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Simplified treatment of diffusion in ionic systems and molten slags

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1. Background

- Ionic systems are technologically important, e.g.
  - Oxidation of alloys
  - Molten slags
  - Aging of Li-ion batteries
  - …
- A detailed phenomenological analysis of multicomponent diffusion is complex.
- For ionic systems there are additional complications making the analysis particularly challenging.

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- The analysis of such systems involves many quantities that are difficult to measure and to store in a database.
- A simplified analysis should be based on well defined quantities that are measured in practice.
- The thermodynamic analysis based on CALPHAD now is largely available and should be used in a simplified treatment.
- The vector-matrix notation makes equations more direct and should be used.

2. Vector-Matrix notation of multicomponent diffusion

$$J_k = -\sum_{j=1}^{N-1} D_{kj}^N \nabla c_j$$

In 1-D planar geometry: $\nabla c_j = \frac{1}{V_m}\nabla x_j = \frac{1}{V_m}\frac{\partial x_j}{\partial z}$

$$\mathbf{J} = -\mathbf{D}^N \nabla C \qquad \mathbf{J} = -\frac{1}{V_m}\mathbf{D}^N \nabla \mathbf{x}$$

$$\mathbf{J} = \begin{pmatrix} J_1 \\ J_2 \\ . \\ . \\ J_N \end{pmatrix}, \qquad \mathbf{D}^N = \begin{pmatrix} D_{11}^N & D_{12}^N & . & . & 0 \\ D_{21}^N & D_{22}^N & & & 0 \\ . & & . & & . \\ . & & & . & 0 \\ D_{N1}^N & . & . & D_{NN-1}^N & 0 \end{pmatrix}, \qquad \nabla \mathbf{x} = \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \\ . \\ . \\ \nabla x_N \end{pmatrix}$$

Introducing mobilities and thermodynamic forces

$$J_k = -M_k \frac{x_k}{V_m} \nabla \mu_k => \mathbf{J} = -\mathbf{L} \nabla \boldsymbol{\mu}$$

$$\mathbf{L} = \frac{1}{V_m} \begin{pmatrix} x_1 M_1 & 0 & . & . & 0 \\ 0 & x_2 M_2 & & & . \\ . & & . & & . \\ . & & & . & 0 \\ 0 & & . & 0 & x_N M_N \end{pmatrix}$$

$$\nabla \boldsymbol{\mu} = \begin{pmatrix} \nabla \mu_1 \\ \nabla \mu_2 \\ . \\ . \\ \nabla \mu_N \end{pmatrix}$$

The matrix $\mathbf{L}$ is diagonal and the Onsager reciprocal relations are obeyed, i.e. $L_{ik} = L_{ki}$ or $\mathbf{L} = \mathbf{L}^T$.

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3. Ionic systems

(NIST diffusion workshop 14-15 May 2007 with slightly different notation.
See also In-Ho Jung et al. Calphad 72 (2021)102246

- Distinguish between
  - Diffusing consistuent species, some ionic and some neutral. Not necessarily conserved.
  - Components which are conserved.

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Wagner's analysis: The flux for a constituent ionic species i with charge Z_i is

$$J_i' = -L'_i(\nabla\Lambda_i + Z_i F \nabla\psi)$$

Λ_i = chemical potential of species i

$L'_i = y_i M_i / V_m$, M_i is the mobility of i

$\nabla\psi$ = electric potential gradient

F = Faraday constant

The steps in deriving a more useful expression

- Condition of no net charge transport: $\sum Z_i J_i' = 0 \rightarrow$ $\nabla\psi$ can be eliminated.

$$F\nabla\psi = -\frac{\sum Z_i L'_i \nabla\Lambda_i}{\sum {Z_i}^2 L'_i}$$

- Introduce the matrix **B** with elements b_{ki} as the number of moles of component k contained in species i. It then follows $\Lambda_i = \sum_k b_{ki}\mu_k$ or $\boldsymbol{\Lambda} = \mathbf{B}^T\boldsymbol{\mu}$ and $J_k = \sum_i b_{ki}J_i'$ or $\mathbf{J} = \mathbf{B}\mathbf{J}'$

