Thermo-Calc Software

TCS Metal Oxide Solutions Database (TCOX)

Validation and Calculation Examples Collection

Document created 2025-01-09

Contents

About the Database Examples

The *Validation and Calculation Examples Collection* that is available for many databases demonstrates both the *validity* of the database itself as well as demonstrates some of its *calculation* capabilities when combined with Thermo-Calc software and its Add-on Modules and features.

For each database, the type and number of available examples varies. In some cases an example can belong to both a validation and calculation type.

- *Validation* examples generally include experimental data in the plot or diagram to show how close to the predicted data sets the Thermo-Calc calculations are. It uses the most recent version of the software and relevant database(s) unless otherwise specified.
- *Calculation* examples are intended to demonstrate a use case of the database. This might be showing a binary or ternary system calculated in a phase diagram, or demonstrate how the database and relevant software features would be applied to a heat treatment application, process metallurgy, soldering process, and so forth. In the case of heat treatment, it might include the result of calculating solidification segregation, determining homogenization temperature and then predicting the time needed to homogenize. There are many other examples specifically related to each database.

Where relevant, most references related to each example set are included at the end of the individual section. You can also find additional references specific to the database itself when using the database within Thermo-Calc. You can also contact us directly should you have any questions.

If you are interested in sharing your own examples using Thermo-Calc products in unique or surprising ways, or if you want to share your results from a peer reviewed paper, send an email to info@thermocalc.com.

TCS Metal Oxide Solutions Database (TCOX) Resources

Information about the database is available on our website and in the Thermo-Calc software online Help.

- **Website**: On our website the information is both searchable and the database specific PDFs are available to download.
- **Online Help**: Technical database information is included with the Thermo-Calc software online Help. When in Thermo-Calc, press F1 to search for the same information as is contained in the PDF documents described. Depending on the database, there are additional examples available on the website.

Database Specific Documentation

- The *TCS Metal Oxide Solutions Database (TCOX) Technical Information* PDF document contains version specific information such as the binary, ternary, and higher-order assessed systems, phases, and models. It also includes a list of the included elements, details about the properties (e.g. viscosity, molar volume, etc.), and a summary of the database revision history by version.
- The *TCS Metal Oxide Solutions Database (TCOX) Validation and Calculation Examples Collection* PDF document contains a series of validation examples using experimental data, and a set of calculation examples showing some of the ways the database can be used. Additional examples are available on the website.

Go to the Metal Slag and Oxides Database page on our website where you can access a Validation and Calculation Examples Collection and the Technical Information plus learn about its many applications with the Process Metallurgy Module. Also explore further applications of Thermo-Calc to Refractory Oxides and Slags including links to resources such as examples, publications, and more.

Learn more on our website about the CALPHAD Method and how it is applied to the Thermo-Calc databases.

TCOX Validation Examples

Some diagrams are calculated with earlier versions of the database. Negligible differences might be observed if these are recalculated with the most recent version. The diagrams are updated when there are considerable or significant improvements.

Acknowledgement

Professor Malin Selleby, Dr. Bengt Hallstedt and David Dilner are acknowledged for many valuable discussions and important contributions.

In this section:

$CaO\text{-}SiO_2\text{-}YO_{1.5}$ and $CaO\text{-}SiO_2\text{-}GdO_{1.5}$

The isothermal sections comparing data on 3-phase corners and tie-lines for this example using the TCS Metal Oxide Solutions Database (TCOX) are taken from Poerschke [2017/2016a/2016bPoe].

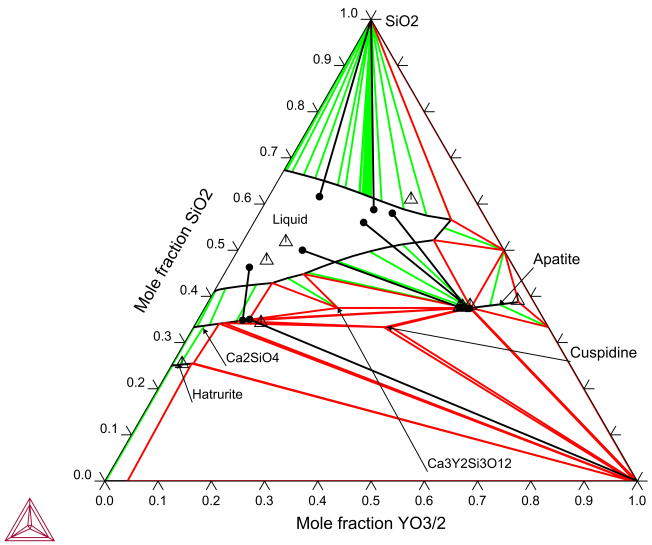

Figure 1: Calculated isothermal section of $CaO\text{-}SiO_2\text{-}YO_{1.5}$ at 1600 °C, compared to data on 3-phase corners and tie-lines.

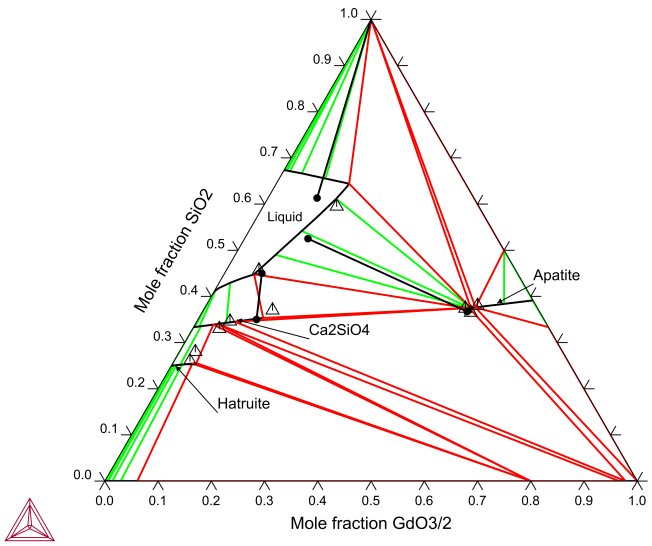

Figure 2: Calculated isothermal section of CaO-SiO_2-$GdO_{1.5}$ at 1600 °C, compared to data on 3-phase corners and tie-lines.

References

[2016aPoe] D. L. Poerschke, T. L. Barth, O. Fabrichnaya, C. G. Levi, Phase equilibria and crystal chemistry in the calcia–silica–yttria system. J. Eur. Ceram. Soc. 36, 1743–1754 (2016).

[2016bPoe] D. L. Poerschke, T. L. Barth, C. G. Levi, Equilibrium relationships between thermal barrier oxides and silicate melts. Acta Mater. 120, 302–314 (2016).

[2017Poe] D. L. Poerschke, C. G. Levi, Phase equilibria in the calcia-gadolinia-silica system. J. Alloys Compd. 695, 1397–1404 (2017).

$CaO\text{-}ZrO_2$ and $MgO\text{-}ZrO_2$

Infiltration of molten Calcium-Magnesium Alumino-Silicate (CMAS) deposits is a primary cause of failure of thermal barrier coatings (TBCs) on aero-turbine engine blades. The TCS Metal Oxide Solutions Database (TCOX) is available to examine the most commonly applied TBC material, yttria stabilized zirconia (YSZ). $CaO\text{-}ZrO_2$ and $MgO\text{-}ZrO_2$ are thus two of the core systems to be able to calculate CMAS/TBC interactions.

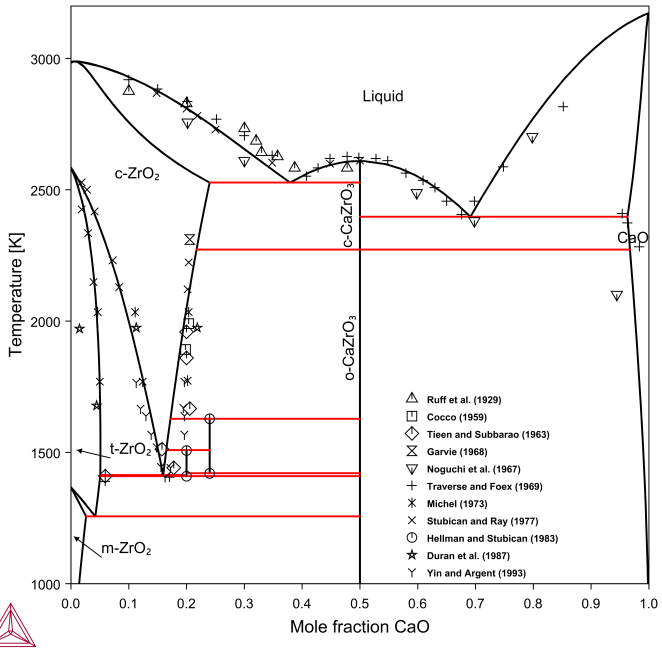

Figure 3: Calculated and experimental phase diagram for $CaO\text{-}ZrO_2$.

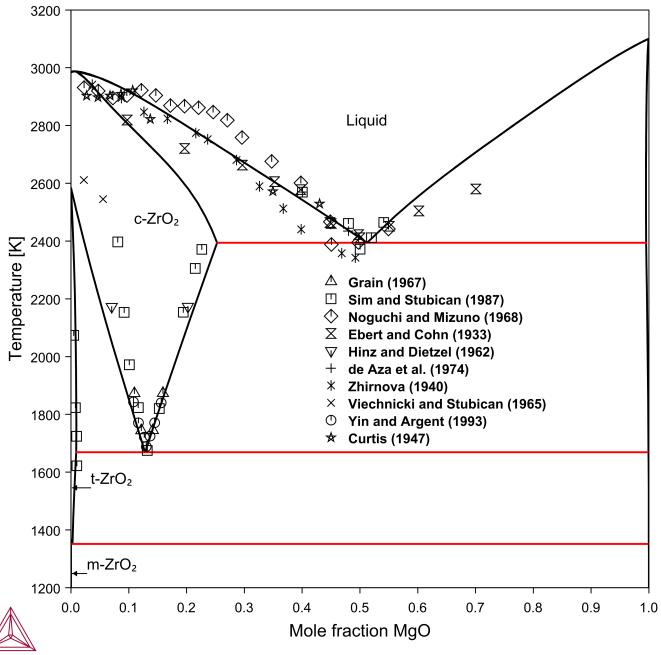

Figure 4: Calculated and experimental phase diagram for MgO-ZrO_2.

Ca-Fe-Mg-O-P-Si

The TCS Metal Oxide Solutions Database (TCOX) can be used to estimate the phosphorus solubility in liquid iron which is in equilibrium with steelmaking slags. The figure below compares the phosphorus solubility estimated based on the database and the corresponding experimental data in the Ca-Fe-Mg-O-P-Si system.

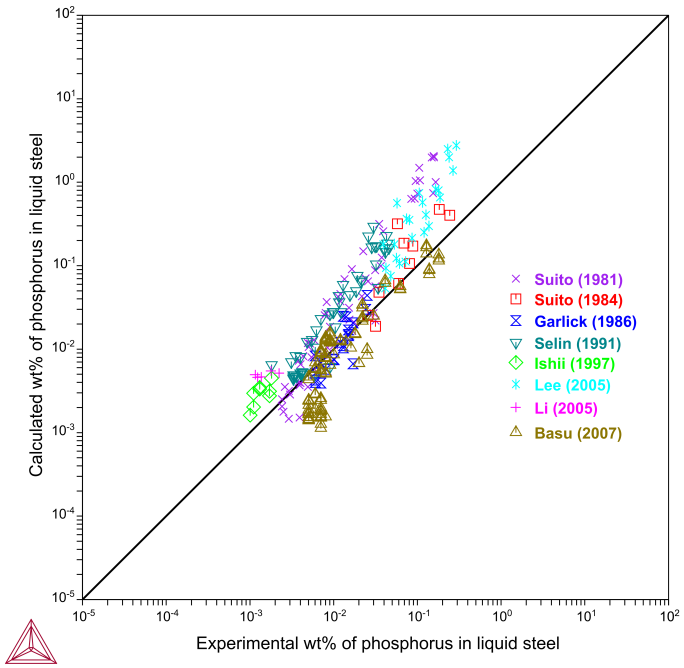

Figure 5: Comparison of experimental and calculated phosphorus solubility in liquid iron in equilibrium with slag in the Ca-Fe-Mg-O-P-Si system.

Sulfur in Ladle Slag

An impressive amount of sulfide capacity measurements have been made for a variety of slag systems over the years, but the results are scattered. Allertz [2016All] used a different method with equilibrium between copper and slag. Sulfur was added as Cu_2S. Different CMAS slags were then equilibrated with Cu and Cu_2S under controlled oxygen partial pressures. The equilibrium sulfur contents in the copper and slag were then analyzed as shown in this example using the TCS Metal Oxide Solutions Database (TCOX).

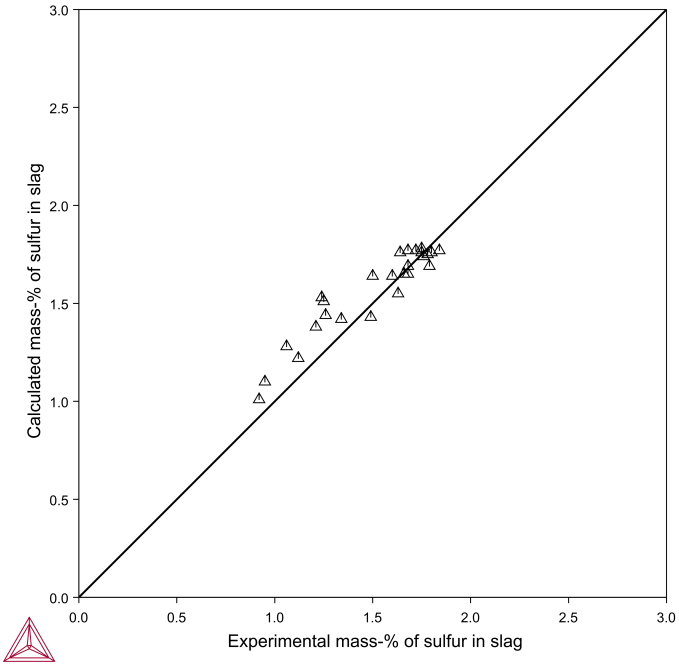

Figure 6: Experimental obtained composition of sulfur in the slag against calculated values.

