Ideal Solution

A solution that behaves like a mixture of ideal gases. Dalton´s law:

$$a_i = x_i$$

$$\Delta G_m = \sum_{i=1}^{c} \Delta \overline{G}_i X_i$$

$$a_i = e^{\frac{\mu_i - \mu_i^0}{RT}} = e^{\frac{\overline{G}_i - G_i^0}{RT}} \rightarrow \Delta \overline{G}_i = RT \ln a_i$$

$$\Delta G_m^{ideal} = \sum_{i=1}^{c} \Delta \overline{G}_i X_i = \sum_{i=1}^{c} X_i RT \ln a_i = RT \sum_{i=1}^{c} X_i \ln X_i$$

Ideal Solution- Only configurational entropy

$$S = k \ln \Omega$$

For a mol of mixture containing $N_A + N_B = N_0$ atoms

$$\Omega_{total} = \frac{N_0 !}{N_A ! N_B !}$$

$$S = k \ln \Omega_{total} = k \ln \frac{N_0 !}{N_A ! N_B !} = k \ln N_0 ! - k \ln N_A ! - k \ln N_B !$$

$$\ln N ! = N \ln N - N \qquad \text{After Stirling}$$

$$S = -R(X_A \ln(\frac{N_A}{N_0}) + X_B \ln(\frac{N_B}{N_0})) = -R(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta S_m^{ideal} = -R(X_A \ln X_A + X_B \ln X_B) - 0 - 0$$

Model complexity- Physical Chemistry

- **Ideal** $\Delta H_m = 0$
- **Regular: pairs interact and define U (internal energy)**

$$\Delta H_m = \alpha x_A x_B$$

- **Regular with different coordinations**

$$\Delta U_m^{regular} = \alpha X_A X_B + \beta X_B$$

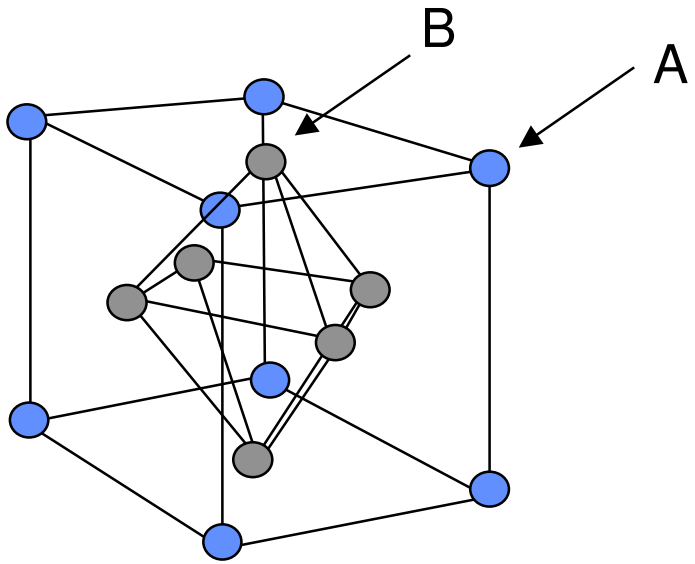
- **Pair interaction energy affects number of pairs: Quasi-chemical:** *Entropy change is not ideal*

Compound Energy Model (or Sub-lattices model)

Hillert e Staffansson Acta Chem. Scand. 24(1970)3618-3626

From Temkin´s model for salt mixtures (e.g. (Na,K)(Cl,F))

- For a phase such as $(A,B)_a\ (C,D)_c$ we assume that each type of crystallographic position ("sub-lattice") can be occupied by certain elements only.