Example: metal-deficit oxide $M_{1-x}O$ with constituents M^{+2}, M^{+3}, O^{-2} and e^{-1} and components M, O and the electron e^{-1}.

$$\mathbf{B} = \begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -2 & -3 & 2 & 1 \end{pmatrix}$$

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- Change to component chemical potentials: $\nabla\Lambda = \mathbf{B}^{\mathrm{T}}\ \nabla\boldsymbol{\mu}$

$$\nabla\Lambda_{M^{+2}} = \nabla\mu_M - 2\nabla\mu_{e^{-1}}$$
$$\nabla\Lambda_{M^{+3}} = \nabla\mu_M - 3\nabla\mu_{e^{-1}}$$
$$\nabla\Lambda_{O^{-2}} = \nabla\mu_{MO} + 2\nabla\mu_{e^{-1}}$$
$$\nabla\Lambda_{e^{-1}} = \nabla\mu_{e^{-1}}$$

- Change from flux of constituents J_i' to flux of components J_k: $\mathbf{J} = \mathbf{B}\mathbf{J}'$

$$J_M = J'_{M^{+2}} + J'_{M^{+3}}$$
$$J_O = J'_{O^{-2}}$$
$$J_{e^{-1}} = -2J'_{M^{+2}} - 3J'_{M^{+3}} + J'_{O^{-2}} + J'_{e^{-1}}$$

Phenomenological matrix referring to components

$$\mathbf{J} = -\frac{1}{V_m}\mathbf{L}\nabla\boldsymbol{\mu}$$

$$\mathbf{L} = \begin{pmatrix} L'_{M^{+2}} + L'_{M^{+3}} - L'^{2}_{M}/_{(L'+L_{e^{-1}})} & L'_{M}L'_{O}/(L' + L_{e^{-1}}) \\ L'_{M}L'_{O}/(L' + L_{e^{-1}}) & -L'_{O}(1 - 2L'_{O}/(L' + L_{e^{-1}})) \end{pmatrix}$$

where

$$L'_{M} = 2L'_{M^{+2}} + 3L'_{M^{+3}}$$

$$L'_{O} = 2L'_{O^{-2}}$$

$$L' = 4L'_{M^{+2}} + 9L'_{M^{+3}} + 4L'_{O^{-2}}$$

Onsager relations are obeyed!

Example $MO - A_2O_3$

Oxide solution $MO - A_2O_3$ with constituents M^{+2}, A^{+3} and O^{-2} and components MO and A_2O_3.

$$J'_{M^{+2}} = -L'_{M^{+2}}[\nabla\Lambda_{M^{+2}} + 2F\nabla\varphi]$$
$$J'_{A^{+3}} = -L'_{A^{+3}}[\nabla\Lambda_{A^{+3}} + 3F\nabla\varphi]$$
$$J'_{O^{-2}} = -L'_{O^{-2}}[\nabla\Lambda_{O^{-2}} - 2F\nabla\varphi]$$

$$\mathbf{B} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & \frac{1}{2} & \frac{1}{3} \end{pmatrix} \qquad \mathbf{B^T} = \begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{2} \\ 1 & \frac{1}{3} \end{pmatrix}$$

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- No net charge transport: $\sum Z_i J_i' = 0 \rightarrow \nabla\psi$ can be eliminated

$$F\nabla\psi = -\frac{\sum Z_i L'_i \nabla\Lambda_i}{\sum Z_i^2 L'_i}$$
$$= -\frac{2L'_{M^{+2}}\nabla\Lambda_{M^{+2}} + 3L'_{A^{+3}}\nabla\Lambda_{A^{+3}} + 2L'_{O^{-2}}\nabla\Lambda_{O^{-2}}}{L'}$$

