Outline

- **Thermodynamic Models**
  - Regular Solution Models
  - Sublattice Model
  - Associated Solutions
  - Cluster Variation Model
  - Quasichemical Model
  - Cluster Expansion Model
- **Thermodynamic Data**
- ***Order – Disorder* transformation**

Thermodynamic Models – *Multicomponent Systems*

- The Gibbs energy per mole for a solution phase is normally divided into four contributions:

$$G = G^{rsf} + G^{id} + G^{xs} + G^{phys}$$

Where,
G^{rsf} is the reference surface for Gibbs energy
G^{id} is the ideal mixing or configurational entropy contribution
G^{xs} is the excess Gibbs energy
G^{phys} is a physical contribution (*magnetic*)

- Modeling by physicists have mainly concentrated on finding a correct configurational entropy (*Quasichemical, CVM*) to describe main features.
- Modeling among material scientists has mainly focused on finding a representative excess Gibbs energy to reproduce the experimental data.

Regular Solutions

- Regular solution models are based on ideal entropy of mixing of the constituents. As these, in the general case, are different from the components their fraction is denoted y_i.

$$G^{\varphi}_m = \Sigma_i\, y_i\, {}^oG^{\varphi}_i + RT\, \Sigma_i\, y_i \ln(y_i) + {}^EG^{\varphi}_m$$

Where, ${}^oG^{\varphi}_i$ is the Gibbs energy of constituent i in phase φ
${}^EG^{\varphi}_m$ is the excess Gibbs energy

- The excess Gibbs energy for a binary system modeled as a regular solution:

$${}^EG_m = \Sigma_i\, \Sigma_{j>i}\, y_i\, y_j\, L_{ij}$$

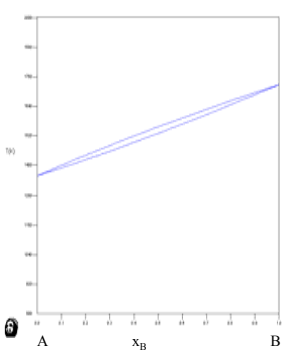
$$L_{ij} = \Sigma_\nu\, (y_i - y_j)^\nu\ {}^\nu L_{ij} \rightarrow \ldots\ldots\ldots\ldots\ \textit{polynomial}$$

${}^\nu L_{ij}$ are so called Redlich-Kister coefficients.

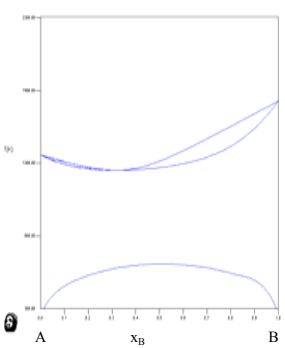
Of course, other types of polynomial can be used and should give '*identical*' results for binary systems. However, they are expected to differ in ternary and higher order extrapolations.

Example 1: *Regular Solutions*

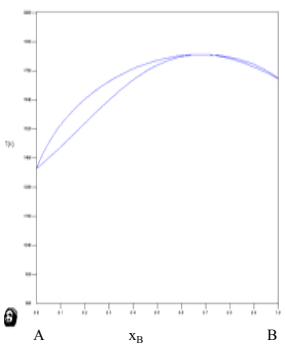
For regular Solutions, $G^{xs} = \Omega X_A X_B$



Liquid: Ideal solution
Solid Solution: Ideal



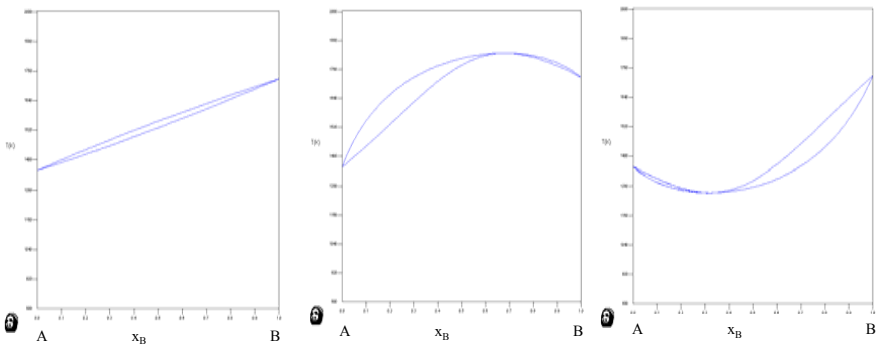
Liquid: Ideal solution
Solid Solution: Regular with Ω = 10000J/mol



