

## Computer Calculation of Equilibria and Phase Diagrams

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3rd lecture

## Homework

- Running assessment example tcex36
- Collecting experimental data for own system
- Selecting models for phases for own system
- Give me floppy or send E-mail with setup and POP file!!!

## Repetition: Data for assessments

- Theoretical information
- Experimental data
- Estimated data
- Assessments of similar systems

## Repetition: Theoretical information

- Thermodynamic relations.
- Stability conditions
- First principle calculations of enthalpies of formation of given compounds.

## Repetition: Experimental data

1. Crystallographic data
2. Physical property data (magnetism)
3. Thermochemical data
4. Phase Diagram data

## Common lattices

<http://cst-www.nrl.navy.mil/lattice/>

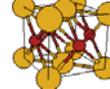
A1



B1



L1<sub>n</sub>



L1<sub>2</sub>



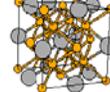
A2



B2



D0<sub>3</sub>



L2<sub>1</sub>



## Entering a phase with sublattices

- Sublattices are specified when the phase is entered in the Gibbs Energy System (G-E-S)

ENTER-PHASE

Name: SIGMA

Type:

Number of sublattices /1/:3

Number of sites in sublattice 1/1.0/: 10

Number of sites in sublattice 2/1.0/: 4

Number of sites in sublattice 3 /1.0/: 16

## Entering constituents

Constituents in sublattice 1:

Name of constituent: Fe

Name of constituent:

Constituent in sublattice 2:

Name of constituent: Cr;

Constituent in sublattice 3:

Name of constituent: Fe Cr

Name of constituent:

Will you add constituents later /N/:

Do you want a list of possible parameters /N/:

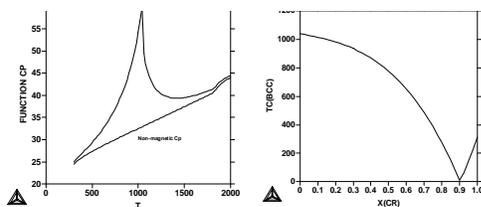
## Physical property data

- Magnetic phases have a Curie temperature and Bohr magneton number that are composition dependent. The magnetic contribution is calculated as
- $G_m^{\text{magn}} = RT f(\tau) \ln(\beta + 1)$
- $\tau = T/TC$ . TC and  $\beta$  are composition dependent.
- The function  $f(\tau)$  is empirical.

## Physical property data

- Magnetic phases are specified with the AMEND-PHASE-DESCRIPTION command in G-E-S. This command requires the "anti-ferromagnetic factor" and the fraction of magnetic enthalpy above the Curie temperature. For FCC phases these are -3 and 0.28, for BCC they are -1 and 0.4
- Note that magnetic transitions at low temperatures may be ignored as the paramagnetic state at high temperature is the reference state.

## Physical property data



## Volume data

- $V0(\text{phase, constituent array})$  is the volume at 298.15 K and 1 bar
- $VA(\text{phase, constituent array})$  is the integrated thermal expansivity at 1 bar.
- Both of these can be composition dependent
- $V = V0(y) \cdot \exp(VA(y, T))$
- $G = p V$
- NOTE: TC (magnetic ordering temperature) can be pressure dependent which affects the volume

### Thermochemical data

- Calorimetric data: enthalpy of formation, ~ of transformation, ~ of mixing
- EMF, Knudsen cell data: chemical potentials, activities
- Partial pressure: activities
- DSC: heat capacity, enthalpy of transformation

### Thermochemical data

- Enthalpy of mixing in the liquid is very useful. Unfortunately almost no one is measuring this any more.
- A theoretical technique to estimate the enthalpy of mixing in the liquid state would be the most useful estimated property.

