3.020 Lecture 30

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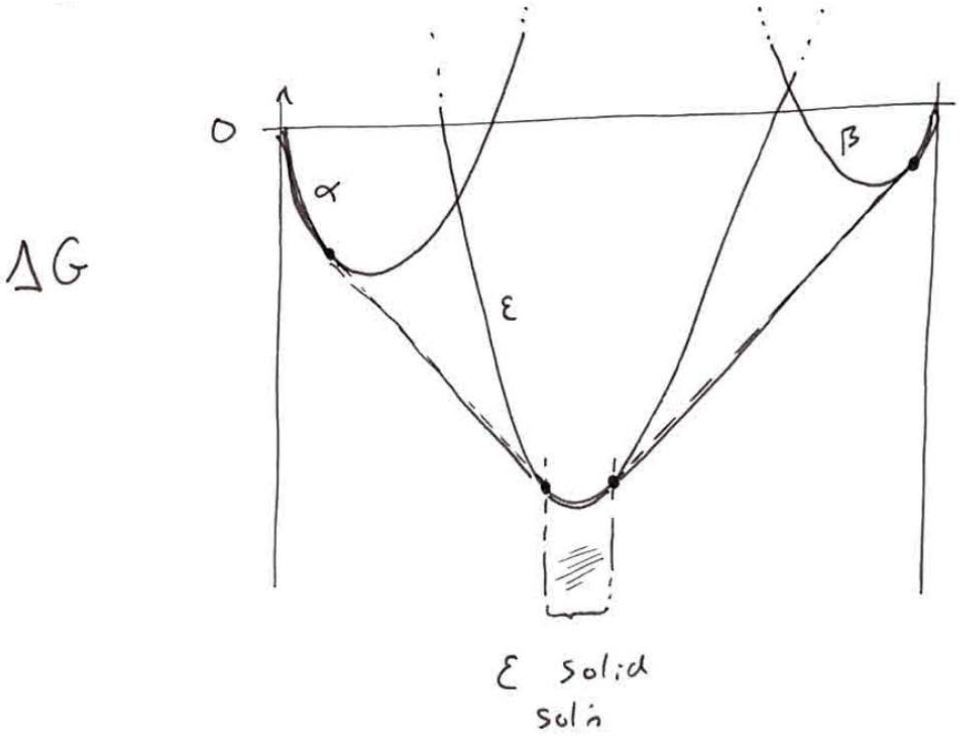
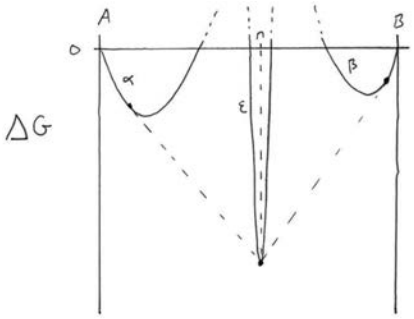
1 Intermediate phases and line compounds

recall : intermediate phase in a three-phase system



- Suppose that, instead of being a solid solution, the ϵ phase is very intolerant of deviations from stoichiometry
  e.g. $A_{1-n}B_n$, n fixed



- "Solution" model for ϵ phase becomes very steep
- All possible common tangents converge at the same point, at fixed composition $A_{1-n}B_n$
- $\Longrightarrow$ No longer need solution model, only need this one point

