Aalto University

CHEM-E6105
Thermodynamics of modeling and simulation

Lecture 2

Spring 2022

Non-ideal solutions & Thermodynamic solution models

Daniel Lindberg

Overview

- Ideal solution and regular solution
- Metals and alloys
  - Compound Energy Formalism
- Ionic solutions
  - Sublattice models
- Slags/liquid oxides
  - Associate model
  - Quasichemical model
- Quadruplet model

Solution phase

- Solutions are thermodynamic phases with varying compositions:
- Gas
- Supercritical fluids
- Liquid phase
  - Aqueous solutions
  - Organic liquids
  - Molten slags, molten salts, etc.
- Solid solutions
  - Alloys, minerals

For a binary system A-B we have for **each solution phase** at constant temperature

$$G_T = \underline{x_A{}^0G_A + x_B{}^0G_B} + \boxed{RT(x_A\ln x_A + x_B\ln x_B) + G^E}$$

G^{id}_{mix} **Excess Gibbs energy**

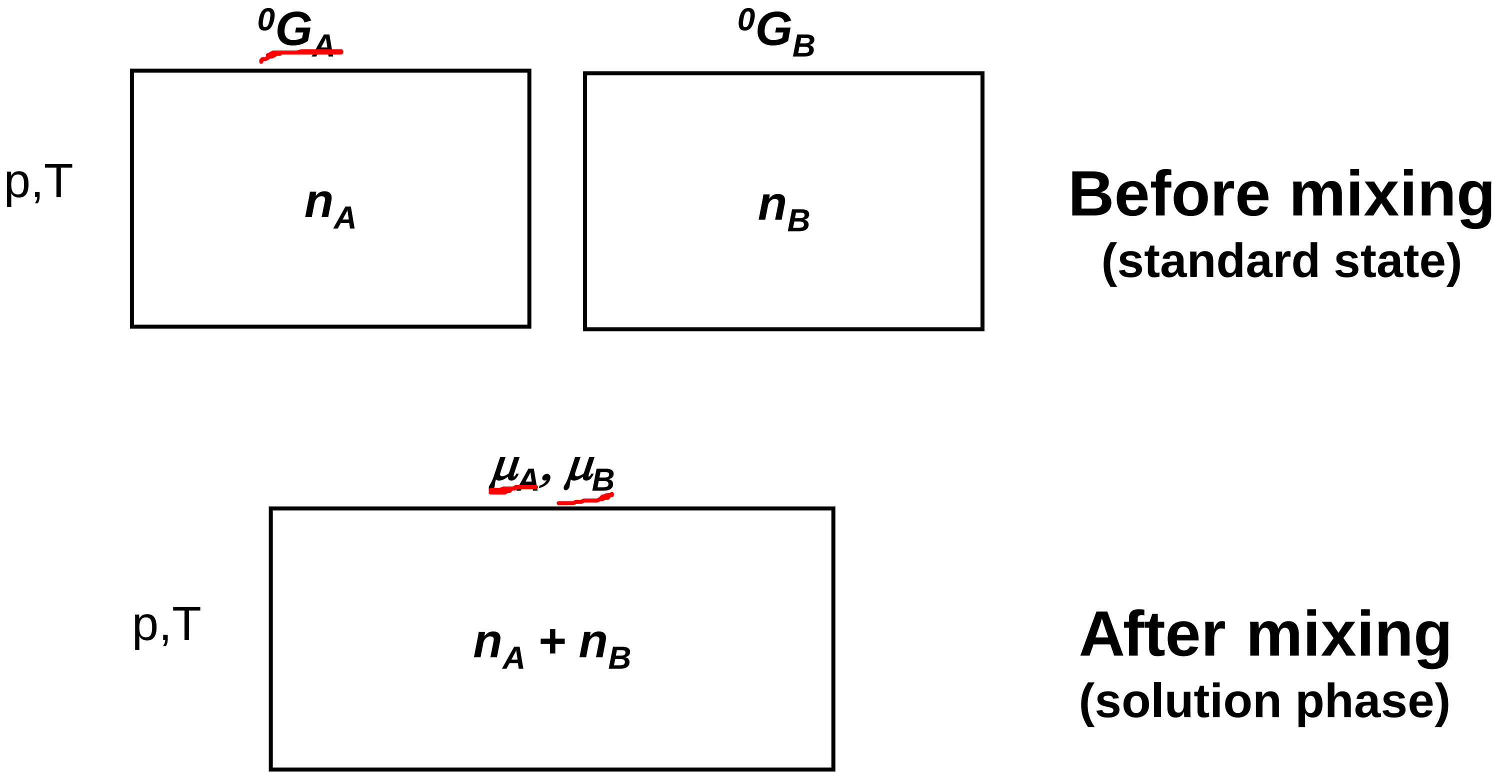
$G_{mix} = \underline{G^{id}_{mix}} + \boxed{G^E}$ **Gibbs energy of mixing**

^0G_A and ^0G_B are the Gibbs energies for **pure, unmixed A and B**

At equilibrium the sum of *G* for all phases present is at **minimum** and the *chemical potential* (partial Gibbs energy) for A and B is **equal** in all phases present at equilibrium

$$\mu_A = G'_A = x_A{}^oG_A + RTx_A\ln x_A + G^E_A$$

Illustation of mixing properties



${}^0G_A$ ${}^0G_B$

p,T n_A n_B

Before mixing

(standard state)

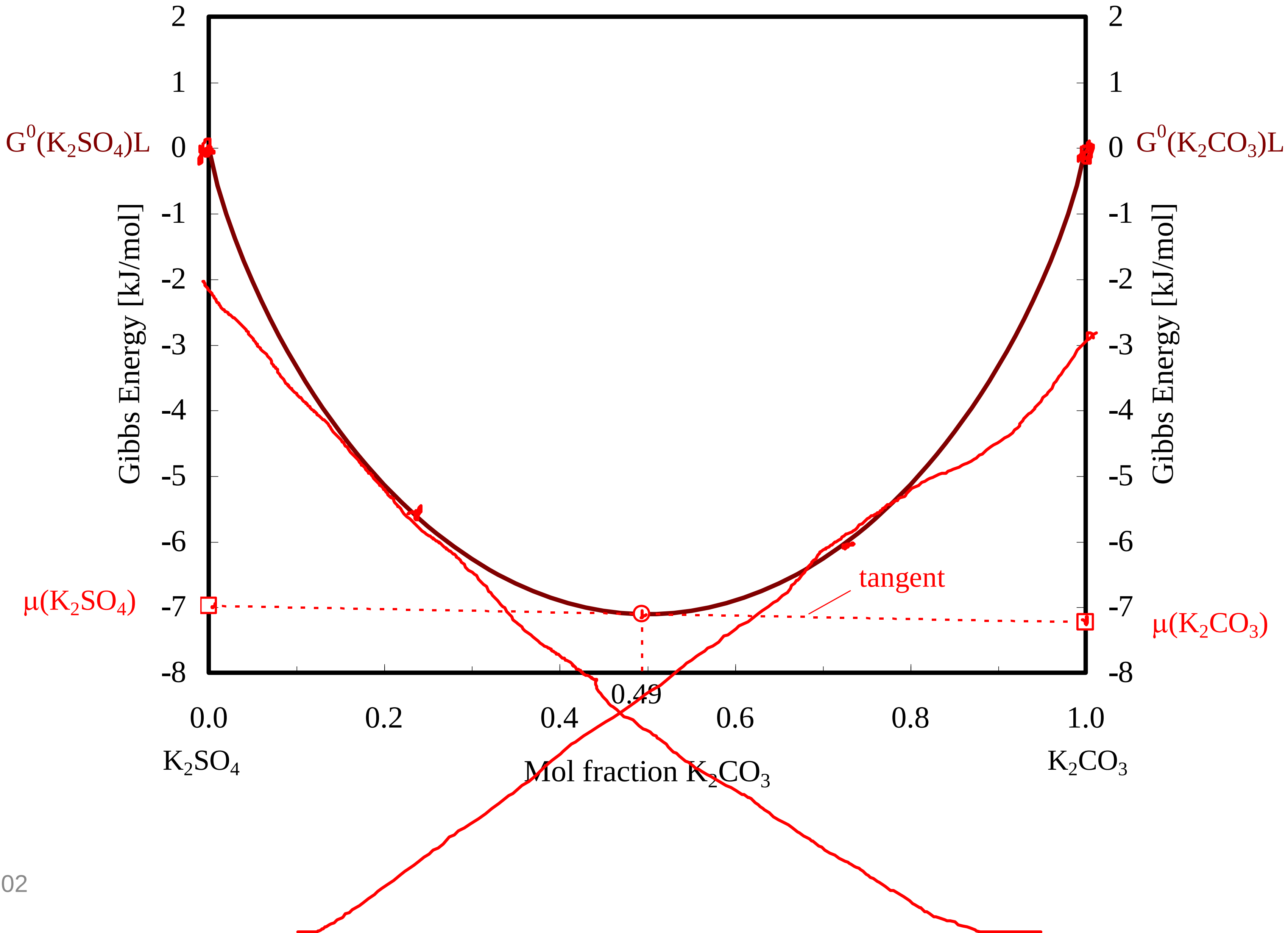
μ_A, μ_B

p,T $n_A + n_B$

After mixing

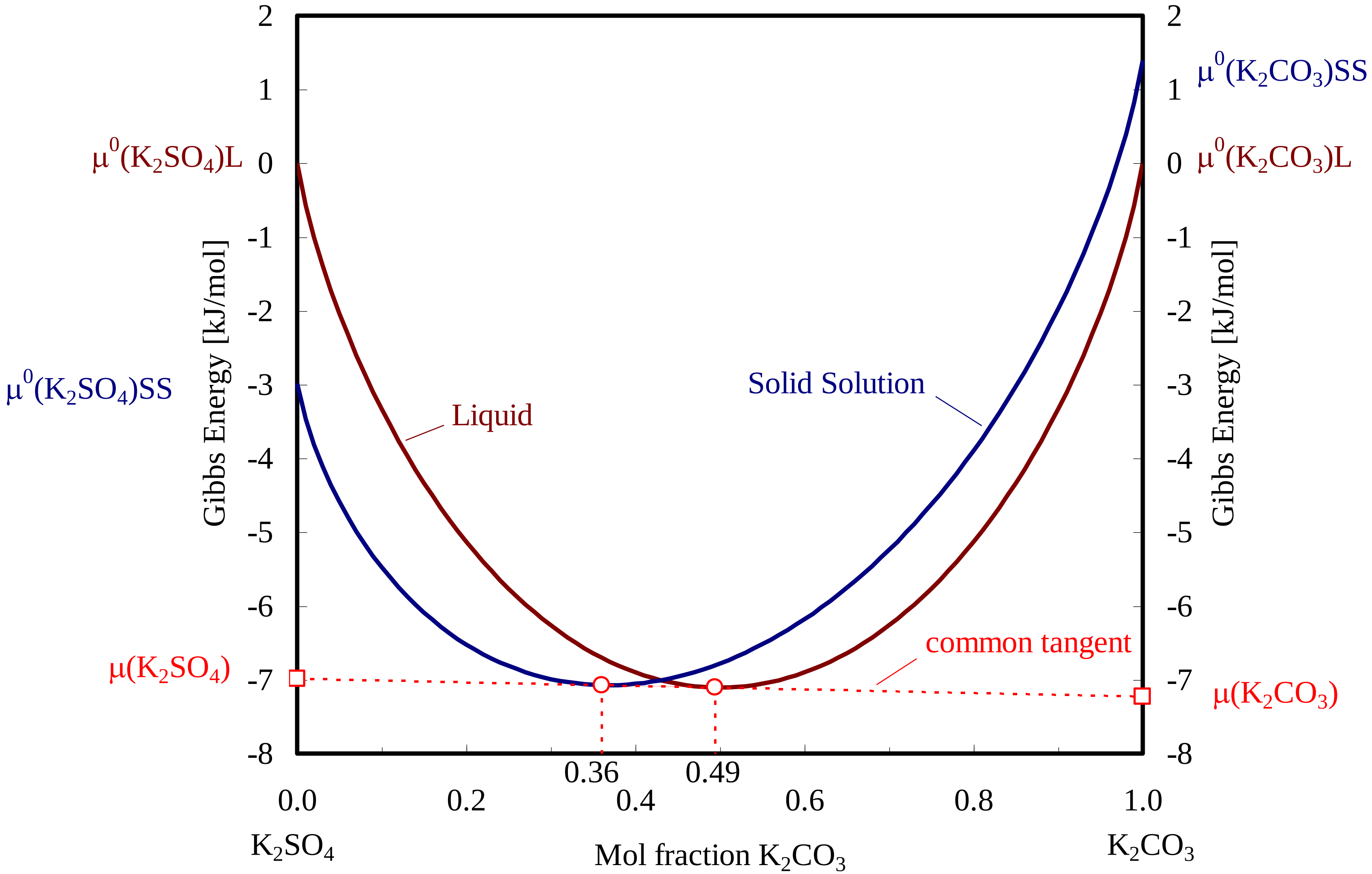
(solution phase)

