Rovnovážné diagramy, fázové pravidlo, Fe-C (Fe_3C) diagram

… v souvislosti s mechanickými vlastnostmi

A. Kroupa, T. Kruml, Ústav fyziky materiálů, AV ČR
kroupa@ipm.cz, kruml@ipm.cz

Contents

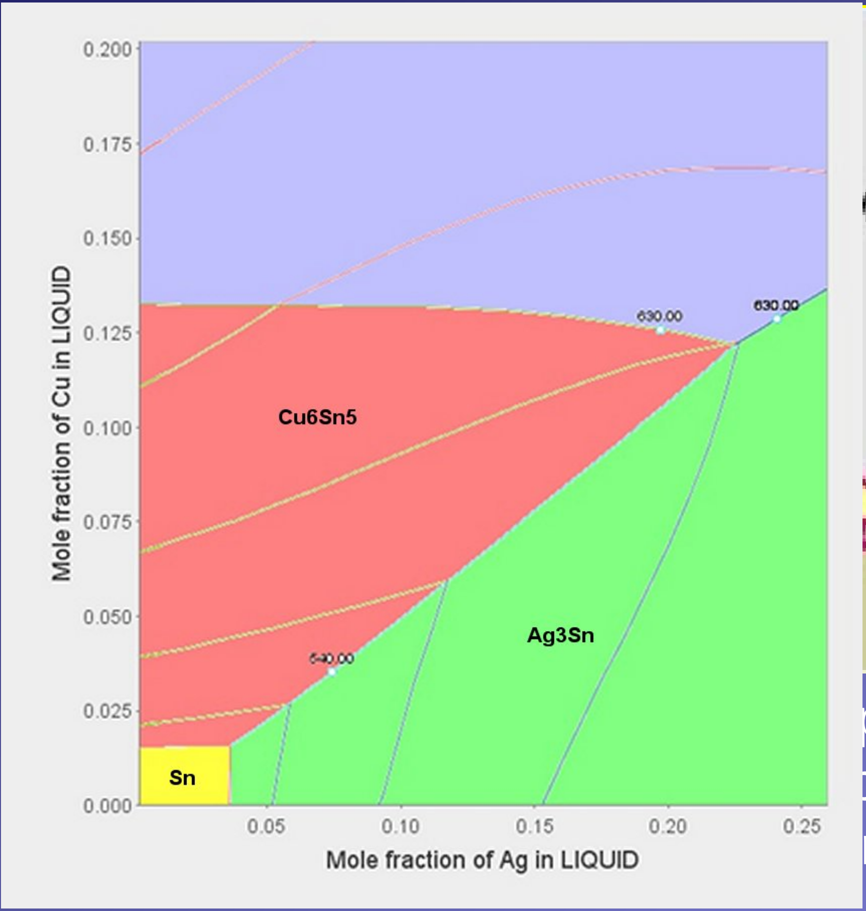
- Laws of Thermodynamics
  - Essentially a reflection of what we see around us
- Thermodynamic quantities
  - Heat capacity
  - Enthalpy
  - Gibbs energy
  - Entropy
- Properties pure substances e.g. elements
- Properties of mixtures
- Types of phase diagrams
- Fe-Fe3C (Fe-C) phase diagrams
- TTT and CCT diagrams
- Software – thermodynamics made easy

What is a Phase Diagram?

A phase diagram is the graphical representation of the state of a system in thermodynamic equilibrium as a function of selected state variables

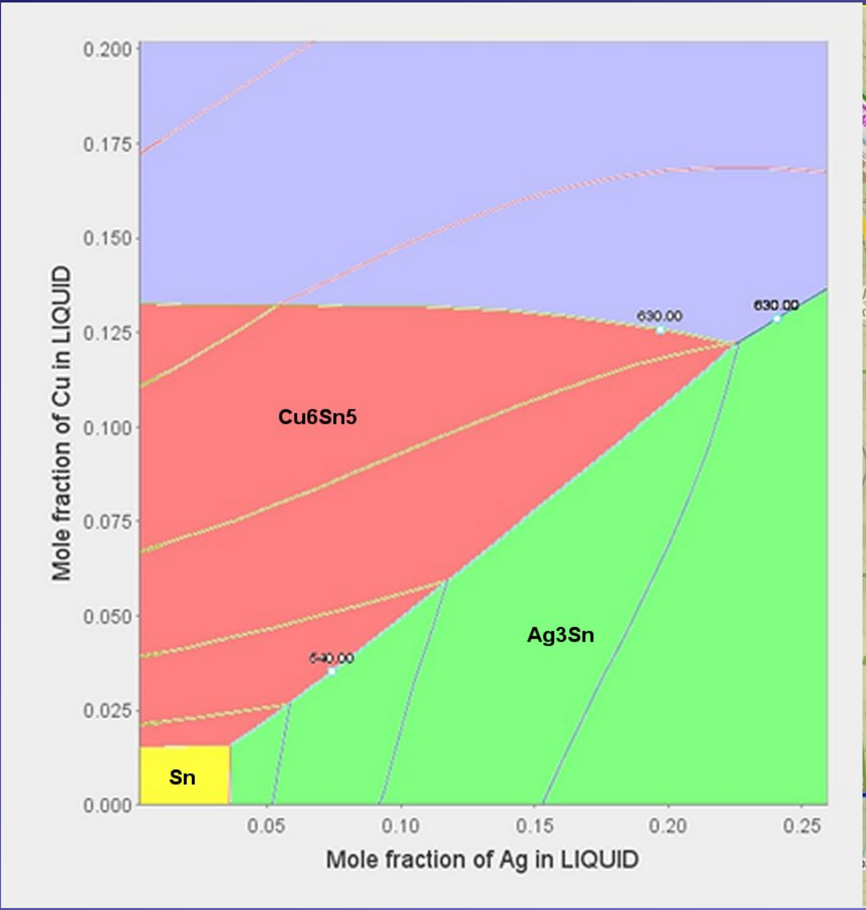
- Phase diagrams are strictly connected with the rules of thermodynamics
- Phase diagrams differ from “normal” (property) diagrams. They carry a different type of information
- Phase diagrams are powerful tools to help materials scientists to solve specific problems related to the equilibrium state of their material system

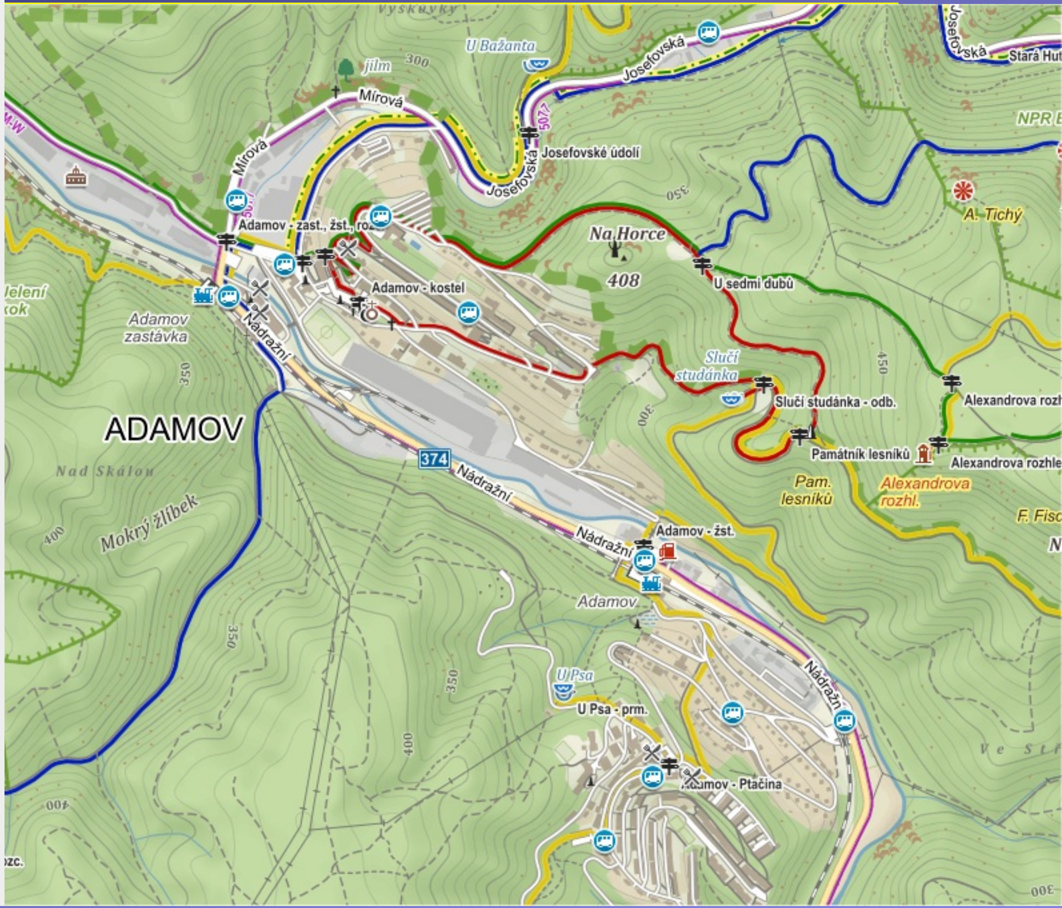
What is a Phase Diagram?



powerful tools to help materials pecific problems related to the r material system

What is a Phase Diagram?



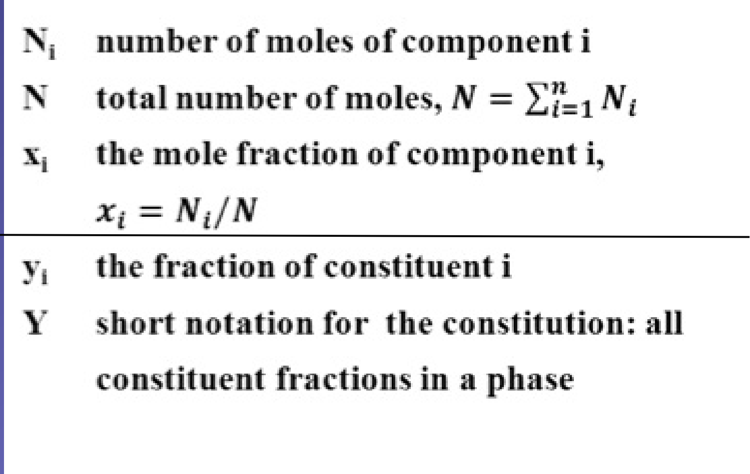


Some Terms and Symbols

A system consists of components (element or specie – ion, molecule, ...)

A phase is of homogeneous part of the system in equilibrium. It is determined by its crystal structure. It can also be liquid or gaseous.

A constituent is a species that can be treated as an independent entity to describe the constitution of a phase. E.g.: element, stoichiometric compound (e.g. oxide), a molecule in the gas phase, or a defect in a crystalline phase



System	N_i	number of moles of component i
	N	total number of moles, $N = \sum_{i=1}^{n} N_i$
	x_i	the mole fraction of component i, $x_i = N_i/N$
Phase	y_i	the fraction of constituent i
	Y	short notation for the constitution: all constituent fractions in a phase

G	**total Gibbs energy of a system**
G_m	**molar Gibbs energy of a system**
G_m^α	**molar Gibbs energy of the phase α**
G_i^α	**partial Gibbs energy of component i in the phase α**
$^0G_i^\alpha$	**Gibbs energy of the pure component i in the phase α**

Thermodynamics: State Variables

The state of a system is described by a set of state variables

- Intensive state variables: p, T, μ_i, ….
  - do not depend on the size of the system. In equilibrium they are the same everywhere in the system

- Extensive state variables: N, N_i, V, S, G, H, …
  - are proportional to the size of the system

- Molar variables: $G_m = G/N$, $S_m = S/N$….
  - derived from extensive variables by dividing them by N. They are not dependent on the size of the system, but have different values for different phases in equilibrium

Thermodynamic Equilibrium Conditions

The intensive state variables are constant in the entire system:

T=const., p = const., μ_i = const. for all components i in all phases

The state function G (Gibbs energy) reaches a minimum at

T, p, N_i = const.

The number of state variables necessary to describe the system is therefore the number of independent components (c) + 2

The Gibbs phase rule relates this to the number of phases present in the system (p) and the degree of freedom (f)

$$p + f = c + 2$$

Thermodynamics

- Interpretation of what we see around us
  - 1st - In any process or event, energy can only be converted from one form to another; the total energy must remain constant
    - perpetual motion machines of the first kind are impossible
  - 2nd - It is not possible to convert all energy into useful work
    - perpetual motion machines of the second kind are impossible
  - 3rd - It is not possible to reach a temperature of absolute zero
    - The entropy of a perfect crystal at absolute zero is exactly equal to zero.

Thermodynamics

0th - Materials in thermal equilibrium have the same temperature

- *4th* ? – Materials at infinite high temperature behave like ideal systems

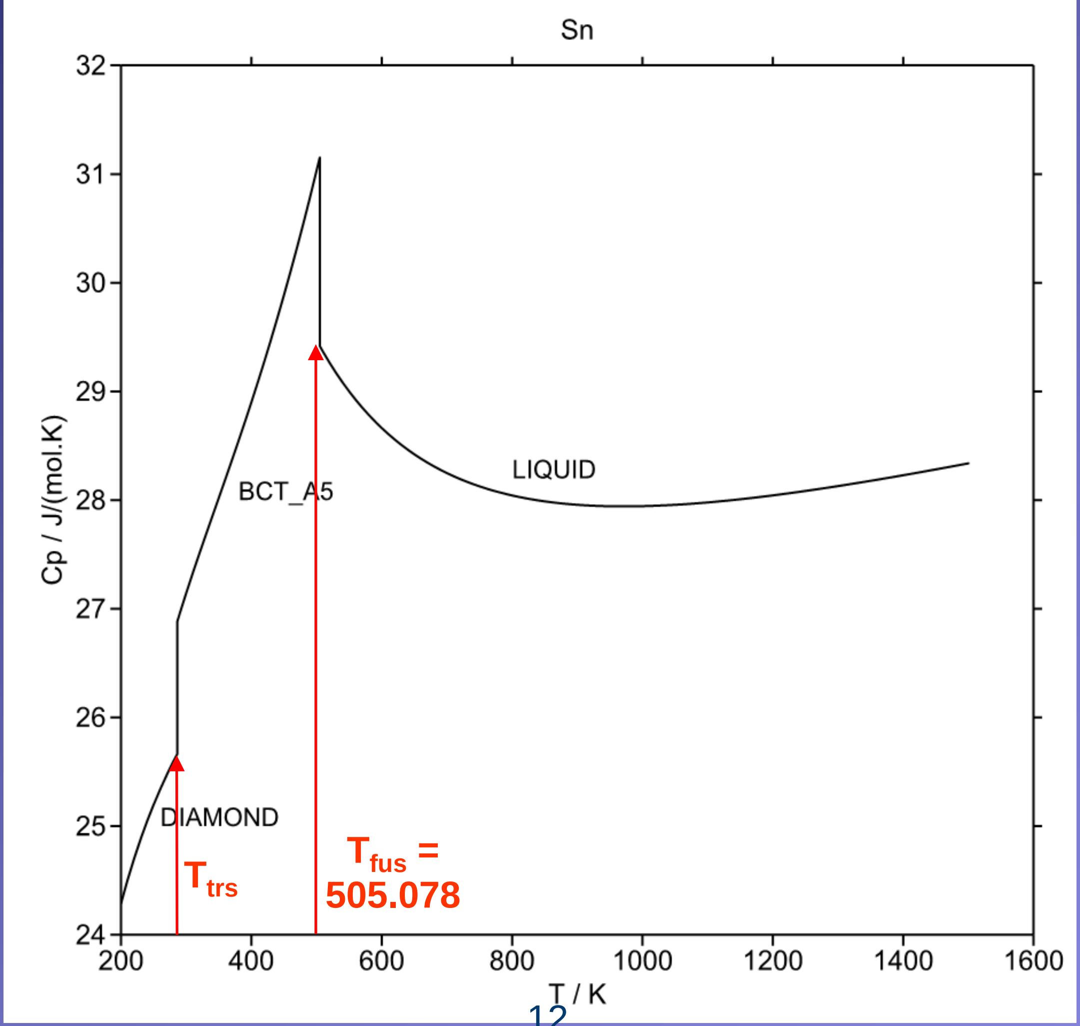
Leads to definitions of all thermodynamic quantities

Thermodynamics enables us to understand why things happen in the way they do and to make predictions about what is likely to happen under conditions yet to be studied

Heat capacity

- For most materials we consider constant pressure
- Heat capacity is amount of heat required to raise temperature of the unit amount of material by 1°
- Measure of capacity of material to absorb heat
- Differs from one phase to another
- Also a measure of change within the material
  - Monotonous change in the heat capacity indicates stability
  - Big changes with temperature indicates bond breaking
    - Magnetic transition, melting of alloy
    - Gas speciation
    - Electronic effects in gas species

Heat capacity of Sn for different phases



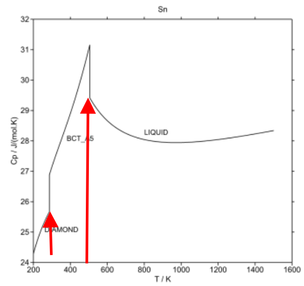
Enthalpy

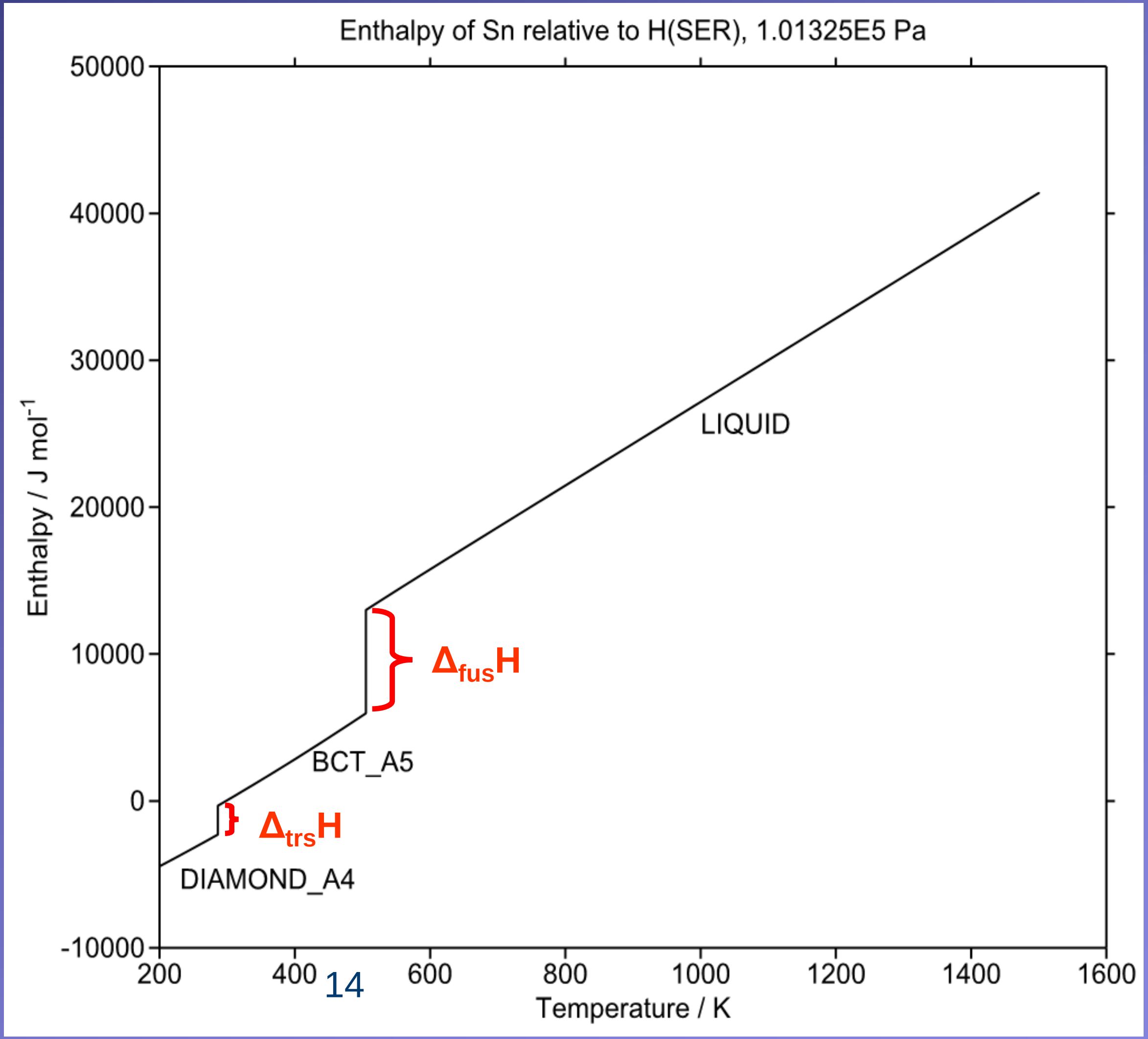
- Amount of heat stored in a material $H = U + pV$
- Has no absolute value – possible to talk only about changes in enthalpy or differences between two states
  - Need standard reference state (SER – stable phase at room temp. and standard pressure)
- Integrated heat capacity between temperatures
- Different phases have different enthalpies
  - Melting requires energy to be absorbed
- Substances reacting together give off or absorb heat

