Thermo-Calc Software

Thermo-Calc On-line Training

Day 2 *April 10, 2024*

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Schedule

Thermo-Calc Day 2

9:00	About the home assignment.
9:10	Thermodynamic Databases.
9:30	Step 3: Al alloy 6053
9:55	Map 1: Phase diagram for a cemented carbide.
10:25	Q & A
10:40	Map 2: HEA phase diagram.
11:05	Map 3: Phase diagram from base material to weld.
11:40	Q & A
11:55	Handing out home assignment.

Step = One-axis Step Calculation

Map = Phase diagram mapping, 2 axes or more.

Home assignment 1 – Fixing phase

Material: Tool Steels - Database: TCFE13 !

1) Fe-4Cr-8Mo-2V-0.3Mn-0.3Si-1C (wt-%)

   a) Calculate the liquidus temperature for the steel.

   b) How does the liquidus temperature change with carbon content?

More than one way to solve!

Home assignment 1 - solution

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At least two methods to solve this:

1) Graphic
   a) One-axis stepping in T and read Liquidus-T from a T vs. “Mole-fraction of phase”-diagram
   b) Phase diagram mapping, plot wt-% C vs. T

2) Using phase status
   a) Single-equilibrium calculation with LIQUID as FIX phase with 1 mole (in a system where N=1).
   b) One-axis step calculation in W(C) with the same condition on the LIQUID’s phase status.

Home assignment 1 - Results

Material: Tool Steels

1) Fe-4Cr-8Mo-2V-0.3Mn-0.3Si-1C

a) What is the liquidus temperature for the steel?

- 1686K (1413°C)

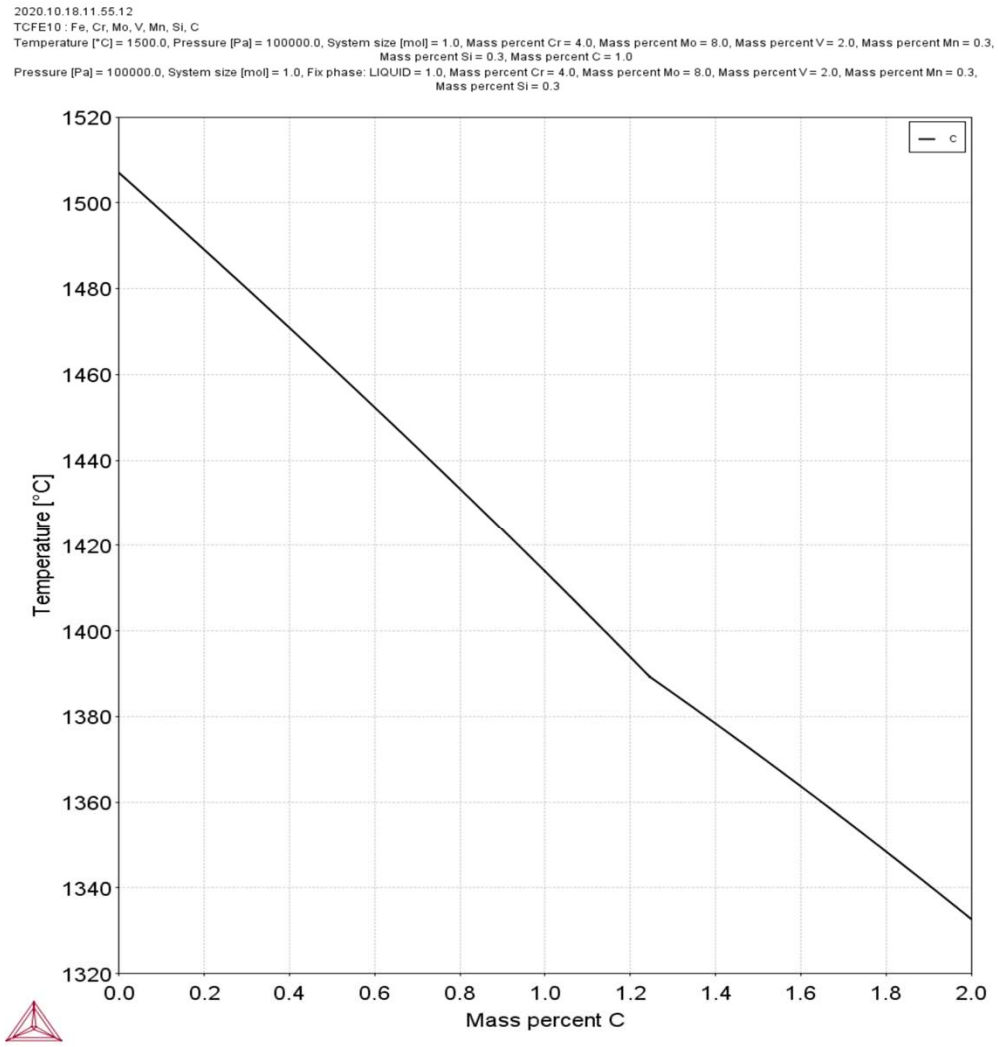
b) How does the liquidus temperature change with carbon content?

- Decreasing with increasing carbon content in a fairly linear fashion (as long as the stable phases are the same). See next slide.

Home assignment 1 - Results

1) Fe-4Cr-8Mo-2V-0.3Mn-0.3Si-1C

b) Step with the conditions on FIX LIQUID still on.



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Thermodynamic Databases

Databases

A database in our understanding means *a collection of polynomials describing some property for the individual phases of a system, as a function of temperature, (pressure) and composition.*

Databases are developed using the CALPHAD method.

- ❑ Thermodynamic data ⇒ All our software tools
  - Gibbs free energy, i.e. $G_m^{\phi} = f\left(T, P, x_i^{\phi}\right)$

- ❑ Kinetic data ⇒ DICTRA, TC-PRISMA
  - Atomic mobility

- ❑ Property data
  - Molar volume ⇒ TC, TC-PRISMA
  - Interfacial energies (no database) ⇒ TC-PRISMA
  - Thermal conductivity ⇒ TC
  - Electric conductivity ⇒ TC
  - Viscosity in liquid ⇒ TC
  - Liquid surface tension ⇒ TC
  - *….more will follow*

Thermodynamic Databases

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- Unary systems. G=G(T) for all stable and metastable phases included in database.
- Binary systems (or parts of). G=G(T,x) for stable and metastable phases, including binary phases.
- Ternary systems (or parts of). See above.
- Higher order systems (parts of).

- Databases are produced by critical assessment of experimental data and optimization of model parameters (the CALPHAD method).

- PARROT in Thermo-Calc Console Mode can be used as a tool in this process.

The CALPHAD Method

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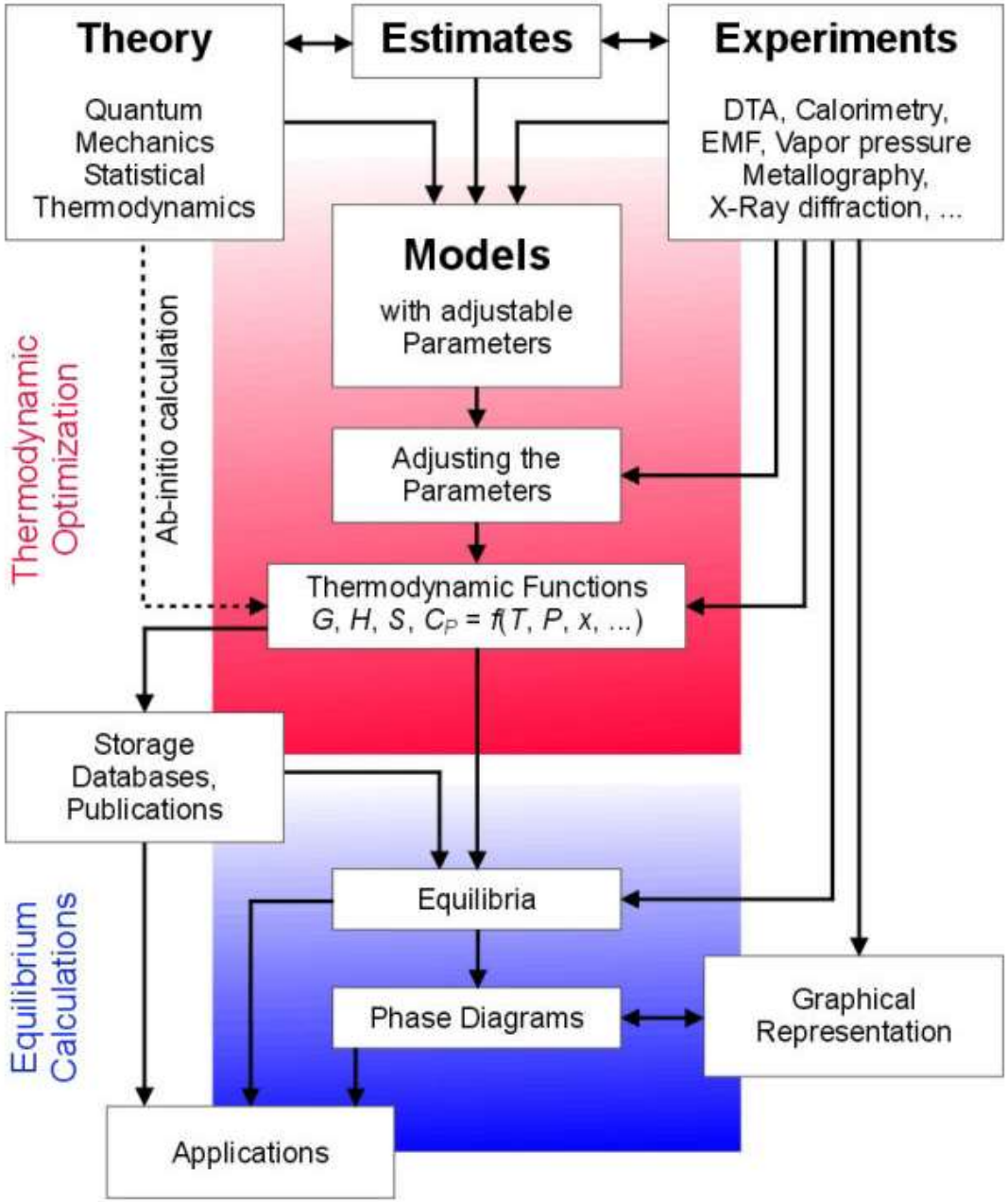
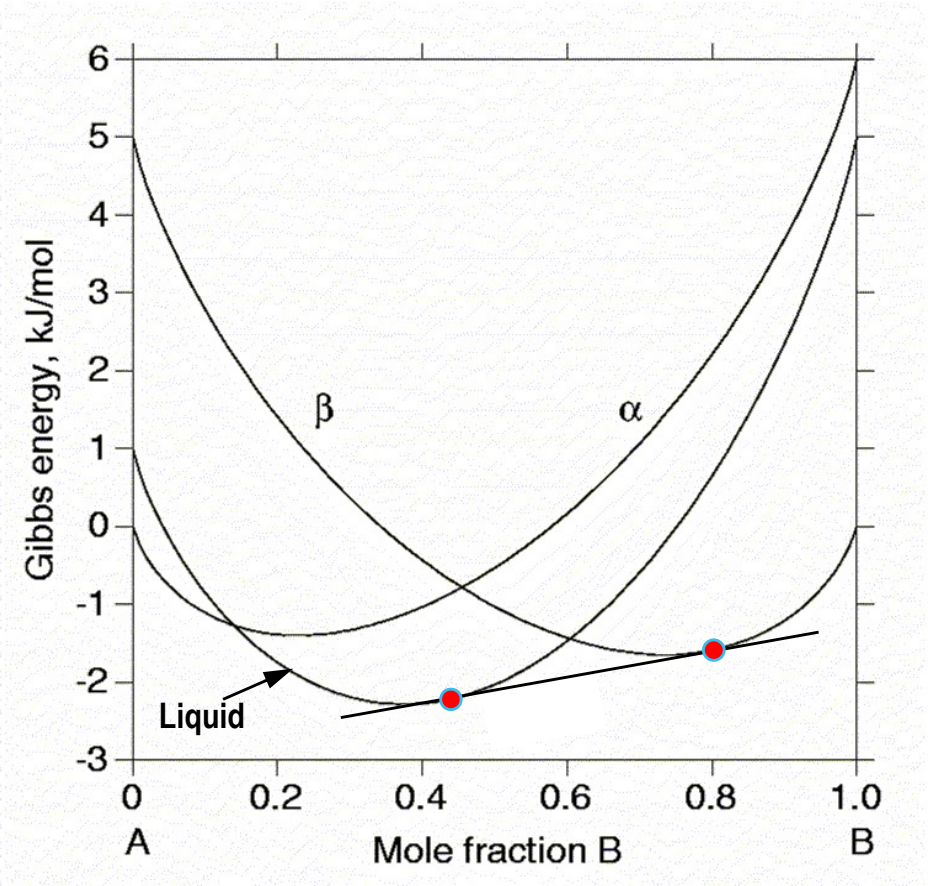
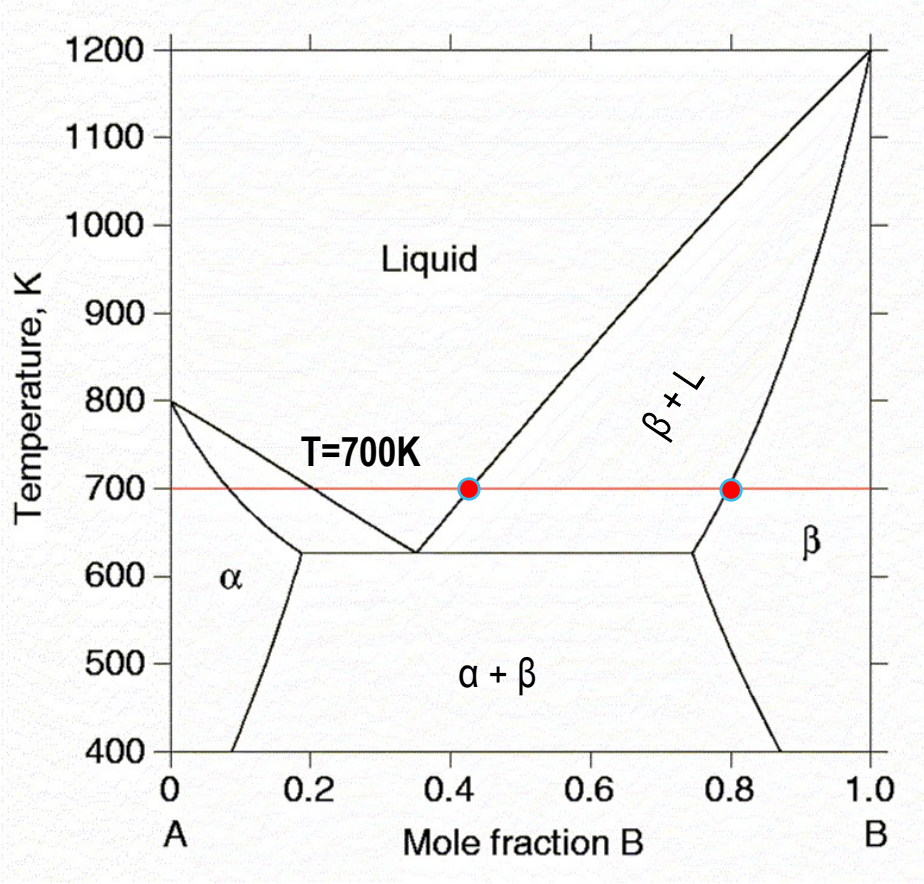


