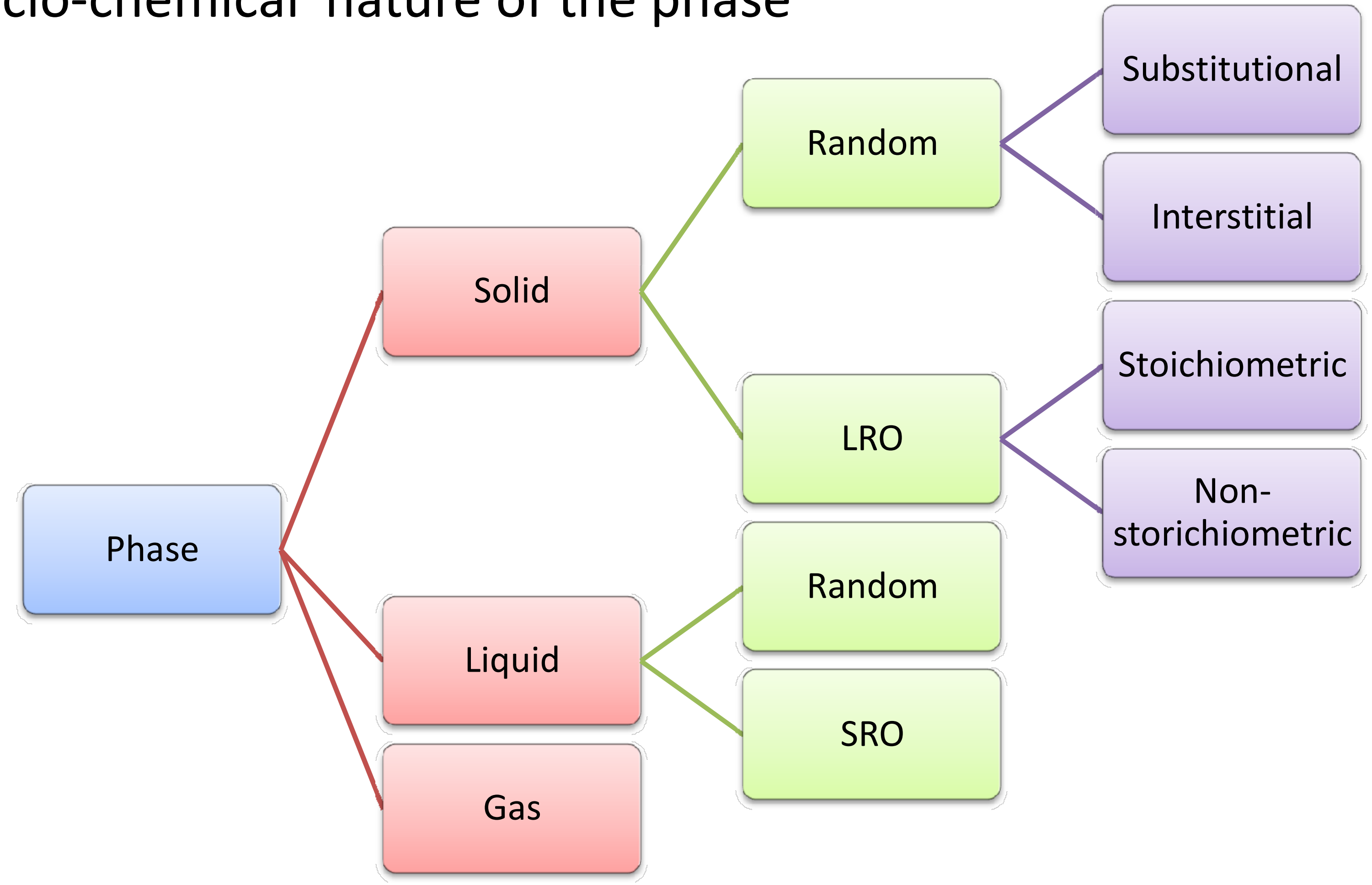
Gibbs Energy Model

Gibbs Energy Models

- Models for T, P and composition dependence of Gibbs energy
- Choice of a particular Gibbs energy model depends on the physcio-chemical nature of the phase



Phase

Solid

Liquid

Gas

Random

LRO

Random

SRO

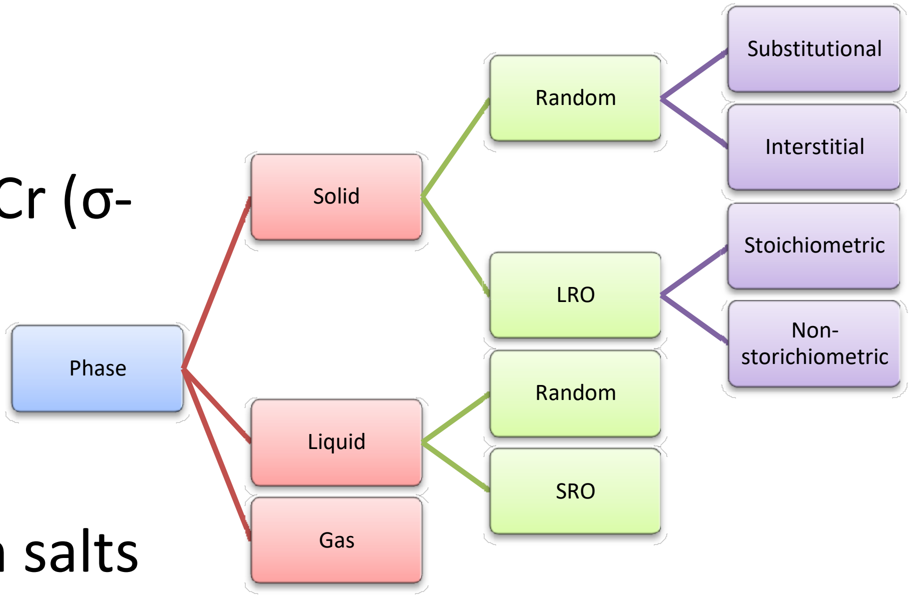
Substitutional

Interstitial

Stoichiometric

Non-storichiometric

- Random-Substitutional: α-brass
- Random-Interstittial: C in (α-Fe)
- LRO Non-stoichiometric: NiAl, FeCr (σ-phase), FeO (Wustite)
- LRO-Stoichiometric: Fe_3C, Al_2O_3
- Liquid-Random: molten steel
- Liquid-SRO: slags, mattes, molten salts



