The CALPHAD method – basis and applications

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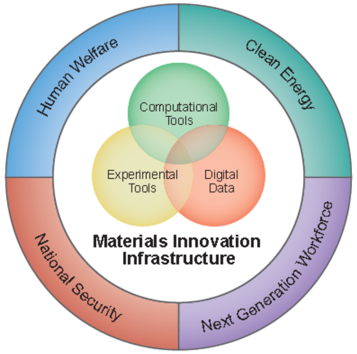
eit RawMaterials

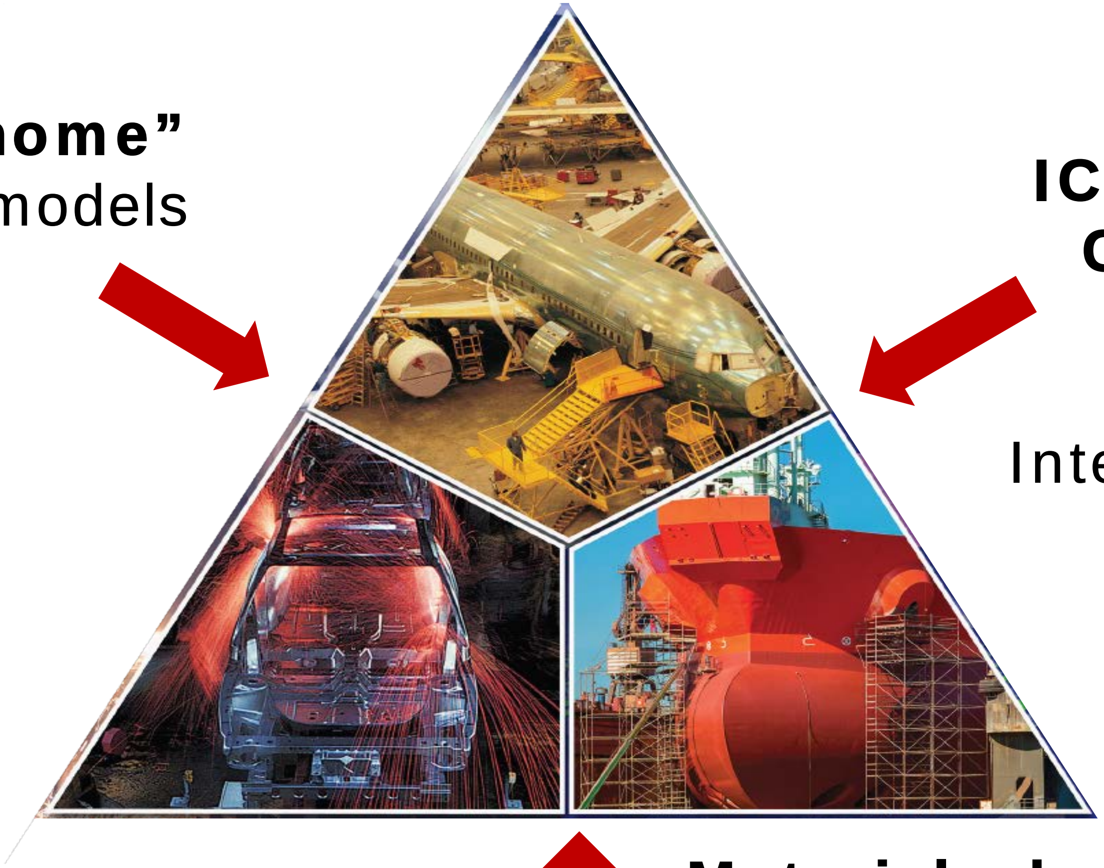
Content

1. Introduction - A shift in Paradigm!

New possibilities: Development time for new materials can be decreased from 10-20 years to 3-4 years.

”Materials Genome”
Databases and models





ICME - Integrated Computational Materials Engineering
Integration of models

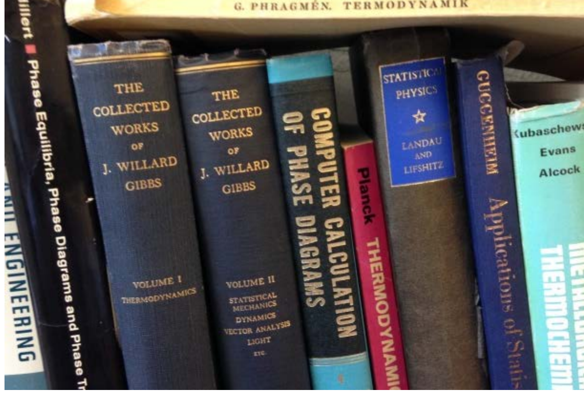
Materials design
Method for a purpose

CALPHAD - the first materials genome because it is …

- the most efficient way of integrating various pieces of information
  - different character (thermochemistry, phase diagrams etc)
  - coherent and useful form
- extendable far beyond the traditional thermochemistry
- increasingly being used outside the traditional CALPHAD community

A major enabling technology in Materials science and engineering.

CALPHAD – a brief history



- Was born 1970 with the book (Kaufman and Bernstein: *Computer calculation of phase diagrams,* 1970)
- In the 50:ies and 60:ies Kaufman and Cohen and Hillert had outlined the general principles.
- Early predecessors – van Laar 1908 and later several others.
- CALPHAD was introduced as an alternative to the quantum-based approach PHACOMP (1964).
- The annual meetings (Later called CALPHAD conferences) and the CALPHAD journal both initiated by Kaufman were instrumental for the rapid expansion of the field.

1. Introduction – A shift in Paradigm!
2. **General idea behind CALPHAD**
3. Thermodynamic basis
4. Thermodynamic models
5. Some Examples:
6. Extension of CALPHAD beyond thermochemistry
7. Conclusions

2. General idea behind CALPHAD

Properties such as

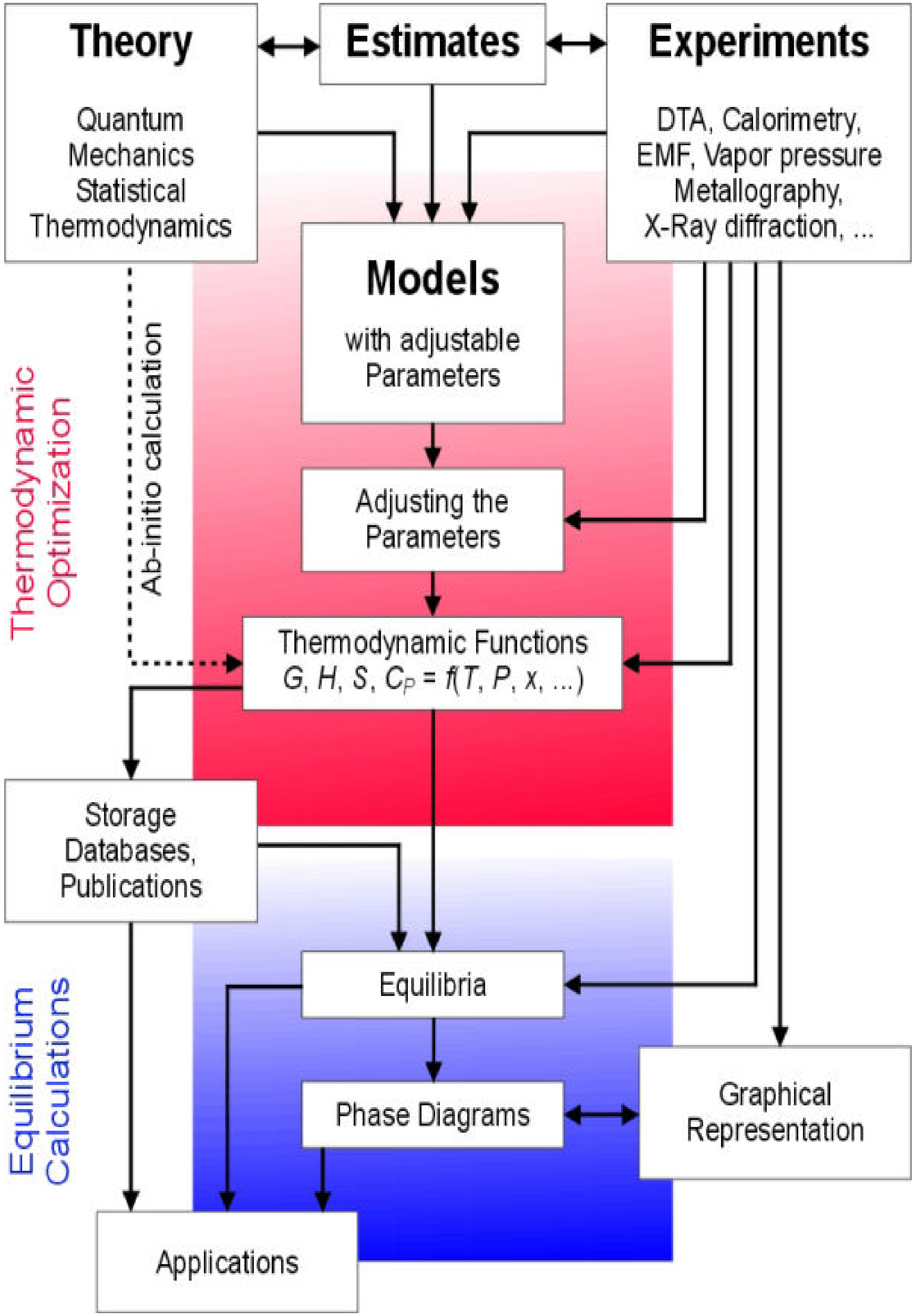
- Phase equilibrium
  - Phase diagrams
  - Composition of phases and compounds
  - Partition coefficients and equilibrium constants…
- Thermochemical data
  - Heat of reactions and transformations
  - Heat capacities
  - Vapour pressures…
- Elastic properties
  - Bulk modulus
  - Elastic constants…
- Volume and its thermal expansion…

all stem from a single thermodynamic function of the system of interest.

If that function is known…

then

- all these properties may be calculated using that function.
- also other quantities of interest may be calculated such as
  - Driving forces for reactions and transformations if the system is not at equilibrium (e.g. In phase-field simulations)
  - Properties of metastable states, e.g. metastable phase diagrams.



Theory

Quantum Mechanics

Statistical Thermodynamics

Estimates

Experiments

DTA, Calorimetry, EMF, Vapor pressure Metallography, X-Ray diffraction, ...

Models

with adjustable Parameters

Adjusting the Parameters

Thermodynamic Functions

$G, H, S, C_P = f(T, P, x, \ldots)$

Ab-initio calculation

Thermodynamic Optimization

Storage Databases, Publications

Equilibria

Phase Diagrams

Graphical Representation

Applications

Equilibrium Calculations

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3. Thermodynamic basis

- What is the equilibrium state of a system aged under given external conditions?

- What are the driving forces for internal changes if the system is not in equilibrium?

Important remark:

Thermodynamics <u>does not only</u> apply at equilibrium, i.e. the condition when nothing more can change.

- measurements can be performed sometimes quite far outside equilibrium and be extrapolated further into the non-equilibrium regime.

- Thus thermodynamics applies considerably outside equilibrium. But how far outside would it apply? Here we will demonstrate how thermodynamics may be applied as far as needed to solve certain problems.