K_2SO_4-K_2CO_3: Partial Gibbs Energy for liquid at 960°C
Reference State: K_2SO_4(l) and K_2CO_3(l)



ÅA/PCG/CMC/RB/2002

K_2SO_4-K_2CO_3: Total Gibbs Energy at 960°C
Reference State: $K_2SO_4(l)$ and $K_2CO_3(l)$



$\boldsymbol{G^E}$ is dependent on the physical properties of the solution
i.e. **interaction** between different atoms or molecular groups

The numerical value of $\boldsymbol{G^E}$ is dependent of the **solution model** used for the description of the phase

Thus, $\boldsymbol{G^E}$ is the quantity to be **modeled** as a function of phase composition and temperature

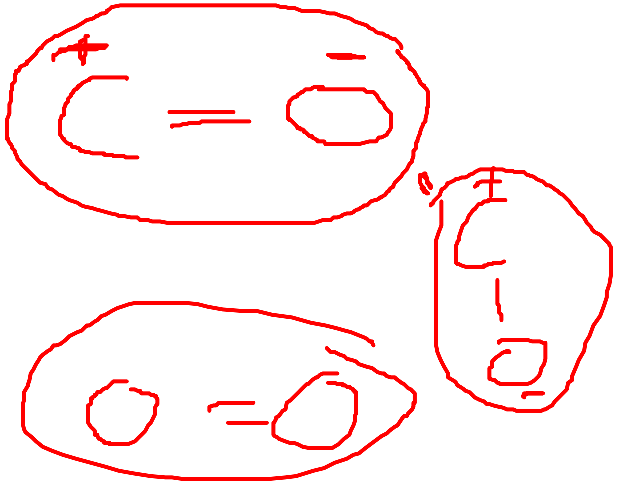
Solution phase

- Gases
  - Ideal gas: follows the ideal gas law
    - PV=nRT
    - $P_{tot} = \Sigma P_i$, $P_i = x_i \cdot P_{tot}$
    - $a_i = P_i / P_i°$
  - Real gas
    - Requires other equations of state for real gases
    - Largest deviations are observed for low T and high P
    - $a_i = f_i / P_i°$ (f = fugacity)

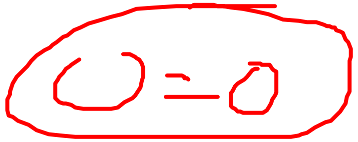
Solution phase

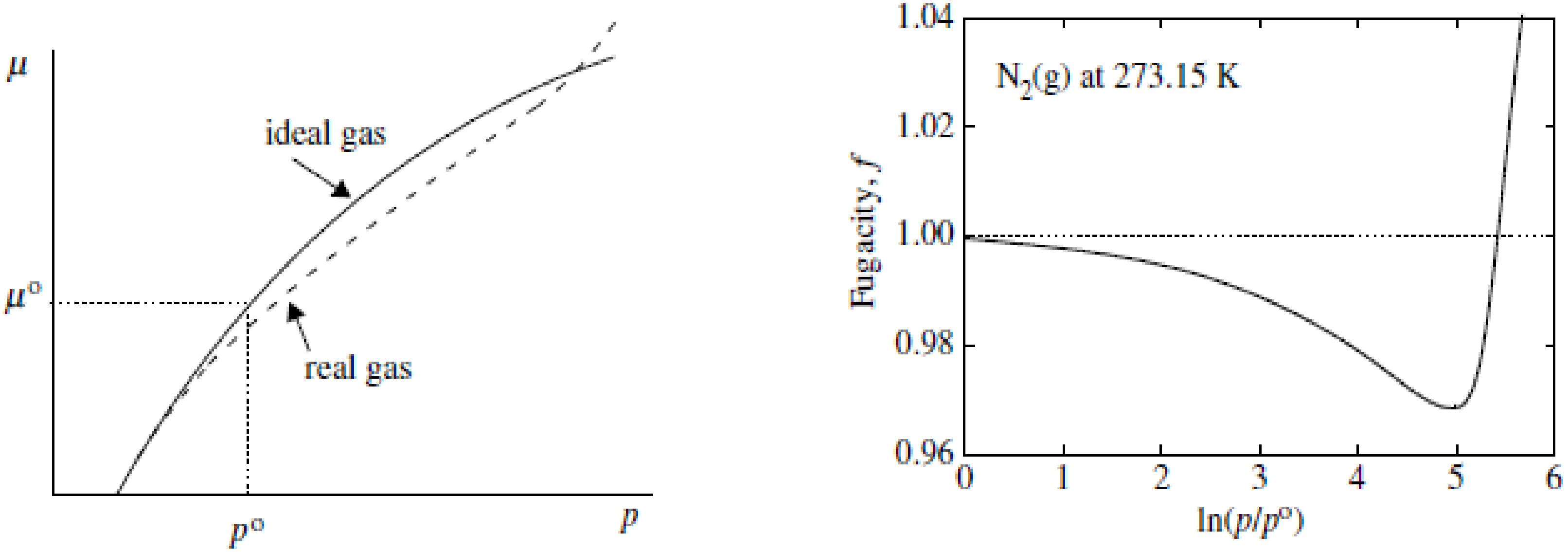
- Real gas

$$\left[p + a\left(\frac{n}{V}\right)^2\right](V - nb) = nRT$$



Example: van der Waal’s equation

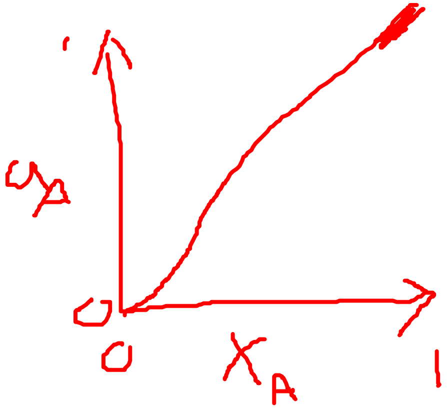




Deviations from ideality

Ideal solution

- A solution where the thermodynamic activity is proportional to its mole fraction
- Follows Raoult's law
- For A(l) + B(l) → A + B (liquid solution)



$\Delta V = 0$

$\Delta H_{mixing} = 0$

$S_{mixing} = \underline{-R(x_A \ln x_A + x_B \ln x_B)}$ (ideal entropy of mixing) $\underline{a = x}$

$\underline{G^{ideal}_{mixing}} = \underbrace{\Delta H_{mixing}}_{=0} \underline{-TS_{mixing}} = \underline{RT(x_A \ln x_A + x_B \ln x_B)}$

$a = \gamma \cdot x$

$$\underline{G_m = \sum_i \underline{x_i G_i^o} + RT \sum_i x_i \ln x_i}$$

Regular solution

- Simplest non-ideal solution model
- For A(l) + B(l) → A + B (liquid solution)

$$\Delta H_{mixing} = \Omega x_A x_B$$

$$\Delta S_{mixing} = -R(x_A \ln x_A + x_B \ln x_B) \text{ (ideal entropy of mixing)}$$

$$\Delta G_{mixing} = \Delta H_{mixing} - T\Delta S_{mixing} =$$

$$\Omega x_A x_B + RT(x_A \ln x_A + x_B \ln x_B)$$

Regular solution

$$G_m = \sum_i x_i G_i^o + RT\sum_i x_i \ln x_i + \sum_i \sum_{j>i} x_i x_j \Omega_{ij}$$

Ideal mixing Excess mixing

Regular solution

- often expanded into simple power series
  sub-regular, sub-sub-regular....

$\omega_0 = a + bT \ldots$

$$G^E = \underline{x_1x_2}(\underline{\omega_0} + \omega_1 x_2 + \omega_2 x_2^2 + \ldots)$$

- coefficients can be made temperature dependent

- correlation between coefficients

- terms have maximum value at $x_2 = 1$, zero at $x_2 = 0$

- The model works well for many non-polar molecular solutions and simple binary ionic solutions

- For statistical explanation of regular solution model, see Gaskell Chap. 9.10

Regular solution

- Redlich-Kister expansion

$$G^E = \boxed{x_1 x_2 (L_0} + L_1(x_2 - x_1) + L_2(x_2 - x_1)^2 + \;....)$$

- coefficients can be made temperature dependent

- decreased correlation between coefficients:
  $(x_2 - x_1) = 0$ at $x_1 = x_2 = 0.5$

- terms do not have maximum value at the same composition

$$\underline{G_m = \underline{\sum_i x_i G_i^o} + RT \underline{\sum_i x_i \ln x_i} + \underline{\sum_i \sum_{j>i} x_i x_j \sum_n \Omega_{ij}^n (x_i - x_j)^n}}$$

