Alternatively, thinking of entropy (not energy) as the basic thermo function

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$$
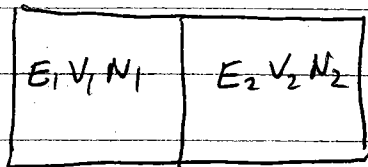
$$TdS = dE + pdV - \mu dN$$

$$\Rightarrow dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

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

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

Thermal equilibrium

$$E = E_1 + E_2$$

$$S = S_1(E_1, N_1, V_1) + S_2(E_2, N_2, V_2)$$

↖ imoveable, impermiable, insulating wall.
("adiabatic" wall → no flow of heat)

as long as wall is in place, subsystems cannot exchange energy, volume, or particles.

("diathermal" wall - conducts heat)

1) suppose now the wall is changed to a thermally conducting one, so the systems can exchange energy? what will be the new E_1 and $\overset{\circ}{E_2}$ after the system equilibrates?

$E = E_1 + E_2$ is fixed constant by consew of energy.

But E_1 and $E_2 = E - E_1$ can change

$$E = E_1 + E_2 \quad \text{fixed} \quad \Rightarrow \quad dE = dE_1 + dE_2 = 0$$
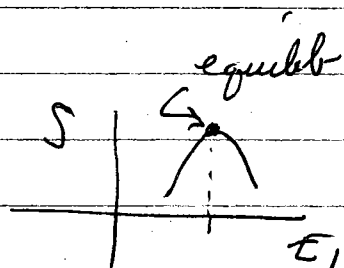
$$dE_2 = -dE_1$$

change in entropy
as system equilibrates $\qquad S = S_1 + S_2$

$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1 N_1} dE_1 + \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2 N_2} dE_2$$

$$= \frac{1}{T_1} dE_1 + \frac{1}{T_2} dE_2$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1$$

equilibrium is when S becomes maximum

$\Rightarrow dS = 0$, ie S will not change for small

changes in dE_1

$$\Rightarrow \boxed{T_1 = T_2} \qquad \text{system is in equilibrium when the}$$
two subsystems have the same
temperature.

Mechanical Equilibrium

2) Now suppose the wall is made thermally conducting
AND it is allowed to slide.

$$E = E_1 + E_2$$
$$V = V_1 + V_2 \qquad\qquad V_1 \text{ and } V_2 = V - V_1 \text{ may change, but}$$
total volume V stays fixed

$$\Rightarrow dE_1 = -dE_2$$
$$dV_1 = -dV_2 \qquad\qquad \text{assume wall moves slowly so}$$
that no energy is dissipated in
friction of moving wall.

as system equilibrates the change in entropy is

$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1 N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1 N_1} dV_1 + \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2 N_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2 N_2} dV_2$$

$$= \frac{1}{T_1} dE_1 + \frac{P_1}{T_1} dV_1 + \frac{1}{T_2} dE_2 + \frac{P_2}{T_2} dV_2$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_2$$

$$dS = 0 \quad \text{at equilib so} \quad \Rightarrow \quad T_1 = T_2$$
$$P_1 = P_2$$

when volume can change, equilib is reached when pressure of both subsystems are equal.

Chemical Equilibrium

3) Now suppose wall becomes conducting, can slide, and is permeable to particles?

$$E = E_1 + E_2 \quad \Rightarrow \quad dE_1 = -dE_2$$
$$V = V_1 + V_2 \quad \Rightarrow \quad dV_1 = -dV_2$$
$$N = N_1 + N_2 \quad \Rightarrow \quad dN_1 = -dN_2$$

tot number N fixed, but N_1 and $N_2 = N - N_1$ vary

$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1 N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1 N_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{E_1 V_1} dN_1$$

$$+ \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2 N_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2 N_2} dV_2 + \left(\frac{\partial S_2}{\partial N_2}\right)_{E_2 V_2} dN_2$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right)dE_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)dN_1$$

$$dS = 0 \Rightarrow T_1 = T_2, \quad p_1 = p_2, \quad \mu_1 = \mu_2$$

when particles can be exchanged, equilib is reached when the subsystems have equal chemical potential.

The role of statistical mechanics is to calculate the entropy from the microscopic details of the system. Once the entropy is known, all thermodynamic properties follow.