### Phase Diagram data

- DTA: start/end temperatures of transformations
- Microscope: phase identification, determining phase amounts
- X-ray: phase identification, lattice parameters
- Microsond: phase identification, phase compositions (tie-lines)
- Neutron diffraction: site occupancies

### Estimation of missing data

Missing data that are essential for a good assessment can be estimated in various ways:

- Comparisons with similar systems
- Calculations using first principles
- Miedema or similar estimation formulae

- 3. Creating the experimental data file. Modelling intermetallics like sigma, mu and phases with order/disorder transformations like A2/B2, A1/L1\_2/L1\_0. Partitioning the Gibbs energy. Creating databases from assessments, extrapolations to multicomponent systems.
- Articles: Re-W paper, Ringberg paper.
- Homework: TC example 31, Assessment of Co-V

## The POP file

- Experiments are described like an equilibrium calculation in POLY. Additional information provided as EXPERIMENT or as SET-ALTERNATE-COND. LABEL and GRAPHICAL are useful during optimization.
- ```

CREATE-NEW 5 1
CHANGE-STATUS PHASE FCC LIQ=FIX 1
SET-COND T=1000 P=1E5
LABEL AFL
EXPERIMENT X(LIQ,CR)=0.22 : 0.02
SET-ALTERNATE-COND X(FCC,CR)=0.18
GRAPHICAL 1 0.22 1000 4
COMMENT From Acta Met ?????

```

## The POP file

- Experiments are described independently of the models used for the phases.
- All kinds of experiments can be used in the same POP file.
- Use raw data, not polished or fitted. Never read data from a hand-drawn phase diagram.
- Use GRAPHICAL to plot experimental data from the POP file, SET-ALTERNATE-COND to help with start values, LABEL to handle weights.

## The POP file

- Tables in POP files require only one description of the equilibrium, the same is repeated for each line in table
- ```

TABLE-HEAD 100
CREATE-NEW @@ 1
CHANGE-STATUS PHASE @1 @2 =FIX 1
SET-COND T=@3 P=1E5
EXPERIMENT X(@1,CR)=@4:5% X(@2,CR)=@5:10%
GRAPHICAL 1 @4 @3 5
GRAPHICAL 1 @5 @3 6
LABEL @6
TABLE-VALUES
FCC LIQ 1000 0.18 0.22 AFL
BCC LIQ 1100 0.16 0.20 ABL
...

```

## The POP file

- Thermochemical data can also be used for example this showing an enthalpy of mixing in the liquid

```
CREATE-NEW 200 1
CHANGE-STATUS LIQ=FIX 1
SET-REFERENCE-STATE CR LIQ * 1E5
SET-REFERENCE-STATE FE LIQ * 1E5
SET-COND T=2000 P=1E5 X(CR)=.15
EXPERIMENT HMR=-4500:500
```

## POP file: invariant equilibria

### 3-phase equilibrium

```
CREATE-NEW 1 1
CHANGE-STATUS LIQ BCC FCC=FIX 1
SET-COND P=1E5
EXPERIMENT T=1430:10 X(LIQ,B)=0.23:0.02
SET-ALTERNATE X(BCC,B)=0.15 X(FCC,B)=0.27
```

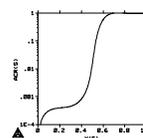
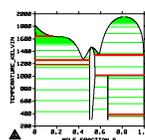
### Congruent melting

```
CREATE-NEW 2 1
CHANGE-STATUS LIQ PYRRHO=FIX 1
SET-COND P=1E5 X(LIQ,S)-X(PYRR,S)=0
EXPERIMENT T=1462:5 X(S)=0.52:0.02
```

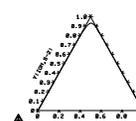
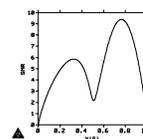
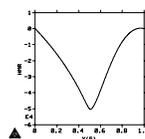
## Model selection

- Special behaviour of data, like strong "V" shaped enthalpy of mixing (sharp raise of activity). In a crystalline phase this indicates long range order, in a liquid short range order.
- Same phase may occur in several places in the system (or related phases like ordered superstructures)
- Use same models as in previous assessments of the same phase.

