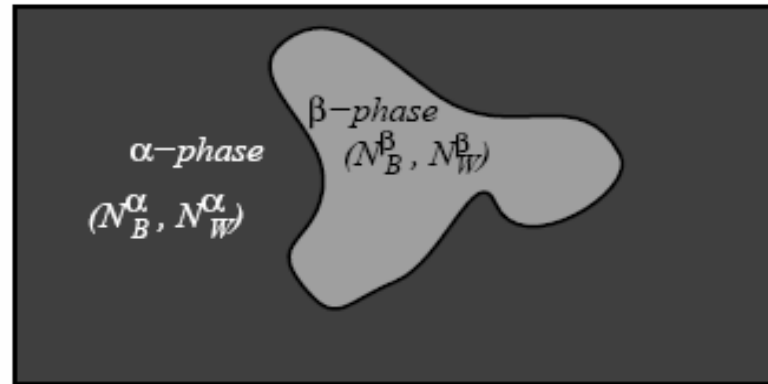
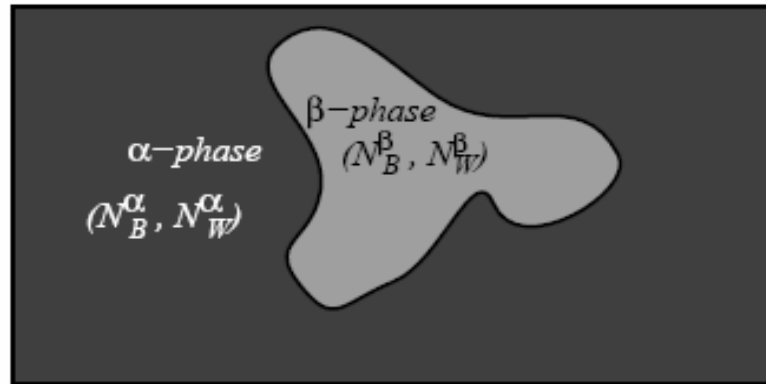

Composition variations and phase fractions

Composition variations and phase fractions



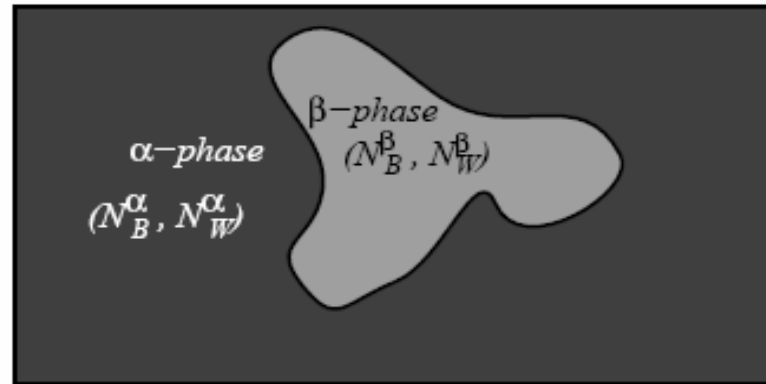
- Consider a system composed of variable chemical elements and various phases.
- The internal degrees of freedom are the compositions of the various regions that compose our system.

Phases



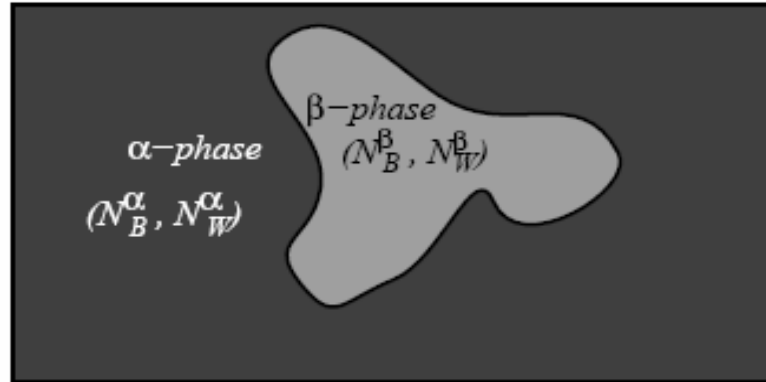
- **Phase:** A part of the system that can be identified as 'different' from another part of the system.
- Examples of phases are a solution of iron and carbon in an FCC structure and a solution of iron and carbon in a BCC structure.

Composition of each phase



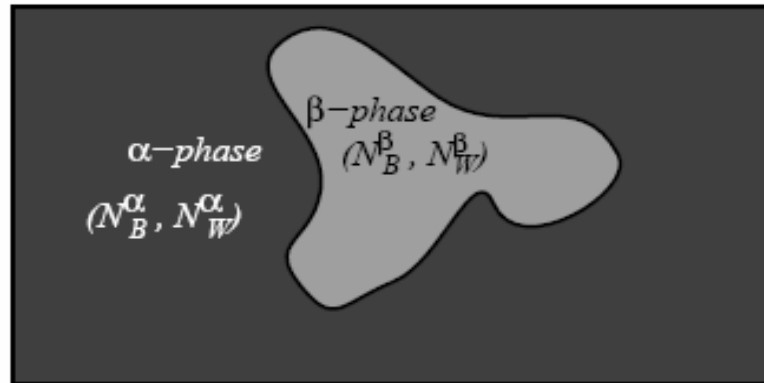
- **Composition:** The fractions of the various chemical components that comprise the system.
- **Phase fraction:** The fraction of the system that is in each phase ($\alpha, \beta, \gamma, \dots$).
- **Composition of phase α :** The composition of the subsystem composed α -phase alone.

Composition variations and phase fractions



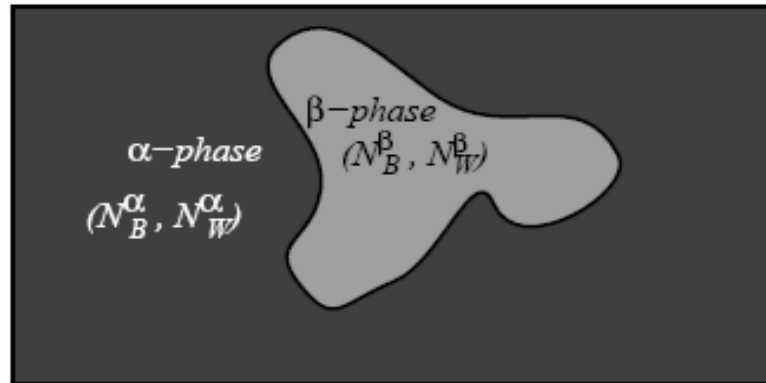
- Let N_B and N_W represent numbers of B and W-type molecules.
- The number of moles in phases α and β can be varied.

Composition variations and phase fractions



Notation	
N_B^α	Number of B atoms (or molecules) in α -phase
N_W^α	Number of W atom in α -phase
N_B^β	Number of B atom in β -phase
N_W^β	Number of W atom in β -phase

Composition variations and phase fractions



The total number of B and W molecules in the system are:

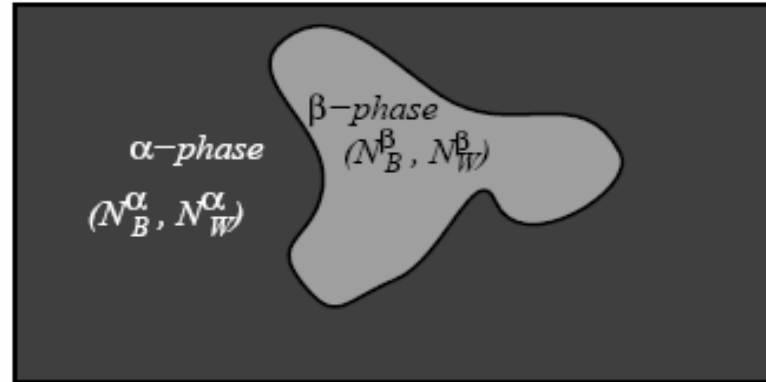
$$N_B = N_B^\alpha + N_B^\beta = \quad (\text{general}) \quad \sum_{i=1}^f N_B^i$$

$$N_W = N_W^\alpha + N_W^\beta = \quad (\text{general}) \quad \sum_{i=1}^f N_W^i$$

