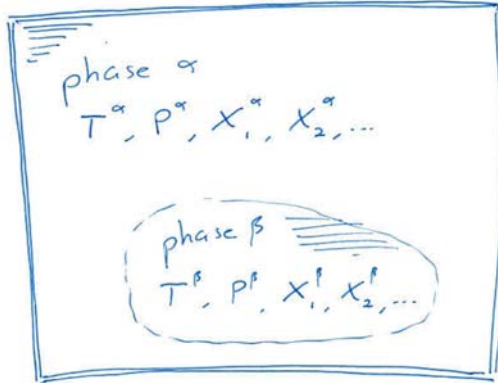


# 3.020 Lecture 20

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# 1 Equilibrium in multicomponent, heterogeneous systems



- Overall system is isolated
- Q. What is condition for phase equilibrium between  $\alpha$  &  $\beta$  if phase boundary is
  - open
  - non-rigid
  - thermally conductive

- For total system

$$dS' = \underbrace{\sum_j}_{\text{sum over phases}} \left( \frac{dU^j}{T^j} + \frac{P^j}{T^j} dV^j + \underbrace{\sum_k}_{\text{sum over components}} \frac{\mu_k^j}{T^j} dn_k^j \right)$$

- $dS' = 0$  at equilibrium leads to conditions

$$T^\alpha = T^\beta, \quad P^\alpha = P^\beta, \quad \mu_k^\alpha = \mu_k^\beta$$

thermal, mechanical, chemical

## 2 Gibbs phase rule, revised for multicomponent systems

Ph phases, C components

$$\begin{array}{l}
 \overline{\# \text{ variables}} \\
 \left. \begin{array}{l}
 T^\alpha, P^\alpha, X_1^\alpha, X_2^\alpha, \dots, X_{C-1}^\alpha \\
 T^\beta, P^\beta, X_1^\beta, X_2^\beta, \dots, X_{C-1}^\beta \\
 \vdots
 \end{array} \right\} \text{Ph phases} \Rightarrow \# \text{ vars} = \text{Ph} \cdot (C+1) \\
 \underbrace{\hspace{10em}}_{2 + (C-1)} \\
 \text{variables per phase}
 \end{array}$$

$\overline{\# \text{ constraints from equilibrium conditions}}$

$$\begin{array}{l}
 T^\alpha = T^\beta = \dots \\
 P^\alpha = P^\beta = \dots \\
 \mu_1^\alpha = \mu_1^\beta = \dots \\
 \mu_2^\alpha = \mu_2^\beta = \dots \\
 \vdots \\
 \mu_c^\alpha = \mu_c^\beta = \dots
 \end{array}
 \left. \vphantom{\begin{array}{l} T^\alpha = T^\beta = \dots \\ P^\alpha = P^\beta = \dots \\ \mu_1^\alpha = \mu_1^\beta = \dots \\ \mu_2^\alpha = \mu_2^\beta = \dots \\ \vdots \\ \mu_c^\alpha = \mu_c^\beta = \dots \end{array}} \right\} C+2 \text{ rows} \Rightarrow \# \text{ constraints} = (C+2)(\text{Ph}-1)$$

$(\text{Ph}-1)$  independent equations per row

## 3 Degrees of freedom (DoF) = $\text{Ph}(C+1) - (C+2)(\text{Ph}-1) = C+2 - \text{Ph}$

Case of binary system, C = 2

Gibbs phase rule for multicomponent systems

- Ph =1,  $\rightarrow$  DoF =3, can vary  $T$ ,  $P$  and composition
- 

- Ph =2,  $\rightarrow$  DoF =2, can vary 2 parameters, but 3<sup>rd</sup> will be determined e.g. Vary  $T$  and  $P$ , composition variables  $X_i^\alpha$  &  $X_i^\beta$  will co-vary to remain in 2-phase region
- Ph =3,  $\rightarrow$  DoF =1, can only vary 1 parameter, others co-vary to remain in 3-phase region
- Ph =4,  $\rightarrow$  DoF =0, Quadruple point, stationary in binary systems

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