Overview of thermodynamics

State variables
- External
- Internal

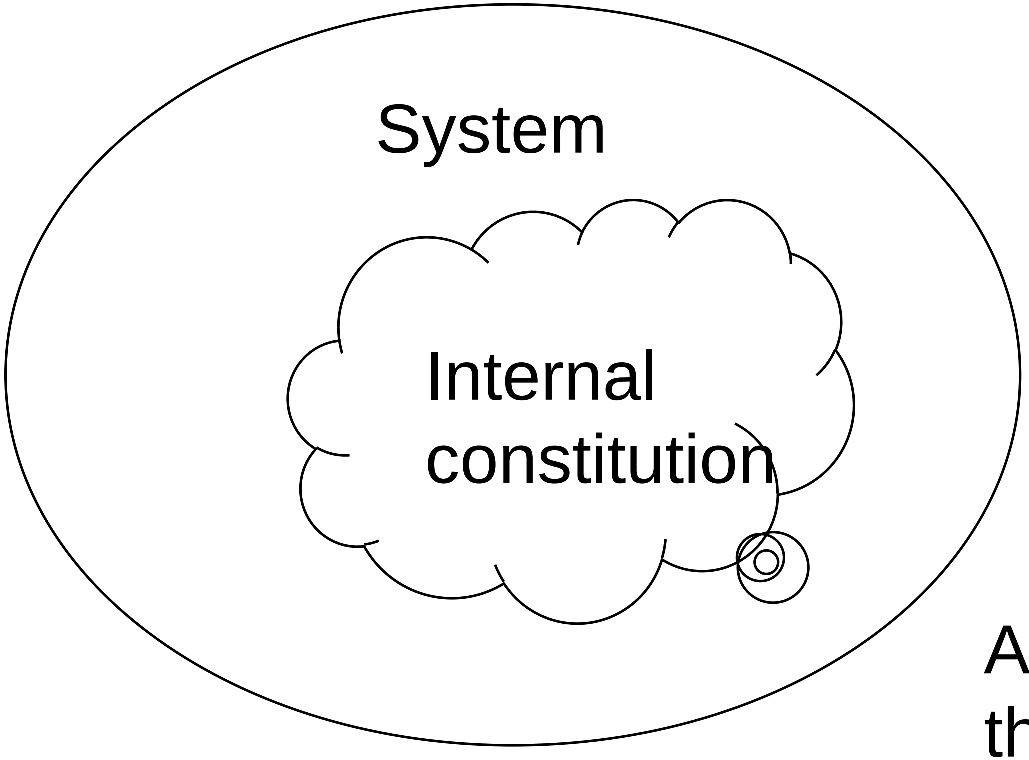
First law: Energy, heat and work

Second law: Entropy, equilibrium, driving force

Multicomponent systems –chemical potential

Surroundings

External conditions: $P, V, T, n_k \ldots$



System

Internal constitution

Interactions between system and surroundings:

composition	C
thermal	1
mechanical	1
	C + 2

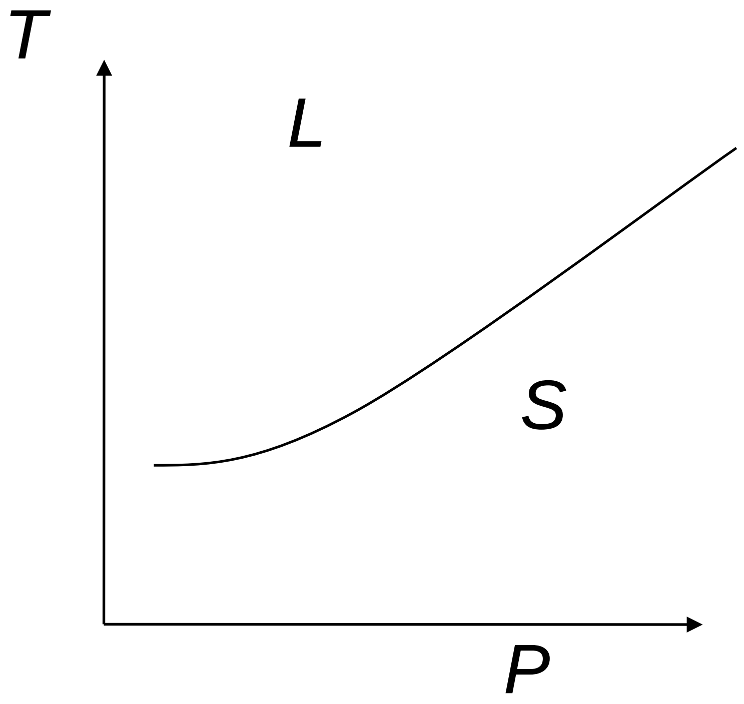
After fixing the external conditions the system will approach a <u>state of equilibrium</u> at which there are no further changes.

C + 2 external variables must be fixed in order to define a unique equilibrium state.

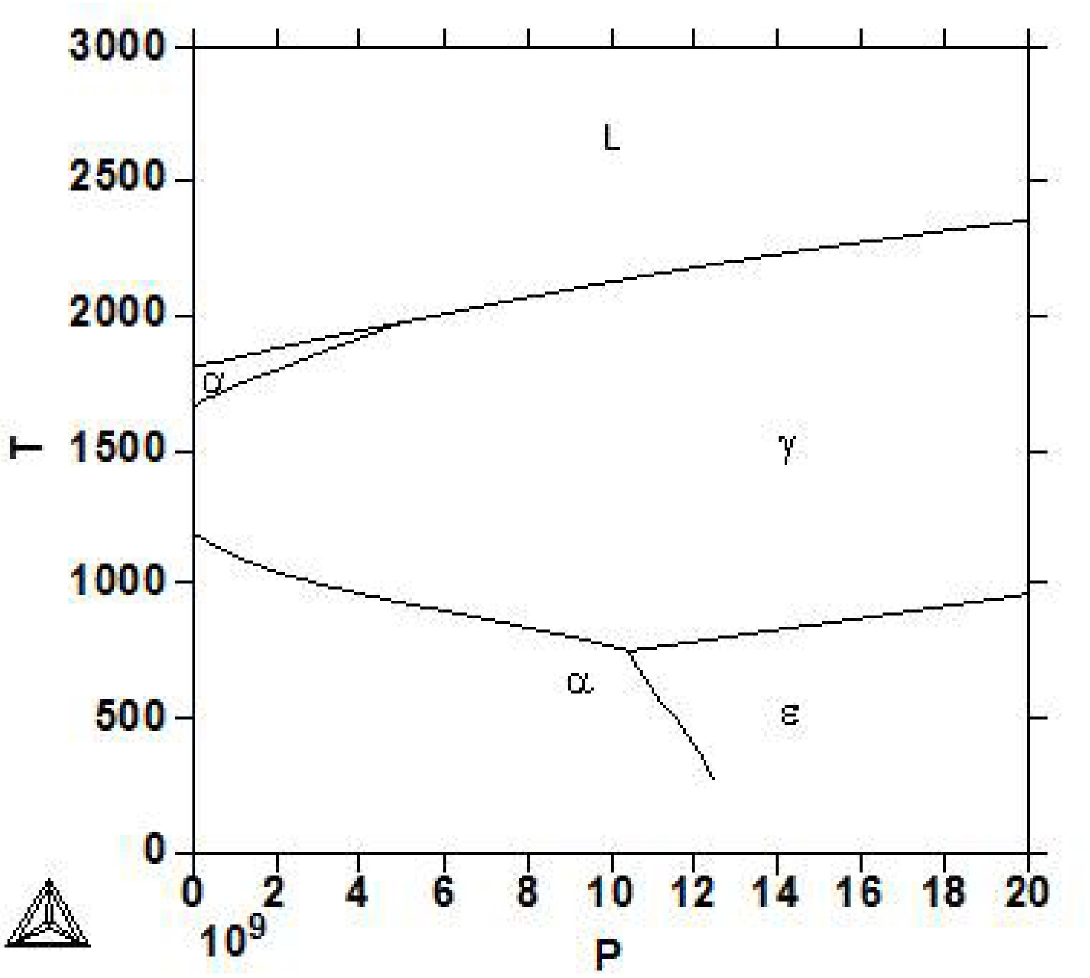
The equilibrium state may be represented by a point in a C + 2 dimensional space; a **state diagram.**

A state diagram containing information about what phase is stable is a **phase diagram.**

Example:
1-component system, n = fix, let *P* and *T* vary =>
2-dimensional state diagram.
Add information on phases => unary phase diagram



Example: Phase diagram of pure iron. Pressure in Pa and temperature in K.



External and internal state variables

External state variables

may be controlled outside the system by the experimentalist or the processing conditions

Internal state variables

In a system out of equilibrium additional variables are needed to fully characterize the system. These variables

- describe the internal constitution of the system
- vary until they reach their equilibrium values and the system comes to rest

Intensive variables

If a new system is formed by merging two identical systems the values of all intensive variables remain constant.

Ex: P, T, ρ, c_k, H_m *etc*

Extensive variables

If a new systems is formed by merging two identical systems the values of all extensive variables will become twice as large.

Ex: V, U, n_k,

Additative rule:

$$\boxed{V = V_1 + V_2}$$

Two types of intensive variables:

- Potentials
  ex: *P*, *T*

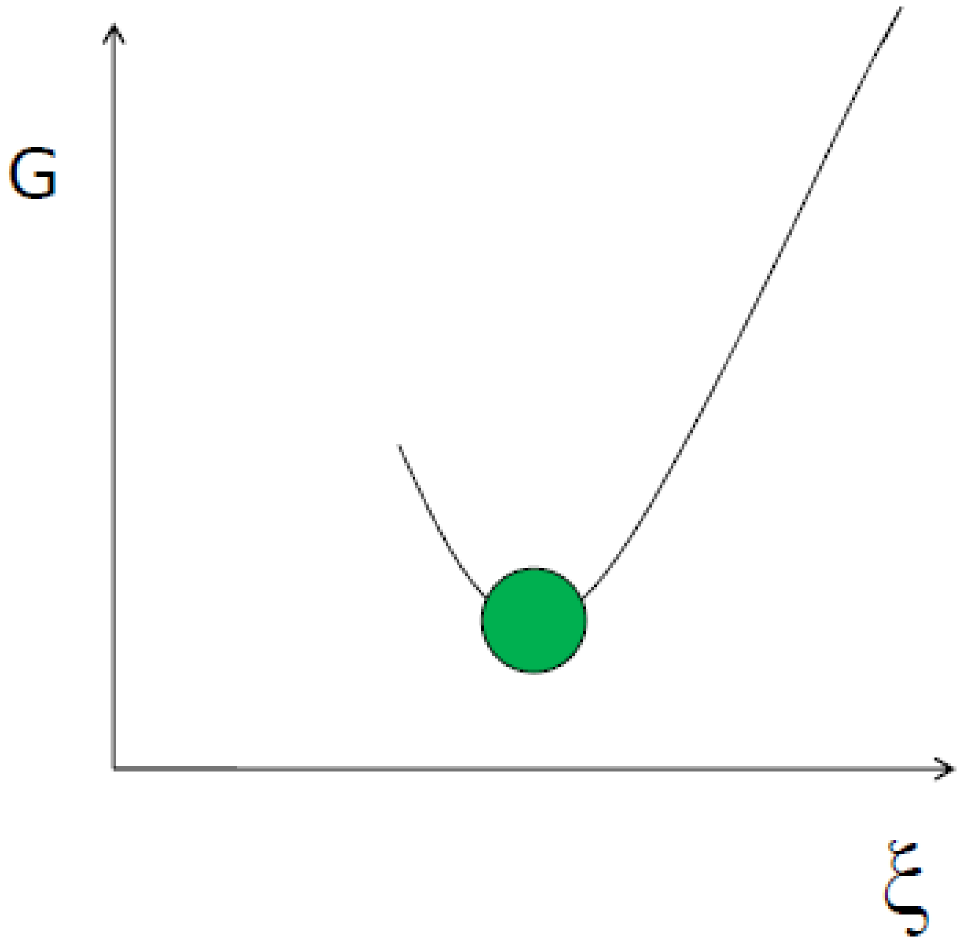
- Densities or specific variables =

$$\frac{\text{extensive variable}}{\text{size}}$$

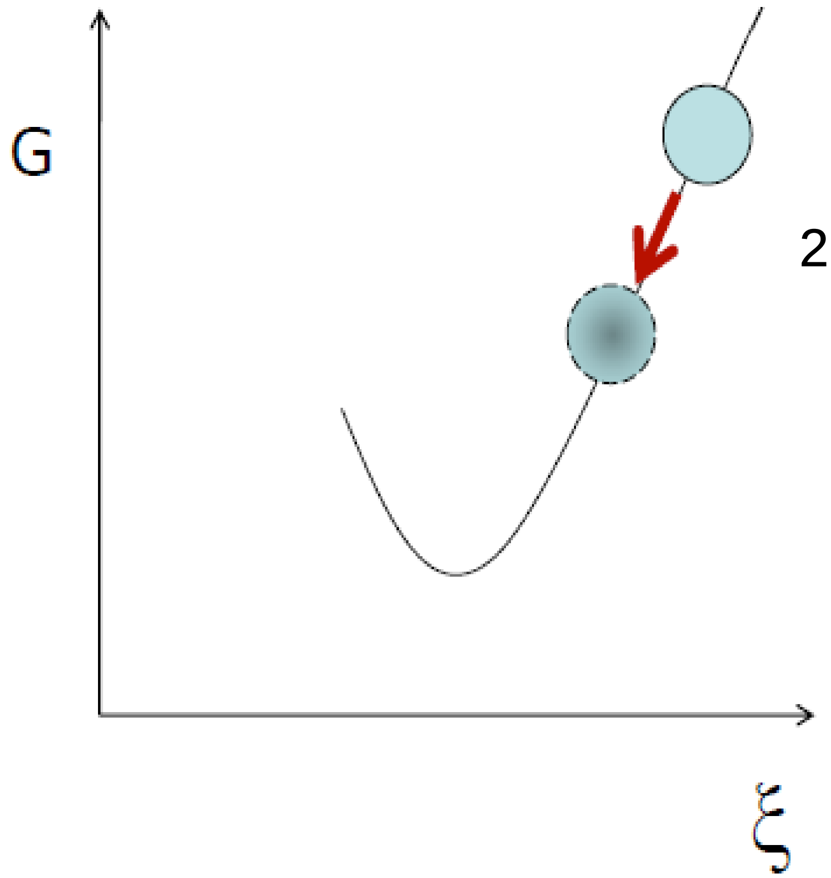
$$\rho = \frac{\text{mass}}{\text{volume}} \quad c_k = \frac{n_k}{\text{volume}} \quad x_k = \frac{n_k}{\sum n_j} \quad \ldots$$

The state of equilibrium at given pressure, temperature and composition

Equilibrium for the value of the internal variable ξ that gives the lowest Gibbs energy.