The total number of atoms in the system are:

$$N^{\text{total}} = N_B + N_W = \quad (\text{in general}) \quad \sum_{j=1}^c N_j$$

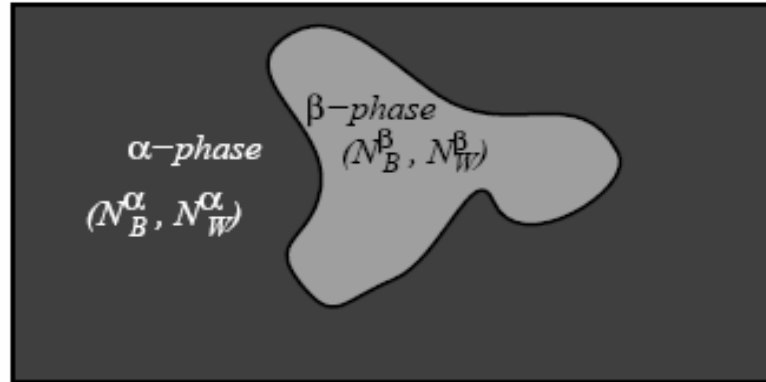
Composition variations and phase fractions



The average composition in the system is:

$$\overline{N_B} \equiv X_B = \frac{N_B}{N^{\text{total}}}$$
$$\overline{N_W} \equiv X_W = \frac{N_W}{N^{\text{total}}}$$

Composition variations and phase fractions



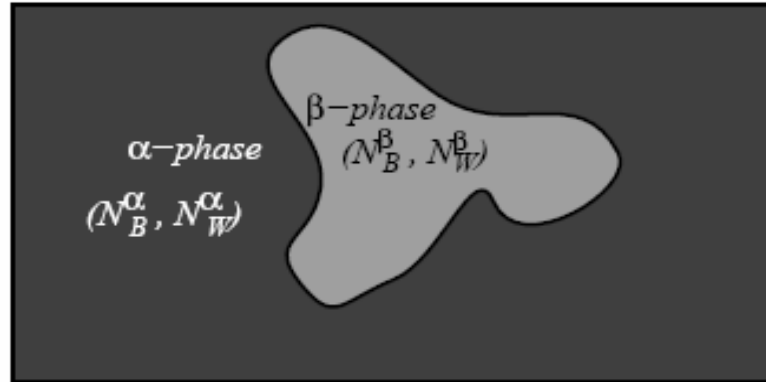
The total number of atoms in each phase is:

$$N^{\alpha\text{total}} = N_B^\alpha + N_W^\alpha = \quad (\text{in general}) \quad \sum_{j=1}^C N_j^\alpha$$

$$N^{\beta\text{total}} = N_B^\beta + N_W^\beta = \quad (\text{in general}) \quad \sum_{j=1}^C N_j^\beta$$

$$(\text{general, for phase } i) \quad N^{i\text{total}} = \sum_{j=1}^C N_j^i$$

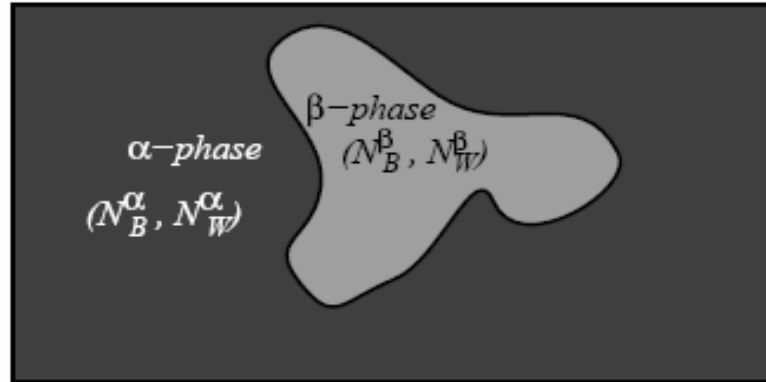
Composition variations and phase fractions



The compositions of each phase can now be defined as:

$$X_B^\alpha = \frac{N_B^\alpha}{N^{\alpha\text{total}}} \quad X_W^\alpha = \frac{N_W^\alpha}{N^{\alpha\text{total}}}$$
$$X_B^\beta = \frac{N_B^\beta}{N^{\beta\text{total}}} \quad X_W^\beta = \frac{N_W^\beta}{N^{\beta\text{total}}}$$

Composition variations and phase fractions



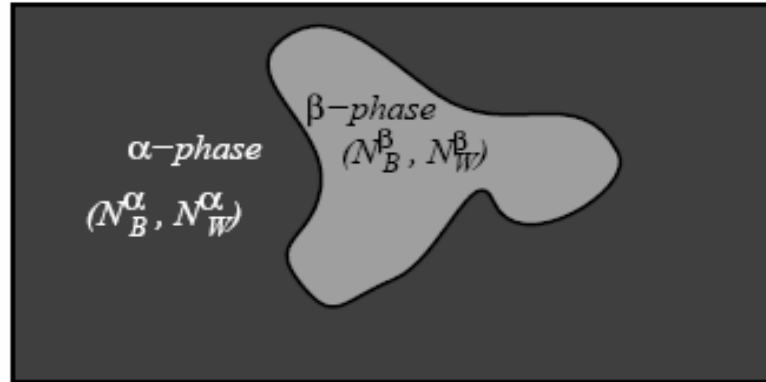
The phase fractions can be computed as:

$$f^\alpha = \frac{N^{\alpha\text{total}}}{N^{\text{total}}} \quad f^\beta = \frac{N^{\beta\text{total}}}{N^{\text{total}}}$$

generally, $f^i = \frac{N^{i\text{total}}}{N^{\text{total}}}$

$$1 = \sum_{i=1}^f f^i$$

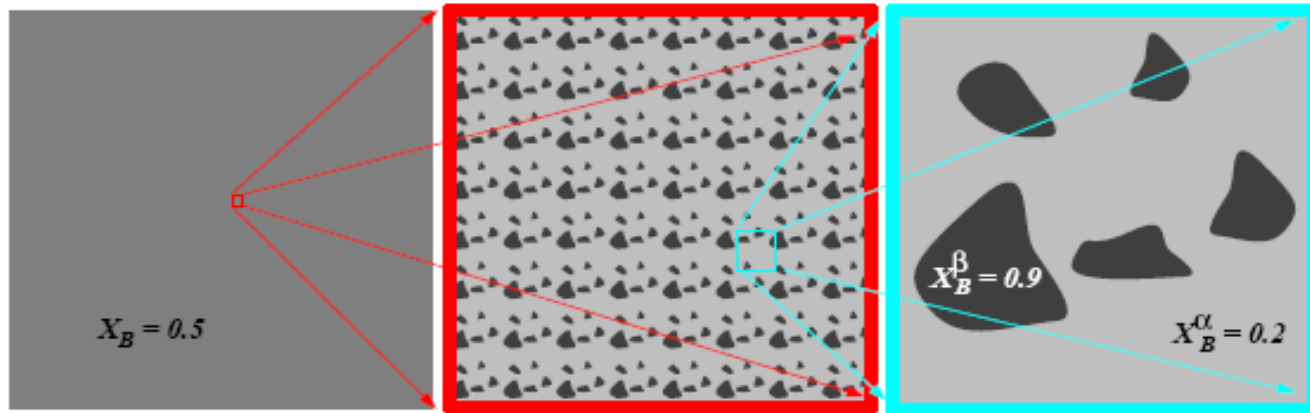
Composition variations and phase fractions



Note the following identity: $X_B = f^\alpha X_B^\alpha + (1 - f^\alpha) X_B^\beta$

From which we derive:
$$f^\alpha = \frac{X_B - X_B^\beta}{X_B^\alpha - X_B^\beta}$$

Composition variations and phase fractions



Consider the example above and think of B as the black spots.

Note that the composition is nowhere equal to the average composition.

The chemical potential

The chemical potential

- Let n_i be the number of moles of substance i .
- Then we have: $U=U(S, V, n_1, n_2, \dots, n_C)$ and:

$$dU = \left. \frac{\partial U}{\partial S} \right|_{V, n_i} dS + \left. \frac{\partial U}{\partial V} \right|_{S, n_i} dV + \sum_{i=1}^c \left. \frac{\partial U}{\partial n_i} \right|_{S, V, n_j} dn_i$$

- For constant n_1, n_2, \dots, n_k , $dU = TdS - PdV \Rightarrow T = \left. \frac{\partial U}{\partial S} \right|_{V, n_i}$, $-P = \left. \frac{\partial U}{\partial V} \right|_{S, n_i}$.