At constant volume, the heat absorbed by the system = ΔU

At constant pressure, the heat absorbed by the system = ΔH

Enthalpy of Sn relative to T=298K

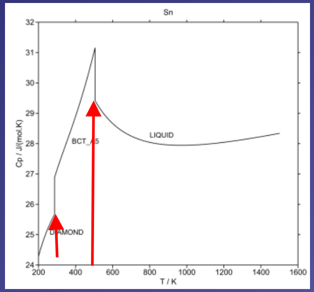


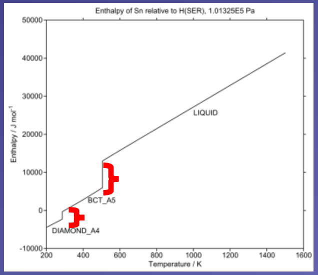


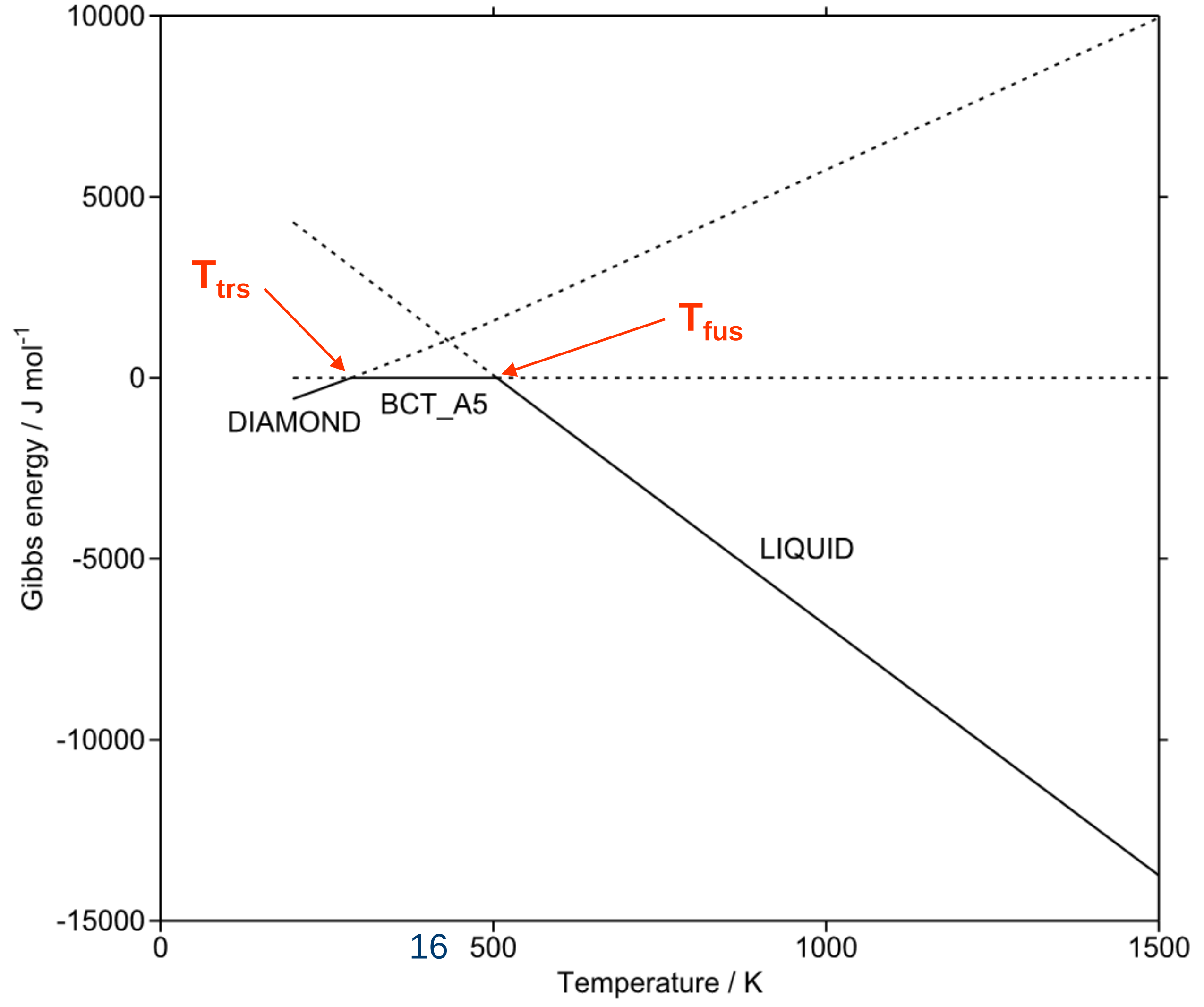
Gibbs energy (G, state function with respect to P, T, n_i)

- Any spontaneous change takes place to increase the stability of the system
- For problems in materials science we tend to express this in terms of Gibbs energy
- Different phases have different Gibbs energies
- At constant temperature and pressure the state with lowest Gibbs energy is the equilibrium state
- Like enthalpy, Gibbs energy has no absolute value i.e. it is possible to talk only about changes in the Gibbs energy
- Depends on temperature
  - Material melts when you raise the temperature, i.e. difference in Gibbs energy between liquid and solid changes with temperature
- Depends on pressure
  - Reducing the pressure causes a liquid to boil
- $G = U - T S + P V$ Play off between lowest energy state (enthalpy) and increased disorder (entropy)

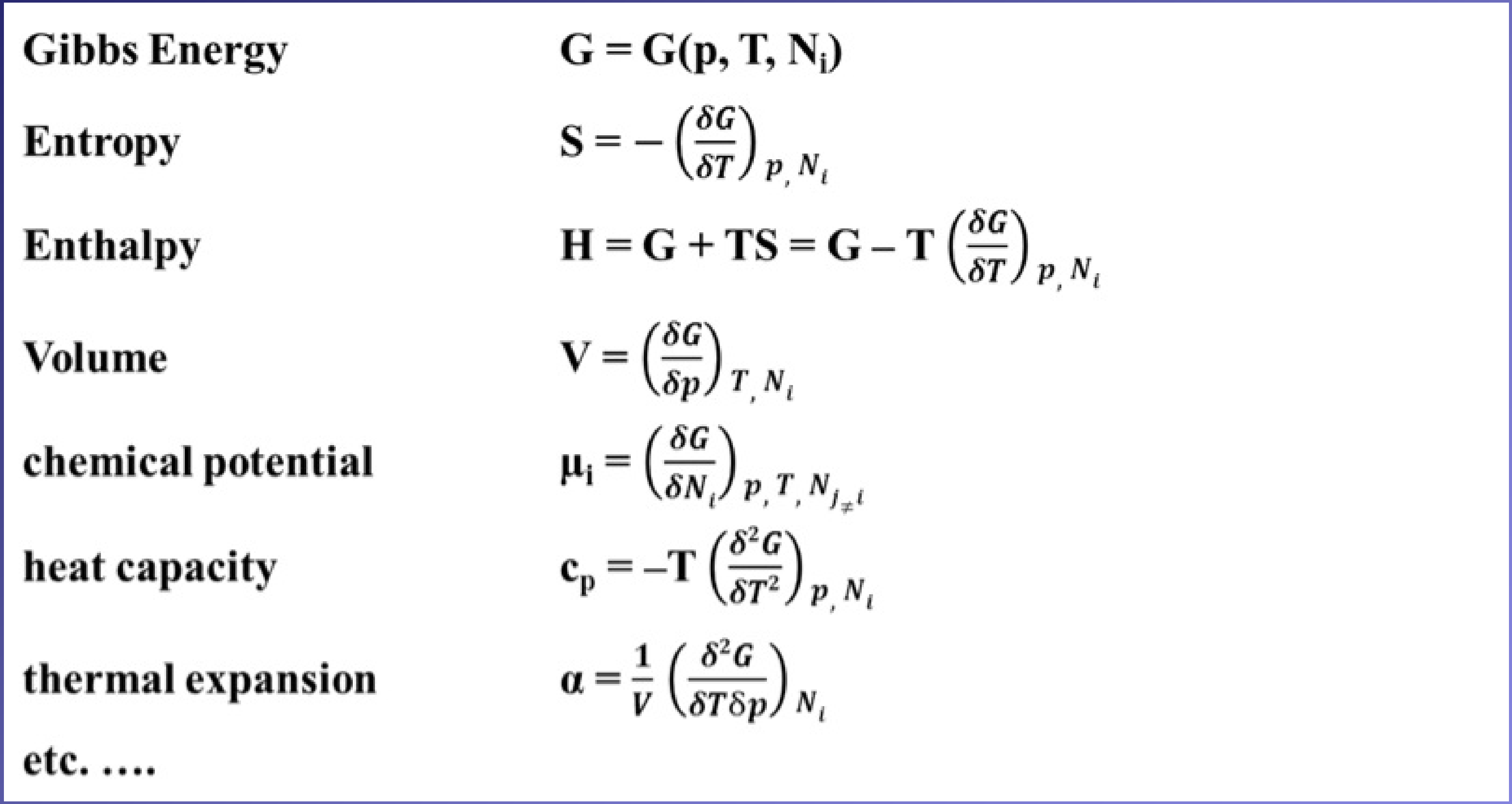
Gibbs energy of phases of Sn relative to BCT







Derivatives of the Gibbs Energy

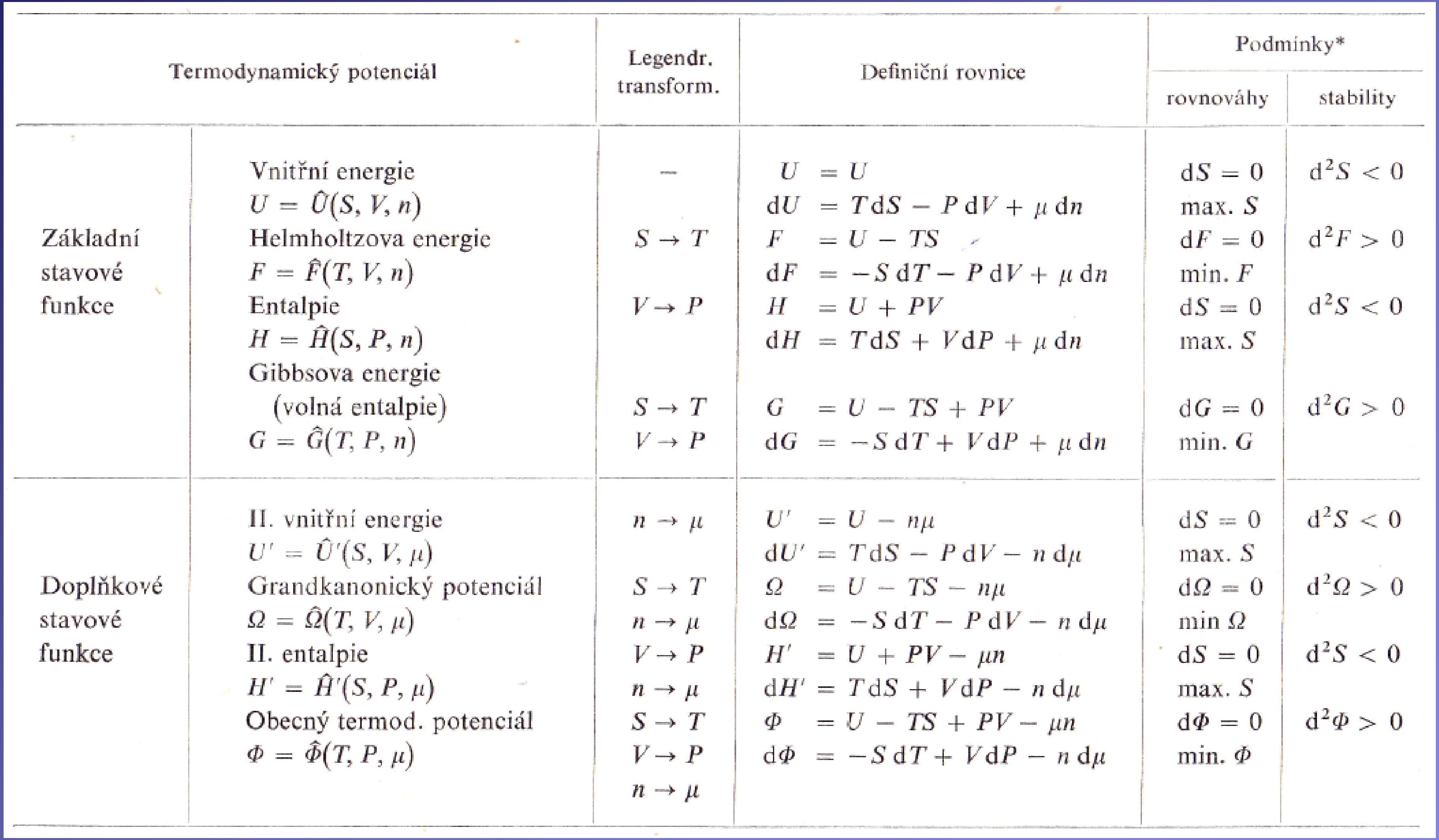


Gibbs Energy	$G = G(p, T, N_i)$
Entropy	$S = -\left(\frac{\delta G}{\delta T}\right)_{p, N_i}$
Enthalpy	$H = G + TS = G - T\left(\frac{\delta G}{\delta T}\right)_{p, N_i}$
Volume	$V = \left(\frac{\delta G}{\delta p}\right)_{T, N_i}$
chemical potential	$\mu_i = \left(\frac{\delta G}{\delta N_i}\right)_{p, T, N_{j \neq i}}$
heat capacity	$c_p = -T\left(\frac{\delta^2 G}{\delta T^2}\right)_{p, N_i}$
thermal expansion	$\alpha = \frac{1}{V}\left(\frac{\delta^2 G}{\delta T \delta p}\right)_{N_i}$
etc. ….	

Entropy

- Entropy associated with disorder
- Effect more significant at higher temperatures
- Entropy has definite value
- At low temperatures the entropy should tend towards zero
- The effect of entropy usually offsets enthalpy
  - Pure substance at transition temperature, the enthalpy change equals entropy change * T

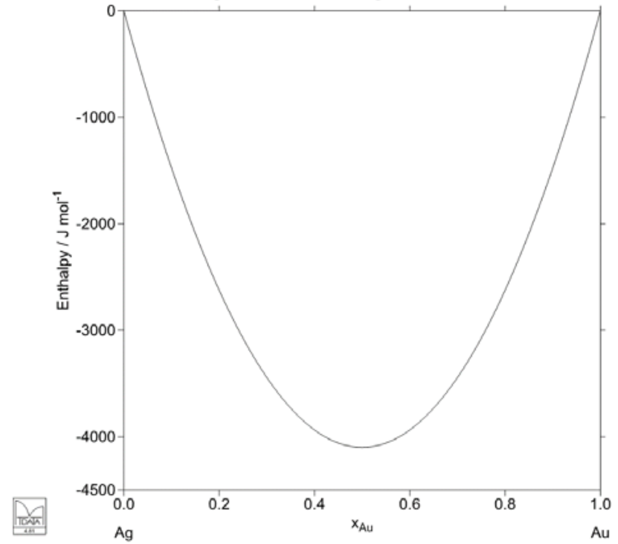
Přehled stavových funkcí:



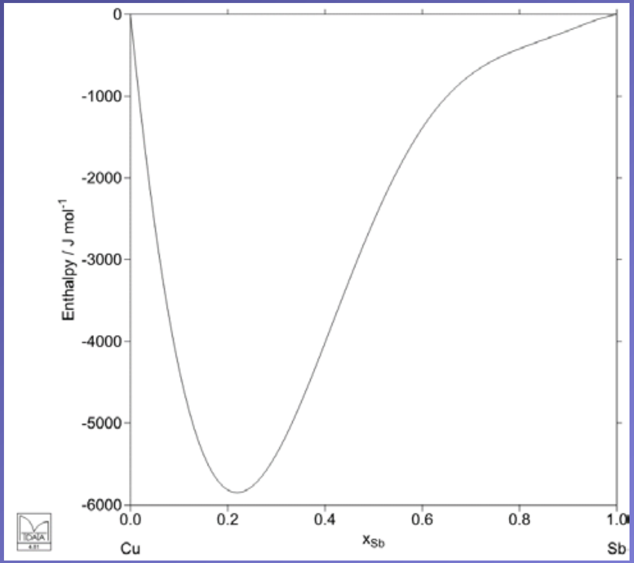
Termodynamický potenciál		Legendr. transform.	Definiční rovnice	Podmínky*	
				rovnováhy	stability
Základní stavové funkce	Vnitřní energie	–	$U = U$	$\mathrm{d}S = 0$	$\mathrm{d}^2S < 0$
	$U = \hat{U}(S, V, n)$		$\mathrm{d}U = T\mathrm{d}S - P\,\mathrm{d}V + \mu\,\mathrm{d}n$	max. S	
	Helmholtzova energie	$S \to T$	$F = U - TS$	$\mathrm{d}F = 0$	$\mathrm{d}^2F > 0$
	$F = \hat{F}(T, V, n)$		$\mathrm{d}F = -S\,\mathrm{d}T - P\,\mathrm{d}V + \mu\,\mathrm{d}n$	min. F	
	Entalpie	$V \to P$	$H = U + PV$	$\mathrm{d}S = 0$	$\mathrm{d}^2S < 0$
	$H = \hat{H}(S, P, n)$		$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P + \mu\,\mathrm{d}n$	max. S	
	Gibbsova energie				
	(volná entalpie)	$S \to T$	$G = U - TS + PV$	$\mathrm{d}G = 0$	$\mathrm{d}^2G > 0$
	$G = \hat{G}(T, P, n)$	$V \to P$	$\mathrm{d}G = -S\,\mathrm{d}T + V\mathrm{d}P + \mu\,\mathrm{d}n$	min. G	
Doplňkové stavové funkce	II. vnitřní energie	$n \to \mu$	$U' = U - n\mu$	$\mathrm{d}S = 0$	$\mathrm{d}^2S < 0$
	$U' = \hat{U}'(S, V, \mu)$		$\mathrm{d}U' = T\mathrm{d}S - P\,\mathrm{d}V - n\,\mathrm{d}\mu$	max. S	
	Grandkanonický potenciál	$S \to T$	$\Omega = U - TS - n\mu$	$\mathrm{d}\Omega = 0$	$\mathrm{d}^2\Omega > 0$
	$\Omega = \hat{\Omega}(T, V, \mu)$	$n \to \mu$	$\mathrm{d}\Omega = -S\,\mathrm{d}T - P\,\mathrm{d}V - n\,\mathrm{d}\mu$	min Ω	
	II. entalpie	$V \to P$	$H' = U + PV - \mu n$	$\mathrm{d}S = 0$	$\mathrm{d}^2S < 0$
	$H' = \hat{H}'(S, P, \mu)$	$n \to \mu$	$\mathrm{d}H' = T\mathrm{d}S + V\mathrm{d}P - n\,\mathrm{d}\mu$	max. S	
	Obecný termod. potenciál	$S \to T$	$\Phi = U - TS + PV - \mu n$	$\mathrm{d}\Phi = 0$	$\mathrm{d}^2\Phi > 0$
	$\Phi = \hat{\Phi}(T, P, \mu)$	$V \to P$	$\mathrm{d}\Phi = -S\,\mathrm{d}T + V\mathrm{d}P - n\,\mathrm{d}\mu$	min. Φ	
		$n \to \mu$			

What happens when things mix?

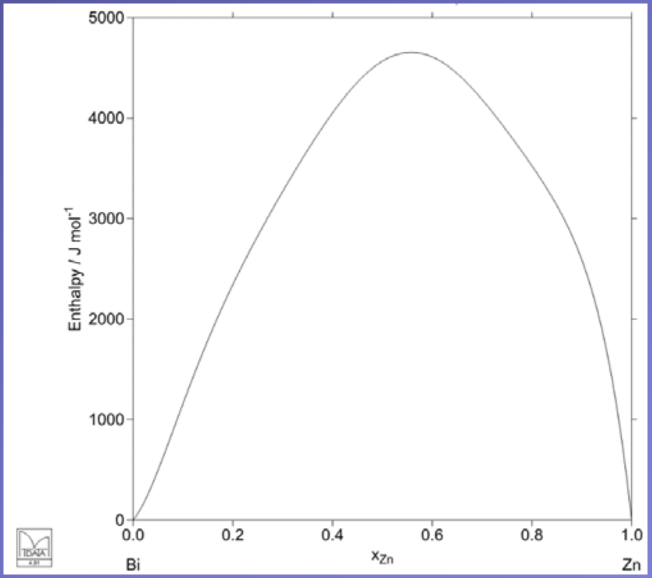
- Some elements mix together (eg in the liquid phase) without giving out or absorbing heat – said to mix ideally eg Co and Ni
- Normally there is a net heat effect which could be either negative (giving out heat) or positive (heat is absorbed) … or even more complex



regular solution



negative enthalpy of mixing

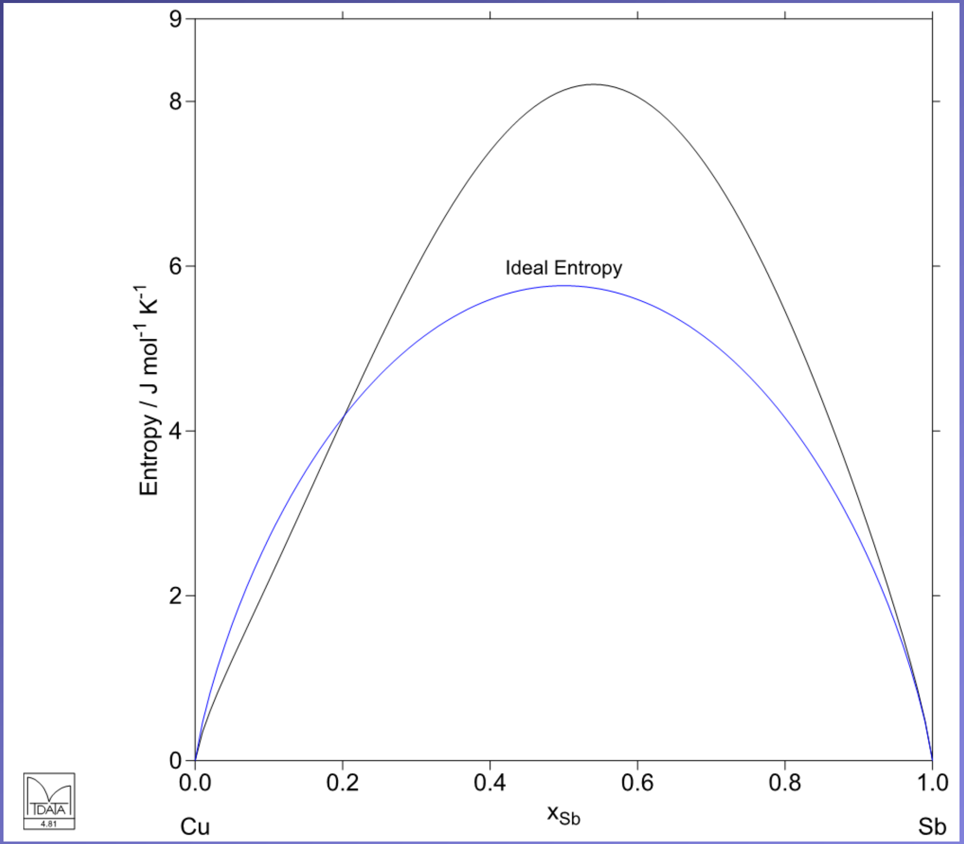


Positive enthalpy of mixing

Entropy of mixing

Generally two contributions

- First from random mixing of the elements (ideal contribution)
- “So called” excess entropy of mixing - *really to account for deviations from ideality*



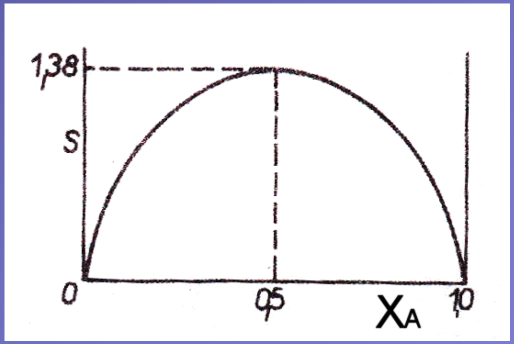
Konfigurační entropie systému:

opět máme krystal s N atomy: n atomů A a (N-n) atomů B

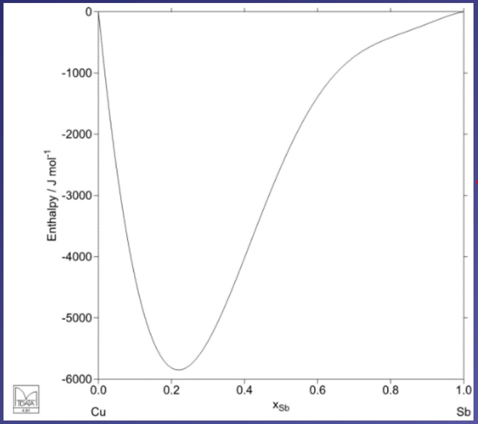
$$S = k \ln w, \qquad w = \frac{N!}{n!(N-n)!}$$

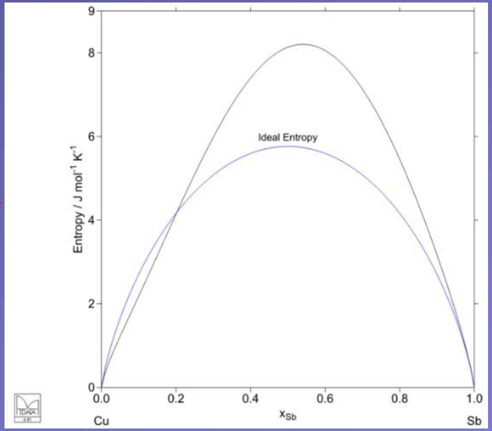
$$S = k\left[N \ln N - n \ln n - (N-n)\ln(N-n)\right]$$

