

# Thermodynamics

*Review of Engineering Thermodynamics  
and  
FactSage software*

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# Contents

- Review of Engineering Thermodynamics
- FactSage thermodynamic database

# **REVIEW OF ENGINEERING THERMODYNAMICS**

# Gibbs energy

$G = H - TS$ ; G: Gibbs Energy, H: Enthalpy, S: Entropy

## 1. For pure element or pure compound (Al, O<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.)

$$G_T^o = H_T^o - TS_T^o$$

$$H_T^o = \Delta H_{298K}^o + \int_{298K}^T C_p dT \quad S_T^o = S_{298K}^o + \int_{298K}^T \frac{C_p}{T} dT \quad : C_p = a + bT + cT^2 + dT \ln T + \dots$$

*is known (measurable)*

is enthalpy for compound at 298 K with reference of pure stable elemental species  
At 298 K 1 atm (  $H_{0K}^o \neq 0$  , unknown)

is standard entropy at 298 K  
(  $S_{0K}^o = 0$  )

Standard state for H :  $\Delta H_{298K}^o = 0$

for all stable elements at 1atm and 298K.

~~Fe(bcc), Fe(fcc), Fe(l), H<sub>2</sub>O(l), H<sub>2</sub>O(g), H<sub>2</sub>(g), O<sub>2</sub>(g), O(g), CaO, FeO, C(s), CO<sub>2</sub>, CO, ..~~

\* In FactSage compound database,  $\Delta H_{298K}^o$ ,  $S_{298K}^o$ ,  $C_p$  are stored  
→ Absolute Gibbs Energy of compound relative to elemental species.

# Gibbs energy

## 2. Chemical reaction between pure compounds (No solution)



$$\begin{aligned}\Delta G_{rxn} &= G_{A_nB_m}^o - (nG_A^o + mG_B^o) \\ &= \Delta H_{rxn}^o - T\Delta S_{rxn}^o\end{aligned}$$

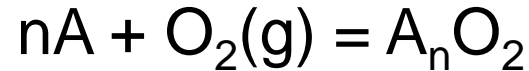
In many thermo books, these  $\Delta H_{rxn}^o$ ,  $S_{rxn}^o$  are given.

These values are not absolute values, but dependent on each chemical reaction.

→ In the FactSage, therefore, absolute Gibbs energy of each species (relative to elemental species) is stored. Then, the reaction Gibbs energy for each reaction can be automatically calculated from the Gibbs energy of each species.

# Gibbs energy

## 3. Chemical reaction involving gas



$$\Delta G_{rxn} = G_{A_nO_2}^o - (nG_A^o + mG_{O_2}^o)$$



$$G_i = G_i^o + RT \ln P_i$$

for gas species i

$$= \Delta G^o - mRT \ln P_{O_2}$$

**At Equilibrium state**  $\Delta G_{rxn} = 0$

$$\therefore \Delta G^o = -RT \ln\left(\frac{1}{P_{O_2}^m}\right)$$

# Gibbs energy

## 3. Chemical reaction involving gas (continue)

In general, for  $aA + bB(g) = cC + dD(g)$

**At Equilibrium**

$$\Delta G^o = -RT \ln\left(\frac{P_D^d}{P_B^b}\right)$$

$$\Delta G^o = -RT \ln K$$

**K: Equilibrium constant**

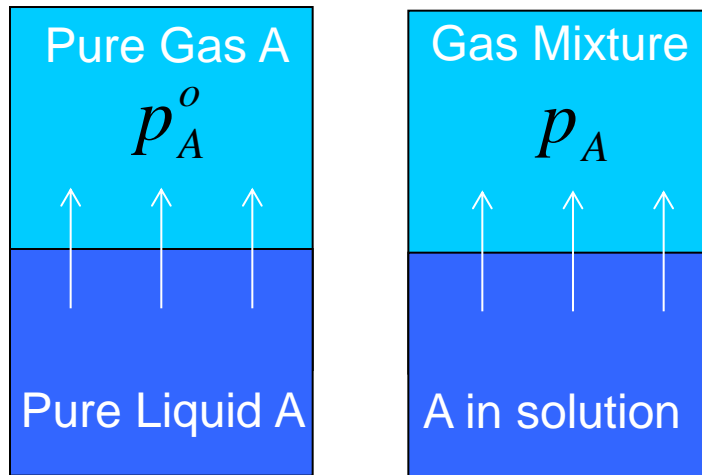
# Gibbs energy

## 4. Chemical reaction involving solid or liquid solution

$$G_{i(\text{in soln})} = G_{i(\text{pure})}^{\circ} + RT \ln(a_i) \quad \mathbf{a: \text{ activity}}$$

change of Gibbs energy of  $i$  in solution  
by interacting with surrounding species

### Definition of activity



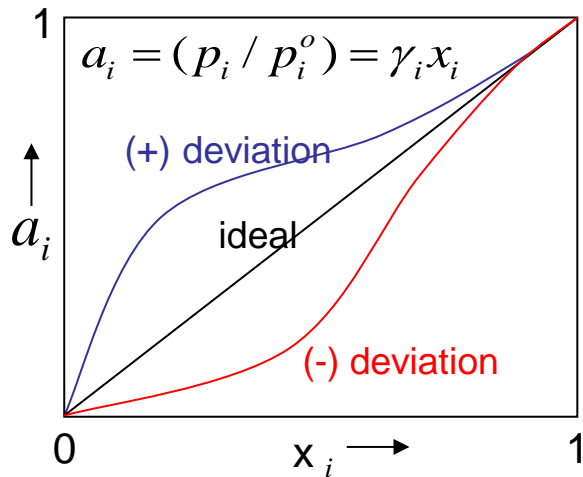
$$a_A = \frac{P_A}{P_A^{\circ}} = \gamma_A x_A$$

$\therefore$  activity is movement of species in solution

# Gibbs energy

## 4. Chemical reaction involving solid or liquid solution

### Definition of activity



(+) deviation: repulsion between  $i$  and other species  
→  $a_i > x_i$  : more active chemical reaction of  $i$

(-) deviation: attraction between  $i$  and other species  
→  $a_i < x_i$  : less active chemical reaction of  $i$

In general, for  $aA + bB(g) = cC + dD(g)$

$$\Delta G_{rxn} = \sum G_{products} - \sum G_{reactants}$$

**At Equilibrium**

$$\Delta G^o = -RT \ln\left(\frac{a_C^c P_D^d}{a_A^a P_B^b}\right)$$

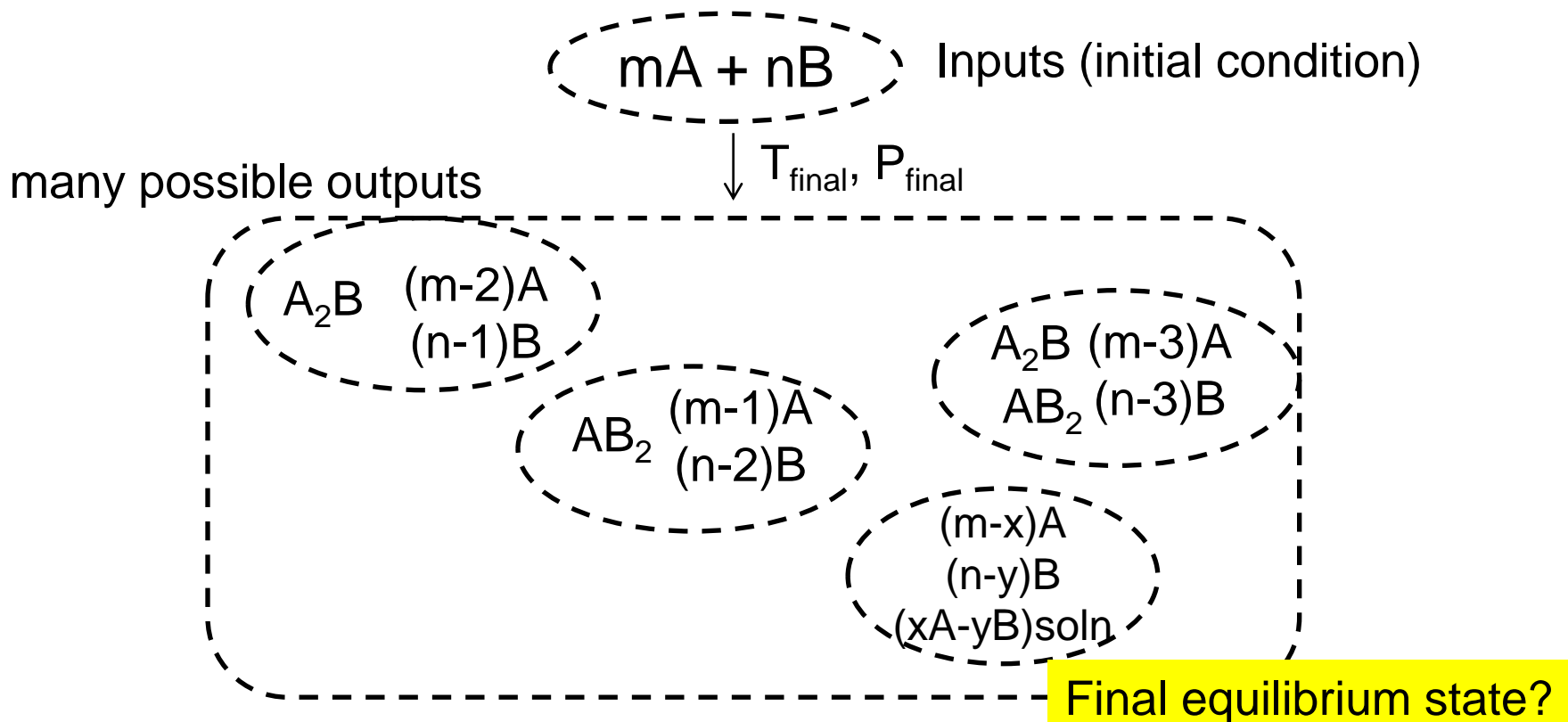
\* FactSage solution database contain the model and model parameters to calculate  $G_i \rightarrow a_i$

# Gibbs energy minimization

In most of thermodynamic book, we always calculate equilibrium condition

$$\Delta G_{rxn} = 0 \longrightarrow \Delta G^o = -RT \ln K_{eq}$$

But in reality, we want to first know the direction of reaction



# Gibbs energy minimization

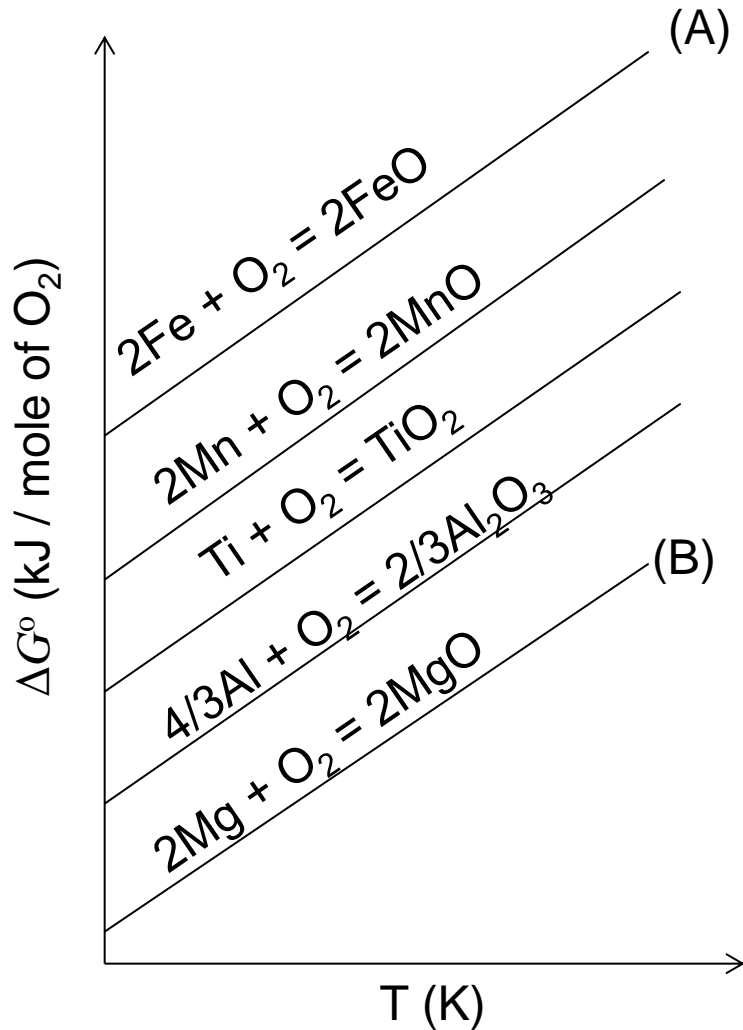
(continue)

- We have to find out which phase assemblage is most stable at given  $T_f$  and  $P_f$  with respect to the mass balance with inputs.
- Gibbs energy minimization routine. (ChemSage, Solgas-mix, etc.)  
The most stable phase assemblage has the lowest Gibbs energy.

