
The Van't Hoff equation

Gibbs function - chemical potential

$$\begin{aligned}\mu_i &= \bar{g}_i = \bar{h}_i(T) - T\bar{s}_i(P, T) \\ &= \bar{h}_i(T) - T \left[\bar{s}_i^0 - \bar{R} \ln \left(\frac{y_i P}{P_{ref}} \right) \right] \\ &= \bar{h}_i(T) - T\bar{s}_i^0 + \bar{R}T \ln \left(\frac{y_i P}{P_{ref}} \right)\end{aligned}$$

Recall the equilibrium constant

$$\frac{-\Delta G_{RP}^{\circ}}{RT} = \ln(K_p)$$

Expand ΔG_{RP}°

$$\bar{R}T \ln(K) = - \left[\left(\sum_{prod.} \nu \bar{h} - \sum_{react.} \nu \bar{h} \right) - T \left(\sum_{prod.} \nu \bar{s}^{\circ} - \sum_{react.} \nu \bar{s}^{\circ} \right) \right]$$

Differentiate the previous equation with respect to T

$$\frac{d}{dT} (\bar{R}T \ln(K_p)) = \bar{R}T \frac{d \ln K_p}{dT} + \bar{R} \ln K_p$$

$$= - \left[\begin{array}{c} \sum_{prod.} \nu \left(\frac{d\bar{h}}{dT} - T \frac{d\bar{s}^o}{dT} \right) \\ - \sum_{react.} \nu \left(\frac{d\bar{h}}{dT} - T \frac{d\bar{s}^o}{dT} \right) \end{array} \right] + \left(\begin{array}{c} \sum_{prod.} \nu \bar{s}^o \\ - \sum_{react.} \nu \bar{s}^o \end{array} \right)$$

Using definition of C_p

$$\frac{d\bar{h}}{dT} = \bar{C}_p \quad \text{and} \quad \frac{d\bar{s}^o}{dT} = \frac{\bar{C}_p}{T}$$

Use definition of C_p to eliminate the first term on the r.h.s.

$$\bar{R}T \frac{d \ln K}{dT} + \bar{R} \ln K_p$$

$$= - \left[\sum_{prod.} \nu \left(\frac{d\bar{h}}{dT} - T \frac{d\bar{s}^o}{dT} \right) - \sum_{react.} \nu \left(\frac{d\bar{h}}{dT} - T \frac{d\bar{s}^o}{dT} \right) \right] + \left(\sum_{prod.} \nu \bar{s}^o - \sum_{react.} \nu \bar{s}^o \right)$$

$$= 0$$

Result....

$$\bar{R}T \frac{d \ln K}{dT} + \bar{R} \ln K = \left(\begin{array}{c} \sum_{\text{prod.}} \nu \bar{s}^o \\ - \sum_{\text{react.}} \nu \bar{s}^o \end{array} \right)$$

Multiply this result by T to obtain...

Result...

$$\bar{R}T^2 \frac{d \ln K}{dT} + \bar{R}T \ln K = T \left(\begin{array}{c} \sum_{prod.} \nu \bar{s}^o \\ - \sum_{react.} \nu \bar{s}^o \end{array} \right)$$

Combine this result with the definition of K_p , to get...

$$\bar{R}T \ln (K) = - \left[\begin{array}{c} \left(\sum_{prod.} \nu \bar{h} - \sum_{react.} \nu \bar{h} \right) - \\ T \left(\sum_{prod.} \nu \bar{s}^o - \sum_{react.} \nu \bar{s}^o \right) \end{array} \right]$$

The Van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{1}{\overline{RT}^2} \left(\begin{array}{c} \sum_{prod.} \overline{v}h \\ - \sum_{react.} \overline{v}h \end{array} \right)$$

The Van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta H_{R-P}}{\bar{R} T^2}$$

Integrate the Van't Hoff equation with
 ΔH approximately constant

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H_{R-P}}{\bar{R}} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\frac{d \ln K}{dT} = \frac{\Delta H_{R-P}}{\bar{R} T^2}$$

When ΔH is approximately constant, then

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H_{R-P}}{\bar{R}} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Evaluating enthalpies of a compound

(look at Eq. 13.9 in the text)

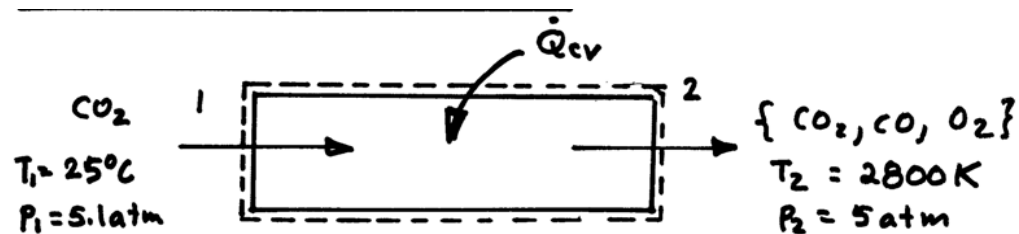
$$\bar{h} = \bar{h}_f^0 + [\bar{h}(T) - \bar{h}(T_{ref})]$$