Elements and Stoichiometric Phases

- G has no composition dependence,

$$\boxed{G(T,p) = G^{lattice} + G^{phys} + G^{pres}}$$

where $G^{lattice}$ is the lattice (chemical) contribution

G^{phys} is the physical contribution like magnetic, ordering

G^{pres} is the pressure contribution

- For elements one should use G functions recommended by SGTE
- SGTE expression for $G^{lattice}$ of an element i has the following format (Meyer-Kelly Polynomial):

$$\boxed{G_i^0(T,1bar) = H_i^{SER} + a + bT + cT\ln T + \sum_{n=2,3,-1} d_n T^n}$$

Where a, b, c, ... are the model parameters

H_i^{SER} serves as the reference energy term

$$\boxed{G_i^0(T,1bar) = H_i^{SER} + a + bT + cT\ln T + \sum_{n=2,3,-1} d_n T^n}$$

- SER refers to Standard Element Reference, the reference state adopted by SGTE (Scientific Group Thermodata Europe)
- According to SER,

$$\boxed{\begin{aligned} &H_i^{SER} = H_i^{0,\phi}(298.15K,1bar) = 0 \\ &S_i^{0,\phi}(0K,1bar) = 0 \\ &S_i^{0,\phi}(298.15K,1bar) = \int_0^{298.15} C_{pi}^{0,\phi}\, d\ln T \end{aligned}}$$

Where ϕ corresponds to the phase of i that is stable at 298.15K and 1 bar.

NOTE: SGTE expressions are valid only above 298.15 K

$$\boxed{G_i^0(T,1bar) = H_i^{SER} + a + bT + cT\ln T + \sum_{n=2,3,-1} d_n T^n}$$

- Following can be deduced from the SGTE expression for G_i^0

$$\boxed{\begin{aligned} S_i^0 &= -b - c(1+\ln T) - \sum_{n=2,3,-2} d_n T^{n-1} \\ H_i^0 - H_i^{SER} &= a - cT - \sum_{n=2,3,-2} (n-1) d_n T^n \\ C_{p,i}^0 &= -c - \sum_{n=2,3,-2} n(n-1) d_n T^{n-1} \end{aligned}}$$

- For stoichiometric phases (compounds) $G^{lattice}$ is represented as

$$\boxed{G^0(T,1bar) = \sum_i \nu_i H_i^{SER} + A + BT + CT\ln T + \sum_{n=2,3,-1} D_n T^n}$$

where ν_i are the stoichiometric coefficients

A, B, C, ... are the model parameters.

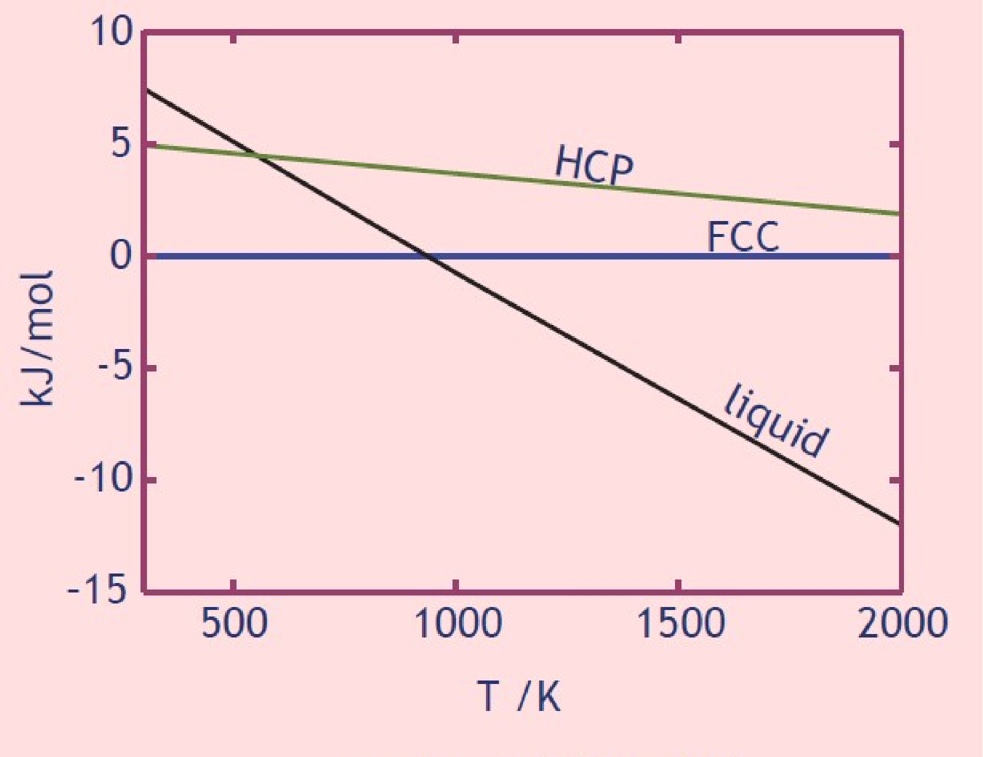
For compounds with no C_p of formation (Neumann and Kopp rule, $\Delta_f C_p = 0$), one can use a simple format

$$\boxed{\begin{array}{l} G^0(T,1bar) = \sum_i \nu_i G_i^{0,ref} + \Delta_f G \\ \Delta_f G = h + sT \end{array}}$$