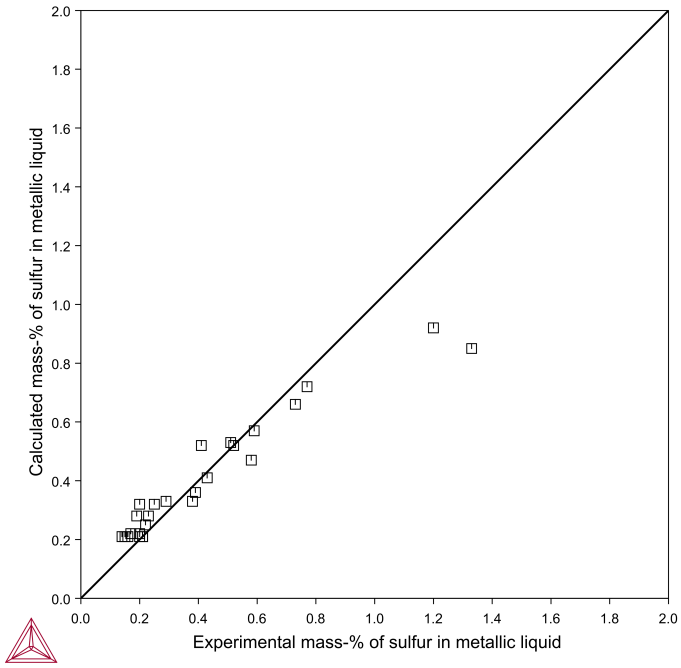

Figure 7: Experimentally obtained composition of sulfur in the metallic liquid against calculated values.

Reference

[2016All] C. Allertz, PhD. thesis, KTH Royal Institute of Technology, Stockholm, Sweden (2016).

Al_2O_3-CaO-CaS

Control of sulfide and oxysulfide inclusions in steels has been an important issue in the steelmaking process for many years. One of the typical sulfide inclusions found in steel is CaS. CaS is known to be harmful, to cause nozzle clogging and to cause the physical properties of the steel to deteriorate. Therefore, it is necessary to remove or tightly control the CaS during the refining and casting processes. The solubility of CaS in liquid CaO-Al_2O_3-CaS is thus an important property and can be examined using the TCS Metal Oxide Solutions Database (TCOX).

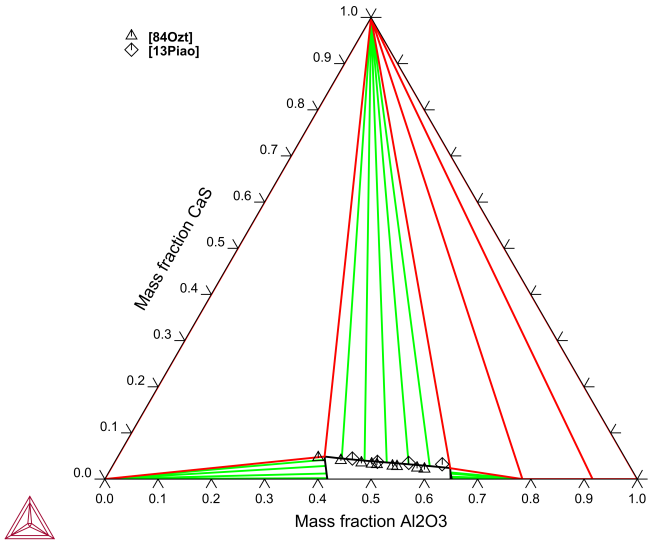

Figure 8: An isothermal section of the Al_2O_3-CaO-CaS system at 1600 °C with experimental data [1984Ozt; 2013Pia].

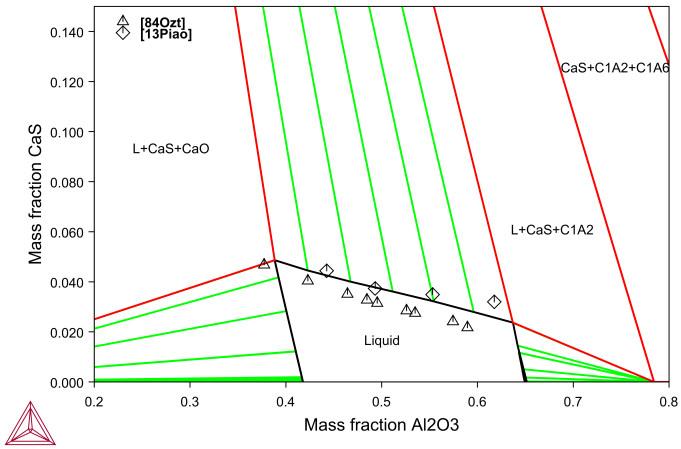

Figure 9: Close up of the isothermal section of the Al_2O_3-CaO-CaS system at 1600 °C.

References

[1984Ozt] B. Ozturk, E. T. Turkdogan, Equilibrium S distribution between molten calcium aluminate and steel. Met. Sci. 18, 299–305 (1984).

[2013Pia] R. Piao, H.-G. Lee, Y.-B. Kang, Experimental investigation of phase equilibria and thermodynamic modeling of the CaO–Al2O3–CaS and the CaO–SiO2–CaS oxysulfide systems. Acta Mater. 61, 683–696 (2013).

Ti+3/Ti+4 Ratio

In metallurgical operations, the distribution of titanium between liquid metal and slag, as well as the partitioning among Ti+4, Ti+3 and Ti+2 valency states in the slag, is determined by the oxygen partial pressure, slag composition, and temperature. The oxides associated with the three valencies of titanium are expected to exhibit inherently different properties, affecting both the physical and thermodynamic behavior of slags containing these oxides. Experimental results show that the Ti+3/Ti+4 ratio in CaO-SiO_2-TiO_x slags increase with decreasing oxygen partial pressure and decreased with increasing CaO/SiO_2 ratio and decreasing temperature as shown in this example using the TCS Metal Oxide Solutions Database (TCOX).

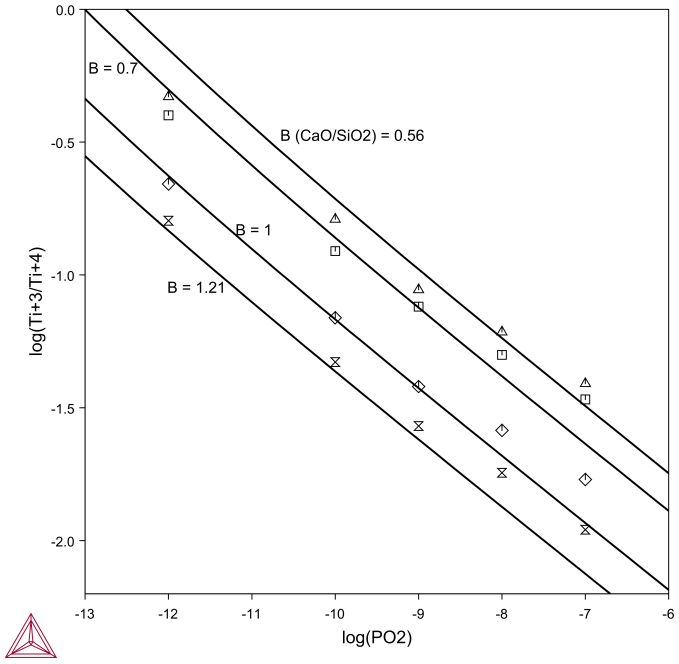

Figure 10: Variation of the Ti+3/Ti+4 ratio with oxygen partial pressure at 1600 °C with different CaO/SiO_2 ratios with experimental data.

V+3/V+4/V+5 Ratio

Vanadium is a multivalent element which can occur as V+2, V+3, V+4, and V+5. The distribution of vanadium between liquid metal and slag, as well as the partitioning among the different valency states in the slag, is determined by the oxygen partial pressure, slag composition, and temperature.

At the production of ferroalloys, slags can include large quantities of vanadium. In order to understand the activity of vanadium during the process, it is of great importance to know the oxidation behavior, something that can be further understood using the TCS Metal Oxide Solutions Database (TCOX).

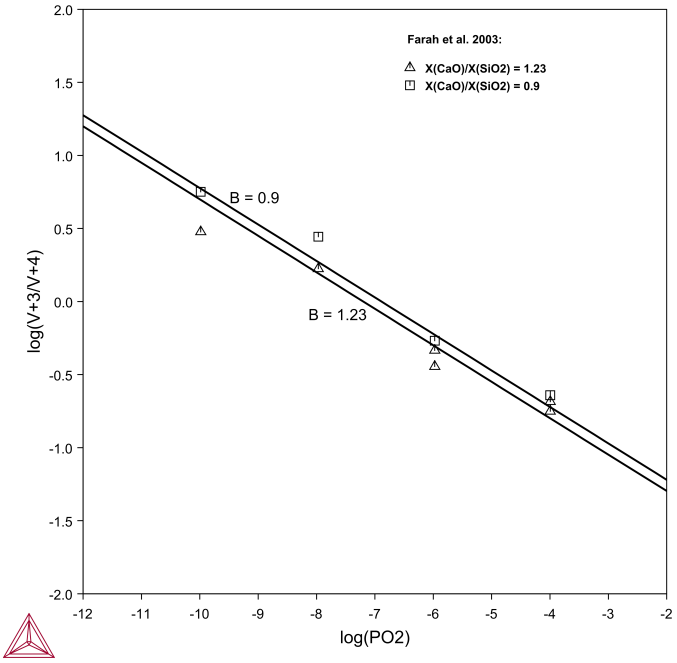

Figure 11: Variation of the V+3/V+4 ratio with oxygen partial pressure with different CaO/SiO_2 ratios. Calculated at 1600 °C with experimental data.

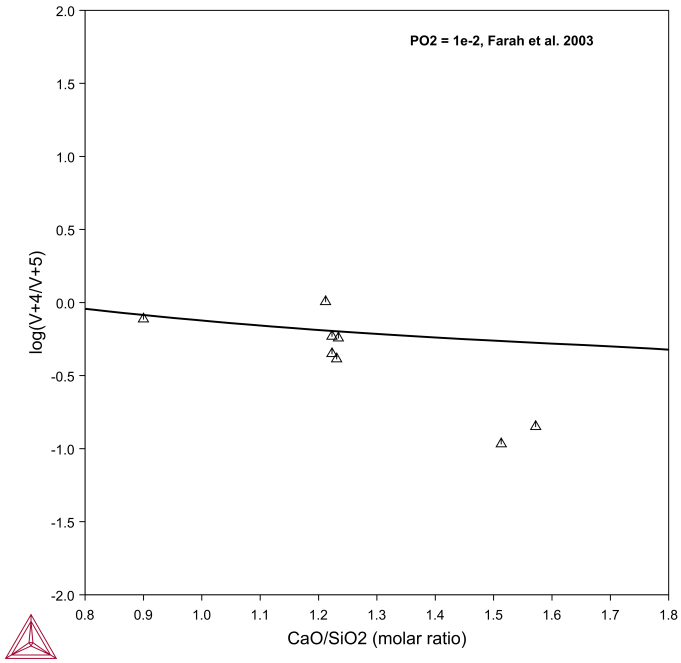

Figure 12: Variation of the V+4/V+5 ratio with basicity at a fixed oxygen partial pressure. Calculated at 1600 °C with experimental data.

The Equilibrium Between SiO_2 and Al_2O_3 in Slag, and Si and Al in Steel

The ratio SiO_2/Si for lime saturated slags in the CaO-Al_2O_3-SiO_2 system in equilibrium with steel, as a function of aluminum content of steel. Results of Bannenberg et al. [1992Ban] for post degassing ladle stirring compared against calculated result from TCS Metal Oxide Solutions Database (TCOX).

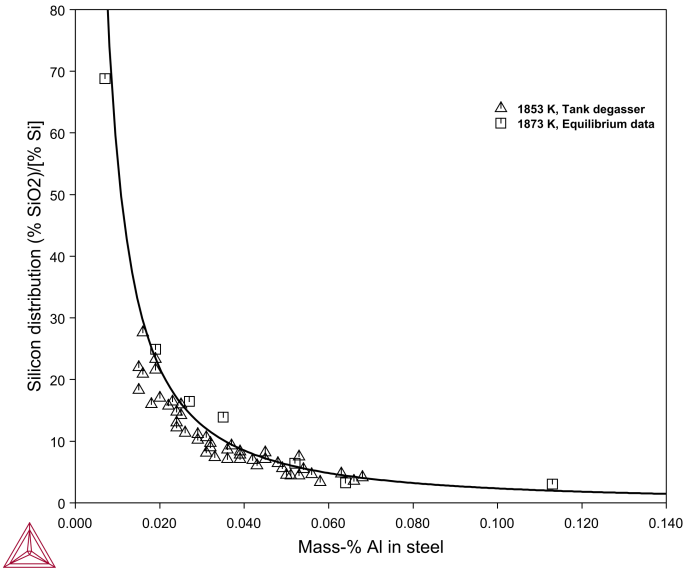

Figure 13: The ratio SiO_2/Si for lime saturated slags in the CaO-Al_2O_3-SiO_2 system in equilibrium with steel as a function of aluminum content of steel.

Reference

[1992Ban] N. Bannenberg, B. Bergmann, H. Gaye, Combined decrease of sulphur, nitrogen, hydrogen and total oxygen in only one secondary steelmaking operation. Steel Res. 63, 431–437 (1992).

Viscosity: Diopside-Albite and Diopside-Anorthite Systems

Diopside-anorthite-albite is a key system of petrological interest and the system has several literature references available describing the phase relationships. However, there is an increased demand to study viscosity and density of oxide melts. When you have details about the viscosity of silicate melts and magmas, it allows for the investigation of the generation, transport, and emplacement of igneous rocks, which then enables you to get information about the melt structure [1983/1986Sca] .

Measurements of viscosity-temperature relationships along the two pseudo-binary joins were made by Scarfe et al. [1983Sca] and Scarfe and Cronin [1986Sca] over the temperature range 1423 K to 1873 K in air.

Examples using the TCS Metal Oxide Solutions Database (TCOX) show the diopside-albite ($MgCaSi_2O_6$-$NaAlSi_3O_8$) and diopside-anorthite ($MgCaSi_2O_6$-$CaAl_2Si_2O_8$) systems.

Diopside-Albite ($MgCaSi_2O_6$-$NaAlSi_3O_8$) System

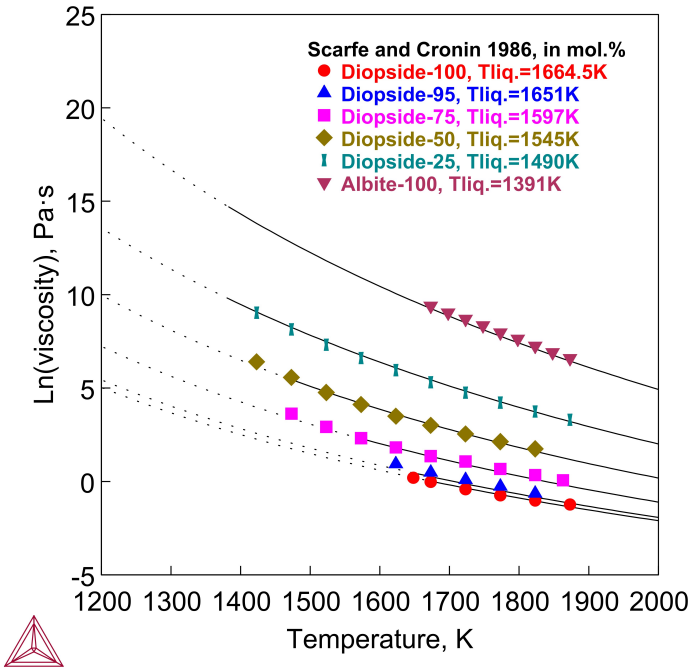

Figure 14: The solid lines represent the calculated viscosities of $MgCaSi_2O_6$-$NaAlSi_3O_8$ system, which are compared with the experimental data by [198Sca].

