

GET entropy of ideal gas from TEMP

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, N} \rightarrow T \text{ quantity of}$$

2 systems in thermodynamic
Equilibrium, \neq EXCHANGING
ENERGY ONLY
V & N of EACH SYSTEM
FIXED.

$$\text{ideal gas} - \left(\frac{\partial S}{\partial U} \right)_{N, V} = \frac{\partial}{\partial U} \left(NK \ln U^{3/2} + U \text{ INDEP STUFF} \right)$$

$$= \frac{3}{2} NK \left(\frac{\partial \ln U}{\partial U} + 0 \right)$$

$$= \frac{3}{2} NK \frac{1}{U} = \frac{1}{T}$$

$$U = \frac{3}{2} NKT \leftarrow \text{which we already knew}$$

Gibbs Paradox

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

for 2 different gases too

$$S_1 = N_1 k \left[\ln \left(\frac{V_1}{N_1} \left[\frac{4\pi m u}{3N_1 h^2} \right]^{3/2} \right) + \frac{5}{2} \right]$$

$$S_2 = N_2 k \left[\ln \left(\frac{V_2}{N_2} \left[\frac{4\pi m u}{3N_2 h^2} \right]^{3/2} \right) + \frac{5}{2} \right]$$

$$V_1 = V_2, N_1 = N_2$$

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

but take doubling the amount of gas \rightarrow "two" gases are identical

remains same.

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

double \rightarrow

$$\frac{u}{N} \rightarrow \frac{2u}{2N} = \frac{u}{N} \quad \text{unchanged}$$

but have $\ln \left(\frac{2V}{2N} \right) \dots$

see over.

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

so entropy is

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

↑
original
entropy

so it doesn't double by factor

$$\underbrace{2Nk \ln 2}_{\text{entropy of mixing}}$$

$$S_{\text{FINAL}} = S_{\text{INITIAL}} + Nk \ln 2$$

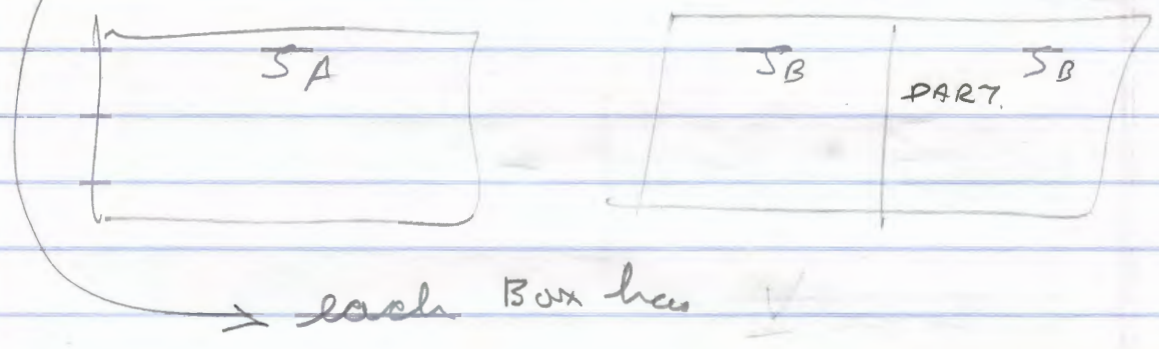
where does $\ln \left(\frac{V}{N} \right)$ this N come from

— from $\frac{1}{N!}$ → in multiply to account for INDISTINGUISHABLE

If didn't have N factorial

$$S_A = Nk \left[\ln \left(V \left(\frac{4\pi m u}{3Nh^2} \right)^{3/2} \right) + \frac{3}{2} \right]$$

DISTINGUISHABLE



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

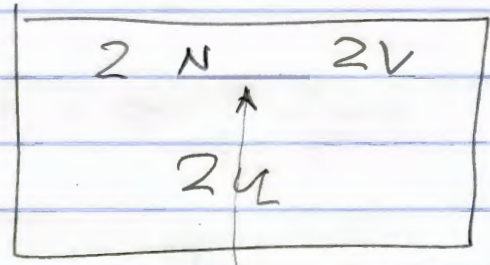
$$S_B < \frac{S_A}{2}$$

Violates second law.