Convexity of the Entropy

From postulate II we know S will be maximized whenever a constraint is removed. We can use this to show that S is a convex function of its variables. Consider a system that we conceptually split in half (no physical wall
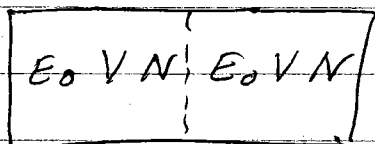
$\frac{E}{2} + \Delta E$	$\frac{E}{2} - \Delta E$
$\frac{N}{2} \quad \frac{V}{2}$	$\frac{N}{2} \quad \frac{V}{2}$

in equilib, $\Delta E = 0$, as the two halfs must have equal energy. But consider how the entropy changes if ΔE is allowed to vary.

Concavity

~~Convexity~~ of the Entropy   Callen Chpt 3 + 5
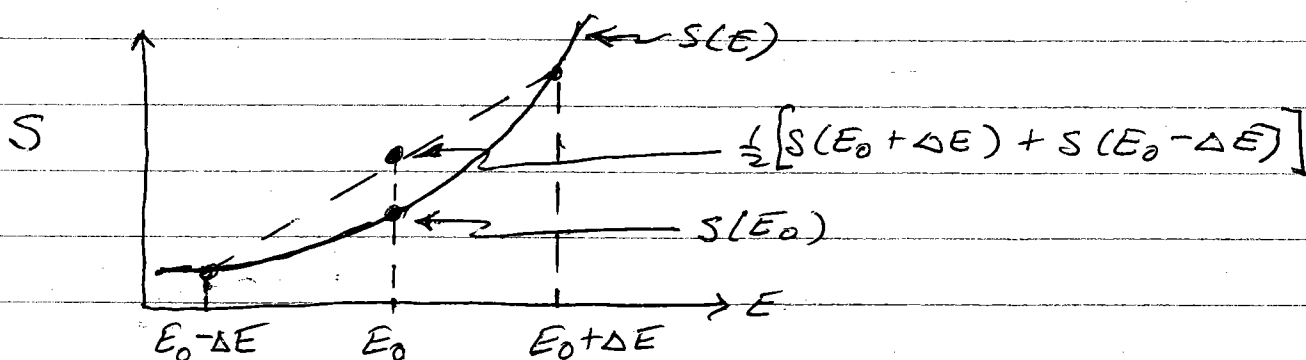
consider a container of gas conceptually divide into two equal halves (no physical wall)

$$\boxed{E_0 \; V \; N \; | \; E_0 \; V \; N}$$

If N and V are fixed to be the same on both sides, we expect the energy will be equal on both sides

$$S^{total} = S(2E_0, 2V, 2N) = S(E_0, V, N) + S(E_0, V, N)$$

Consider how S depends on E. If S were not
a ~~convex~~ [concave] function of E (ie if $\partial^2 S / \partial E^2 > 0$) then the system would be unstable as follows:
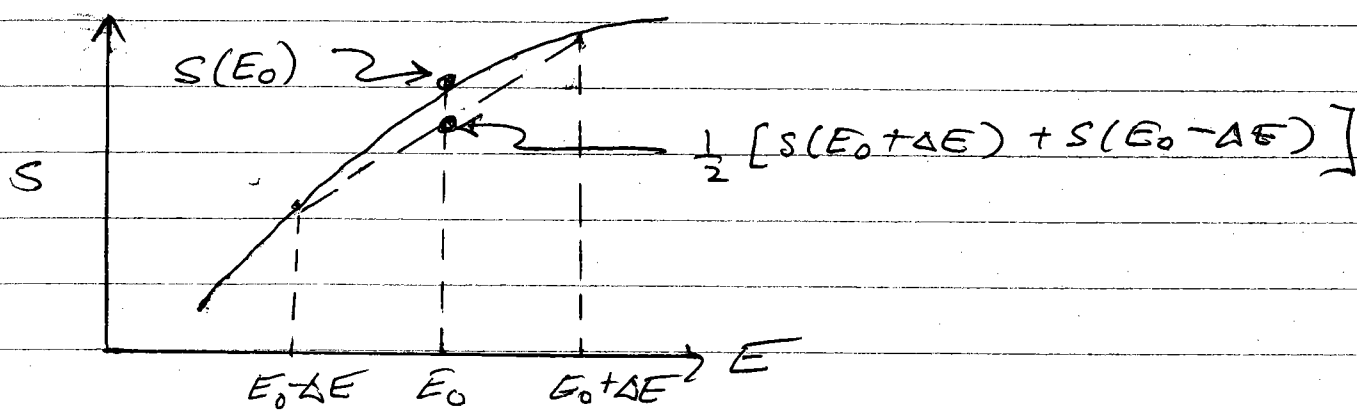

