AUXILIARY FUNCTIONS

In the previous treatments, $E, V$ and $N$ were the independent variables. giving a function $S$ that defines the equilibrium and approach to equilibrium extensive quantities.

When a system is in equilibrium, then it is in contact with a bath and control of extensive variables (there are easier to measure).

$E, V, N$ can fluctuate (exchange with the bath).

In actual experiments, we introduce a bath, we control $T$ and not $E$. So we need a function that depends on $T$ and not $E$ to describe equilibrium state of such a system placed in a bath.

$E, V, N$ are natural variables of $S$ which is to be maximized. $T, V, N$ are not natural variables of $S$.

We define a new function $F$ which has $T, V, N$ as natural variables: Helmholz's free energy.

Here's how we do it:

$$dS_{\text{system}} + dS_{\text{bath}} = 0 \quad \text{Second law}$$

Total energy of isolated system or universe = constant

$$dE_{\text{system}} + dE_{\text{bath}} = 0 \quad \text{or} \quad dE_{\text{bath}} = -dE_{\text{system}}$$

$$dS_{\text{bath}} = \frac{dE_{\text{bath}}}{T} + \frac{p}{T} dV_{\text{bath}} - \frac{M}{T} dN_{\text{bath}}$$

$\text{constant } V, N$

$$dS_{\text{bath}} = -\frac{dE_{\text{system}}}{T}$$

$$dS_{\text{system}} - \frac{dE_{\text{system}}}{T} \geq 0 \quad \text{another form of second law}$$

$$dE_{\text{system}} - TdS_{\text{system}} \leq 0 \quad \text{for a fixed temperature}$$

Left: Define new function $F$ of properties of the system alone.

$$F = E - TS$$

$$dF = dE - TdS - SdT \quad \text{at constant temp}$$
Thus we get for spontaneous process
\[ dF = 0 \]

Thus \( F = E - TS \) is minimized in any spontaneous process

\( F \) represents a balance between energy and entropy. At constant \( T \), system tries to minimize energy and maximize entropy at the same time. The balance depends on temperature.

At low temperature, energy of system dominates.
At high temperature, entropy of system dominates.

Now \( dF = dE - TdS - SdT \)
\[ = (TdS - pdV + \sum_j \mu_j dN_j) - TdS - SdT \]
\[ dF = -pdV + \sum_j \mu_j dN_j \Rightarrow \text{Thus } F \text{ is a function of variables } T, V, N. \]
\[ \frac{\partial F}{\partial V} \text{ and } \frac{\partial F}{\partial N_j} \text{ are } -p \text{ and } \mu_j \text{ respectively.} \]

So \( F \) is expressed as a function of \( T, V, N \).

\[ dF = \left( \frac{\partial F}{\partial T} \right)_{V,N} dT + \left( \frac{\partial F}{\partial V} \right)_{T,N} dV + \sum_j \left( \frac{\partial F}{\partial N_j} \right)_{T,V,N \neq j} dN_j \]

\[ S = -\left( \frac{\partial F}{\partial T} \right)_{V,N} \quad p = -\left( \frac{\partial F}{\partial V} \right)_{T,N} \quad \mu_j = \left( \frac{\partial F}{\partial N_j} \right)_{V,T,N \neq j} \]

We arrived at \( F(T,V,N) \) from \( S(E,V,N) \) by logic. We can arrive here by a mathematical approach called Legendre transform.

This allows us to exchange a thermodynamic variable by its conjugate. Exchange between non-conjugate variables is not possible. If it were then you would have less knowledge of the macrostate.

\[ y = f(x) \Rightarrow \alpha = f(p) \]
\[ \text{intercept} \quad \text{slope} \quad \text{defines equivalent function but in terms of } p \text{ as an independent variable} \]

Eq. \( y = a + px \Rightarrow \alpha = y - px \). where \( \alpha = \frac{\partial y}{\partial x} \).
\[ E(S,V,N) \xrightarrow{\text{Legendre transform}} F(T,V,N) \]

\[
\left( \frac{\partial E}{\partial S} \right)_{V,N} = T \quad \Rightarrow \text{slope}
\]

\[ F = E - TS \text{ would do the job} \]

\[ dF = dE - T dS - S dT \]