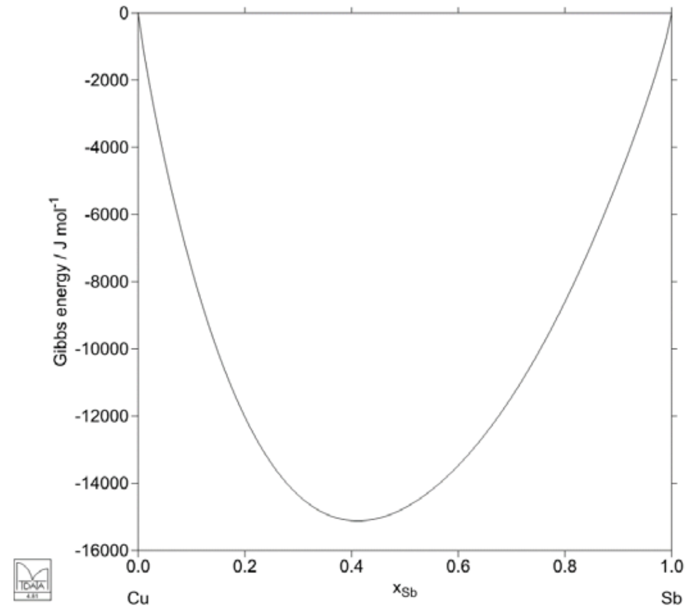
$$S = -kN\left[x_A \ln x_A + (1-x_A)\ln(1-x_A)\right]$$



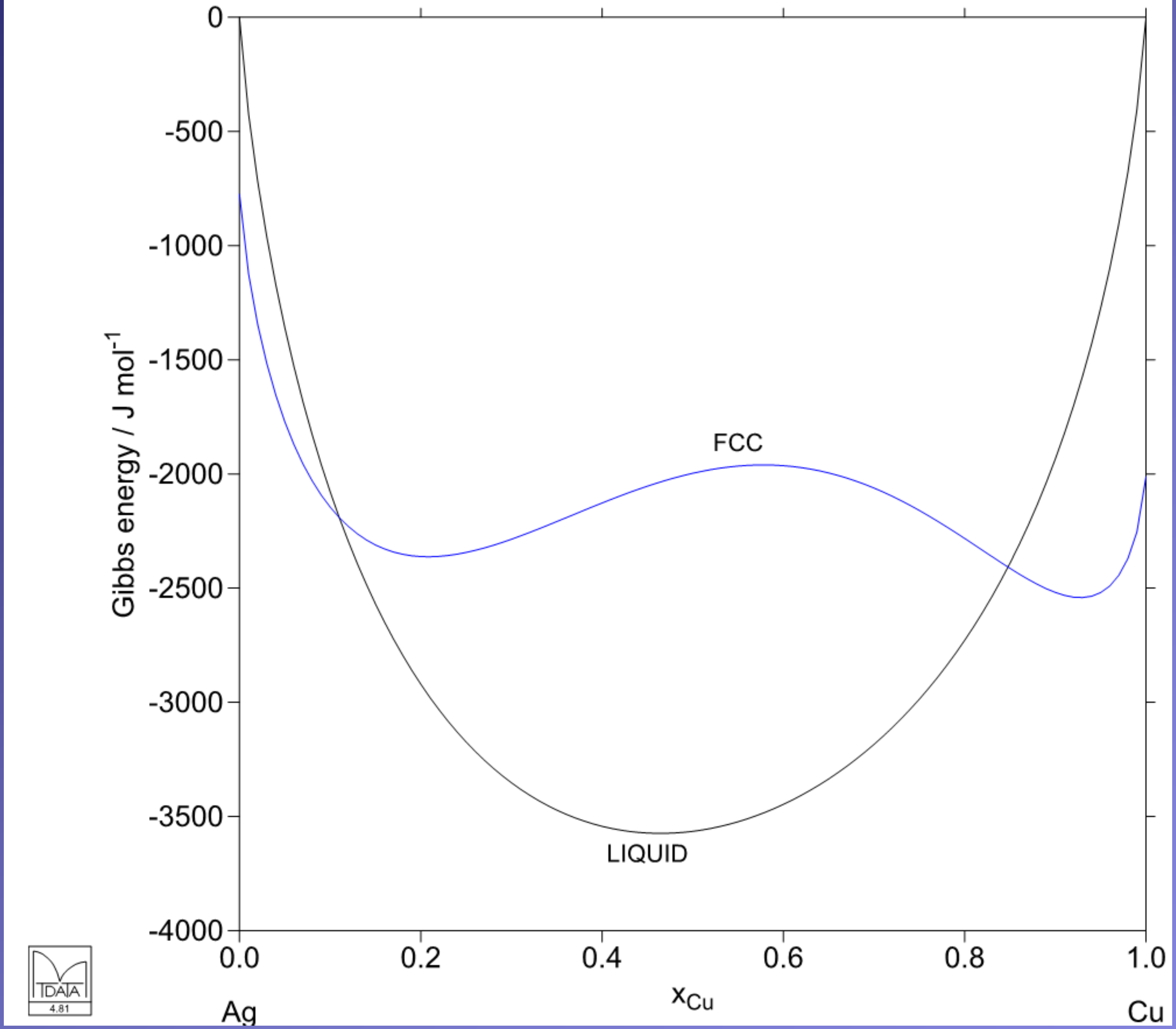
Gibbs energy of mixing G = H – T S



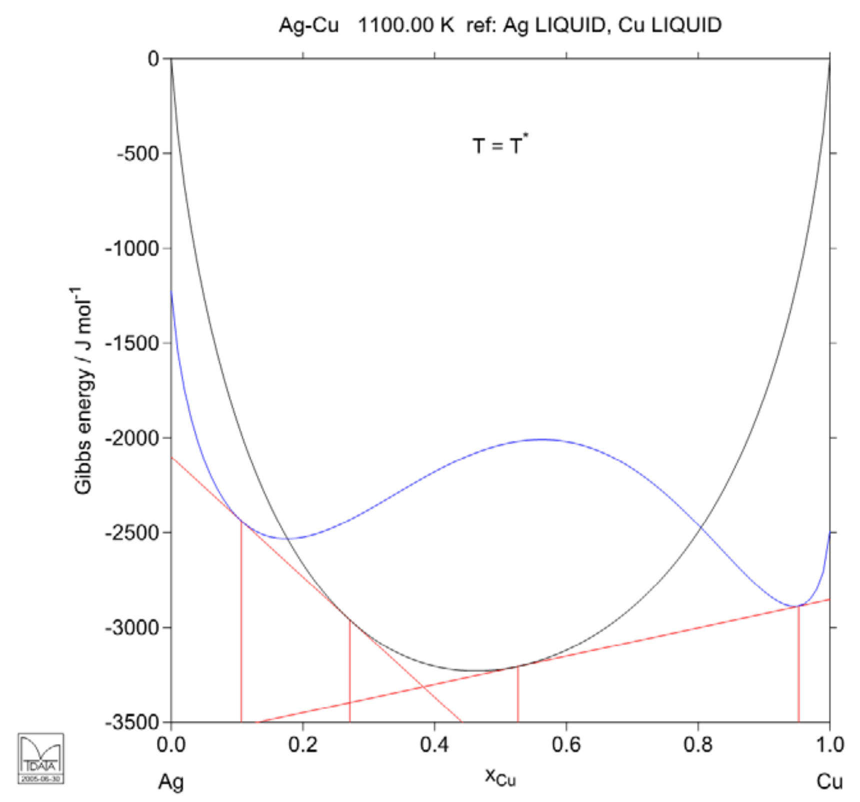


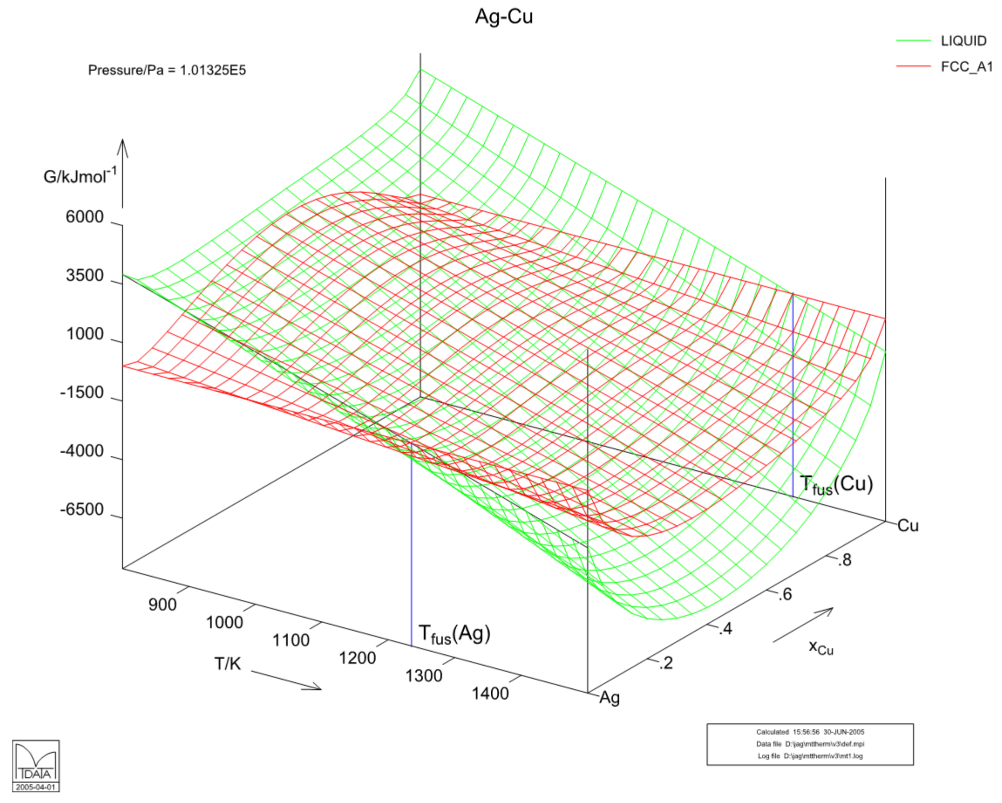


Gibbs energies of two phases

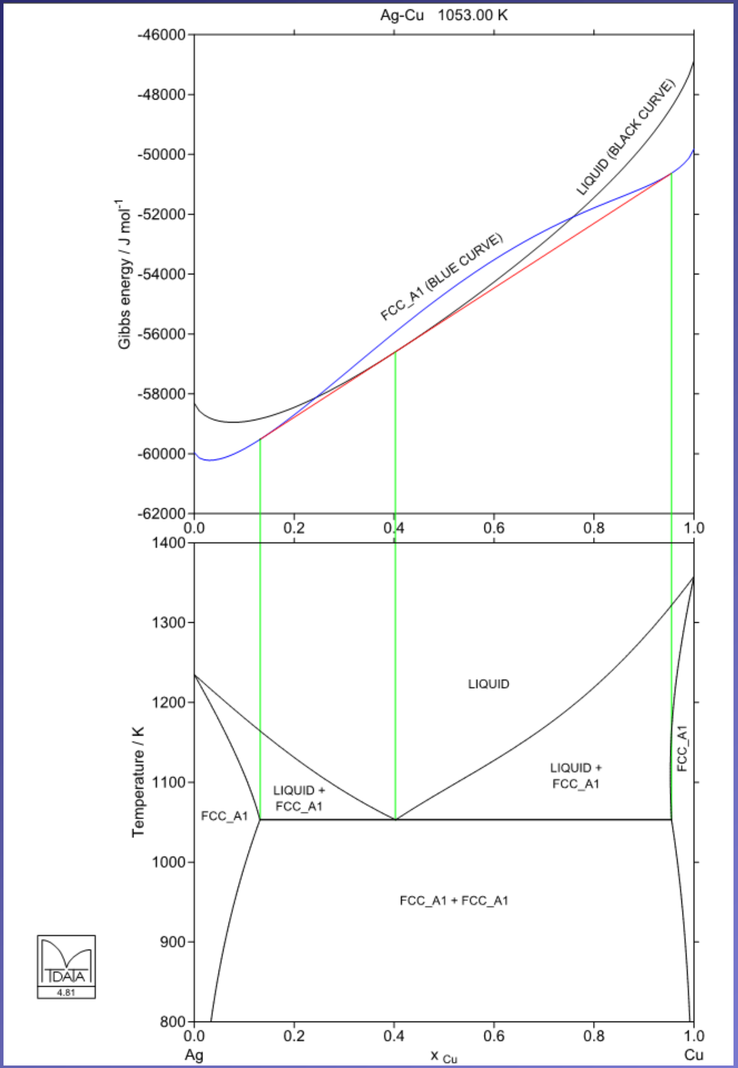


Calculation of binary phase equilibria



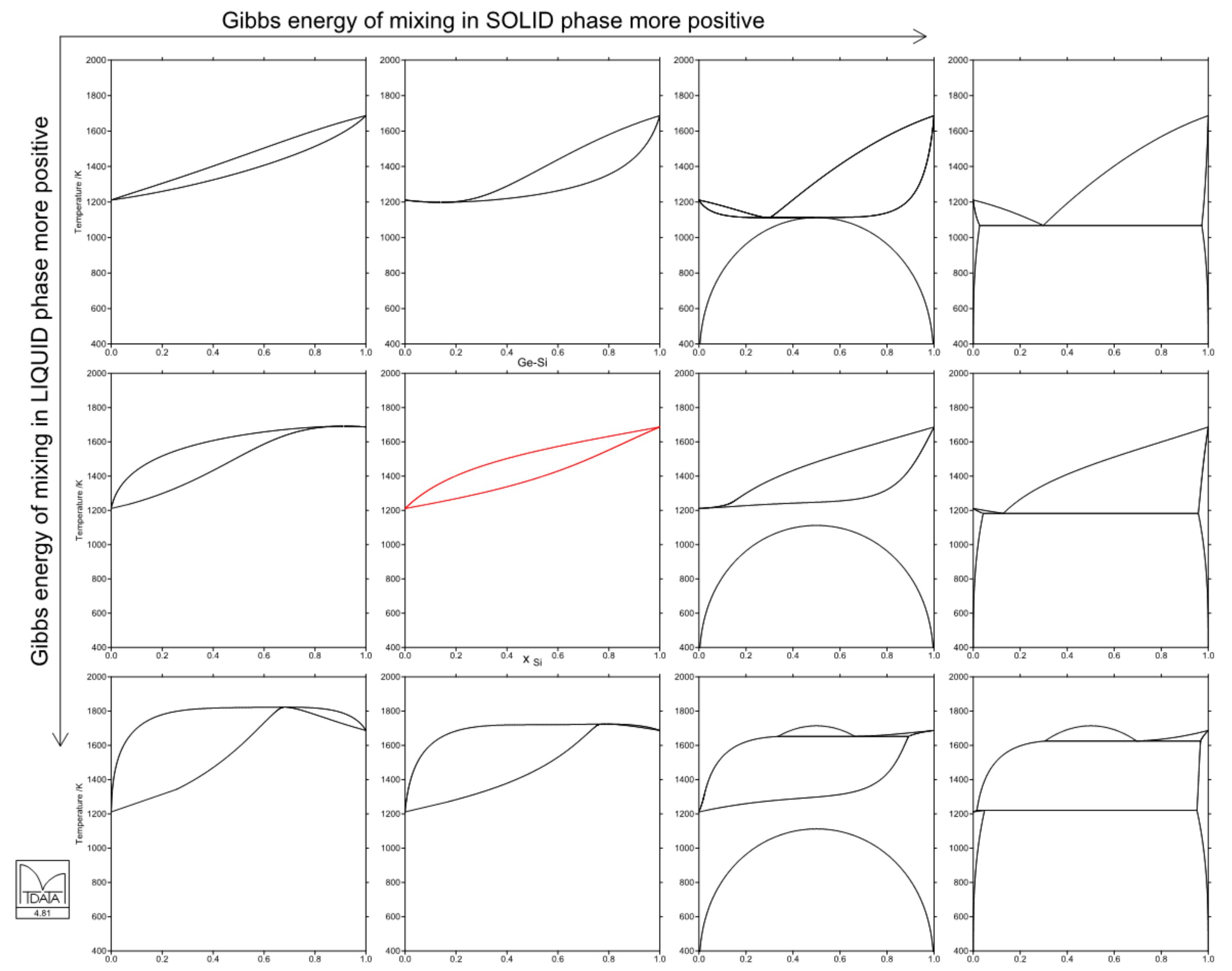


Calculation of binary phase equilibria

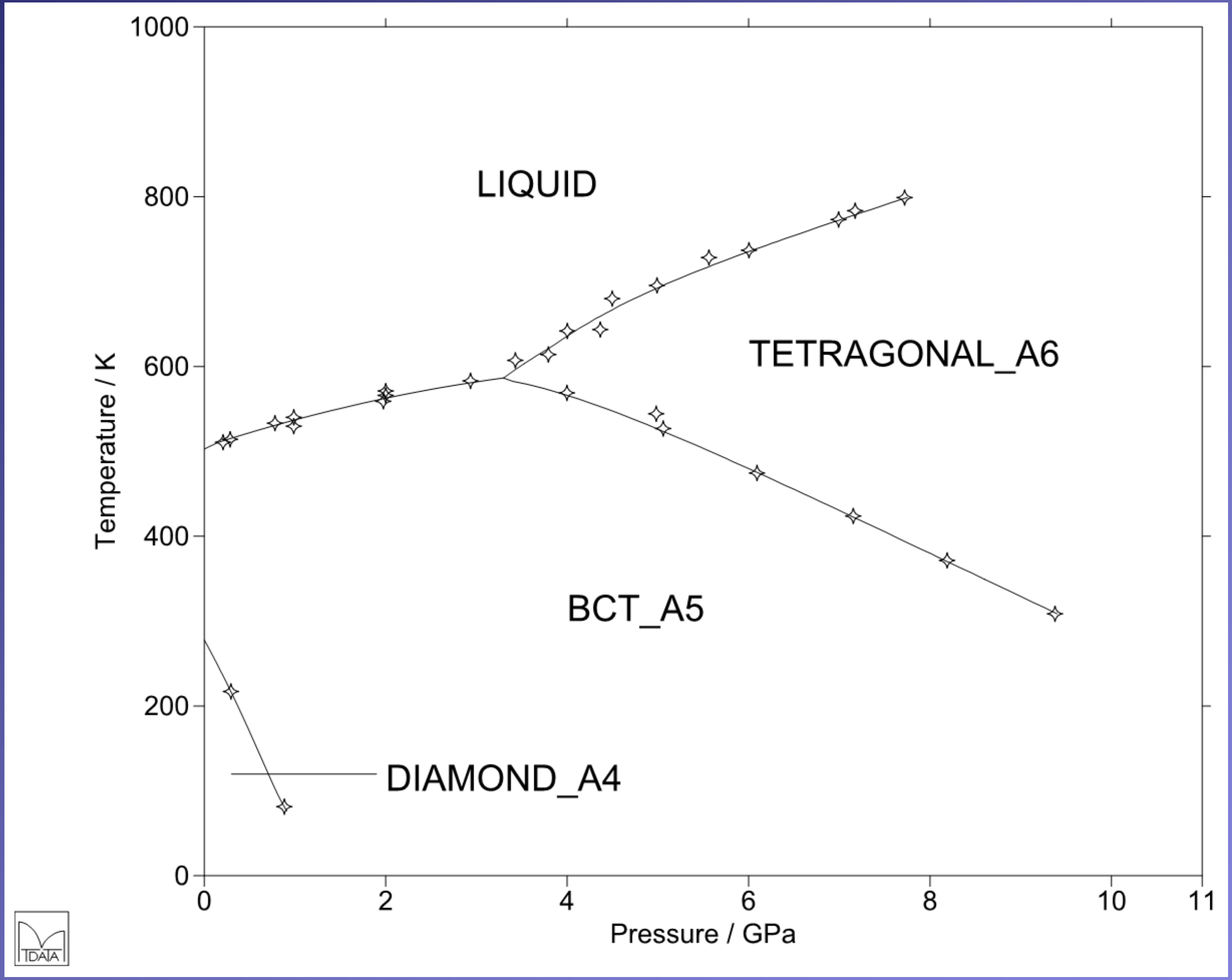


.... over a range of temperatures

Calculation of binary phase equilibria



Phase diagram and property diagram



Types of Phase Diagrams

A system in equilibrium is defined by a set of c+2 state variables. By varying two of them and keeping the others constant, a two-dimensional phase diagram can be drawn.

The maximal dimension of the phase diagram is c+1, because one extensive variable can be diminished by dividing them by N:

e.g.: $T, p, N_1 \ldots N_j \rightarrow T, p, x_1 \ldots x_{j-1}$

Types of phase diagrams:

a) two intensive variables
b) one intensive, one extensive (molar) variable
c) two extensive (molar) variables
d) Sections through higher dimensional phase diagrams defined by special restraints on extensive variables

Types of Phase Diagrams

A system in equilibrium is defined by a set of c+2 state variables. By varying two of them and keeping the others constant, a two-dimensional phase diagram can be drawn.

The maximal dimension of the phase diagram is c+1, because one extensive variable can be diminished by dividing them by N:

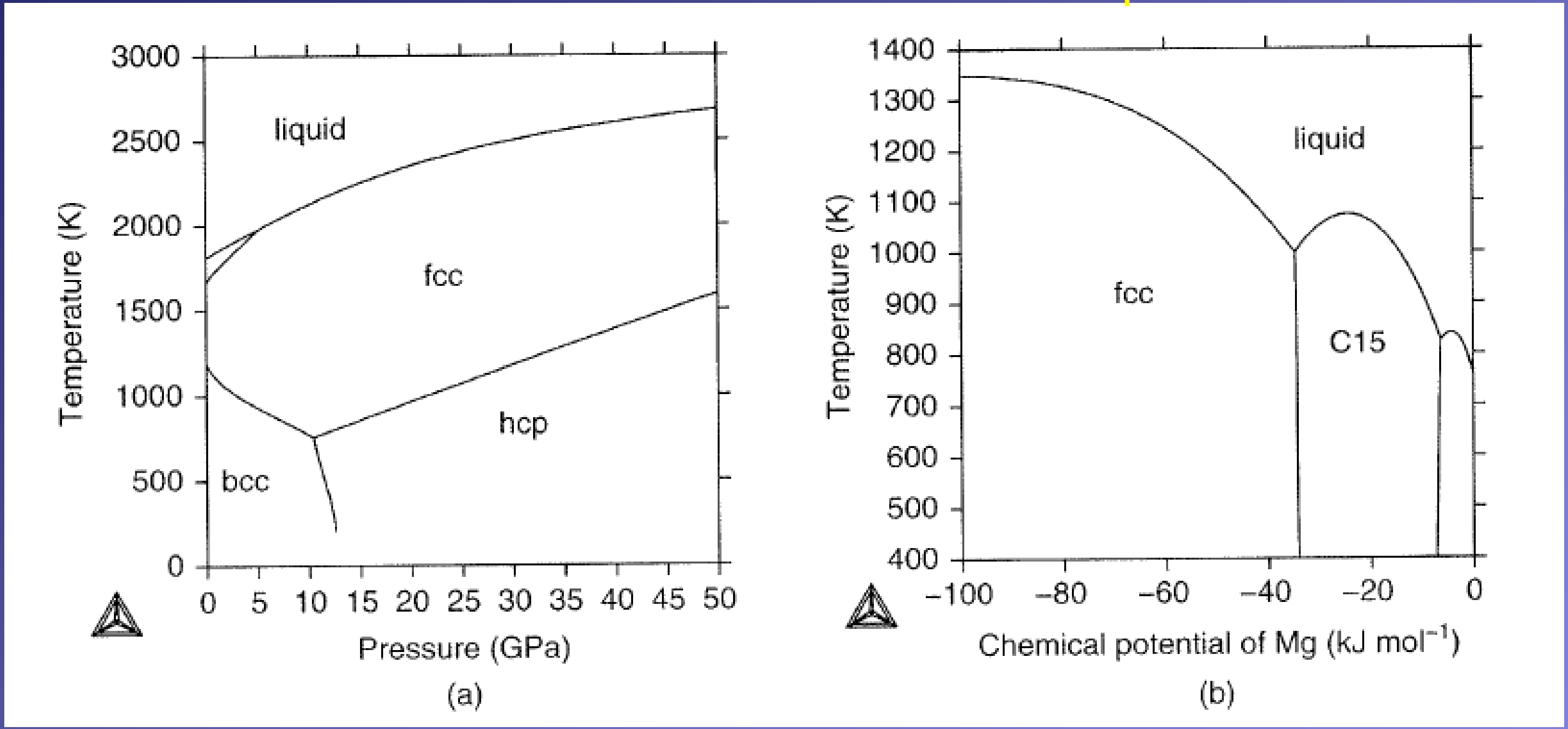
e.g.: $T, p, N_1 \ldots N_j \quad \rightarrow T, p, x_1 \ldots x_{j-1}$

Types of phase diagrams:

a) two intensive variables
b) one intensive, one extensive (molar) variable
c) two extensive (molar) variables
d) Sections through higher dimensional phase diagrams defined by special restraints on extensive variables

Types of Phase Diagrams

p = const.



