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

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

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

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

\[ dS = 0 \text{ at equilibrium so } \Rightarrow T_1 = T_2, \quad P_1 = P_2 \]

When volume can change, equilibrium is reached when pressure of subsystems are equal.

Chemical equilibrium

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

\[ E = E_1 + E_2 \Rightarrow dE = -dE_2 \]

\[ V = V_1 + V_2 \Rightarrow dV = -dV_2 \]

\[ N = N_1 + N_2 \Rightarrow dN = -dN_2 \]

If number \( N \) fixed, but \( N_1 \) and \( N_2 = N - N_1 \) vary

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

\[ + \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2N_2} dE_2 + \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2N_2} dV_2 + \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2V_2} dN_2 \]
\[
\Delta S = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left( \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_1 - \left( \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_2.
\]

\[dS = 0 \Rightarrow T_1 = T_2, \quad \mu_1 = \mu_2, \quad N_1 = N_2,\]

When particles can be exchanged, equilibrium 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) in equal volumes \( V = \frac{V}{2} \). As the two halves must have equal energy. But consider how the entropy changes if \( \Delta E \) is allowed to vary.
Return to a previous problem

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

\[ E_{1}, V_{1} \quad \text{and} \quad E_{2}, V_{2} \]

\[ N_{1}, N_{2} \text{ fixed so we ignore them} \]

Initially well is adiabatic and
invariant - subsystem are in equilibrium with energies and volumes \( E, V \) on left, \( E_{2}, V_{2} \) on right.

Now well is allowed to move ad to conduct heat

\[ E = E_{1} + E_{2} \text{ stays fixed } \Rightarrow E_{2} = E - E_{1} \]
\[ V = V_{1} + V_{2} \text{ stays fixed } \Rightarrow V_{2} = V - V_{1} \]

Total entropy is

\[ S = S_{1}(E_{1}, V_{1}) + S_{2}(E - E_{1}, V - V_{1}) \]

is maximized when system reaches equilibrium

\[ \Rightarrow \text{ equilibrium is when} \]

\[ 0 = \left( \frac{\partial S}{\partial E} \right)_{V_{1}} = \left( \frac{\partial S_{1}}{\partial E_{1}} \right)_{V_{1}} + \left( \frac{\partial S_{2}}{\partial E_{2}} \right)_{V_{2}} \frac{\partial E_{2}}{\partial E_{1}} = \frac{1}{T_{1}} - \frac{1}{T_{2}} \]

\[ 0 = \left( \frac{\partial S}{\partial V} \right)_{E_{1}} = \left( \frac{\partial S_{1}}{\partial V_{1}} \right)_{E_{1}} + \left( \frac{\partial S_{2}}{\partial V_{2}} \right)_{E_{2}} \frac{\partial V_{2}}{\partial V_{1}} = \frac{p_{1}}{T_{1}} - \frac{p_{2}}{T_{2}} \]

\[ \Rightarrow T_{1} = T_{2} \quad \text{and} \quad p_{1} = p_{2} \]
or more specifically, since $T$ and $p$ are functions of $E$ and $V$,

\[
\begin{align*}
T_1(E_1, V_1) &= T_2(E - E_1, V - V_1) \\
p_1(E, V) &= p_2(E - E_1, V - V_1)
\end{align*}
\]

above is two equations for the two 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.

\[\Box\]

However, consider the same initial situation, but now the wall is made moveable but stays adiabatic, i.e., still no heat can be transported across the wall between the two subsystems. Since $dQ = T dS = 0$ (no heat flows through wall)

\[
\Rightarrow dS_1 = dS_2 = 0
\]

Total entropy of system cannot change.

\[
dS_1 = \left( \frac{dS_1}{dE_1} \right)_{V_1} dE_1 + \left( \frac{dS_1}{dV_1} \right)_{E_1} dV_1
\]

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

\[
\Rightarrow dE_1 = -p_1 dV_1
\]

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 \( \Rightarrow V = V_1 + V_2 \) is fixed
\[ \Rightarrow dV_2 = -dV_1 \]
\[ dE_1 = -p_1 dV_1 \]
\[ dE_2 = -p_2 dV_2 \]
\[ \Rightarrow -dE_1 = p_2 dV_1 \]
\[ \Rightarrow p_1 = p_2 \]
\[ \phi_1(E_1, V_1) = p_2 (E - E_1, V - V_1) \]

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, I 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.
Consider a container of gas conceptually divided 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.

$$S_{\text{total}} = S(2E_0, 2V, 2N) = S(E_0, V, N) + S(E_0, V, N)$$

Consider how $S$ depends on $E$. If $S$ were not a convex function of $E$ (i.e., if $\frac{d^2S}{dE^2} < 0$), then the system would be unstable as follows:

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

$$S_{\text{final}} = 2S(E_0) < S(E_0 + \Delta E) + S(E_0 - \Delta E)$$

Therefore, the total system would increase its entropy by changing 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 concave.

If \( S(E) \) is concave, i.e. \( \frac{d^2S}{dE^2} < 0 \), this does not happen.