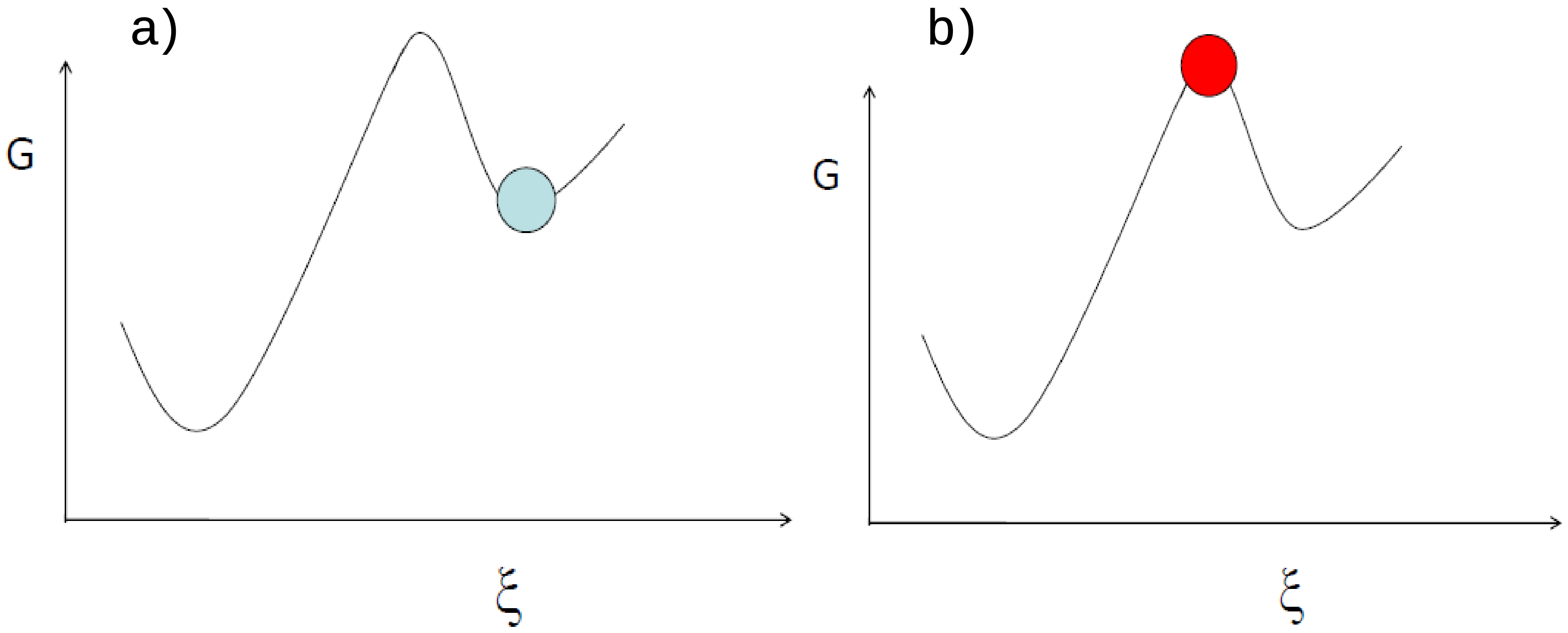


Change in Gibbs energy during a phase transformation.



2:nd law of thermodynamics

a) Metastable equilibrium b) Unstable equilibrium (critical state).



Combined 1:st and 2:nd law of thermodynamics in an open system (i.e. Exchange of matter with surroundings), i.e. multicomponent

$$dU = TdS - PdV + \sum_k \mu_k dN_k - Td_iS \quad \text{(combined law)}$$

$$Td_iS = \sum_j D_j d\xi_j \geq 0 \quad \text{(2:nd law)}$$

$D_j =$ driving force for process j

$d\xi_j = 0$ Process j is frozen in

$$U = U(S, V, N_k, \xi_j)$$

S, V, N_k, ξ_j are natural variables for U!

From the combined law:

Each derivative tells how much the internal energy changes per unit amount of an extensive quantity, i.e. entropy, volume or number of moles of *k*, added to the system: Potentials!

$$\frac{\partial U}{\partial S} = T \quad \longleftarrow$$

Thermal potential (temperature)

$$\frac{\partial U}{\partial V} = -P \quad \longleftarrow$$

Volume potential (negative pressure)

$$\frac{\partial U}{\partial N_k} = \mu_k \quad \longleftarrow$$

Chemical potential

$$\frac{\partial U}{\partial \xi_j} = -D_j \quad \longleftarrow$$

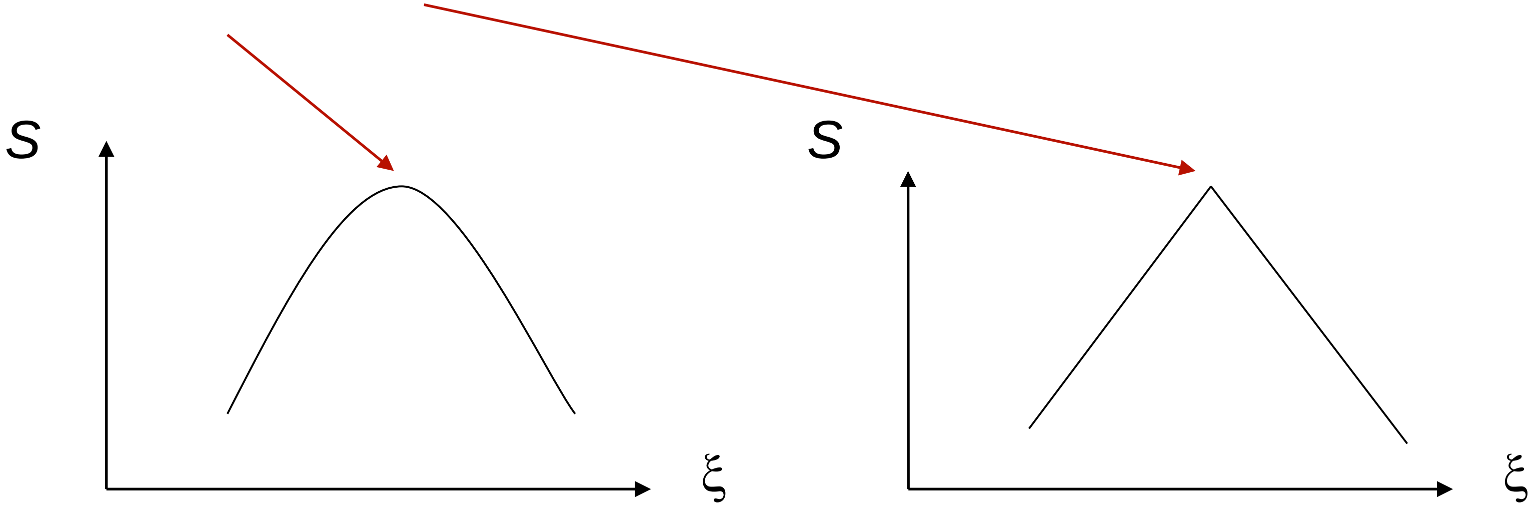
Reaction potential (negative driving force)

Equilibrium conditions come from second law:

For a closed system with a constant energy $dU = 0$ under constant volume:

$$\cancel{dU} = TdS - P\cancel{dV} + \sum_k \mu_k \cancel{dN_k} - Td_iS$$

The condition $dS = d_iS > 0$ implies that S must increase towards a maximum which is reached at equilibrium.



A more convenient equilibrium condition

Equilibrium conditions fixed T and P we obtain from the combined law:

$$dU = TdS - PdV - D\,d\xi$$

$$d(U - TS + PV) = -SdT + VdP - D\,d\xi$$

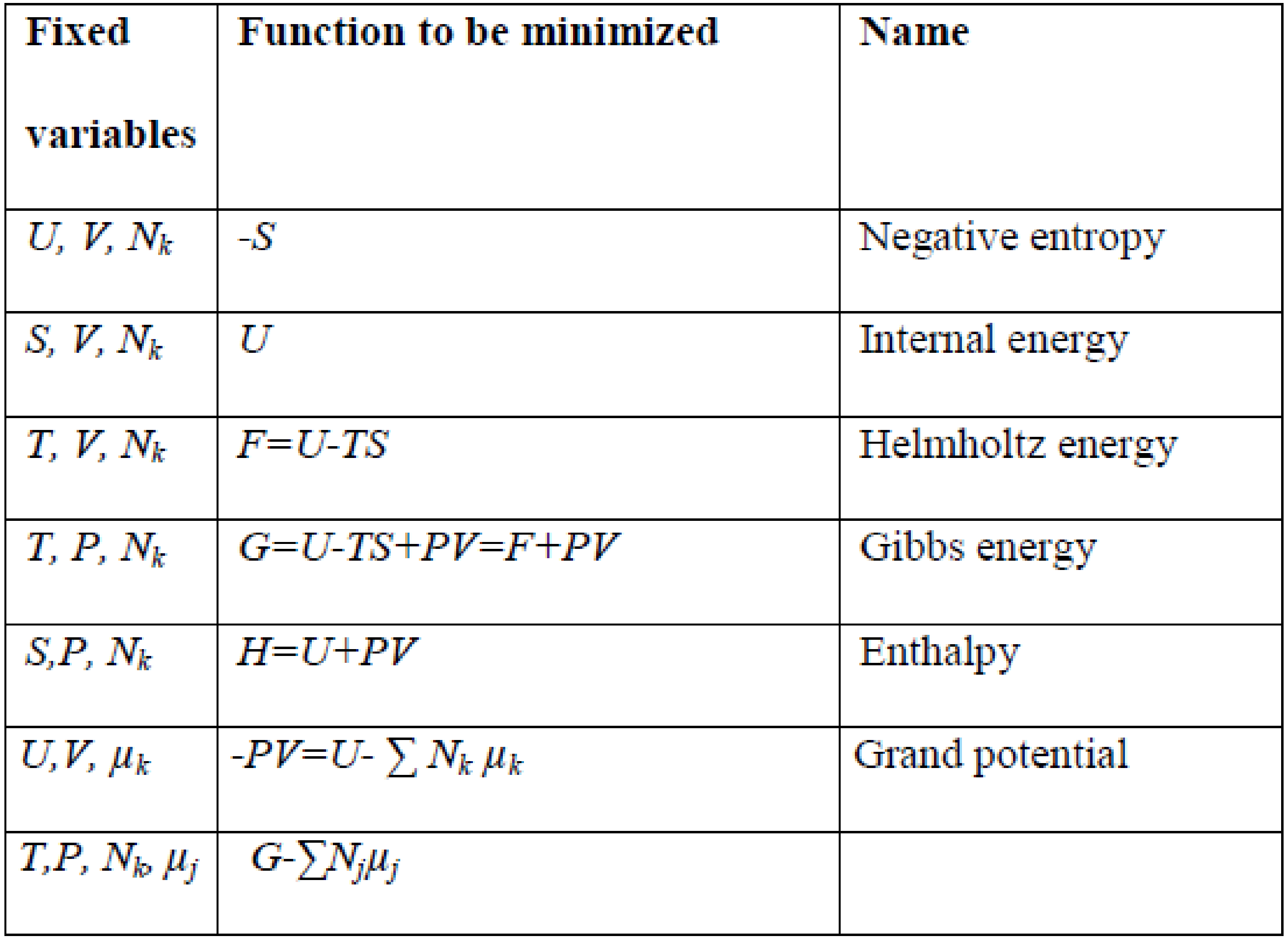
At constant T and P: $d(U - TS + PV) = -D\,d\xi$

$G = U - TS + PV$ Gibbs energy

$\left(\frac{\partial G}{\partial \xi}\right)_{TP} = -D = 0$ at equilibrium.

At given T and P the Gibbs energy G is minimized at equilibrium.

Most useful!



