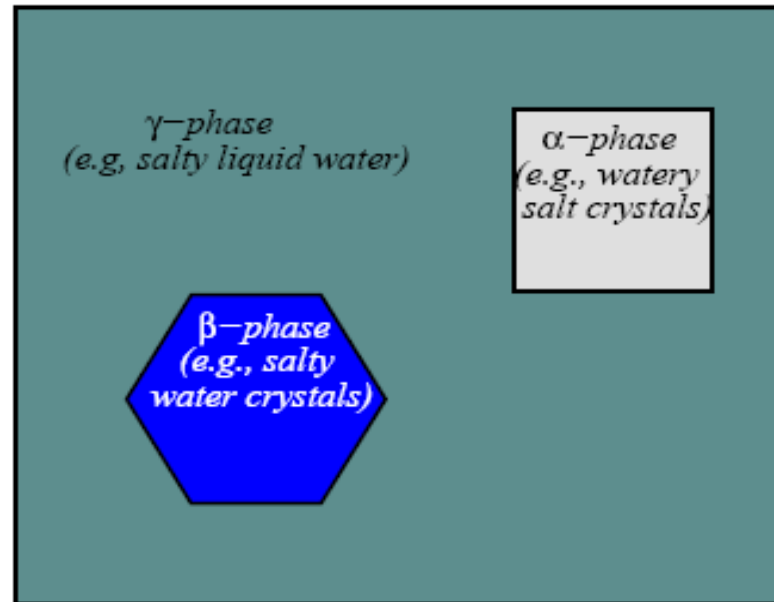


---

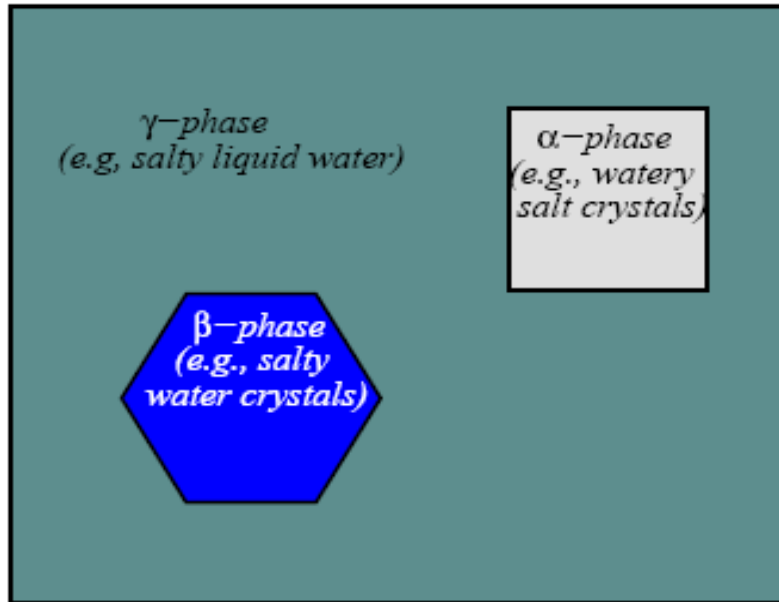
# *Return to Chemical Equilibrium*

# 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



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

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

$\mu_i^j$  is the chemical potential of chemical species  $i$  in phase  $j$ .

# Composition variations and phase fractions

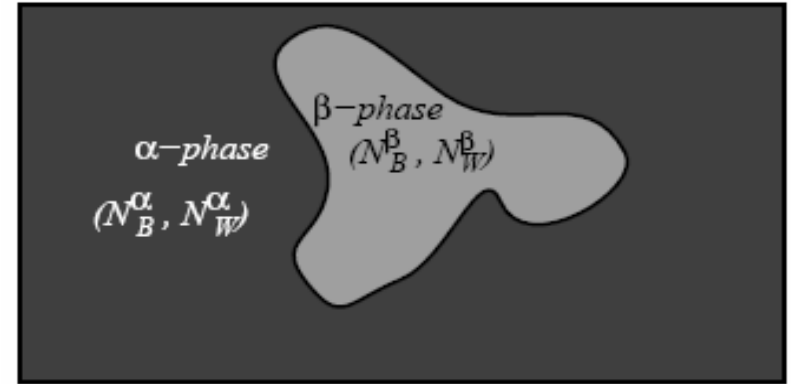
---

Consider e.g. two phases  $\alpha$ ,  $\beta$ :