- We can thus write: $dU = TdS - PdV + \sum_{i=1}^c \left. \frac{\partial U}{\partial n_i} \right|_{S, V, n_j} dn_i$

- We introduce the chemical potential as: $\mu_i = \left. \frac{\partial U}{\partial n_i} \right|_{S, V, n_j}$.

μ_i is an intensive property. It represents the tendency of a substance to diffuse from one phase to another.

The chemical potential through G

$$dU = TdS - PdV + \sum_{i=1}^C \mu_i dn_i$$

- We can also introduce the chemical potential through G.
- Let $G=G(T,P,n_1,n_2,\dots,n_C)$. Then:

$$dG = \left. \frac{\partial G}{\partial T} \right|_{P,n_i} dT + \left. \frac{\partial G}{\partial P} \right|_{T,n_i} dV + \sum_{i=1}^C \left. \frac{\partial G}{\partial n_i} \right|_{T,P,n_j} dn_i$$

- For constant n_1,n_2,\dots,n_k , $dG = -SdT + VdP$.
- We can thus write: $dG = -SdT + VdP + \sum_{i=1}^C \left. \frac{\partial G}{\partial n_i} \right|_{T,P,n_j} dn_i$
- We can show that $\mu_i = \left. \frac{\partial G}{\partial n_i} \right|_{T,P,n_j}$

The chemical potential through G

$$\mu_i = \left. \frac{\partial U}{\partial n_i} \right|_{S,V,n_j} = \left. \frac{\partial G}{\partial n_i} \right|_{T,P,n_j}$$

- Recall that $dU = TdS - PdV + \sum_{i=1}^C \mu_i dn_i$

- Add on both sides $d(PV-TS)$

$$dG = TdS - PdV + \sum_{i=1}^C \mu_i dn_i + d(PV - TS) = -SdT + VdP + \sum_{i=1}^C \mu_i dn_i$$

- μ_i is thus given as $\mu_i = \left. \frac{\partial G}{\partial n_i} \right|_{T,P,n_j}$
- μ_i is thus the amount by which the capacity of the phase for doing work other than work of expansion is increased per unit amount of substance i added for an infinitesimal addition at constant T and P .

Combined first and second laws

$$U = U(S, V, n_1, n_2, \dots, n_C) : dU = TdS - PdV + \sum_{i=1}^C \mu_i dn_i$$

$$H = H(S, P, n_1, n_2, \dots, n_C) : dH = TdS + VdP + \sum_{i=1}^C \mu_i dn_i$$

$$F = F(T, V, n_1, n_2, \dots, n_C) : dF = -SdT - PdV + \sum_{i=1}^C \mu_i dn_i$$

$$G = G(T, P, n_1, n_2, \dots, n_C) : dG = -SdT + VdP + \sum_{i=1}^C \mu_i dn_i$$

where:
$$\mu_i = \left. \frac{\partial U}{\partial n_i} \right|_{S, V, n_j} = \left. \frac{\partial H}{\partial n_i} \right|_{S, P, n_j} = \left. \frac{\partial F}{\partial n_i} \right|_{T, V, n_j} = \left. \frac{\partial G}{\partial n_i} \right|_{T, P, n_j}$$

The chemical potential

$$dG = \sum_{i=1}^c \mu_i dN_i \quad (\text{constant pressure and temperature for the system})$$

$$d\bar{G} = \sum_{i=1}^c \mu_i dX_i \quad (\text{constant pressure and temperature for the system per mole})$$

$$dG^\alpha = \sum_{i=1}^c \mu_i^\alpha dN_i^\alpha \quad (\text{constant pressure and temperature for the } \alpha \text{ subsystem})$$

$$d\bar{G}^\alpha = \sum_{i=1}^c \mu_i^\alpha dX_i^\alpha \quad (\text{constant pressure and temperature per mole of the } \alpha \text{ subsystem})$$

$$\mu_i^\alpha = \left(\frac{\partial G^\alpha}{\partial N_i} \right)_{\text{const } P, \text{const } T, \text{const } N_j \text{ where } j \neq i} = \left(\frac{\partial \bar{G}^\alpha}{\partial X_i} \right)_{\text{const } P, \text{const } T, \text{const } X_j \text{ where } j \neq i}$$

The chemical potential is an intensive variable. $\mu_i^\alpha(T, P)$ is the chemical potential of species i in phase α . It is the rate at which reversible work must be done on the subsystem α to add a species i at constant P and T .

The chemical potential

Recall the method that was used to demonstrate the uniformity of P and T: from a conservation principle (constant U and V) for the extensive variables (U and V), and with the maximal entropy principle $dS=0$, it followed that the intensive variables (T and P) associated with the conserved quantities must be equal to equilibrium.

At constant T and P, G_{system} is minimized at equilibrium.

With another conservation principle, another equality can be derived. What will that be? Consider a closed system constraint:

The chemical potential

With another conservation principle, another equality can be derived. What will that be? Consider a closed system constraint (a closed system with f phases & C components):

$$dN_A^\alpha + dN_A^\beta + \dots + dN_A^f = 0 \Rightarrow dN_A^\alpha + dN_A^\beta + \dots + dN_A^{f-1} = -dN_A^f$$

$$dN_B^\alpha + dN_B^\beta + \dots + dN_B^f = 0 \Rightarrow dN_B^\alpha + dN_B^\beta + \dots + dN_B^{f-1} = -dN_B^f$$

.....

$$dN_C^\alpha + dN_C^\beta + \dots + dN_C^f = 0 \Rightarrow dN_C^\alpha + dN_C^\beta + \dots + dN_C^{f-1} = -dN_C^f$$

At equilibrium, the chemical potential for any transportable species must be uniform throughout the system.

$$\mu_i = \left. \frac{\partial G}{\partial N_i} \right|_{P,T,N_j \neq N_i} = \left. \frac{\partial \bar{G}}{\partial X_i} \right|_{P,T,X_j \neq X_i}$$

Note that in the last partial derivative there is a constraint to be considered

$$\sum_i X_i = 1$$

The chemical potential

If we can calculate the chemical potential in some phase we know its value in any other phase that is in equilibrium with it.

A clever approach would be to determine the chemical potential in the phase where it is most simple to calculate!
What would that be?

An ideal gas?

More to come in another lecture

Coefficient and Maxwell relations

$$U = G(S, V, n_1, n_2, \dots, n_C) : dU = TdS - PdV + \sum_{i=1}^C \mu_i dn_i$$

$$H = H(S, P, n_1, n_2, \dots, n_C) : dH = TdS + VdP + \sum_{i=1}^C \mu_i dn_i$$

$$F = G(T, V, n_1, n_2, \dots, n_C) : dF = -SdT - PdV + \sum_{i=1}^C \mu_i dn_i$$

$$G = G(T, P, n_1, n_2, \dots, n_C) : dG = -SdT + VdP + \sum_{i=1}^C \mu_i dn_i$$

Coefficient relations

$$T = \left. \frac{\partial U}{\partial S} \right|_{V, n_i} = \left. \frac{\partial H}{\partial S} \right|_{P, n_i}$$

$$P = -\left. \frac{\partial U}{\partial V} \right|_{S, n_i} = -\left. \frac{\partial F}{\partial V} \right|_{T, n_i}$$

$$S = -\left. \frac{\partial F}{\partial T} \right|_{V, n_i} = -\left. \frac{\partial G}{\partial T} \right|_{P, n_i}$$

$$V = \left. \frac{\partial H}{\partial P} \right|_{S, n_i} = \left. \frac{\partial G}{\partial P} \right|_{T, n_i}$$

Maxwell relations

$$\left. \frac{\partial T}{\partial V} \right|_{S, n_i} = -\left. \frac{\partial P}{\partial S} \right|_{V, n_i}$$

$$\left. \frac{\partial T}{\partial P} \right|_{S, n_i} = \left. \frac{\partial V}{\partial S} \right|_{P, n_i}$$

$$\left. \frac{\partial S}{\partial V} \right|_{T, n_i} = \left. \frac{\partial P}{\partial T} \right|_{V, n_i}$$

$$\left. \frac{\partial S}{\partial P} \right|_{T, n_i} = -\left. \frac{\partial V}{\partial T} \right|_{P, n_i}$$

