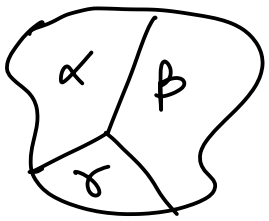
* MULTI-PHASE SYSTEMS:

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:

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

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) $\longrightarrow$ $N_c + 2$ equations of state

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

Hessian:

	T	p	N_i	
T	$-C_p/T$	αV	$\partial^2 G / \partial N_i \partial T$	$= -\frac{\partial S}{\partial N_i} = -\overline{S}_i$ → Partial Molar Entropy of i
p	αV	$-V\kappa$	$\partial^2 G / \partial N_i \partial p$	$\frac{\partial V}{\partial N_i} = \overline{V}_i$ → Partial Molar Volume of i
N_i			$\partial^2 G / \partial N_i^2$	$\left(\frac{\partial \mu}{\partial N_i}\right) = \chi_{ii}$

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

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

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

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

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

↳ not to be confused with partial molar quantities

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

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

↳ 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

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

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

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

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

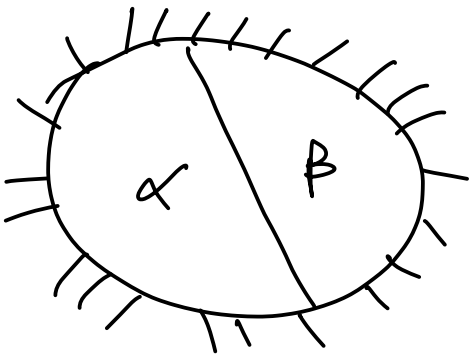
$$\left(\frac{\partial G}{\partial n_A}\right)_{p,T,n_{tot}} = \mu_A - \mu_B$$

(n_{tot}: Constant)

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

$(\mu_A - \mu_B)$ ⟶ 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

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

* ASIDE:

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

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

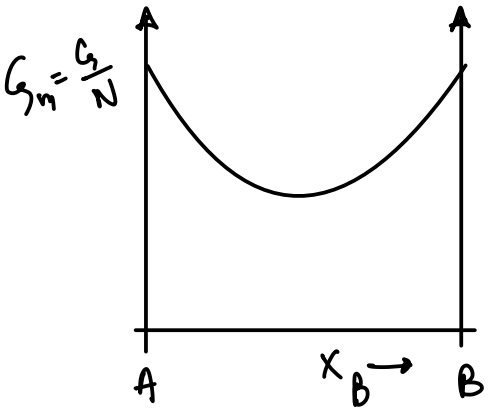
$$\Rightarrow \boxed{d\mu_1 = \sum_i -\frac{N_i}{N_1} d\mu_i}$$

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?

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

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

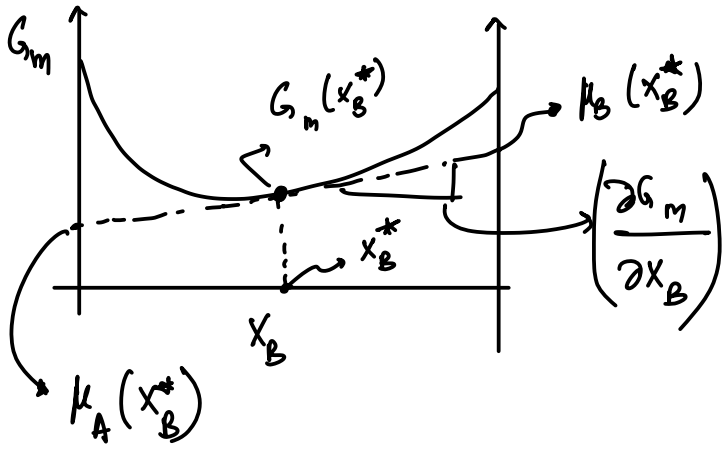
$$= G_m + N_A \frac{\partial G_m}{\partial N_A} + N_B \frac{\partial G_m}{\partial N_A} = G_m + N\left(\frac{\partial G_m}{\partial N_A}\right)_{N_B}$$

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

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

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

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



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

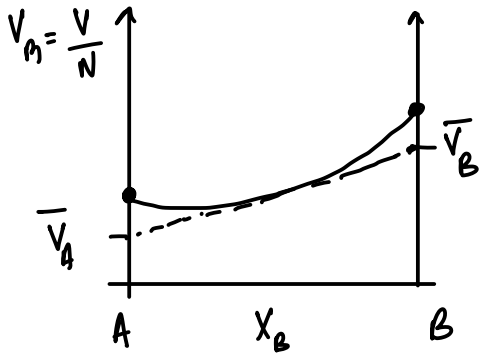
$$\boxed{\lambda = \mu_B}$$

Notice also that:

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

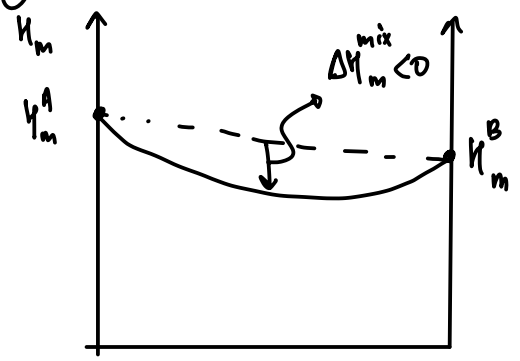
→ Notice that μ_A & μ_B are functions of composition!