Consider two components 1,2:

Consider constant T and P

(already shown to be required for equilibrium):



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

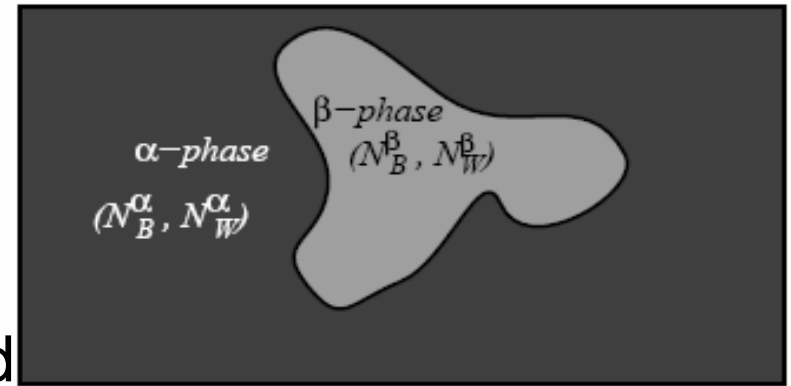
$$dG = \mu_1^\alpha dN_1^\alpha + \mu_2^\alpha dN_2^\alpha + \mu_1^\beta dN_1^\beta + \mu_2^\beta dN_2^\beta$$

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

# 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  $dN_1^\alpha$  and  $dN_2^\alpha$  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  $\alpha$  to phase  $\beta$ !

# Composition variations and phase fractions

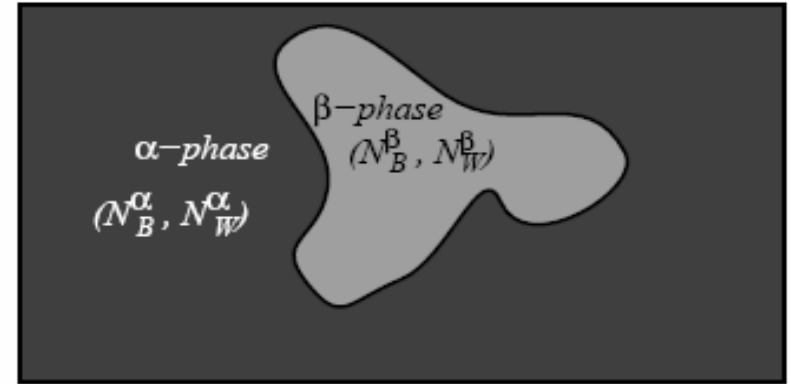
---

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

For equilibrium  $dG=0$ :

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

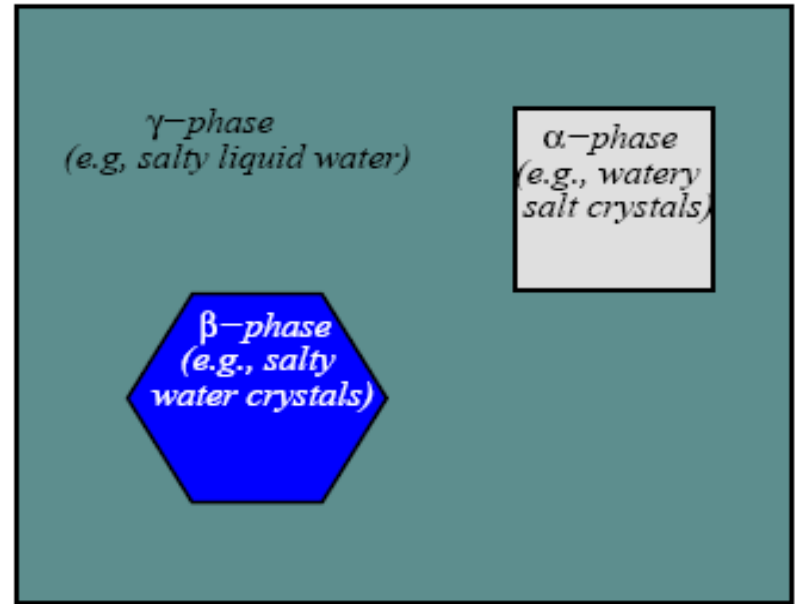
$$\mu_2^\alpha = \mu_2^\beta$$



# 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

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

$$dG = -SdT + VdP +$$

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

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

+ .....

