac{1}{K_T} > 0 \text{ or simply } K_T > 0$$

## Chemical Equilibrium

Can use Gibbs to determine equilibrium condition...

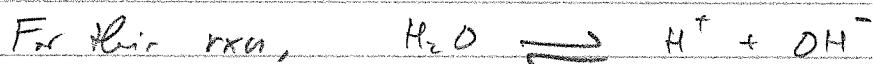


Mixture of  $H_2O$ - ions is most stable state (lower G)

$$G = U - TS$$

@ Eq.  $\Delta G = 0$ . Ions have a higher entropy. But additional entropy of mixing makes the mixture more stable.

@ Eq.  $dG = dH - TdS = \mu N_i = \sum_i \mu_i dN_i = \sum_i \mu_i dN_i$



$$dN_{H_2O} = -1, \quad dN_H^+ = +1, \quad dN_{OH^-} = +1 \quad \Leftarrow @ \text{eq. } dG = 0 = \sum_i \mu_i dN_i$$

$$\text{Eq} \quad -\mu_{H_2O} + \mu_{OH^-} + \mu_{H^+} = 0$$

$$\text{Eq} \quad \boxed{\mu_{OH^-} + \mu_{H^+} = \mu_{H_2O}}$$

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 solution, which is a mixture of a solvent (primary component) + solute (secondary comp)

Dilute solution { # of solute molecules  $\ll$  # of solvent molecules  
 and solute molecules don't interact  
 with each other  
 $\rightarrow$  can treat them as an ideal gas!

Q Need to calculate  $\mu$  for solvent & solute in order to predict eq.

Hypo 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

$$dG = \underbrace{dU}_{\substack{\downarrow \\ \text{index of } N_A}} + \underbrace{PdV}_{\substack{\downarrow \\ \text{only dep on } N_B}} - TdS \quad \rightarrow \text{dep on } N_A \quad (S \sim N_A)$$

$dS = k \ln N_A \rightarrow$  additional terms index of  $N_A$ ...

$$\text{Eq} \quad \boxed{dG = -kT \ln N_A + f(T, P)} \quad \substack{\text{for adding 1 mol} \\ \text{index of } N_A}$$

Adding 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...

$$\begin{aligned} dG' &= 2f(T, P) - T[2k \ln N_A - k \ln 2] \\ &= 2f(T, P) - 2kT \ln N_A + kT \ln 2 \end{aligned}$$

Generalizing (for  $N_B$  molecules)

$$kT N_B \ln N_B - kT N_B$$

$$dG = N_B f(T, P) - N_B kT \ln N_A + kT \ln(N_B!)$$

One 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  $\mu_A$  &  $\mu_B$

$$\boxed{\mu_A = \left( \frac{\partial G}{\partial N_A} \right)_{T, P, N_B} = \mu^0(T, P) - N_B kT / N_A} \quad \begin{array}{l} \text{chem pot} \\ \text{of solvent} \end{array}$$

$$\boxed{\mu_B = \left( \frac{\partial G}{\partial N_B} \right)_{T, P, N_A} = f(T, P) - kT \ln N_A - kT + kT + kT \ln N_B} \quad \begin{array}{l} \text{chem pot} \\ \text{of solute} \end{array}$$

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

$$dG = \underbrace{dU + PdV - TdS}_{\text{some terms dep. on } N_A} \rightarrow \text{some terms dep. on } N_A$$

$f(T, P)$  independent of  $N_A$

$$\Omega = \frac{N_A!}{N_B!(N_A - N_B)!}, \text{ and since } N_A > N_B \Rightarrow \Omega \approx \frac{N_A^{N_B}}{N_B!}$$

$$\begin{aligned} S &= k \ln \Omega = k \ln \left[ \frac{N_A^{N_B}}{N_B!} \right] = k \ln (N_A^{N_B}) - k \ln (N_B!) \\ &\approx N_B k \ln (N_A) - N_B k \ln N_B + N_B k \end{aligned}$$

Now,  $G = G_A + dG$

$$\text{So } dG = N_B f(T, P) - N_B k T \ln N_A + k T \ln N_B - N_B k T$$

$$\text{So } \boxed{G = \mu^\circ(T, P) N_A + N_B f(T, P) + N_B k T \ln \left( \frac{N_B}{N_A} \right) - N_B k T}$$

Now,

$$\mu = \left( \frac{\partial G}{\partial N} \right)_{T, P} \Rightarrow \boxed{\mu_A = \left( \frac{\partial G}{\partial N_A} \right)_{T, P} = \mu^\circ(T, P) - \frac{N_B k T}{N_A}}$$

(solvent)

$$\boxed{\mu_B = \left( \frac{\partial G}{\partial N_B} \right)_{T, P} = f(T, P) + k T \ln \frac{N_B}{N_A}}$$

(solute)

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  $\mu_B$  in terms of  $m$ :  $\rightarrow$  absorbed ... extraction ...

$$\star \mu_B = f'(T, P) + RT \ln(m_B) \quad (?)$$

$$\star \mu_B^\circ(T, P) \xrightarrow{S} \text{standard condition for molality } = 1 = m_B$$

$$\text{So when } m_B = 1 \rightarrow \boxed{\mu_B = \mu_B^\circ(T, P) + RT \ln(m_B)}$$

### Example Dissociation of water



Treat as dilute solution  $\Rightarrow$  solvent  $H_2O$

$$\star \mu_{H_2O} = \mu_{H_2O}^\circ - \frac{N_A k T}{m_{H_2O}} \left. \begin{array}{l} \xrightarrow{T=0} \\ \xrightarrow{N_A=1} \end{array} \right\} \mu_{H_2O}^\circ - \frac{N_A k T}{m_{H_2O}}$$

$$\star \mu_{H^+} = \mu_{H^+}^\circ(T, P) + RT \ln m_{H^+}$$

$$\star \mu_{OH^-} = \mu_{OH^-}^\circ(T, P) + RT \ln m_{OH^-}$$

at room temp,  $kT \sim 4 \times 10^{-21} J$

$$\text{So } \mu_{H_2O} = \mu_{H^+} + \mu_{OH^-} \Rightarrow \mu_{H_2O} - \mu_{H^+} - \mu_{OH^-} = 0$$

$$\Rightarrow \mu_{H_2O}^\circ - \mu_{H^+}^\circ - \mu_{OH^-}^\circ = RT \ln(m_{H^+}) + RT \ln(m_{OH^-}) \\ = RT \ln(m_{H^+} \cdot m_{OH^-})$$

$$\text{So } -N_A \underbrace{[\mu_{H^+}^\circ + \mu_{OH^-}^\circ - \mu_{H_2O}^\circ]}_{=} = RT \ln(m_{H^+} \cdot m_{OH^-})$$

$$\boxed{-\Delta G^\circ = RT \ln(m_{H^+} \cdot m_{OH^-})}$$

Ex  $\Delta G^\circ$  dissociation of water =  $-29.9 \text{ kJ/mol}$

Naw

$$\Rightarrow m_{H^+} \cdot m_{OH^-} = e^{-\frac{\Delta G^\circ}{RT}}$$

$K$  equilibrium constant

For room temp & standard  $P$ ,

$$K_{H_2O} = 10^{-14}$$

$$\therefore m_{H^+} \cdot m_{OH^-} = 10^{-14} = (m_{OH^-})^2 = (m_{H^+})^2$$

$$\therefore m_{H^+} = m_{OH^-} = 10^{-7} \rightarrow \text{moles/kg H}_2\text{O}$$

$$\boxed{pH = -\log_{10}(m_{H^+})} \Rightarrow pH = 7 \text{ for "pure" H}_2\text{O}$$

{ if fewer  $H^+$  conc. then basic,  $pH \uparrow$   
 { if more  $H^+$  conc. then acidic  $\rightarrow pH \downarrow$

partial pressure



Treat as ideal gas :  $\boxed{\mu(T, P) = \mu^\circ(T) + RT \ln\left(\frac{P}{P^\circ}\right)}$

std. atm. pressure

$$(\mu_{p^+}^\circ + \mu_{e^-}^\circ - \mu_H^\circ) = RT \ln\left(\frac{P_H}{P^\circ}\right) - RT \ln\left(\frac{P_{p^+}}{P^\circ}\right) - RT \ln\left(\frac{P_{e^-}}{P^\circ}\right)$$

$$\Rightarrow -\Delta G^\circ = N_A RT \ln \left[ \frac{P_H P^\circ}{P_{p^+} P_{e^-}} \right] \xrightarrow{P^\circ} \frac{RT}{P^\circ}$$

So Recall, for ideal gas  $\mu^\circ = -RT \ln \left[ \frac{V}{N} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right]$

But  $\mu$  for H should be less than  $-13.6 \text{ eV}$  when at rest ( $kT = 0$ )

$$\therefore \boxed{\mu_H^o = -kT \ln \left[ \frac{kT}{P_0} \left( \frac{2\pi m_p kT}{h^2} \right)^{3/2} \right] - 13.6 \text{ eV}}$$

Ansatz Rent  $p^+$ ,  $e^-$  unbond  $\Rightarrow$

$$\rightarrow \mu_{p^+}^o = -kT \ln \left[ \frac{kT}{P_0} \left( \frac{2\pi m_p kT}{h^2} \right)^{3/2} \right]$$

$$\mu_{e^-}^o = -kT \ln \left[ \frac{kT}{P_0} \left( \frac{2\pi m_e kT}{h^2} \right)^{3/2} \right]$$

$$\text{Now, } m_H \approx m_e$$

$$\therefore \mu_{p^+}^o + \mu_{e^-}^o - \mu_{H_2^o}^o = -kT \ln \left( \frac{kT}{P_0} \left( \frac{2\pi m_e kT}{h^2} \right)^{3/2} \right) + 13.6 \text{ eV}$$

