

Thermo-Calc Software

Data Organization and Knowledge Discovery

Thermo-Chemistry to Phase Diagrams and More

Paul Mason

Thermo-Calc Software, Inc.

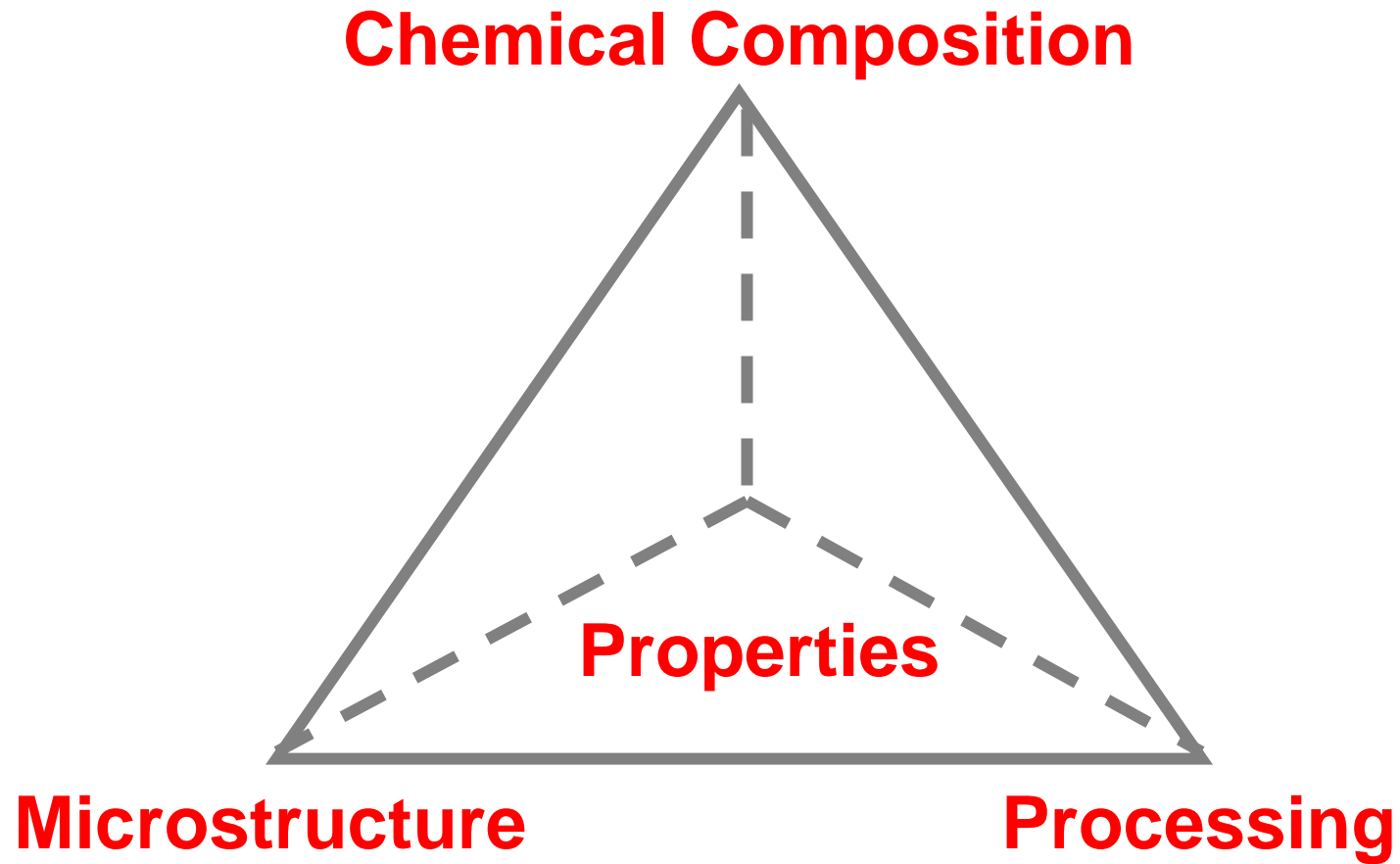
<http://www.thermocalc.com>
E-mail: paul@thermo-calc.com

Tel: (724) 731 0074
Fax: (724) 731 0078

Introduction

- **This part of the program will focus on the role of computational thermodynamics in the broader scheme of Materials Informatics.**
- **Computational thermodynamics and the so-called CALPHAD method is well established. As will be seen, it is in a sense a microcosm of the broader framework of Materials Informatics, as it integrates numerous aspects of data manipulation and transformation in a collection and self-consistent transformational scheme to get out much more than the basic data provide.**

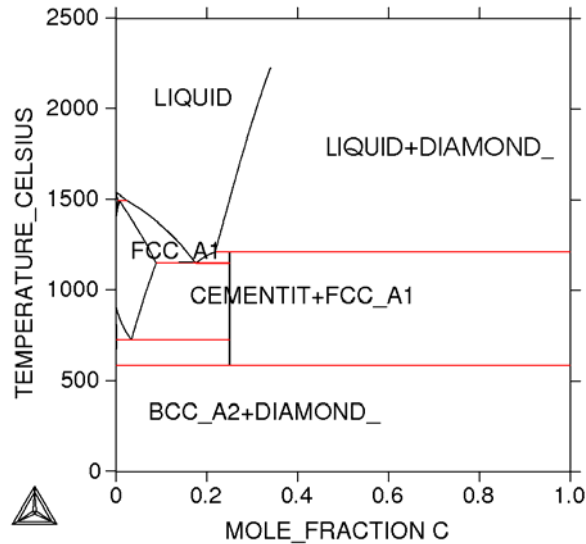
Paradigm of Materials Science and Engineering



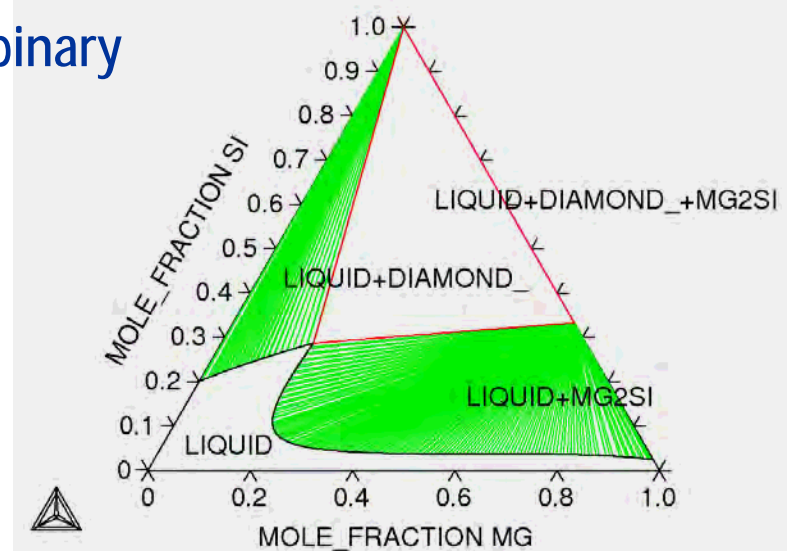
What is Computational thermodynamics / CALPHAD? (1)

- **“CALPHAD (Computer Coupling of Phase Diagrams and Thermo chemistry) aims to promote computational thermodynamics through development of models to represent thermodynamic properties for various phases which permit prediction of properties of multicomponent systems from those of binary and ternary subsystems, critical assessment of data and their incorporation into self-consistent databases, development of software to optimize and derive thermodynamic parameters and the development and use of databanks for calculations to improve understanding of various industrial and technological processes.”**
- **<http://www.calphad.org>**

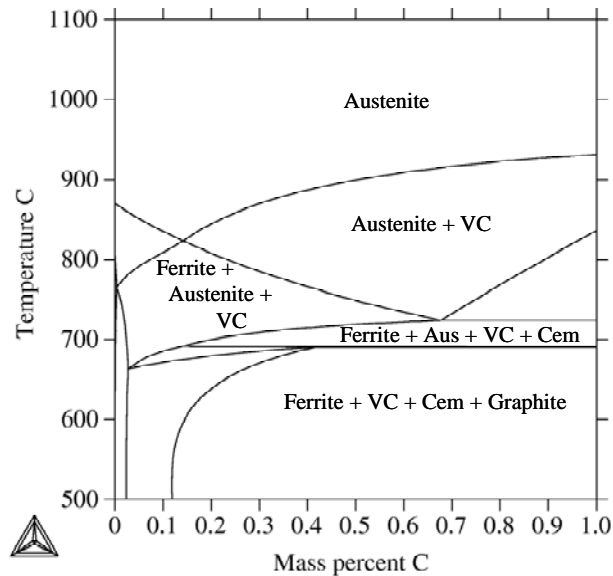
What is Computational thermodynamics / CALPHAD? (2)