The CALPHAD Method

Originally «CALculation of PHAse Diagrams»

Now: «Computer coupling of phase diagrams and thermodynamics»





$$G^{\alpha}(x)_T = x_A G^{\alpha} + x_B G^{\alpha} + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L^E$$

$$G^{\alpha}(T)_x = A + BT + CT\ln(T) + ET^{-1} + FT^2 + \ldots$$

Thermodynamic Modeling

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Gibbs free energy per mole for a solution phase is normally divided in:

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

reference surface

configurational contribution

excess term

physical contribution
(e.g. from magnetics)

Solution phase = solid solution (e.g. FCC, BCC, HCP….) or LIQUID.

Example Fe-C

Per Gustafson, 1985, *Scand. Journal of Metallurgy* **14**(5):259-267

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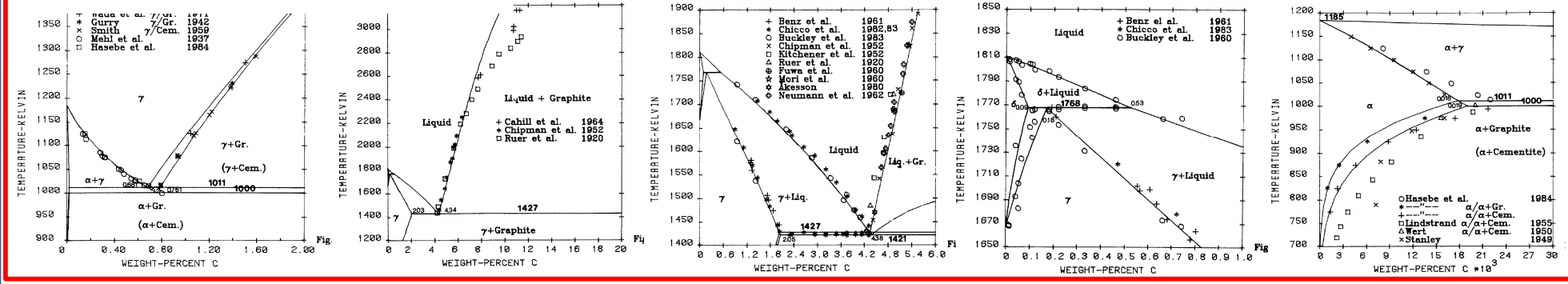
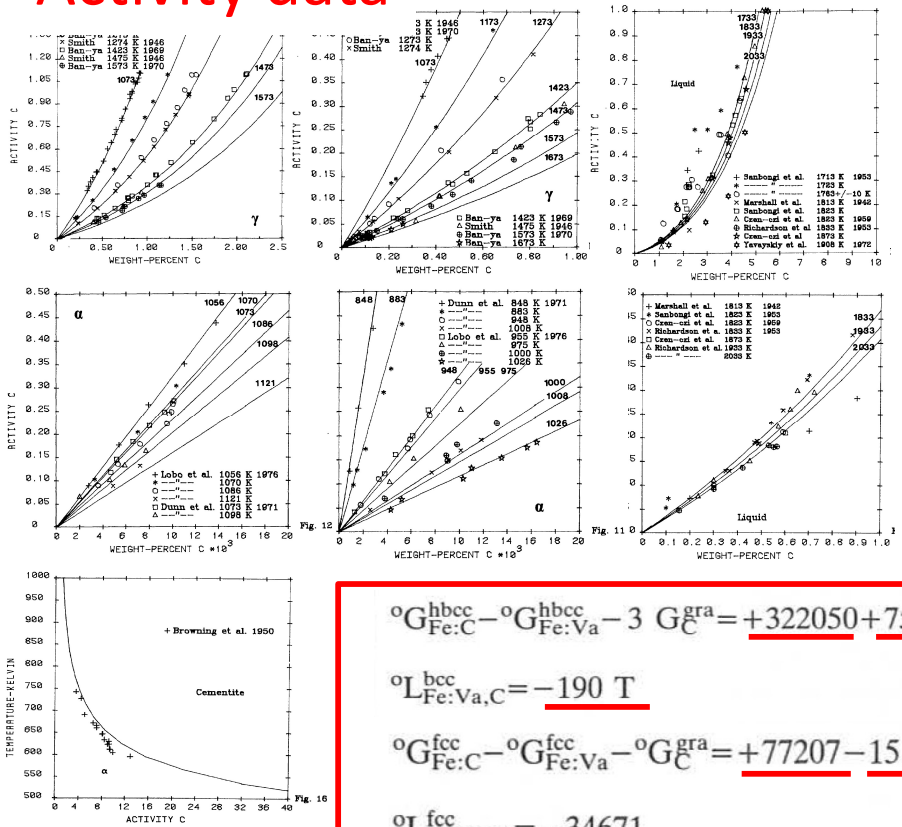
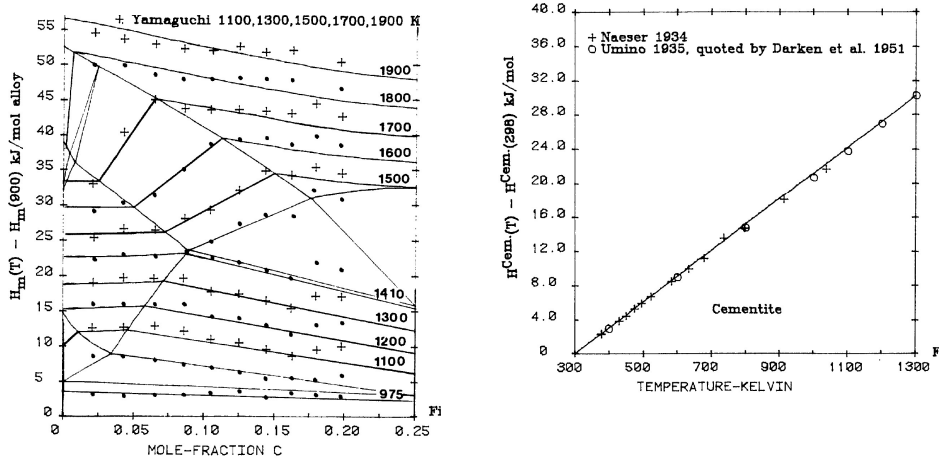
Phase diagram data



Activity data



Enthalpy data



$${}^{o}G^{hbcc}_{Fe:C} - {}^{o}G^{hbcc}_{Fe:Va} - 3\ G^{gra}_{C} = +322050 + 75.667\ T$$

$${}^{o}L^{bcc}_{Fe:Va,C} = -190\ T$$

$${}^{o}G^{fcc}_{Fe:C} - {}^{o}G^{fcc}_{Fe:Va} - {}^{o}G^{gra}_{C} = +77207 - 15.877\ T$$

$${}^{o}L^{fcc}_{Fe:Va,C} = -34671$$

$${}^{o}G^{cem}_{Fe:C} - H^{SER}_{C} - 3\ H^{SER}_{Fe} = -10745 + 706.04\ T - 120.6\ T\ \ln(T)$$