Where $\Delta_f H = h$ and $\Delta_f S = s$

Lattice Stability

- Gibbs energy difference between two phases of an element is called lattice stability.
- Ex.: $G_{Al}^{0,HCP} - G_{Al}^{0,FCC}$



Lattice stability of Al

Example

$$G_C^{0,gr} = H_C^{SER} - 17368.441 + 170.73T - 24.3T\ln(T)$$

$$-4.723X10^{-4} + \frac{2562600}{T} - \frac{2.643X10^{8}}{T^{2}} + \frac{1.2X10^{10}}{T^{3}}$$

$$G^{0,cem} = 3H_{Fe}^{SER} + H_C^{SER} - 10745 + 706.04T - 120.6T\ln(T)$$

$$G^{0,AlB_2} = G_{Al}^{0,FCC} + G_B^{0,r\hom b} - 85808.76 + 45.46923T$$

$$G_{Al}^{0,HCP} - G_{Al}^{0,FCC} = +5481 - 1.8T$$

- T dependence of heat capacity is no longer simple when phonomena such as magnentic transitions are involved
- Accounting Gibbs energy due to such physical phenomena separately is more appropriate
- Inden-Hillert-Jarl model for magnetic transitions

$$G^{ma} = RT\ln(\beta + 1)g(\tau)$$

where, $\tau = T/T_c$

T_c is the critical temperature for the magnetic transition

β is the mean magnetic moment expressed in Bohr magnetons

The function $g(\tau)$ is

$$g(\tau) = 1 - \frac{1}{A}\left(\frac{79\tau^{-1}}{140} + \frac{474}{497}\left(\frac{1}{s} - 1\right)\left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600}\right)\right) \qquad \tau < 1$$

$$g(\tau) = -\frac{1}{A}\left(\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500}\right) \qquad \tau \geq 1$$

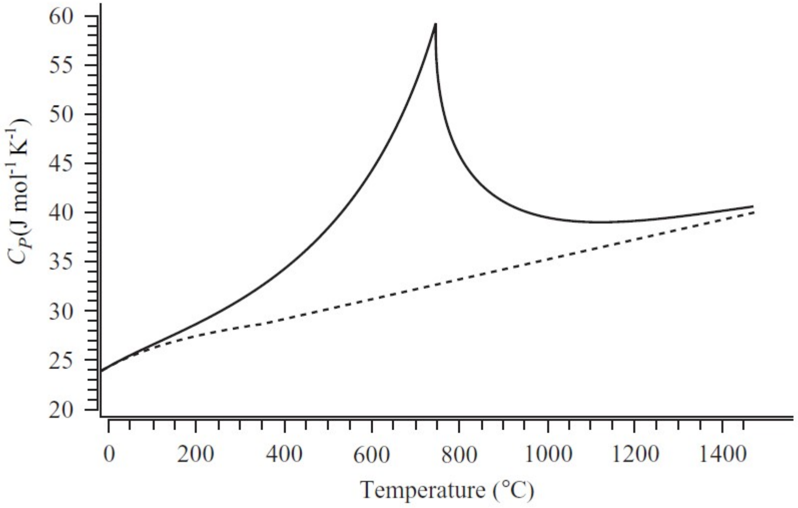
Where,

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

P is a structure dependent constant $p = \frac{(s+1)}{s(z-1)}$

Z is the CN (Z=8 for BCC, Z=12 for FCC, HCP)

S (=1/2) electron spin quantum number



Heat capacity of α-Fe

Gas Phase

- Gas (Vapour) phase may consist of several species.

  Example: with components O and S we have O, O_2, O_3, S, S_2 etc. constituent species.
- It is common to treat gas phase as ideal (V=RT/p)