where $L' = 4L'_{M^{+2}} + 9L'_{A^{+3}} + 4L'_{O^{-2}}$

Change to component chemical potentials: $\nabla\Lambda = \mathbf{B}^{\mathrm{T}}\ \nabla\boldsymbol{\mu}$

$$\nabla\Lambda_{M^{+2}} = \nabla\mu_{MO}$$

$$\nabla\Lambda_{A^{+3}} = \frac{1}{2}\nabla\mu_{A_2O_3}$$

$$\nabla\Lambda_{O^{-2}} = \nabla\mu_{MO} + \frac{1}{3}\nabla\mu_{A_2O_3}$$

Thus $F\nabla\psi = -\frac{2L'_{M^{+2}}\nabla\mu_{MO} + 3L'_{A^{+3}}\frac{1}{2}\nabla\mu_{A_2O_3} + 2L'_{O^{-2}}\left(\nabla\mu_{MO} + \frac{1}{3}\nabla\mu_{A_2O_3}\right)}{L'}$

$$F\nabla\psi = -\frac{L'_{MO}\nabla\mu_{MO} + L'_{A_2O_3}\nabla\mu_{A_2O_3}}{L'}$$

where

$$2L'_{M^{+2}} + 2L'_{O^{-2}} = L'_{MO}$$

$$\frac{3}{2}L'_{A^{+3}} + \frac{2}{3}L'_{O^{-2}} = L'_{A_2O_3}$$

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And:

$$J'_{M^{+2}} = -L'_{M^{+2}}\left[\nabla\mu_{MO} - 2\frac{L'_{MO}\nabla\mu_{MO} + L'_{A_2O_3}\nabla\mu_{A_2O_3}}{L'}\right]$$

$$J'_{A^{+3}} = -L'_{A^{+3}}\left[\frac{1}{2}\nabla\mu_{A_2O_3} - 3\frac{L'_{MO}\nabla\mu_{MO} + L'_{A_2O_3}\nabla\mu_{A_2O_3}}{L'}\right]$$

$$J'_{O^{-2}} = -L'_{O^{-2}}\left[\nabla\mu_{MO} + \frac{1}{3}\nabla\mu_{A_2O_3} + 2\frac{L'_{MO}\nabla\mu_{MO} + L'_{A_2O_3}\nabla\mu_{A_2O_3}}{L'}\right]$$

Change from flux of constituents J_i' to flux of components J_k: $\mathbf{J} = \mathbf{B}\mathbf{J}'$

$$J_{MO} = J'_{M^{+2}} + J'_{O^{-2}}$$

$$J_{A_2O_3} = \frac{1}{2} J'_{A^{+3}} + \frac{1}{3} J'_{O^{-2}}$$

Thus:

$$\begin{pmatrix} J_{MO} \\ J_{A_2O_3} \end{pmatrix} = \begin{pmatrix} -\left(L'_{M^{+2}}\left[1 - 2\frac{L'_{MO}}{L'}\right] + L'_{O^{-2}}\left[1 + 2\frac{L'_{MO}}{L'}\right]\right) & \left(2L'_{M^{+2}}\frac{L'_{A_2O_3}}{L'} - L'_{O^{-2}}\left[\frac{1}{3} - 2\frac{L'_{A_2O_3}}{L'}\right]\right) \\ \left(\frac{3}{2}L'_{A^{+3}}\frac{L'_{MO}}{L'} - \frac{1}{3}L'_{O^{-2}}\left[1 + 2\frac{L'_{MO}}{L'}\right]\right) & -\left(\frac{1}{2}L'_{A^{+3}}\left[\frac{1}{2} - 3\frac{L'_{A_2O_3}}{L'}\right] + \frac{1}{3}L'_{O^{-2}}\left[\frac{1}{3} + 2\frac{L'_{A_2O_3}}{L'}\right]\right) \end{pmatrix} \begin{pmatrix} \nabla\mu_{MO} \\ \nabla\mu_{A_2O_3} \end{pmatrix}$$

Inserting the expressions for L'_{MO} and $L'_{A_2O_3}$ one finds that Onsager reciprocal relations hold.