Use fundamental energy equation

\[ dE = T dS - p dV + \sum_j \mu_j dN_j \quad \text{for a reversible step} \]

\[ dF = -S dT - p dV + \sum_j \mu_j dN_j \quad \text{differential form of } F \]

\[ F = F(T,V,N_j) \text{ as desired where } T,V,N \text{ are independent variables. Note we have one intensive variable } T \text{ and other extensive variables } T,V,N_1,N_2,\ldots,N_j \]

We already showed for a spontaneous process \( dF < 0 \) i.e. \( F \) is minimized w.r.t. partitioning of \( V \) and each \( N_j \). \( T \) cannot be partitioned. \( dT \) term gives temperature dependence of the function. \( dV \) and \( dN_j \) terms represent change in free energy in response to repartitioning of \( V \) and \( N_j \). When this repartitioning minimizes \( F \) until it can not be reduced any further \((dF = 0)\) then equilibrium is reached.

So \( F \) is a quantity that is minimized at constant temperature and constant total \( V \) and \( N \)'s by repartitioning of \( V \) and \( N \). (Useful for processes involving gaseous mixtures in a chamber)

Another form

\[ F = E - TS \]

\[ E = TS - PV + \sum_j \mu_j N_j \quad (\text{Euler's theorem}) \]
\[ F = -PV + \sum_{j} \mu_j N_j \]
where \( P \) and \( \mu_j \) are defined at a given temperature. This implies at every temperature, there is a corresponding form for \( F \):

\[ F_{T_c} = -P_{T_c} V + \sum_{j} \mu_j N_j \]

This \( F \) needs to be minimized at given temperature by repartitioning of \( V \) and \( N_j \), keeping their total constant.
Other such auxiliary functions \( \Rightarrow \)
\( H(S, p, N) \Rightarrow \) more useful than energy or entropy for experiments involving a constant pressure bath.
\( G(T, p, N) \Rightarrow \) most useful quantity for experiments (constant \( T \) and \( P \)), especially for chemical reactions.

**Enthalpy or \( H(S, p, N) \)**

\[
\begin{align*}
E(S, V, N) & \rightarrow H(S, p, N) \quad \text{so swap } p \text{ for } V \\
\frac{\partial E}{\partial V}_{S,N} & = -p \quad \text{... from fundamental energy equation.}
\end{align*}
\]
\[

\therefore H = E + pV \\
\Delta H = \Delta E + p\Delta V + V\Delta p \\
\Delta H = T\Delta S - p\Delta V + \sum_{j} \mu_j \Delta N_j + p\Delta V + V\Delta p \\
\Delta H = T\Delta S + V\Delta p + \sum_{j} \mu_j \Delta N_j \quad \text{... differential form}
\]
\[
H = H(S, p, N) \quad \text{... } H \text{ is dependent on } S, p \text{ and } N
\]

Using Euler's theorem: \( E = TS - pV + \sum_{j} \mu_j N_j \)

\[
H = TS + \sum_{j} \mu_j N_j \\
\text{where } S \text{ and } \mu_j \text{'s are defined at constant pressure.}
\]

and equilibrium requires \( S \) and \( \mu_j \text{'s} \) be repartitioned for constant total \( S \) and \( \mu_j \text{'s} \) until \( H \) reaches an extremum.

At this point the temperatures of all partitions become equal & chemical potential of each species is the same in all partitions.

