Unary System

- **Finding the equilibrium configuration (G´ minimum) is easy IF G_m^{Φ} is known for ALL phases as a function of P and T.**

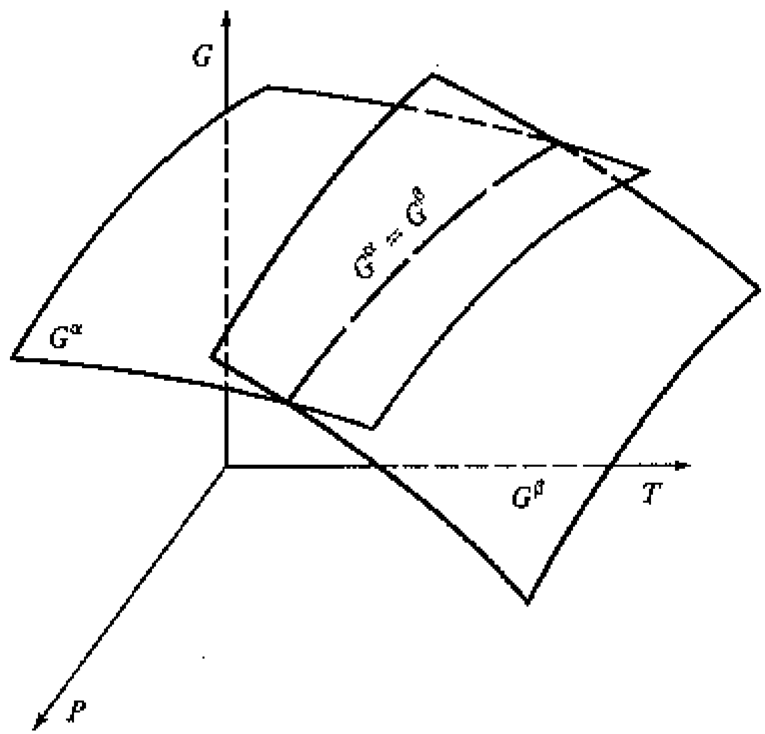
- **How can G_m^{Φ} be known?**
  - Outside of stability range?
  - For phases that are not ever "seen"?

Lattice stability?

$^oG^T_{i},^{\phi} - {}^oH_{i},^{\Phi}$ (298.15 K)= $^oG^T_{i},^{\phi} - {}^oG^T_{i},^{\Phi}$ + GHSERi =[Lattice Stability Π] + GHSERi

