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

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

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

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

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

$P_1 = P_2$

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?

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

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

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

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

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1$$

$$dS = 0 \Rightarrow T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2$$

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

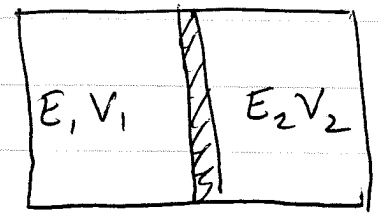
From postulate II we know S will be maximized whenever a constraint is removed. We can use this to show that S is a convex function of its variables. Consider a system that we conceptually split in half (no physical wall)

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

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.

Return to a previous problem

(1) another way to look at the problem of thermal + mechanical equilibrium



N_1, N_2 fixed so we ignore them

Initially wall is adiabatic and immoveable - subsystems are in equilib with energies and volumes E, V_1 on left, $E_2 V_2$ on right

Now wall is allowed to move and to conduct heat.

$E = E_1 + E_2$ stays fixed $\Rightarrow E_2 = E - E_1$

$V = V_1 + V_2$ stays fixed $\Rightarrow V_2 = V - V_1$

total entropy is

$$S = S_1(E_1, V_1) + S_2(E - E_1, V - V_1)$$

is maximized when system reaches equilibrium

$\Rightarrow$ equilibrium is when

$$0 = \left(\frac{\partial S}{\partial E_1}\right)_{V_1} = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1} + \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2} \frac{\partial E_2}{\partial E_1} = \frac{1}{T_1} - \frac{1}{T_2}$$

$$0 = \left(\frac{\partial S}{\partial V_1}\right)_{E_1} = \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1} + \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2} \frac{\partial V_2}{\partial V_1} = \frac{p_1}{T_1} - \frac{p_2}{T_2}$$

$\Rightarrow T_1 = T_2$ and $p_1 = p_2$

or more specifically, since T and p are functions of E and V,

$$\begin{cases} T_1(E_1, V_1) = T_2(E - E_1, V - V_1) \\ p_1(E_1, V_1) = p_2(E - E_1, V - V_1) \end{cases}$$

above is <u>two</u> equations for the <u>two</u> unknowns E_1 and V_1. In principle one can therefore solve them to find E_1 and V_1 (and hence $E_2 = E - E_1$, $V_2 = V - V_1$) of the new equilibrium state.

(2) However, consider the same initial situation, but now the wall is made moveable but stays <u>adiabatic</u> ie still no heat can be transported across the wall between the two subsystems. Since $dQ = TdS = 0$ (no heat flows through wall)

$$\Rightarrow dS_1 = dS_2 = 0$$

total entropy of system cannot change

$$dS_1 = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1} dV_1$$

$$= \frac{1}{T_1} dE_1 + \frac{p_1}{T_1} dV_1 = 0$$

$$\Rightarrow dE_1 = -p_1 dV_1$$

similarly $dE_2 = -p_2 dV_2$

} energy of each side can change only due to mechanical work done in moving the wall

Total Energy is still conserved $\Rightarrow E = E_1 + E_2$ is fixed

$\Rightarrow dE_2 = -dE_1$

Total Volume is fixed $\Rightarrow V = V_1 + V_2$ fixed

$\Rightarrow dV_2 = -dV_1$

$$\left.\begin{aligned} dE_1 &= -p_1 dV_1 \\ dE_2 &= -p_2 dV_2 \Rightarrow -dE_1 = p_2 dV_1 \end{aligned}\right\} \Rightarrow p_1 = p_2$$

or $p_1(E_1, V_1) = p_2(E - E_1, V - V_1)$

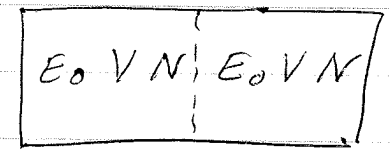
in equilibrium the pressures of the two subsystems must be equal - so net force on the wall is zero.
But above is just <u>one</u> equation for <u>two</u> unknowns E_1 and V_1. Thermodynamics alone does <u>not</u> give us enough information to determine the new equilibrium state, [postulate of maximizing the entropy does not help here since total entropy does not change $dS = dS_1 + dS_2 = 0$ when the wall is adiabatic].

The new equilibrium state will depend on details such as the viscosity of the gases in each subsystem. Viscosity is the mechanism by which the energy added to one subsystem via the mechanical work done by the wall goes into increasing the temperature of that gas. If the gases had <u>no</u> viscosity, the wall would just oscillate in simple harmonic motion, and no equilibrium would ever be reached.