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

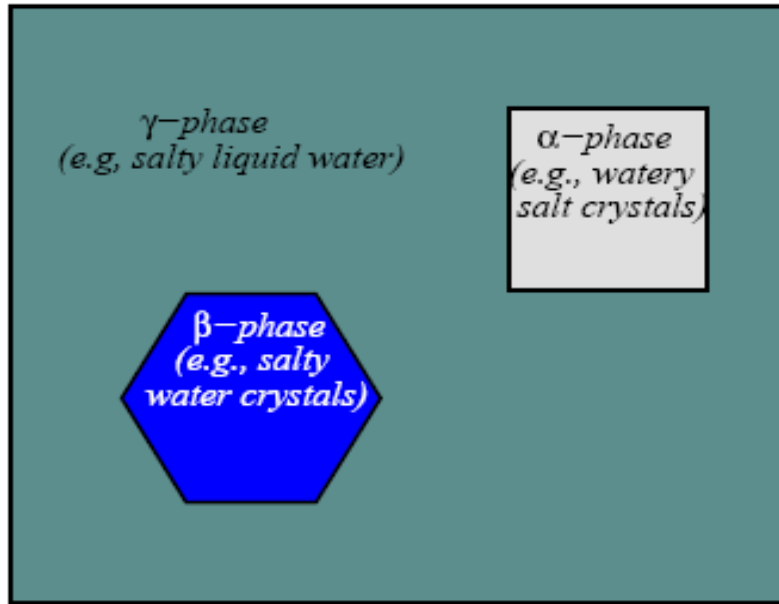
$$- \mu_B^f (dN_B^\alpha + dN_B^\beta + \dots + dN_B^{f-1}) - \dots$$

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

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

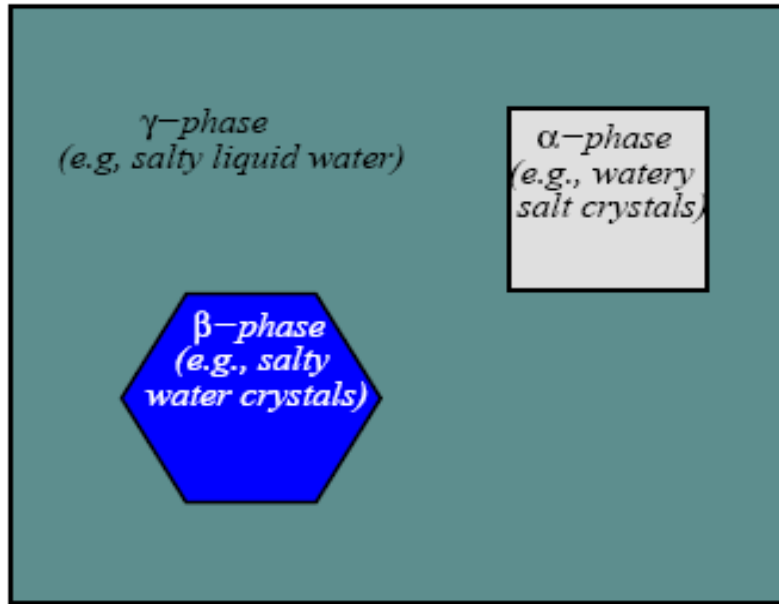


$$dG = -SdT + VdP + \sum_{j=1}^{f-1} \sum_{i=1}^C (\mu_i^j - \mu_i^f) dN_i^j$$

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.