Coefficient and Maxwell relations

Enthalpy H			
$H = U + PV$		$H = G + TS$	$H = F + PV - TS$
Second Law Formulation	Independent Variables	Conjugate Variables	Maxwell Relations
$dH =$ TdS $+VdP$ $+ \sum_{i=1}^C \mu_i dN_i$	S P N_i	$T = \left(\frac{\partial H}{\partial S}\right)_{V, N_i}$ $V = \left(\frac{\partial H}{\partial P}\right)_{S, N_i}$ $\mu_i = \left(\frac{\partial H}{\partial N_i}\right)_{S, P, N_j \neq N_i}$	$\left(\frac{\partial T}{\partial P}\right)_{S, N_i} = \left(\frac{\partial V}{\partial S}\right)_{P, N_i}$ $\left(\frac{\partial \mu_i}{\partial P}\right)_{S, N_i} = \left(\frac{\partial V}{\partial N_i}\right)_{S, P, N_j \neq N_i}$ $\left(\frac{\partial \mu_i}{\partial S}\right)_{P, N_i} = \left(\frac{\partial T}{\partial N_i}\right)_{S, P, N_j \neq N_i}$

Coefficient and Maxwell relations

Helmholtz Free Energy F					
$F = U - TS$		$F = H - PV - TS$		$F = G + PV$	
Second Law Formulation	Independent Variables	Conjugate Variables	Maxwell Relations		
$dF =$	T	$-S = \left(\frac{\partial F}{\partial T}\right)_{V, N_i}$	$\left(\frac{\partial S}{\partial V}\right)_{T, N_i} = \left(\frac{\partial P}{\partial T}\right)_{V, N_i}$		
$-SdT$	V	$-P = \left(\frac{\partial F}{\partial V}\right)_{T, N_i}$	$\left(\frac{\partial \mu_i}{\partial V}\right)_{T, N_i} = -\left(\frac{\partial P}{\partial N_i}\right)_{T, V, N_j \neq N_i}$		
$-PdV$	N_i	$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T, V, N_j \neq N_i}$	$\left(\frac{\partial \mu_i}{\partial T}\right)_{V, N_i} = -\left(\frac{\partial S}{\partial N_i}\right)_{T, V, N_j \neq N_i}$		
$+ \sum_{i=1}^C \mu_i dN_i$					

Coefficient and Maxwell relations

Gibbs Free Energy G			
$G = U - TS + PV$		$G = F + PV$	$G = H - TS$
Second Law Formulation	Independent Variables	Conjugate Variables	Maxwell Relations
$dG =$ $-SdT$ $+VdP$ $+ \sum_{i=1}^C \mu_i dN_i$	T P N_i	$-S = \left(\frac{\partial G}{\partial T}\right)_{P,N_i}$ $V = \left(\frac{\partial G}{\partial V}\right)_{T,N_i}$ $\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j \neq N_i}$	$\left(\frac{\partial S}{\partial P}\right)_{T,N_i} = -\left(\frac{\partial V}{\partial T}\right)_{P,N_i}$ $\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N_i} = -\left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_j \neq N_i}$ $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N_i} = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j \neq N_i}$

Coefficient and Maxwell relations

Enthalpy H			
$H = U + PV$		$H = G + TS$	$H = F + PV - TS$
Second Law Formulation	Independent Variables	Conjugate Variables	Maxwell Relations
$dH =$ TdS $+VdP$ $+ \sum_{i=1}^C \mu_i dN_i$	S P N_i	$T = \left(\frac{\partial H}{\partial S}\right)_{V, N_i}$ $V = \left(\frac{\partial H}{\partial P}\right)_{S, N_i}$ $\mu_i = \left(\frac{\partial H}{\partial N_i}\right)_{S, P, N_j \neq N_i}$	$\left(\frac{\partial T}{\partial P}\right)_{S, N_i} = \left(\frac{\partial V}{\partial S}\right)_{P, N_i}$ $\left(\frac{\partial \mu_i}{\partial P}\right)_{S, N_i} = \left(\frac{\partial V}{\partial N_i}\right)_{S, P, N_j \neq N_i}$ $\left(\frac{\partial \mu_i}{\partial S}\right)_{P, N_i} = \left(\frac{\partial T}{\partial N_i}\right)_{S, P, N_j \neq N_i}$

$\sum_{i=1}^C \mu_i dn_i$ as a work term

$$dU = TdS - PdV + \sum_{i=1}^C \mu_i dn_i$$

- For a reversible change in composition of a closed system, $\sum_{i=1}^C \mu_i dn_i$ can be interpreted as the ‘chemical work’ (work other than compression work)

Integration of the basic equations

- Let us consider $dU = TdS - PdV + \sum_{i=1}^C \mu_i dn_i$
- Let the phase under examination is enlarged from V to kV .
- T, P and μ_i remain unchanged (intensive variables).

Thus we can write:

$$\Delta U = T\Delta S - P\Delta V + \sum_{i=1}^C \mu_i \Delta n_i$$

- Because U, S and n_i are extensive variables:

$$\Delta U = (k-1)U, \Delta S = (k-1)S, \Delta n_i = (k-1)n_i$$

- Thus:
 $(k-1)U = T(k-1)S - P(k-1)V + \sum_{i=1}^k \mu_i (k-1)n_i \Rightarrow U = TS - PV + \sum_{i=1}^C \mu_i n_i \Rightarrow G = \sum_{i=1}^C \mu_i n_i$

Integration of the basic equations

$$dG = -SdT + VdP + \sum_{i=1}^C \mu_i dn_i \Rightarrow G = \sum_{i=1}^C \mu_i n_i$$

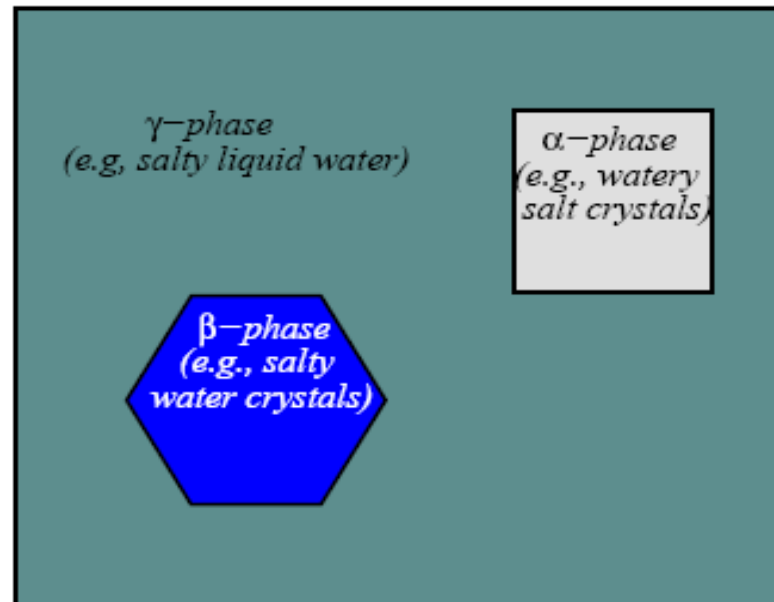
$$dH = TdS + VdP + \sum_{i=1}^C \mu_i dn_i \Rightarrow H = TS + \sum_{i=1}^C \mu_i n_i \quad (H = G + TS)$$

$$dF = -SdT - PdV + \sum_{i=1}^C \mu_i dn_i \Rightarrow F = -PV + \sum_{i=1}^C \mu_i n_i \quad (F = G - PV)$$

μ_i is the partial molar G

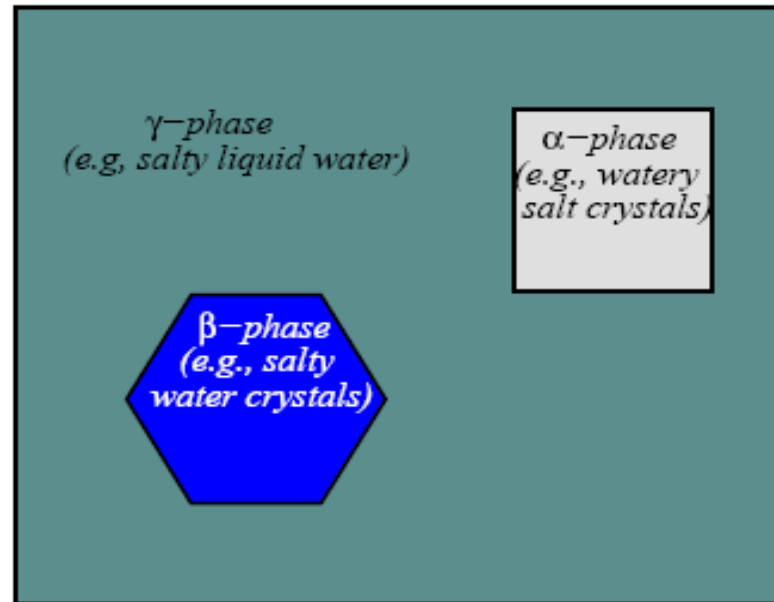
Conditions of multiphase equilibrium

- We will show that for a multiphase system, the chemical potential in each phase must be uniform and equal.