Regular solution

Negative deviation =
Liq. more stable

Ideal liquid

Positive deviation =
Liq. less stable

Positive deviation =
ss less stable

Ideal solid solution

Negative deviation =
ss more stable

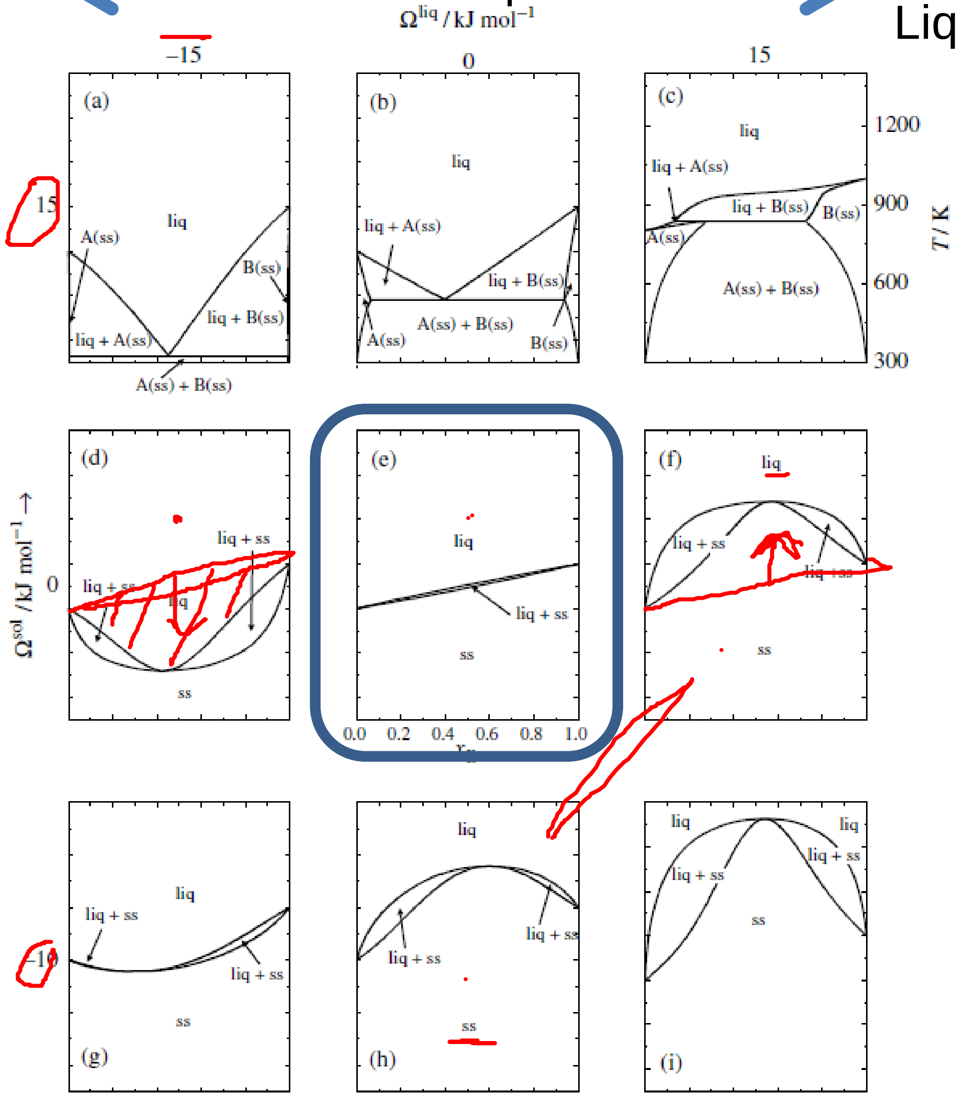


Figure 4.10 (a)–(i) Phase diagrams of the hypothetical binary system A–B consisting of regular solid and liquid solution phases for selected combinations of Ω^{liq} and Ω^{sol}. The entropy of fusion of compounds A and B is 10 J K^{-1} mol^{-1} while the melting temperatures are 800 and 1000 K.

$G_i = {}^{\circ}G_i + \underline{RT \ln a_i}$

μ_i

Excess functions

- Gibbs energy of a dissolved substance i is divided into two parts in the following way:

$$G_i = \boxed{{}^{\circ}G_i} + RT \ln x_i + RT \ln \gamma_i,$$

$$\ln(\gamma \cdot x) = \ln \gamma + \ln x$$

where $a_i \equiv \gamma_i \times x_i$ and the variable γ_i is the *activity coefficient* of i in the solution.

- G-function for the total system can thus be written as:

$$G = \Sigma\, x_i G_i = \Sigma\, x_i {}^{\circ}G_i + RT\, \Sigma (x_i \ln x_i) + RT\, \Sigma (x_i \ln \gamma_i).$$

- Its third term is called Gibbs energy *excess function* ${}^{Ex}G$ (of the solution), and each of its term is called excess Gibbs energy ${}^{Ex}G_i$ of substance i . We can also summarise:

$${}^{Ex}G = RT\, \Sigma x_i \ln \gamma_i. = \Omega\, x_A x_B$$

Industrial melts

Industrial process	Melt composition	Role of melt	Temperature
Biomass/waste combustion /gasification	Alkali salt mixtures and complex silicates	Facilitates increased corrosion, deposition and agglomeration in boilers and furnaces	<400 °C to >1000 °C
Black liquor combustion	Sodium salt mixtures (smelt)	Forms smelt bed for sulfur reduction, can cause deposition and corrosion	500-1200 °C
Batteries and fuel cells	Molten carbonates	Electrolyte	>650 °C
Flash smelting	Matte (liquid metal sulfide) and oxide slag	Liquid phase captures impurities from copper/nickel ore	>1000 °C
Aluminum electrolysis	Cryolite (NaF-AlF_3) liquid and liquid aluminum	Cryolite dissolves Al_2O_3 and acts as electrolyte, liquid aluminum is a product	~1000 °C
Iron- and steelmaking (Blast furnaces & BOF)	Liquid metal and silicate/oxide slags	Liquid metal is a product, slag captures impurities from liquid iron and steel	~1000 °C-2000 °C
Cement manufacturing	Ca-rich silicate liquid	Acts as solvent and reaction medium in the cement kiln	>1000 °C
Glass manufacturing	Oxide/silicate mixtures	Glass forms from a cooling liquid phase	500-1500 °C
Ionic liquids	Complex organic salts	Reaction medium, solvent, etc.	<100°C

Different type of phases

- Metals and alloys
  - Ex. Fe-Cu
- Simple ionic phases
  - Ex. KCl-NaCl, K^+,Na^+//Cl^-,SO_4^{2-}
- Polymeric oxide phases
  - Ex. SiO_2-P_2O_5-B_2O_3(+metal oxides)
  - May also show ionic character and strong short-range ordering in the liquid phase
- Sulfides
  - May show ionic, metallic or covalent characteristics depending on the metal sulfide

Metals and alloys

- The so-called Calphad community (Calculations of Phase Diagrams) studies mainly phase equilibria and thermodynamic properties of metals and alloys with focus on material properties

  →

  Thermodynamic models for the liquid phase are often simple compared to solid phases

Simplified binary atomic structures

Substitutional

A A B A B B A B
B A B B A B A A
B B A A B A B A
A B A B B A B B
A B A B B A A A

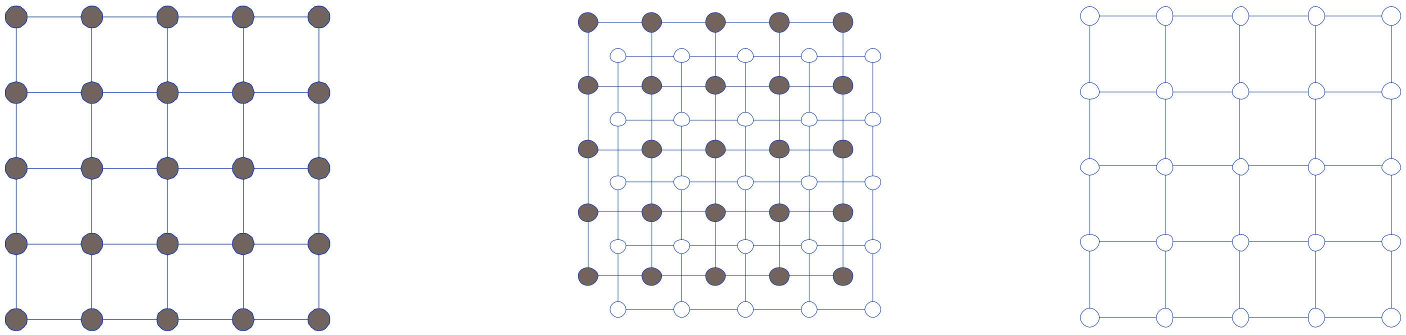
With vacancies

A A B A B   A B
B A   B A B A A
B B A A B   B A
A B A B   A B B
A B A B B A A A

Interstitial

A A B A B B A B
B A B B A B A A
B B A A B A B A
A B A B B A B B
A B A B B A A A

Sublattice structures



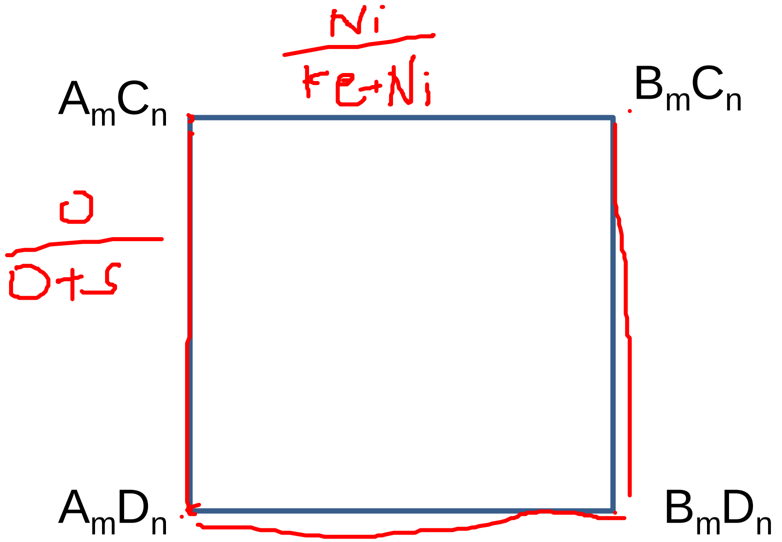
Metals and alloys

- **Compound Energy Formalism (CEF)** is a mathematical description for the thermodynamic properties of phases with several sublattices
- Often used for complicated metallic phases, but also solid solutions of oxides, sulfides, ionic salts
- Assume a reciprocal phase $(A,B)_m(C,D)_n$

$(Fe,Ni)_1(O,S)_1$

A = Fe
B = Ni

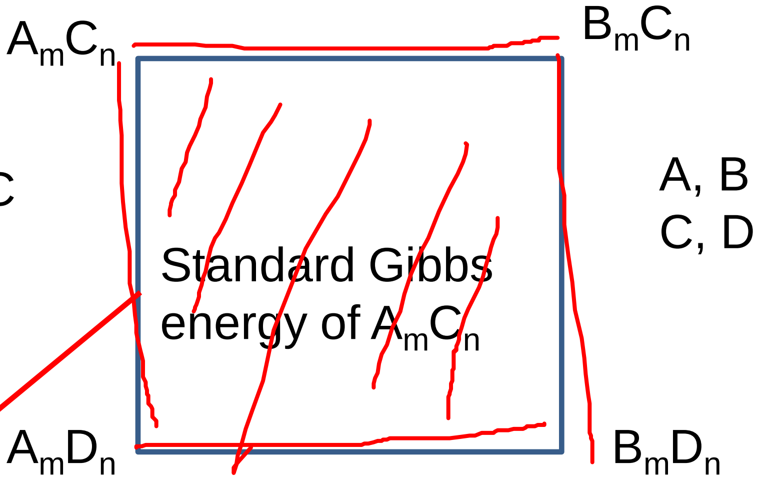
C = O
D = S



A, B on sublattice *S*
C, D on sublattice *T*

Compound Energy Formalism

$$y_A^S = \frac{A}{A+B}$$



Standard Gibbs energy of A_mC_n

A, B on sublattice *S*
C, D on sublattice *T*

Site fraction of C on sublattice T

Site fraction of A on sublattice S

$$G_m = y_A^S y_C^T G^\circ_{A:C} + y_A^S y_D^T G^\circ_{A:D} + y_B^S y_C^T G^\circ_{B:C} + y_B^S y_D^T G^\circ_{B:D}$$
$$+ (mRT(y_A^S \ln y_A^S + y_B^S \ln y_B^S) + nRT(y_C^T \ln y_C^T + y_D^T \ln y_D^T)) + G^E$$