Therefore,

$$-\ln \left( \frac{P_H P^o}{P_{p^+} P_{e^-}} \right) = \ln \left( \frac{kT}{P_0} \left( \frac{2\pi m_e kT}{h^2} \right)^{3/2} \right) - \frac{13.6 \text{ eV}}{kT}$$

$$\therefore \left( \frac{P_H P^o}{P_{p^+} P_{e^-}} \right)^{-1} = \frac{kT}{P_0} \left( \frac{2\pi m_e kT}{h^2} \right)^{3/2} \cdot e^{-\frac{13.6 \text{ eV}}{kT}}$$

$$\therefore \frac{P_{p^+} P_{e^-}}{P_H} = \frac{kT}{P_0} \left( \frac{2\pi m_e kT}{h^2} \right)^{3/2} \cdot e^{-\frac{13.6 \text{ eV}}{kT}}$$

$$\therefore \boxed{\frac{P_{p^+}}{P_H} = \frac{kT}{P_0} \left( \frac{2\pi m_e kT}{h^2} \right)^{3/2} \cdot e^{-\frac{13.6 \text{ eV}}{kT}}} \quad \text{Saha's Eqn}$$

$$\frac{N_{p^+}}{N_H}$$

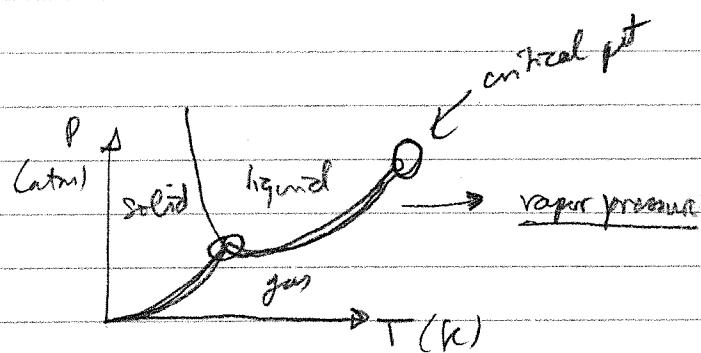
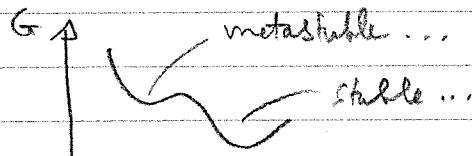
## PHASE TRANSFORMATION

def { A continuous change in property 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.  $P, T, B, \dots$

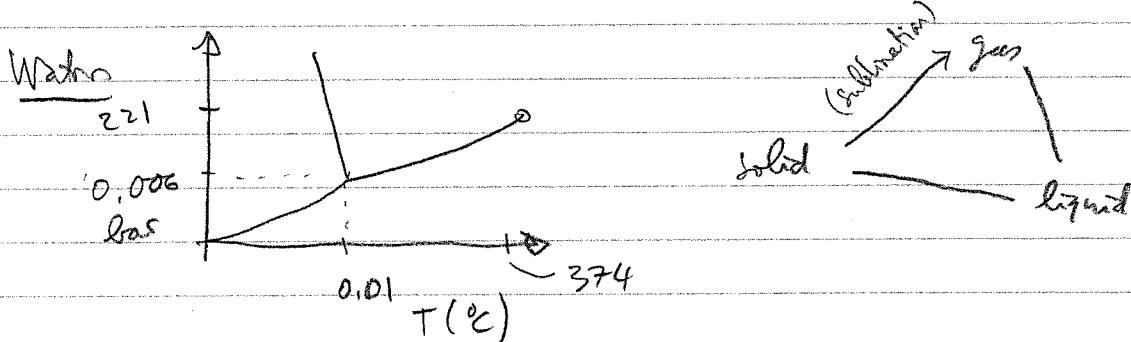
↳ Gibbs free energy is key to understanding these...



• Phase diagram for water

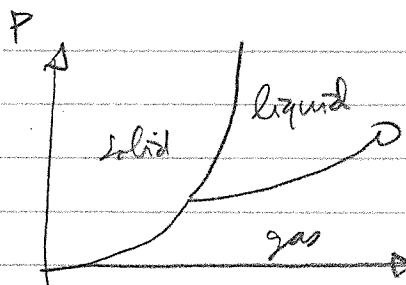
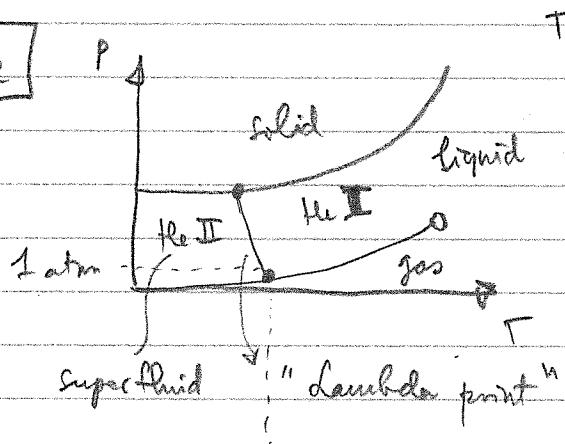
Vapor pressure → pressure at which liquid or solid phase can coexist with gas

• Triple point → precise  $T, P$  at which all 3 phases (liquid, gas, solid) can coexist...



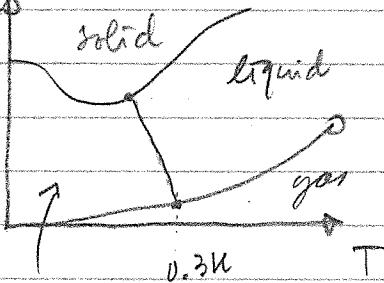
• Critical point As  $P$  or  $T$  increases, we reach a point where liquid & gaseous phases are indistinguishable.

Ex plasma ...

Ex  $\text{CO}_2$  ${}^4\text{He}$ 

${}^4\text{He}$  is a superfluid below the lambda point (@1 atm,  $2.17 \text{ K}$ )

**Superfluid**  $\rightarrow$  **zero viscosity**  
 $\left. \begin{array}{l} \text{zero entropy} \\ \text{high conductivity} \end{array} \right\}$

 ${}^3\text{He}$ 

2 superfluid phases:

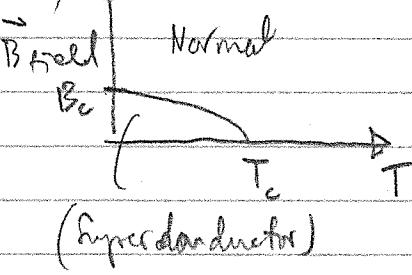
Other variables that can cause phase change:

- chemical composition:

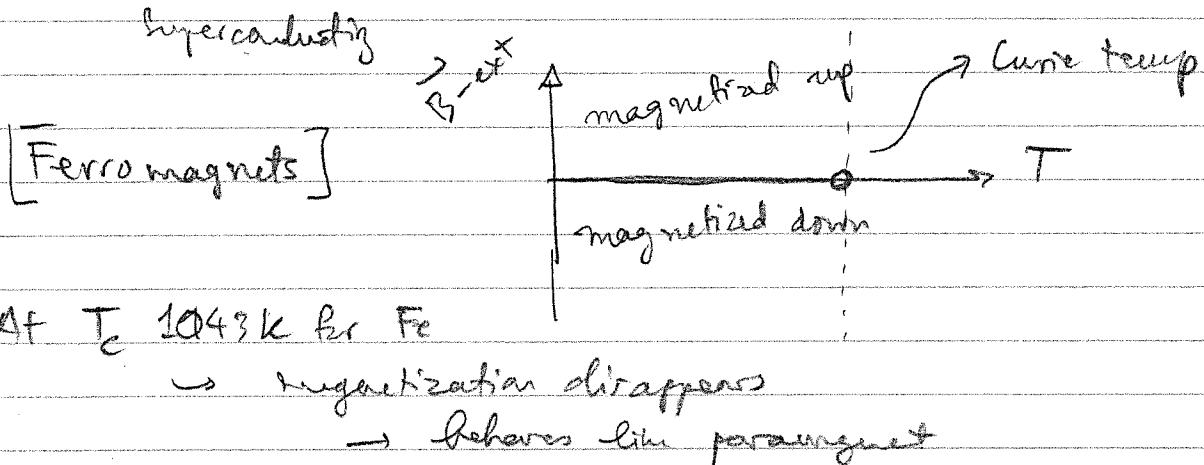
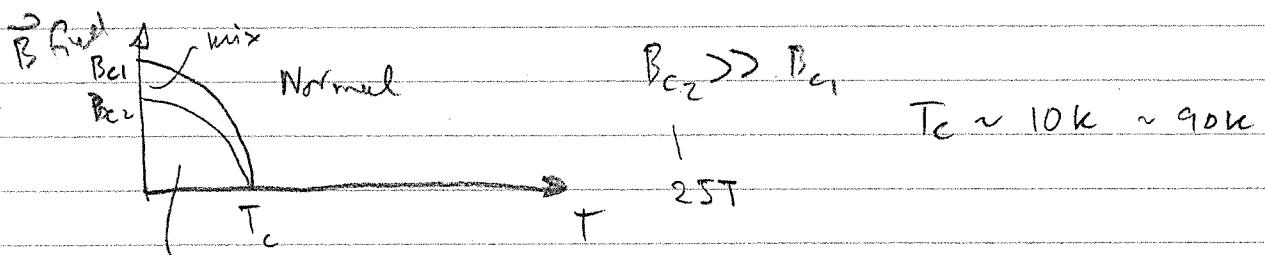
- external  $\vec{B}$  field strength  $\rightarrow$  (Type I superconductor)  
 $(0 \text{ resistivity})$

(Type I superconductor)

Typical  $B_c \sim 0.01 - 0.1 \text{ T}$   
 $T_c \sim 10 \text{ K}$



## Axide Type II - Superconductor



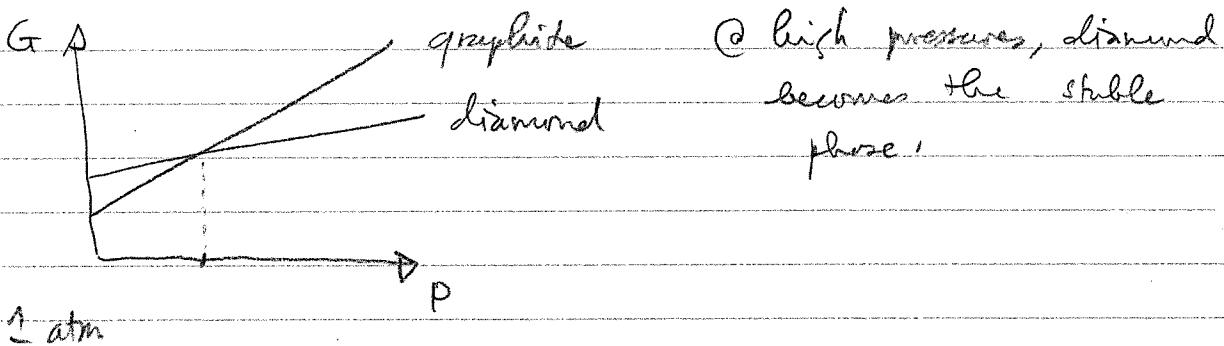
## Using Gibbs free energy to evaluate stable phase for substances

$$dG = -SdT + VdP + \mu dN$$

$$\text{So } \left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad ; \quad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V$$