Fixed variables	**Function to be minimized**	**Name**
U, V, N_k	$-S$	Negative entropy
S, V, N_k	U	Internal energy
T, V, N_k	$F=U-TS$	Helmholtz energy
T, P, N_k	$G=U-TS+PV=F+PV$	Gibbs energy
S,P, N_k	$H=U+PV$	Enthalpy
U,V, μ_k	$-PV=U-\sum N_k \mu_k$	Grand potential
T,P, N_k, μ_j	$G-\sum N_j\mu_j$	

Characteristic state functions with their natural variables

$$U(S,V,\xi)$$

$$F(T,V,\xi)$$

$$G(T,P,\xi)$$

$$H(S,P,\xi)$$

$$S(U,V,\xi)$$

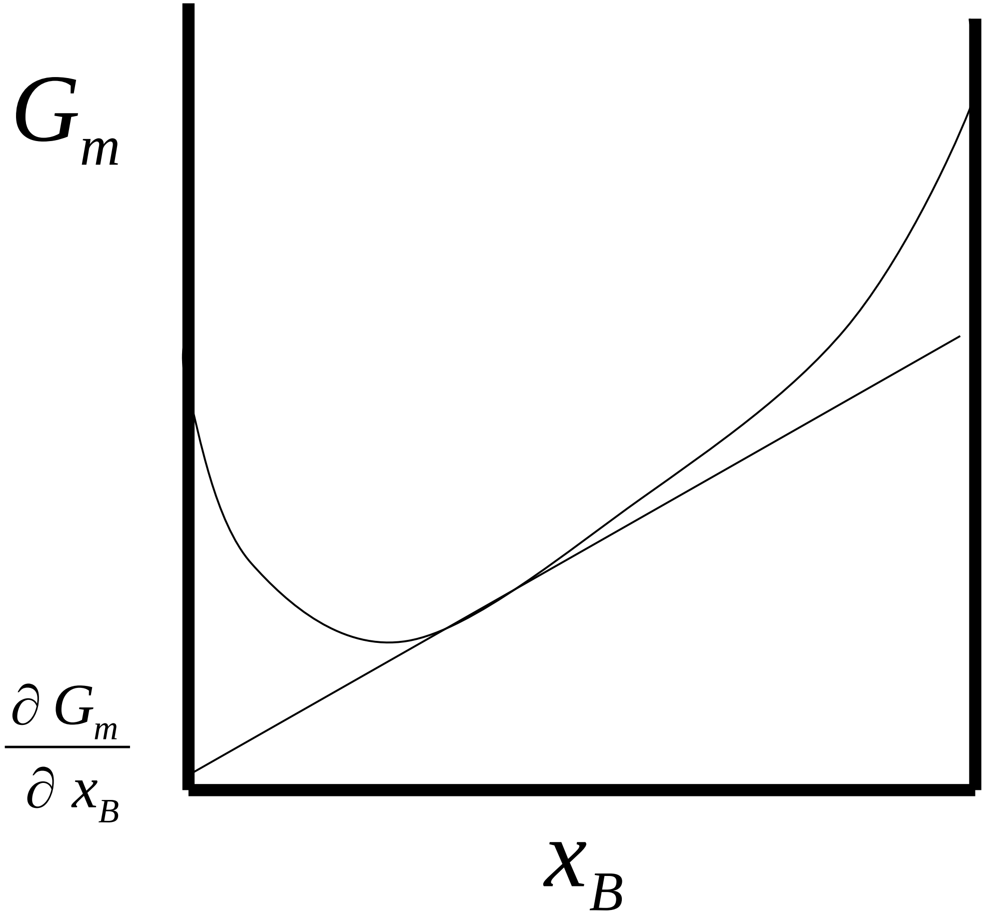
Either one of these functions fully characterize a system.

If $G_m(T, P, x_1, x_2 \ldots x_n)$ is known, what is μ_j?

It is straight forward to show that

$$\mu_j = G_m + \frac{\partial G_m}{\partial x_j} - \sum_{i=1}^{n} x_i \frac{\partial G_m}{\partial x_i}$$

Example:
Binary system – The tangent construction



$$\mu_B = G_m + (1 - x_B)\frac{\partial G_m}{\partial x_B}$$

$$\mu_A = G_m - x_B \frac{\partial G_m}{\partial x_B}$$

Some properties derived from Gibbs energy of a phase:

$$G_m = G_m(T, P, x_1, x_2 \ldots \xi_1, \xi_2 \ldots)$$

$$V_m = \partial G_m / \partial P$$

$$S_m = \partial G_m / \partial T$$

$$\alpha = (\partial^2 G_m / \partial P \partial T) / \partial\, G_m / \partial P$$

$$c_P = -T \partial^2 G_m / \partial T^2$$

$$\ldots$$

$$\mu_k = G_m + \frac{\partial G_m}{\partial x_k} - \sum x_j \frac{\partial G_m}{\partial x_j}$$

$$D_j = -\frac{\partial G_m}{\partial \xi_j}$$

$$G = \sum_\alpha N^\alpha G_m{}^\alpha (T, P, x_1^\alpha, x_2^\alpha \ldots \xi_1^\alpha, \xi_2^\alpha \ldots)$$

Driving force under fixed P, T and composition

Combined law yields:

$$dG = -\sum D_j d\xi_j$$

Consider now a process where the ξ variables change from an initial state to a final state.

The driving forces may vary in a complicated way during the integration the integral

$$\int dG = G^{final} - G^{start} = -\sum \int_{start}^{final} D_j d\xi_j$$

The integrated driving force.

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4. Thermodynamic models

If we know Gibbs energy as a function

$$G_m = G_m(P, T, x_1, x_2, \ldots \xi_1, \xi_2, \ldots)$$

for the individual phases in a system:

- We may calculate a lot of properties of practical interest.
- Calculate equilibrium state and phase diagram by minimizing G.
- Calculate driving forces to use in kinetic simulations.

Modeling of solutions

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

$$G_m = {}^{\circ}G_m + \Delta G_m^{ideal} + {}^{E}G_m + \Delta G_m^{ph}$$

reference surface

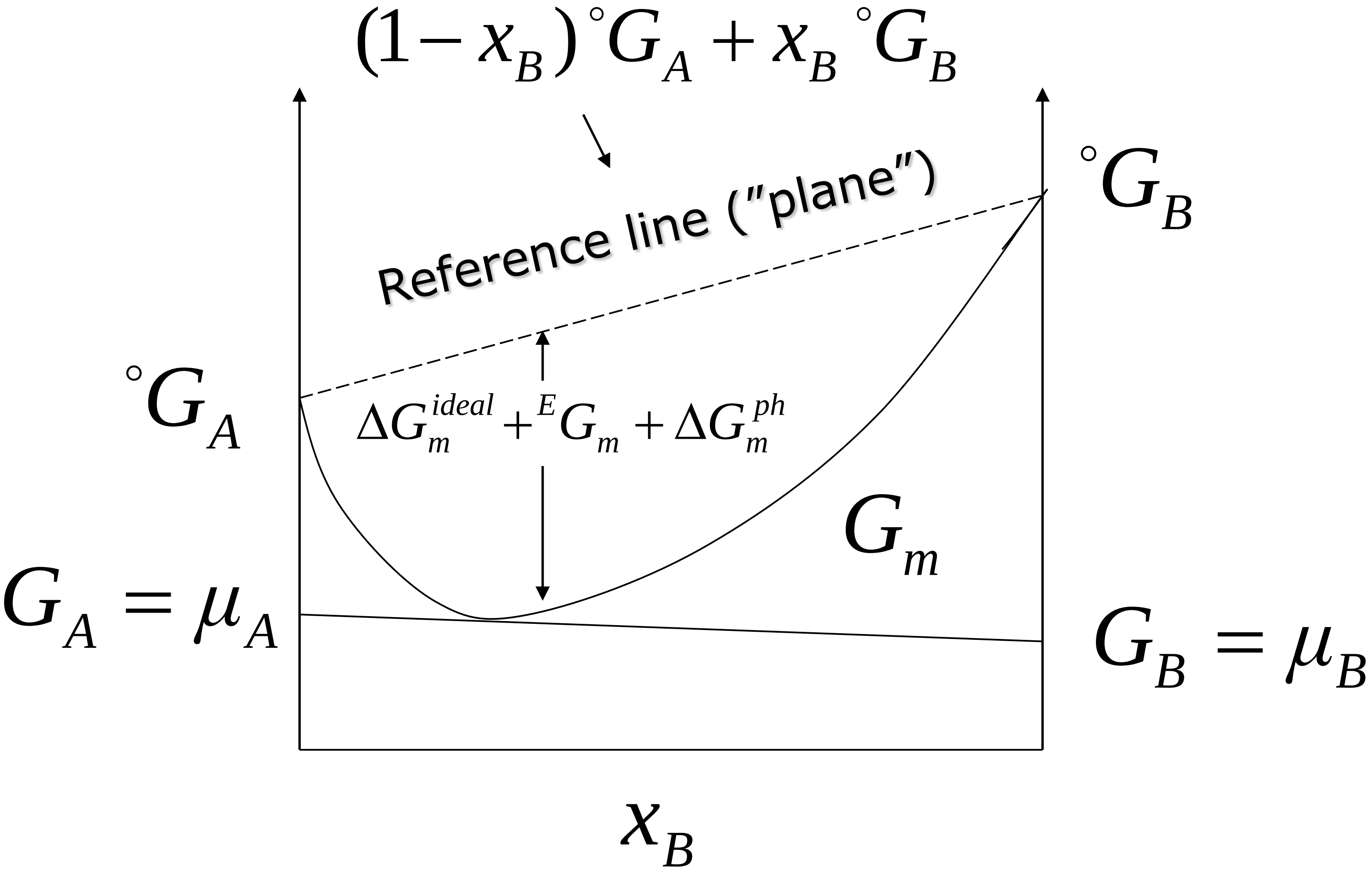
configurational contribution
(random mixing)

excess term

physical contribution

$${}^{\circ}G_m = \sum_{i=1}^{C} x_i \, {}^{\circ}G_i \, , \quad \Delta G_m^{ideal} = RT \sum_{i=1}^{C} x_i \ln x_i \, , \quad {}^{E}G_m = \text{e.g. regular solution}$$

$$\Delta G_m^{ph} = \text{e.g. ordering (magnetic/chemical)}$$


$(1-x_B)\,{}^{\circ}G_A + x_B\,{}^{\circ}G_B$
Reference line ("plane")
${}^{\circ}G_B$
${}^{\circ}G_A$
$\Delta G_m^{ideal} + {}^{E}G_m + \Delta G_m^{ph}$
G_m
$G_A = \mu_A$
$G_B = \mu_B$
x_B

Regular-solution type of models

$$^{E}G_m = \sum_{i>j}\sum_{j} x_i x_j L_{ij}$$

where

$$L_{ij} = {}^{\circ}L_{ij} + \sum_{k}(x_i - x_j)^k \; {}^{k}L_{ij} = {}^{\circ}L_{ij} + (x_i - x_j)^1 \; {}^{1}L_{ij} + (x_i - x_j)^2 \; {}^{2}L_{ij} + \dots$$

