The theoretical background of

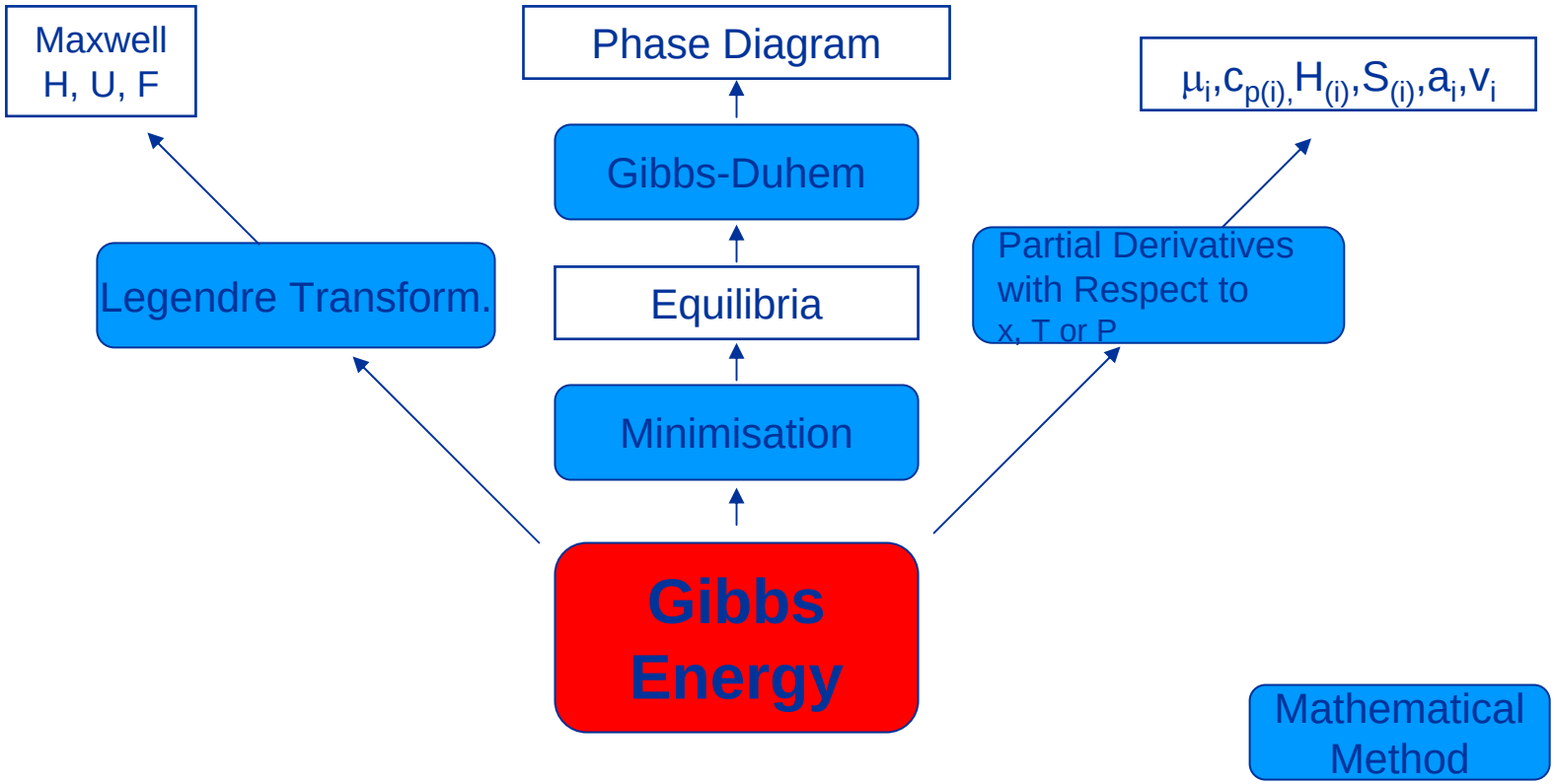
FactSage™

CRCT

The theoretical background of FactSage

The following slides give an
abridged overview
of the major
underlying principles
of the
calculational modules
of
FactSage.