## In FactSage

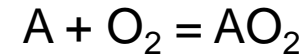
- Put inputs amount
- Select all possible phases (solid compounds, solid solutions, liquid solutions, gases)
- Set  $T_{\text{final}}$  and  $P_{\text{final}}$
- Calculation (Gibbs energy minimization routine)
- Equilibrium phases

# Ellingham diagram



- Collection of  $\Delta G^\circ$  for oxidation reaction  
 $mA + O_2 = A_m O_2$  (reference: 1 mol of  $O_2$ )

- Only consider for pure species.  
 (No solutions are considered.)



$$\Delta G = \Delta G^\circ + RT \ln \frac{(a_{AO_2})}{(a_A) (p_{O_2})}, (\Delta G = 0: \text{Equilibrium})$$

$$\Delta G^\circ = RT \ln p_{O_2}$$

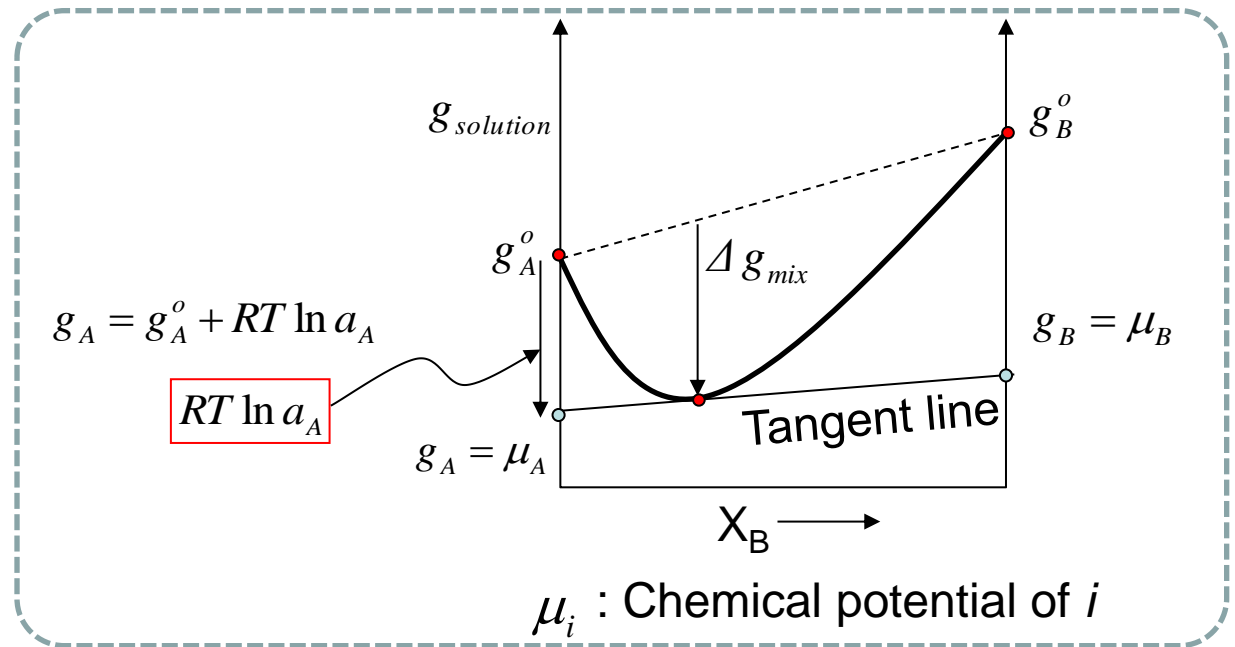
$$\Delta G^\circ = (R \ln p_{O_2}) \times T$$

# Solution thermodynamics

A-B solution, (Solid or Liquid solution)

$$G_{\text{solution}} = \sum x_i G_i$$

$$G_i = G_i^{\circ} + RT \ln a_i \quad \mathbf{G_i: \text{partial Gibbs energy of } i \text{ in solution}}$$



$$= (x_A G_A^{\circ} + x_B G_B^{\circ}) + RT (x_A \ln a_A + x_B \ln a_B)$$

# Solution thermodynamics

A-B solution, (Solid or Liquid solution)

$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln a_A + x_B \ln a_B)$$

**1. Ideal solution:**  $\gamma_A = 1, \gamma_B = 1$

$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln x_A + x_B \ln x_B)$$

**2. Regular solution:**  $RT \ln \gamma_A = \Omega_{AB} x_B^2$   **$\Omega$ : Regular solution parameter**

$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln x_A + x_B \ln x_B) + \Omega_{AB} x_A x_B$$

# Solution thermodynamics

A-B solution, (Solid or Liquid solution)

$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln a_A + x_B \ln a_B)$$

**3. General solution:**  $\gamma_A = f(x, T)$

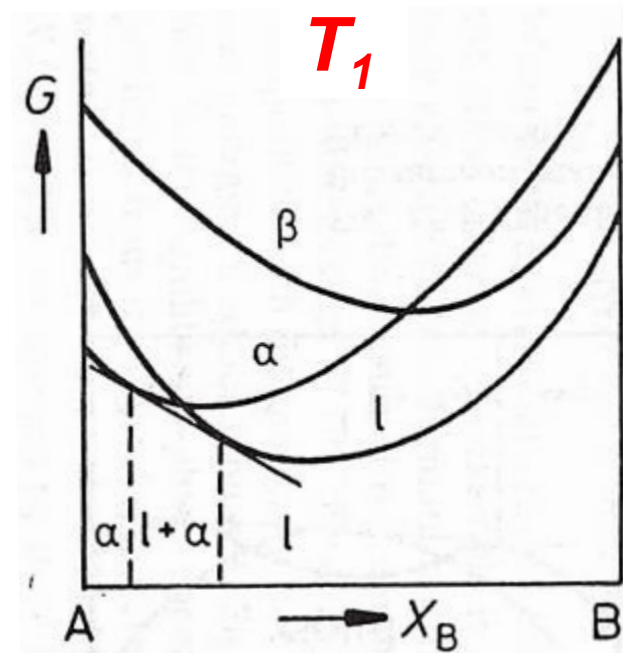
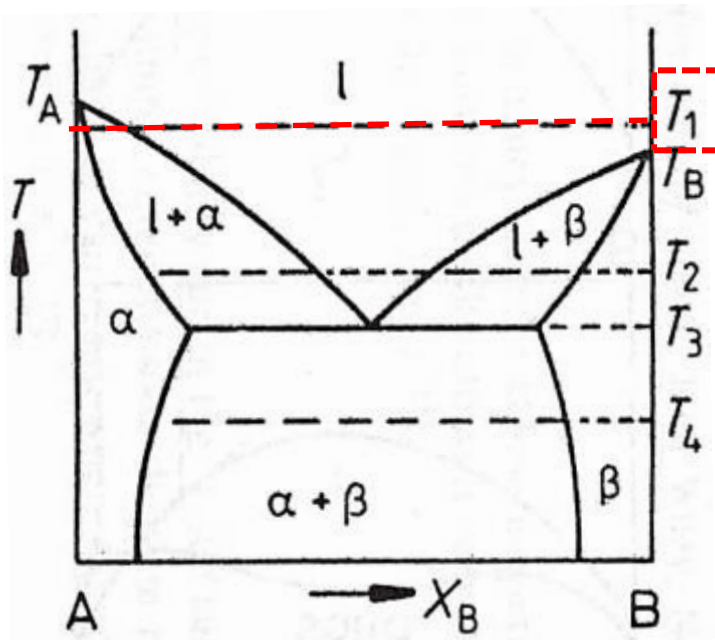
$$G_{soln} = (x_A G_A^o + x_B G_B^o) + RT(x_A \ln x_A + x_B \ln x_B) + G^{ex}$$

$$G^{ex} = \sum_{i,j \geq 1} \omega_{AB}^{ij} x_A^i x_B^j$$

\* FactSage supports many complex solution models. Solution database (FToxid, FTSalt, ....) contains optimized model parameters reproducing Gibbs energy of solution.

# Gibbs Energy vs. Phase Diagram

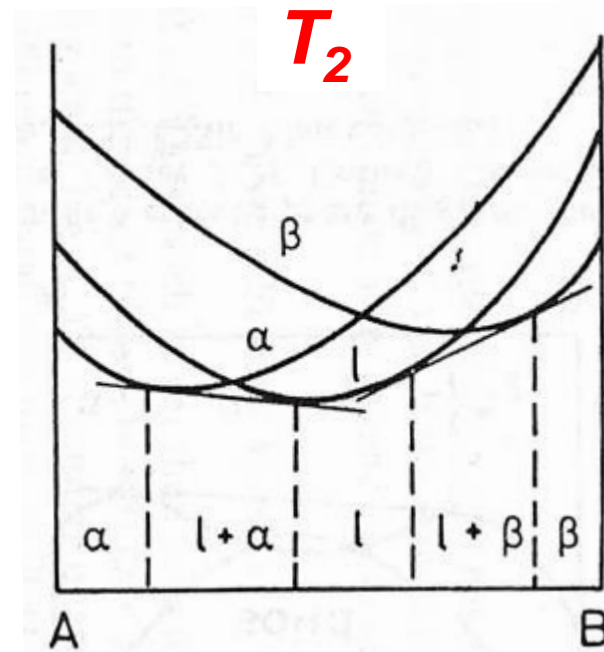
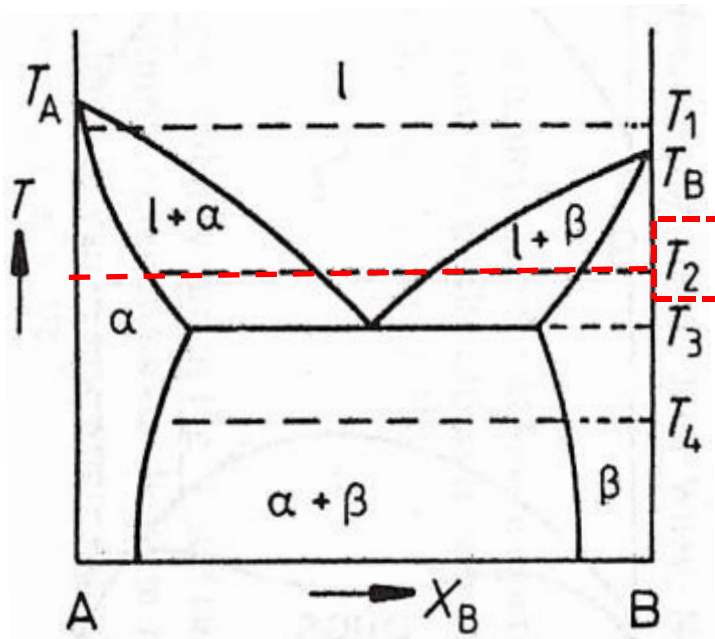
→ Phase diagram is the collection of minimum Gibbs energy assemblage of given system with temperature.



Porter, D.A., and Easterling, K.E., Phase Transformation in Metals and Alloys, 2<sup>nd</sup> Ed. CHAMAN & HALL (1992)

# Gibbs Energy vs. Phase Diagram

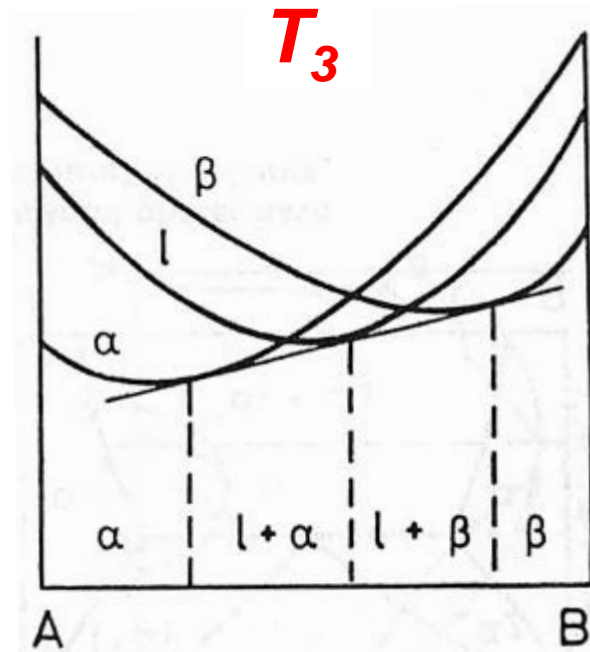
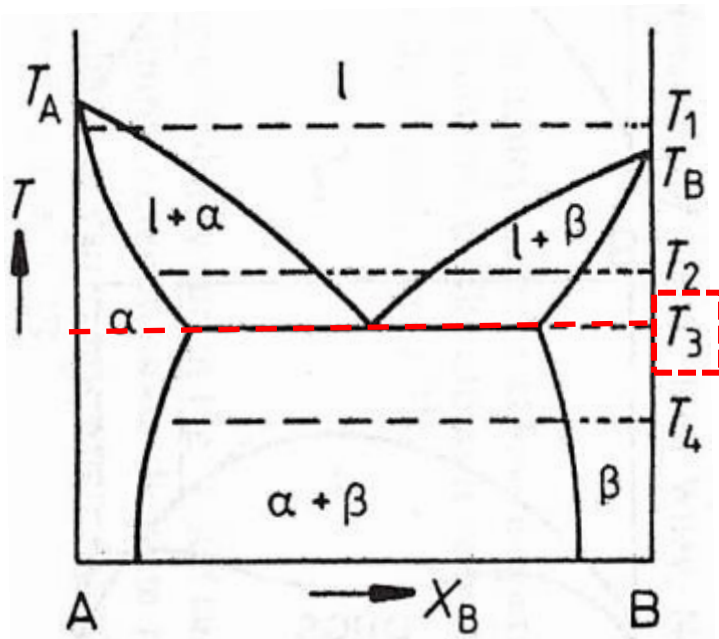
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# Gibbs Energy vs. Phase Diagram

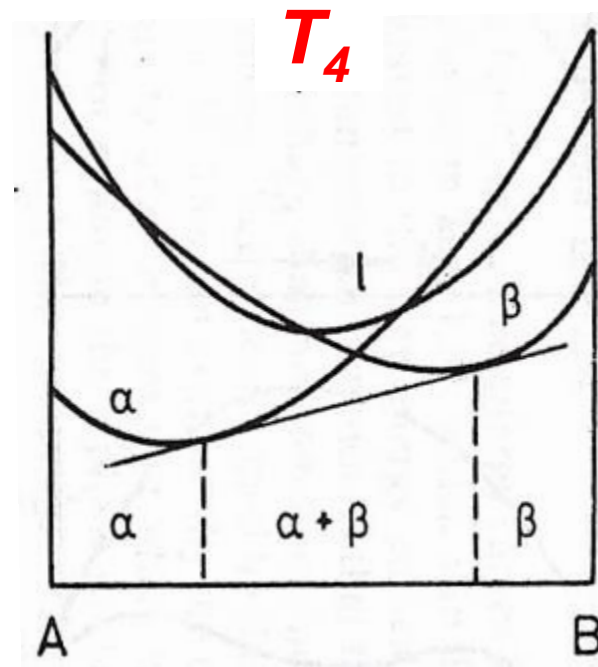
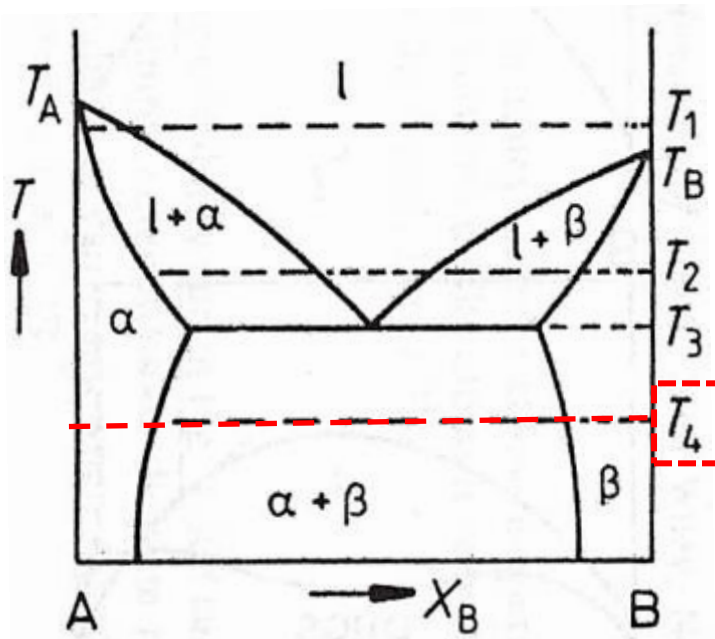
→ Phase diagram is the collection of minimum Gibbs energy assemblage of given system with temperature.



Porter, D.A., and Easterling, K.E., Phase Transformation in Metals and Alloys, 2<sup>nd</sup> Ed. CHAMAN & HALL (1992)

# Gibbs Energy vs. Phase Diagram

→ Phase diagram is the collection of minimum Gibbs energy assemblage of given system with temperature.



