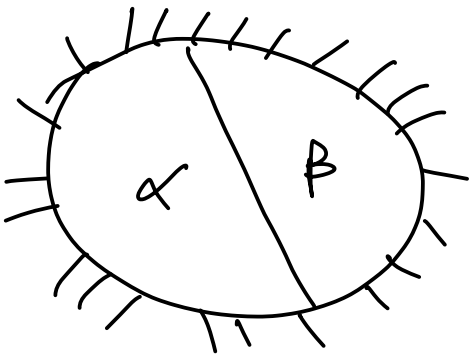
* EQ^m IN MULTIPHASE SYSTEMS:



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

$\longrightarrow$ **HOW DOES μ_i DEPEND ON COMPOSITION?**

* ASIDE:

GIBBS-DUHEM: $SdT - Vdp + \sum_i N_i d\mu_i = 0$

@ Constant T, P: $\sum_i N_i d\mu_i = 0$

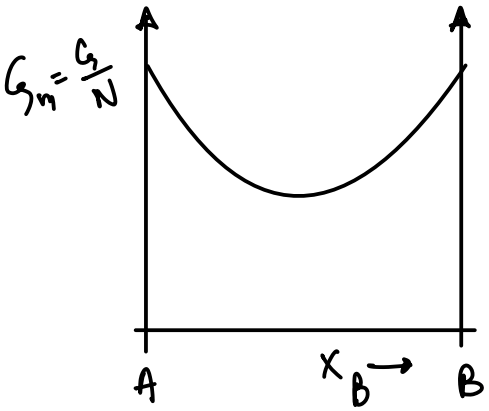
$$\Rightarrow \boxed{d\mu_1 = \sum_i -\frac{N_i}{N_1} d\mu_i}$$

If I know how μ_i vary with composition
I can compute μ_1

CHEMICAL POTENTIALS: GRAPHICAL INTERPRETATION:

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

$$Z = NZ_m \qquad N = N_A + N_B \qquad X_A = \frac{N_A}{N} \qquad X_B = \frac{N_B}{N} \qquad \boxed{X_B = 1 - X_A}$$



How do we read chemical potentials from these plots?

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

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

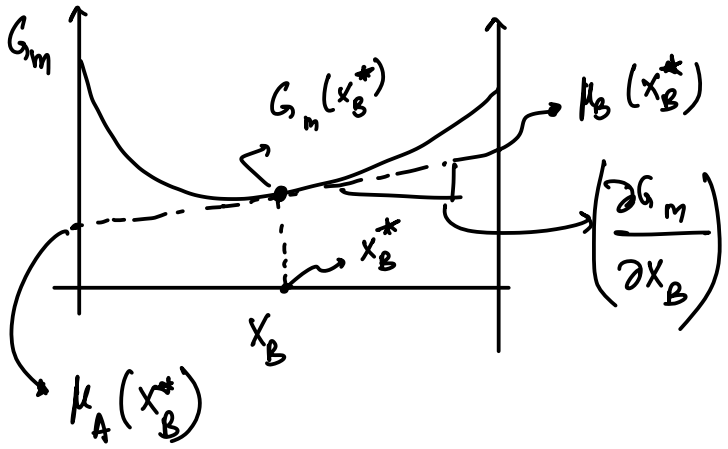
$$= G_m + N_A \frac{\partial G_m}{\partial N_A} + N_B \frac{\partial G_m}{\partial N_A} = G_m + N\left(\frac{\partial G_m}{\partial N_A}\right)_{N_B}$$

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

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

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

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



equation of the line

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

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

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

Comparing with our equation for μ_B

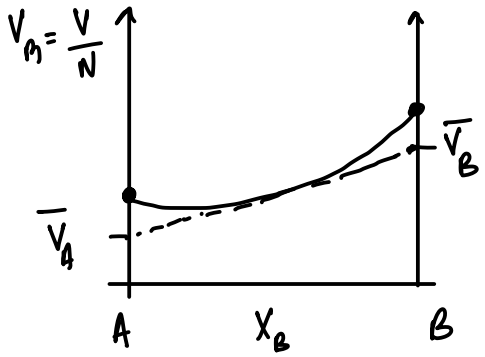
$$\boxed{\lambda = \mu_B}$$

Notice also that:

$$G_m(X_B^*) = (1 - X_B^*)\mu_A(x_B^*) + X_B^*\mu_B(x_B^*)$$
$$= X_A\mu_A + X_B\mu_B = X_A\bar{G}_A + X_B\bar{G}_B$$