Diopside-Anorthite ($MgCaSi_2O_6$-$CaAl_2Si_2O_8$) System

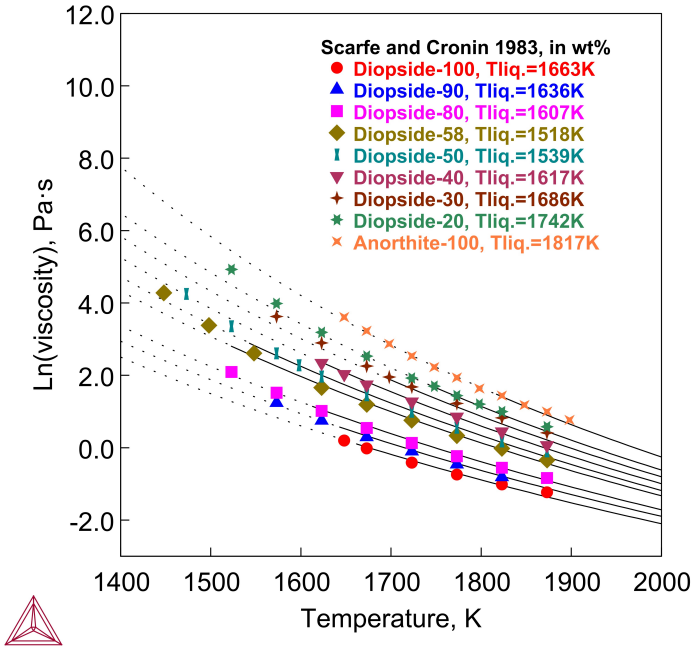

Figure 15: The solid lines represent the calculated viscosities of MgCaSi2O6-CaAl2Si2O8 system, which are compared with the experimental data by [198Sca].

References

[1983Sca] C. M. Scarfe, D. J. Cronin, J. T. Wenzel, D. A. Kauffman, Viscosity-temperature relationships at 1 atm in the system diopside-anorthite. Am. Mineral. 68, 1083–1088 (1983).

[1986Sca] C. M. Scarfe, D. J. Cronin, Viscosity-temperature relationships of melts at I atm in the system diopside-albite, Am. Mineral. 71, 767–771 (1986).

Viscosity: $FeO-CaO-Al_2O_3-SiO_2$

It is beneficial to get the viscosity for coal ash and fluxed coal slags at the tapping temperatures of entrained flow gasifiers. In the work by Hurst et al. [1999/2000Hur], slags derived by fluxing Australian bituminous coal ashes with limestones have properties that may be approximated by the $FeO-CaO-Al_2O_3-SiO_2$ system.

In this example using the TCS Metal Oxide Solutions Database (TCOX), viscosity-temperature curves were determined for a range of slag compositions at the 5 and 15 mass% FeO levels.

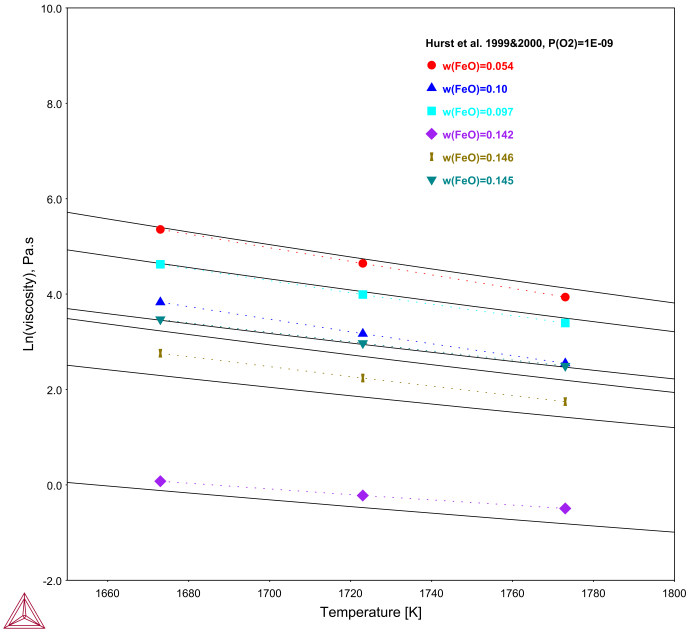

Figure 16: The solid lines represent the calculated viscosities of the $FeO-CaO-Al_2O_3-SiO_2$ system, which are compared with the experimental data by Hurst et al. [1999/2000Hur].

References

[1999Hur] H. J. Hurst, F. Novak, J. Patterson, Viscosity measurements and empirical predictions for some model gasifier slags, Fuel. 78, 439–444 (1999).

[2000Hur] H. J. Hurst, J. Patterson, A. Quintanar, Viscosity measurements and empirical predictions for some model gasifier slags—II, Fuel. 79, 1797–1799 (2000).

Viscosity: $CaSiO_3$-TiO_2

The viscosity along the $CaSiO_3$-TiO_2 join was measured in equilibrium with air by Dingwell [1992Din]. The example using the TCS Metal Oxide Solutions Database (TCOX) shows the comparison between the calculations and this experimental data.

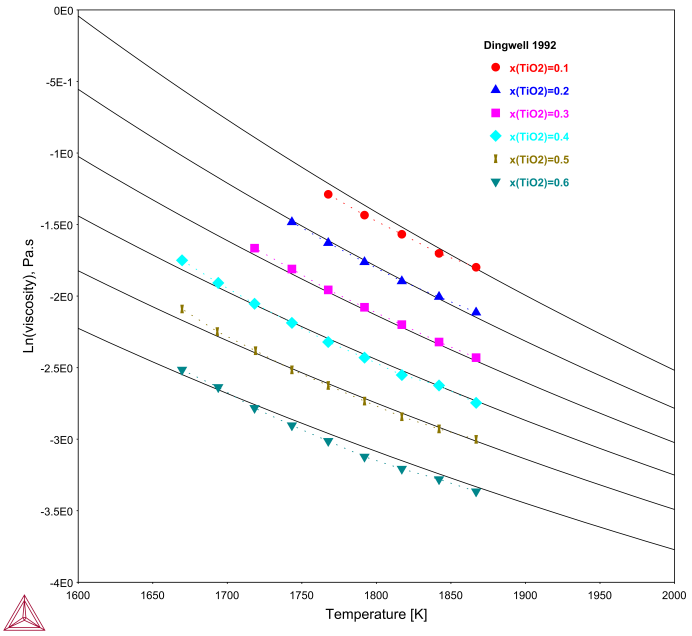

Figure 17: The solid lines represent the calculated viscosities of the $CaSiO_3$-TiO_2 system, which are compared with the experimental data from [1992Din].

Reference

[1992Din] D. B. Dingwell, Shear viscosity of alkali and alkaline earth titanium silicate liquids, Am. Mineral. 77, 270–274 (1992).

Surface Tension of Slag

Surface tension of slag is an important property for mineral processing, metal processing, slagging combustion, and slagging gasification. In the case of slagging gasification, slag properties impact the efficiency, reliability, maintenance cost, and environmental performance of the process [2017Duc]. The calculation of the surface tension using Thermo-Calc and TCS Metal Oxide Solutions Database (TCOX) is validated by comparing with two synthetic slags and one real slag with the various compositions listed in the table below.

	Synthetic coal ash, wt. %	*Real Coal ash, wt. %*	*Synthetic petroleum coke ash, wt. %*
SiO_2	45.4	37.59	54.1
Al_2O_3	20.0	16.61	22.69
Fe_2O_3	6.7	5.54	8.6
TiO_2	0.8	0.69	4.2
P_2O_5	-	0.41	-
CaO	15.9	13.16	2.9
MgO	3.5	2.93	1.5
Na_2O	7.7	6.36	0.7
K_2O	-	0.28	-
V_2O_5	-	-	4.1
NiO	-	-	1.0
MnO	-	0.0245	-
CuO	-	0.0076	-

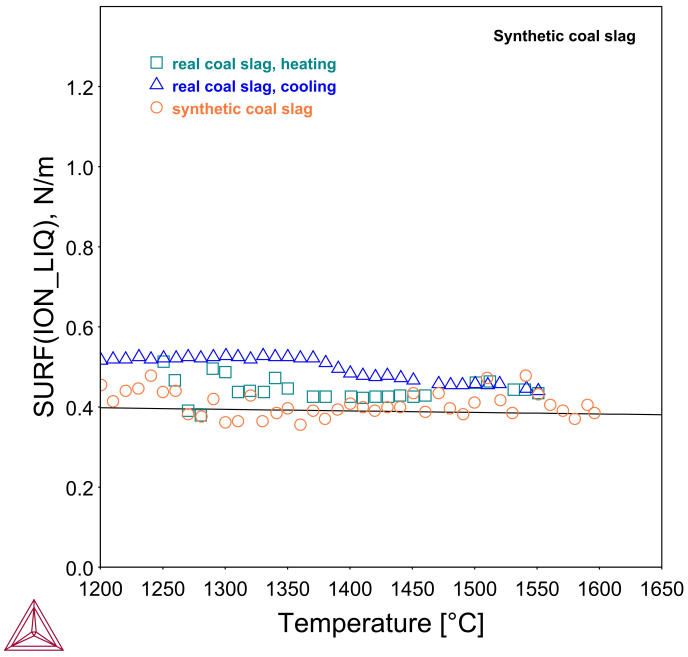

Figure 18: Calculated surface tension under $P(O_2)$ =1e-9 bar compared with the surface tension of synthetic coal slag measured on 8 mm substrates of molybdenum in Ar/H_2 [2017Duc].

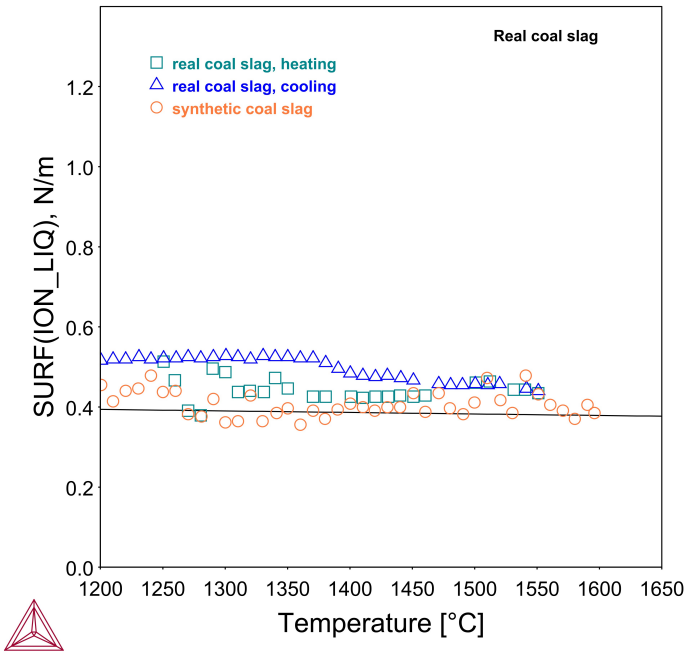

Figure 19: Calculated surface tension under $P(O_2)$ =1e-9 bar compared with the surface tension of real coal slag measured on 8 mm substrates of molybdenum in Ar/H_2 [2017Duc].

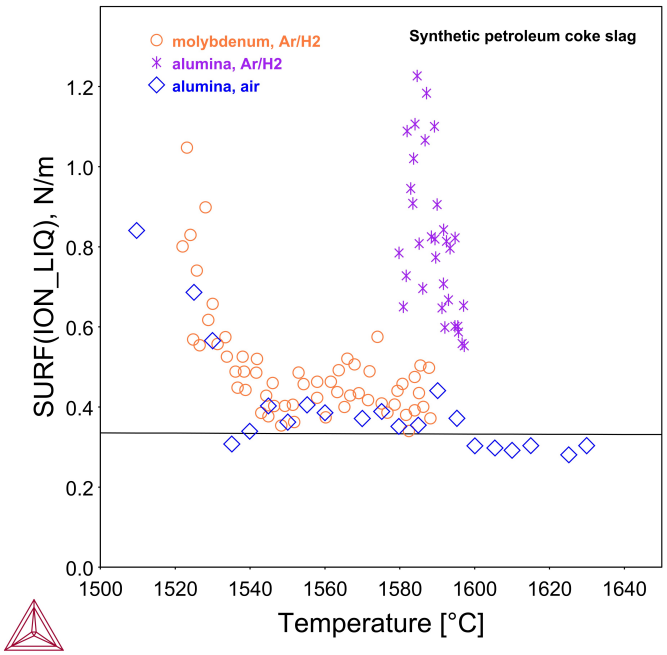

Figure 20: Calculated surface tension in air compared with the surface tension of synthetic petroleum coke slag measured on 8 mm substrates of molybdenum in Ar/H_2, alumina in Ar/H_2, and alumina in air [2017Duc].

Reference

[2017Duc] M.A. Duchesne, R.W. Hughes, Slag density and surface tension measurements by the constrained sessile drop method, Fuel, 188, 173-181 (2017).

Electrical Conductivity in Ionic Liquids

Electrical conductivity (ELCD) of ionic liquids can be calculated using Thermo-Calc and the TCS Metal Oxide Solutions Database (TCOX). Below are examples of how this is simulated.

The electrical conductivity for ionic liquids thermophysical property data is included starting with version 13 (TCOX13).

For more information about the various thermophysical, thermomechanical, and properties models, and when in Thermo-Calc, press F1 to search the online help. The details are found under a *General Reference* section.

You can find information on our website about the properties that can be calculated with Thermo-Calc and the Add-on Modules. Additional resources are added on a regular basis so keep checking back or subscribe to our newsletter.

Fe-O-SiO_2

By changing the partial pressure of oxygen, the electrical conductivity of iron silicate slags was measured by Pastukhov et al. [1966Pas] and Fontana et al. [1984Fon]. The present model can well reproduce the measurements. The comparisons between the calculated electrical conductivity and experimental data are shown as the amount of Fe^{+3} changes.