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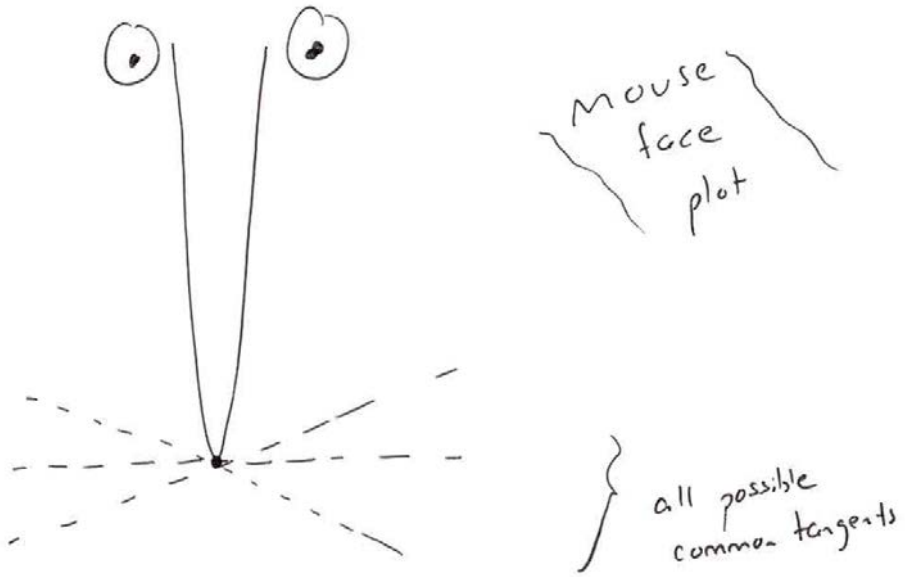

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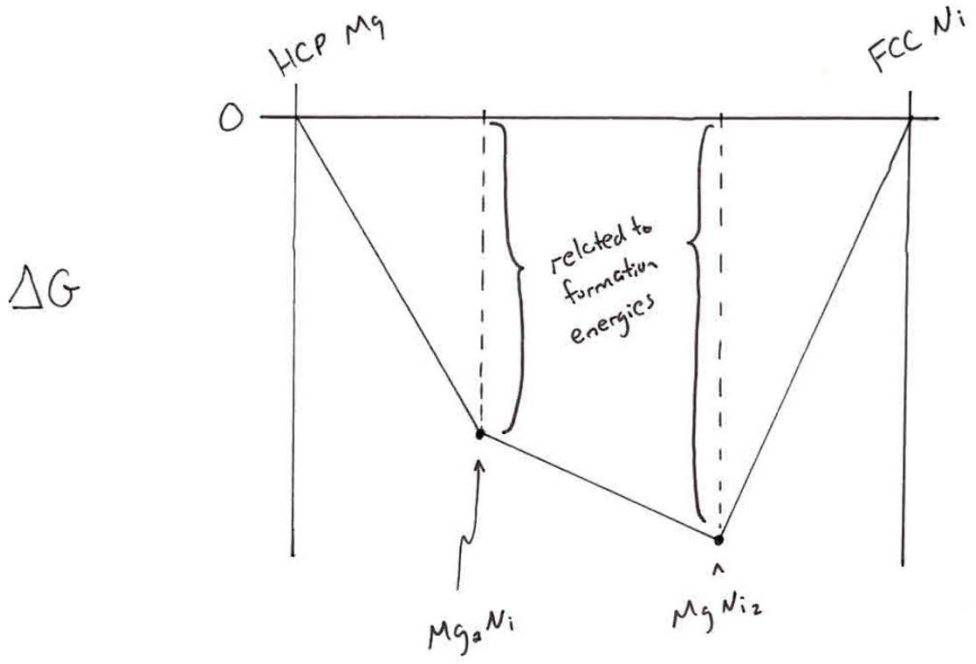
e.g. Mg-Ni



