3.020 Lecture 20

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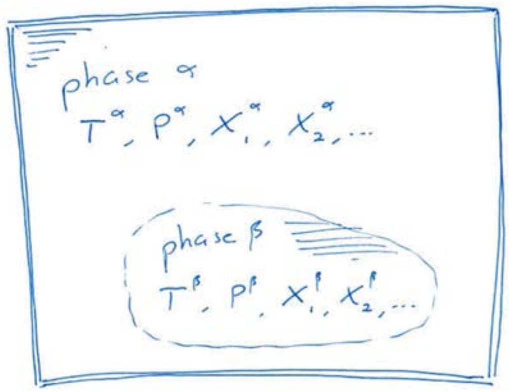
1 Equilibrium in multicomponent, heterogeneous systems



- Overall system is isolated
  Q. What is condition for phase equilibrium between α & β if phase boundary is
  - open
  - non-rigid
  - thermally conductive

- For total system

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

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

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

thermal, mechanical, chemical

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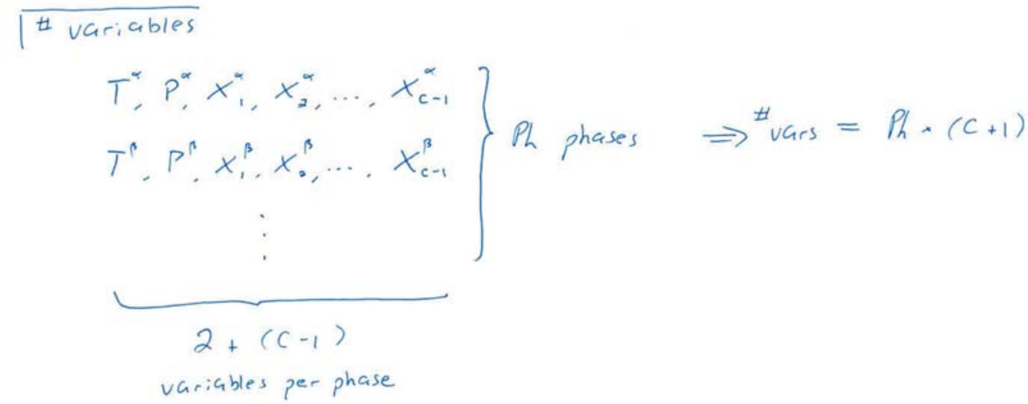
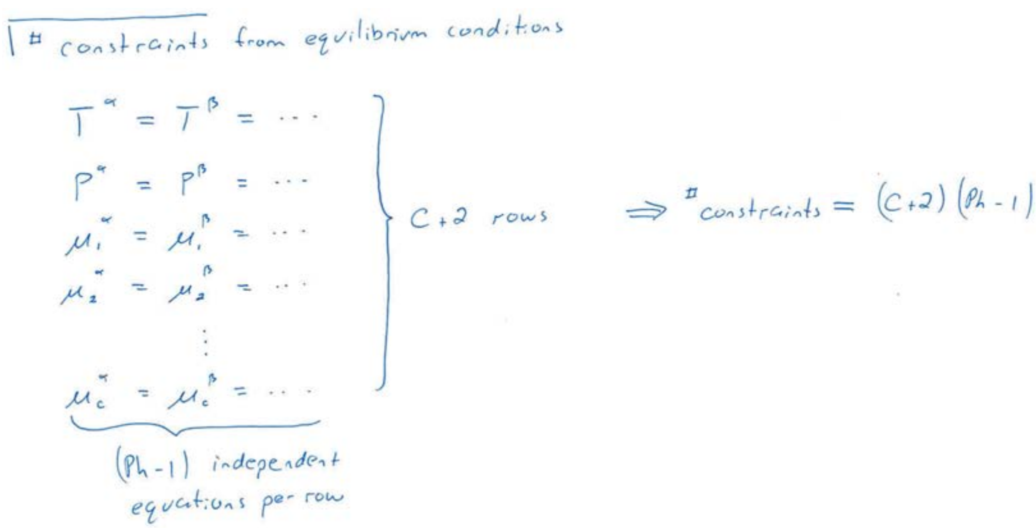
2 Gibbs phase rule, revised for multicomponent systems

Ph phases, C components





3 Degrees of freedom (DoF) = Ph(C+1)-(C+2)(Ph-1)=C+2-Ph

Case of binary system, C =2

Gibbs phase rule for multicomponent systems

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

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- Ph =2, $\longrightarrow$ DoF =2, can vary 2 parameters, but 3^{rd} will be determined e.g. Vary T and P, composition variables X_i^α & X_i^β will co-vary to remain in 2-phase region
- Ph =3, $\longrightarrow$ DoF =1, can only vary 1 parameter, others co-vary to remain in 3-phase region
- Ph =4, $\longrightarrow$ DoF =0, Quadruple point, stationary in binary systems