Ideal mixing on *S* sublattice

Ideal mixing on *T* sublattice

Excess term

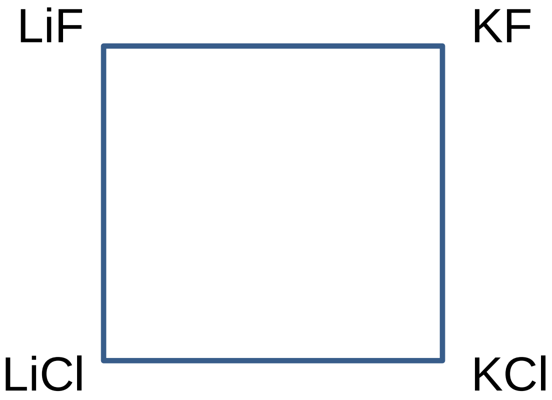
$$G^E = y_A^S y_B^S y_C^T L_{A,B:C} + y_A^S y_B^S y_D^T L_{A,B:D} + y_A^S y_C^T y_D^T L_{A:C,D} + y_B^S y_C^T y_D^T L_{B:C,D} + y_A^S y_B^S y_C^T y_D^T L_{A,B:C,D}$$

Binary interactions

Reciprocal term

Ionic solutions

- Models for ionic phases consider the physical nature by assuming cations mix on a cationic sublattice and anions on an anionic sublattice
- Sublattice assumption for liquid phase is appropriate due to cation-anion interactions



LiF

KF

LiCl

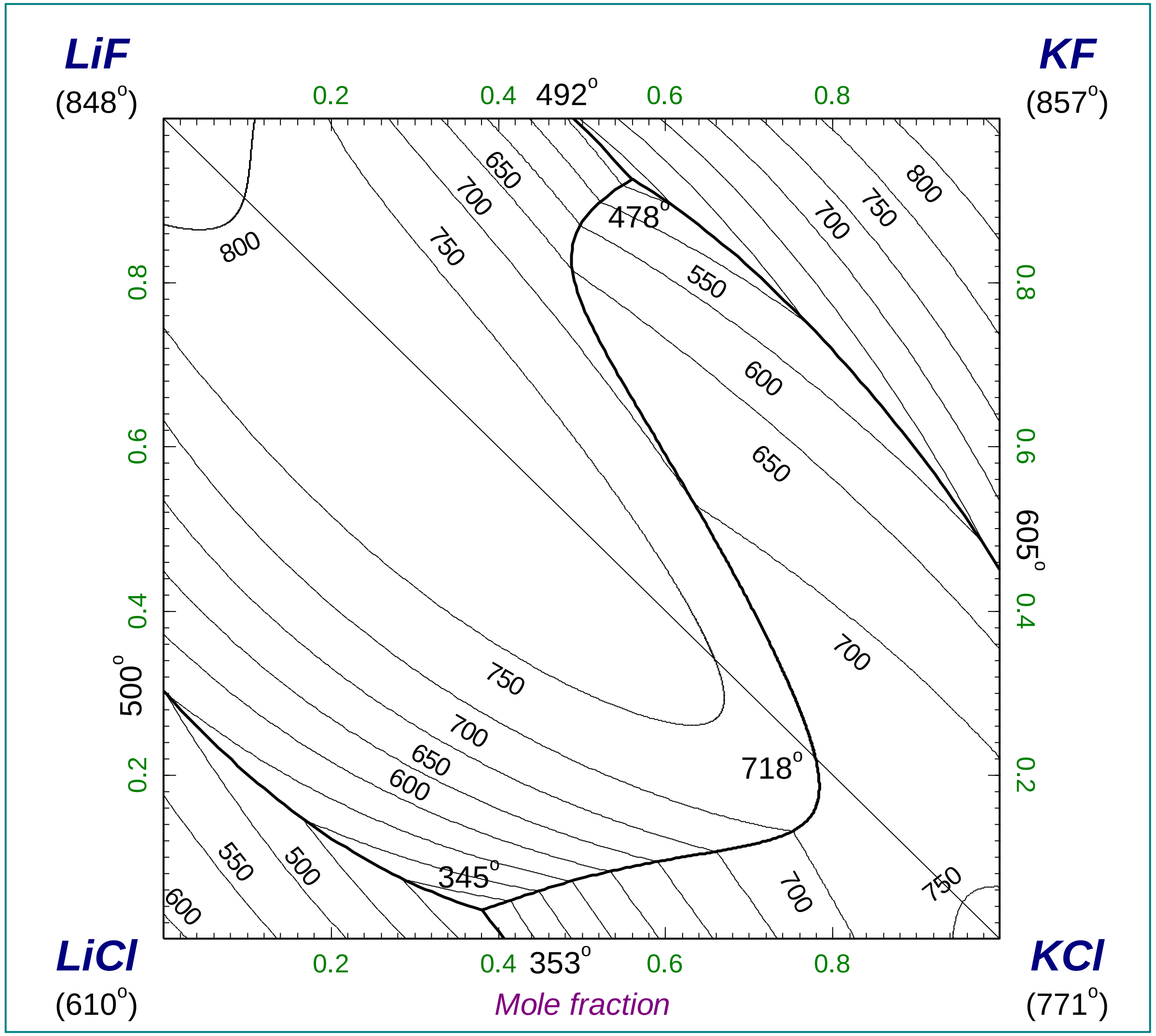
KCl

Na^+, K^+ on cationic sublattice
Cl^-, F^- on anionic sublattice

$$G_m = x_A^{cation} x_X^{anion} G_{AX}^{\circ} + x_A^{cation} x_Y^{anion} G_{AY}^{\circ} + x_B^{cation} x_X^{anion} G_{BX}^{\circ} + x_B^{cation} x_Y^{anion} G_{BY}^{\circ} + RT(x_A^{cation} \ln(x_A^{cation}) + x_B^{cation} \ln(x_B^{cation})) + RT(x_X^{anion} \ln(x_X^{anion}) + x_Y^{anion} \ln(x_Y^{anion})) + G^E.$$

Reciprocal molten salt system Li,K/F,Cl

- Liquidus projection



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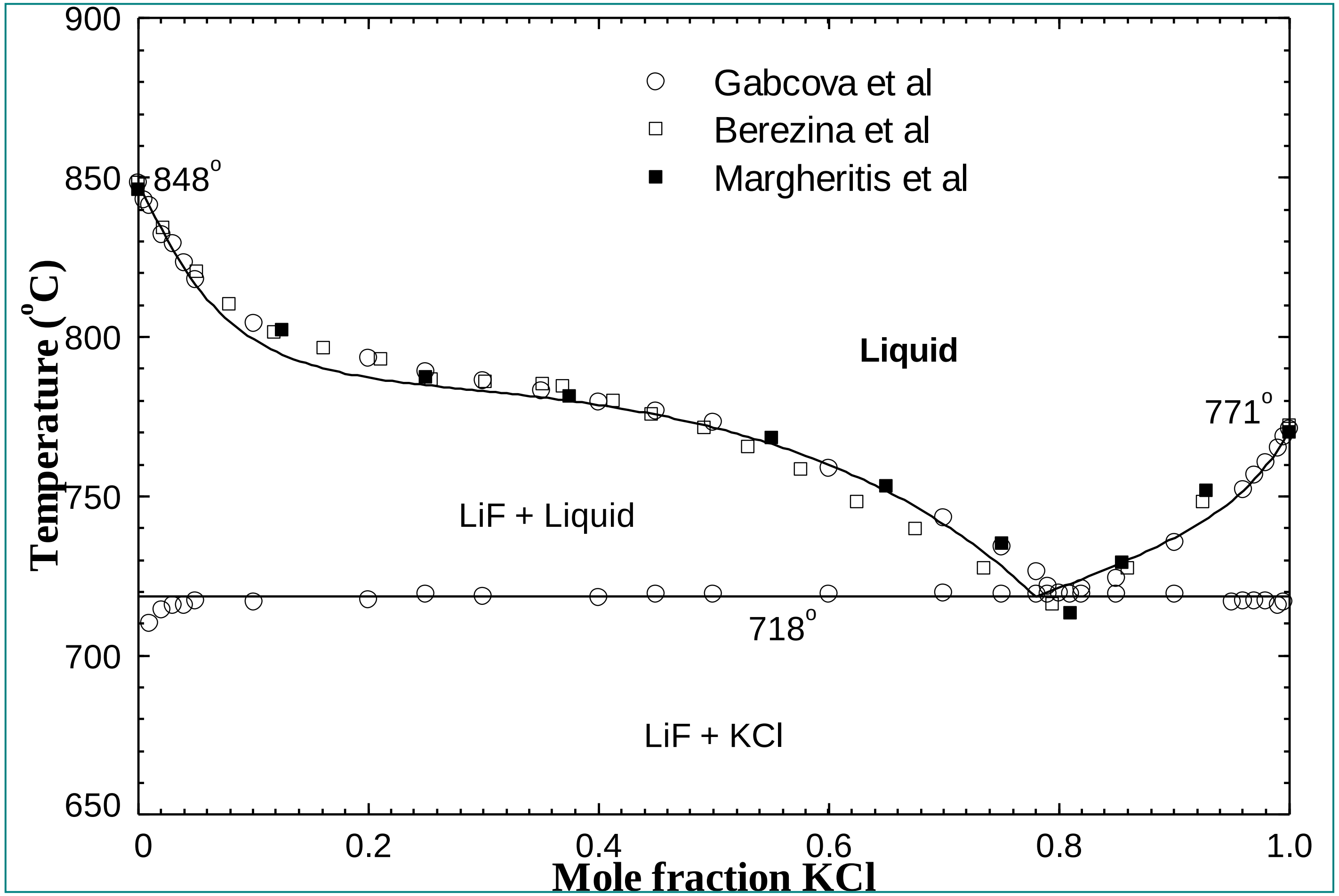
Section of the preceding phase diagram along the LiF-KCl diagonal



- A tendency to de-mixing (immiscibility) is evident.
- This is typical of reciprocal salt systems, many of which exhibit an actual miscibility gap oriented along one diagonal.