Concavity

~~Convexity~~ of the Entropy

Callen Chpt 3 + 5

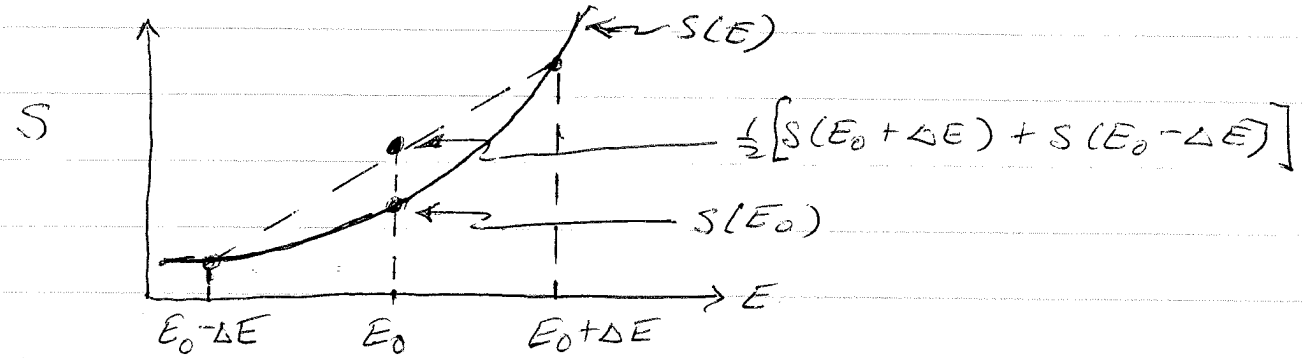


consider a container of gas conceptually divide into two equal halves (no physical wall)

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:



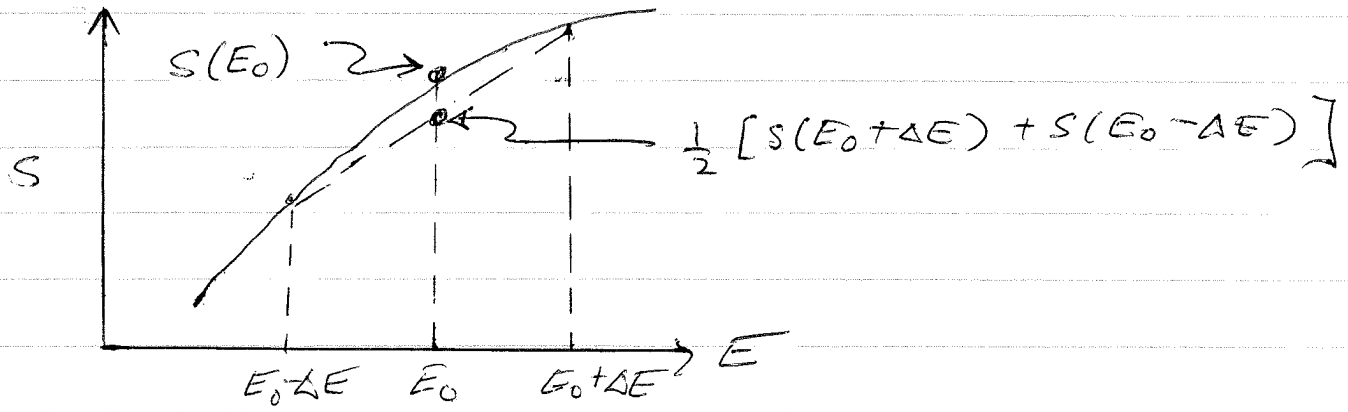
If S(E) is not ~~convex~~ concave, then we have from above

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

Therefore, the total system would 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 system 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 $2S(E_0) > S(E_0+\Delta E) + S(E_0-\Delta E)$

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

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

By similar argument, 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

$$\left.\begin{aligned} T(S,V,N) &= T\left(\frac{S}{N}, \frac{V}{N}, 1\right) = T(s,v) \\ P(S,V,N) &= P\left(\frac{S}{N}, \frac{V}{N}, 1\right) = p(s,v) \\ \mu(S,V,N) &= \mu\left(\frac{S}{N}, \frac{V}{N}, 1\right) = \mu(s,v) \end{aligned}\right\}$$ "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 u, 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 the 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 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

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

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

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

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

Now take $\lambda = 1$,

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

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

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

$$\boxed{S\,dT - V\,dp + N\,d\mu = 0}$$

or

$$\boxed{d\mu = -s\,dT + v\,dp}$$

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 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