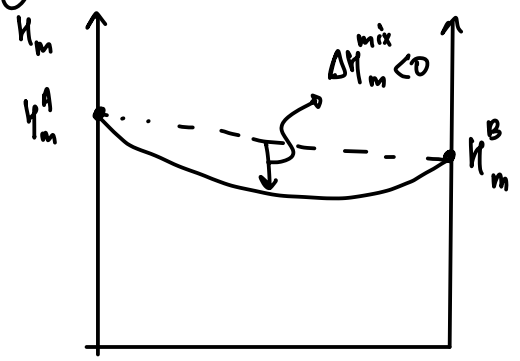
→ Notice that μ_A & μ_B are functions of composition!

NOTE: the equations can be derived for ALL PARTIAL MOLAR QUANTITIES (eg)



$$\boxed{V_m = \bar{V}_A x_A + \bar{V}_B x_B}$$

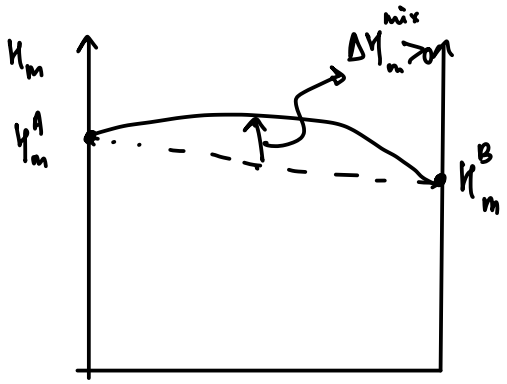
* Other mixing quantities:

① 

$$\Delta H_m^{mix} = H_m(x_B) - (1-x_B) H_m^A - x_B H_m^B$$

physical significance of ΔH_m^{mix} ?

mix A & B @ const. T & p



$\Delta H_m^{mix} < 0 \Rightarrow$ heat is given off when you mix these elements.

$$Q = (N_A + N_B)\, \Delta H_m^{mix}$$

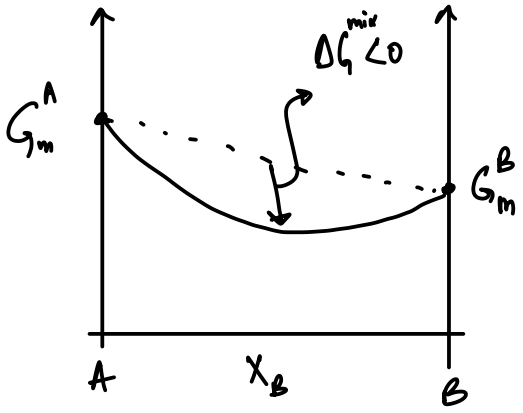
$\Delta H_m^{mix} > 0 \Rightarrow$ heat is absorbed upon mixing.

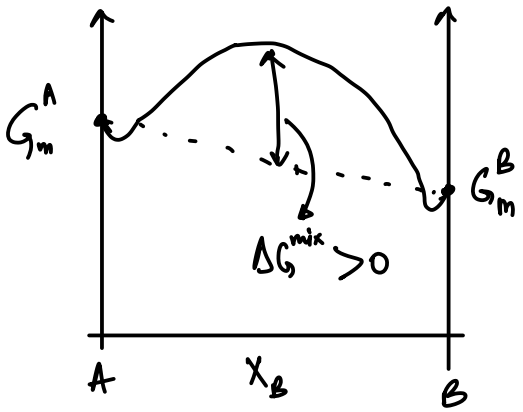
② Entropy of mixing:

$$\Delta S_m^{mix} = S_m(x_B) - (1-x_B) S_m^A - x_B S_m^B$$

③ Gibbs free energy of mixing:

$$\Delta G_m^{mix} = G_m(x_B) - (1-x_B) G_m^A - x_B G_m^B$$





which system will spontaneously mix?