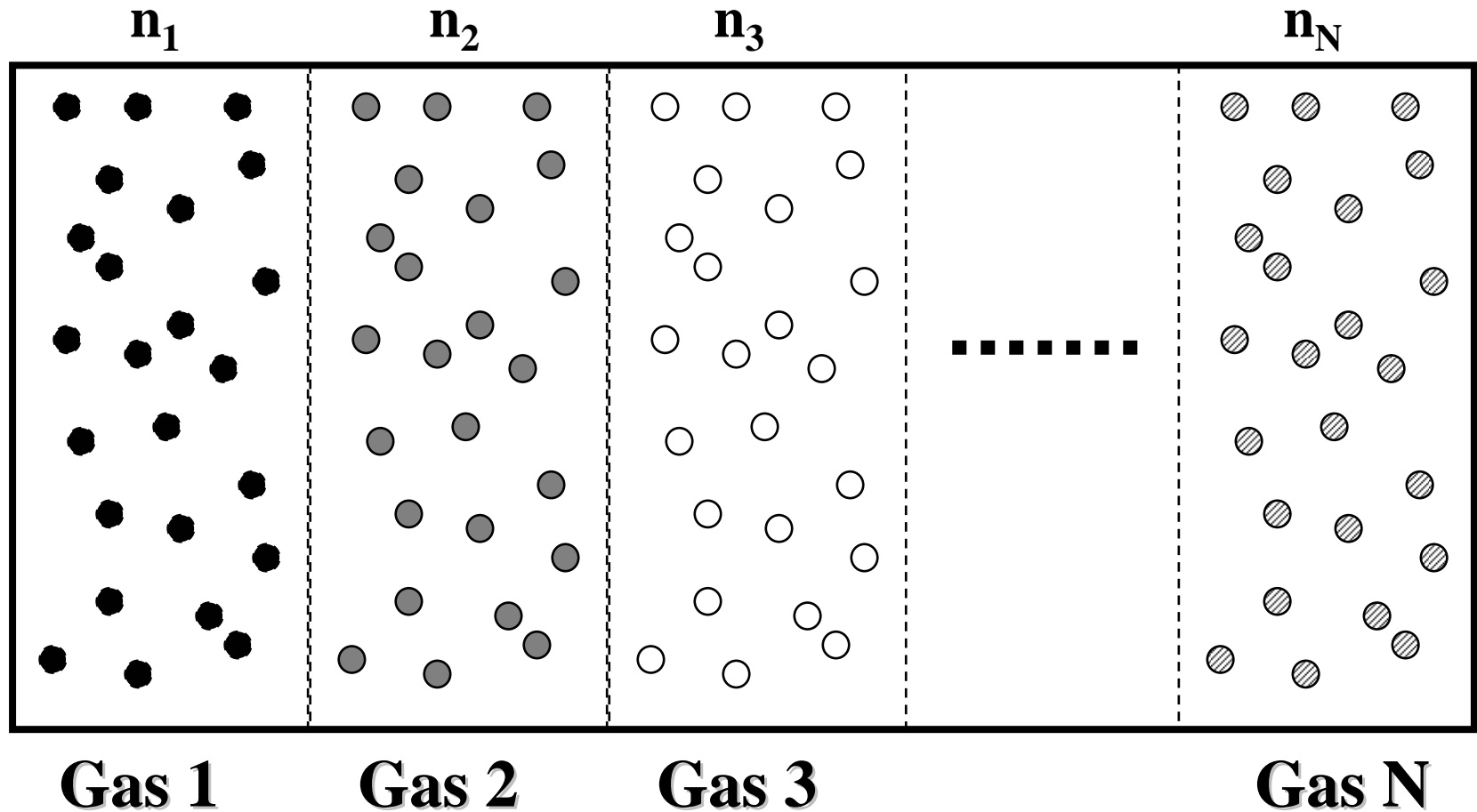
$$\begin{aligned}\mu_1^{\text{I}} &= \mu_1^{\text{II}} = \mu_1^{\text{III}} = \dots = \mu_1^{\text{f}} \\ \mu_2^{\text{I}} &= \mu_2^{\text{II}} = \mu_2^{\text{III}} = \dots = \mu_2^{\text{f}} \\ &\vdots \\ \mu_C^{\text{I}} &= \mu_C^{\text{II}} = \mu_C^{\text{III}} = \dots = \mu_C^{\text{f}}\end{aligned}$$