Porter, D.A., and Easterling, K.E., Phase Transformation in Metals and Alloys, 2<sup>nd</sup> Ed. CHAMAN & HALL (1992)

# Thermodynamic Database Development: FactSage

## Pure compound

$$G_T^o = H_T^o - TS_T^o$$

$$H_T^o = \Delta H_{298K}^o + \int_{298K}^T C_p dT$$

$$S_T^o = S_{298K}^o + \int_{298K}^T \frac{C_p}{T} dT$$

$$S_{298K}^o = \int_{0K}^{298K} \frac{C_p}{T} dT$$

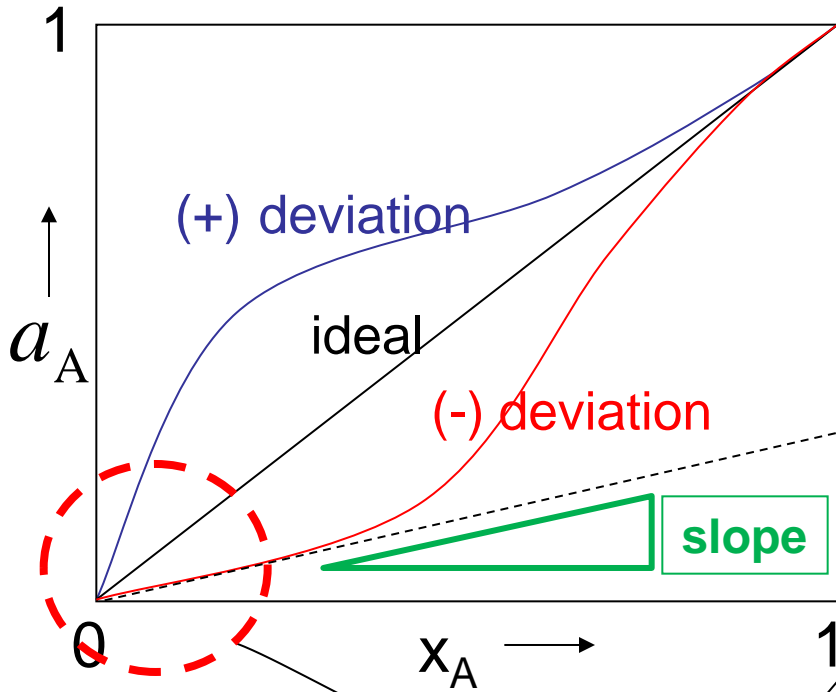
- Calorimetry
- emf
- Knudsen cell
- Vapor pressure

## Solution

$$G^{ex} = \sum_{i,j \geq 1} \omega_{AB}^{ij} x_A^i x_B^j$$

- emf (activity)
- Knudsen cell (activity)
- Vapor pressure (activity)
- Solution calorimetry (enthalpy)
- Phase diagram

# Dilute Solution



$a_A = \gamma_A^o x_A$  : Henry's law

$\gamma_A = \gamma_A^o$

↓

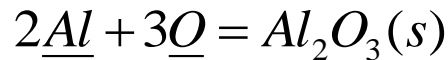
Constant slope

Henrian activity coefficient

# Dilute Solution

Most of refining process involves impurity elements (dilute solutes)  
→ Henrian activity is important

For example, Al-deoxidation process in steelmaking,



$$\Delta G^o = -RT \ln \frac{(a_{Al_2O_3})}{(a_{Al}^2) (a_O^3)} = -RT \ln \frac{(a_{Al_2O_3})}{(\gamma_{Al}^o X_{Al}^2) (\gamma_O^o X_O^3)}$$

$\gamma_{Al}^o$  is the Henrian activity coefficient of Al in pure liquid Fe

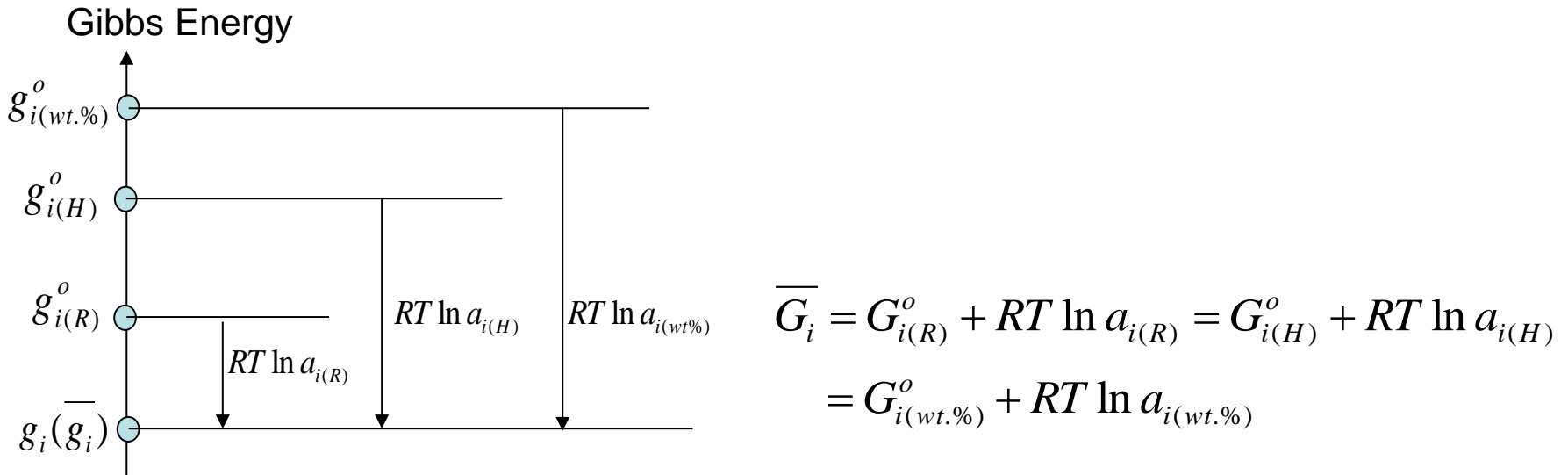
**Now, if we have other elements in Fe such as O, Mn, C, etc. there is interaction between Al and these elements.**

→ Change of  $\gamma_{Al}$  from  $\gamma_{Al}^o$  : interaction coefficients

$$\ln \gamma_{Al} = \ln \gamma_{Al}^o + \varepsilon_{Al}^{Al} x_{Al} + \varepsilon_{Al}^O x_O + \varepsilon_{Al}^C x_C + \dots$$

\* *FactSage FTmisc-FeLQ database contains these Henrian activity coefficients and interaction parameters for liquid steel.*

# Change of Standard State



➤ Raoultian standard state → Henrian standard state

$$\Delta G_{i(R \rightarrow H)}^o = RT \ln \gamma_i^o \quad a_{i(H)} = f_i x_i$$

$$\ln f_i = \varepsilon_i^i x_i + \varepsilon_i^j x_j + \varepsilon_i^k x_k + \dots$$

➤ Raoultian standard state → 1 wt.% standard state

$$\Delta G_{i(R \rightarrow wt\%)}^o = RT \ln \left( \frac{\gamma_i^o M_{Bulk}}{100 M_i} \right) \quad a_{i(wt.\%)} = f_i x_i$$

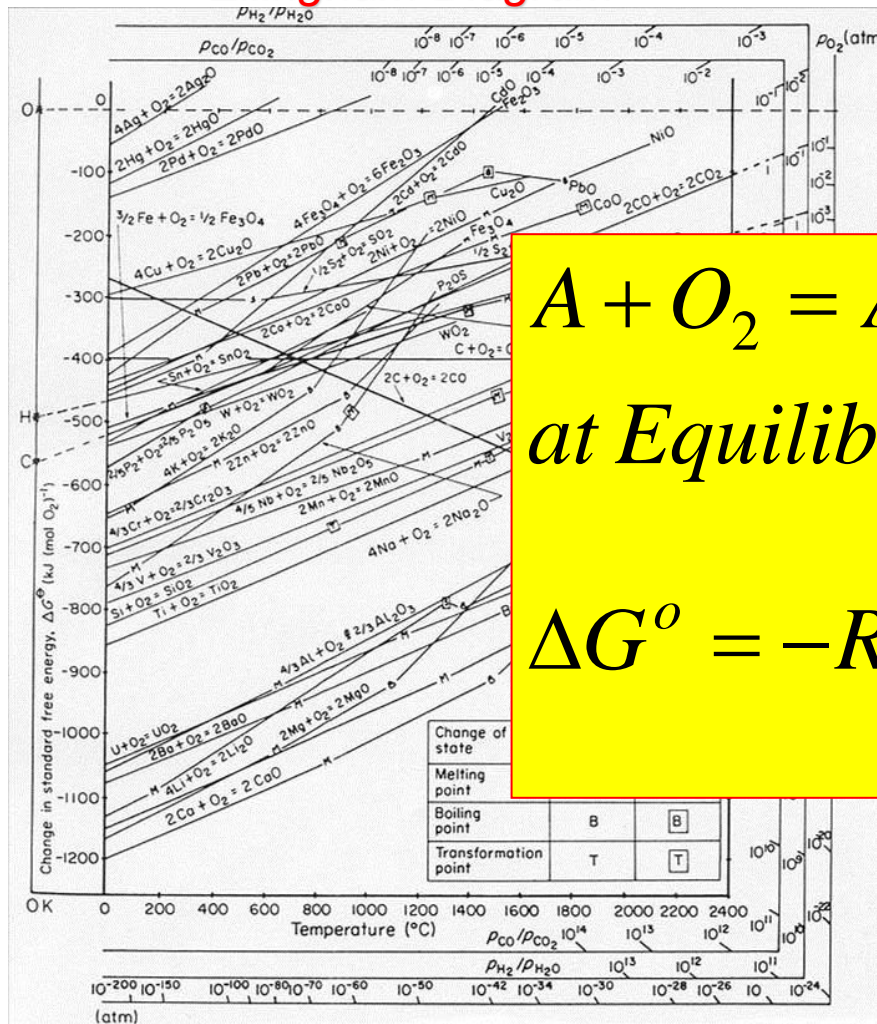
$$\log f_i = e_i^i [wt\% i] + e_i^j [wt\% j] + e_i^k [wt\% k] + \dots$$

# COMPUTATIONAL THERMODYNAMICS & FACTSAGE THERMODYNAMIC DATABASE

# Advantage of thermodynamic database

## Ellingham Diagram

## FactSage calculations



(gram) 58.4 MgO + 28.5 Cr2O3 + 5.4 Al2O3 + 6.1 Fe2O3 =

0.00000	gram	(	9.6630	wt. %	Al2O3	
			+ 62.986	wt. %	Cr2O3	<b>Corundum</b>
			+ 27.351	wt. %	Fe2O3	
			(1600.00 C, 1 atm, M2O3(Corundum), a=0.25426)			
+ 44.369	gram	(	0.87098	wt. %	Fe3O4[1+]	Spin
			+ 0.17265E-05	wt. %	Fe104[5-]	Spin
			+ 1.4285	wt. %	Al304[1+]	Spin
			+ 0.17705E-05	wt. %	Al104[5-]	Spin
			+ 1.2681	wt. %	Fe1Al204[1+]	Spin
			+ 1.0299	wt. %	Al1Fe204[1+]	Spin
			+ 9.7943	wt. %	Mg1Al204	Spin
			+ 0.87538	wt. %	Al1Mg204[1-]	Spin
			+ 5.9975	wt. %	Mg304[2-]	
			+ 0.12004E-04	wt. %	Mg104[6-]	<b>Spinel</b>
			+ 7.0989	wt. %	Mg1Fe204	
			+ 0.78203	wt. %	Fe1Mg204[1-]	Spin
			+ 55.811	wt. %	Mg1Cr204	Spin
			+ 0.40158E-01	wt. %	Cr1Cr204[1+]	Spin
			+ 0.45352E-02	wt. %	Cr1Mg204[1-]	Spin
			+ 6.8849	wt. %	Fe1Cr204[1+]	Spin
			+ 0.50832E-02	wt. %	Cr1Fe204[1+]	Spin
			+ 8.1011	wt. %	Al1Cr204[1+]	Spin
			+ 0.73593E-02	wt. %	Cr1Al204[1+]	Spin
			+ 0.99174E-08	wt. %	Cr104[5-]	Spin
			(1600.00 C, 1 atm, Cubic)			
+ 54.031	gram	(	2.4263	wt. %	Fe2O3	
			+ 89.953	wt. %	MgO	<b>Monoxide</b>
			+ 0.16289	wt. %	Al2O3	
			+ 7.4575	wt. %	Cr2O3	
			(1600.00 C, 1 atm, Monoxide)			
+ 0.00000	gram	(	34.012	wt. %	MgO	
			+ 31.916	wt. %	Al2O3	
			+ 25.317	wt. %	Fe2O3	
			+ 8.7552	wt. %	Cr2O3	<b>Slag</b>
			(1600.00 C, 1 atm, ASlag-liq/glass, a=0.44534)			

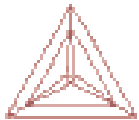
- Ellingham diagram : Reaction between pure stoichiometric oxide phases.
- FactSage calc.: Multicomponent phase equilibria including many solid/liquid/gas solutions.
  - for example, Spinel/Slag/Monoxide/Corundum/Fe-steel/Gas/etc....