Classical Examples

- Carbonitides in steels (Nb,Ti)(C,N)
- Interstitial solutes in Fe
  - CCC $(Fe)_1(C,Va)_3$
  - CFC $(Fe)_1(C,Va)_1$
- Intermetallics
  - $(Mo)_1(Si)_2$ ou $(Mo)_{0.333}(Si)_{0.667}$ $(Mo,W)_1(Si,Al)_2$
  - NiAl (B2, CsCl)
    - For $x_{Al}>0.5$ defect is a vacancy in Ni sub-lattice
    - Para $x_{Al}<0.5$ defect is substitutional Ni in Al sub-lattice
    - Modelo: (Ni,Va) (Al,Ni)
- **Liquids:**
  - Ex: (Fe,Va)(S,Va)

  Fernandez Guillermet, Hillert e Jansson Met Trans B 12B(1981)745-754

The Model

- Define y_i as site fractions for each element in a given sub-lattice
- For $(A,B)_a\ (C,D)_c$:

$$X_A = \frac{n_A}{n_A + n_B + n_C + n_D}\ ;\ \sum X_i = 1$$

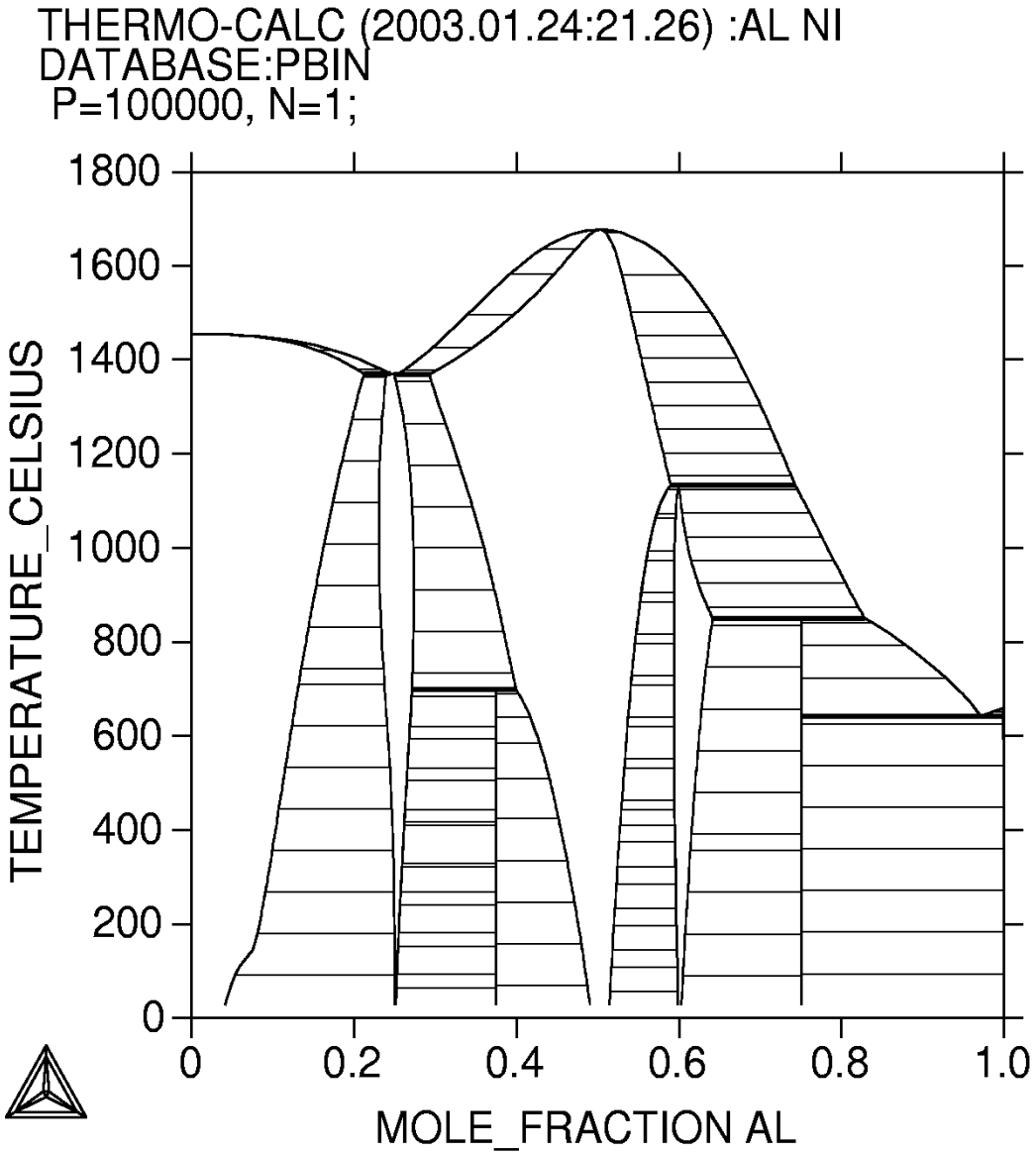
$$y_A = \frac{n_A}{n_A + n_B}\ ;\ y_A + y_B = 1$$

