Estimating the physical properties of slags

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Transaction Paper

Synopsis

The objective of this work was to provide process engineers with values of the physical properties of various slag systems involved in high-temperature processes. Software that calculates the thermo-physical properties of slags from chemical composition is available on the www.pyrometallurgy.co.za website. This paper outlines the principles underlying the various models available in the program. The software calculates the following properties of crystalline, glassy, and liquid slags (where appropriate) as a function of temperature: heat capacity, enthalpy, density, viscosity, thermal conductivity, electrical conductivity, and surface tension. We hope, in the future, to update the program to (i) add new models as they become available, (ii) remove any 'bugs' discovered in existing programs, and (iii) provide guidance on the limitations of individual programs.

Keywords
pyrometallurgy, molten, slag, physical properties, heat capacity, enthalpy, density, viscosity, thermal conductivity, electrical conductivity, surface tension.

Introduction

Slags play an important part in many processes in metal production and refining, coal gasification, continuous casting, etc. The properties of these slags have a significant effect on the performance of the process, e.g. the selection of viscosity and solidification temperature are key to minimizing defects in the continuous casting of steel[1], and the electrical conductivity of the slag determines the power supply requirements of many electric smelting processes[2]. The physical properties of these slags are needed to solve process problems and to improve product quality. However, in recent years there has been an exponential increase in the use of mathematical models to solve process and quality problems, and these models require reliable input data for the physical properties of the slags used in the process. As there are a large number of processes, a wide range of slag compositions used in any one process, and a large number of properties involved, there is a need for a vast amount of property data. The measurement of thermo-physical properties of molten slags is both difficult and expensive. Consequently, there has been a drive to develop empirical rules and models to estimate the various properties of slags from their chemical compositions, as this information is available on a routine basis. Furthermore, the properties of glasses and enamels are also related to those of slags, and so the models developed can, in some cases, be applied to these materials too.

A significant number of models have been reported to estimate the thermo-physical properties of slags. For some properties (e.g. viscosity) there are a large number of reported models available, whereas, in other cases, there are few reported models (e.g. electrical and thermal conductivities) and these are frequently available only for either simple slag systems (e.g. ternaries) or for a limited compositional range.

Silicates are the basis of most metallurgical slags, and their physical properties are very dependent on the silicate structure developed in the molten slag[3]. The dependence of property on structure is in the hierarchy, viscosity (η) > electrical conductivity (κ) and thermal conductivity (k) > thermal expansion coefficient (α) > density (ρ) > surface tension (γ) > C_p and enthalpy. In fact, some workers have proposed that the viscosity is a convenient form to represent slag structure[4,5]. In recent years, the capabilities of commercial thermodynamic software packages have expanded from the estimation of thermo-dynamic properties to the estimation of parameters to represent the slag structure and which lead to the calculation of slag densities and viscosities[6–10]. The reliability of the property values estimated by the various

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thermodynamic packages will be evaluated in the future. Most process engineers do not have either the time or the specific expertise required to implement the reported models. Consequently, we have developed here a simple program that will enable engineers to estimate thermo-physical properties from the chemical composition of the slag in mass per cent.

Objectives of this work

The objectives of this work are:

(i) To develop a program to calculate various physical properties of slags from their chemical compositions and to make this openly available by placing it on the www.pyrometallurgy.co.za website
(ii) To write a set of notes to accompany the program to aid its use, point out the limitations of predictions of individual models, range of applicability, etc., and provide guidance on which model to use for the slag system in question
(iii) To identify any 'bugs' within the program and correct them continually
(iv) To add new models as they become available.

Effect of structure and other factors on properties

A full list of the symbols and abbreviations used is given at the end of this paper.

Structure of silicate and alumino-silicate slags

Slags are formed of ions, and slag reactions are electro-chemical in nature, involving the exchange of ions. Slags contain two forms of bonds: (i) covalent Si-O bonds that form into chains, rings etc., and (ii) ionic bonds involving cations such as Na^+ or Ca^{2+} that break the silicate chains, etc., to form Na^+-O^- bonds[11]. The silicate structural unit (SiO_4^{4-}) consists of one Si^{4+} ion surrounded tetrahedrally by four O^{2-} ions (Figure 1)[11]. Each of these O ions has a negative charge, and so can connect to either another O^- ion and thereby add to the network (denoted as a bridging oxygen (BO or O^o)) or to a cation, thereby breaking the chain (denoted as a non-bridging oxygen (NBO or O^-). Oxygen ions that are not associated with Si ions are referred to as free oxygen (denoted O^{2-})[11].

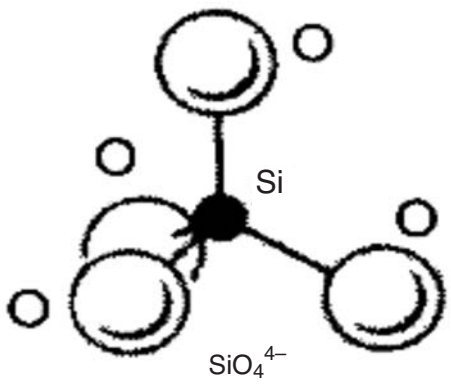

Figure 1—Silicate structure showing four O^- in tetrahedral positions surrounding a Si^{4+} ion

The structure of a slag can thus be represented by the mole fractions (X) of O^o, O^-, and O^{2-} present. Consequently, it is customary to divide various constituents into either network formers (e.g. SiO_2) or network breakers (CaO, Na_2O, etc.). However, when Al_2O_3 is added to a silicate slag, the Al^{3+} ion can be absorbed into the Si^{4+} chain but requires charge-balancing cations (e.g. Na^+ or $0.5Ca^{2+}$) to create a $(NaAl)^{4+}$ ion which must be located near the Al^{3+} as shown in Figure 2. Cations on charge-balancing duties cannot act as network-breakers.

Parameters used to represent structure

Several parameters have been used to represent the structure of the slag. The earliest models used the basicity (%CaO/%SiO_2) or basicity indices where different weights were given to different basic oxides (e.g. CaO, MgO, or FeO). The most widely used parameter is the ratio of NBO to tetragonal ions (NBO/T), which is calculated using Equation [1]. NBO/T is a measure of the depolymerization of the slag.

$$\text{NBO/T} = 2(X_{MO}+X_{M_2O}+3f X_{M_2O_3} - X_{Al_2O_3} - (1-f) X_{M_2O_3})/(X_{SiO_2} + 2 X_{Al_2O_3} +2(1-f)X_{M_2O_3}) \quad [1]$$

where X = mole fraction, f = fraction of M_2O_3 acting as a network breaker MO=CaO, FeO etc. M_2O=Na_2O etc. and M_2O_3 =Fe_2O_3, Cr_2O_3 etc.

