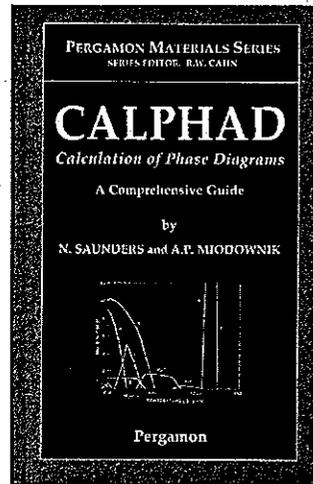
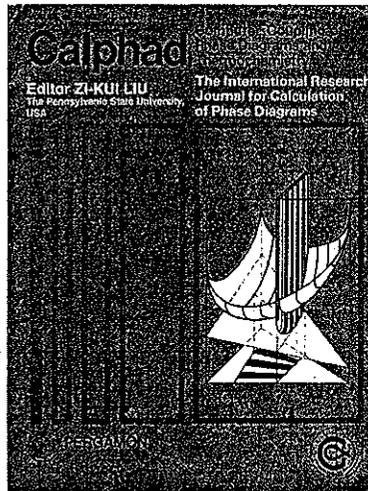


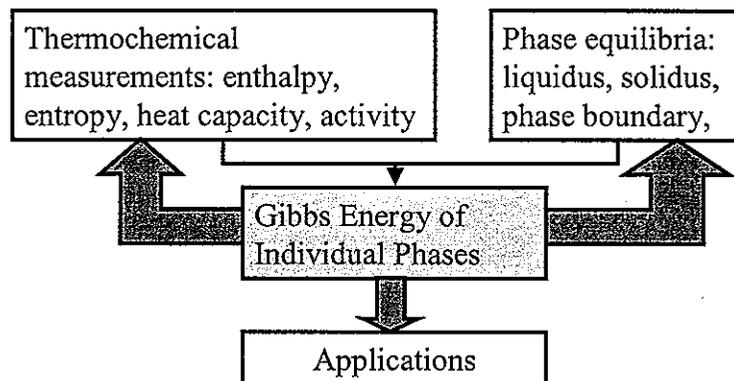
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Thermodynamic Modeling



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Using Gibbs Energy

- Gibbs energy is the state function minimized under constant T and P at the state of equilibrium
- Most experiments are carried out under constant T and P.

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Modeling of Multicomponent Systems

- Consider lower-order systems in a seven-component system
 - Pure element: 7
 - Binary: $7 \times 6 / 2 = 21$
 - Ternary: $7 \times 6 \times 5 / 2 / 3 = 35$
 - *Quaternary*: $7 \times 6 \times 5 \times 4 / 2 / 3 / 4 = 35$
 - *Quinary*: $7 \times 6 \times 5 \times 4 \times 3 / 2 / 3 / 4 / 5 = 14$
 - *Six-component*: 7
- Thermodynamic modeling starts from low-order systems.

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Thermodynamic Modeling Steps

- **Understand the system**
 - Search and read ALL references and select experimental data
- **Create a setup file for the system**
 - Define thermodynamic models
- **Create an “experimental” data file**
 - Make a pop file.
- **Evaluate thermodynamic model parameters**
 - Use Parrot
- **Compare experimental and calculated results**
 - Use Poly_3
- **Make a thermodynamic database**
 - add to an existing database

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Understand the System

- **Collect and understand all information available in the literature about the system**
 - Thermochemical, crystal structure, phase equilibria.
 - Sort out the discrepancies among data from different sources.
 - Examine similar systems.
 - Check higher-order systems when possible.
 - Create new data by experiments, first-principles calculations, and estimations if needed.
- **Know the destination**
 - Compile a set of data to be reproduced.

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Thermodynamic Models

- **Primarily based on crystal structures**
 - Sublattice models
 - Homogeneity range
- **Compatible with other systems**
 - Combine with other modeling results for higher-order systems
 - More value: Others can use the results in developing database for their higher-order systems.