Ex Diamond vs Graphite. look up  $S_f G$  for both now  $T = 1\text{ atm}$

$S_f G_{\text{graphite}} \approx 2900\text{ J}$  less than  $S_f G_{\text{diamond}} @ 218\text{ K, 1 atm}$

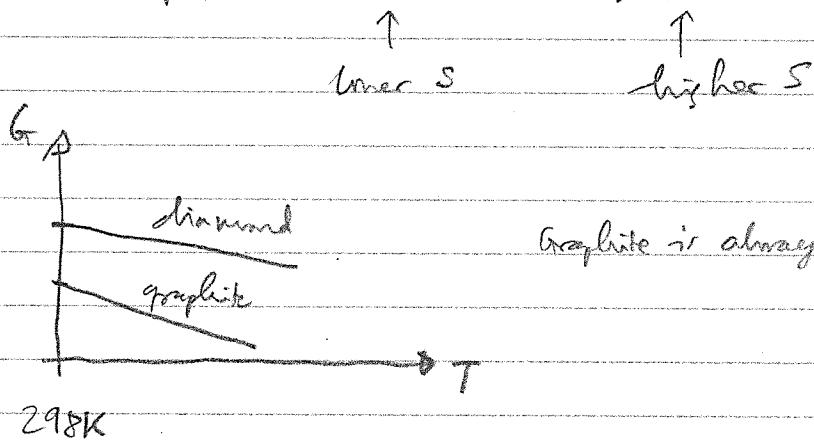


(III)

## Now look at T dependence

$$\left(\frac{\partial G}{\partial T}\right) = -S \text{ as } T \uparrow, G \downarrow$$

Entropy of diamond vs graphite.



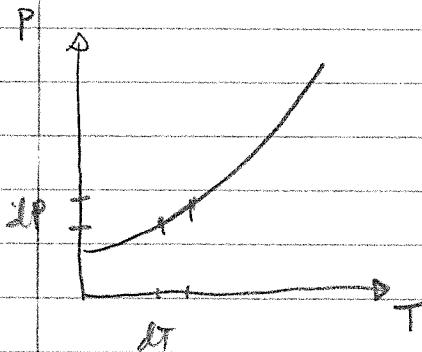
## Clausius - Clapeyron relation

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  $P \times T$  diagram is related to  $S \propto V$  of the two phases...

Phase boundary between liquid, gas

assume 1 mole of substance

On the boundary  $\Delta G_L = \Delta G_g$



increase  $P$  &  $T$  st 2 phases remain in eq.

$$\Delta G = -SdT + VdP + \mu dN^0$$

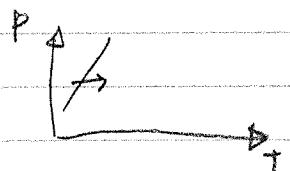
$$\therefore SdT = VdP$$

$$\begin{aligned} \Delta G_L &= -S_LdT + V_LdP \\ \Delta G_g &= -S_gdT + V_gdP \end{aligned} \quad \text{equal}$$

$$\text{So } (V_g - V_e) dP = (S_g - S_e) dT$$

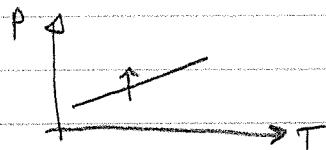
$$\boxed{\frac{dP}{dT} = \frac{S_g - S_e}{V_g - V_e}}$$

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

$$\boxed{\frac{dP}{dT} = \frac{L}{T\Delta V}}$$

$L$ : total latent heat of vaporization  
 $\Delta V = V_g - V_e$

Clausius - Clapeyron Egn.

$L = L/m \rightarrow$  extensive }  $\Rightarrow$  ratio  $\frac{L}{\Delta V}$   $\rightarrow$  intensive.  
 $\Delta V =$  extensive

Example Use Clausius - Clapeyron to explain why H<sub>2</sub>O has negative  $\frac{dP}{dT}$  between solid - liquid phases.

$$\frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{\Delta S}{\Delta V}$$

$$\rho_{sl} = 917 \text{ kg/m}^3, \rho_{liq} = 1000 \text{ kg/m}^3 \rightarrow \text{use 1 mol of H}_2\text{O}$$

$$V_e = m/p = \frac{1000\text{kg}}{1000\text{kg/m}^3} = 1\text{m}^3 \quad V_{ie} = \frac{1000\text{kg}}{917\text{kg/m}^3} = 1.09\text{m}^3$$

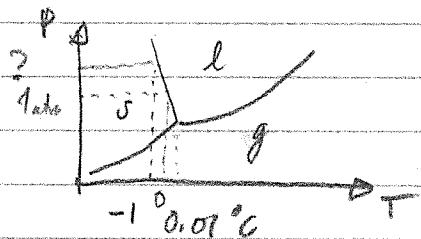
$$(V_e - V_{ie}) = -0.09\text{m}^3$$

As we go from ice to water,  $V \downarrow, ST$

So  $\frac{dP}{dT}$  is negative

$$\text{Assume } L \text{ is constant with } t, T : \frac{dP}{dT} = \frac{333\text{J/g} \times 10^6\text{g}}{(273\text{K})(-0.09\text{m}^3)} = -1.35 \times 10^9 \text{ Pa/K}$$

How much pressure is required to melt ice at  $-1^\circ\text{C}$ ?

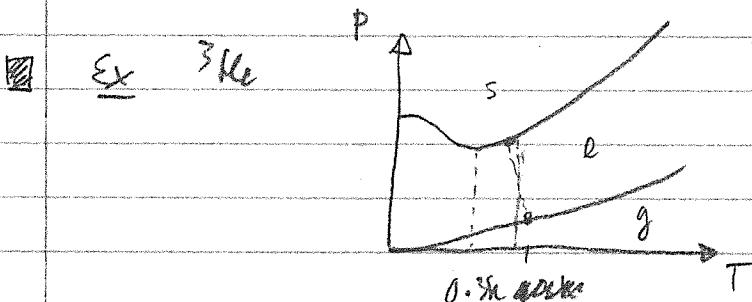


$$\frac{dP}{dT} = -1.35 \times 10^9 \text{ Pa/K}$$

$$dP = (-1.35 \times 10^9 \text{ Pa/K})(-1\text{K})$$

$$dP = 1.35 \times 10^9 \text{ Pa} \approx 135 \text{ atm}$$

$$= 135 \text{ bars}$$



- At  $T < 0.3\text{K}$ , slope between solid - liquid is negative

- Which phase is more dense? Remember that  $(\frac{\partial G}{\partial T})_{P,N} = V$

Solid  ${}^3\text{He}$  is stable phase at high  $P$ , so it must have smaller  $V$ . Shallower  $dG/dP$   
→ Solid is more dense.

Which phase has more entropy?

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} < 0 \quad @ \quad T < 0.3k$$

If  $V \downarrow$  as we go  $l \rightarrow s$ ,  $S^l > S^s$  as we go from  $l \rightarrow s$

↳ solid  $^3He$  has more entropy.

Q: What is the slope of the phase boundary at  $T=0$ ?

3<sup>rd</sup> law: As  $T \rightarrow 0K$ ,  $S \rightarrow$  minimum value.

↳  $\Delta S = 0$  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  $V \rightarrow V - V_b \rightarrow$  can't compress gas to  $V=0$   
 "b" represents volume per particle  
 min volume =  $Nb$  @  $P=\infty$

②  $P \rightarrow P + \frac{\alpha N^2}{V^2}$  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.

$$PE_{\text{mfp}} \propto N/V \Rightarrow PE_{\Sigma} \propto \frac{N}{V} \cdot N$$

$$\Rightarrow PE_{\text{eff}} = -\frac{\alpha N^2}{V}, \text{ negative since it works against KE}$$

• "a" constant depending on type of molecules  $\text{O}_2, \text{O}_3, \text{NO}_2$

$$\bullet \text{To calculate } P, dV = TdS - PdV \Rightarrow P = -\left(\frac{\partial V}{\partial S}\right)_{T=0} \quad (T=0)$$

• Contribution to  $P$  from  $PE$

$$\hookrightarrow P = -\left(\frac{\partial V}{\partial S}\right)_{T=0} \Rightarrow \boxed{P = \frac{NkT}{V-Nb} - \frac{\alpha N^2}{V^2}}$$

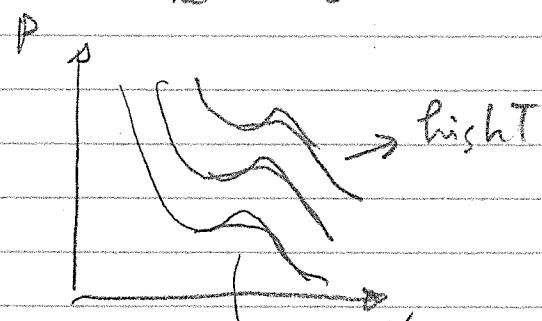
Ex Molecular Interaction  $\text{H}_2\text{O}: b \approx 6 \times 10^{-24} \text{ m}^3 \sim (4\text{\AA})^3$   
 $\text{N}_2$  similar

"a" varies between molecules...  $\text{N}_2: a \sim 2.5 \text{ eV A}^3$

$\text{H}_2\text{O} \sim a_{\text{N}_2}$  due to dipole interaction  
 $\text{He}: a_{\text{He}} < a_{\text{N}_2}$  (nonattractive)