Some workers prefer using the parameter Q (defined in Equation [2]) since this provides a measure of the polymerization of the slag that is easier to visualize; Q will be used here. Table I provides some examples of the physical reality of various Q and (NBO/T) values.

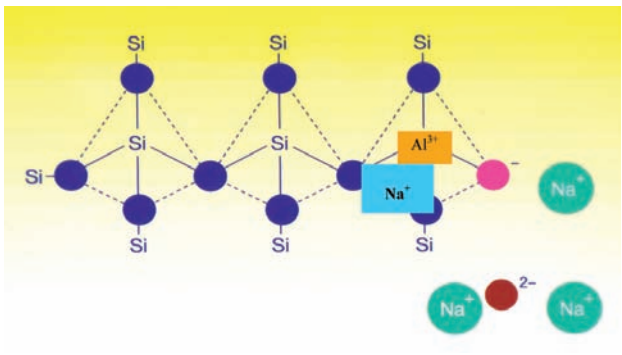

Figure 2—Formation of a silicate network showing (a) bridging oxygens and (b) charge–balancing by a Na^+ (denoted as a rectangle) when Al^{3+} cations are incorporated into the network (denoted as a rectangle)

Table I

NBO/T and Q for various CaO-SiO_2 slag compositions

Unit	Equivalent	NBO/T	Q	Examples
SiO_4^{4-} (monomer)	$2CaO.SiO_2$	4	0	BOS slag ; Q=ca. 0
$Si_2O_7^{6-}$ (polyhedra)	$3CaO.2SiO_2$	3	1	Mould flux; billets; Q= 1
$Si_2O_6^{4-}$ (chain)	$CaO.SiO_2$	2	2	BF slag Q>2 Mould fluxes; Q= 2-2.5
$Si_2O_5^{2-}$ (sheet)	$CaO.2SiO_2$	1	3	Glasses, Coal slags
SiO_2 (3-dim)	SiO_2	0	4	Glasses

Q=4-NBO/T [2]

Other models[10] calculate the mole fractions of O°, O^{-}, and O^{2-} (which are usually calculated using the Gaye modification[12] of the Kapoor-Frohberg cell model[13]) and relate these to the property values.

Structural data for slags can be determined using Raman spectroscopy; in these cases the structural parameters can be expressed as the mole fractions of Q_1 (equivalent to $2CaO.SiO_2$ or O^{2-} units), Q_2 ($3CaO.\ 2SiO_2$ units), Q_3 ($CaO.SiO_2$ units), and Q_4 (SiO_2 or O^0 units).

One difficulty when using both (NBO/T) and Q is that they do not differentiate between the effects of the different cations on the structure or property (e.g. CaO, MgO, and Na_2O). For this reason, the optical basicity (Λ) has been used to represent the structure as it does differentiate between cations but this parameter (Λ_{corr}) is usually corrected for the cations used in charge-balancing duties[14].

Du and Seetharaman[15,16] took a different approach and represented the activation energy for viscous flow as a function of the excess free energy (ΔG^{xs}) of the molten slag.

Effect of different cations on properties

Property values are affected by the nature of the cation as can be seen from Table II. The cations affect the various properties in different ways:

(i) Divalent ions (e.g. Ca^{2+}) will break two different chains and the resulting ionic bonds hold these two chains together (O^{-}–Ca^{2+}–O^{-}), whereas monovalent ions (O^{-}–Na^{+}) will break only one chain; consequently, for the viscosities of slags with equivalent compositions, $\eta\ CaO > \eta\ Na_2O$.

(ii) For equivalent slag compositions (identical Q) there are twice as many Na^{+} ions as Ca^{2+} ions; since the electrical conductivity is dependent upon the number of ions available, it follows that the electrical conductivity of $\kappa_{Na_2O} > \kappa_{CaO}$.

(iii) The electrical conductivity is also dependent upon the mobility of the cations; thus it would be expected that the conductivity would be greater for smaller cations; this is valid for Li, Na, and K ions, but the reverse trend can be seen with Ba, Ca, and Mg. This is probably due to the effects of increased polarization with decreasing ionic radius that could also affect the cationic mobility.

Inspection of Table II indicates that, although property values are affected by different cations, the effect differs according to the property.

Effect of temperature on physical properties

Increasing temperature tends to loosen the network structure. Thus properties such as viscosity and thermal conductivity tend to decrease with increasing temperature[3]. For other properties where the network offers a resistance to movement (e.g. electrical conductivity and thermal expansion), property values tend to increase with increasing temperature.

When looking at the effect of temperature on solid slags it is necessary to divide slags into (i) glassy slags and (ii) crystalline slags. It is customary to express structure-related properties (e.g. viscosity, electrical conductivity) by either the Arrhenius or Weymann equations shown in Equations [3] and [4] respectively, where A and B are constants and ($B = E/R$) where E = activation energy for viscous flow and R = gas constant.

$$\eta(dPas) = A_A\ exp\ (B_A/T) \quad [3]$$

$$\eta(dPas) = A_W T\ exp\ (B_W/T) \quad [4]$$

$$\eta(dPas) = A_V\ exp\ (B_V/(T-T_o)) \quad [5]$$

When heating a glassy slag from room temperature, there is an abrupt change in property (e.g. C_p, α) at the glass transition temperature (T_g) where the slag transforms into a supercooled liquid (*scl*). This transition at T_g is accompanied by a step-like increase in C_p and a 3-fold increase in α above T_g. The viscosity of the *scl* decreases smoothly with increasing temperature above T_g and is usually expressed in the form of the Vogel-Fulcher relation (Equation [5]) with the viscosity value at T_g, $\eta\ T_g(dPas) = 10^{13.4}$ (Figure 3a). Thus for supercooled liquids there are no abrupt changes in property at T_{liq} (e.g. no enthalpy of fusion). In contrast, when a liquid slag is cooled to the point where crystals are precipitated (known as the break temperature, T_{br}) there is a sudden increase in viscosity (Figure 3b).