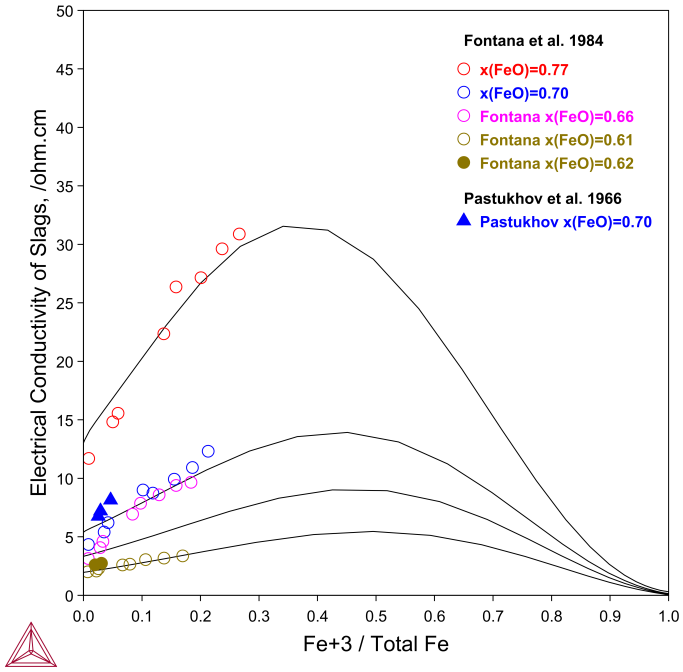

Figure 21: Calculated electrical conductivity of iron silicate slags at 1623 K, compared with the measurements by [1984Fon] and [1966Pas].

$CaO-MgO-Al_2O_3-SiO_2$

In most pyrometallurgical processes, CMAS containing slags are used as the base. Due to its significance, the properties of viscosity, surface tension and electrical conductivity have been measured by several work. The electrical conductivity of three CMAS slags were investigated by Winterhager et al. [1966Win] and Hundermark [2003Hun].

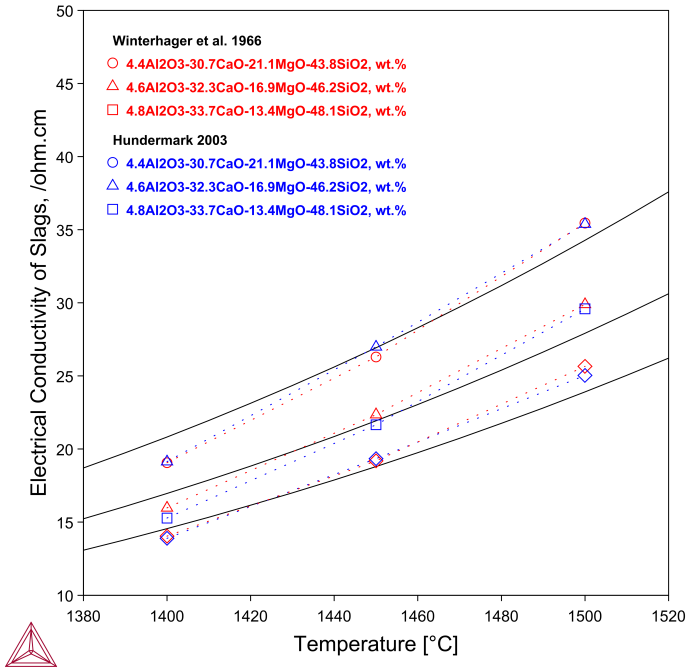

Figure 22: Calculated temperature dependence of electrical conductivity of CaO-MgO-Al_2O_3-SiO_2 slags, compared with the measurements from [1966Win] and [2003Hun].

References

[1966Pas] E. Pastukhov, O. Esin, S. Chuchmarev, Electric conductivity of silicate melts containing iron oxides. Elektrokhimiya. 2, 209–215 (1966).

[1966Win] H. Winterhager, L. Greiner, R. Kammel, Investigations of the density and electrical conductivity of melts in the system CaO-Al2O3-SiO2 and CaO-MgO-Al2O3-SiO2 (Westdeutscher Verlag, Cologne, 1966).

[1984Fon] A. Fontana, L. Segers, K. Twite, R. Winand, Electrical conductivity of ferrous silicate melts from slag cleaning operations, in TMS-AIME Paper Selection, Paper no A84-38 (1984): 13 pp.

[2003Hun] R. Hundermark, The electrical conductivity of melter type slags, Master's thesis, University of Cape Town (2003).

TCOX Calculation Examples

Acknowledgement

Professor Malin Selleby, Dr. Bengt Hallstedt and David Dilner are acknowledged for many valuable discussions and important contributions.

In this section:

Fe-O

The Fe-O system is well known experimentally and has a number of characteristic features in both liquid and solid phases—for example extended solubility of the solid oxides, magnetic transitions, and a liquid miscibility gap. The Fe-O system is interesting since Fe can be both ferrous (+2) or ferric (+3), as shown in this example using the TCS Metal Oxide Solutions Database (TCOX).

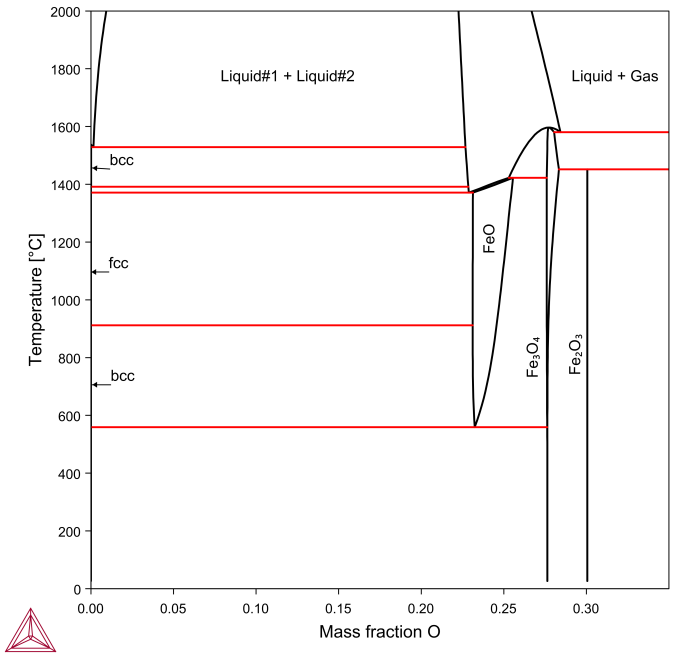

Figure 23: Calculated Fe-O phase diagram [1991Sun].

Reference

[1991Sun] B. Sundman, An assessment of the Fe-O system. J. Phase Equilibria. 12, 127–140 (1991).

Al_2O_3-MgO

The system Al_2O_3-MgO is one of the basic systems to understand metallurgical slags and refractories as is shown in this example using the TCS Metal Oxide Solutions Database (TCOX).

You might want to define the components Al_2O_3, MgO instead of the elements Al, Mg, O. Since there are three elements, also three components are needed. Al_2O_3, MgO, and O are chosen here, but other sets are possible and give the same result. When the conditions are set for the Al_2O_3-MgO "binary", there is one condition missing after giving temperature, pressure, size of system, and composition, e.g. P=1E5 N=1 T=2000 X(AL2O3)=0.3. One option is to give the oxygen activity as a condition. For systems containing only single valent elements, the absolute value on the activity is not very important.

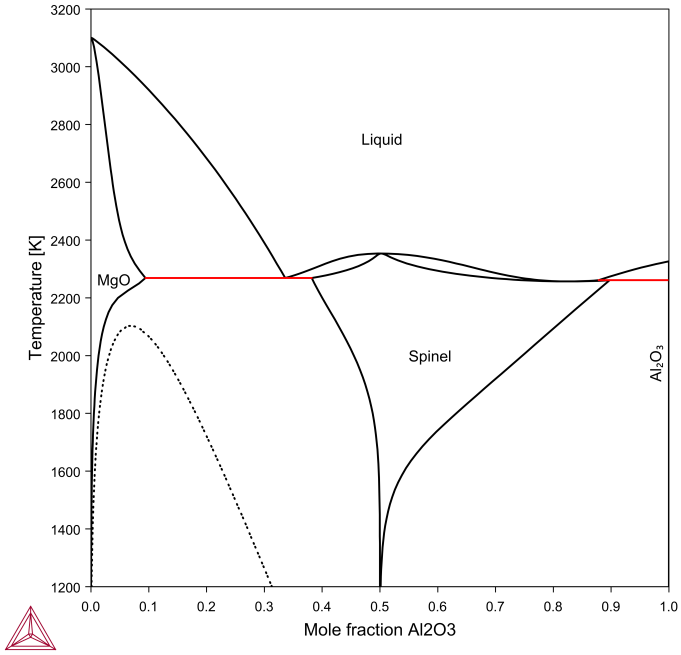

Figure 24: Calculated MgO-Al_2O_3 section with experimental data.

References

[1992Hal] B. Hallstedt, Thermodynamic Assessment of the System MgO-Al2O3. J. Am. Ceram. Soc. 75, 1497–1507 (1992).

[2004Mao] H. Mao, M. Selleby, B. Sundman, A re-evaluation of the liquid phases in the CaO–Al2O3 and MgO–Al2O3 systems. Calphad. 28, 307–312 (2004).

Fe-Mg-O

Magnesium is of great importance for the steelmaking process. Ladle walls are often made of MgO bricks. Due to its importance in the steelmaking process it is vital to have thermodynamic descriptions containing Mg together with Fe and O, as is shown in this example using the TCS Metal Oxide Solutions Database (TCOX).

In contrast to Al_2O_3-MgO, the “missing” condition is really important in systems with multivalent atoms, for example Fe. Experimental phase diagrams are often presented as MgO-FeO or MgO-Fe_2O_3.

- MgO-FeO: with excess iron, often referred to as iron-saturated section, where the iron oxide consists mainly of FeO. This can be calculated in Thermo-Calc by using the condition AC(FE,FCC)=1.
- MgO-Fe_2O_3: Often the phase diagram in air (or oxygen) is presented. This can be calculated in Thermo-Calc by using the condition AC(O2,GAS)=0.21 (air) or =1 (in oxygen).

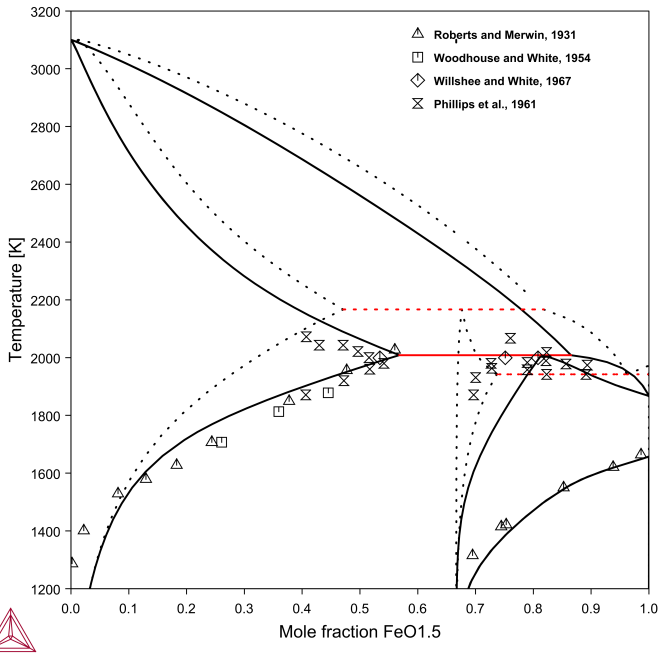

Figure 25: Calculated MgO-"Fe_2O_3" in air. Dashed line is the true binary system MgO-Fe_2O_3 calculated by setting a very high oxygen potential.

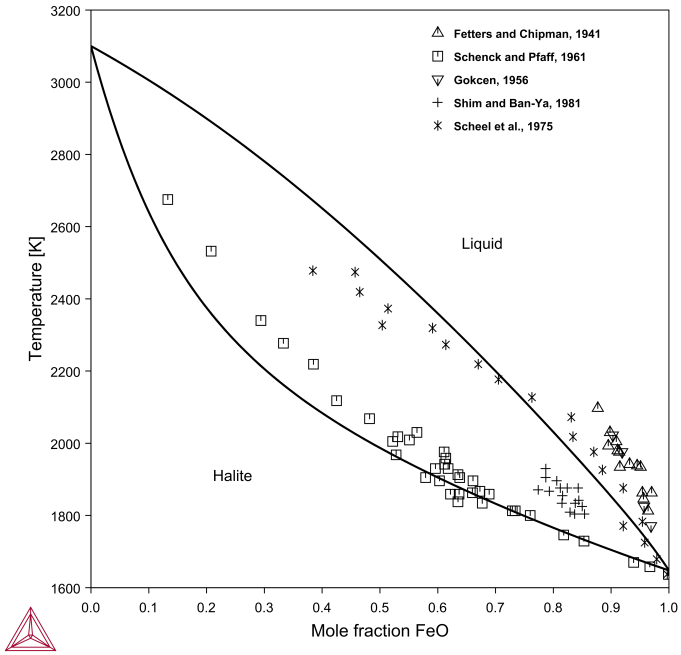

Figure 26: Calculated MgO-"FeO", assuming excess iron.

Reference

[2016Dil] D. Dilner, L. Kjellqvist, M. Selleby, Thermodynamic Assessment of the Fe-Ca-S, Fe-Mg-O and Fe-Mg-S Systems. J. Phase Equilibria Diffus. 37, 277–292 (2016).

Fe-Si-O

Calculating the iron-saturated section in "FeO"-SiO_2 (ac(fe,fcc)=1), there is still some amount of Fe_2O_3 in the liquid as is shown in this example using the TCS Metal Oxide Solutions Database (TCOX).

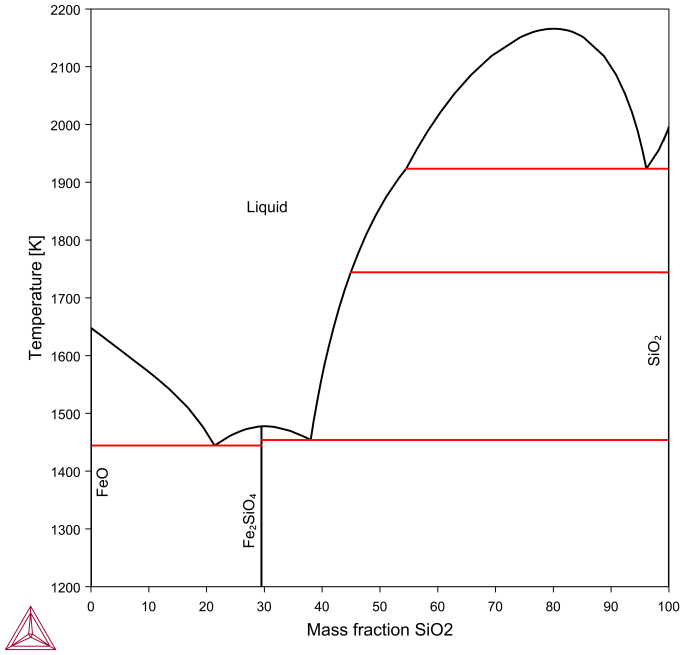

Figure 27: Calculated "FeO"-SiO_2 phase diagram.