# Commercial Databases and Programs



F\*A\*C\*T + ChemSage: CRCT, Canada + GTT Tech., Germany  
[www.crct.polymtl.ca](http://www.crct.polymtl.ca), [www.factsage.com](http://www.factsage.com)

TD: Oxide (slag, inclusion, refractory), Salt, Steel, Light alloy (very good)  
Fully Window Interface



Thermo-Calc Software

KTH, Sweden, [www.thermocalc.se](http://www.thermocalc.se)

TD: Steel, Light Alloy (very good) + poor Oxide  
DICTRA (Diffusion Process)  
DOS Interface, Window Interface

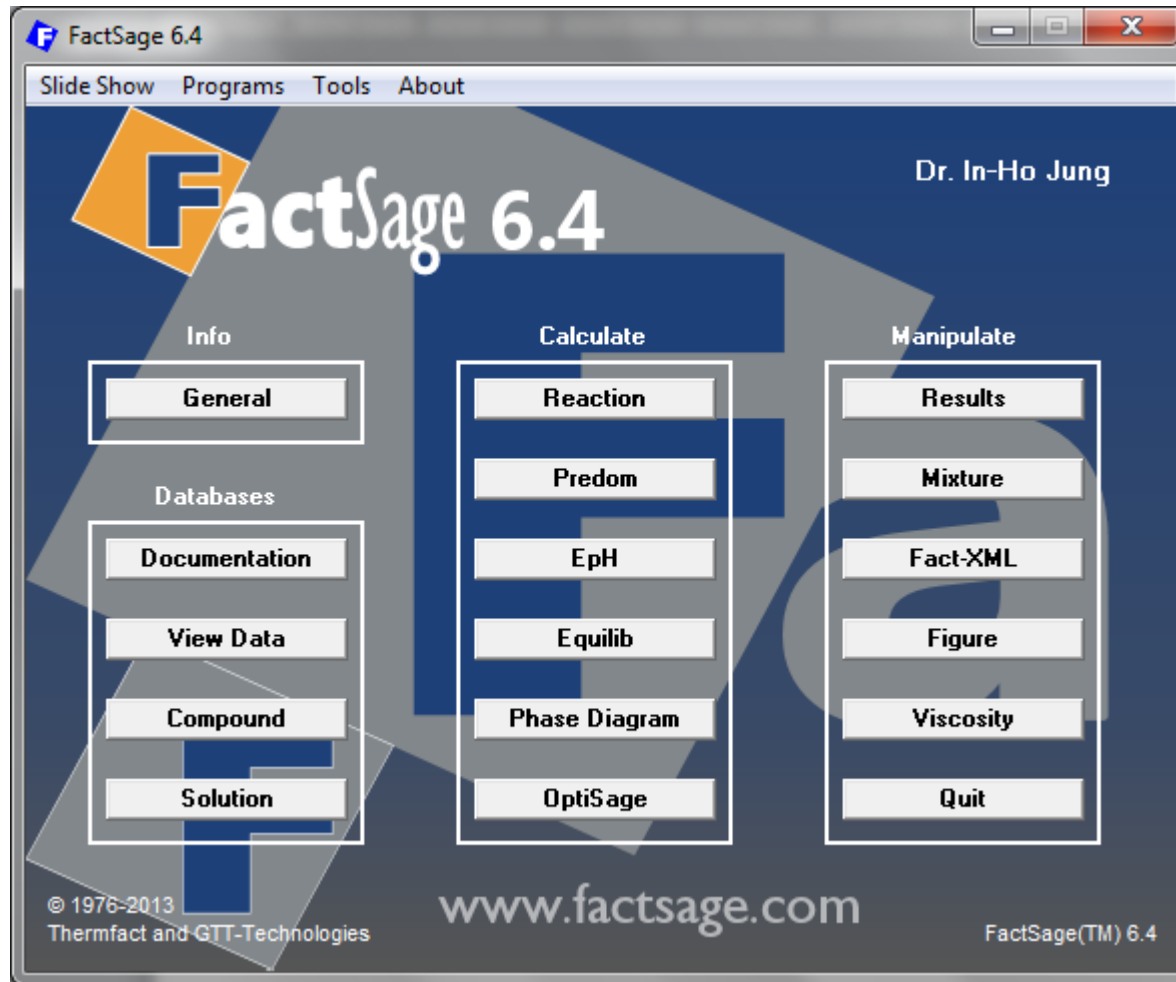


NPL, UK, [www.npl.co.uk/npl/cmmt/mtdata](http://www.npl.co.uk/npl/cmmt/mtdata)  
TD: Oxide, Salt, Steel, Light alloy (good)  
Window Interface

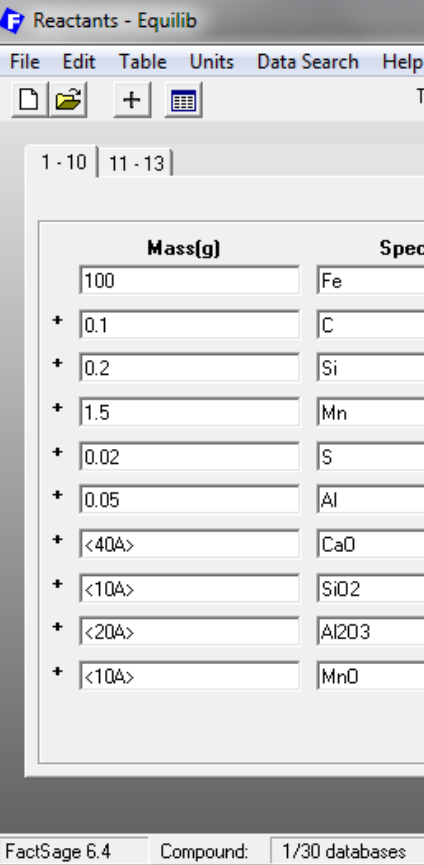


SGTE (Europe + Canada + US), [www.sgte.org](http://www.sgte.org)  
Organization of Database Development

Since 1976



# Desulfurizing a Steel by CaSi Addition.



Reactants - Equilib

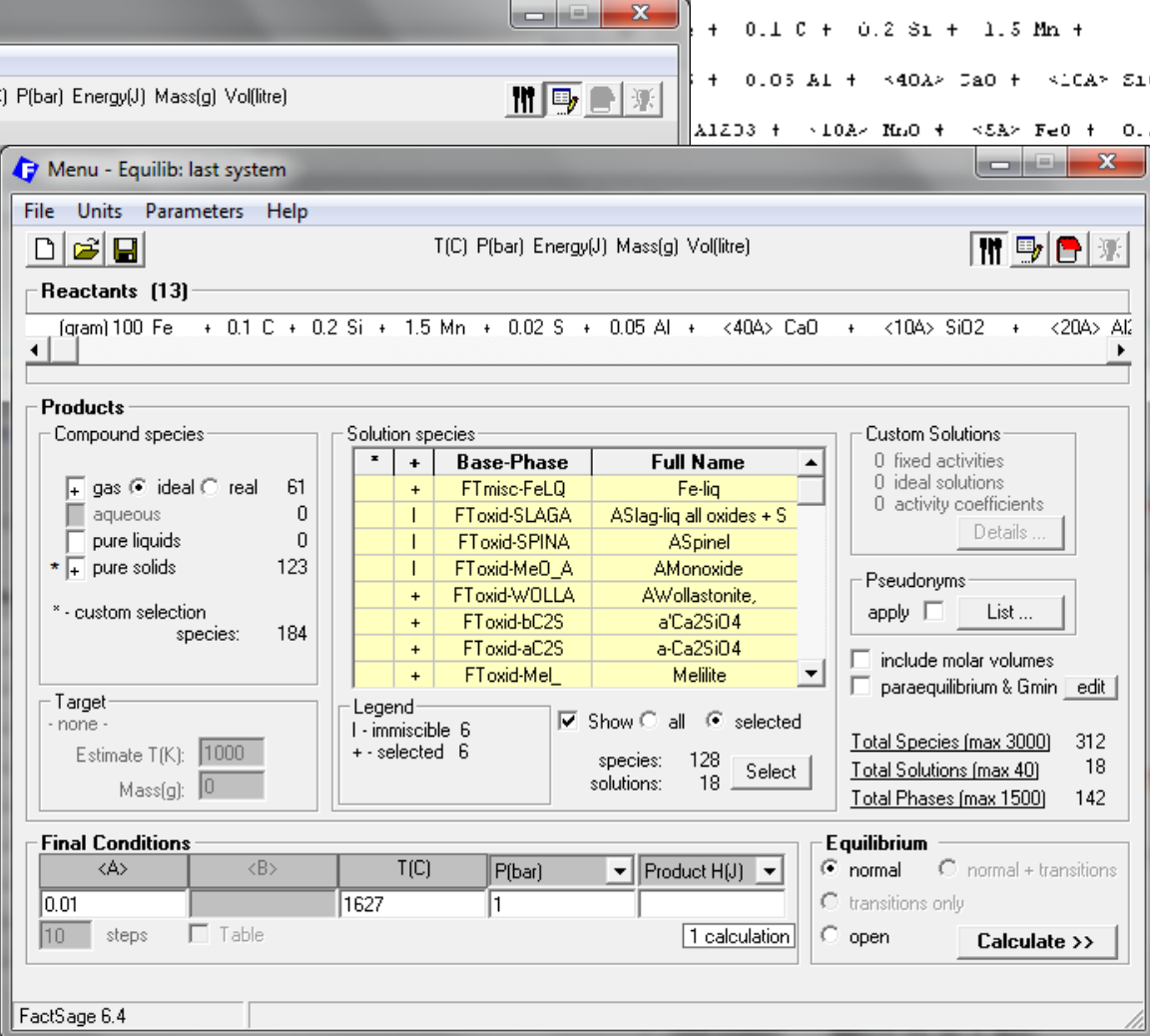
File Edit Table Units Data Search Help

T(C) P(bar) Energy(J) Mass(g) Vol(litre)

1 - 10 | 11 - 13

Mass(g)	Species
100	Fe
+ 0.1	C
+ 0.2	Si
+ 1.5	Mn
+ 0.02	S
+ 0.05	Al
+ <40A>	CaO
+ <10A>	SiO2
+ <20A>	Al2O3
+ <10A>	MnO

FactSage 6.4 Compound: 1/30 databases



Menu - Equilib: last system

File Units Parameters Help

T(C) P(bar) Energy(J) Mass(g) Vol(litre)

Reactants (13)

(gram) 100 Fe + 0.1 C + 0.2 Si + 1.5 Mn + 0.02 S + 0.05 Al + <40A> CaO + <10A> SiO2 + <20A> Al2O3 + <10A> MnO

Products

Compound species

Phase	Count
gas	61
aqueous	0
pure liquids	0
pure solids	123
custom selection	0
<b>species:</b>	<b>184</b>

Target: none - Estimate T(K): 1000 Mass(g): 0

Solution species

+	Base-Phase	Full Name
+	FTmisc-FeLQ	Fe-liq
	FToxid-SLAGA	ASlag-liq all oxides + S
	FToxid-SPINA	ASpinel
	FToxid-MeO_A	AMonoxide
+	FToxid-WOLLA	AWollastonite
+	FToxid-bc2S	aCa2SiO4
+	FToxid-aC2S	aCa2SiO4
+	FToxid-Mel_	Mellite

Legend: | - immiscible 6, + - selected 6

Final Conditions: <A> 0.01, <B> 10, T(C) 1627, P(bar) 1, 1 calculation

Equilibrium: normal selected

Total Species (max 3000) 312  
Total Solutions (max 40) 18  
Total Phases (max 1500) 142

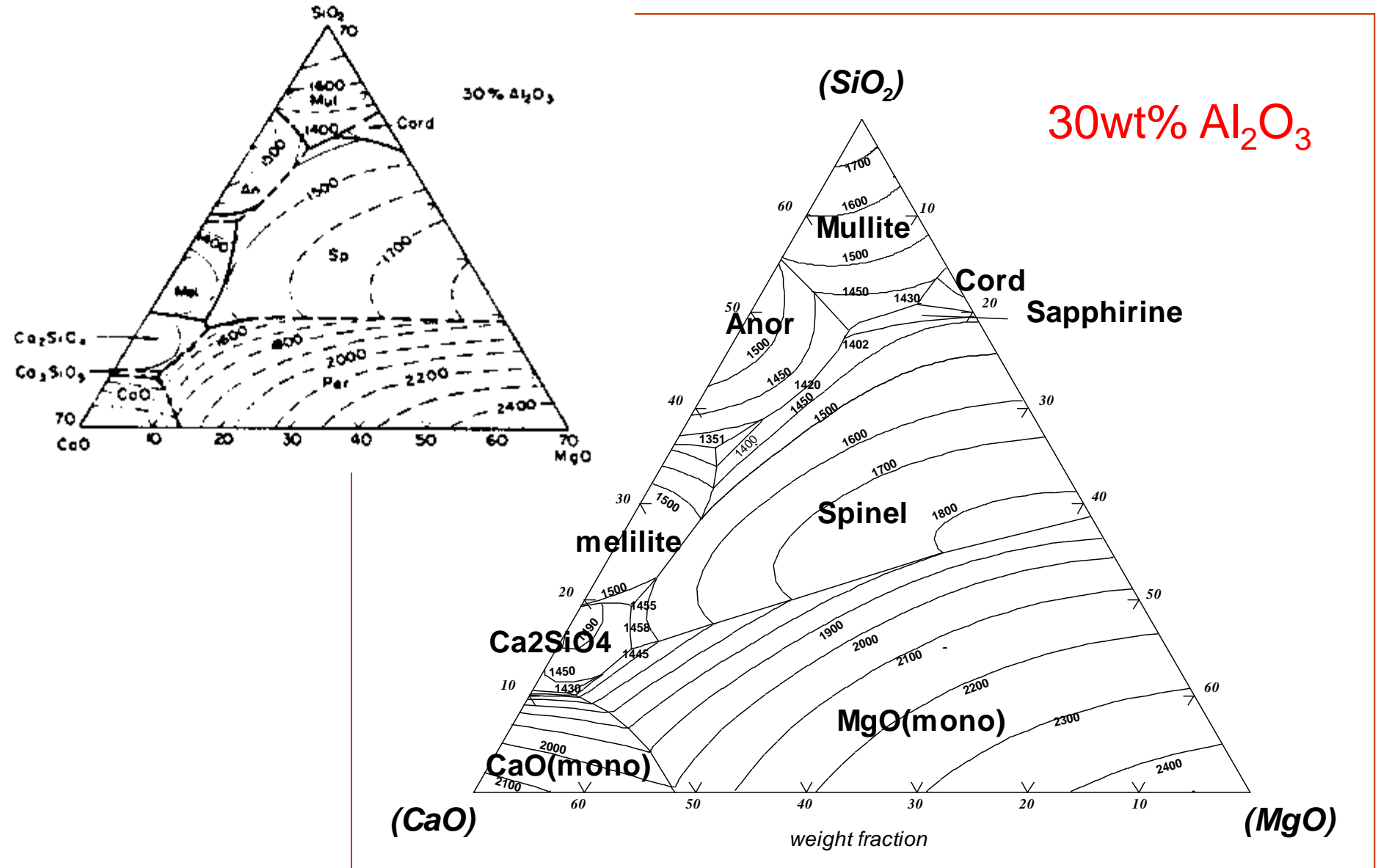
2.5599E-04 g/(ml)

No solid phases (activity<1)

```

+ 0.00000 gram Fe_bcc
+1627.70 C, 1 atm, S1, a=0.93200:
+ 0.00000 gram Fe_icc
+1627.70 C, 1 atm, S2, a=0.92352:
                    
```

# Prediction of Phase diagrams



# FactSage for Steelmaking

The thermodynamic database can be used along with the Gibbs energy minimization software of **FactSage** to calculate:

- Slag/Metal/Inclusion/Gas/Refractory equilibration
  - Inclusion chemistry
  - Maximum solubility of refractories
  - Slag/metal equilibration
  - de-O, de-S, de-P, ...
  - Etc.
- any phase diagram section for multicomponent systems  
*isothermal, isoplethal, etc.*
- cooling paths of slag and alloys  
*(Equilibrium, Scheil-Gulliver, etc.)*
- Mass/Heat balances: alloying
- Viscosity of slag

# Merits of Using Thermodynamic Calculations in Alloy and Process Design

- Reduce Time/Cost/Manpower by effective searching for optimal conditions, compositions, etc. through thermodynamic calculations.
- Eliminate “Trial and Error” Approach.
- Calculations are rapid.
- Does not require expert knowledge of thermodynamics.

# Thermodynamic Modeling / Applications

## Phase diagram data

- Phase diagram
- S/L/G phase equilibria

## Crystal Structural data

## Thermodynamic data

- Calorimetric data: Heat capacity, H of mixing, H of melting, etc.
- Vapour pressures
- Chemical Potentials: activity
- etc.