Heating a crystalline slag results in no abrupt changes in property at T_g, and both C_p and α values tend to be lower than those of glassy slags for the region where $T_g < T < T_{liq}$. However, for crystalline slags, there is an abrupt change in both enthalpy (ΔH_{fus}) and volume (ΔV_{fus}) when the crystalline solid transforms to liquid in the fusion region. Thus it is necessary to differentiate between glassy and crystalline

Table II

Effect of different cations on properties of slags; α, β = linear and volume thermal expansion coefficients; k = thermal conductivity; κ = electrical conductivity; η = viscosity

Property	Structure dependence	Cation dependence	[Ref] Comments *T* dependence
T_{liq}		Mg>Ca>Sr>Ba>Li>Ca>Sr>Ba: T_{liq}↑as (Z/r^2) ↑	For same X_{SiO_2}
α,β	α,β ↑ as Q↓	K>Na>Li>Ba>Ca>Mg; α ↑-as (Z/r^2) ↓	[3]
k	k↑ as Q ↑	Li seems to ↑ k at 298& T_g	[3]
κ	κ ↑ as Q ↓:	Li>Na>K>Ba>Ca>Mg; $\kappa_I > \kappa_{II}$	[17]
η	η ↑ as Q↑	$\eta_{Mg}>\eta_{Ca}>\eta_{Sr}>\eta_{Ba}>\eta_{Fe}$: -η↓ as (Z/r^2) ↓ $\eta_{Mg}>\eta_{Ba}>\eta_{Sr}>\eta_{Ca}>\eta_{Fe}$;	[18] [19]

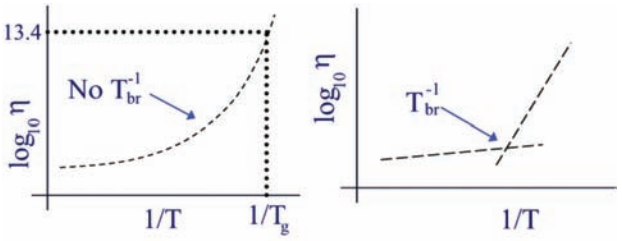

Figure 3—Plots of $\log_{10}$ viscosity as functions for reciprocal temperature (K^{-1}) for (a) glassy slag (Q>2.5) and (b) for a less-glassy slag (Q=2)

slags when estimating property values in the solid state; as a rough rule of thumb, glassy slags occur when Q>2.5 and crystalline slags when Q=<2.

Modelling thermo-physical properties of slags

The fundamentals underlying the various methods used to calculate individual properties in the program are described below. All temperatures in this paper refer to the thermodynamic temperature, *K*.

Liquidus temperature (T_{liq})

It is essential to have a value for the liquidus temperature when modelling the thermo-physical properties of both solid and liquid slags. In the commercial thermodynamic models T_{liq} can be calculated for the temperature where the activity of the liquid is unity. This facility is not available for the present software and a value should be provided by the user. If the user does not provide a T_{liq} value, the model will insert a default value (Equation [6]). This was obtained by carrying out regression analysis on 124 T_{liq} values taken from several sources[20,21]. This approach provides general trends for the effect of individual oxides on T_{liq}. However, the liquidus surface contains 'peaks and valleys' that frequently occur at compositions corresponding to compound formation, e.g. '2CaO.SiO_2'. The database contains a number of T_{liq} values corresponding to such compounds. The mean uncertainty of the estimated T_{liq} value is ± 130K. This is due mainly to large deviations (± 500K) that can occur for compound 'peaks and valleys' which constitute about a quarter of the database; for the remainder of the database, the uncertainty is < ± 100K. For these reasons, users are recommended to provide a value if they have one.

$$T_{liq}(K)=958+656.9X_{SiO_2}+1040.7X_{CaO}+1343.2X_{Al_2O_3}+1090.5X_{MgO}+137X_{Na_2O}-668X_{K_2O}+408.7X_{Li_2O}+522X_{FeO}+760.9X_{MnO}+1022X_{CrO}+794X_{Fe_2O_3}+2198X_{Cr_2O_3}-532X_{CaF_2}+844X_{TiO_2}-12.6X_{B_2O_3}+1207X_{BaO}+1768X_{SrO}+2234X_{ZrO_2} \quad [6]$$

Glass transition temperature (T_g)

It is also essential to have a value of T_g for the estimation of the thermo-physical properties of solid, glassy materials. The following equation was derived by regression analysis of experimental data for T_g and chemical compositions of the slags.

$$T_g(K)= 1028 - 26X_{SiO_2}+189.5X_{CaO}-95.6X_{Al_2O_3}-996X_{Na_2O}-850X_{Li_2O}-600X_{K_2O}-59760X_{MgO}+7034X_{CaF_2}-6366X_{MnO}+3608X_{FeO} \quad [7]$$

It should be noted that the constants associated with MgO, MnO, and FeO are 'unrealistic' since they are based on values for slags with ca. 1% of these oxides, which leads to unrealistic estimates of T_g when applied to slags with much higher concentrations of these oxides.

Heat capacity (C_p) and enthalpy (HT-H298)

Crystalline slags

The heat capacities of slags are little affected by the structure of the slag; thus it is possible to obtain reasonable estimates of C_p from partial molar C_p values for individual components (Equation [8] where 1, 2 = CaO, SiO_2, etc.).

$$C_p = \Sigma (X_1C_{p1}) + (X_2C_{p2}) + (X_3C_{p3}) + (X_4C_{p2}) \quad [8]$$

It is customary to express the temperature dependence of C_p of crystalline slags in the form:

$$C_p = a + bT - c/T^2 \quad [9]$$

Thus it is possible to derive individual values of the parameters, *a*, *b*, and *c* by:[19]

$$a = \Sigma (X_1a_1) + (X_2a_2) + (X_3a_3) + (X_4a_4) \quad [10]$$

The enthalpy $(H_T\text{-}H_{298})$ is given by

$$(H_T\text{-}H_{298}) = \int_{298}^{T} C_p\,dT = a\,(T\text{-}298) + 0.5bT^2 - 0.5b\,(298)^2 + (c/T) - (c/298) \quad [11]$$

Consequently, $(H_T\text{-}H_{298})$ for the crystalline state can be calculated from the *a*, *b*, and *c* values.