Enthalpy of formation
Tables A-25
or A-25E

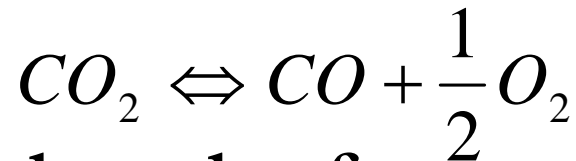
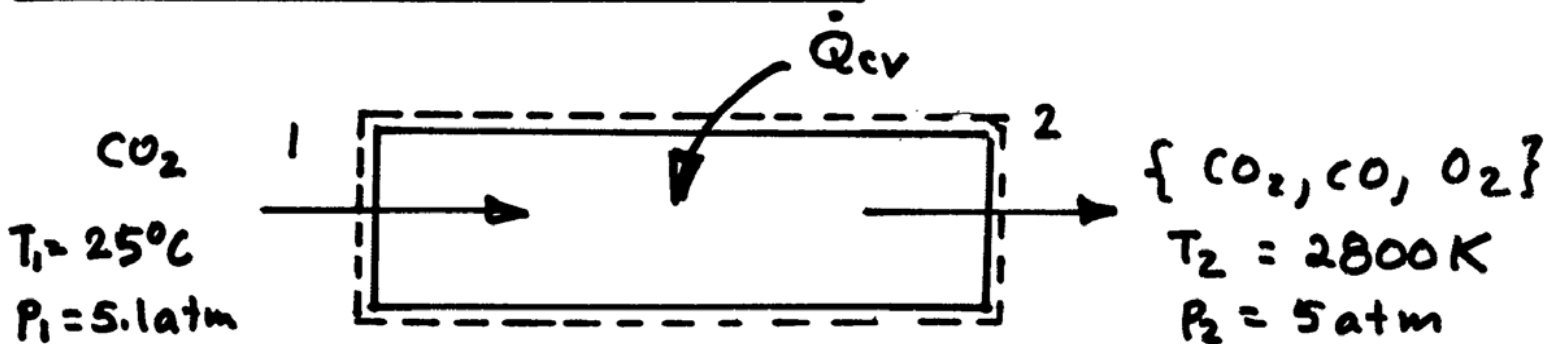
Change of enthalpy from
temperature T_{ref} to T
(Tables A23, A23-E or A-21)

Example problem

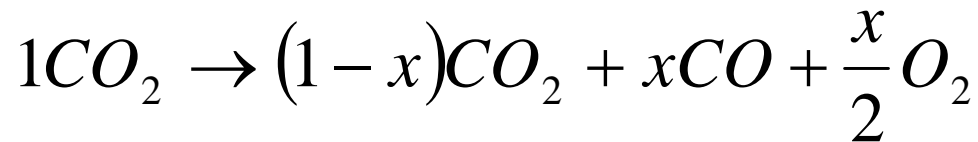
- CO_2 gas at 25°C , 5.1 atm enters a heat exchanger operating at steady state. An equilibrium mixture of CO_2 , CO , and O_2 exits at 2800 K , 5 atm . Determine per kmol entering:
 - (a) the composition of the exiting mixture (b) the heat transfer to the gas stream, in KJ
- Neglect kinetic and potential energy effects.



Example problem



- The reaction has the form:



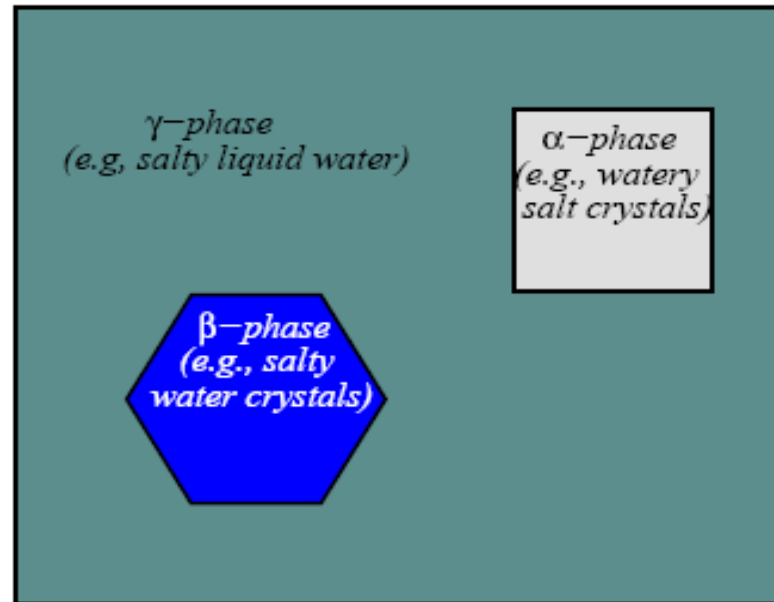
- The amount of mixture is:

