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

If \( N \) at \( V \) 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:

\[
2S(E_0) < S(E_0 + \Delta E) + S(E_0 - \Delta E)
\]

Therefore, the total system would increase its entropy by switching the LHS with \( E_0 - \Delta E \), as 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.

Now, \( 2S(E_0) > S(E_0 + AE) + S(E_0 - AE) \)

The maximum total entropy \( S_{\text{tot}} \) will be when both halves have equal energy \( E_0 \).

\( \Rightarrow S(E) \) is concave.

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

\( d^2S < 0 \) concave
Further consequences of $S$ being a 1st order homogeneous function

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

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

Differentiate with respect to $S$.

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

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

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

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

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

$T, p, \mu$ are homogeneous functions of 0th order.

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

$$T(S, V, N) = T\left( \frac{S}{N}, \frac{V}{N}, 1 \right) = T(\lambda S, \lambda V)$$

$$p(S, V, N) = p\left( \frac{S}{N}, \frac{V}{N}, 1 \right) = p(\lambda S, \lambda V)$$

$$\mu(S, V, N) = \mu\left( \frac{S}{N}, \frac{V}{N}, 1 \right) = \mu(\lambda S, \lambda V)$$
\[ E(s,v,N) = T(s,v,N)S - p(s,v,N)V + \mu(s,v,N)N \]

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

or dividing by \( N \)

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

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

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

\[ dE = Ts\text{d}s - pd\text{d}V + \mu dN \]

But from (*) above we can write

\[ dE = Ts\text{d}s + \text{sdT} - pd\text{d}V - Vdp + \mu dN - Ndp \]

Subtracting these two differential relations gives

\[ \text{sdT} - Vdp + Nd\mu = 0 \quad \text{Gibbs-Duhem relation} \]

or

\[ d\mu = -sdT + Vdp \]
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 \( T = T(u, v) \) and \( p = p(u, v) \) and solving for \( u \) and \( v \) in terms of \( T \) and \( p \), one could then take this result and substitute it into the third equation \( μ = μ(u, v) \) to get a relation \( μ = μ(T, p) \).

The differential form for this constraint on \( T, p, μ \) is known as the Gibbs-Duhem relation. We derive it as follows:

Consider:

\[
\frac{\partial E(s, v, N)}{\partial s} = E(\lambda s, \lambda v, \lambda N)
\]

differentiate with respect to \( λ \):

\[
E(s, v, N) = \left( \frac{\partial E(\lambda s, \lambda v, \lambda N)}{\partial (\lambda s)} \right) \frac{\partial (\lambda s)}{\partial s} + \left( \frac{\partial E(\lambda s, \lambda v, \lambda N)}{\partial (\lambda v)} \right) \frac{\partial (\lambda v)}{\partial v} + \left( \frac{\partial E(\lambda s, \lambda v, \lambda N)}{\partial (\lambda N)} \right) \frac{\partial (\lambda N)}{\partial N}
\]
one cannot vary $T$, $P$, or $\mu$ independently.

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

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

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

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

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:

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

Combining with the above we get:

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

or $d(\frac{\mu}{T}) = -ud(\frac{1}{T}) + \nu d(\frac{P}{T})$
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.
Example: The ideal monatomic gas

From expt: \[ PV = Nk_B T \implies \frac{P}{T} = \frac{Nk_B}{V} = \frac{k_B}{V} \]

\[ E = \frac{3}{2} Nk_B T \implies \frac{1}{T} = \frac{3}{2} k_B \frac{N}{E} = \frac{3}{2} \frac{k_B}{U} \]

If we can find \( \mu \), 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

\[ d\left( \frac{\mu}{T} \right) = u d\left( \frac{1}{U} \right) + v d\left( \frac{P}{T} \right) \]

\[ = u \frac{3}{2} k_B d\left( \frac{1}{U} \right) + v k_B d\left( \frac{1}{V} \right) \]

\[ d\left( \frac{\mu}{T} \right) = -\frac{3}{2} \frac{k_B}{U} du - \frac{k_B}{V} dv \]

Integrate to get

\[ \left( \frac{\mu}{T} \right) - \left( \frac{\mu}{T_0} \right) = -\frac{3}{2} k_B \ln\left( \frac{U}{U_0} \right) - k_B \ln\left( \frac{V}{V_0} \right) \]

where \( U_0 \) at \( V_0 \) are some reference state, and \( \frac{\mu}{T} \) is an unknown constant of integration. Then one gets

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

\[ + \frac{3}{2} Nk_B \ln\left( \frac{U}{U_0} \right) + k_B N \ln\left( \frac{V}{V_0} \right) + \left( \frac{\mu}{T} \right)_0 \]

\[ S = \frac{3}{2} k_B N + k_B N + \left( \frac{\mu}{T} \right)_0 + N k_B \ln\left[ \left( \frac{U}{U_0} \right)^{3/2} \left( \frac{V}{V_0} \right) \right] \]
\[ E = uN, \quad E_0 = u_0N_0, \quad V = vN, \quad V_0 = v_0N_0 \]

\[ S = \frac{N}{N_0} S_0 + Nk_B \ln \left[ \left( \frac{E}{E_0} \right)^{\frac{3}{2}} \left( \frac{V}{V_0} \right) \left( \frac{N}{N_0} \right)^{-\frac{3}{2}} \right] \]

where \( S_0 = \frac{5}{2} k_B N_0 + \frac{\mu}{k_B T_0} N_0 \) a constant

Fundamental equation, expresses \( S \) in terms of \( E, V, N \)

Alternatively

\[ dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN \]

\[ \Rightarrow dS = \frac{1}{T} du + \frac{P}{T} dv \]

\[ = \frac{3}{2} \frac{k_B}{u} du + \frac{k_B}{v} dv \]

\[ \Delta - \Delta_0 = \frac{3}{2} k_B \ln \left( \frac{u}{u_0} \right) + k_B \ln \left( \frac{v}{v_0} \right) \]

\[ \Delta = \Delta_0 + \frac{3}{2} k_B \ln \left( \frac{u}{u_0} \right) + k_B \ln \left( \frac{v}{v_0} \right) \]

\[ \Delta = \Delta_0 + k_B \ln \left[ \left( \frac{u}{u_0} \right)^{\frac{3}{2}} \left( \frac{v}{v_0} \right)^{-\frac{3}{2}} \right] \quad \text{same as above} \]

Fundamental equation, expresses \( \Delta \) in terms of \( u \) at \( v \)
Energy minimum Principle

Postulate II stated that when constraints are removed, the equilibrium state will be the one that maximizes the entropy \( S(E, V, N, \ldots) \), which is concave.

We saw that entropy is a concave function of its 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 equilibrium 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 \( E = E_0 \).

\( X_0 \) is given by the point \( A \) that maximizes \( S \) along the curve of intersection.

\[
S_0 = \max_{X} S(E_0, X)
\]

[Cellin 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 constant $S = S_0$.

Callin Fig 5.2

\[ E_0 = \min_X \{ E(S_0, X) \} \]

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 concave total energy $E$. In equilib, $d^2S < 0$, $S$ concave.

**Energy formulation:** fundamental function is $E(S, X_1, X_2)$ 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 equilibrium state for which $E$ was not the minimum possible value for the given $S$.

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

Start do mechanical and heat

\[ E_0, S_0 \xrightarrow{\text{work}} E_1, S_0 \rightarrow E_0, S_1 \]

where $E_1 < E_0$ and $S_1 > S_0$.

Now return the 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 equilibrium state was a maxmin of entropy. \( \Rightarrow \) original $E$ had to have been the minimum.