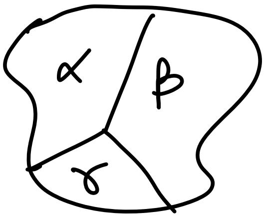
* MULTI-PHASE SYSTEMS:

Objective: describe multi-phase systems with multiple chemical elements.



① Compute properties of each phase as a function of composition
② " " " total system as a function of composition.
③ How do I compute eq^m in multi-phase systems?

- The system has c components (different species)
- $N_1, N_2, \dots, N_c \longrightarrow$ # of mole of each component

FUNDAMENTAL EQUATION OF THERMO:

$U(S, X_i, N_i)$:

$$dU = TdS + \sum Y_i dX_i + \sum_{i=1}^{c} \mu_i dN_i$$

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{T, X_i, N_{j \neq i}}$$ ⟵ definition of the chemical potential

* Review of some eqns. we derived before

- EULER: $U = TS - pV + \sum_i \mu_i N_i$

  other potentials:

  $H(S, p, N_i)$ = enthalpy = $U + pV = TS + \sum \mu_i N_i$

  $F(T, V, N_i)$ = Helmholtz free energy = $U - TS = -pV + \sum_i \mu_i N_i$

  $G(T, p, N_i) = U - TS + pV = \sum_i \mu_i N_i$

- GIBBS-DUHEM:

$$S d\underset{\uparrow}{T} - V d\underset{\uparrow}{p} + \sum_i N_i d\underset{\uparrow}{\mu_i} = 0$$

all intensive

$$G = U - TS + pV$$

$$dG = V\,dp - S\,dT + \sum_{i=1}^{c} \mu_i \, dN_i$$

EOS (for the multicomponent free energy) ⟶ $N_c + 2$ equations of state

new eos: $\left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}} = \mu_i \longrightarrow \mu_i\left(T, p, \{N_j\}\right) \xrightarrow{} $ all mole numbers!

Hessian:

$$\begin{array}{c|cc:c}
 & T & p & N_i \\
\hline
T & -C_p/T & \alpha V & \partial^2 G/\partial N_i \partial T \\
p & \alpha V & -V\underline{K} & \partial^2 G/\partial N_i \partial p \\
\hdashline
N_i & & & \partial^2 G/\partial N_i^2
\end{array}$$

$$\partial^2 G/\partial N_i \partial T \longrightarrow = \frac{-\partial S}{\partial N_i} = -\overline{S}_i \longrightarrow \text{PARTIAL MOLAR ENTROPY of } i$$

$$\partial^2 G/\partial N_i \partial p \longrightarrow \frac{\partial V}{\partial N_i} = \overline{V}_i \longrightarrow \text{PARTIAL MOLAR VOLUME of } i$$

$$\partial^2 G/\partial N_i^2 \longrightarrow \left(\frac{\partial \mu}{\partial N_i}\right) = \chi_{ii}$$

In general: A partial molar quantity:

$$\left(\frac{\partial X}{\partial N_i}\right)_{N_{j\neq i}; T, p} = \overline{X}_i$$

New Maxwell relations:

$$\overline{V}_i = \left(\frac{\partial V}{\partial N_i}\right)_{T,p,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial p}\right)_{N_i, T}$$

$$\overline{S}_i = \left(\frac{\partial S}{\partial N_i}\right) = -\left(\frac{\partial \mu_i}{\partial T}\right)_{N_i, p}$$

* DEFINITIONS:

total number of atoms

$$N = N_1 + N_2 + \cdots + N_c$$

* molar quantity: So far we have avoided normalizing extensive variables

$$X_m \rightsquigarrow \text{(eg)} \quad G_m = \frac{G}{N} = g$$

$$H_m = \frac{H}{N} = h$$

$$V_m = \frac{V}{N} = v$$

NOTE: Sometimes these quantities are also written as $\bar{G}, \bar{H}, \bar{V}$

$\hookrightarrow$ not to be confused with partial molar quantities

* What is the chemical potential @ const. T, p?

$$\left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}} = \mu_i$$

$\rightsquigarrow$ change in Gibbs free energy when I add a small amount of element i

N is NOT constant!

what we usually want is to compute the effects of changing compositions.

