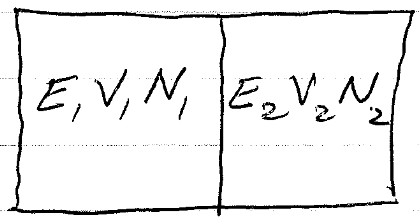
Thermal Equilibrium



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

immoveable, unpermeable,
insulating wall

thermally insulating wall is often called an "adiabatic" wall — no heat can flow across it.
(A "diathermal" wall is a wall that can conduct heat)
As long as the wall is in place, the two subsystems cannot exchange energy, volume, or particles.

1) Suppose now that the wall is changed to a thermally conducting one, so the systems can exchange energy? What will be the new E_1 and E_2 after the system equilibrates?

$E = E_1 + E_2$ is a fixed constant by conservation of energy

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

$E = E_1 + E_2$ fixed $\Rightarrow dE = dE_1 + dE_2 = 0$

so $dE_2 = -dE_1$

Change in entropy $S = S_1 + S_2$ as system equilibrates is then

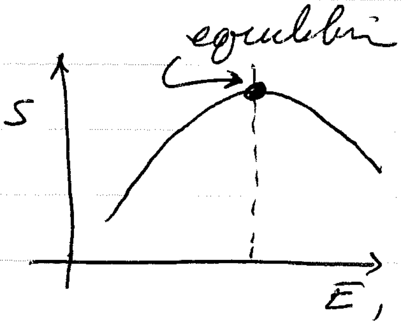
$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1 N_1} dE_1 + \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2 N_2} dE_2$$

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

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 \qquad \text{as } dE_2 = -dE_1$$

equilibrium is when <u>S becomes maximum</u>

At the maximum, $dS = 0$, ie S will not change for small changes in dE_1



$$dS = 0 \Rightarrow \boxed{T_1 = T_2}$$

System is in equilibrium when the two subsystems have the same temperature.

<u>Note:</u> $dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 \Rightarrow$ If $T_1 > T_2$ then since system evolves so that $dS > 0$ always (entropy increases as one approaches equilibrium) $\Rightarrow dE_1 < 0$. So energy flows from (1) to (2) ie from higher T_1 to lower T_2. Agrees with our intuition about temperature that heat flows from hot to cold.

Mechanical Equilibrium

2) Now suppose the wall is thermally conducting AND it is allowed to slide so that volumes V_1 and V_2 can change.

Still the total volume $V = V_1 + V_2$ is fixed so $V_2 = V - V_1$ and $dV_2 = -dV_1$

We have

$$E = E_1 + E_2 \text{ fixed} \Rightarrow dE_2 = -dE_1$$
$$V = V_1 + V_2 \text{ fixed} \Rightarrow dV_2 = -dV_1$$

We will also assume that the wall moves slowly so that no energy is dissipated in friction of the moving wall as system equilibrates the change in entropy is

$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1N_1} dV_1 + \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2N_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2N_2} dV_2$$

$$= \frac{1}{T_1} dE_1 + \frac{p_1}{T_1} dV_1 + \frac{1}{T_2} dE_2 + \frac{p_2}{T_2} dV_2$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_2$$

$dS = 0$ at equilib so $\Rightarrow$ $T_1 = T_2$
$p_1 = p_2$

When volume can change, equilib is reached when pressure of ~~[illegible]~~ subsystems are equal.

Chemical Equilibrium

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

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

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

$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1N_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{E_1V_1} dN_1$$

$$+ \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2N_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2N_2} dV_2 + \left(\frac{\partial S_2}{\partial N_2}\right)_{E_2V_2} dN_2$$

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

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

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

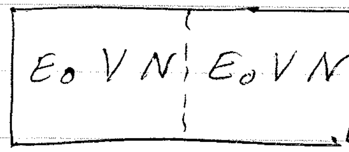
From posulate II we know S will be maximized whenever a constraint is removed. We can use this to show that S is a convex function of its variables. Consider a system that we conceptually split in half (no physical wall)

$\frac{E}{2}+\Delta E$	$\frac{E}{2}-\Delta E$
$\frac{N}{2}$ $\frac{V}{2}$	$\frac{N}{2}$ $\frac{V}{2}$

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.