Liquid: Ideal solution
Solid Solution: Regular with Ω = -10000J/mol

Example 2: *Regular Solutions*

For regular Solutions, $G^{xs} = \Omega X_A X_B$



Liquid: Ideal solution
Solid Solution: Ideal

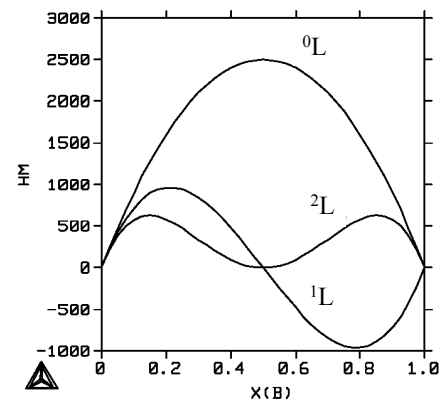
Liquid: Regular with Ω = 10000J/mol
Solid Solution: Ideal

Liquid: Regular with Ω = -10000J/mol
Solid Solution: Ideal

Redlich-Kister Coefficients

$$^{E}G_m = \Sigma_i \Sigma_{j>i} y_i y_j L_{ij}$$

$$L_{ij} = \Sigma_v (y_i - y_j)^v \; {}^vL_{ij}$$



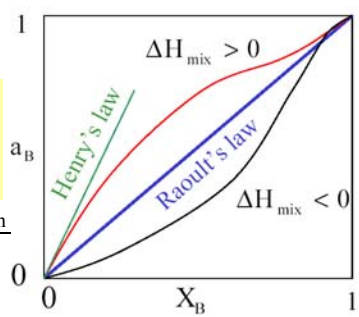
Dilute Solution Model

$$\gamma_B = \frac{a_B}{X_B} \approx const$$ → Henry's law

When a solution is sufficiently dilute in component *B*, the vapor pressure exerted by component *B* (i.e. a_B) is linearly proportional to the concentration of this component.

$$a_B = \frac{\text{Vapor pressure exerted by component B in a solution}}{\text{Vapor pressure of B in equilibrium with pure B}}$$

$$\gamma_A = \frac{a_A}{X_A} \approx 1$$ → Raoult's law



- Component *B* obeys Henry's law up to X_1.
- Note that if the slope of the tangent drawn from the zero concentration (i.e. *the constant in Henry's law*) is ……., Henry's law becomes identical to that of Raoult → Henry's law is more general.
- In a binary solution, if the **solute** follows Henry's law, the **solvent** will obey Raoult's law. (*this can be proven using Gibbs-Duhem equation*)
- Also note that these laws cannot be used in a software for calculating the phase equilibrium in wide range of composition.

Sublattice Model

- Crystalline phases with different types of sublattices can be described with the Sublattice Model. Different constituents may enter in the different sublattices and ideal mixing can be assumed in each sublattice.
- The simplest case is $(A,B)_a(C,D)_c$ and its Gibbs energy and entropy expressions can be written as:

$$G_m^{rsf} = \Sigma_i \Sigma_j y'_i y''_j \, {}^oG_{ij}$$

$$S_m^{cfg} = -R(a\Sigma_i y'_i \ln(y'_i) + c\Sigma_j y''_j \ln(y''_j))$$

$^oG_{ij}$ is the Gibbs energy of formation of the compound $i_a j_c$. Where, a and c are the site ratios

- The excess and physical contributions are as for a **regular solution** for each sublattice. For instance, Excess Gibbs energy for $(A,B)_a(C,D)_c$ is:

$$G^{xs} = y'_A y'_B (y''_C L_{A,B:C} + y''_D L_{A,B:D}) + y''_C y''_D (y'_A L_{A:C,D} + y''_B L_{B:C,D}) + y'_A y'_B y''_C y''_D L_{A,B:C,D}$$

- Each L can be expressed as Redlich-Kister coefficient.