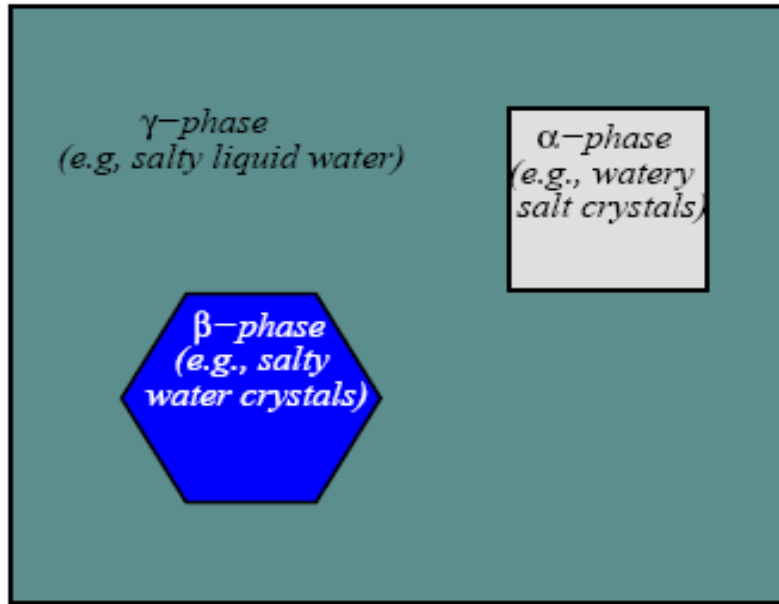


Conditions of multiphase equilibrium

- Consider the conditions of internal equilibrium to the entire system considering that is composed of f phases:



Conditions of multiphase equilibrium



$$dG = -SdT + VdP + \sum_{j=1}^f \sum_{i=1}^C \mu_i^j dN_i^j$$

$$\begin{aligned} dG = & -SdT + VdP + \\ & + \mu_A^\alpha dN_A^\alpha + \mu_B^\alpha dN_B^\alpha + \dots + \mu_C^\alpha dN_C^\alpha \\ & + \mu_A^\beta dN_A^\beta + \mu_B^\beta dN_B^\beta + \dots + \mu_C^\beta dN_C^\beta \\ & + \dots \\ & + \mu_A^f dN_A^f + \mu_B^f dN_B^f + \dots + \mu_C^f dN_C^f \end{aligned}$$

μ_i^j is the chemical potential of chemical species i in phase j .

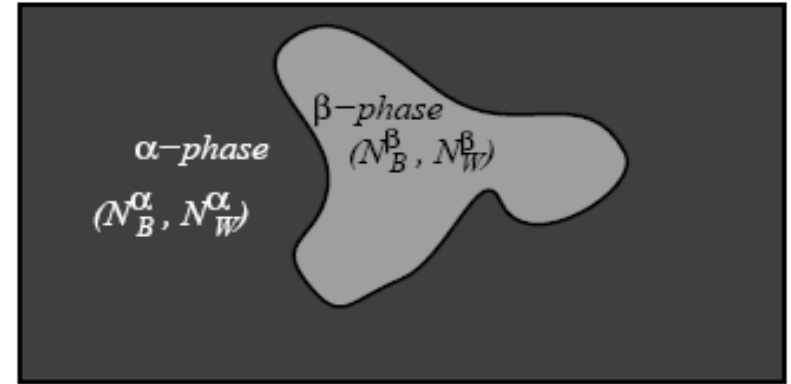
Composition variations and phase fractions

Consider e.g. two phases α , β :

Consider two components 1,2:

Consider constant T and P

(already shown to be required for equilibrium):



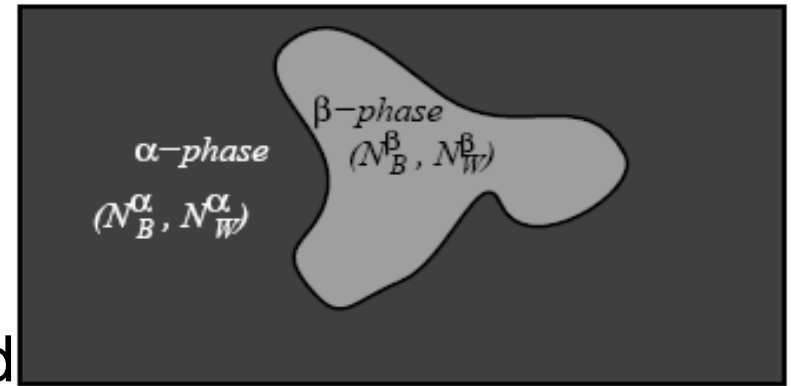
$$dG = -SdT + VdP + \sum_{j=1}^2 \sum_{i=1}^2 \mu_i^j dN_i^j \quad \text{But note that:} \quad \begin{aligned} dN_1^\alpha + dN_1^\beta &= 0, \\ dN_2^\alpha + dN_2^\beta &= 0 \end{aligned}$$

$$dG = \mu_1^\alpha dN_1^\alpha + \mu_2^\alpha dN_2^\alpha + \mu_1^\beta dN_1^\beta + \mu_2^\beta dN_2^\beta$$

$$dG = (\mu_1^\alpha - \mu_1^\beta) dN_1^\alpha + (\mu_2^\alpha - \mu_2^\beta) dN_2^\alpha$$

Composition variations and phase fractions

$$dG = (\mu_1^\alpha - \mu_1^\beta) dN_1^\alpha + (\mu_2^\alpha - \mu_2^\beta) dN_2^\alpha$$



A chemical species is transported

from the a phase of high potential to

a phase of low potential. Indeed, lets assume that $\mu_1^\alpha > \mu_1^\beta$

Since dN_1^α and dN_2^α are independent of each other, let's

consider only: $dG = (\mu_1^\alpha - \mu_1^\beta) dN_1^\alpha$

For spontaneous processes: $dG < 0 \Rightarrow dN_1^\alpha < 0 \Rightarrow$

Component 1 is transported from phase α to phase β !