Fe-C metastable binary

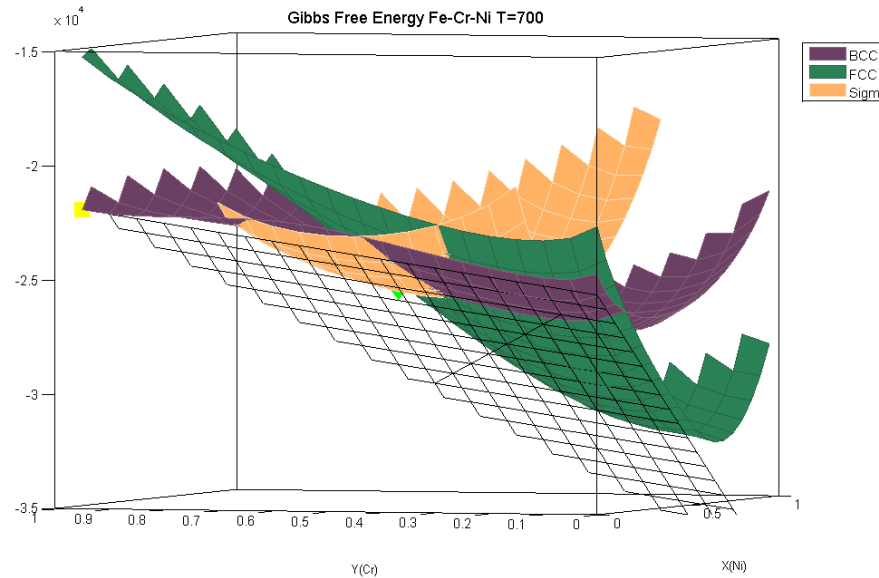


Al-Mg-Si ternary at 700 deg. C



Fe-1.5Mn-0.3Si-0.1V-C HSLA Steel

What is Computational thermodynamics / CALPHAD? (3)



- In the CALPHAD approach to modeling thermodynamics, the modeling of the Gibbs energy of individual phases and the coupling of phase equilibria and thermo-chemistry are key to developing internally consistent thermodynamic descriptions of multi-component materials with sound fundamentals and predictive power because these two sets of data are deduced from the minimization of the Gibbs energy of individual phases under given constraints.

Early History of CALPHAD and Thermo-Calc

1969 Formation of CALPHAD.

1971 Sublattice model for 2 comp. (Hillert and Staffansson, KTH).

1977 Development of Thermo-Calc starts. KTH member of SGTE.

1981 First version of Thermo-Calc.

1981 Sublattice model for multicomponent systems.

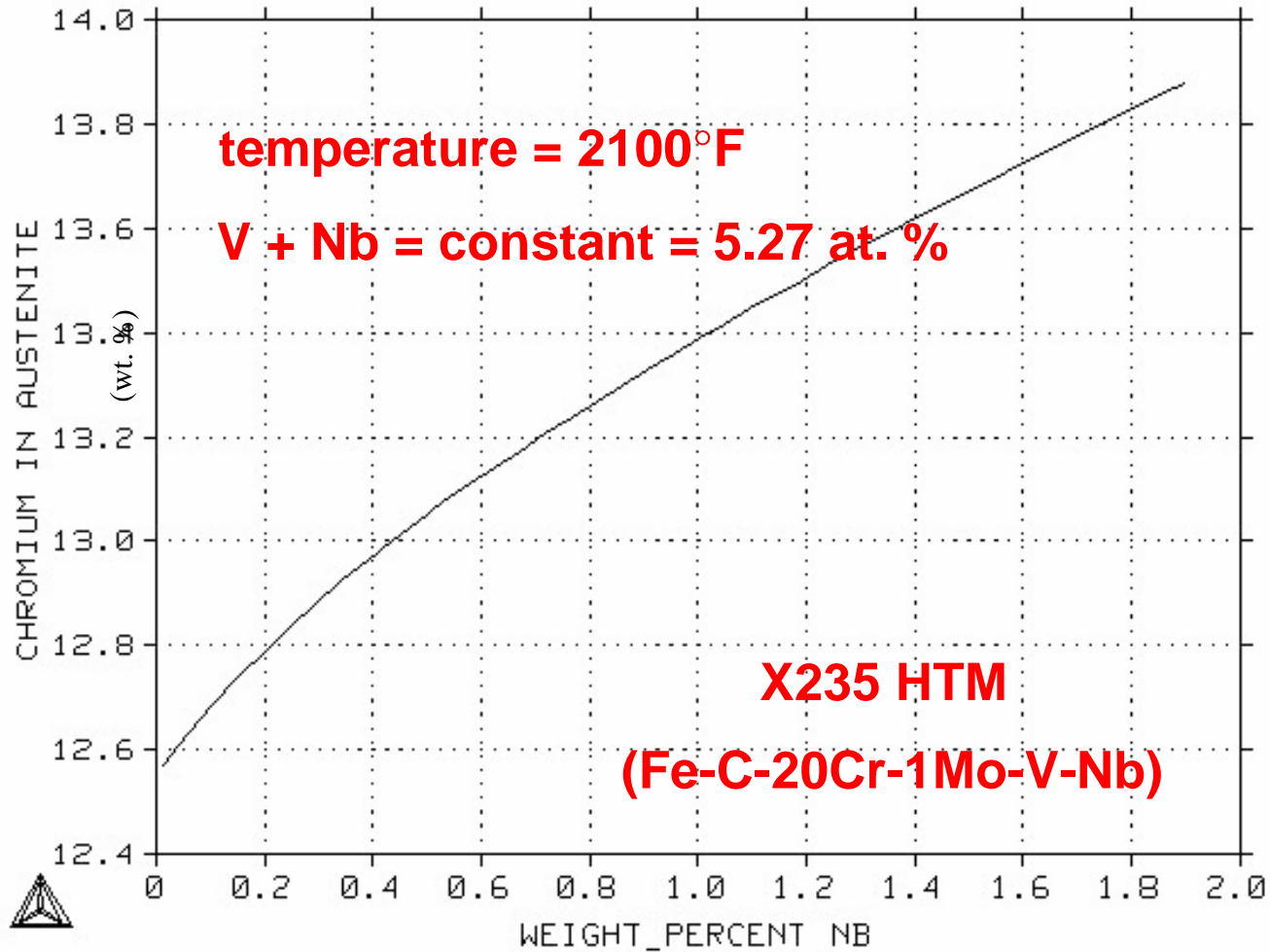
1984 First sale of TC and the Fe-data base.