## Thermochemical properties for Fe-S



The phase diagram and some thermodynamic properties: activity, enthalpy and entropy at 2000 K



## Model selection

- The **liquid phase** in metallic systems is most often modelled with a substitutional regular solution model.
- For metal-nonmetal systems with strongly asymmetric miscibility gaps or rapid change of activities this is often not good and an *associated*, *quasichemical* or *ionic liquid* model may be used instead. These will be described later.

## Model selection

- An **intermediate phase** is any phase which does not extend to the pure elements (or end-members).
- The name **intermediate** is preferred to **intermetallic** as it can also be used for carbides and oxides.
- 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.

## Intermediate phases

- These phases usually have different types of sites with different elements entering these sublattices. For example the  $\sigma$  phase modelled with 3 sublattices with 10:4:16 sites and with "fcc" elements on the first, "bcc" elements on the second and all elements on the third.
- Example  
 $(\text{Co,Fe,Ni})_{10}(\text{Cr,Mo})_4(\text{Co,Cr,Fe,Mo,Ni})_{16}$

## Intermediate phases

- An initial set of parameters for an intermediate phase with sublattices are using the GHSERxx functions like
- $G(\text{MU,FE:MO:FE})=7*\text{GFEECC} + 2*\text{GHSERMO} + 4*\text{GHSERFE}+V1+V2*T$
- V1 is a heat of formation and V2 is an entropy of formation.
- With no  $T \ln(T)$  term one assumes Kopp-Neuman rule for the heat capacity. Only if there are experimental heat capacities one may use a  $T \ln(T)$  term
- It is often enough to use just the G parameters for intermediate phases, one should avoid using interaction parameters.

## Intermediate phases

- Laves phases have the stoichiometry  $A_2B$  and there are several different called C14, C15 and C36. Additionally there are other phases with the same stoichiometry that are not Laves phases.
- It has been a general agreement to model the Laves phases as  $(A,B)_2(B,A)$  assuming that the only defects are anti-sites atoms.
- There is also a general agreement that the pure elements in a Laves phase are given as  $G(\text{Laves},A:A)=3*GHSERAA+15000$

## Intermediate phases

- Carbides and nitrides are usually modelled with one sublattice for the metals and one for the carbon or nitrogen. But sometimes there are several sublattices for the metals.
- The fcc carbonitride, like TiC or VN is modelled as an FCC phase with most of the interstitial sites filled with carbon or nitrogen. This is a second composition set.
- The hcp carbonitride, like  $M_2C$  or  $M_2N$  is also modelled as a second composition set of the HCP phase

## Phases with order/disorder transformations

- Some intermediate phases represent ordered BCC, FCC and HCP lattices. 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
- $G_m = G_m^{\text{dis}}(x) + \Delta G_m^{\text{ord}}(y)$   
 $\Delta G_m^{\text{ord}}$  is zero when the phase is disordered

## Advantages with partitioning

- Simpler assessment of binaries and ternaries as the ordering part can be assessed independently of the disordered phase
- Simpler merging with other systems where the phase is only disordered. Those parameters are just added to the disordered part.

### Entering a partitioned phase

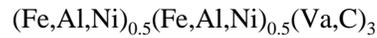
```
ENTER-PHASE BCC_A2 2 1 3 AL FE; VA; N N
ENTER-PHASE BCC_B2 3 0.5 0.5 3
AL FE; AL FE; VA; N N
AMEND-PHASE BCC_B2 DISORD_CONTR BCC_A2
```

Some checks are made on constituents and sites. The first two or four sublattices of the ordered phase must be equivalent to the first sublattice of the disordered phase. One may have a sublattice for interstitials added.

The BCC\_A2 phase will be hidden from POLY and PARROT.