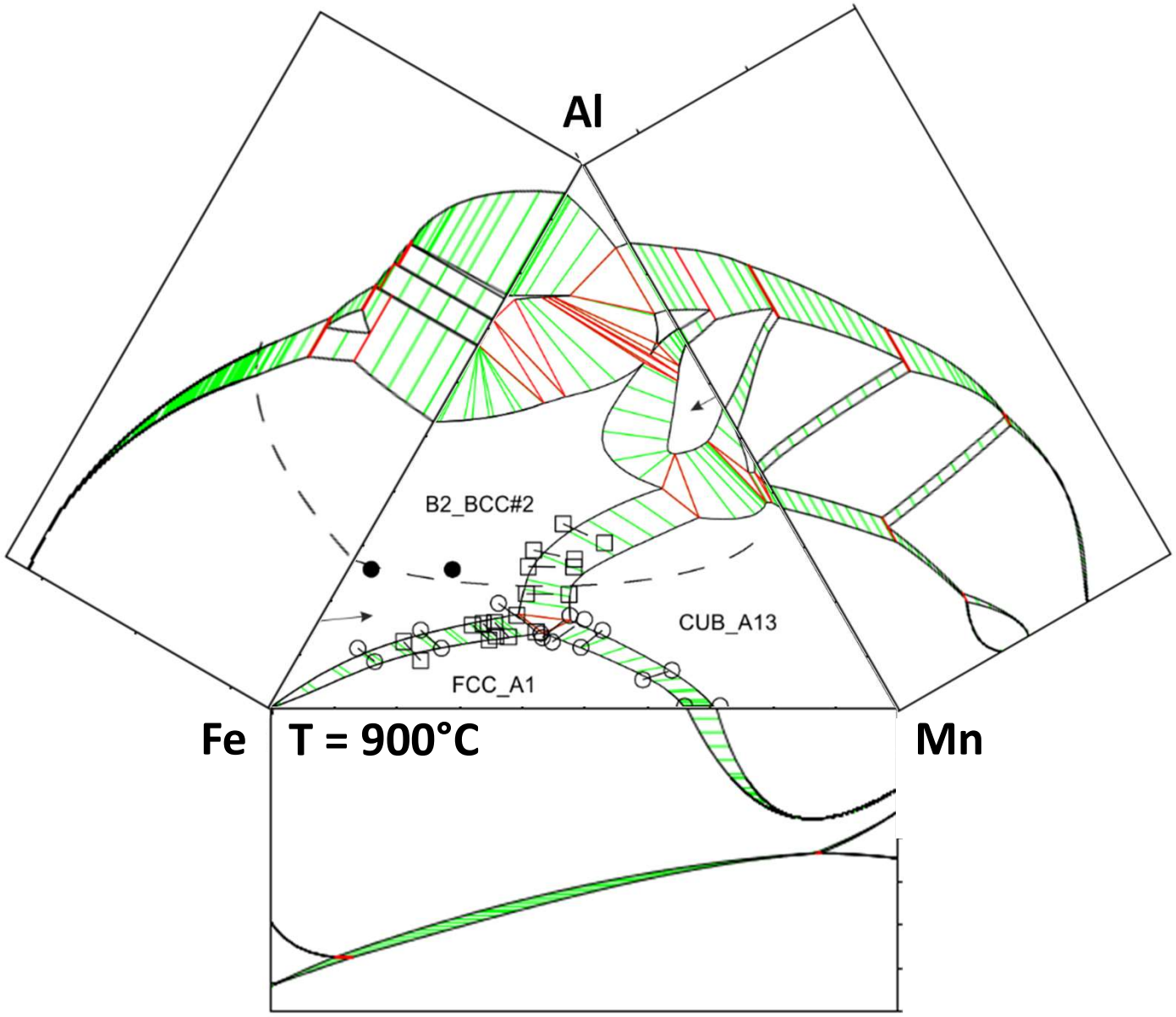
$${}^{0}L^{liq}_{Fe,C} = -124320 + 28.5\ T$$

$${}^{1}L^{liq}_{Fe,C} = +19300$$

$${}^{2}L^{liq}_{Fe,C} = +49260 - 19\ T$$

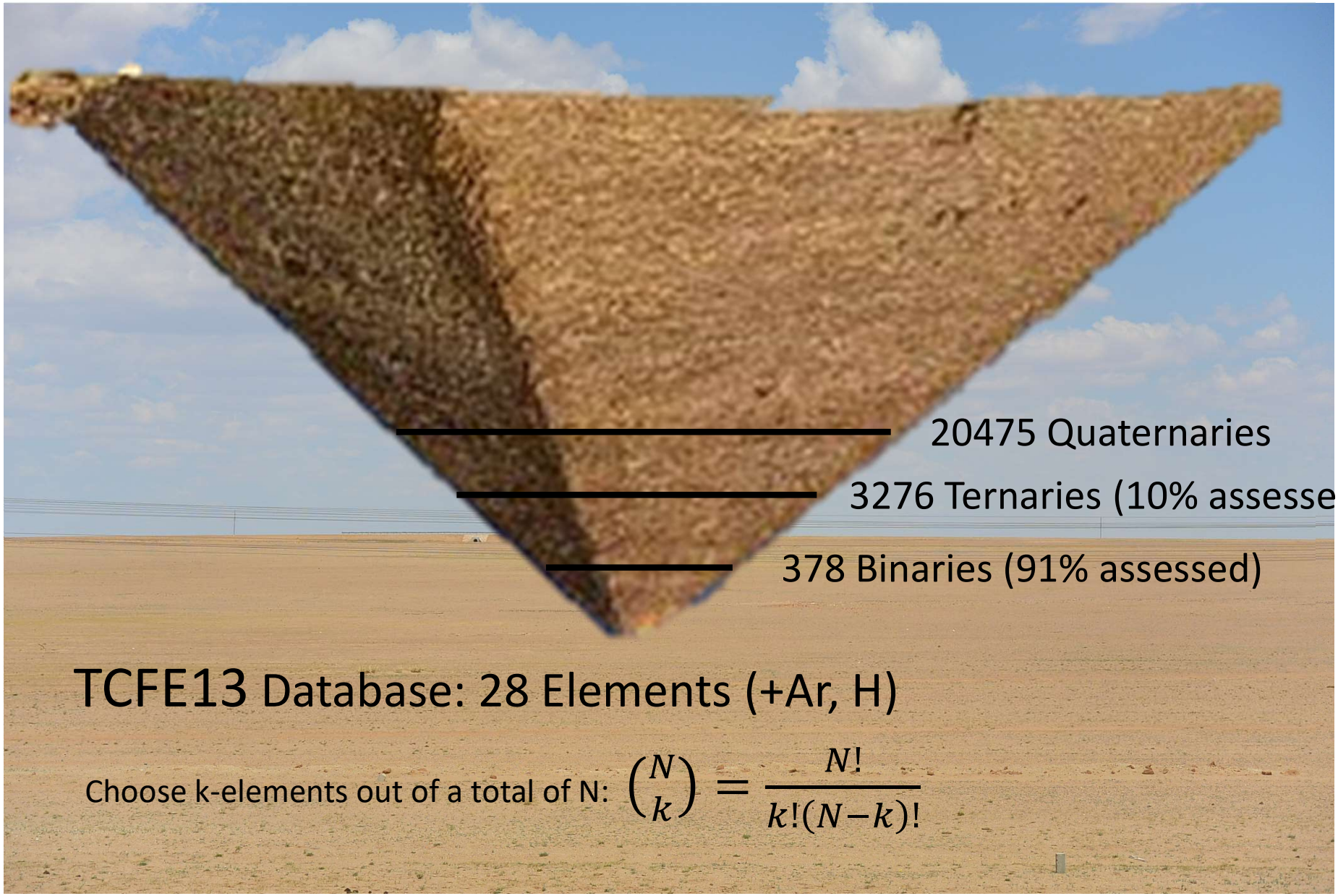
4 phases, >1000 experiments reproduced with 14 parameters

From binaries to ternaries



Extrapolation

→How to predict multi-component materials?
Extrapolation from binaries to ternaries, etc...



Intermediate phases

Carbides and nitrides are usually modelled with one sub-lattice for the metallic atoms and one for atoms that occupy the spaces in-between (interstitial positions), such as carbon or nitrogen. These interstitial sites are defined as a separate sub-lattice.

In many cases there are more than one sub-lattice for the metals.

The FCC carbonitride, e.g. TiC or VN is modelled as an a normal solid solution FCC phase, but in this case most of the interstitial sites are filled with carbon or nitrogen. This is handled in Thermo-Calc as second composition set of FCC and designated for instance FCC_A1#2.

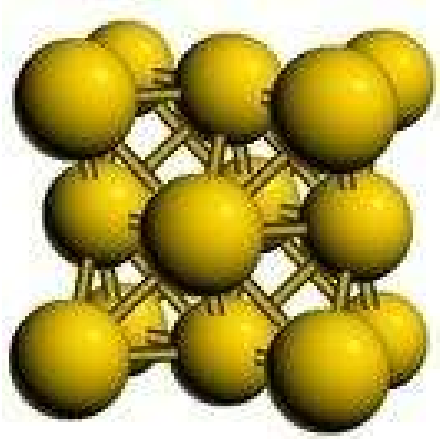
The HCP carbonitride, M_2C or M_2N is in the same way modelled as a second composition set of the HCP phase.

Other intermetallic phases can be modelled in many different ways.

Compound Energy Formalism (CEF)

Thermo-Calc Software

Fcc



Austenite

$[Co,Cr,Fe,Mn,Mo,Si,V,W]_1\,[C,N,Va]_1$

Carbide/Carbonitride

$[Co,Cr,Fe,Mn,Mo,Si,V,W]_1\,[C,N,Va]_1$

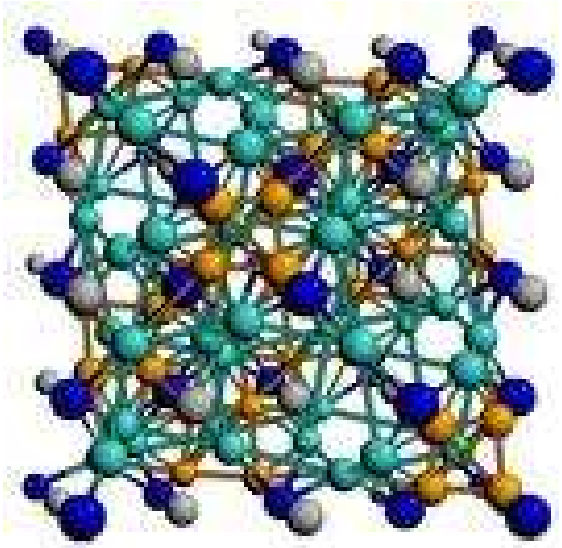
$$G_m^{\phi} = \sum_M \sum_I y_M y_I {}^{\circ}G_{M:I}^{\phi} + RT(a\sum_M y_M \ln y_M + c\sum_I y_I \ln y_I) + {}^{E}G_m^{\phi} + G_m^{\phi\,mg}$$

- ${}^{o}G_{M:I}$ is the Gibbs energy of formation of the compound M_aI_c.
- y *i*s the site fraction, and a and c are the site ratios.
- The excess and physical contributions are as for a regular solution on each sublattice.

Compound Energy Formalism (CEF)

Thermo-Calc Software

More complex structures needs more sublattices



M_6C Carbide

$[Co,Fe]_2\ [Co,Cr,Fe,Mo,Si,V,W]_2\ [Mo,W]_2\ [C]_1$

$$G_m = \sum y_I^1 y_J^2 y_K^3\ {}^oG_{I:J:K:C} + RT\sum\sum n^S y_J^S \ln(y_J^S) + {}^EG_m$$

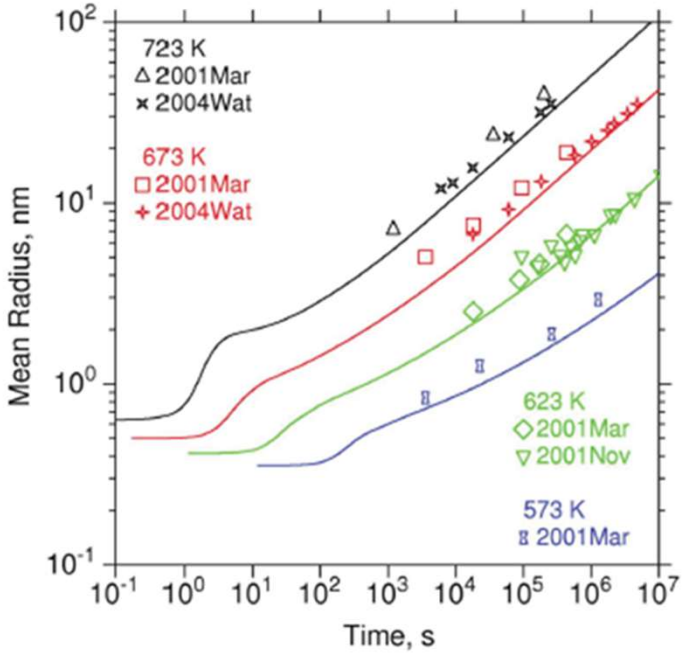
Extensions of CALPHAD

CALPHAD was initially only applied for representing **thermochemical** and **phase-equilibrium** information (the first materials genome), but has since a long time been proven to be extended to other phase-based properties, e.g.