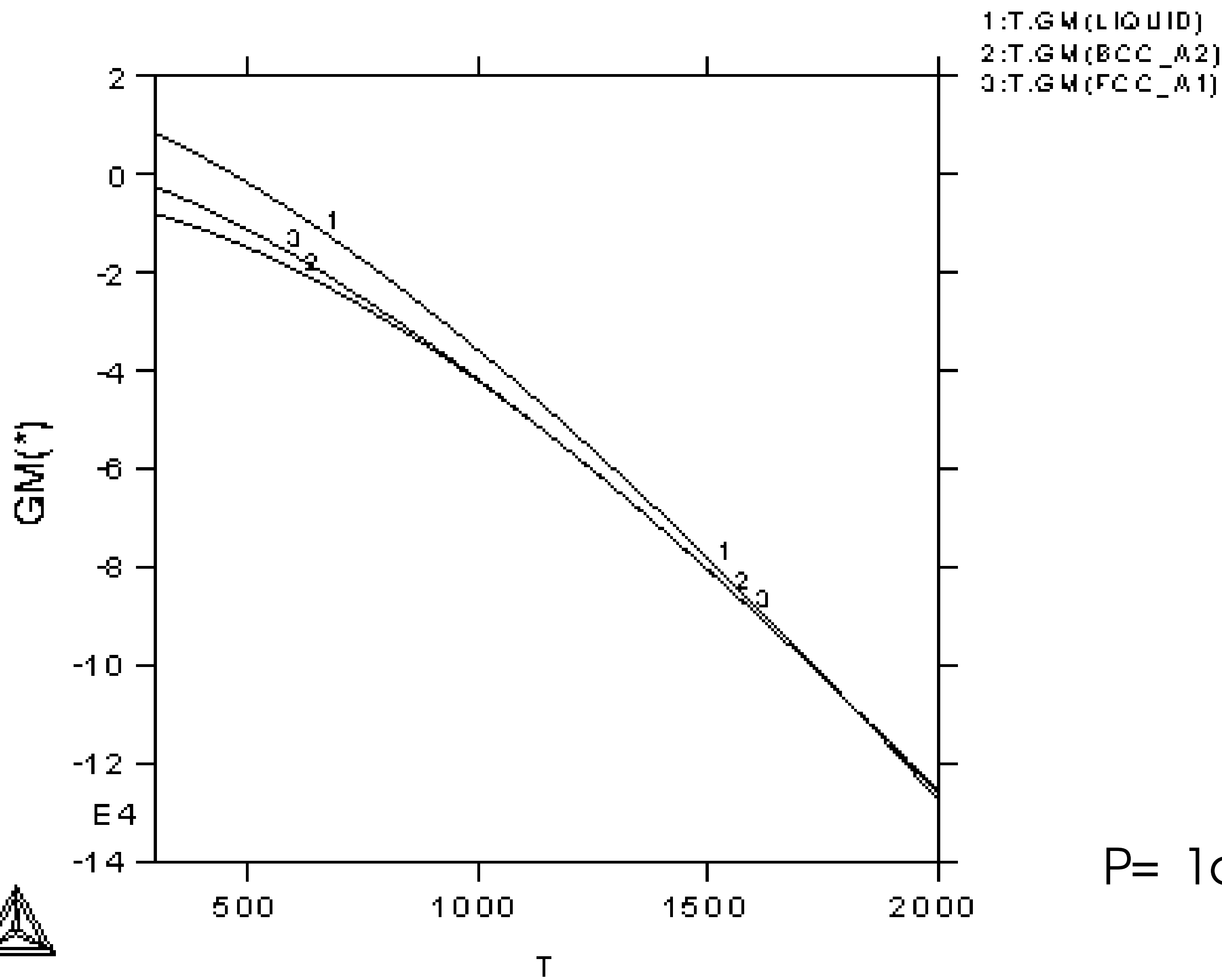
Ab-initio calculations? Miedema?