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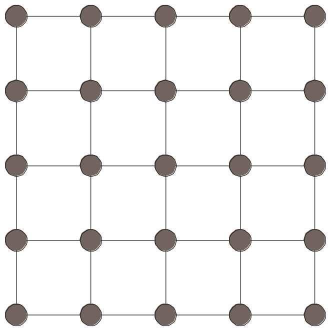
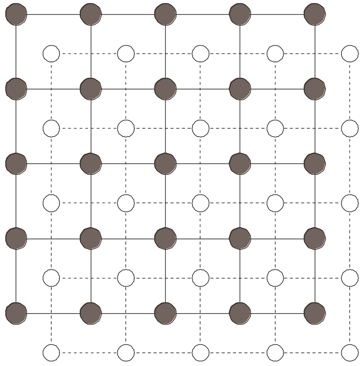
Ionic sublattice model

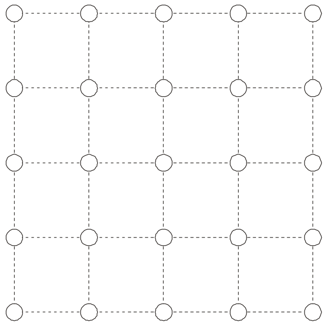
$(Na^{+},K^{+})_x(CO_3^{=},SO_4^{=},S^{=},Cl^{-})_y$



Cationic sublattice

Na^{+}, K^{+}





Anionic sublattice

$CO_3^{=},SO_4^{=},S^{=},Cl^{-}$

Equivalents on cationic sublattice = Equivalents on anionic sublattice

Equivalent cationic fraction =

$Y_{Na}=q_{Na}n_{Na}/(q_{Na}n_{Na}+q_{K}n_{K})$

Equivalent anionic fraction =

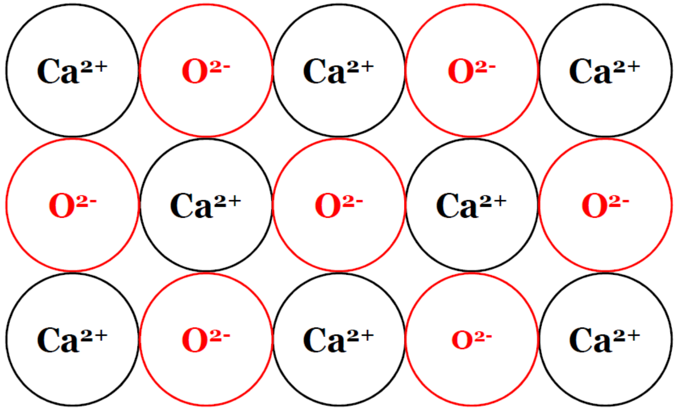
$Y_{CO3=}q_{CO3}n_{CO3}/(q_{CO3}n_{CO3}+q_{SO4}n_{SO4}+ q_{S}n_{S}+q_{Cl}n_{Cl})$

q_i = absolute ionic charge of ***i***, n_i = number of molesof ***i*** in solution

PELTON, A.D. A database and sublattice model for molten salts. CALPHAD: Comput. Coupling Phase Diagrams Thermochem. 1988, 12(2), 127-142.

Slags/liquid oxides

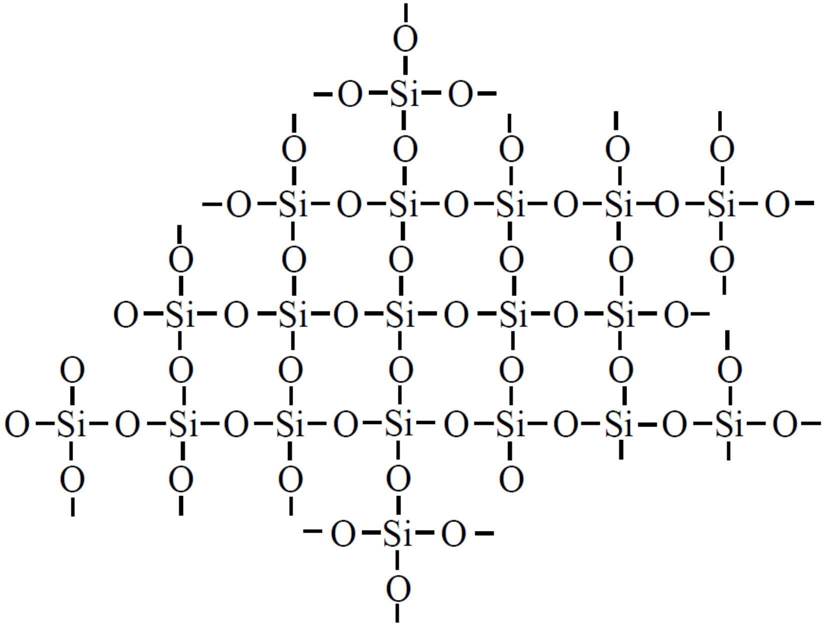
Ionic (“Basic”) Oxides



CaO, MgO, FeO, MnO, ...

Na_2O, K_2O, ...

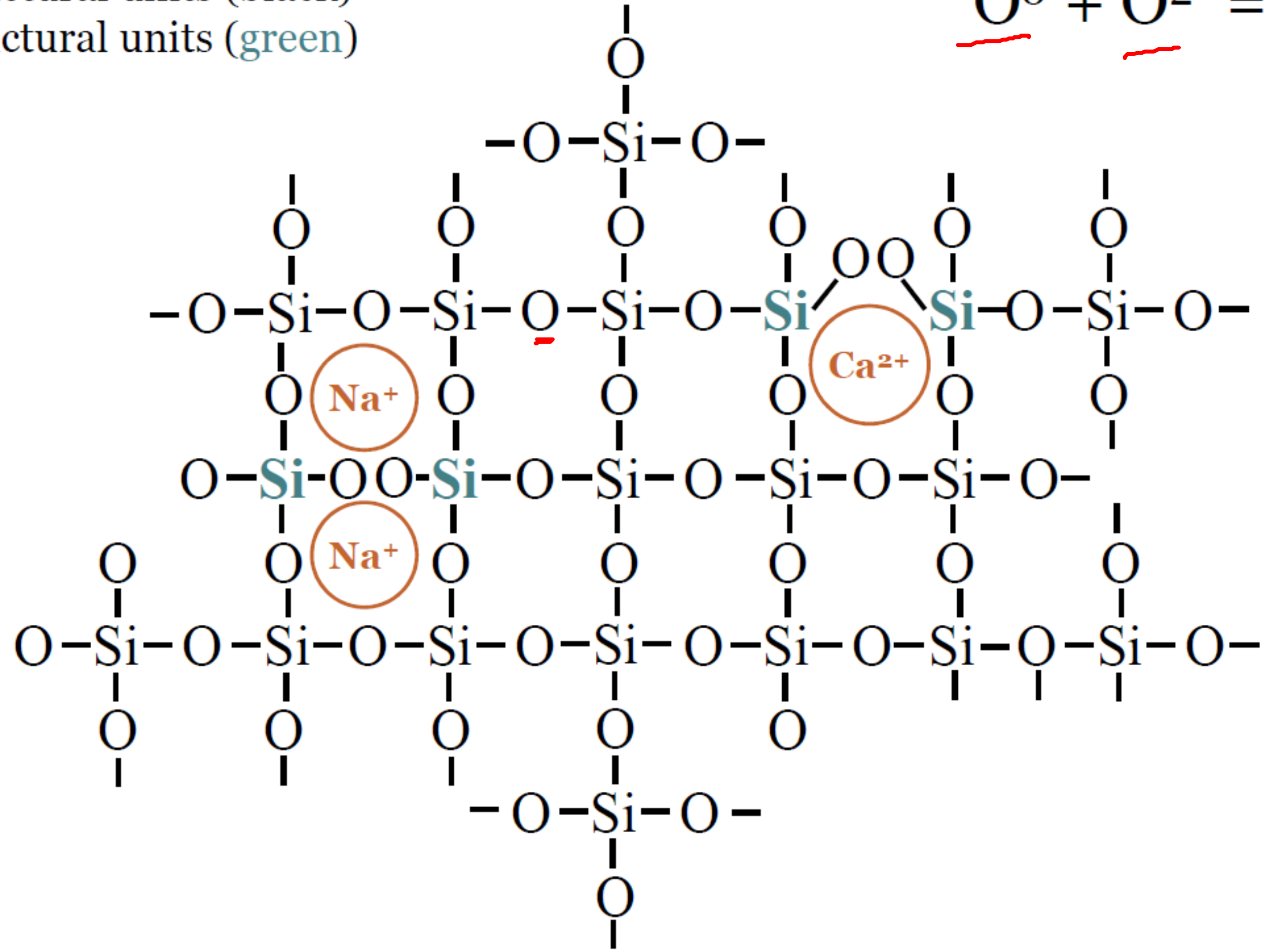
Structure of SiO_2



Network Modification by Basic Oxides

Q4 structural units (black)
Q3 structural units (green)

$$O^0 + O^{2-} = 2\ O^-$$



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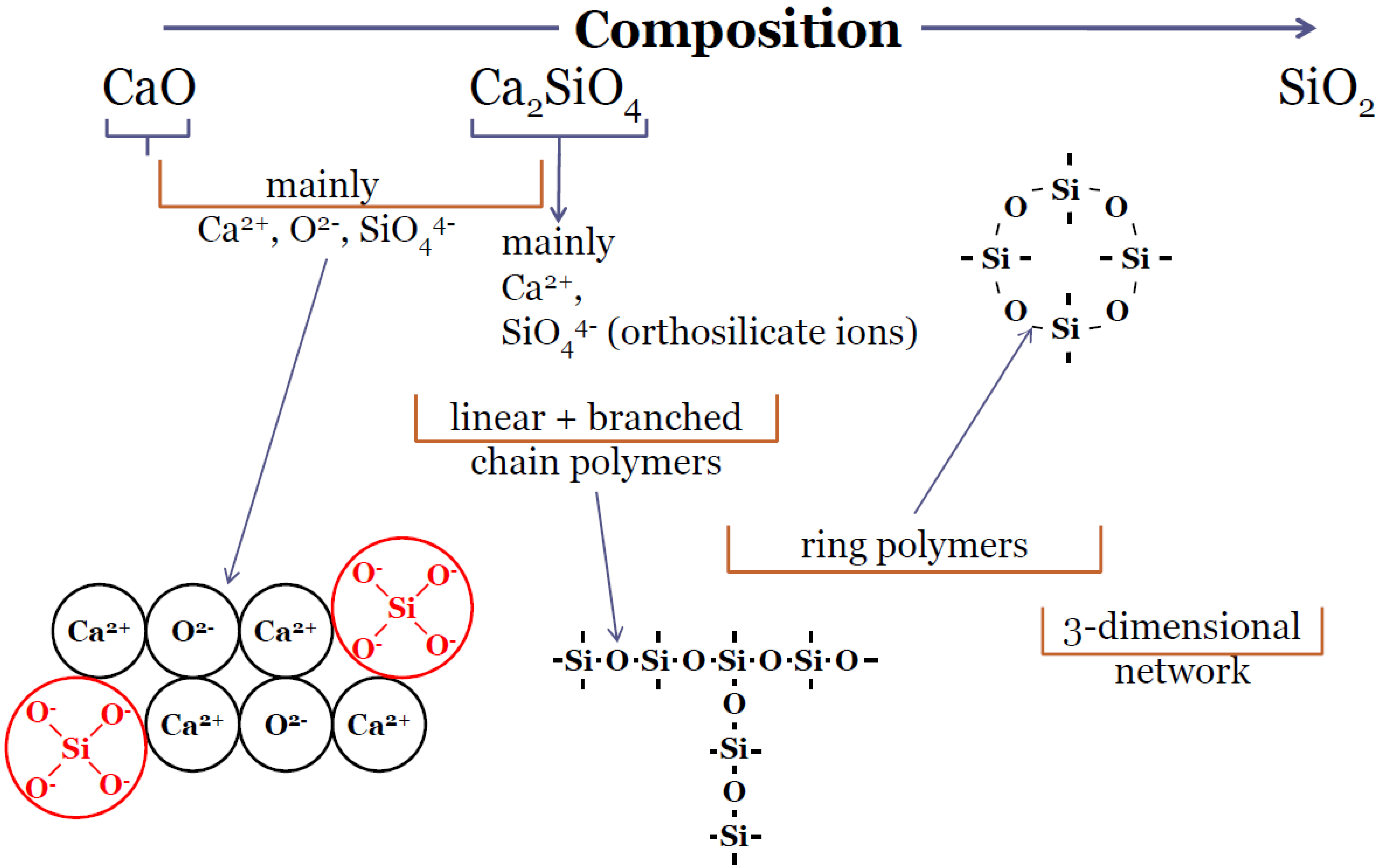
Structure of CaO-SiO_2 Liquid Solutions