- ✓ Thermodynamic data
- ✓ Multicomponent mobility data
- ✓ Molar volume

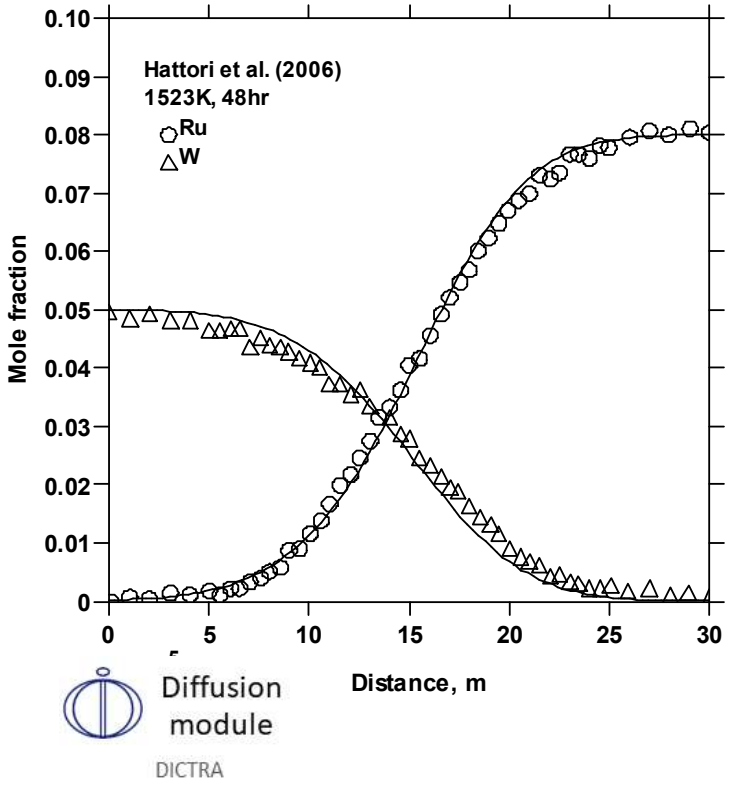
+ Interfacial energy

→ **Precipitation and growth**



Precipitation module

TC-PRISMA



Diffusion module

DICTRA

Later extensions of CALPHAD

- ✓ Thermodynamic data
- ✓ Multicomponent mobility data
- ✓ Molar volume

+ Interfacial energy

- ✓ Precipitation and growth

And more recently (from 2020 in our software) also:

- ✓ *Thermal conductivity*
- ✓ *Thermal resistivity*
- ✓ *Electrical conductivity*
- ✓ *Electrical resistivity*
- ✓ *Viscosity in Liquid phase*
- ✓ *Surface tension of Liquid phase*

Related is:

- ✓ *Yield strength*: not a database quantity but software models making this possible to calculate.

Selecting the right database(s) (1)

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Three most common types of databases:

Substance database (e.g. SSUB7, NUMT2):

Database for condensed phase compounds and gases
Advantage: Many elements, many compounds
Limitation: Not suitable for phase diagrams, phase transformations

Solution database (e.g. TCFE13, TCNI12, SSOL8, TCOX12, etc):

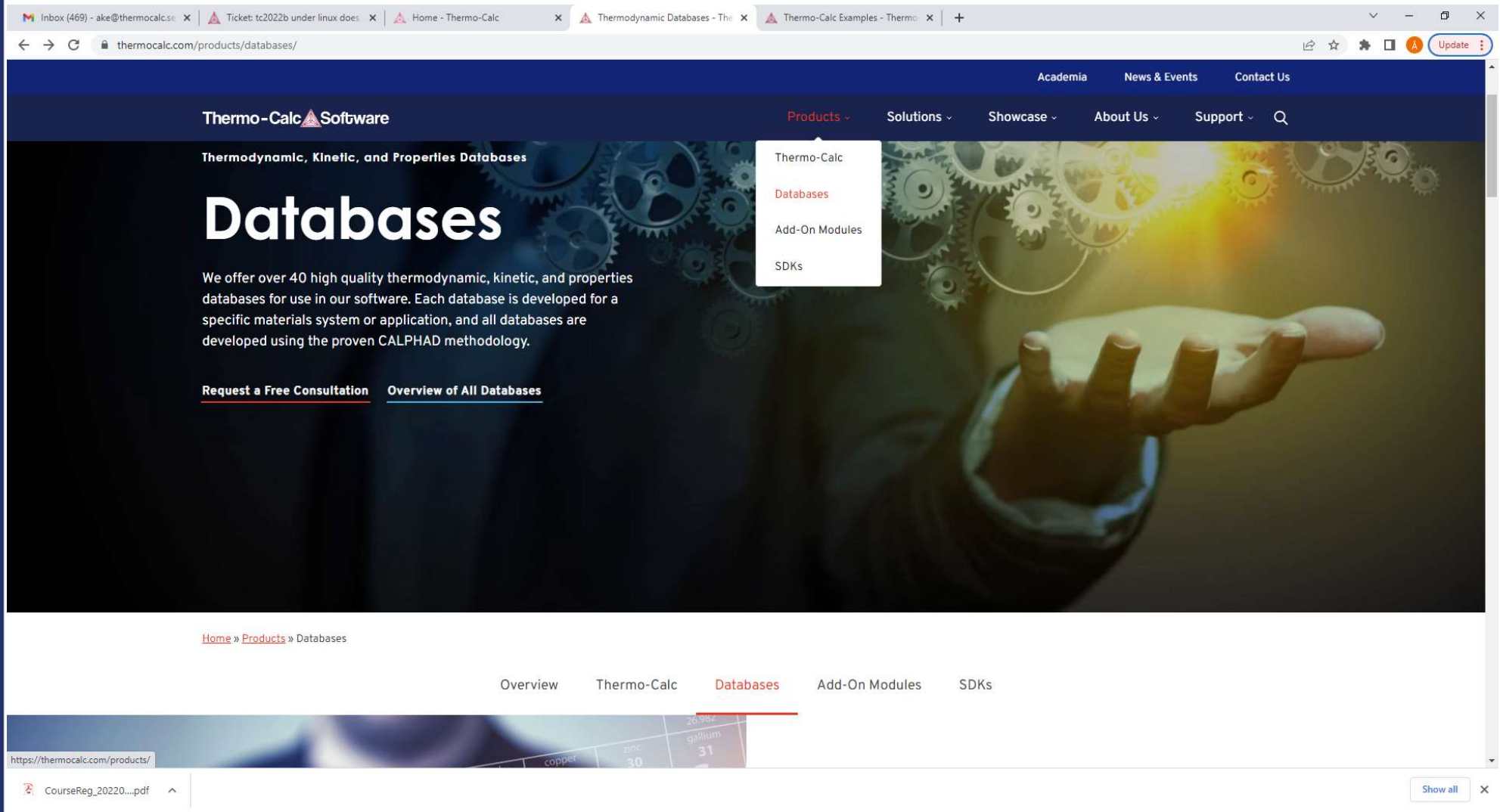
Databases for alloys and solid solutions
Advantage: Describes phase diagrams, phase transformations
Limitation: Generally fewer elements than substance database/ SSOL6 has many elements but most assessments limited to binaries

Aqueous databases (e.g. TCAQ3, AQS2):

Advantage: Consists of various free cations and anions, inorganic and organic complexes
Limitation: Needs to be used in conjunction with substance or solution databases

Selecting the right database(s) (2)

For a list of available thermodynamic and mobility databases refer to the database overview or www.thermocalc.com



Selecting the right database(s) (2)

For a list of available thermodynamic and mobility databases refer to the database overview or www.thermocalc.com/products/databases

Selecting the right database(s) (3)

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The Technical information sheet for each database contains a list of binary and ternary systems evaluated.

TCHEA6 Assessed Binary Systems

These are the assessed binary systems (310 in total) in the full range of composition and temperature.

	Al	B	C	Co	Cr	Cu	Fe	Hf	Ir	Mn	Mo	N	Nb	Ni	Re	Rh	Ru	Si	Sn	Ta	Ti	V	W	Y	Zn	Zr
B	x	B																								
C	x	x	C																							
Co	x	x	x	Co																						
Cr	x	x	x	x	Cr																					
Cu	x	x	x	x	x	Cu																				
Fe	x	x	x	x	x	x	Fe																			
Hf	x	x	x	x	x	x	x	Hf																		
Ir	x	x	x	x	x	x	x	x	Ir																	
Mn	x	x	x	x	x	x	x	x	x	Mn																
Mo	x	x	x	x	x	x	x	x	x	x	Mo															
N	x	x		x	x	x	x	x		x	x	N														
Nb	x	x	x	x	x	x	x	x	x	x	x	x	Nb													
Ni	x	x	x	x	x	x	x	x	x	x	x	x	x	Ni												
Re	x	x	x	x	x	x	x	x	x	x	x		x	x	Re											
Rh	x	x	x	x	x	x	x	x	x	x	x			x	x	Rh										
Ru	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	Ru									
Si	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	Si								
Sn	x	x	x	x	x	x	x	x	x	x			x	x	x	x	x	x	Sn							
Ta	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	Ta						
Ti	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	Ti					
V	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	V				
W	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	W			
Y	x	x	x	x	x	x	x	x		x	x		x	x	x		x	x	x	x	x	x	x	Y		
Zn	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	Zn	
Zr	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	Zr
	Al	B	C	Co	Cr	Cu	Fe	Hf	Ir	Mn	Mo	N	Nb	Ni	Re	Rh	Ru	Si	Sn	Ta	Ti	V	W	Y	Zn	

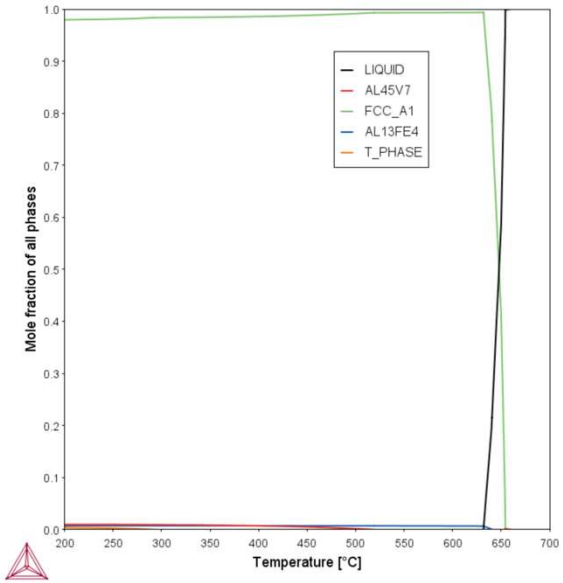
Step 3: Al alloy UNS A_96053. Volume change at solidification and other properties.

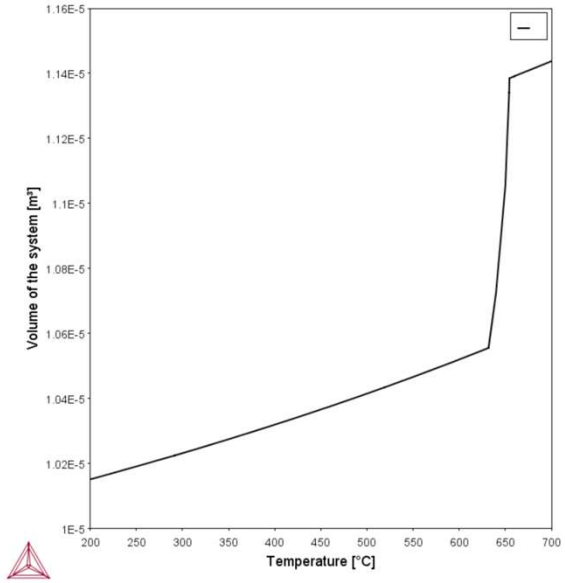
Property diagrams for Al-Alloy 6053
Step example 3.

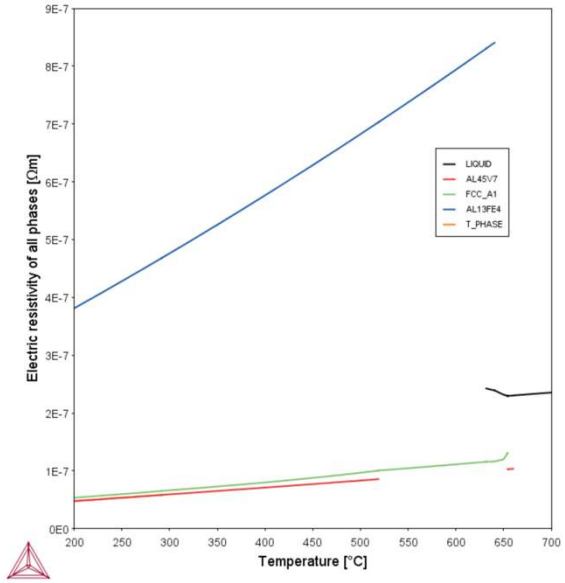
Calculate different properties as a function of T for this alloy:

Al – 1.2 Mg - 0.35 Fe – 0.25 Cr – 0.1 Cu – 0.1 Zn (wt-%)

Use the “Load Material” option in System Definer. Remember to make sure the database is TCAL8.