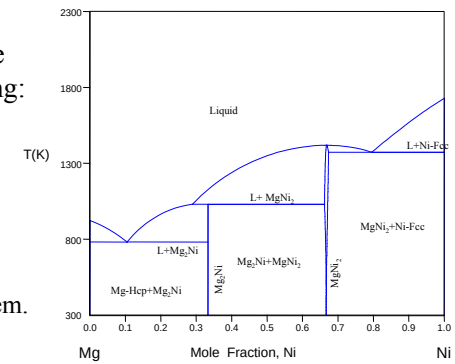
Sublattice Model

- The sublattice model has been used extensively to describe interstitial solutions, carbides, oxides, intermetallic phases etc.
- It is often called the compound energy formalism (CEF) because it is assumed that the compound energies are independent of composition.
- In this model, Gibbs energy is usually expressed in moles per *formula units*, instead of moles of atoms because …….. can be constituents.
- Sublattices are used to describe Long Range Order (LRO) when the atoms are regularly arranged on sublattices over large distances.
- Short Range Order (SRO) means that the fraction of atoms in the neighborhood of an atom deviate from the overall composition.

There are special models that deal with SRO such as the …… and …… models.

Example: *Laves- Phase in the Mg-Ni system*

- Two important aspects must be considered in sublattice modeling:
  1) Crystallographic information
  2) Solubility range of phase
- Crystallographic information mainly used for deciding the
  - number of sublattices to be used
  - the species present in each of them.



- In order to model the homogeneity range, it is necessary to allow mixing of species in one or more sublattices.
- For phases with relatively narrow ranges of homogeneity the mixing may be attributed to the presence of structural defects.
- The number of end members can be reduced by combining sublattices with similar crystallographic character:
  - same …….. - and same …….

Example: *Sublattice model of $MgNi_2$*

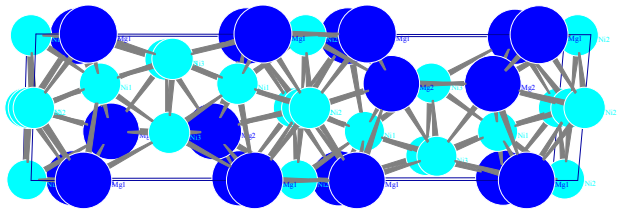
Crystallographic information of $MgNi_2$

Space group number	194
Lattice parameter (A)	a=4.824, c=15.826

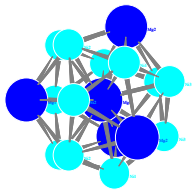
Sublattice model:
$MgNi_2$=AB2
WP position= 4:4:4:6:6
=2:2:2:3:3
(A)2: (A)2: (B)2: (B)3: (B)3
(A)4: (B)8
(A): (B)2
(A,B): (A,B)2

Atom	WP	CN	PS	Atomic position
Mg1	4e	16	3m	x=0, y=0,z=0.09400
Mg2	4f	16	3m	x=1/3,y=2/3,z=0.84417
Ni1	4f	12	3m	x=1/3,y=2/3,z=.12514
Ni2	6g	12	.2/m.	x=1/2,y=0,z=.346
Ni3	6h	12	mm2	x=0.16429,y=0.32858, z=1/4

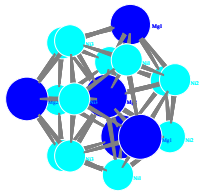
Unit cell of **$MgNi_2$**



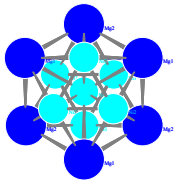
Example: *$MgNi_2$ – Coordination Numbers*



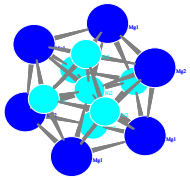
Mg1: CN=….



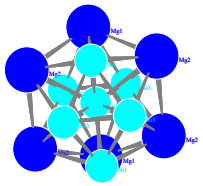
Mg2: CN =….



Ni1: CN=……



Ni2: CN=….,



Ni3 :CN=….