(a)

(b)

Unary Fe, type A

Binary Cu-Mg, type A

In type A diagrams, lines denote two phase (monovariant) equilibria and points three phase (invariant) equilibria

Types of Phase Diagrams

A system in equilibrium is defined by a set of c+2 state variables. By varying two of them and keeping the others constant, a two-dimensional phase diagram can be drawn.

The maximal dimension of the phase diagram is c+1, because one extensive variable can be diminished by dividing them by N:

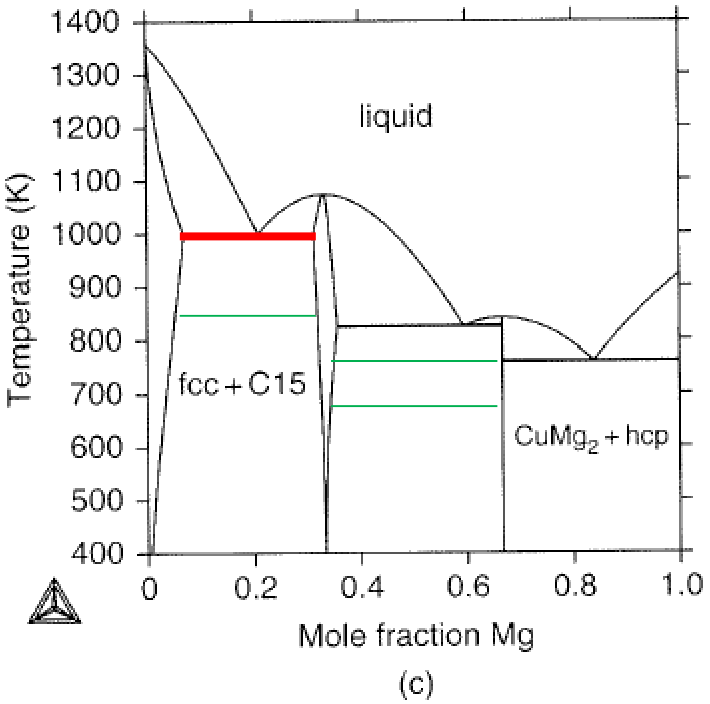
e.g.: $T, p, N_1 \ldots N_j \rightarrow T, p, x_1 \ldots x_{j-1}$

Types of phase diagrams:

a) two intensive variables
b) one intensive, one extensive (molar) variable
c) two extensive (molar) variables
d) Sections through higher dimensional phase diagrams defined by special restraints on extensive variables

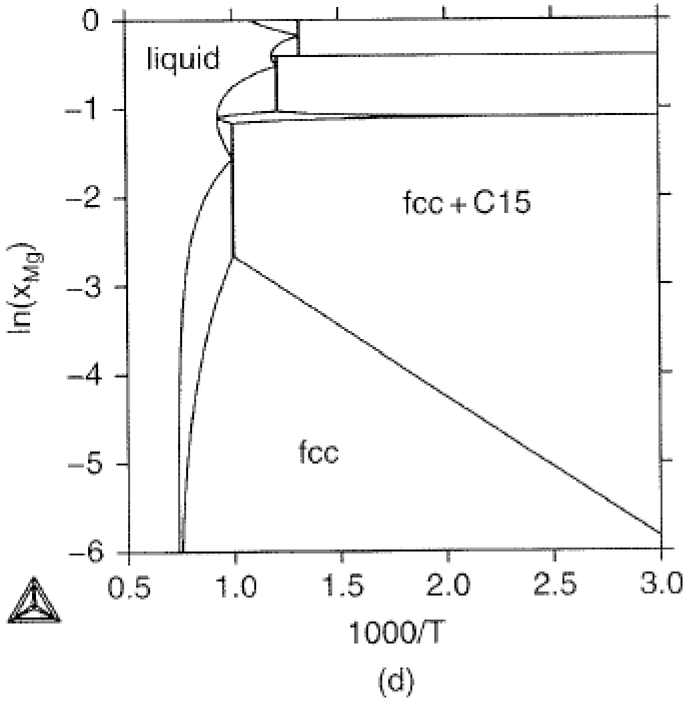
Types of Phase Diagrams

p = const.



Binary Cu-Mg, type B

p = const.



Binary Cu-Mg, type B

In type B diagrams, tie-lines connect two separated phases in equilibrium. Tie-lines are parallel to the extensive axis. Three phase equilibria are defined by special tie-lines.

Types of Phase Diagrams

A system in equilibrium is defined by a set of c+2 state variables. By varying two of them and keeping the others constant, a two-dimensional phase diagram can be drawn.

The maximal dimension of the phase diagram is c+1, because one extensive variable can be diminished by dividing them by N:

e.g.: $T, p, N_1 \ldots N_j \quad \rightarrow T, p, x_1 \ldots x_{j-1}$

Types of phase diagrams:

a) two intensive variables

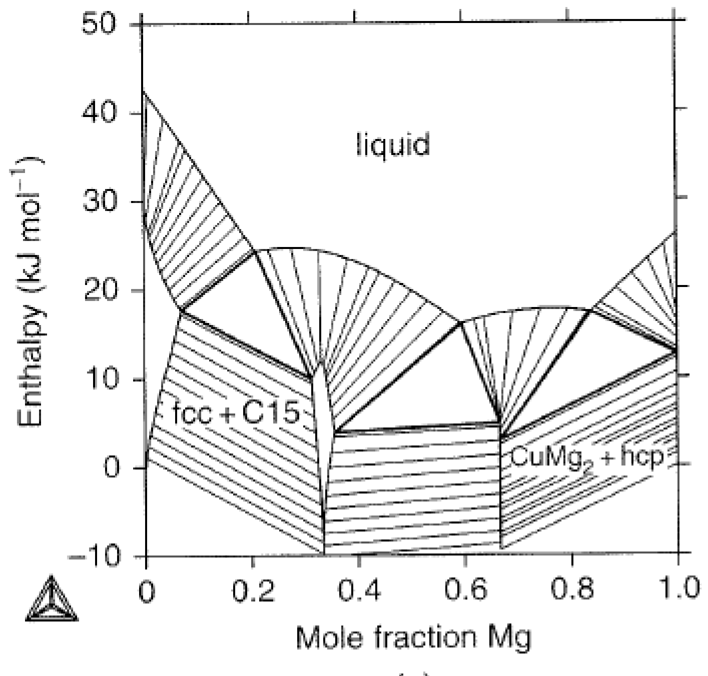
b) one intensive, one extensive (molar) variable

c) two extensive (molar) variables

d) Sections through higher dimensional phase diagrams defined by special restraints on extensive variables

Types of Phase Diagrams

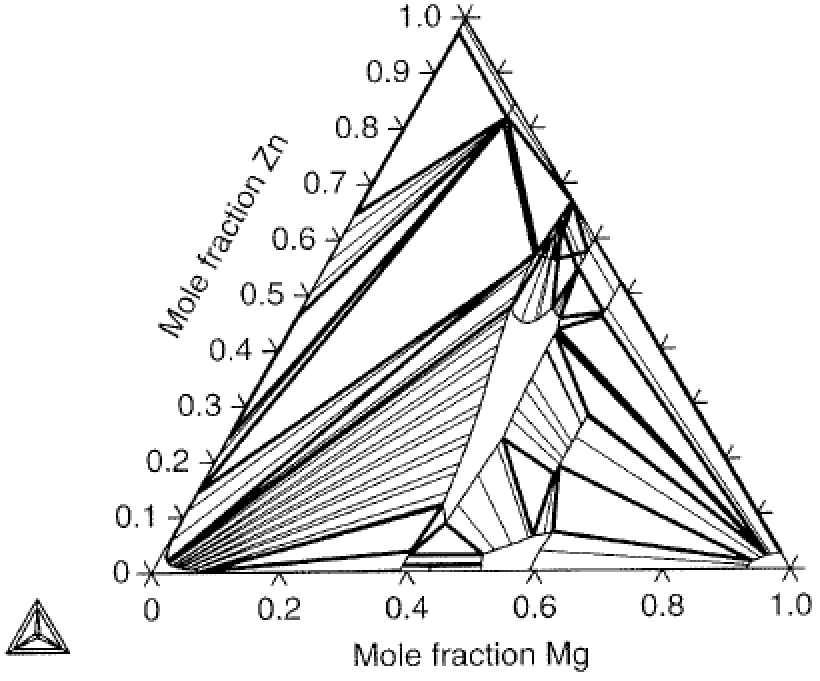
p = const.



(e)

Binary Cu-Mg, type C

p = const., T = 608K

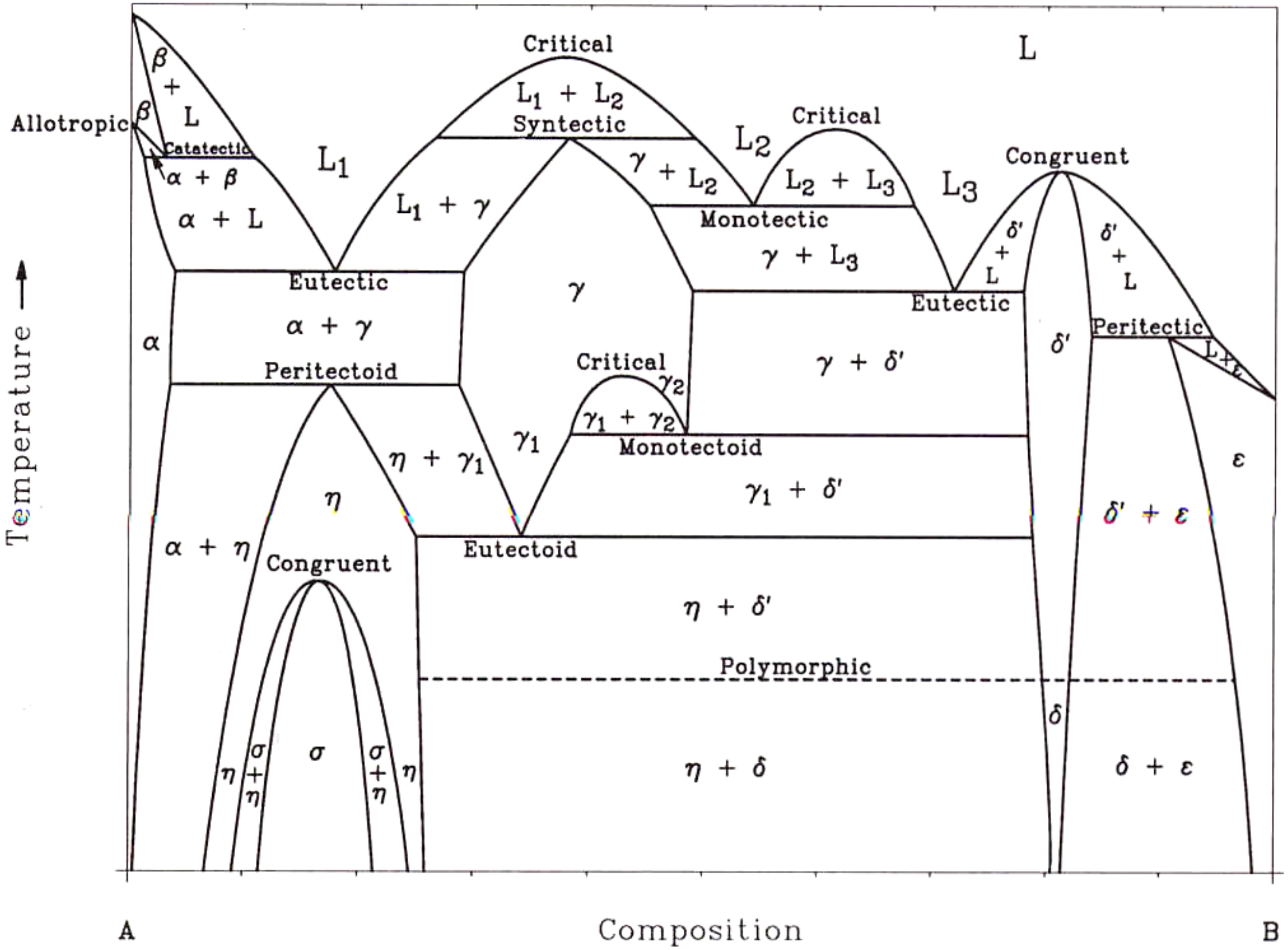


(f)

Ternary Al-Mg-Zn, type C

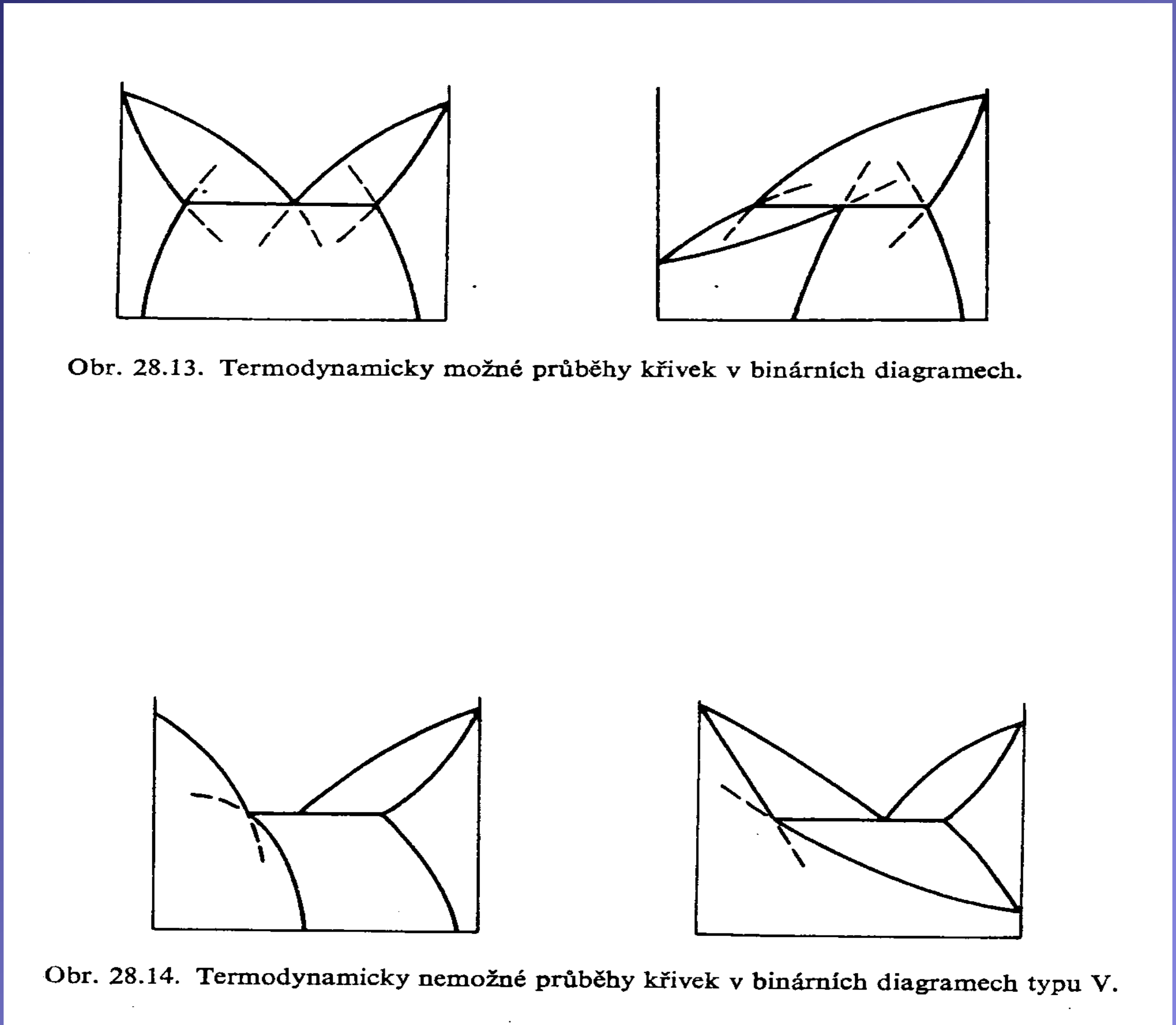
In type C diagrams, tie-lines can have any direction and have to be drawn separately. Three phase equilibria are tie-triangles.

Reading of binary phase diagram



Hypothetical binary phase diagram showing intermediate phases formed by various invariant reactions and a polymorphic transformation

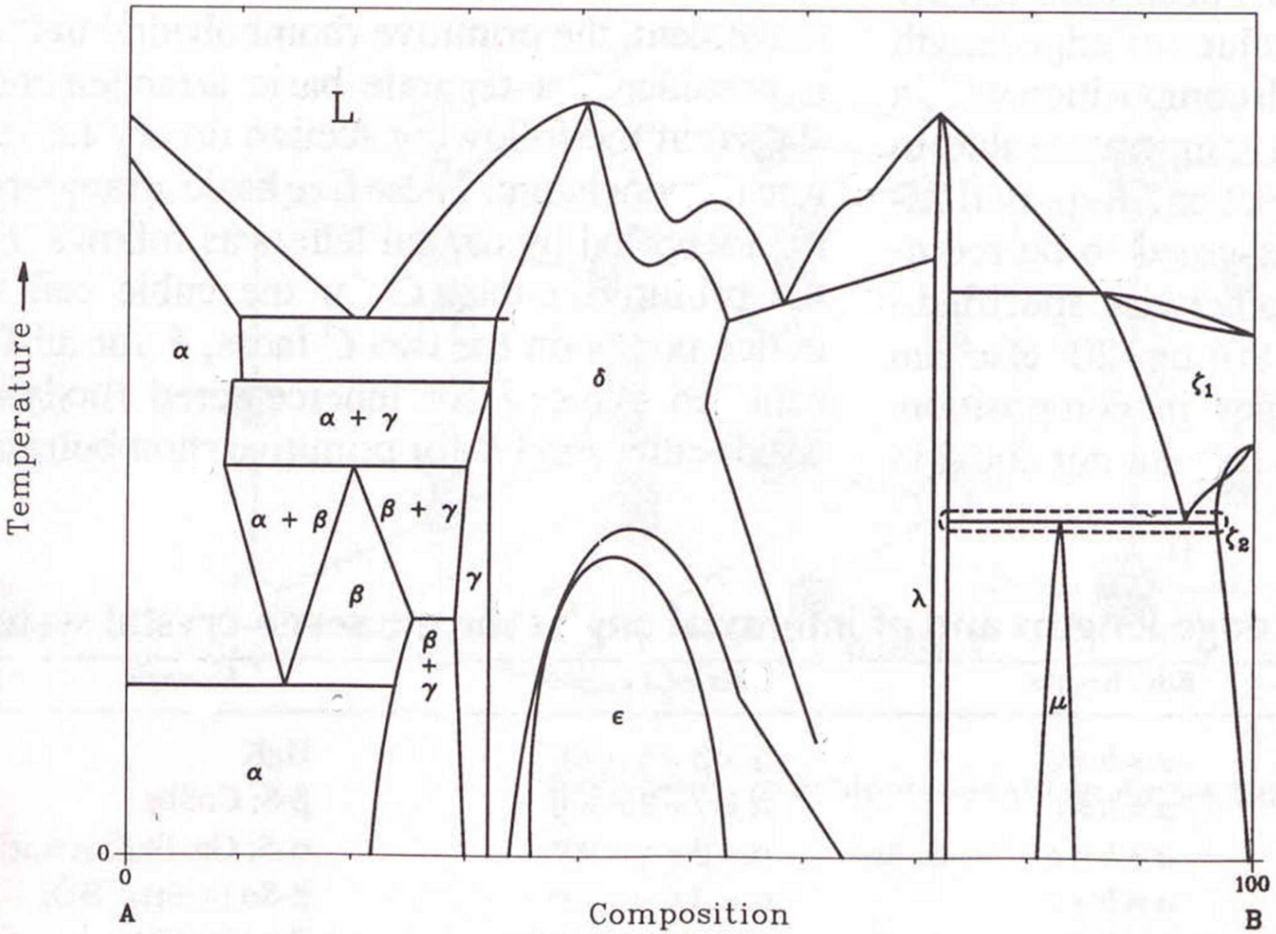
Rules for phase boundaries



Obr. 28.13. Termodynamicky možné průběhy křivek v binárních diagramech.