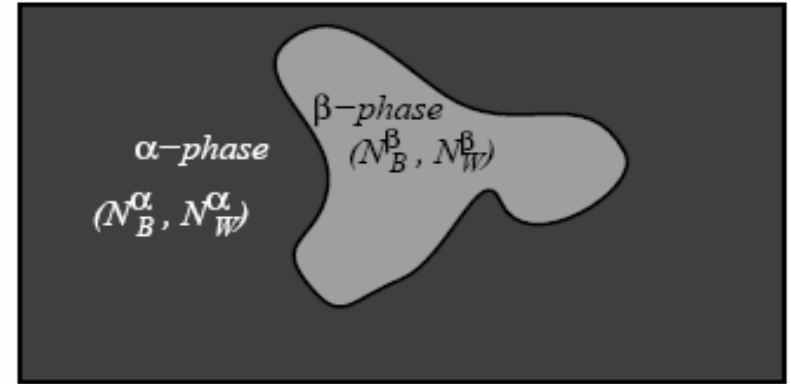
Composition variations and phase fractions

$$dG = (\mu_1^\alpha - \mu_1^\beta) dN_1^\alpha + (\mu_2^\alpha - \mu_2^\beta) dN_2^\alpha$$

For equilibrium $dG=0$:

$$\mu_1^\alpha = \mu_1^\beta$$

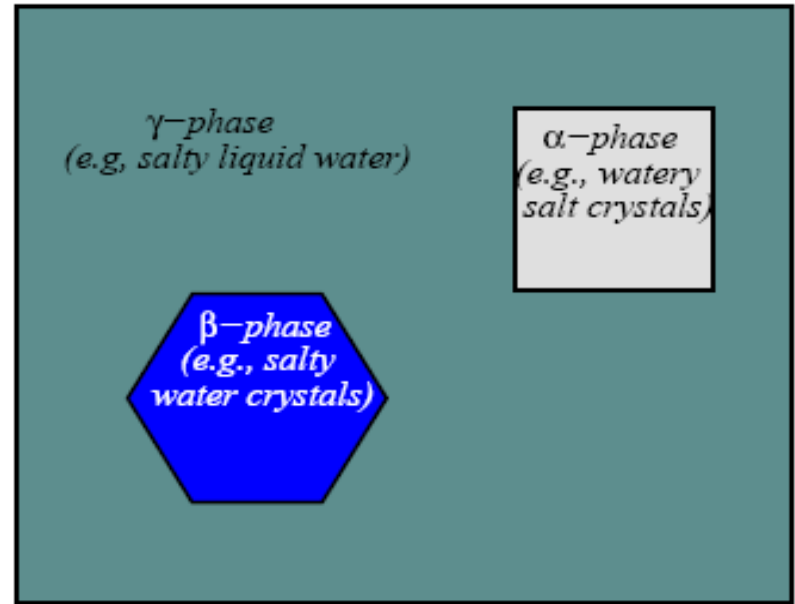
$$\mu_2^\alpha = \mu_2^\beta$$



Composition variations and phase fractions

$$dG = -SdT + VdP + \sum_{j=1}^f \sum_{i=1}^C \mu_i^j dN_i^j$$

$$\begin{aligned} dG = -SdT + VdP + \\ + \mu_A^\alpha dN_A^\alpha + \mu_B^\alpha dN_B^\alpha + \dots + \mu_C^\alpha dN_C^\alpha \\ + \mu_A^\beta dN_A^\beta + \mu_B^\beta dN_B^\beta + \dots + \mu_C^\beta dN_C^\beta \\ + \dots \\ + \mu_A^f dN_A^f + \mu_B^f dN_B^f + \dots + \mu_C^f dN_C^f \end{aligned}$$



We can simplify using the following constrains:

$$dN_A^\alpha + dN_A^\beta + \dots + dN_A^f = 0 \Rightarrow dN_A^f = -(dN_A^\alpha + dN_A^\beta + \dots + dN_A^{f-1})$$

$$dN_B^\alpha + dN_B^\beta + \dots + dN_B^f = 0 \Rightarrow dN_B^f = -(dN_B^\alpha + dN_B^\beta + \dots + dN_B^{f-1})$$

.....

$$dN_C^\alpha + dN_C^\beta + \dots + dN_C^f = 0 \Rightarrow dN_C^f = -(dN_C^\alpha + dN_C^\beta + \dots + dN_C^{f-1})$$

Composition variations and phase fractions

$$dG = -SdT + VdP + \sum_{j=1}^f \sum_{i=1}^C \mu_i^j dN_i^j$$

$$dG = -SdT + VdP +$$

$$+ \mu_A^\alpha dN_A^\alpha + \mu_B^\alpha dN_B^\alpha + \dots + \mu_C^\alpha dN_C^\alpha$$

$$+ \mu_A^\beta dN_A^\beta + \mu_B^\beta dN_B^\beta + \dots + \mu_C^\beta dN_C^\beta$$

+

$$- \mu_A^f (dN_A^\alpha + dN_A^\beta + \dots + dN_A^{f-1})$$

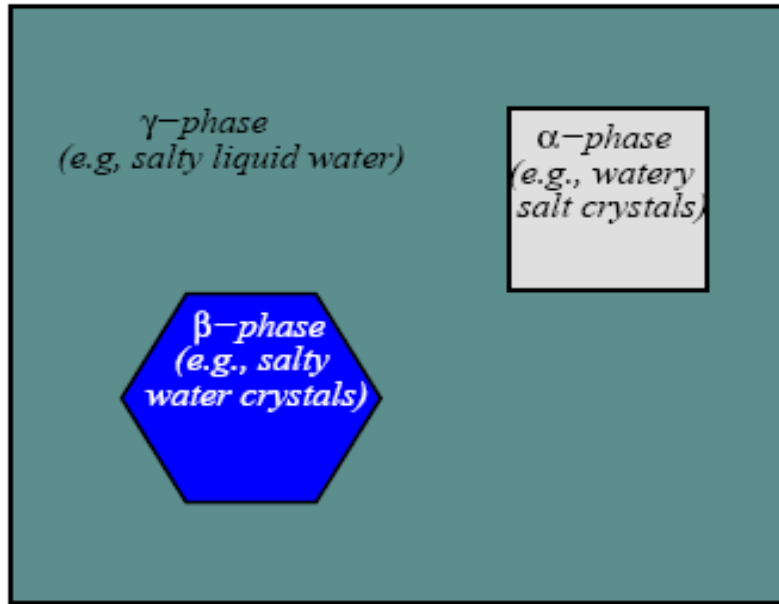
$$- \mu_B^f (dN_B^\alpha + dN_B^\beta + \dots + dN_B^{f-1}) - \dots$$

$$- \mu_C^f (dN_C^\alpha + dN_C^\beta + \dots + dN_C^{f-1})$$

We can simplify as: $dG = -SdT + VdP + \sum_{j=1}^{f-1} \sum_{i=1}^C (\mu_i^j - \mu_i^f) dN_i^j$

These remaining dN_1^j are independent of each other

Conditions of multiphase equilibrium

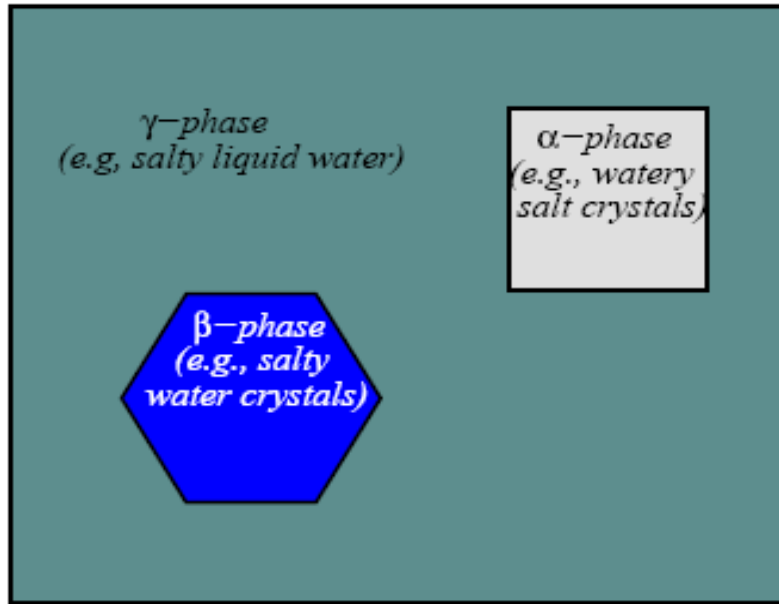


$$dG = -SdT + VdP + \sum_{j=1}^{f-1} \sum_{i=1}^C (\mu_i^j - \mu_i^f) dN_i^j$$

Because G is minimized at equilibrium at constant T and P , it follows that if any species i can be exchanged between the j -phase and the f -phase (i.e. one can consider virtual changes with $dN_i^j = -dN_i^f$), then it follows that at equilibrium:

$$\mu_i^j = \mu_i^f$$

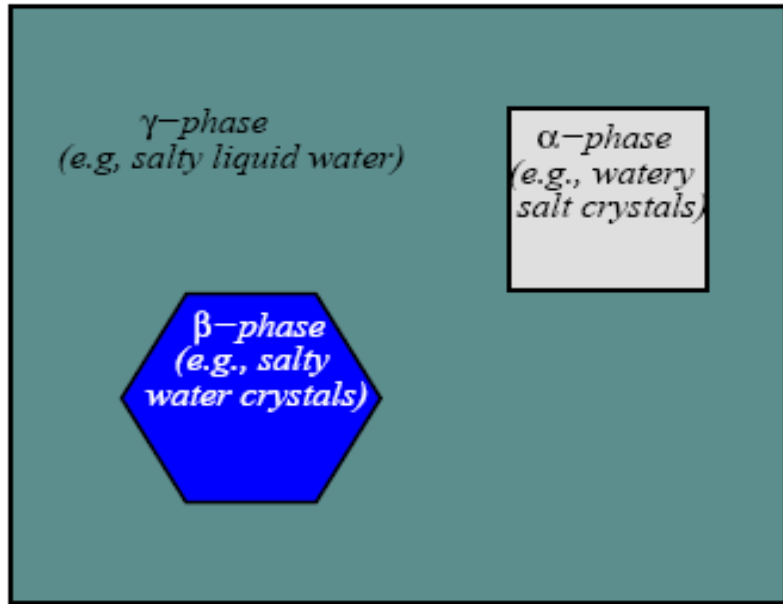
Conditions of multiphase equilibrium



A chemical species could be spontaneously transported from a phase of larger potential to one of lower potential.

$$\begin{aligned}\mu_1^{\text{I}} &= \mu_1^{\text{II}} = \mu_1^{\text{III}} = \dots = \mu_1^{\text{f}} \\ \mu_2^{\text{I}} &= \mu_2^{\text{II}} = \mu_2^{\text{III}} = \dots = \mu_2^{\text{f}} \\ &\vdots \\ \mu_C^{\text{I}} &= \mu_C^{\text{II}} = \mu_C^{\text{III}} = \dots = \mu_C^{\text{f}}\end{aligned}$$

The Gibbs Duhem equation



Consider our initial fundamental equation (for each phase):

$$dU = TdS - PdV + \sum_{i=1}^C \mu_i dN_i \quad (*)$$

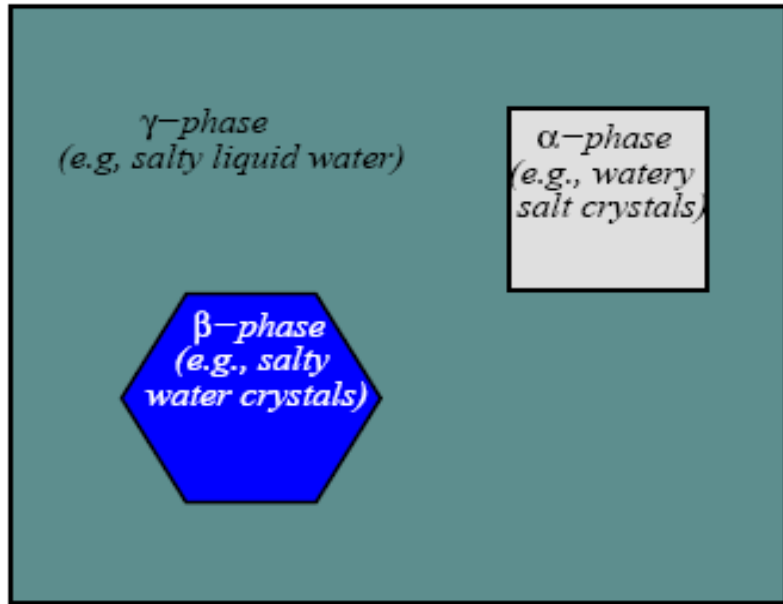
Using $U = TS - PV + \sum_{i=1}^C \mu_i N_i \Rightarrow$

$$dU = SdT + TdS - VdP - PdV + \sum_{i=1}^C \mu_i dN_i + \sum_{i=1}^C d\mu_i N_i \quad (**)$$

Eqs. (*) and (**) lead to the following Gibbs-Duhem equation:

$$SdT - VdP + \sum_{i=1}^C N_i d\mu_i = 0$$

The Gibbs Duhem equation



For f phases at equilibrium, we have f Gibbs-Duhem equations:

$$0 = S^{\text{I}}dT - V^{\text{I}}dP + \sum_{i=1}^c N_i^{\text{I}}d\mu_i^{\text{I}}$$

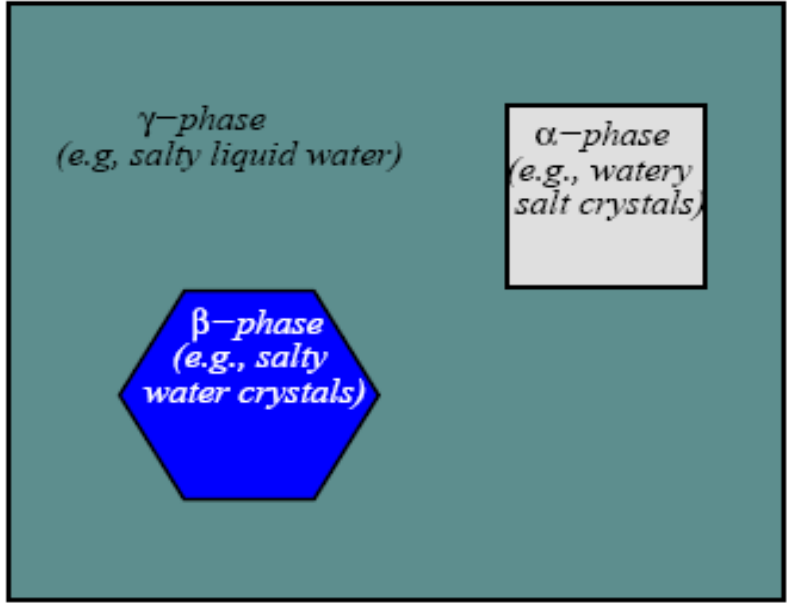
$$0 = S^{\text{II}}dT - V^{\text{II}}dP + \sum_{i=1}^c N_i^{\text{II}}d\mu_i^{\text{II}}$$

$\vdots = \vdots$

$$0 = S^{\text{f}}dT - V^{\text{f}}dP + \sum_{i=1}^c N_i^{\text{f}}d\mu_i^{\text{f}}$$

The Gibbs-Duhem equations provide constraints on the independent variables at equilibrium.

Number of independent degrees of freedom



Consider f phases (of a C component system) at equilibrium.

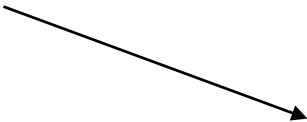
What are the independent degrees of freedom at equilibrium?

1. T and P (2 variables)
2. Chemical potentials μ_i^j (total of Cf variables)

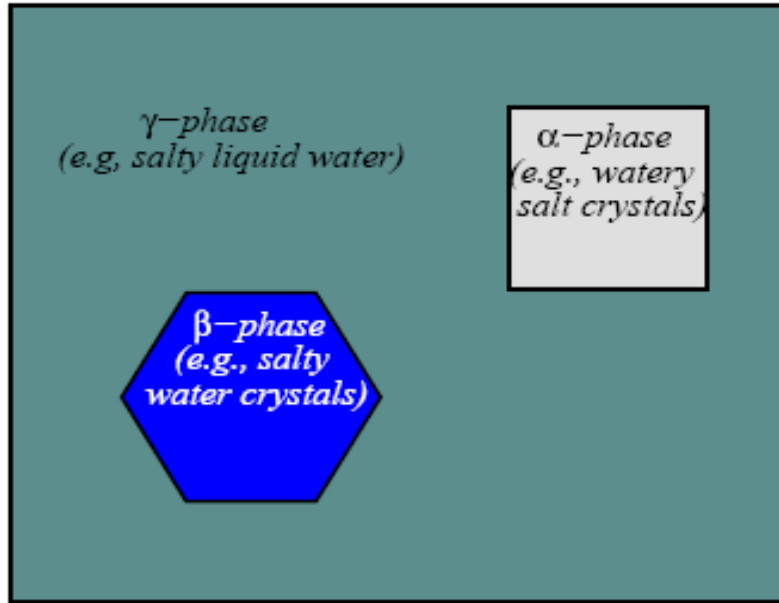
How many constrains we have from equilibrium?

