example : The ideal monatomic gas

From expt: $PV = Nk_BT$ $\Rightarrow \frac{P}{T} = \frac{N}{V} k_B = \frac{k_B}{v}$

$E = \frac{3}{2} Nk_BT$ $\Rightarrow \frac{1}{T} = \frac{3}{2} k_B \frac{N}{E} = \frac{3}{2} \frac{k_B}{u}$

if we can find μ, then we have entropy S via

$$S = \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N$$

From Gibbs-Duhem relation in entropy representation

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

$$= u \frac{3}{2} k_B \, d\left(\frac{1}{u}\right) + v k_B \, d\left(\frac{1}{v}\right)$$

$$d\left(\frac{\mu}{T}\right) = -\frac{3}{2} \frac{k_B}{u} du - \frac{k_B}{v} dv$$

integrate to get

$$\left(\frac{\mu}{T}\right) - \left(\frac{\mu}{T}\right)_0 = -\frac{3}{2} k_B \ln\left(\frac{u}{u_0}\right) - k_B \ln\left(\frac{v}{v_0}\right)$$

where u_0 at v_0 are some reference state, and $\left(\frac{\mu}{T}\right)_0$ is an unknown constant of integration. Then one gets

$$S = \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N = \frac{3}{2} k_B \frac{E}{(E/N)} + \frac{k_B}{(V/N)} V$$

$$+ \frac{3}{2} Nk_B \ln\left(\frac{u}{u_0}\right) + k_B N \ln\left(\frac{v}{v_0}\right) - \left(\frac{\mu}{T}\right)_0 N$$

$$S = \frac{3}{2} k_B N + k_B N - \left(\frac{\mu}{T}\right)_0 N + Nk_B \ln\left[\left(\frac{u}{u_0}\right)^{3/2}\left(\frac{v}{v_0}\right)\right]$$

use $E = uN$, $E_0 \equiv u_0 N_0$, $V = vN$, $V_0 \equiv v_0 N_0$

$$\Rightarrow \boxed{S(E,V,N) = \frac{N}{N_0} S_0 + N k_B \ln \left[\left(\frac{E}{E_0}\right)^{3/2} \left(\frac{V}{V_0}\right) \left(\frac{N}{N_0}\right)^{-5/2} \right]}$$

where $S_0 = \frac{5}{2} k_B N_0 - \left(\frac{\mu}{T}\right)_0 N_0$ is a constant

So from experimental knowledge of two of the equations of state $\frac{1}{T}$ and $\frac{P}{T}$ as functions of E, N, V, we have derived the entropy $S(E,V,N)$. All behaviors of the ideal gas can now be deduced from knowledge of S.

Alternatively, we could derive $s = \frac{S}{N}$ as follows:

$$E = TS - pV + \mu N \quad \Rightarrow \quad S = \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N$$

$$\Rightarrow s = \frac{u}{T} + \frac{P}{T} v - \frac{\mu}{T} \qquad \text{where } u = \frac{E}{N}, \ v = \frac{V}{N}$$

$$ds = \frac{1}{T} du + \frac{P}{T} dv + \underbrace{u\, d\left(\frac{1}{T}\right) + v\, d\left(\frac{P}{T}\right) - d\left(\frac{\mu}{T}\right)}$$

these cancel due to the Gibbs-Duhem relation as expressed in the entropy formulation

So
$$\Rightarrow \boxed{ds = \frac{1}{T} du + \frac{P}{T} dv}$$

$$ds = \frac{1}{T} du + \frac{P}{T} dv$$

$$= \frac{3}{2} \frac{k_B}{u} du + \frac{k_B}{v} dv \qquad \text{since} \begin{cases} \frac{1}{T} = \frac{3}{2} \frac{k_B}{u} \\ \frac{P}{T} = \frac{k_B}{v} \end{cases}$$

integrate

$$s - s_0 = \frac{3}{2} k_B \ln(u/u_0) + k_B \ln(v/v_0)$$

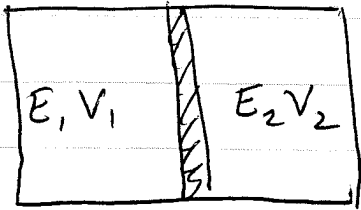$$\boxed{s = s_0 + k_B \ln\left[\left(\frac{u}{u_0}\right)^{3/2} \left(\frac{v}{v_0}\right)\right]}$$

substitute in $S = Ns$, $\quad E = Nu$, $\quad V = Nv$

$$S_0 = N_0 s_0, \quad E_0 = N_0 u_0, \quad V_0 = N_0 v_0$$

and we recover the earlier result for $S(E, V, N)$

Return to a previous problem

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 $E_1 V_1$ on left, $E_2 V_2$ on right

Now wall is allowed to move and to conduct heat.

$$E = E_1 + E_2 \quad \text{stays fixed} \Rightarrow E_2 = E - E_1$$
$$V = V_1 + V_2 \quad \text{stays fixed} \Rightarrow V_2 = V - V_1$$

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

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

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

$$\Rightarrow T_1 = T_2 \quad \text{and} \quad p_1 = p_2$$

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.