1988 SGTE Solution database (SSOL)

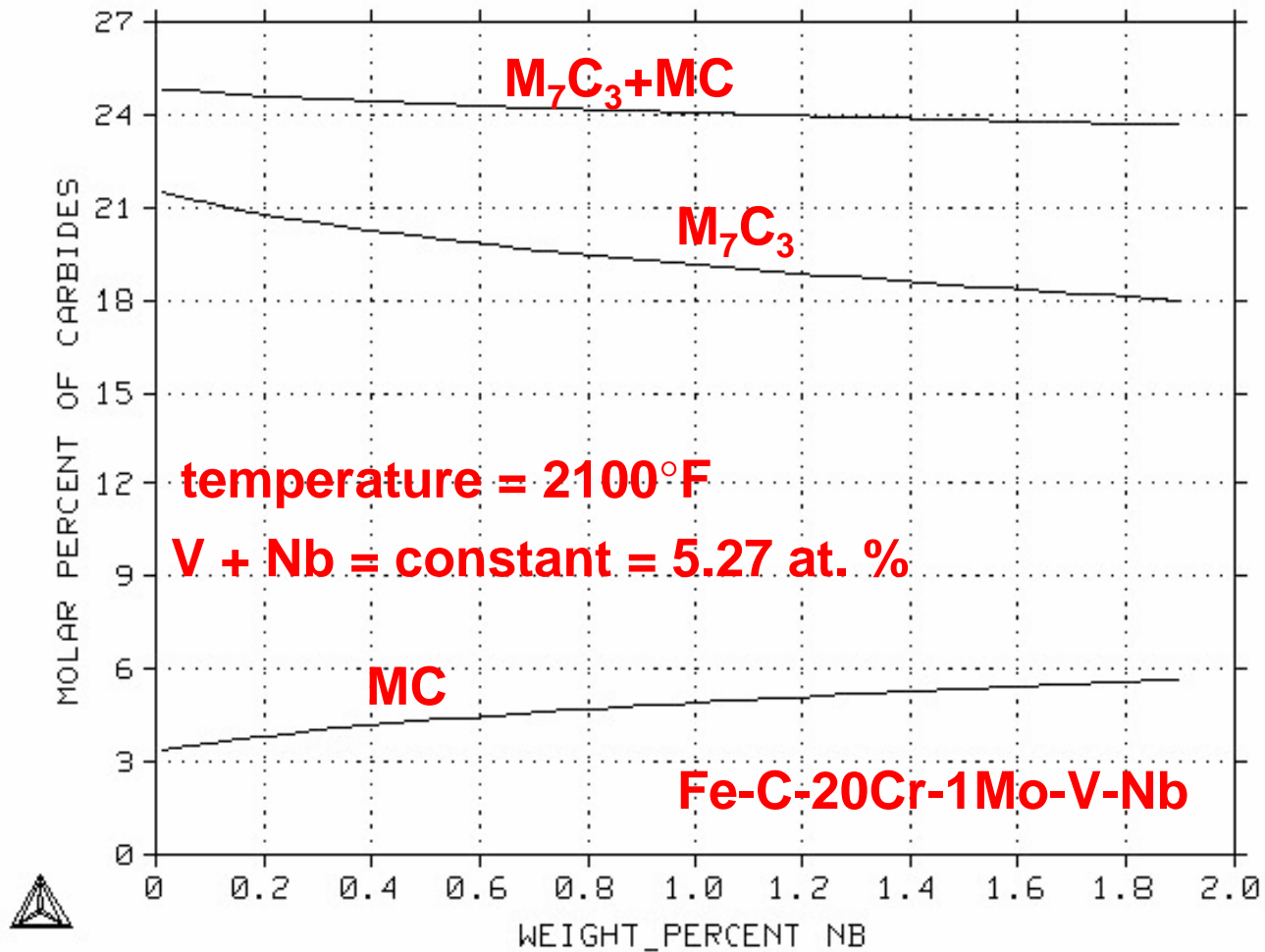
Success stories (1)

- **CALPHAD (and broader Computational Thermodynamics) has been successful over many years in extending phase diagram knowledge from binary and ternary systems into multi-component systems for real alloys and other systems and processes of interest as the following examples illustrate.**

Success stories (2)



Success stories (3)



Success stories (4)

Carburizing and decarburization

Microsegregation during solidification

Precipitate growth and dissolution

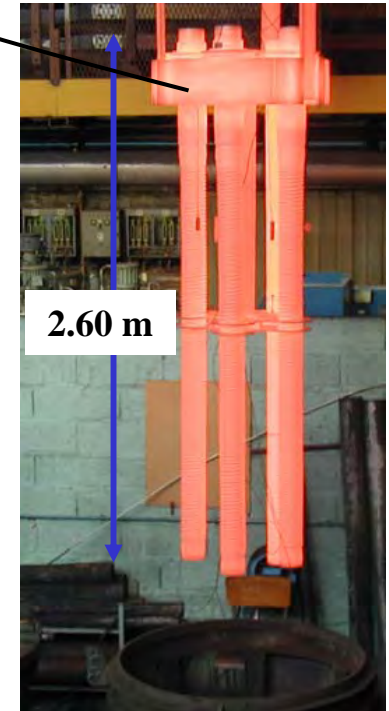
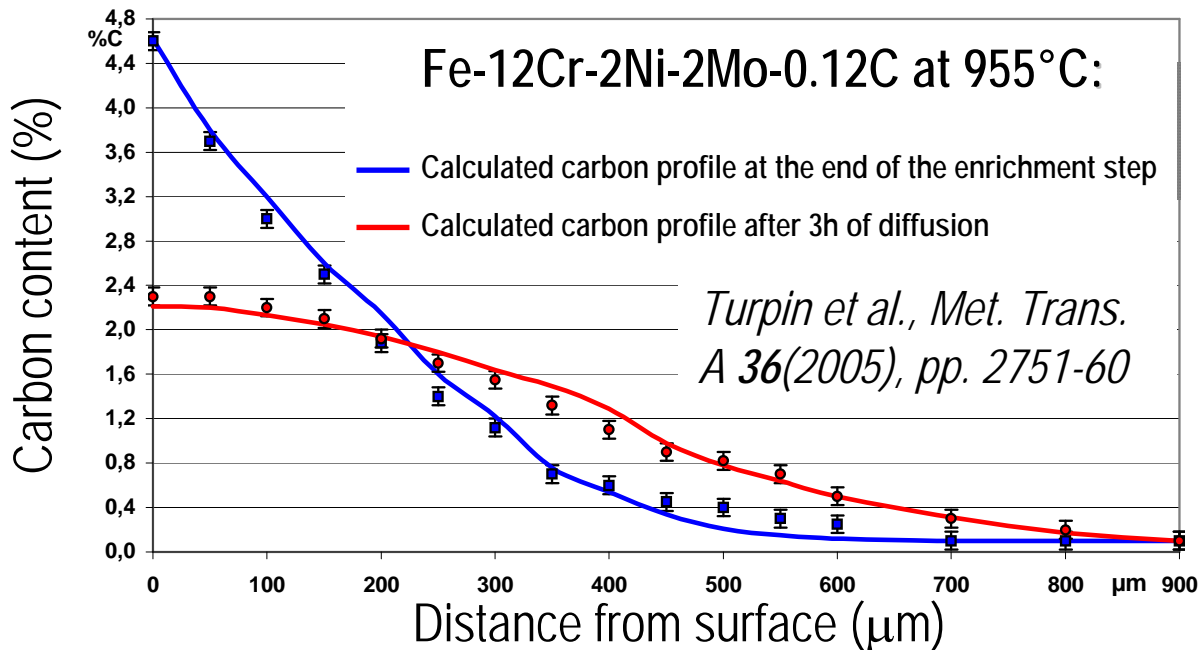
Precipitate coarsening

Interdiffusion in coating/substrate

TLP bonding of alloys and more...



Example: *Simulation of carbon evolution in high alloyed steels by Aubert & Duval, France.*



Behind Thermo-Calc

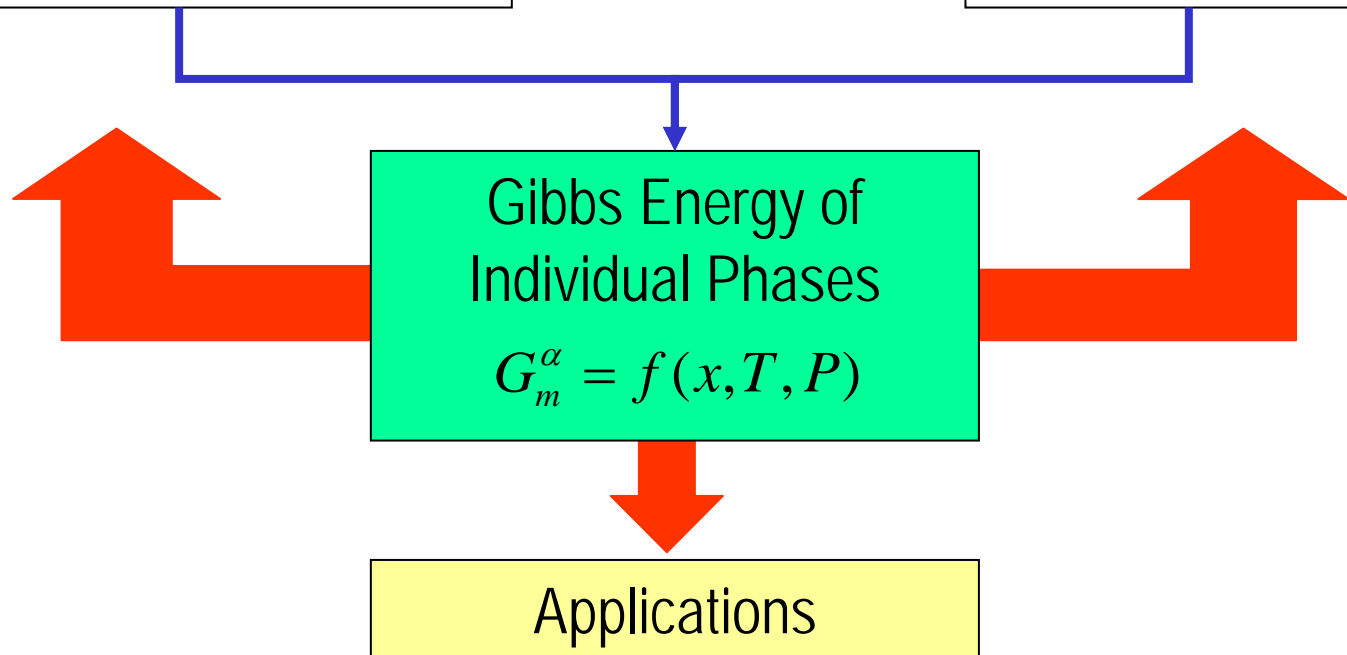
Thermodynamic Databases (*The CALPHAD approach*)