$$G = G^{ref} + G^{conf} + G^{pres}$$

$$G = G^{ref} - TS^{conf} + G^{pres}$$

$$G^{ref} = \sum_i y_i \left(G_i^{0,gas} - \sum_j b_{ij} H_i^{SER} \right)$$

$$-TS^{conf} = RT \sum_i y_i \ln y_i$$

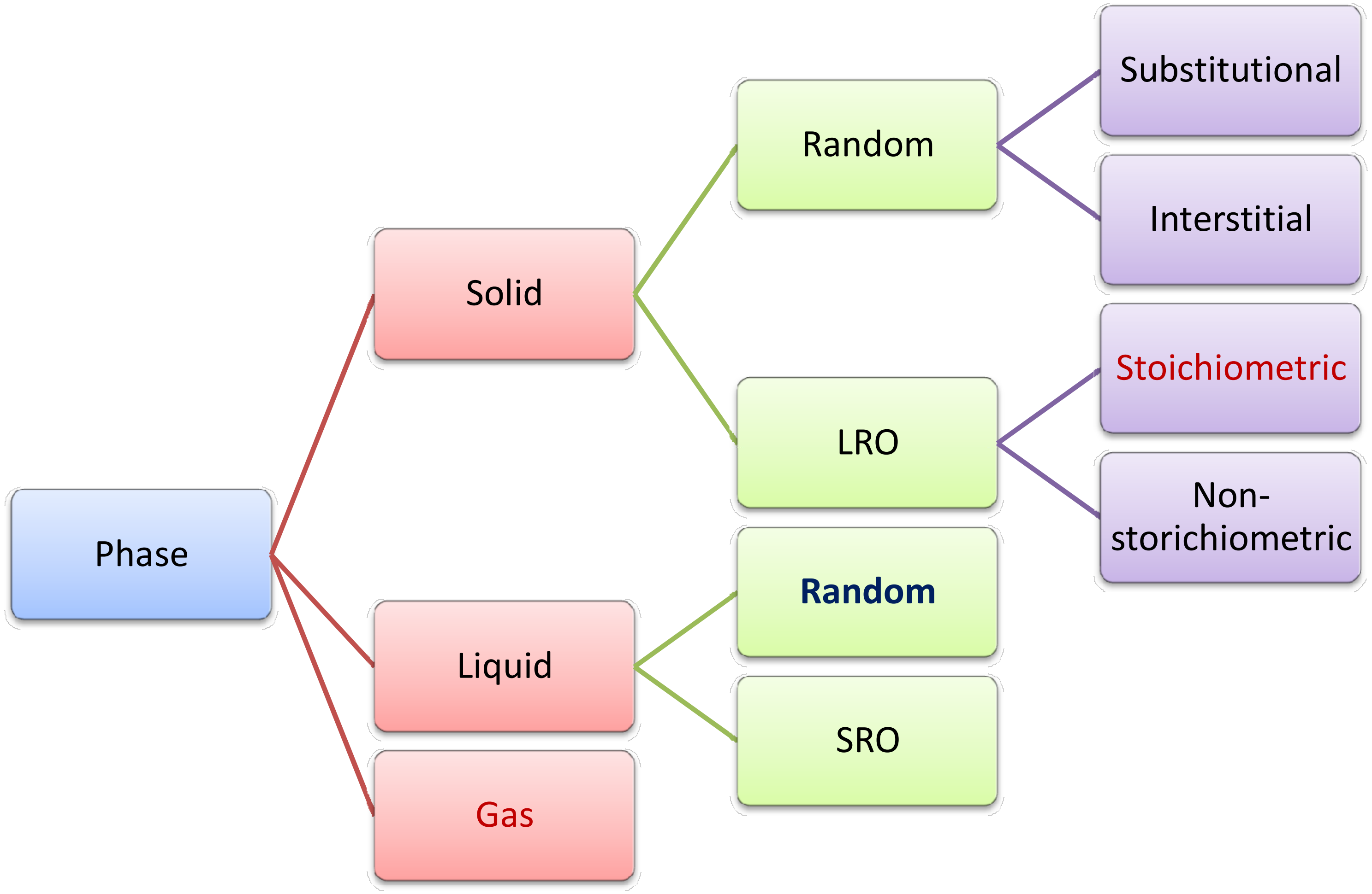
$$G^{pres} = RT \int_{p^\circ}^{p} \frac{dp}{p} = RT \ln\left(\frac{p}{p^0}\right)$$

Where

y_i is the mole fraction of species *i*

b_{ij} is the stoichiometric coefficient of component *j* in species *i*

P^o is the standard pressure (1 bar)



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Stoichiometric

Non-storichiometric

Random Substitutional Solutions

- There is random substitution of one type of constituents by other. Ex.: molten steel, α-brass
- In its most general form, molar Gibbs energy of a solution phase consists of five parts

$$G = G^{ref} + G^{conf} + G^{E} + G^{pres} + G^{phys}$$

- G^E is the excess Gibbs energy term
- For an *ideal solution* last three terms are absent, i.e.

$$G = G^{ref} + G^{conf}$$

$$G = G^{ref} - TS^{conf}$$

$$G = \sum_i x_i \left(G_i^o - H_i^{SER} \right) + RT \sum_i x_i \ln x_i$$

- For real solutions, $G^E \neq 0$

$$G = \underbrace{\sum_{i=A,B} x_i \left(G_i^o + H_i^{SER}\right)}_{G^{ref}} + \underbrace{RT \sum_{i=A,B} x_i \ln x_i}_{G^{conf}} + \underbrace{x_A x_B L_{A,B}}_{G^E}$$

- Substitutional regular solution model for a phase in binary A-B

- Real solutions often need a model for composition dependence of G^E with many adjustable parameters
- Power series: polynomial functions of composition
- Examples: Redlich-Kister, Legendre, Margules, ...
- All polynomial models are inter-convertible
- Some are numerically superior than others
- Redlich-Kister (R-K) polynomial is the most commonly used since they have some advantages in multi-component systems

$$\boxed{\begin{gathered} G^E = x_A x_B L_{A,B}\left(x_{A,} x_B\right) \\ G^E = x_A x_B \sum_{\nu=0}^{n} {}^{\nu}L_{A,B}\left(x_A - x_B\right)^{\nu} \end{gathered}}$$

- Where ${}^{\nu}L_{A,B}$ are the R-K interaction parameters
- Their T dependence can be described using

$$\boxed{{}^{i}L_{A,B} = {}^{i}a + {}^{i}bT + {}^{i}cT\ln T}$$

Extrapolation models for ternary and higher order systems

- Allow us to express excess property of a multicomponent system in terms of excess properties of limiting binary systems.
- It is accomplished through geometrical extrapolation of binary G^E, resulting in