Data File for Optimization

- **Data to be calculated from Gibbs energy functions**
 - *Original* experimental data
 - *Original* theoretical data
 - Constraints on phase stability
- **Define $n+2$ conditions as in the equilibrium calculations.**
- **Create a single equilibrium for one data point.**
- **Create a table for a group of data.**

Optimization of Model Parameters

- Start from data for single phases
- Start from simple phase relationships
- Know the relationships between model parameters and data
 - Signs of the parameters: positive or negative
 - Temperature dependent: temperature range of data
- Compare the calculated results with the “experimental” data regularly.
- Many iterations

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Thermodynamic Modeling

- Pure elements
$$G_m - H_m^{SER} = a + bT + cT \ln(T) + \sum d_i T^i$$
- Solution phases
$$G_m = G_m^0 + \Delta G_m^{ideal} + \Delta G_m^{xs}$$
- Stoichiometric compounds
 - Similar to pure elements
 - Or combination of pure elements plus Gibbs energy of formation

$$G_{AB} = G_{AB}^0 + \Delta G^{formation}$$

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Reference State

- **Standard Element Reference(SER)**
 - Enthalpy of the stable structure at 298.15K
 - Entropy at 0K ($S=0$).
 - GHSERAG means the Gibbs energy of Ag under SER state.
- **Reference state can be easily changed in software such as reference phase, temperature, and pressure.**

Data for Pure Element

- **Experimental data**
 - Heat capacity
 - Structure transition: temperature, enthalpy.
 - Volume / Lattice parameter

Binary System

- **Lattice stability**
 - Gibbs energy of non-stable structures: for example, Mg in fcc and bcc structures. Pure elements in Laves phase structures.
 - Needed when considering the formation of solution phases
- **Formation of binary phases**

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Solution Phase $G_m = G_m^0 + \Delta G_m^{ideal} + \Delta G_m^{xs}$

- **For a A-B binary solution phase: (A,B)**

$$G_m^0 = x_A G_A^0 + x_B G_B^0 \quad \text{Both } G^0 \text{ in same crystal structure}$$

$$\Delta G_m^{ideal} = RT(x_A \ln x_A + x_B \ln x_B)$$

$$\begin{aligned} \Delta G_m^{xs} &= x_A x_B \sum_{k=0}^{\infty} {}^k L_{A,B} (x_A - x_B)^k \\ &= x_A x_B ({}^0 L_{A,B} + {}^1 L_{A,B} (x_A - x_B) + {}^2 L_{A,B} (x_A - x_B)^2 + \dots) \end{aligned}$$

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Contribution of L parameters

$$\Delta G_m^{xs} = x_A x_B ({}^0L_{A,B} + {}^1L_{A,B}(x_A - x_B) + {}^2L_{A,B}(x_A - x_B)^2 \dots)$$

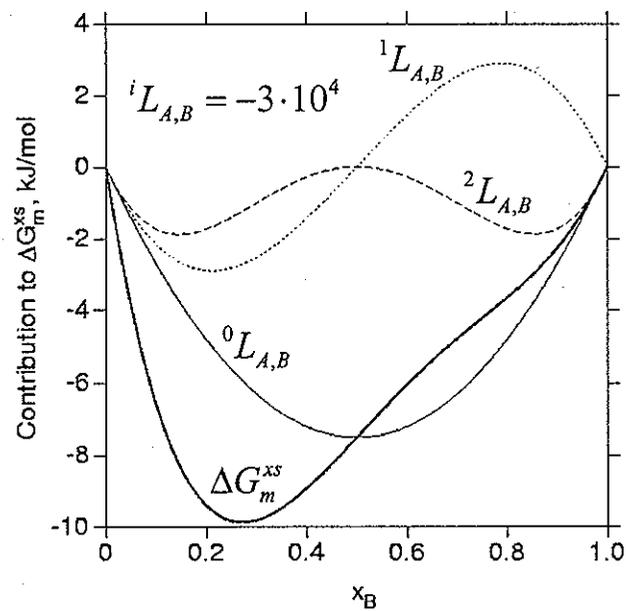
${}^0L_{A,B}$: Symmetric to both A and B