## Critical Evaluation/Optimization

one set of  $G_{\text{phase}} = f(T, x, P)$  for all phases  
(Good thermodynamic model → High predictive ability)

## Construction of Thermodynamic Database

Unary → Binary → Ternary → Multicomponents

## Applications to Materials / Process Design/Analysis

- Complex chemical reactions
- Solidification / Equilibration calculations (as-cast/as-annealed)
- Multicomponent phase diagrams
- Mass/Heat balance with stream: process simulation

 FactSage™

ThermoCalc  
Pandat



# FactSage thermodynamic database for Steelmaking

Gases + Pure elements and compounds : > 4400

Slag (molten oxide)

CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub>-MnO-CrO-Cr<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-Ti<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-CoO-NiO-Na<sub>2</sub>O, K<sub>2</sub>O, B<sub>2</sub>O<sub>3</sub>, Cu<sub>2</sub>O, As<sub>2</sub>O<sub>3</sub>, GeO<sub>2</sub>, PbO, SnO, ZnO...

Gases: S, SO<sub>4</sub>, PO<sub>4</sub>, H<sub>2</sub>O, F, Cl, C, N, ... (up to ~5% solubility. Higher for S)

Solid oxides (refractories, inclusions)

Spinel: Fe<sub>3</sub>O<sub>4</sub>, MgFe<sub>2</sub>O<sub>4</sub>, MgAl<sub>2</sub>O<sub>4</sub>, MgCr<sub>2</sub>O<sub>4</sub>, FeAl<sub>2</sub>O<sub>4</sub>,... (Al-Co-Cr-Fe-Mg-Mn-Ni-Zn-O)

Olivine: Fe<sub>2</sub>SiO<sub>4</sub>, Mg<sub>2</sub>SiO<sub>4</sub>, Ca<sub>2</sub>SiO<sub>4</sub>, Mn<sub>2</sub>SiO<sub>4</sub>, etc. (Co, Ni, Zn)

Monoxide: CaO-MgO-FeO-MnO-NiO-CoO-Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-etc.

Melilite, Perovskite, Corundum, Pyroxenes, Wollastonite, Ilmenite, Pseudobrookite, etc.

+ Pure Compounds

Steel

Steel database (Liquid (deoxidation), FCC, BCC, Carbides, (Ti,Nb)(C,N), etc. )

Fe-Ag-Al-B-Ca-Ce-Co-Cr-Cu-La-Mg-Mn-Mo-N-Nb-Ni-Pb-Pd-Si-Sn-Ta-Ti-U-V-W-C-H-N-O-P-S

## Pure compounds

$$G_T^o = H_T^o - TS_T^o$$

$$H_T^o = \Delta H_{298}^o + \int_{298}^T C_p dT \quad S_T^o = S_{298}^o + \int_{298}^T \frac{C_p}{T} dT$$

## Solutions

For example, Random mixing solution (ideal, regular, sub-regular solutions)

$$G^L = X_A G_A^{o,L} + X_B G_B^{o,L} + RT(X_A \ln X_A + X_B \ln X_B) + G^{ex}$$

$$G^{ex} = \sum q_{AB}^{mn} X_A^m X_B^n$$

To get high predictive ability, thermodynamic model should reflect the **structure of solutions** (phases)

In our databases, many different models are used such as:

- **Slag:** Modified Quasichemical Model (short-range-ordering)
- **Solid solution:** Compound Energy Formalism (crystallographic information)
- **Liquid Fe:** Generalized Interaction formalism (dilute solution)

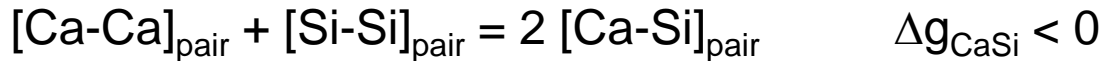
# Quasichemical Model for Short-Range Ordering

- Used for the liquid oxide solution



Consider a random distribution of second-nearest-neighbor cation pairs.

Model parameters are the Gibbs energies of the pair-exchange reactions such as:



This is equivalent to  $\text{O}^{2-} + \text{O}^{\circ} = 2\text{O}^{\cdot}$

$$G = \left( n_{\text{SiO}_2} G_{\text{SiO}_2}^0 + n_{\text{CaO}} G_{\text{CaO}}^0 + \dots \right) - T \Delta S^{\text{config}} + \sum_{n>m} n_{mn} (\Delta g_{mn}/2)$$

**where :**  $n_i$ ,  $G_i^0$  = number of moles and Gibbs energy of component  $i$  in solution

$n_{mn}$  = number of moles of  $[m-n]$  pairs at equilibrium

$\Delta S^{\text{config}}$  = (Ising) entropy for random distribution of pairs = function of  $n_i$  and  $n_{mn}$

$\Delta g_{mn}$  = binary model parameters

(which may be functions of composition and  $T$ )

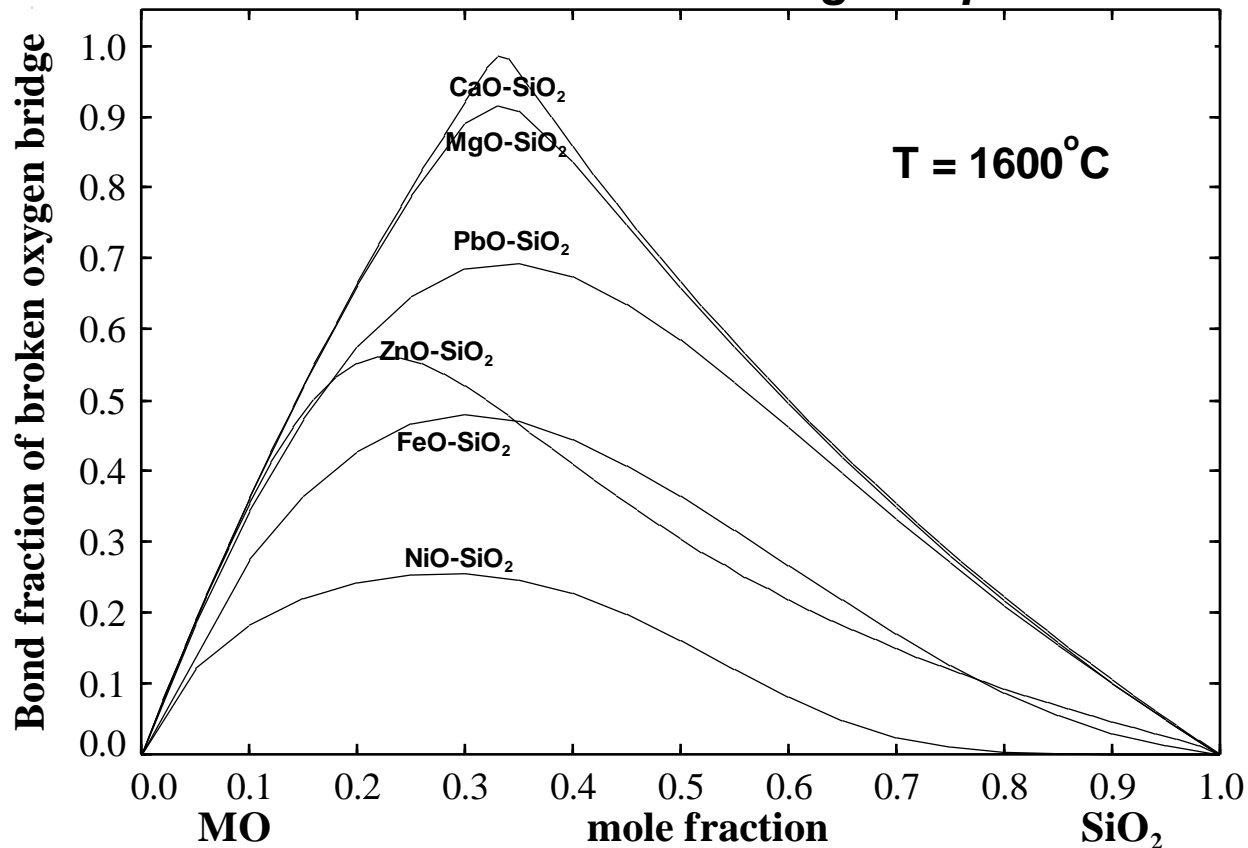
(The equilibrium values of  $n_{mn}$  are obtained by setting  $\partial G / \partial n_{mn} = 0$  at constant  $n_i$ )

# Silicate Slag: Network structure

*-Consideration of Second Nearest Neighbor Short-Range-Ordering-*



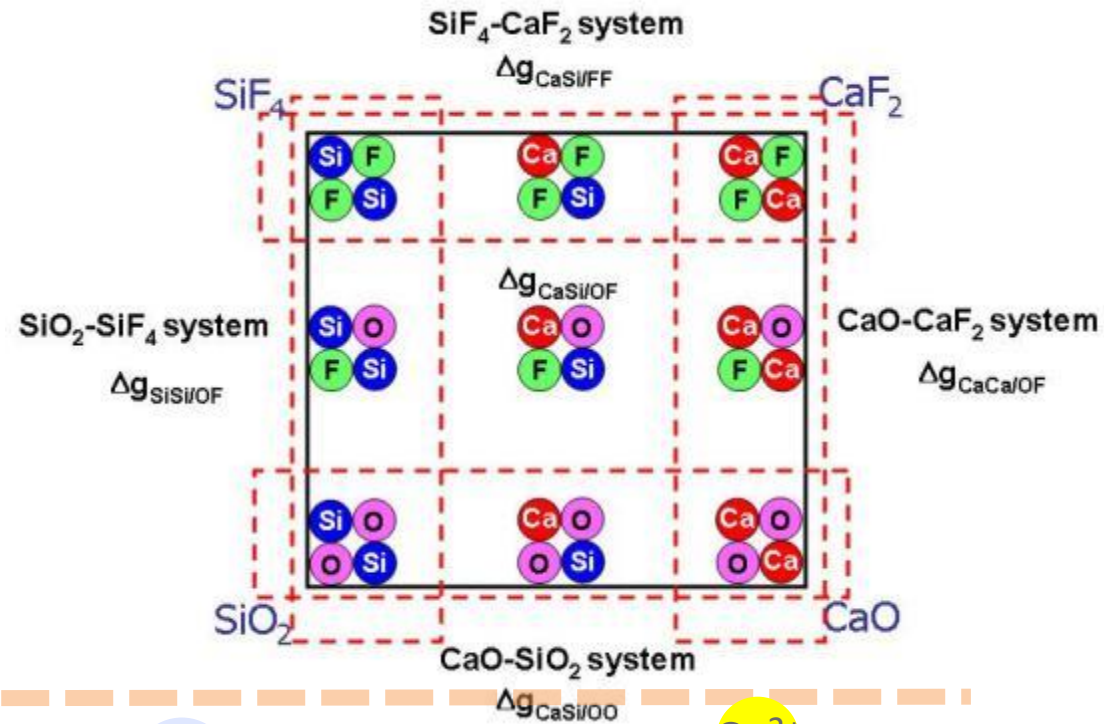
*Calculated bonding in liquid silicates*



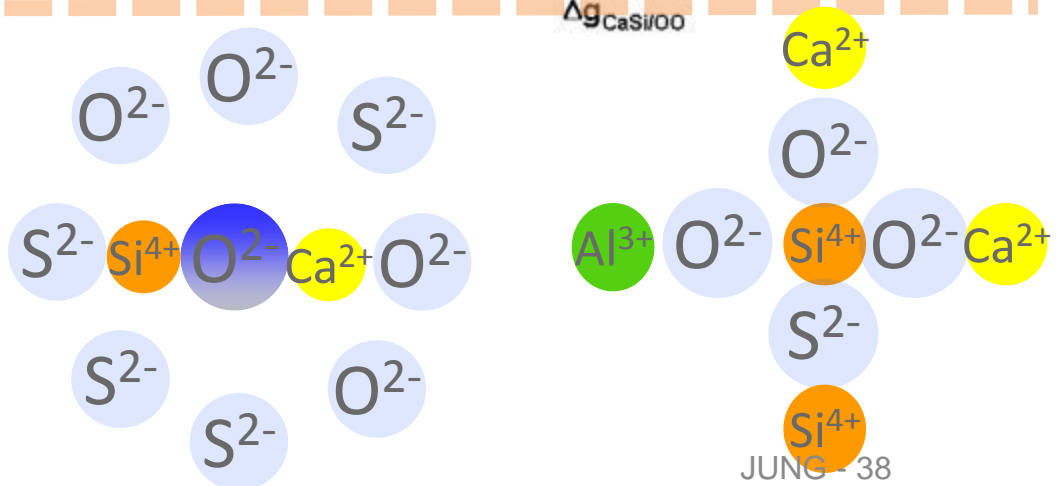
# Slag system like OxySulfide, OxyFluoride, etc.