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

$$dG = -SdT + VdP + \mu dN, \text{ fix } T, N = \left(\frac{\partial G}{\partial V}\right)_{T, N} = V \left(\frac{\partial P}{\partial V}\right)_{T, N}$$

$$P = \frac{NkT}{V-Nb} - \frac{\alpha N^2}{V^2} \quad \text{So,}$$

$$V \left( \frac{\partial P}{\partial V} \right)_{T,N} = V \frac{\partial}{\partial V} \left[ \frac{NkT}{V-Nb} - \frac{aN^2}{V^2} \right]$$

$$= V \left[ \frac{-NkT}{(V-Nb)^2} + \frac{2aN^2}{V^3} \right]$$

$$\rightarrow \left( \frac{\partial G}{\partial V} \right)_{T,N} = -\frac{NkTV}{(V-Nb)^2} + \frac{2aN^2}{V^2}$$

$$\therefore dG = \int [ ] dV$$

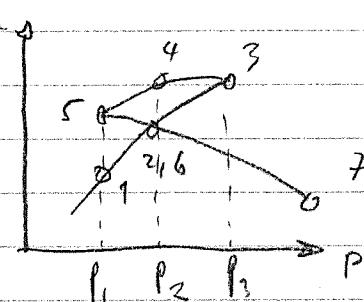
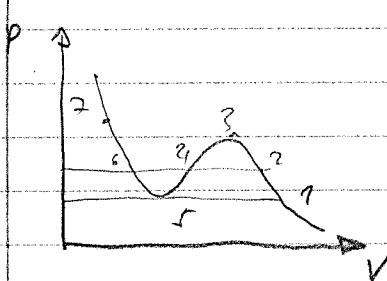
$$= \int -\frac{NkT(V-Nb+Nb)}{(V-Nb)^2} + \frac{2aN^2}{V^2} dV$$

$$= \int -\frac{NkT(V-Nb)}{(V-Nb)^2} - \frac{NkT}{(V-Nb)^2} + \frac{2aN^2}{V^2} dV$$

constant  
of int

$$\rightarrow G = -NkT \ln(V-Nb) + \frac{NkT(Nb)}{(V-Nb)} - \frac{2aN^2}{V} + c(T)$$

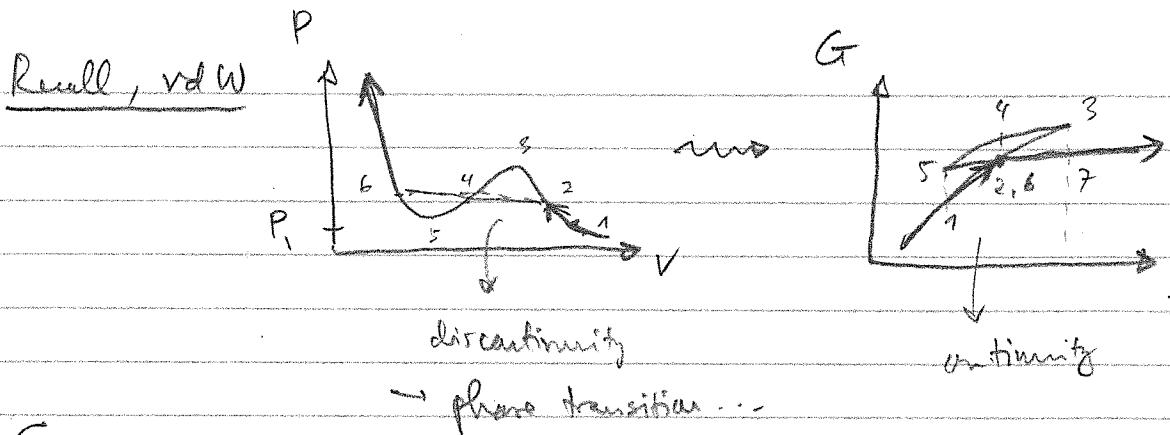
Want to know  $G$  vs.  $P$



- J2 & J6 are unstable.
- Solvent will go directly from vol @ 2  $\rightarrow$  vol @ 6 as it's compressed.
- Discontinuity = phase change.

$$\Delta G \text{ around loop} = 0 \quad \int_{\text{loop}} dG = 0, \quad \left( \frac{\partial G}{\partial P} \right)_T = V \Rightarrow \int \left( \frac{\partial G}{\partial P} \right)_T dP = 0$$

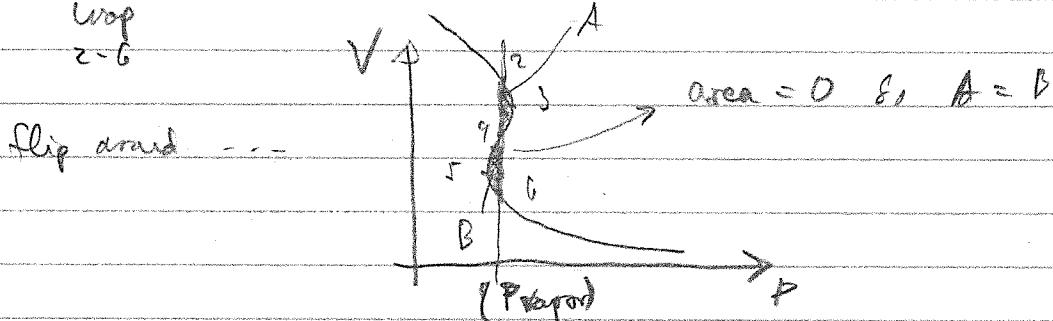
$$\therefore \boxed{0 = \int_{\text{loop}} V dP}$$



$$\int_{\text{loop } 2-6} dG = 0 = \int_{\text{loop } 2-6} dG = 0 \quad \text{where } dG = -SdT + PdV$$

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

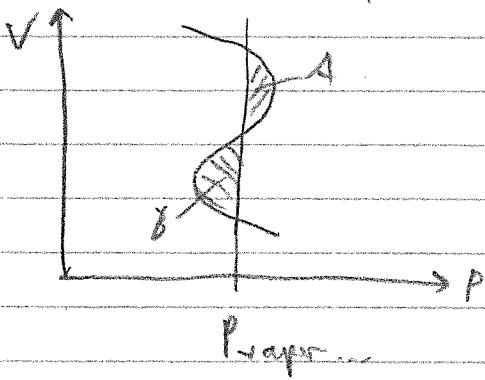
b  $\int_{\text{loop } 2-6} VdP_T = 0$



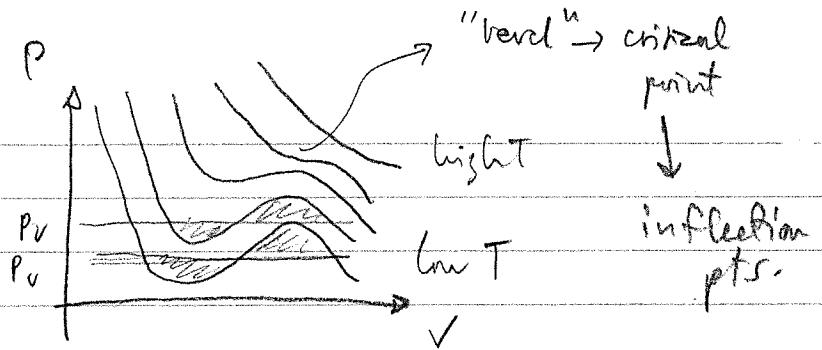
$\rightarrow \text{area}(A) = \text{area}(B)$  for  $\int VdP_T = 0$

$\hookrightarrow$  "Maxwell's construction"

$\Rightarrow$  P of phase transformation occurs where vertical P divides the area in equal halves

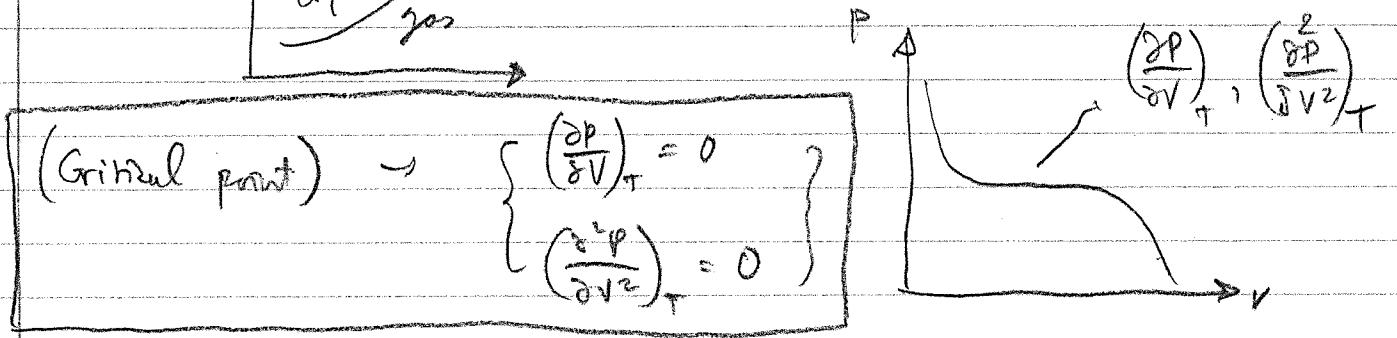


Isotherms at different T



↳ By finding  $P_{\text{cav}}$  based on Isotherms . . .

↳ ↑ or critical point.



{  
T<sub>c</sub> = critical temp. is where 1<sup>st</sup> & 2<sup>nd</sup> derivs of  $\frac{\partial P}{\partial V}$  wrt V are zero. }

### 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-mechanical equilibrium  
 $\rightarrow T_A = T_B = P_A = P_B$

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

$$G = U - TS + PV \quad , \text{ Assume these changes are small}$$

$$\Delta G = \Delta U - T\Delta S + PV$$

Initially,  $G_{\text{tot}}^{\circ} \approx (1-x)G_A^{\circ} + xG_B^{\circ}$

Recall,  $\Delta S_{\text{mixing}} = -Nk[x \ln x + (1-x) \ln(1-x)]$

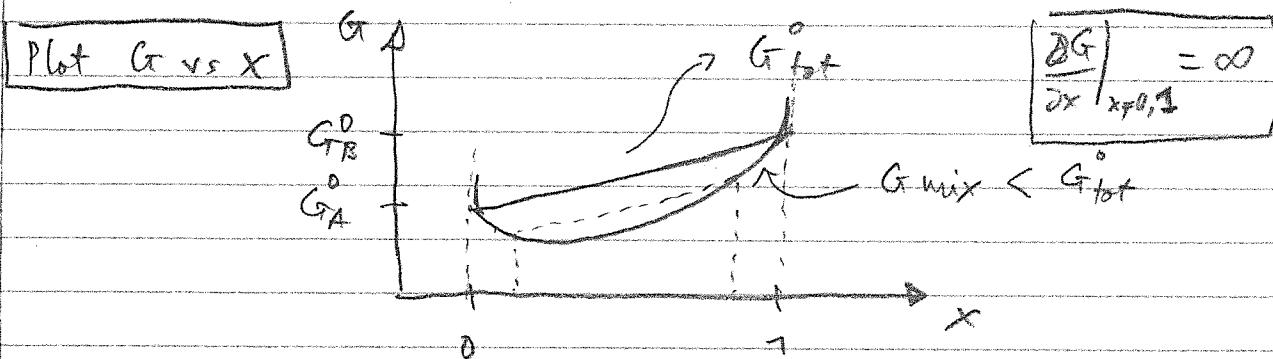
So assuming  $\Delta U = 0$ ,  $\Delta V = 0$ , then,

$$G_{\text{mixed}} = G_{\text{tot}}^{\circ} - T\Delta S$$

$$= G_{\text{tot}}^{\circ} + NkT[x \ln x + (1-x) \ln(1-x)]$$

E  $G_{\text{mixed}} = (1-x)G_A^{\circ} + xG_B^{\circ} + NkT[x \ln x + (1-x) \ln(1-x)]$

→ We call this an ideal mixture  $\Rightarrow$  derived from ideal gas...