The Gibbs Energy Tree



Mathematical methods are used to derive more information from the Gibbs energy (of phase(s) or whole systems)

Thermodynamic potentials and their natural variables

Variables

Gibbs energy: $G = G(T, p, n_i, \ldots)$

Enthalpy: $H = H(S, P, n_i, \ldots)$

Free energy: $A = A(T, V, n_i, \ldots)$

Internal energy: $U = U(S, V, n_i, \ldots)$

Interrelationships:

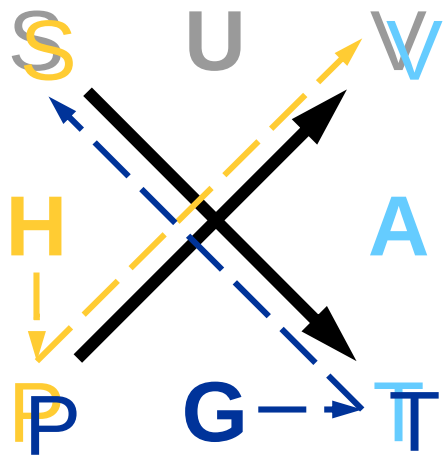
$$A = U - T \cdot S$$

$$H = U + P \cdot V$$

$$G = H - T \cdot S = U + P \cdot V - T \cdot S$$

Thermodynamic potentials and their natural variables

Maxwell-relations:



$$\frac{\partial H}{\partial P} = V$$

$$\frac{\partial G}{\partial T} = -S$$

and

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V}$$

Thermodynamic potentials and their natural

Equilibrium condition:

$$\left.\begin{aligned} G &= \min \\ dG &= 0 \end{aligned}\right\} \text{ for const. } T, p, n_i, \ldots$$

$$\left.\begin{aligned} H &= \min \\ dH &= 0 \end{aligned}\right\} \text{ for const. } S, p, n_i, \ldots$$

$$\left.\begin{aligned} A &= \min \\ dT &= 0 \end{aligned}\right\} \text{ for const. } T, U, n_i, \ldots$$

$$\left.\begin{aligned} U &= \min \\ dU &= 0 \end{aligned}\right\} \text{ for const. } S, V, n_i, \ldots$$

$$\left.\begin{aligned} S &= \max \\ dS &= 0 \end{aligned}\right\} \text{ for const. } U, V, n_i, \ldots$$

Thermodynamic properties
from the Gibbs-energy

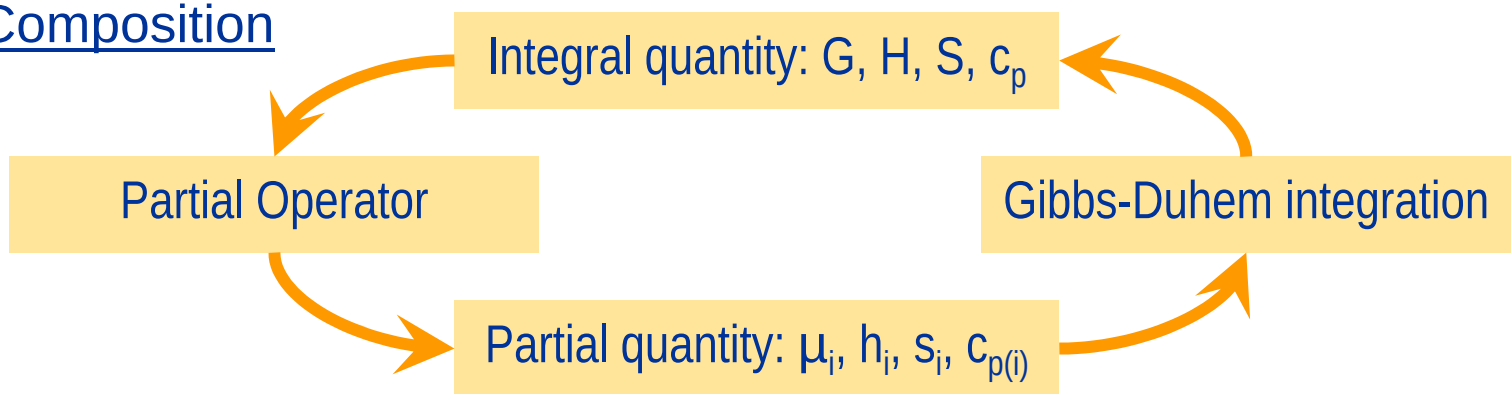
Temperature

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,n_i}$$

$$H = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_{p,n_i}$$

$$c_p = \left(\frac{\partial H}{\partial T}\right)_{p,n_i} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,n_i}$$

Composition



Use of model equations permits to start at either end!