If S(E) is not ~~convex~~ [concave], then we have from above

$$S^{total} = 2S(E_0) < S(E_0 + \Delta E) + S(E_0 - \Delta E)$$

therefore, the total system would increase its entropy by having the LHS with $E_0 - \Delta E$, and the RHS with $E_0 + \Delta E$ — the system would not be stable with equal energies on both sides!

Since, by Postulate II, the systems acts so as to maximize its entropy, we see that the system will be unstable if $S(E)$ is not ~~convex~~ concave.

If $S(E)$ is ~~convex~~ concave, ie $\frac{\partial^2 S}{\partial E^2} < 0$, this does not happen

$$S(E_0)$$

$$\frac{1}{2}\left[S(E_0 + \Delta E) + S(E_0 - \Delta E)\right]$$

S

$E_0 - \Delta E \qquad E_0 \qquad E_0 + \Delta E \qquad E$

Now $\qquad 2S(E_0) > S(E_0 + \Delta E) + S(E_0 - \Delta E)$

The maximum total entropy S^{total} will be when both halves have ~~equal~~ equal energy E_0

$\Rightarrow \quad S(E)$ is ~~convex~~ concave

By similar argument, S must be a ~~convex~~ concave function of all its variables.

$$d^2 S < 0 \qquad\qquad \text{~~convex~~ concave}$$

Further consequences of S being a 1st order homogeneous function

$$\lambda S(E, V, N) = S(\lambda E, \lambda V, \lambda N)$$

$$\Rightarrow \quad \lambda E(S, V, N) = E(\lambda S, \lambda V, \lambda N) \qquad E \text{ is also a } 1^{st} \text{ order}$$
homogeneous function

differentiate with respect to S.

$$\Rightarrow \quad \lambda \left(\frac{\partial E(S, V, N)}{\partial S} \right)_{V, N} = \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial (\lambda S)} \right)_{\lambda V, \lambda N} \left(\frac{\partial (\lambda S)}{\partial S} \right)$$

$$\Rightarrow \quad \lambda \, T(S, V, N) = T(\lambda S, \lambda V, \lambda N) \, \lambda$$

$$T(S, V, N) = T(\lambda S, \lambda V, \lambda N)$$

similarly from $p = -\left(\frac{\partial E}{\partial V} \right)_{S, N}$ and $\mu = \left(\frac{\partial E}{\partial N} \right)_{S, V}$
we conclude

$$\left. \begin{array}{l} T(S, V, N) = T(\lambda S, \lambda V, \lambda N) \\ p(S, V, N) = p(\lambda S, \lambda V, \lambda N) \\ \mu(S, V, N) = \mu(\lambda S, \lambda V, \lambda N) \end{array} \right\}$$

T, p, μ are homogeneous functions of <u>zeroth</u> order

let $\lambda = \frac{1}{N}$, then

$$\left. \begin{array}{l} T(S, V, N) = T\left(\frac{S}{N}, \frac{V}{N}, 1 \right) = T(s, v) \\ P(S, V, N) = P\left(\frac{S}{N}, \frac{V}{N}, 1 \right) = P(s, v) \\ \mu(S, V, N) = \mu\left(\frac{S}{N}, \frac{V}{N}, 1 \right) = \mu(s, v) \end{array} \right\} \begin{array}{l} \text{4} \\ \text{equation} \\ \text{of state} \end{array}$$

T, p, μ are really functions of only _two_ intensive variables $s = S/N$ and $v = V/N$

Since the three variables T, p, μ are all functions of the two variables u, v, there must exist a relation among them — T, p, μ are _not independent_.