$$y_C = \frac{n_C}{n_C + n_D}\ ;\ y_C + y_D = 1$$

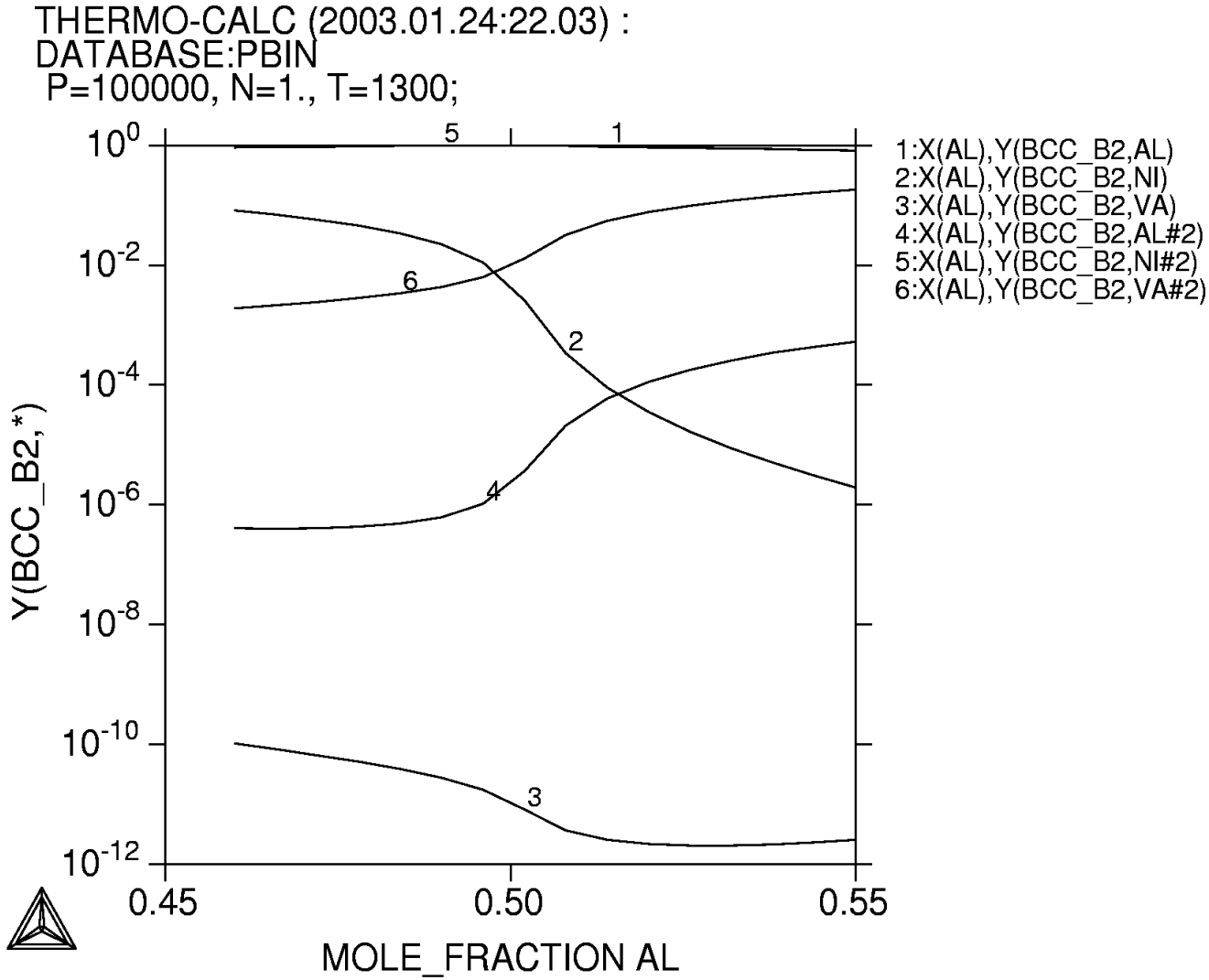
$$y_A = \frac{a + c}{a} X_A \quad y_B = \frac{a + c}{a} X_B$$