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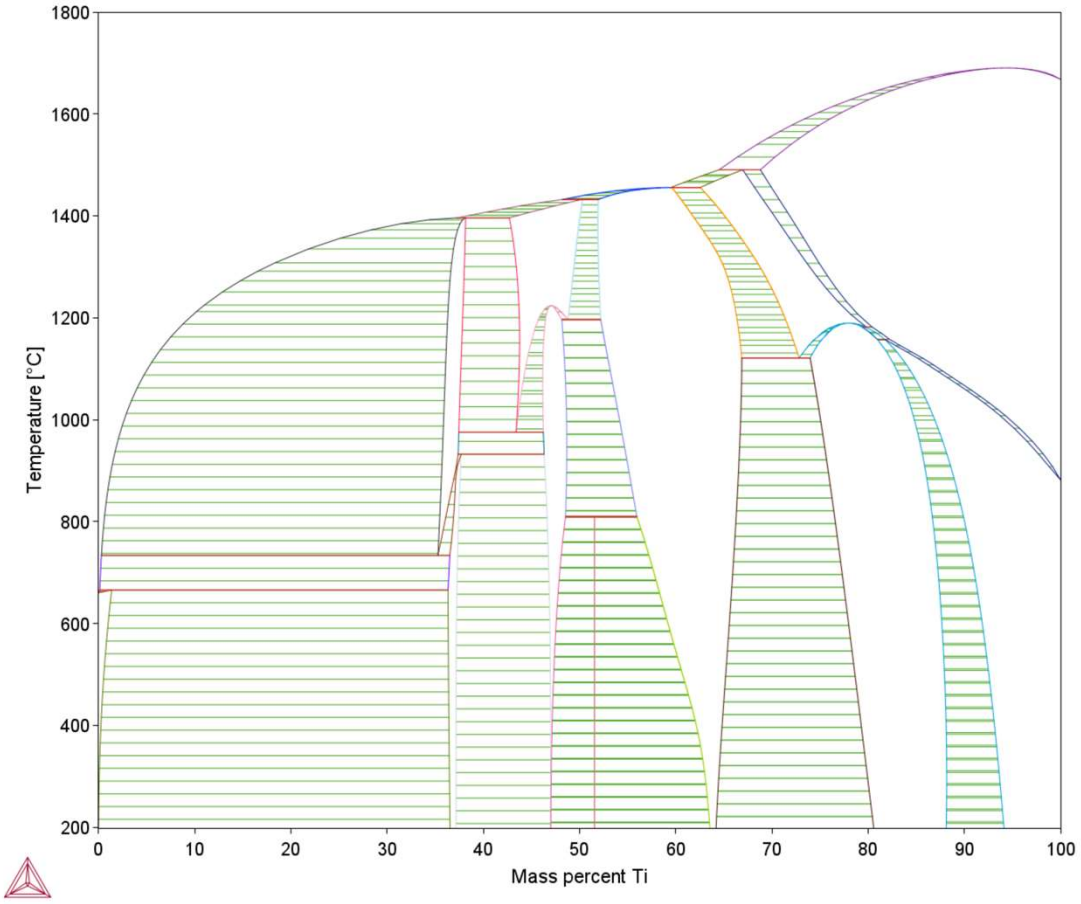
Map calculations – two axes (or more) → Phase diagrams

Binary phase diagram

Thermo-Calc Software

Al-Ti Binary



Use the ”Binary Phase Diagram” template.

TCBIN, the special binary database, is default.

But also several other databases can be used. This diagram from TCAL8.

Phase diagram calculations

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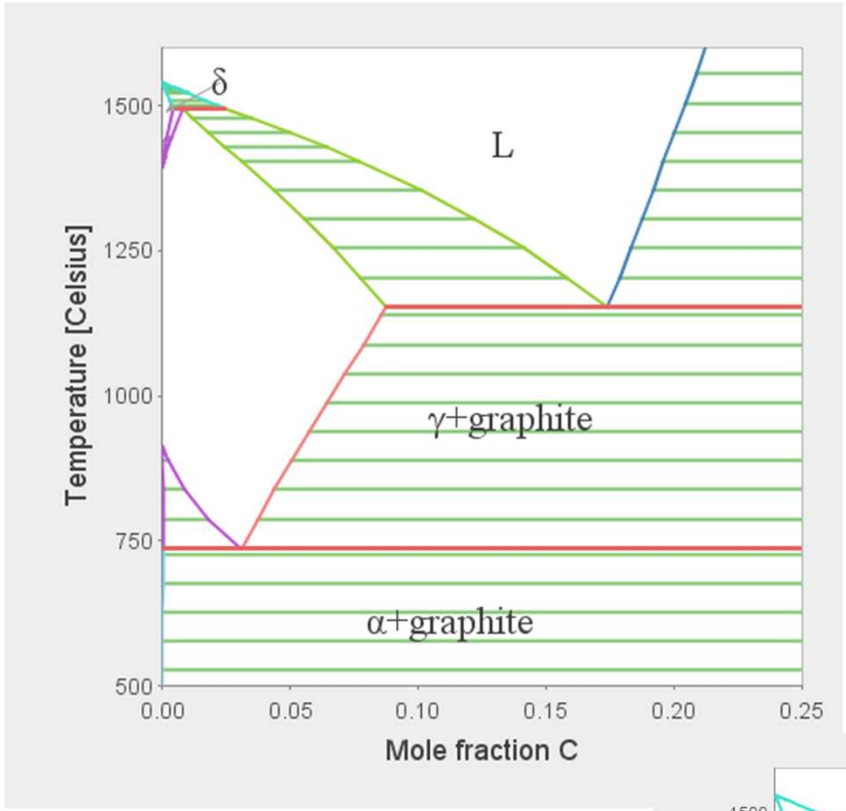
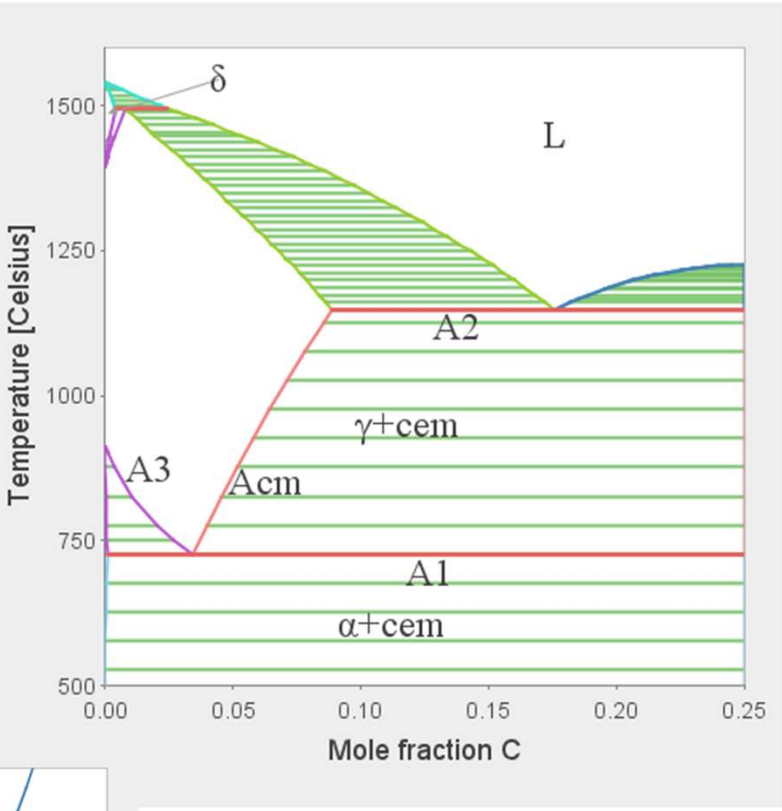
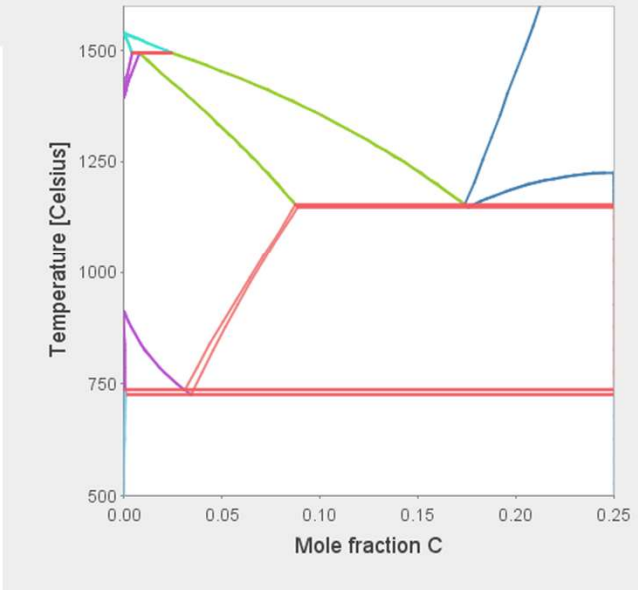


Stable diagram



Metastable diagram



Combined diagram

Examples – Isothermal Section

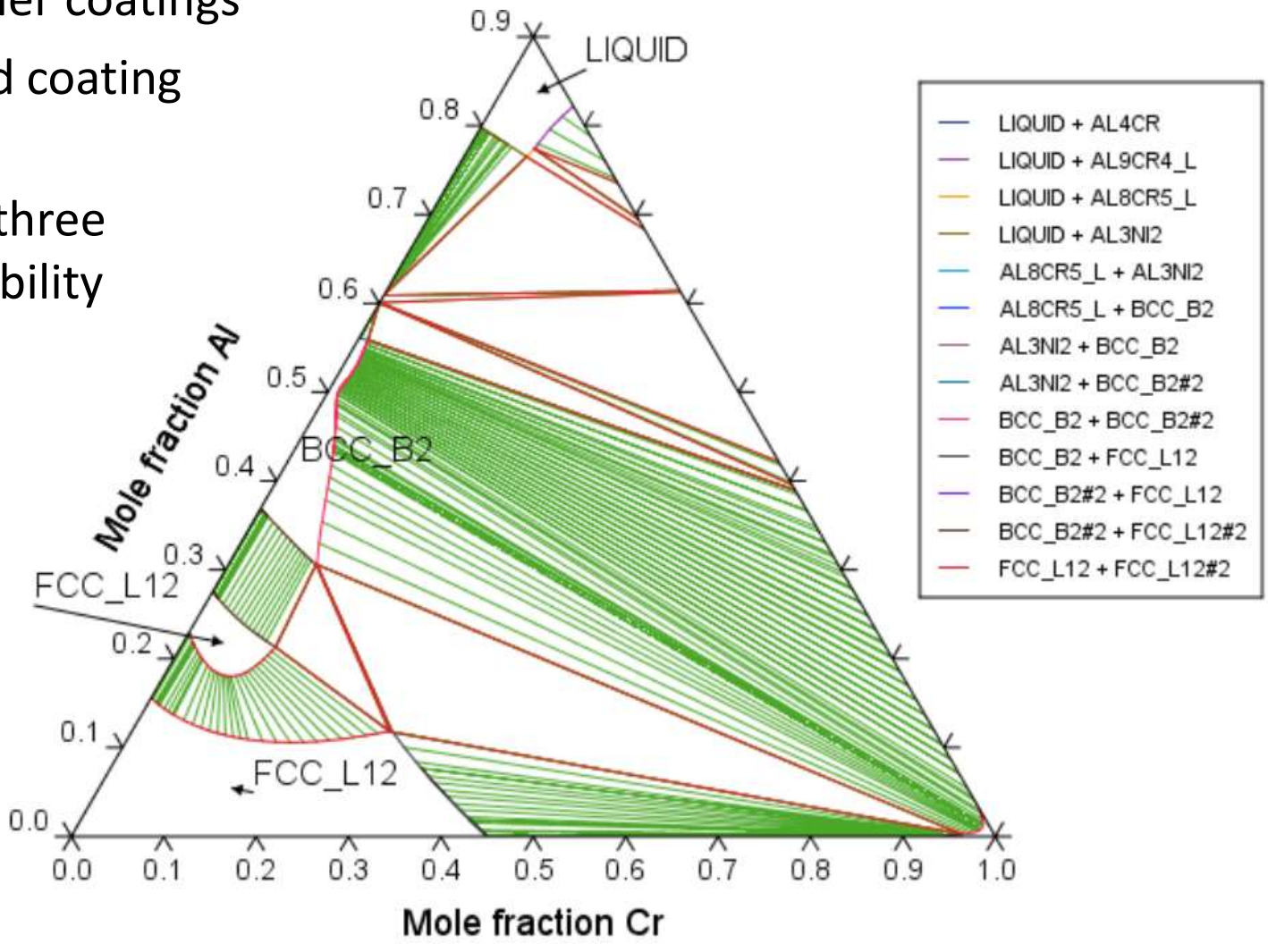
Thermo-Calc Software

Ni-Al shows γ + γ’