This can be seen from differential form:
\[ dH = TdS + VdP + \sum_j u_j dN_j \]

At constant pressure \( dP = 0 \)

\[ dH = TdS + \sum_j u_j dN_j \]

Across all partitions \( (1, 2, 3, \ldots, r) \)

\[ dH = \sum_r dH_r = \sum_r \frac{1}{r} T_r ds_r + \sum_r \left( \frac{1}{r} \sum_j u_j dN_j \right) \]

For 2 partitions,

\[ dH = T_1 dS_1 + T_2 dS_2 + \sum_j \frac{1}{r} u_j dN_j^1 + \sum_j r^2 u_j dN_j^2 \]

At equilibrium, \( dH = 0 \)

Note: Total entropy constant: \( ds_1 = -ds_2 \)

Likewise: \( dN_j^1 = -dN_j^2 \)

\( \therefore \) at equilibrium \( T_1 = T_2 \) and \( u_j^1 = u_j^2 \) \( \ldots \) for all species \( (1 \to \ldots j) \)

Thus we arrive at the same conditions for thermal and chemical equilibrium as from the entropy approach.

Of course here the pressure is held constant by the bath over all partitions hence it is not necessary to state condition for mechanical equilibrium. It is implied.

One can perform similar exercises for other auxiliary functions.
Thus two Legendre transforms reqd

\[ E(S,V,N_j) \rightarrow F(T,V,N_j) \rightarrow G(T,P,N_j) \]

Let's perform \( F(V) \rightarrow G(P) \)

\[
\left( \frac{\partial F}{\partial V} \right)_{T,N_j} = -P
\]

\[ G = F + PV = E - TS + PV \]

\[ \text{d}G = \text{d}E - T \text{d}S - S \text{d}T + P \text{d}V + V \text{d}P \]

using fundamental energy equation

\[ \text{d}G = -S \text{d}T + V \text{d}P + \sum_j \mu_j \text{d}N_j \ldots \text{differential form} \]

\[ \therefore G \text{ is a function of } T, P, N_j \text{ as desired.} \]

The \( \text{d}T \) and \( \text{d}P \) terms describe temperature and pressure dependence. \( \text{d}N_j \) term describes effect on \( G \) on partitioning of \# of particles of each species while keeping each \( N_j \) constant. Once \( G \) reaches an extremum, we get equilibrium partitioning. Thus at given temp and pressure (most common conditions)

\[ \text{d}G = \sum_j \mu_j \text{d}N_j \]

\[ \text{d}P = 0, \text{d}T = 0 \]

At equilibrium \( \text{d}G = 0 \) implying for each species \( N_j \) is partitioned such that \( \mu_1 = \mu_2 = \ldots = \mu_j \) (for \( r \) partitions)

This describes chemical equilibrium.
Mechanical equilibrium and thermal equilibrium is always enforced on the system by the T,p bath.

Summary of auxiliary functions

\( \Rightarrow S \) is a quantity maximized by partitioning \( E,V,N \) at constant total \( E,V,N \).

\( \Rightarrow E \) is a quantity that is minimized by partitioning \( S,V,N \) at constant total \( S,V,N \). Note \( E \) being minimized as saying \(-E\) is maximized. So it's a sign convention matter, no fundamental difference.

\( \Rightarrow H \) is qty that is minimized by partitioning \( S,N_j \) at constant \( P \), total \( S,N_j \). Remember intensive variables cannot be partitioned. \( P \) is held fixed due to application of a pressure bath.

\( \Rightarrow F \) is a qty minimized by partitioning \( V,N_j \) at constant \( T \) (thermal bath) and total \( V,N_j \).

\( \Rightarrow G \) is a qty minimized by partitioning \( N_j \)’s at constant \( P \) and \( T \) (thermal & pressure bath) and total \( N_j \).

Most fundamental for completely isolated system

\( S \Rightarrow F \Rightarrow H \Rightarrow G \)

1 no intensive variables

1 intensive variable

2 intensive variables
Flask isolated (a universe in itself)
$E, V, N = \text{constant}$

There are partitioned within flask until entropy within flask is maximized
$\Delta S_{\text{system}} > 0$  $\Delta S_{\text{bath}} = 0$ (no interaction with system)
$\Delta S_{\text{universe}} > 0$

Flask exchanges energy with surroundings $S, V, N$ while flask held constant.
These are partitioned within flask until $E$ in flask is minimized.
$\Delta S_{\text{system}} = 0$  $\Delta S_{\text{bath}} > 0$  $\Delta S_{\text{universe}} > 0$