$$y_C = \frac{a + c}{c} X_C \quad y_D = \frac{a + c}{c} X_D$$

Ni-Al


THERMO-CALC (2003.01.24:21.26) :AL NI
DATABASE:PBIN
P=100000, N=1;
TEMPERATURE_CELSIUS
1800
1600
1400
1200
1000
800
600
400
200
0
0
0.2
0.4
0.6
0.8
1.0
MOLE_FRACTION AL

Ni-Al BCC_B2


THERMO-CALC (2003.01.24:22.03) :
DATABASE:PBIN
P=100000, N=1., T=1300;
1:X(AL),Y(BCC_B2,AL)
2:X(AL),Y(BCC_B2,NI)
3:X(AL),Y(BCC_B2,VA)
4:X(AL),Y(BCC_B2,AL#2)
5:X(AL),Y(BCC_B2,NI#2)
6:X(AL),Y(BCC_B2,VA#2)
Y(BCC_B2,*)
MOLE_FRACTION AL
0.45
0.50
0.55

Calculating the properties

- "Ideal" Entropy and ΔS also:

$$-\frac{S_m^{ideal}}{R} = a(y_A \ln y_A + y_B \ln y_B) + c(y_C \ln y_C + y_D \ln y_D)$$

- The choice of a reference:

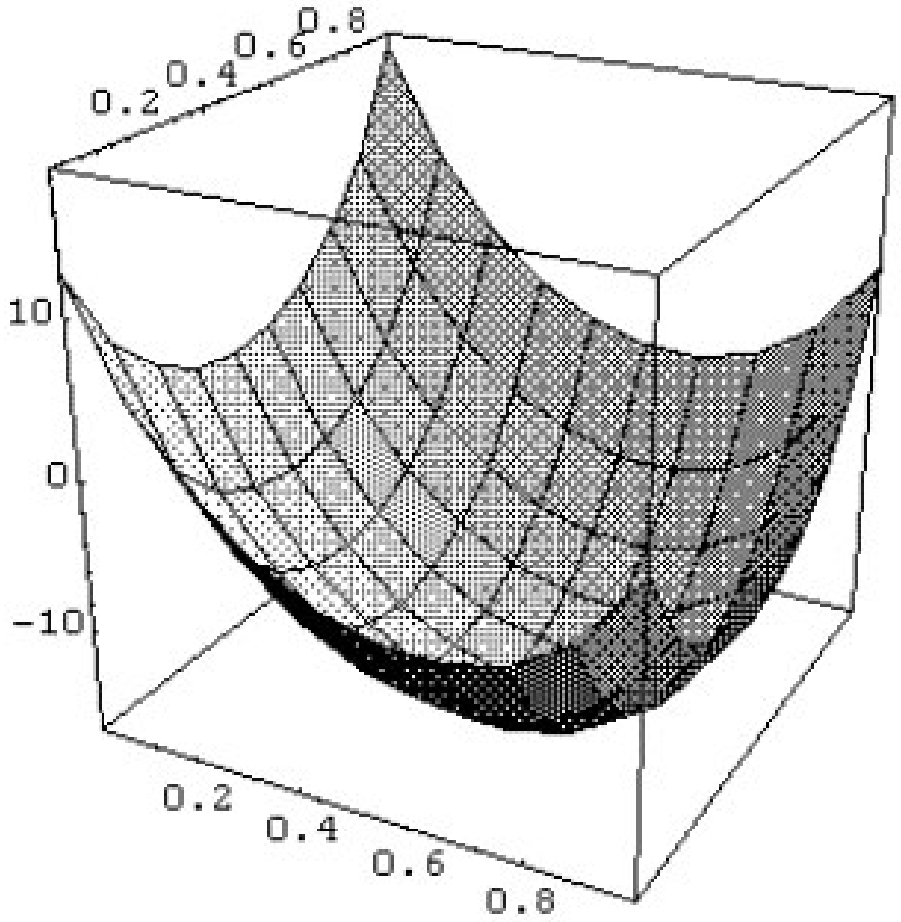
$$G_m^{\varphi} = \sum_i x_i \, {}^{o}G_i^{\varphi} + \Delta G_m^{ideal} + \Delta G_m^{excesso}$$