• Slope of  $G$  vs.  $x$  @  $0, 1$  is  $\infty$

• mixture (mixed) is always more stable bc of entropy of mixing...

## Phase changes of mixtures

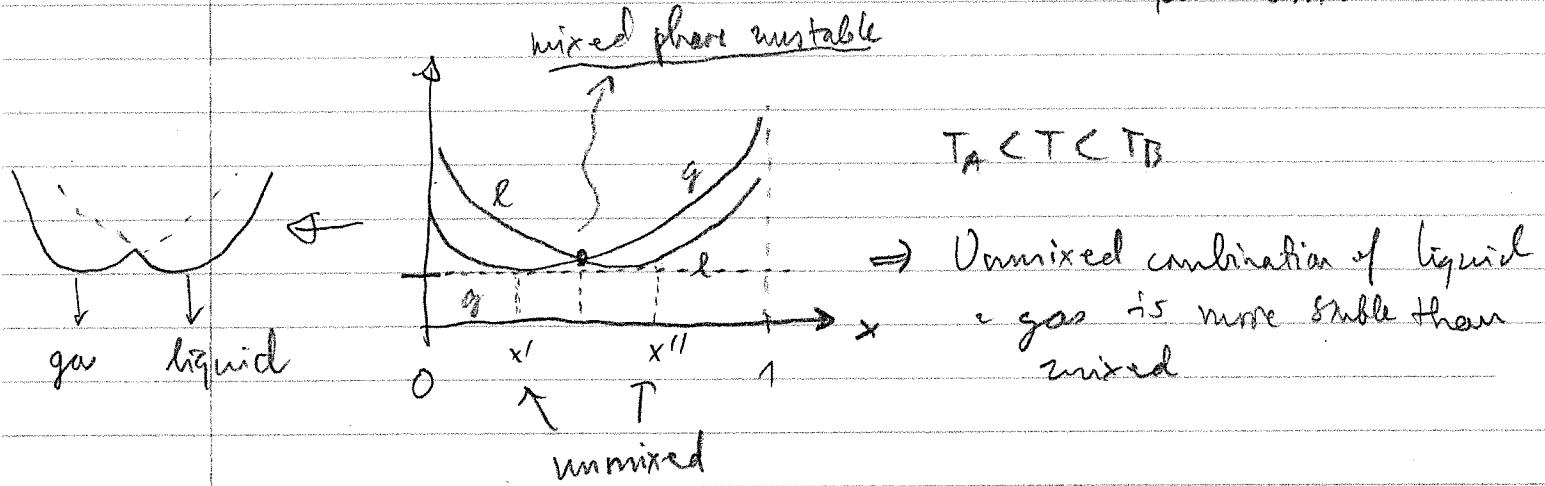
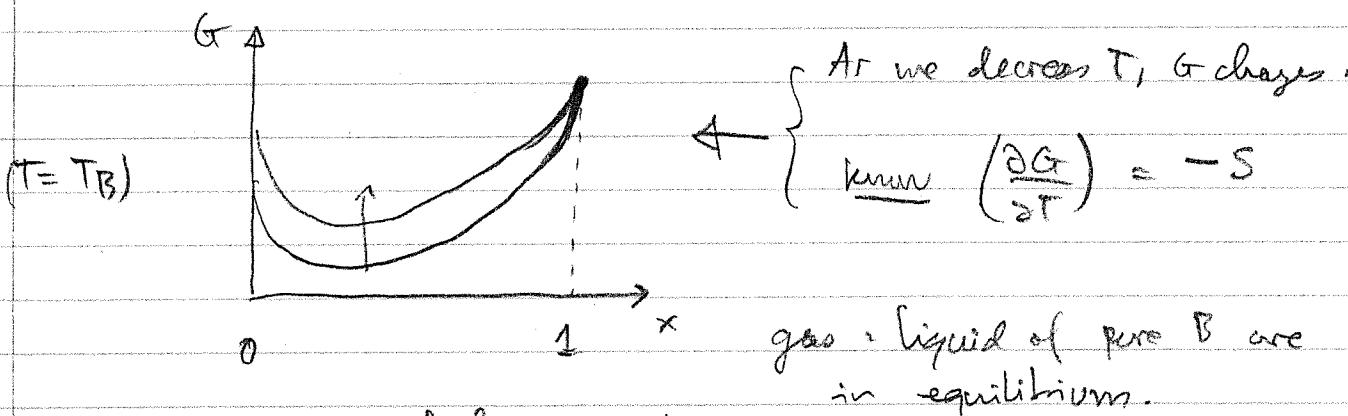
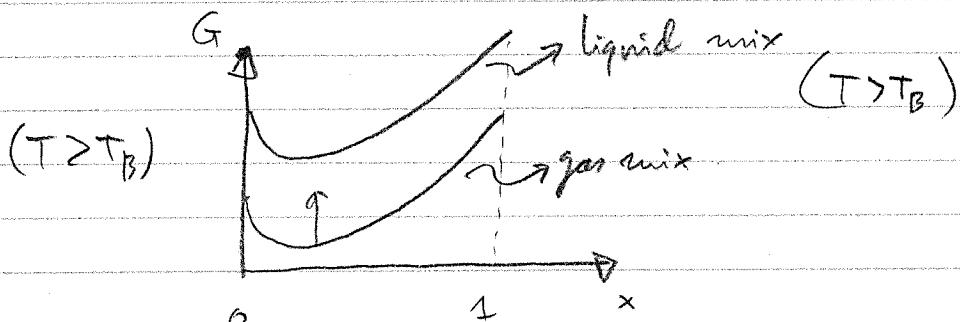
e.g.  $N_2 + O_2$

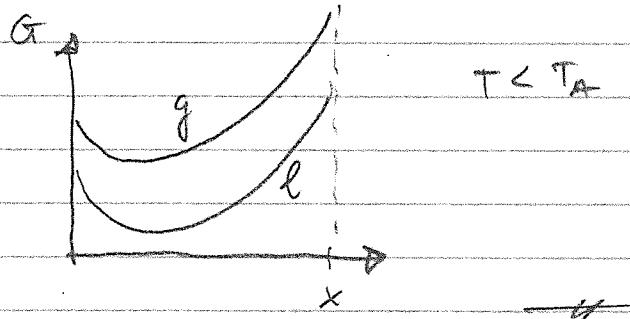
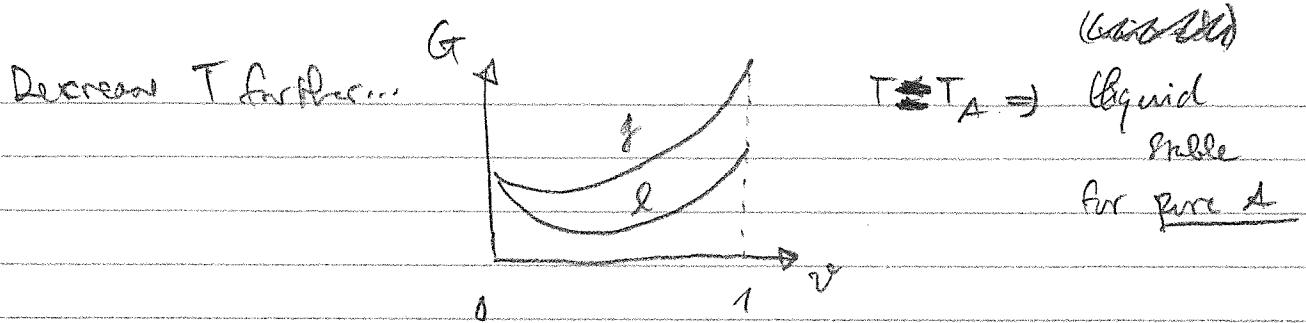
Let  $T_A$  = boiling point of pure substance A

$T_B$  = boiling point of pure substance B

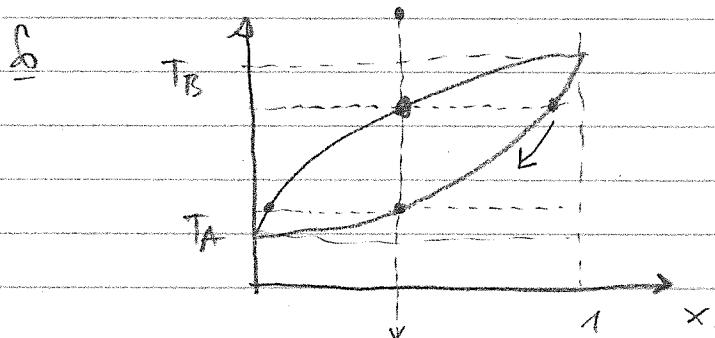
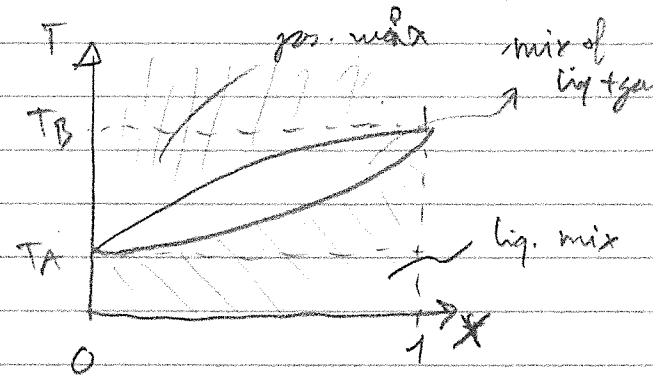
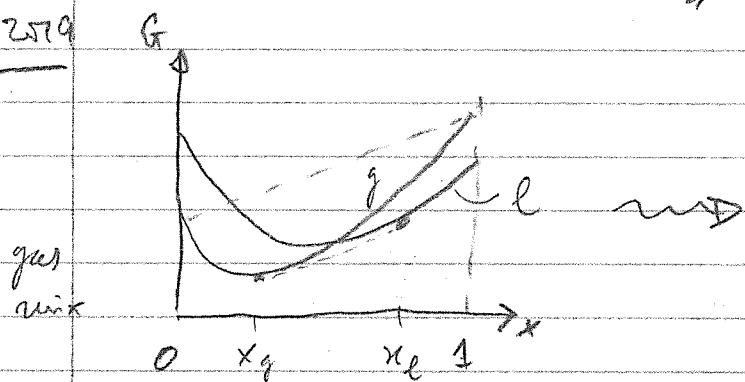
Let  $T_B > T_A$ . Then at high temp.  $T > T_B > T_A$

→ stable phase is a gas regardless of composition ...



