# Thermodynamic potentials

## Fundamental equation

According to the first law

$$dU = T\,dS - p\,dV + \mu\,dN \qquad (*)$$

$S$, $V$ and $N$ are the natural variables of the internal energy $U$, i.e.

$$U = U(S, V, N).$$

Furthermore, from the law $(*)$ one can read the relations

$$\begin{aligned} \left(\frac{\partial U}{\partial S}\right)_{V,N} &= T \\ \left(\frac{\partial U}{\partial V}\right)_{S,N} &= -p \\ \left(\frac{\partial U}{\partial N}\right)_{S,V} &= \mu. \end{aligned} \qquad (**)$$

Now $U$, $S$, $V$ and $N$ are extensive so we have

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)\ \forall\lambda. \qquad (***)$$

Let $S \to S + \epsilon S$, $V \to V + \epsilon V$ and $N \to N + \epsilon N$, when $\epsilon$ is infinitesimal. Then

$$U(S + \epsilon S, V + \epsilon V, n + \epsilon N) = U(S, V, N) + \left(\frac{\partial U}{\partial S}\right)_{V,N} \epsilon S + \left(\frac{\partial U}{\partial V}\right)_{S,N} \epsilon V + \left(\frac{\partial U}{\partial N}\right)_{S,V} \epsilon N.$$

On the other hand, according to the equation $(***)$ we have

$$U(S + \epsilon S, V + \epsilon V, N + \epsilon N) = U(S, V, N) + \epsilon U(S, V, N).$$

We end up with the *Euler equation for homogenous functions*

$$U = S\left(\frac{\partial U}{\partial S}\right)_{V,N} + V\left(\frac{\partial U}{\partial V}\right)_{S,N} + N\left(\frac{\partial U}{\partial N}\right)_{S,V}.$$

Substituting the partial derivatives $(**)$ this takes the form

$$U = TS - pV + \mu N$$

or

$$S = \frac{1}{T}(U + pV - \mu N).$$

This is called the *fundamental equation.*

## Internal energy and Maxwell relations

Because

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

and

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N},$$

so

$$\frac{\partial T}{\partial V} = \frac{\partial}{\partial V}\frac{\partial U}{\partial S} = \frac{\partial}{\partial S}\frac{\partial U}{\partial V} = -\frac{\partial p}{\partial S}.$$

Similar relations can be derived also for other partial derivatives of $U$ and we get so called *Maxwell's relations*

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

In an irreversible process

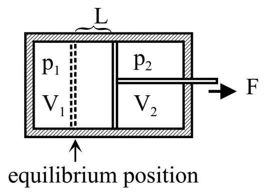
$$T\,\Delta S > \Delta Q = \Delta U + \Delta W,$$

so

$$\Delta U < T\,\Delta S - p\,\Delta V + \mu\,\Delta N.$$

If $S$, $V$ and $N$ stay constant in the process then the internal energy decreases. Thus we can deduce that *In an equilibrium with given $S$, $V$ and $N$ the internal energy is at the minimum.*

We consider a reversible process in an isolated system




We partition $\Delta W$ into the components

$$\begin{aligned} \int p\,dV &= \begin{bmatrix}\text{work due to the} \\ \text{change of the} \\ \text{volume}\end{bmatrix} \\ \Delta W_{\text{free}} &= \begin{bmatrix}\text{work done by the} \\ \text{gas against the} \\ \text{force } \boldsymbol{F}\end{bmatrix}. \end{aligned}$$

Now

$$\begin{aligned} \Delta W_{\text{free}} &= \Delta W_1 + \Delta W_2 = p_1 \Delta V_1 + p_2 \Delta V_2 \\ &= (p_1 - p_2)\Delta V_1 = (p_1 - p_2) A\,\Delta L \\ &= -F\,\Delta L. \end{aligned}$$

According to the first law we have

$$\begin{aligned} \Delta U &= \Delta Q - \Delta W = \Delta Q - \int p\,dV - \Delta W_{\text{free}} \\ &= \Delta Q - \Delta W_{\text{free}}. \end{aligned}$$

Because now $\Delta Q = 0$, we have

$$\Delta U = -\Delta W_{\text{free}} = F\,\Delta L,$$

i.e. when the variables $S$, $V$ and $N$ are kept constant the change of the internal energy is completely exhangeable with the work. $\Delta U$ is then called *free energy* and $U$ *thermodynamic potential.*