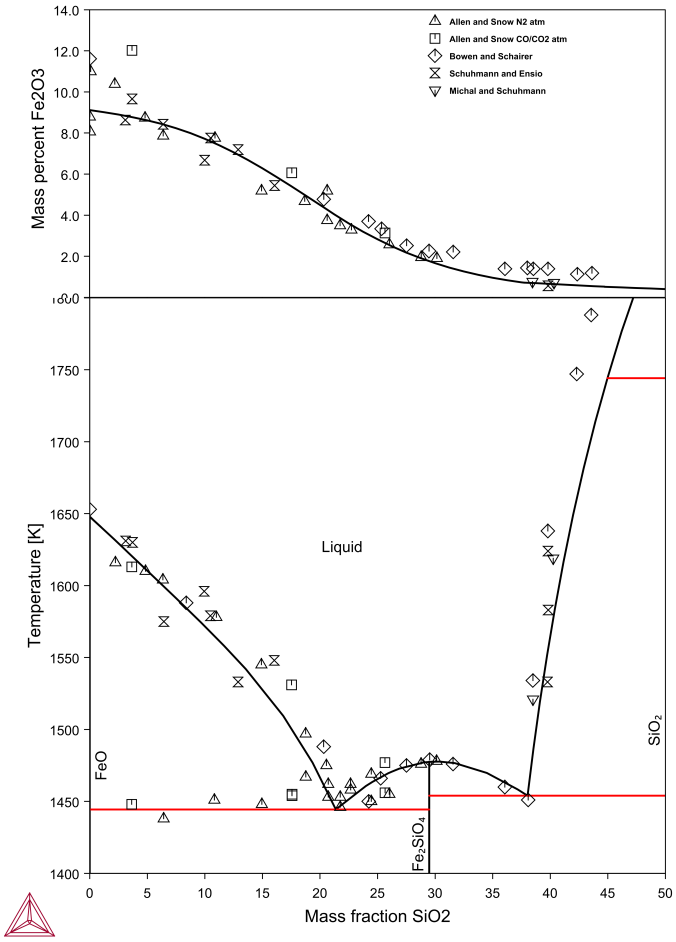

Figure 28: Magnification of the calculated "FeO"-SiO_2 phase diagram. The upper part shows the Fe_2O_3 content in the slag at the liquidus.

Reference

[1997Sel] M. Selleby, An assessment of the Fe-O-Si system. Metall. Mater. Trans. B. 28, 563–576 (1997).

Oxidation Behavior

Oxidation diagrams can be calculated with the TCS Metal Oxide Solutions Database (TCOX) at a fixed oxygen partial pressure (Cr-Fe-O) or at a fixed temperature (Fe-Mn-O).

Cr-Fe-O

Cr and Mn are two of the most important alloying elements in steels and their oxidation behavior is important.

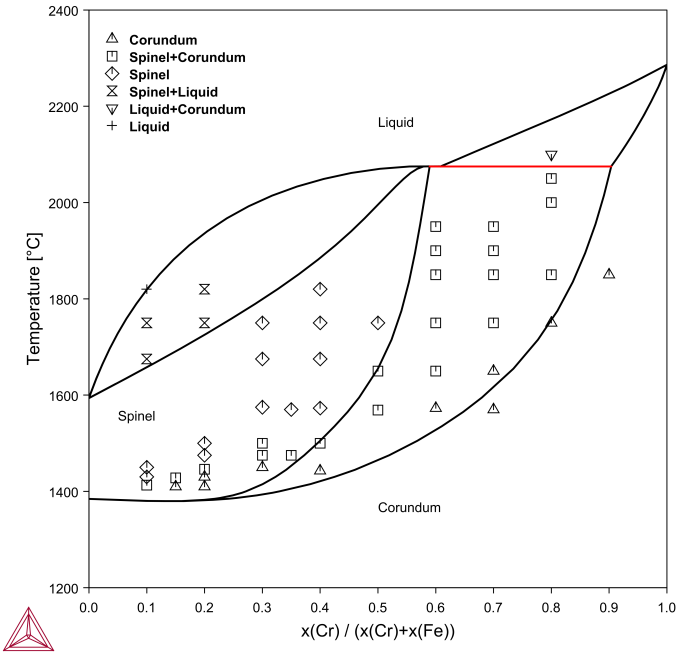

Figure 29: Calculated [2008Kje] and experimental phase diagram of Cr-Fe-O in air.

Fe-Mn-O

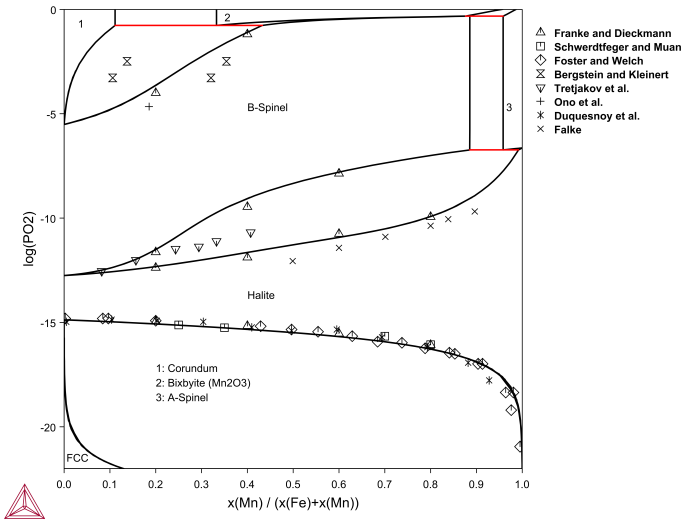

Figure 30: Phase diagram of Fe-Mn-O at 1000 °C, both calculated [2010Kje] and experimental.

References

[2008Kje] L. Kjellqvist, M. Selleby, B. Sundman, Thermodynamic modelling of the Cr–Fe–Ni–O system. Calphad. 32, 577–592 (2008).

[2010Kje] L. Kjellqvist, M. Selleby, Thermodynamic Assessment of the Fe-Mn-O System. J. Phase Equilibria Diffus. 31, 113–134 (2010).

Miscibility Gaps

Miscibility gaps are frequently found in, for example, silicate systems in the liquid slag phase.

Also see the Fe-Si-O system example.

Metastable miscibility gaps in the liquid phase can also be calculated as is shown in this example using the TCS Metal Oxide Solutions Database (TCOX).

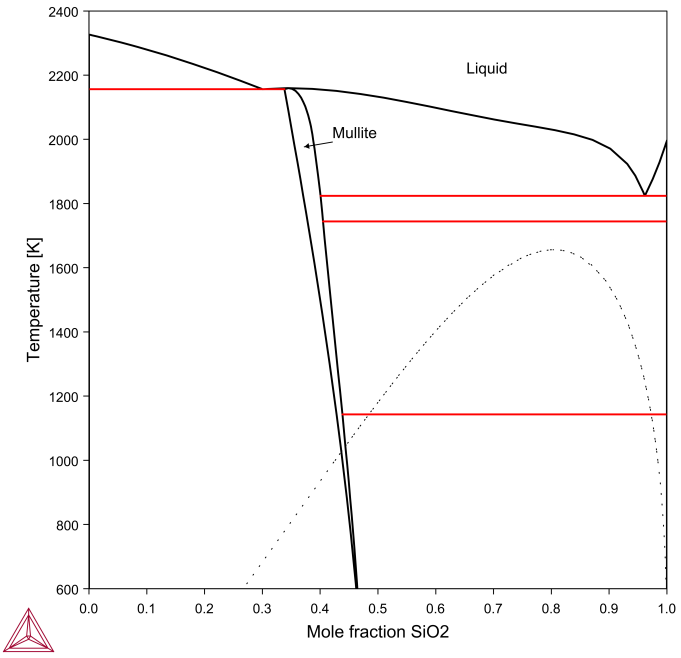

Figure 31: Calculated Al_2O_3-SiO_2 phase diagram. Dashed curve is a metastable liquid miscibility gap [1989aHil; 2007Mao].

Miscibility gaps can also be found in solid phases, both stable and metastable.

CaO and MgO both have the NaCl structure and are modeled as the same phase: halite. These have some mutual solubility and MgO dissolves some Al_2O_3.

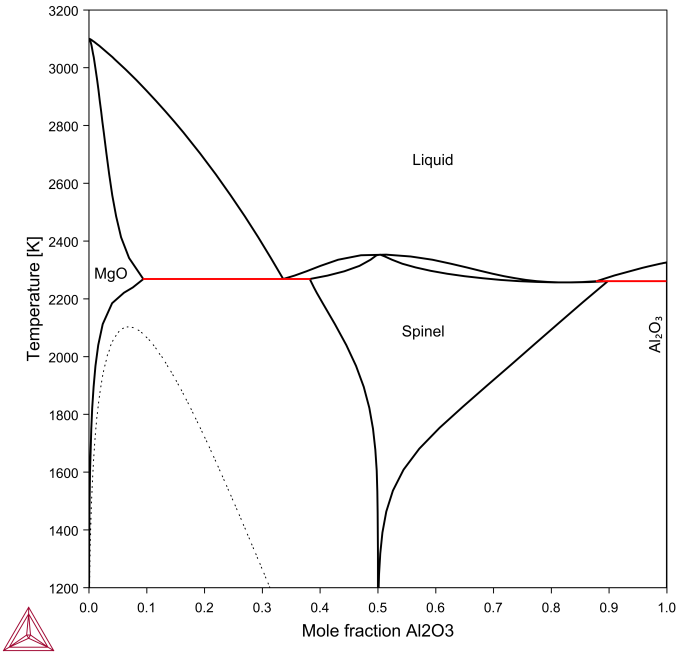

Figure 32: Calculated MgO-Al_2O_3 phase diagram. Dashed curve is a calculated metastable miscibility gap in MgO [1992Hal; 2004Mao].

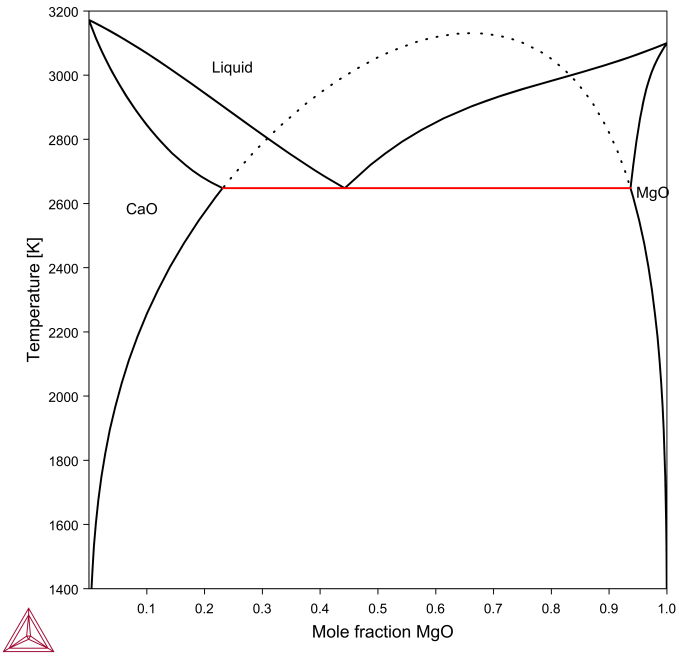

Figure 33: Calculated CaO-MgO phase diagram. Dashed curve is a calculated metastable miscibility gap [1989bHil].

References

[1989aHil] M. Hillert, B. Sundman, X. Wang, A Thermodynamic Evaluation of the Al2O3 -SiO2 System, Trita-Mac. 402, 24 (1989).

[1989bHil] M. Hillert, X. Wang, Thermodynamic calculation of the CaO-MgO system, Calphad. 13, 267–271 (1989).

[1992Hal] B. Hallstedt, Thermodynamic Assessment of the System MgO-Al2O3, J. Am. Ceram. Soc. 75, 1497–1507 (1992).

[2004Mao] H. Mao, M. Selleby, B. Sundman, A re-evaluation of the liquid phases in the CaO–Al2O3 and MgO–Al2O3 systems, Calphad. 28, 307–312 (2004).

[2007Mao] H. Mao, M. Selleby, Thermodynamic reassessment of the Si3N4–AlN–Al2O3–SiO2 system—Modeling of the SiAlON and liquid phases, Calphad. 31, 269–280 (2007).

Isothermal Sections

A pseudo-ternary isothermal section is calculated with two composition axes at a fixed temperature. The oxygen activity could be used as a condition. These are isothermal section examples using the TCS Metal Oxide Solutions Database (TCOX).

Li_2O-MgO-Al_2O_3

An application with a high potential for resource efficient solutions is the pyrometallurgical processing of Li ion batteries. To safeguard raw material sources especially for critical elements such as Co, Ni, and Li as key components of this technology, efficient recycling processes are essential. One of the most important routes to recycle these battery types is the pyrometallurgical processing. While Co, Ni and other valuable heavy metals report into the alloy melt, Li is transferred at least in major amounts into the slag phase of this process. A resource and energy efficient recovery of Li from the slag could be accomplished, if Li were concentrated in specific Li-rich mineral phases, which could then be separated after crystallization and cooling of the slag by means of mineral processing technologies, generating concentrates for subsequent hydrometallurgical processing.

In the system Li_2O-MgO-Al_2O_3, three important primary crystallization fields can be predicted: spinel ($MgAl_2O_4$), MgO and γ-$LiAlO_2$. Interesting isopleths are spinel-$LiAl_5O_8$ and MgO-$LiAlO_2$. From these sections, it can be concluded that a limited amount of $LiAlO_2$ can be dissolved in MgO. Additionally, the compounds $LiAl_5O_8$ and $MgAl_2O_4$ can be combined to form an ideal spinel solid solution.

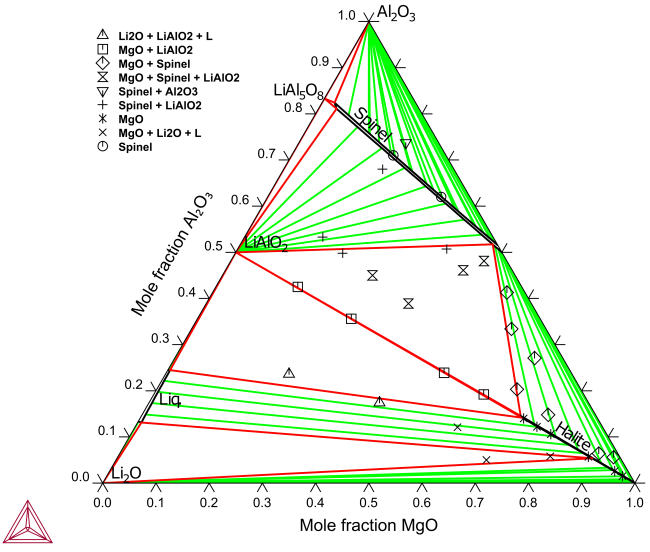

Figure 34: Calculated and experimental Li_2O-MgO-Al_2O_3 isothermal section at 1473 K.