$$n = (1-x) + x + \frac{x}{2} = \frac{2+x}{2}$$

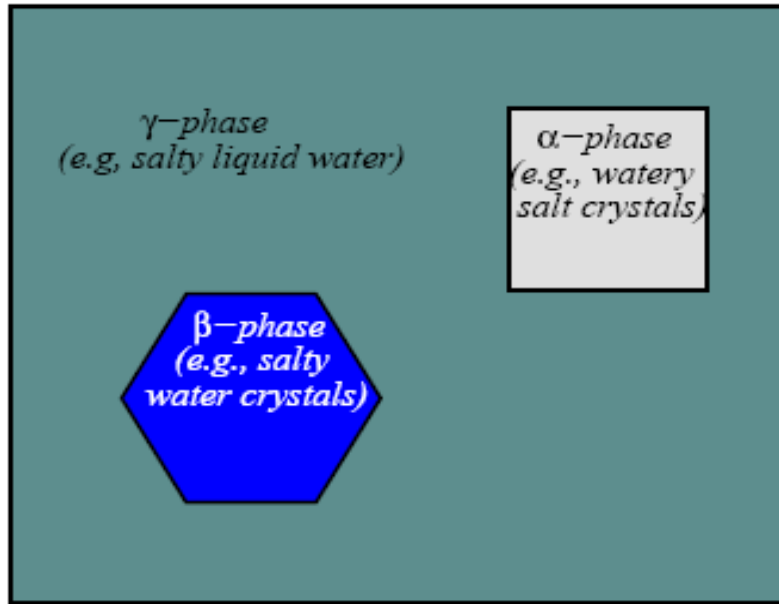
Return to Chemical Equilibrium

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



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

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

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

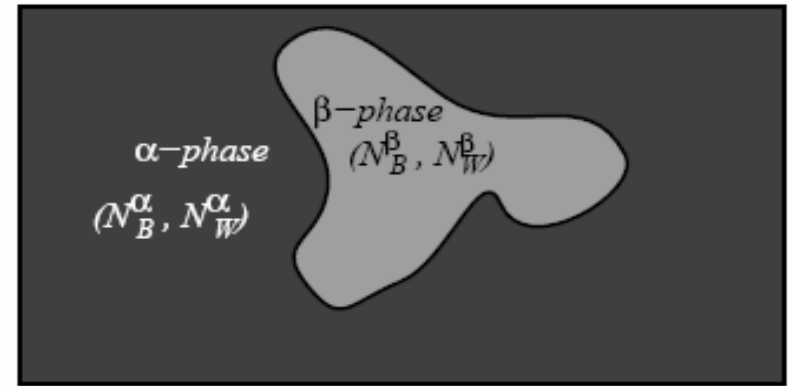
Composition variations and phase fractions

Consider e.g. two phases α , β :

Consider two components 1,2:

Consider constant T and P

(already shown to be required for equilibrium):



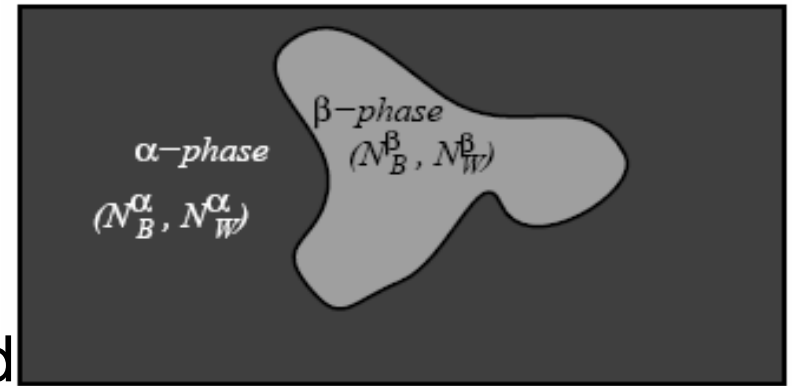
$$dG = -SdT + VdP + \sum_{j=1}^2 \sum_{i=1}^2 \mu_i^j dN_i^j \quad \text{But note that:} \quad \begin{aligned} dN_1^\alpha + dN_1^\beta &= 0, \\ dN_2^\alpha + dN_2^\beta &= 0 \end{aligned}$$

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

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

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 !