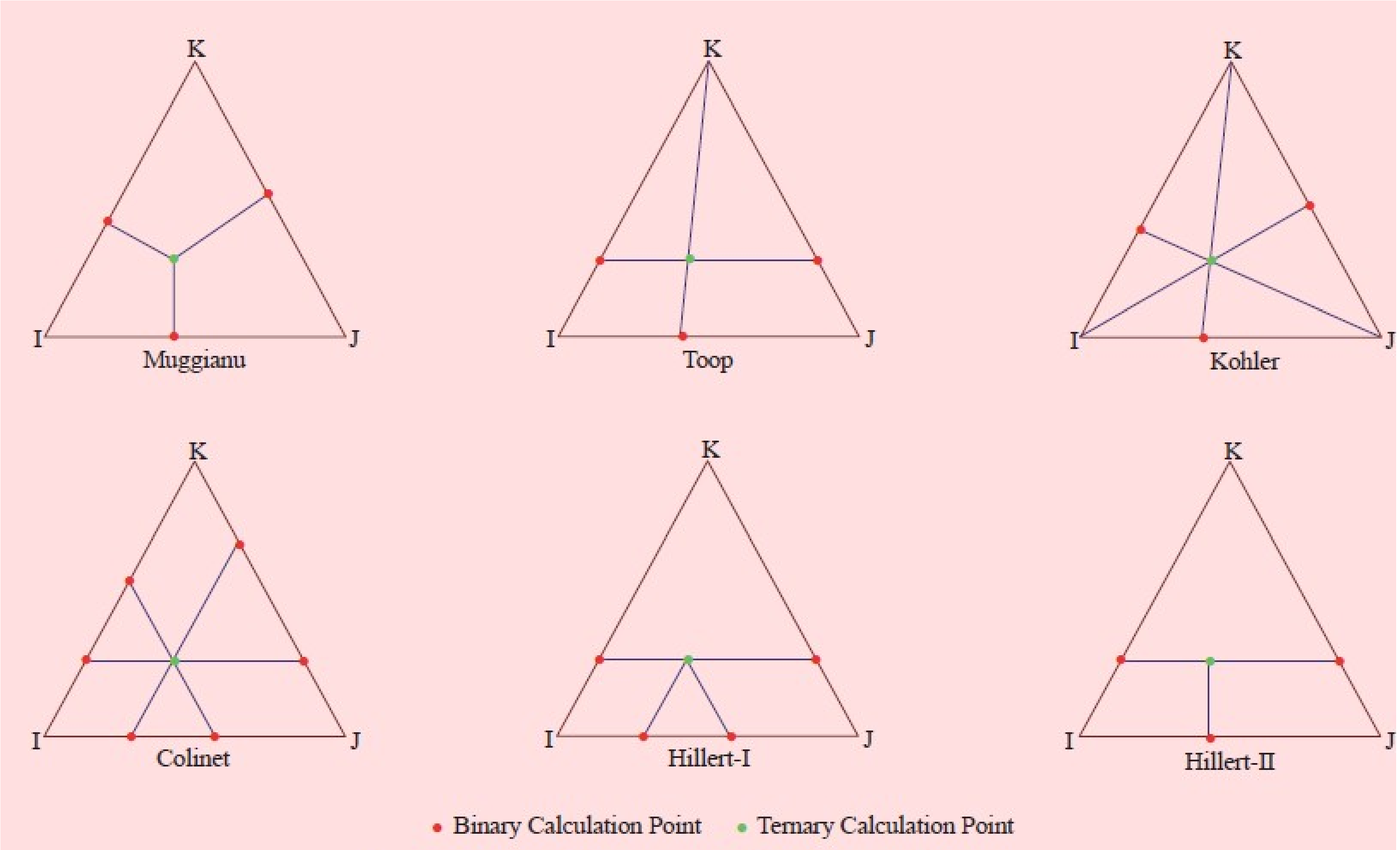
$$\left(G^{E}\right)_{m-c}=\left(G^{E}\right)_{\mathrm{exp}ld}+Correction-terms$$

- Correction terms are

ternary → $X_iX_jX_kL_{i,j,k}$

quaternary → $X_iX_jX_kX_lL_{i,j,k,l}$

- Many schemes exists for the extrapolation



Geometrical Extrapolation Schemes

- Muggianu extrapolation scheme:

$$\boxed{\left(G^{E}\right)_{\exp ld}=\sum_{i=1}^{c-1}\sum_{j=i+1}^{c}\frac{X_iX_j}{V_{ij}V_{ji}}\left(G^{E}\left(V_{ij},V_{ji}\right)\right)_{i-j}}$$

- Where, $\left(G^{E}\left(V_{ij},V_{ji}\right)\right)_{i-j}=V_{ij}V_{ji}L_{i,j}\left(V_{ij},V_{ji}\right)$

$$V_{ij}=X_i+\frac{(1-X_i-X_j)}{2}\qquad V_{ji}=X_j+\frac{(1-X_i-X_j)}{2}$$

- The quantity $\frac{X_iX_j}{V_{ij}V_{ji}}$ is a weighting factor
- If we use R-K polynomials for $\left(G^{E}\left(V_{ij},V_{ji}\right)\right)_{i-j}$ above equation can be considerably simplified

$$\boxed{\left(G^{E}\right)_{\exp ld}=\sum_{i=1}^{c-1}\sum_{j=i+1}^{c}\left(G^{E}\left(V_{ij},V_{ji}\right)\right)_{i-j}}$$

- In the case of ternary system R-K-M scheme gives

$$\boxed{G^{E}=\sum_{i=1}^{2}\sum_{j=i+1}^{3}X_iX_j\sum_{\nu=0}^{n_{i-j}}{}^{\nu}L_{i,j}\left(X_i-X_j\right)^{\nu}+X_iX_jX_kL_{i,j,k}}$$