ⓔ 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

$\Rightarrow dV_2 = -dV_1$

$$\left.\begin{array}{l} dE_1 = -p_1 dV_1 \\ dE_2 = -p_2 dV_2 \Rightarrow -dE_1 = p_2 dV_1 \end{array}\right\} \Rightarrow P_1 = P_2$$

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

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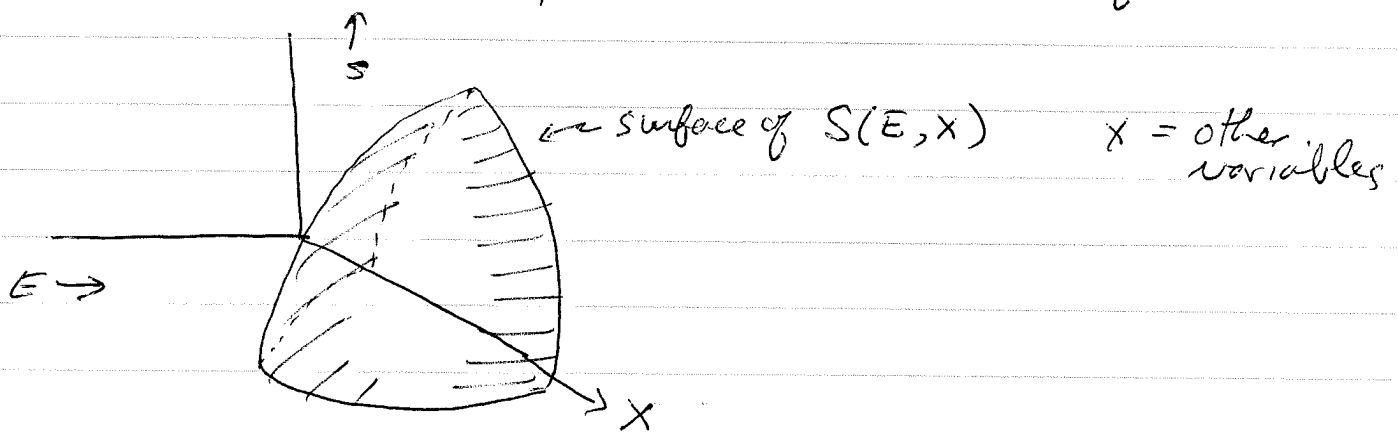
But above is just one equation for two unknowns E_1 and V_1. Thermodynamics alone does not give us enough information to determine the new equilibrium state. [postulate of maximizing the entropy does not help here since total entropy does not change $dS = dS_1 + dS_2 = 0$ when the wall is adiabatic].

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 no viscosity, the wall would just oscillate in simple harmonic motion, and no equilibrium would ever be reached.

Energy Minimum Principle

Postulate II stated that when constraints are removed, the equilibrium state will be the one that maximizes the entropy $S(E, V, N, \ldots)$
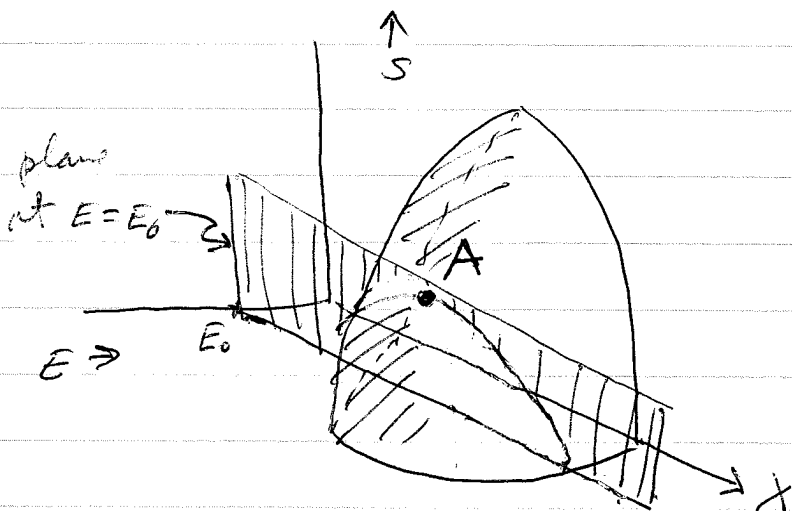
We saw that entropy is a ~~convex~~ concave function of its variables