Ionic Liquid Model

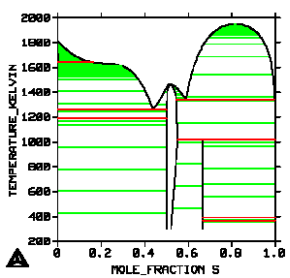
It is possible to use the idea of sublattice model to describe liquid phases

- For example, the ionic liquid model is the modified sublattice model, where the constituents are cations (M^{q+}), vacancies (Va^{q-}), anions (X^{p-}), and neutral species (B^{o}).
- Assumes separate "sublattices" for M^{q+} and Va^{q-}, X^{p-}, B^{o}, e.g., $(Cu^{+})_P(S^{2-}, Va^{-}, S^{o})_Q$, $(Ca^{2+}, Al^{3+})_P(O^{2-}, AlO_{1.5}^{o})_Q$ or $(Ca^{2+})_P(O^{2-}, SiO_4^{4-}, Va^{2-}, SiO_2^{o})_Q$
- The number of "sites" (P, Q) varies with composition to maintain electro-neutrality.
- It is possible to handle the whole range of compositions from pure metal to pure non-metal.

Associated Solutions

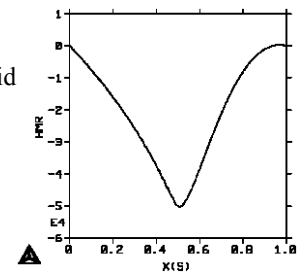
- These are identical to regular solutions except that …… constituents can be introduced in these models, for example FeS molecules in the Fe-S liquid. The reason to introduce this is to describe short range order around the FeS composition. In this case, a parameter ${}^{o}G^{FeS}$ would be added.
- Interaction parameters between '*Fe-FeS*' and '*FeS-S*' are added to those between Fe-S. In other words this system can be modeled like a "*ternary*" system.
- Note that a gas mixture is similar to an associated solution but in the case of gas mixture the constituents are real.

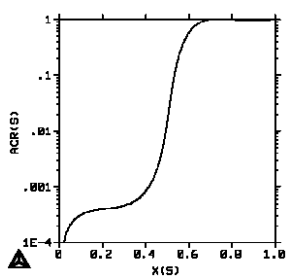
Example: *Associated Solution Model (Fe-S)*



Fe-S phase diagram

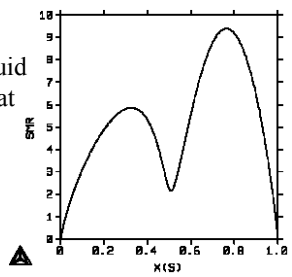
Enthalpy of liquid Fe-S mixing at 2000K





Activity of S in Fe-S liquid

Entropy of liquid Fe-S mixing at 2000K



Quasichemical Model

- Quasichemical model (QCM) is derived using the fractions of bonds y_{AA}, y_{AB} and y_{BB} rather than constituents y_A and y_B. But one may also treat this as a model with the additional constituents AB and BA.
- The configurational entropy in this model can be expressed as:

$$S^{cfg} = -R/2\,(y_{AA}\ln(y_{AA}/y_A y_A) + y_{AB}\ln(y_{AB}/y_A y_B) + y_{BA}\ln(y_{BA}/y_B y_A) + y_{BB}\ln(y_{BB}/y_B y_B)) - R(y_A\ln(y_A)+y_B\ln(y_B))$$

- The fraction of the constituents can be calculated from the bond fractions as: $y'_A = 0.5(y_{AA} + y_{AB})$ $\quad y'_B = 0.5(y_{BA} + y_{BB})$

  $y''_A = 0.5(y_{AA}+y_{BA})$ $\quad y''_B = 0.5(y_{AB} + y_{BB})$

- It is possible to include long range order in the quasichemical model by allowing y'_A and y''_A to be different, i.e. y_{AB} unequal to y_{BA}. This is similar to an ordered model (A,B)(A,B)

$$y_{AA} = y_A y_A - \varepsilon$$
$$y_{AB} = y_A y_B + \varepsilon$$
$$y_{BA} = y_B y_A + \varepsilon$$
$$y_{BB} = y_B y_B - \varepsilon$$

The degree of short range order, ε, can be evaluated from the difference between the *fraction of bonds* and the product of the constituent fractions

Cluster Variation Method

• An improved method to treat short range order in crystalline solids was developed in 1951 by Kikuchi and called Cluster Variation Method (CVM).