**Note** If there are irreversible processes in an isolated system ($V$ and $N$ constants) then

$$\Delta W_{\text{free}} \leq -\Delta U.$$

## Enthalpy

Using the Legendre transform

$$U \to H = U - V\left(\frac{\partial U}{\partial V}\right)_{S,N} = U + pV$$

We move from the variables $(S,V,N)$ to the varaiables $(S,p;N)$. The quantity

$$H = U + pV$$

is called *enthalpy*.
Now

$$\begin{aligned} dH &= dU + p\,dV + V\,dp \\ &= T\,dS - p\,dV + \mu\,dN + p\,dV + V\,dp \end{aligned}$$

or

$$dH = T\,dS + V\,dp + \mu\,dN.$$

From this we can read the partial derivatives

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

Corresponding Maxwell relations are

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

In an irreversible process one has

$$\Delta Q = \Delta U + \Delta W - \mu\,\Delta N < T\,\Delta S.$$

Now $\Delta U = \Delta(H - pV)$, so that

$$\Delta H < T\,\Delta S + V\,\Delta p + \mu\,\Delta N.$$

We see that
*In a process where $S$, $p$ and $N$ are constant spontaneous changes lead to the minimum of $H$, i.e. in an equilibrium of a $(S,p,N)$-system the enthalpy is at the minimum.*
The enthalpy is a suitable potential for an isolated system in a *pressure bath* ($p$ is constant).
Let us look at an isolated system in a pressure bath. Now

$$dH = dU + d(pV)$$

and

$$dU = \bar{d}Q - \bar{d}W + \mu\,dN.$$

Again we partition the work into two components:

$$\bar{d}W = p\,dV + \bar{d}W_{\text{free}}.$$

Now

$$dH = \bar{d}Q + V\,dp - \bar{d}W_{\text{free}} + \mu\,dN$$

and for a finete process

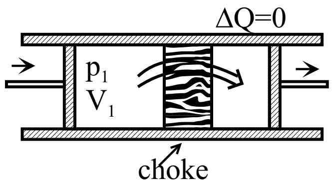
$$\Delta H \leq \int T\,dS + \int V\,dp - \Delta W_{\text{free}} + \int \mu\,dN.$$

When $(S,p,N)$ is constant one has

$$\Delta H \leq -\Delta W_{\text{free}}$$

i.e. $\Delta W_{\text{free}}$ is the minimum work required for the change $\Delta H$.
**Note** An other name of enthalpy is *heat function* (in constant pressure).

### Joule-Thomson phenomenon




$p_1$ and $p_2$ are temporal constants, $p_1 > p_2$ and the process irreversible. When a differential amount of matter passes through the choke the work done by the system is

$$\bar{d}W = p_2 dV_2 + p_1 dV_1.$$

| | $V_1$ | $V_2$ |
|---|---|---|
| Initial state | $V_{\text{init}}$ | 0 |
| Final state | 0 | $V_{\text{final}}$ |

The work done by the system is

$$\Delta W = \int \bar{d}W = p_2 V_{\text{final}} - p_1 V_{\text{init}}.$$

According to the first law we have

$$\Delta U = U_{\text{final}} - U_{\text{init}} = \Delta Q - \Delta W = -\Delta W,$$

so that

$$U_{\text{init}} + p_1 V_{\text{init}} = U_{\text{final}} + p_2 V_{\text{final}}.$$

Thus in this process the enthalpy $H = U + pV$ is constant, i.e. the process is *isenthalpic*,

$$\Delta H = H_{\text{loppu}} - H_{\text{alku}} = 0.$$

We consider now a *reversibel* isenthalpic (and $dN = 0$) process init→final. Here

$$dH = T\,dS + V\,dp = 0,$$

so

$$dS = -\frac{V}{T}\,dp. \qquad (*)$$

Now $T = T(S,p)$, so that

$$dT = \left(\frac{\partial T}{\partial S}\right)_p dS + \left(\frac{\partial T}{\partial p}\right)_S dp.$$

On the other hand

$$\left(\frac{\partial T}{\partial S}\right)_p = \frac{T}{C_p},$$

where $C_p$ is the isobaric heat capacity (see thermodynamical responses).
Using the Maxwell relation

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

and the partial derivative relation

$$\left(\frac{\partial V}{\partial S}\right)_p = \frac{\left(\frac{\partial T}{\partial S}\right)_p}{\left(\frac{\partial T}{\partial V}\right)_p}$$

we can write

$$dT = \frac{T}{C_p}\, dS + \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p dp.$$