Isothermal Section with Four Components

The CMAS (CaO-MgO-Al_2O_3-SiO_2) system is important for slags and non-metallic inclusions. The Al_2O_3-MgO-CS ($CaO.SiO_2$) isothermal section at 1873 K is calculated with the TCS Metal Oxide Solutions Database (TCOX) using the components AL_2O_3, CAO, MGO, SIO_2, O and the condition X(SIO2)-X(CAO)=0.

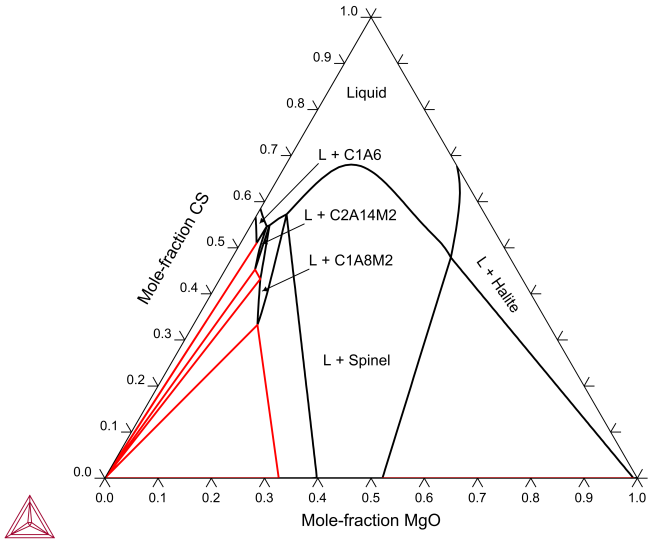

Figure 35: Calculated Al_2O_3-MgO-CS isothermal section at 1873 K.

Liquidus Projections

Liquidus surface calculations have two compositions axis and one temperature axis. When the liquid phase is set in Console Mode as PRESENT, only the monovariant lines with the liquid phase is mapped, as shown in this example using the TCS Metal Oxide Solutions Database (TCOX).

Calculating liquidus projections with more than three elements is not possible in Thermo-Calc Graphical Mode.

"FeO"-MgO-SiO_2

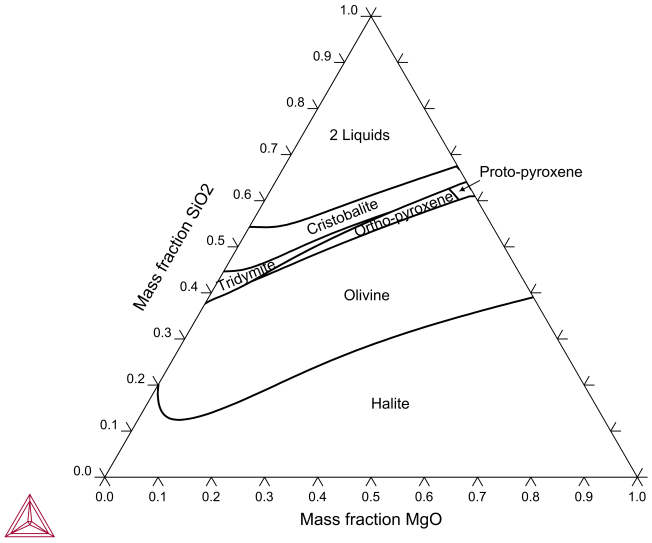

Figure 36: Calculated liquidus surface "FeO"-MgO-SiO_2 in Fe-saturation.

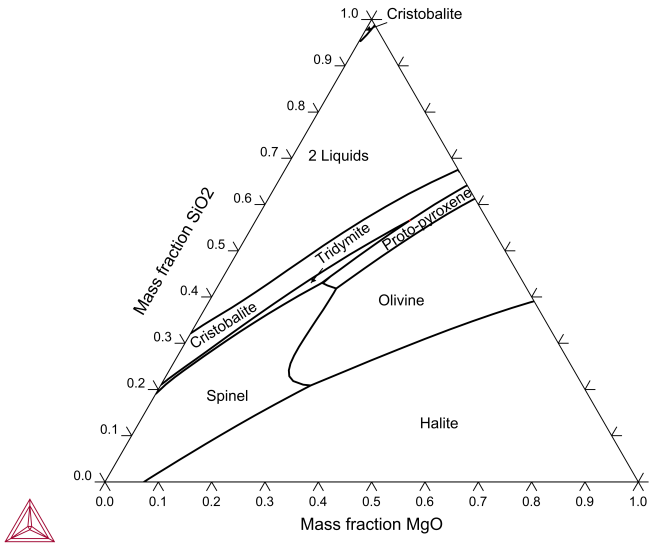

Figure 37: Calculated liquidus surface "Fe_2O_3"-MgO-SiO_2 in air.

CaO-Al_2O_3-SiO_2

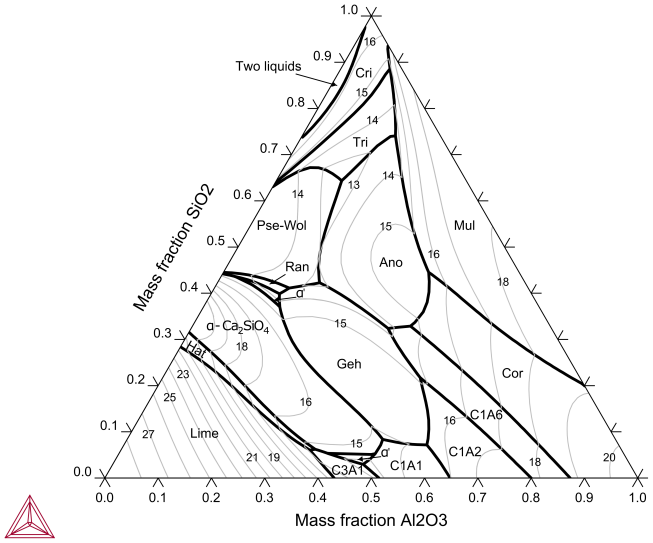

Figure 38: Calculated phase diagram of the CaO-Al_2O_3-SiO_2 system. See the text for a key to the abbreviations.

Key to Plot Abbreviations

Ano: anorthite	Cor: corundum	Pse-Wol: pseudo-wollastonite
C1A1: $CaAl_2O_4$	Cri: cristobalite	Ran: rankinite
C1A2: $CaAl_4O_7$	Geh: gehlenite	Tri: tridymite
C1A6: $CaAl_{12}O_{19}$	Hat: hatrurite	
C3A1: $Ca_3Al_2O_8$	Mul: mullite	

Solidification

A slag with a given composition: 52% CaO-25% SiO_2-13.5% Al_2O_3-1.5% FeO-MgO. The solidus is calculated using the TCS Metal Oxide Solutions Database (TCOX) with increasing MgO content.

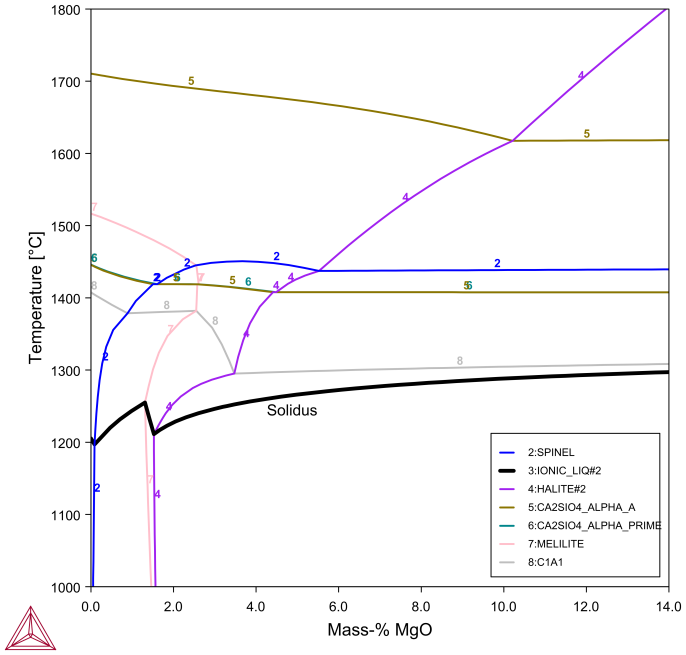

Figure 39: A slag with a given composition where the solidus is calculated with an increasing MgO content.

Vertical Sections

Vertical sections can be calculated in different ways. The components can be redefined to match the endmembers, or you can find a condition that matches the section, as shown in these examples using the TCS Metal Oxide Solutions Database (TCOX).

$MgSiO_3$-$FeSiO_3$

The $MgSiO_3$-$FeSiO_3$ section shown in this example is calculated using the components MGO, FEO, SIO2, O and the conditions AC(FE,FCC)=1, X(SIO2)=0.5.

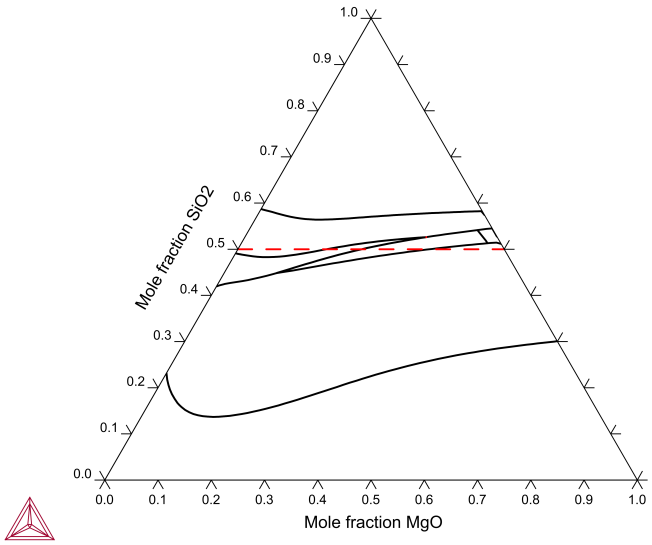

Figure 40: Calculated "FeO"-MgO-SiO_2 liquidus projection. Dashed curve is the pyroxene section $MgSiO_3$-$FeSiO_3$.

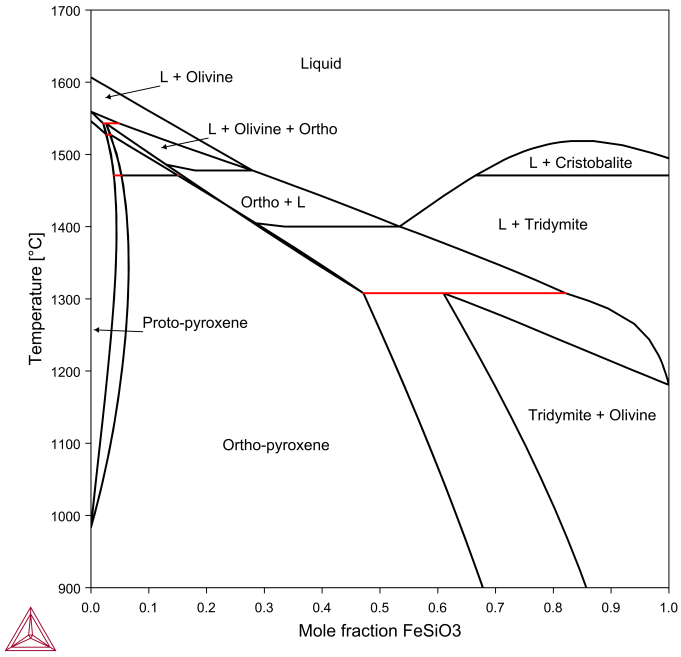

Figure 41: Calculated $MgSiO_3$-$FeSiO_3$ section in equilibrium with Fe.

Fe_2O_3-Mg_2SiO_4

The Fe_2O_3-Mg_2SiO_4 section is calculated using the components MGO, FE2O3, SIO2, O. The section is calculated along a line where the MgO content is twice that of the SiO_2 content, this can be used as a condition: AC(O2,GAS)=0.21, 2*X(SIO2)-X(MGO)=0.

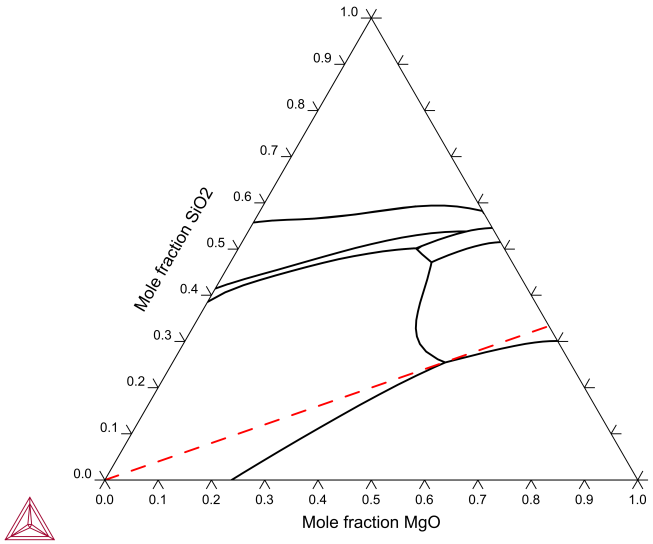

Figure 42: Calculated "Fe_2O_3"-MgO-SiO_2 liquidus projection. Dashed curve is the Fe_2O_3-Mg_2SiO_4 section.

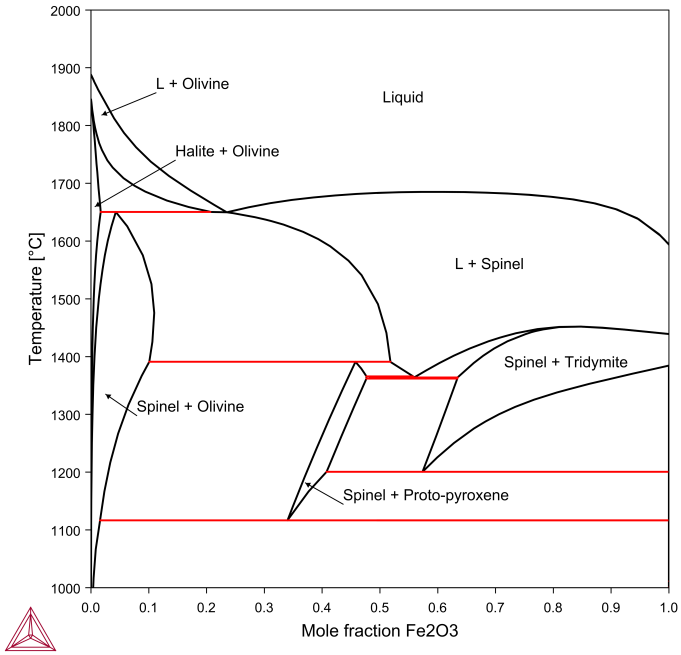

Figure 43: Calculated Mg_2SiO_4-Fe_2O_3 section in air.