Thermochemical measurements:

- Enthalpy
- Entropy
- Heat capacity
- Activity

Phase equilibria:

- Liquidus
- Solidus
- Phase boundary



Transforming Data

- **Thermo-Calc Software as a company (and through our products, Thermo-Calc and DICTRA) rely on data and use data to add value to the data collection and modeling process.**
- **Our products and databases are built on good quality experimental data (and where necessary supplemented using theoretical techniques). As such, data is an input for us.**
- **Our products also generate and output data. Value is added by taking experimental and theoretical data, developing modular databases based on the well established CALPHAD methodology which allows calculations to be made for higher order, multicomponent multiphase systems of industrial relevance (e.g. alloy design / process optimization and operational performance).**
- **This approach makes data re-usable and applicable across a broad range of systems and also provides an important building block for multi-scale modeling approaches.**

What do we mean by a database? (1)

A (thermodynamic) database in our understanding means a collection of polynomials describing the Gibbs energy of individual phases of a system as a function of temperature, (pressure) and composition.

What do we mean by a database? (2)

$$G_m^{hcp} = x_{Co} {}^0G_{Co}^{nhcp} + x_{Ni} {}^0G_{Ni}^{nhcp} + RT(x_{Co} \ln x_{Co} + x_{Ni} \ln x_{Ni}) \\ + {}^{ex}G_m^{nhcp} + {}^{mag}G_m^{hcp},$$

where

$${}^0G_{elem}^{ph} = a + bT + cT \ln T + dT^{-1} + eT^2 + fT^{-2} + \dots$$

$${}^{ex}G_m^{nhcp} = x_{Co} x_{Ni} \sum_{i=0}^j (x_{Co} - x_{Ni})^i {}^iL_{Co,Ni}^{hcp}$$

$${}^iL_{Co,Ni}^{hcp} = A + BT$$

$${}^{mag}G_m^{hcp} = \text{an expression of similar form as } G_m^{hcp}$$

What do we mean by a database? (3)