Substituting into this the differential $dS$ in constant enthalpy $(*)$ we get so called *Joule-Thomson coefficients*

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{T}{C_p}\left[\left(\frac{\partial V}{\partial T}\right)_p - \frac{V}{T}\right].$$

Defining the *heat expansion coefficient* $\alpha_p$ so that

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p,$$

we can rewrite the Joule-Thomson coefficient as

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p}(T\alpha_p - 1).$$

We see that when the pressure decreases the gas

- cools down, if $T\alpha_p > 1$.
- warms up, if $T\alpha_p < 1$.

For ideal gases $\left(\frac{\partial T}{\partial p}\right)_H = 0$ holds. For real gases $\left(\frac{\partial T}{\partial p}\right)_H$ is below the *inversion temperature* positive, so the gas cools down.

## Free energy

The Legendre transform

$$U \to F = U - S\left(\frac{\partial U}{\partial S}\right)_{V,N}$$

or

$$F = U - TS$$

defines the (*Helmholtz*) *free energy.*

Now

$$dF = -S\, dT - p\, dV + \mu\, dN,$$

so the natural variables of $F$ are $T$, $V$ and $N$. We can read the partial derivateves

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_{V,N} \\ p &= -\left(\frac{\partial F}{\partial V}\right)_{T,N} \\ \mu &= \left(\frac{\partial F}{\partial N}\right)_{T,V}. \end{aligned}$$

From these we obtain the Maxwell relations

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

In an irreversible change we have

$$\Delta F < -S\,\Delta T - p\,\Delta V + \mu\,\Delta N,$$

i.e. when the variables $T$, $V$ and $N$ are constant the system drifts to the minimum of the free energy.
Correspondingly

$$\Delta W_{\text{free}} \le -\Delta F,$$

when $(T,V,N)$ is constant.
Free energy is suitable for systems where the exchange of heat is allowed.

## Gibbs' function

The Legendre transformation

$$U \to G = U - S\left(\frac{\partial U}{\partial S}\right)_{V,N} - V\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

defines the *Gibbs function* or the *Gibbs free energy*

$$G = U - TS + pV.$$

Its differential is

$$dG = -S\, dT + V\, dp + \mu\, dN,$$

so the natural variables are $T$, $p$ and $N$. For the partial derivatives we can read the expressions

$$\begin{aligned} S &= -\left(\frac{\partial G}{\partial T}\right)_{p,N} \\ V &= \left(\frac{\partial G}{\partial p}\right)_{T,N} \\ \mu &= \left(\frac{\partial G}{\partial N}\right)_{T,p}. \end{aligned}$$

From these we obtain the Maxwell relations

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

In an irreversible process

$$\Delta G < -S\,\Delta T + V\,\Delta p + \mu\,\Delta N,$$

holds, i.e. when the variables $T$, $p$ and $N$ stay constant the system drifts to the minimum of $G$.
Correspondingly

$$\Delta W_{\text{free}} \leq -\Delta G,$$

when $(T, p, N)$ is constant.
The Gibbs function is suitable for systems which are allowed to exchange mechanical energy and heat.

## Grand potential

The Legendre transform

$$U \to \Omega = U - S\left(\frac{\partial U}{\partial S}\right)_{V,N} - N\left(\frac{\partial U}{\partial N}\right)_{S,V}$$

defines the *grand potential*

$$\Omega = U - TS - \mu N.$$

Its differential is

$$d\Omega = -S\,dT - p\,dV - N\,d\mu,$$

so the natural variables are $T$, $p$ and$\mu$.
The partial derivatives are now

$$\begin{aligned}S &= -\left(\frac{\partial \Omega}{\partial T}\right)_{p,\mu}\\ p &= -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu}\\ N &= -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}.\end{aligned}$$

We get the Maxwell relations

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

In an irreversible process

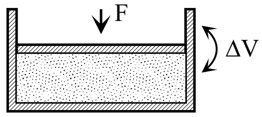
$$\Delta\Omega < -S\,\Delta T - p\,\Delta V - N\,\Delta\mu,$$

holds, i.e. when the variables $T$, $V$ and$\mu$ are kept constant the system moves to the minimum of $\Omega$.
Correspondingly

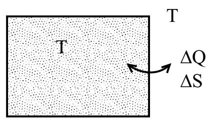
$$\Delta W_{\text{free}} \leq -\Delta\Omega,$$

when $(T, V, \mu)$ is constant.
The grand potential is suitable for systems that are allowed to exchange heat and particles.