• It can treat arbitrarily large clusters of lattice sites but the entropy expression must be derived for each lattice. Therefore, even for binary systems it can be …….. to use. More importantly, it is ……. to apply to multi-component systems.

• For most phases the contribution to Gibbs energy due to *SRO* is small.

A model describing SRO should have ideal entropy of mixing when $^{o}G_{AB}$ is zero. This is satisfied by the quasichemical model but not the associated model.

The reason why the associated model is still used is that it is easier to handle.

Cluster Variation Method

• The Cluster Variation Method (CVM) divides the lattice into *clusters of different sizes*. The smallest cluster is an atom at a lattice point, then two atoms forming a bond, then 3 atoms forming a triangle (i.e. *there may be several different clusters with 3 atoms*), then 4 atoms etc

• By taking fractions of different clusters into account CVM can describe the short range order.

• The disadvantage of CVM is the large number of clusters needed to describe multicomponent systems.

Cluster Expansion Model

• From **first principles,** one may calculate the energy at 0 K for different configurations of atoms on specific lattices. These energies can be expanded in different ways to describe states for compositions between the calculated configurations. A popular model to use is the Cluster Expansion Model (CEM) by *Connally and Williams*. Then, one way to calculate the cluster energies and phase diagram is by CVM calculation.

• The energies from a **first principle** calculation can also be used directly in a sublattice model if the configurations correspond to the compounds. However, the error made by ignoring the short range order contribution should be taken into consideration.

• Also, **first principle** calculations are used to calculate thermodynamic properties (e.g. heat of formation of compounds) which are not available experimentally.

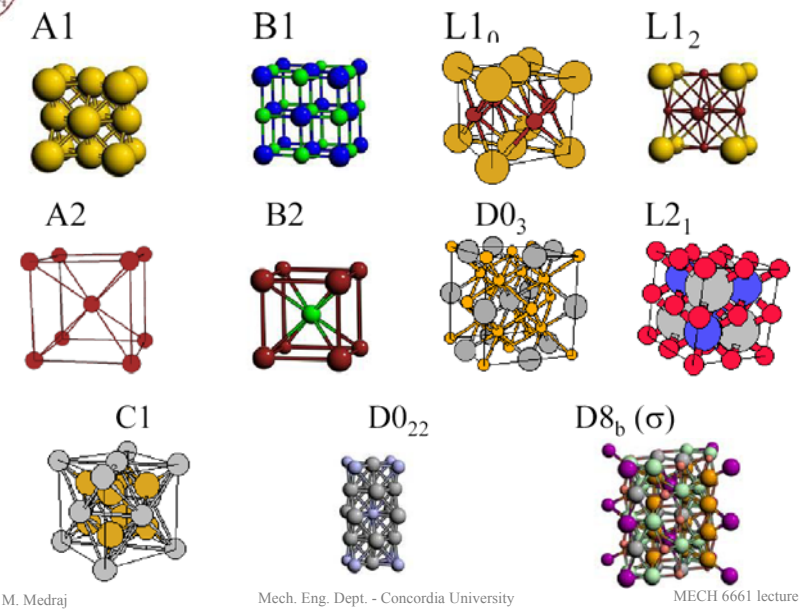
10 MINUTES *BREAK*

Experimental data

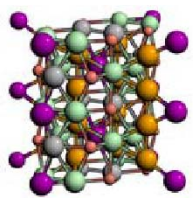
$$G = G^{rsf} + G^{id} + G^{xs} + G^{phys}$$

- The interaction parameters in the thermodynamic models are determined using different experimental data by optimization. The experimental data needed for the optimization include:
  - Phase Diagram data
  - Thermochemical data
  - Crystallographic data
  - Physical property data (magnetism)
- Therefore we should first find the nature (liquid, ordered solid solution, compound… etc) and structure of the phases in the system. Determine the appropriate model to be used. If the *compound energy formalism* is used, the number and type of sublattices for different constituents should be determined. Also, the types of defects (e.g. vacancies) for non-stoichiometric compounds should be known.