${}^1L_{A,B}$: Asymmetric to A and B

${}^2L_{A,B}$: Symmetric to both A and B

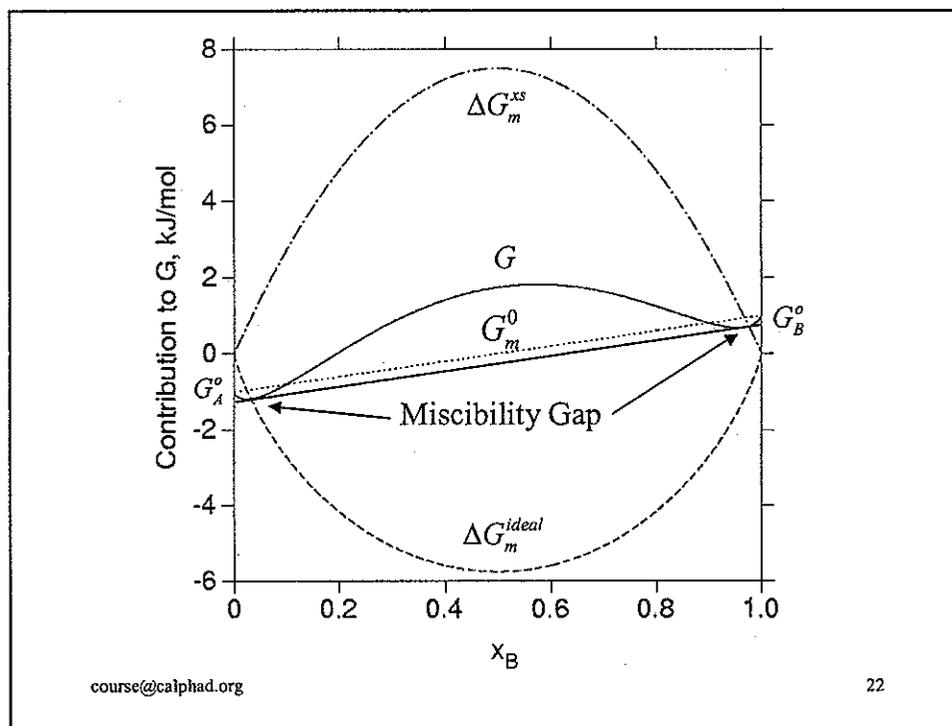
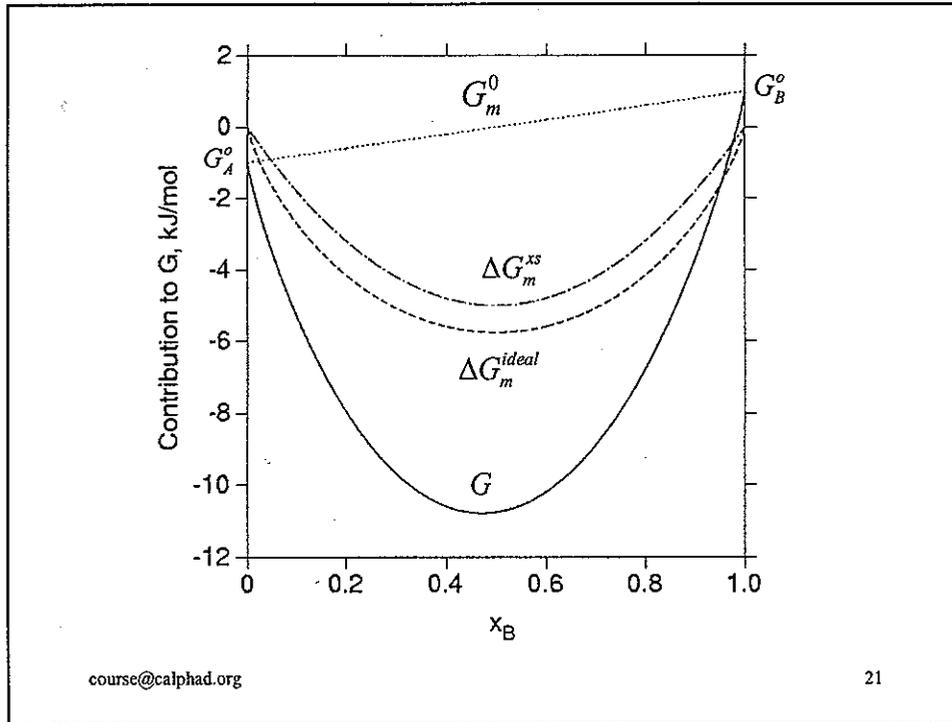
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Ternary system