$$G_m^{\varphi} = y_A y_C \, {}^{0}G_{A_a C_c}^{\varphi} + y_A y_D \, {}^{0}G_{A_a D_c}^{\varphi} + y_B y_C \, {}^{0}G_{B_a C_c}^{\varphi} + y_B y_D \, {}^{0}G_{B_a D_c}^{\varphi} + \Delta S_m^{ideal} + \Delta G_m^{xs}$$

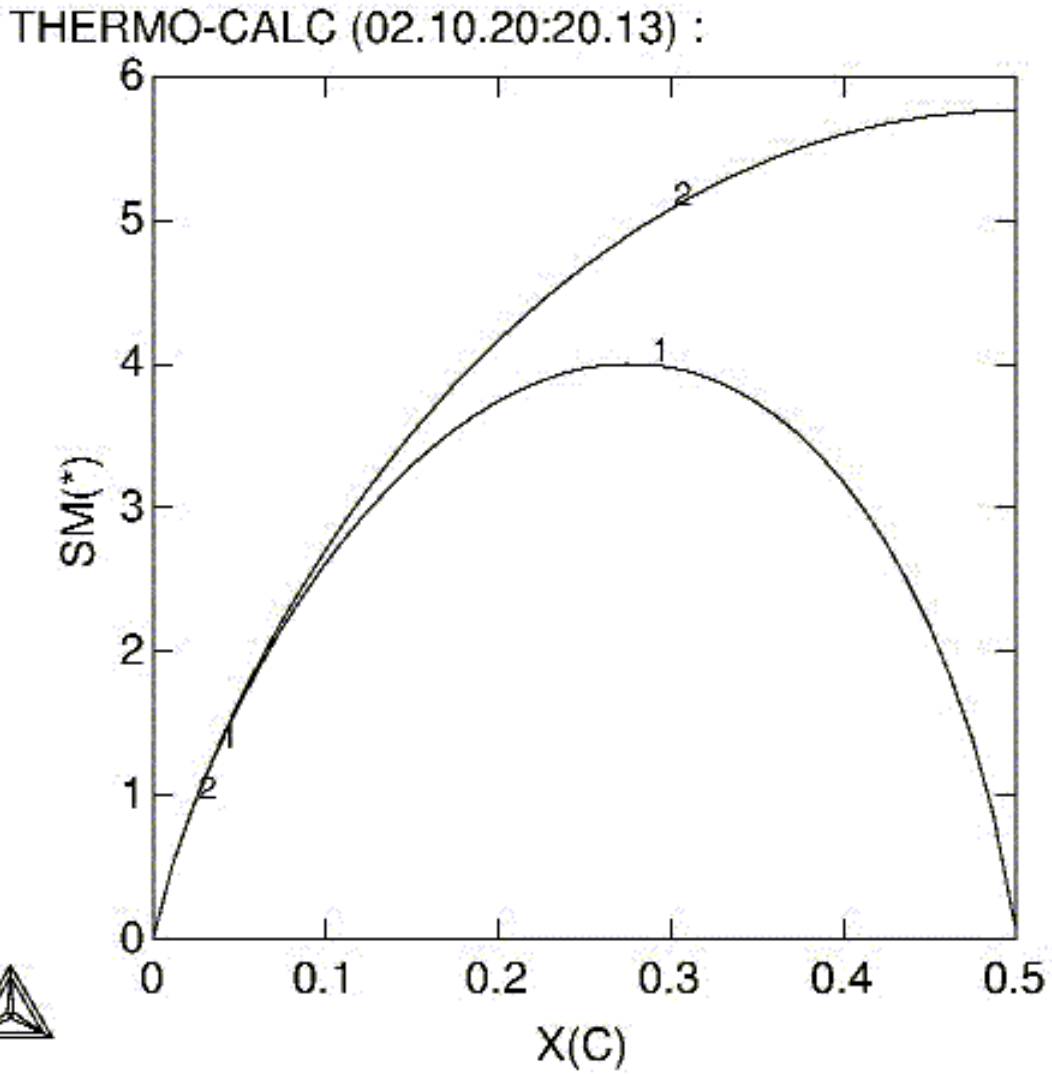
Example

$$G_m^{\varphi} = y_{Nb} y_C \, {}^{0}G_{NbC}^{\varphi} + y_{Nb} y_N \, {}^{0}G_{NbN}^{\varphi} + y_{Ti} y_C \, {}^{0}G_{TiC}^{\varphi} + y_{Ti} y_{ND} \, {}^{0}G_{TiN}^{\varphi} + \Delta S_m^{ideal} + \Delta G_m^{xs}$$

The Free Energy of the Mixture



Be careful with what you define!



Defining
Latt as $(Fe)_1(C,Va)_1$
Subst as $(Fe,C)_1$
gives us this result!

Sub.tcm

The excess Free Energy

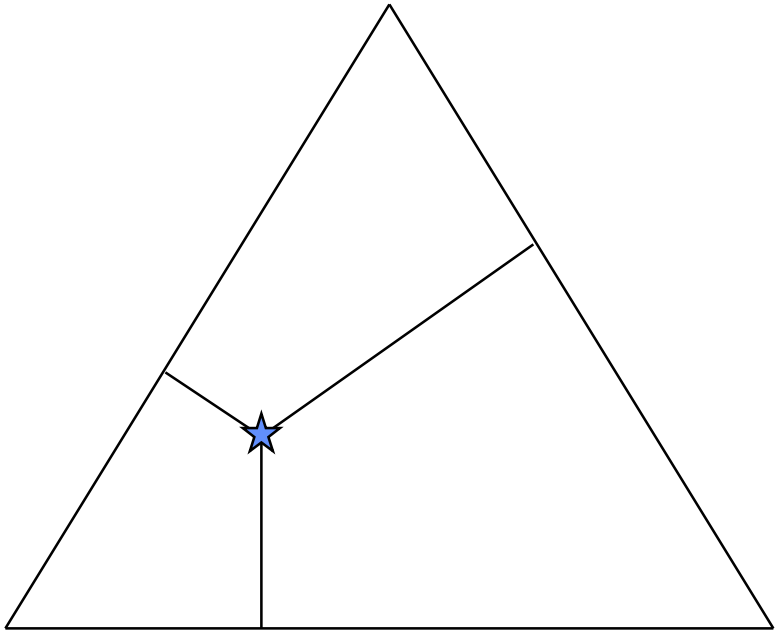
- **Redlich-Kister** *(Ind. Eng. Chem.,40(1948) 345-348)*