One approach for an Unary system



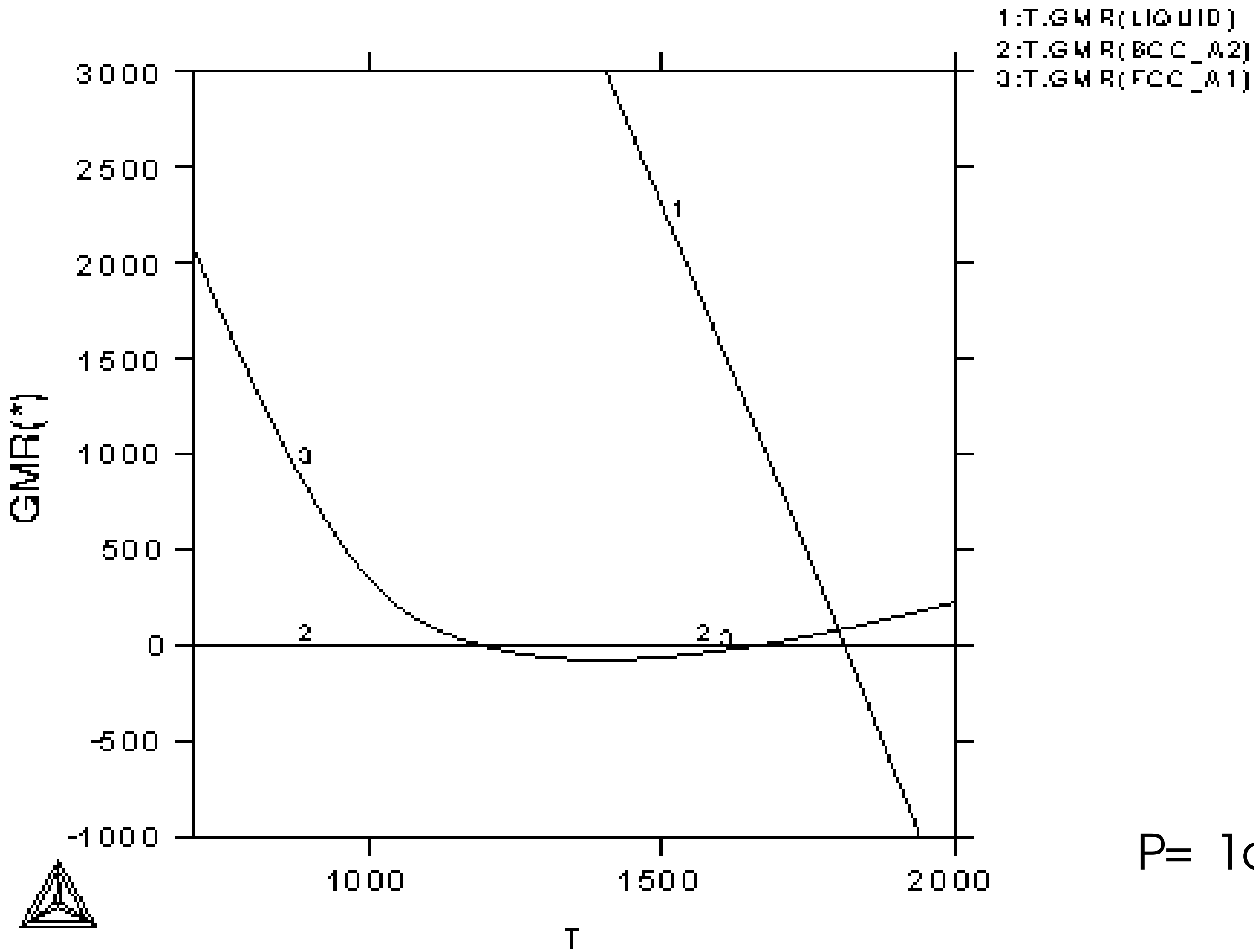
After DeHoff

Free Energy of Iron $G_{Fe}^{\varphi} - H_{Fe}^{SER}$



P= 1atm

Free Energy of Iron $G_{Fe}^{\varphi} - G_{Fe}^{BCC}$



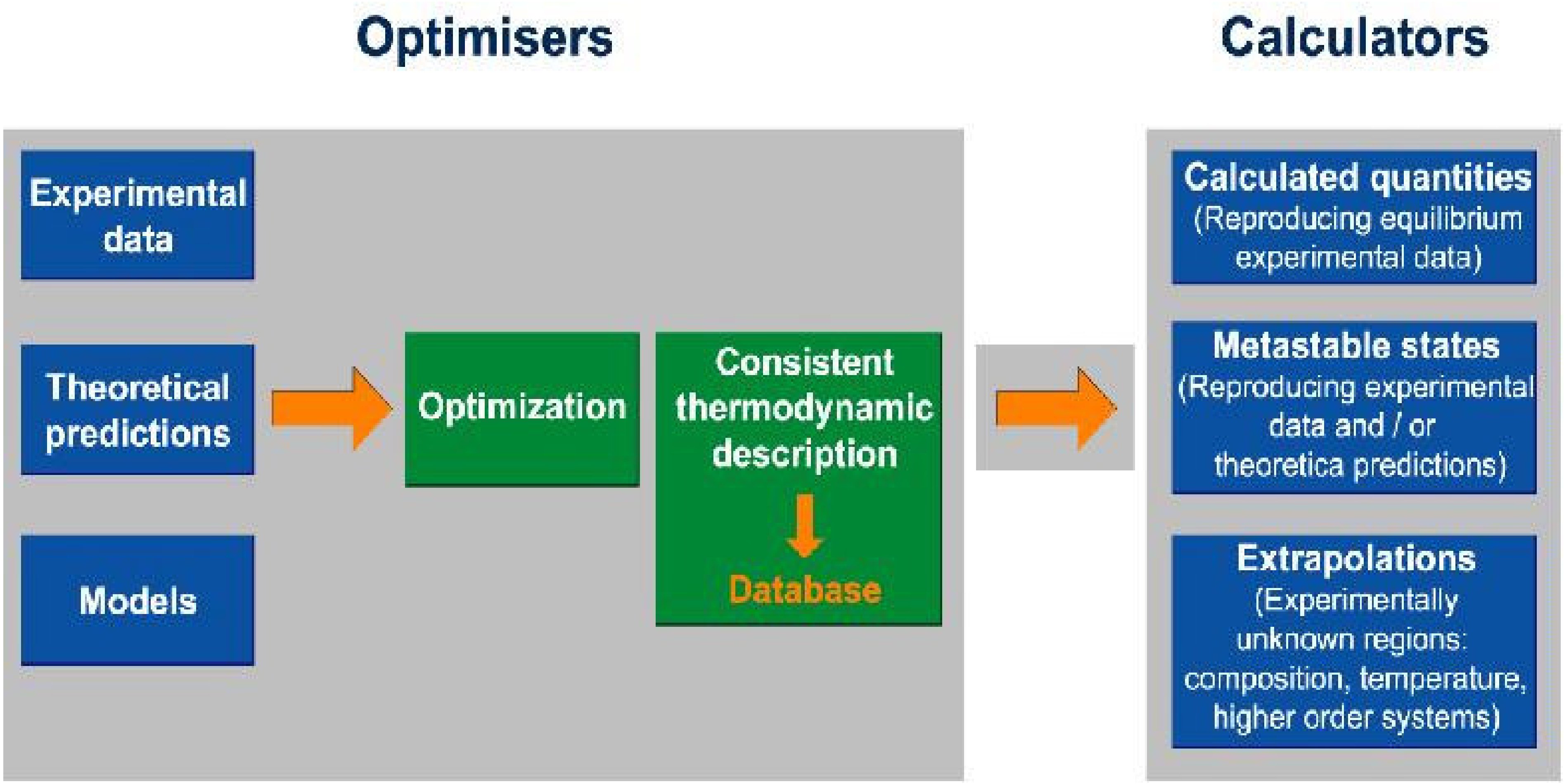
P= 1atm

Multi-component system

- **If more than one element is present, besides structure, composition is a variable.**
- **Mixing (or not!) becomes an option!**
- **For all possible compositions and structures (including liquid and gas) nature "knows" G_m^Φ (P,T, structure Φ, composition).**
- **For all combinations of phases and elements, nature determines the phases and their compositions such that G´ is minimum at constant P and T.** (recall, there are several methods for us, humans, to try to do it!)