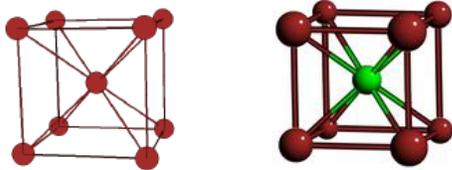
### Order/disorder for BCC

- A2/B2 ordering in BCC is modelled with two sublattices, sometimes also with a third for interstitials.



- B2 ordering require  $G(\text{B2,Fe:Al})=G(\text{B2,Al:Fe})$  as the two sublattices are identical. All interaction parameters on both sublattices must also be equal, for example  $L(\text{B2,Al,Fe:Al:Va})=L(\text{B2,Al:Fe,Al:Va})$ .

### The BCC and B2 structures

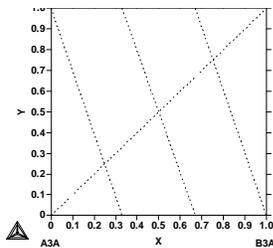


All nearest neighbour bonds are between elements in different sublattices

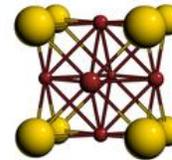
### Order/disorder for FCC and HCP

- A1/L1<sub>2</sub> ordering is often modelled with two sublattices (or 3 with interstitials)  $(\text{Ni,Al,Fe})_{0.75}(\text{Al,Fe,Ni})_{0.25}(\text{Va,C})_1$
- This model has many complicated relations between the parameters because there are nearest neighbour bonds both between the sublattices and within the sublattice with 0.75 sites.

## Constitutional square $A_3B_1$



## The $L1_2$ structure



In a 2 sublattice model the red atoms have 8 nearest neighbours one the same sublattice and 4 nearest neighbours on the other sublattice.

## Order/disorder for FCC

- A better description of ordering in FCC\_A1 is obtained with four sublattices. In this case both  $L1_2$  and  $L1_0$  ordering can be described. The 4 sublattices represent a tetrahedron in the lattice. The relations between the parameters are also simpler as all nearest neighbours are on another sublattice.
- Ordering in HCP\_A3 is treated identically with ordering in FCC\_A1 with 4 sublattice CEF.

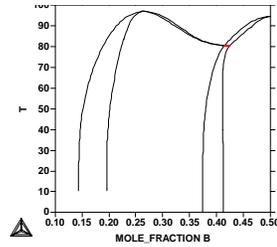
## CVM modelling of FCC ordering

- 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 (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.

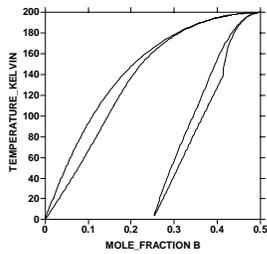
## CVM modelling of FCC ordering

- The disadvantage of CVM is the large number of clusters needed to describe multicomponent systems. With the "tetrahedron" approximation of the FCC lattice one has  $N^4$  clusters (constituents) in an  $N$  component system. The CEF 4 sublattice model would give  $4N$  constituents. As the calculation time increases approximately with  $N^2$  it is important to have as few constituents as possible in the model

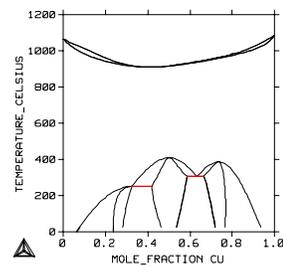
## FCC ordering with CVM



## FCC ordering without SRO



## FCC ordering in Au-Cu



## FCC ordering with 4 sublattices

- All parameters  $G(\text{ORDFCC}, A:A:A:B)$  must be equal independently which sublattice with B.
- All interaction parameters like  $L(\text{ORDFCC}, A,B:A:A:A)$  must be equal independently which sublattice have interaction.
- The 4 sublattice model is a tetrahedron in the FCC lattice and  $G_{A:A:A:B}$  has 3 bonds between A and B.
- $G_{A:A:B:B}$  has 4 bonds between A and B