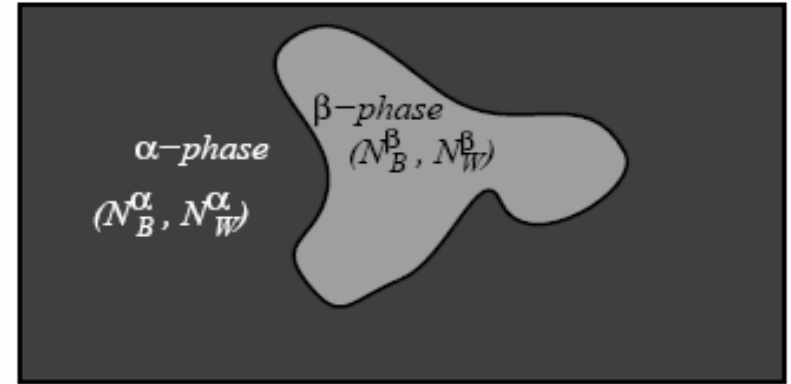
Composition variations and phase fractions

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

For equilibrium $dG=0$:

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

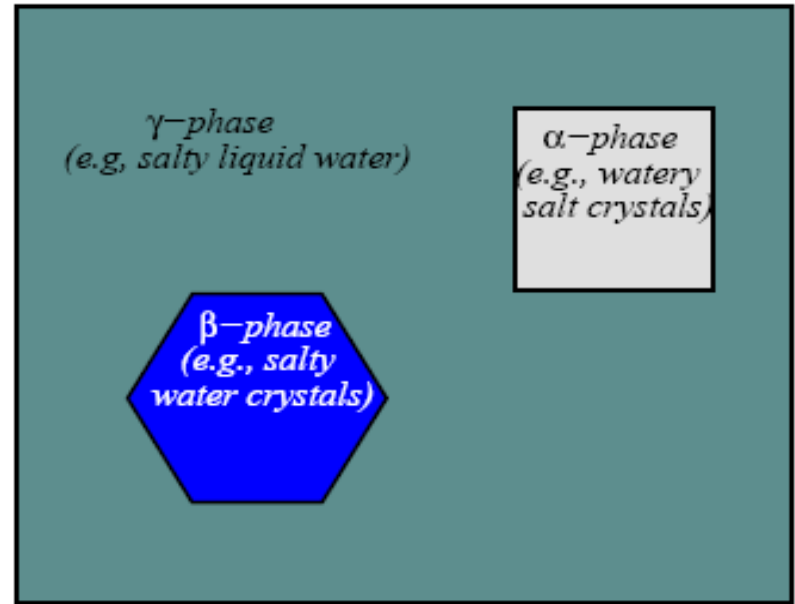
$$\mu_2^\alpha = \mu_2^\beta$$



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

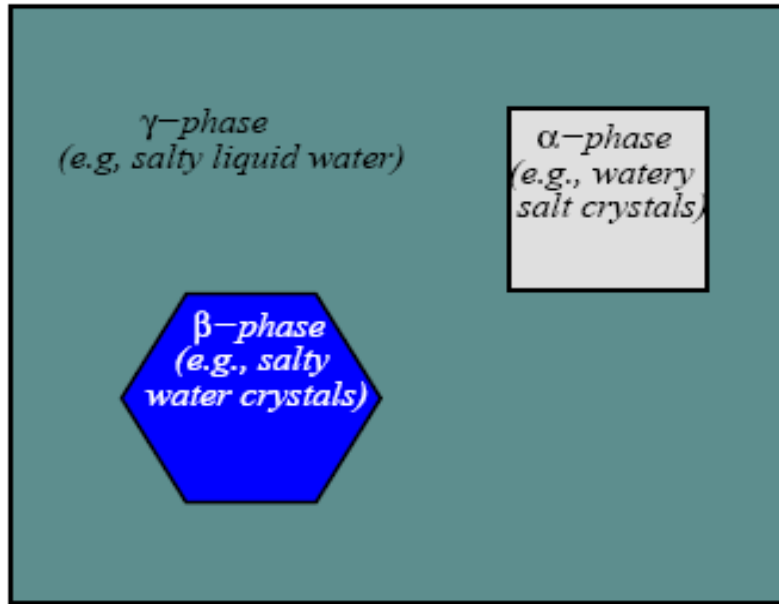
$$dG = -SdT + VdP + \sum_{j=1}^f \sum_{i=1}^C \mu_i^j dN_i^j$$

$$\begin{aligned} dG = & -SdT + VdP + \\ & + \mu_A^\alpha dN_A^\alpha + \mu_B^\alpha dN_B^\alpha + \dots + \mu_C^\alpha dN_C^\alpha \\ & + \mu_A^\beta dN_A^\beta + \mu_B^\beta dN_B^\beta + \dots + \mu_C^\beta dN_C^\beta \\ & + \dots \\ & - \mu_A^f (dN_A^\alpha + dN_A^\beta + \dots + dN_A^{f-1}) \\ & - \mu_B^f (dN_B^\alpha + dN_B^\beta + \dots + dN_B^{f-1}) - \dots \\ & - \mu_C^f (dN_C^\alpha + dN_C^\beta + \dots + dN_C^{f-1}) \end{aligned}$$