EQUILIBRIUM CRITERIA FOR MULTICOMPONENT ALLOYS: (revisited)

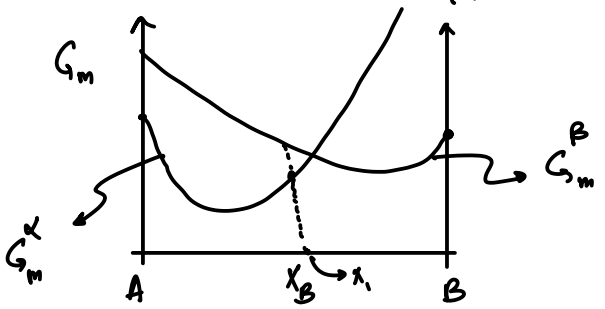
System @ constant P, T, N_A, N_B

$\Rightarrow$ characteristic potential is $G(T, P, N_A, N_B)$

$\Rightarrow$ eq^m is achieved when G is minimized.

Consider a system that can form 2 phases [(eg) water + salt]

phases $\longrightarrow \alpha$ & β



$G_m^\alpha(X_A=1) < G_m^\beta(X_A=1) \Rightarrow$ only α is formed when we have $N_B = 0$

$G_m^\beta(X_B=1) < G_m^\alpha(X_B=1)$

$\Rightarrow$ only β is formed when $N_A = 0$

what about X_1?

$G_m^\alpha(X_1) < G_m^\beta(X_1)$

free energy of the system: $G(N) = G^\alpha(N^\alpha, x^\alpha) + G^\beta(N^\beta, x^\beta)$

$NG_m(X) = N_\alpha G_m^\alpha(x^\alpha) + N_\beta G_m^\beta(x^\beta)$

N_α → # of moles that correspond to α

x^α → composition of the α phase

$G_m(X) = f^\alpha G_m^\alpha(x^\alpha) + f^\beta G_m^\beta(x^\beta)$

$f^\alpha = \frac{N^\alpha}{N}$ & $f^\beta = \frac{N^\beta}{N}$

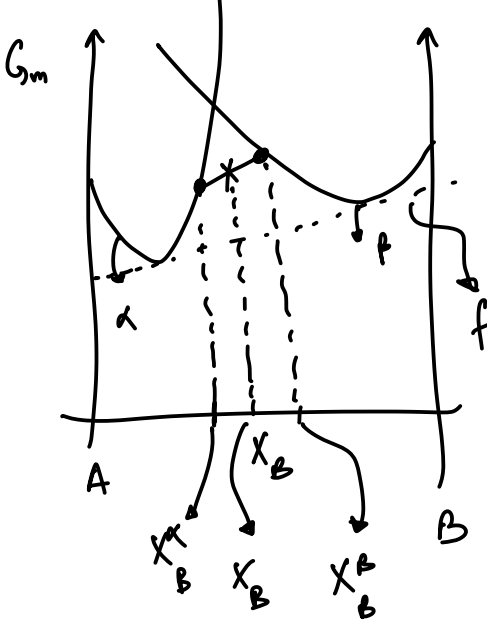
Lever rule:

$N_B = N_B^\alpha + N_B^\beta \longrightarrow X_B = \frac{N_B}{N}$

$\Rightarrow NX_B = X_B^\alpha N^\alpha + X_B^\beta N^\beta$

$= X_B^\alpha (N - N^\beta) + X_B^\beta N^\beta \longrightarrow N^\alpha + N^\beta = N$

$N(X_B - X_B^\alpha) = N^\beta(X_B^\beta - X_B^\alpha) \Rightarrow \frac{X_B - X_B^\alpha}{X_B^\beta - X_B^\alpha} = \frac{N^\beta}{N} = f^\beta$



f^α & f^β are fixed based on the choice of X_B^α & X_B^β

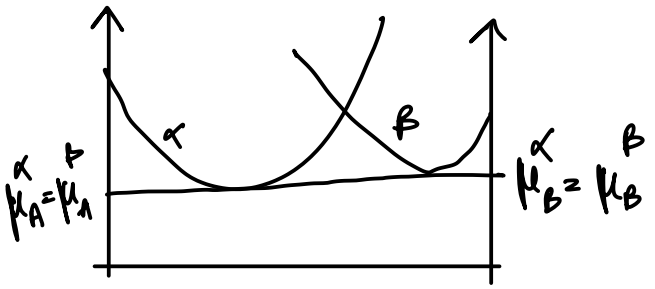
$G_m(X_B)$ ⟶ is on a chord connecting $G_m^\alpha(X^\alpha)$ and $G_m^\beta(X^\beta)$

free energy is minimized when we are on the common tangent

* EQ^m CRITERIA:

$$\mu_i^\alpha = \mu_i^\beta$$

Graphical representation:



"COMMON TANGENT" construction corresponds to a minimum in G