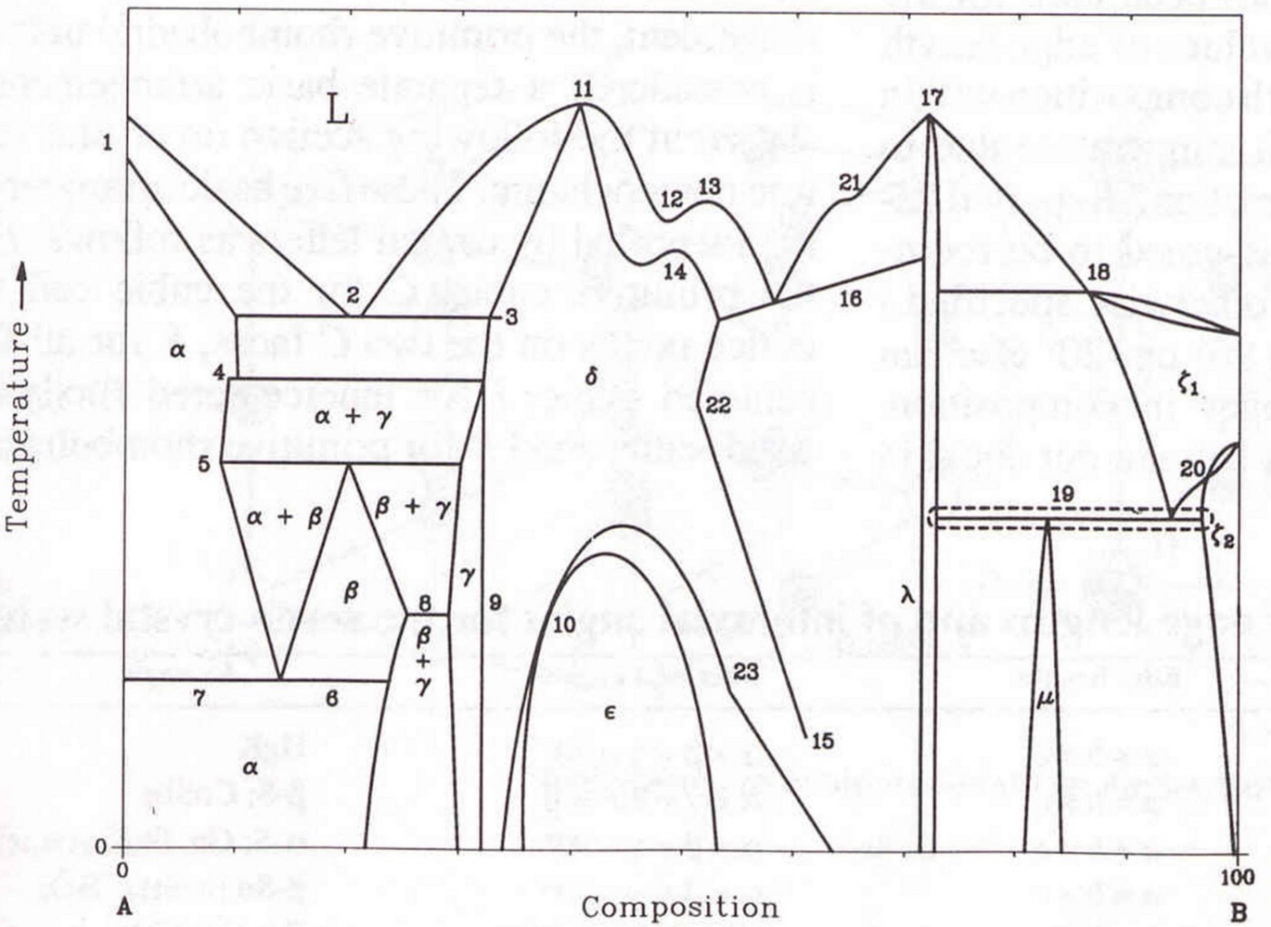
Obr. 28.14. Termodynamicky nemožné průběhy křivek v binárních diagramech typu V.

Rules for phase boundaries



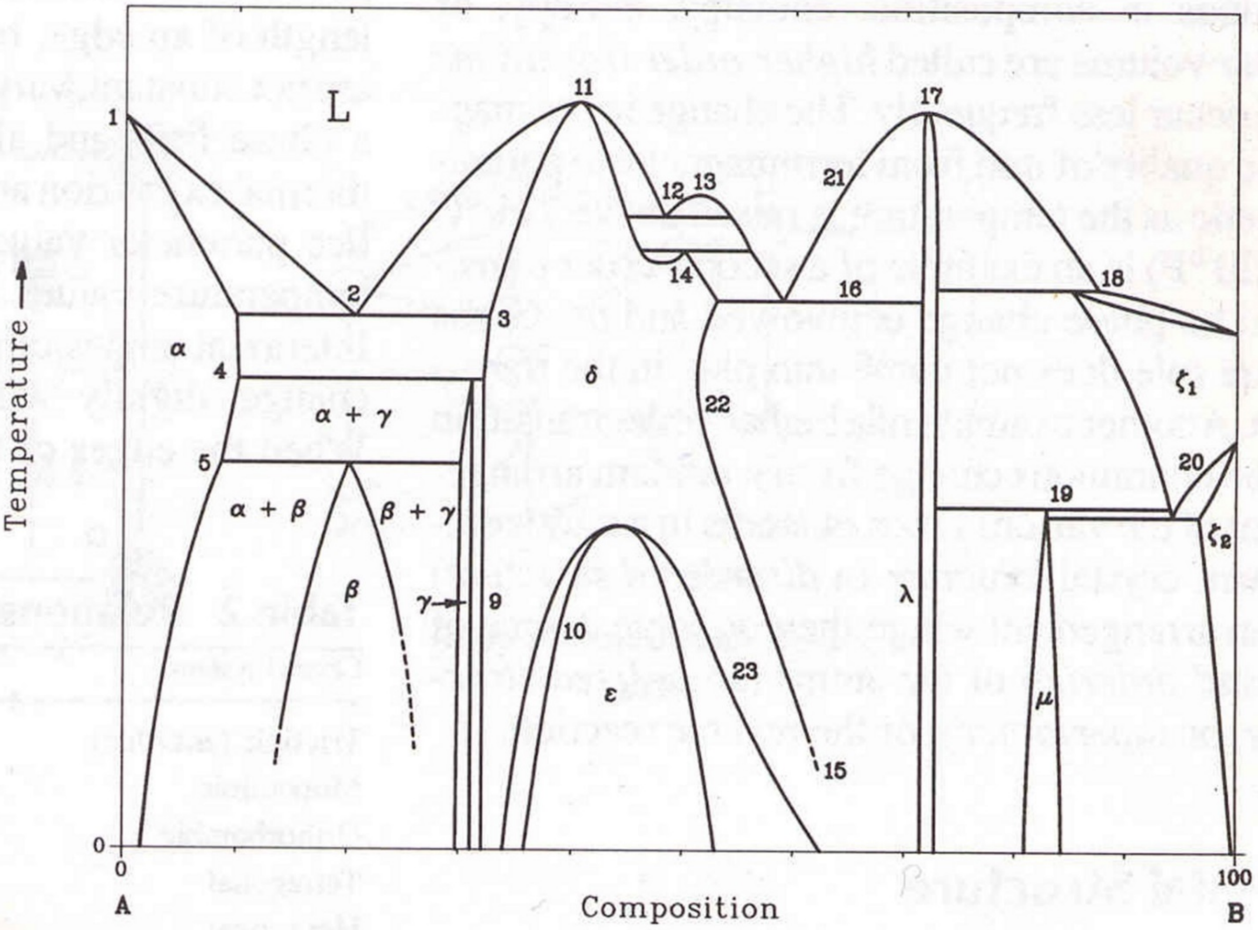
Hypothetical binary phase diagram showing many typical errors of construction. See the accompanying text for discussion of the errors at points 1 to 23.

Rules for phase boundaries



Hypothetical binary phase diagram showing many typical errors of construction. See the accompanying text for discussion of the errors at points 1 to 23.

Rules for phase boundaries



Error-free version of the phase diagram

Types of Phase Diagrams

A system in equilibrium is defined by a set of c+2 state variables. By varying two of them and keeping the others constant, a two-dimensional phase diagram can be drawn.

The maximal dimension of the phase diagram is c+1, because one extensive variable can be diminished by dividing them by N:

e.g.: $T, p, N_1 \ldots N_j \rightarrow T, p, x_1 \ldots x_{j-1}$

Types of phase diagrams:

a) two intensive variables
b) one intensive, one extensive (molar) variable
c) two extensive (molar) variables
d) Sections through higher dimensional phase diagrams defined by special restraints on extensive variables

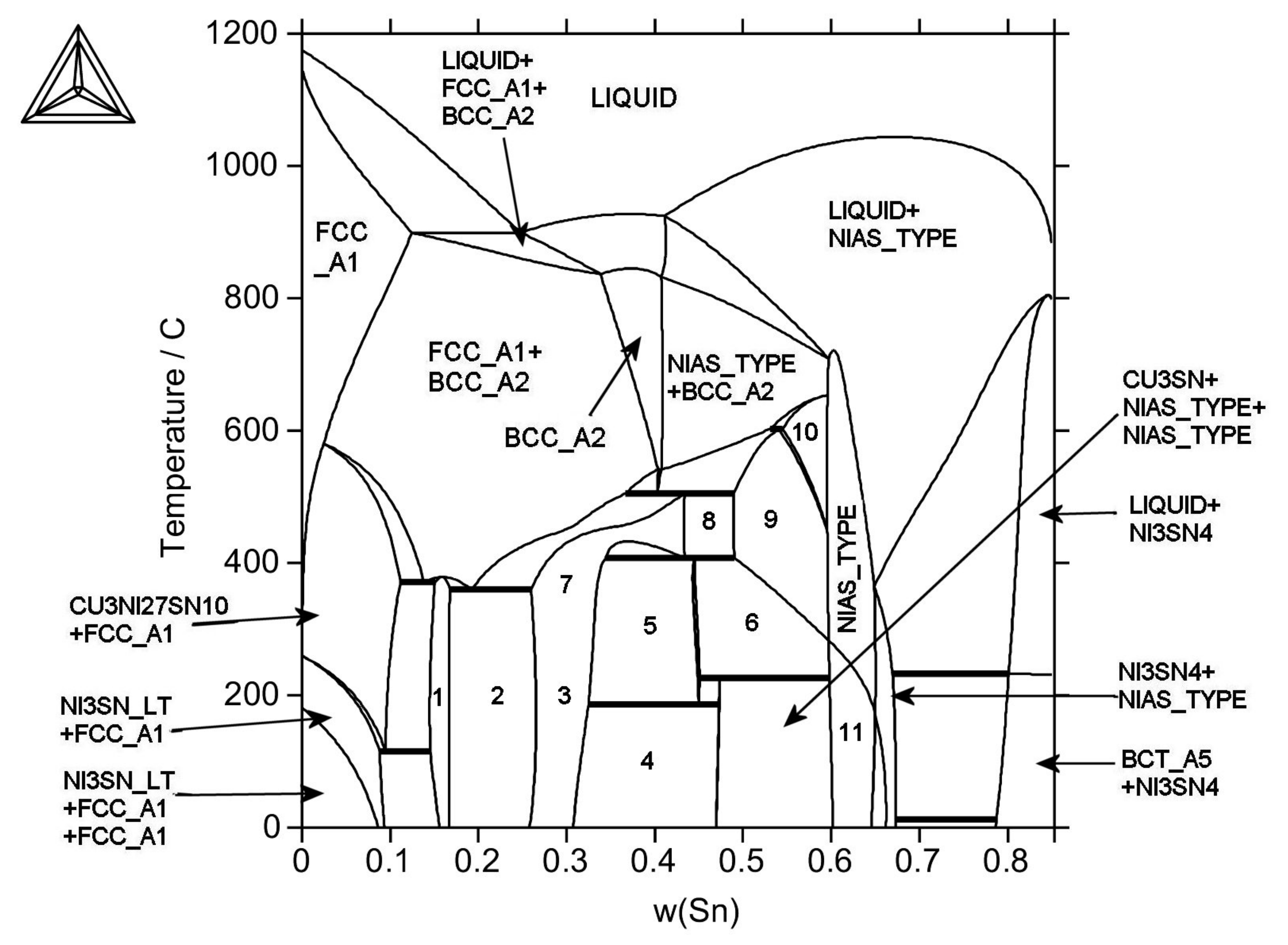
Vertical sections of ternary systems (isopleths)

- Tie-lines generally are not in the plane of section!

- The lines do not belong to monovariant equilibria - they show „zero-phase-fraction“ equilibria.

- Lines show boundaries between an n- and (n-1)-phase field (calculated from equilibrium condition for the n-phase equilibrium with additional condition that amount of one phase is zero, although still present in equilibrium).

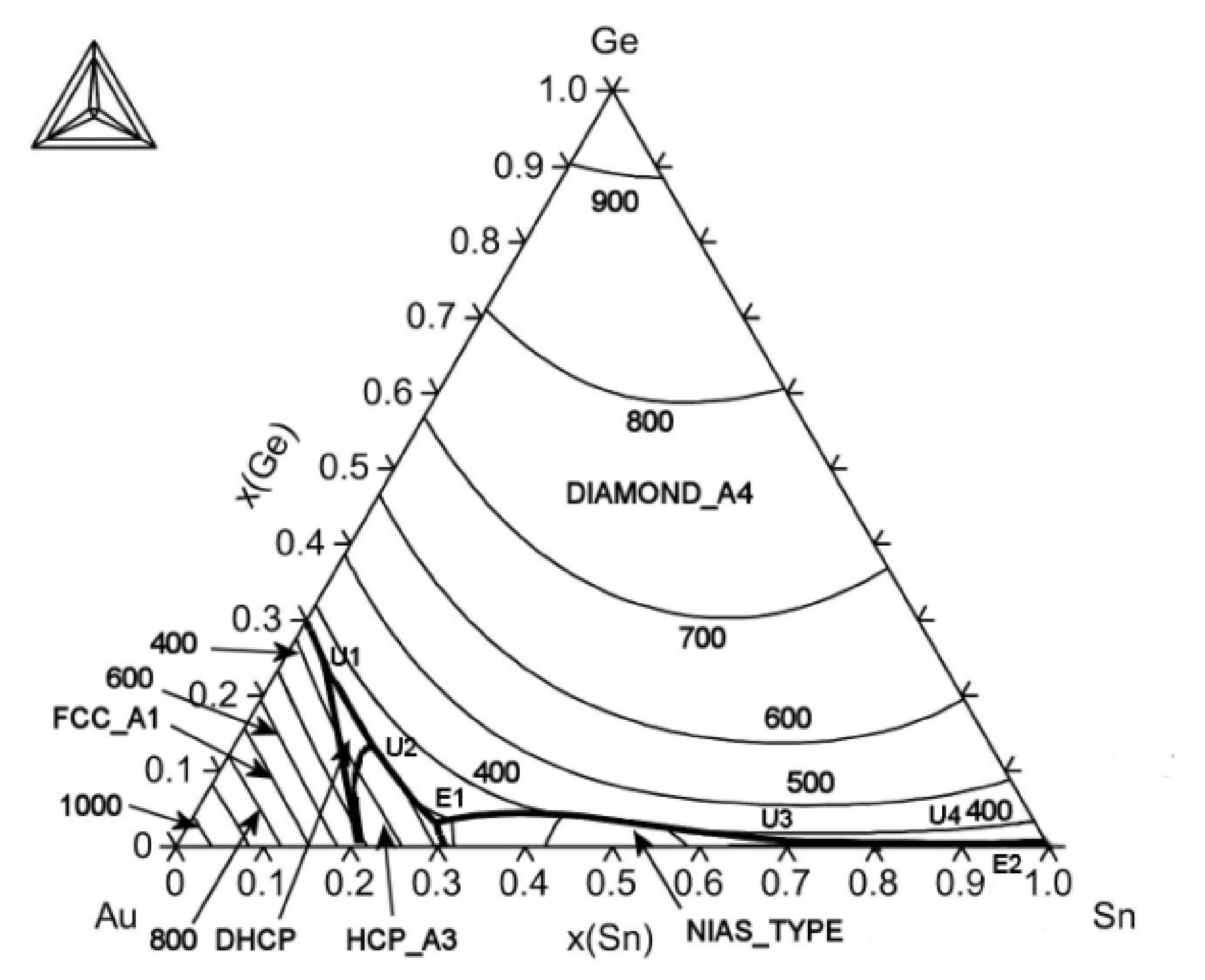
Vertical sections of ternary systems (isopleths)



Reading ternary phase diagram

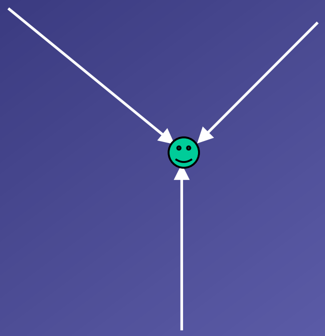
Liquidus projection: eutectic, peritectic, phase transformation

Example: Au-Ge-Sn

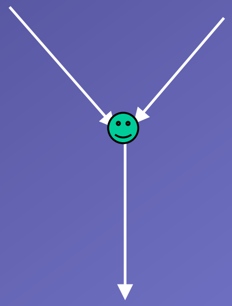


Phase transformations on liquidus surface

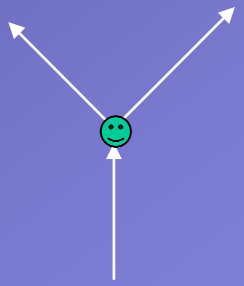
E (eutectic)



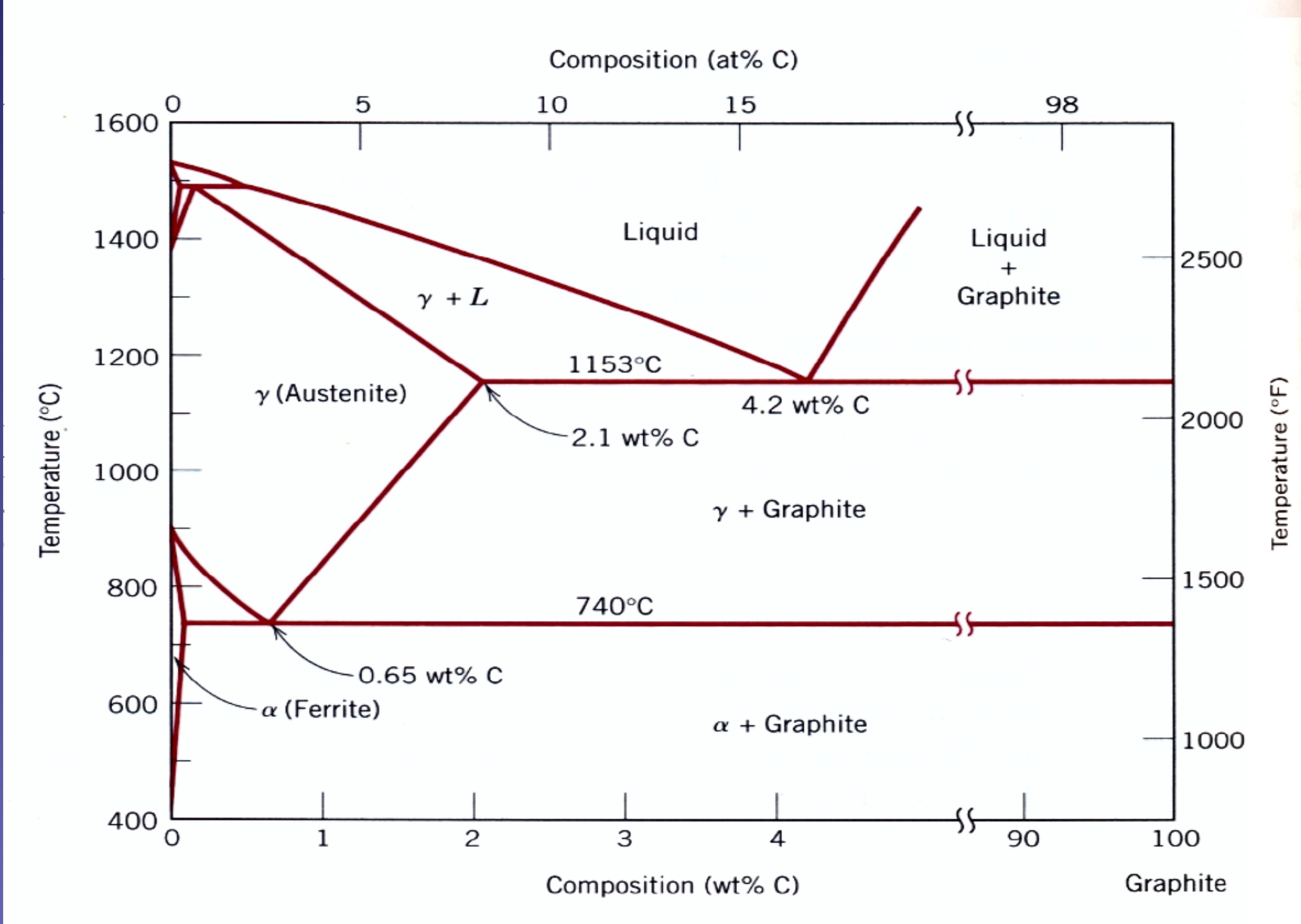
U (phase transformation)



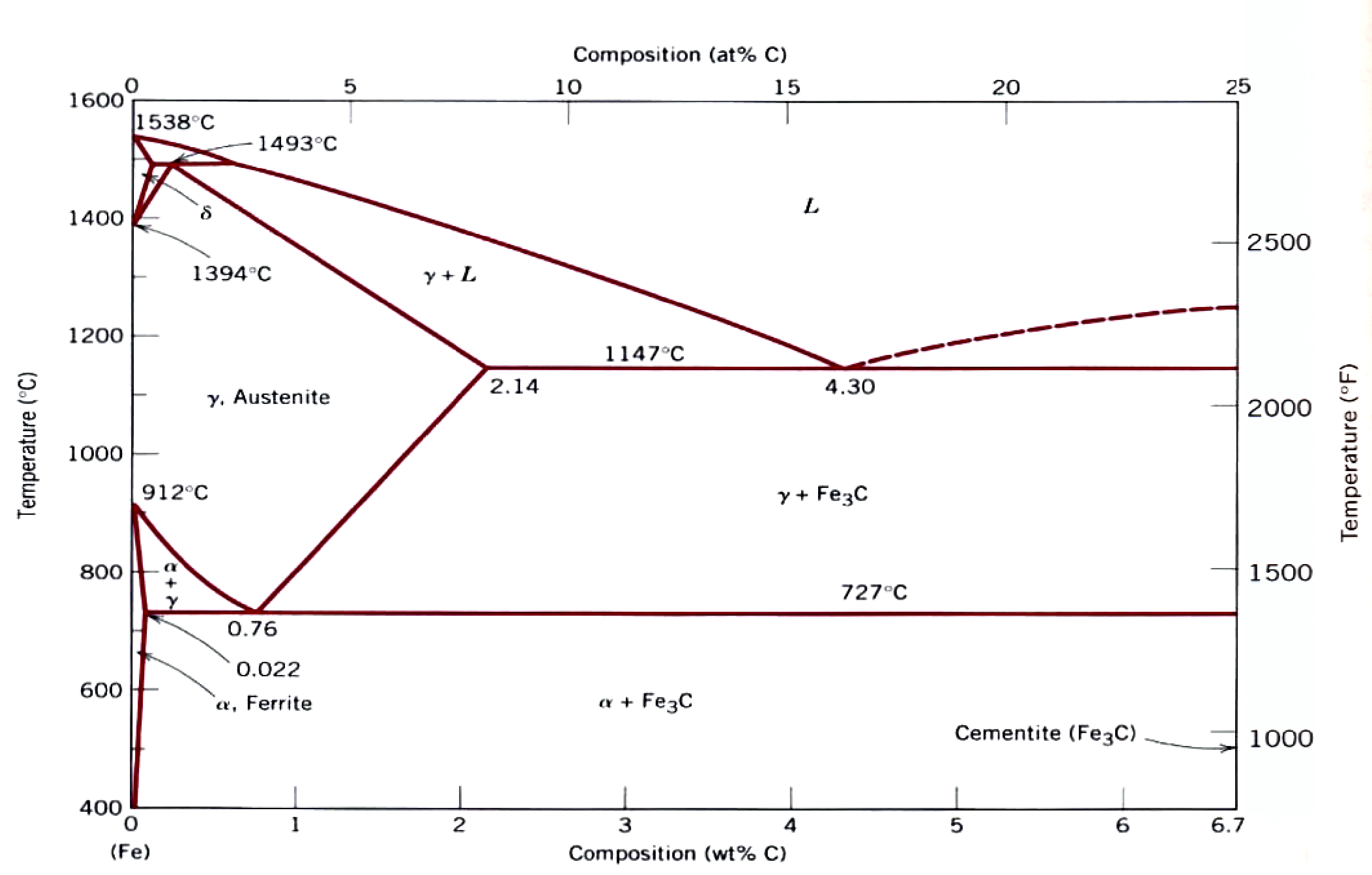
P (peritectic)



Fázový diagram Fe–C:

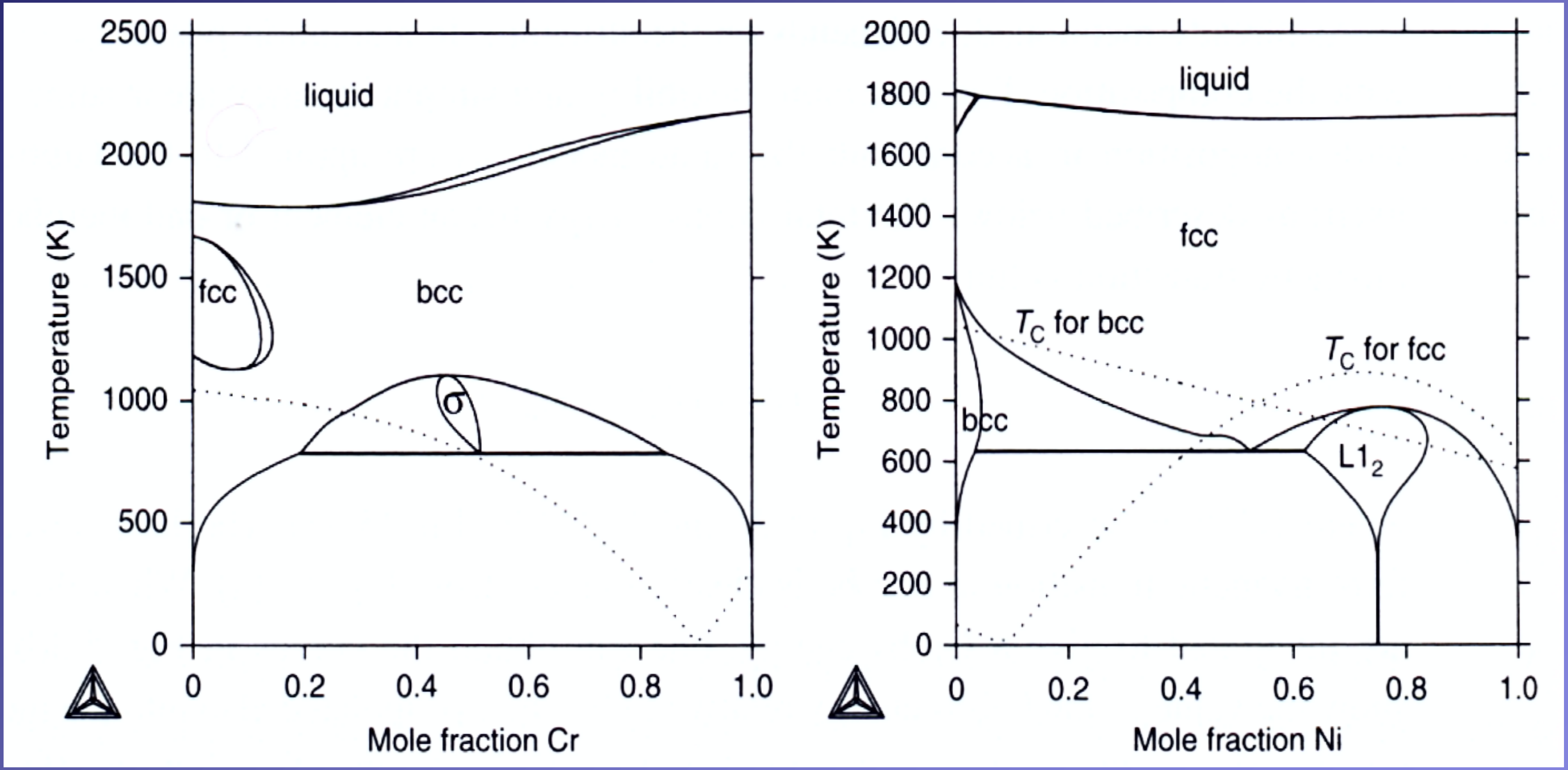


Fázový diagram Fe–Fe_3C:

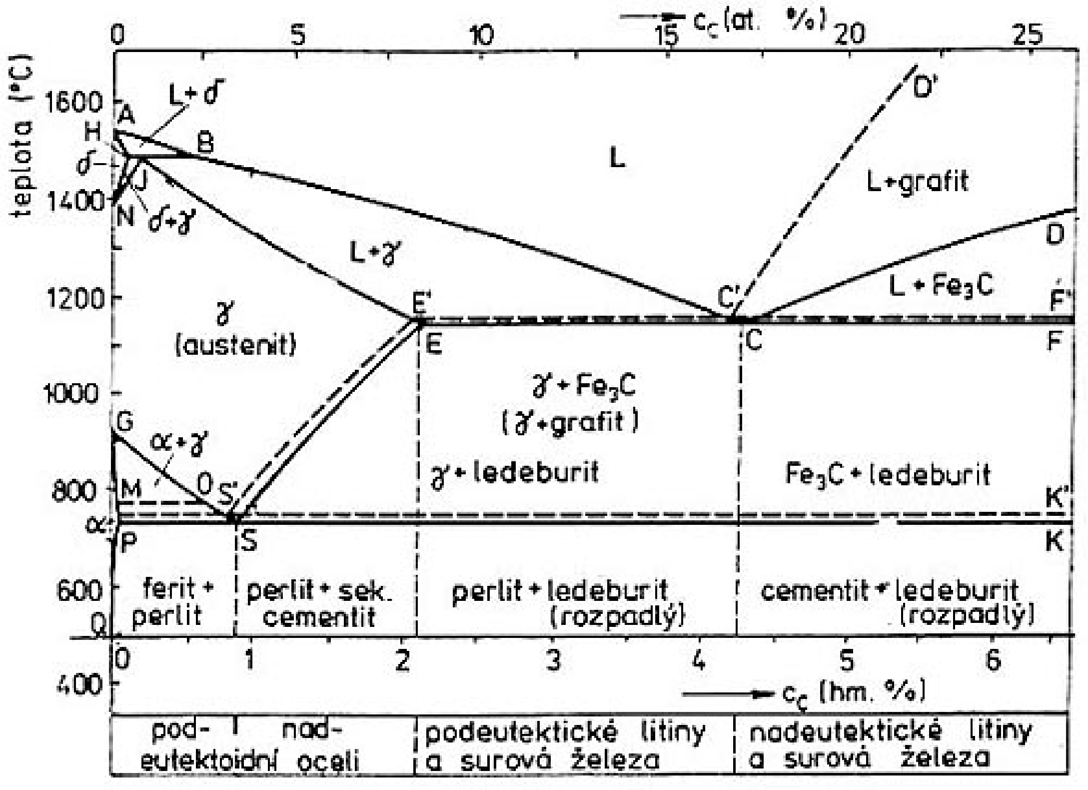


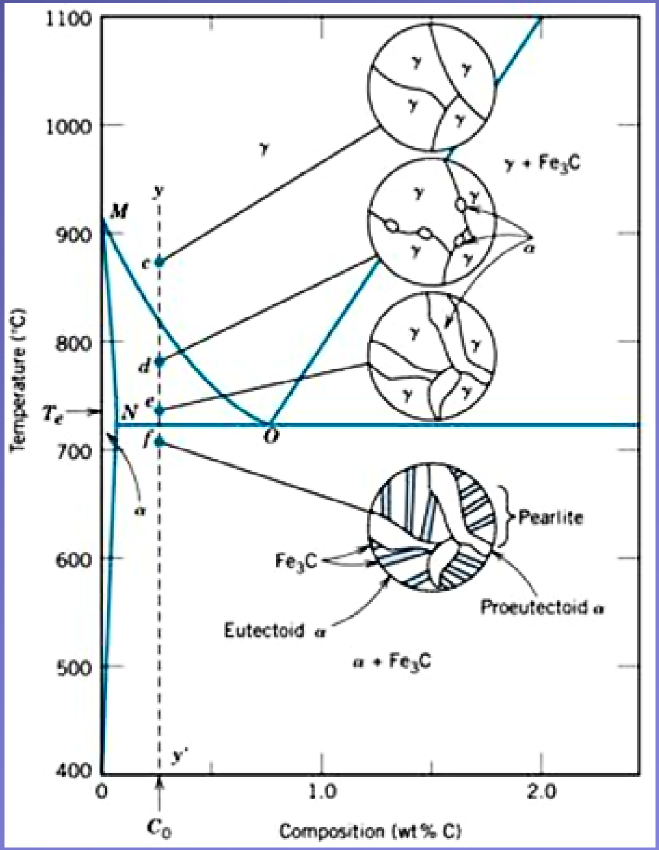
(metastabilní)

Legury železa: feritotvorné a austenitotvorné



Mikrostruktura oceli v závislosti na zpracování:





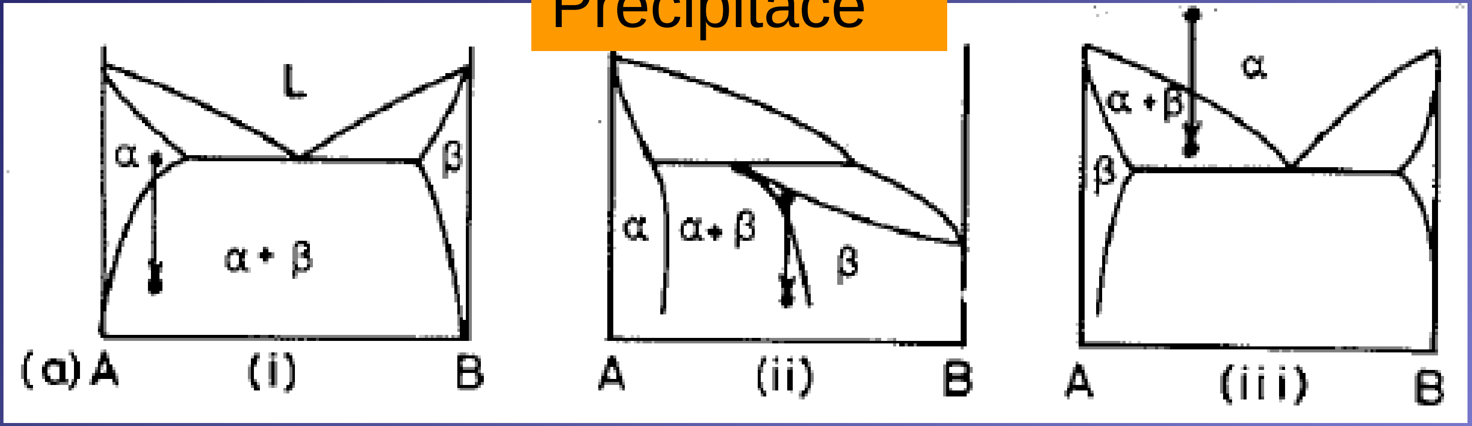
Jednofázové materiály: souvislost složení tuhého roztoku s mechanickými vlastnostmi

substituční nebo intersticiální zpevnění (dobře rozpracovaná teorie, Fischer, Labusch, Lukáč),
tj. zvýšení zejména skluzového napětí a posunutí celé deformační křivky k vyšším napětím, interakce dislokací s cizími atomy (P.-L. jev)
Hume-Rotheryho empirická pravidla pro rozpustnost příměsí (velikost atomů, elektronegativita, mocenství prvků)

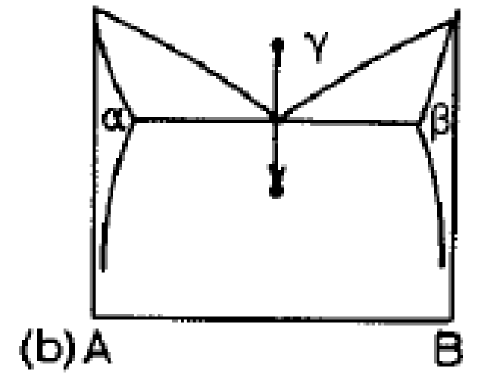
Vícefázové materiály:
Vliv mikrostruktury a fázového složení na průběh plastické deformace (geometrie rozložení fází, složení fází a jejich objemový podíl, velikost a rozložení částic jednotlivých fází).

Typy fázových transformací řízených difúzí:

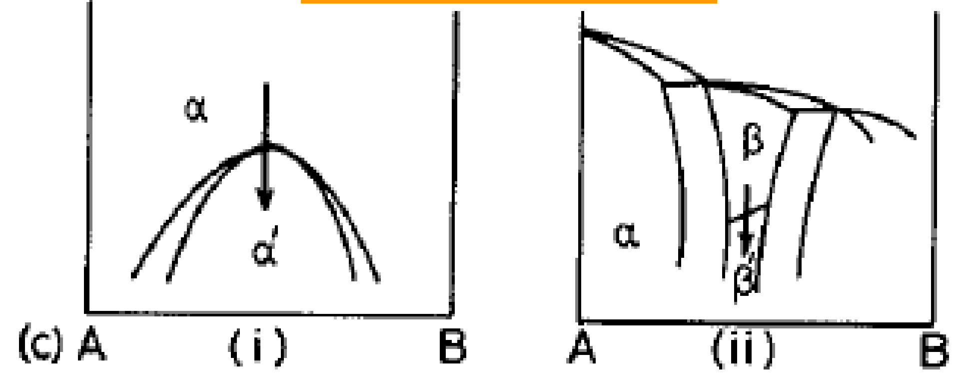
Precipitace



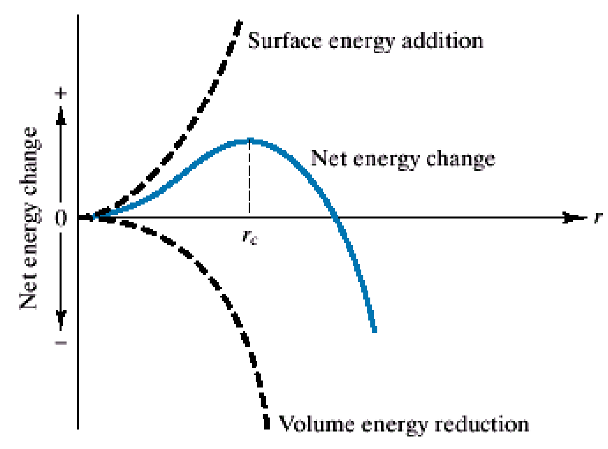
Eutektoidní FT



Uspořádání



Stadia: nukleace, růst a hrubnutí (precipitátů, zrn)



Kulovitý precipitát: $\Delta G = -\frac{4}{3}\pi r^3(\Delta G_v - \Delta G_s) + 4\pi r^2\gamma$

Energie mechanických napětí může snižovat i zvyšovat energetickou bariéru!

Nukleace homogenní nebo heterogenní na různých poruchách (vakance, dislokace, vrstevné chyby, hranice zrn, volný povrch) (pozn.)

Hnací síla nukleace roste s rostoucím podchlazením pod křivku rozpustnosti a významně ovlivňuje rychlost nukleace.

Za malého podchlazení je hnací síla nukleace malá. Za příliš vysokého podchlazení je mobilita atomů malá. Tedy existuje optimum pro rychlost nukleace.

Scheil –Gulliverova rovnice

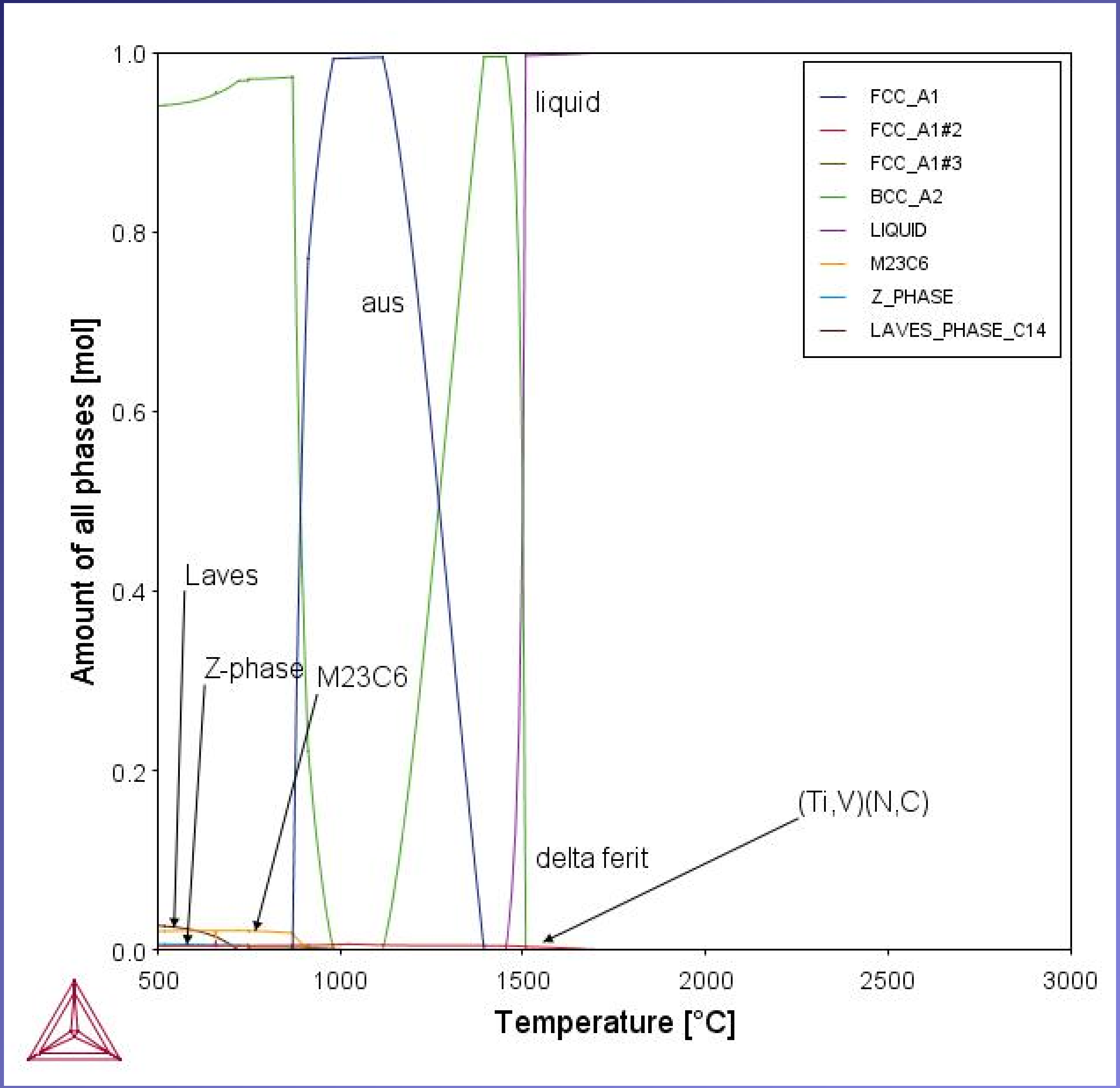
Při běžném ochlazování nejsou obecně splněny podmínky pro ustavení kompletní termodynamické rovnováhy

Lépe situaci popisuje přístup použitý v práci Scheila a Gulivera
Předpoklady:
1 – Žádná difuze v pevné fázi, jakmile se jednou zformuje
2 – Nekonečně rychlá difuze v tavenině
3 – Termodynamická rovnováha existuje přímo na rozhraní
(4 – Křivky liquidu a solidu mohou být extrapolovány přímkami)

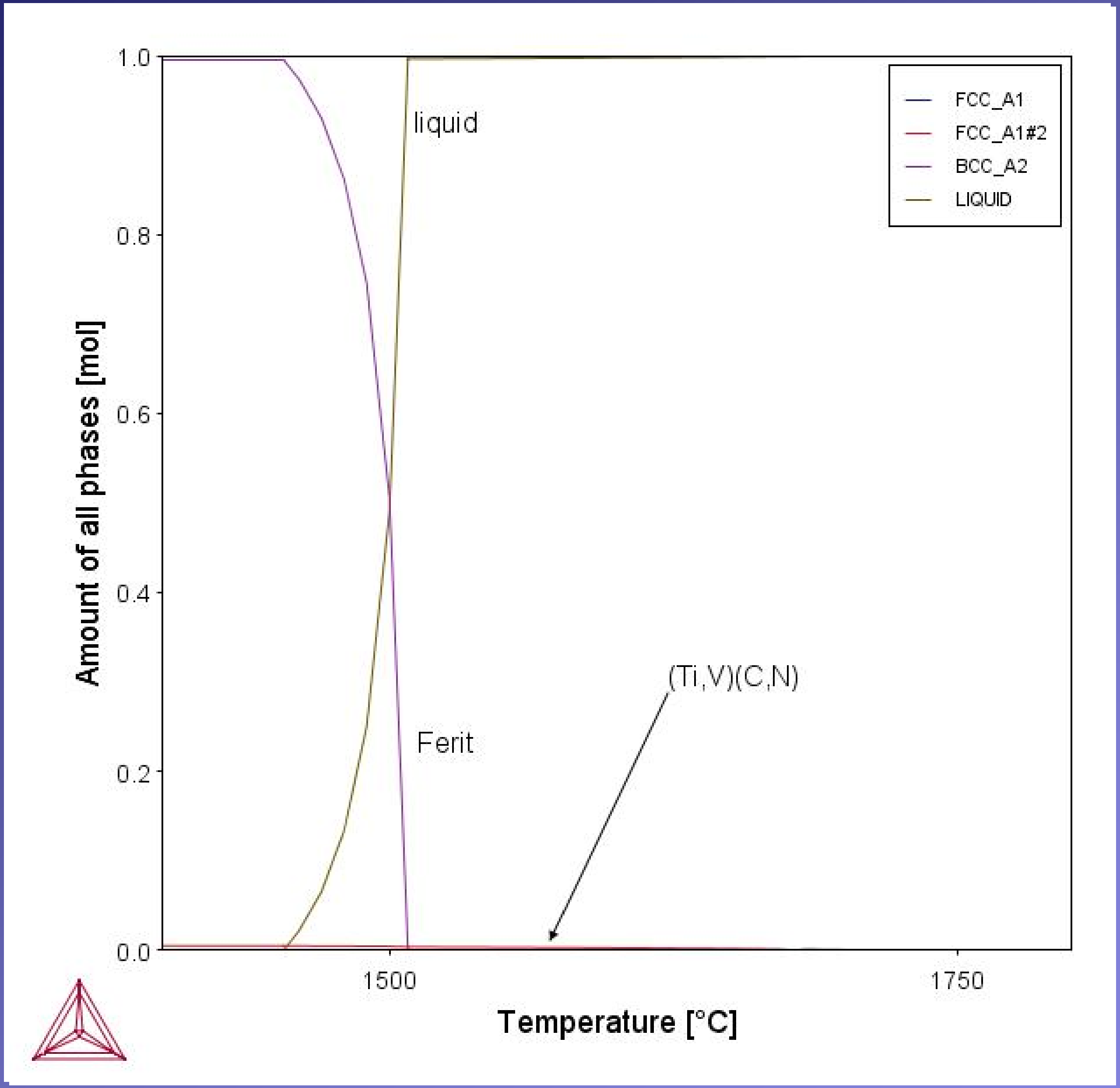
$C_L = C_0 . (f_L)^{k-1}$
$C_S = k.C_0 . (1-f_S)^{k-1}$