Ni-Cr-Al is used for bond layer to join to thermal barrier coatings

Used to design bond coating composition

Need to stay in the three phase region for stability after diffusion



Isothermal sections of Al-Cr-Ni at 1000°C

Multicomponent Phase Diagrams

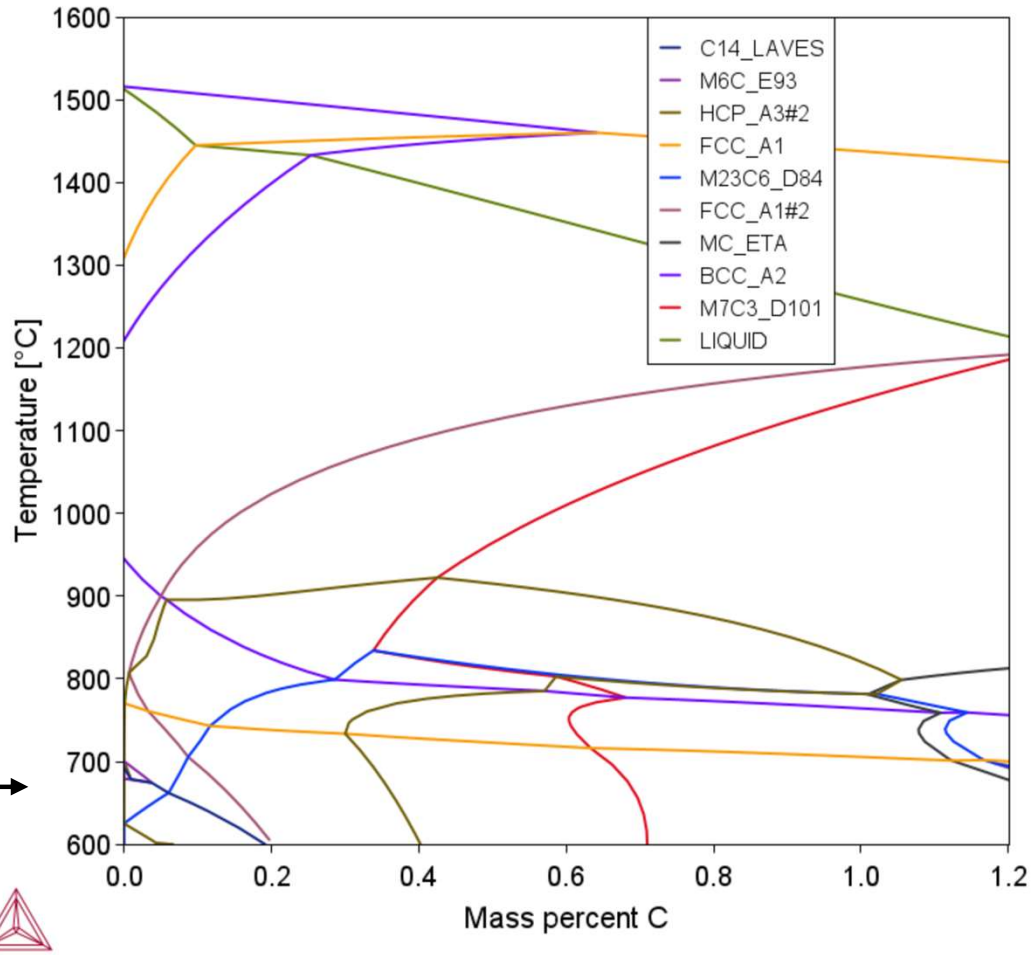
When making phase diagrams of more complicated alloys (more components) the diagrams can get very confusing

Because it's not a binary, the tie-lines do not lie in the plane of the calculation so the lever rule is not possible

Hard to label the diagram as well with so many small regions

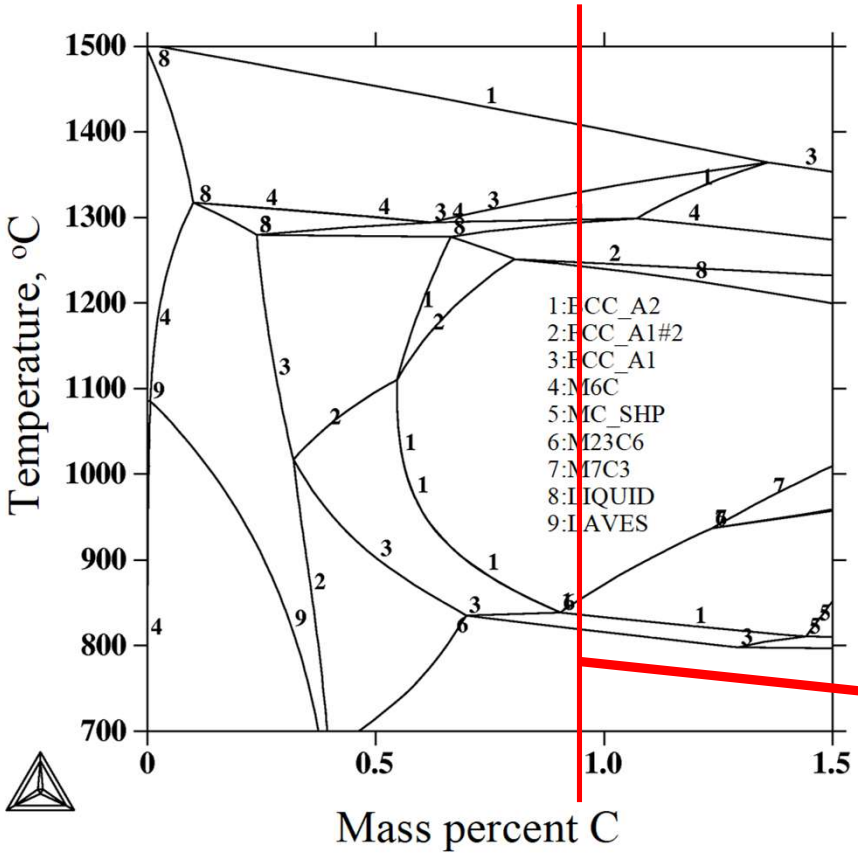
Coloured lines indicate a phase is stable on one side of the line and not stable on the other side

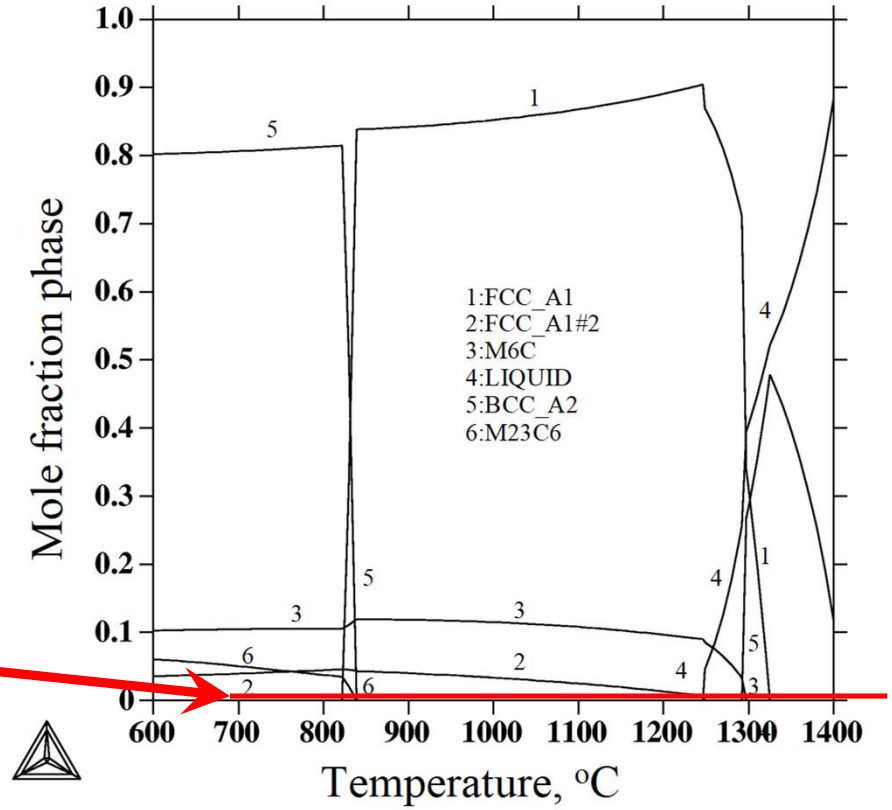
Tool steel with Fe-5 Cr-1.5 Mo-1.5 Ni-1 V-0.5 Mn – (0--1.2) C



Thermo-Calc - Examples

Example: Carbon in M42 High Speed Steel





Phase diagram for a M42 high speed steel.
The lines represent where a phase appears or disappears. The alloy is Fe-4Cr-5Mo-8W-2V-0.3Mn-0.3Si-C(wt%). **Isoplethal section.**

Property diagram for a M42 high speed steel.
Shows how the fractions of the phases in the system vary with temperature. The alloy is Fe-4Cr- 5Mo-8W-2V-0.3Mn-0.3Si-0.9C.

Map 1: Phase diagram for a cemented carbide.

Cemented carbide phase diagram. Map ex. 1.

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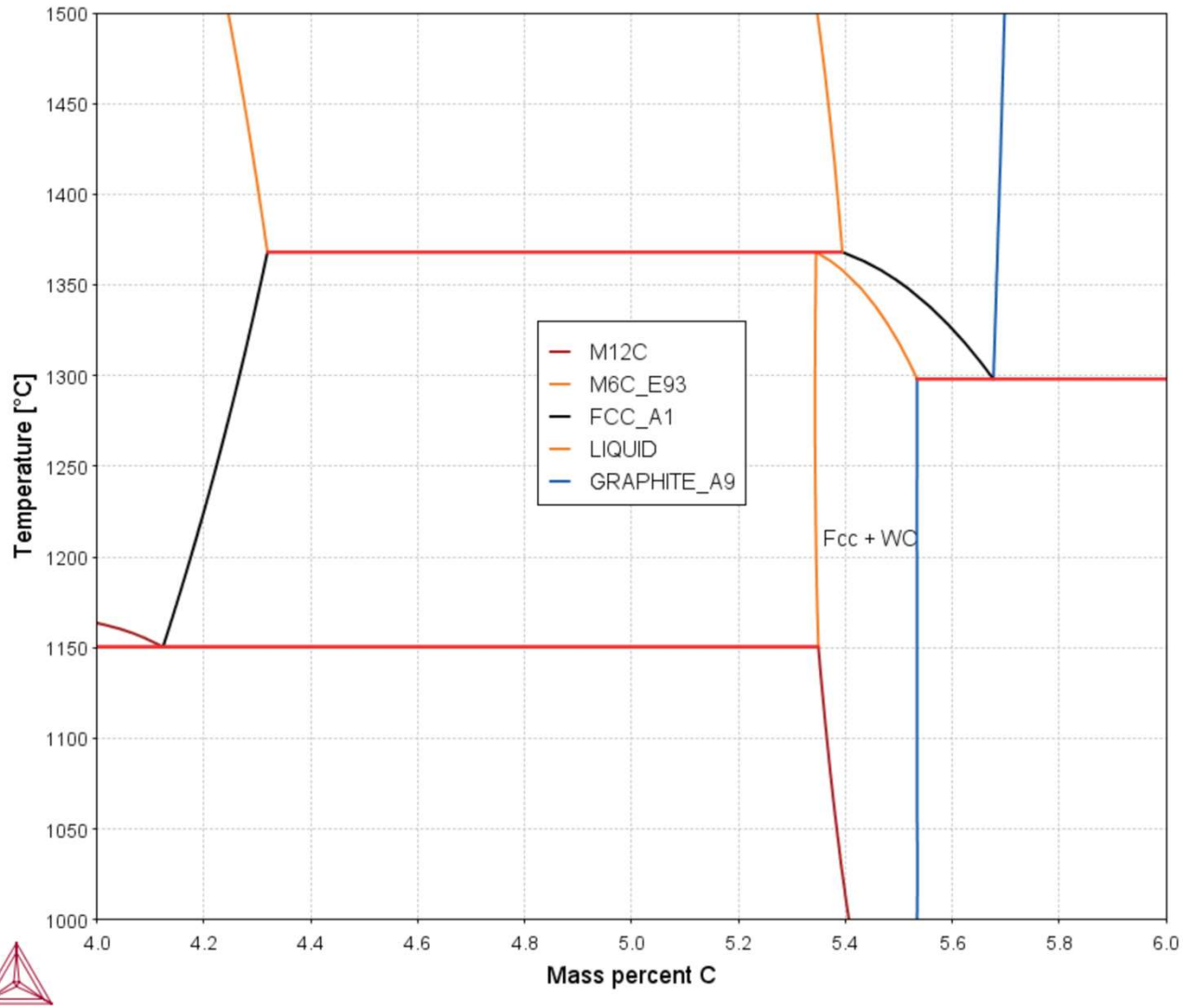
Typical hard metal (cemented carbide): W + C + 10 wt-% Co binder. Calculate this diagram. Then replace 3 wt-% Co with Fe and calculate a second diagram.