Thermodynamic properties
from the Gibbs-energy

J.W. Gibbs defined the chemical potential of a component as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p}$$

With $$G = \left(\sum n_i\right) G_m$$ (G is an extensive property!)

one obtains

$$\mu_i = \frac{\partial}{\partial n_i}\left(\sum n_i\right) G_m$$

$$= G_m + \left(\sum n_i\right)\frac{\partial}{\partial n_i} G_m$$

Thermodynamic properties
from the Gibbs-energy

Transformation to mole fractions : $n_i \rightarrow x_i$

$$\mu_i = G_m + \frac{\partial}{\partial x_i} G_m - \sum x_i \frac{\partial}{\partial x_i} G_m$$

$$1 + \frac{\partial}{\partial x_i} - \sum x_i \frac{\partial}{\partial x_i}$$ = partial operator

$$h_i = H_m + \frac{\partial}{\partial x_i} H_m - \sum x_i \frac{\partial}{\partial x_i} H_m$$

s_i S_m S_m S_m

c_{p_i} C_{p_m} C_{p_m} C_{p_m}

Gibbs energy function
for a pure substance

- *G(T)* (i.e. neglecting pressure terms) is calculated from the enthalpy *H(T)* and the entropy *S(T)* using the well-known Gibbs-Helmholtz relation: $G = H - TS$

- In this *H(T)* is $$H = H_{298} + \int_{298}^{T} c_p \cdot dT$$

- and S(T) is $$S = S_{298} + \int_{298}^{T} c_p / T \cdot dT$$

- Thus for a given T-dependence of the c_p-polynomial (for example after Meyer and Kelley) one obtains for *G(T)*:

$$G(T) = A + B \cdot T + C \cdot T \cdot \ln T + D \cdot T^2 + E \cdot T^3 + F / T^2$$

Gibbs energy function
for a solution

- As shown above $G_m(T,x)$ for a solution φ consists of three contributions: the **reference term**, the **ideal term** and the **excess term**.
- For a simple substitutional solution (only one lattice site with random occupation) one obtains using the well-known ***Redlich-Kister-Muggianu*** polynomial for the excess terms:

$$G_m^{\varphi}(T,x_i) = \sum_i x_i G_i^{o,\varphi} + RT\sum_i x_i \ln x_i + \sum_i \sum_{\prec j} x_i x_j \sum_{\nu=0}^{n_{ij}} L_{ij}^{(\nu)}(T)(x_i - x_j)^{\nu}$$
$$+ \sum_i \sum_{\prec j} \sum_{\prec k} x_i x_j x_k (x_i L_i^{ijk}(T) + x_j L_j^{ijk}(T) + x_k L_k^{ijk}(T))/(x_i + x_j + x_k)$$

Equilibrium considerations

a) Stoichiometric reactions

Equilibrium condition:

$$G = \min \quad \text{or} \quad dG = 0$$

Reaction : $n_A A + n_B B + ... = n_S S + n_T T + ...$

Generally :

$$\sum_i \nu_i B_i = 0$$

For constant T and p, i.e. **dT = 0** and **dp = 0**,

and no other work terms:

$$dG = \sum_i \mu_i dn_i$$

Equilibrium considerations

a) Stoichiometric reactions

For a stoichiometric reaction the **changes dn_i** are given by the stoichiometric coefficients n_i and the **change in extend of reaction $d\xi$**.

$$dn_i = \nu_i d\xi$$

Thus the problem becomes ***one-dimensional***.