It takes energy for a crystalline solid to transform into a liquid slag, and this energy (enthalpy of fusion, ΔH^{fus}) can be calculated from the entropy of fusion (ΔS^{fus}) that represents the structural changes accompanying this transition. The ΔH^{fus} can be calculated in the following way[22]:

$$\Delta S^{fus} = \Sigma (X_1\,\Delta S^{fus}_1) + (X_2\,\Delta S^{fus}_2) + (X_3\,\Delta S^{fus}_3) + (X_4\,\Delta S^{fus}_4) + \ldots \quad [12]$$

$$\Delta H^{fus} = T_{liq}\,\Delta S^{fus} \quad [13]$$

Glassy slags

The C_p values for glassy slags are very similar to those of crystalline slags in the range (298K to T_g), but glassy slags show a stepwise increase of ca. 0.2 kJ $K^{-1}kg^{-1}$ at T_g (C_pT_g usually occurs around 1100 $JK^{-1}kg^{-1}$ (=1.1 kJ $K^{-1}kg^{-1}$). The enthalpy $(H_T\text{-}H_{298})$ value at T_{liq} (=T^m) for the liquid phase must be identical for both glassy and crystalline phases of the same composition. Thus we can calculate C_p and $(H_T\text{-}H_{T_g})$ values by Equation [14] for the $(T_g\text{-}T_{liq})$ range by assuming that C_p = a'+ b'T in this range.

$$b' = 2\{(\Delta/(T^m\text{-}T_g)) - a'\} / (T^m + T_g) \quad [14]$$

where $\Delta = (H_{Tm} - H_{298})_{crys} - (H_{T_g} - H_{298})_{glass}$ and $a' = C_p^{scl}{}_{T_g}$. There is no enthalpy of fusion term at T_{liq} for the super-cooled liquid.

Liquid slags

Values for the liquid can be calculated from Equation [8] using the values C_p(l) for the various slag constituents (e.g. *CaO*, SiO_2, etc.)[22]

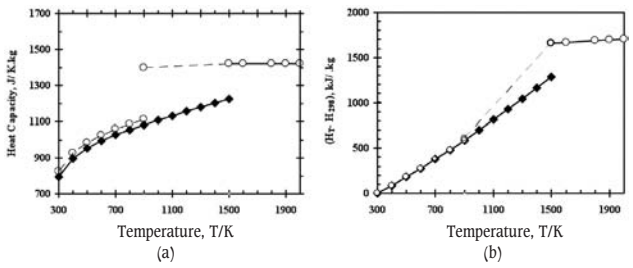

Figure 4—Schematic diagrams showing (a) C_p and (b) enthalpy (H_T-H_{298}) of glassy and crystalline slags as functions of temperature; solid line, ♦= crystalline phase; - - -,O= liquid, supercooled liquid and glass phases; vertical dotted lines represent T_g and T_{liq}

Density (ρ) and Thermal expansion(α, β)

Liquid slags

The densities of most of the components of the slag tend to be similar, so Keene[23] proposed a simple relation for calculating the densities of molten steelmaking slags at 1673K with an uncertainty of ca. ± 5%.

$$\rho_{1673}(\text{kgm}^{-3}) = 2490 + 12\,(\%FeO + \%Fe_2O_3 + \%MnO + \%NiO) \quad [15]$$

The densities of molten slags (ρ) can be modelled[19] using the partial molar volumes (V, Equations [16] and [17], where M= molecular weight) of the various slag constituents. The effect of the SiO_2 and Al_2O_3 on the molar volume (i.e. structure) of the slag can be represented by simple relations (Equations [18] and [19] respectively) derived from an analysis of density measurements[22]. The densities are calculated for a reference temperature of 1773K and then adjusted to other temperatures by applying a temperature coefficient of -0.01% K^{-1}. The calculated densities usually lie within ± 2% of measured values.

$$V = \Sigma\,(X_1V_1) + (X_2V_2) + (X_3V_3) + (X_4V_4) + \ldots. \quad [16]$$

$$\rho = M/V \quad [17]$$

$$V_{SiO_2} = (19.55 + 7.97X_{SiO_2}) \quad [18]$$

$$V_{Al_2O_3} = (28.3 + 32X_{Al_2O_3} - 31.45X^2_{Al_2O_3}) \quad [19]$$

Solid slags

Thermal expansion coefficients (α) for crystalline and glassy slags are very similar for temperatures in the range (298K to T_g). However, for glassy slags, the transition into a super-cooled liquid (scl) is accompanied by a three-fold increase in α, whereas, in contrast, for crystalline slags, α maintains its gradual increase with increasing temperature. Consequently, for any specific temperature in the range (T_g to T_{liq}), $V_T^{scl} > V_T^{crys}$. However, at T_{liq}, there is a sudden increase in volume (ΔV^{fus}) as the crystalline solid transforms into a liquid; in contrast, there is no volume change associated with the transition of a scl into a liquid (i.e. ΔV^{fus}=0). Thus the enhanced volume change associated with α^{scl} in the (T_g to T_{liq}) range is offset by ΔV^{fus}.

Crystalline slags

Slags with crystalline phases have a higher density than glassy, amorphous slags, and will show a marked change in density at T_{liq} ($\Delta\rho^{fus}$.). The slag densities are estimated at 298 K by using a very similar method to that adopted for the liquid phase. The values at T>298 K were calculated by using an average linear thermal expansion coefficient (α) of 9 **x** 10^{-6} K^{-1}.

Glassy slags

Molar volumes (V_T) are calculated in an identical manner to that for crystalline phases up to T_g. For temperatures above T_g, the molar volume of scl (V_T) is calculated using Equation [20] and the liquid molar volume at T_{liq} (V^m) and the molar volume of the scl at T_g (VT_g):

$$V_T = V_{T_g} + (T\text{-}T_g)\{(V^m - V_{T_g})/(T_{liq}\text{-}T_g)\} \quad [20]$$

Viscosity (η)

Viscosity is a measure of the resistance encountered when moving one set of atoms over a lower layer of atoms. Thus, as the network structure becomes more polymerized (i.e. Q increases) the resistance to viscous flow will increase and thus the viscosity (η) will increase. Since increased temperature loosens up the structure, the viscosity will decrease with increasing temperature. The viscosity has been used as a measure of the slag's structure[5].

The Riboud[24], Urbain[25], and Iida[26] models have been implemented in the software.