- **Combine three binaries**
 - Muggianu, Toop, Kohler, and Colinet models
 - **Solution of third element in binary compounds**
 - Mixture of $(A)_a(C)_b$ and $(B)_a(C)_b$ when both stable
 - **Lattice stability of compounds**
 - $(A,B)_a(C)_b$ when $(B)_a(C)_b$ not stable in the B-C system.
 - **Ternary compounds**
 - Line compounds
 - With homogeneity

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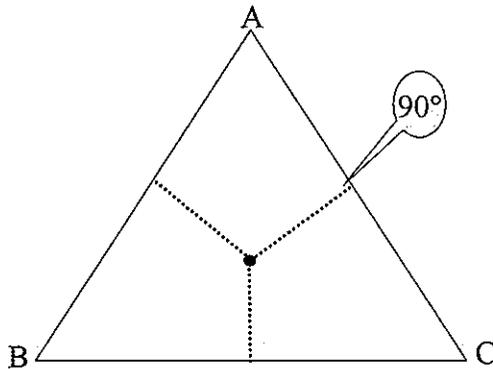
Geometrical models

- Expressions for ternary system must be able to be reduced to binary system when the amount of one component becomes zero
- **Models in the literature: The detailed formulae are in the book by Hillert.**
 - Toop model: asymmetric
 - Kohler model: symmetric
 - Colinet model: symmetric
 - Muggianu model: symmetric

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Muggianu model



Can reproduce all $x_i x_j^k L_{i,j}(x_i - x_j)^k$

Ternary solutions

$$G_m^0 = x_A G_A^0 + x_B G_B^0 + x_C G_C^0$$

$$\Delta G_m^{ideal} = RT(x_A \ln x_A + x_B \ln x_B + x_C \ln x_C)$$

$$\Delta G_m^{xs} = \sum_i \sum_{j>i} x_i x_j I_{ij} + \sum_i \sum_{j>i} \sum_{k>j} x_i x_j x_k I_{ijk} + \dots$$

From Binary

From Ternary

$$I_{ijk} = x_i^0 L_i + x_j^1 L_j + x_k^2 L_k$$

Sublattice Model

- Interstitial $(A)_a(B, Va)_b$
- Intermetallics $(A, B)_a(C, D)_b$
- Ordering $(A, B)_a(A, B)_b$
- Ionic phase $(A^+)_P(C^-, B^0)_Q$

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Mole fraction vs site fraction

- $(Fe)_a(Va, C)_b$: Per mole of formula, a sites for the first sublattice and b sites for the second sublattice.
- The mole of atoms is $a + y_C b$.
- Site fractions: Mole fractions in individual sublattices

$$x_C = \frac{by_C}{a + by_C} \quad x_{Fe} = \frac{a}{a + by_C}$$

$$y_C = \frac{a}{b} \frac{x_C}{1 - x_C} \quad y_{Va} + y_C = 1 \quad y_{Fe} = 1$$

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Gibbs Energy

- For a compound: $(A,B)_a(C,D)_b$

$$G^{\circ} = y_A^I y_C^II G_{AC}^{\circ} + y_A^I y_D^II G_{AD}^{\circ} + y_B^I y_C^II G_{BC}^{\circ} + y_B^I y_D^II G_{BD}^{\circ}$$