Sublattice Formalism

- General modeling concept for many types of phases: Stoichiometric compounds, random substitutional solutions, interstitial solutions, intermediate phases with homogeneity range, ionic and non-ionic melts, etc.
- Based on Temkin's model (1945) for molten salts

  Salt system – $(Cs^+, Na^+)(Cl^-, F^-)$

  - Cations and anions occupy separate sublattices and mixing is random on each sublattice.
- Hillert and Staffanson (1970)

  Formula unit containing two sublattices

$$(A,B)_{a1}(C,D)_{a2}$$

a_s →relative number of lattice sites on sublattice 's'

$$\sum_s a_s = 1 \quad \text{(or a positive integer)}$$

- Harvig (1971)

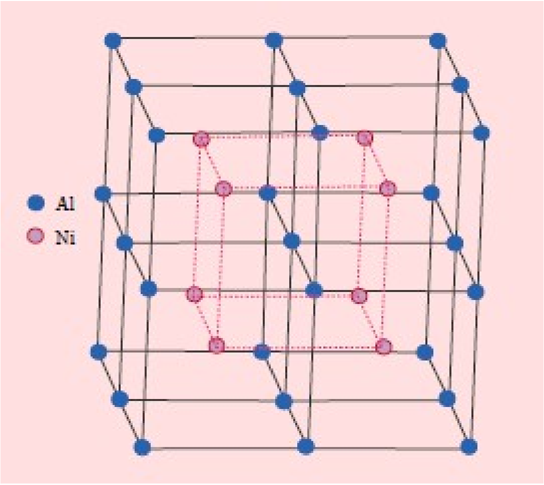
$$(A,B,C...)_{a1}(A,C,E,...)_{a2}$$

- Arbitrary number of constituent species
- Sundman and Ågren (1981): general formalism

$$(A,B,C...)_{a1}(A,C,E,...)_{a2}...(B,C,D,...)a_{n}$$

- A,B, C,....=atoms, molecules, charges species, vacancy
- Arbitrary number of constituent species and sublattices allowed
- For solid phases: Compound Energy Formalism (CEF)
- A species is permitted only once in each sublattice
- Suitable for computer implementation

Crystallographic data for the AlNi phase



Prototype	CsCl	
Space Group	Pm/3m(221)	
Pearson Symbol	*cP2*	
Strukturbericht	B2	
Point Group Symmetry	m/3m	m/3m
Site Occupation	Al	Ni
Wykoff Notation	1a	1b
Coordination Number	8	8

Sublattice model for perfectly ordered AlNi: $(Al)_1(Ni)_1$

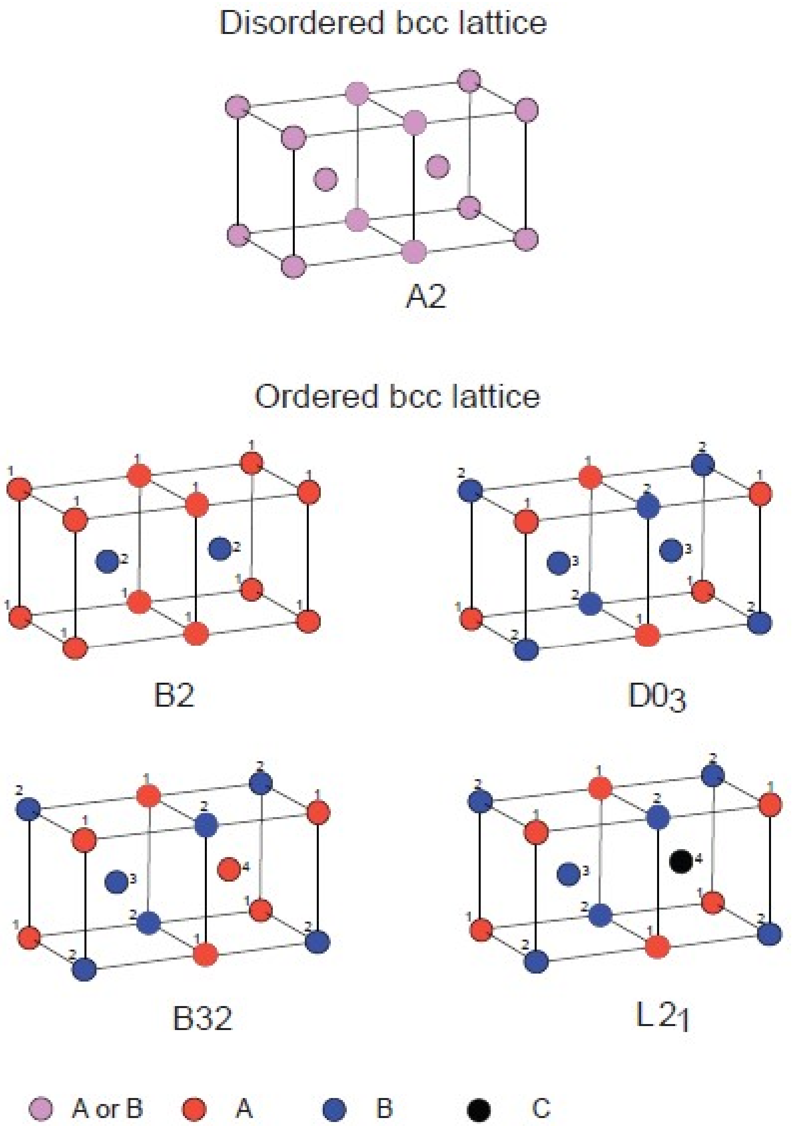


Figure 2.5: Sublattices of bcc based structures. (1, 2, 3 and 4 denotes sublattices)

- Site fractions: mole fractions defined for a particular sublattice.