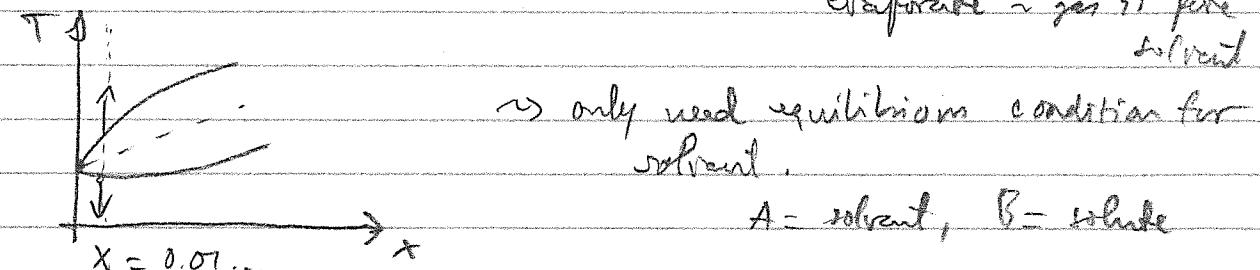


part 15, 2079



as we go down  
in temp

For dilute solutions,  $x$  is small. Thus solute does not evaporate ~ gas is pure solvent



$$\text{Ansatz: } \mu_{A, \text{liq}}(T, P) = \mu_{A, \text{gas}}(T, P) \rightarrow A \text{ in equil.}$$

$$\text{Solvent, } \mu_{A, \text{liq}}(T, P) = \mu_0(T, P) - \frac{N_B k T}{N_A}$$

Also,

$$\mu_0(T, P) - \frac{N_B k T}{N_A} = \mu_{A, \text{gas}}(T, P)$$

Let  $T_0$  be boiling point of pure solvent (A). Hold pressure steady, vary temperature around  $T_0$  to see how  $\mu$  changes.

$$\mu_0(T_0, P) + (T-T_0) \left( \frac{\partial \mu_0}{\partial T} \right) - \frac{N_B k T}{N_A} = \mu_{A, \text{gas}}(T_0, P) + (T-T_0) \left( \frac{\partial \mu_{A, \text{gas}}}{\partial T} \right)$$

at  $T=T_0$ , by assumption  $\mu_{A, \text{gas}}(T_0, P) = \mu_{A, \text{gas}}^0(T_0, P)$  @ eq.  
(assuming gas is pure solvent)

a

$$(T-T_0) \left( \frac{\partial \mu_0}{\partial T} \right) - \frac{N_B k T}{N_A} = (T-T_0) \left( \frac{\partial \mu_{A, \text{gas}}}{\partial T} \right)$$

Also,

$$\mu = \frac{G}{N} \Rightarrow \frac{\partial \mu}{\partial T} = \frac{1}{N} \left( \frac{\partial G}{\partial T} \right)_{V, N} = -\frac{s}{N}$$

b

$$(T-T_0) \left( -\frac{s_{\text{liq}}}{N_A} \right) - \frac{N_B k T}{N_A} = (T-T_0) \left( -\frac{s_{\text{gas}}}{N_A} \right)$$

c

$$(T-T_0) \left[ \frac{s_{\text{gas}}}{N_A} - \frac{s_{\text{liq}}}{N_A} \right] = \frac{N_B k T}{N_A}$$

d

$$(T-T_0) = \frac{N_B k T}{s_{\text{gas}} - s_{\text{liq}}} = \frac{N_B k T}{\Delta s} = \frac{N_B k T}{Q/T_0} = \frac{N_B k T_0}{L}$$

$Q = L = \text{Latent heat}$

Assuming  $T_0 \approx T$

$$\rightarrow T - T_0 = \frac{N_B k T_0^2}{L}$$

e

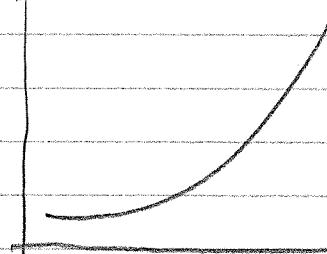
$$T - T_0 = \frac{n_B R T_0^2}{L}$$

shift in boiling point of solvent due to  $n_B$  solute

### Shift in vapor pressure

... (deviation in Boh)

P



Raoult's law

$$\frac{P}{P_0} = 1 - \frac{N_B}{N_A}$$

only for dilute solutions...

### Ch. 6 Boltzmann Statistics

Goal: Get multiplicity for more complicated systems

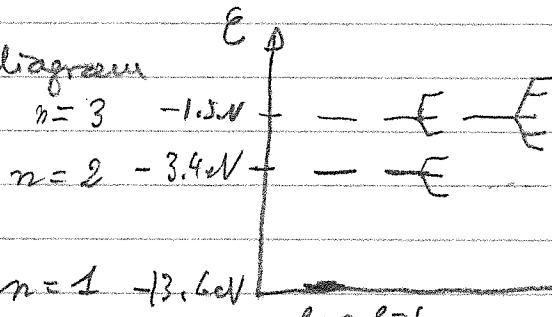
April 16, 2019

~~Ch. 6~~ "System" of a single atom in a reservoir of other atoms at some temperature T

• Macrostate = energy level. These energy levels are degenerate.  
→ multiple microstates.

Ex hydrogen atom.  $n, l, m_l, m_s$

• Energy level diagram



principal quantum number,  $n$  is #  $> 1$

$l = 0, 1, \dots$

$n$  is #  $> 1$

$l$ : orbital angular momentum.  $l$  is 0, 1, ...,  $(n-1)$

$m_l$ : z-component of orbital angular momentum

$$-l \leq m_l \leq l$$

$m_s$ : z-component of spin angular momentum

$$m_s = \pm \frac{1}{2}$$

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 :  $P(A) = \frac{\# A}{\# S_A} \rightarrow \Sigma$

Use ratios instead to avoid #s. Take 2 possible states of atom  
 $s_1 \neq s_2$ .

$E(s_1)$  = 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.

$\Sigma_R(s_i) \rightarrow$  multiplicity of reservoir when atom is in state  $s_i$

$$P_R(s_i) \propto \Sigma_R(s_i) \Rightarrow \frac{P(s_2)}{P(s_1)} = \frac{\Sigma_R(s_2)}{\Sigma_R(s_1)} \quad S = k \ln \Sigma$$

$$S = k \ln \Sigma \rightarrow \boxed{\frac{P(s_2)}{P(s_1)} = \frac{e^{S_R(s_2)/k}}{e^{S_R(s_1)/k}} = e^{\underbrace{(S_R(s_2) - S_R(s_1))}_{\downarrow}/k}}$$

$$dS = \frac{1}{T} [dU + PdV - \nu dN_R]$$

$\uparrow \quad \uparrow \quad \uparrow$

equal & opposite  
to the atoms ...

infinitesimal  
change in entropy of reservoir

$$\rightarrow PdV_R \sim (1\text{ Å})^3 \text{ at 1 atm} \rightarrow (10^5 \text{ Pa})(10^{-10})^3 \approx 10^{-25} \text{ J}$$

$$dV_R \sim \text{few eV} \sim 10^{-11} \text{ J}$$

$$\therefore PdV_R \ll dV_R \rightarrow \text{ignore} \rightarrow dV_R \approx 0$$

$$\text{Also, } dN_R \approx 0$$

reservoir  
...

$$\therefore [S_R(s_2) - S_R(s_1)] = \frac{1}{T_R} [U_R(s_2) - U_R(s_1)]$$

atom ...

$$[S_R(s_2) - S_R(s_1)] = -\frac{1}{T_R} [E(s_2) - E(s_1)]$$

And so,

$$P(s_2) = e^{-[E(s_2) - E(s_1)]/kT}$$

$$\frac{P(s_1)}{P(s_2)} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}}$$

$\Rightarrow$  Boltzmann factor...

$$e^{-E(s)/kT}$$

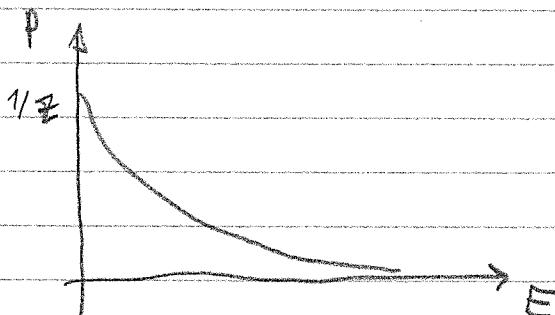
$$\therefore \frac{P(s_2)}{P(s_1)} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}} \Rightarrow \text{must be constant.}$$

$\uparrow$  indep. of  $s_1$        $\downarrow$  indep. of  $s_2$

$$\therefore \frac{P(s_2)}{e^{-E(s_2)/kT}} = \frac{P(s_1)}{e^{-E(s_1)/kT}} = \text{constant} = \frac{1}{Z}$$

$$P(s) = \frac{1}{Z} e^{-E(s)/kT}$$

$\Rightarrow$  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 
$$Z = \sum_s e^{-E(s)/kT}$$
  $\sim$  partition function...

April 17, 2019

constant

$Z \rightarrow$  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  $e^0 = 1$

tiny...

$\rightarrow$  @ low T,  $Z=1 \rightsquigarrow 1$  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...