Thermo-Calc Software

Questions

&

Answers

Map 2: Phase diagram for a HEA with one element replacing all the other.

High Entropy Alloys
(= Multi Principal-Element Alloys)

Thermo-Calc Software

High-entropy alloys (**HEAs**) are alloys that are formed by mixing equal of relatively large proportions of (usually) five or more elements.

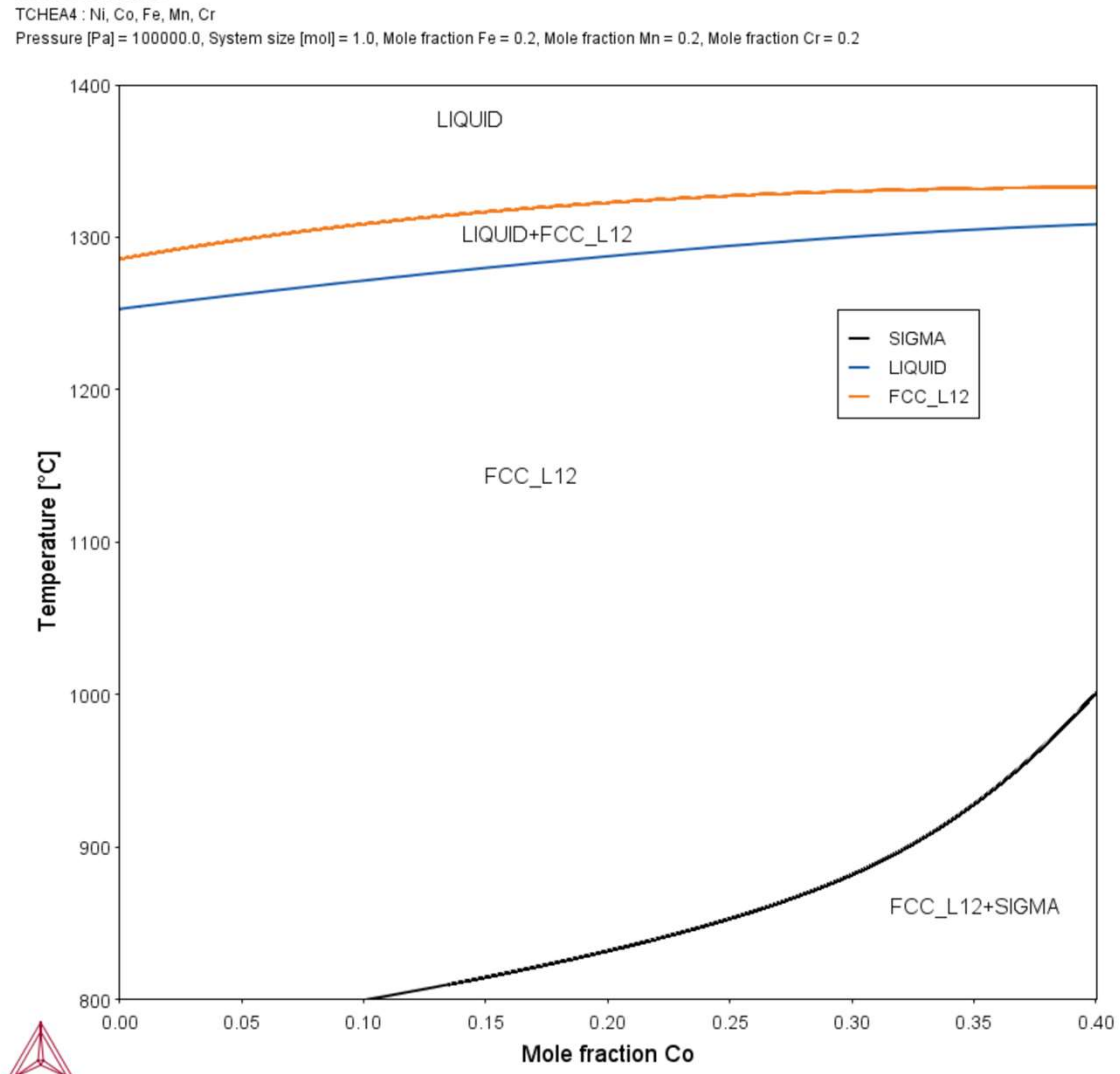
The entropy increase of mixing is substantially higher when there is a larger number of elements in the mix.

There is no universally agreed-upon definition of a **HEA**. The original definition of **HEAs** was alloys containing at least 5 elements with concentrations between 5 and 35 atomic percent. Later research has suggested that this definition could be expanded.

From Wikipedia, the free encyclopedia.

High Entropy Alloy phase diagram, Map ex. 2

This is a standard phase diagram with Co replacing Ni with conditions x(Fe)= x(Mn)= x(Cr)= 0.2. This means x(Ni) + x(Co) = 0.4

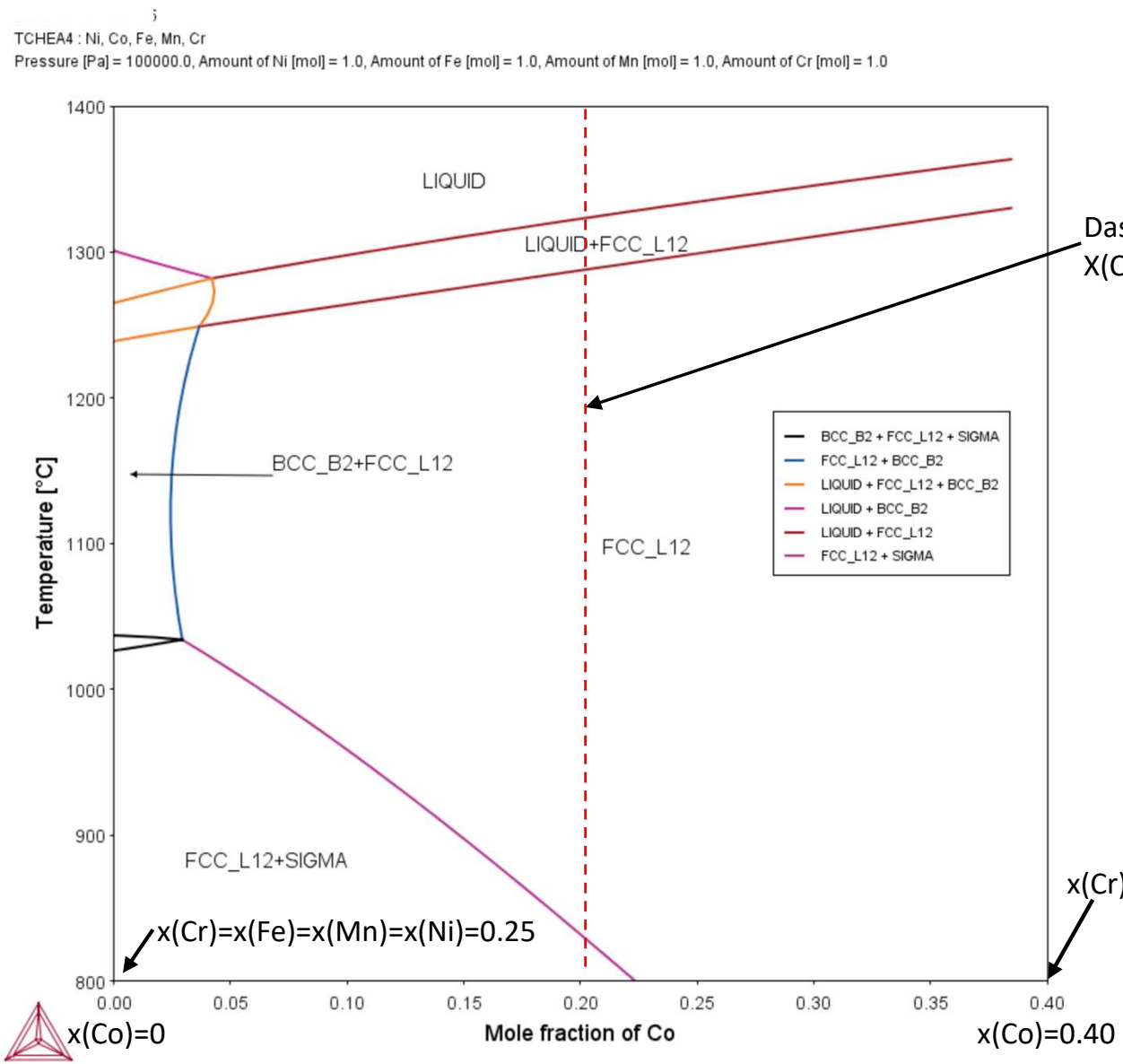


x(Co)=0 x(Ni)=0

High Entropy Alloy phase diagram, Map ex. 2

Thermo-Calc Software

Adding Co to an alloy with equal parts Cr – Fe – Mn – Ni (in mole-fraction).
Co is not replacing just one base metal (unlike standard phase diagrams).



Dashed line: All five elements
X(Co)=x(Cr)=x(Fe)=x(Mn)=x(Ni)=0.2

x(Cr)=x(Fe)=x(Mn)=x(Ni)=0.25

x(Cr)=x(Fe)=x(Mn)=x(Ni)=0.15

x(Co)=0

x(Co)=0.40

Map 3: Base metal to Weld phase diagram.

Multicomponent ”mapped” diagrams, Map ex. 3

Thermo-Calc Software

Calculate a phase diagram between two high alloyed stainless steels. All alloying elements are changing along the x-axis. This used to require functions as conditions.