---

# *Example: Entropy of mixing*

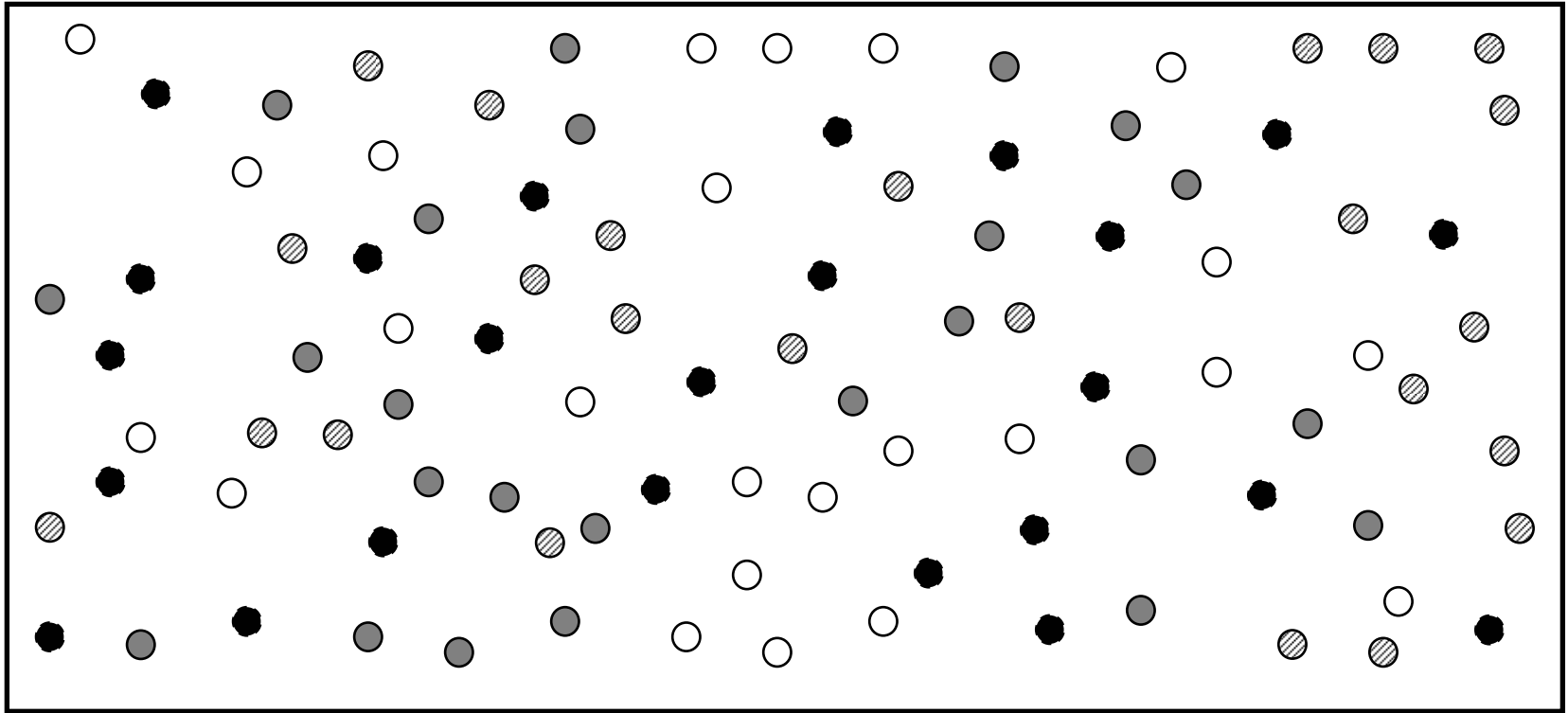
# *System of “N” Ideal Gases*

---



*The Mixture occupies the entire volume  
with pressure  $p$  and temperature  $T$*