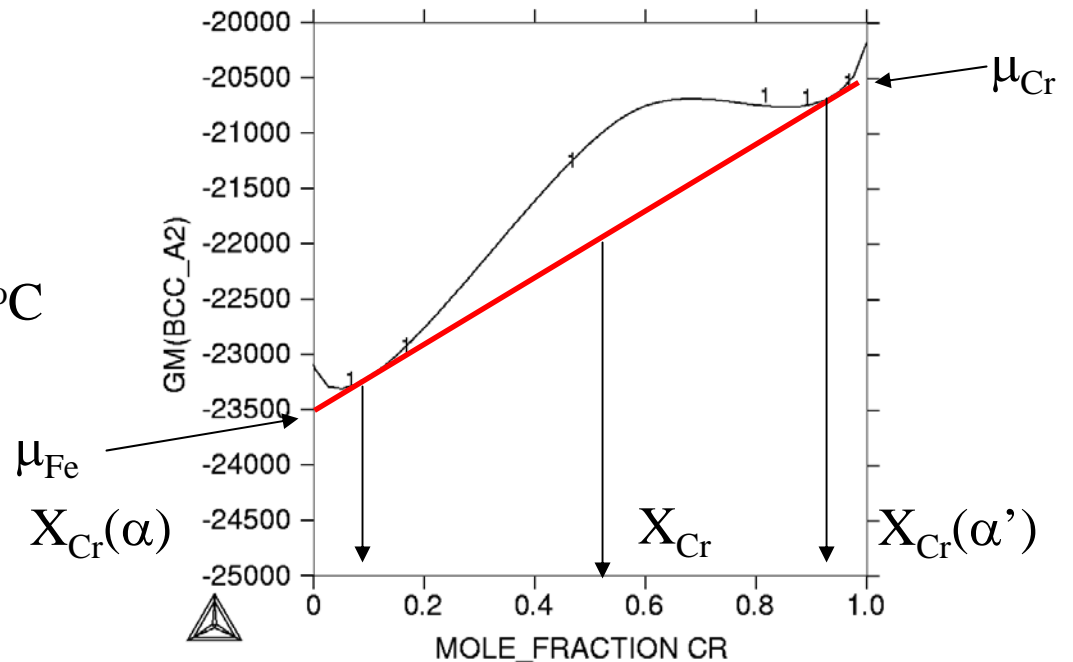
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PARAMETER G(HCP_A3,CO:VA;0) 298.15 +GHSERCO;,,N !
PARAMETER G(HCP_A3,NI:VA;0) 298.15 +GHCPNI;,,N !
FUNCTION GHSERCO 298.15 +310.241+133.36601*T
-25.0861*T*LN(T)-.002654739*T**2-1.7348E-07*T**3
+72527*T**(-1) 1768.0 Y -17197.666+253.28374*T
-40.5*T*LN(T)+9.3488E+30*T**(-9);,, N !
FUNCTION GHSERNI 298.15 -5179.159+117.854*T
-22.096*T*LN(T)-.0048407*T**2;
1728.0 Y -27840.655+279.135*T-43.1*T*LN(T)
+1.12754E+31*T**(-9);,, N !
PARAMETER L(HCP_A3,CO,NI:VA;0) 298.15 -1620-.385*T;,,N !
PARAMETER TC(HCP_A3,CO:VA;0) 298.15 +1396;,,N !
PARAMETER BMAGN(HCP_A3,CO:VA;0) 298.15 1.35;,,N !
PARAMETER TC(HCP_A3,NI:VA;0) 298.15 633;,,N !
PARAMETER BMAGN(HCP_A3,NI:VA;0) 298.15 .52;,,N !
PARAMETER TC(HCP_A3,CO,NI:VA;0) 298.15 411;,,N !
```


Calculation of Equilibrium

Equilibrium can be calculated from a minimisation of Gibbs Energy. The common tangent construction in a binary system

Example:

G_m for ferrite in Fe-Cr at 400°C



Data in, Data transformed, Data stored and Data out

3 Categories of data

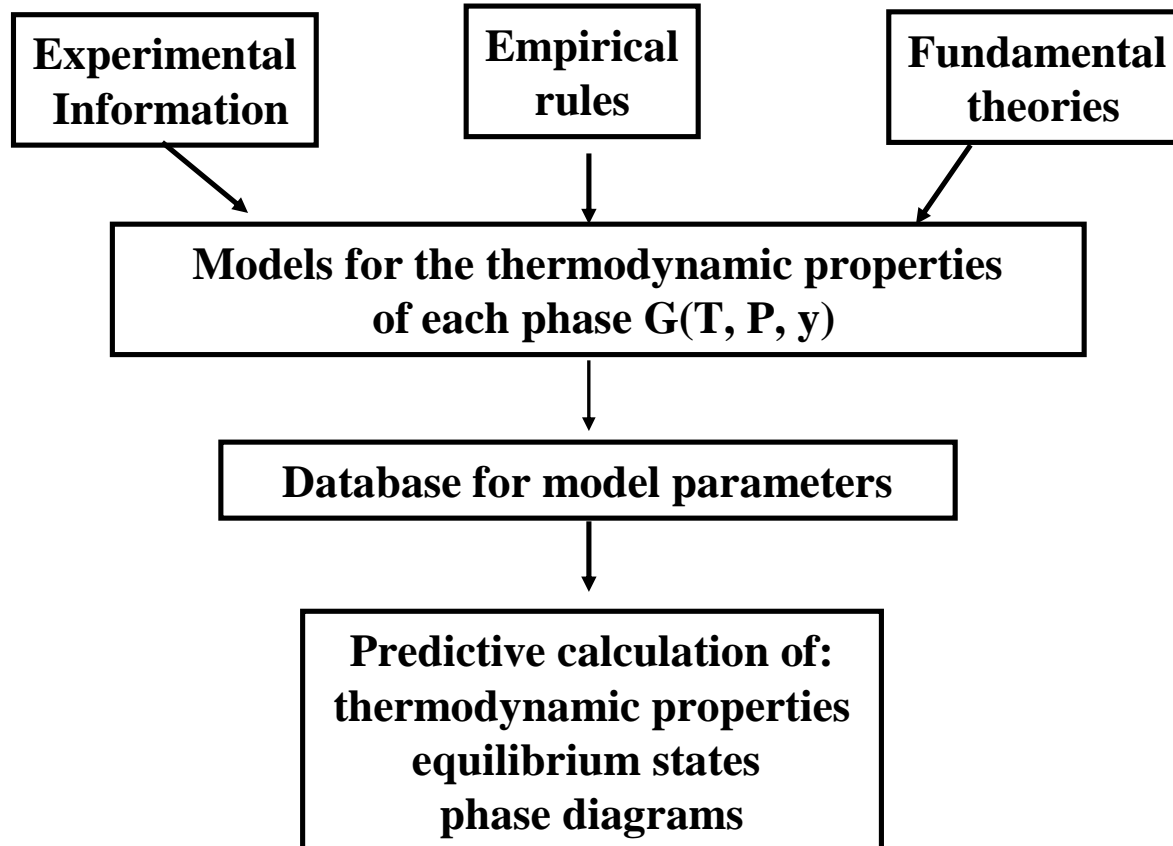
- **Raw Data (data in)**
 - **Experimental data**
 - **Theoretical data**

- **Refined/Assessed/Transformed Data (data stored, databases)**
 - **Do not store raw data**
 - **Gibbs energies stored as polynomial functions**
 - **Critically assessed interaction parameters enable calculated reproduction of experimental data**

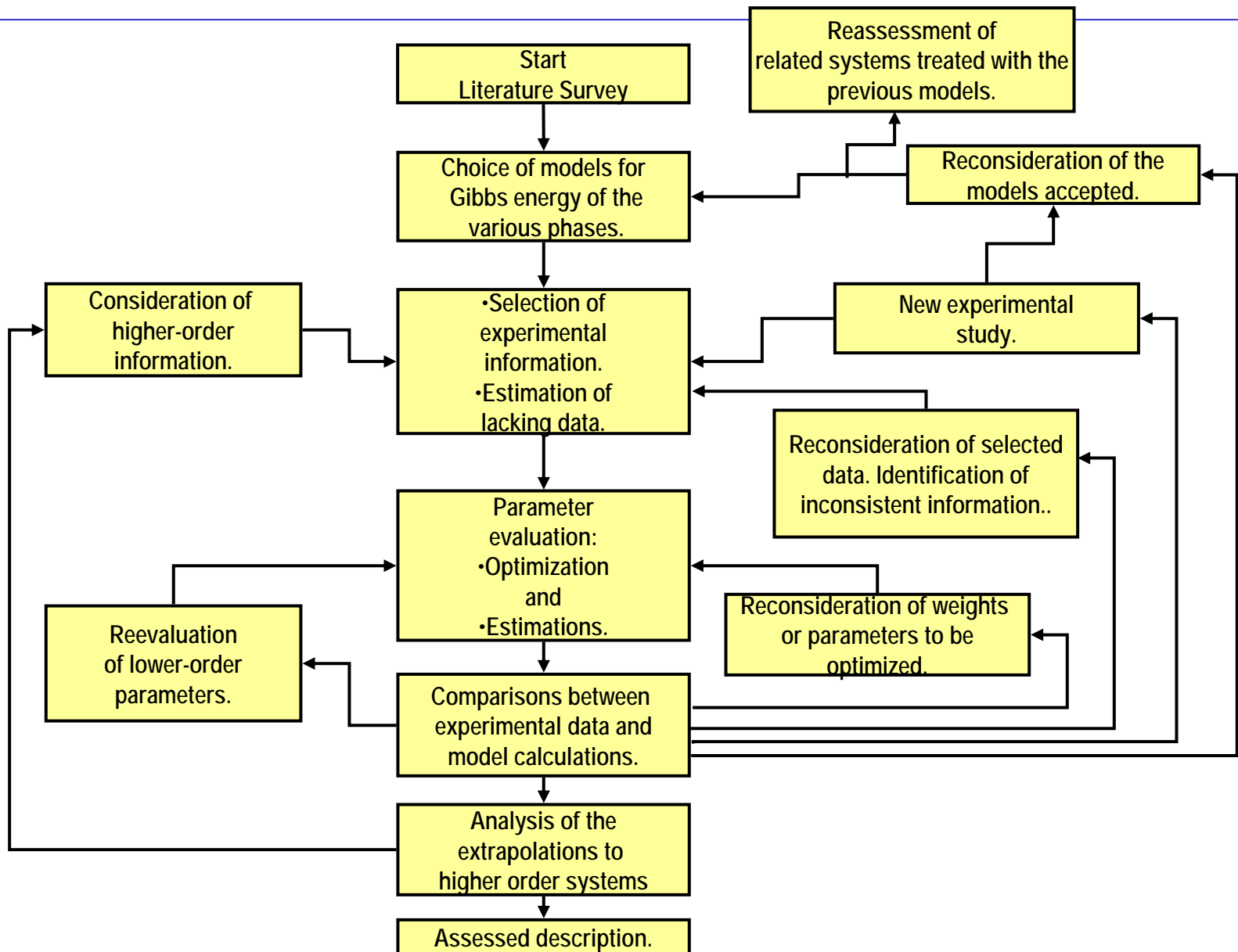
- **Calculated Data (Data out)**
 - **Reproduce most of the raw data.**
 - **Make predictions in industry-relevant high-order multicomponent systems with just data from the constituent low-order systems**

The CALPHAD method

CALculation of PHase Diagrams



Optimization Procedure



Sources of thermodynamic data

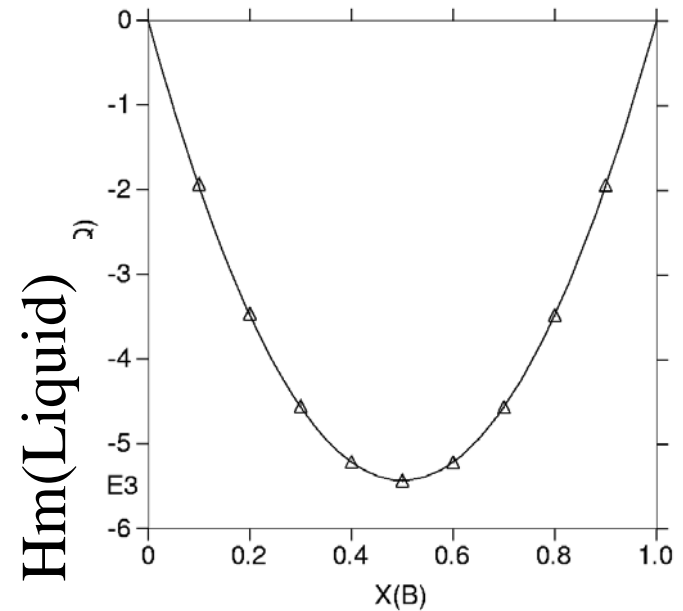
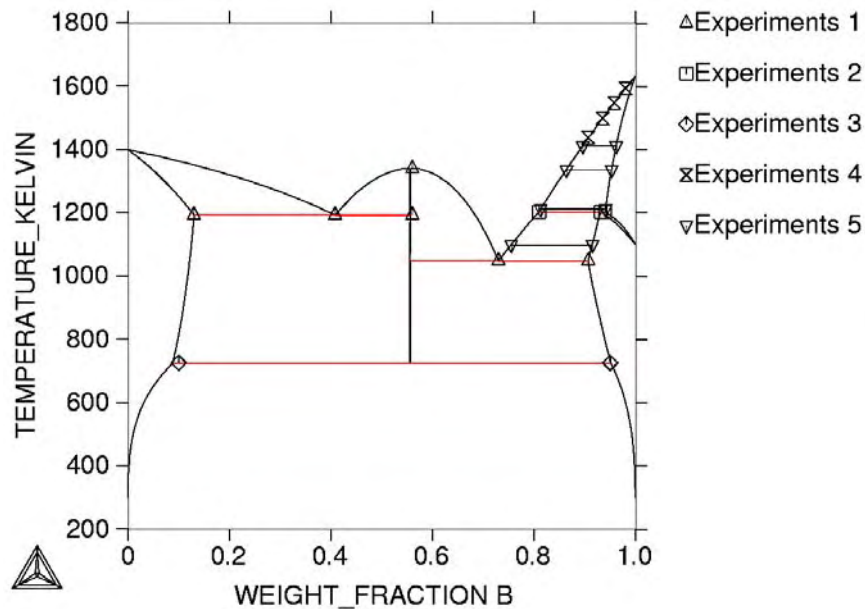
Two types of data

- Basic thermodynamic and phase equilibrium data – the building blocks of thermodynamic databases
 - Experimental
 - Phase equilibrium (phase diagrams) for binary and ternary system (liquidus/solidus/phase boundary)
 - Thermodynamic data for compounds/stoichiometric phases
 - Activity measurements etc