*-Consideration of First and Second Nearest neighbor Short-Range-Ordering-*

**Two Sublattice  
Modified Quasichemical  
Model  
(Quadruplet Approximation)**



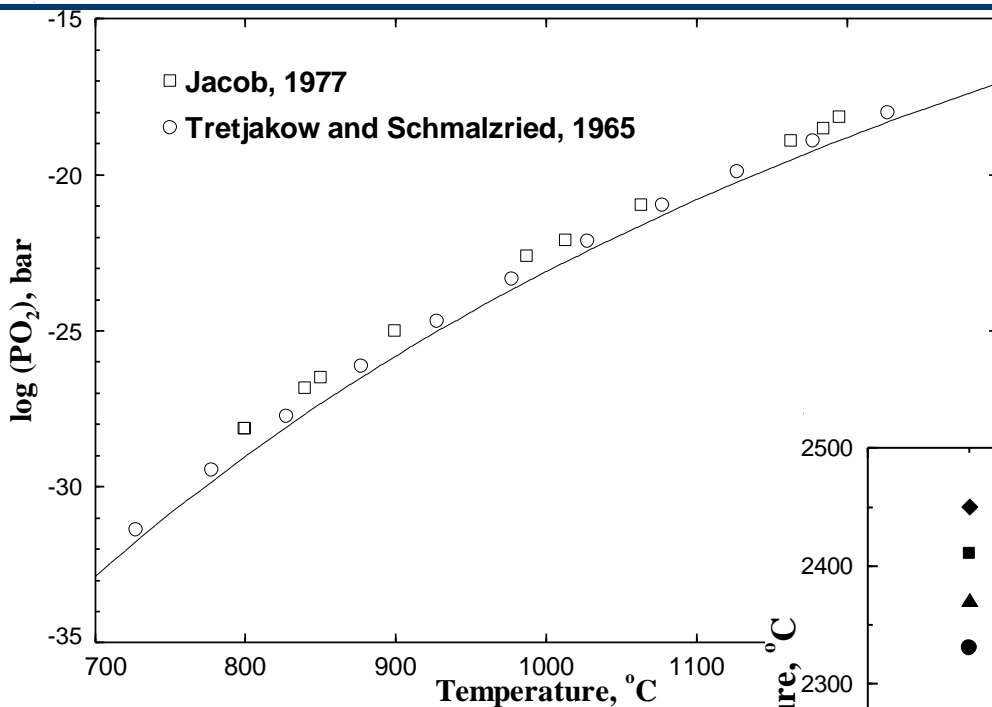
**General Central  
Atom (GCA) Model**



# Thermodynamic Database Development

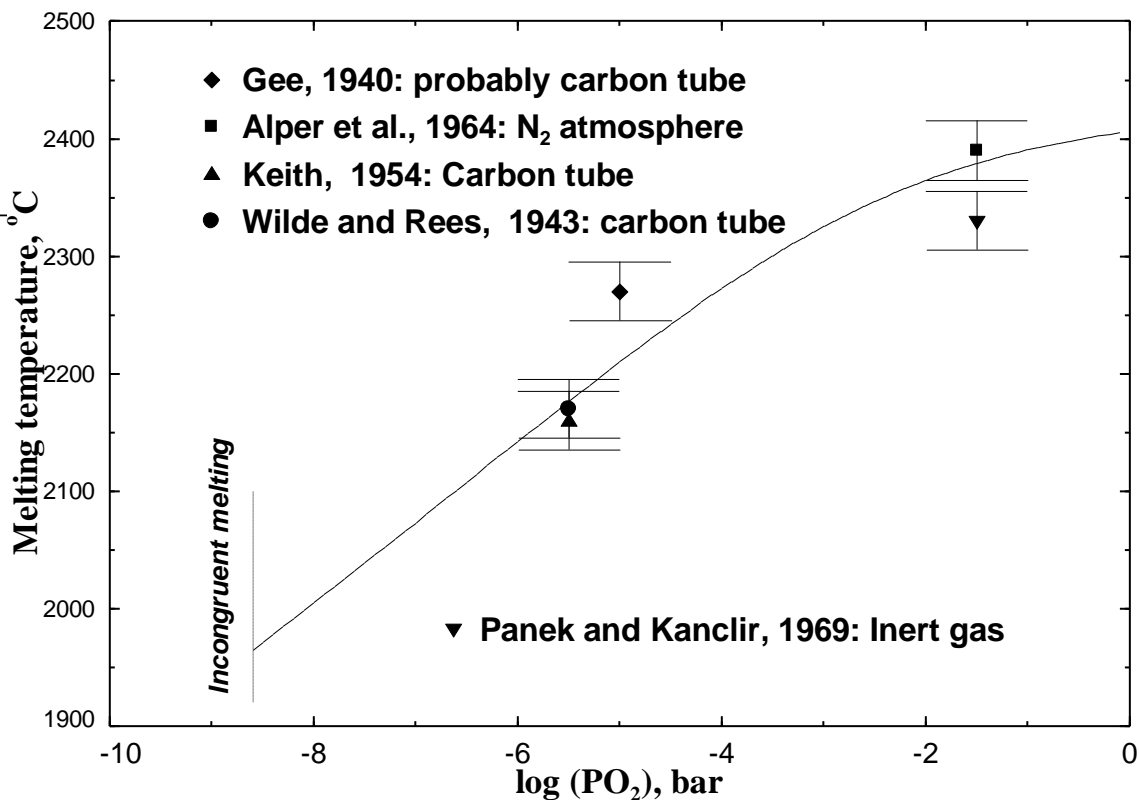
Mg-Cr-Al-O system  
Mg-Fe-Si-O system

# Thermodynamic properties of $\text{MgCr}_2\text{O}_4$

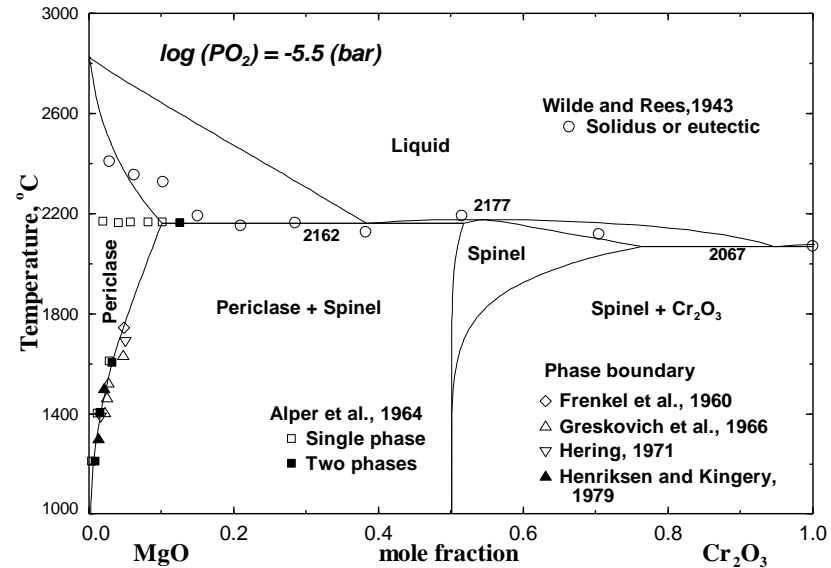
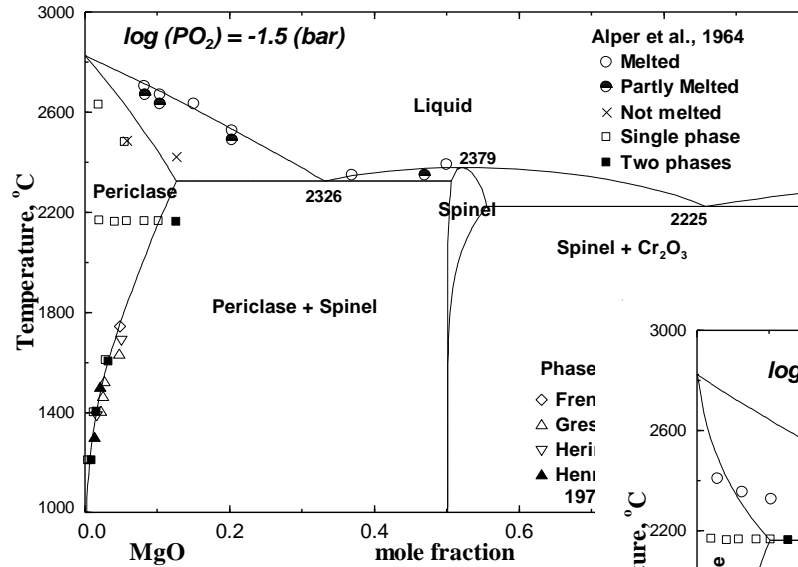
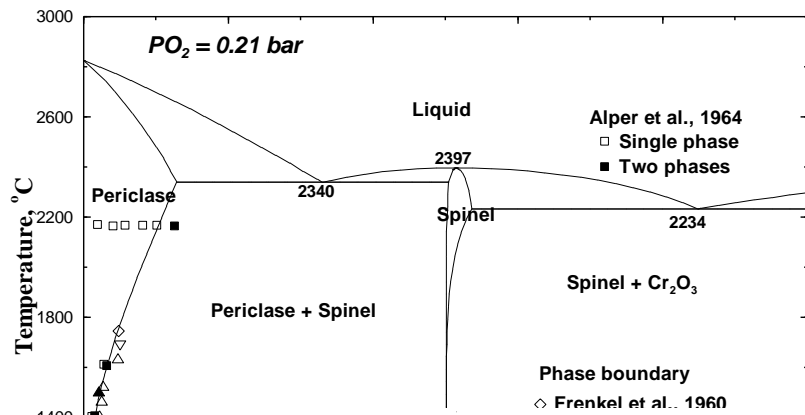


Emf measurement for  
Gibbs energy of  $\text{MgCr}_2\text{O}_4$   
from  $(\text{MgCr}_2\text{O}_4 + \text{MgO} + \text{Cr})$

Melting temperature of  
 $\text{MgCr}_2\text{O}_4$  with  $\text{PO}_2$



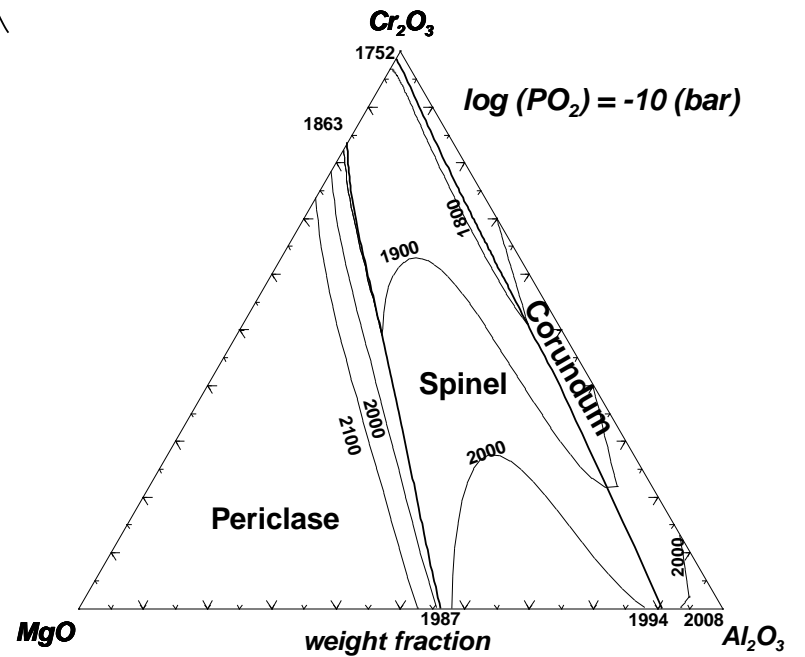
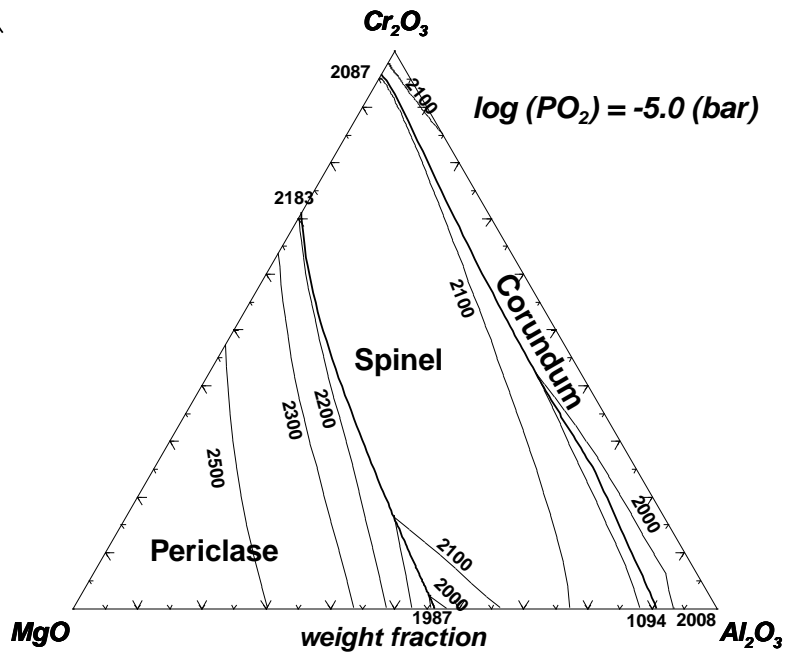
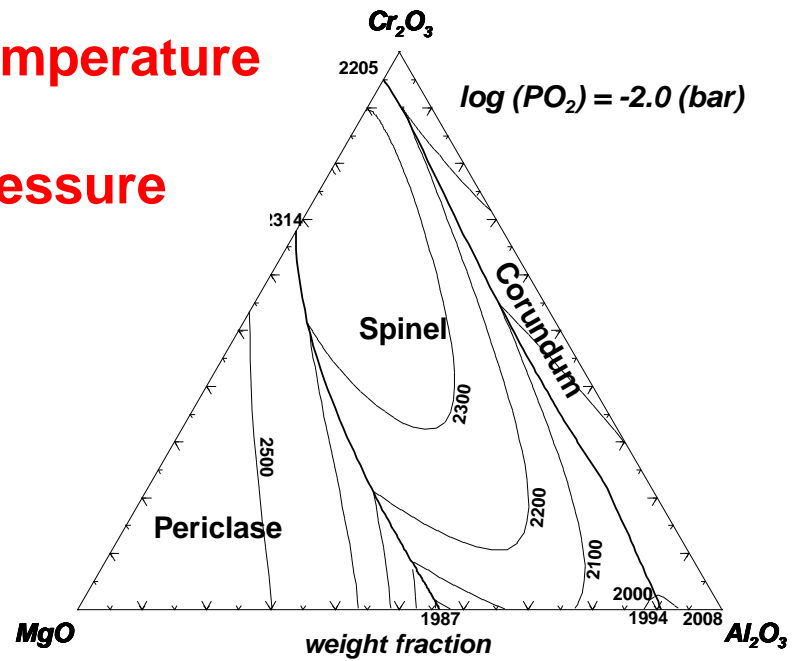
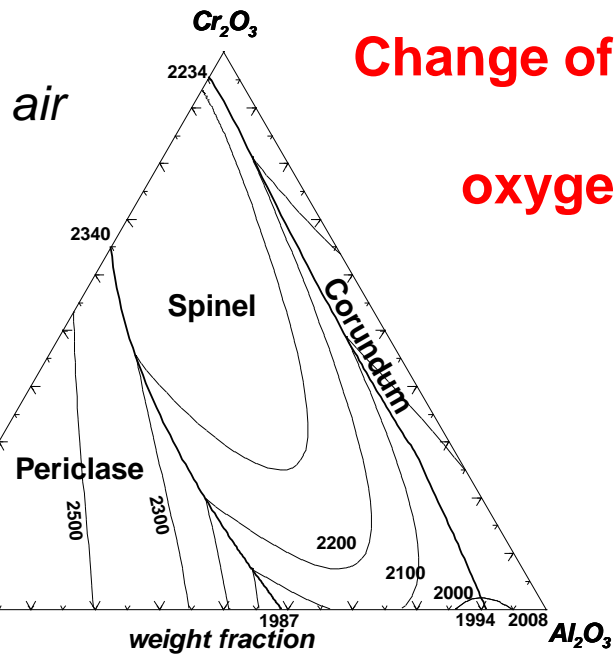
# MgO-Cr<sub>2</sub>O<sub>3</sub> phase diagram