Temperature bath kept $T$ constant. No energy exchange/partitioning required. $V$ and $N$ are partitioned in flask until $F$ in flask is minimized.
$\Delta F_{\text{system}} < 0$ implies $-(\Delta S_{\text{bath}} + \Delta S_{\text{system}}) < 0$
$\therefore \Delta S_{\text{universe}} > 0$

Pressure bath kept $P$ constant. No volume exchange/partitioning required. $S$ and $N$ are partitioned in flask until $H$ in flask is minimized.
$\Delta H_{\text{system}} < 0$ Note $AN$ is equivalent to heat absorbed by closed system at constant pressure, i.e. $\Delta S_{\text{sur}} > 0$ or $\Delta S_{\text{sur}} > 0$
$\therefore \Delta S_{\text{system}} = 0$  $\Delta S_{\text{universe}} > 0$

Temperature and pressure held constant by bath. $N$ within flask partitioned until $G$ in flask is minimized
$\Delta G_{\text{system}} < 0$ implies $\Delta H - T \Delta S_{\text{system}} < 0$
$\therefore -T(\Delta S_{\text{sur}} + \Delta S_{\text{system}}) < 0$ or $\Delta S_{\text{universe}} > 0$
Discussion and clarification

* Fundamental relation: If the fundamental relation of a particular system is known, all possible thermodynamic information about the system is discernible.

* Internal constraints: are constraints that restrict the partitioning of extensive variables but do not alter the total value of those extensive variables.

* When an internal constraint is removed, repartitioning of the independent extensive variables occurs such that $S$ is maximized. ($E, V, N$)

* If $(S, V, N)$ are repartitioned, $E$ is minimized (same as $-E$ being maximized).

In the universe, constraints are constantly being removed (mixing & randomization).

The Legendre transformation $E(S) \Rightarrow F(T)$ is equivalent to $S(E) \Rightarrow F(T)$.

* $F(T, V, N)$ defines a function which is maximized by repartitioning $V$ and $N$ once such partitioning is permitted. $T$ is intensive so is not partitioned, but held constant. It makes no sense to repartition intensive variables.

* $G(T, p, N)$ defines a function which is minimized by repartitioning $N$ (chemical reactions!) once such partitioning is permitted. $T$ and $p$ are intensive so they are not partitioned, but held constant. As above, intensive properties (system size independent) cannot be partitioned.
Euler's Theorem: For a homogeneous first-order function, Extensive properties depend linearly on size of system.

E.g. \( E(S, V, N) = \lambda E(S, x) \) for any \( \lambda \)

\( E(S, V, N) \) is a first-order homogeneous function.

Any general \( f(x_1, x_2, \ldots, x_r) \)

let \( u_i = \lambda x_i \)

\[ f(u_1, u_2, \ldots, u_r) = \lambda f(x_1, x_2, \ldots, x_r) \]

differentiated w.r.t. \( \lambda \)

\[ \left( \frac{\partial f(u_1, u_2, \ldots, u_r)}{\partial \lambda} \right)_{u_i} = f(x_1, x_2, \ldots, x_r) \]

\[ \sum_{i=1}^{r} \left( \frac{\partial f}{\partial u_i} \right)_{u_j} \left( \frac{\partial u_i}{\partial \lambda} \right)_{u_i} = f(x_1, x_2, \ldots, x_r) \]

\[ \sum_{i=1}^{r} \left( \frac{\partial f}{\partial u_i} \right)_{u_i} x_i = f(x_1, x_2, \ldots, x_r) \]

Take \( \lambda = 1 \)

\[ f(x_1, x_2, \ldots, x_r) = \sum_{i=1}^{r} \left( \frac{\partial f}{\partial u_i} \right)_{u_i} x_i \]