Crystallographic Data



Crystallographic Data: *Example*



D8$_b$ (σ)

- In many cases the crystallographic data must be simplified before used in a thermodynamic model. Thus the σ phase is modeled with 3 sublattices and not 5 and all elements are not entered in all sublattices.
- Many intermediate phases have *little or no* crystallographic information. One may then use a prototype of the structure to determine the number and nature of sublattices. For the same reasons some times, specially in case of narrow homogeneity range, we assume these solid solutions linear compounds and use a chemical formula for their composition.

Calorimetric Data

- Calorimetric data include enthalpy of:
  - formation,
  - transformation, and
  - mixing
- EMF, Knudsen cell data which include:
  - chemical potentials, and
  - activities
- Partial pressure to measure activities.
- DSC to measure: heat capacity and enthalpy of transformation

Phase Diagram Data

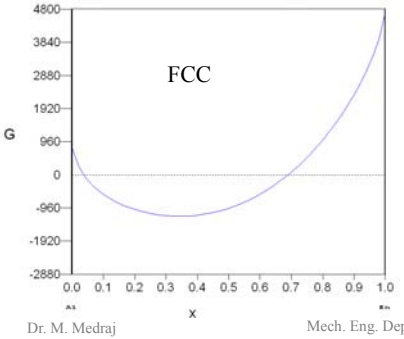
- DTA: start/end temperatures of transformations
- Microscope: phase identification, determining phase amounts and their composition (EDS and EPMA)
- X-ray: phase identification and crystal structure
- Microsound: phase identification
- Neutron diffraction: site occupancies

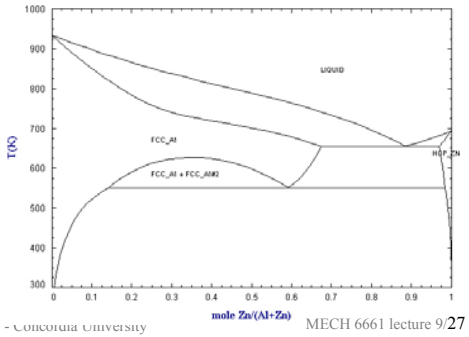
Thermodynamic Modeling

- Missing data that are essential for thermodynamic modeling can be estimated in various ways:
  - Comparisons with similar systems
  - Calculations using first principles
- Special behavior of data, like strong "V" shaped enthalpy of mixing or sharp raise of activity. In a crystalline phase this indicates *long range order*, in a liquid *short range order*.
- The liquid phase in metallic systems is most often modeled with a substitutional regular solution model.
- For metal-nonmetal systems with strongly asymmetric miscibility gaps or rapid change of activities Regular Model is often not suitable and an associated, quasichemical or ionic liquid model is used in the literature. Our preference at TMG is the modified QCM because it is more scientifically sound.

Solid Solutions

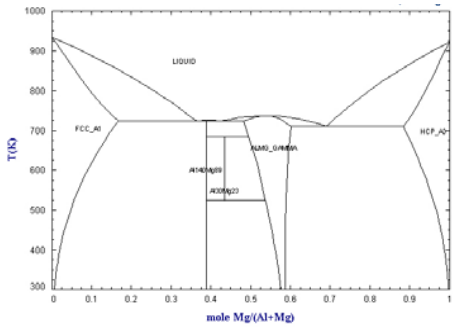
- The mixing in a terminal solid solutions may be substitutional or interstitial.
- Some terminal phases may extend far into the system and this makes it possible to determine the excess Gibbs energy accurately. But often the solubility is very low and one must use few excess parameters.
- In some cases one may have the same terminal phase on both sides but one or more intermediate phases in between. In this case, the terminal phase **must** be modeled as the same phase.