Riboud model[24]

This model is simple and is applicable to a wide range of slags. The model divides the slag constituents into five different categories (see below). Additional slag constituents are covered in the software and these have been allocated to the various groups and are denoted by {}. The model applies to the following ranges: SiO_2 (28–48%), CaO (13–52%), Al_2O_3 (0–17%), CaF_2 (0–21%), Na_2O (0–27%).

$$X_{`SiO_2'} = X_{SiO_2} + X_{P_2O_5} + X_{TiO_2} + X_{ZrO_2} \quad [21]$$

$$X_{`CaO'} = X_{CaO} + X_{MgO} + X_{FeO} + X_{Fe_2O_2} + \{X_{MnO} + X_{NiO} + X_{CrO} + X_{ZnO} + X_{Cr_2O_3}\} \quad [22]$$

$$X_{`Al_2O_3'} = X_{`Al_2O_3'} + \{X_{`B_2O_3'}\} \quad [23]$$

X_{CaF_2}

$$X_{`Na_2O'} = X_{Na_2O} + X_{K_2O} + \{X_{Li_2O}\} \quad [24]$$

The temperature dependence is expressed via the Weymann equation {$\eta(dPas) = A_W\,T \exp(B_W/T)$}and the viscosity is calculated from this relation where A_W and B_W are calculated using Equations [25] and [26].

$$A = exp\,(-19.81 + 1.73X_{`CaO'} + 5.82X_{CaF_2} + 7.02\,X_{`Na_2O'} - 35.76X_{Al_2O_3} \quad [25]$$

$$B = 31140 - 23896\,X_{`CaO'} - 46356X_{CaF_2} - 39159X_{`Na_2O'} + 68833X_{`Al_2O_3'} \quad [26]$$

Urbain model[25]

This model divides the various slag constituents into the following groups:

Glass formers $X_G = X_{SiO_2}$ [27]

Network modifiers:

$$X_M = X_{CaO} + X_{MgO} + X_{CaF_2} + X_{FeO} + X_{MnO} + X_{CrO} + X_{NiO} + X_{Na_2O} + X_{K_2O} + X_{Li_2O} + 2\,X_{TiO_2} + X_{ZrO_2} \quad [28]$$

Amphoterics: $X_A = X_{Al_2O_3} + X_{B_2O_3} + X_{Fe_2O_3} + X_{Cr_2O_3}$ [29]

Here it has been assumed that Fe_2O_3 and Cr_2O_3 behave both as network breakers and as amphoterics, where f is the fraction (f) behaving as network modifiers and a value f=0.6 is assumed.

The Urbain model works predominantly on a basis of M_xO so this creates extra ions and it is necessary to normalize X_G, X_M, and X_A by dividing by the term (1+ $0.5X_{FeO_{1.5}}$+ X_{TiO_2} + X_{ZrO_2}+ X_{CaF_2}) to give X_G^* X_M^* and X_A^*.

The model assumes the Weymann relation

$$\eta(dPas) = A_W\, T \exp(B_W/T) \quad [30]$$

Urbain[25] found that A and B were linked through the equation

$$-\ln A_W = 0.29B_W + 11.57 \quad [31]$$

The B_W value must be calculated via the equations

$$\alpha^* = X_M/(X_M + X_A) \quad [32]$$

$$B_i = a_i + b_i\alpha + c_i\,\alpha^2 \quad [33]$$

where subscript i can be 0, 1, 2, or 3 and a, b, and c are given constants for each case e.g. 0, 1, 2, 3.

$$B = B_o + B_1X_{SiO_2} + B_2X^2_{SiO_2} + B_3X^3_{SiO_2} \quad [34]$$

Different values for a, b, and c are given for 0,1,2,3 to calculate B values for the CaO–Al_2O_3 +SiO_2, MgO–Al_2O_3 +SiO_2, and MnO–Al_2O_3 +SiO_2 systems. In this study, we have modified X_{MnO}, to represent $X_{MnO} + X_{FeO} + X_{NiO} + X_{CrO}$ +0.6($X_{Fe_2O_3} + X_{Cr_2O_3}$). The global B (B_{global}) is given by

$$B_{global} = (X_{MnO}\,B_{MnO} + B_{CaO}\,X_{CaO} + B_{MgO}\,X_{MgO}) / (X_{MnO} + X_{CaO} + X_{MgO})) \quad [35]$$

The values calculated with this software are in good agreement with the values cited by Urbain[24] but the model does not have B_i values covering monovalent oxides (e.g. Na_2O).

Iida model[26]

The model[26] makes use of the basicity index (B_i) to represent structure:

$$\eta(Pas) = A\ \eta_0 \exp(E/Bi) \quad [36]$$

where A = pre-exponential term, E = activation energy; η_0 = hypothetical viscosity for each slag constituent (i); the parameters A, E, and η_0 are all given as functions of temperature.

$$A = 1.029 - 2.078 \times 10^{-3}T + 1.05 \times 10^{-6}T^2 \quad [37]$$

$$E = 28.46 - 2.884 \times 10^{-2}T + 4.0 \times 10^{-6}T^2 \quad [38]$$

$$\eta_0 = \Sigma\,\eta_0\,X_{SiO_2} + \eta_0\,X_{CaO} + \eta_0\,X_{Al_2O_3} + \eta_0\,X_{MgO} + \ldots \quad [39]$$

$$\eta_0 = 1.8\times10^{-7}\,\{(M_iT_i^m)^{0.5} \exp(H_i/R^*T)\} / \{V_m\}_i^{0.6667} \exp(H_i/RT)\} \quad [40]$$

where V_m = molar volume for each constituent, and H_i = 5.1 $(T^m)_i$ and R^* = gas constant

The various constituents are divided into the following categories: (1) acidic (SiO_2, ZrO_2, TiO_2) denoted by subscript A, (2) basic (CaO, MgO, Na_2O, K_2O, Li_2O, FeO, MnO, CrO, CaF_2, etc.) denoted by subscript B, and (3) amphoteric (Al_2O_3, B_2O_3, Fe_2O_3, Cr_2O_3). The basicity index B_i is calculated by

$$B_i = \Sigma\,(\alpha_i.\%i)_B / \Sigma\,(\alpha_i.\%i)_A \quad [41]$$

where α_i.=constant for each constituent expressing its relative basicity and %i = mass %.