 - Theoretical
 - Estimation and Ab initio calculations

- Higher order (multi-component data) – validation for alloys etc
 - Experimental
 - Cp, liquidus/solidus/phase boundary data etc for “real” alloys
 - Volume fraction of carbides etc

Binary and ternary systems

- Normally collected from the literature
- Reliable data is selected and critically assessed
- Both phase diagram data or thermodynamic data ($\Delta H, C_p, \dots$) can be used



Higher order systems: Real alloys for validation (1)

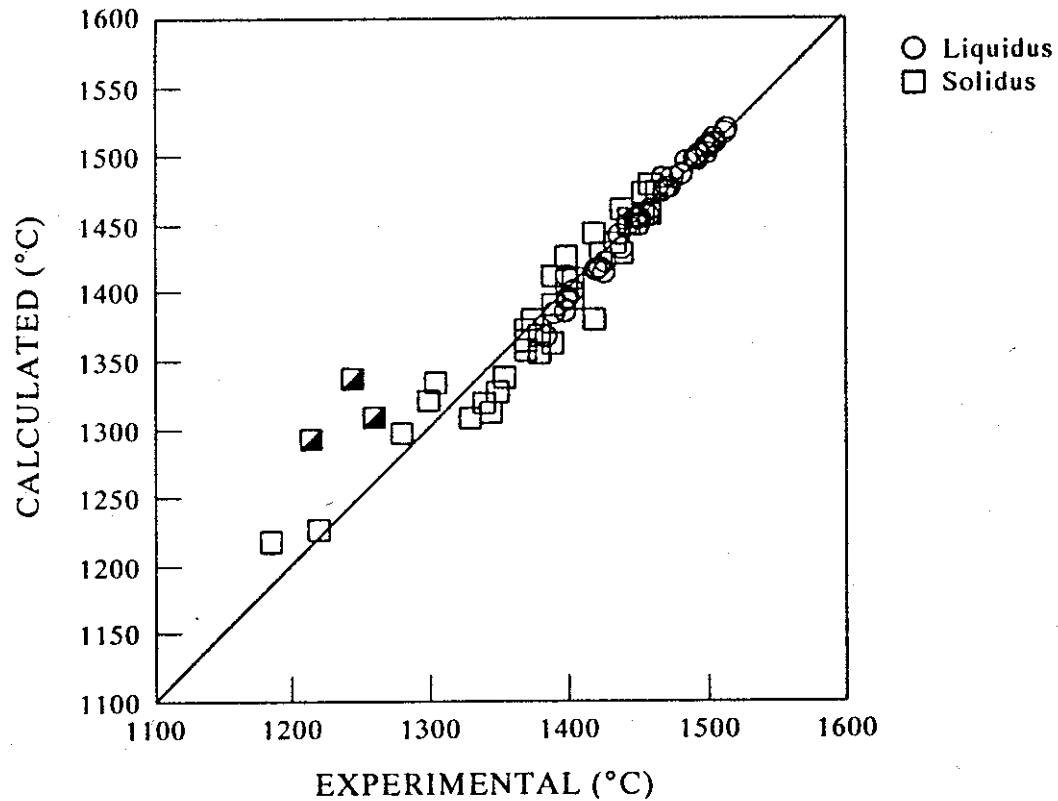


Figure 10.37 Comparison between calculated and experimental (Jernkonteret 1977) solidus and liquidus values of a range of steels.

From: Saunders & Miedownik: "Calphad -a comprehensive review"

Higher order systems: Real alloys for validation (2)

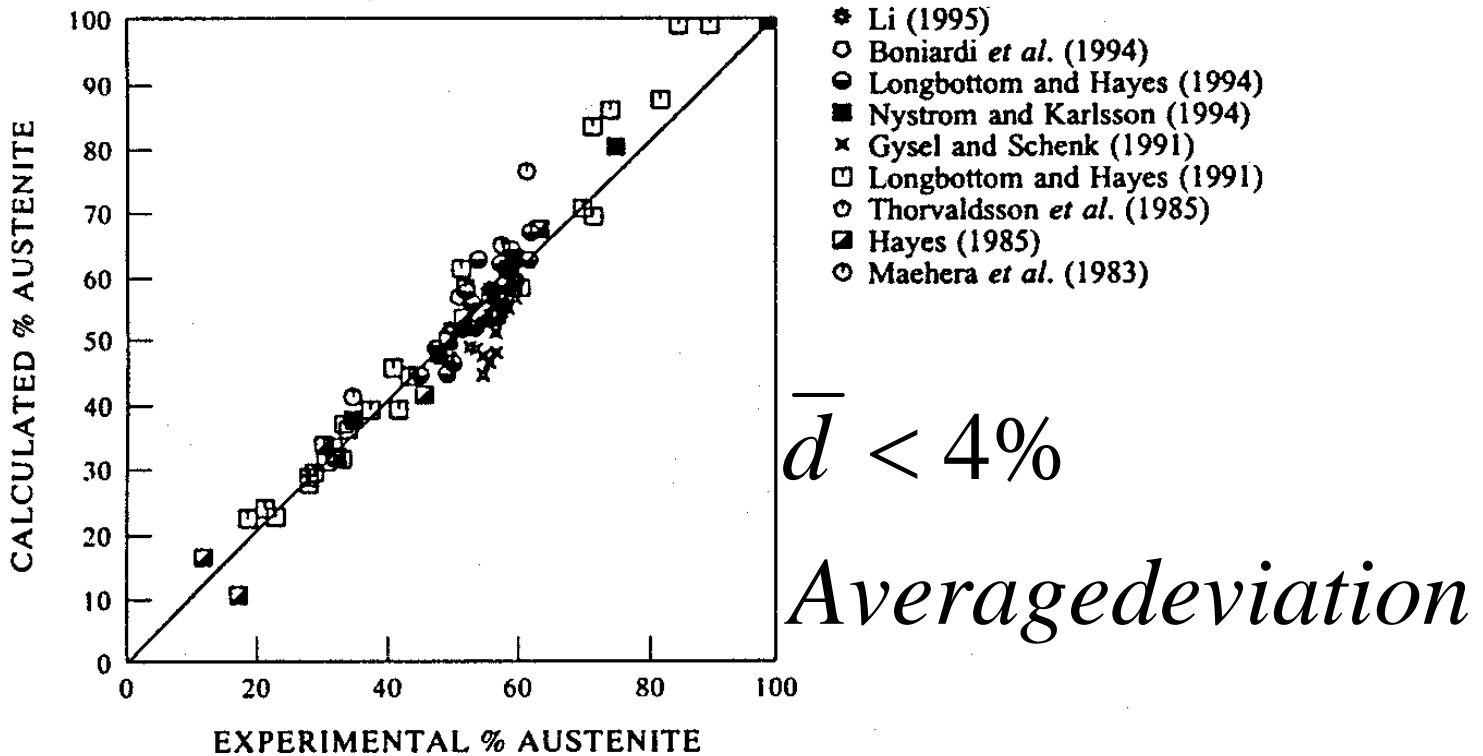


Figure 10.40 Comparison between calculated and experimentally observed % of austenite in duplex stainless steels. (Data from Longbottom and Hayes (1991) represent dual phase steels.).

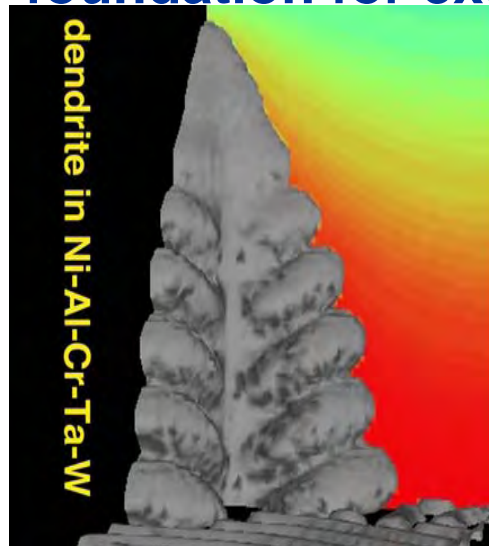
Thermodynamic databases

A wide range of thermodynamic databases are available for:

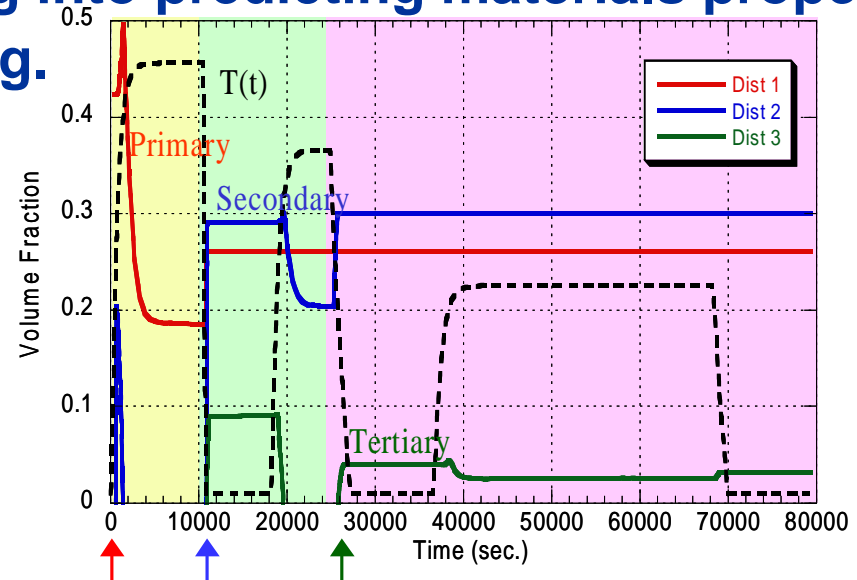
- **Steels and Fe-alloys**
- **Nickel-base superalloys**
- **Aluminium/Titanium/Magnesium-base alloys**
- **Gases, pure inorganic/organic substances, & general alloys**
- **Slag, metallic liquids, and molten salts**
- **Ceramic systems, and hard materials**
- **Semiconductors, and solder alloys**
- **Nobel metal alloys**
- **Materials processing, process metallurgical & environmental aspects**
- **Aqueous solutions, materials corrosion & hydrometallurgical systems**
- **Minerals, and geochemical/environmental processes**

Beyond phase diagrams (1)

- Computational thermodynamics can be used to predict phase equilibria and thermodynamic properties for complex multi-component systems. But in the broader scale of materials informatics, alloy design and process optimization, such information is only one part of a much bigger story. Through direct coupling of computer models and data, and also indirect feeding of results from one model to another, computational thermodynamics provides an important foundation for extending into predicting materials properties