For example, one could imagine taking the two equations $T = T(s, v)$ and $p = p(s, v)$ and solving for s and v in terms of T and p, one could then take this result and substitute it into the third equation $\mu = \mu(s, v)$ to get a relation $\mu = \mu(T, p)$.

The differential form for this constraint on T, p, μ is known as the <u>Gibbs-Duhem</u> relation. We derive it as follows:

<u>Consider:</u>
$$\lambda E(S, V, N) = E(\lambda S, \lambda V, \lambda N)$$
differentiate with respect to λ

$$E(S, V, N) = \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} \right)_{\lambda V, \lambda N} \left(\frac{\partial(\lambda S)}{\partial \lambda} \right)$$

$$+ \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} \right)_{\lambda S, \lambda N} \left(\frac{\partial(\lambda V)}{\partial \lambda} \right)$$

$$+ \left(\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} \right)_{\lambda S, \lambda V} \left(\frac{\partial(\lambda N)}{\partial \lambda} \right)$$

$$\Rightarrow E(s,v,N) = T(\lambda s, \lambda v, \lambda N)\, S$$
$$- p(\lambda s, \lambda v, \lambda N)\, V$$
$$+ \mu(\lambda s, \lambda v, \lambda N)\, N$$

$$E(s,v,N) = T(s,v,N)\, S - p(s,v,N)\, V + \mu(s,v,N)\, N$$

$(*)$ $\boxed{E = TS - pV + \mu N}$ Euler relation

or dividing by N

$$u = Ts - pv + \mu$$

Now from the fundamental definitions of T, p, μ we can write

$$dE = \left(\frac{\partial E}{\partial s}\right)_{v,N} ds + \left(\frac{\partial E}{\partial v}\right)_{s,N} dV + \left(\frac{\partial E}{\partial N}\right)_{s,v} dN$$

$$\Rightarrow dE = TdS - pdV + \mu dN$$

But from $(*)$ above we can write

$$dE = TdS + SdT - pdV - Vdp + \mu dN - Nd\mu$$

Subtracting these two differential relations gives

$$\boxed{\begin{array}{l} SdT - Vdp + Nd\mu = 0 \\[2mm] \text{or} \qquad d\mu = -sdT + vdp \end{array}}$$ Gibbs - Duhem relation

one cannot vary T, P, and μ <u>independently</u>.

The Gibbs-Duhem relation gives the variation of one in terms of the variation in the other two.

We can also derive a Gibbs-Duhem relation in the entropy formulation:

$$S = \frac{E}{T} + \frac{P}{T}V - \frac{\mu}{T}N \qquad \text{from Euler relation}$$

$$\Rightarrow dS = E\,d\left(\frac{1}{T}\right) + \frac{1}{T}dE + V\,d\left(\frac{P}{T}\right) + \frac{P}{T}dV - N\,d\left(\frac{\mu}{T}\right) - \frac{\mu}{T}dN$$

but from definitions $\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$, $\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}$, $\left(\frac{\partial S}{\partial N}\right)_{E,V} = \frac{-\mu}{T}$
we get

$$dS = \left(\frac{1}{T}\right)dE + \left(\frac{P}{T}\right)dV - \left(\frac{\mu}{T}\right)dN$$

combining with the above we get

$$E\,d\left(\frac{1}{T}\right) + V\,d\left(\frac{P}{T}\right) - N\,d\left(\frac{\mu}{T}\right) = 0$$

$$\text{or} \quad d\left(\frac{\mu}{T}\right) = u\,d\left(\frac{1}{T}\right) + v\,d\left(\frac{P}{T}\right)$$

Summary

The fundamental thermodynamic function, which determines all thermodynamic behavior, is the _entropy_

$$S(E, V, N)$$ as function of the extensive variables E, V, N

or equivalently the total _internal energy_

$$E(S, V, N)$$ as function of the extensive variable S, V, N

The partial derivatives

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

give the three "equations of state"

If one knows the three equations of state, then it is equivalent to knowing the fundamental thermodynamic function since by Euler's relation

$$E = TS - pV + \mu N$$

If one knows any two of the equations of state one can find the third by using the Gibbs-Duhem relation