---



**Gas Mixture:  $n_1+n_2+n_3+\dots+n_N = n_{\text{Total}}$**

---

# Entropy of mixing

When a mixture of N gases exists,

$$S - S^0 = \sum_i n_i (\bar{s}_i - \bar{s}_i^0) = \sum_i n_i \left[ \bar{C}_{p,i} \ln \left( \frac{T}{T_0} \right) - \bar{R} \ln \left( \frac{p_i}{p_0} \right) \right]$$

Prior to mixing, if the system of gases existed at the same temperature and each gas was at the same pressure,

$$S - S^0 = \sum_i n_i (\bar{s}_i - \bar{s}_i^0) = \sum_i n_i \left[ \bar{C}_{p,i} \ln \left( \frac{T}{T_0} \right) - \bar{R} \ln \left( \frac{p}{p_0} \right) \right]$$

# *Entropy of Mixing*

---

Thus consider the entropy change from the pre-mixed to the final mixed state.

$$\Delta S_{mixing} = - \sum_i n_i \bar{R} \ln(y_i)$$

This entropy increase is always positive, and is equal to the entropy change of the universe and entropy production.

# Example

---

A half a mole of H and a half mole of He are mixed at constant T and P. What is the entropy change due to mixing of the two gases?

**Solution:**

$$y_{H_2} = \frac{0.5}{0.5 + 0.5} \quad y_{He} = \frac{0.5}{0.5 + 0.5}$$
$$\Delta s = -\sum_i n_i \bar{R} \ln y_i = -\bar{R} [0.5 \ln(0.5) + 0.5 \ln(0.5)]$$
$$= \bar{R} \ln(2)$$

# *The Gibbs Paradox*

---

What if the the two gases are the same? Is there an entropy increase?

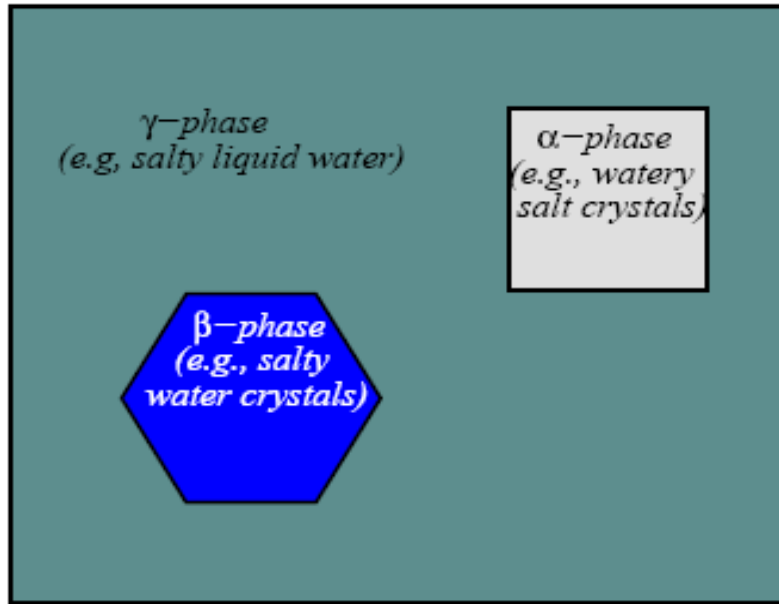
In this case, there is no entropy change as the free expansion of identical gases has no meaning.

However, if the gases are tagged in some way, then the entropy change is realized.

The Gibbs Paradox is just this anomalous result when the gases become indistinguishable.

---

# The Gibbs Duhem equation: Review



Consider our initial fundamental equation (one for each phase):