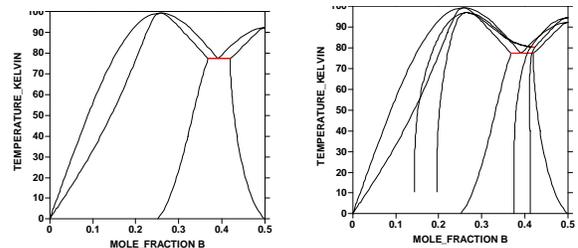
## More about FCC ordering

- In a simple bond energy model when the bond between A and B is independent of the composition we would thus have
- $G_{A:A:A:B} = 3u_{AB}$
- $G_{A:A:B:B} = 4u_{AB}$
- $G_{A:B:B:B} = 3u_{AB}$
- It is possible to calculate metastable G by first principle techniques.

## More about FCC ordering

- In CEF there is no explicit short range order (sro) but it is possible to show that a first approximation of the contribution to the Gibbs energy from sro can be modelled by the reciprocal parameters  $L_{A,B:A,B:A:A}$
- If these cannot be fitted to experimental data one can use the approximation  $L_{A,B:A,B:A:A} = u_{AB}$

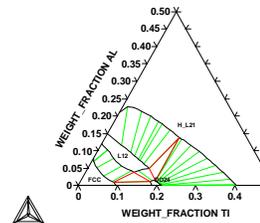
## FCC ordning with CVM and CEF



## Ordering in ternaries

A third component added to an ordered phase may stabilize or destabilize the ordering. If the third component does not form this ordered phase it may be necessary to use first principle calculations to determine if the component would enhance the ordering or not.

## Al-Ni-Ti at 1273 K



## Creating databases

- From an assessment (the PAR file) one can create a template for a database with the command LIST-DATA in G-E-S.
- LIST-DATA myfile N
- After creating the template all optimized V coefficients must be replaced by their numeric value in the TDB file.

## Creating databases

- One should add references to the parameters
- One should add an automatic calculation of the binary system with ASSESSED\_SYSTEM
- One can merge TDB files with a check of parameters and functions with the MERGE program.
- One can add various features like creating several composition sets for miscibility gaps depending on selected elements etc.

## Sample TDB file This is from tcex21

```

$ The basic syntax is  KEYWORD DATA !
$ DATA can be several lines. The KEYWORD is terminated by !
$
$ Keyword ELEMENT <symbol> <refer. phase> <mass> <H298-H0> <S298> !
$ The electron is denoted by /- and the vacancy by VA
ELEMENT /-  ELECTRON_GAS  0.0000E+00  0.0000E+00  0.0000E+00!
ELEMENT VA  VACUUM       0.0000E+00  0.0000E+00  0.0000E+00!
ELEMENT CR  BCC_A2      5.1996E+01  4.0500E+03  2.3560E+01!
ELEMENT FE  BCC_A2      5.5847E+01  4.4890E+03  2.7280E+01!
ELEMENT NI  FCC_A1      5.8690E+01  4.7870E+03  2.9796E+01!

```

```

$ Keyword FUNCTION <symbol> <expression> !
$ <expression> is explained in manual
FUNCTION GHSERCR  298.15  -8856.94+157.48*T-26.908*T*LN(T)
+0.00189435*T**2-1.47721E-06*T**3+139250*T**(-1);  2.18000E+03  Y
-34869.344+344.18*T-50*T*LN(T)-2.88526E+32*T**(-9);  6000  N !
FUNCTION GFELIQ  298.15  +12040.17-6.55843*T-3.6751551E-21*T**7
+GHSERFE#;  1.81100E+03  Y
-10839.7+291.302*T-46*T*LN(T);  6000  N !