## Applications of Boltzmann factors

(a) 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.

$$\frac{P(S_2)}{P(S_1)} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}} = e^{-(E_2 - E_1)/kT} \quad \text{Eq}$$

$$\text{For H, } E_2 - E_1 = \Delta E = -3.4\text{eV} - (-13.6\text{eV}) = 10.2\text{eV}$$

$$\text{And } kT = (8.62 \times 10^{-5} \text{eV/K})(5800\text{K}) = 0.50\text{eV}$$

$$\frac{P(S_2)}{P(S_1)} = e^{-10.2\text{eV}/0.50\text{eV}} = 1.4 \times 10^{-9}$$

But we need to add "statistical weights" to account for degeneracy of energy levels ...

$$\begin{aligned} g_2 &= 8 \quad (2n^2) \quad \& P(E_2)/P(E_1) &= \frac{g_e}{g_1} \cdot e^{-\Delta E/kT} \\ g_1 &= 2 \\ &= 4 \left[ 1.4 \times 10^{-9} \right] \\ &= 5.6 \times 10^{-9} \end{aligned}$$

**Caveat**

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. Salts eqn i:

$$\frac{\text{pressure} \rightarrow \text{H ionized}}{P_{\text{H neutral}}} = \frac{1}{ne} \left( \frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-E_I/kT}$$

— 4 —

Average values

S 5.2.

$$P(s) = \frac{1}{Z} e^{-E(s)/kT} = \frac{1}{Z} e^{-\beta E(s)}$$

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 real atoms, 2 in ground, 2 in 1<sup>st</sup> state,  
1, in 2<sup>nd</sup> state.

Average energy of all 5 atoms is:

$$\bar{E} = \frac{0 \cdot 2 + 4 \cdot 2 + 7 \cdot 1}{5} = \frac{11eV}{5} = 2.2eV \dots$$

or

$$E = \left( \frac{2}{5} \cdot 0eV \right) + \left( \frac{2}{5} \cdot 4eV \right) + \left( \frac{1}{5} \cdot 7eV \right)$$

$$= P(0), 0eV + P(1), 4eV + \dots$$

Generalise

$$\bar{E} = \sum_s E(s) N(s) = \sum_s E(s) \frac{N(s)}{N} = \sum_s E(s) P(s)$$

So  $\bar{E} = \frac{1}{Z} \sum_s E(s) e^{-\beta E(s)}$

Can do this for avg values of any property

$$\bar{X} = \sum_{s=1}^z X(s) P(s) = \frac{1}{z} \sum_{s=1}^z X(s) e^{-\beta E(s)}$$

Also note that average values are additive ...

if  $\bar{E}$  is avg value of single atom, so in general,

$$\langle u \rangle = N \bar{E} \quad \rightarrow \text{avg energy of ensemble of } N \text{ particles}$$

Calculate deviation about the mean

For our 5 atoms @ 3 energy level  $\bar{E} = 3 \text{ eV}$  ... then the difference from the mean

$$2 \text{ atoms } @ 0 \text{ eV} : \Delta E = E_1 - \bar{E} = 0 - 3 \text{ eV} = -3 \text{ eV}$$

$$2 \text{ atoms } @ 4 \text{ eV} : \Delta E = E_2 - \bar{E} = 4 - 3 = 1 \text{ eV}$$

$$= 4 \text{ eV}$$

$(\Delta E)^2 \rightarrow$  average of the square deviation

$$\bar{\Delta E}^2 = \frac{(-3)^2 \cdot 2 + (1)^2 \cdot 2 + 4^2}{5} = 7.2 \text{ eV}^2$$

Then,  $\sqrt{\bar{\Delta E}^2} = \text{rms/ std dev} \dots = \sigma_E = \sqrt{7.2 \text{ eV}^2} = 2.7 \text{ eV}$

But we observed that

$$\sigma_E^2 = \bar{E}^2 - \bar{E}^2$$

For any system 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

$$-\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{1}{Z} \sum_s +E(s) e^{-\beta E(s)} = \sum_s \left( \frac{1}{Z} E(s) e^{-\beta E(s)} \right) = \sum_s E(s) \cdot p(s)$$

$$\text{So} \quad -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \bar{E}$$

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  $\Rightarrow W = \int F \cdot dx \approx \sum F_i \Delta x$   
where  $F_i \rightarrow$  i.e. change in Energy w.r.t  $x$ .

$$F = \frac{\partial E_s}{\partial x}$$

$$\sum_s \frac{\partial E_s}{\partial x} e^{-\beta E(s)} \Delta x$$

. Work done on system  $W = \frac{\sum_s \frac{\partial E_s}{\partial x} e^{-\beta E(s)} \Delta x}{\sum_s e^{-\beta E(s)}}$

Re-write numerator

$$\sum_s e^{-\beta E(s)} \frac{\partial E(s)}{\partial x} = -\frac{1}{\beta} \frac{\partial}{\partial x} \left( \sum_s e^{-\beta E(s)} \right)$$

So

$$\begin{aligned} \cancel{\sum_s e^{-\beta E(s)} \frac{\partial E(s)}{\partial x}} &= \frac{-1}{\beta} \frac{\partial}{\partial x} \left( \sum_s e^{-\beta E(s)} \right) \\ &= \frac{-1}{\beta} \frac{\partial z}{\partial x} \end{aligned}$$

So,

$$W = \frac{-1}{\beta} \frac{\partial z}{\partial x} dx / z$$

or

$$W = \frac{-1}{\beta} \frac{\partial z}{z} dx = \frac{-1}{\beta z} \frac{\partial z}{\partial x} dx = \frac{-1}{\beta} \frac{\partial \ln z}{\partial x} dx$$

So

$$W_{on} = \frac{-1}{\beta} \frac{\partial \ln z}{\partial x} dx$$

For example,  $x = V$  (volume)

$$W_{on} = -\bar{P} dV = \frac{-1}{\beta} \frac{\partial \ln z}{\partial V} dV$$

or

$$\bar{P} = \frac{1}{\beta} \frac{\partial \ln z}{\partial V}$$

How is  $z$  related to  $s$ ?

$z = z(\beta, x)$ . For small changes in  $z$ ,

$$d \ln z = \underbrace{\frac{\partial \ln z}{\partial x} dx}_{\text{ }} + \underbrace{\frac{\partial \ln z}{\partial \beta} d\beta}_{\text{ }}$$

or

$$d \ln(z) = -\beta W_{on} + -\bar{E} d\beta$$

$\uparrow$

$dW_{on}$

$$\text{Re-writing } d\ln Z = -\beta dW - d(\bar{E}_P) + \beta d\bar{E}$$

$$\text{So } d(\ln Z + \bar{E}_P) = \beta (\underbrace{d\bar{E} - dW}_{dQ \text{ (First law)}}) = \beta dQ = \frac{dQ}{kT} = \frac{1}{k} dS$$

$$\text{So } d(\ln Z + \bar{E}_P) = \frac{dS}{k}$$

$$\text{Now, } S = k \ln Z$$

$$\boxed{S = k(\ln Z + \beta \bar{E})}$$

$$\text{So } \ln Z + \beta \bar{E} = \ln Z$$

$$\boxed{\ln Z = \ln Z - \beta \bar{E}}$$

### Example of paramagnetism

$$\hookrightarrow \text{Before: } \textcircled{1} \quad Z(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!}$$

$$\textcircled{2} \quad S = k \ln Z \quad (\text{use sterling approximation})$$

$$\textcircled{3} \quad \frac{1}{T} = \left( \frac{\partial S}{\partial T} \right)$$

$$\textcircled{4} \quad U = 0(+) \rightarrow u = -N_\uparrow \beta \tanh\left(\frac{\mu}{kT}\right)$$

$$\textcircled{5} \quad M = -\frac{u}{B}$$

$$\textcircled{6} \quad C_B = \left( \frac{\partial U}{\partial T} \right)_B$$

Now, we'll redo this with Boltzmann statistics... Two possible energy states...

$$\begin{aligned} \text{"up"} \quad \mu &= -\mu B \\ \text{"down"} \quad \mu &= \mu B \end{aligned} \quad \left. \right\} \text{ then } Z = \sum_i e^{-\beta E(i)} = e^{-\beta(-\mu B)} + e^{-\beta(\mu B)} = e^{\mu B} + e^{-\mu B}$$

$$\text{So, } \boxed{Z = 2 \cosh(\mu B)}$$

Q) Probability of finding in up / down direction.

$$P_U = \frac{e^{-\beta \mu B}}{2 \cosh(\mu B \beta)} \quad , \quad P_D = \frac{e^{\beta \mu B}}{2 \cosh(\mu B \beta)}, \quad P_U + P_D = 1$$

Average energy of a dipole

$$\begin{aligned} \bar{E} &= \sum E(s) P(s) = (-\mu B) \frac{e^{\beta \mu B}}{2 \cosh(\mu B \beta)} + (\mu B) \frac{e^{-\beta \mu B}}{2 \cosh(\mu B \beta)} \\ &= (\mu B) \frac{2 \tanh(\mu B \beta)}{2 \cosh(\mu B \beta)} \\ &= -\mu B \tanh(\mu B \beta) \end{aligned}$$

$\therefore \bar{E} = -\mu B \tanh(\mu B \beta)$

$\therefore \boxed{E_{\text{int}} = -N \mu B \tanh(\mu B \beta) = -N \mu B \tanh\left(\frac{\mu B}{kT}\right)}$

Alternate approach

$$\begin{aligned} \bar{E} &= \frac{-1}{Z} \frac{\partial Z}{\partial \beta} \\ &= \frac{-1}{Z} \frac{\partial}{\partial \beta} \left[ 2 \cosh(\mu B \beta) \right] \\ &= \frac{-1}{Z} \cdot 2 \left( \mu B \sinh(\mu B \beta) \right) \\ &= (2 \mu B) \frac{-1}{2 \cosh(\mu B \beta)} \cdot \sinh(\mu B \beta) \\ &= -\mu B \tanh(\mu B \beta) \end{aligned}$$

$\therefore \boxed{\bar{E}_{\text{int}} = -N \mu B \tanh(\mu B \beta)}$

Magnetization  $\Rightarrow M = N \bar{\mu}_x + \bar{\mu}_z = \sum \mu_s P(s) \dots$

$$= \mu P_U + (-\mu) P_D$$

April 22, 2019

## The Equipartition Theorem

G applies to systems with quadratic degrees of freedom.