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

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

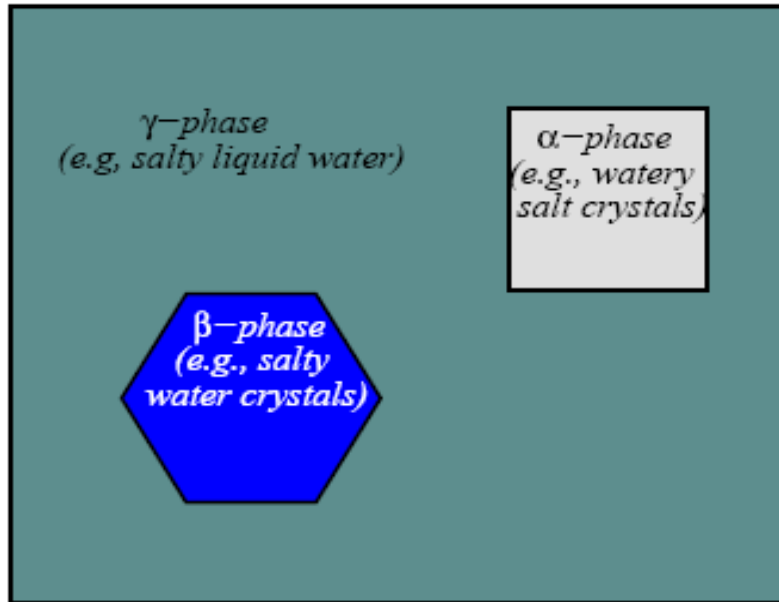
$$dU = SdT + TdS - VdP - PdV + \sum_{i=1}^C \mu_i dN_i + \sum_{i=1}^C d\mu_i N_i \quad (**)$$

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:

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

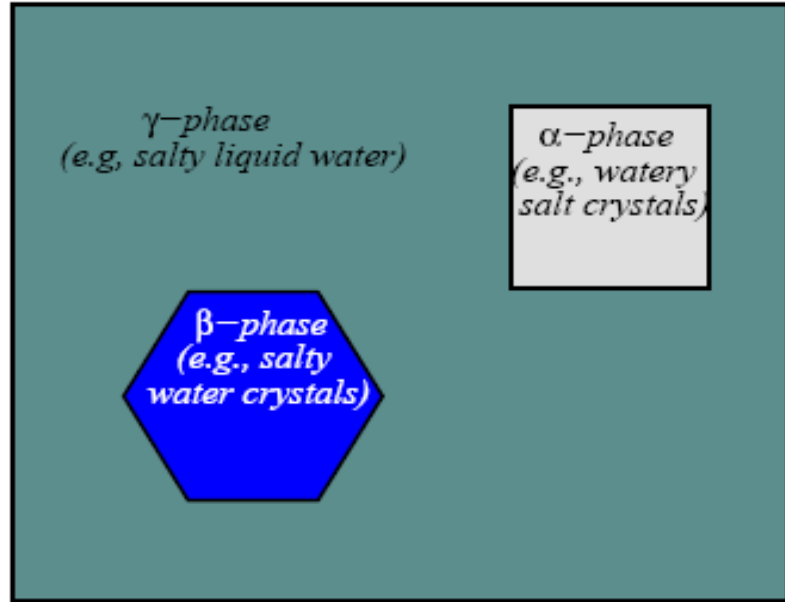
$$0 = S^{\text{II}}dT - V^{\text{II}}dP + \sum_{i=1}^c N_i^{\text{II}}d\mu_i^{\text{II}}$$

$\vdots = \vdots$

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

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  $\mu_i^j$  (total of  $Cf$  variables)

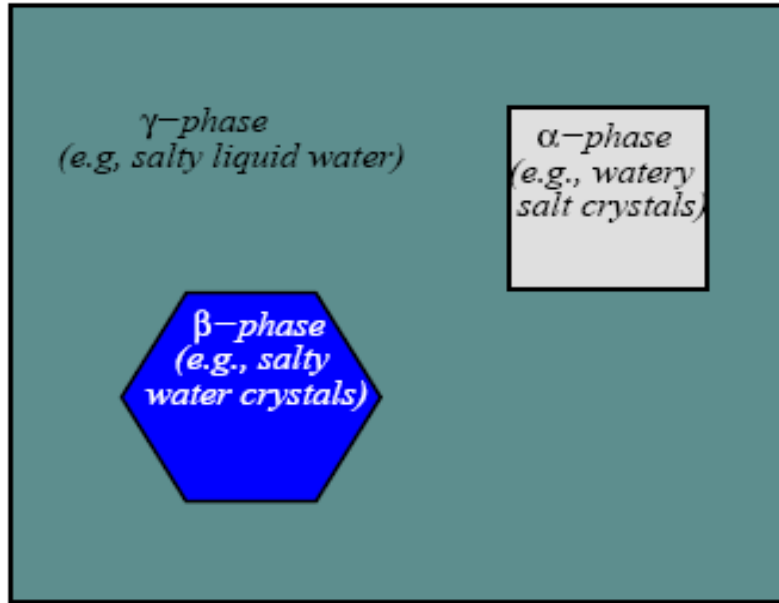
How many constraints we have from equilibrium?