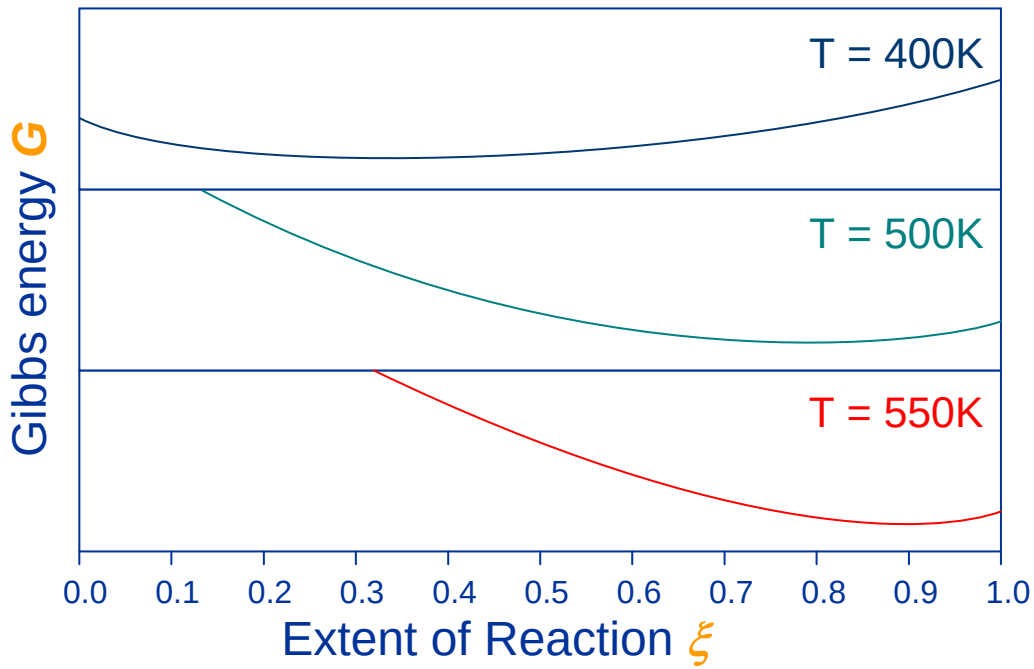
One obtains:

$$dG = \sum_i \mu_i \nu_i d\xi = 0$$

[see the following graph for an example of G = G(x)]

Equilibrium considerations

a) Stoichiometric reactions



Gibbs Energy as a function of extent of the reaction $2NH_3 <=> N_2 + 3H_2$ for various temperatures. It is assumed, that the changes of enthalpy and entropy are constant.

Equilibrium considerations

a) Stoichiometric reactions

Separation of variables results in : $$\frac{dG}{d\xi} = \sum_i \nu_i \mu_i = 0$$

Thus the equilibrium condition for a stoichiometric reaction is: $$\Delta G = \sum_i \nu_i \mu_i = 0$$

Introduction of standard potentials μ_i° and activities a_i yields: $$\mu_i = \mu_i^\circ + RT \ln a_i$$

One obtains: $$\sum_i \nu_i \mu_i^\circ + RT \sum_i \left(\nu_i \ln a_i\right) = 0$$

Equilibrium considerations

a) Stoichiometric reactions

It follows the **Law of Mass Action**:

$$\Delta G^{\circ} = \sum_i \nu_i \mu_i^{\circ} = -RT \ln \prod_i a_i^{\nu_i}$$

where the product

$$K = \prod_i a_i^{\nu_i} \quad \text{or} \quad K = \exp\left(-\frac{\Delta G^{\circ}}{RT}\right)$$

is the well-known Equilibrium Constant.

The **REACTION** module permits a multitude of calculations which are based on the Law of Mass Action.

Equilibrium considerations

b) Multi-component multi-phase approach

Complex Equilibria

Many components, many phases (solution phases), constant T and p :

$$G = \min$$

with

$$G = \sum_i n_i \mu_i = \sum_i n_i \left(\mu_i^o + RT \ln a_i \right)$$

or

$$G = \sum_\varphi \left(\sum_i^{m_p} n_m^\varphi \right) G_m^\varphi$$

Equilibrium considerations

b) Multi-component multi-phase approach

Massbalance constraint

$$\sum_i a_{ij} n_i = b_j$$

j = 1, ... , n of components b

Lagrangeian Multipliers M_j turn out to be the chemical potentials of the system components at equilibrium:

$$G = \sum_j b_j M_j$$

Equilibrium considerations

b) Multi-component multi-phase approach

$a_{ij} \rightarrow j$

$\downarrow$

i

Phase	Components	System Components						
		Fe	N	O	C	Ca	Si	Mg
Gas	Fe	1	0	0	0	0	0	0
	N_2	0	2	0	0	0	0	0
	O_2	0	0	2	0	0	0	0
	C	0	0	0	1	0	0	0
	CO	0	0	1	1	0	0	0
	CO_2	0	0	2	1	0	0	0
	Ca	0	0	0	1	0	0	0
	CaO	0	0	1	0	1	0	0
	Si	0	0	0	0	0	1	0
	SiO	0	0	1	0	0	1	0
	Mg	0	0	0	0	0	0	1
Slag	SiO_2	0	0	2	0	0	1	0
	Fe_2O_3	2	0	3	0	0	0	0
	CaO	0	0	1	0	1	0	0
	FeO	1	0	1	0	0	0	0
	MgO	0	0	1	0	0	0	1
Liq. Fe	Fe	1	0	0	0	0	0	0
	N	0	1	0	0	0	0	0
	O	0	0	1	0	0	0	0
	C	0	0	0	1	0	0	0
	Ca	0	0	0	0	1	0	0
	Si	0	0	0	0	0	1	0
	Mg	0	0	0	0	0	0	1

Example of a stoichiometric matrix for the gas-metal-slag system Fe-N-O-C-Ca-Si-Mg

Equilibrium considerations

b) Multi-component multi-phase approach

Modelling of Gibbs energy of (solution) phases

$$G_m^{\varphi} = G_m^{\varphi}\left(T, n_i^{\varphi}, p\right)$$

Pure Substance $G_m^{\varphi} = \mu^{o,\varphi} = G^{o,\varphi}(T,p)$ (stoichiometric)

Solution phase

$$\begin{aligned} G_m^{\varphi} &= G_m^{\varphi,ref} \\ &\quad + G_m^{\varphi,id} \quad \left(= -T\Delta S_m^{id}\right) \\ &\quad + G_m^{\varphi,ex} \end{aligned}$$

Choose appropriate reference state and ideal term, then check for deviations from ideality.
See Page 11 for the simple substitutional case.

Equilibrium considerations

Multi-component multi-phase approach

Use the EQUILIB module to execute a multitude of calculations based on the complex equilibrium approach outlined above, e.g. for combustion of carbon or gases, aqueous solutions, metal inclusions, gas-metal-slag cases, and many others .

NOTE: The use of constraints in such calculations (such as fixed heat balances, or the occurrence of a predefined phase) makes this module even more versatile.

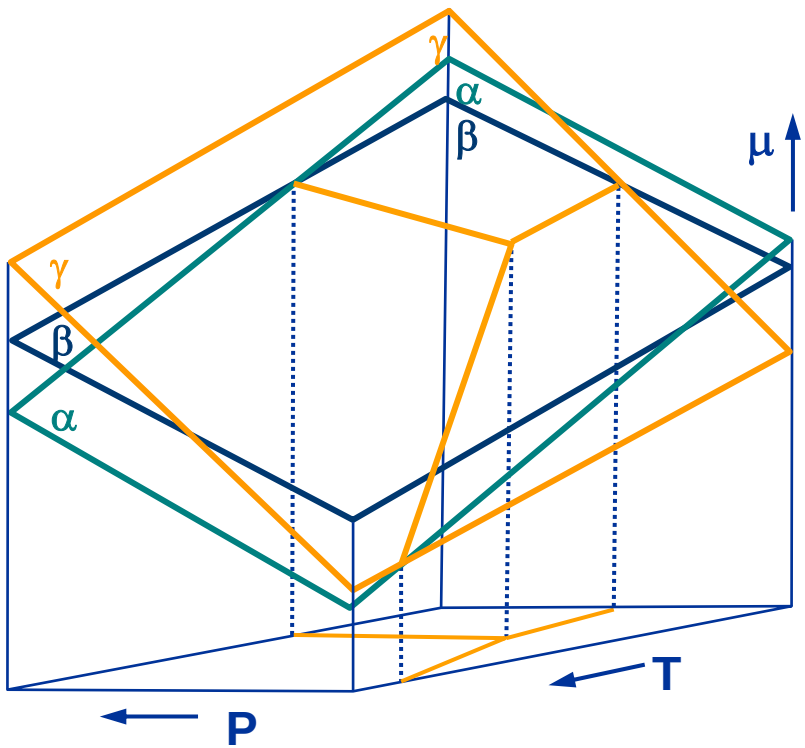
Phase diagrams as projections of Gibbs energy plots