$$\rightarrow E = \frac{P^2}{2m}$$

$$E = cq^2 \text{ where } q = \text{position or momentum coordinate}$$

- $Z = \sum_q e^{-\beta cq^2}$ , and assuming that the spacing  $\Delta q$  is constant and small...

$$\therefore Z = \frac{1}{\Delta q} \sum_q e^{-\beta cq^2} \Delta q$$

$$= \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta cq^2} dq$$

Change of variable: Let  $x = \sqrt{\beta c} \cdot q \rightarrow x^2 = \beta cq^2$

$$dq = \frac{dx}{\sqrt{\beta c}}$$

$$\therefore Z = \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-x^2} dx \cdot \frac{1}{\sqrt{\beta c}} = \frac{1}{\Delta q} \frac{1}{\sqrt{\beta c}} \int_{-\infty}^{\infty} e^{-x^2} dx \quad \begin{matrix} \nearrow \text{assumption} \\ \nearrow \end{matrix}$$

$$Z = \frac{\sqrt{\pi}}{\Delta q \sqrt{\beta c}}$$

(\*) As long as  $\Delta q \ll kT$ , the equipartition holds (high temp)

$$\boxed{Z = \frac{1}{\Delta q} \sqrt{\frac{\pi}{\beta c}}}$$

Or equivalently,

$$\boxed{Z = C \beta^{-1/2}}$$

$C$  is some constant...

$$\therefore E = \frac{1}{2} \frac{\partial Z}{\partial \beta} = \frac{-1}{C \beta^{-1/2}} \left( \frac{-1}{2} C \beta^{-3/2} \right) \Rightarrow \boxed{E = \frac{1}{2} \beta^{-1}}$$

$$\therefore \boxed{E = \frac{1}{2} kT}$$

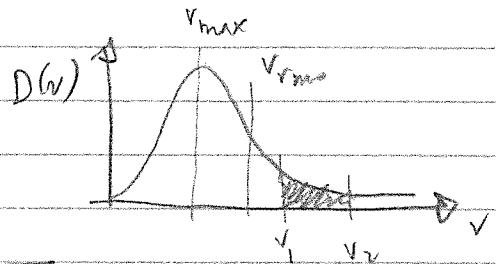
$\rightarrow$  Eq. partition theorem for sys k df.

## Note Conditions

☒ Equipartition doesn't hold for quantum mechanical system,  
since it requires a continuum of  $\Delta E$ .

☒ Equipartition holds if  $\Delta E \ll kT$  (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  $\vec{v}$  -  $\Rightarrow$  # of vectors  $\vec{v}$  corresponding to speed  $v$ .

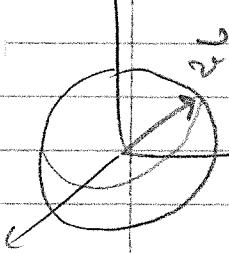
$$D(v) \propto \underbrace{\left( \text{prob. of molecule w/ velocity } \vec{v} \right)}_{\boxed{?}} \times \underbrace{\left( \# \text{ of vectors, } \vec{v} \text{ corresponding to speed } v \right)}_{\text{as } \boxed{??}}$$

know,

$$\boxed{?} \propto \text{ Boltzmann factor } \cdot E = \frac{1}{2}mv^2 \rightarrow = e^{-mv^2/2kT}$$

$$\boxed{?} \propto 4\pi v^2$$

$\rightarrow$  larger  $v$ , more surface area, higher  $\Sigma$  for  $\vec{v}$ .



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 ...

$$1 = 4\pi C \int_0^\infty x^2 e^{-x^2} dx \left( \sqrt{\frac{2kT}{m}} \right)^3$$

$$= 4\pi C \cdot \left( \frac{2kT}{m} \right)^{3/2} \int_0^\infty x^2 e^{-x^2} dx$$

$\underbrace{\qquad\qquad\qquad}_{\sqrt{\pi}/4}$

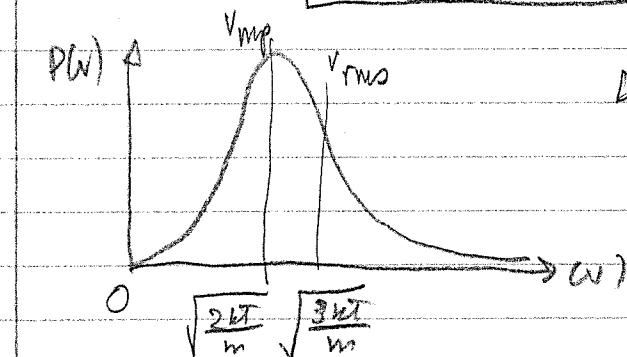
Q

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

Maxwell's speed distribution ...

Thus,

$$D(v) = 4\pi v^2 \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT}$$



$$D(v) = 0 @ v=0 - v \rightarrow \infty$$

Q Calculate  $v_{mp}$  (most probable)

$$0 = \frac{d}{dv} D(v) = 0 \rightarrow 0 = \frac{d}{dv} \left[ v^2 e^{-mv^2/2kT} \right]$$

Q

$$0 = 2v e^{-mv^2/2kT} + v^2 \cdot \left( \frac{-mv}{kT} \right) e^{-mv^2/2kT}$$

$$= 2v + \frac{-mv^3}{kT} \Rightarrow 0 = 2 - \frac{mv^2}{kT} \Rightarrow$$

$$v_{mp} = \sqrt{\frac{2kT}{m}}$$

8) Calculate  $\bar{v}$

$$\bar{v} = E(v) = \int_0^\infty v D(v) dv = \int_0^\infty 4\pi v^3 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} dv$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^3 e^{-\frac{mv^2}{2kT}} dv$$

$$\bar{v} = \left(\frac{m}{2\pi kT}\right)^{3/2} (4\pi) \cdot \frac{1}{2} \left(\frac{2kT}{m}\right)^2$$

$$\therefore \bar{v} = \left(\frac{2kT}{m}\right)^{1/2} \cdot \frac{2}{\sqrt{\pi}}$$

$$\therefore \boxed{\bar{v} = \left(\frac{8kT}{m\pi}\right)^{1/2}}$$

$$M = m N_A$$

Ex N<sub>2</sub> in air @ room temp ... T ~ 298 K, m<sub>N<sub>2</sub></sub> = 14 g/mol  
 $m_{N_2} = 28 \text{ g/mol}$

$$\bar{v}_{mp} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2(1.38 \times 10^{-23})(298K)}{28 \times 10^{-3} \text{ kg/mol} / 6.023 \times 10^{23}}} \approx \boxed{420.5 \text{ m/s}}$$

April 23, 2019

PARTITION FUNCTION = FREE ENERGY

$\Omega(u)$  @ const u  $\Rightarrow S$  tends to T,  $S = k \ln \Omega$

$Z(T) \leftrightarrow F$  @ constant T

Recall  $F = U - TS \rightarrow \frac{F-U}{T} = -S$

$$dF = -PdV - SdT + \mu dN \rightarrow \left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$$

$$\therefore \left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{F-U}{T} \quad \textcircled{1}$$

Guess  $\tilde{F} = -kT \ln Z \Rightarrow Z = e^{-\tilde{F}/kT}$

Check deriv w.r.t T:  $\frac{\partial}{\partial T} \tilde{F} = \frac{\partial}{\partial T} (-kT \ln Z)$

$$= -k \ln Z - kT \frac{\partial}{\partial T} \ln Z$$

$$= -k \ln Z - kT \underbrace{\frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \ln Z}_{\frac{-1}{kT^2} \frac{1}{Z} \frac{\partial Z}{\partial \beta}}$$

$$\Rightarrow \frac{\partial \tilde{F}}{\partial T} = -k \ln Z - \frac{U}{T}$$

$$\frac{\partial \tilde{F}}{\partial T} = \frac{\tilde{F}}{T} - \frac{U}{T} = \frac{\tilde{F} - U}{T}, \text{ same as (1), so } -U$$

$\gg$  we know given

were correct, except there might be a constant

Check initial condition (to determine constant)

$$F = 0 - TS \quad \text{Let's use } T=0 \rightarrow \text{then } F(T=0) = U.$$

$$\begin{aligned} Z(T=0) &= \psi_0 \sum_S e^{-F(S)/kT} \\ &= e^{-U_0/kT} + \text{high order terms, negligible because } U \gg kT \end{aligned}$$

$T$   
lowest possible  
energy,

$$\therefore \tilde{F}(T=0) = -kT \ln Z = -kT(u_0/kT) = -U_0$$

$$\therefore \tilde{F}(T=0) = U_0 \text{ no constant!}$$

S  $F = -kT \ln Z$

$$dF = -pdV - SdT + \mu dN$$

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

Example

$$\left( \frac{\partial F}{\partial T} \right)_{V,N} = -S \quad F = -kT \ln Z, \quad S = -\frac{\partial}{\partial T} (-kT \ln Z)$$

$$S = -\frac{\partial}{\partial T} (-kT \ln Z) = k \ln Z + \frac{\partial P}{\partial T} \frac{\partial}{\partial P} \ln Z$$

$$= k \ln Z + \frac{E}{T}$$

$\hookrightarrow S = k (\ln Z + \beta E)$  ✓ 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

1<sup>st</sup>: determine how  $Z_{\text{tot}}$  depends on  $Z$  for each individual particle -

Start w/ system off 2 particles. If they do not interact, total energy

$$E_{\text{tot}} = E_1 + E_2$$

$$Z_{\text{tot}} = \sum_c e^{-\beta [E_1(c) + E_2(c)]} = \sum_s e^{-\beta E_1(s)} e^{-\beta E_2(s)}$$

If we also assume that states of individual particles are independent of each other:

$$Z_{\text{tot}} = \underbrace{\sum_s e^{-\beta E_1(s)}}_{Z_1} \underbrace{\sum_s e^{-\beta [E_2(s)]}}_{Z_2} \Rightarrow Z_{\text{tot}} = Z_1 Z_2$$

(non-interacting distinguishable system particles)

If particles are indistinguishable, we have double counted states.

$$\hookrightarrow Z_{\text{tot}} \approx \frac{1}{2} Z_1 Z_2$$

$$\text{or } Z_{\text{tot}} = Z_1^N$$

Generalize this to  $N$  particles  $\rightarrow Z_{\text{tot}} = Z_1 Z_2 \dots Z_N$  distinguishable

For distinguishable

$$Z_{\text{tot}} = \frac{1}{N!} Z_1^N$$