Redlich-Kister polynomial

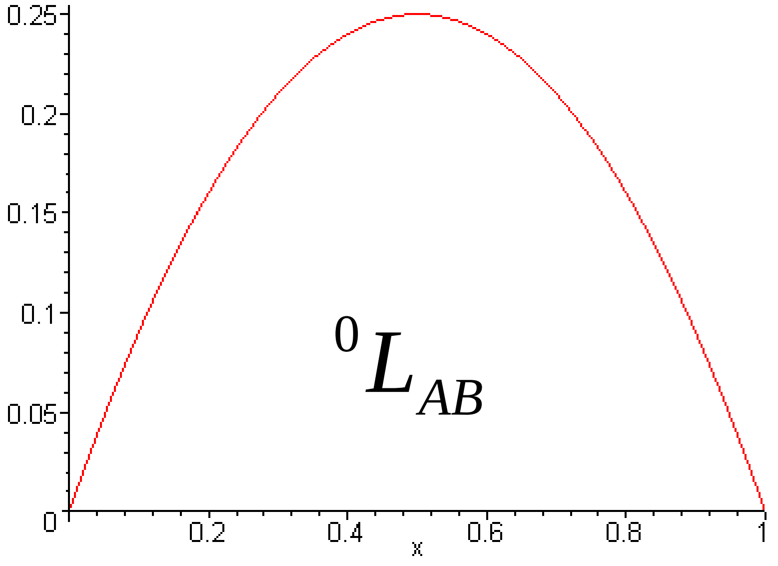
$k = 0$: Regular solution

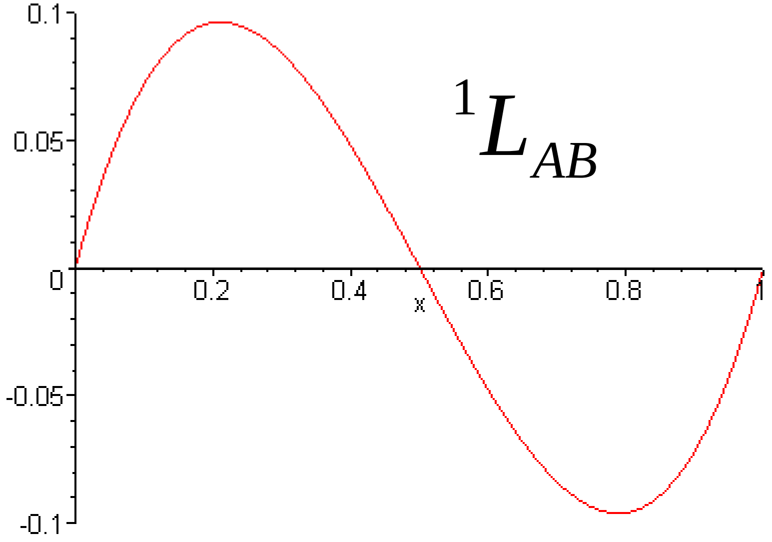
$k = 1$: Sub-regular solution

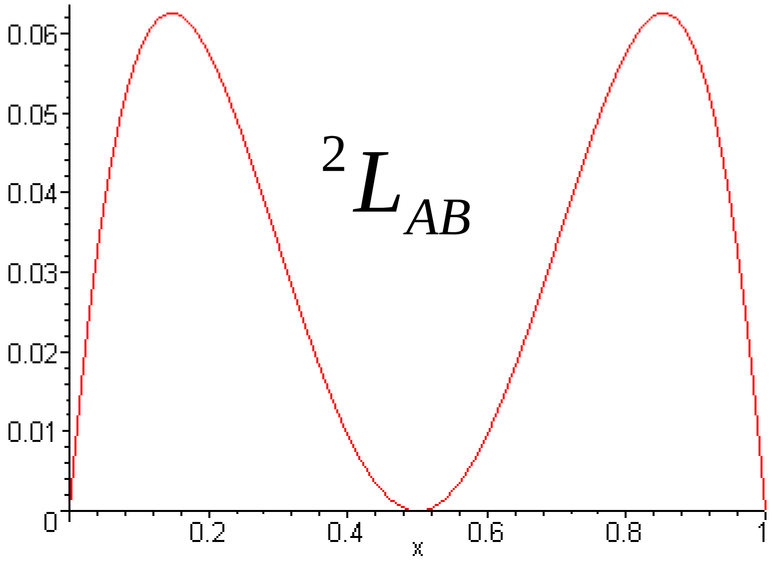
$k = 2$: Sub-sub-regular solution

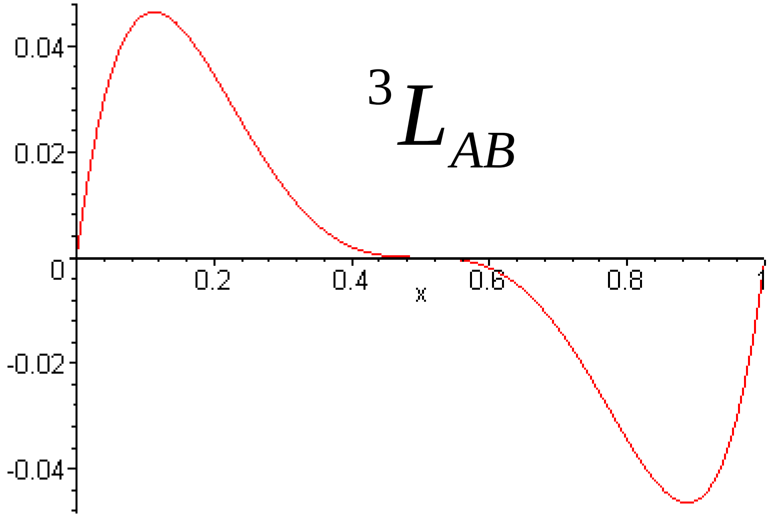
etc

Contributions to ${}^{E}G_m$:

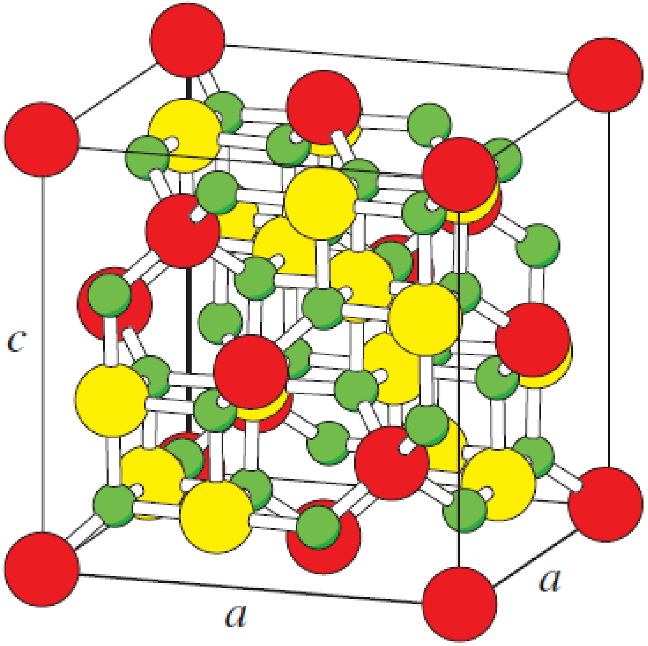








Phases with sublattices



$(A_1A_2...)_{a_1}(B_1B_2...)_{a_2}.....(....)_{a_t}.....$

For example:

Oxides, e.g. $(Ni,Mn)(O,N)$

Carbo-nitrides, e.g. $(Cr,Fe,Mo)_{23}(C,N)_6$

Interstitials, e.g. $(Fe,Mn,Si...)(C,Va)$

Salts, e.g. $(Na^{+1},K^{+1})(Cl^{-1},F^{-1})$

The site fraction y_j^t is the fraction of lattice sites on sublattice t that are occupied by component k.

$$y_j^t = N_k^t / \sum_j N_j^t$$

$N =$ number of formula units

$$G_m = G / N$$

One can usually not calculate the chemical potential of a component because the derivative $\partial G / \partial N_k$ cannot be taken without violating the constraints.

In general,

$$(A_1, A_2 \ldots .)_{a_1} (B_1, B_2 \ldots .)_{a_2} (C_1, C_2 \ldots .)_{a_3} \ldots$$

$$\mu_I = G_m + \sum_t \frac{\partial G_m}{\partial y_{I_t}^t} - \sum_t \sum_k y_k^t \frac{\partial G_m}{\partial y_k^t}$$

where I is a hypothetical compound:

$$I = (I_1)_{a_1} (I_2)_{a_2} (I_3)_{a_3} \ldots$$

eg $Cr_{23}C_6$

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The compound energy formalism

For example: how to represent the Gibbs energy of

$(Cr, Fe)_{23}(C, N)_6$?

G_m per mole of formula unit.

Random mixture on each sublattice

$$-S_m^{mix}/R = 23\left(y_{Cr}\ln y_{Cr} + y_{Fe}\ln y_{Fe}\right) + 6\left(y_C\ln y_C + y_N\ln y_N\right)$$

What about the reference and excess energies?

Note: in the reference mixing entropy and excess energy vanish.

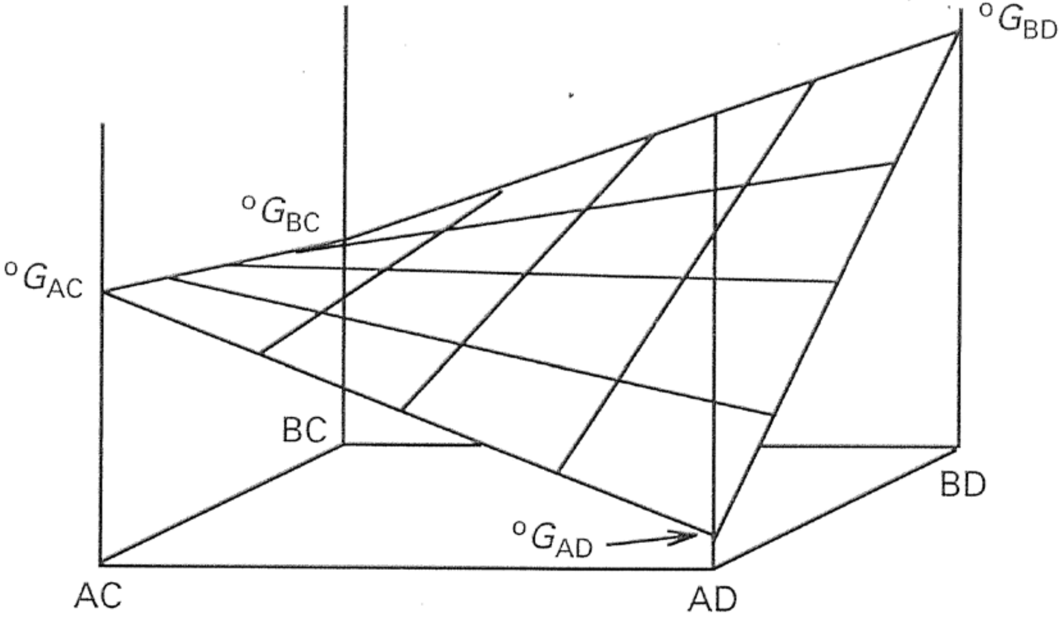
The reference energy "surface"

4 compounds:

$(Cr)_{23}(C)_6$ $\quad$ $(Cr)_{23}(N)_6$

$(Fe)_{23}(C)_6$ $\quad$ $(Fe)_{23}(N)_6$

$$G_m^{ref} = y_{Cr}y_C\,{}^{\circ}G_m^{Cr_{23}C_6} + y_{Cr}y_N\,{}^{\circ}G_m^{Cr_{23}N_6} + y_{Fe}y_C\,{}^{\circ}G_m^{Fe_{23}C_6} + y_{Fe}y_N\,{}^{\circ}G_m^{Fe_{23}N_6}$$



The chemical potentials

$$\mu_{Cr_{23}C_6} = \left[G_m + \frac{\partial G_m}{\partial y^1_{Cr}} + \frac{\partial G_m}{\partial y^2_{C}} - \sum_t \sum_k y^t_k \frac{\partial G_m}{\partial y^t_k} \right]$$

$$\mu_{Cr_{23}C_6} = {}^{\circ}G_m^{Cr_{23}C_6} + y_{Fe} y_N \Delta {}^{\circ}G_{CrN+FeC} + RT\left[23 \ln y_{Cr} + 6 \ln y_C \right] + \ldots$$

$$\Delta {}^{\circ}G_{CrN+FeC} = {}^{\circ}G_m^{Cr_{23}N_6} + {}^{\circ}G_m^{Fe_{23}C_6} - {}^{\circ}G_m^{Cr_{23}C_6} - {}^{\circ}G_m^{Fe_{23}N_6})$$

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5. Some examples

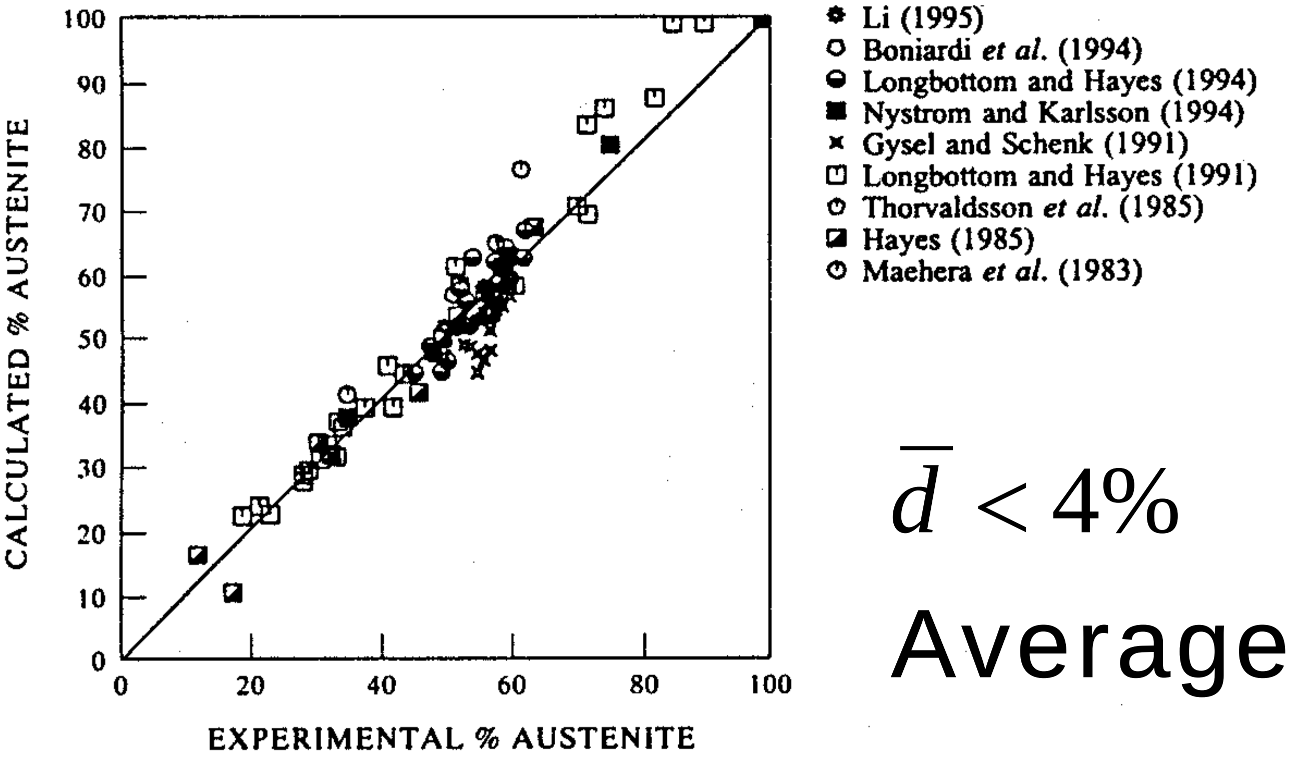


Figure 10.40 Comparison between calculated and experimentally observed % of austenite in duplex stainless steels. (Data from Longbottom and Hayes (1991) represent dual phase steels.).