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- The procedure thus yields expression of the type

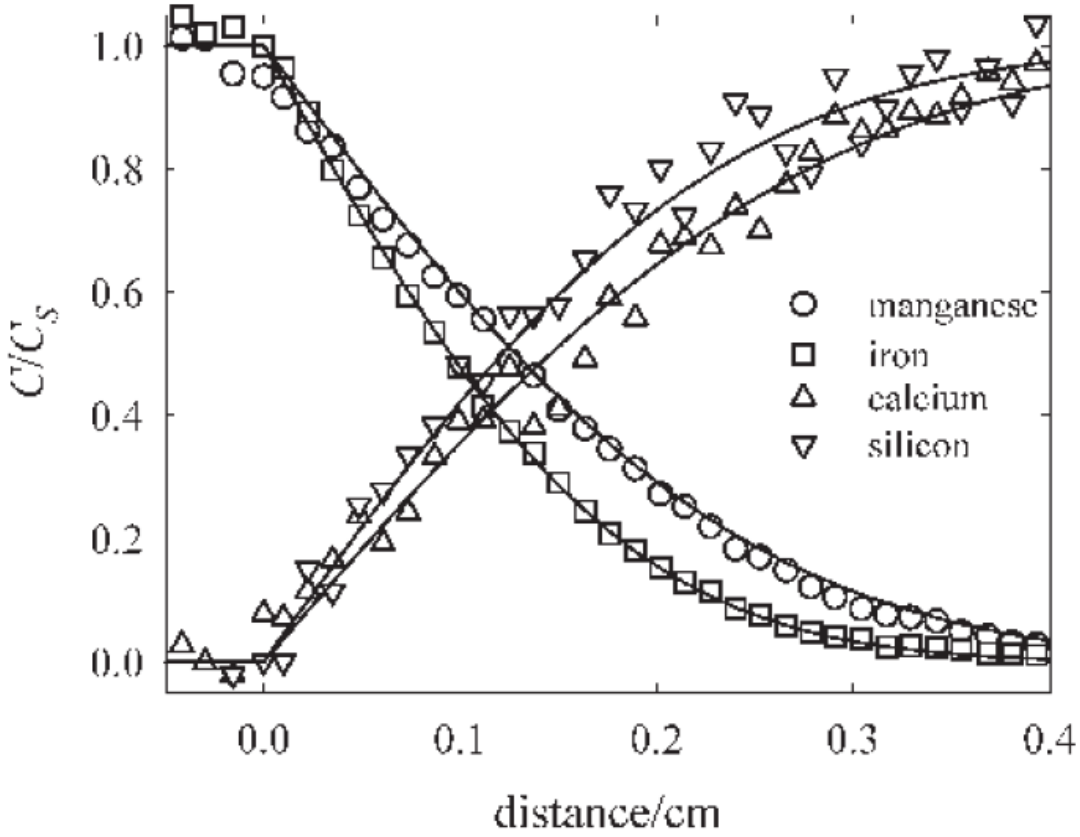
$$J_{MO} = -L_{MOMO}\nabla\mu_{MO} - L_{MOA_2O_3}\nabla\mu_{A_2O_3}$$
$$J_{A_2O_3} = -L_{A_2O_3MO}\nabla\mu_{MO} - L_{A_2O_3A_2O_3}\nabla\mu_{A_2O_3}$$

$$L_{MOA_2O_3} = L_{A_2O_3MO}$$

- The expressions for the L matrix are quite complex and contains the parameters $L'_{M^{+2}}$, $L'_{A^{+3}}$, $L'_{O^{-2}}$ that are difficult to determine.
- Simplifications are needed.

Experimental information (example)

CaO-Al2O3-SiO2 slags



Dolan and Johnston 2004
(x-ray or electron microprobe)

Fitted by error-function.