$CaMgSi_2O_6$ (diopside)-FeO_x

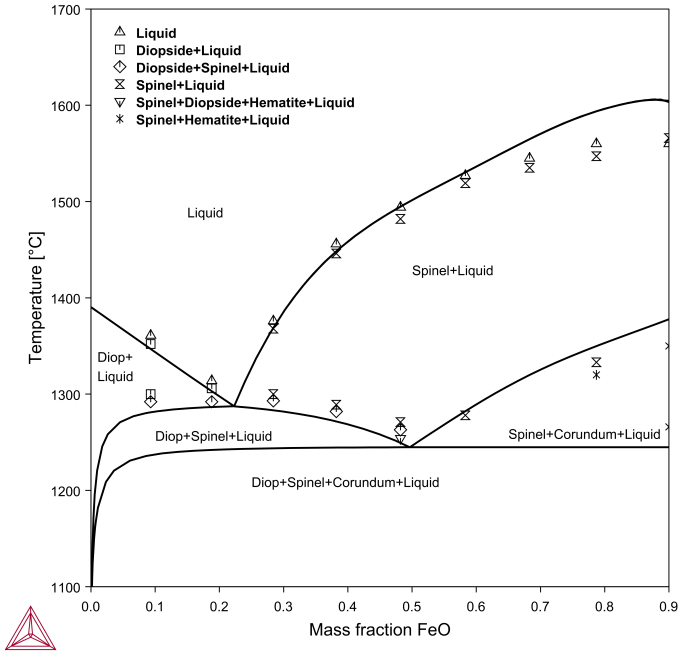

Figure 44: Calculated $CaMgSi_2O_6$ (diopside)-FeO_x section in air.

(50% Al_2O_3, 50% HfO_2)-Y_2O_3

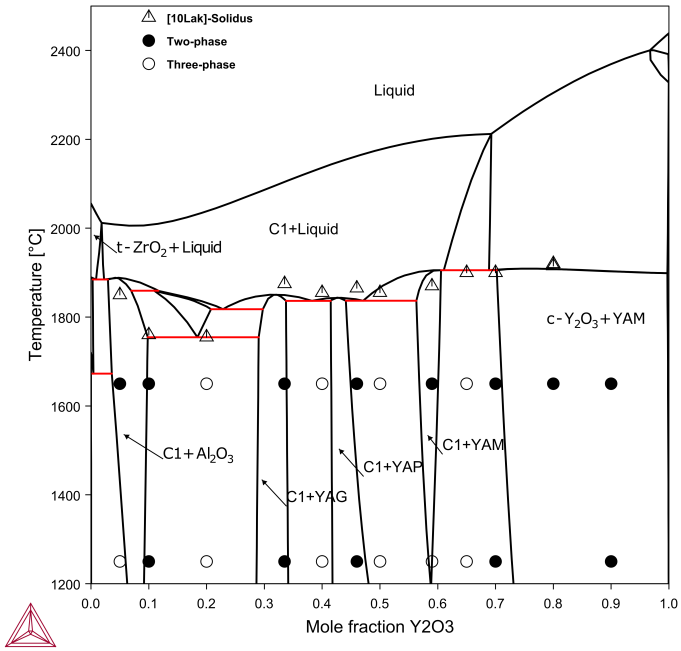

Figure 45: Calculated and experimental (50% Al_2O_3, 50% HfO_2)-Y_2O_3 section.

CaB_2O_4-$Ca_3Si_2O_7$

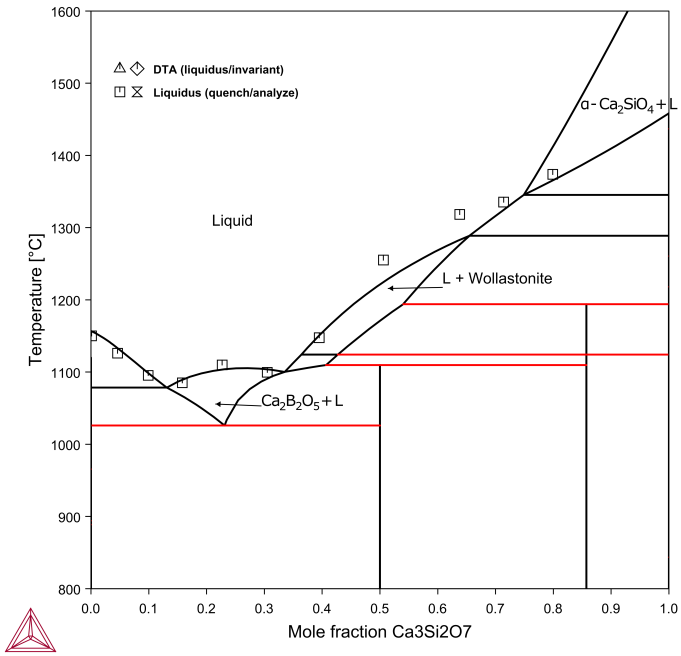

Figure 46: Calculated and experimental CaB_2O_4-$Ca_3Si_2O_7$ section.

BaB_2O_4-$LiBO_2$

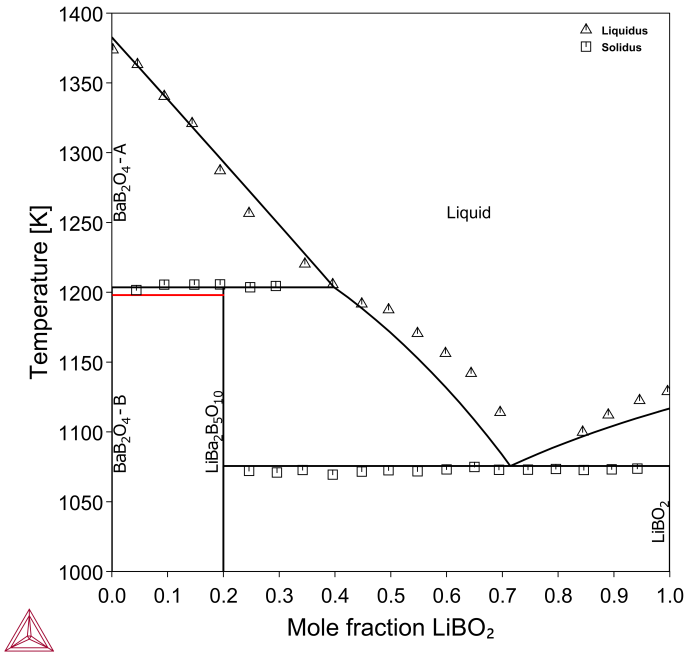

Figure 47: Calculated and experimental BaB_2O_4-$LiBO_2$ section.

Inclusions

Given a steel with 20 ppm O and 0.01%S. Vary the amount of Al and Ca at 1813 K and see which inclusions are formed, something you can examine using the TCS Metal Oxide Solutions Database (TCOX).

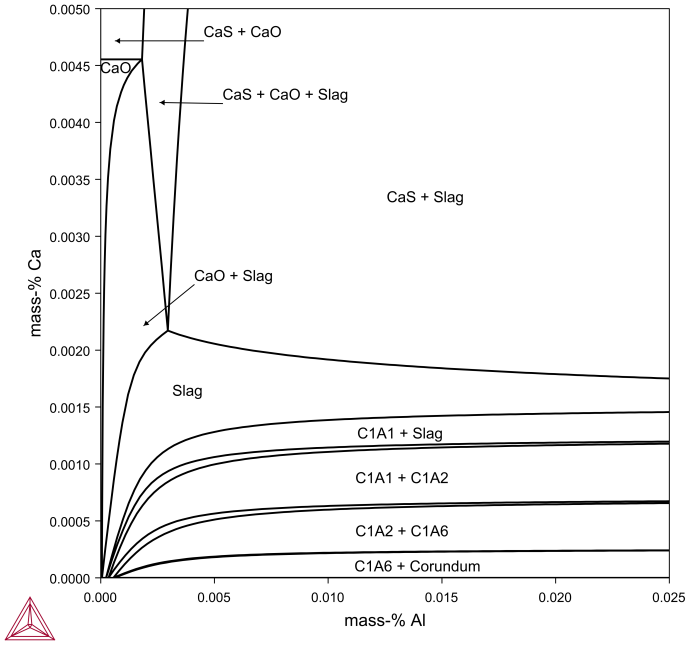

Figure 48: Calculated effect of formed inclusions in a steel with 20 ppm O with varied amounts of Al and Ca at 1813 K. C1A1, C1A2 and C1A6 are short for $CaO.Al_2O_3$, $CaO.2Al_2O_3$, $CaO.6Al_2O_3$.

Effect of Inclusion Composition of 18-8 Stainless Steel

The stability and composition of sulfides were investigated [1980Ono] at 1100 °C by varying the Mn concentration of the steel: Fe - 0.06% C - 0.6% Si - 0.2% S - 8.4% Ni - 18.2% Cr.

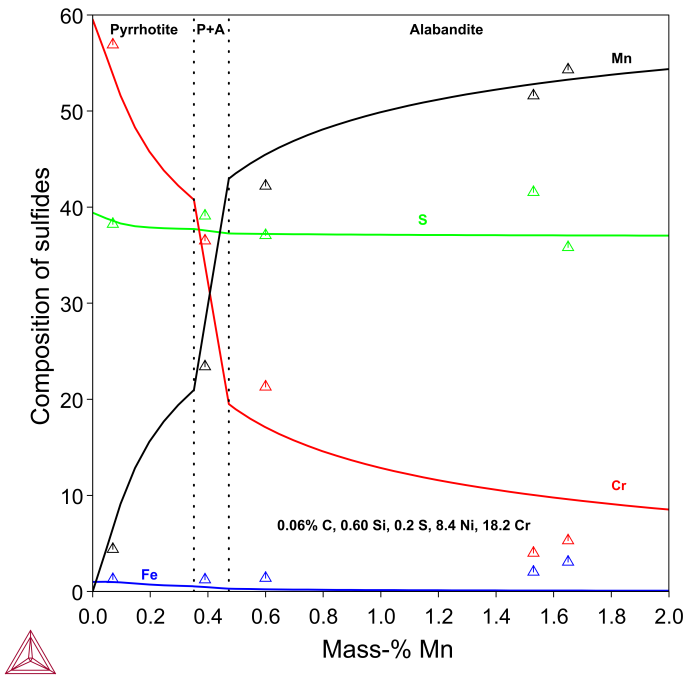

Figure 49: Calculated effect of inclusion composition of 18-8 stainless steel.

Reference

[1980Ono] K. Ono, T. Kohno, Effect of Inclusion Composition on Stability of Inclusions and Corrosion Resistance of 18-8 Stainless Steel. Denki-Seiko[Electric Furn. Steel]. 51, 122–131 (1980).

Effect of CaF_2 on the Al_2O_3-CaO-SiO_2 Liquidus

Calcium fluoride is known as a powerful reagent in hot metal pretreatment and steelmaking slag, which is based on lime. In recent years, steelmakers were advised to limit the fluorine consumption because of its harmful effects on refractory walls and environmental issues.

The CaO-Al_2O_3-SiO_2 (CAS) system is one of the basic systems for metallurgical slags and has been extensively studied. The effect of CaF_2 on the viscosity of slags have been widely investigated and CaF_2 is well known to decrease slag melting point and increases lime solubility and slag fluidity as well and improves hot metal refining process, as shown in this example using the TCS Metal Oxide Solutions Database (TCOX).

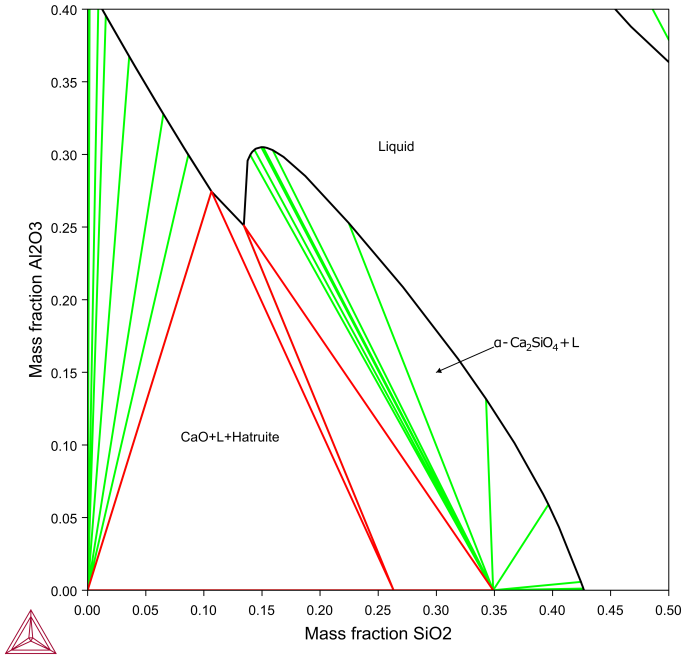

Figure 50: Calculated isothermal section of the Al_2O_3-CaO-SiO_2 system at 1600 °C.

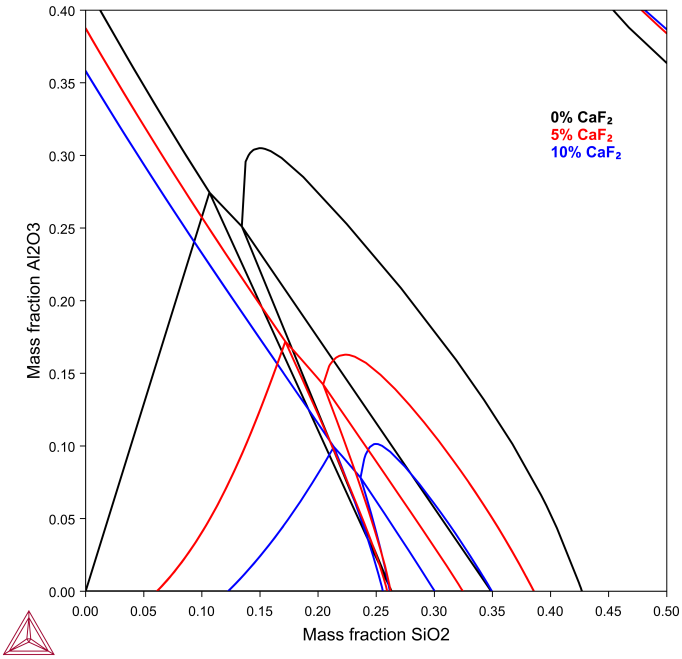

Figure 51: The calculated effect of CaF_2 on the Al_2O_3-CaO-SiO_2 system at 1600 °C with no, 5 and 10% CaF_2. The stability of the liquid one-phase area increases with increasing CaF_2 additions.