This was the original Iida model. Subsequently, the model was modified[26] to account for the amphoterics where their basicity changed according to the temperature. This was done through the modified basicity index (B_i^j), particularly for Al_2O_3, which was done through back-calculation from experimental viscosity data (Equation [42]). It was concluded that Fe_2O_3 and Cr_2O_3 worked basically as basic oxides so they appear on the top line. The model gets exceedingly complicated because the modified α (denoted α^*) for Al_2O_3 was obtained from experimental viscosity data for certain systems, e.g. $CaO + MgO + Al_2O_3 + SiO_2$, and then expressed by Equation [42].

$$(B_i^j) = \{\Sigma\,(\alpha_i.\%i)B + (\alpha_i.\%i)\,Fe_2O_3 + (\alpha_i.\%i)_{BCr2O3}\} / \{\Sigma\,(\alpha_i.\%i)_A + \Sigma\,(\alpha_i.^*\,\%i)\,Al_2O_3\} \quad [42]$$

$$\alpha_i.^* = aB_i + b\,\%Al_2O_3 + c \quad [43]$$

It is difficult to apply the Iida model to systems where there is no experimental data since $\alpha_i.^*$values are determined for each system/family and there is no general overall value for α_i^*. For example, one can calculate α_i^* from a, b, and c values for $CaO + MgO + Al_2O_3 + SiO_2$ but other a, b, c values (leading to a different $\alpha_i.^*Al_2O_3$) are given for $Li_2O + Al_2O_3 + SiO_2$. The high accuracy claimed with this model comes from its calibration with experimental data for each family of slags.

Thermal conductivity (k)

There are no extant models for estimating thermal conductivities but Mills[3] noted that the thermal conductivity of liquid silicate slags at T_{liq} (k^m) increased linearly as (NBO/T) decreased (i.e. Q increased). Phonon conduction is considered to occur as lattice waves. Slags exhibit covalent bonding (in chains, etc.) and ionic bonding. Since k^m increases with increasing Q, it is obvious that thermal conduction is greater along the covalent chain than across the cationic bonds. Consequently, a relationship between thermal conductivity and viscosity might be expected, and recent work[4,27] has shown that such a link exists. Further evidence for this link between thermal conductivity and viscosity lies in the temperature dependence of the thermal conductivities of molten slags that can be satisfactorily represented by the Arrhenius relation, which is widely used for the temperature dependence of viscosity[27,28].

Thermal conductivity (k_R) measurements at temperatures on glassy and liquid slags contain a significant and unknown contribution from radiation conduction[29]. These k_R contributions are much smaller in transient hot wire (THW) measurements than for those obtained with the laser pulse (LP) method, because the emitting surface area in LP experiments is 10x that in THW studies. Therefore, only thermal conductivity data from THW studies were accepted here. Typical examples of the temperature dependence of glassy, crystalline, and liquid slags are shown in Figure 5. The maximum in k occurs at T_g and it is our contention that the thermal conductivity in the range (T_g to T_{liq}) can be represented by a Vogel-Fulcher relation (see Equation. [5]), which is widely used for viscosities in this range.

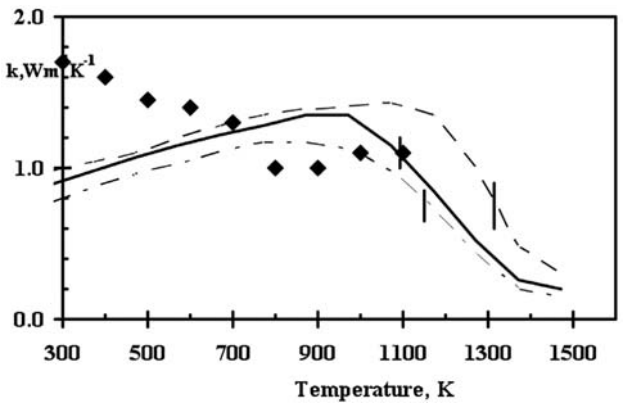

Figure 5—Thermal conductivity as a function of temperature for $Na_2O.2SiO_2$ (dash-dot line), $Na_2O.3SiO_2$ (solid line), and $Na_2O.4SiO_2$ (dashed line)[29], ♦=crystalline $CaO.SiO_2$[30]; vertical lines; solid=T_{liq} and dotted =T_g. it can be seen that k increases with increasing SiO_2 content (i.e. increasing Q)

Liquid slags

Method 1—relation with viscosity

This uses the relation of thermal conductivity (k) of the liquid at T_{liq} (k^m) with viscosity. Reported line source data for ln k^m[4,27, 30-32] were correlated with Riboud calculations of ln η^m[24]. The data showed some scatter because of (i) uncertainties in the calculated ln η^m values, (ii) experimental uncertainties associated with ln k^m, and (iii) sensitivities of both η^m and k^m in the region around T_{liq} and the uncertainties in T_{liq} itself. The following relation was obtained.

$$\ln k^m = -2.178 + 0.282.\ln \eta^m \quad [44]$$

Method 2—relation to both Q and ln η^m

This method is similar to Method 1 in that it uses a relation between ln η^m and ln k^m. The data is shown in Figure 6, and has been expressed as an exponential relation.

$$\eta^m = 0.165 \exp (Q / 0.817) \quad [45]$$

Then ln k^m can be calculated using the equation

$$\ln k^m = -1.8755 - 0.0893 (\ln \eta^m) + 0.0352 (\ln \eta^m)^2.) \quad 46]$$

The values of k^m obtained are valid only for the range Q = 2 to 3.2. Care should be taken particularly for slags with Q > 3.2 and for slags with high Al_2O_3 contents (e.g. 45% CaO + 10% SiO_2 + 45% Al_2O_3 which would show a high Q value but, in actual fact, is largely made up of calcium aluminates and will show relatively low η^m and k^m values).

Method 3—relation with Q

The relation between ln k^m and Q is shown in Figure 6b and it can be seen that it has similarities to the equation between ln η^m and Q (Figure 6a, Equation [47]). There is significant dispersion in the scattered data for k^m but the upward trend with increasing Q is obvious. Unfortunately, the experimental values for k^m lie within the range Q = 2 to 3.2. The following relation was derived:

$$\ln k^m = -1.914 + 0.00037 \exp (Q/0.402) \quad [47]$$

This equation is valid only for the range Q = 2 to 3.2.