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

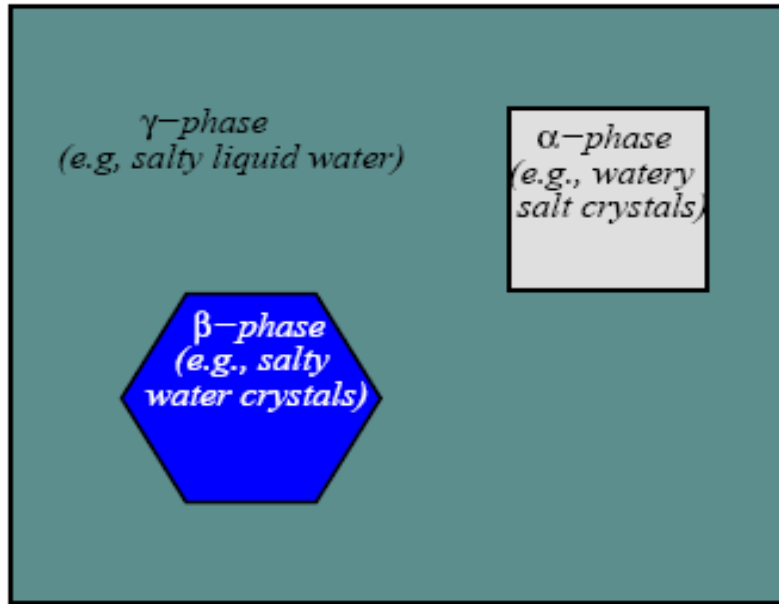


$$dG = -SdT + VdP + \sum_{j=1}^{f-1} \sum_{i=1}^C (\mu_i^j - \mu_i^f) dN_i^j$$

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.

$$\mu_1^{\text{I}} = \mu_1^{\text{II}} = \mu_1^{\text{III}} = \dots = \mu_1^{\text{f}}$$

$$\mu_2^{\text{I}} = \mu_2^{\text{II}} = \mu_2^{\text{III}} = \dots = \mu_2^{\text{f}}$$

\vdots

$$\mu_C^{\text{I}} = \mu_C^{\text{II}} = \mu_C^{\text{III}} = \dots = \mu_C^{\text{f}}$$

Example

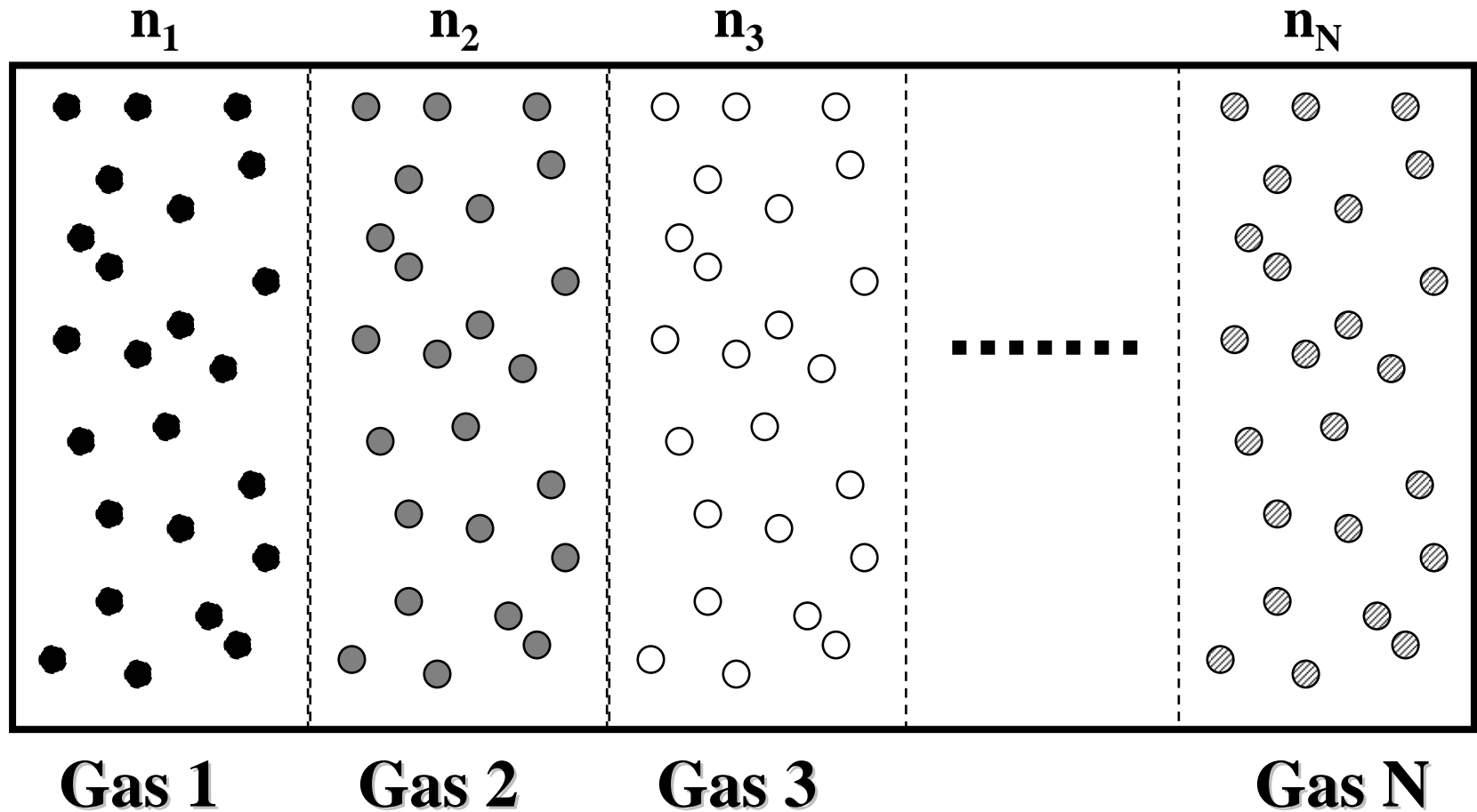
- Consider a closed chamber of fixed volume that is divided into two equal parts by a rigid membrane. Initially each part contains an ideal gas mixture of He and Xe with partial pressures specified in the figure below. Note that the membrane cannot move so there are always two chambers each at 1 m^3 .