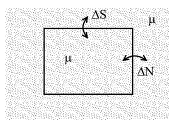
**Bath**
A *bath* is an equilibrium system, much larger than the system under consideration, which can exchange given extensive property with our system.
*Pressure heat*




The exchanged property is the volume or a corresponding generalized displacement; for example magnetization in a magnetic field.
*Heat bath*




*Particle path*




Baths can also be combined; for example a suitable potential for a pressure and heat bath is the Gibbs function $G$.

## Thermodynamic responses

**1) Volume heat expansion coefficient**

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N}$$

or

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{p,N},$$

where $\rho = N/V$.

**2) Isothermic compressibility**

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_{T,N}$$

**3) Adiabatic compressibility**

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S,N} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_{S,N}.$$

The velocity of sound depends on the adiabatic compressibility like

$$c_S = \sqrt{\frac{1}{m\rho\kappa_S}},$$

where $m$ the particle mass.
One can show that

$$\kappa_T = \kappa_S + VT\,\frac{\alpha_p^2}{C_p}.$$

**4) Isochoric heat capacity**
In a reversible process we have

$$\Delta Q = T\,\Delta S.$$

The heat capacity $C$ is defined so that

$$C = \frac{\Delta Q}{\Delta T} = T\,\frac{\Delta S}{\Delta T}.$$

In constant pressure we define

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N}.$$

In constant volume and the number particles being fixed, according to the first law

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

we can write

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}.$$

**5) Isobaric heat capacity**

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N}$$

Because

$$dH = T\,dS + V\,dp + \mu\,dN,$$

one can write

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,N}.$$

Now

$$\begin{aligned}\left(\frac{\partial S}{\partial T}\right)_p &= \left(\frac{\partial S\,(V(p,T),T)}{\partial T}\right)_p \\ &= \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p\end{aligned}$$

and (a Maxwell relation)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V,$$

so

$$C_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p.$$

Since

$$\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial V}{\partial p}\right)_T = -1$$

or

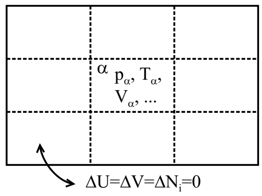
$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\alpha_p}{\kappa_T},$$

so

$$C_p = C_V + VT\frac{\alpha_p^2}{\kappa_T}.$$

## Thermodynamic equilibrium conditions

We divide the system into fictive semimicroscopic parts:




Extensive variables satisfy

$$\begin{aligned} S &= \sum_\alpha S_\alpha \\ V &= \sum_\alpha V_\alpha \\ U &= \sum_\alpha U_\alpha \\ N_j &= \sum_\alpha N_{j\alpha}.\end{aligned}$$

Since each element is in equlibrium the state variables are defined in each element, e.g.

$$S_\alpha = S_\alpha(U_\alpha, V_\alpha, \{N_{j\alpha}\})$$

and

$$\Delta S_\alpha = \frac{1}{T_\alpha}\,\Delta U_\alpha + \frac{p_\alpha}{T_\alpha}\,\Delta V_\alpha - \frac{\mu_{j\alpha}}{T_\alpha}\,\Delta N_{j\alpha}.$$

We suppose that the system is composed of two parts: $\alpha \in \{A, B\}$. Then

$$\Delta U_B = -\Delta U_A,\ \Delta V_B = -\Delta V_A \text{ and } \Delta N_{jB} = -\Delta N_{jA}$$

so

$$\begin{aligned}\Delta S &= \sum_\alpha \Delta S_\alpha \\ &= \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\Delta U_A + \left(\frac{p_A}{T_A} - \frac{p_B}{T_B}\right)\Delta V_A \\ &\quad -\sum_j\left(\frac{\mu_{jA}}{T_A} - \frac{\mu_{jB}}{T_B}\right)\Delta N_{jA}.\end{aligned}$$

In an equilibrium $S$ is at its maximum, so $\Delta S = 0$ and

$$\begin{aligned} T_A &= T_B \\ p_A &= p_B \\ \mu_{jA} &= \mu_{jB}.\end{aligned}$$

This is valid also when the system consists of several phases.