The temperature dependence would be expected to follow an Arrhenius–type relation because of the correlation between η and k.

$$\ln k_T (l) = A \exp (B/T) \quad [48]$$

There are insufficient data to determine B values as a function of Q, so an approximate relation for dk/dT was obtained but should be used with caution.

$$dk/dT = 0.0005 \exp (0.5551Q) \quad [49]$$

Solid slags

Method 1

The experimental data for ln k_{298} and ln k_{T_g} show appreciable scatter when plotted vs Q, but they do show k increasing with increasing Q. The data were assumed to follow an exponential relation similar to that used for ln η^m (Equation [47], Figure 6b). It was noted that the experimental data for solid Li_2O- containing slags were significantly higher than the curve values and so a correction for Li_2O was added to the exponential relation:

$$\ln k_{298} = -0.424 + 0.00002 \exp(Q / 0.299) + 3.2.X_{Li_2O} \quad [50]$$

$$\ln k_{T_g} = -0.435 + 0.00005 \exp(Q / 0.332) + 3.0\ X_{Li_2O} \quad [51]$$

This equation should not be used out of range i.e. Q > 3.3 or Q < 2.

Values can be calculated at other temperatures by linear interpolation between 298 K and T_g, and values have also been calculated in the same manner for T_g to T_{liq} (but this should in fact follow a Vogel-Fulcher relation, Equation [5], but there was not enough data to establish the necessary constants). This procedure should be accepted only for slags in the range Q = 2 to 3.3.

Method 2

A second method is also shown. It was found that for slags with Q around 2.5 the thermal diffusivity between 298 K and T_g tends to have a constant value $a = 4 \times 10^{-7}$ m^2s^{-1}. Values calculated from $k = a.C_p.\rho$ using the calculated values of C_p and ρ are also shown. These values apply only when Q = 2 to 3.

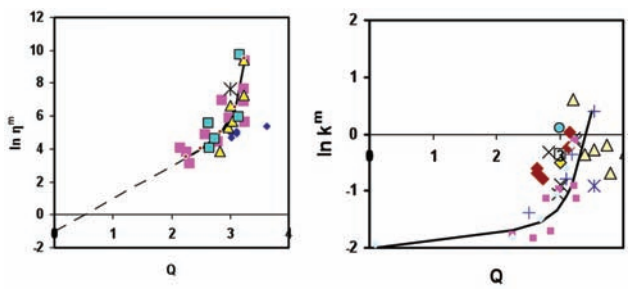

Figure 6—(a) Viscosity and (b) thermal conductivity at the liquidus temperature as function of the parameter Q

Estimating the physical properties of slags

Crystalline slags

Nishioka *et al.*[31] report that k values for crystalline slags are between 1.5 and 2.5 times higher than that for the glassy slag and are independent of temperature (Figure 5). Thus it has been assumed that $k_{cryst} = 2k_{glass}$ and is independent of temperature from 298 to 1000K.

Electrical conductivity (κ) of liquid slags

The electrical conductivity involves the movement of cations under the influence of an applied field. In this case, the polymeric silicate network hinders the movement of the cations. Thus the factors affecting the electrical conductivity (κ) are (i) the concentration, charge, and size of the cations and (ii) the polymeric network (as represented by $\mathcal{Q}$) which hinders the movement of cations. Smaller cations are more mobile, but the increased mobility of smaller cations is offset by the increased polarization in the M-O bond. For instance, for M_2O-SiO_2 slags, the hierarchy is $\kappa_{Li} > \kappa_{Na} > \kappa_K$ i.e. decreasing with increasing cation radius. However, the trend is reversed for the MO-SiO_2 slags where $\kappa_{Ba} > \kappa_{Sr} > \kappa_{Ca} > \kappa_{Mg}$[5,16] i.e. κ decreases as (z/r^2), possibly because of the higher charge (z) in this slag series which would be expected to increase polarization. As increasing temperature gradually loosens up the structure, the hindrance to the movement of cations by the silicate network is reduced, and hence the conductivity increases with increasing temperature. It should also be noted that factors causing an increase in electrical conductivity would cause a decrease in thermal conductivity. The electrical conductivities of slags containing Li^+, Na^+, and K^+ are significantly higher than those containing Ca^{2+}, Mg^{2+}, etc., because, for an equivalent slag structure ($\mathcal{Q}$), $n_{Na^+} = n_{Ca^{2+}}$ where n = number of cations present.

The electrical conductivities have been estimated using recent papers by Zhang and Chou[5, 36], both of which involve using the relation between conductivity and viscosity.

Method 1

Chou and Zhang[35, 5] proposed a relationship for slags containing CaO, MgO, Al_2O_3, and SiO_2.

$$\ln \kappa = (-0.08 - \ln \eta)/1.18 \quad [52]$$

Zhang calculated values of ln k using this equation and parameters to calculate the viscosity. These parameters are not generally available for all slag systems, so ln η values were calculated here using the Riboud, Iida, and Urbain models.

Method 2

Zhang *et al.* [5,36] reported that the following equations apply for M_2O–SiO_2 (where $M_2O = Na_2O$ etc.) and MO–SiO_2 (e.g. CaO) systems.

$$M_2O\text{–}SiO_2: \quad \ln \kappa = (0.02 - \ln \eta)/ 2.87 \quad [53]$$

$$MO\text{–}SiO_2 \quad \ln \kappa = (0.15 - \ln \eta)/1.1 \quad [54]$$

The model assumes (i) that cations on charge balancing duties are not available for electrical conduction and (ii) the charge balancing is directly related to the concentrations of the various cations present (i.e. a statistical distribution). The differences between Equations [53] and [54] were attributed to the fact that there are twice as many Na^+ ions as Ca^{2+} for equivalent compositions. Here the model calculates the ratio (r^*) of M^+ ions present in the slag (Equation [55]) and then calculates the conductivity using Equation [56] (which was derived from the product of r^* multiplied by the differences between Equations [53] and [54]). It is recommended that this method be used when the slag contains M^+ ions e.g. Na^+, K^+, or Li^+.

$$r^* = 2 \Sigma X_{M^+} / \Sigma (2 X_{M^+} + X_{M^{2+}} 0.667 X_{M^{3+}} + 0.5 X_{M^{4+}}). \quad [55]$$

$$\ln \kappa = 0.15 + r^* 3.87 - (\ln \eta / \{1.1 + 1.77 r^*\}) \quad [56]$$

Surface tension (γ)

Method 1

Surface tension is not a bulk property but is a surface property. The free surface of the molten slag contains higher concentrations of the constituents with lower surface tension. Values of surface tension and the trends in surface tension can be calculated using a partial molar approach (Equation [57]), and are shown in Figure 7[37]. The model divides slag components into two classes: (i) oxides with higher surface tension values where values of $X_2\ \gamma_2$ tend to be similar to that shown in Figure 7a and (ii) components with lower γ values (surfactants B_2O_3, CaF_2, Na_2O, K_2O, Fe_2O_3, and Cr_2O_3) where values of $X_2\ \gamma_2$ tend to be similar to those shown in Figure 7a.