E.g. \( dE = Tds - pDV + \sum_j \delta u_j \delta N_j \)

\[ E(T, V, N) = \left( \frac{\partial E}{\partial S} \right)_{V, N} S + \left( \frac{\partial E}{\partial V} \right)_{S, N} V + \sum_j \left( \frac{\partial E}{\partial N_j} \right)_{S, V, N_{-j}} \]

\[ E = TS - pV + \sum_j \delta u_j \delta N_j \]
Total Differential
\[ dE = Tds + sdt - p\,dV - V\,dp + \sum_j \mu_j \,dN_j + \sum_j \eta_j \,d\eta_j \]

Subtracting from fundamental energy equation
\[ 0 = s\,dT + V\,dp - \sum_j \eta_j \,d\eta_j \]

\[ \sum_j \eta_j = - s\,dT + V\,dp \quad \Rightarrow \text{Gibb's Duhem equation} \]

At constant \( T, p \)

\[ \sum_j \eta_j \,d\eta_j = 0 \]

Relation between chemical potentials of different species in a system. How molecular interactions are coupled in osmotic, ligand binding and phase transitions; also how chemical potentials depend on temperature and pressure.
Heat capacities: \[ dE = dq - pdV + udN \]

At constant volume, particle no, \( dE = dq \), heat capacity is the amount of heat needed to be absorbed to raise the temperature by a unit amount, \( C_v = \left( \frac{\partial q}{\partial T} \right)_{V,N} = \left( \frac{\partial E}{\partial T} \right)_{V,N} = T \left( \frac{\partial S}{\partial T} \right)_{V,N} \). Note \( C_v \) is extensive.

At constant pressure, we need a different fundamental \( dq \) to calculate the amount of heat needed to be absorbed.

\[
\begin{align*}
\Delta H &= dq - pdV + udN + pdV + Vdp \\
\Delta H &= dq + udN + Vdp \\
\end{align*}
\]

(valid for all processes)

\[ C_p = \left( \frac{\partial q}{\partial T} \right)_{p,N} = \left( \frac{\partial H}{\partial T} \right)_{p,N} \]

How does internal energy change as a function of temperature?

\[
\Delta E = \int_{T_A}^{T_B} dq = \int_{T_A}^{T_B} C_v(T) dT \quad \text{\( C_v \) can be a function of temperature or volume}
\]

\[
\Delta S = \int_{T_A}^{T_B} \frac{C_v(T)}{T} dT \quad \Rightarrow \text{This is the change in entropy when temperature is increased from } T_A \text{ to } T_B
\]

\[
\Delta H = \int_{T_A}^{T_B} C_p(T) dT \quad \Rightarrow \text{This is the change in enthalpy when temperature is increased from } T_A \text{ to } T_B
\]

Thus, \( \Delta E \& \Delta S \) can be obtained by constant volume calorimetry

\( \Delta H \) by constant pressure calorimetry.
Fundamental properties are seldom measurable. Measurable properties are seldom fundamental.

Maxwell's relations ⇒ relate different measurements

\[ f = f(x, y) \]
\[ \delta f = \left( \frac{\partial f}{\partial x} \right)_{y} \delta x + \left( \frac{\partial f}{\partial y} \right)_{x} \delta y = a \delta x + b \delta y \]

Now \[ \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \] …… for any smooth function

\[ \Rightarrow \frac{\partial a}{\partial y} \bigg|_{x} = \frac{\partial b}{\partial x} \bigg|_{y} \]

\[ dp = - \delta p \delta T + T dp + \sum_{J} \Xi_{m} dN_{j} \]

\[ \therefore \frac{\partial s}{\partial p} = \frac{\partial ^{2} s}{\partial p \partial T} \]

\[ \frac{\partial V}{\partial T} = \frac{\partial ^{2} s}{\partial T \partial p} \]

\[ \therefore \frac{\partial s}{\partial p} = \left( \frac{\partial V}{\partial T} \right)_{p,N} \]

fundamental \<—\> easy to measure

impart into

molecular behavior.

\[ \therefore \ ds = \ -\left( \frac{\partial V}{\partial T} \right)_{p,N} \ dp \] \text{ at given temperature}

\[ \therefore \ ds = \ -\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{p,N} V dp \]

\[ \therefore \ ds = -\alpha V dp \] \text{ thermal expansion coefficient}

\[ \Delta s = \int_{P_{1}}^{P_{2}} \alpha(p) V(p) dp \] \text{ at a given temperature and pressure.}
The thermal expansion coefficient $\alpha$ can be measured. 
$\alpha$ is small for a system with "rigid bonds".