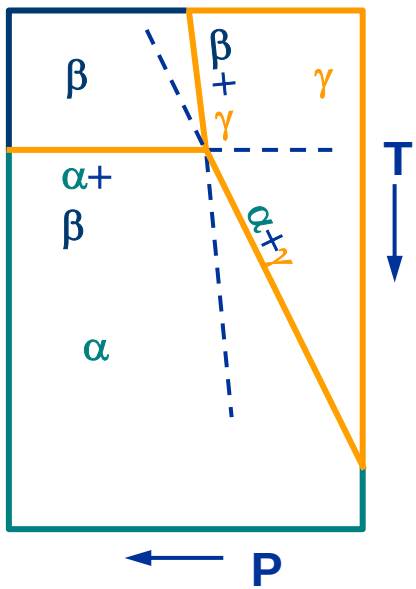
Hillert has pointed out, that what is called a phase diagram is derivable from a projection of a so-called property diagram. The Gibbs energy as the property is plotted along the z-axis as a function of two other variables x and y.

From the *minimum condition* for the *equilibrium* the phase diagram can be derived as a projection onto the x-y-plane.

(See the following graphs for illustrations of this principle.)

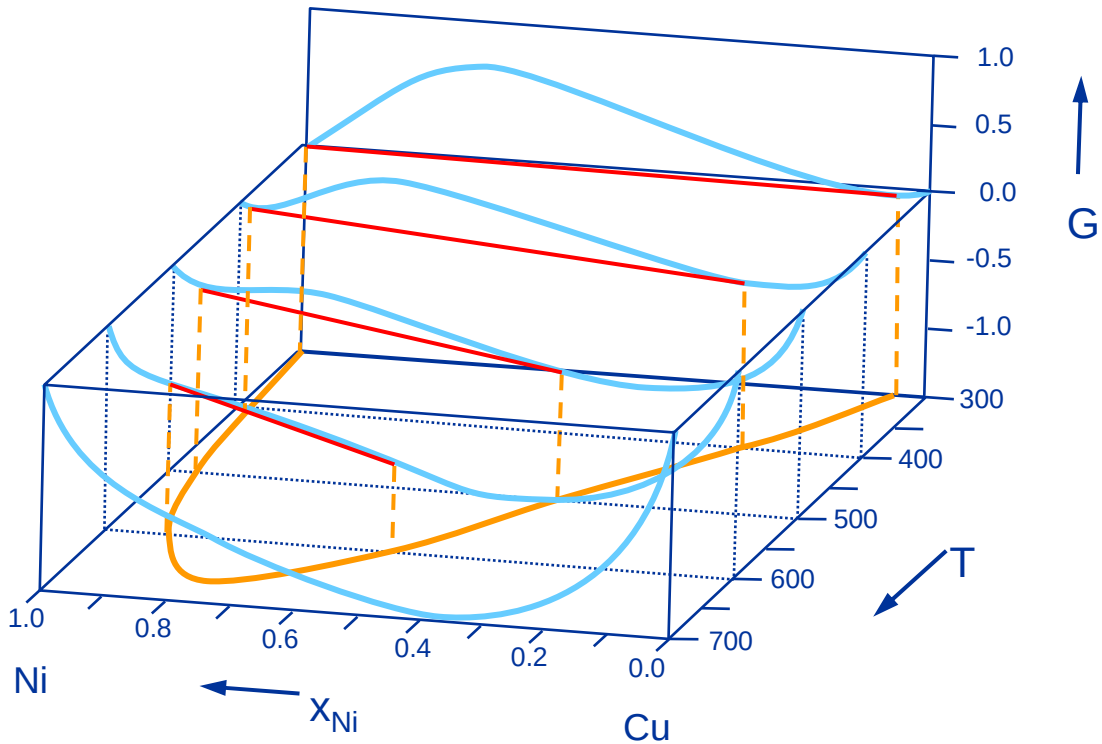
Phase diagrams
as projections of Gibbs energy plots