Viscosity of SiO_2

SiO_2 is one of the most fundamental components for metallurgical oxide slags, which is why there are many studies conducted about the viscosity of SiO_2. This example is an outline of the steps to calculate the viscosity of SiO_2 using Thermo-Calc and the TCS Metal Oxide Solutions Database (TCOX).

You can either define the elements of Si and O or the oxides of SiO_2 and O. Since in most industrial applications, the component SiO_2 is preferred in practice, SiO_2 and O are used as the input components.

After entering the conditions of temperature, pressure, size of the system and composition, for example, `T=2000K, P=1E5, X(SiO2)=1`, you can perform the equilibrium calculation and plot the property of viscosity of SiO_2 by using the parameter of `dvis(ion)`, which in Thermo-Calc is the viscosity of ionic liquid.

Considering the sharp change of viscosity of SiO_2 as temperature changes, an option is to plot `ln (viscosity) (natural log)` as `ln(dvis(ionic))`.

The calculation below the melting point of SiO_2 is the extrapolation from the viscosity of SiO_2 melt.

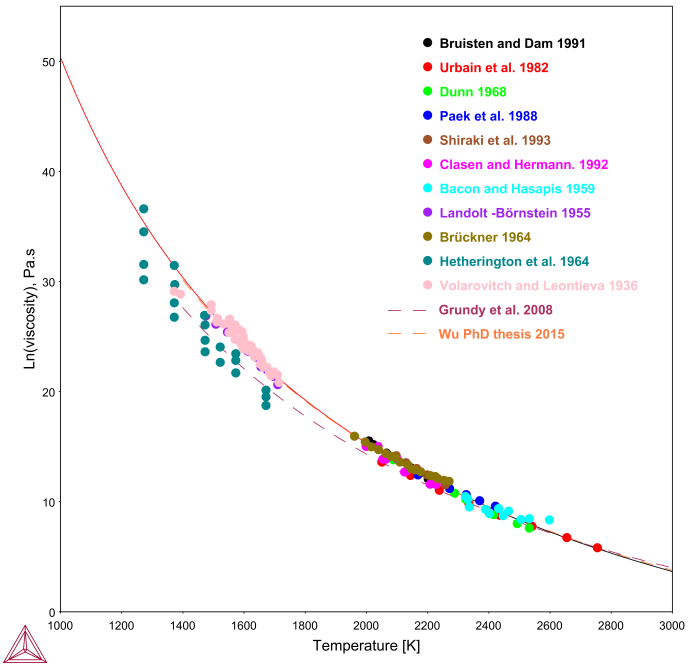

Figure 52: Calculated viscosity of SiO_2 compared to the literature data.

Viscosity of the Fe-Si-O System

When iron is included in the study of viscosity, it is of great importance to know the atmosphere under which the measurements are made since Fe exists as ferrous (+2) or ferric (+3), or both. The experimental data that reports the partial pressure of oxygen is given a higher weight during the assessment. In Thermo-Calc:

- when the system is consisted of mainly FeO (often referred to as iron-saturated), you can use the condition of `AC(FE,FCC)=1`;
- when the system is in equilibrium in air, you can use the condition of `AC(O2,GAS)=0.21` (air) or `AC(O2,GAS)=1` (oxygen).

This example, using the TCS Metal Oxide Solutions Database (TCOX), shows how you can calculate the viscosity for the Fe-Si-O system with iron saturation. In the work by Kucharski et al. [1989Kuc], the partial pressure of oxygen was reported to be 6.08e-6 N/m2 that it tends to form Fe+2, and the mass ratio of Fe/Si was measured. Therefore, one can define the components as Fe, Si and O. Since the PO2 was reported, one only needs to define the AC(O2,GAS) instead of AC(FE,FCC).

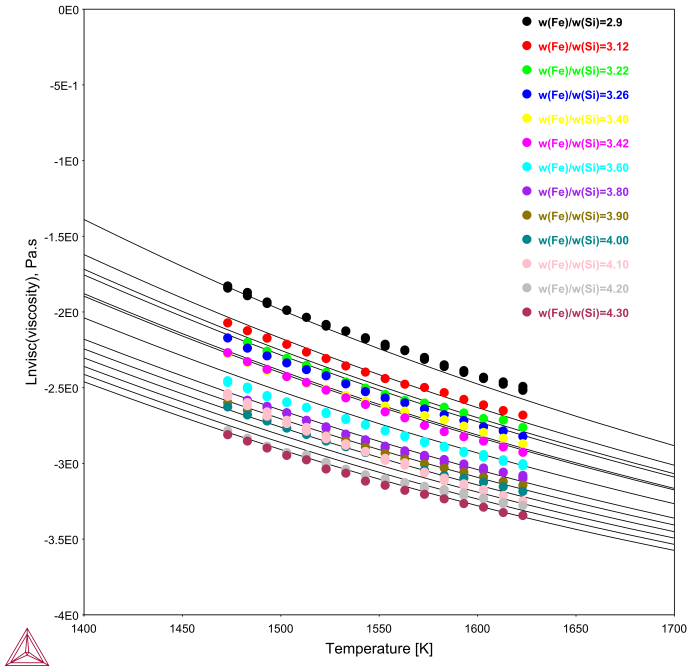

Figure 53: Comparison between the calculations and literature data.

Reference

[1989Kuc] M. Kucharski, N. M. Stubina, J. M. Toguri, Viscosity Measurements of Molten Fe–O–SiO2 , Fe–O–CaO–SiO2, and Fe–O–MgO–SiO2 Slags. Can. Metall. Q. 28, 7–11 (1989).

Viscosity of the CaO-MgO-Al_2O_3-SiO_2 System

The CaO-MgO-Al_2O_3-SiO_2 system, often abbreviated as CMAS, is one of the major systems for blast furnace slags and steelmaking and ironmaking slags.

This example using the TCS Metal Oxide Solutions Database (TCOX) demonstrates the comparison between the present calculation and the literature data regarding the viscosity of a blast furnace slag. The calculation is performed by using the components of CaO, MgO, Al_2O_3, SiO_2 and O. After giving the temperature, pressure, size of the system and compositions, one more condition is needed to make the degree of freedom of the system as zero, so oxygen activity is used as a condition in this example. The CMAS system contains only single valent elements, so the absolute value of the activity has no effect on the final calculation.

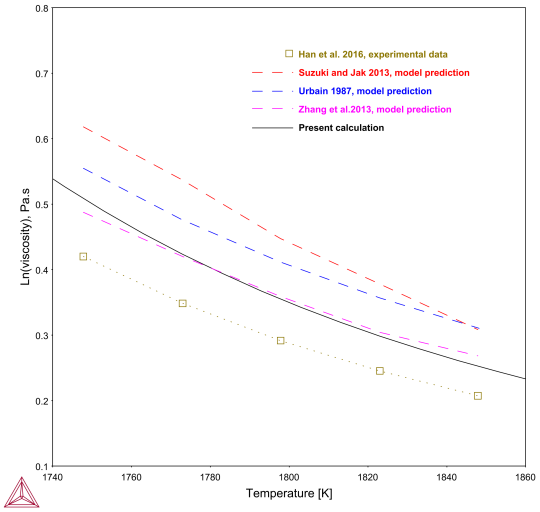

Figure 54: Comparison between the literature data and the present calculation for the slag composition of 35.6 wt.%SiO2, 15wt.%Al2O3, 46.3 wt.% CaO, and 3 wt.%MgO.

References

[1987Urb] G. Urbain, Viscosity estimation of slags, Steel Res. 58, 111–116 (1987).

[2013Suz] M. Suzuki, E. Jak, Quasi-Chemical Viscosity Model for Fully Liquid Slag in the Al2O3-CaO-MgO-SiO2 System. Part II: Evaluation of Slag Viscosities, Metall. Mater. Trans. B. 44, 1451–1465 (2013).

[2013Zha] G.-H. Zhang, K.-C. Chou, K. Mills, A Structurally Based Viscosity Model for Oxide Melts, Metall. Mater. Trans. B. 45, 698–706 (2014).

[2016Han] C. Han, M. Chen, W. Zhang, Z. Zhao, T. Evans, B. Zhao, Evaluation of Existing Viscosity Data and Models and Developments of New Viscosity Model for Fully Liquid Slag in the SiO2-Al2O3-CaO-MgO System, Metall. Mater. Trans. B. 47, 2861–2874 (2016).

Surface Tension of CaF_2-CaO and CaO-Al_2O_3-SiO_2

The thermophysical properties available with the TCS Metal Oxide Solutions Database (TCOX) include surface tension.

For more information about the various thermophysical, thermomechanical, and properties models, and when in Thermo-Calc, press F1 to search the online help. The details are found under a *General Reference* section.

You can find information on our website about the properties that can be calculated with Thermo-Calc and the Add-on Modules. Additional resources are added on a regular basis so keep checking back or subscribe to our newsletter.

CaF_2-CaO

The CaF_2 component is well known as network modifier and surface-active constituents in mold flux. With the addition of CaF_2 into the slag, it decreases the surface tension.

This example is an outline of the steps to calculate the surface tension of CaF_2-CaO using Thermo-Calc and the TCS Metal Oxide Solutions Database (TCOX).

You can define the components of CaF_2, CaO, and O as in most industrial applications, and these components are preferred in practice. The gas atmosphere is usually fixed as in air by using P=1E5 and ac (O_2,gas)=0.21, but can be changed according to the specific experimental conditions reported. By using the variable of `SURF(ION)`, you can plot the property of surface tension of the ionic liquid phase.

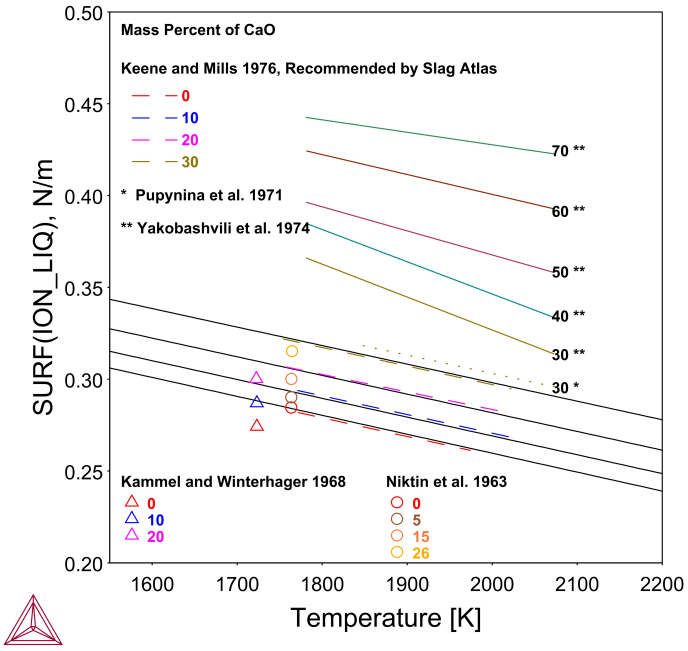

Figure 55: Variation of the surface tension of CaF_2-CaO melt with temperature.

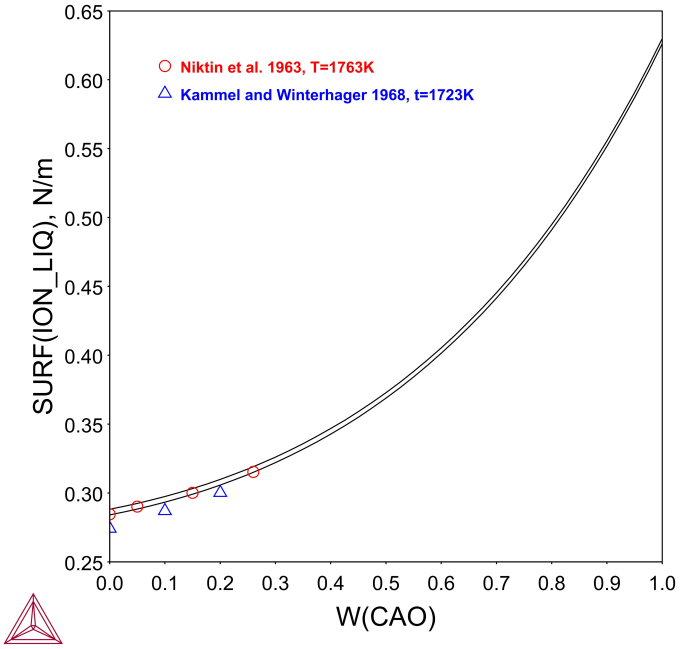

Figure 56: Variation of the surface tension of CaF_2-CaO melt with composition of CaO.

$CaO-Al_2O_3-SiO_2$

This example using the TCS Metal Oxide Solutions Database (TCOX) demonstrates the comparison between the present calculation and the literature data regarding the surface tension of Al_2O_3-CaO-SiO_2. The calculation is performed by defining the components of Al_2O_3, CaO, SiO2 and O. After giving the temperature, pressure, size of the system, compositions and oxygen activity, one can calculate the equilibria and then plot the surface tension by using the variable of `SURF(ION)`.

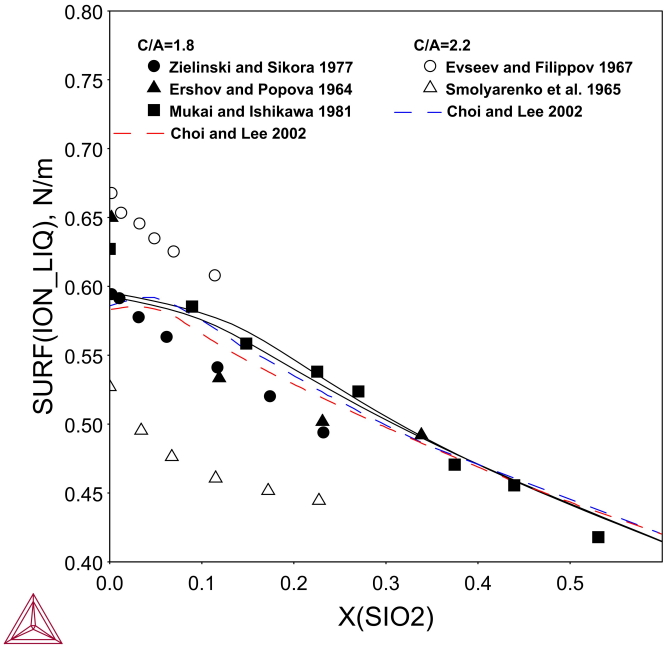

Figure 57: Surface tension of the CaO-Al_2O_3-SiO_2 system with x(CaO)/x(Al_2O_3)=1.8 and 2.2 at 1873 K.