Example of theoretical attempts

- Ukyo and Goto 1981: diffusion in liquid slags of Fe_2O_3-CaO-SiO_2.
- Melt quite complex with ionic species of Ca^{+2}, Fe^{+2}, O^{-2}, silicate and various degree of polymerization.
- Assumed local equilibrium and considered the flux of 5 elementary ions, Ca^{+2}, Fe^{+2}, Fe^{+3}, O^{-2}, Si^{+4} and O^{-2}.
- As further simplification they considered a ternary system with fluxes of Fe_2O_3, CaO and SiO_2 and evaluated 4 diffusion coefficients of the type $D^{SiO_2}_{Fe_2O_3\ CaO}$.

4. Simplified approach for molten slags of the type $CaO - SiO_2 - Al_2O_3 - \ldots$

- The approach should be based on the chemical potential of the oxide components.
- Us the equation: $\mathbf{J} = -\mathbf{L}\nabla\boldsymbol{\mu}$
- Neglect off-diagonal elements in $\mathbf{L}$, introduce mobilities of the oxide components:

$$J_{CaO} = -\frac{x_{CaO}}{V_m} M_{CaO} \nabla \mu_{CaO}$$

$$J_{SiO_2} = -\frac{x_{SiO_2}}{V_m} M_{SiO_2} \nabla \mu_{SiO_2}$$

…

- We consider one mole of cations, i.e. Al_2O_3 is treated as $Al_1O_{3/2}$.

- This gives the same mathematics as for substitutional diffusion of atoms in a lattice-fixed frame of reference.

$$J_A = -\frac{x_A}{V_m} M_A \nabla \mu_A$$

Etc. One may then transform to other frames of reference.

- We assume that the mobilities depend only on temperature and the basicity B of the slag.

$$M_A = \frac{1}{RT} M_A^0 \exp(\lambda B)$$

λ is fitted to the experimental data and depends on what measure of basicity that is used. For optical basicity Dolan and Johnston (2004) gave $\lambda = 12.5$.

5. Basicity of slags, B

- Is not a trivial concept and is not easy to measure.
- It stems from the traditional division of oxides into basic (CaO, MgO, FeO) and acid oxides (SiO2, Al2O3), See Flood and Förland 1947).
- Simplest approach $B = {\%CaO}/{\%SiO2}$ or $B = {(\%CaO+MgO)}/{\%SiO2}$
- A more refined concept is the electron donor power of the oxygen ions. This can be measured spectroscopically (optical basicity).

Values of optical basicity of oxides from different scales.

Oxide	Ion-Oxygen Attraction, $I = (2Z)/d^2$	Ionic Bond Fraction	Optical Basicity, Λ Derived from Pauling electronegativity	Optical Basicity, Λ Derived from Average Electron Density	Optical basicity, Λ, Recommended
K_2O	0.27	0.68	1.40	1.15	1.40
Na_2O	0.36	0.65	1.15	1.10	1.20
Li_2O	0.50	0.63	1.07	1.05	1.05
BaO	0.53	0.65	1.15	1.08	1.10
SrO	0.63	0.61	1.07	1.04	1.05
CaO	0.70	0.61	1.00	1.00	1.00
MnO	0.83	0.47	0.59	0.95	0.95
FeO	0.87	0.38	0.51	0.93	0.93
MgO	0.95	0.54	0.78	0.92	0.85
Cr_2O_3	1.44	0.41	0.55	0.69	0.69
Fe_2O_3	1.50	0.36	0.48	0.69	0.69
Al_2O_3	1.66	0.44	0.61	0.68	0.65
TiO_2	1.85	0.41	0.61	0.64	0.65
B_2O_3	2.34	0.31	0.42	0.42	0.42
SiO_2	2.44	0.36	0.48	0.47	0.48
P_2O_5	3.31	0.28	0.40	0.38	0.40