$$^{E}G_i^T = X_1 X_2 \sum_{\nu} L_{\nu}^T (X_1 - X_2)^{\nu}$$

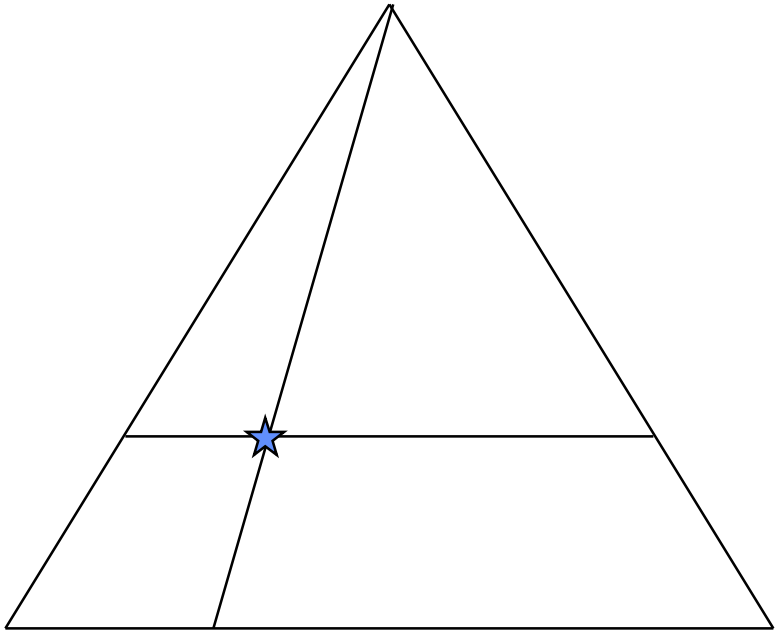
- **Other polynomia (Legendre, etc.)** *(Belton, Gokcen)*

- **Geometric models to extrapolate to high order systems**
  Hillert, CALPHAD, 4(1980)1-12, p.ex.

Going to Ternary from Binaries

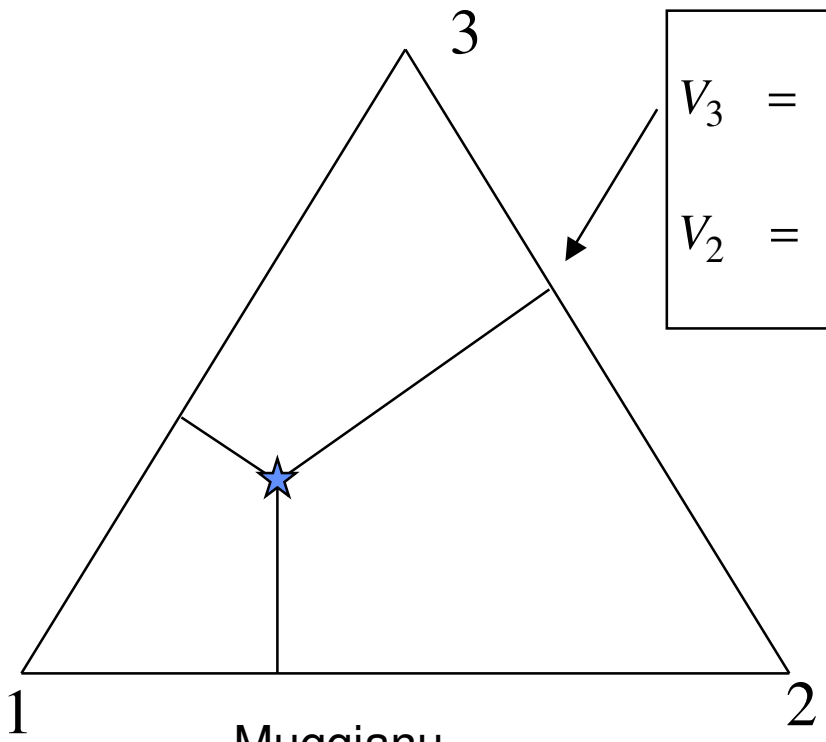


Muggianu



Toop ou Bonnier

Muggianu's model



Muggianu

$$V_3 = \frac{1 + x_3 - x_2}{2}$$

$$V_2 = \frac{1 + x_2 - x_3}{2}$$

$$\Delta G^{xs} = \sum_{3\ bin} \frac{x_i x_j}{V_i V_j}\ \Delta G^{xs}\left(V_i;\ V_j\right)$$

Quaternário ⇨

$$\Delta G^{xs} = \sum_{4ter} \frac{x_i x_j x_k}{V_i V_j V_k}\ \Delta G^{xs}\left(V_i;\ V_j;\ V_k\right)$$

Higher order interaction terms

Risky!

:

$$\Delta G^{xs}_{ter} = x_1 x_2 x_3 \sum (V_1 L^{v}_{1} + V_2 L^{v}_{2} + V_3 L^{v}_{3})$$