➤ y : Site fraction, i.e. the mole fraction in each sublattices

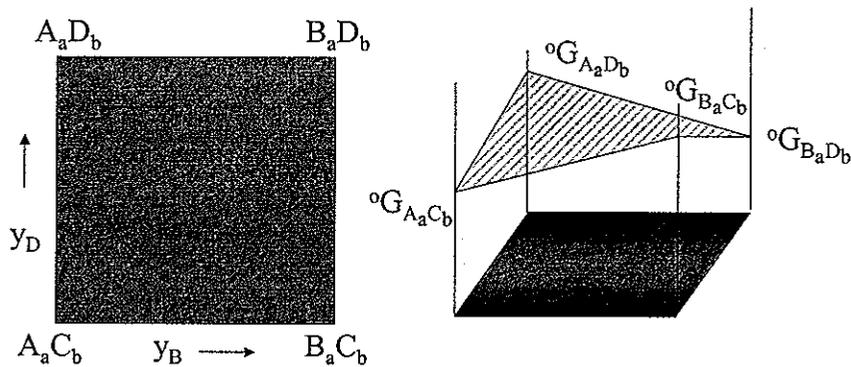
$$G_{mix}^{ideal} = aRT(y_A^I \ln y_A^I + y_B^I \ln y_B^I) + bRT(y_C^II \ln y_C^II + y_D^II \ln y_D^II)$$

$$G_{mix}^{xs} = y_A^I y_B^I \left(y_C^II \sum_{k=0}^k L_{A,BC} (y_A^I - y_B^I)^k + y_D^II \sum_{k=0}^k L_{A,B,D} (y_A^I - y_B^I)^k \right) \\ + y_C^II y_D^II \left(y_A^I \sum_{k=0}^k L_{AC,D} (y_C^II - y_D^II)^k + y_B^I \sum_{k=0}^k L_{B,C,D} (y_C^II - y_D^II)^k \right)$$

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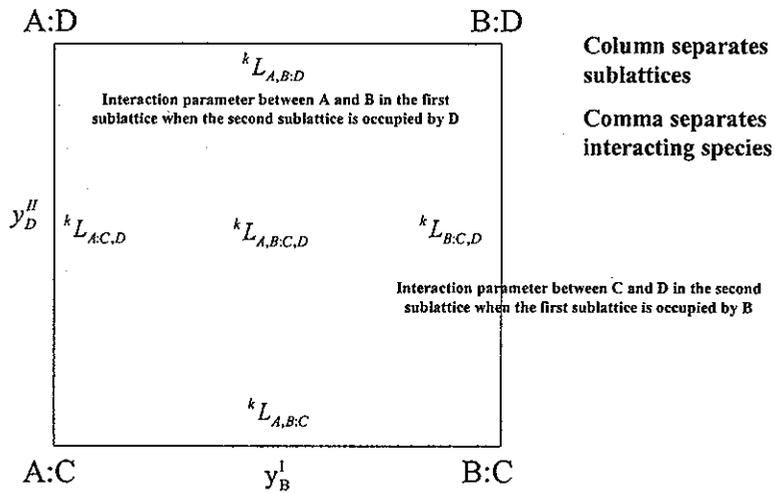
Sublattice Model: $(A,B)_a(C,D)_b$