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

\[\begin{align*}
E_0 - \Delta E & \quad E_0 & \quad E_0 + \Delta E \\
S & \quad S(E_0) & \quad S(E_0)
\end{align*}\]

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

The maximum total entropy state will be when both halves have equal energy \( E_0 \).

\[\Rightarrow S(E) \text{ is concave} \]

By similar argument, \( S \) must be a concave function of all its variables.

\[d^2S < 0 \quad \text{concave} \]
Further consequences of \( S \) being a 1st order homogeneous function

\[
AS(E, V, N) = S(\lambda E, \lambda V, \lambda N)
\]

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

differentiate with respect to \( S \).

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

\[\Rightarrow \lambda T(S, V, N) = T(\lambda S, \lambda V, \lambda N) \lambda
\]

\[
T(S, V, N) = T(\lambda S, \lambda V, \lambda N)
\]

Similarly, from \( \rho = -\left( \frac{\partial E}{\partial V} \right)_{s, N} \) and \( \mu = \left( \frac{\partial E}{\partial N} \right)_{s, V} \)

we conclude

\[
T(S, V, N) = T(\lambda S, \lambda V, \lambda N) \tag{1}
\]

\[
\rho(S, V, N) = \rho(\lambda S, \lambda V, \lambda N) \tag{2}
\]

\[
\mu(S, V, N) = \mu(\lambda S, \lambda V, \lambda N) \tag{3}
\]

\( T, \rho, \mu \) are homogeneous functions of \( 2 \)nd order

let \( \lambda = \frac{1}{N} \), then

\[
T(S, V, N) = T(\frac{S}{N}, \frac{V}{N}, 1) = T(\lambda, \lambda) \quad \text{"equations of state"}
\]

\[
\rho(S, V, N) = \rho(\frac{S}{N}, \frac{V}{N}, 1) = \rho(\lambda, \lambda)
\]

\[
\mu(S, V, N) = \mu(\frac{S}{N}, \frac{V}{N}, 1) = \mu(\lambda, \lambda)
\]
$T, P, \mu$ are really functions of only two intensive variables $s = s(N), v = v(N)$.

Since the three variables $T, P, \mu$ are all functions of the two variables $s, v$, there must exist a relation among them — $T, P, \mu$ 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 $T, P, \mu$ is known as the Gibbs–Duhem relation. We derive it as follows:

Consider:

$$\partial E(s, v, N) = E(\lambda s, \lambda v, \lambda N)$$

Differentiate with respect to $\lambda$:

$$E(s, v, N) = \left( \frac{\partial E(\lambda s, \lambda v, \lambda N)}{\partial \lambda} \right)_{\lambda s, \lambda v, \lambda N} \left( \frac{\partial (\lambda s)}{\partial \lambda} \right)_{s, v, N} + \left( \frac{\partial E(\lambda s, \lambda v, \lambda N)}{\partial \lambda} \right)_{s, \lambda v, \lambda N} \left( \frac{\partial (\lambda v)}{\partial \lambda} \right)_{s, v, N} + \left( \frac{\partial E(\lambda s, \lambda v, \lambda N)}{\partial \lambda} \right)_{\lambda s, \lambda v, \lambda N} \left( \frac{\partial (\lambda N)}{\partial \lambda} \right)_{s, v, N}.$$
\[ E(s,v,N) = T(s,v,N) S - p(s,v,N) V + \mu(s,v,N) N \]

Now take \( b = 1 \),

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

\[(*) \quad E = TS - pV + \mu N \quad \text{Euler relation} \]

or dividing by \( N \)

\[ u = Ts - pV + \mu \]

Now from the fundamental definitions of \( T, p, \mu \) we can write

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

\[ \Rightarrow dE = Ts \, ds - p \, dv + \mu \, dN \]

But from \((*)\) above we can write

\[ dE = Ts \, ds + s \, dT - p \, dv - V \, dp + \mu \, dN + N \, d\mu \]

Subtracting these two differential relations give

\[ 3dT - V \, dp + N \, d\mu = 0 \]

\[ \text{Gibbs-Duhem relation} \]

\[ \Rightarrow \, d\mu = -s \, dT + V \, dp \]
one cannot vary $T$, $p$, $a$, and $\mu$ 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:

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

$$ \Rightarrow dS = Ed\left(\frac{1}{T}\right) + \frac{1}{T} dE + Vd\left(\frac{p}{T}\right) + \frac{p}{T} dV - N d\left(\frac{\mu}{T}\right) - \frac{\mu}{T} dN $$

But from definitions \((\frac{\partial S}{\partial E})_{V,N} = \frac{1}{T}\), \((\frac{\partial S}{\partial V})_{E,N} = \frac{p}{T}\), \((\frac{\partial S}{\partial N})_{E,V} = -\frac{\mu}{T}\)

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

$$ d\left(\frac{\mu}{T}\right) = \mu d\left(\frac{1}{T}\right) + N d\left(\frac{p}{T}\right) $$
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

\[
\begin{align*}
\left( \frac{\partial E}{\partial S} \right)_{V,N} &= T(S,V,N) \\
-\left( \frac{\partial E}{\partial V} \right)_{S,N} &= p(S,V,N) \\
\left( \frac{\partial E}{\partial N} \right)_{S,V} &= \mu(S,V,N)
\end{align*}
\]

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