$$\bar{d} < 4\%$$

Average deviation

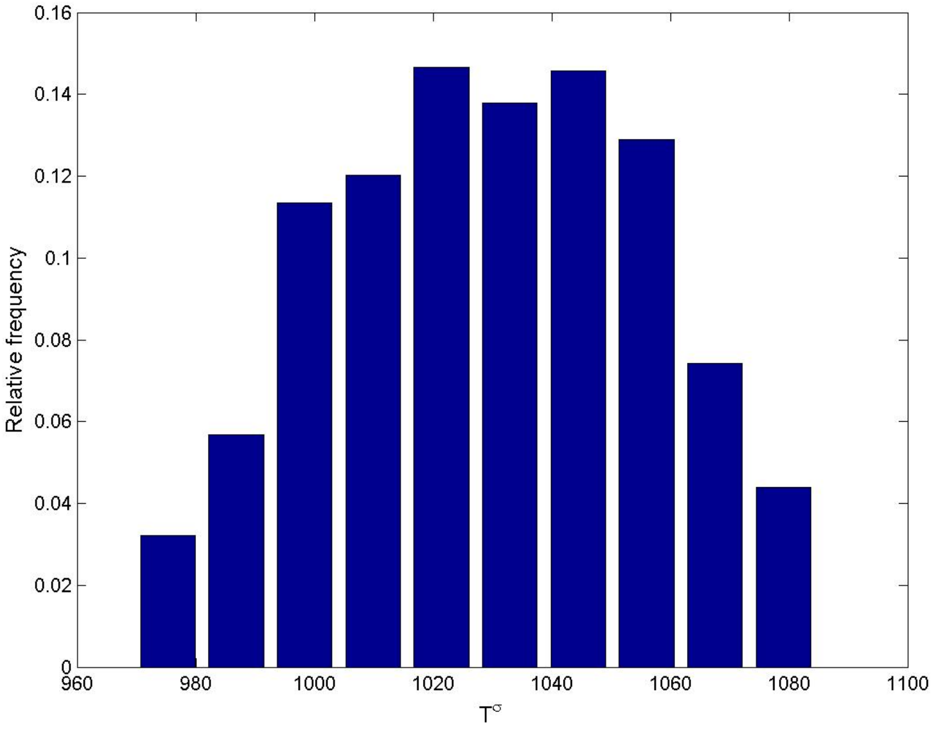
From: Saunders & Miedownik: ”Calphad -a comprehensive review”

Nominal composition (SAF 2507):

Fe – 25% Cr – 7% Ni – 4% Mo – 0.27% N – 0.02% C

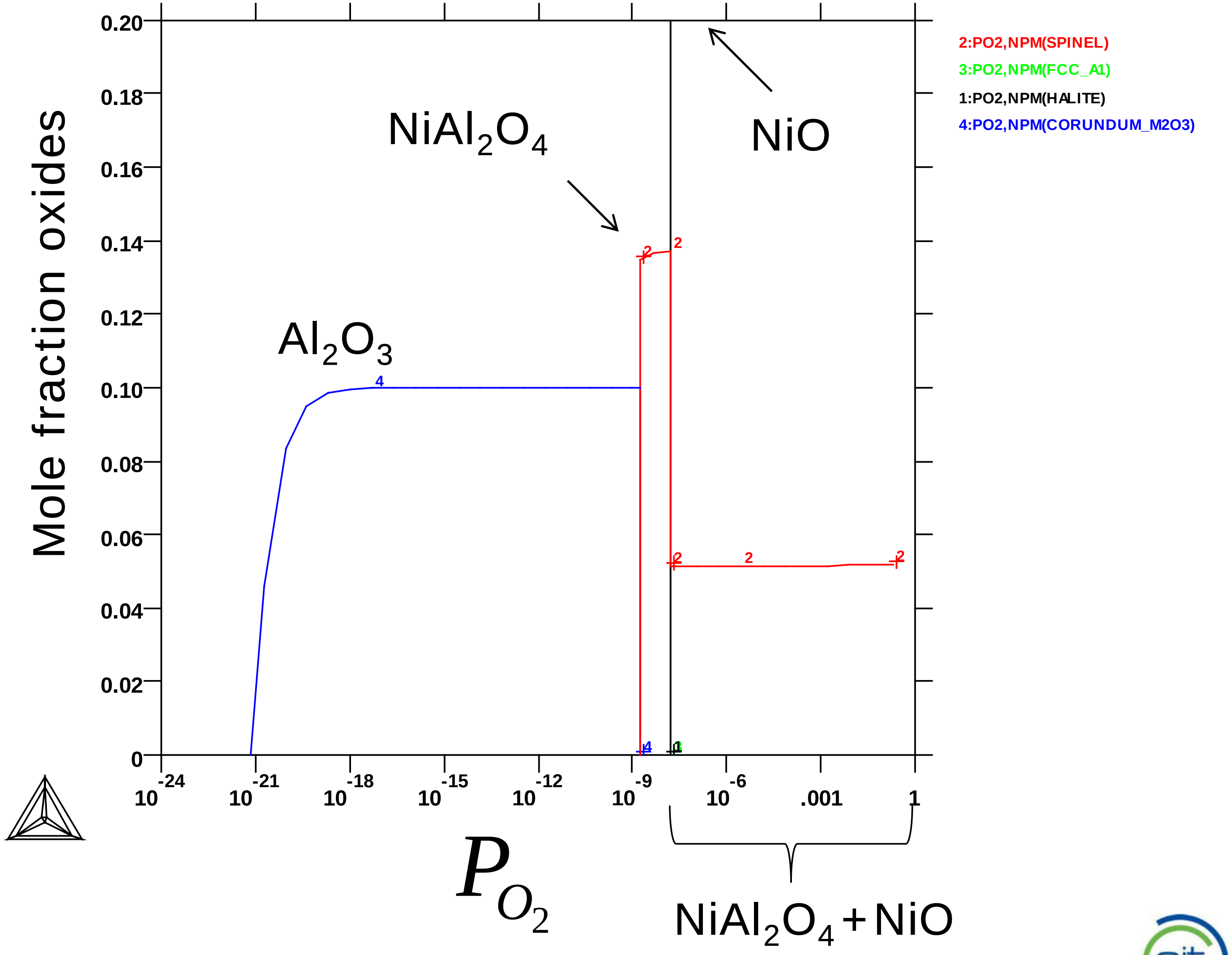
Predict the temperature when sigma-phase becomes stable within some composition variation:

- Fe Base
- Cr 23 – 27%
- Ni 6 – 8%
- Mo 3 – 5%
- N 0.25 – 0.29%
- C 0 – 0.03%



Oxidation of Ni-base alloy

Ni-2 mass% Al at 1200 °C (TCFE7)



The data challenge (ex. Ni-base alloys)

	Al	B	C	Co	Cr	Fe	Hf	Mo	N	Nb	Ni	Pd	Pt	Re	Si	Ta	Ti	V	W
B	x	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
C	x	x	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Co	x	x	x	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Cr	x	x	x	x	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Fe	x	x	x	x	x	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Hf	x	x	x	x	x	x	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Mo	x	x	x	x	x	x	x	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
N	x	x		x	x	x		x	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Nb	x	x	x	x	x	x	x	x	x	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Ni	x	x	x	x	x	x	x	x	x	x	▨	▨	▨	▨	▨	▨	▨	▨	▨
Pd	x	x	x	x	x	x	x	x		x	x	▨	▨	▨	▨	▨	▨	▨	▨
Pt	x	x	x	x	x	x	x			x	x	x	▨	▨	▨	▨	▨	▨	▨
Re	x	x	x	x	x	x	x	x		x	x	x	x	▨	▨	▨	▨	▨	▨
Si	x	x	x	x	x	x	x	x	x	x	x	x	x	x	▨	▨	▨	▨	▨
Ta	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	▨	▨	▨	▨
Ti	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	▨	▨	▨
V	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	▨	▨
W	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	▨
Zr	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x

- 20 elements: 190 binary systems
- 184 of the 190 binary systems assessed for full range composition
- All Ni containing ternaries plus other ternary systems also assessed to full range of composition (184 in total)
- 292 intermetallic and solution phases

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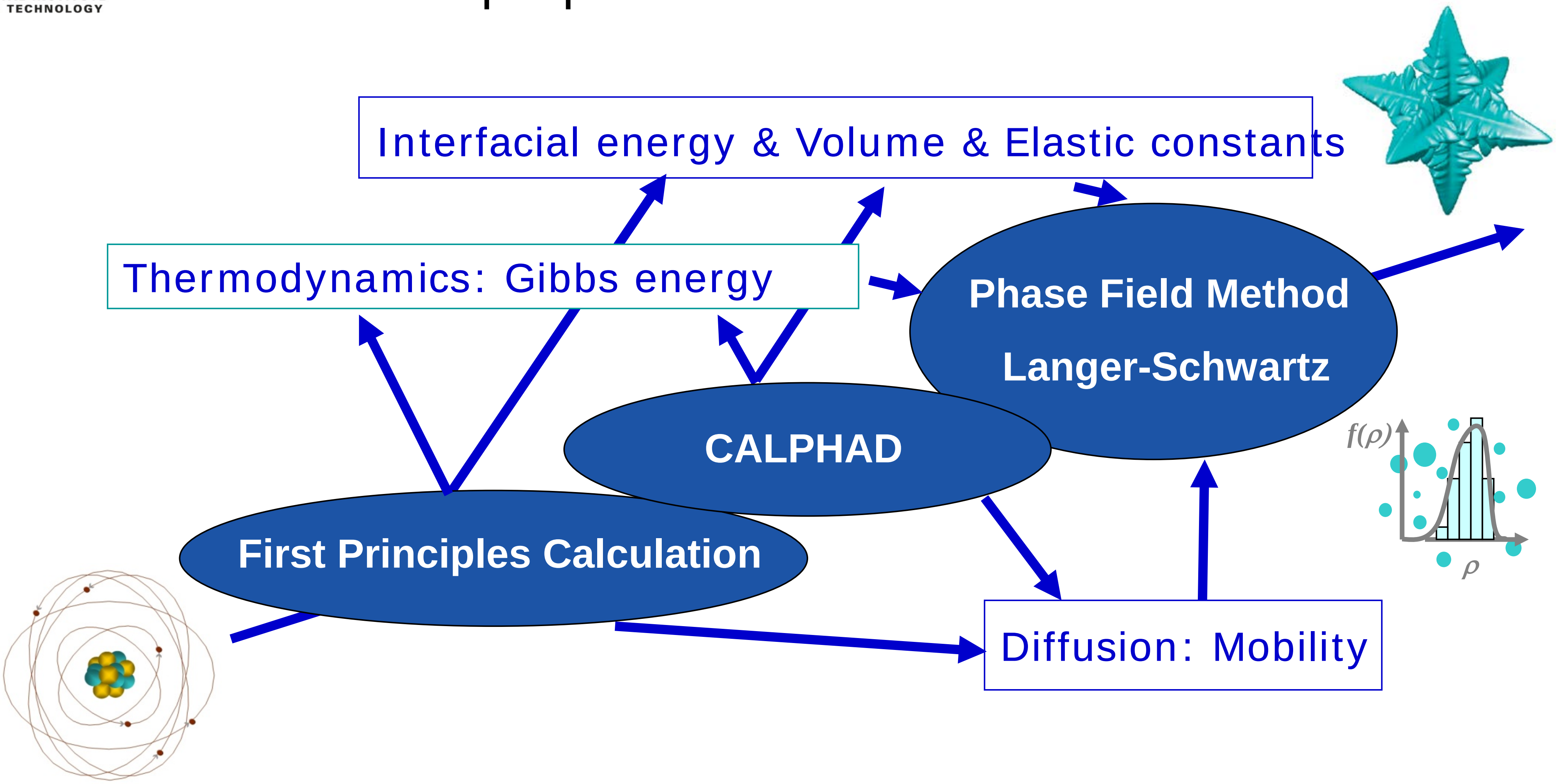
6. Extension of CALPHAD beyond thermochemistry

- Diffusion and phase transformations: driving forces from CALPHAD thermodynamics
- Other properties
  - Diffusion coefficients
  - Interfacial mobilities
  - Interfacial energies
  - Stacking fault energy
  - Elastic constants (anisotropic behaviour)
  - Optical
  - Electronic
  - Magnetic
  - Strength, ductility etc…

From atoms to microstructure: The aim is to predict microstructure evolution and materials properties.