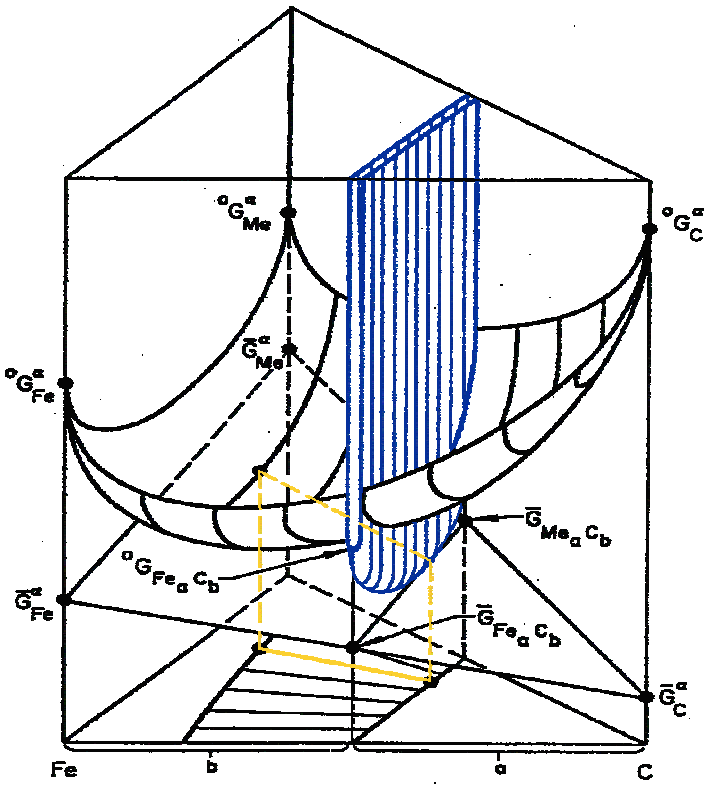
Unary system: projection from μ-T-p diagram

Phase diagrams
as projections of Gibbs energy plots



Binary system: projection from G-T-x diagram, p = const.

Phase diagrams
as projections of Gibbs energy plots



Ternary system: projection from G-x_1-x_2 diagram,
T = const and p = const

Phase diagrams generated with FactSage

Use the **PHASE DIAGRAM** module to generate a multitude of phase diagrams for unary, binary, ternary or even higher order systems.

NOTE: The **PHASE DIAGRAM** module permits the choice of T, P, m (as RT *ln* a), a (as *ln* a), mol (x) or weight (w) fraction as axis variables. Multi-component phase diagrams require the use of an appropriate number of constants, e.g. in a ternary isopleth diagram T vs x one molar ratio has to be kept constant.

N-Component **System** (A-B-C-…-N)

Extensive variables q_i	Corresponding potentials $\phi_i = \left(\frac{\partial U}{\partial q_i}\right)_{q_j}$
S	T
V	-P
n_A	μ_A
n_B	μ_B
.	.
.	.
.	.
n_N	μ_N

$$dU = TdS - PdV + \sum \mu_i dn_i = \sum \phi_i dq_i$$

Gibbs-Duhem: $SdT + VdP + \sum n_i d\mu_i = \sum q_i d\phi_i = 0$

Choice of Variables which always give a True Phase Diagram

N-component system

(1) Choose n potentials: $\phi_1, \phi_2, \ldots, \phi_n$ $\quad (n \leq N+1)$

(2) From the non-corresponding extensive variables ($q_{n+1}, q_{n+2}, \ldots$), form (N+1-n) independent ratios ($Q_{n+1}, Q_{n+2}, \ldots, Q_{N+1}$).

Example:

$$Q_j = \frac{q_i}{\sum_{J=n+1}^{N+2} q_j} \qquad (n+1 \leq i \leq N+1)$$

[$\phi_1, \phi_2, \ldots, \phi_n$; $Q_{n+1}, Q_{n+2}, \ldots, Q_{N+1}$] are then the ($N$+1) variables of which 2 are chosen as axes and the remainder are held constant.