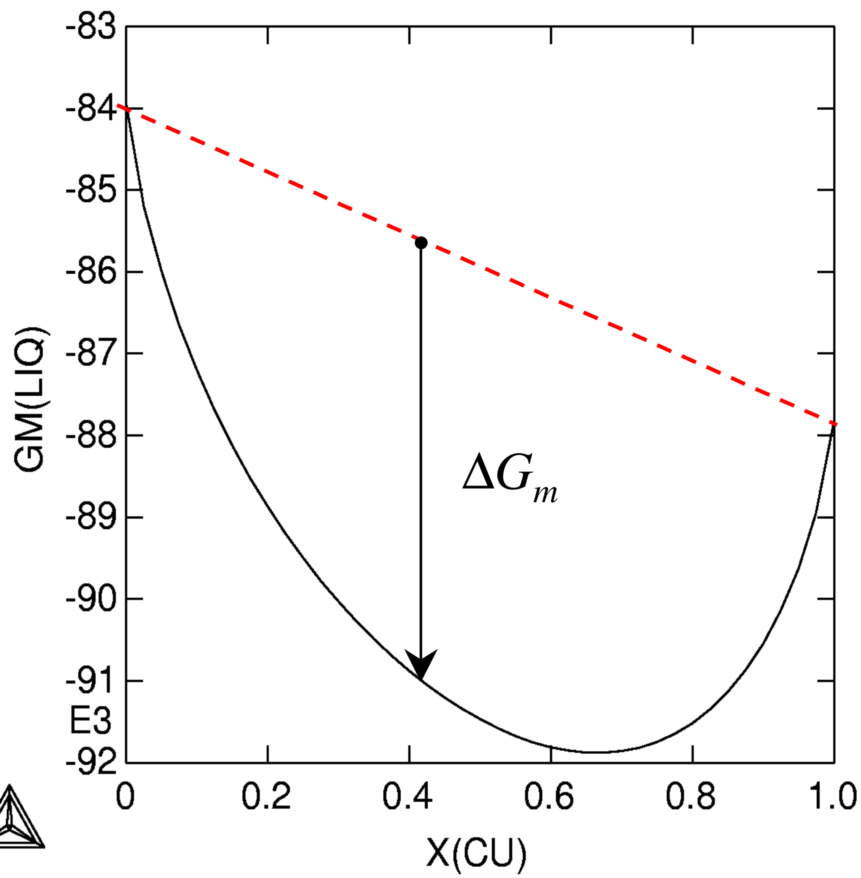
Can we model it?