$$\boxed{{}^{s}y_i = \frac{{}^{s}N_i}{{}^{s}N}}$$

- ${}^{s}y_i$ → site fraction of constituent species i on sublattice s
- ${}^{s}N_i$ → number of sites occupied by species i in sublattice s
- ${}^{s}N$ → total number of sites on sublattice s, given by

$$\boxed{{}^{s}N = {}^{s}N_{va} + \sum_i {}^{s}N_i}$$

- ${}^{s}N_{va}$ → number of vacant sites on sublattice s
- Sum of site fractions in a given sublattice is unity

$$\boxed{{}^{s}Y_{va} + \sum_i {}^{s}y_i = 1}$$

- Mole fraction of a component j can always be calculated from site fractions of constituent species

$$\boxed{X_j = \sum_i \left(\frac{{}^i b_j}{\sum_k {}^i b_k} \left(\frac{\sum_s a_s \, {}^s y_i}{\sum_s a_s \left(1 - {}^s y_{va}\right)} \right) \right)}$$

- ${}^i b_j$ → stoichiometry of component j in species i.

  e.g. $(A, AB)_1(B,Va)_3$

$$\boxed{X_B = \frac{0.5\,{}^1 y_{AB} + 3\,{}^2 y_B}{1 + 3(1 - {}^1 y_{Va})}}$$

- If all constituent species are monoatomic

$$\boxed{X_j = \frac{\sum_s a_s \, {}^s y_j}{\sum_s a_s (1 - {}^s y_{va})}}$$

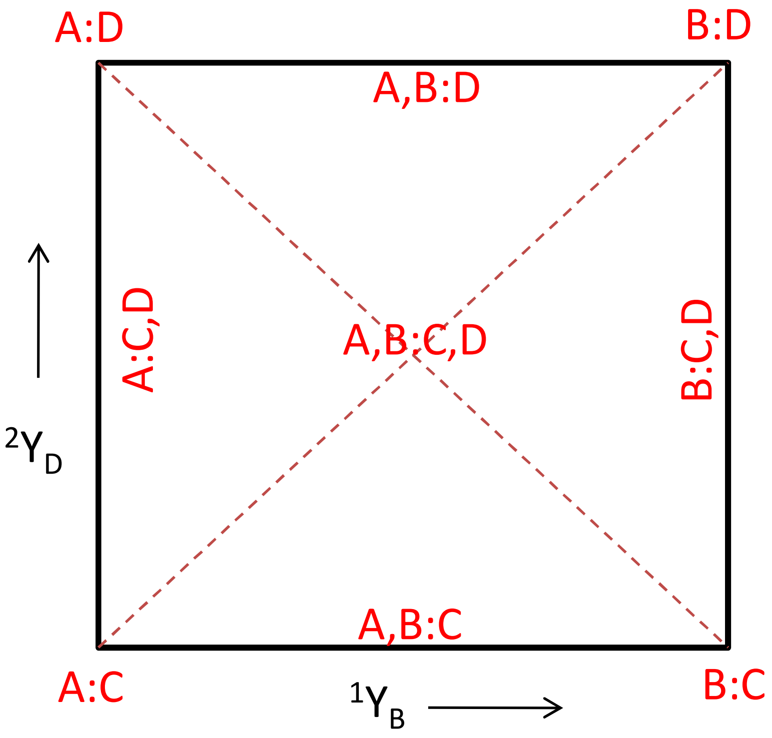
- Site fractions have mixed character of an external and internal state variable
- They are obtained through Gibbs energy minimization
  - In simple cases site fractions can be calculated from mole fractions without resorting to a Gibbs energy minimization
  - For this, the number of independent site fractions should be equal to the number of independent mole fractions

e.g. $(A,B)_{a1}(C,Va)_{a2}$

$$X_A = \frac{a_1\,{}^1y_A}{a_1 + a_2(1 - {}^2y_{Va})} \qquad X_B = \frac{a_1\,{}^1y_B}{a_1 + a_2(1 - {}^2y_{Va})}$$

$$ {}^1y_A = \frac{X_A}{1 - X_C} \qquad {}^2y_A = \left(\frac{a_1}{a_2}\right)\frac{X_C}{1 - X_C}$$

- Constituent array: A unit of the sublattice model having one or more constituent species on each sublattice
- Constituent array of Z^{th} order: I(z)
- Constituent arrays of $(A,B)_{a1}(C,D)_{a2}$
    - I(O)→A:C, A:D, B:C and B:D
    - No interacting constituent species on a sublattice
    - I(1)→A:(C,D), B:(C,D) and (A,B):C   (A,B):D
    - One interacting constituent species on a sublattice
    - I(2)→(A,B):(C,D)
    - Two interacting constituent species on two sublattices or three interacting constituent species on one sublattice.
- “.” is used to separate two sublattices and a “.” to separate two constituent species within a sublattice
- Generally, we need not consider constituent arrays larger than I(2), since their influence on G is negligible
- I(0) are also known as the “end members” of the sublattice model.