← surface of $S(E, X)$ X = other variables

For a situation where the total E is held fixed, at value E_0, then if X is an unconstrained degree of freedom, it will take in equilib that value X_0 that maximizes S for the given fixed E_0. This is determined by the intersection of the surface $S(E, X)$ with the plane at fixed $E = E_0$

plane at $E = E_0$ →

X_0 is given by the point A that maximizes S along this curve of intersection

$$S_0 = \max_{X} \left[S(E_0, X) \right]$$
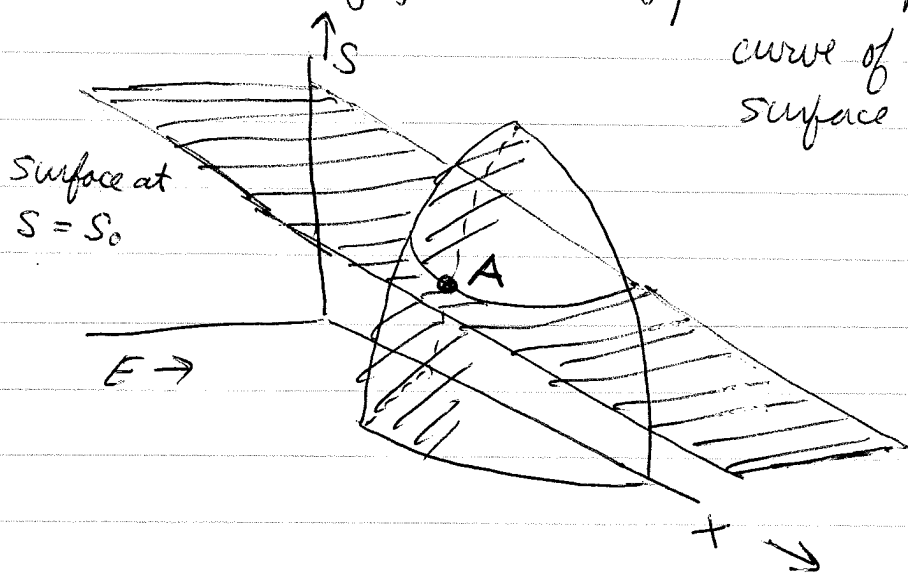
Callen Fig 5.1

Suppose now an alternative situation in which
the total entropy S is held fixed at value S_0.
Then if X is an unconstrained degree of freedom
we see that the equilibrium state at S_0, E_0 corresponds
to minimizing the energy with respect to X, along the
curve of intersection between $S(E,X)$
surface and plane of const $S = S_0$

surface at
$S = S_0$

$E \rightarrow$

A

$X \rightarrow$

Callen Fig 5.2

$$E_0 = \min_{X} \left[E(S_0, X) \right]$$

We thus have two contrasting formulations.

entropy formulation: fundamental function is $S(E, X_1, X_2, \ldots)$
if constraint on some X_i is removed, X_i will
take the value that maximizes S for the fixed
total energy E. In equilib, $d^2S < 0$. S ~~convex~~ concave

energy formulation: fundamental function is $E(S, X_1, X_2, \ldots)$
if constraint on some X_i is removed, X_i will
take the value that minimizes E for the
fixed total entropy S. In equilib $d^2E > 0$
E ~~concave~~ convex

Suppose we had some equilib. state for which E was not the minimum possible value for the given S.

Then can withdraw energy from the system by doing mechanical work (for example drive a piston) while keeping S constant.

start $\qquad$ do mechanical work $\qquad$ add heat

$E_0, S_0 \xrightarrow{\qquad} E_1, S_0 \xrightarrow{\qquad} E_0, S_1$

$\qquad\qquad\qquad$ where $E_1 < E_0$ $\qquad$ where $S_1 > S_0$

now return this energy to the system in the form of heat $E_0 - E_1 = dQ = TdS$. The energy is now back to E_0, but the entropy has increased by $dS = (E_0 - E_1)/T$.

The system is restored to its original energy but with a higher value of entropy. But this contradicts the requirement that the original equilib. state was a max min of entropy. $\Rightarrow$ original E had to have been the minimum.

We have now two equivalent representations

1) entropy $S(E, V, N)$ energy E, volume V, number N held fixed

2) energy $E(S, V, N)$ entropy S, volume V, number N held fixed

In certain cases it is more natural to regard temperature T as held constant, rather than S; or to regard pressure p as held constant, rather than V; or to regard chemical potential μ as held constant, rather than N.

We therefore wish to develop new formulations of thermodynamics that will allow us to regard T, p, or μ as a fundamental variable rather than S, V, or N. These new formulations will lead to the Helmholtz and Gibb free energies that play the role ~~of~~ ~~entropy~~ analogues to ~~entropy~~ energy as the fundamental thermodynamic function of these new formulations.

For example, we have $E(S, V, N)$ with $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$

How can we make a thermodynamic "potential" that contains all the information of $E(S, V, N)$ but depends on T rather than S.