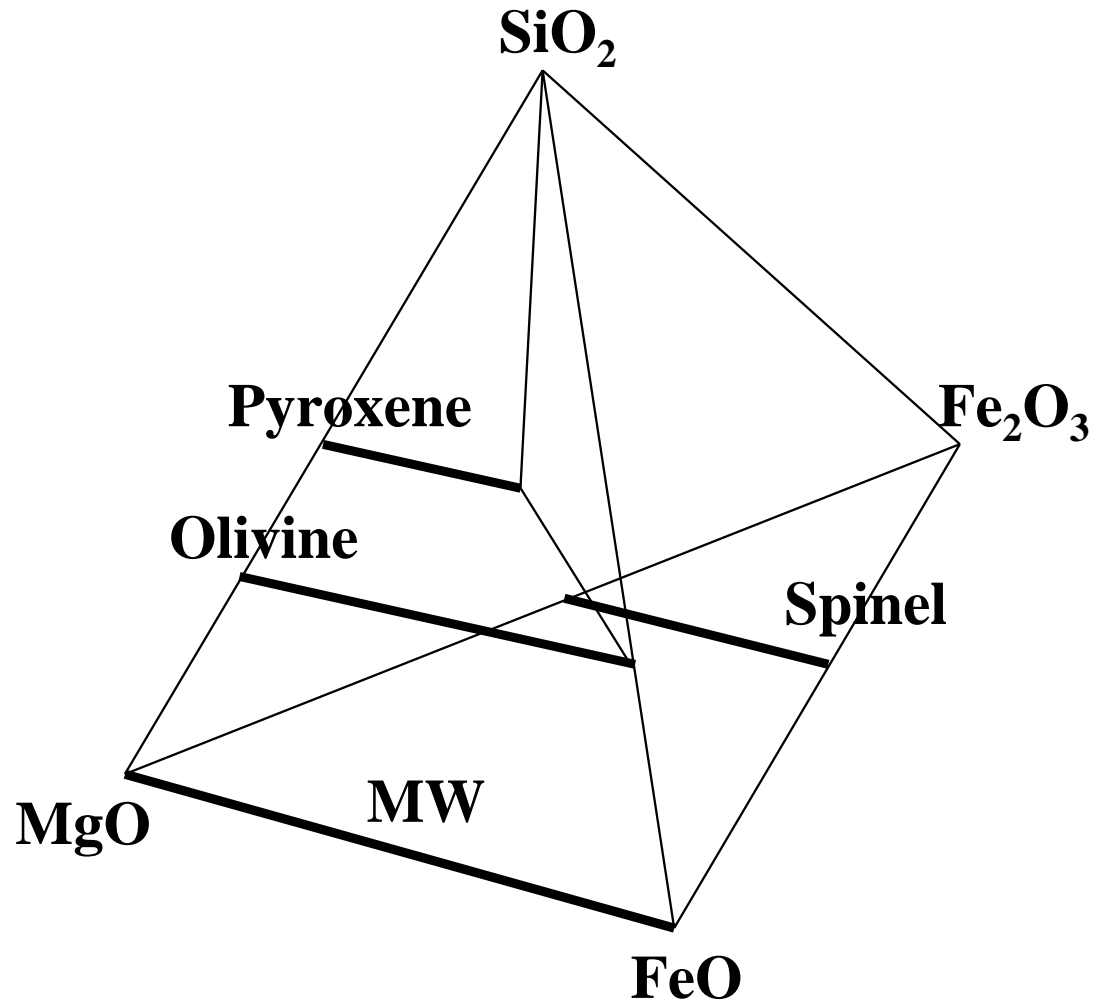
Decreasing  
PO<sub>2</sub>

Jung et al., *J. Amer. Ceram. Soc.*,  
vol. 88, 2005, p. 1921

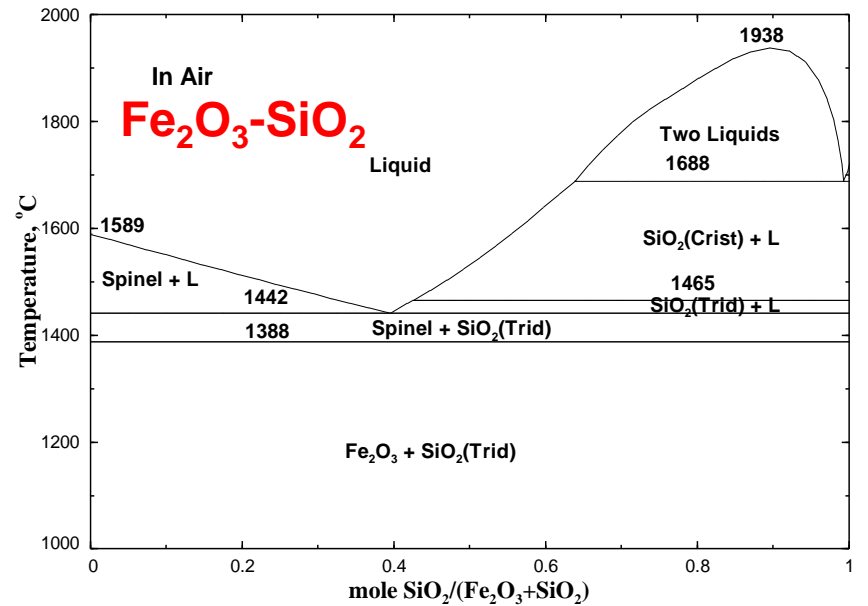
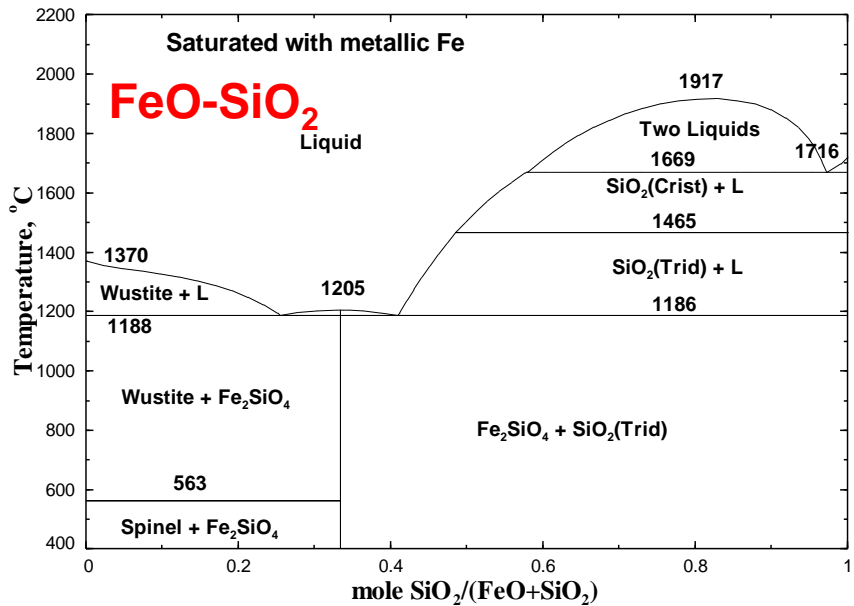
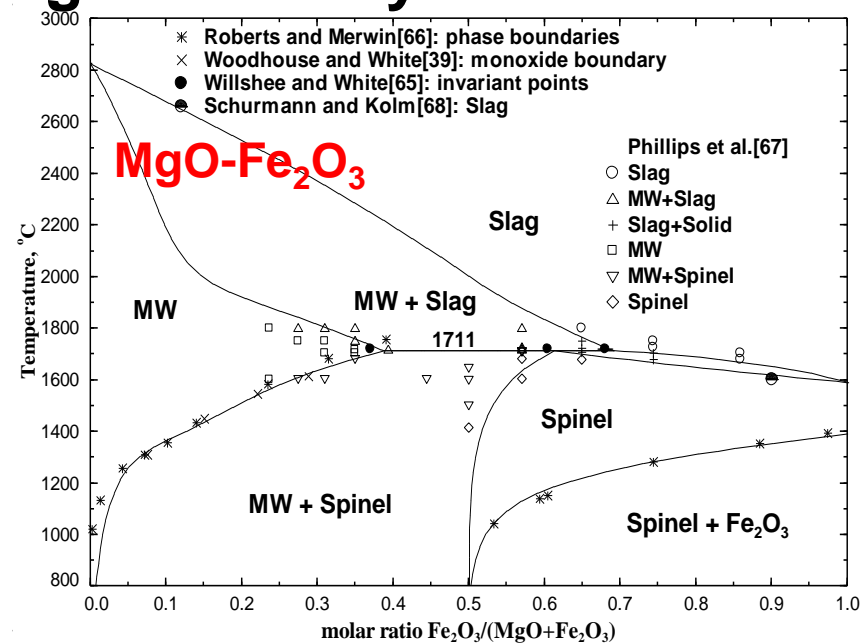
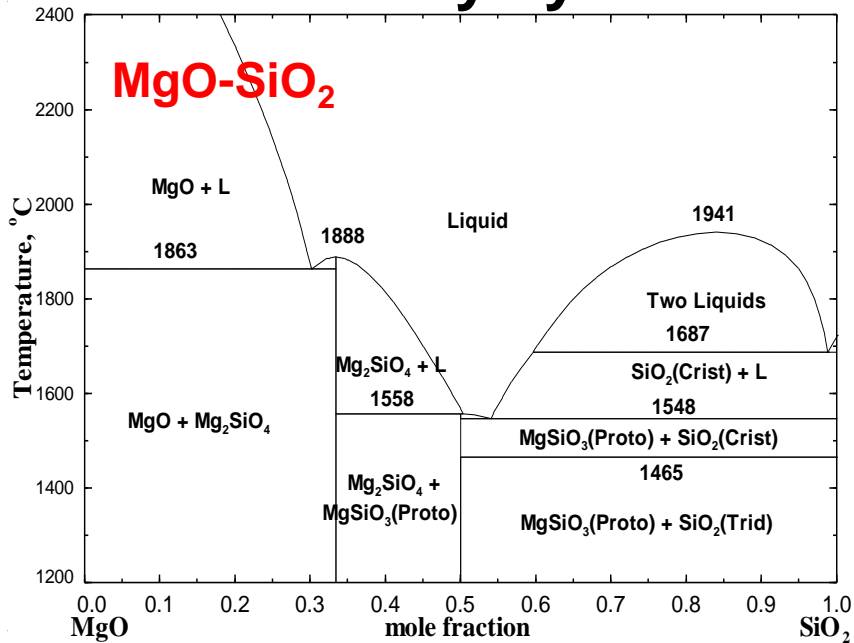
# Change of liquidus temperature with oxygen partial pressure



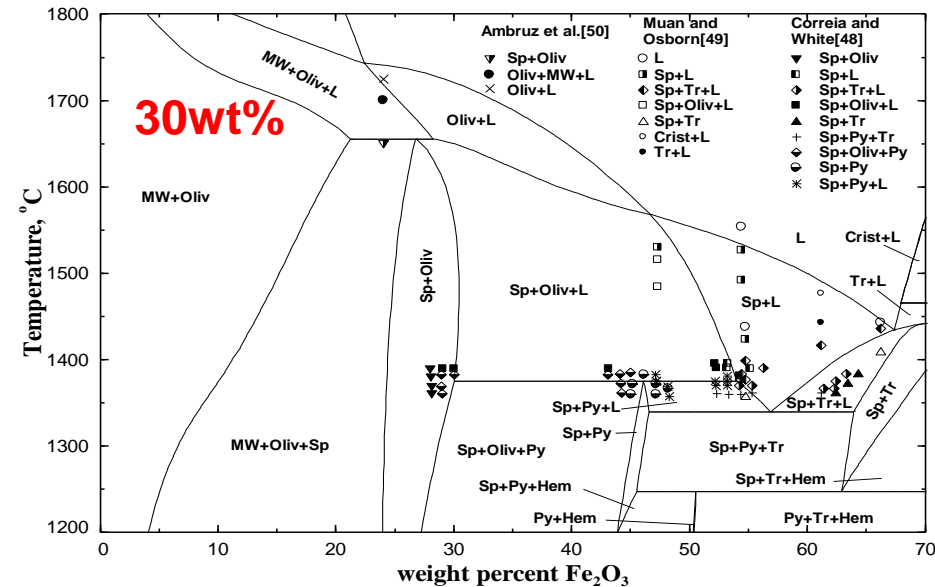
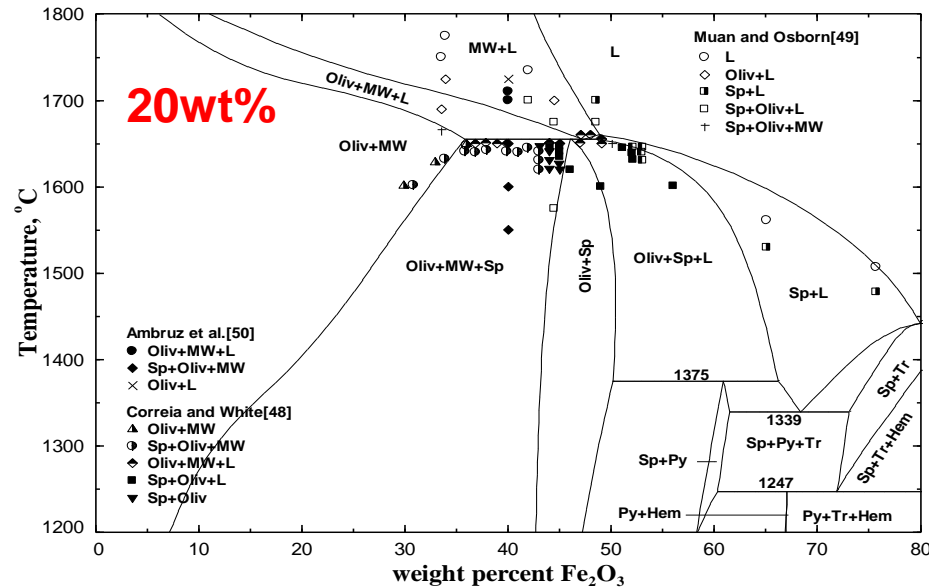
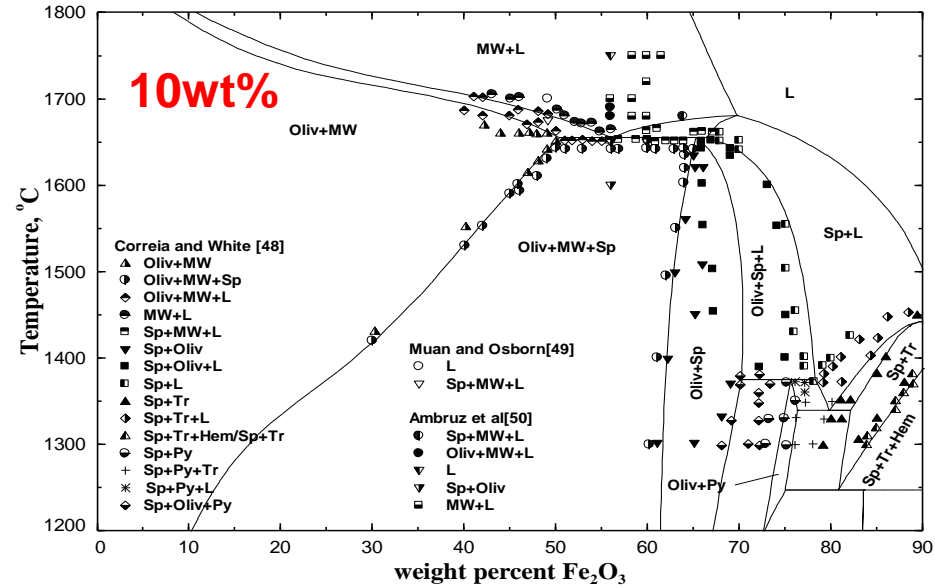
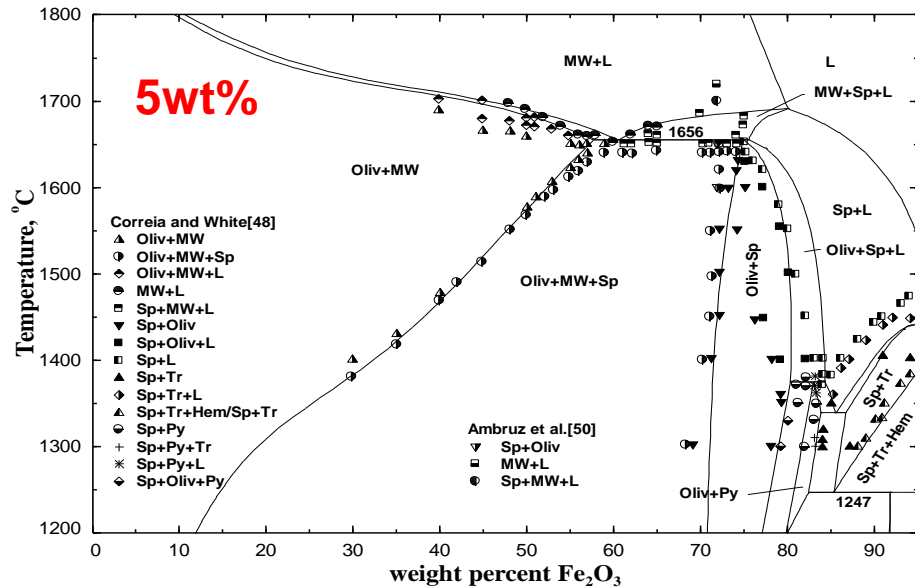
# Mg-Fe-Si-O system