The "CALPHAD" approach

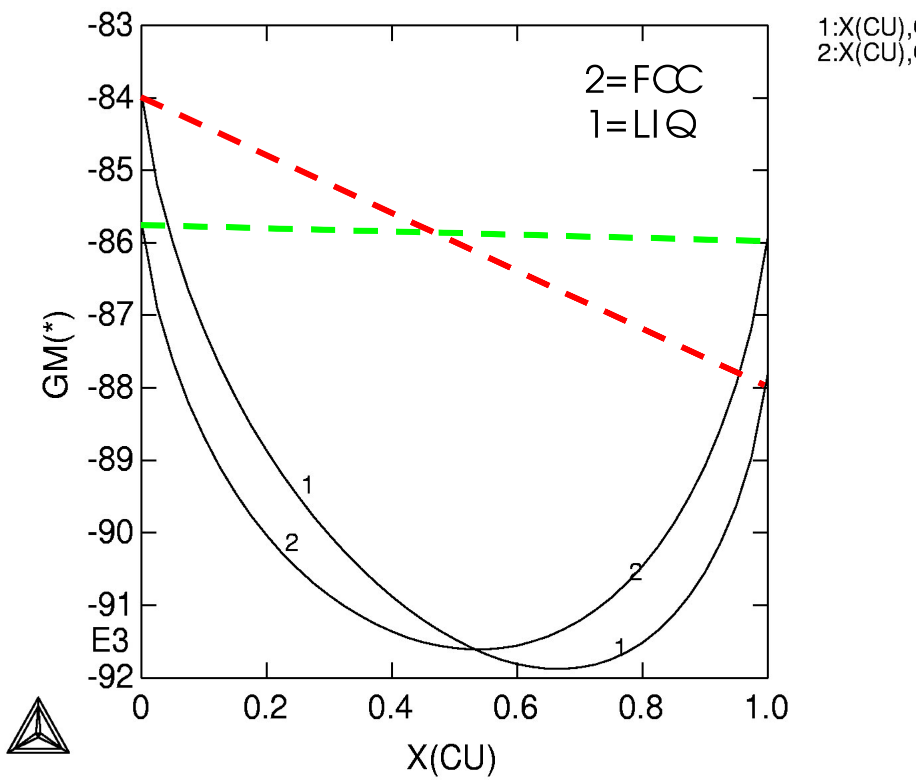


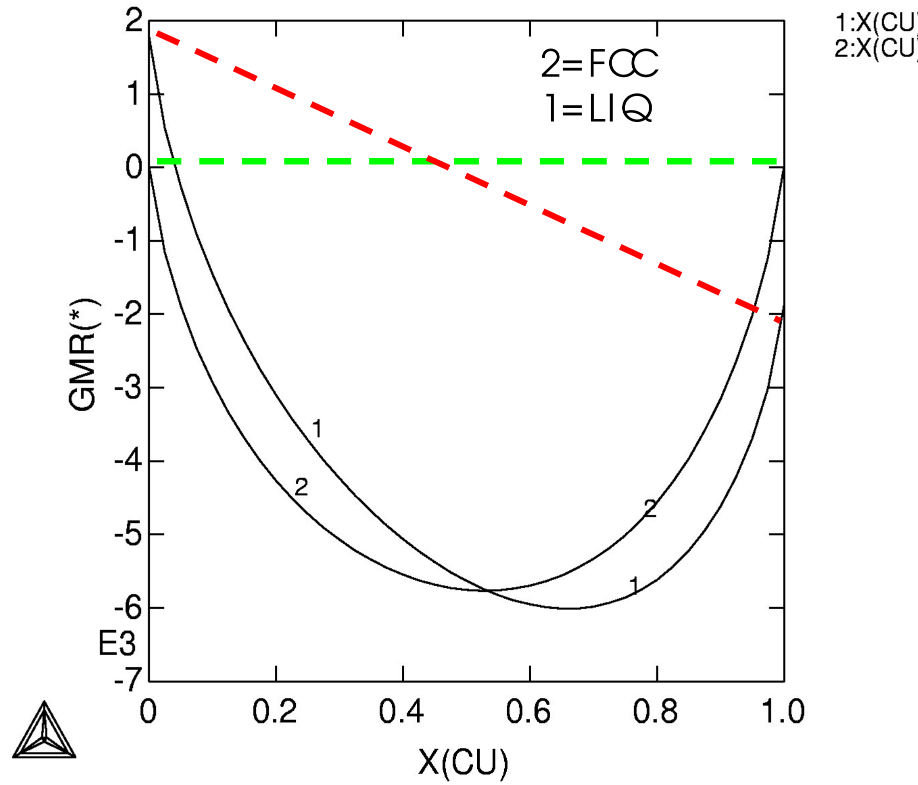
Multicomponent System (Binary and more)

$$G_m^{\varphi}(T, P, x_1 \ldots x_{n-1}) = \sum_i x_i \, {}^oG_i^{\varphi} + \Delta G_m^{ideal} + \Delta G_m^{excess}$$



Where are the “ends” of the curve?





The "parts" of G of a mixture

$$G_m^{\varphi}(T, P, x_1 \ldots x_{n-1}) = \sum_i x_i \, {}^oG_i^{\varphi} + \Delta G_m^{ideal} + \Delta G_m^{excess}$$

$$G^{\Phi,T} - H^{SER} = ({}^{ref}G^{\Phi,T} - H^{SER}) + {}^{id}G_m^{\Phi} + {}^{E,bin}G_m^{\Phi}$$

$$({}^{ref}G^{\Phi,T} - H^{SER}) = \sum_{i=1}^{2} x_i ({}^0G_i^{\Phi,T} - H_i^{SER})$$

depends on the solution model:

$${}^{id}G_m^{\Phi} = R \cdot T \cdot \sum_{i=1}^{2} x_i \ln(x_i)$$

$${}^{id}G_m^{\Phi} = R \cdot T \cdot \sum_{Y=1}^{L} I_Y \sum_{i=1}^{l} y_i \ln(y_i)$$

$${}^{E,bin}G_m^{\Phi} = \sum_{\nu=0}^{n} L_{i,j}^{\Phi,\nu} (x_i - x_j)^{\nu}$$

$${}^{E,ter}G_m^{\Phi} = \sum_{i=1}^{2} \sum_{j=i+1}^{3} x_i \cdot x_j \cdot \sum_{\nu=0}^{n} L_{i,j}^{\Phi,\nu} (x_i - x_j)^{\nu}$$