~~Convexity~~ Concavity of the Entropy

Callen Chpt 3 + 5

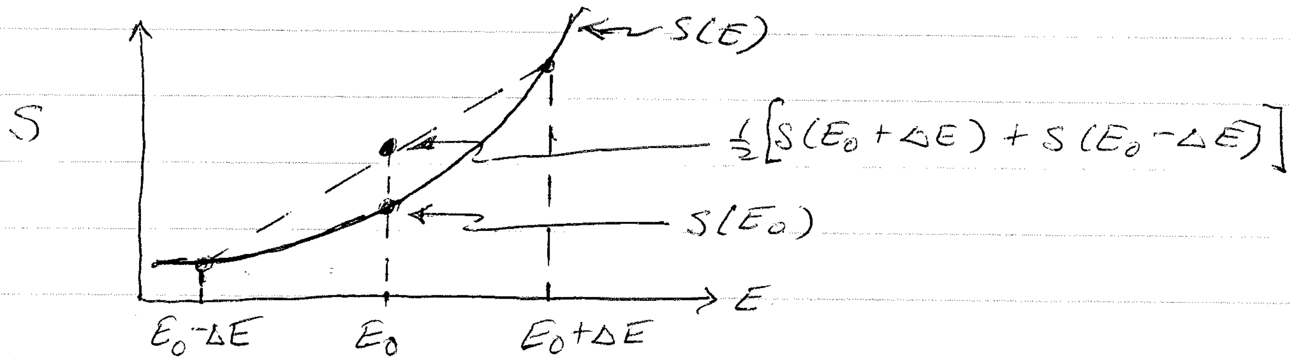


consider a container of gas conceptually divide into two equal halves (no physical wall)

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:



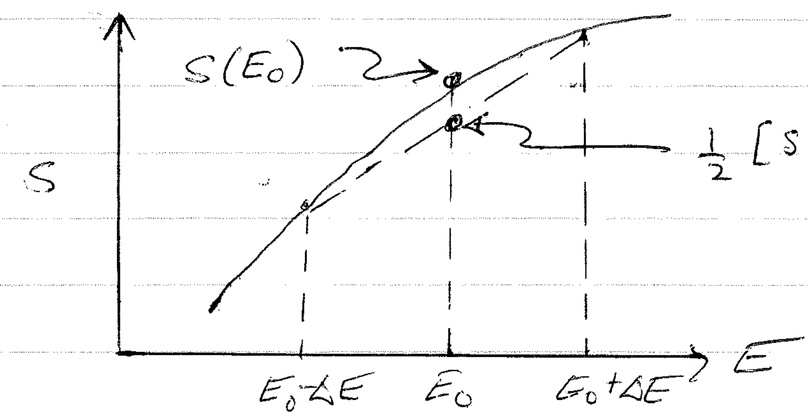
If S(E) is not ~~convex~~ concave, then we have from above

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

Therefore, the total system would <u>increase</u> 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



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

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

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

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

$d^2S < 0$ ~~convex~~ concave

__Further consequences of__ S being a 1st order homogeneous function

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

$$\Rightarrow \lambda E(S,V,N) = E(\lambda S, \lambda V, \lambda N)$$ E is also a 1st order homogeneous function

__differentiate with respect to S.__

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

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

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

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

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

T, p, μ are homogeneous functions of __zeroth__ order

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

$$\left.\begin{aligned} T(S,V,N) &= T\left(\tfrac{S}{N}, \tfrac{V}{N}, 1\right) = T(s, v) \\ P(S,V,N) &= P\left(\tfrac{S}{N}, \tfrac{V}{N}, 1\right) = P(s, v) \\ \mu(S,V,N) &= \mu\left(\tfrac{S}{N}, \tfrac{V}{N}, 1\right) = \mu(s, v) \end{aligned}\right\}$$ "equations of state"

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

Since the three variables T, p, μ are all functions of the two variables s, v, there must exist a relation among them — T, p, μ are <u>not independent</u>.
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> <u>relation</u>. 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

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

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

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

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

Now take $\lambda = 1$,

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

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

or dividing by N

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

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

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN$$

$$\Rightarrow dE = T\,dS - p\,dV + \mu\,dN$$

But from $(*)$ above we can write

$$dE = T\,dS + S\,dT - p\,dV - V\,dp + \mu\,dN - N\,d\mu$$

Subtracting these two differential relations gives

$$\boxed{\begin{aligned} & S\,dT - V\,dp + N\,d\mu = 0 \\ \text{or} \quad & d\mu = -s\,dT + v\,dp \end{aligned}} \qquad \underline{\text{Gibbs-Duhem relation}}$$

one cannot vary T, p, and μ independently.
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

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

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

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 variables S, V, N

The partial derivatives

$$\left.\begin{aligned} \left(\frac{\partial E}{\partial S}\right)_{V,N} &= T(S,V,N) \\ -\left(\frac{\partial E}{\partial V}\right)_{V,N} &= p(S,V,N) \\ \left(\frac{\partial E}{\partial N}\right)_{S,V} &= \mu(S,V,N) \end{aligned}\right\} \text{ give the three "equations of state"}$$

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