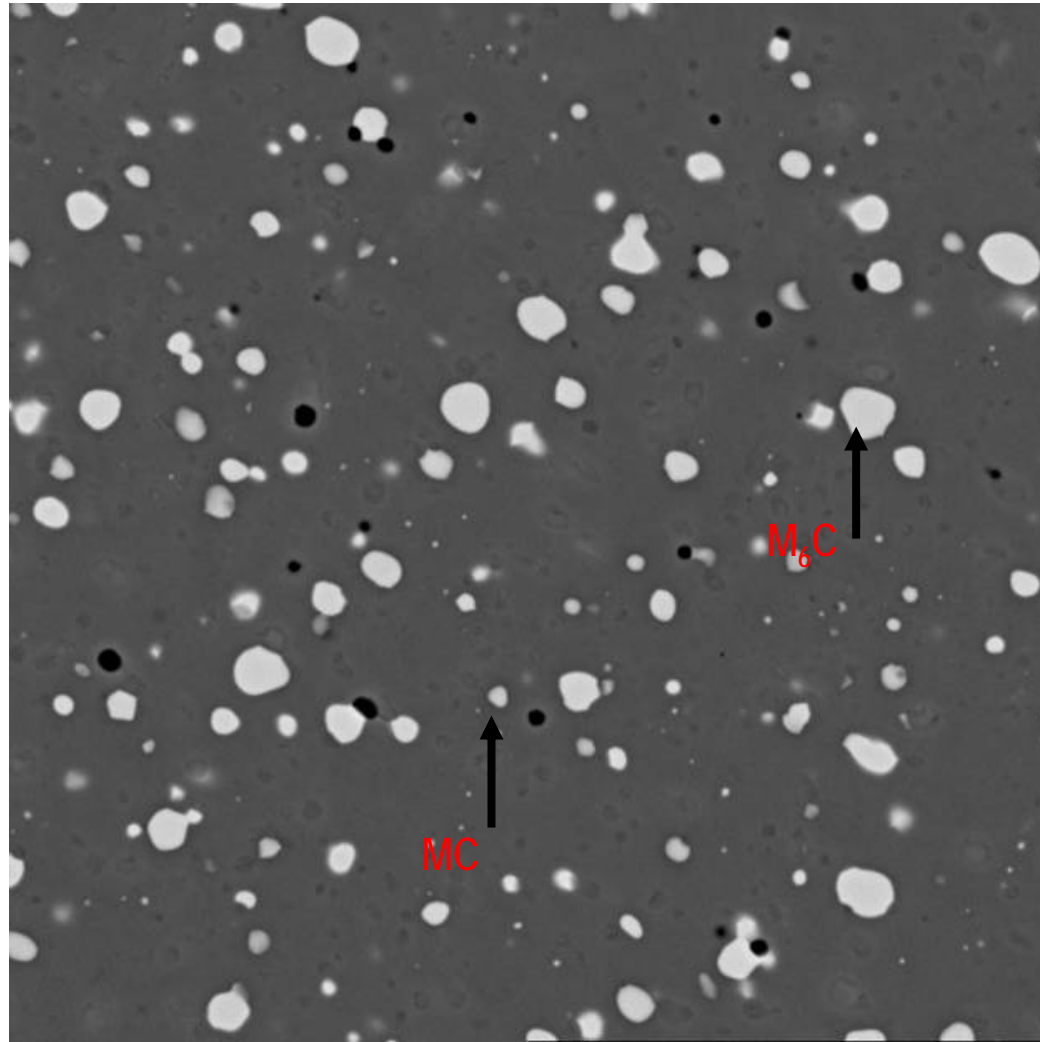


odeling.



Beyond phase diagrams (2)

Microstructure of P/M M4 under SEM



Beyond phase diagrams (3)

Modeling of Volume Fractions of Primary Carbides

Molar fractions and chemical compositions of primary carbides calculated with Thermo-Calc

Density of a phase (carbide and matrix) calculated based on its crystallography and chemistry

Volume fraction of primary carbides calculated based on densities and weights of phases

Beyond phase diagrams (4)

Modeling of Volume Fractions of Primary Carbides in M4

Grade	[°F]	Thermo-Calc						LOM Total
		Density, [g/cm ³]			Prim. Carb. [vol. %]			
		MC	M6C	γ	MC	M6C	Total	
M4	2050	6.58	10.61	7.74	6.6	6.3	12.9	13.0

Beyond phase diagrams (5)

Proof strength of austenitic stainless steels at elevated temperatures

A linear relationship for the proof stress $R_{p0.2}$ as a function of composition is frequently applied for austenitic stainless Steels, e.g.

$$R_{p0.2T} = A_T + \sum_{m=1}^n B_{mT} C_m$$

where,

A_T Base proof strength (MPa)

B_{mT} Regression constant (MPa/%)

C_m Concentration of alloying element (%)

Beyond phase diagrams (6)

Example of regression data

Table 3. Influence on proof strength from each alloying element as a function of temperature with the range of alloying elements analysed. Method I is based on the amount of elements in solid solution and the amount of precipitates. Method II is based on the total composition

Alloying element	range of alloying element %	influence on proof strength (I) MPa/element in %	influence on proof strength (II) MPa/element in %
C	0.01 - 0.12	$B_C = 575 - 0.3686T$	$F_C = 605 - 0.3401T$
Si	0.3 - 2.15	$B_{Si} = 24.76 + 1.129 \cdot 10^{-4} T^2 - 0.09T$	$F_{Si} = 24.5 + 5 \cdot 10^{-5} T^2 - 0.0457T$
Mn	0.4 - 2.1	$B_{Mn} = -1.4 - 7 \cdot 10^{-3} T$	$F_{Mn} = -1.2 - 8.1 \cdot 10^{-3} T$
Cr	16.6 - 24.7	$B_{Cr} = 0.3 - 7 \cdot 10^{-4} T$	$F_{Cr} = -0.07 - 1.1 \cdot 10^{-3} T$
Ni	8.8 - 25.8	$B_{Ni} = 5.3 - 3.3 \cdot 10^{-3} T$	$F_{Ni} = 5.8 - 2.3 \cdot 10^{-3} T$
Mo	0 - 4.7	$B_{Mo} = 6 - 3.3 \cdot 10^{-3} T$	$F_{Mo} = 5.2 - 4.2 \cdot 10^{-3} T$
Cu	0.2 - 1.5	$B_{Cu} = -14 + 0.0116T$	$F_{Cu} = -17.5 + 1 \cdot 10^{-3} T$