$P_{Xe}^{left, init} = 1/4 \text{ atm}$	$P_{Xe}^{right, init} = 1 \text{ atm}$
$P_{He}^{left, init} = 1/2 \text{ atm}$	$P_{He}^{right, init} = 1 \text{ atm}$

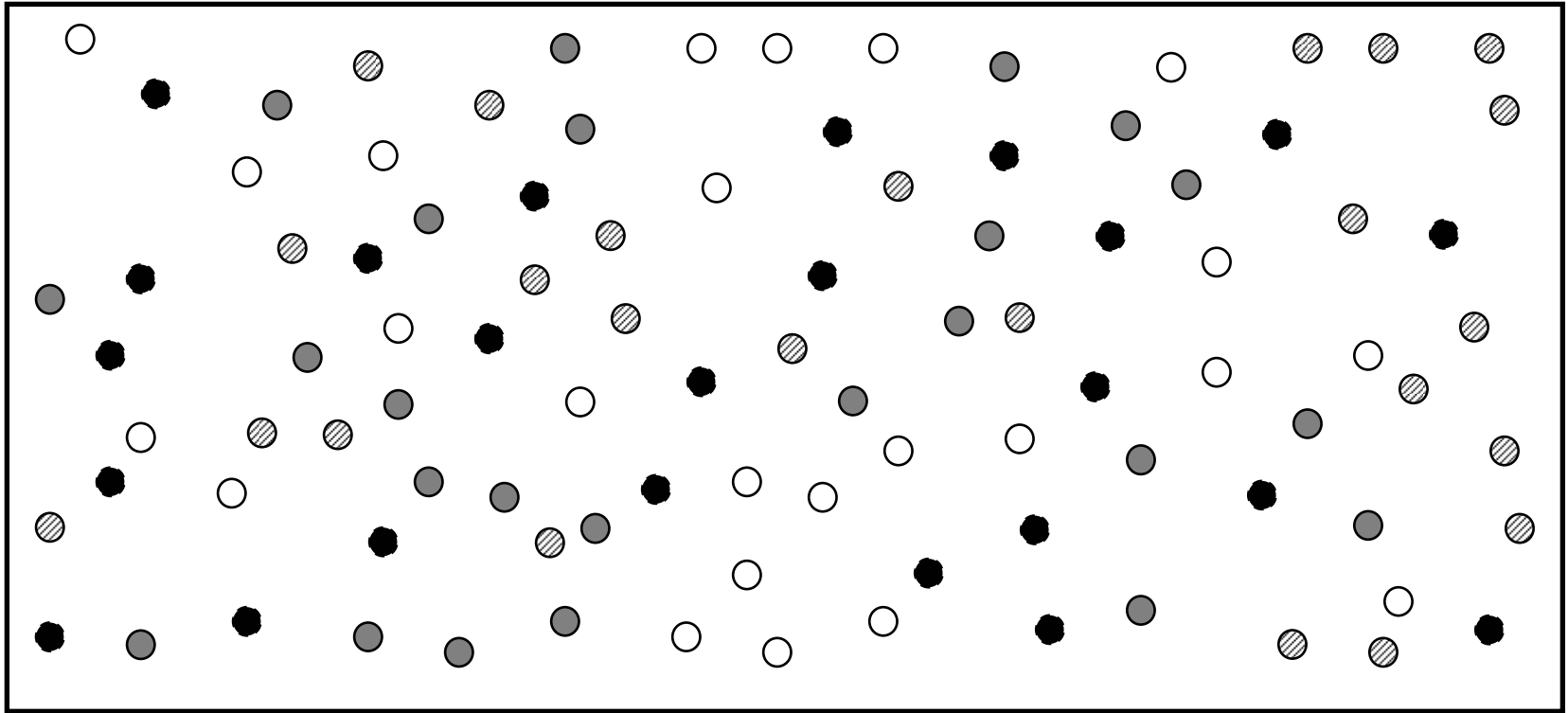
- The membrane allows He to pass through it but does not allow Xe to pass through it. Assume the temperature is constant and that He and Xe are the only species present.