Gibbs realized how to have $\frac{1}{N!}$

↳ before Quantum mechanics and understanding of INDISTINGUISH

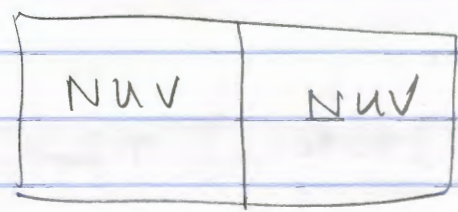
↳ $N!$ NOT there



insert partition

insert partition adiabatically

↳ do no WORK



↑ has lower entropy

Gibbs did NOT believe that you

can LOWER ENTROPY ADIABATICALLY

GENERAL PROCEDURE

MICRO \rightarrow MACRO

Description

for any ISOLATED SYSTEM.

- Assume one knows MICROSCOPIC THEORY

this TELLS us.

$$U = \sum_{i=1}^N \left(\begin{array}{c} \text{kinetic} \\ \text{energies} \end{array} \right) + \sum_{i \neq j}^N \left(\begin{array}{c} \text{interaction energies} \\ \text{between particles} \end{array} \right) + \sum_{i=1}^N \left(\begin{array}{c} \text{potential energy} \\ \text{in external field} \end{array} \right)$$

- then assuming one can find

the number of ACCESSIBLE MICROSTATES

$$= \Omega(U, N, V)$$

Can calculate MACROSCOPIC QUANTITIES.

$$S = k \ln \Omega(u, N, V)$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial u} \right)_{N, V} (u, N, V) \rightarrow \text{solve for } u$$

MEASURABLE QUANTITY

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

u - MICROSCOPIC

Example - for ideal gas, we get

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

$$\frac{du}{dT} = \frac{3}{2} Nk \rightarrow C_V$$

(7)

SO FAR — Considered thermodynamic Equilibrium
between systems only allowed to

Exchange Energy

Condition that TOTAL ENTROPY
EXTREMIZED in thermodynamic

Equilibrium

$$\frac{1}{T_1} = \left(\frac{\partial s_1}{\partial u_1} \right)_{N_1, V_1}$$

$$\frac{1}{T_2} = \left(\frac{\partial s_2}{\partial u_2} \right)_{N_2, V_2}$$

should be
EQUAL

this also yielded

STATISTICAL DEFINITION
OF

TEMPERATURE

Can use analogous procedure to get

STATISTICAL DEFINITIONS of

- PRESSURE

- CHEMICAL POTENTIAL

by maximizing S at thermodynamic Equilibrium with

"Exchange of Volume" \rightarrow Mechanical Equilibrium.

\rightarrow Equal pressure

"Exchange of Particles" \rightarrow Chemical Equilibrium

Chemical Potential — energy absorbed or

emitted by change in PARTICLE NUMBER

of a given SPECIES.

$$U_1, N_1, V_1$$

$$U_2, N_2, V_2$$

$$U_1 + U_2 = U \leftarrow \text{fixed}$$

put them together

U_1'	U_2'
N_1, V_1	N_2, V_2

$$U_1' = U - U_2'$$

2nd Law says that in thermodynamic Equilibrium Combined Entropy is a maximum.

$$S_{1+2} = S_1(U - U_2', N_1, V_1) + S_2(U_2', N_2, V_2)$$

Should be extremum w.r.t U_2'