```

```

$ Keyword TYPE_DEFINITION <character> <directive> !
$ Character is any single character except ,
$ This keyword is used for many different things. Some more examples
$ are shown
$ below, read the manual for full description.
$ The type definition here is to specify that the parameters for a
$ phase
$ should be read sequentially from the current file.
TYPE_DEFINITION % SEQ *!
$ These are directives to the TDB module, explained in manual
DEFINE_SYSTEM_DEFAULT ELEMENT 2 !
DEFAULT_COMMAND DEF_SYS_ELEMENT VA !

```

```

$ Keyword PHASE <name> <type codes> <number of sublattices>
$ <sites in each> !
$ Name must start with letter followed by max 23 letters, digits and _
$ Type codes are single letters that can give extra info about the
$ phase,
$ if magnetic etc. All phases must have a type code specifying where
$ the parameters are. Here all has the type code % for that. This type
$ code is explained above
PHASE LIQUID:L % 1 1.0 !
$ Keyword CONSTITUENT <phase name> : <const. in first subl.> : ... !
$ Constituents that should be major in a sublattice is suffixed with %
$ (See FCC below)
CONSTITUENT LIQUID:L :CR,FE,NI : !

```

```

$ Keyword PARAMETER <name> <expression> <reference symbol> !
$ The parameter name consist of
$ <identifier> ( <phase> , <constituent array> ; <degree> )
$ Identifier can be G, L, TC, BMAGN, VO, VKAPPA etc.
$ Expression is the same as for function
$ Reference symbol can be any 8 character symbol
PARAMETER G(LIQUID,CR;0) 298.15 +24339.955-11.420225*T
+2.37615E-21*T**7+GHSERCR#; 2.18000E+03 Y
+18409.36-8.563683*T+2.88526E+32*T**(-9)+GHSERCR#; 6000 N 91Din !
PARAMETER G(LIQUID,FE;0) 298.15 +GFELIQ#; 6000 N 91Din !
PARAMETER G(LIQUID,NI;0) 298.15 +11235.527+108.457*T
-22.096*T*LN(T)-.0048407*T**2-3.82318E-21*T**7; 1.72800E+03 Y
-9549.775+268.598*T-43.1*T*LN(T); 3.00000E+03 N 91Din !
PARAMETER G(LIQUID,CR,FE;0) 298.15 -14550+6.65*T; 6000 N 87And2 !

```

```

$ The type definition below specifies that BCC_A2 is a magnetic phase
$ The arguments to AMEND_PHASE:DESCRIPTION are the same as in G-E-S
TYPE_DEFINITION & GES AMEND_PHASE_DESCRIPTION BCC_A2 MAGNETIC -1.0 0.4 !
$ The second sublattice is for interstitials like C and N
PHASE BCC_A2 %& 2 1 3 !
$ The suffix % indicates that CR and FE can be major in BCC
$ The major constituents are used when setting automatic start values.
$ The only interstitials in 2nd sublattice is vacancies.
CONSTITUENT BCC_A2 :CR%,FE%,NI :VA% : !
PARAMETER G(BCC_A2,CR:VA;0) 298.15 +GHSERCR#; 6000 N 91Din !
PARAMETER TC(BCC_A2,CR:VA;0) 298.15 -311.5; 6000 N 91Din !
PARAMETER BMAGN(BCC_A2,CR:VA;0) 298.15 -.008; 6000 N 91Din !
PARAMETER G(BCC_A2,FE:VA;0) 298.15 +GHSERFE#; 6000 N 91Din !
PARAMETER TC(BCC_A2,FE:VA;0) 298.15 1043; 6000 N 91Din !
PARAMETER BMAGN(BCC_A2,FE:VA;0) 298.15 2.22; 6000 N 91Din !
PARAMETER G(BCC_A2,NI:VA;0) 298.15 +GNIBCC#; 3.00000E+03 N 91Din !
PARAMETER TC(BCC_A2,NI:VA;0) 298.15 575; 6000 N 91Din !
PARAMETER BMAGN(BCC_A2,NI:VA;0) 298.15 .85; 6000 N 91Din !
PARAMETER G(BCC_A2,CR,FE:VA;0) 298.15 +20500-9.68*T; 6000 N 87And2 !
PARAMETER BMAGN(BCC_A2,CR,FE:VA;0) 298.15 -.85; 6000 N 87And2 !
PARAMETER TC(BCC_A2,CR,FE:VA;0) 298.15 1650; 6000 N 87And2 !
PARAMETER TC(BCC_A2,CR,FE:VA;1) 298.15 550; 6000 N 87And2 !