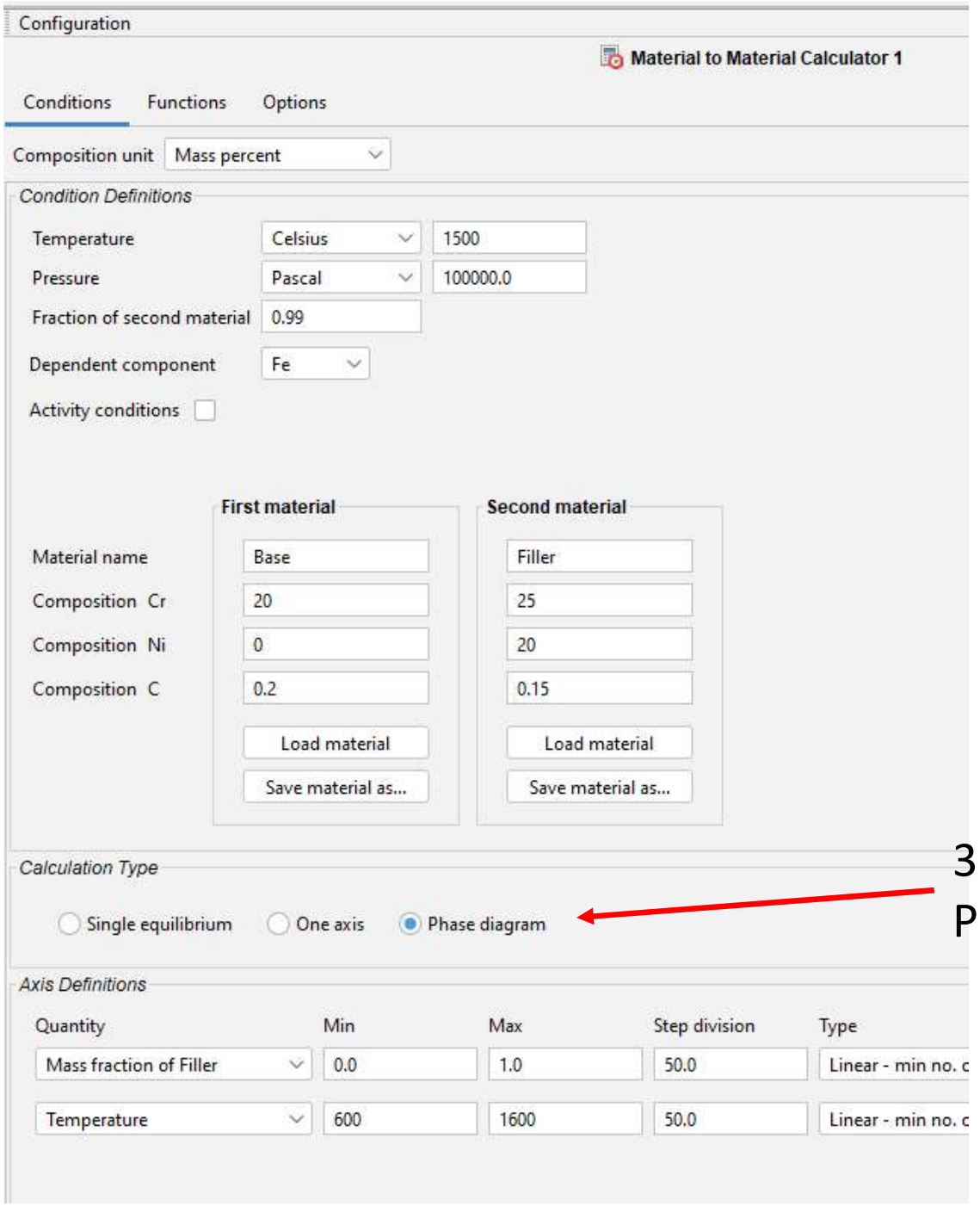
(Functions can be written in console mode syntax. Must use W(ii) = Weight-fraction and not wt-%.)

Material to Material Calculator. New since 2 years.
This template makes such a calculation much easier to set up.

Base Fe – 0.0 Ni – 20 Cr – 0.2 C (wt-%)
Filler Fe – 20 Ni – 25 Cr – 0.15 C (wt-%)

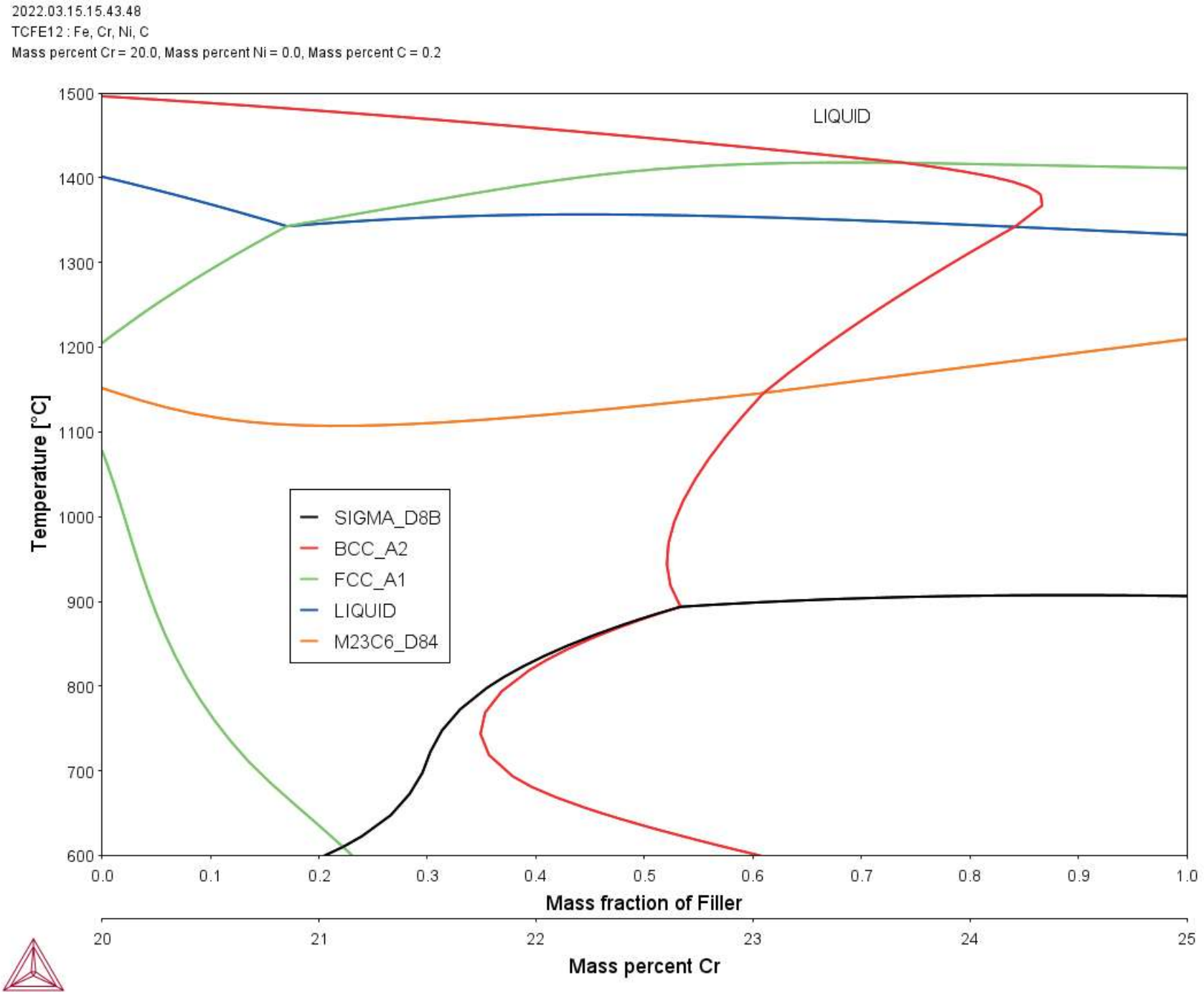
See next slide.

Multicomponent ”mapped” diagrams, Map ex. 3



3 types of calculations,
Phase diagram is one.

Multicomponent ”mapped” diagrams, Map ex. 3



Thermo-Calc Software

Questions

&

Answers

Thermo-Calc Software

Home Assignment 2

Home Assignment 2

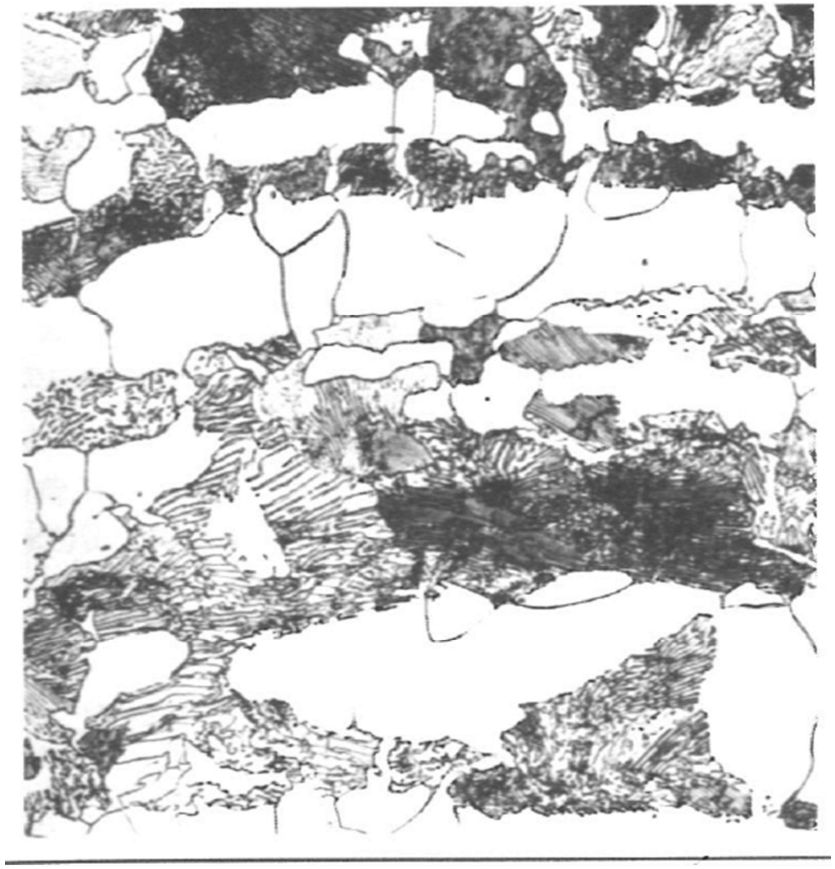
Thermo-Calc Software

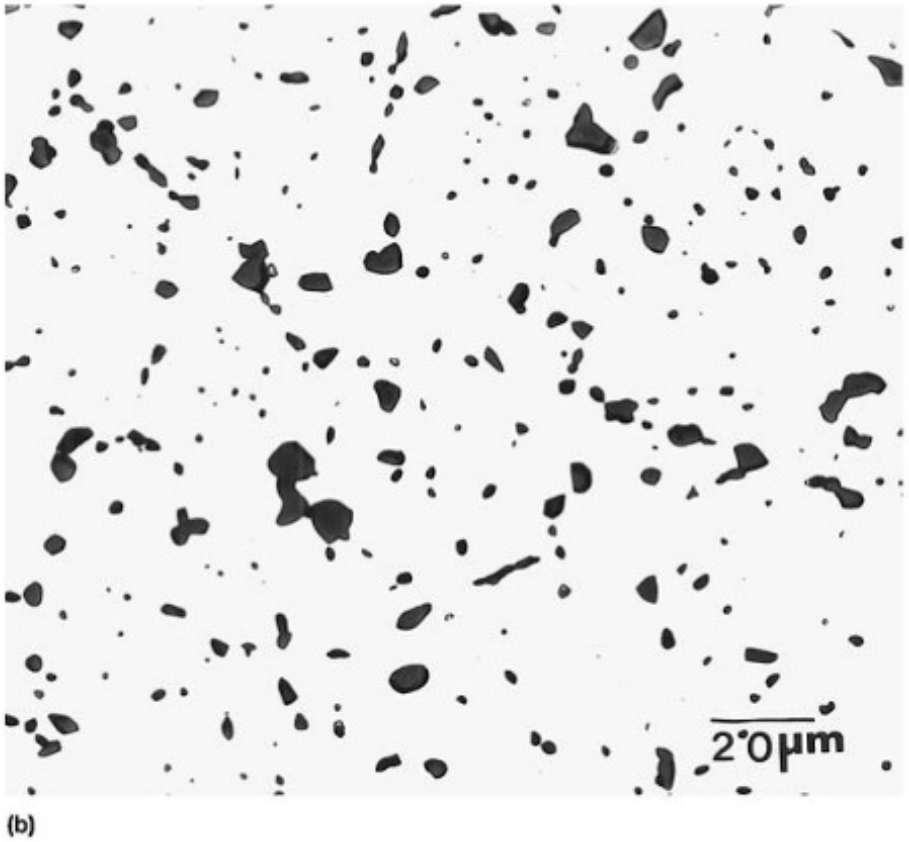
Calculate Equilibrium at 600 ºC for the following steel:

- AISI 1040 with Fe (bal.) – 0.4C - 0.7Mn (wt-%)

Which microstructure aligns with your result?

Is this Graphite or Fe_3C (Cementite)?





From ASM International: Heat Treaters Guide (1995).

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https://download.thermocalc.com/courses/TC-Day3/