Say we have a binary: n_A, n_B, p, T

$$dG = Vdp - SdT + \mu_A dN_A + \mu_B dN_B$$

$$n_A + n_B = n_{tot} \Rightarrow n_B = n_{tot} - n_A$$

$$\Rightarrow dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_{tot} - \mu_B dn_A$$

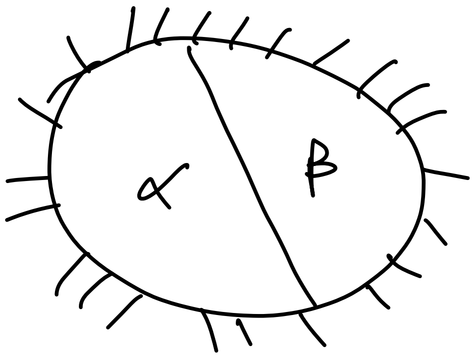
$$dG = Vdp - SdT + (\mu_A - \mu_B)\, dn_A + \mu_B dn_{tot}$$

$$\left(\frac{\partial G}{\partial n_A}\right)_{p,T,\underset{\overset{\uparrow}{\text{Constant}}}{n_{tot}}} = \mu_A - \mu_B$$

$$\Rightarrow \left(\frac{\partial \left(G/n_{tot}\right)}{\partial \left(n_A/n_{tot}\right)}\right)_{p,T,n_{tot}} = \left(\frac{\partial G_m}{\partial x_A}\right)_{p,T,n_{tot}} = \mu_A - \mu_B$$

$$\boxed{(\mu_A - \mu_B) \longrightarrow \text{Molar Gibbs energy change when we change the composition}}$$

* EQ^m IN MULTIPHASE SYSTEMS:



Overall the system is closed.
Constant T, p.
mass can flow between the two phases α & β.

$G^{total} = G^{\alpha} + G^{\beta}$; minimize G_{total} to find eq^m.

$$dG^{total} = dG^{\alpha} + dG^{\beta} = \sum_i \mu_i^{\alpha} dN_i^{\alpha} + \sum_j \mu_j^{\beta} dN_j^{\beta}$$

system is closed:

$$N_i^{total} = N_i^{\alpha} + N_i^{\beta}$$

$$dN_i^{total} = 0 \Rightarrow dN_i^{\alpha} = -dN_i^{\beta}$$

$$dG^{total} = \sum_i (\mu_i^{\alpha} - \mu_i^{\beta}) dN_i^{\alpha} = 0 \longrightarrow @ \text{ eq}^m.$$

$\Rightarrow$ for eq^m: $\boxed{\mu_i^{\alpha} = \mu_i^{\beta}}$ for all i

* CHEMICAL POTENTIALS & COMMON TANGENTS

- LEVER RULE

$\alpha, \beta \longrightarrow$ Two phases in a binary alloy

$$X^A_\alpha = \frac{N^A_\alpha}{N^A_\alpha + N^B_\alpha} \qquad X^A_\beta = \frac{N^A_\beta}{N^A_\beta + N^B_\beta}$$

$f_\alpha \longrightarrow$ fraction of the α phase

$$f_\alpha = \frac{N^A_\alpha + N^B_\alpha}{N^A_\alpha + N^B_\alpha + N^A_\beta + N^B_\beta} = \frac{N_\alpha}{N_\alpha + N_\beta.} \; ; \; f_\beta = \frac{N_\beta}{N_\alpha + N_\beta}$$

$$X^A = \frac{N^A}{N^A + N^B} = \frac{N^A_\alpha + N^A_\beta}{N^A_\alpha + N^A_\beta + N^B_\alpha + N^B_\beta} = X^A_\alpha f_\alpha + X^A_\beta f_\beta$$

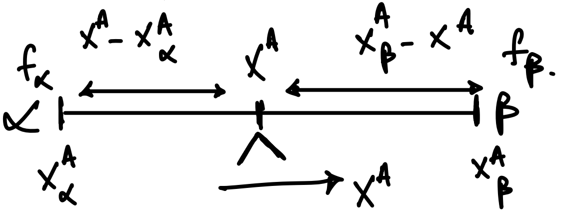
$$X^A = X^A(f_\alpha + f_\beta) = X^A_\alpha f_\alpha + X^A_\beta f_\beta$$

$$\Rightarrow (X^A_\alpha - X^A) f_\alpha + (X^A_\beta - X^A) f_\beta = 0$$

$$\Rightarrow \frac{X^A_\alpha - X^A}{f_\beta} = \frac{X^A - X^A_\beta}{f_\alpha} = \frac{X^A - X^A_\beta}{1 - f_\beta} \Rightarrow \frac{1}{f_\beta} - 1 = \frac{X^A - X^A_\beta}{X^A_\alpha - X^A}$$

$$\Rightarrow f_\beta = \frac{X^A_\alpha - X^A}{X^A - X^A_\beta + X^A_\alpha - X^A} \; ; \; \boxed{f_\beta = \frac{X^A - X^A_\alpha}{X^A_\alpha - X^A_\beta}}$$

Similarly: $\boxed{f_\alpha = \frac{X^A_\beta - X^A}{X^A_\beta - X^A_\alpha}}$



– Free energy of a two-phase mixture

$\alpha \longrightarrow g_\alpha(x_\alpha)$ $\longrightarrow$ composition of element A in the α phase