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

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

# 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  $\mu_i^j$  (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.

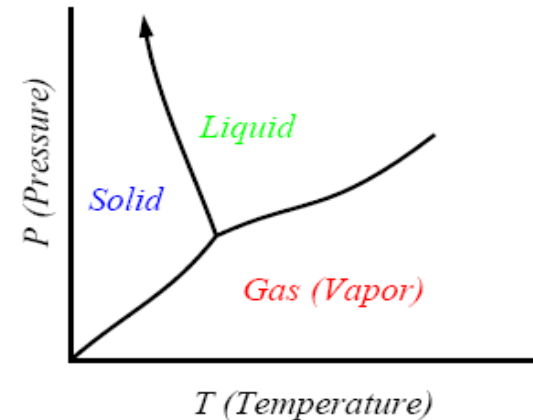
$C=1$ , and  $f=2$ . Then  $D=1+2-2=1$

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  $D=1+2-3=0$

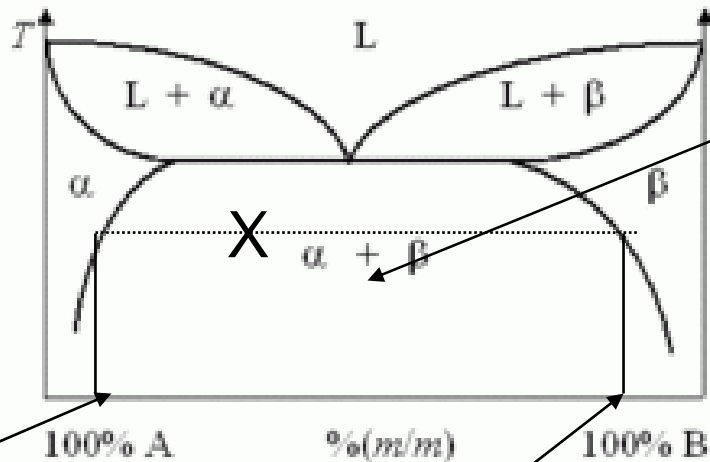
Indeed this is the triple point (well defined  $T$  and  $P$ ). Cannot change any of them and still maintain water, ice and vapor in equilibrium)



# *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  $\alpha$  and  $\beta$  coexist?  $C=2$ , and  $f=2$ . Then  $D=2+1-2=1$ . You can change  $T$  but the composition is specified.



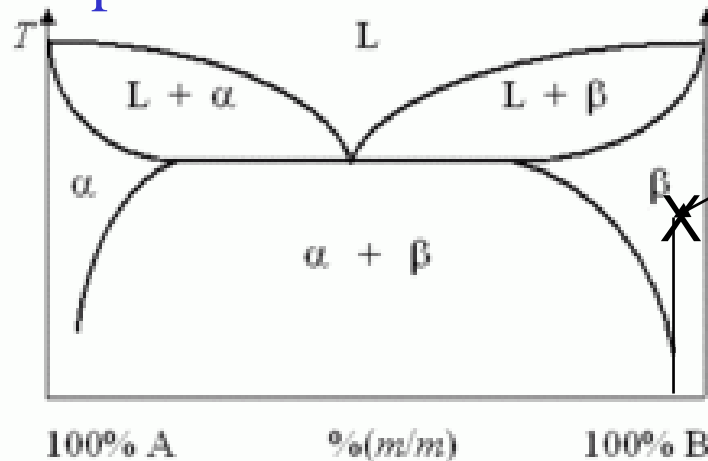
Region of interest

Composition of the  $\alpha$  and  $\beta$  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  $\beta$  phase can change independently and still maintain a  $\beta$  phase in equilibrium