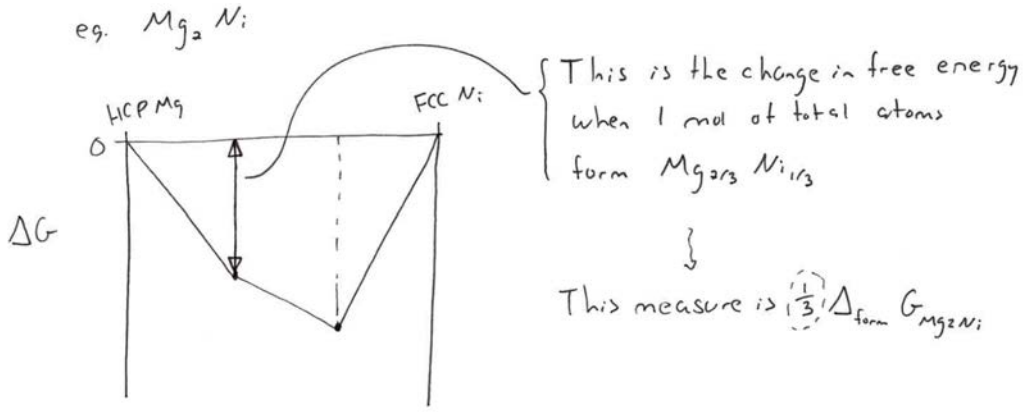
- taut rope construction becomes series of straight lines

- Compound formation energy $\Delta_{form}G$
  - Free energy change for formation of one mole of compound from the elements in their standard state

    e.g.

$$2\,\mathrm{Mg}^{\alpha} + \mathrm{Ni}^{\alpha} \xleftrightarrow{\Delta_{\mathrm{form}}\,\mathrm{G}} \mathrm{Mg_2\,Ni}$$
$$2\,\mathrm{Al}^{\alpha} + \tfrac{3}{2}\mathrm{O_2}^{v} \xleftrightarrow{\Delta_{\mathrm{form}}\,\mathrm{G}} \mathrm{Al_2O_3}$$

  - Need normalization to use $\Delta_f G$ on a free energy-composition plot



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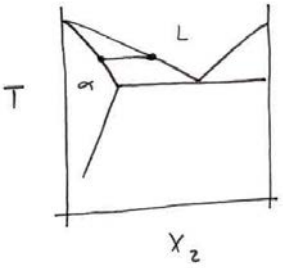
2 Comparing solutions of equilibrium to line compounds at equil.

- Two solutions, e.g. α & L



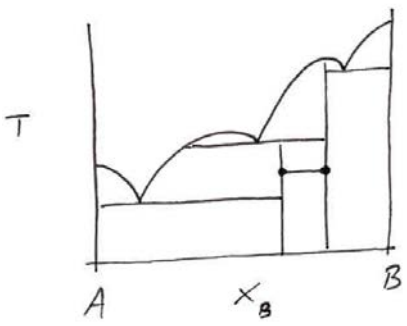
- $dG' = (\mu_i^\alpha - \mu_i^L)\ dn_i^\alpha + (\mu_2^\alpha - \mu_2^L)\ dn_2^\alpha$
- Internal composition variables

$$n_1^\alpha, n_2^\alpha, n_1^L, n_2^L \quad \longrightarrow \quad X_1^\alpha, X_1^L$$

- Equilibrium condition $dG' = 0$ satisfied by common tangent construction s.t.

$$\mu_i^\alpha = \mu_1^L, \qquad \mu_2^\alpha = \mu_2^L$$

- Two line compounds, e.g. B_3A_2 & B_4A_3



- $G_{B3A2} = 3G_B^o + 2G_A^o + \Delta_{form}G_{B3A2}$
- $G_{B4A3} = 4G_B^o + 3G_A^o + \Delta_{form}G_{B4A3}$
- No internal composition variables
- Equilibrium condition $dG' = 0$ is satisfied trivially
- $G' = f^{B3A2}\ (\frac{1}{5}G_{B3A2}) + f^{B4A3}\ (\frac{1}{7}G_{B4A3})$
  f^{B3A2}, f^{B4A3}: phase fractions determined by lever rule

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3 Metal oxides

- React metal M with 1 mole of O_2 to form an oxide
- M in its reference state
- Could by solid, liquid or even gas
- O_2 nearly always in gas reference state

$$Z\,M + {O_2}^g \longleftrightarrow M_z\,O_2$$

- Z determined by charge balance
- oxides are line compounds
- oxygen always O^{2-} in compounds
- metals have various oxidation states, many have more than one

3.020 Thermodynamics of Materials

Spring 2021