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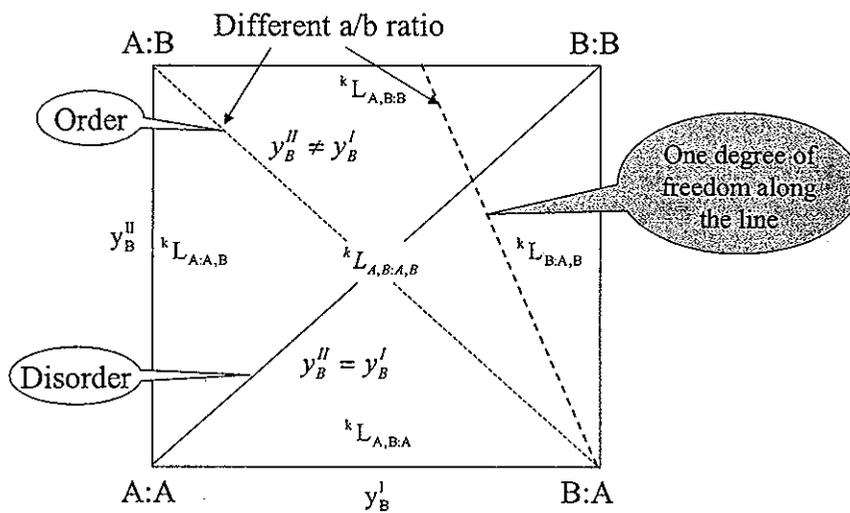
Interaction Parameters for $(A,B)_a(C,D)_b$



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Order-disorder: concentration map for $(A,B)_a(A,B)_b$



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Gibbs Energy

• (A,B)_a(A,B)_b

$(a+b)G^0$

$(a+b)G^0$

$$G^{o,order} = y_A^I y_A^{II} G_{A:A}^o + y_A^I y_B^{II} G_{A:B}^o + y_B^I y_A^{II} G_{B:A}^o + y_B^I y_B^{II} G_{B:B}^o$$

$$\Delta G_m^{ideal,order} = aRT(y_A^I \ln y_A^I + y_B^I \ln y_B^I) + bRT(y_A^{II} \ln y_A^{II} + y_B^{II} \ln y_B^{II})$$

$$G_{mix}^{xs,order} = y_A^I y_B^I \left(y_A^{II} \sum_{k=0}^k L_{A,B,A} (y_A^I - y_B^I)^k + y_B^{II} \sum_{k=0}^k L_{A,B,B} (y_A^I - y_B^I)^k \right) \\ + y_A^{II} y_B^{II} \left(y_A^I \sum_{k=0}^k L_{A,A,B} (y_A^{II} - y_B^{II})^k + y_B^I \sum_{k=0}^k L_{B,A,B} (y_A^{II} - y_B^{II})^k \right)$$

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Combining order and disorder parts

$$G_m = G_m^{dis} + \Delta G_m^{ordering}$$

$$\Delta G_m^{ordering} = G_m^{order}(y_i^I, y_i^{II}) - G_m^{order}(x_i)$$

$$G_m^{dis} = G_m^{0,dis} + \Delta G_m^{ideal,dis} + \Delta G_m^{xs,dis}$$

$$G_m^{order} = G_m^{0,order} + \Delta G_m^{ideal,order} + \Delta G_m^{xs,order}$$

Site fractions are replaced by mole fractions using the same formula

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Example of B2 in Al-Fe

TYPE_DEFINITION & GES A_P_D BCC_A2 MAGNETIC -1.0 4.00000E-01 !

PHASE BCC_A2 %& 2 1 3 !

CONSTITUENT BCC_A2 :AL,FE% : VA% : !

PARAMETER G(BCC_A2,AL:VA;0) 2.98140E+02 +GBCCAL#; 2.90000E+03 N REF: 1 !

PARAMETER G(BCC_A2,FE:VA;0) 2.98150E+02 +GHSERFE#; 6.00000E+03 N REF: 1 !

PARAMETER TC(BCC_A2,FE:VA;0) 2.98150E+02 1043; 6.00000E+03 N REF: 1 !

PARAMETER BMAGN(BCC_A2,FE:VA;0) 2.98150E+02 2.22; 6.00000E+03 N REF: 1 !

PARAMETER G(BCC_A2,AL,FE:VA;0) 2.98150E+02 +4*LALFEB0#-4*ALFEW1#; 6.E+03 N REF: 76 !

PARAMETER G(BCC_A2,AL,FE:VA;1) 2.98150E+02 +8*LALFEB1#; 6.00000E+03 N REF: 76 !

PARAMETER TC(BCC_A2,AL,FE:VA;1) 2.98150E+02 +8*ETCALFE#; 6.00000E+03 N REF: 76 !