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

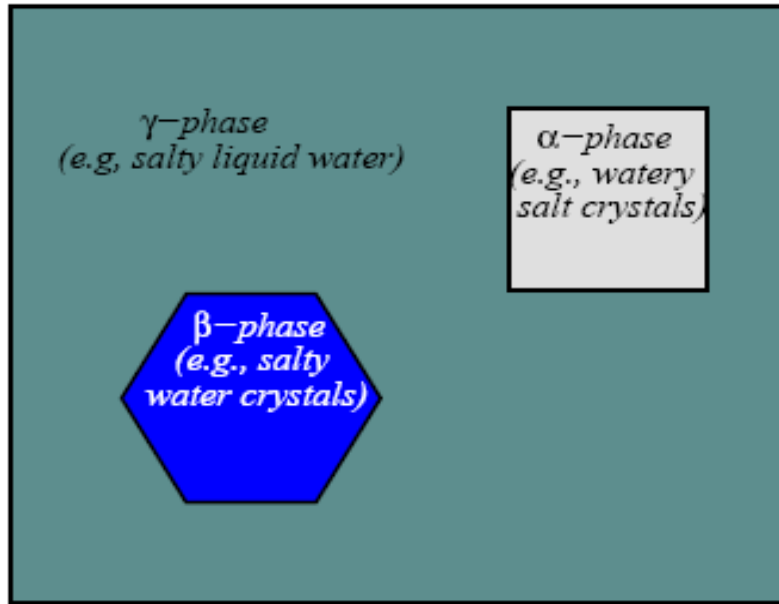
What if the the two gases are the same? Is there an entropy increase?

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):

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

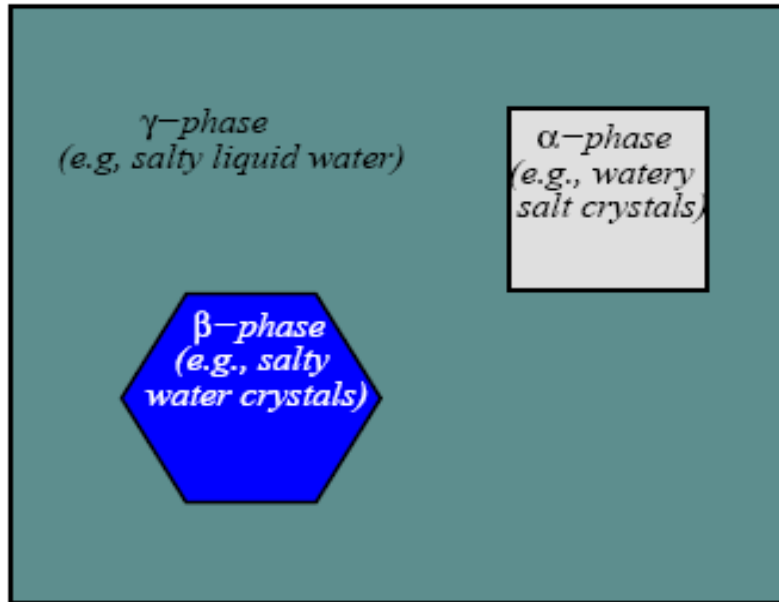
Using $U = TS - PV + \sum_{i=1}^C \mu_i N_i \Rightarrow$

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

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:

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

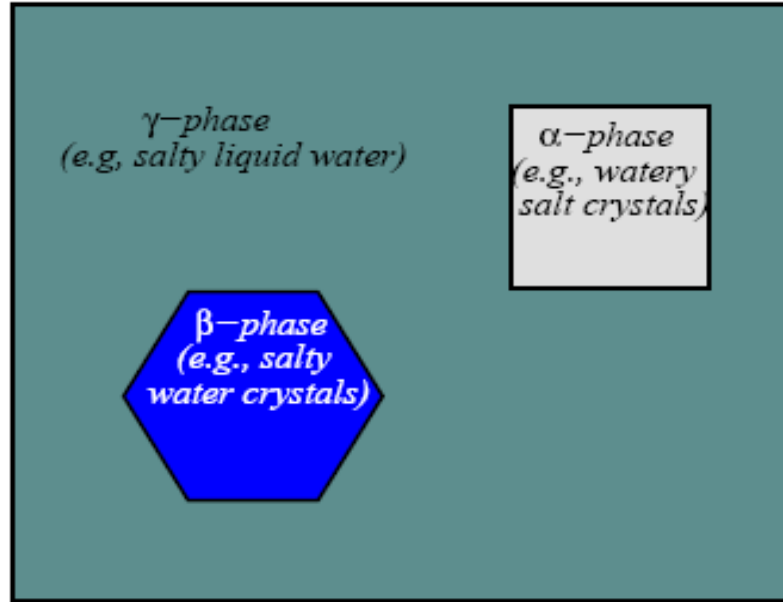
$$0 = S^{\text{II}}dT - V^{\text{II}}dP + \sum_{i=1}^c N_i^{\text{II}}d\mu_i^{\text{II}}$$

$\vdots = \vdots$

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

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?