# Binary systems of the Mg-Fe-Si-O system



# Iso-%SiO<sub>2</sub> sections of MgO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> in air





# Slag Viscosity: Structural Viscosity Model

Modified Quasichemical Model

- Bond fraction (Silicate network structure)
- Activation energy of bond breaking reaction: Binary parameters + Association energy for  $M^+Al^{3+}$  replacing  $Si^{4+}$  in silicate network
- Prediction of multicomponent system (oxide and oxy-fluoride)
- Heterogeneous (solid + liquid): Einstein-Rosco equation

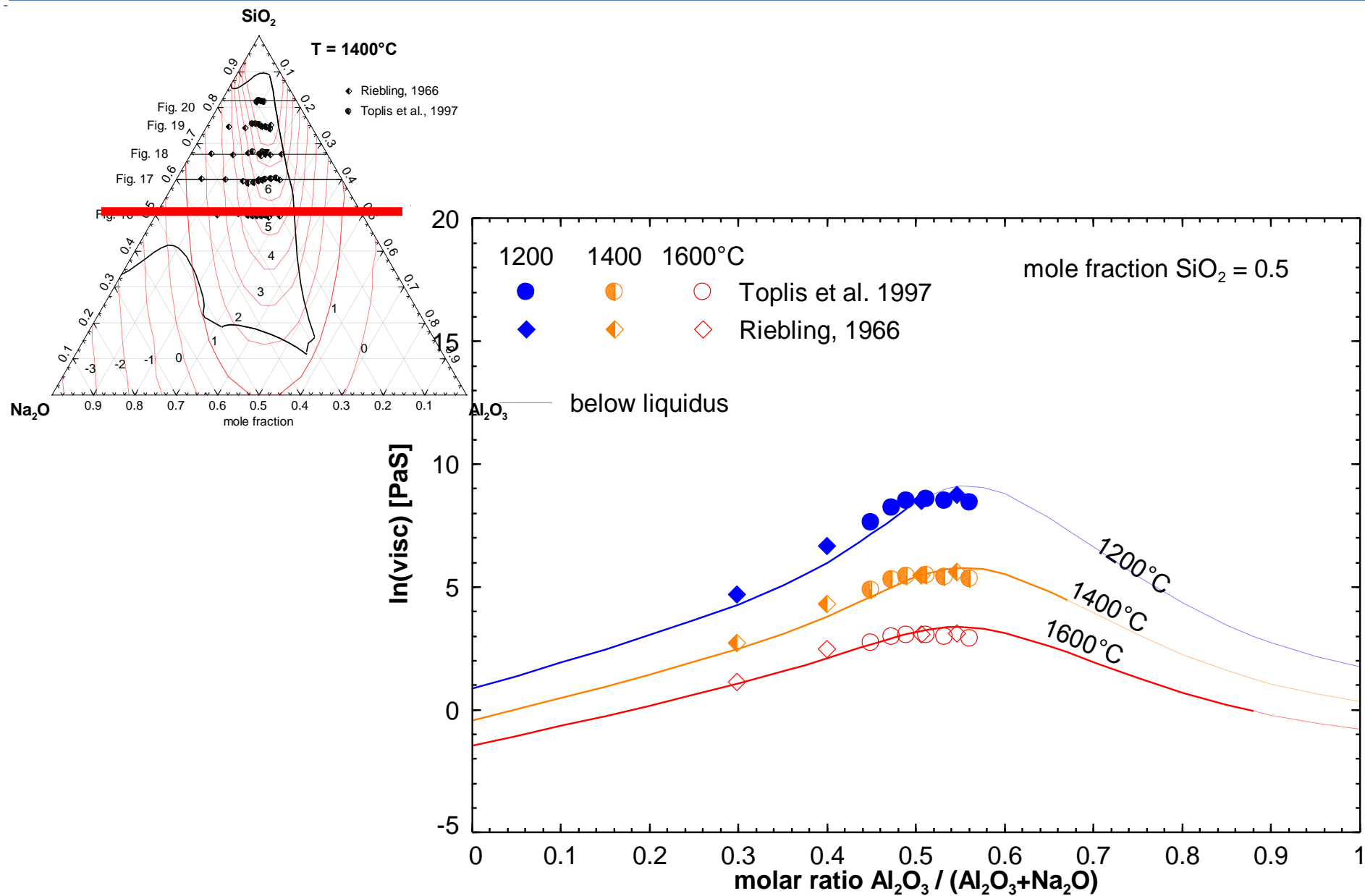
Database for molten slag

CaO-MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub>-MnO-TiO-TiO<sub>2</sub>-Na<sub>2</sub>O-K<sub>2</sub>O-Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-F (-PbO-NiO)

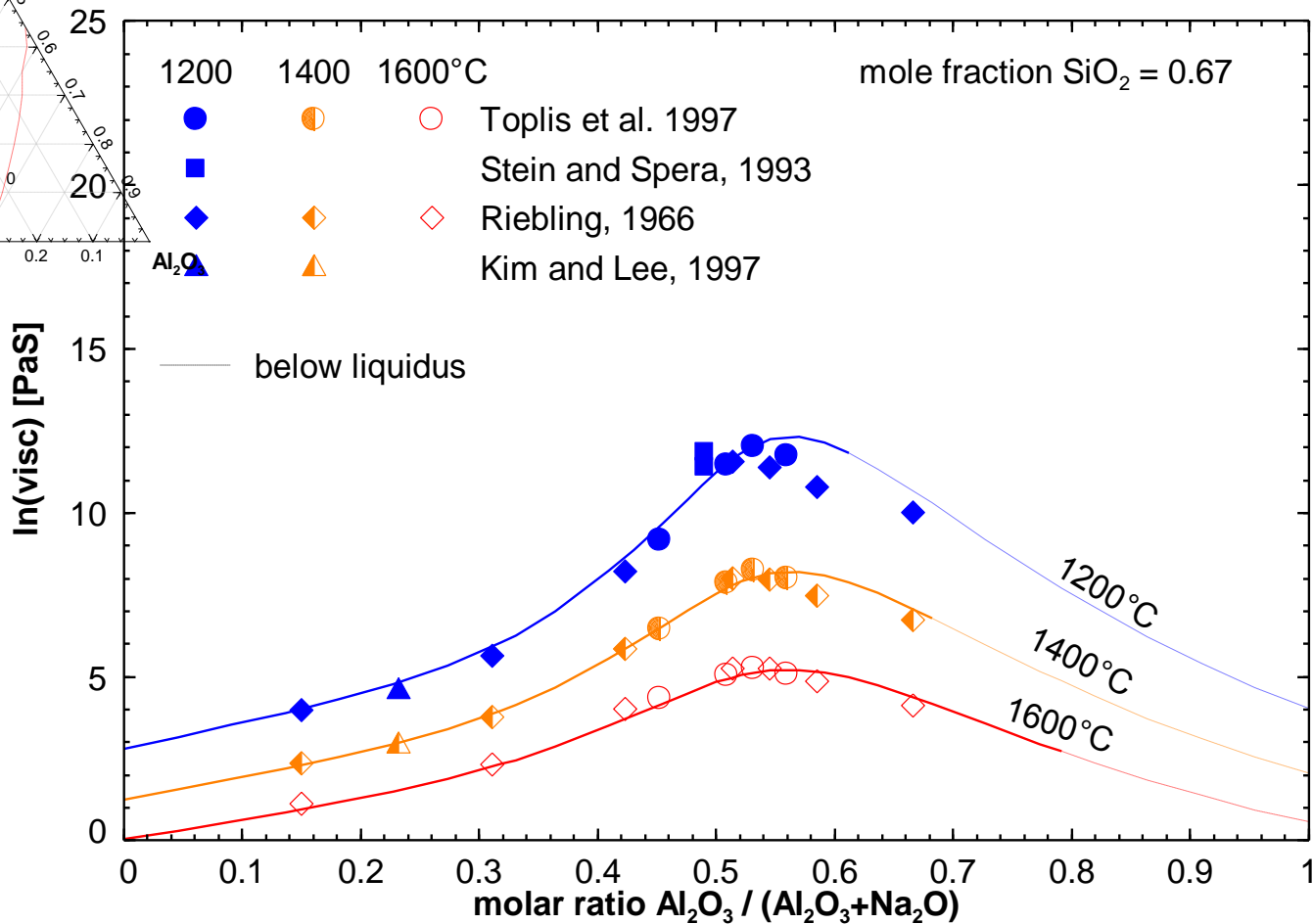
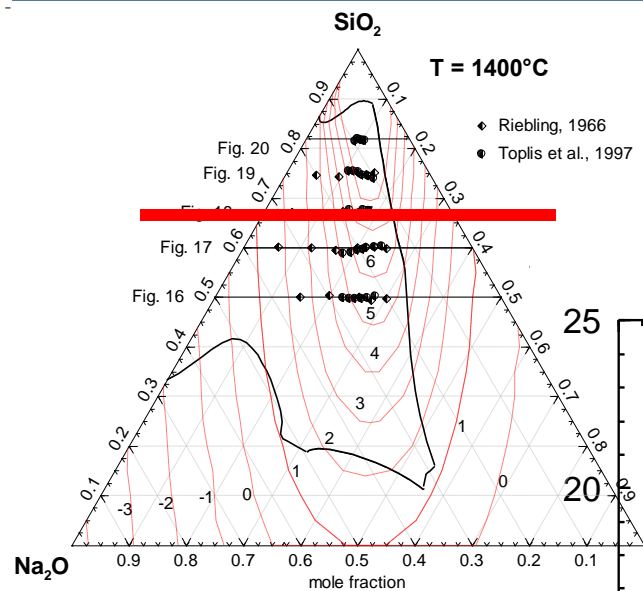
Database for glass (supercooled melt)

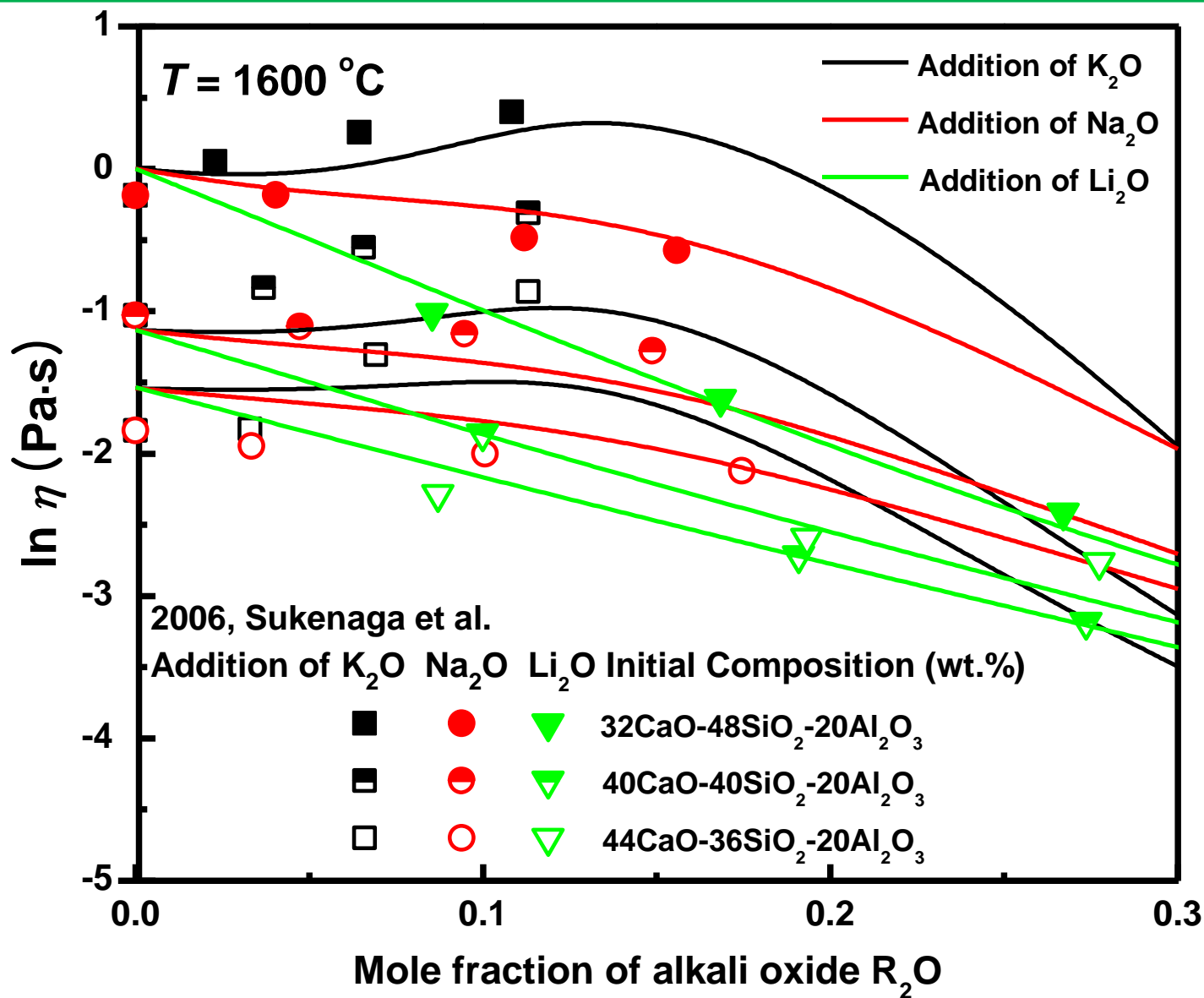
CaO-MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-K<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-PbO

# The Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system



# The $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system





# Viscosities of various systems