MgO-CaO Binary System

Extensive variables and corresponding potentials → Chosen axes variables and constants

S	T
V	-P
n_{MgO}	μ_{MgO}
n_{CaO}	μ_{CaO}

→

$\phi_1 = T$ for y-axis

$\phi_2 = -P$ constant

$$\left.\begin{aligned} q_3 &= n_{MgO} \\ q_4 &= n_{CaO} \end{aligned}\right\} Q_3 = \frac{n_{CaO}}{\left(n_{MgO} + n_{CaO}\right)}$$

for x-axis

Fe - Cr - S - O System

S	T	
V		$-P$
n_{O_2}		μ_{O_2}
n_{S_2}		μ_{S_2}
n_{Fe}		m_{Fe}
n_{Cr}		m_{Cr}

$\longrightarrow$

$f_1 = T$	(constant)
$f_2 = -P$	(constant)
$\phi_3 = \mu_{O_2}$	x-axis
$\phi_4 = \mu_{S_2}$	x-axis
$\left.\begin{array}{l} q_5 = n_{Cr} \\ q_6 = n_{Fe} \end{array}\right\} Q_5 = \dfrac{n_{Cr}}{n_{Fe}}$	(constant)

Fe - Cr - C System - improper choice of axes variables

S	T
V	$-P$
n_C	m_C
n_{Fe}	m_{Fe}
n_{Cr}	m_{Cr}

$f_1 = T$ (constant)

$f_2 = -P$ (constant)

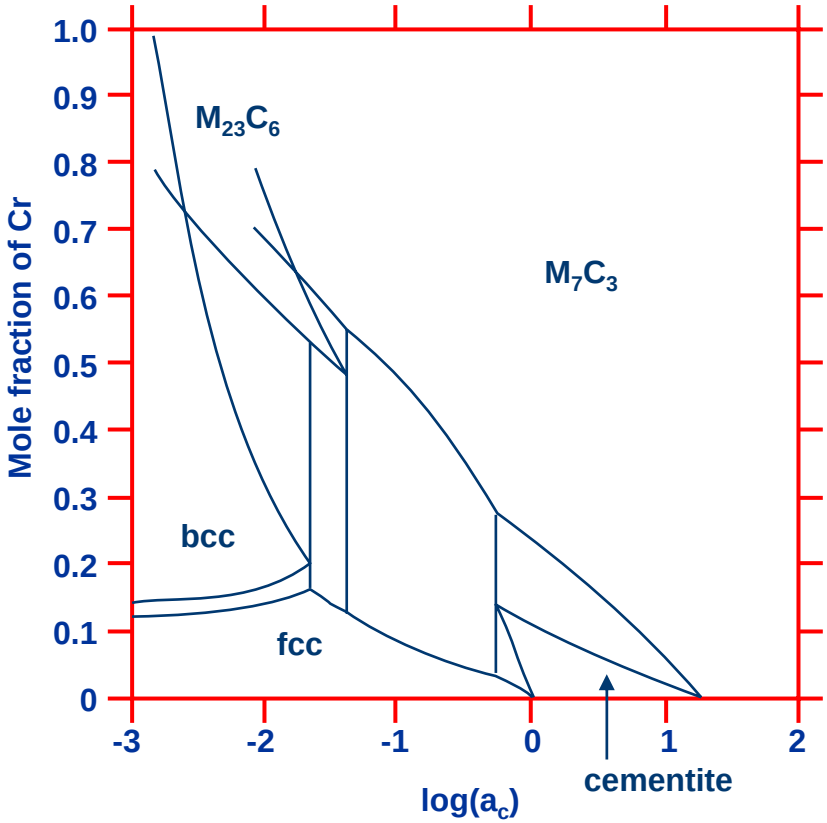
$f_3 = m_C$ $\rightarrow$ a_C for x-axis and Q_4 for y-axis

$$Q_4 = \frac{n_{Cr}}{(n_{Fe} + n_{Cr} + n_C)}$$ **(NOT OK)**

$$Q_4 = \frac{n_{Cr}}{(n_{Fe} + n_{Cr})}$$ **(OK)**

Requirement: $\frac{dQ_j}{dq_i} = 0 \quad for \quad i \leq 3$

Fe - Cr - C System - improper choice of axes variables



This is NOT a true phase diagram.

Reason: n_C must NOT be used in formula for mole fraction when a_C is an axis variable.

NOTE: FactSage users are safe since they are not given this particular choice of axes variables.