## Stability conditions of matter

In a steady equilibrium the entropy has the true maximum so that small variations can only reduce the entropy.

We denote the equilibrium values common for all fictive parts by the symbols $T$, $p$ and $\{\mu_j\}$ and the equilibrium values of other variables by the superscript $^0$.

We write the entropy $S_\alpha$ of the fictive partial system $\alpha$ close to an equilibrium as the Tatlor series

$$S_\alpha(U_\alpha, V_\alpha, \{N_{j\alpha}\}) = S^0_\alpha(U^0_\alpha, V^0_\alpha, \{N^0_{j\alpha}\}) + \left(\frac{\partial S}{\partial U_\alpha}\right)^0_{V,N} \Delta U_\alpha + \left(\frac{\partial S}{\partial V_\alpha}\right)^0_{U,N} \Delta V_\alpha + \sum_j \left(\frac{\partial S}{\partial N_{j\alpha}}\right)^0_{U,V} \Delta N_{j\alpha} + \frac{1}{2}\left\{\Delta\left(\frac{\partial S}{\partial U_\alpha}\right)^0_{V,N} \Delta U_\alpha + \Delta\left(\frac{\partial S}{\partial V_\alpha}\right)^0_{U,N} \Delta V_\alpha + \sum_j \Delta\left(\frac{\partial S}{\partial N_{j\alpha}}\right)^0_{U,V} \Delta N_{j\alpha}\right\} + \cdots.$$

Here $\Delta U_\alpha = U_\alpha - U^0_\alpha$ and correspondingly for other quantities. The variations of partial derivatives stand for

$$\Delta\left(\frac{\partial S}{\partial U_\alpha}\right)^0_{V,N} = \left(\frac{\partial^2 S}{\partial U^2}\right)^0_{V,N} \Delta U_\alpha + \left[\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial U}\right)_{V,N}\right]^0_{U,N} \Delta V_\alpha + \sum_j \left[\frac{\partial}{\partial N_j}\left(\frac{\partial S}{\partial U}\right)_{V,N}\right]^0_{U,V} \Delta N_{j\alpha}$$

and similarly for other partial derivatives.

In an equilibrium

$$\left(\frac{\partial S}{\partial U}\right)^0 = \left(\frac{\partial S}{\partial V}\right)^0 = \left(\frac{\partial S}{\partial N_j}\right)^0 = 0,$$

so

$$\Delta S_\alpha = \frac{1}{2}\left\{\Delta\left(\frac{\partial S}{\partial U_\alpha}\right)^0_{V,N} \Delta U_\alpha + \Delta\left(\frac{\partial S}{\partial V_\alpha}\right)^0_{U,N} \Delta V_\alpha + \sum_j \Delta\left(\frac{\partial S}{\partial N_{j\alpha}}\right)^0_{U,V} \Delta N_{j\alpha}\right\}.$$

This can be rewritten as

$$\Delta S_\alpha = \frac{1}{2}\left\{\Delta\left(\frac{1}{T_\alpha}\right) \Delta U_\alpha + \Delta\left(\frac{p_\alpha}{T_\alpha}\right) \Delta V_\alpha - \sum_j \Delta\left(\frac{\mu_{j\alpha}}{T_\alpha}\right) \Delta N_{j\alpha}\right\}.$$

Using the first law we get

$$\Delta S = \frac{1}{2T}\sum_\alpha \left\{ -\Delta T_\alpha \Delta S_\alpha + \Delta p_\alpha \Delta V_\alpha - \sum_j \Delta\mu_{j\alpha}\Delta N_{j\alpha}\right\}.$$

This can be further written as

$$\Delta S = -\frac{1}{2T}\sum_\alpha \left\{ \frac{C_V}{T}(\Delta T_\alpha)^2 + \frac{1}{\kappa_T V}[(\Delta V_\alpha)^2_{N_\alpha}] + \left(\frac{\partial \mu}{\partial N}\right)^0_{p,T} (\Delta N_\alpha)^2\right\},$$

where

$$(\Delta V_\alpha)_{N_\alpha} = \left(\frac{\partial V}{\partial T}\right)^0_{N,p} \Delta T_\alpha + \left(\frac{\partial V}{\partial p}\right)^0_{N,T} \Delta p_\alpha.$$

Since $\Delta S \le 0$, we must have

$$C_V \ge 0,\ \kappa_T \ge 0,\ \frac{\partial \mu}{\partial N} \ge 0.$$