TYPE_DEFINITION ' GES A_P_D BCC_B2 DISORDERED_PART BCC_A2 !

PHASE BCC_B2 %' 3 .5 .5 3 !

CONSTITUENT BCC_B2 :AL,FE : AL,FE : VA : !

PARAMETER G(BCC_B2,FE:AL;0) 2.98150E+02 -2*ALFEW1#; 6.00000E+03 N REF: 76 !

PARAMETER G(BCC_B2,AL:FE;0) 2.98150E+02 -2*ALFEW1#; 6.00000E+03 N REF: 76 !

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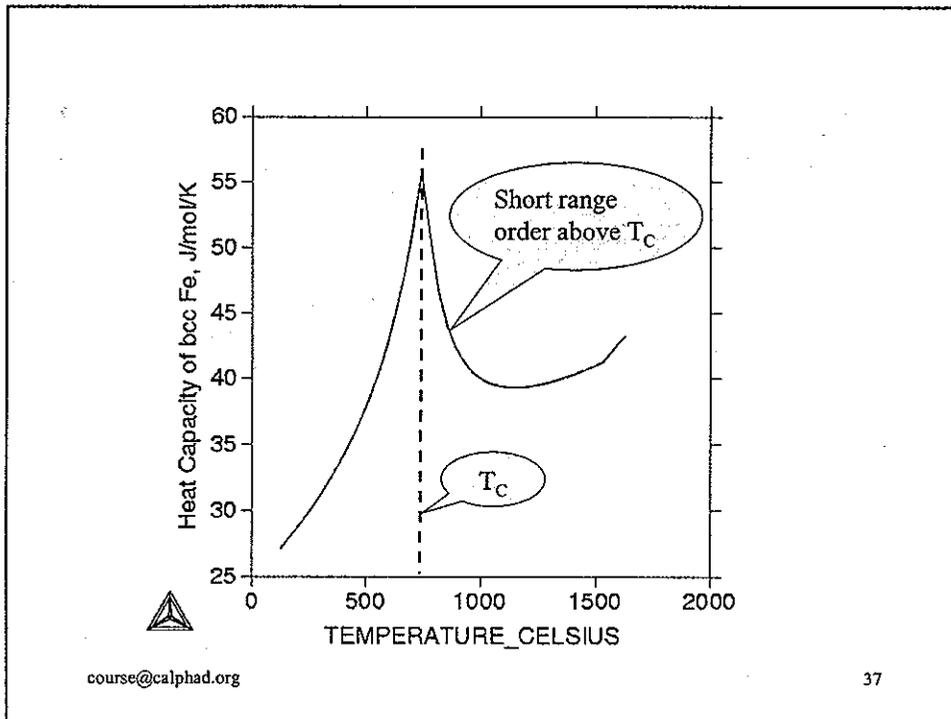
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Magnetic ordering

- Important in Fe, Co, Ni, and rare earth elements
- Ferromagnetism: parallel spins, Curie temperature, short range order above Curie temperature
- Anti-ferromagnetism: anti-parallel spins, Neel temperature
- Ferri-magnetism: anti-parallel with different values of spins resulting a net spin in one direction, behaves like ferromagnetic with a Curie temperature.

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Gibbs Energy

$$G_m = G_m^0 + \Delta G_m^{ideal} + \Delta G_m^{xs} + \Delta G_m^{mag}$$

$$\Delta G_m^{mag} = RT \ln(\beta + 1) f(\tau)$$

- β is the mean Bohr magnetic moment per mole of formula unit
- τ is T/T_c , where T_c is the Curie/Neel temperature.