Příklad: ocel Fe-9%Cr-2%Mo-0,3%V-0,3%Ti-0,1%C-0,1%N

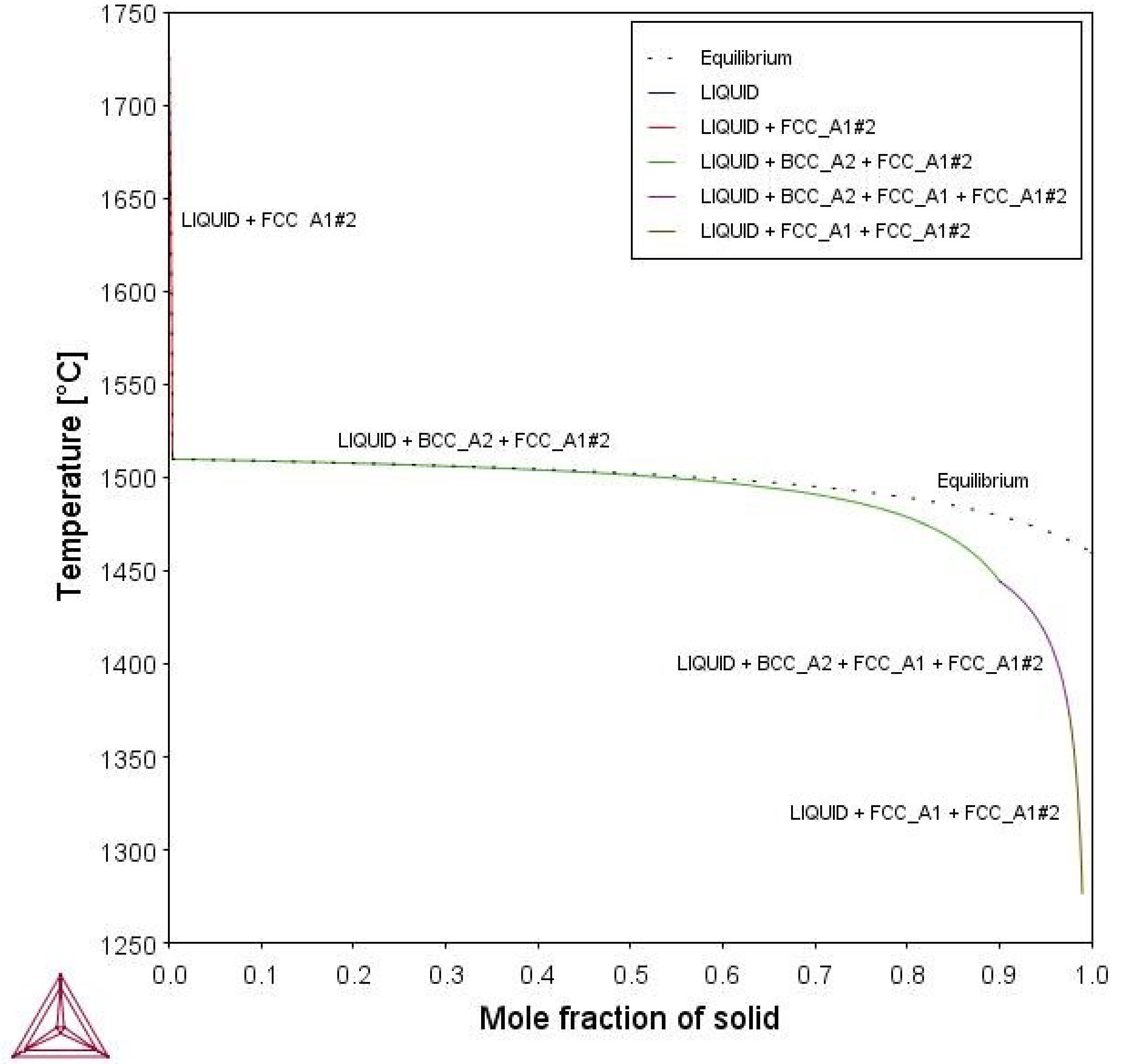
Scheil –Gulliverova rovnice



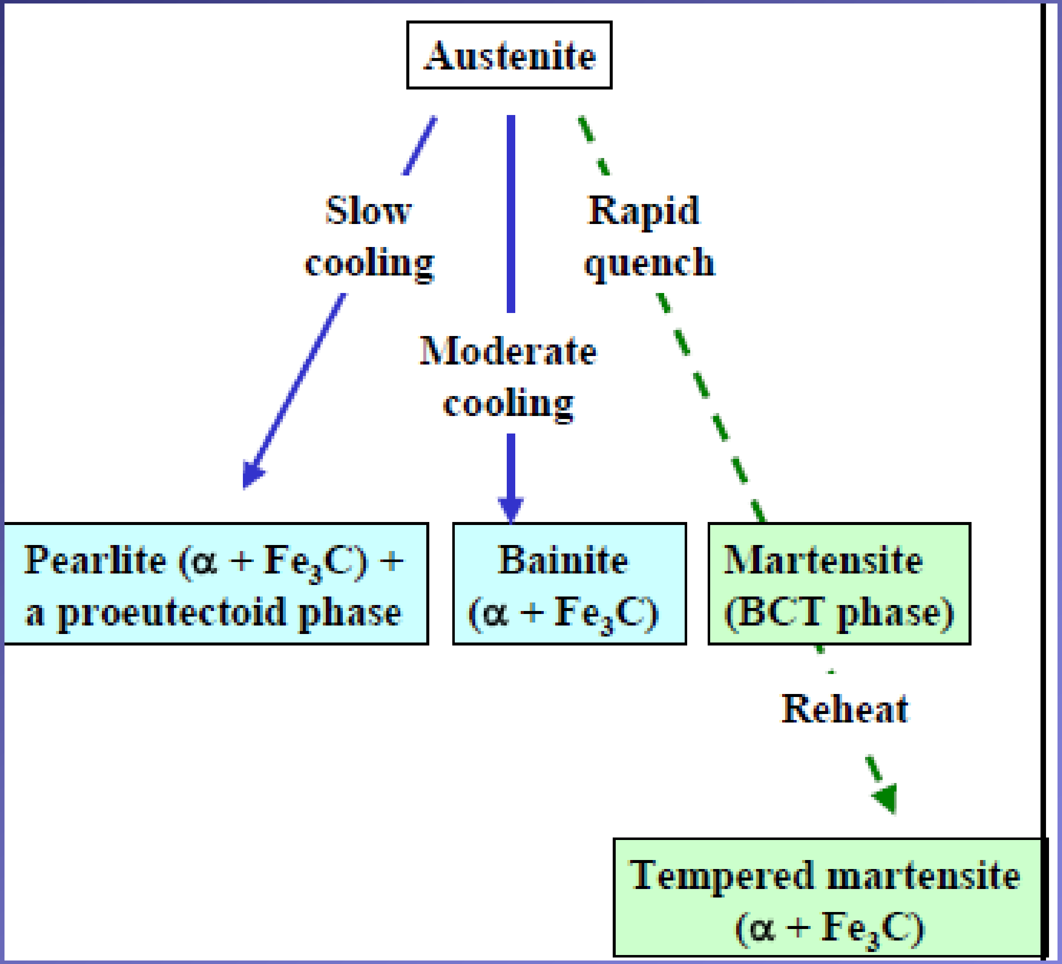
Scheil –Gulliverova rovnice



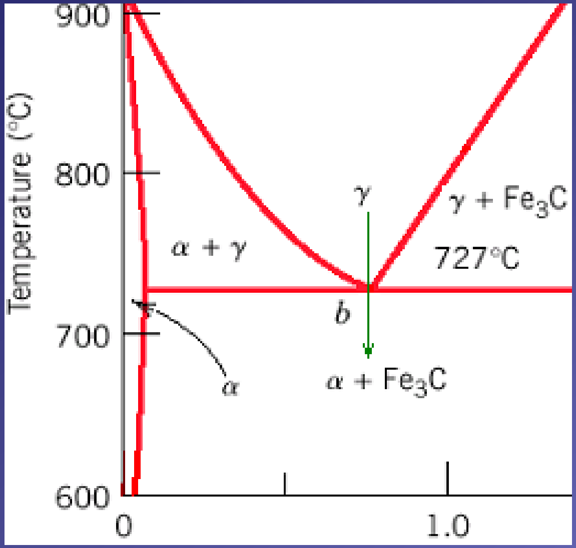
Scheil –Gulliverova rovnice



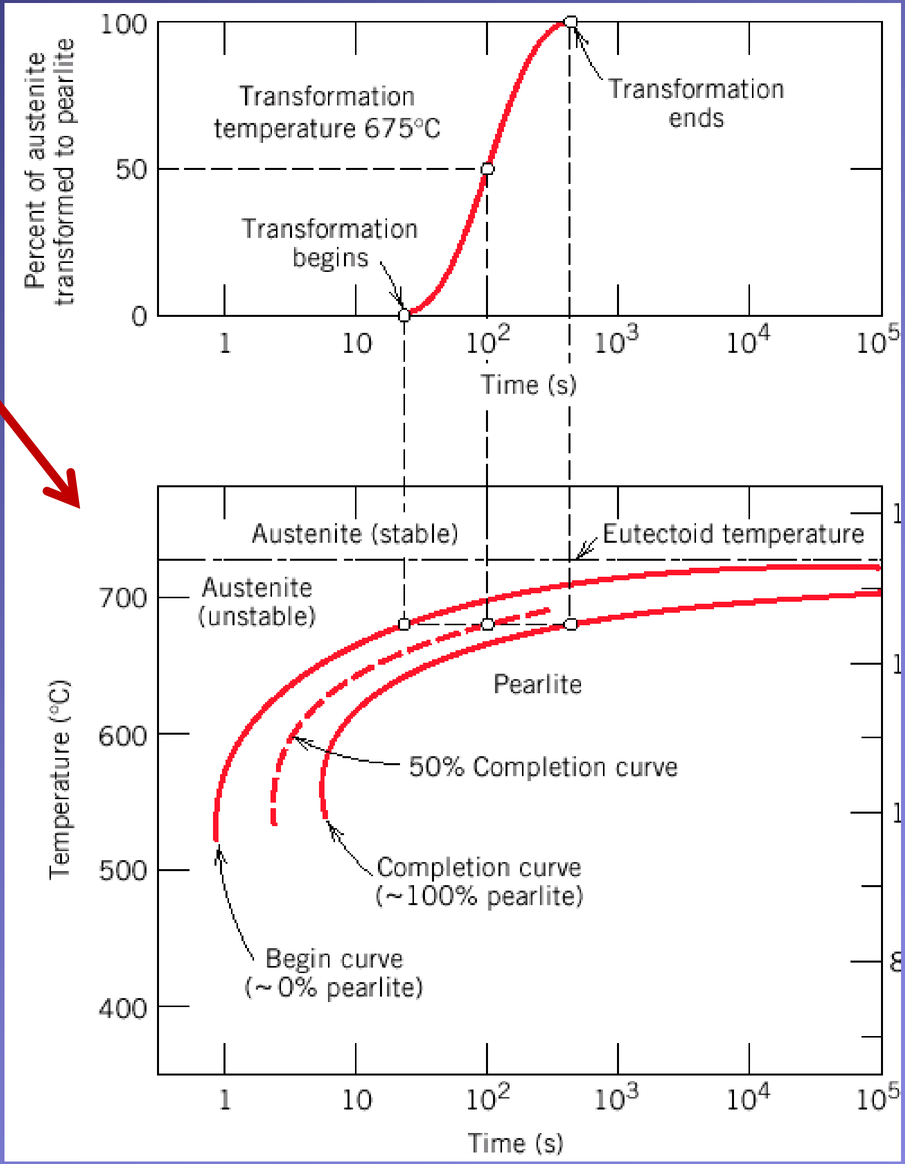
Zpracování Fe-C slitin:



TTT křivky Fe–C

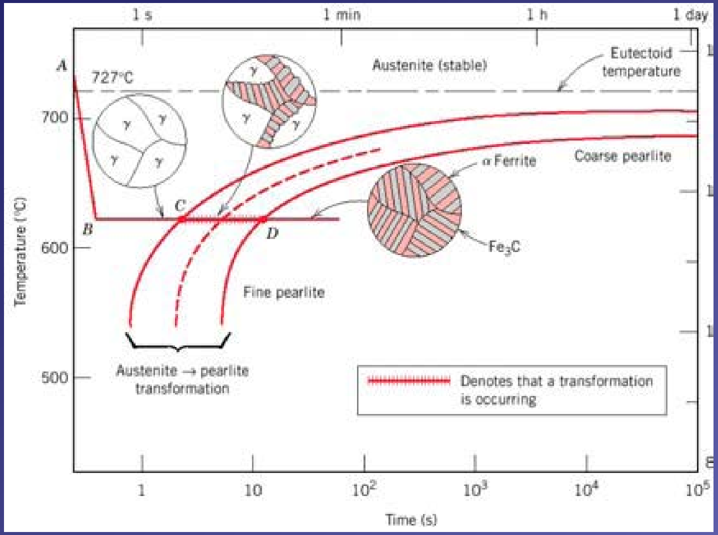


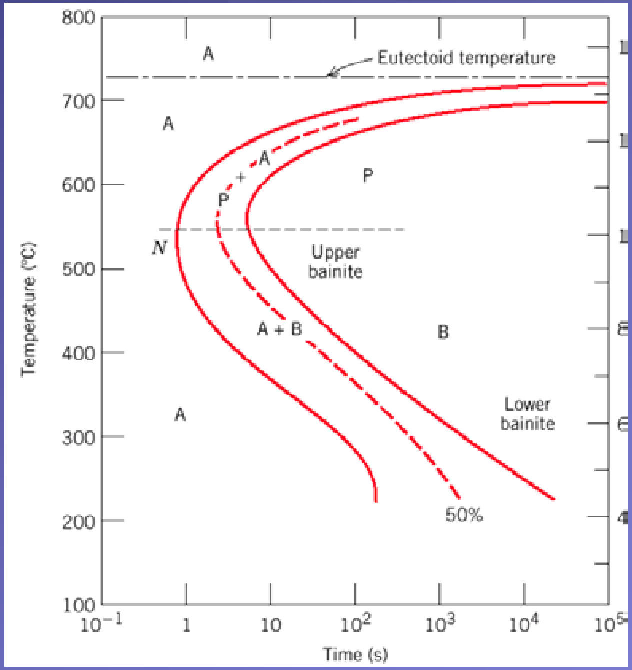
Perlit Fe-0,8wt%C

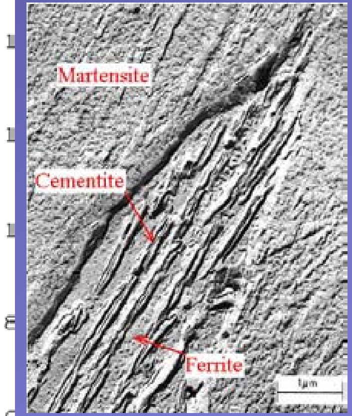


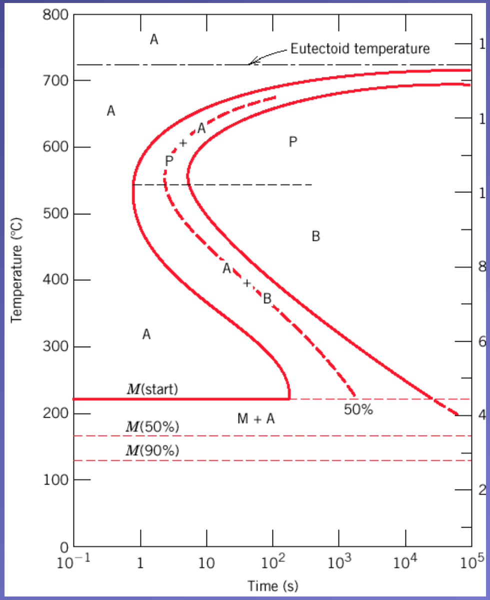
TD-60

Souvislost mikrostruktury se způsobem tepelného zpracování:



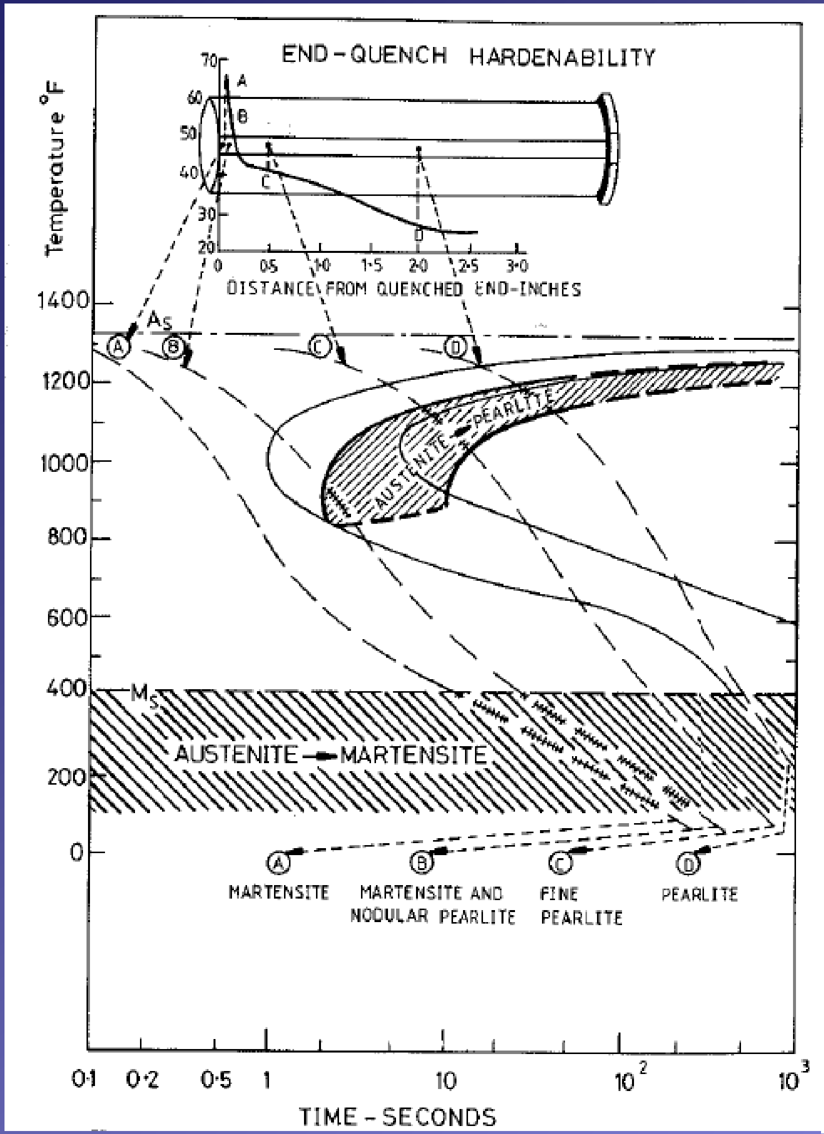


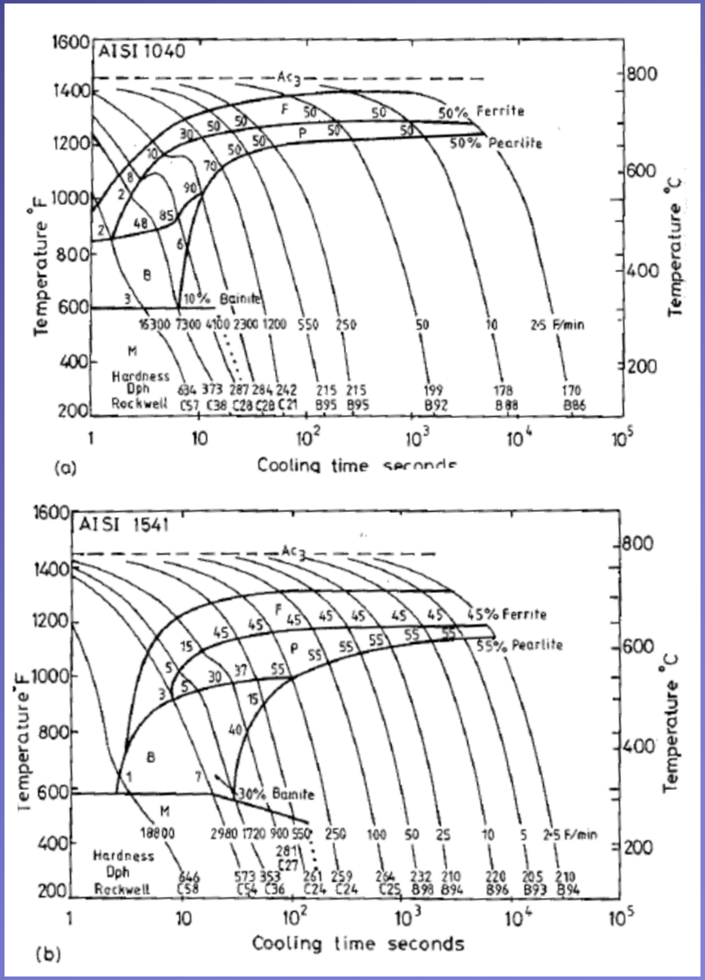


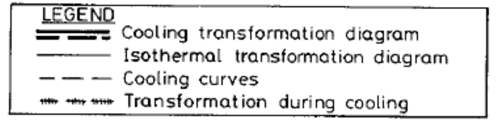


Výrazné a rychlé podchlazení: bezdifúzní transformace austenitu na (nerovnovážný) martensit

CCT diagramy:

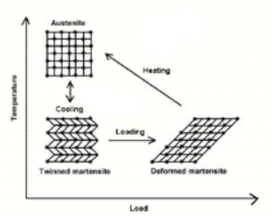






Další témata:

- Jak pracují programy pro výpočet fázových diagramů (fenomenologický přístup, CALPHAD metoda, extrapolace unárních a binárních f.d. na složitější soustavy, rozvoj dodatkových příspěvků v mocninách molárních zlomů, optimalizace parametrů na základě exp. dat)
- Existují i programy pro modelování kinetiky fázových transformací (teorie difúze, aktivity složek, mobility, ...)
- TD databáze mohou být spojené s diagramy vlastností materiálů
- Tvarová paměť (NiTi, ...)