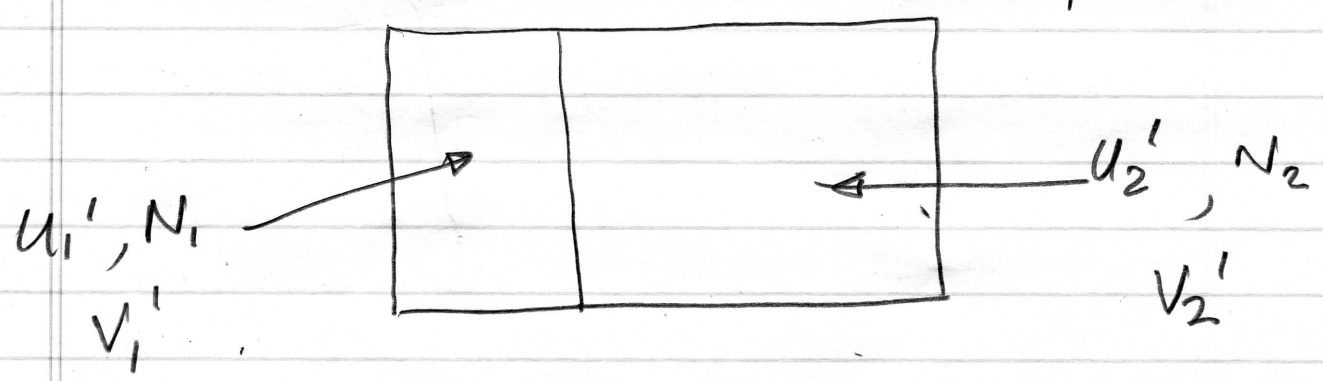
$$0 = \frac{\partial}{\partial u_2'} [S_1 + S_2] = \frac{\partial S_1}{\partial u_1'} (u_1', N_1, V_1) \Big|_{u_1' = u - u_2'} + \frac{\partial S_2}{\partial u_2'} (u_2', N_2, V_2)$$

$$\frac{\partial S_1}{\partial u_1'} (u_1', N_1, V_1) \Big|_{u_1' = u - u_2'} = \frac{\partial S_2}{\partial u_2'} (u_2', N_2, V_2)$$

MECHANICAL EQUILIBRIUM.

↳ allow energy AND volume to change.

↳ moving partition



How to find u_1', u_2', v_1', v_2'

such that $u_1' = u - u_2'$

$v_1' = v - v_2'$

initial values

$u = u_1 + u_2$

$v = v_1 + v_2$

POSTULATE! S_{1+2} should be extremum

w.r.t both u_2' and v_2' | u, v fixed.

$$S_{1+2} = S_1(u - u_2', N_1, v - v_2')$$

$$+ S_2(u_2', N_2, v_2')$$

for $f(x, y)$ to have extremum: $\vec{\nabla} f = 0$

$$\frac{\partial f}{\partial x}(x, y) \Big|_{y \text{ const}} = 0$$

and $\frac{\partial f}{\partial y}(x, y) \Big|_{x \text{ const}} = 0$

Extremum of S_{1+2} wrt u_2' $\rightarrow T_1 = T_2$

do same thing for v_2'

$$\frac{\partial S_{1+2}}{\partial v_2'} = 0 \quad ; \quad V = \text{const}$$

$$u_1', u_2', N_1, N_2 \text{ all fixed}$$

As usual

$$-\left. \frac{\partial S_1}{\partial v_1'} \right|_{v_1' = V - v_2'} + \frac{\partial S_2}{\partial v_2'} = 0$$

$$\left(\frac{\partial S_1}{\partial v_1'} \right)_{N_1, u_1' \text{ fixed}} = \left(\frac{\partial S_2}{\partial v_2'} \right)_{N_2, u_2' \text{ fixed}}$$

for MECHANICAL EQUILIBRIUM.

each of these depends only on the properties of system 1, or 2.

Define $\frac{P_i}{T_i} = \left(\frac{\partial S_i}{\partial V_i} \right) \Big|_{N_i, U_i}$

$P = T \left(\frac{\partial S}{\partial V} \right)_{N, U}$ $T^{-1} = \left(\frac{\partial S}{\partial U} \right)_{N, V}$

STATISTICAL DEFINITION of PRESSURE

$\frac{P}{T} = \frac{\partial}{\partial V} S(N, U, V) \Big|_{N, U}$ ideal gas

$= \frac{\partial}{\partial V} \left\{ Nk \left(\ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right) \right\}_{N, U}$

$= Nk \frac{\partial}{\partial V} \left\{ \ln V + \underbrace{\ln(V - \text{indep}) + \frac{5}{2}}_{\frac{\partial}{\partial V} \rightarrow 0} \right\}$

$= \frac{Nk}{V}$

So $PV = NkT \leftarrow \nabla$