What we find is that the entropy change is small for small value of $\alpha$.

Thus from measurable $\alpha$ we learn about fundamental behavior. How bonds can be organized by applying pressure, etc.,...

**Partial molar quantities**

Describes how a quantity changes when a small amount of a species is added to the system.

These are typically defined at constant temperature and pressure.

Now $\mu = -(\frac{\partial G}{\partial N})_V = (\frac{\partial H}{\partial N})_p = (\frac{\partial E}{\partial N})_{sv} = (\frac{\partial F}{\partial N})_T = (\frac{\partial G}{\partial N})_P$

So chemical potential is partial molar free energy.

Remember $G = E- TS + PV$

$E = TS - PV \equiv \sum_{i} \mu_i N_i$ (Euler's theorem)

$\therefore G = \sum_{i} \mu_i N_i$

$j = 1, 2, 3, \ldots$ different species

chemical potentials or partial molar free energies

we allow

If chemical reactions between species, then total $N$ across all species constant rather than each $N_j$. Thus total $N$ partitioned across different species such that $G$ is minimized until it can be minimized no further.
Chemical equilibrium and Gibb's free energy

\[ G = \sum_{i} \mu_i N_i \]

where \( i = 1, 2, 3, \ldots \) for different species / quasiparticles

If \( \sum_{i} N_i = N \)

\[ G = \frac{\sum_{i} \mu_i N_i}{N} \]

\[ \therefore \text{Free energy} = \frac{\sum_{i} \mu_i x_i}{\mathbb{E}x_i} \text{ where } x_i \Rightarrow \text{mole fraction per mole} \text{ and } \mathbb{E}x_i = 1 \]

\[ \therefore \text{Chemical potentials are partial molar free energies} \]

For only type of species

\[ G = \mu_i \]

So here, there is only one component.

But do note \( \mu \) depends on temperature and pressure.
This is via the Gibb's-Duhem equation.

When you have a multicomponent system (r components)

\[ G = \frac{\sum_{i} \mu_i x_1 + \mu_i x_2 + \ldots + \mu_i x_r}{N} \]

Imagine a chemical reaction between these species \( A, A, \ldots \)

\[ \underset{\Delta}{\sum_{i}} A_i \rightarrow 0 \]

A chemical reaction is a type of partitioning.
\( f_i \) are stoichiometric coefficients \( \Rightarrow \) from mass conservation.
\[ \Delta G = -s \Delta T + v \Delta P + \sum \varepsilon_{\text{mi}} \Delta N_i \]

Changes in mole numbers must be in proportion to stoichiometric coefficients.

\[
\frac{\Delta N_1}{f_1} = \frac{\Delta N_2}{f_2} = \cdots = \frac{\Delta N}{f_r} \]

proportionality factor.

\[ \therefore \Delta N_i = f_i \Delta N \]

If chemical reaction carried out constant temperature and pressure the condition of equilibrium implies:

\[ \Delta G = \Delta \bar{N} \bar{E}_{\text{fi} \Delta N_i} = 0 \]

\[ \boxed{\bar{E}_{\text{fi} \Delta N_i} = 0} \Rightarrow \text{This gives law of mass action as we will see soon.} \]

Condition for equilibrium \[ \sum \bar{E}_{\text{fi} \Delta N_i} = \bar{E}_{\text{f_i} \Delta N_i} \]

Note \( \mu_i \)'s here are chemical potentials of different species.

So, for chemical equilibrium \( \Rightarrow \) we partition \# of molecules partitioned between reactants and products.