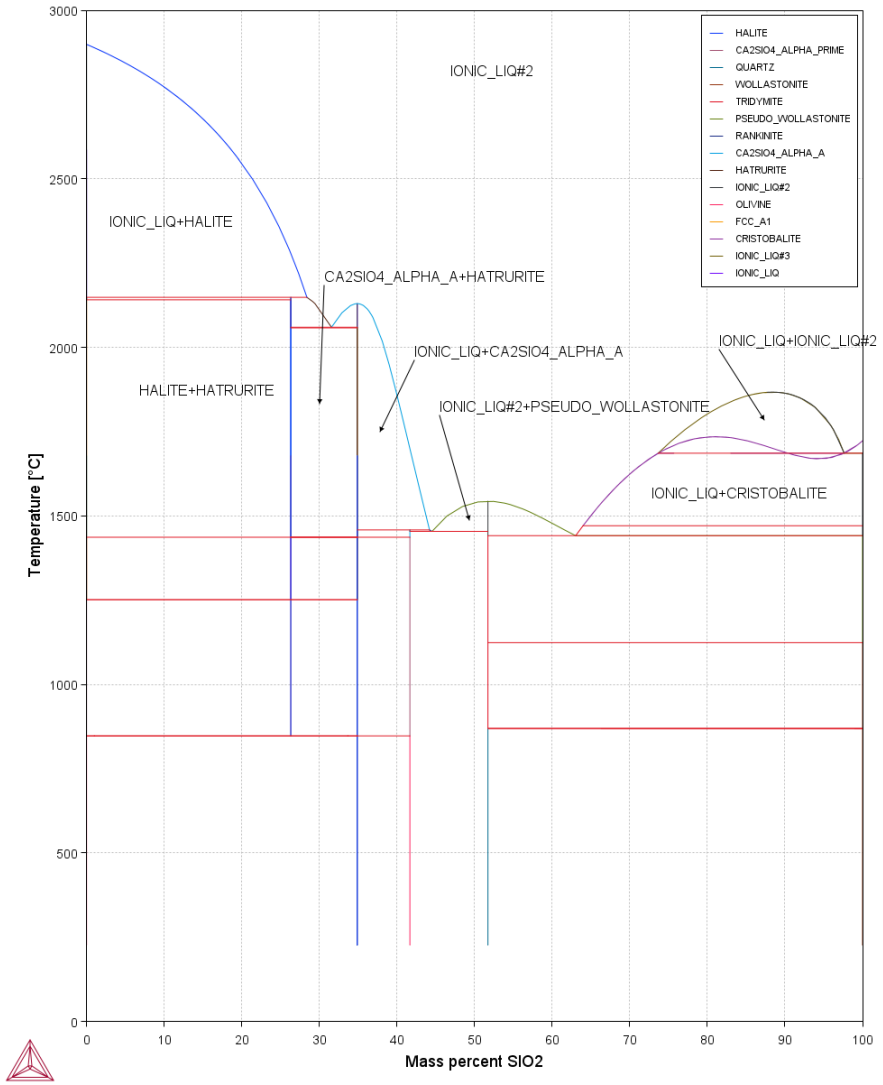
Sommerville and Yang 2000

6. Fickian diffusion coefficients

$$J = -V_m L \frac{d\mu}{dX} \nabla c = -D \nabla c$$

Thermodynamic factor $\frac{d\mu}{dX} = \begin{pmatrix} \frac{\partial \mu_1}{\partial x_1} & \cdots & \frac{\partial \mu_1}{\partial x_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial \mu_n}{\partial x_1} & \cdots & \frac{\partial \mu_n}{\partial x_n} \end{pmatrix}$