```

```

LIST_OF_REFERENCES
NUMBER SOURCE
91Din 'A.T. Dinsdale, SGTE Data for Pure Elements,
Calphad 15(1991)4, p 317-425; '
87And2 'J.O. Andersson, B. Sundman, Calphad 11(1987)1 p 83-92
TRITA-MAC 270 (1986); Cr-Fe'
91Lee1 'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
92Lee3 'Byeong-Joo Lee, Calphad 16(1992)2, p 121-149; carbides'
86Din1 'A. Dinsdale, T. Chart, MTDS NPL, unpublished work (1986); Fe-Ni'
86Din2 'A. Dinsdale, T. Chart, MTDS NPL, unpublished work (1986); Cr-Ni'
88Gui2 'A.F. Guillermet, Z. Metallkde. 79(1988)8 p 524-536,
TRITA-MAC 362 (1988); C-Co-Ni, C-Co-Fe-Ni'
90Fri1 'K. Frisk, Metall. Trans. 21A (1990)9 p 2477-2488, Cr-Fe-N'
UNASS2 'Unassessed parameter, linear combination of unary data.'
88Gus6 'P. Gustafson, Calphad 12(1987)3 p 277-292, Cr-Ni-W '
!

```

```

ASSESSED_SYSTEM
CR-FE(TDB -HCP ;G5 C_S:BCC/CR:VA MAJ:BCC/FE:VA ;P3 STP:.6/1200/1/-2/2)
!

```

## Parameter notation

A parameter is denoted <symbol><phase>, <constituent-array>;<degree> <function of T and p>

- <symbol> can be G or L for energy parameters, TC for magnetic transition temperature, V0 for volume at 298.15 and 1 bar etc.
- A constituent array has at least one constituent in each sublattice. These constituents are separated by colon ":".
- An interaction parameter has two or more constituents in one or more sublattices. The interaction constituents are separated by a comma ",".
- An interaction parameter may have a "degree" and the meaning of this depends on the excess model of the phase. Default degree is zero.

## Parameter notation

- The <function> is written with a <low T limit>, <expression terminated with semicolon ";">, <high T limit> followed by a Y or N if there is an expression above the high T limit.
- Examples: Gibbs energy of pure FCC Cr  
G(FCC,Cr) 298.15 GHSERCR+7284+0.163\*T; 6000 N
- GHSERCR is the name of a function that describes the properties of pure BCC Cr and is entered separately and can be used for several parameters.

## Parameter notation

- The vacancy, Va, is a possible constituent in a sublattice. Interstitial sublattices are normally mainly vacant i.e. filled with vacancies. Note that parameters are for a formula unit of a phase. Thus G(FCC,Fe:Va) is for one mole of Fe and G(FCC,Ti:C) is for two moles of atoms, one Ti and one C.
- Example of interaction parameters are  
L(FCC,Fe,Cr:Va;0) 298.15 10833-7.48\*T; 6000 N  
L(FCC,Fe,Cr:Va;1) 298.15 1410; 6000 N

## kursPM

- 3: Modelling intermetallics. Order/disorder. Partitioning of Gibbs energy. Creating databases
- Papers: CVM by Colinet, CVM implemented in TC, Al-Ni, Au-Cu, Al-Cr-Ni, Fe-Si-C, Re-W, Cd-Te,