Another situation \( \Rightarrow \) in a phase transformation \( \Rightarrow \) at equilibrium, \# of molecules/ particles partitioned between different phases.
Application to phase equilibria

At given $T, p$ for $j$ phases of one component only

$$dG = \sum_j \mu_j dN_j$$

where $\mu_j$ is defined at given $T, p$, (no other component present, constant).

Say for two phases (e.g. water & ice or atomic & molecular oxygen)

$$dG = \mu_{\alpha} dN_{\alpha} + \mu_{\beta} dN_{\beta}$$

If total no. of particles of our single component system is held constant, then $dN_{\alpha} = -dN_{\beta}$

Exchange of particles between phases allowed.

$$\therefore dG = \mu_{\alpha} dN_{\alpha} + \mu_{\beta} dN_{\beta} = (\mu_{\alpha} - \mu_{\beta}) dN_{\alpha}$$

At equi. $dG = 0$

This is possible only if $\mu_{\alpha} = \mu_{\beta}$

Note $\mu_{\alpha}$ and $\mu_{\beta}$ are defined at given $T, p$.

$\alpha$ and $\beta$ phases can co-exist.

So at some $P, T$, $\mu_{\alpha} = \mu_{\beta}$. This is the curve along which phases $\alpha$ and $\beta$ can co-exist, both equally likely. On left side of this curve $\mu_{\alpha} < \mu_{\beta}$, therefore $G$ is smaller if material exists as $\alpha$ phase. On right side of this curve $\mu_{\alpha} < \mu_{\beta}$, $\beta$ exists. Minimum $G$ achieved if all of the particles are in phase $\beta$.

At one point $\mu_{\alpha} = \mu_{\beta} = \mu_{\gamma}$, all three phases co-exist.
For any general case:

\( \pi \) phases and \( r \) components. Let \( x_i \) be mole fraction of \( i^{th} \) species in \( \pi \) phases.

At equilibrium for each component

\[ \mu(T, P, x_1, x_2, \ldots x_r) \]

has to be the same across all \( \alpha = 1, 2, \ldots, \pi \) phases.

* Each \( \mu \) has \((r-1)\) independent variables besides \( T, P \).

\[ \text{Total \# of variables} = \pi \cdot (r-1) + 2 \quad \text{for} \quad T, P \]

* For each component \((r-1)\) independent equations, involving equating the chemical potentials of component for the \( \pi \) phases. Total \# of equations = \( r \cdot (r-1) \)

So degrees of freedom = \# of independent variables - \# of independent equations

\[ = 2 + \pi (r-1) - r (r-1) \]

\[ = 2 + \pi - r - r^2 + r \]

\[ = (2 + r) - r \]

For 1 component and 1 phase, \# of degrees of freedom = 2 \( \rightarrow \) a phase can exist anywhere on a plane.

For one component and 2 phases.

\# of degrees of freedom = \((2+1)-2 = 1 \rightarrow 2 \) phases can exist anywhere along a line.

For one component and 3 phases.

\# of degrees of freedom = 0 \( \rightarrow \) 3 phases can exist only at one point.
Phase transition = changes in interatomic & intermolecular behavior in macroscopic systems.

Intersection of the two surfaces represents co-existence line

Chemical potential surfaces for two phases.
Phase transition = intersection of two Gibb's surfaces.

\[ N d u = -S d T + V d P \]

\[ \left( \frac{\partial u}{\partial P} \right)_T = \frac{V}{N} = u \Rightarrow \text{molar volume} \]

\[ \left( \frac{\partial u}{\partial T} \right)_P = -\frac{S}{N} = -S \Rightarrow \text{molar entropy} \]

At phase transition change in \( u \) is given by change in \( (\partial u)/(\partial P)_T \) and change in \( S \) is given by change in \( (\partial u)/(\partial T)_P \)

If the two surfaces are smoothly connected, i.e.

\[ (\partial u)_T^a = (\partial u)_T^b \quad \text{and} \quad (\partial u)_P^a = (\partial u)_P^b \]

then \( u(T,P) \) and \( s(T,P) \) are continuous.
This is a second order transition.