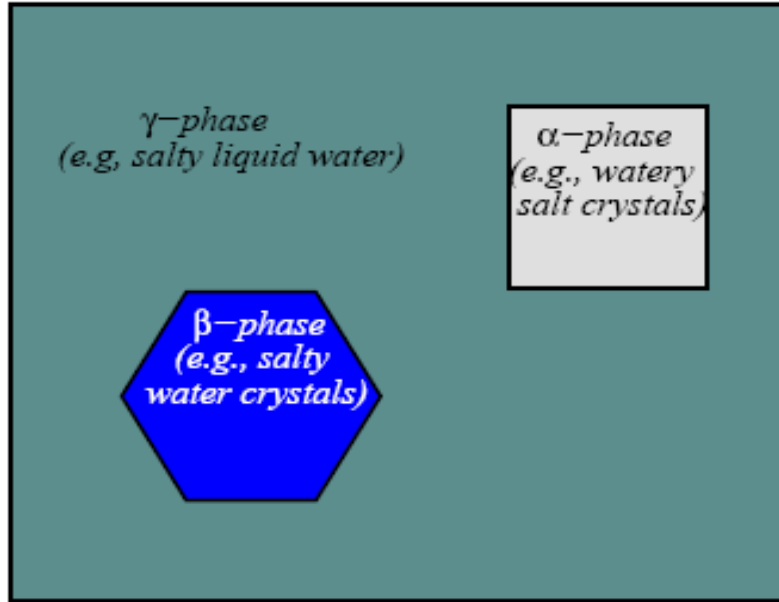
1. T and P (2 variables)
2. Chemical potentials μ_i^j (total of Cf variables)

How many constraints we have from equilibrium?

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

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

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.

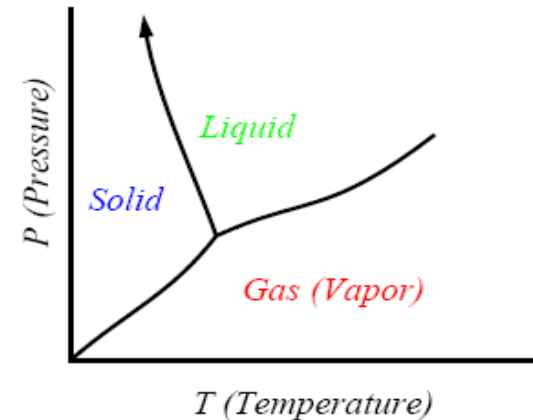
$C=1$, and $f=2$. Then $D=1+2-2=1$

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 $D=1+2-3=0$

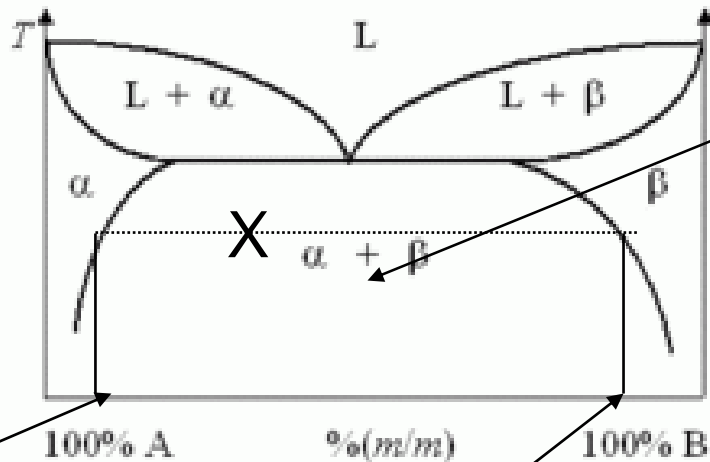
Indeed this is the triple point (well defined T and P). Cannot change any of them and still maintain water, ice and vapor in equilibrium)



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.



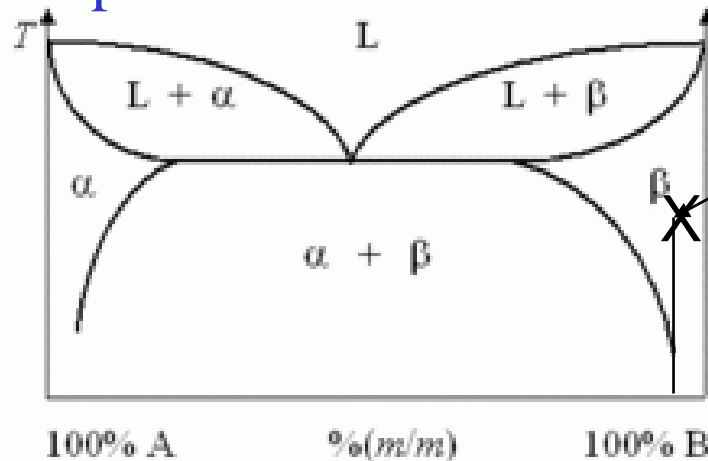
Region of interest

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