$$\tau < 1 \quad f(\tau) = 1 - \left\{ \frac{79\tau^{-1}}{140p} + \frac{474}{497} \left(\frac{1}{p} - 1 \right) \left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right) \right\} / A$$

$$\tau > 1 \quad f(\tau) = - \left(\frac{\tau^5}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right) / A$$

$$A = \frac{518}{1125} + \frac{11692}{15975} \left(\frac{1}{p} - 1 \right)$$

Short range order fraction

$p = 0.28$ for fcc and hcp

$p = 0.4$ for bcc

$$T_C = \sum_i x_i T_i + \sum_{i,j} x_i x_j T_{i,j} + x_A x_B x_C T_{A,B,C}$$

$$\beta = \sum_i x_i \beta_i + \sum_{i,j} x_i x_j \beta_{i,j} + x_A x_B x_C \beta_{A,B,C}$$

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Liquid phase

- **No lattice structure: model is not structure-based**
- **No long rang order, but some with a large degree of short range order**
 - Expression for entropy needs to be modified.
- **Extrapolation below the melting points**
 - Entropy of fusion:

$$\Delta S_{fusion} = S^{liquid} - S^{solid} \geq 0$$

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Models for Liquid Phase

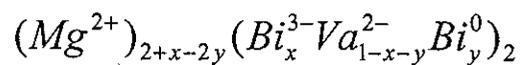
- **Associate model:** Assume associates such as A_aB_b as a component exist in the liquid.
 - Consider the reaction $aA+bB=A_aB_b$.
 - Entropy for the mixing of the three component, A, B and A_aB_b .
- **One sublattice Quasi-chemical model**
 - Consider bond reaction, $A-A+B-B=2(A-B)$.
 - Entropy for the mixing of three kinds of bonds.
- **These two can be inter-reformulated.**

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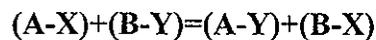
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Models for Liquid Phase

- **Ionic model:**



- **Two sublattice quasichemical model:**

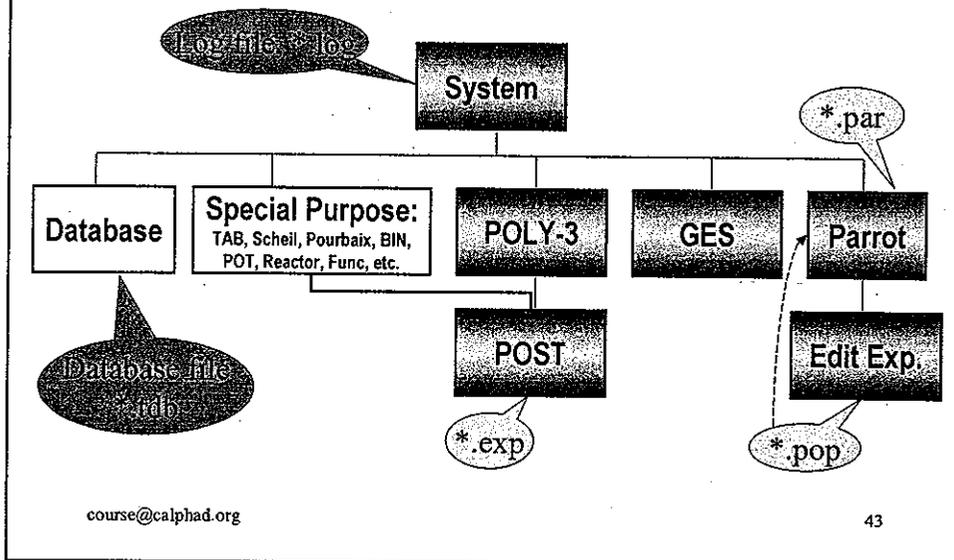


- **Glass transition:** $T_{\text{glass}}(\Delta S_{\text{fusion}}=0)$

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Files in Thermo-Calc



Files

- **Log file (*.log):** Record all commands and can be modified and saved as a macro-file (*.tcm) for repeated calculations (text file)
- **Database file (*.tdb):** Store thermodynamic functions (text file)
- **Pop file (*.pop):** Experimental data for evaluating thermodynamic parameters, to be used in Parrot (text file)
- **Parrot file (*.par):** Store thermodynamic data, thermodynamic parameters to be evaluated, and experimental data (formatted file)
- **Experimental file (*.exp):** Experimental data for plotting to compare with calculations (text file)