Composition

CaO

Ca_2SiO_4

SiO_2

mainly

Ca^{2+}, O^{2-}, SiO_4^{4-}

mainly

Ca^{2+},

SiO_4^{4-} (orthosilicate ions)

linear + branched chain polymers

ring polymers

3-dimensional network

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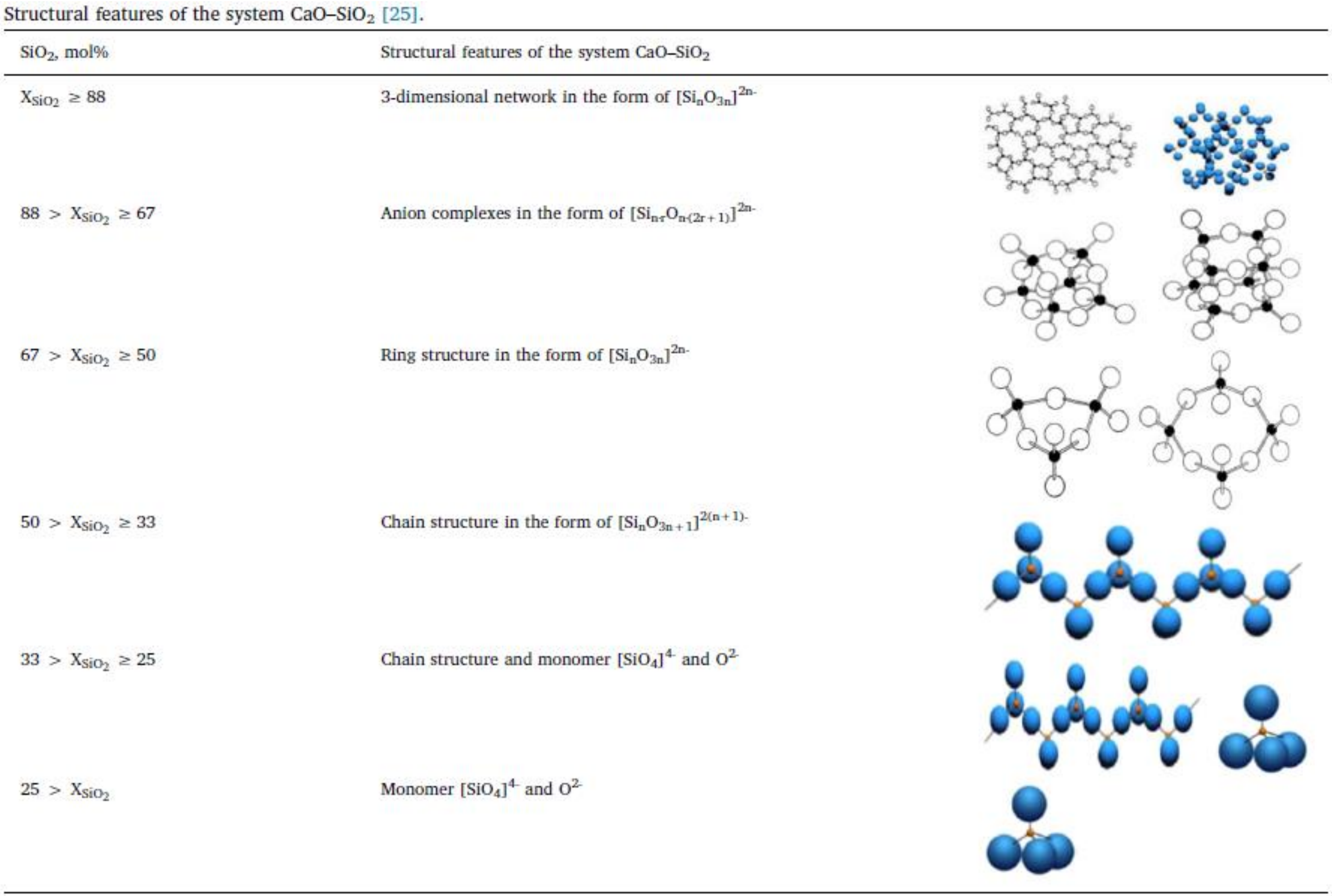
Structural features of the CaO-SiO_2 system



Structural features of the system CaO–SiO_2 [25].

SiO_2, mol%	Structural features of the system CaO–SiO_2
$X_{SiO_2} \geq 88$	3-dimensional network in the form of $[Si_nO_{3n}]^{2n-}$
$88 > X_{SiO_2} \geq 67$	Anion complexes in the form of $[Si_{n-r}O_{n-(2r+1)}]^{2n-}$
$67 > X_{SiO_2} \geq 50$	Ring structure in the form of $[Si_nO_{3n}]^{2n-}$
$50 > X_{SiO_2} \geq 33$	Chain structure in the form of $[Si_nO_{3n+1}]^{2(n+1)-}$
$33 > X_{SiO_2} \geq 25$	Chain structure and monomer $[SiO_4]^{4-}$ and O^{2-}
$25 > X_{SiO_2}$	Monomer $[SiO_4]^{4-}$ and O^{2-}

Slags/liquid oxides

- Several types of models are used for liquid oxides
    - Quasichemical model (Factsage, CRCT Montreal)
    - Associate model (MTdata, Mtox, NPL)
    - Reciprocal Ionic models (Thermo-calc)
    - Cell model

- Quasichemical model, associate model, and cell model consider short-range ordering

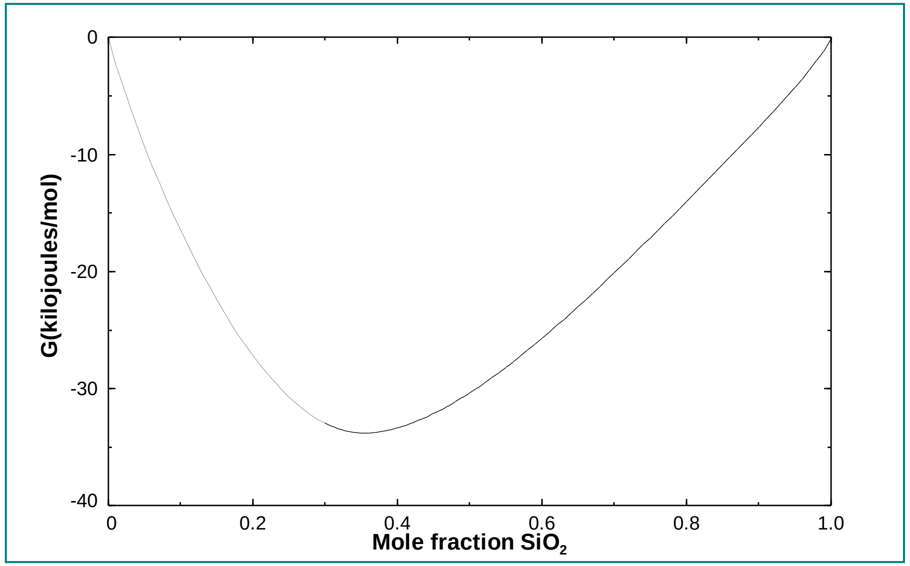
Associate Models

- Model the MgO-SiO_2 binary liquid assuming MgO, SiO_2 and Mg_2SiO_4 «molecules»

$$2\,\underline{MgO} + \underline{SiO_2} = \underline{Mg_2SiO_4} \quad ; \Delta G^o$$

$$K = \frac{X_{Mg_2SiO_4}}{X_{MgO}^2 X_{SiO_2}} = \exp\left(\frac{-\Delta G^o}{RT}\right)$$

- With the model parameter $\Delta G° < 0$, one can reproduce the Gibbs energy of the binary liquid reasonably well:



Gibbs energy of liquid MgO-SiO_2 solutions

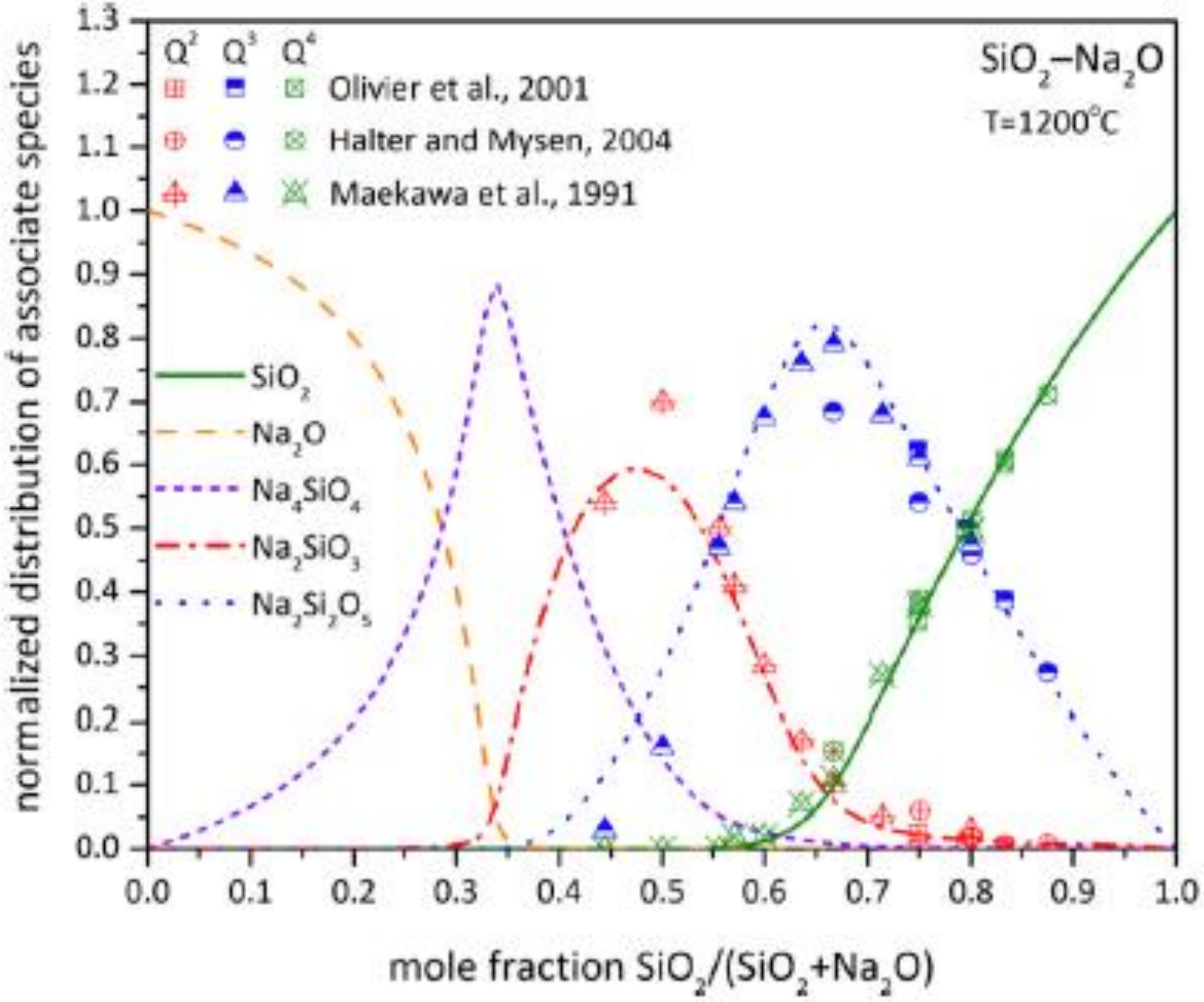


Fig. 2. Q-species distribution as calculated from the non-ideal associate model together with experimental information [41–43] in the system SiO_2–Na_2O [32].