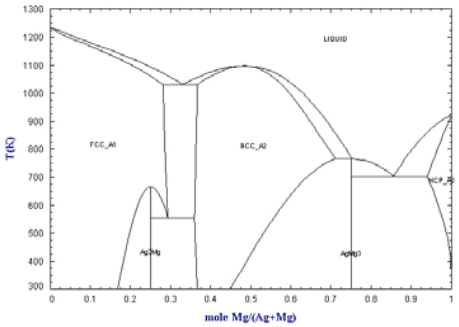




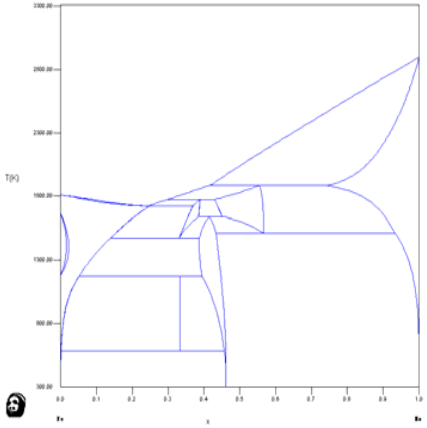
Solid Solutions

- An intermediate phase is any phase which does not extend to the pure elements.
- An intermediate phase can have extensive solubility and a simple lattice like BCC or FCC but often it has restricted solubility and sometimes the structure is unknown. Most often they have at least two sublattices with different constituents. The Compound Energy Formalism (CEF) can often provide a reasonable model.

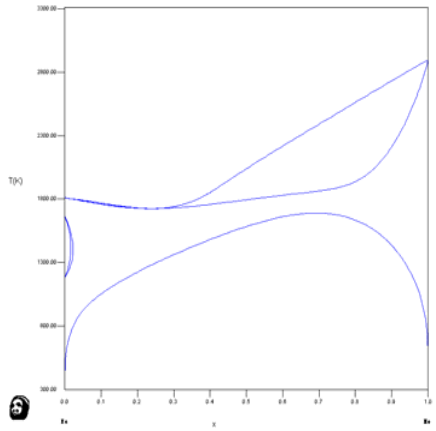




Example: Fe-Mo System



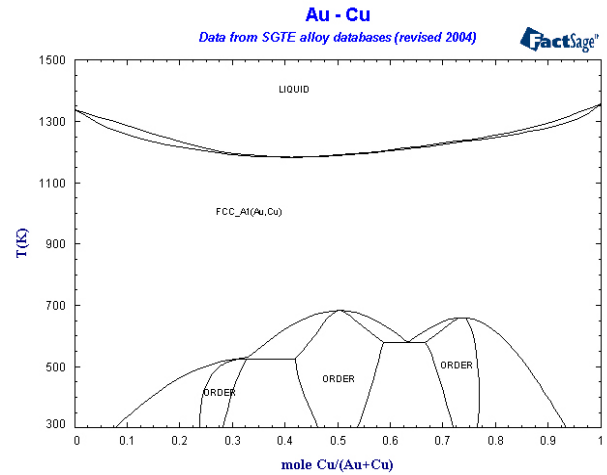
Fe-Mo system



Meta stable phase diagram of Fe-Mo (*without intermediate phases*)

Phases with Order/Disorder Transformations

• Some intermediate phases represent ordered BCC, FCC and HCP lattices.



Phases with Order/Disorder Transformations

• There are a number of established techniques to model phases with order/disorder as the ordered phases should become identical to the disordered phase when the ordering is no longer stable.

• This is achieved by partitioning the Gibbs energy in two parts:

$$G = G^{dis} + \Delta G^{ord}$$

ΔG^{ord} is zero when the phase is disordered

• Partitioning is advantageous because it provides simpler assessment of binaries and ternaries as the ordering part can be assessed independently of the disordered phase. Also, easier merging with other systems where the phase is only disordered. The terms of ΔG^{ord} are just added to the disordered part.

Selection of Model Parameters

• For the liquid and terminal phases the excess parameters need to be optimized.

- *Usually expressed in Redlich-Kister terms*

• For intermediate phases there are Gibbs energy of formation parameters to be optimized.

- *Usually expressed as:* $\Delta G^f = a + bT = \Delta H^f - \Delta S^f T$

• Sometimes those are sufficient but for phases with large solubility, interaction parameters may be assessed also.

Next time:

Ternary Systems