Example system CaO -SiO_2



TCOX12

Example system CaO -SiO_2

$$\begin{pmatrix} J_{CaO} \\ J_{SiO_2} \end{pmatrix} = -\begin{pmatrix} L_{CaOCaO} & 0 \\ 0 & L_{SiO_2SiO_2} \end{pmatrix}\begin{pmatrix} \nabla\mu_{CaO} \\ \nabla\mu_{SiO_2} \end{pmatrix}$$

$$L_{CaOCaO} = \frac{x_{CaO}}{V_m} M_{CaO}$$

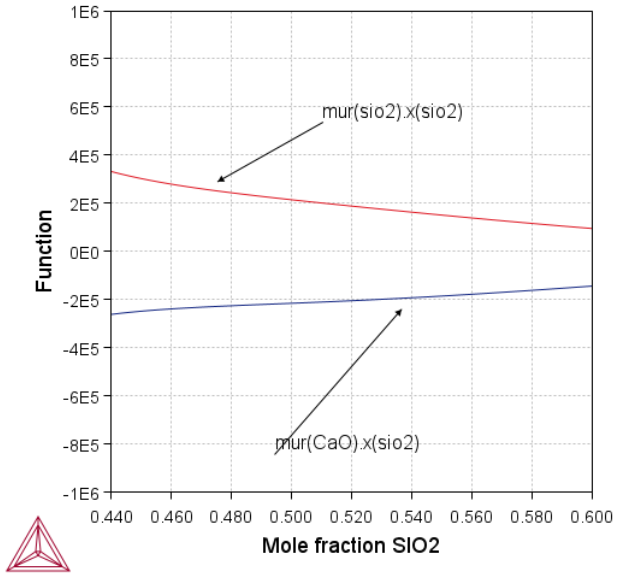
$$L_{SiO_2SiO_2} = \frac{x_{SiO_2}}{V_m} M_{SiO_2}$$

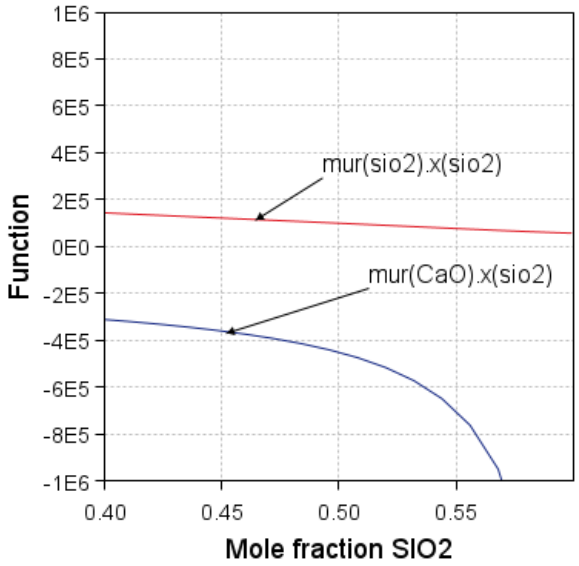
Using x_{SiO_2} as independent variable, i.e. $x_{CaO} = 1 - x_{SiO_2}$

and $\frac{\partial \mu_{CaO}}{\partial x_{CaO}} = -\frac{\partial \mu_{CaO}}{\partial x_{SiO_2}}$ and $\frac{\partial \mu_{SiO_2}}{\partial x_{CaO}} = -\frac{\partial \mu_{SiO_2}}{\partial x_{SiO_2}}$

$$\frac{d\mu}{dX} = \begin{pmatrix} -\frac{\partial \mu_{CaO}}{\partial x_{SiO_2}} & \frac{\partial \mu_{CaO}}{\partial x_{x_{SiO_2}}} \\ -\frac{\partial \mu_{SiO_2}}{\partial x_{SiO_2}} & \frac{\partial \mu_{SiO_2}}{\partial x_{SiO_2}} \end{pmatrix}$$

The derivatives are calculated as mur(CaO).x(sio2) and mur(sio2).x(sio2). The calculation is performed at 1600 C in the composition range where only the molten slag is stable. The same calculation is shown in Fig. to the right for an additional mole fraction Al_2O_3 of 0.4.





mole fraction Al_2O_3 of 0.4

The advantages with the suggested simplified method

- It uses well defined quantities.
- It uses the same formalism as diffusion in a substitutional solution as discussed by Andersson and Ågren 1992.
- The construction of a useful database should be rather straight forward.

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Thanks!