Reciprocal Ionic Liquid Model

(M. Hillert, B. Jansson, B. Sundman, J. Ågren)

- Ca^{2+} and Mg^{2+} randomly distributed on cationic sublattice
- O^{2-}, $(SiO_4)^{4-}$ and neutral SiO_2 species randomly distributed on anionic sublattice
- An equilibrium is established:

$$SiO_2^0 + 2O^{2-} = SiO_4^{4-}$$

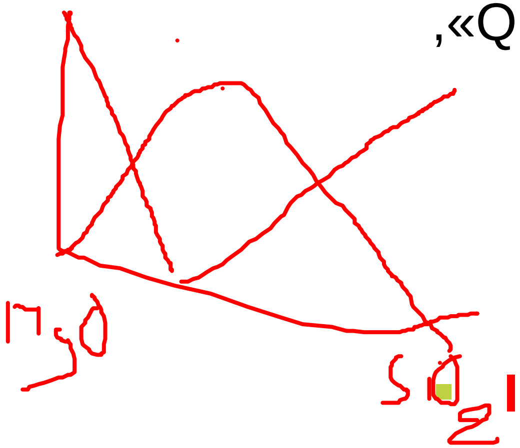
$$\Delta G^0 < 0$$

(Very similar to: $O^0 + O^{2-} = 2\ O^-$)

- In basic melts mainly Ca^{2+}, Mg^{2+}, O^{2-}, $(SiO_4)^{4-}$ **randomly** distributed on two sublattices.

Short-range-ordering is neglected.

Modified Quasichemical Model



„«Quasichemical» reaction among second-nearest-neighbour pairs:

$$(Mg\text{-}Mg)_{pair} + (Si\text{-}Si)_{pair} = \underline{2(Mg\text{-}Si)_{pair}}$$

$$\Delta G° < 0$$

(Very similar to: $O^0 + O^{2-} = 2\ O^-$)

- **In basic melts:**
  - Mainly (Mg-Mg) and (Mg-Si) pairs (because $\Delta G° < 0$).
  - That is, most Si atoms have **only** Mg ions in their second coordination shell.
  - This configuration is equivalent to $(SiO_4)^{4-}$ anions.
  - In very basic ($MgO\text{-}SiO_2$) melts, the model is essentially equivalent to a sublattice model of Mg^{2+}, Ca^{2+}, O^{2-}, $(SiO_4)^{4-}$ ions.

At higher SiO_2 contents, more (Si-Si) pairs are formed, thereby modeling polymerization.

A.D. Pelton and M. Blander "Thermodynamic Analysis of Ordered Liquid Solutions by a Modified Quasichemical Approach - Application to Silicate Slags", Met. Trans., 17B, 805-815 (1986).

The Cell Model

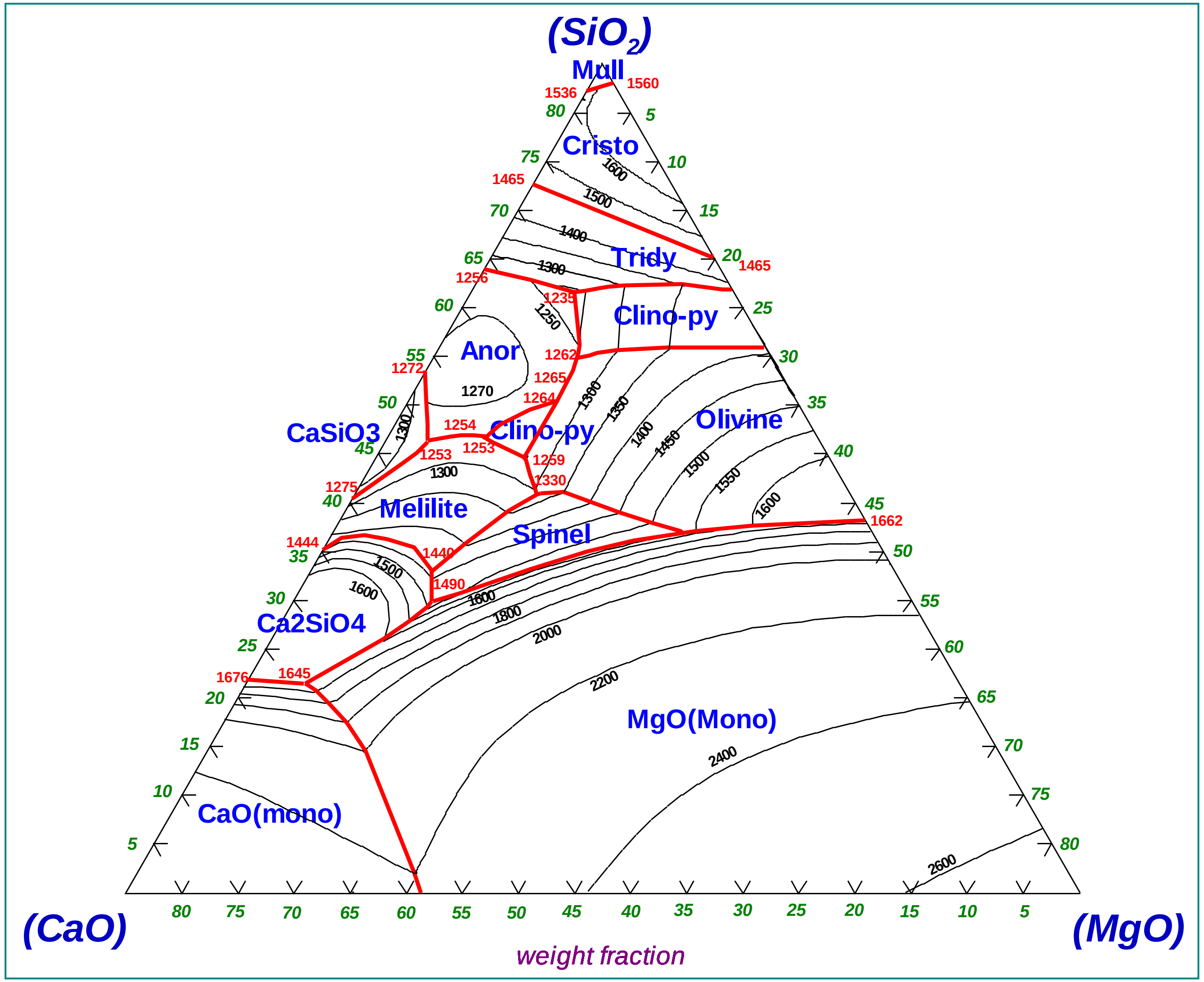
M.L. Kapoor, G.M. Frohberg, H. Gaye and J. Welfringer

- Slag considered to consist of «cells» which mix essentially ideally, with equilibria among the cells:

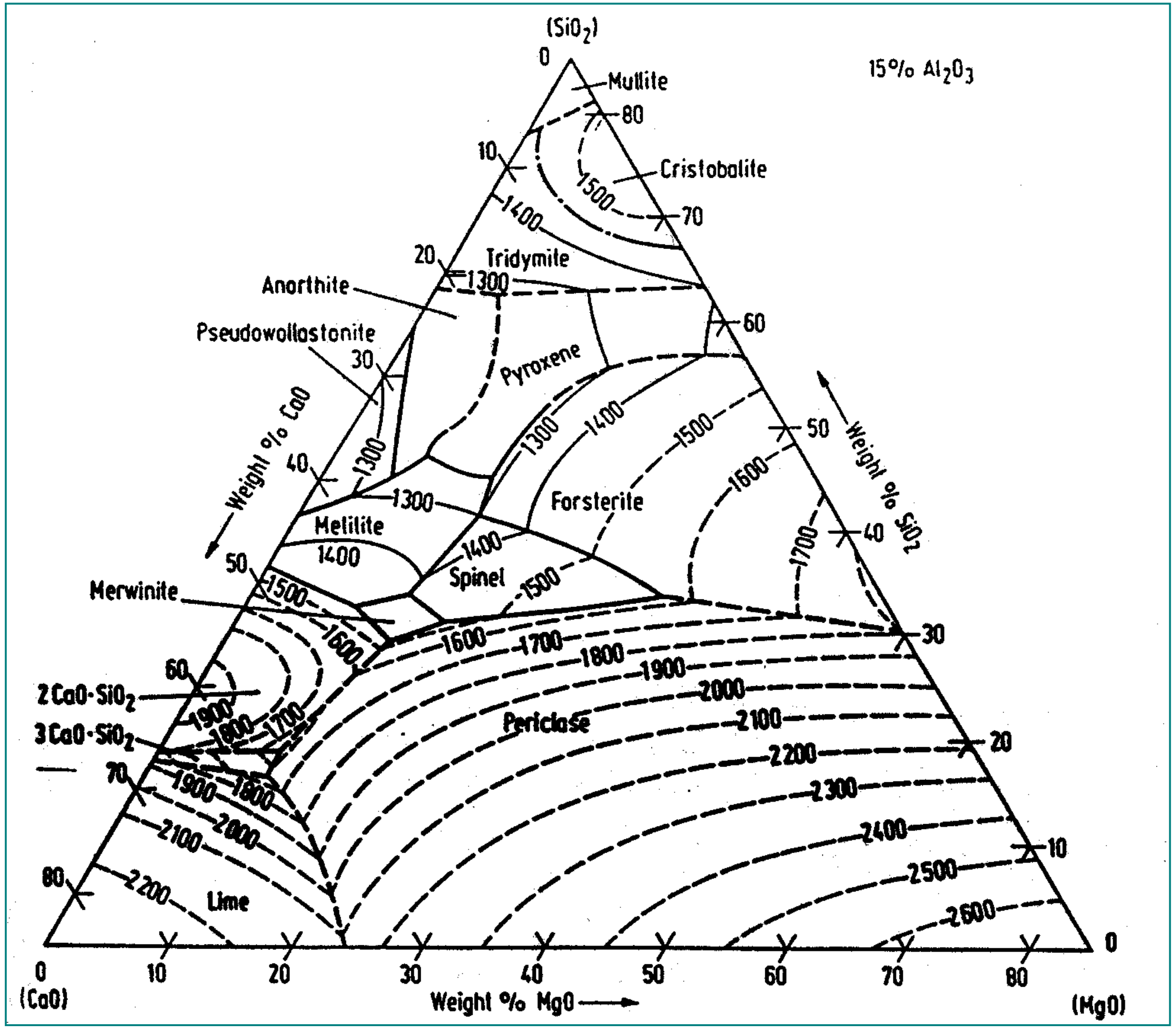
$$[\text{Mg-O-Mg}] + [\text{Si-O-Si}] = 2\,[\text{Mg-O-Si}]$$

$$\Delta G° < 0$$

- Quite similar to Modified Quasichemical Model
- Accounts for ionic nature of slags **and** short-range-ordering.