N	0.01 - 0.27	$B_N = 937 - 2.74 \cdot 10^{-6} T^3 + 5.24 \cdot 10^{-3} T^2 - 3.08T$	$F_N = 938 - 2.827 \cdot 10^{-6} T^3 + 5.44 \cdot 10^{-3} T^2 - 3.195T$
Ti	0 - 0.64	$B_{Ti} = 124 - 0.064T$	$F_{Ti} = 117 + 0.0356T$
TiC	-	$B_{TiC} = 181 + 0.031T$	-
M ₂₃ C ₆	-	$B_{M_{23}C_6} = 48 + 0.0135T$	-
Fe	51 - 70	$B_{Fe} = 1.68 + 4.248 \cdot 10^{-6} T^2 - 4.22 \cdot 10^{-3} T$	$F_{Fe} = 1.67 + 4.184 \cdot 10^{-6} T^2 - 4.22 \cdot 10^{-3} T$

T - temperature in °C

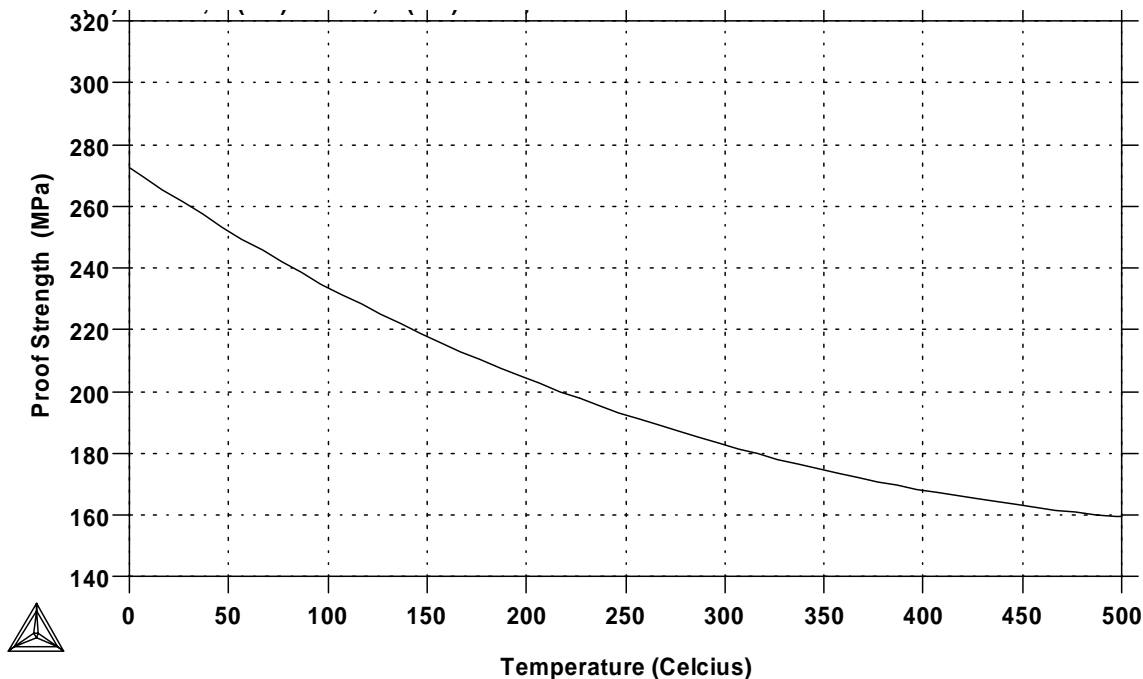
From: Eliasson and Sandström

Beyond phase diagrams (7)

Example – SS2361 (310S)

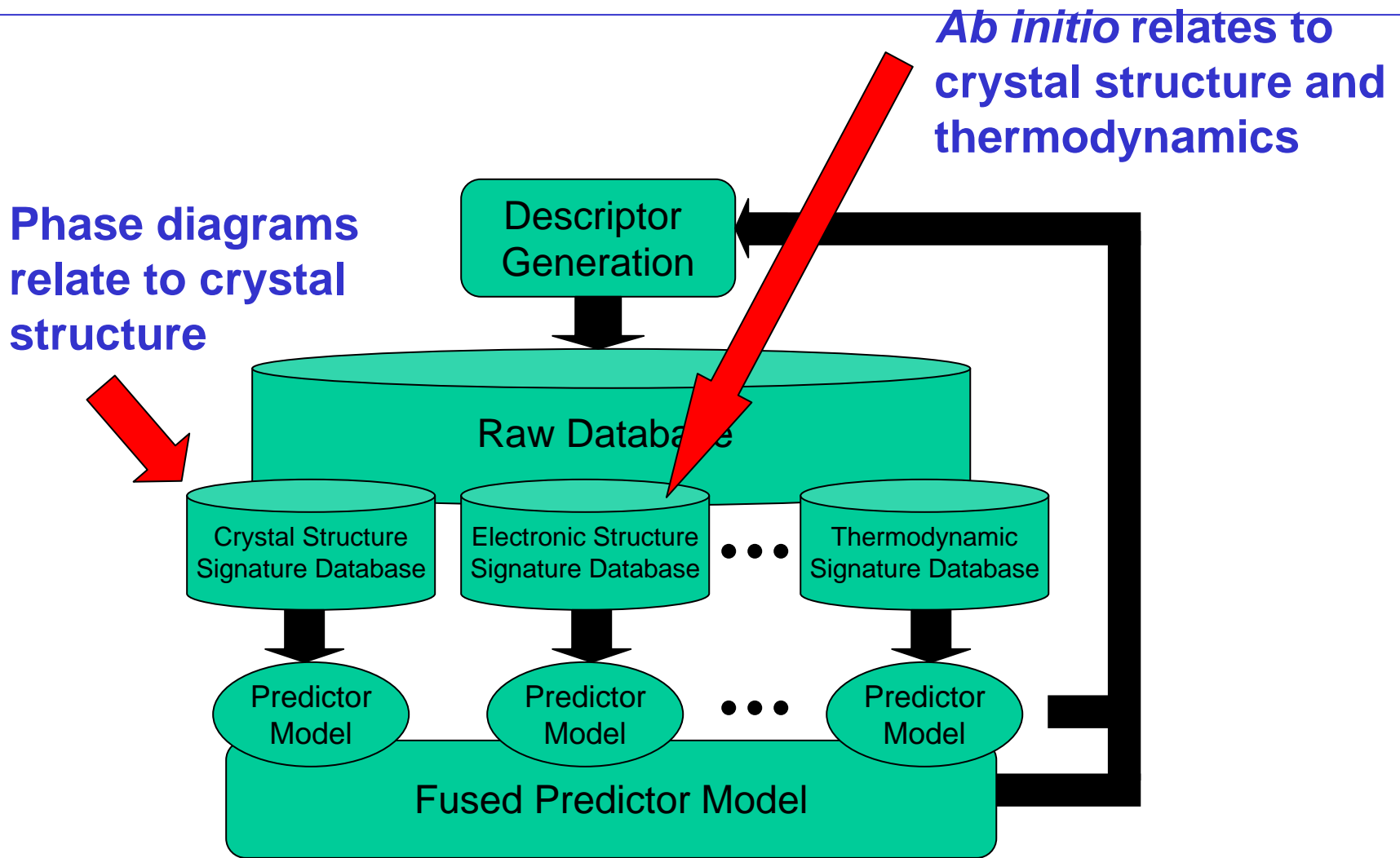
Element	C	N	Cr	Ni	Mn	Si	Cu	Mo	Fe
Mass %	0.09	0.07	24.6	20	1.3	1.3	0.24	0.3	Base

Solution treatment at 1100 °C followed by quenching



Prediction from using Method I in previous slide

Putting CALPHAD in a broader context of Materials Informatics (1)



Putting CALPHAD in a broader context of Materials Informatics (2)

How can Computational Thermodynamics benefit from Materials Informatics?

- **Thermodynamic data and phase descriptions are fundamentally linked to the crystal structures – hence information linked to a crystallographic database is inherently useful. Also, crystal structures are an underlying basis of ab initio calculations which also can complete holes in the experimental data-sets.**
- **On a wider scale, data mining and statistical tools can be used to search for data and pre-process it in preparation for the CALPHAD type optimizations.**

Putting CALPHAD in a broader context of Materials Informatics (3)

How can Materials Informatics benefit from Computational Thermodynamics?

- **Computational thermodynamics provides an important foundation for multi-scale models and the modeling of physical and mechanical properties of materials. Coupling with other methods in the framework of an integrated materials informatics scheme allows for:**
 - **a) holes in experimental data to be filled by computation**
 - **b) predictions to be made for multi-component materials (not just simplified systems restricted to 2 or 3 elements).**
 - **c) a self-consistent linkage of data from small binary and ternary systems (which are well measured and understood) to complex multi-component alloys**