In a first order transition, \( u(T,P) \) is discontinuous.
Sharp/quick change in volume and entropy at phase transition.
An activation barrier exists. No barrier exists for second higher order transitions. A continuous transition.
One-component system \( \rightarrow \) 2\textsuperscript{nd} order transition can occur at only one point — a critical point.

A two-component system \( \rightarrow \) 2\textsuperscript{nd} order transition can occur along lines, called critical lines.

For a first order transition,

The \( p-T \) co-existence line satisfies a differential equation obtained from:

\[
\mu^x(T, p) = \mu^y(T, p).
\]

\[
\Rightarrow \quad \frac{\partial \mu}{\partial T} = s^x dT + v^x dp
\]

Hence:

\[
\frac{d\mu^x}{dT} = \frac{d\mu^y}{dT} = s^y dT + v^y dp
\]

\[\frac{dp}{dT} = \frac{\Delta s(T, p)}{\Delta v_x(T, p)} \quad \text{Clausius-Clapeyron Eq.}
\]

This tells you what the co-existence line looks like.

\[\Delta s(T) = s^x(T, p) - s^y(T, p) \quad \text{and}.
\]

\[\Delta v_x(T) = v^x(T, p) - v^y(T, p)
\]

At \( T/P \) for which \( x \) and \( y \) are in equilibrium.
Stability and equilibrium criteria in terms of driving forces.

\[ \Delta A = -SdT - pdV + \sum \mu_i dN_i \]

For \( V \) partitioning over two sub-systems:

\[ 8V_1 = -8V_2 \quad \Rightarrow \quad V = \text{constant} \]

Let's say particle exchange is not allowed: \( S_{N_1} - S_{N_2} = 0 \)

At constant temperature, volume and no. of particles:

\( (\Delta A)_{T,V,N} > 0 \) as you move away from equilibrium.

\( (8A)_{T,V,N} = 0 \) for small displacements.

Equilibrium condition gives \( \rho_1 = \rho_2 \) - we have seen thus.

But what does stability require? It tells us about processes to equilibrium.

\( (8^2A)_{T,V,N} \geq 0 \)

Second-order difference in \( A \) w.r.t. of a small volume fluctuation:

\[ 8V_1 = -8V_2 = 8V \]

\[ (8V)^2 = (8V_1)^2 = (8V_2)^2 = (8V)^2 \]

\[ 8^2A = \frac{1}{2} (8V)^2 \left[ \left( \frac{\partial^2 A}{\partial V_T^2} \right) + \left( \frac{\partial^2 A}{\partial V_N^2} \right) \right] \]

\[ = -\frac{1}{2} (8V)^2 \left[ \left( \frac{\partial \rho}{\partial V} \right)^2 + \left( \frac{\partial \rho}{\partial V} \right)^2 \right] \]

\( \therefore (8^2A)_{T,V,N} \geq 0 \) implies \( -\left( \frac{\partial \rho}{\partial V} + \frac{\partial \rho}{\partial V} \right) \geq 0 \)

\( \therefore \frac{\partial \rho}{\partial V}_{T,N} > 0 \) ... if the pressure of a stable system is increased isothermally, its volume will decrease.
Isothermal compressibility

\[ \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T,N} \]

Thus \( \kappa \) is positive.

Same way \( \left( \frac{\partial m_i}{\partial N_i} \right)_{T,U,N_2} \geq 0 \)

General case

For any function \( \phi \) obtained from Legendre transformation of \( E \) and a function of independent extensive variables \( f(x_1, x_2, \ldots, x_r) \) and intensive variables \( (I_{r+1}, \ldots, I_n) \)

Then

\[ d\phi = \sum_{i=1}^{r} x_i \, dI_i - \sum_{j=r+1}^{n} x_j \, dI_j \]

and the stability criteria are

\[ 0 \leq \left( \frac{\partial I_i}{\partial x_i} \right)_{x_1, \ldots, x_i, x_{i+1}, \ldots, x_r, I_{r+1}, \ldots, I_n} \]