Interfacial energy & Volume & Elastic constants

Thermodynamics: Gibbs energy

Phase Field Method

Langer-Schwartz

CALPHAD

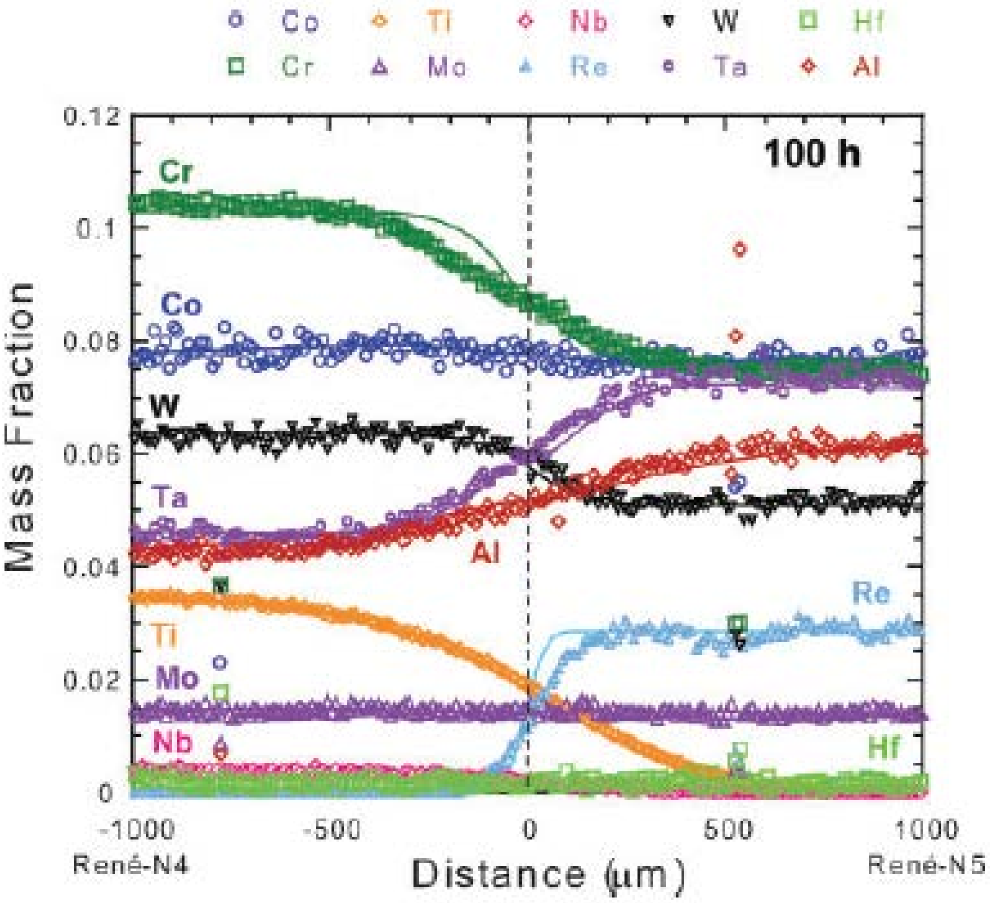
First Principles Calculation

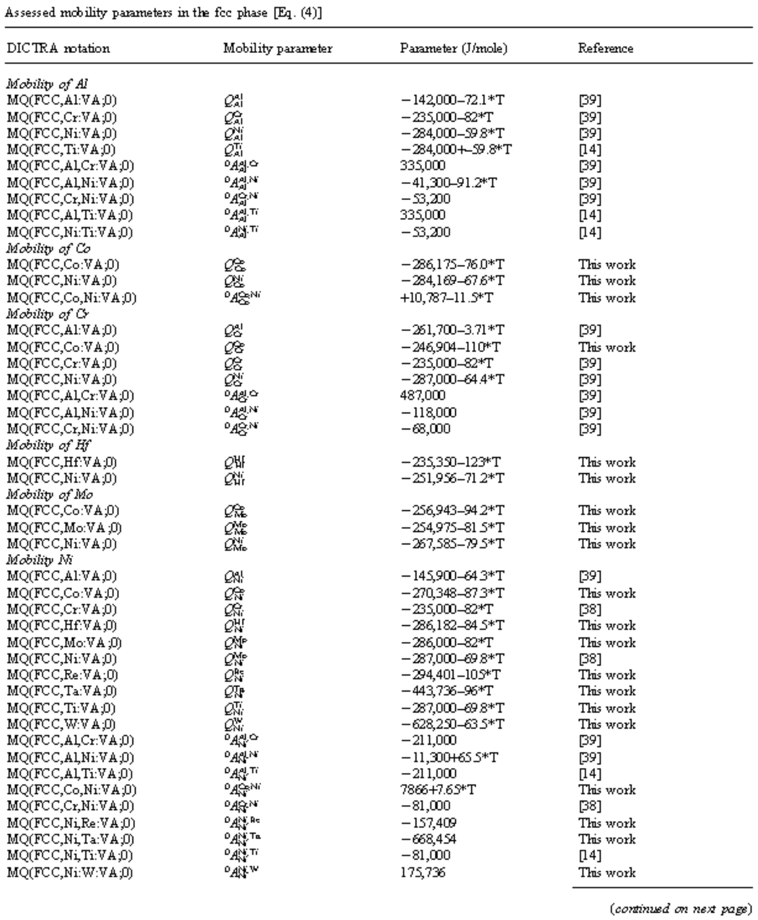
Diffusion: Mobility

Genomic database for diffusion

- Multicomponent systems: many diffusion coefficients!
- Various type of coupling effects may make it more complicated than Fick’s law.
- A CALPHAD-type of approach was suggested for information on diffusion kinetics (Andersson-Ågren 1992)
  - Allowed systematic representatation of the kinetic behaviour of multicomponent alloy systems.
- DICTRA was developed in the 1990s for numerical solution of multicomponent diffusion problems in simple geometries.

Diffusion in Ni-base alloys: Campbell et al. 2002





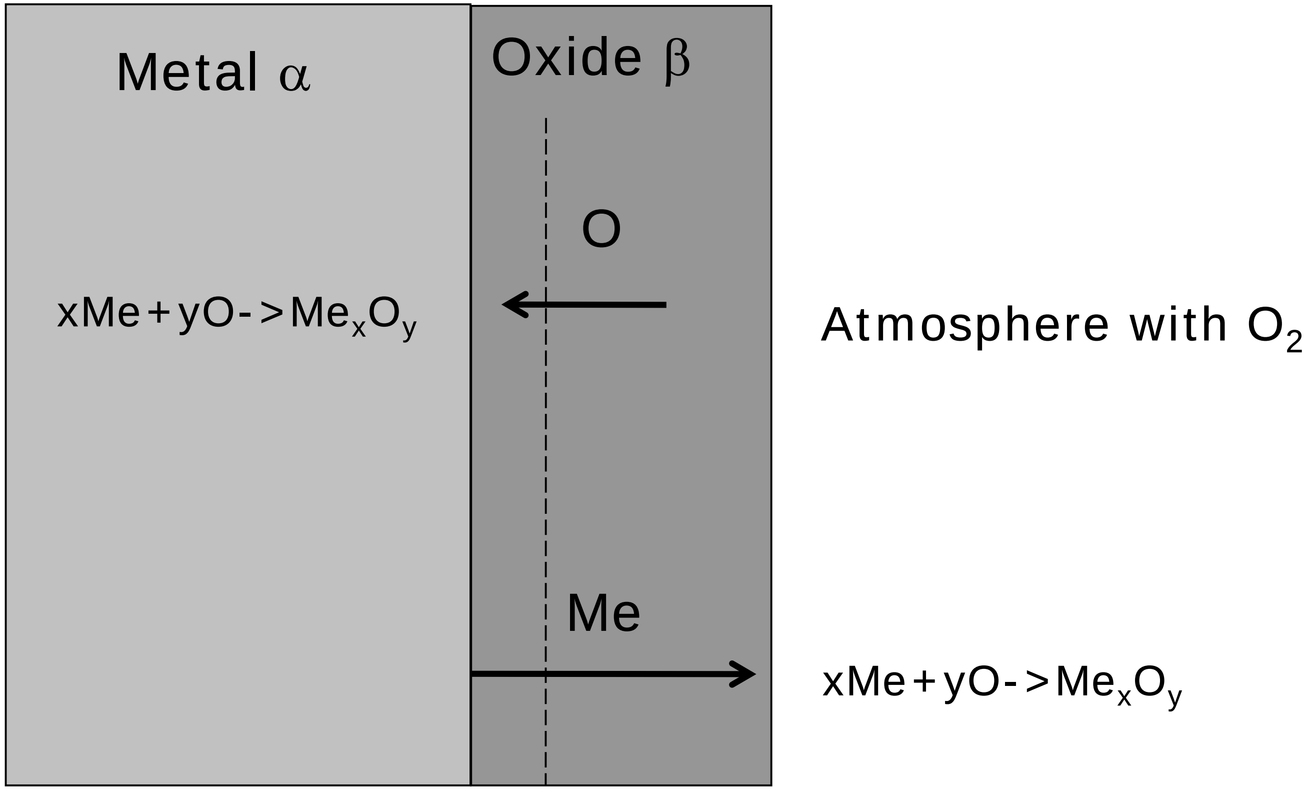
Assessed mobility parameters in the fcc phase [Eq. (4)]

DICTRA notation	Mobility parameter	Parameter (J/mole)	Reference
Mobility of Al			
MQ(FCC,Al:VA;0)	Q_{Al}^{Al}	−142,000–72.1*T	[39]
MQ(FCC,Cr:VA;0)	Q_{Al}^{Cr}	−235,000–82*T	[39]
MQ(FCC,Ni:VA;0)	Q_{Al}^{Ni}	−284,000–59.8*T	[39]
MQ(FCC,Ti:VA;0)	Q_{Al}^{Ti}	−284,000+–59.8*T	[14]
MQ(FCC,Al,Cr:VA;0)	$^{0}A_{Al}^{Al,Cr}$	335,000	[39]
MQ(FCC,Al,Ni:VA;0)	$^{0}A_{Al}^{Al,Ni}$	−41,300–91.2*T	[39]
MQ(FCC,Cr,Ni:VA;0)	$^{0}A_{Al}^{Cr,Ni}$	−53,200	[39]
MQ(FCC,Al,Ti:VA;0)	$^{0}A_{Al}^{Al,Ti}$	335,000	[14]
MQ(FCC,Ni:Ti:VA;0)	$^{0}A_{Al}^{Ni,Ti}$	−53,200	[14]
Mobility of Co			
MQ(FCC,Co:VA;0)	Q_{Co}^{Co}	−286,175–76.0*T	This work
MQ(FCC,Ni:VA;0)	Q_{Co}^{Ni}	−284,169–67.6*T	This work
MQ(FCC,Co,Ni:VA;0)	$^{0}A_{Co}^{Co,Ni}$	+10,787–11.5*T	This work
Mobility of Cr			
MQ(FCC,Al:VA;0)	Q_{Cr}^{Al}	−261,700–3.71*T	[39]
MQ(FCC,Co:VA;0)	Q_{Cr}^{Co}	−246,904–110*T	This work
MQ(FCC,Cr:VA;0)	Q_{Cr}^{Cr}	−235,000–82*T	[39]
MQ(FCC,Ni:VA;0)	Q_{Cr}^{Ni}	−287,000–64.4*T	[39]
MQ(FCC,Al,Cr:VA;0)	$^{0}A_{Cr}^{Al,Cr}$	487,000	[39]
MQ(FCC,Al,Ni:VA;0)	$^{0}A_{Cr}^{Al,Ni}$	−118,000	[39]
MQ(FCC,Cr,Ni:VA;0)	$^{0}A_{Cr}^{Cr,Ni}$	−68,000	[39]
Mobility of Hf			
MQ(FCC,Hf:VA;0)	Q_{Hf}^{Hf}	−235,350–123*T	This work
MQ(FCC,Ni:VA;0)	Q_{Hf}^{Ni}	−251,956–71.2*T	This work
Mobility of Mo			
MQ(FCC,Co:VA;0)	Q_{Mo}^{Co}	−256,943–94.2*T	This work
MQ(FCC,Mo:VA;0)	Q_{Mo}^{Mo}	−254,975–81.5*T	This work
MQ(FCC,Ni:VA;0)	Q_{Mo}^{Ni}	−267,585–79.5*T	This work
Mobility Ni			
MQ(FCC,Al:VA;0)	Q_{Ni}^{Al}	−145,900–64.3*T	[39]
MQ(FCC,Co:VA;0)	Q_{Ni}^{Co}	−270,348–87.3*T	This work
MQ(FCC,Cr:VA;0)	Q_{Ni}^{Cr}	−235,000–82*T	[38]
MQ(FCC,Hf:VA;0)	Q_{Ni}^{Hf}	−286,182–84.5*T	This work
MQ(FCC,Mo:VA;0)	Q_{Ni}^{Mo}	−286,000–82*T	This work
MQ(FCC,Ni:VA;0)	Q_{Ni}^{Mo}	−287,000–69.8*T	[38]
MQ(FCC,Re:VA;0)	Q_{Ni}^{Re}	−294,401–105*T	This work
MQ(FCC,Ta:VA;0)	Q_{Ni}^{Ta}	−443,736–96*T	This work
MQ(FCC,Ti:VA;0)	Q_{Ni}^{Ti}	−287,000–69.8*T	This work
MQ(FCC,W:VA;0)	Q_{Ni}^{W}	−628,250–63.5*T	This work
MQ(FCC,Al,Cr:VA;0)	$^{0}A_{Ni}^{Al,Cr}$	−211,000	[39]
MQ(FCC,Al,Ni:VA;0)	$^{0}A_{Ni}^{Al,Ni}$	−11,300+65.5*T	[39]
MQ(FCC,Al,Ti:VA;0)	$^{0}A_{Ni}^{Al,Ti}$	−211,000	[14]
MQ(FCC,Co,Ni:VA;0)	$^{0}A_{Ni}^{Co,Ni}$	7866+7.65*T	This work
MQ(FCC,Cr,Ni:VA;0)	$^{0}A_{Ni}^{Cr,Ni}$	−81,000	[38]
MQ(FCC,Ni,Re:VA;0)	$^{0}A_{Ni}^{Ni,Re}$	−157,409	This work
MQ(FCC,Ni,Ta:VA;0)	$^{0}A_{Ni}^{Ni,Ta}$	−668,454	This work
MQ(FCC,Ni,Ti:VA;0)	$^{0}A_{Ni}^{Ni,Ti}$	−81,000	[14]
MQ(FCC,Ni:W:VA;0)	$^{0}A_{Ni}^{Ni,W}$	175,736	This work