1. f Gibbs-Duhem eqs
2. Chemical potentials C(f-1) equations

$$\begin{aligned} \mu_1^I &= \mu_1^{II} = \mu_1^{III} = \dots = \mu_1^f \\ \mu_2^I &= \mu_2^{II} = \mu_2^{III} = \dots = \mu_2^f \\ &\vdots \\ \mu_C^I &= \mu_C^{II} = \mu_C^{III} = \dots = \mu_C^f \end{aligned}$$



Gibbs phase rule



$$D = (Cf + 2) - [C(f - 1) + f]$$

$$D + f = C + 2$$

Consider f phases (of a C component system) at equilibrium.

What are the independent degrees of freedom at equilibrium?

1. T and P (2 variables)
2. Chemical potentials μ_i^j (total of Cf variables)

How many constraints we have from equilibrium?

1. f Gibbs-Duhem eqs
2. Chemical potentials $C(f-1)$ equations

Gibbs Phase rule $D+f=C+2$

Example 1: Consider water + ice at equilibrium.

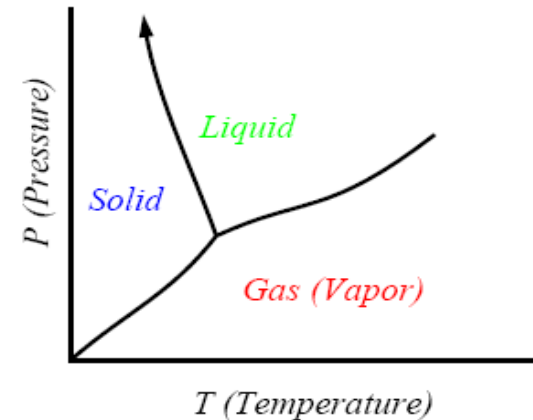
$C=1$, and $f=2$. Then $D=1+2-2=1$

Indeed we can only change one variable T or P and still maintain equilibrium (once you change T (P) you know what P (T) should be).

Example 2: Consider water + ice+vapor at equilibrium.

$C=1$, and $f=3$. Then $D=1+2-3=0$

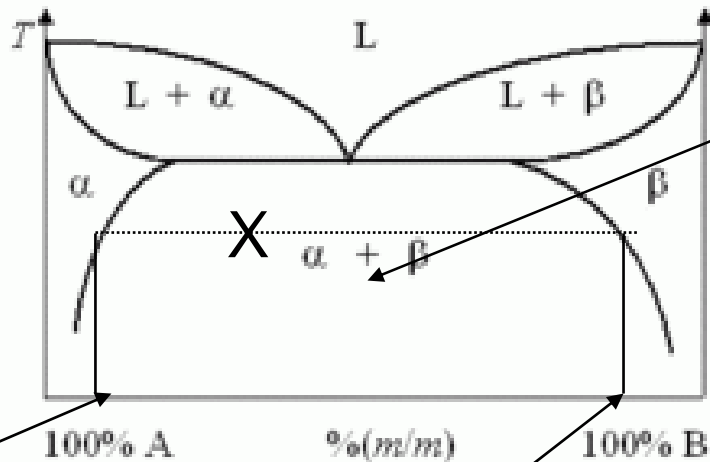
Indeed this is the triple point (well defined T and P). Cannot change any of them and still maintain water, ice and vapor in equilibrium)



Phase rule $D+f=C+1$ (pressure not counting)

Example 3: Consider a two component binary system as follows:

How many independent DOF we have when 2 solid phases α and β coexist? $C=2$, and $f=2$. Then $D=2+1-2=1$. You can change T but the composition is specified.



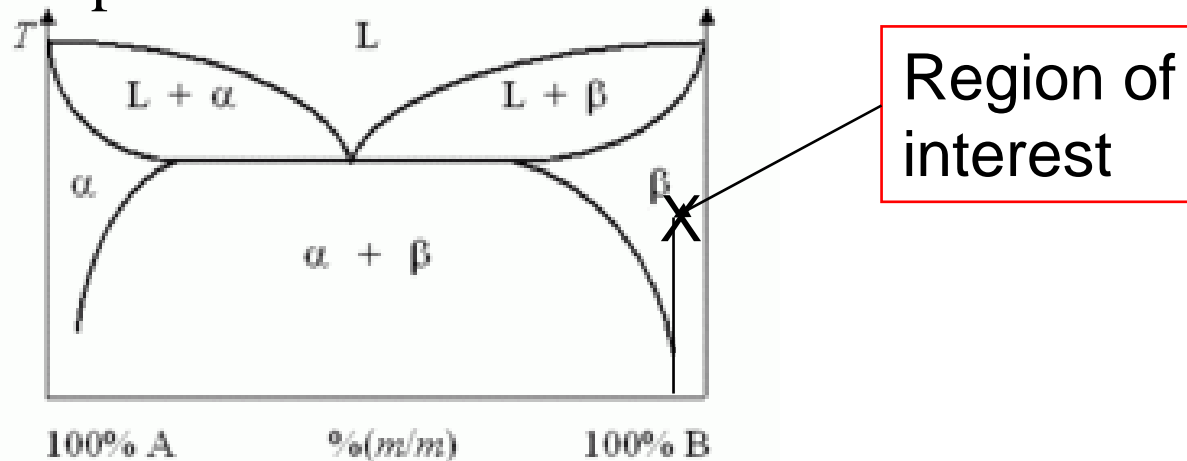
Region of interest

Composition of the α and β phases are fixed for a given temperature

Phase rule $D+f=C+1$ (pressure not counting)

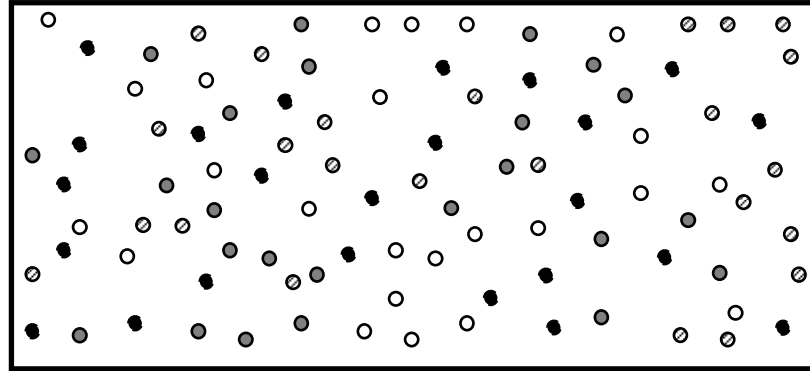
Example 3: Consider the one-phase region of a two component binary system :

Here $C=2$, and $f=1$. Then $D=2+1-1=2$. You can independently change T and composition!



Temperature and composition of the β phase can change independently and still maintain a β phase in equilibrium

Mixture of ideal gases at T and p



$$n_1 + n_2 + n_3 + \dots + n_N = n_{\text{Total}}$$

Assume all components are in thermal and mechanical equilibrium, i.e., each at T and its respective partial pressure for each components.

Gibbs function for the mixture

$$G = G(p, T, n_1, n_2, \dots, n_N)$$

Processes at constant T and p

G is an extensive property. Let each of the constituents change by an arbitrary amount α .

$$\alpha G = G(P, T, \alpha n_1, \alpha n_2, \dots, \alpha n_N)$$

$$\left. \frac{\partial}{\partial \alpha} \right|_{P, T} \alpha G = G(P, T, \alpha n_1, \alpha n_2, \dots, \alpha n_N)$$

Processes at constant T and p

$$\left. \frac{\partial}{\partial \alpha} \right|_{p,T} \alpha G = G(p, T, \alpha n_1, \alpha n_2, \dots, \alpha n_N)$$

$$\left(\frac{\partial \alpha G}{\partial \alpha} \right)_{p,T} = \sum_{k=1}^N \frac{\partial G}{\partial n_k} \frac{\partial \alpha n_k}{\partial \alpha}$$

$$G = \sum_k n_k \left(\frac{\partial G}{\partial n_k} \right)_{P,T, n_{i \neq k}} = \sum_k n_k \mu_k$$

Equilibrium

At equilibrium, $dG = 0$ and G is a minimum, i.e.,

$$dG = 0 = \sum_i \mu_i dn_i$$