$$\gamma\ (\mathrm{mNm^{-1}}) = \Sigma X_1\ \gamma_1 + X_2\ \gamma_2 + X_3\ \gamma_3 + \ldots \quad [57]$$

These surface active components cause a rapid decrease in surface tension and, in these cases, $X_2\ \gamma_2$ and can be represented by two curves determined by a critical point N (corresponding to the minimum in Figure 7b) (i) for <N as a polynomial by $X_2 . \gamma_2 = a + bX + cX^2$ and (ii) >N by $X_2\ \gamma_2 = a' + b'X$ (which are shown by the dashed line in Figure 7b). The method has the advantage that it can easily be applied to multicomponent industrial slags, but uncertainties in the estimated values are ca. ± 10%. The biggest problem with this method lies in its inability to deal with two, or more, surface-active components simultaneously (e.g. CaF_2 and B_2O_3) and, for these conditions, Method 1 tends to exaggerate the decrease in γ in these cases (i.e. $\gamma_{meas} > \gamma_{calc}$).

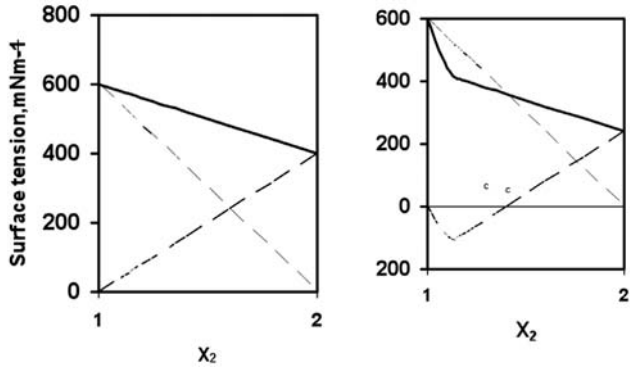

Figure 7—Schematic diagram showing compositional dependence (X) of surface tension (γ = solid line) and $X_1\ \gamma_1$ and $X_2\ \gamma_2$ (= dashed lines) for a binary slag system containing (a) no surface active constituents and (b) one surface active constituent where 1 and 2 represent the slag components

Method 2

Method 2 was devised to address this problem. It was assumed that (i) occupation of the surface occurs in the hierarchy (of lowest surface tension) $B_2O_3 > K_2O > Na_2O > CaF_2 > Fe_2O_3 > Cr_2O_3$ and (ii) surface saturation occurs at N=0.12. The various surfactant contributions were calculated from the various oxides until the value N=0.12 was attained. When N>0.12 all contributions from these surfactants were taken as positive contributions ($=X_i\gamma_i$) i.e. they were not considered to be present in the surface layer and thus contributed normally to the bulk surface tension. The values calculated using Method 2 are preferred.

Most slags have negative temperature coefficients ($d\gamma/dT$)[20]. However, it is known that slags with high SiO_2 contents exhibit positive ($d\gamma/dT$) values[38]. This is related to the fact that SiO_2 has a relatively low surface tension value. Ideally, ($d\gamma/dT$) could be calculated on a partial molar basis but we do not have ($d\gamma/dT$) data for all the slag constituents. Consequently, a constant value of ($d\gamma/dT$) has been assumed. However, ($d\gamma/dT$) values were calculated on a partial molar basis for those slag constituents where data were available (e.g. Equation [58]).

$$(d\gamma/dT)\ (\mathrm{mNm^{-1}K^{-1}}) = \Sigma\, X_1\,(d\gamma_1/dT) + X_2\,(d\gamma_2/dT) + X_3\,(d\gamma_3/dT) + \ldots \quad [58]$$

Using the software

The intention behind this work is to provide a practical set of models that can be used by process engineers as working tools in everyday pyrometallurgical work. The software is available from http://www.pyrometallurgy.co.za/KenMills/, initially in the form of a spreadsheet, but other interactive calculation methods may be available in due course. The attractive feature of having the software available on a website is that the latest version can always be available to all users, and the burden of sending out software updates is relieved. Specific detailed instructions for the use of the software are available on the same website, so are not repeated here. The software requires the specification of the composition and liquidus temperature of the slag. If the glass transition temperature for glassy slags is known, this can also be specified; otherwise this will be estimated by the software.

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Symbols, abbreviations, units

a	= Thermal diffusivity (m^2s^{-1})
C_p	= Heat capacity (JK^{-1}/ mol^{-1} or JK^{-1}/kg^{-1})
E	= Activation energy ($kJ\ mol^{-1}$)
f	= Fraction of M^{3+} ions acting as network breaker
(H_T-H_{298})	= Enthalpy ($Jmol^{-1}$ or Jkg^{-1})
ΔH^{fus}	= Enthalpy of fusion ($Jmol^{-1}$ or Jkg^{-1})
k	= Thermal conductivity ($Wm^{-1}K^{-1}$)
(l)	= Liquid phase
M	= Molecular weight ($g\ mol^{-1}$)
p	= Partial pressure (atm, bar)
Q	= 4-(NBO/t)= measure of polymerization
R	= Gas Constant= 8.314 ($J\ mol^{-1}\ K^{-1}$)
r	= Cation radius (10^{-10}m)
(s)	= Solid phase
scl	= Supercooled liquid
T	= Temperature (K or °C)
T_g	= Glass transition temperature (K or °C)
T_{liq}	= Liquidus temperature (K or °C)
V	= Molar volume ($m^3\ mol^{-1}$)
Z	= Charge on cation (=2 for Fe^{2+})
α	= Linear thermal expansion coefficient (K^{-1})
β	= Volume thermal expansion coefficient (K^{-1})
γ	= Surface tension (mNm^{-1})
γ_{ms}	= Slag/metal interfacial tension (mNm^{-1})
κ	= Electrical conductivity ($\Omega^{-1}m^{-1}$)
Λ	= Optical basicity
η	= Viscosity (Pas or dPas)
θ	= Contact angle (°)
ρ	= Density (kgm^{-3})
BO	= Bridging oxygen (O^0)
NBO	= Non-bridging oxygen ((O^-))

Subscripts

br	= Break (temperature)
liq	= Liquidus
$_m$(subscript)	= Metal
s	= Slag
sol	= Solidus

Superscripts

^{m}(superscript)	= Value at T_{liq} ◆