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



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

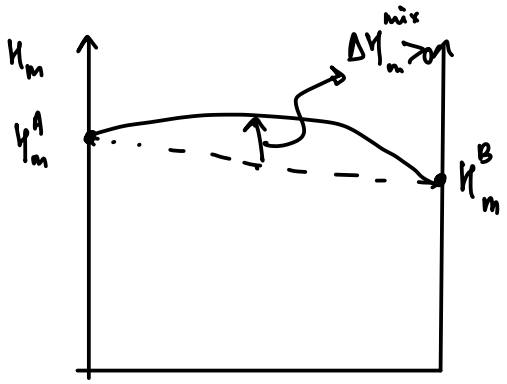
* Other mixing quantities:

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.

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

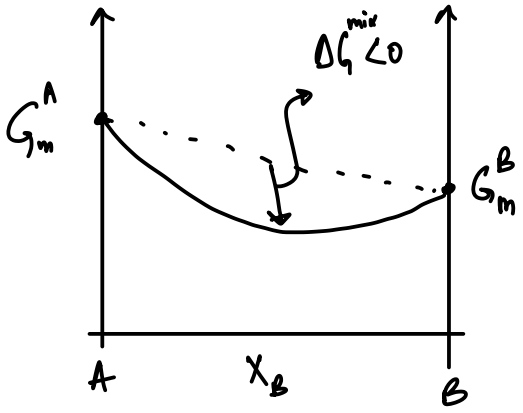
$\Delta H_m^{mix} > 0 \Rightarrow$ heat is absorbed upon mixing.

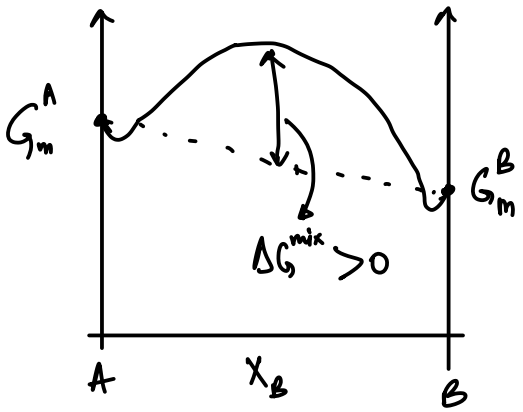
② Entropy of mixing:

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

③ Gibbs free energy of mixing:

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

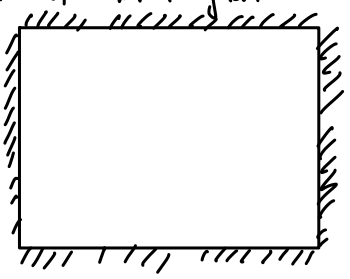




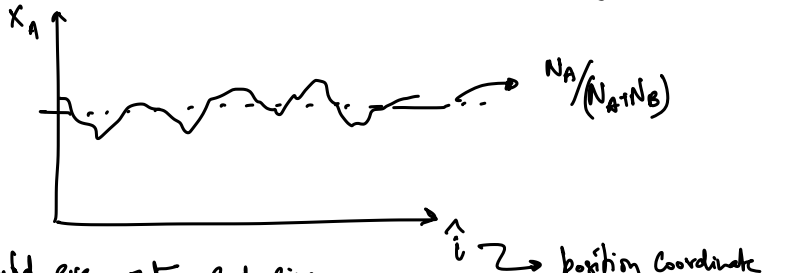
which system will spontaneously mix?

PHENOMENOLOGICAL TREATMENT OF NON-EQUILIBRIUM PROCESSES:

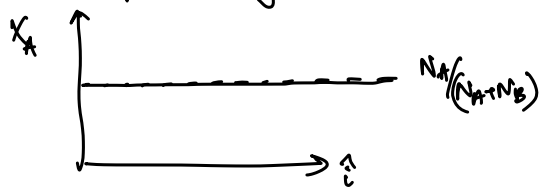
Let us consider an isolated system that is out of eqm



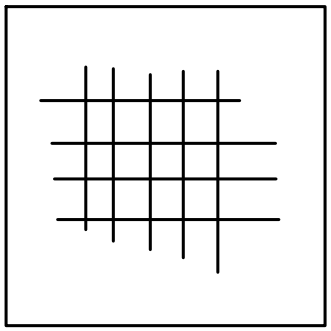
Say it contains N_A, N_B atoms with a total internal energy of $U(N_A, N_B)$



After a long-time composition fluctuations should even out and give a constant composition profile everywhere.



To study the evolution of the system we will begin by making the "local equilibrium" approximation:



divide the system into smaller sub-systems

- small enough such that local variations in extensive variables are minimal within a sub-system
- not so small that statistical mechanics breaks down. (ie) not atomic scale.

Local eqm approximation holds as long as extensive variables vary slowly from sub region to sub region.

$$\frac{U}{V_0} = u(\vec{r}) \qquad \frac{N_i}{V_0} = c_i(\vec{r}) \qquad \frac{S}{V_0} = s(\vec{r}) \qquad \frac{N_i}{N} = x_i(\vec{r})$$

$\vec{r}$ → location of the sub-region

→ mole fraction.

Consider a sub-region within the larger system.

$(u, s, c_i, x_i, T, \mu_i, p, \cdots)$ → a set of well-defined state variables for the sub-region.

⇒ Start from the fundamental equation of thermodynamics:

$$\boxed{du = Tds - pdV + \sum_i \mu_i dc_i}$$

neglect volume change for simplicity $dV = 0$

$$du = Tds + \sum_i \mu_i dc_i$$

$$\Rightarrow \boxed{ds = \left(\frac{1}{T}\right) du - \sum_i \left(\frac{\mu_i}{T}\right) dc_i} \quad \text{——— (1)}$$

the system is overall out of eqm ⇒ heat and matter will flow in and out of each element

ALL LOCAL THERMODYNAMIC STATE VARIABLES WILL EVOLVE OVER TIME

Take the time derivative of (1)