Composition domain for $(A,B)_{a1}(C,D)_{a2}$

- I(0) represent the corners of the composition domain of the model, I(1) the edges, and I(2) the diagonals

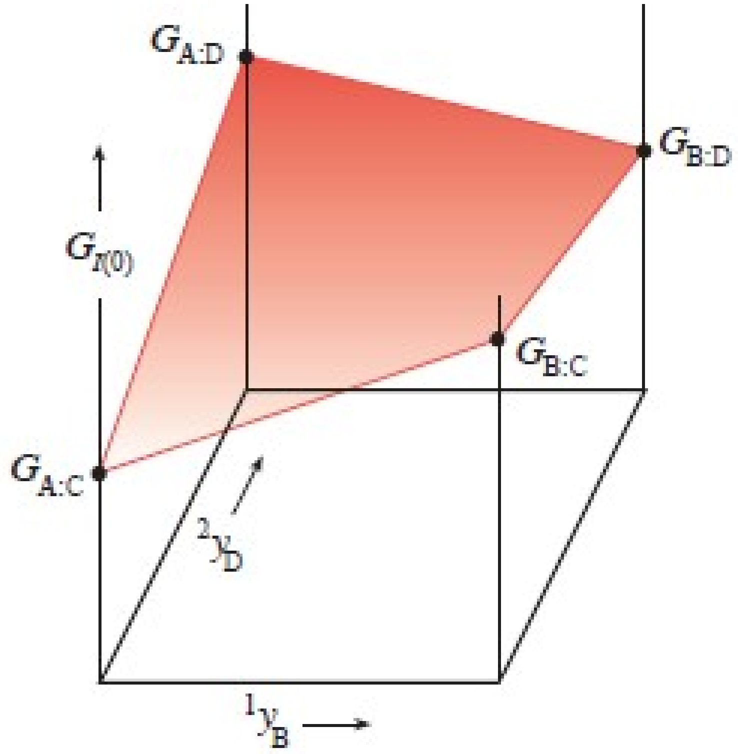


Fig.: Reference surface for (A,B)$_{a1}$(C,D)$_{a2}$ at constant p and T

- Reference surface is non-planar, defined by the function

$$G^{ref} = {}^1y_A\left({}^2y_C G^o_{A:C} + {}^2y_D G^o_{A:D}\right) + {}^1y_B\left({}^2y_C G^o_{B:C} + {}^2y_D G^o_{B:D}\right)$$

- It is planar when

$$G^o_{A:C} + G^o_{B:D} = G^o_{B:C} + G^o_{A:D}$$

- For the general case, we can write

$$\boxed{G^{ref} = \Sigma_{I(0)}\left(\Pi_{I(0)}{}^{s}y_i\right)G^{o}_{I(0)}}$$

- $\Pi_{I(0)}{}^{s}y_i$ is a product of site fractions from I(0)
- The degreee of the product is equal to the number of sublattices having mixing of constituent species.

$$\Sigma_{I(0)}\Pi_{I(0)}{}^{s}y_i = 1$$

- $G^{o}_{I(0)}$ is the Gibbs energy per mole of formula unit (mfu) of the end member compound –i.e. the compound energy
- Compound eneryg is the mose significant part of the Gibbs energy of the phase and for this reasong the sublattice model is popularly known as the “Compound Energy Formalism (CEF)”
- The number of terms (number of end members) is obtained by taking the product of number of species on each sublattice.
- $G^{o}_{I(0)} = f(T, p = 1bar),$ may have several adjustable parameters.

- Constituent species on each sublattice mix randomly
- For the specific case of $(A,B)_{a1}(C,D)_{a2}$ configurational entropy is given by

$$S^{conf} = -R\left\lfloor a_1\left({}^1y_A \ln\left({}^1y_A\right) + {}^1y_B \ln\left({}^1y_B\right)\right) + a_2\left({}^2y_C \ln\left({}^2y_C\right) + {}^2y_D \ln\left({}^2y_D\right)\right)\right\rfloor$$

- For the general case, S^{conf} can be written as

$$S^{conf} = -R\sum_s a_s \sum_i {}^s y_i \ln\left({}^s y_i\right)$$

- The ideal Gibbs energy of mixing is given by

$$G^{conf} = -T.S^{conf} = -RT\sum_s a_s \sum_i {}^s y_i \ln\left({}^s y_i\right)$$

- Excess Gibbs energy (G^E) represents interaction between constituent species within same sublattice
- G^E involves only constituent arrays larger than *I(0)*
- For the specific case of $(A,B)_{a1}(C,D)_{a2}$:

$$\begin{aligned} G^E = {}&{}^1y_A\,{}^1y_B\left({}^2y_C L_{A,B:C} + {}^2y_D L_{A,B:D}\right) + \\ &{}^2y_C\,{}^2y_D\left({}^1y_A L_{A:C,D} + {}^1y_B L_{B:C,D}\right) + \\ &{}^1y_A\,{}^1y_B\,{}^2y_C\,{}^2y_D L_{A,B:C,D} \end{aligned}$$

- $L_{I(Z)}$ → interaction energies between constituent species in *I(Z)*
- Influence of $L_{I(1)}$ interaction terms ($L_{A,B:C}$, $L_{A,B:D}$, $L_{A:C,D}$ and $L_{B:C,D}$) are along the sides of the composition domain
- Influence of $L_{I(2)}$ term ($L_{A,B:C,D}$) is along the diagonals, maximum effect being at the canter of the composition domain

- One may introduce further composition dependence for GE by expanding LI(1) terms as R-K polynomials for example,

$$L_{A,B:C} = \sum_{\nu=0}^{k} {}^{\nu}L_{A,B:C} \left({}^{1}y_A - {}^{1}y_B\right)^{\nu}$$

- ${}^{\nu}L_{I(Z)}$ are adjustable model parameters
- They may have a temperature dependence

$${}^{\nu}L_{A,B:C} = {}^{\nu}a_{A,B:C} + {}^{\nu}b_{A,B:C}T + \ldots$$

- Only in rare cases we need to expand $L_{I(2)}$ terms

$$L_{A,B:C,D} = {}^{0}L_{A,B:C,D} + {}^{1}L_{A,B:C,D}({}^{1}y_A - {}^{1}y_B) + {}^{2}L_{A,B:C,D}({}^{2}y_C - {}^{2}y_D)$$