Liquidus projection of the CaO-MgO-SiO_2-Al_2O_3 system at 15 wt % Al_2O_3, calculated from the Modified Quasichemical Model



Liquidus projection of the CaO-MgO-SiO$_2$-Al$_2$O$_3$ system at 15 wt % Al$_2$O$_3$, as reported by E. Osborn, R.C. DeVries, K.H. Gee and H.M. Kramer

Thermodynamic models for liquid phase

Molten salts

a) Quasichemical model for common-anion(cation) systems, e.g. KCl-NaCl-$CaCl_2$-$MgCl_2$-$ZnCl_2$-$PbCl_2$ (K_2O-Na_2O-CaO-SiO_2) taking into account short-range ordering. Additional anions, such as SO_4^{2-} can't be added (Only one sublattice)

b) Simple two-sublattice models, e.g. $Na^+,K^+//SO_4^{2-}, CO_3^{2-}, Cl^-$

Can give reasonable results for alkali salts but can't take into account short-range order, which is important for systems such as KCl-$ZnCl_2$

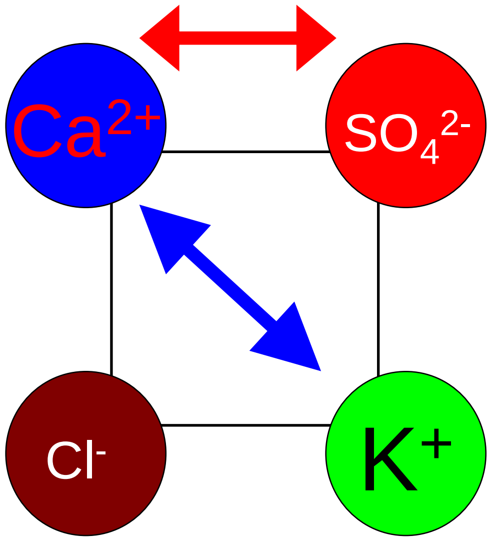
c) Quasichemical model with quadruplet approximation

Can consider mixing on cationic and anionic sublattices and takes into account short-range ordering

Thermodynamic model for ionic solution phases (liquid/solid)

Modified quasichemical model in the quadruplet approximation

Takes into account anion-cation and cation-cation /anion-anion interactions



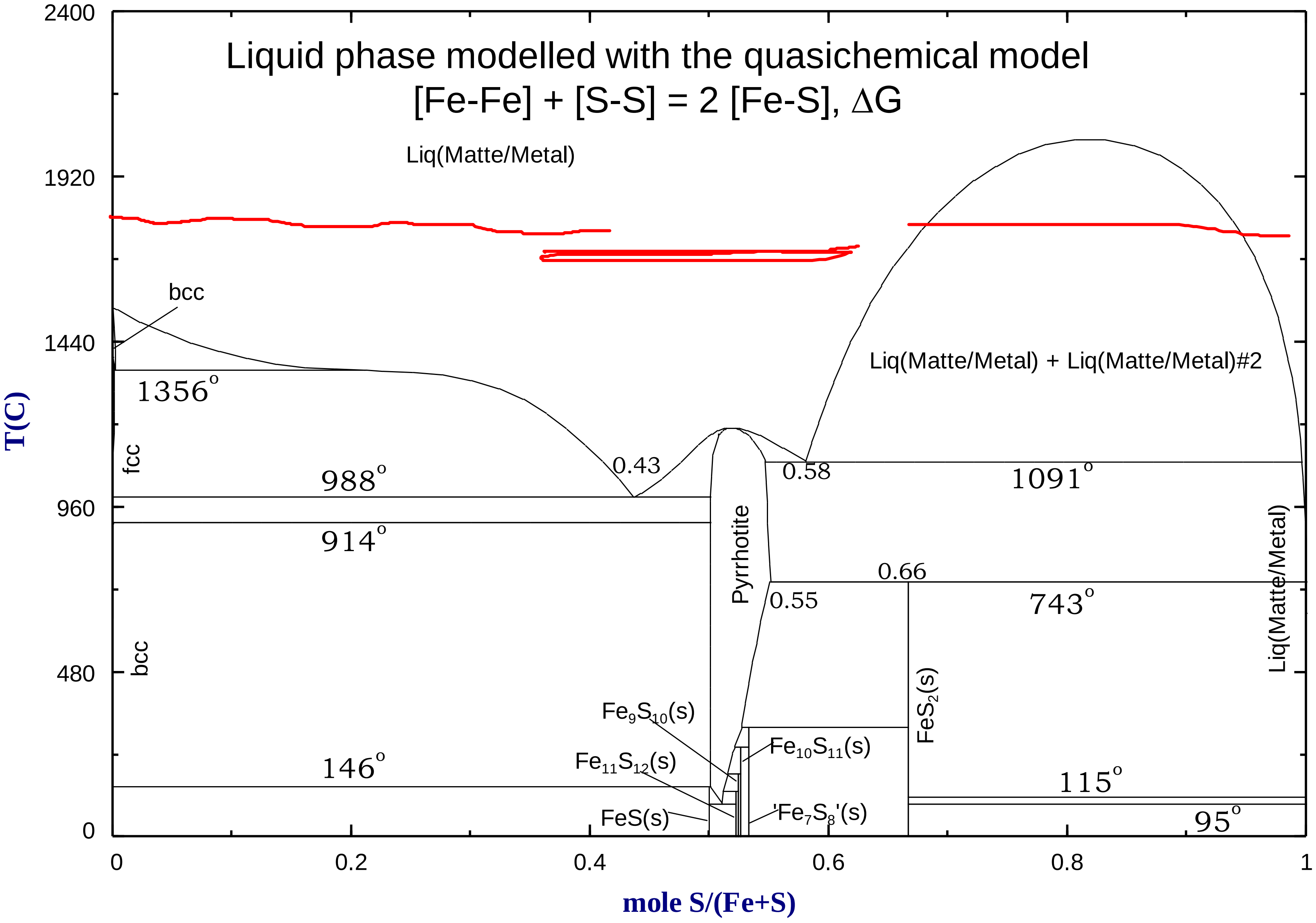
A.D. Pelton & P. Chartrand, G. Eriksson"The Modified Quasichemical Model IV - Two Sublattice Quadruplet Approximation", Met. & Mat. Trans., 32A, 1409-16 (2001).

Liquid sulfides

- Liquid metal sulfides behave very differently depending on the metal
- Na-S and K-S are ionic with long polymerized polysulfide ion (S^{2-} to S_8^{2-})
  - Can be modelled with ionic models
- Fe-S, Ni-S shows strong short-range ordering around the FeS or NiS composition
  - Can be modelled with associate or quasichemical models

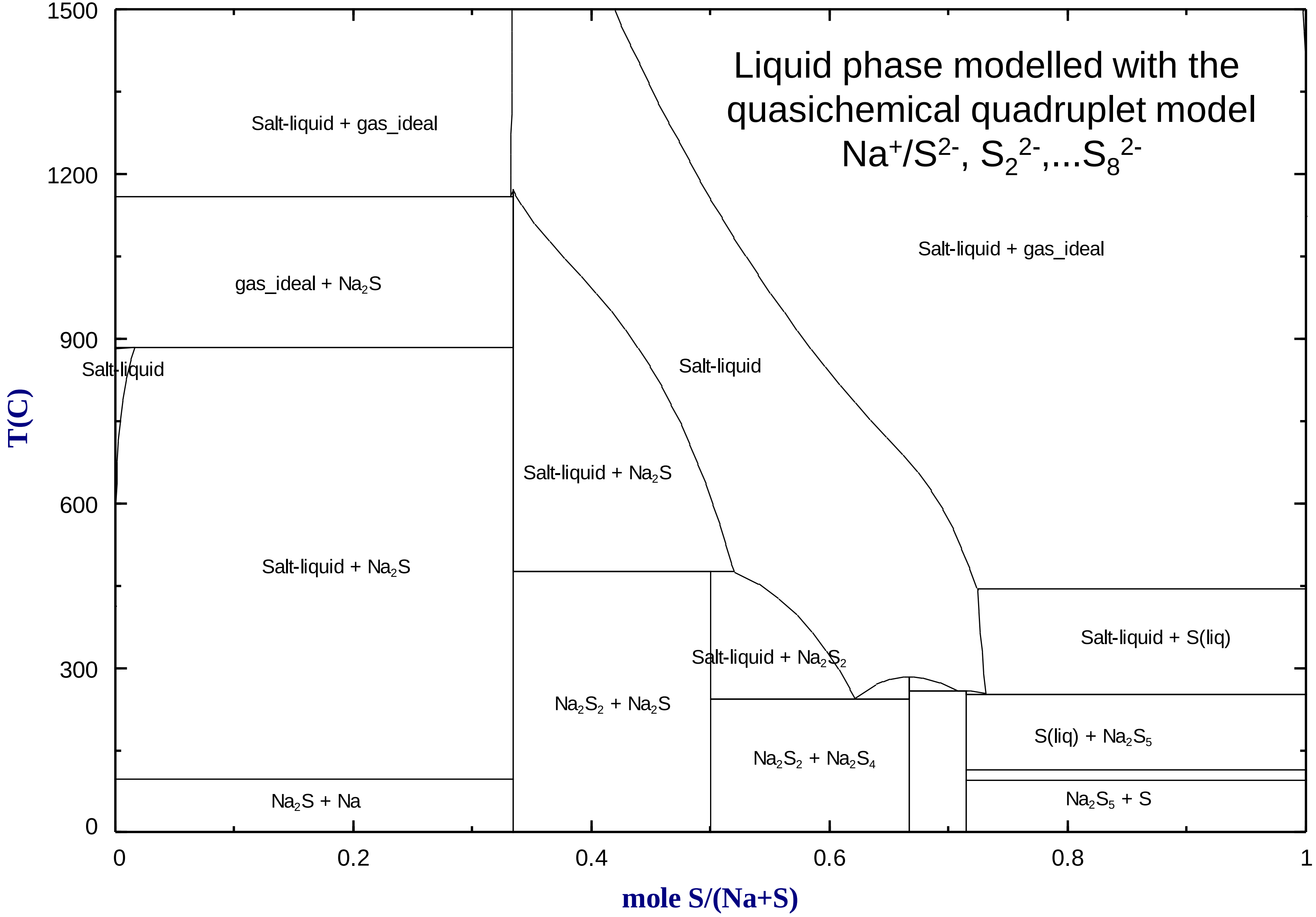
Fe - S - Gas phase suppressed

Data from FTmisc - FACT miscellaneous database 2010



Na - S

Data from FTpulp - FACT pulp and paper databases



Liquid phase modelled with the quasichemical quadruplet model $Na^+/S^{2-}, S_2^{2-},...S_8^{2-}$

Terms and concepts

- Ideal solution and regular solution
- Metals and alloys
  - Compound Energy Formalism
- Ionic solutions
  - Sublattice models
- Slags/liquid oxides
  - Associate model
  - Quasichemical model
- Quadruplet model