(continued on next page)

Simple substitutional model

Growth of oxides controlled by diffusion



- Oxygen diffusion in the oxide layer gives inward growth
- Metal diffusion in the oxide layer gives outward growth
- Internal oxidation needs oxygen diffusion into the metal, i.e. Oxygen diffusion through the oxide scale and the metal

Defect based models of diffusion in oxides

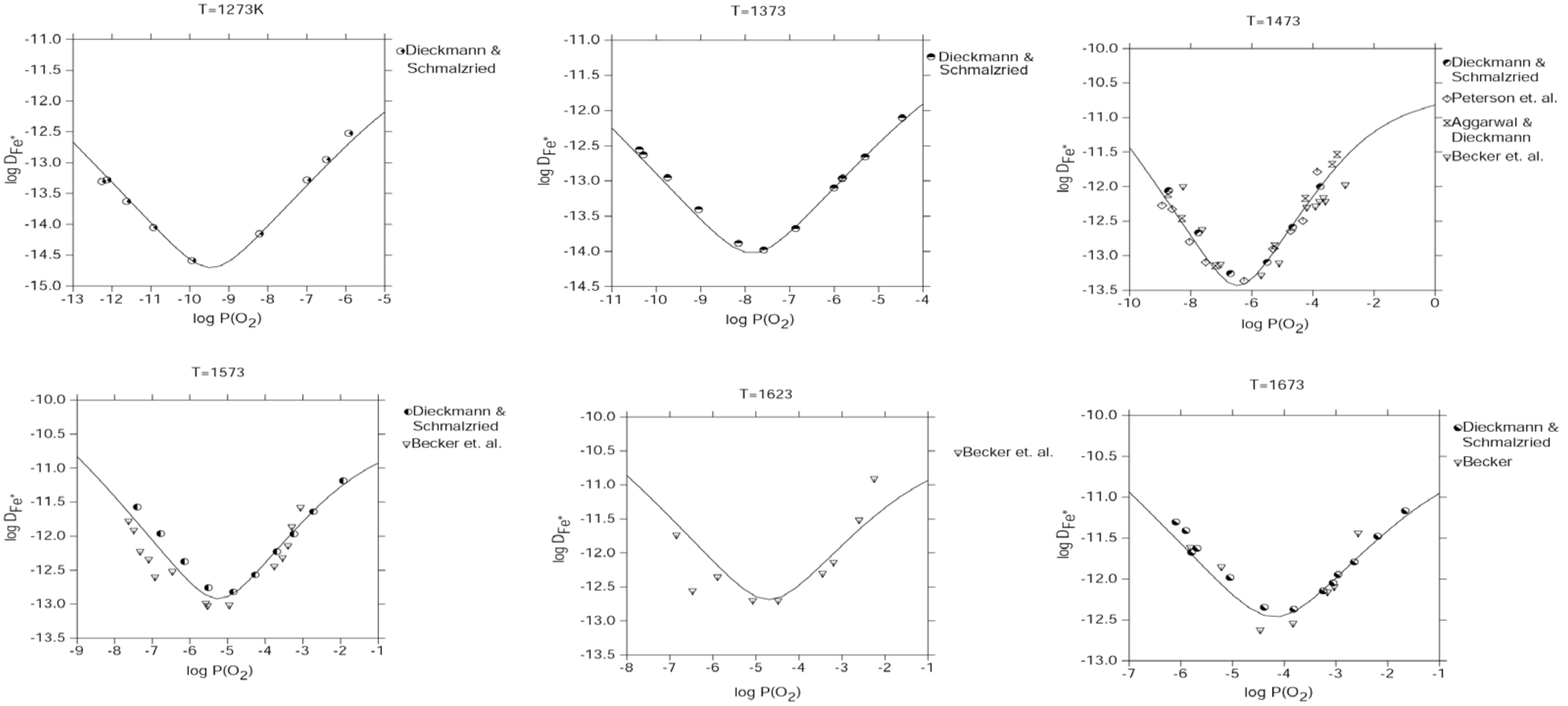
Vacancy mechanism operative on different sublattices. The defect structure, the vcancy content, calculated from CALPHAD databases, and the mobility parameters are stored in mobility databases.

Generalization the Wagner model!

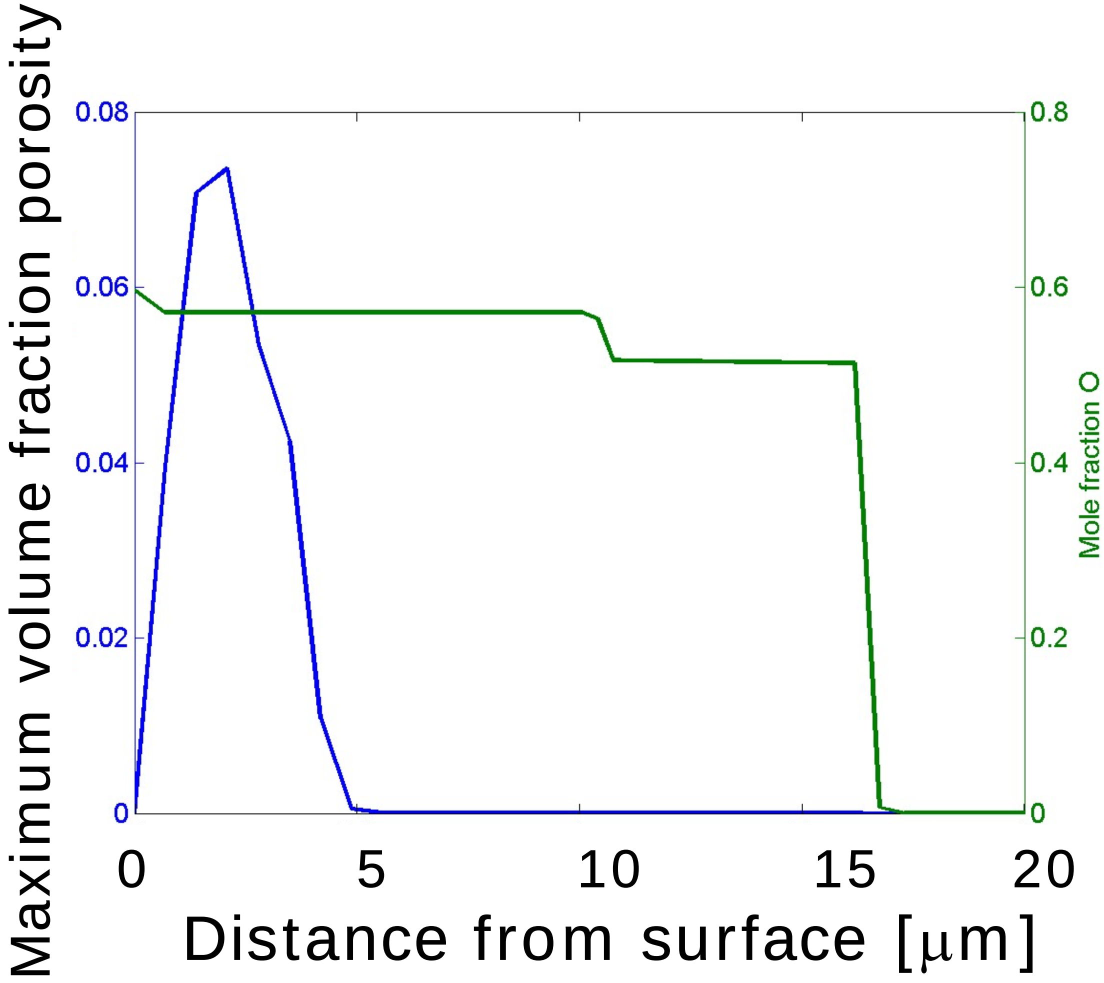
Account for type A grain-boundary diffusion.

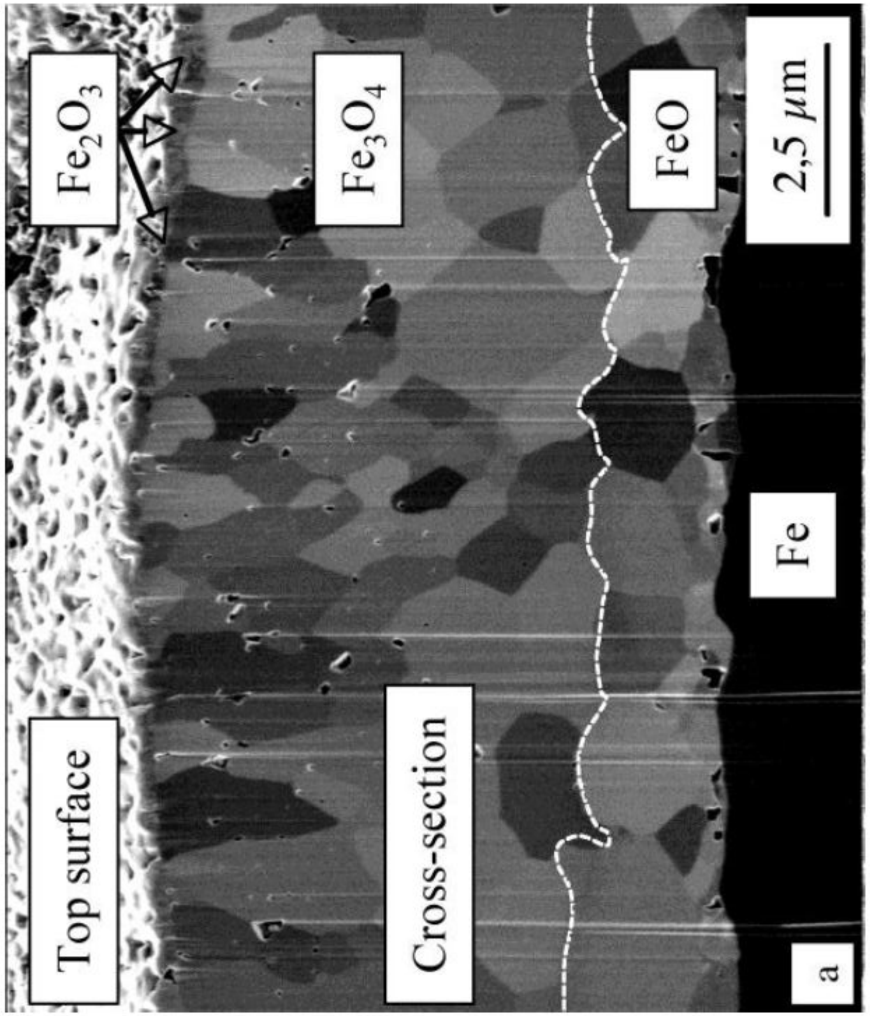
Experimental data on Fe tracer diffusion in spinel - Optimization of Fe mobilities

(Hallström et al. 2011)



Simulation of oxidation of iron using the homogenization model in DICTRA





Jonsson et al Mat Sci Forum 595-598(2008)1005

Mechanical properties

- Solution hardening (use the ”compound energy formalism”):

Formula unit: $(M_1M_2...)(C,N,Va)_b$

Yield stress

$$\sigma_y = \sum_{ij} y_i^{'} y_j^{''} \sigma_{yij}^{\circ} + \Delta\sigma_y^{SSH}$$

$$\Delta\sigma_y^{SSH} = \sum_{ij}\sum_{k} \left(y_i^{'} y_j^{'}\right)^n y_k^{''} A_{ijk} + \sum_{i}\sum_{k\ell} y_i^{'}\left(y_k^{''} y_\ell^{''}\right)^m A_{ik\ell}$$

In classical models

$$n = m = 2/3$$

and the A parameters represent a combination of mismatch in lattice parameter and elastic constants.

Here they are taken as adjustable parameters!

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7. Conclusive remarks

- Models in CALPHAD can have <u>any level</u> of sophistication and account for:
  - Crystallographic structure
  - Lattice vibrations
  - Chemical order and disorder
  - Other phenomena such as magnetic order disorder...
- Different phases in the same material can be represented by different models and require different type of parameters.
- Quantities which are experimentally unknown, uncertain or show a large scatter may be calcaluated by ab-initio methods.

CALPHAD is the most efficient method to organise our experimental and theoretical knowledge on thermodynamics and phase equilibria.