$\beta \longrightarrow g_\beta(x_\beta)$

2-phase mixture with phase fractions f_α, f_β, & total composition of A is X

$$G(f_\alpha, f_\beta, x_\alpha, x_\beta, N) = N_\alpha g_\alpha(x_\alpha) + N_\beta g_\beta(x_\beta)$$

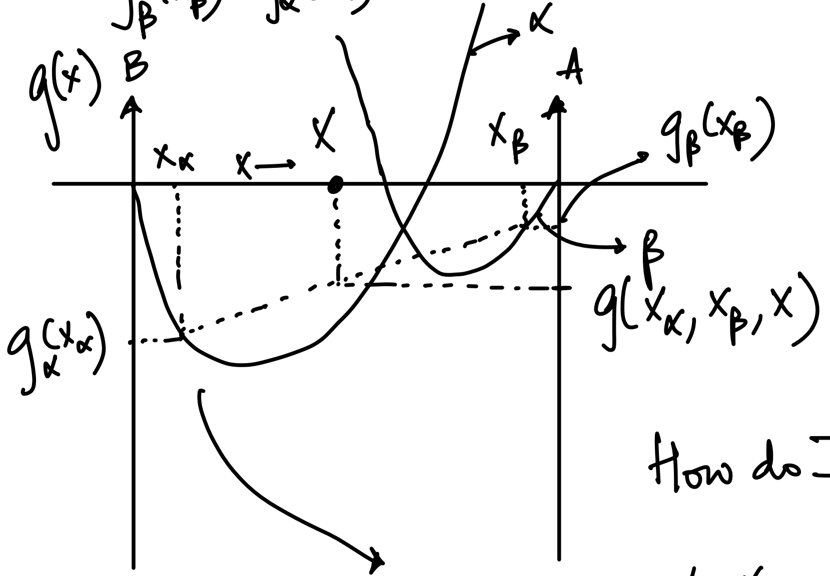
$$g(f_\alpha, f_\beta, x_\alpha, x_\beta) = \frac{G}{N} = f_\alpha g_\alpha(x_\alpha) + f_\beta g_\beta(x_\beta) = (1-f_\beta) g_\alpha + f_\beta g_\beta(x_\beta)$$

$$= g_\alpha(x_\alpha) + f_\beta\left(g_\beta(x_\beta) - g_\alpha(x_\alpha)\right)$$

$$g(x_\alpha, x_\beta, X) = g_\alpha(x_\alpha) + \left[\frac{X - x_\alpha}{x_\beta - x_\alpha}\right]\left(g_\beta(x_\beta) - g_\alpha(x_\alpha)\right)$$

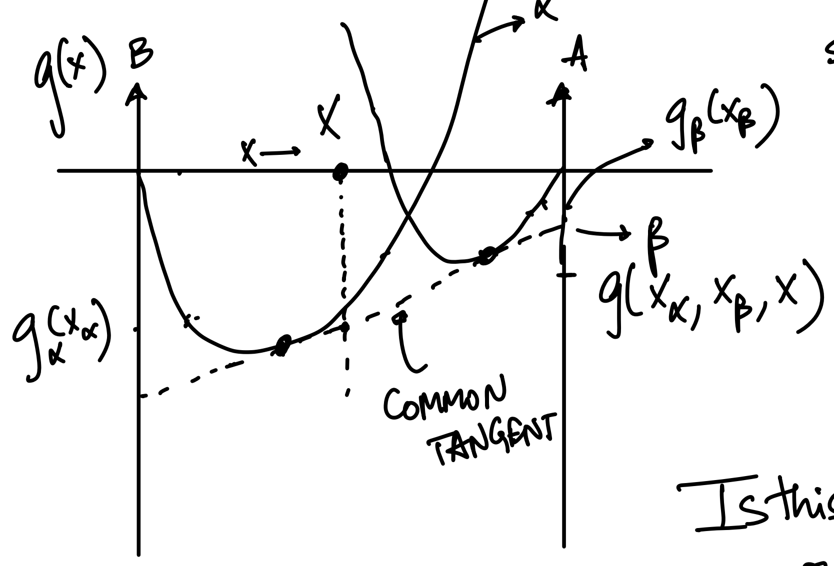
$$\Rightarrow \frac{g - g_\alpha(x_\alpha)}{g_\beta(x_\beta) - g_\alpha(x_\alpha)} = \frac{X - x_\alpha}{x_\beta - x_\alpha} \Rightarrow \boxed{\frac{g_\beta(x_\beta) - g_\alpha(x_\alpha)}{x_\beta - x_\alpha} = \frac{g - g_\alpha(x_\alpha)}{X - x_\alpha}}$$

equation of a line.