Few comments about the software

Thermo-Calc

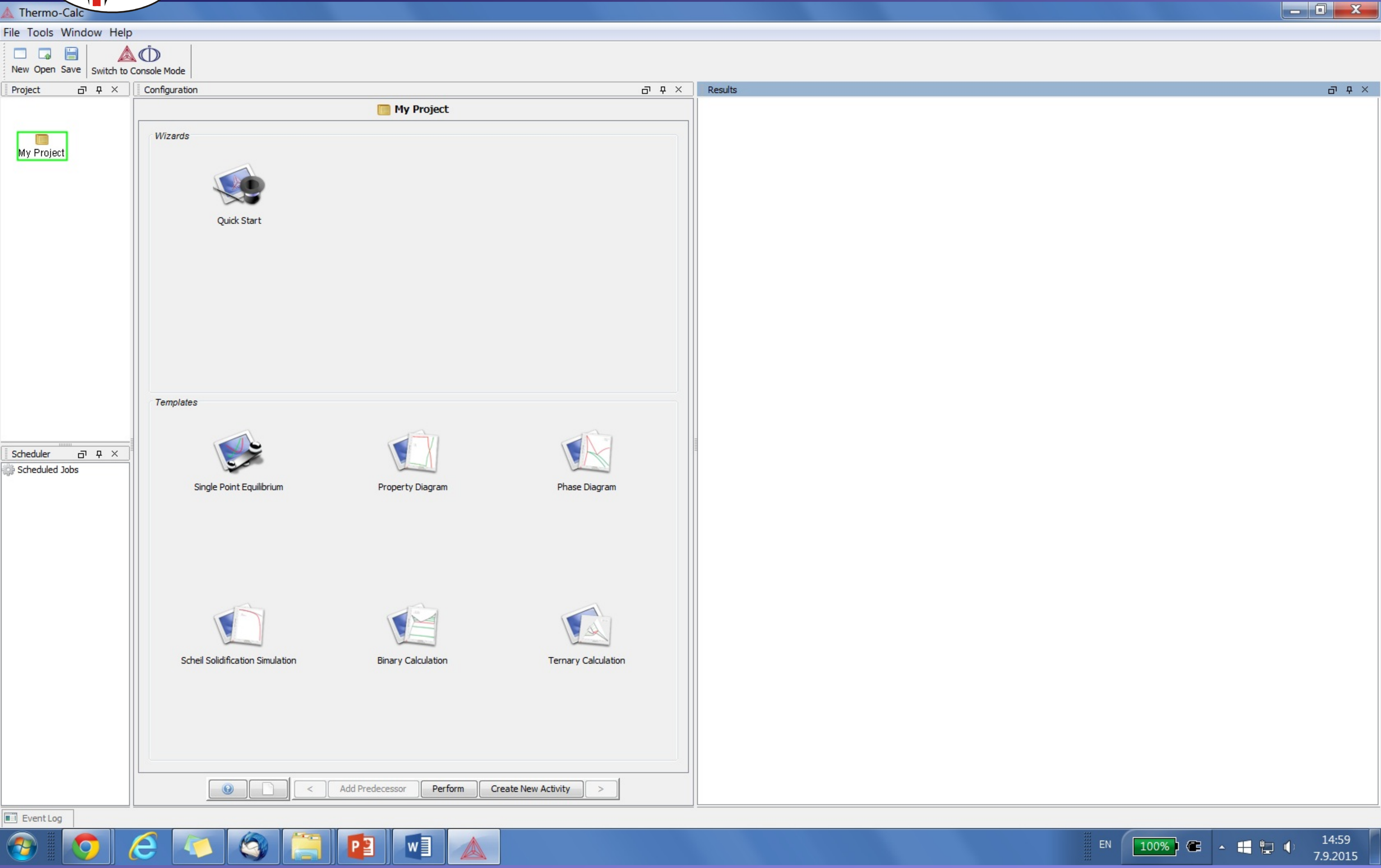
Pandat

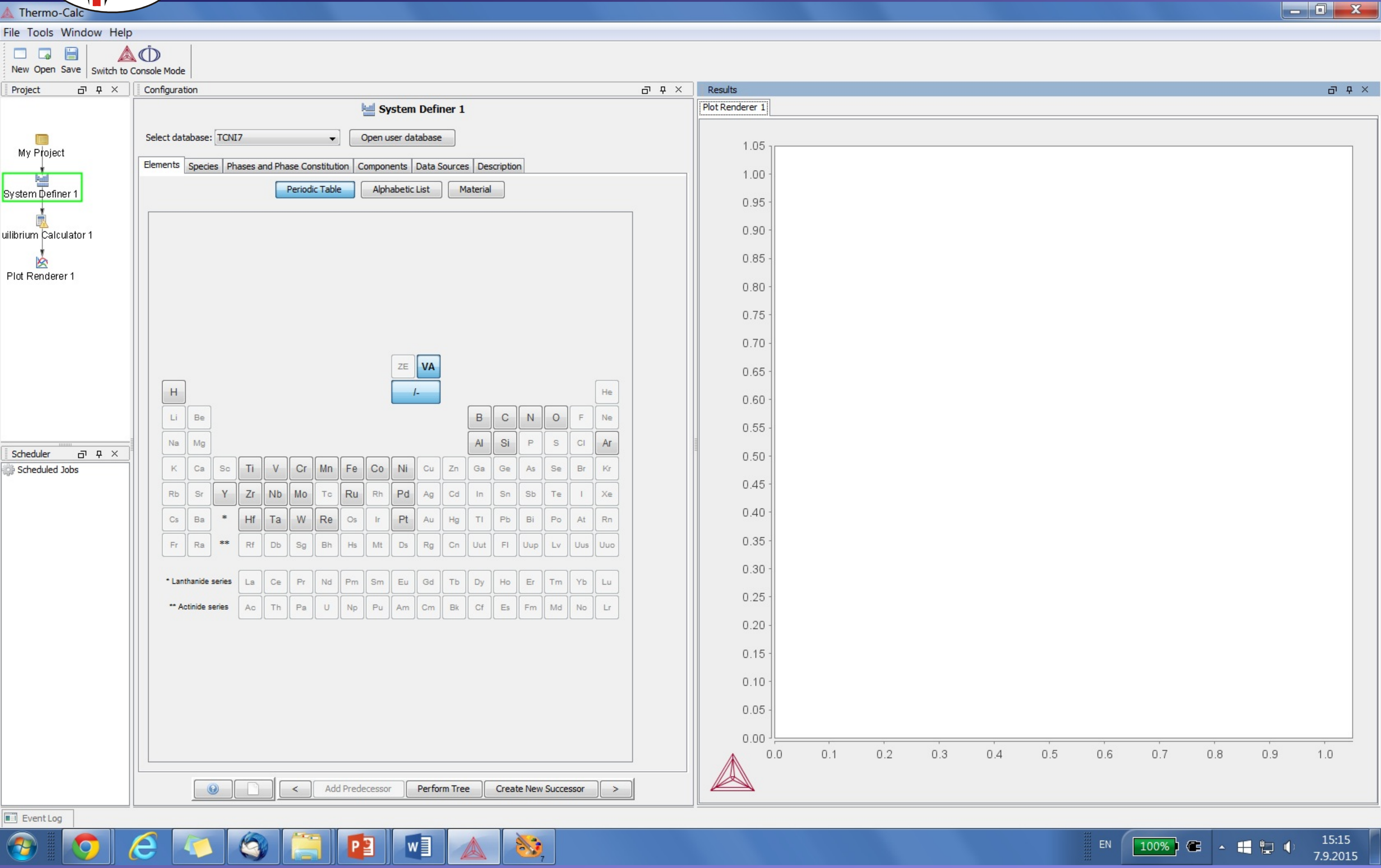
MT DATA

FactSage

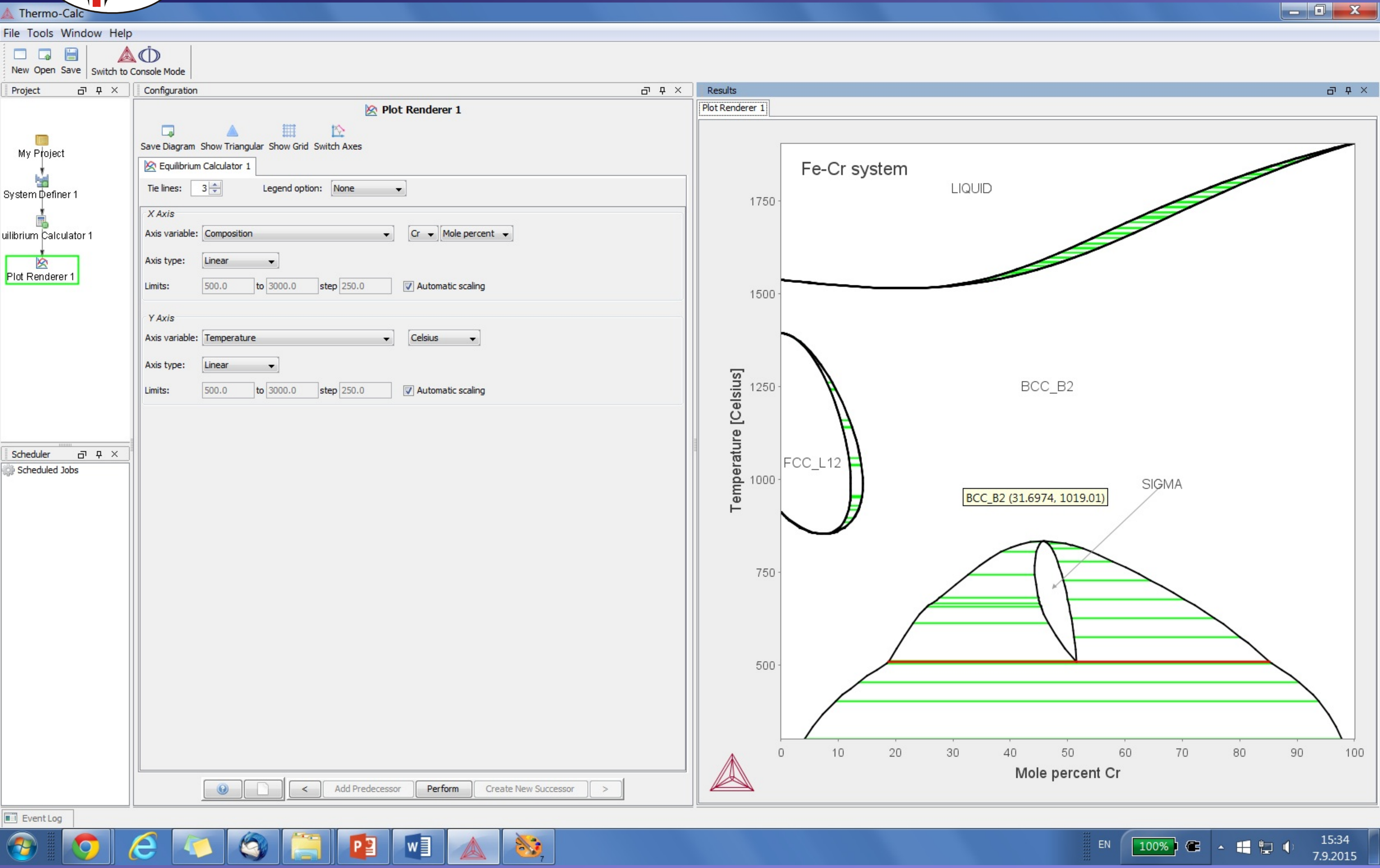
- All are based on global minimization of total Gibbs energy of system in dependence of temperature, pressure and overall composition,
- Thermodynamic data valid from the room temperature
- Different level of user-friendliness
- Originally different level of versatility and power, but now more closer to each other, the differences are small, depends on personal preferences
- The thermodynamic databases in the form of black boxes, mostly not compatible (conversion software usually not commercially available)
- Different qualities of graphical outputs
- Different reliability of global minimum search, detection of miscibility gaps, detection of errors of the assessment (liquid MG, LT phases at HT etc.)

- Thermo–Calc (grandpa of all softwares) (http://www.thermocalc.com)
    - Probably most powerful, most versatile
    - Two regimes – command mode, “windows”type mode
    - Keeps all results for given session, can be extracted later
    - Less user friendly, the user-friendly version just for routine calculations
    - Free download of limited version for academic use (ternary systems only, limited time use only)
    - The assessment modulus PARROT accessible only in Command mode
    - It is possible to define all quantities derived as partial derivations of the Gibbs energy
- DICTRA (software for modelling of diffusion processes)
    - Older versions “”hate users”
    - Uses mobilities instead of diffusion coeficients
    - Local equilibrium at interface


Thermo-Calc
File Tools Window Help
New Open Save
Switch to Console Mode
Project
Configuration
Results
My Project
Wizards
Quick Start
Templates
Single Point Equilibrium
Property Diagram
Phase Diagram
Scheil Solidification Simulation
Binary Calculation
Ternary Calculation
Scheduler
Scheduled Jobs
<
Add Predecessor
Perform
Create New Activity
>
Event Log
EN
100%
14:59
7.9.2015



Select database: TCNI7



Tie lines: 3 Legend option: None

X Axis

Axis variable: Composition Cr Mole percent

Axis type: Linear

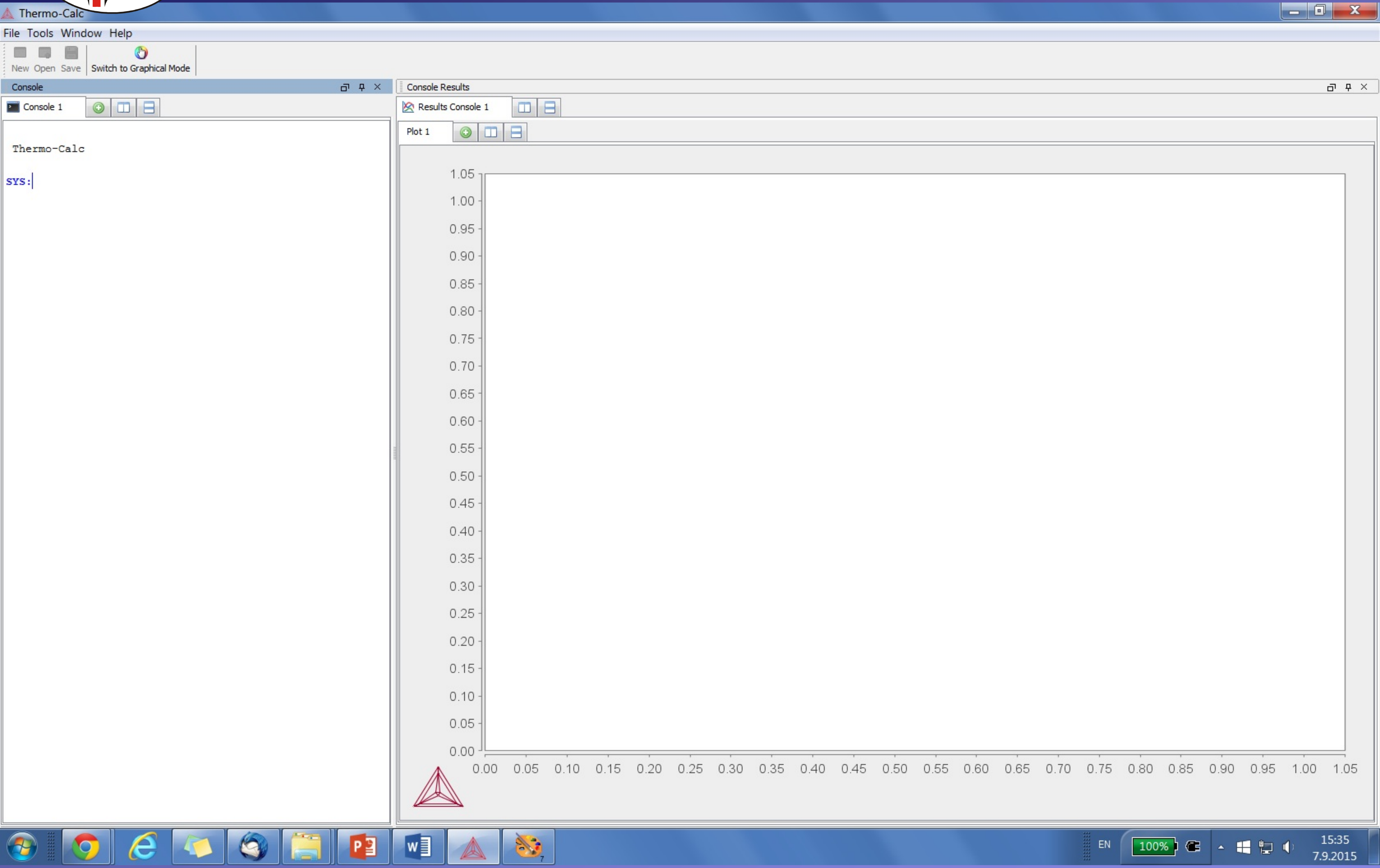
Limits: 500.0 to 3000.0 step 250.0 ☑ Automatic scaling

Y Axis

Axis variable: Temperature Celsius

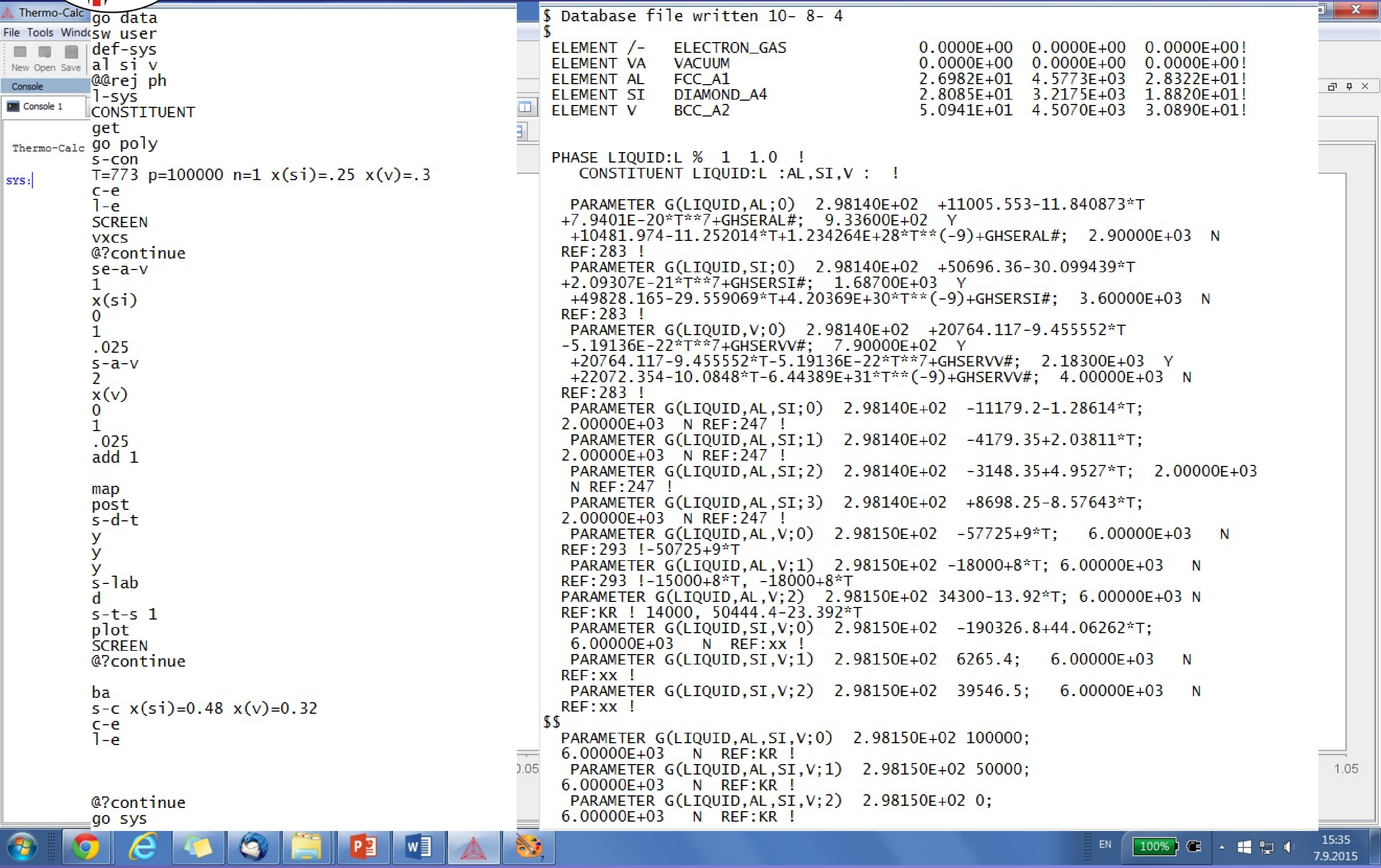
Axis type: Linear

Limits: 500.0 to 3000.0 step 250.0 ☑ Automatic scaling



```
Thermo-Calc

SYS:
```



```
go data
sw user
def-sys
al si v
@@rej ph
l-sys
CONSTITUENT
get
go poly
s-con
T=773 p=100000 n=1 x(si)=.25 x(v)=.3
c-e
l-e
SCREEN
vxcs
@?continue
se-a-v
1
x(si)
0
1
.025
s-a-v
2
x(v)
0
1
.025
add 1

map
post
s-d-t
y
y
y
s-lab
d
s-t-s 1
plot
SCREEN
@?continue

ba
s-c x(si)=0.48 x(v)=0.32
c-e
l-e


@?continue
go sys
```

```
$ Database file written 10- 8- 4
$
 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 AL   FCC_A1                    2.6982E+01  4.5773E+03  2.8322E+01!
 ELEMENT SI   DIAMOND_A4                2.8085E+01  3.2175E+03  1.8820E+01!
 ELEMENT V    BCC_A2                    5.0941E+01  4.5070E+03  3.0890E+01!


 PHASE LIQUID:L %  1  1.0  !
    CONSTITUENT LIQUID:L :AL,SI,V :  !

   PARAMETER G(LIQUID,AL;0)  2.98140E+02  +11005.553-11.840873*T
  +7.9401E-20*T**7+GHSERAL#;  9.33600E+02  Y
   +10481.974-11.252014*T+1.234264E+28*T**(-9)+GHSERAL#;  2.90000E+03  N
  REF:283 !
   PARAMETER G(LIQUID,SI;0)  2.98140E+02  +50696.36-30.099439*T
  +2.09307E-21*T**7+GHSERSI#;  1.68700E+03  Y
   +49828.165-29.559069*T+4.20369E+30*T**(-9)+GHSERSI#;  3.60000E+03  N
  REF:283 !
   PARAMETER G(LIQUID,V;0)  2.98140E+02  +20764.117-9.455552*T
  -5.19136E-22*T**7+GHSERVV#;  7.90000E+02  Y
   +20764.117-9.455552*T-5.19136E-22*T**7+GHSERVV#;  2.18300E+03  Y
   +22072.354-10.0848*T-6.44389E+31*T**(-9)+GHSERVV#;  4.00000E+03  N
  REF:283 !
   PARAMETER G(LIQUID,AL,SI;0)  2.98140E+02  -11179.2-1.28614*T;
  2.00000E+03  N REF:247 !
   PARAMETER G(LIQUID,AL,SI;1)  2.98140E+02  -4179.35+2.03811*T;
  2.00000E+03  N REF:247 !
   PARAMETER G(LIQUID,AL,SI;2)  2.98140E+02  -3148.35+4.9527*T;  2.00000E+03
   N REF:247 !
   PARAMETER G(LIQUID,AL,SI;3)  2.98140E+02  +8698.25-8.57643*T;
  2.00000E+03  N REF:247 !
   PARAMETER G(LIQUID,AL,V;0)  2.98150E+02  -57725+9*T;   6.00000E+03   N
  REF:293 !-50725+9*T
   PARAMETER G(LIQUID,AL,V;1)  2.98150E+02 -18000+8*T; 6.00000E+03   N
  REF:293 !-15000+8*T, -18000+8*T
  PARAMETER G(LIQUID,AL,V;2)  2.98150E+02 34300-13.92*T; 6.00000E+03 N
  REF:KR ! 14000, 50444.4-23.392*T
   PARAMETER G(LIQUID,SI,V;0)  2.98150E+02  -190326.8+44.06262*T;
   6.00000E+03    N   REF:xx !
   PARAMETER G(LIQUID,SI,V;1)  2.98150E+02  6265.4;   6.00000E+03    N
  REF:xx !
   PARAMETER G(LIQUID,SI,V;2)  2.98150E+02  39546.5;   6.00000E+03    N
  REF:xx !
$$
  PARAMETER G(LIQUID,AL,SI,V;0)  2.98150E+02 100000;
  6.00000E+03    N   REF:KR !
   PARAMETER G(LIQUID,AL,SI,V;1)  2.98150E+02 50000;
  6.00000E+03    N   REF:KR !
   PARAMETER G(LIQUID,AL,SI,V;2)  2.98150E+02 0;
  6.00000E+03    N   REF:KR !
```

]

- **Open CALPHAD (free software and databases)**
  http://www.opencalphad.com/

- OpenCalphad is an informal international collaboration of scientists and researchers interested in the development of high quality software and databases for thermodynamic calculations for all kinds of applications.
- The intention is to allow interested scientists to develop more fundamental models to incorporate results from DFT calculations as well as to provide scientists interested in materials simulations a flexible and reliable software using consistent thermodynamic databases.
- Basic principles are identical with Thermo-Calc, main author is Dr. Sundman, who was one of authors of original CALPHAD method and ThermoCalc software
- Currently includes only basic modules and limited amount of databases
- Anybody can download the code
- Anybody can take part in the collaboration

Trying to incorporate the description of thermodynamic function from 0K