How do I find eq^m?

⇒ Minimize g (Not g_α or g_β) subject to fixed X

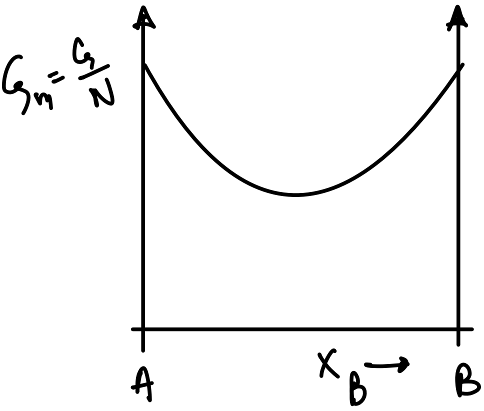


Is this the same as our eq^n criterion?

CHEMICAL POTENTIALS: GRAPHICAL INTERPRETATION:

Consider a binary alloy: A - B @ constant T, p

$Z = N Z_m \quad N = N_A + N_B \quad x_A = \frac{N_A}{N} \quad x_B = \frac{N_B}{N} \quad \boxed{x_B = 1 - x_A}$



How do we read chemical potentials from these plots?

$$\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{T,p,N_B} = \left(\frac{\partial (N G_m)}{\partial N_A}\right)_{T,p,N_B} = \left(\frac{\partial (N_A + N_B) G_m}{\partial N_A}\right)_{T,p,N_B}$$

$$\mu_A = \frac{\partial (N_A G_m)}{\partial N_A} + \left(\frac{\partial (N_B G_m)}{\partial N_A}\right)_{N_B}$$

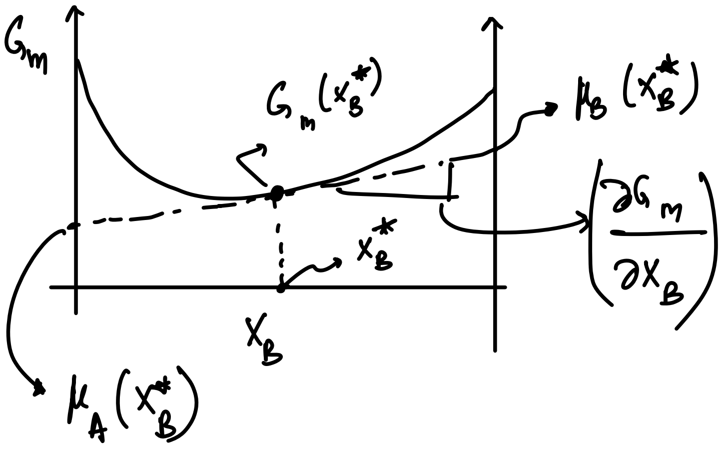
$$= G_m + N_A \frac{\partial G_m}{\partial N_A} + N_B \frac{\partial G_m}{\partial N_A} = G_m + N\left(\frac{\partial G_m}{\partial N_A}\right)_{N_B}$$

$$\mu_A = G_m + N \left(\frac{\partial G_m}{\partial x_A}\right)_{T,p,N_B} \left(\frac{\partial x_A}{\partial N_A}\right)_{T,p,N_B}$$

$$\left(\frac{\partial x_A}{\partial N_A}\right)_{T,p,N_B} = \frac{\partial \left(\frac{N_A}{N_A + N_B}\right)}{\partial N_A} = \frac{1}{N} - \frac{N_A}{N^2} = N_B / N^2 = x_B / N$$

$$\mu_A = G_m + \left(\frac{\partial G_m}{\partial x_A}\right)_{T,p,N_B} x_B = G_m - \left(\frac{\partial G_m}{\partial x_B}\right) x_B$$

$$\mu_B = G_m + \left(\frac{\partial G_m}{\partial x_B}\right)_{T,p,x_A} x_A = G_m + \left(\frac{\partial G_m}{\partial x_B}\right)(1 - x_B)$$



equaton of the line

let the intercept of the line @ $X_B=1$ be denoted as λ

$$\frac{\lambda - G_m(x_B^*)}{1-x_B^*} = \left(\frac{\partial G_m}{\partial x_B}\right)\Bigg|_{x_B^*}$$

$$\lambda = G_m(x_B^*) + (1-x_B^*)\left(\frac{\partial G_m}{\partial x_B}\right)\Bigg|_{x_B^*}$$

Comparing with our equation for μ_B

$$\boxed{\lambda = \mu_B}$$

- Common tangents

$$\Rightarrow \boxed{\mu_A^\alpha = \mu_A^\beta \quad \& \quad \mu_B^\alpha = \mu_B^\beta}$$

- Phase Diagrams: