# THE ESTIMATION OF SLAG PROPERTIES

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Short course presented as part of

## Southern African Pyrometallurgy 2011

**7 March 2011**

## Symbols and Units

a=thermal diffusivity ($m^2s^{-1}$)
Cp= Heat capacity ( $JK^{-1}$/ mol or kg)
E= Extinction coefficient ($m^{-1}$)
E= Activation energy ( $kJ\ mol^{-1}$)
f= fraction of $M^{3+}$ ions acting as network breaker
($H_T$-$H_{298}$)= Enthalpy ( J/ mol or kg)
$\Delta H^{fus}$ = enthalpy of fusion ( JK/ mol or kg)
k= thermal conductivity ($Wm^{-1}K^{-1}$)
K= Electrical conductivity ($\Omega m^{-1}$)
k=Thermal conductivity ($W^{-1}K^{-1}$)
(l)= liquid phase
M= molecular weight ($g\ mol^{-1}$)
n= refractive index
P= property
p= partial pressure (atm, bar)
Q= 4-(NBO/T)= measure of polymerisation
R= electrical resistivity (=1/ $\kappa$) ($\Omega m$)
R*= Gas Constant= 8.314 ( $JK^{-1}mol^{-1}$)
s*= scattering coefficient ($m^{-1}$)
(s)= solid phase
T= temperature ( K or $^oC$)
$T_g$= Glass transition temperature ( K or $^oC$)
$T_{liq}$= liquidus temperature ( K or $^oC$)
$T_{sol}$= solidus temperature ( K or $^oC$)
V= molar volume ($m^3\ mol^{-1}$)
$\alpha$= linear thermal expansion coefficient ($K^{-1}$)
$\alpha$*= Absorption coefficient ($m^{-1}$)
$\beta$= volume thermal expansion coefficient ($K^{-1}$)
$\varepsilon$= emissivity
$\gamma$=surface tension ($mNm^{-1}$)
$\gamma_{ms}$=slag/metal interfacial tension ($mNm^{-1}$)

$\varepsilon$= emissivity
$\kappa$=electrical conductivity ($\Omega^{-1}m^{-1}$)
$\Lambda$= Optical basicity
$\eta$= viscosity (Pas or dPas)
$\theta$= contact angle ($^o$)
$\rho$= density ($kgm^{-3}$)

## Subscripts and superscripts

br = break (temperature)
liq= liquidus
$^m$ (supersript)=value at $T_{liq}$
$_m$(subscript)= metal
$^m$(supersript)=value at $T^{liq}$
s= slag
sol= solidus

## Abbreviations

AL=   aerodynamic levitation
BF= Blast furnace
BO= Bridging Oxygen
BOS =Basic Oxygen Steelmaking process
CC= Continuous casting of steel
de-S= de-sulphurisation
EML= Electro-magnetic levitation
ESL= Electro-static levitation
ESR= Electro-slag refining
NBO= Non-bridging Oxygen
NBO/T= non bridging O/ tetragonal O
scl= super-cooled liquid

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# 1. SLAGS

The word "slags" may not have a pleasant connotation with the man in the street but they are very important to metal production. They protect the metal and remove undesirable impurities. Usually a liquid slag layer covers the molten metal and carries out the following functions:

- (i) It seals off the metal from oxygen and prevents oxidation
- (ii) It removes undesirable elements (eg. S ,P) from the metal
- (iii) It helps to remove non-metallic inclusions (eg by flotation etc)
- (iv) It reduces the heat losses from the metal surface and prevents the "*skull formation*" and
- (v) in the continuous casting of steel liquid slag infiltrates continuously between the metal and mould and it provides both lubrication and control of the heat extraction.

Slags are very important to the production of clean metals. The old adage *"Look after the slag and the metal will look after itself"* is very appropriate.

Slags have a wide range of composition:
*Metallurgical slags* are usually based on the $CaO$-$Al_2O_3$- $SiO_2$ system
*Non- ferrous slags* are frequently based on fayalite- eg $FeO.SiO_2$
*Coal slags/ fly ashes* are basically $CaO+Al_2O_3 + SiO_2$ with relatively low CaO levels (<10%) and tend to be very viscous
*ESR-slags* are made of oxides and fluorides (in significant amounts) eg $CaF_2$+ $CaO$+ $Al_2O_3$
*Continuous casting fluxes and welding fluxes* are made up of oxides with <10% $CaF_2$
Slags have similarities to glasses and slags.
*Glasses*- tend to have high $SiO_2$ contents
*Enamels* contain appreciable amounts of $B_2O_3$

Liquid slags are thought to be made up of ions. We know that ions are involved in reactions between metal and slag; eg reaction 1 can be expressed by Equation 2 (where M indicates in metal) :

$$\underline{2Al} +1.5\ SiO_2\ (slag) = \underline{3Si} + Al_2O_3\ (slag) \tag{1}$$
$$\underline{2Al} +1.5Si^{4+} = 1.5\ \underline{Si} + 2\ Al^{3+} \tag{2}$$

These electro-chemical reactions are accompanied by changes in properties. Mass transfer (in Equation 1) across the metal/slag interface is accompanied (Figure 1)by (i) decrease in interfacial tension (which causes local turbulence and easy transfer across the interface) and (ii)a gradual decrease in the potential difference between metal and slag. The local interfacial turbulence is also a result of the changes in electrical potential which result in local changes in surface tension which, in turn, induce Marangoni flows (arising from surface tension gradients).
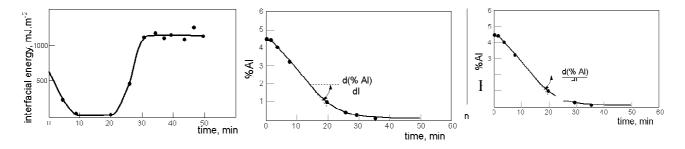


Figure 1 Figure Changes in (i) interfacial tension (ii)Mass transfer (iii) Electrical potential for reaction 1 [1]..

## 1.1 Slag properties
Slag properties are important since they:
- (i) have a decisive effect on both process control and on the quality of the product and

(ii)     good quality property data are needed to develop reliable mathematical models of the process and to optimise the efficiency of the process and quality control.

An example of process control is that the slag compositions should have a high S-capacity to maximise transfer of S from the metal to slag; this is usually achieved by using a liquid, high-basicity flux. If de-sulphurisation (d-S) is below requirement more CaO is added to increase basicity but it could also increase the liquidus temperature ($T_{liq}$) of the slag and thereby reduce the amount of liquid slag formed,which, in turn, results in less de-sulphurisation.

An example of the effect on product quality occurs in continuous casting (CC). Longitudinal cracks occur on the surface of the steel and have to be scarfed off, thereby reducing yield and increasing expenditure and energy. It is known that flux viscosity ($\eta$) and break temperature ($T_{br}$) of mould fluxes used in CC must be optimised to eradicate longitudinal cracking.

There are several types of mathematical model namely (i) **thermodynamic models** (to establish the viability of the process and the optimum conditions) (ii) **kinetic models** (to establish that the productivity rate) (iii) **heat and fluid flow models** (to improve process design and control) and (iv) models of **environmental and financial impact** of the process. Reliable property values are principally needed as input data for heat and fluid flow models.

### 1.1.1   Reactivity of slag with container, metal and atmosphere

The unofficial First law of High Temperatures states:
"*At high temperatures everything reacts with everything else*"
and the Second Law states
"**They react bloody quickly and it gets exponentially- worse as the temperature increases** ".

Slags react with the container and any other contact materials (eg. bobs) with the metal and with the atmosphere. Their reactivity varies between the viscously aggressive (eg coal slags and ashes) to benign (glasses) and is very dependent upon the slag composition.

Some slags are basically unstable at high temperatures since two or more components in the slag will react and the composition will change continuously eg ESR slags where fluorides and oxides react eg.

$$3CaF_2 + Al_2O_3 = 2AlF_3 \text{ (g)} + 3CaO \qquad\qquad (3)$$

and the slag composition shows a steady increase in CaO concentration and a decrease in $Al_2O_3$.

### Slag/container reactions

Some slags are so aggressive and reactive towards the refractory walls that a process has had to be abandoned because no suitable refractory could be identified. (Slag /refractory erosion is discussed in more detail below).

A major problem in performing measurements on slags involves the selection of a crucible material which is inert to the slag. The general rule in selecting crucibles is "*Use a metal to contain an oxide melt and use a refractory oxide to contain liquid metals* ". The most commonly-used materials are either (i) Pt metals and alloys (eg. Pt, Ir) or (ii) refractory metals (Mo, Ta , W). Pt-alloys are not suitable for reducing conditions and Mo etc are not suitable for oxidising conditions. FeO- containing slags are notoriously aggressive since FeO is easily reduced by the container ( see Figure 2 ); it is customary to use Fe crucibles but this limits the temperature range to <1400$^o$C. Graphite is also widely used but (i) reacts with slag oxides (eg. $FeO_{slag}$ + C= CO(g) + Fe ) and (ii) is non-wetting which affects viscosity measurements) Container-less methods have been used to avoid slag/container reactions (eg levitation (EML, ESL, AL and micro-gravity conditions) [2]

```
        0        2Fe +O₂=FeO
       200
       400        2Mn +O₂=2 MnO
ΔG,
kJ     600        Si +O₂=SiO₂
        80        4/3 Al+O₂=2/3 Al₂O₃
       100
      1200        2Ca+O₂=2CaO

         300        100        2000
              Temperature,
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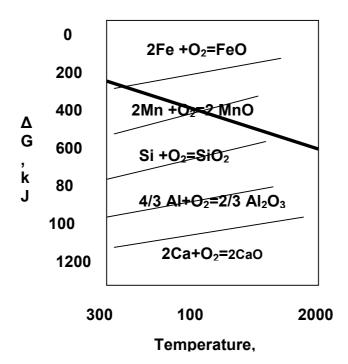
*Figure 2: Schematic Ellingham diagram;  (i) Any element lower in the diagram will capture O from an element above (Al will take O from FeO) (ii) Oxides reduced by C when T> T $_{crossover}$ of 2C +O₂=2CO (Bold line) with other curves*

### Slag/metal reactions

Slag/metal reactions are very important in the production of clean metals (eg. de-S and de-P) but they can sometimes produce unwanted reactions  (eg Equn 1   ie, $SiO_{2 \, slag}$ +$\underline{Al}$= $\underline{Si}$  +$Al_2O_{3 \, slag}$) in continuous casting (CC).  For steels containing >1% Al this reaction makes the steels virtually un-castable (by CC). Slag/metal reactions involve ions (Equn 1) and involve charge exchange resulting in the changes shown in Figure 1.

### Slag/atmosphere reactions

The slag is used in many processes to shield the metal from oxidation; oxygen can have a significant effect on transition-metal, multi-valent oxides (eg $Fe^{2+}$/ $Fe^{3+}$, $Cr^{2+}$/ $Cr^{3+}$, Ti- Nb- oxides) . In the case of $Fe^{2+}$/ $Fe^{3+}$, the $Fe_2O_3$ concentration has a significant effect on the properties (eg. viscosity, electrical resistivity). Thus it is important that the partial pressure of oxygen, $p_{O2}$, in an experiment be selected to reflect the conditions of the industrial process being studied.

Nitrogen tends to be inert to most slags but those containing Ti and Nb will react with $N_2$ to form TiN and NbN inclusions, which can have significant effects on the process.

Reactions of slags with moisture can have important effects. In oxide slags with the $H_2O$ being both chemically-bonded to the slag and adsorbed on the slag; this can affect the performance of the slags. However, the effects of moisture are more severe when dealing with slags containing fluorides, (or chlorides) such as ESR fluxes, CC fluxes and Al fluxes because of the reaction :

$$CaF_{2 \, slag} + H_2O \, (g) = CaO \,_{slag} + 2HF \, (g) \qquad (4)$$

The HF(g) emitted can cause plant corrosion and pose a threat to health of the plant personnel.

### Corrosion and Erosion of refractories

**Corrosion** is the chemical attack of refractories
**Erosion** involves both the chemical attack (erosion) and the mechanical abrasion of the refractory.

Refractories (eg $Al_2O_3$, CaO , MgO and $ZrO_2$) used for furnace linings are usually oxides with great chemical stability (see Ellingham diagram, Figure 2) and have high melting points. These properties arise from the great chemical affinity of Al, Ca, Mg and Zr for oxygen (the bond strength Al-O etc. is very high) – these elements lie at the bottom of the Ellingham diagram and it is very difficult for metals to break the Al-O bond and form a metal- oxide bond. However, most slags will dissolve a certain amount of the refractory oxide *eg*. CC fluxes dissolve up to 40% $Al_2O_3$, up to 10%$TiO_2$ and only 2 %$ZrO_2$ and 0.5% TiN.



*Figure 3: Schematic drawing of BOS process and the turbulence generated which causes refractory erosion*

Erosion frequently arises from turbulent flows generated in the converter eg. the BOS process (Figure 3 ) or from mechanical erosion eg the feeding of scrap to the converter. Enhanced erosion tends to occur in furnace linings at the metal / slag and slag/ atmosphere interfaces; this is known as *"slag line erosion"*.

### Mechanism of slag line erosion
The refractories used in industrial furnaces frequently exhibit a n area of wear (deep groove) in the region between the slag/metal and slag/gas interfaces. Figure 4 shows the case of slag line attack at the slag/atmosphere interface for a $SiO_2$ refractory; the same mechanism is thought to apply to other refractories. When the slag first comes in contact with the silica it forms a meniscus. Some SiO2 dissolves in the slag in the meniscus and this alters the surface tension (eg. $\gamma_{SiO2} > \gamma_{PbO}$ but $\gamma_{SiO2} < \gamma_{FeO}$) thus for the PbO –$SiO_2$ system the surface tension is greater at the tip than the base of the meniscus . Marangoni flow (surface-tension –driven flow) causes a flow from low to high surface tension so a flow is established which results in a vortex being formed; this vortex flow causes the gradual erosion of the refractory in this region [3]. The same mechanism applies to the FeO- $SiO_2$ slag but the direction of the slag flow will be the reverse of that for PbO- $SiO_2$.

*Figure 4: Schematic drawings showing (a) direction of Marangoni flow and (b) mechanism for slag line attack in PbO-SiO2 slag [3]*

In the case of the PbO- $SiO_2$ the slag film at the meniscus tip is higher than that at the base and the upward, Marangoni flow causes the slag to cover new refractory, this dissolves in the thin slag layer and creates a higher γ and so the slag is pulled further up to new area of refractory; this results in the slag creeping up the crucible and it will only flow back when the gravity force> upward Marangoni flow (Figure 5). This is known as *slag creeping*.
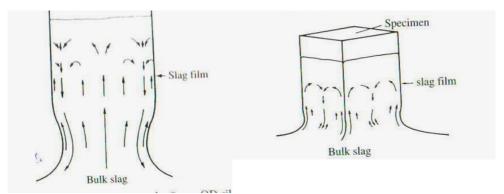


*Figure 5: Schematic diagrams showing refractory erosion and creeping for PbO- $SiO_2$ for round and square-sectioned silica[3].*

### Mechanism of erosion in carbon/oxide refractories

Oxide refractories are prone to thermal shock. Modern refractories have much better thermal shock resistance through the addition of graphite particles, which absorb much of the stress generated by the expansion on heating of the oxide particles. The erosion/corrosion of these oxide/C refractories occurs by a different mechanism [3] to that for slag line attack. Figure 6 shows wetting and non-wetting conditions. At high temperatures *reactive wetting* is the norm *ie* wetting will occur when there is reaction (*eg* (i) oxide in the slag and (ii) C in the metal). If the refractory surface at any one time consists mostly of oxides, the conditions will favour the covering of the surface by slag (since the oxide is non-wetting to the metal but slag reacts with and "wets" the oxide). The slag will then gradually dissolve these oxide particles (Figure 7a). When the dissolution process results in a surface comprising mostly of graphite flakes the conditions become non-wetting to slag and the refractory is covered by metal since metal wets graphite. (Figure 7b) The dissolution of the graphite by the metal will occur until the majority of the surface is mostly covered by oxide (Figure 7a) at which point the metal will retreat and the surface will be covered by slag once more and then another cycle of dissolution will occur.
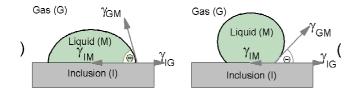
*Figure 6:  Schematic diagrams showing typical contact angles for wetting and non-wetting systems*



(a)                                                                                                    (b)
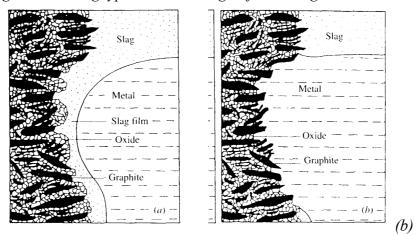
*Figure 7: Schematic drawings showing the refractory erosion for Oxide/carbon refractories [3] where the refractory surface is predominantly (a) oxide and (b) graphite, respectively.*


**How to combat slag/erosion of refractories**
The following methods are used:
(i) Since erosion rates are directly related to the flow rates of the slag, then erosion rates can be reduced by (a) increasing the viscosity of the slag or  (b) by reducing the flow rates of the metal (*eg.* by using electro-magnetic braking on the liquid metal) since these produce a drag force in the slag.
(ii) The driving force for erosion is ($C_{sat}$- $C_o$) where $C_{sat}$ and $C_o$ are the saturation concentration and actual concentrations, respectively; for  $ZrO_2$ and $ZrO_2$/ C refractories  erosion can be decreased by  adding $2\%ZrO_2$ to the slag to saturate it with $ZrO_2$ (for CC fluxes) .
   (iii)     It has been reported that making the slag non-wetting to refractory can extend refractory lives by the application of an electrical potential to the refractory and the slag [4,5].



*Figure 8: Effect of applying electrical potentials to a molten slag after 2 mins at (a) 0V (b)-1V and (c) -2V*


(iv) $ZrO_2$ undergoes a high-temperature transition and is usually stabilised by CaO or $Y_2O_3$; it has been reported that $CaF_2$ attacks the stabilisers and promotes erosion [6].
(v) Creation of a *freeze lining* on the refractory surface; this is done by blowing the molten slag left in the vessel after draining the metal in order to produce a protective, consumable slag layer. ***Slag splashing*** is used in BOS practice; for successful slag splashing the  FeO  should equal ca 13% to get good adhesion with the refractory and the MgO % should be  saturated (ca 8%) to create a high-temperature phase which slows down the erosion rate of the freeze lining [7].

S – 6

### 1.1.2 Thermo-physical properties

We have seen above that thermo–physical property data are needed to (i) solve industrial problems with process control and improve product quality and (ii) the development of mathematical models of the process. These models often involve simulation of the fluid flow and heat transfer in the process and it has been shown that reliable predictions (for the process) require accurate data for the input data for the properties (eg. viscosity, density, thermal conductivity of the slag) [8].Such measurements are frequently tricky because of the high temperatures involved and the consequent slag/container reactions. When you consider the large number of processes and the large number of properties required as input data, you soon realise that this is a massive job. This is further aggravated by the fact that compositions of reactants frequently vary. In mathematical modelling sensitivity analysis can ease this problem by indicating which property data are more important and the accuracy needed in such measurements. However, sensitivity analyses also show that the required accuracy required depends on what parameter is modelled eg. density may be required to 1% when modelling, say, porosity but, say, to 20% when modelling micro-structure. It is obvious that a large body of property values are needed for a wide range of slag compositions. Given the difficulties of making these measurements it follows what we need are models and routines which will calculate reliable and accurate property values from chemical composition since this available on a routine basis for most processes.

### 1.1.3 Estimation of thermo-physical properties

Various approaches have been used to derive estimated property values. These vary from at a simplest level to a numerical analysis of property values, for instance, analysis of $T_{liq}$ as a function of chemical composition. More complex models relate the property to the structure of the slag and for the case of $T_{liq}$ to phase diagram plus thermodynamic data for binary systems expressed as equations. Recently, models based on neural networks have been reported. The following should be noted:

- The accuracy of model predictions of properties can never be greater than that of the database; if the data are based on measurements from a single laboratory and contain a systematic error then the predicted values will also contain a systematic error.
- There are some discrepancies between the property values measured in different laboratories and thus a database based on such measurements will tend to be more scattered but will be applicable to a wider range of slags; the optimum condition is to use a database based on assessed property data.
- Models based on the structure of the slag which use one of the following (i) parameters such as (NBO/T) or the optical basicity ($\Lambda$) which can be calculated from the chemical composition or (ii) properties which are considered to represent the structure such as the excess free energy change $\Delta G^{xs}$ (since this is a measure of the strength of the bonding) or (iii)$N_{Oo}$ , $N_{O-}$ ,and $N_{O2-}$ ie the number of BO, NBO and free-oxygens present.

***Partial molar properties***

Some properties (P) (such as $C_p$ and $\Delta S^{fus}$) are not affected much by the structure of the slag; in these cases, good estimates can be derived using the partial molar property values (P) using the Equation 5 where X= mole fraction (calculated by Equn 6) and 1,2 etc represent the slag components eg. $SiO_2$, CaO etc. and M= Molecular weight of component = 60 for $SiO_2$ and $(\%)_1$= mass % $SiO_2$ etc:

$$P = \Sigma \left[ \left( X_1 \overline{P_1} \right) + \left( X_2 \overline{P_2} \right) + \left( X_3 \overline{P_3} \right) + \left( X_4 \overline{P_4} \right) \right] \qquad (5)$$

$$X_{SiO2}= X_1= \{(\%)_1 / M_1\} / [\{(\%)_1 / M_1\} + \{(\%)_2 / M_2\} + \{(\%)_3 / M_3\} + \{(\%)_4 / M_4\} + \ldots \qquad (6)$$

The values for $P_T$ are those for the pure component (eg. $SiO_2$) for the temperature of interest.
.

## 2. The Structure of slags

### 2.1 Structure of slags and glasses

The structure of $SiO_2$ is a 3D –array (Figure 9a,b) with (i) each $Si^{4+}$ surrounded by 4 $O^{2-}$ arranged tetrahedrally and (ii) and each $O^{2-}$ connected to two $O^{2-}$ (denoted ***bridging O***) which causes the formation

of a 3-D array. Cations eg $Na^+$ or $Ca^{2+}$ break the chain by forming a bond, $O^{2-}$ -- $Na^+$ (denoted ***non-bridging O***). The methods used to determine structure are summarised in Appendix 1. Slags and glasses are polymers in the form of chains, rings etc made up of $SiO_4^{4-}$ tetrahedral units (Figures 9,10). They have the following characteristics [9-12]:

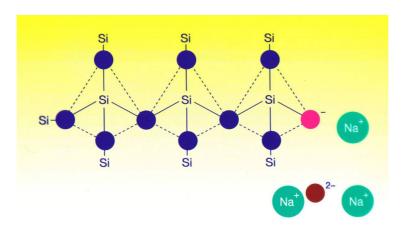

*Figure 9: Structure of SiO₂ showing 3-D characteristics*



*Figure 10. Schematic drawings and silicate chain with Bridging O (Oᵒ) shown in black, non- bridging O (O⁻) as free O²⁻ as green.*

- Each Si (with a valence of 4) is surrounded (tetrahedrally) by 4 $O^{2-}$ ions (with a valence of 2) each connecting to 2Si ions (Figure 9)
- In $SiO_2$ these $SiO_4^{4-}$ polyhedra are connected in a 3-dimensional polymerised structure (Figure 9b, 10) and the oxygens are predominantly ***bridging oxygens*** (denoted $O^o$).
- Cations such as $Ca^{2+}$, $Mg^{2+}$ etc. tend to break up the Si-O bonds and de-polymerise the melt by forming ***non-bridging oxygens*** (NBO denoted $O^-$) and ***free oxygens*** (denoted $O^{2-}$) i.e. not bound to Si at all but to $Na^+$ etc (Figure 10).
- Other cations such as $Al^{3+}$, $P^{5+}$, $Ti^{4+}$ can fit into the Si polymeric chain but need to maintain charge balance *e.g.* if an $Al^{3+}$ is incorporated into a $Si^{4+}$ chain it must have a $Na^+$ (or one half[1] of a $Ca^{2+}$) sitting near the $Al^{3+}$ to maintain local ***charge balance*** (Figure 11). In practice, $Ti^{4+}$ has been reported (on the basis of viscosity measurements [13]) to act as a network breaker (ie is in 6-fold coordination) and has been treated as such in this work.
- Smaller cations such as $Mg^{2+}$ tend to give a wider distribution of chain lengths than larger cations such as $Ba^{2+}$.
- Cations such as $Fe^{3+}$ in small concentrations can act as network breakers but in higher concentrations can be incorporated into the chain in a similar way to $Al^{3+}$.

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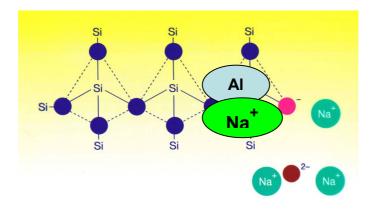[1] The $Ca^{2+}$ would charge balance two neighbouring $Al^{3+}$ ions

*Figure 11: Schematic drawing showing Al $^{3+}$ incorporated into silicate (Si$^{4+}$) chain, which requires cation (shown here as Na$^+$) to maintain charge balance*

- The degree of polymerisation can be expressed in terms of the numbers of **bridging** (N$^{Oo}$) **non-bridging** (N$^{O-}$) and **free- oxygens** (N$^{O2-}$). However the degree of de-polymerisation is frequently represented by parameters such as the ratio of {NBO/T (the ratio of the number of non-bridging O atoms to O atoms in tetragonal co-ordination)}which is denoted **(NBO/T)** [9-12] or the optical basicity (Λ) [12] .
- The structure of melts (both slags and metals) can be represented using thermodynamic quantities (*e.g.* excess free energy [14,15]) since thermodynamics provides a description of bond strengths.
- B$^{3+}$ has 3 fold coordination in borosilicates but the structure of borosilicates (used as enamels) is a complex mixture of 3- and 4- co-ordination [16,17].
- The structures of glasses are very similar to those of liquid slags [18].
- Some metallurgical slags have a high basicity (e.g. CaO/SiO$_2$ > 2) and consequently the Si$^{4+}$ ions are predominantly in the form of monomers *i.e.* completely de-polymerised.

## 2.2 Parameters used to represent structure

### *2.2.1 NBO/T and Q*
*NBO/T*= number of **non bridging O** / *tetragonally –bonded* oxygen
(NBO/T) is a measure of the de-polymerisation and can be calculated using the procedures listed below. However, cations  like Na$^+$ or Ca$^{2+}$ act as network –breakers but if an Al$^{3+}$ goes into the chain it requires a cation eg Na$^+$ to be sited near Al$^{3+}$ to provide charge balance (Figure 11). *A cation on charge-balancing duties cannot be used as a network- breaker*. The parameter, **(NBO/T)$_{corr}$ is a measure of the de-polymerisation of the slag**. (NBO/T)$_{corr}$ can be calculated in the following manner where f= fraction of Fe$^{3+}$ ions acting as a network breaker:

1. Calculate

$Y_{NB}$=Σ 2[ $X_{CaO}$ +$X_{MgO}$+$X_{FeO}$ +$X_{MnO}$ +$X_{CaO}$ +2$X_{TiO2}$ +$X_{Na2O}$ +$X_{K2O}$ +3f $X_{Fe2O3}$  -2$X_{Al2O3}$ – 2(1-f)$X_{Fe2O3}$] (7 )

2. Then  calculate  $X_T$= Σ $X_{SiO2}$ +2 $X_{Al2O3}$ + 2 f $X_{Fe2O3}$ + ..... (8)

3. (NBO/T )$_{corr}$ = $Y_{NB}$/ $X_T$

4. **Q  is a measure of the polymerisation**  of the slag and for this reason is often preferred to (NBO/T)

$$Q = 4 - (NBO/T )$$ (9)

*Table 1: NBO/T and Q for various CaO- SiO₂ slag compositions*

| | | NBO/T | Q | |
|---|---|---|---|---|
| $SiO_4^{4-}$ (monomer) | $2CaO.SiO_2$ | 4 | 0 | BOS slag |
| $Si_2O_7^{6-}$ (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 flux; Q= 2.5 |
| $Si_2O_5^{2-}$ (sheet) | $CaO. 2SiO_2$ | 1 | 3 | Glasses, Coal slags |
| $SiO_2$ (3-dim) | $SiO_2$ | 0 | 4 | Glasses |

### 2.2.2 Optical basicity($\Lambda$)

One problem encountered with both (NBO/T) and Q is that they do not differentiate between the effects of different cations on the silicate structure. The optical basicity ($\Lambda$) has been used as a measure of structure' principally because it does provide some measure of differentiating between different cations. It can be calculated in the following manner:

1. $\Lambda = \Sigma (X_1 n_1 \Lambda_1 + X_2 n_2 \Lambda_2 + X_3 n_3 \Lambda_3 + \ldots) / \Sigma (X_1 n_1 + X_2 n_2 + X_3 n_3 + \ldots)$  (10)

where n = number of oxygens in oxide eg n=2 for $SiO_2$ or 3 for $Al_2O_3$

2. $\Lambda^{corr}$ is calculated by deducting the mole fraction of cation required to charge balance the $Al^{3+}$ in the chain, this is usually deducted from the largest cation present eg. $Ba^{2+}$ thus $X^{corr}_{BaO} = (X_{BaO}-X_{Al2O3})$

The following values of optical basicity are recommended:
$Al_2O_3$= 0.60: $B_2O_3$= 0.42: BaO=1.15: CaO= 1.0: FeO= 1.0: $Fe_2O_3$= 0.75: $K_2O$= 1.4; $Li_2O$= 1.0: MgO= 0.78: MnO= 1.0: $Na_2O$= 1.15: $P_2O_5$= 0.40: $SiO_2$= 0.48: SrO= 1.10:$TiO_2$= 0.61:

Various $\Lambda$ values have been cited for $CaF_2$ 0.43, 0.67 but a value of 1.2 should be used for viscosity calculations. However, recent work due to Sasaki et al. [19] indicates that $Ca^{2+}$ bonds with $2F^-$ and thereafter is *"out of the game"* (thus one can correct the slag composition by ignoring F concentration and deducting $2X_F$ from $X_{CaO}$ )[20]

### 2.3 Structural changes in glasses and slags with temperature

When a glass or a glassy slag (Q> ca.2 .5) is heated both $C_p$ and thermal expansion (and other properties, eg. k ) measurements show a marked change at a specific temperature (as can be seen in Figure 12); this is called the **glass transition temperature** ($T_g$). The change in $C_p$ and $\alpha$ is due to the glass transforming into a super-cooled liquid (but which appears to be a solid). This super –cooled liquid (scl) exists until the slag melts into a true liquid. However, some slags (with lower Q say <2) the scl undergoes crystallisation which is an exothermic transition. On heating, the following changes in glassy slag properties occur at $T_g$ (i) a step increase in $C_p$ with $C_p$ of the glass remaining higher than that of the crystalline slag over the entire range between $T_g$ and $T_{liq}$ (ii) a three-fold increase in thermal expansion (iii) a remarkable decrease in viscosity with increasing temperature, the following value is frequently cited, $\eta$ (dPas)=$10^{13.4}$ at $T_g$ and (iv) an abrupt decrease in the slope of k as a function of temperature .
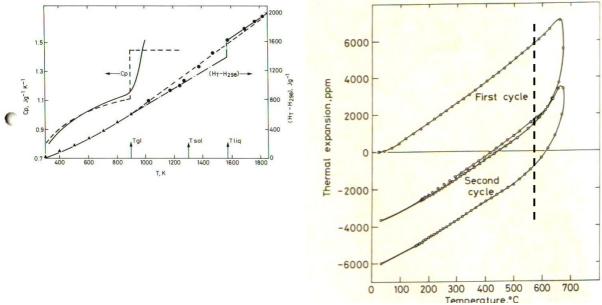
*Figure 12: (a) Heat capacity for a glassy slag and (b) Thermal expansion coefficient
as a function of temperature.*

Viscosity ($\eta$) measurements on glassy samples (Q>2.5) carried out whilst cooling show viscosities (i) with higher values than that of a less-polymerised sample (Q=2) and (ii) a smooth change with temperature as the liquid transforms to scl (with $\eta = 10^{12.4}$ Pas at $T_g$ ). It can be seen from Figure 13b that viscosities for less polymerised slags (Q=<2) show a sharp change in slope (at the *break temperature*, $T_{br}$) when crystalline materials are first precipitated; it should be noted $T_{br}$ decreases as the cooling rate increases.
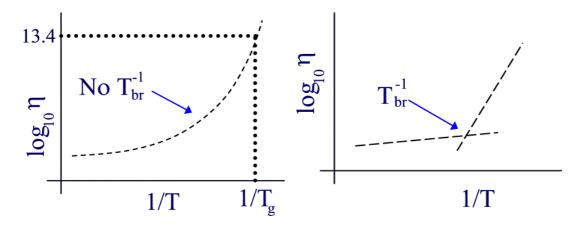


*Figure 13: Plots of $log_{10}$ viscosity as functions for reciprocal temperature ($K^{-1}$) for (a) glassy slag
(Q>2.5) and (b) for a less-glassy slag (Q=2).*

## 2.4 Effect of structure on properties
The effect of polymerisation (or Q) on property values are arranged so the properties showing the biggest dependence on structure first and with diminishing dependence on structure as we go down

## 2.4.1 Effect of structure (Q or (NBO/T)) on properties
Property values for slags and glasses are greatly affected by the degree of polymerisation (ie. Q); polymerisation (or Q) increases as (i) $SiO_2$ and $Al_2O_3$ *(network-former )*concentrations increase and (ii) $Na_2O$, $Li_2O$, CaO, MgO, $K_2O$, SrO and BaO (*network –breakers*) decrease.

## *Viscosity (η)*
Viscosity involves transporting one layer of liquids over another; thus the longer the chain length (or polymerisation) the more difficult this task becomes. It can be seen from Figure 14a  that the viscosity

shows a dramatic decrease between NBO/T=0 and 1 (or Q= 4 to 3)  If we need to represent the structure through a property, the viscosity is the best property to represent the structure of the glass .
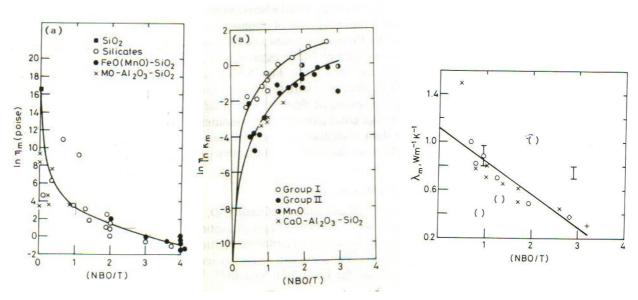


*Figure 14 (a) Viscosity (b) Electrical conductivity and (c) Thermal conductivity as functions of (NBO/T)*
*of liquid slags at $T_{liq}$ [12]*

### Thermal conductivity (k) and electrical conductivity (κ)

The **thermal conductivity** of liquid slags tends to increase with increasing $SiO_2$ content; this can be seen in Figure 14c where the thermal conductivity (k) decreases with increasing NBO/T (or decreasing Q). Thermal conductivity is high for covalently- bonded $Si^{4+}$ and $Al^{3+}$ ions in the chain but is much lower for the NBO and cations at the end of chains. This can be expressed as conduction is easy along the chain (ie. thermal conductivity is much larger) but the transport of phonons is much more difficult for chain-to-chain movement. The thermal conductivity seems to be affected by the nature of the cations with $k_{Li2O} > k_{Na2O} > k_{K2O}$.

**Electrical conductivity** involves the movement of cations through a silicate network when an electrical field is applied; thus a well-developed network will hinder their movement of these cations. It can be seen can be seen from Figure 14b that κ increases sharply (i) as NBO/T increases (or Q decreases) and (ii) when $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$ and $Ba^{2+}$ are replaced by $Li^+$, $Na^+$, or $K^+$. Consequently, there are two factors affecting electrical conductivity (i) the degree of polymerisation of the slag with the electrical resistivity (1/κ) increasing as polymerisation (Q) increases and (ii) the size and concentration of the cations since the number of cations slipping through the "holes" in the network will be greater for high concentrations of cations and for smaller cations.

### Thermal expansion(α,β) and density (ρ)

$SiO_2$ has a very low **thermal expansion coefficient** because of the tight bonding. First order properties (eg α ≡dρ/dT shown in Figure 15a) tend to be more sensitive to temperature than the property itself (eg. ρ) ; the density is only  slightly sensitive to the polymerisation (Q) in the slag. It can be seen from Figure 15a that thermal expansion (1) increases with increasing NBO/T (or decreasing Q) and (2) is greater for $M_2O$ than MO and that increases with increasing cation size (K>Na>Li and Ba>Ca>Mg).  In Figure 15b it can be seen that there is a marked change in thermal expansion when $T>T_g$ (ca. 300%) which occurs when the glass changes into a scl. However, accurate values of thermal expansion of glassy slags are difficult to obtain for $T>T_g$ because the super-cooled liquid tends to collapse under the pressure of the probes.
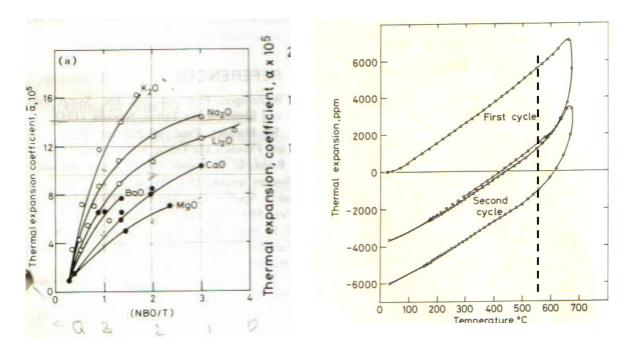
*Figure 15: Thermal expansion of (a) liquid binary slags as a function of (NBO/T) and (b) increase in expansion of solid ( note change of slope at $T_g$)*

### Surface tension (γ) and emissivity (ε)

These properties predominantly depend on the surface and not the bulk. In mixtures, the constituents with the lowest **surface tension** (called "*surfactants*") will tend to occupy the surface layer (eg. S in steels and *surfactants* like $B_2O_3$ in slags). The surface concentration will depend upon both surface tension and the chemical activity of the component (eg $B_2O_3$ in the slag). When there are two or more, surface-active components in the slag (eg $CaF_2$ and $B_2O_3$) there will be competition for the surface sites. The surface tension is a thermodynamic property. Surface tensions of some oxides are given in Table 2 since $\gamma_{SiO2} > \gamma$ for other oxides it follows that γ will decrease with increasing $SiO_2$ and increasing Q.

*Table 2: Surface tensions ($mNm^{-1}$) of pure slag components at 1773K*

| | $SiO_2$ | CaO | BaO | SrO | MgO | $Al_2O_3$ | MgO | FeO | NiO | MnO | CrO | $Na_2O$ | $K_2O$ | $TiO_2$ | $ZrO_2$ | $Cr_2O_3$ | $Fe_2O_3$ | $CaF_2$ | $B_2O_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| γ | 260 | 625 | 560 | 600 | 635 | 655 | 635 | 645 | 645 | 645 | 360 | 295 | 160 | 360 | 400 | 800 | 300 | 290 | 110 |

Slags and glasses are semi-transparent to IR radiation. Slags and glasses are optically- thick if α*d>3 where α*=absorption coefficient. In practice, this means the **emissivity** of liquid slags will depend on the depth of the slag sample. Values are usually cited for the *optically thick condition*.

### Heat capacity ($C_p$), entropy of fusion ($\Delta S^{fus}$)

These properties are little affected by structure and Equations 6 and 7 are valid , where 1,2 etc represent the different components, eg. $SiO_2$ etc. However, $C_p$ is dependent upon the nature of the slag and $C_p$ jumps abruptly at $T_g$ when a glass changes to a scl whereas a crystalline slag (1) shows no jump at $T_g$ (2) $C_{p\ scl} > C_{p\ cryst}$ over the range $T_g$ to $T_{liq}$ and (3) exhibits an enthalpy of fusion ($\Delta H^{fus}$) at $T_{liq}$ wheras a scl exhibits no $\Delta H^{fus}$.

$$P = \Sigma\left[\left(X_1\overline{P_1}\right)+\left(X_2\overline{P_2}\right)+\left(X_3\overline{P_3}\right)+\left(X_4\overline{P_4}\right)\right] \tag{6}$$

# 2. Types of Model

Several types of models have been reported for calculating the properties of slags; these are classified into five groups ie. 1. Numerical fits 2. Neural network models 3. Partial molar models 4. Models based on structural parameters 5. Thermodynamic models (which take structure into account) and 6. Molecular Dynamics (MD) models. These are summarised below.

## 3.1 Numerical fits

With these an experimental database is established covering the compositions of the slags and the property being modelled *eg.* liquidus temperature, $T_{liq}$. A numerical analysis is then carried out to obtain the "best fit" in which $T_{liq}$ is represented as $C_1(comp_1) + C_2 (comp_2) + C_3(comp_3) + . . .$ where C is a constant , comp=either % or X and 1,2,3, =different components eg. $SiO_2$ etc. One problem with this approach is that unrealistic constants can be recorded for components in low concentrations (eg. $K_2O$ in mould fluxes) and it is frequently better for this case to add the % (or X) $K_2O$ to % (or X)$Na_2O$ which is present in greater amounts and exhibits similar behaviour.

This approach is more successful when applied to a family of slags (eg. mould fluxes or ferro-chrome slags) with limited compositional range than for a wide range of slag compositions which involve complex and very different phase equilibria. Some typical applications are for $T_{liq}$ and $T_{br}$ of mould fluxes which allow values to be calculated to better than ± 30K to be calculated [21].

$$T_{liq}(K)=1464+ 11.4\%SiO_2-11\%CaO +4.2\% Al_2O_3+5.7\%MgO-10.1\%Na_2O -15.8\%K_2O +1.9\%F +8.3\%Fe_2O_3 +11.6\%MnO \qquad (11)$$

$$T_{br} (K) = 1393- 8.4\% Al_2O_3- 3.3 \%SiO_2+ 8.65\%CaO-13.86\% MgO -18.4\%Fe_2O_3 -3.2\% MnO -9.2\%TiO_2- 2.2\%K_2O -3.2\%Na_2O -6.47\% F \qquad (12)$$

## 3.2 Neural network models

The human brain contains $>10^{10}$ cells ("neurons") in a neural network consisting of several (3 here) layers. When units are inserted into "input layer" they are transmitted to the "middle layer" and when the intensity exceeds a critical value they are transmitted on to the "output layer" (Figure 16). Signal transmission is represented by a sigmoidal function in the software. In the output layer the output values are (i) compared with teaching values (ie experimental values fed previously) and (ii) errors are computed. These errors are then transmitted back to the nodes between layers to re-calculate the weights. These procedures are called "learning" and learning is repeated until the target attained or errors are within acceptable limits. In the studies of Nakamoto [22, 23] the teaching value is "measured viscosity" and the input values are temperature and compositions of the slags. Neural network models have been used to calculate the viscosities of (i) ferro-chrome ($CaO+Al_2O_3+MgO +CrO_x+SiO_2$) slags [22] see Figure 17 and (ii)mould fluxes [23] which available commercially. Nakamoto et al [22] report uncertainty values for the function $\{100(\eta^{meas}-\eta^{calc}/\eta^{meas})\}$were ± 22% for ferro-chrome-type slags. Neural network values have also been used to determine surface tension [78] and Sulphide capacities.
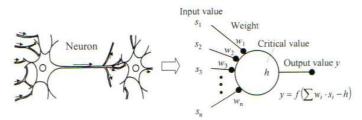
*Figure 16: Schematic diagrams illustrating (i) concept of neuron model and (ii) neural network.*



*Figure 17: (a) Viscosity as a function of temperature for a MgO+CrO+CrO$_{1.5}$+Al$_2$O$_3$+SiO$_2$ slags and (b) Iso-viscosity (dPas) contours for a Fe/Cr process slag at 1923K SAMC= (X$_{MgO}$ =0.41)+ (X$_{CaO}$=0.074)+ (X $_{SiO2}$=0.343)+(X$_{Al2O3}$=0.173) [22]*

### 3.3 Models based on structure

The majority of reported models take the structure into account. Earlier models tended to use basicity (*eg.* CaO/SiO$_2$) ratios to represent the structure. The widely used Riboud model [24] classifies oxides into 5 groups "CaO" "SiO$_2$" "Al$_2$O$_3$" "Na$_2$O" "CaF$_2$" which are network-breakers or network-formers.  More recent models have tended to use one of the following parameters used to represent structure (NBO/T or Q; optical basicity, or the number of Bridging or- Non- bridging and free-O, (N$_{Oo}$ , N$_{O-}$ ,and N$_{O2-}$, respectively).Details of these parameters are given above  in Section 2.2

### 3.4 Thermodynamic models

There are several commercial thermodynamic models available (eg. MTDATA [25], Thermocalc, [27] Factsage [26]). These models are based on database of phase equilibrium and thermodynamic data for various binary systems eg. CaO- $SiO_2$; FeO- $SiO_2$ ; etc. In the case of MTDATA [28] for instance the liquid CaO-$SiO_2$ system is considered to be made up species CaO and $SiO_2$ and by "associate species" such as $CaSiO_3$ and $Ca_2SiO_4$. Polynomial equations are used to represent these data for these species and to account for sharp changes in thermodynamic properties at specific compositions (eg. where miscibility gaps occur). Equations for binary systems are used to predict the equilibrium phase diagrams and chemical activities, free energies, enthalpies, $C_p$ and $T_{liq}$ and $T_{sol}$ values for ternary, quaternary and higher systems .Most crystalline phases are assumed to mix independently on a series of separate sub-lattices

In recent years, these commercial models have been extended to the calculation of physical properties such as densities, viscosities and surface tensions of slag systems. Properties such as viscosity involve the movement of one liquid, slag particle over another and this is related to the strength of the bonding and thermodynamics provides a measure of the strength of the bonding.

Thermodynamic models involve:

- An extensive database of phase equilibrium data and thermodynamic properties which have been assessed to provide reference data for the various binary-, ternary –etc.; These evaluated data are represented as polynomial equations in terms of T, and used to calculate data for ternary and higher systems
- The principal differences between specific models lie in the different ways the liquid is represented eg MTDATA use the *associate species model* for the liquid

There are differences in the approaches taken to model physical properties , such as viscosity, in the various models. For instance in model due to Zhang et al [29,30] the values of $N_{Oo}$ , $N_{O-}$ ,and $N_{O2-}$ are first calculated using the Kapoor-Frohberg cell model (as developed by Gaye et al [31]) and then fitting constants a, b ,c, d, a' and b' are derived for each binary system. Viscosity values for ternary and higher systems are calculated using the fitting constants for the binary systems (Equns13-16) but adjustments are needed in some cases. These quantities are then used to calculate ln A and B for the Weymann equation(Eqn 13). The software is commercially available.

$$\eta = A_w T. \exp (E_W/R^*T) \tag{13}$$

$$E_W = a + b(N_{Oo})^3 + c(N_{Oo})^2 + d(N_{O2-}) \tag{14}$$

$$\text{Ln } A_w = a' + b'.E_W \tag{15}$$

$$a = \Sigma X' a \tag{16}$$

where $E_W$=activation energy, $R^*$=Gas constant and a, b, c, d =fitting constants .

Tanaka et al.[15] also use the Kapoor Frohberg cell model to calculate the $N_{O-}$ and $N_{O2-}$ and the Arrhenius equation and $E\eta = E/ 1+ \{ \Sigma\alpha_{i*} (N_{O-} + N_{O2-})\}^{0.5}$ where A and the constants, $\alpha_i*$ are determined from experimental viscosity data.

In contrast, Seetharaman and Du [32,33] adopt a very different approach. The effect of structure is determined as thermodynamic function (Equn 17) where $\Delta G^*$ =free energy of individual components 1,2 etc ,,$\Delta G_\eta^{mix}$ = free energy of mixing and 1,2=components *eg*. CaO.

$$\Delta G^*_\eta = \Sigma \Delta G^* + \Delta G_\eta^{mix} + 3R^*T X_1 X_2 \tag{17}$$

The viscosity is then calculated using Equn 18 where h=Planck Constant and $N_A$=Avogadro number thus $A_A = hN\rho/ M$ and $B_A = \Delta G^*_\eta$.

$$\eta = hN_A \rho/ M \exp (\Delta G_\eta / RT) \tag{18}$$

S – 16

Although thermodynamic models may provide reliable thermodynamic values, the accuracy of the viscosity prediction will lie in how well the selected thermodynamic functions represent the effect of structure on the viscosity. This model has been adopted by other groups [40].

### 3.5 Molecular Dynamics (MD) models

Molecular dynamics (MD) is a computer simulation where molecules are allowed to interact for a period of time and which is approximated by using the physics of particle motion. MD is based on Statistical Mechanics and makes use of Potential Energy functions to calculate bonding characteristics and motion of the molecules from which the viscosity and self-diffusion of O, Ca, Si, F can be determined. The accuracy of MD calculations is limited by the accuracy of Potential Energy functions for many silicate systems. MD calculations of bonding characteristics and slag viscosities have been reported by Zhang et al [35] and by Ogawa et al. [36] and for Diffusion coefficients by Asada et al.[20]

## 4. Modelling physical properties

### 4.1 Liquidus ($T_{liq}$) and solidus ($T_{sol}$) temperatures

The various commercial models available are capable of calculating reliable values of $T_{liq}$ and $T_{sol}$ for multi-component slags over large compositional ranges..

However, it is difficult to calculate values of $T_{liq}$ and $T_{sol}$ for wide ranges of composition and it may be necessary to make experimental measurements for the calculation of estimated properties. However, it may be possible to estimate $T_{liq}$ and $T_{sol}$ for a specific family of slags (for instance mould fluxes) by creating a database of $T_{liq}$ and $T_{sol}$ and correlating these with their chemical compositions to obtain "best fit" constants. Examples of this approach are determination of $T_{liq}$ and $T_{br}$ of mould fluxes from measured values and chemical composition data [21]. Care must be taken with the constants derived for constituents (eg $K_2O$), which occur in low concentrations since the residuals in the calculations tend to get dumped onto these materials leading to unrealistic constants. In these cases more appropriate constants can be derived by adding the material to a similar material (eg $K_2O + Na_2O$).

$$T_{liq}(K)=1464+ 11.4\%SiO_2-11\%CaO +4.2\% Al_2O_3+5.7\%MgO-10.1\%Na_2O -15.8\%K_2O +1.9\%F +8.3\%Fe_2O_3 +11.6\%MnO \tag{11}$$

$$T_{br} (K) = 1393- 8.4\% Al_2O_3- 3.3 \%SiO_2+ 8.65\%CaO-13.86\% MgO -18.4\%Fe_2O_3 -3.2\% MnO -9.2\%TiO_2- 2.2\%K_2O -3.2\%Na_2O -6.47\% F \tag{12}$$

The principal methods of determining $T_{liq}$ are (i) DTA/DSC [ 37,38 ] (ii) single and double high-temperature thermocouple methods [ 39 ] and (iii) quenching slag samples in Pt capsules from different temperatures followed by metallographic examination to identify melting in the sample .For accurate values the following procedures should be adopted: (i) DSC measurements should be conducted in the heating cycle since significant under-cooling can occur in cooling (ii) the measurement thermocouples should be calibrated using standard reference materials appropriate for the slag samples (eg metals have significantly higher thermal conductivities than slags) (iii) measurements should be carried out using different heating and extrapolated to zero heating rate to determine the magnitude of the correction term.

### 4.2 Heat capacity, enthalpy

*Factors affecting property*: 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 (eg where 1, 2= CaO, $SiO_2$ etc).

$$C_p= \Sigma (X_1 C_{p1}) + (X_2 C_{p2}) + (X_3 C_{p3}) +(X_4 C_{p4}) \tag{19}$$

It is customary to express the temperature dependency of $C_p$ in the form of:

$$C_p =a + bT -c/T^2 \tag{20}$$

Thus it is possible to derive individual values of the parameters, a , b and c in the form of:

$$a = \Sigma \, (X_1 a_1) + (X_2 a_2) + (X_3 a_3) + (X_4 a_4) + \ldots \tag{22}$$

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

$$(H_T\text{-}H_{298}) =_{298}{}^{T}\!\!\int C_p \, dT \quad = a(T\text{-}298) + 0.5bT^2 - 0.5b(298)^2 + (c/T) - (c/298) \tag{22}$$
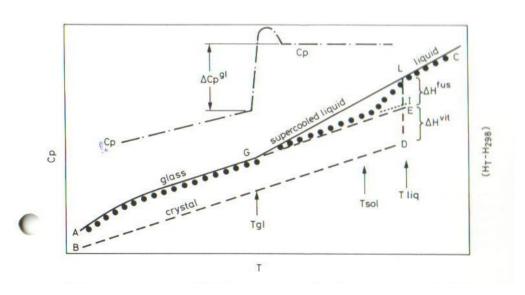
Consequently, $(H_T\text{-}H_{298})$ for the solid state can be calculated from a, b and c values.

It takes energy for a crystalline solid to transform into a liquid slag and this energy is the enthalpy of fusion $(\Delta H^{fus})$ and this is usually is calculated from the entropy of fusion $(\Delta S^{fus})$ which represents the structural changes accompanying this transition. The $\Delta H^{fus}$ can be calculated in the following way:

$$\Delta S^{fus} = \Sigma \, (X_1 \, \Delta S^{fus}{}_1) + (X_2 \, \Delta S^{fus}{}_2) + (X_3 \, \Delta S^{fus}{}_3) + (X_4 \, \Delta S^{fus}{}_4) + \tag{23}$$

$$\Delta H^{fus} = T_{liq} \, \Delta S^{fus} \tag{24}$$

Solid slags can exist in crystalline or glassy forms or as a mixture of glass and crystalline phases. When a glassy slag is heated there is a sharp *"steplike"* increase in $C_p$ (see Figure 18 ) at the glass transition temperature $(T_g)$ which corresponds to the transition of a glass to a super-cooled liquid (scl).Crystallisation usually takes place at a higher temperature ; it should be noted that $Cp^{app}$ valley shown in Figure 18 is not a true change in $C_p$ but is a manifestation of the enthalpy of transition $(\Delta H^{crys})$. It can be seen that for temperatures between $T_g$ and $T_{liq}$ that there are two possible values for the $C_p$ and $(H_T\text{-}H_{298})$ representing the glassy and crystalline phases; the true value for the sample lies between these values and will depend upon the experimental conditions (for both the laboratory specimen and for slag formed in the industrial process).
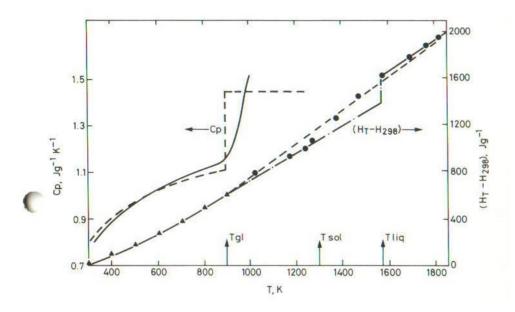
*Figure 18: Schematic representation of heat capacity and enthalpy ($H_T$-$H_{298}$) of glassy and crystalline slag phases.*

### Measurement methods

Various methods are available for measuring $C_p$ and (($H_T$-$H_{298}$)); descriptions of these methods have been given elsewhere [37,38]. The most popular methods today are differential scanning calorimetry (DSC) and drop calorimetry; the experimental uncertainty for both of these methods is ca ± 2%. More accurate $C_p$ values can be derived from ($H_T$-$H_{298}$) values obtained from drop calorimetry with $C_p$ values measured using DSC [38]. It should be noted that cooling rates are very high in drop calorimetry, which will promote the formation of glassy phases.

### Different models available in literature

Thermodynamic models derive $C_p$ and enthalpy values from differentiation of $\Delta G$ data for the slag [40]. Less accurate derived (uncertainty ±2-5%) can be derived from the method described above( Equns 19 to 24 ). The major uncertainty in any estimate lies in the degree of crystallisation of the sample which occurs in the $T_g$ to $T_{liq}$ range and which may be significantly different for industrial conditions from that for DSC conditions.

### 4.3 Thermal expansion

The thermal expansion is frequently expressed through by the volume ($\beta$) and linear thermal expansion coefficients ($\alpha$) which are given in Equns 25 and 26 where $\beta_{(298-T)}$ and $\alpha_{(298-T)}$ are the volume and linear coefficients, respectively and $V_0$, $L_0$=volume or length of sample at the reference temperature ($T^{ref}$), usually 293 or 298K for the solid and $T_{liq}$ for the liquid.

$$\beta_{(298-T)} = \{(V_T - V_0) / V_0 (T - T^{ref})\} \tag{25}$$

$$\alpha_{(298-T)} = \{L_T - L_0) / ( L_0 (T - T^{ref})\} \tag{26}$$

The linear thermal expansion is frequently presented as $\Delta L\%_T$ since densities are readily calculated by Equns 27 and 28 where $L_0$ and $\rho$ are the length and density at the reference temperature ($T^{ref}$) ie 298 or 293 K for the solid and $T^m$ (=$T_{liq}$) for the liquid:

$$\Delta L\%_T = 100 (L_T - L_0) / L_0 \tag{27}$$

$$\rho_T = \rho_0 / [1+\{0.01 \Delta L\%_T\} ]^3 \tag{28}$$

*Factors affecting property:* Thermal expansion parameters ($\alpha$, $\beta$ and $\Delta L\%_T$) are very dependent upon structure since the thermal expansion is very low for $SiO_2$ with its highly polymerised 3-D network (Figure 15a); thus thermal expansion parameters will decrease as Q (polymerisation) in the slag increases.

The transition of glass to scl at $T_g$ is associated with a large increase in $\alpha$ as shown in Figure 15b ($\alpha_{T>Tg} \approx 3\alpha_{T<Tg}$). However, it is quite difficult to obtain thermal expansion data for the scl phase since the pressure of the probes on the specimen in a dilatometer results in a collapse of the sample for the scl phase.

### Measurement methods

At room temperature the density of slags can be measured by accurate measurements of the sample mass and its dimensions. However, it is usually preferable to use the Archimedan method which entails measuring the apparent loss of weight of the sample when immersed in distilled water.

At higher temperatures the following methods are frequently used(i) dilatometry (ii) Archimedan method where a probe(or bob) is immersed in the molten slag.(iii) sessile drop where the volume of the drop is determined (iv) pyknometry (v) Maximum bubble pressure (MBP) method where the density is determined through MBP measurements at different immersion depths [43, 37] The experimental uncertainty is usually in the range ±1-2%.

### 4.4 Density (ρ)

The density is derived directly in thermodynamic models [40].

Persson [41] et al estimated molar volumes (V) by the following equation where the superscript M and subscript m refer to the integral and partial molar quantities and H refers to the enthalpy of mixing and $\lambda$ is a constant; the values of $\Delta G$, $\lambda$ and interaction coefficients were derived from their thermodynamic model:

$$V^M / \Sigma X_i V_m = \lambda H^M / RT \qquad (29)$$

It is possible to derive reasonably accurate density values from a simpler model since the densities of liquid slags are only slightly dependent upon structure. It is customary to model the density through the molar volume (V) where 1, 2 , 3 denotes $SiO_2$,CaO, ,$Al_2O_3$ etc. and M= molecular weight of slag.

$$V = \Sigma (X_1 V_1) + (X_2 V_2) + (X_3 V_3) + (X_4 V_4) + \qquad (30)$$

$$\rho = M / V \qquad (31)$$

for a binary system eg CaO- $SiO_2$ we can determine the value of V for a specific oxide eg. $SiO_2$ from measured V (from ρ for slag ) and the relation:

$$X_1 V_1 = V - X_2 V_2 \qquad (32)$$

If $V_1$ is unaffected by structure it would have a constant value for all mole fractions; in practice it was found that $V_1$ increased as the $SiO_2$ content (ie $X_1$ ) increases. ($V_1 = 19.55 + 7.966 X_{SiO2}$). Similar relations were also found for $Al_2O_3$ and $P_2O_5$ in silicate slags. Similar methods can be used to calculate the density of the solid slag at 298 K and values at higher temperatures can be derived by using the calculated thermal expansion data:

$$\rho_T = \rho_{298} / (1 + \alpha T)^3 . \qquad (33)$$

The densities of many of the components of the slag are similar and Keene [42] proposed a simple relation for calculating the densities of molten steelmaking slags with an uncertainty of ca. ± 5%.

$$\rho_{1673}(kgm^{-3}) = 2490 + 12 (\% \, FeO + \% \, Fe_2O_3\% + \% \, MnO + \% \, FeO) \qquad (34)$$

The transition at $T_g$ of glass→scl results in a larger density- temperature gradient for temperatures>$T_g$.

## *Modelling densities off molten and solid slags*

The densities of many molten slags can be determined to a reasonable accuracy (± 2-3%.) by the simple method outlined above (Equns 30 - 33). The available methods are summarised in Table 3. Various methods are used to account for the dependence on structure eg .via the excess free energy [41]etc.

*Table 3: Details of models to calculate densities of alloys and slags*

| Reference | System | Details of Method | Uncertainty |
|---|---|---|---|
| Bottinga Weill [44] | **Slags** | $V = \Sigma\ X_1V_1 + X_2V_2 + X_3V_3$   Values of V given<br>Corrections to  V values for compositions of $Al_2O_3$, $Na_2O$ , $K_2O$, CaO ,MgO, FeO:<br>Equations for β also corrected for chemical compositions of these oxides | 2-3% |
| Mills Keene[42] | **Slags** | **Method 1:**   $\rho$ ($kgm^{-3}$)= 2460 + 18 (% FeO + %  $Fe_2O_3$% +% MnO + % FeO)<br>**Method 2:**   $V = \Sigma\ X_1V_1 + X_2V_2 + X_3V_3 +$. .at 1773K  V ($10^{-6}m^3mo^{l-1}$) values for:<br>CaO=20.7; FeO= 15.8; $Fe_2O_3$= 38.4: MnO = 15.6; MgO= 16.1; $Na_2O$= 33; $K_2O$ = 51.8:<br>$TiO_2$= 24;$P_2O_5$= 65.7;$SiO_2$= (19.55 + 7.97$X_{SiO2}$) $Al_2O_3$= (28.3+ 32$X_{Al2O3}$ -31.45$X^2_{Al2O3}$)<br>**(dV/dT)** =0.01%$K^{-1}$ | 5%<br><br>2% |
| Robinson et al [40] | **Slags** | Use of  thermodynamic software: Molar  volumes stored for oxides and correction based on molar Gibbs energy of system | 2% |
| Hayashi, Seetharaman [45] | **Slags** | $V / \Sigma\ X_1V_1$= ( $K\Delta^{mix}$ H/R*T) where is the relative integral enthalpy of mixing (determined with thermodynamic software)and K= constant | 2% |
| Persson [ 41] | **Slags** | $V^M$= $\lambda H^M$. $\Sigma Xi\ Vm$ /R*T where M and m indicate integral and partial molar volumes , $\lambda$ is a constant and $H^M$ is the integral enthalpy of mixing<br>Values of $\Delta G^M$ ,$\lambda$ and interaction coefficients obtained from thermodynamic model | 2-5% |
| Priven [46] | **Glasses** | Solids:    $V = \Sigma\ X_1V_1 + X_2V_2 + X_3V_3$      Values and range of applicability given.<br>Special procedures for boro-silicates | |

## *4.5 Viscosity* (η) of slags

Viscosity is the ability to resist the movement of one layer of molecules over another when a stress is applied (via a rotating cylinder in most experiments). *It should be noted that the units of all viscosities cited here are for dPas.*

*4.5.1 Factors affecting property:* Viscosity is very structure dependent upon both structure and on temperature since increased temperature also tends to beak down the structure. The Arrhenius equation (Equn 35) is widely used to express the temperature dependence of viscosity but the Weymann (or Frenkel) relation (Equn 36)  and other equations have been used and  can provide a slightly improved fit.

$$\eta = (A_A.\exp B_A/T) \tag{35}$$

where $A_A$ is constant dependent upon the slag structure and $B_A$=$E_\eta$ /R* where $E_\eta$  is the activation energy for viscous flow (which too is dependent upon structure) and R* is the Gas constant.

$$\eta = (A_W.T.\exp B_W/T) \tag{36}$$

where $A_W$ and $B_W$ are similar to the $A_A$ and $B_A$ parameters in Equn **35**   but will have different values .Some workers [47,29,30] have linked A and B (or $A_W$ and $B_W$) via equations  since both are related to structure.

For glassy slags (*eg* Q>3) there is a rapid increase in viscosity on cooling (Figure 13a) as the slag moves from a liquid to a super-cooled liquid (scl) with the viscosity attaining a value of $10^{13.4}$ dPas at $T_g$.The temperature dependence in this scl range is usually expressed in the form of the Vogel-Fulcher- Tamman relation (Equn 37).which requires the knowledge of three constants A,B and $T^o$.

$$\eta = A_V \exp (B_V /(T-T^o)) \tag{37}$$

### 4.5.2 Methods of measurement

The most popular method of measuring slag viscosities is the concentric cylinder method, which consists of centrally –aligned bob in a cylindrical crucible [43]. The method can be operated by measuring the torque when rotating either the bob or the crucible [43]; the rotating bob method tends to be more popular because of ease of operation. Rotation speed is determined by the viscosity and torque measured and it is usual to make measurements at least two different speeds to ensure the flow is Newtonian.

Falling sphere and capillary viscometers have been used for slags but tend to be difficult to operate at high temperatures because of the need for a large zone of uniform temperature. Oscillating viscometers have been used for measuring de-polymerised slag viscosities[43].

The uncertainty in the measurements for many slags is ca. ± 20% because of changes in slag composition during the measurement and from systematic errors arising from end effects etc. The very best viscosity measurements are probably subject to an uncertainty of ca. ± 10%.

### 4.5.3 Modelling of slag viscosities

A number of models have been reported to estimate viscosity; they all account for the structure in some form and details of the method are given in Table 4. The cited uncertainties in estimated values for different slag systems are also given.

*Table 4: Details of published models for the estimation of slag viscosities; Arr= Arrhenius relation; Wey= Weymann relation; Emp= Empirical relation; Syn= Synthetic slag: BF= Blast furnace slags: $\Delta\%=(\Sigma\ \delta_n\ \%)\ /\ N$ where $\delta\ \% =100\{(\eta_{meas}-\eta_{calc})/\eta_{meas}\}$ and N= number of measurements.*

| Reference | Slag Type | T-Dependence | Details of model and comments | Slag | Δ% |
|---|---|---|---|---|---|
| Riboud et al [ 24 ] | Various | Wey | $A_W$; $B_W$ functions of 5 groups "CaO"+"SiO$_2$"+"Al$_2$O$_3$"+"CaF$_2$"+"Na$_2$O" Where $X_{"CaO"}$ contains $X_{CaO}$ +$X_{MgO}$+$X_{FeO}$+$X_{MnO}$ etc. ln A= -19.81 +1.73 $X_{CaO}$ +3.58 $X_{CaF2}$+7.02 $X_{Na2O}$ - 35.76 $X_{Al2O3}$ B= 31140- 23896 $X_{CaO}$ ""- 46356 $X_{CaF2}$ - 39159 $X_{Na2O}$ -68833$X_{Al2O3}$ Works well (30%) for variety of slags | Slag Mould flux | 30 |
| Urbain [47] | Various | Wey | $A_W$; $B_W$ functions of 3 groups " Glass formers: $X_G = X_{SiO2} + X_{P2O5}$ Amphoterics $X_{Al} = X_{Al2O3} + X_{B2O3} + X_{Fe2O3}$ Modifiers: $X_M = X_{CaO} + X_{MgO} + X_{Na2O} +3 X_{CaF2} + X_{FeO} + X_{MnO} + 2X_{TiO2} +$ $B_W= B_0 + B_1 X_G +B_2 X_G^2 + B_3 X_G^3$ and $Bi= \alpha I +bi\alpha + ci\alpha i^2$ ln $A_W$= 0.2693$B_W$ + 11.6725 Special $B_W$ values for MnO, MgO | Various | 25 |
| Iida et al [48] | Many | Arr | $\eta(Pas)= A\eta_0\ exp\ (E/Bi)$ where $\eta_0$ is viscosity of hypothetical network-forming melt and Bi= basicity index E=11.11- 3.65 x10$^{-3}$ T and a= 1.745 -1.962 x 10$^{-3}$T + 7 x10$^{-7}$ T$^2$ and Bi= $\Sigma(\alpha i\ \%i)_B/ \Sigma(\alpha_i\ \%_I)_A$ where A=acid oxides and B= basic oxides or fluorides : $\eta$=1.8 x 10$^{-7}$ (M=i T$^m$)$^{0.5}$ exp (H$_i$/ RT$^m$) /V$_{)m}^{0.667}$ exp (H$_i$/ RT$^m$) where H$_i$= 5.1 T$^m$ and values of $\alpha$ given | Mould flux  BF | 25  19 |
| Senior [49] | Coal | Wey | A= $a_0 + a_1 B + a_2$ (NBO/ T) where $a_0$= 2.816 $a_1$= 0.4634 : $a_2$= 0.3534 (NBO/T)= $X_{CaO} + X_{MgO} + X_{Na2O} + X_{FeO} + X_{MnO} - X_{Al2O3} + + X_{Fe2O3}$ / { 0.5($X_{SiO2} + X_{TiO2}$) +$X_{Al2O3} + + X_{Fe2O3}$ } Equations also given for low temperatures | | |
| Mills et al [50] | Various | Arr | Optical basicity ($\Lambda$)- measure of depolymerisation Composition adjusted for Al$_2$O$_3$ needed for charge balancing→$\Lambda_{corr}$ ln A= -232.7 ($\Lambda_{corr}$)$^2$ + 357..3 ($\Lambda_{corr}$)- 144.2 ln (B/100= -1.77 + (2.88/$\Lambda_{corr}$)      ln $\eta$(Pas)= ln A +exp(B/T) | Mould flux | 34 |
| Gupta et al [51] | Mould fluxes | Arr | 3 groups "Acidic": $Y_X$= (%SiO$_2$/ 60) + $\alpha$( %Al$_2$O$_3$/102) "Basic" $Y_O$ =(%CaO/56) + (%MgO/40) + (% Na$_2$O/ 63)+.(%FeO/72. " Fluorides" $Y_F$=(%F/19) : $N_F$= $Y_F$/ ($Y_X$+ $Y_O$+ $Y_F$) : $N_X$= $Y_X$/ ($Y_X$+ $Y_O$+ $Y_F$) : $N_O$= $Y_O$/ ($Y_X$+ $Y_O$+ $Y_F$) Na$^+$/ Ca$^{2+}$affected $\eta$ :Values of $a_0$ to $a_5$ given for 1573 and 1673 K $\eta$=$a_0$+ $a_1$(M$^+$/M$^{2+}$)+ $a_2 N_X$+$a_3 Nx$(M$^+$/M$^2$) +$a_4$(M$^+$/M$^2$)$^2$ + $a_5 N_X^2$ | Mould flux | 35 |
| Koyama et al [52] | Mould fluxes | Arr | ln A () -24.2$X_{Al2O3}$ -6.1 $X_{CaO}$ -12.1 $X_{MgO}$ -19 $X_{Na2O}$ +6.3 $X_{CaF2}$ -4.816 B= -9259$X_{SiO2}$ +28319 $X_{Al2O3}$ -16564 $X_{CaO}$ - 41365 $X_{CaF2}$ -45510 $X_{Li2O}$ +29012 | Mould flux | 76 |
| Kim et al [53] | Mould fluxes | Arr | ln A= -2.307 -0.046 $X_{SiO2}$ -0.07 $X_{CaO}$ - 0.041 $X_{MgO}$ - 0.185 $X_{Al2O3}$ +0.035 $X_{CaF2}$ - 0.095 $X_{B2O3}$ B= 6807 + 70.7 $X_{SiO2}$ +32.58 $X_{CaO}$+312.7 $X_{Al2O3}$ - 34.8 $X_{Na2O}$ -176.1 $X_{CaF2}$ - 167.4 $X_{Li2O}$ + 59.7 $X_{B2O3}$  where X in mole % | Mould flux | 45 |
| Utigard et al. | Non- | Emp | log $\eta$(Pas)= -0.49-5.1 (VR)$^{0.5}$ + (-3660+ 12080 (VR)$^{0.5}$/ T | | |

| | | | | | |
|---|---|---|---|---|---|
| [54] | Ferrous | | VR= A/B where A =$SiO_2$ + 1.5 $Cr_2O_3$ +1.2 $ZrO_2$ +1..8 $Al_2O_3$<br>B= 1.2 FeO +0.5($Fe_2O_3$ + PbO) + 0.7 (CaO +$Cu_2O$) +0.8 MgO + 2.3 ($Na_2O$ +$K_2O$) + 1.6 $CaF_2$ where in wt % | | |
| Reddy [55] | Binary Boro-silicate | Emp | $\eta$ (dPas) = 4.9 x$10^{-9}$ $N_{Oo}$ $T^{0.5}$ exp (E/RT )<br>$N_{Oo}$ calculated from atomic pair (thermodynamic )model<br>E related to $N_{Oo}$ | | |
| Du and Seetharaman [32, 33] | Syn | Arr | $\eta$= h$N_A$ $\rho$/ M exp ($\Delta G_\eta$ / RT) where  h= Planck constant, $N_A$= Avogadro No<br>Structure accounted for - thermodynamics:<br>$\Delta G^*_\eta$ = $\Sigma \Delta G^*_\eta$ (oxides) + $\Delta G_\eta^{mix}$+ 3R*T $X_1 X_2$<br>$\Delta G_\eta^{mix}$ for interactions of cations only<br>Works well for synthetic slags ($\pm$ 15%) | Syn | <20 |
| Ling Zhang et al[30,31] | Various | Wey | Structure as $N_O$ .; $N_O$ .; $N_{O2-}$ calculated from cell model (thermodynamic)<br>$A_W$ and Bw as functions of - $N_O$; $N_{O\ 2-}$.<br>Molecular  Dynamics calculations<br>Works well (20%) several slags | Coal | 22 |
| Tanaka [56] | Syn | Arr | $X_O$; $X_O$ .; $X_{O2-}$ calculated from  thermodynamic cell model<br>$N_{MO}$= a * ($X_O$ .+ $X_{O2}$) where a* is a measure of free space available and n is the frequency of the step in MO-$SiO_2$ system: a* values :$Al_2O_3$ = 0.95; MgO =1.8: CaO=2.0 and FeO= 3.8<br> Multicomponent slags: $E_\eta$ =Eo / (1+$\Sigma$ a* $X_O$ .) $^{0.5}$  where Eo = $E_\eta$=for  $SiO_2$ | | |
| Kondratiev, Jak l[57] | Coal; Syn | Wey | Modified Urbain method for CaO +FeO+$Al_2O_3$ + $SiO_2$ system<br>Modification 1: -ln A= mB+N; n=9.322  but m is composition dependent<br>m= $m_1 X_1$+ $m_2 X_2$+ $m_3 X_3$+ $m_4 X_4$+ and values given for various m values<br>Modification 2: Different B values given for FeO and CaO; constants given to calculate B values | Syn | 25 |
| Robinson [40] | Syn | Arr | Uses Thermodynamic software: data for binaries.<br>Based on Du and Seetharaman model | | |
| Nakamoto [22,23] | Syn | | Neural network model based on experimental data | Syn | <22 |

## 4.6 - Electrical conductivity (κ) – Electrical resistivity(R)

Electrical conduction in molten slags occurs through the movement of ions when an electrical field is applied. Since anions are polymeric they tend to be large and do not move readily, so the electrical conductivity is usually associated with the movement of cations eg. $Na^+$, $Ca^{2+}$ etc. Electrical resistivity (R=1/κ) is the measure of the resistance to ionic transport provided by the molten slag.
The specific electrical conductivity (κ) is the conductivity of a 1 metre cube of the sample and is given by the relation:

$$\kappa=F \Sigma cz u \tag{38}$$

where F= Faraday constant, c , z and u are the concentration, charge and mobility of the ionic species. The temperature dependence is usually represented by the Arrhenius equation:

$$\kappa=   A_\kappa exp (-B_\kappa / T) \tag{39}$$

where $A_\kappa$=constant ; $B_\kappa$ =  ($E_\kappa$/ R*), $E_\kappa$ = Activation energy and R* =Gas constant =8.314 $JK^{-1}mol^{-1}$ and T in K

$$\ln \kappa=   \ln A_\kappa – (B_\kappa / T) \tag{40}$$

similarly for resistance

$$\ln R= \ln A_R +(B_R /R*T ) \tag{41}$$

When a metallic electrode is submerged in a molten electrolyte there is a potential difference across the interface. One phase acquires a positive charge and the other a negative charge. The Helmholtz model assumes a layer of charge at the electrode surface to which ions of the opposite charge in the electrolyte are rigidly held (Figure 19 a) and is equivalent to a simple parallel plate capacitor. In the Stern model the charges are adsorbed on the electrode surface and are rigidly fixed there by the presence of an immobile

layer of oppositely charged ions in the melt (Figure 19b). The Stern model allows for the thermal motion of ions.
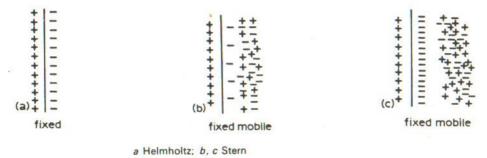


a Helmholtz; b, c Stern

*Figure 19: Schematic drawing of models of double layer (a) Helmholtz (b,c) Stern models*

### 4.6.1 Factors affecting property-

Electrical resistivity (R) will increase as the size of the polymeric units increase. Thus R would be expected to increase as Q increases and (NBO/T) and optical basicity decrease. Since the addition of $Al_2O_3$ effectively increases polymerisation, R will be a function of $Q^{; corr}$;$(NBO/T)^{corr}$ and $\Lambda^{corr}$. The nature of the cations also affects the effects the electrical conductivity. The charge (z) on ions eg 2 for $Ca^{2+}$.affects the resistance since a $Ca^{2+}$ ion will bridge 2 chains whereas a $Na^+$ will not (Figure 20), hence the resistance to the movement of ions will be greater in CaO-slags than in $Na_2O$-slags. However, there are other factors (i) there are twice as many $Na^+$ cations to $Ca^{2+}$ (for any given Q ) -ie. twice the number of potential cations available for transport (ii) smaller cations will slip through the holes in the network more easily than bigger cations but this is offset by the fact that a smaller cation has higher polarisability. Zhang et al. reported that for $M_2O - SiO_2$ slags $\kappa$ decreases as the cation radius (r) increases ($\kappa \downarrow$ as $r\uparrow$) whereas the situation is reversed for Mg, Ca, Sr, and Ba oxide- slags ($\kappa \uparrow$ as $r\uparrow$). It is considered that any cations engaged in charge-balancing duties are not available for movement (ie electrical conduction)

Zhang, Chou et al [58,59] plotted ln $\kappa$ vs ln $\eta$ (Fig 21) and found that for a given viscosity $\kappa(M^+) > \kappa(M^{2+})$. This was attributed to (i) the concentration of $M^+$ ions is twice that of $M^{2+}$ ions and (ii ) increases in the resistance due to the *bridging* of two chains by one $Ca^{2+}$ *cf* no bridging of networks by $Na^+$ (see below)

$$O^- - Ca^{2+} - O^- \qquad O^- - Na^+ \qquad Na^+ - O^-$$

*Figure 20: Schematic diagram showing (a) "bridging " of two O⁻ in chains by $Ca^{2+}$ and (b) absence of "bridging" with $Na^+$ ions.*

Transition metal oxides have more than one valence eg. $Fe^{2+}$ and $Fe^{3+}$. Consequently, there is the possibility that ionic conduction could occur by charge transfer between $Fe^{2+}$ and $Fe^{3+}$.

$$Fe^{3+} \rightarrow Fe^{2+} + e$$

Similar reactions can occur with other transition metal oxides eg $Cr^{3+}$ and $Cr^{2+}$. At high concentrations of $FeO_x$ etc there is the possibility of electronic transport which causes a significant increase in the total conductivity [98]. The electrical conductivity of slags containing $FeO_x$ were determined as a function of $p_{O2}$ and $\kappa$ was found to go through a maximum at ca. $p_{O2}= 10^{-6}$atm [97]. An attempt was made to model the effect of oxidation state into a model of the electrical conductivity [97] according to Jahanshahi et al. [99]; this information was not available to me.

### 4.6.2 Size of cations

The size (r) of the cations affects the conductivity because small cations are more mobile than larger cations and can slip through the "holes" in the network. Zhang, Chou et al. [58,59] plotted data in Figure 21 for $Ba^{2+}$, $Sr^{2+}$, $Ca^{2+}$, $Mg^{2+}$, it can be seen that for a given viscosity the conductivity of $Ca^{2+}$and $Mg^{2+}$ is

slightly greater than $Ba^{2+}$; this may be due to the greater mobility of the smaller cation or may be due to greater resistance to "bridging of chains" with bigger cations.
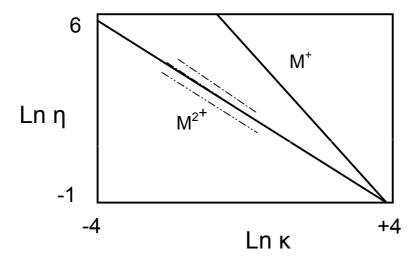


*Figure 21: Schematic diagram representing plot of ln viscosity (Pas) vs ln conductivity ($\Omega^{-1}m^{-1}$) for divalent and monovalent ions.(after Chou) ; dash –dot line= $Ca^{2+}$ dash-double dot line= $Ba^{2+}$[59]*

### 4.6.3 Factors affecting measurements

*Polarisation* is the principal problem and arises from concentration gradients arising in the electrolyte and manifests as a back EMF opposing the normal ionic flow. The 4-wire method is used to minimise polarisation where 2 electrodes carry the current and the other 2 monitor the potential.
Frequency (f) has been reported to affect $\kappa$ [43] ; some workers assume that the impedance of electrolyte region is a function of $f^{-1}$.

### 4.6.4 Measurement methods

The various methods are described in the Slag Atlas [43] and ,in general, it is preferable to have the two electrodes with similar areas (Figures 22 c and d). Methods can be divided into the various 2-electrode (Figure **22**a,b, c) and 4-electrode methods (Figure 22d) with preference being given to the latter since it minimises problems associated with polarisation.
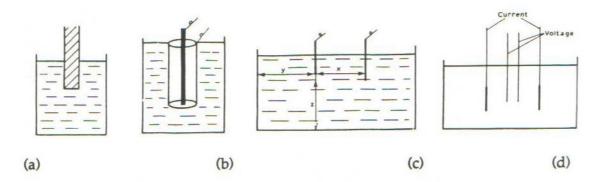


*Figure 22: Cell arrangements for measuring electrical conductivities of molten slags (a) central electrode (b) ring-cell (c) 2-electrode cell (d) 4- electrode cell*

### 4.6.5 Methods of estimating electrical conductivity

Until recently there were no models available to calculate the electrical conductivity ($\kappa$). Jiao and Themelis [96] obtained an empirical relation for CaO+MgO+ MnO+SiO$_2$ slags at 1773K: however, this equation is of limited use for the estimation of the electrical conductivity of industrial slags:

$$\kappa_{1773} = -3.34 + 6.41\ X_{CaO} + 6.45 X_{MgO} + 8.06 X_{MnO} \qquad (42)$$

However, Zhang and Chou [58,59] have recently reported two models to calculate the thermal conductivity of some silicate melts.

## Method 1 Estimation of electrical conductivity using optical basicity
There are two factors affecting the electrical conductivity:
  (i)    The structure of the network which restricts the movement of cations ($\kappa\downarrow$ as polymerisation$\uparrow$)
  (ii)   The nature of the cations which affect (a) the viscosity *ie* structure  (b) the size of the cations (since small cations can move easier through he network) (c) the charge on the cations since there are twice the number of $Na^+$ ions to $Ca^{2+}$ ions available for conduction and (d) the polarisability of the cation which increases as the cation radius decreases.

Zhang and Chou [58] used the corrected optical basicity ($\Lambda^{corr}$)to cover these effects of structure and cation size. The model is described below.

$$\ln \ \kappa = \ln A_\kappa - (B_\kappa/R* T) \tag{43}$$

$$B_\kappa = m(\Lambda^{corr}) + n \tag{44}$$

Experimental data were regressed to obtain best fit values for $A_\kappa$, m and n (*eg* respectively, 5054, 3.24x $10^5$ and -2.768.$10^5$ for the $CaO-MgO-Al_2O_3-SiO_2$ system and 9462, 3.197x$10^5$ and -2.49x$10^5$  for the $CaO-Al_2O_3-SiO_2$ system) .The results are shown in Figure 21  and it is possible to distinguish small deviations for individual cations (Ba to the left and Ca and Mg to the right of the curve). The mean uncertainty in the calculated values was <15%. The model could be applied to slags whose composition lay within the range $\Lambda^{corr}$=0.58-0.67.

## Method 2 Relation between electrical resistivity and viscosity
Zhang and Chou [59] reported that the electrical conductivity could be expressed as a function of the viscosity. They found that for the MO-systems $\ln \eta = 0.15-1.1 \ln \kappa$   and for $M_2O-SiO_2$ systems, $\ln \eta = 4.02-2.87 \ln \kappa$  . These workers also plotted $\ln \kappa$ as a function of ln viscosity (Figure 23) and found a reasonably linear relation with some scatter.
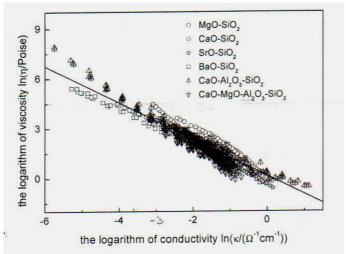


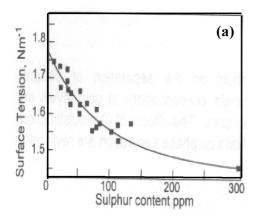Figure 23: ln electrical conductivity as a function of ln viscosity [59].

Thus models for the estimation of electrical conductivities are in their infancy

## 4.7 Surface tension (γ)

*4.7.1 Factors affecting property:* Surface tension is not a bulk property. *Surface-active components* such as S or O in molten metals have a low surface tension compared with the metal and consequently, tend to occupy the surface layer in much higher concentrations (ca 100x) than the exist in the bulk.

Consequently, surface tension and its temperature dependence (dγ/dT) are extremely sensitive to S or O concentrations (Figure  23a); 50ppm S causes a decrease of 25% in surface tension and a negative (dγ/dT)

S – 26

to go to a positive value. In slags there is not such a wide difference between the surface tensions of the surface-active components (eg. $B_2O_3$ and $CaF_2$ and $SiO_2$) and those of the other components (eg. CaO see Table 2 ) in the slag as there is with O or S in metals. Surface tensions of slags tend not to be very structure- dependent but since $\gamma_{SiO2} < \gamma_{CaO}$ the surface tension tends to (i) decrease with increasing Q value and (ii) give positive $(d\gamma/dT)$ values at higher $SiO_2$ (or Q) values (ie similar to High S (>50ppm)steels Fig 23 b). The surface tension of the slag is dependent upon (i) the concentration of the surface active components and (ii) the chemical activity of the surface active component which determines the surface active concentration in the surface layer. Consequently, models of surface tension tend to be based on the thermodynamics of the slag system.
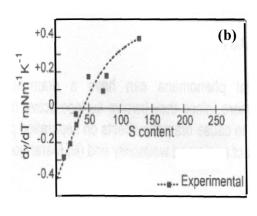


*Figure 24: The effect of S concentrations on the (a) surface tension and (b) temperature coefficient (dγ/dT) of steels containing S*

.

*Table 2: Surface tensions (mNm$^{-1}$) of pure slag components at 1773K*

|  | SiO₂ | CaO | BaO | SrO | MgO | Al₂O₃ | MgO | FeO | NiO | MnO | CrO | Na₂O | K₂O | TiO₂ | ZrO₂ | Cr₂O₃ | Fe₂O₃ | CaF₂ | B₂O₃ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| γ | 260 | 625 | 560 | 600 | 635 | 655 | 635 | 645 | 645 | 645 | 360 | 295 | 160 | 360 | 400 | 800 | 300 | 290 | 110 |

### 4.7.2 Measurement measurements

The principal methods used to measure surface tensions of slags [43,37] are (i) the sessile drop (SD) and pendent drop (PD) methods (ii) the maximum bubble pressure (MBP) method (iii) cylinder detachment method but newer methods like draining crucible and SLLS method may prove useful in the future. The accuracy of the SD and PD values have improved with the introduction of software to derive the parameters giving the "best fit" with the image of the experimental sessile or pendent drop. Surface tensions of many slags fall in the range 400- 500 mNm$^{-1}$. Typical experimental uncertainties are *ca.* ± 5%.

### 4.7.3 Methods of estimating surface tension

Tanaka et al [60,61] have applied their model for alloys to the calculation of the surface tension of slags and molten salts using commercial thermodynamic software to calculate $G^{XS,B}$ where the subscriptsB and S refer to the bulk and surface, respectively. It was found that it was necessary to allow for the fact that the ionic distances in the surface differ from those in the bulk in order to maintain electrical neutrality. This was taken into account using the parameter,$\xi$, which was been applied to ternary systems but would be difficult to apply to multi-component systems.

$$(G^{xs}_{S}/ G^{xs}_{B}) = (Z^{S}/ Z^{B} )/ \xi^{4} = 0.94 / \xi^{4} \tag{45}$$

with $\xi$ having a value of 0.97.

Nakamoto,Tanaka et al [84,85] also reported a model based on the anionic and cationic radii and Butler equation which makes use of the molar volume of the slag components. The system was found to work successfully for a large number of ternary systems (including surfactants like $CaF_2$ and $B_2O_3$) but would be cumbersome when applied to quaternary and higher systems.

Other models have been reported for the calculation of the surface tension of slags [62-65].The model due to Zhang et al. [65] makes use of the excess surface tension ($\gamma^{xs} = \gamma_{meas} - \Sigma X_1 \gamma_1$) and derives constants to express ($\gamma^{xs}$)as a function of composition; good agreement was found for the calculated results with measured values.

Nakamoto et al [78] have developed a model based on the neural network approach. This approach is best applied to certain slag families or slag systems but would be less useful when applied to all slags. Estimated values were found to be within ±4% of the measured values.

Surface tensions and the trends in surface tension can be calculated using a partial molar approach. (Equn 45) and shown in Figure 25 [86]. The model divides slag components into two classes (i) oxides with higher surface tension values where $X_2 \gamma_2$ tends to be similar to that shown in Figure 25a and (ii)components with lower $\gamma$ values (surfactants $B_2O_3$, $CaF_2$, $Na_2O$, $K_2O$, $Fe_2O_3$ and $Cr_2O_3$)where $X_2 \gamma_2$ is similar to that shown in Figures 25b and c.

$$\gamma = \Sigma X_1 \gamma_1 + X_2 \gamma_2 + X_3 \gamma_3 + \quad . \; . \tag{46}$$

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 (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 25b).The biggest problem is the inability of the model to deal with two surface-active components simultaneously.(eg. $CaF_2$ and $B_2O_3$) and the model tends to exaggerate the decrease in $\gamma$ in these cases. The method has the advantage that it can easily be applied to multi-component industrial slags but uncertainties in the estimated values are ca. ± 10%.
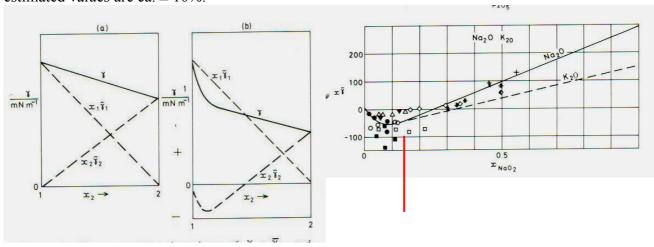


*Figure 25: Composition dependence of γ and $x_i$ $γ_i$ for binary slags with (a) non-surface-active constituents and (b) one surface active constituent (2) and (c) $X_2$ $γ_2$ as function of $X_2$ for Na$_2$O- and K$_2$O- SiO$_2$ slags with N value shown as vertical line.*

**Interfacial tension ($\gamma_{MS}$)**
Interfacial tensions can be calculated using the following relation

$$\gamma_{ms} = \gamma_m + \gamma_s + 2 \phi (\gamma_M . \gamma_S)^{0.5} \tag{47}$$

where $\phi$ is an interaction coefficient. The parameter $\phi$ was found to have a value of 0.5 for slags free of FeO but increased with FeO additions [65]. Tanaka [15] proposed the following equation

S – 28

$$\phi = 0.5 + 0.3X_{FeO} \qquad (48)$$

Qiao et al. [66] have outlined a model for estimating the interfacial tension using the excess interfacial tension ($\gamma^{xs}_{MS}$) and considering the components of a binary alloy separately with regard to the slag. Values were derived for coefficients by fitting experimental data.
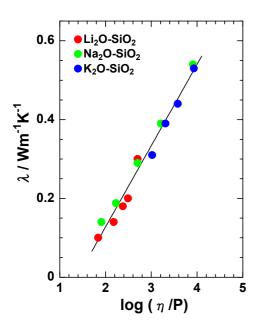
It should be noted that the surface tensions of metals tend to have surface tensions which are 3 to 4 x that for the slag (typically *ca.* 450mNm$^{-1}$) so the largest factor in Equn 47 is $\gamma_m$; it follows that $\gamma_{ms}$ is very dependent upon the soluble O and S contents of the metal (Figure 24).

### 4.8- *Thermal conductivity* –

*4.8.1 Factors affecting thermal conductivity:* The thermal conductivity of slags [68-76] involves the movement of phonons and this is usually referred to as *phonon conduction.* Consequently, the thermal conductivity (k) is very dependent on structure. The thermal conductivity of molten slags *increases* with *increasing* SiO$_2$ content in the slag (*ie.* the direct opposite of electrical conductivity). This is best viewed through the thermal resistance (1/k); the resistance to phonon transport is much smaller when passing along the chain than the resistance of moving phonons from chain to chain. Thus the more the slag is polymerised (ie as Q increases or NBO/T decreases) the higher the thermal conductivity (Figure 26). It follows that because of this dependence on structure:

    a.  the thermal conductivity is a function of the viscosity (see Figure 26a due to Hayashi et al.[68])
    b.  the temperature dependence of k is best represented by similar functions to those for viscosity *ie*. Vogel-Fulcher relation for ($T_g$ to $T_{liq}$ ) and the Arrhenius equation for $T > T_{liq}$)

The thermal conductivity data also show that the cations affect the thermal conductivity values for alkali slags M$_2$O- SiO$_2$ the following hierarchy were observed $k_{Li} > k_{Na} > k_K$ (Hayashi et al.[68]) similar deviations were seen with the viscosity ($B_A$ and ln $A_A$ in hierarchy K>Na>Li). It is difficult to attribute the effect of these cations on (i) their effect on viscosity or (ii) mobility effects on heat transfer for individual cations.



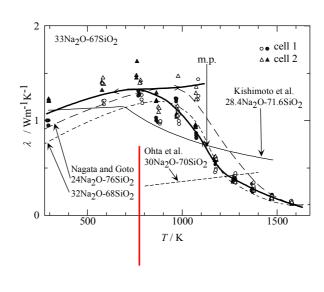*Figure 26: Diagrams showing (a) thermal conductivities of alkali silicates as a function of log viscosity and (b) Thermal conductivity of 0.33 Na$_2$O- 0.67SiO$_2$ as a function of temperature ( after Hayashi [68])(Note $T_g$ coincides with maximum conductivity and $T_{liq}$=mp)*

There are two problems with measuring thermal conductivities of slags and glasses (i) eradicating convection for measurements on liquids and (ii) determining the amount of radiation conductivity; these are described in more detail below.

### 4.8.2 Convection contributions
The measured thermal conductivity for a liquid slag ($k_{meas}$) contains contributions from phonon conductivity ($k_{meas}$) and from convection ($k_{conv}$)

$$k_{meas} = k_{cond} + k_{conv} \qquad (49)$$

These contributions from convection can be large and so it is difficult to determine the true thermal conductivity of the molten slag but $k_{conv}$ decreases as the viscosity of the slag increases. The following methods have been used to minimize $k_{conv}$:
- Using transient techniques (as opposed to steady state methods) where the duration of the experiment is too short (ca 1s) for convection to be initiated.
- Keeping the top of the sample hotter than the bottom
- Carrying out measurements in micro-gravity (space)
- Using magnetic fields to suppress the movement (mostly used on metals).
- It is claimed that measurements of thermal effusivity ($e=(kC_p.\rho)^{0.5}$= the ability to exchange thermal energy with its surroundings) are free of convective contributions.

### 4.8.3 Radiation conductivity ($k_R$)
In the 1960's it was noted that the apparent thermal conductivity ($k_{app}$) of solid glasses increased with increasing sample depth (Figure 27 )until a constant value was attained when the depth exceeded a critical value (denoted as *"optically thick"*)[77]. If a pulse of energy falls on the surface, the temperature of the surface layer increases and this layer is at a higher temperature than the layer 2 below it and so it radiates to layer 2. Now $T_{layer\ 2} > T_{layer\ 3}$ and emits to layer 3 and the process is repeated through the entire sample. Thus radiation conductivity consists of absorption of energy and re-emission of each layer through the sample (Figure 28). The sample becomes *optically thick* when $\alpha^*$ d>3 where $\alpha^*$ = absorption coefficient of the glass and d= thickness or depth of the sample. For optically thick samples $k_R$ can be calculated from following equation where n= refractive index and $\sigma$= Stefan- Boltzmann constant and T is in K.

$$k_R = 16\ \sigma\ n^2\ T^3/3\ \alpha^* \qquad (50)$$

It can be seen that $k_R$ is proportional to $T^3$ and hence increases dramatically at high temperatures. For molten glass 90% of the apparent thermal conductivity comes from $k_R$. In practice, the magnitude of $k_R$ is reduced by:
(i)     transitional metal oxides (eg. FeO, NiO and $Cr_2O_3$) which cause a dramatic increase in $\alpha^*$ ( eg. for FeO, $\alpha^*(m^{-1})$= 1100%FeO ) and thereby reduce $k_R$.
(ii)     scattering of radiation (ie.$k_R$ )by crystallites, grain boundaries etc in solid slag samples; in crystalline solids most of the radiated energy is scattered back to the source.
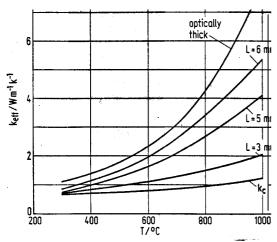
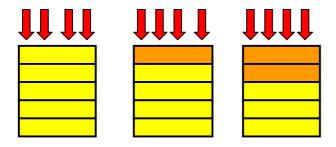*Figure 27: Apparent thermal conductivity as a function of sample thickness*



*Figure 28: Schematic diagram showing the mechanism responsible for radiation conductivity*

### 4.8.4 Measurement methods

There are two *transient* methods available for measuring the thermal conductivity of semi-transparent materials like slags and glasses viz. the laser pulse (LP) and the transient hot wire method (THW). The ***transient hot wire*** (THW) method (Figure 29a ) consists of a thin Pt wire which acts as both a heating element and a temperature sensor (through a known Resistance-T relation).A current is passed through the wire for a short period of time (ca 1s) and the resistance (R) of the wire (which is a measure of the temperature)is monitored continuously and R is plotted as a function of ln time (t). The plot shows 3 regions (i) an initial unstable region (ii) a stable region where the slope of the plot =1/k and (iii) a region where convection kicks in and causes a drop in resistivity due to the cooling of the wire (ie. enhanced conductivity due to convection. Thus it is possible to detect the onset of convection (curvature at left hand side of T-t curve) with this method.
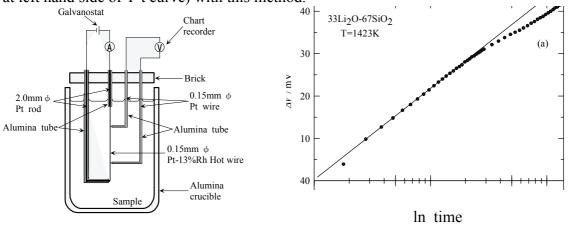


*Figure 29: Schematic drawings showing (a) the transient hot wire method and (b) a typical output for slags.*

In the Laser Pulse (LP) method (when applied to slags and glasses) a short pulse of energy is focused uniformly over a platinum disc located on the upper surface of the sample (ca 10mm diam x 3mm)

(Figure 30b) and the temperature of this disc is monitored continuously; the thermal diffusivity (a) can be calculated from the $T_{disc}$- time relation. Then the thermal conductivity is calculated via k =a $C_p \cdot \rho$
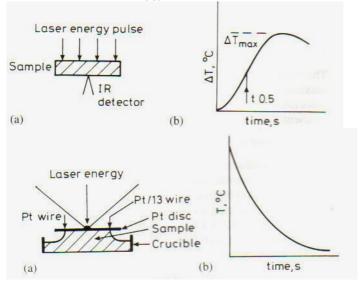


*Figure 30: Schematic drawing of laser pulse method in (a) conventional manner (b) used following the attenuation of a Pt disc on the slag surface on left-hand side and T-t responses on right hand side.*

### 4.8.5 Problems with measurements on slags and glasses

1. Measurements carried out with the THW and LP methods for the same slag composition indicate that $k_{THW} < k_{LP}$ This is thought to be due to a larger $k_R$ contribution for the LP measurements due to the (surface area of disc ) >> (surface area of wire) .Thus values measured contain an unknown contribution from $k_R$ for both solid and liquid samples. However, this should not be the case for crystalline slag samples since most of $k_R$ is reflected back to the source.
2. The measured values may not represent the samples in the industrial process eg. the liquid layer in the CC process is ca. 0.1mm thick and will be *optically thin* but the measurements in the laboratory are for *optically thick* conditions
3. It is very difficult to determine $k_R$ for *optically thin* conditions.
4. Values are needed for optical properties (absorption coefficient and refractive index) are needed to calculate the magnitude of $k_R$ for optically thick conditions

### 4.8.6 Thermal conductivity of crystalline slags

Nishioka et al [76] measured the thermal conductivity of $CaO+Al_2O_3+ SiO_2$ slags in both the glassy and glassy state. As mentioned above it was found that $k_{cryst} = (1.5$ to $2.5) k_{glass}$ due to the increased packing densities. As can be seen from Figure 31 the temperature coefficient (dk/dT) was virtually independent of temperature.over the range covered.
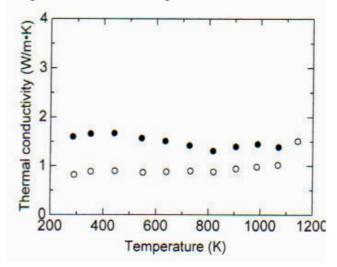


*Figure 31: Thermal conductivity of glassy (O) and crystalline (●) slags as a function of temperature.*

### 4.8.7 Modelling thermal conductivities of slags

The main problem with modelling thermal conductivities of slags is the accuracy of the measured data because of the problems (described above) associated with determining the magnitude of contributions from radiation conductivity and convection.

It has been reported that the thermal conductivity (k) increases as the $SiO_2$ content or the polymerisation (Q) in the slag increases or (NBO/T) decreases. This behaviour is consistent with good conduction along the covalently- bonded $Si^{4+}$ chain and poor conductivity between chains.

For the solid phase the lattice (phonon) thermal conductivity for the crystalline phase is ca 2x larger than that for the glassy or amorphous phase (due to increased packing density).However, this enhanced heat transfer in crystalline slags is more than offset by the decrease in radiation conductivity ($k_R$) due to the scattering of the radiation by the crystallites. Thus $k_{app}$ for glassy material is greater $k_{app}$ of crystalline material ie. $q_{cryst} < q_{glass}$ where q=heat flux density.

Thus for glassy and liquid slags the heat transfer process is complex depends upon the sample thickness and it is important that experiments should provide a reasonable reproduction of the industrial situation Estimation in the case of glassy slags needs data for the various optical properties such as the absorption coefficient, refractive index etc.

***It was decided to only use THW[68-75] data*** because of the difficulties of eradicating $k_R$ effects from LP data when analysing thermal conductivity data. Thermal conductivity data show a reasonable amount of scatter and because of the relation between k and η it was decided to draw the ln $k^m$-Q in a similar way to that of ln $η^m$-Q curve (Figures 32 a and b); unfortunately, there are no data for Q<2 which would have helped in the extrapolation of the curve.

The plots of ln $k_{Tg}$-Q and ln $k_{298}$-Q (Figure 33) show more scatter than the ln $k^m$-Q plot (Figure 32) but curves have been drawn to mirror the ln $k^m$-Q; it was noted that the thermal conductivity of slags containing $Li_2O$ were significantly higher than those for other slags and the curves in Figure 33 were drawn to reflect this. This suggests that the cations do have an effect on the thermal conductivity. The following equations were derived from the plots shown in Figures 32a and 33.
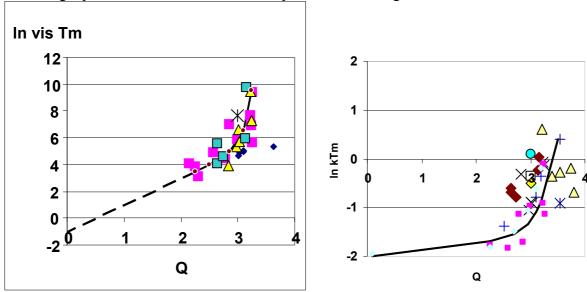


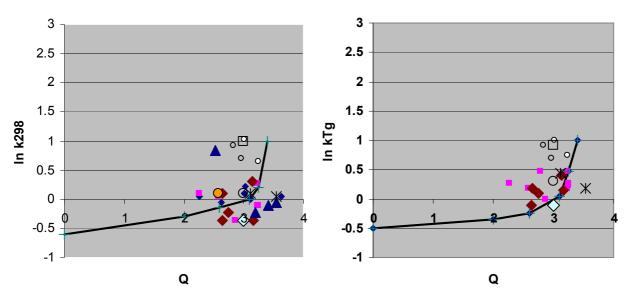*Figure 32: (a) ln $η^m$ and (b) ln $η^m$ as functions of Q: dashed line=extrapolation using data in [12]*

*Figure 33: Values of (a) ln $k_{298}$ and (b) ln $k_{Tg}$ as functions of Q ; o,□ =Li$_2$O-silicate slags.*

Solid, 298K: $\quad\quad\quad\quad\quad$ ln $k_{298}$ = $\;$ -0.424+ 0.00002 exp(Q / 0.299) + 3.2.$X_{Li2O}$ $\quad\quad\quad$ (51)

Solid: $T_g$ $\quad\quad\quad\quad$ ln $k_{Tg}$= $\;$ -0.435+ 0.00005 exp(Q / 0.332) $\;$ + 3.0 $X_{Li2O}$ $\quad\quad\quad$ (52)

Liquid: $T^{liq}$ $\quad$ : $\quad\quad\quad\quad$ ln $k^m$ = -1.914 +0.00037 exp (Q/0.402) $\quad\quad\quad\quad$ (53)

The thermal conductivity data were then used to explore the relation between viscosity and thermal conductivity for liquid slags (shown in Figure 34).The plot due to Hayashi et al [68] is for k vs ln η at various temperatures (Figure 34 a) whereas the other plot is for ln $k^m$ vs ln $η^m$ which yielded the following equation where $k^m$ is in (Wm$^{-1}$K$^{-1}$) and $η^m$ in dPas:

$$Ln\ k^m = -3.43 + 0.4\ ln\ η^m \quad\quad\quad (54)$$

The scatter in the data may be due to the uncertainties in $T_{liq}$ which could lead to significant differences in $η^m$ and $k^m$.
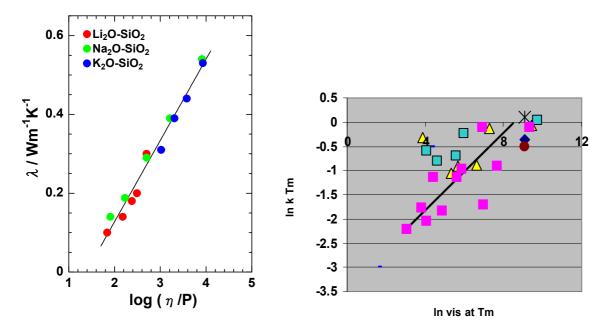


*Figure 34: Thermal conductivity as a function of viscosity (a ) $k^m$ versus ln η [68] and (b) ln $k^m$ vs ln $η^m$*

# 5. The model

**Always work with a copy of the program- the master copy can get corrupted**.
Start on the *Composition worksheet* all input data are fed into this worksheet

## 5.1 Composition worksheet

1. It is is necessary to insert (i) composition of slag in weight % and (ii) the liquidus temperature, $T_{liq}$ or $T^m$ and (iii) the selected temperatures which will be affected by the $T_{liq}$ and $T_g$ values

    (i)     Insert slag composition into column C placing 0% where there is no content for a particular component and

    (ii)     note F is cited as F% and is subsequently converted by the model to $X_{CaF2}$

    (iii)    a blank cell is provided (B 23) for other oxides but you will need to insert Molecular weight of oxides into cell H23 and various other cells in order to calculated the various properties.

    (iv)    Insert $T_{liq}$ into cell B45 on this worksheet – **this must be done. It will appear automatically on other worksheets**

    (v)     If you know the value of the glass transition temperature for glassy slags insert it in cell B –if you choose to let the model to calculate a value for Tg leave 0 in cell B30 and the calculated value ( cell C30) will appear in the temperatures at cell 38.

    **(vi)**   Insert the selected temperatures (a) for glassy slags in cells B32 to B37 and B40 to B44 and for the liquid in cells B48 to B53. **Caution do not insert Tg and Tliq into column B this will be done automatically- if you do mistakenly insert a value it will corrupt this function.**

    (vii)    Insert the temperatures for the crystalline solid phase (no $T_g$ involved) into column E cells 32 to 44-$T_{liq}$ will appear automatically in E45

2. The software

    (i)     sums the slag composition and corrects the input values so that they total 100.0% (column D)

    (ii)     then allows for any pick-up during the process (this is principally aimed at CC fluxes)

    (iii)    the F% is then converted first to %CaF$_2$- this involves deducting (56/38)*F% from the CaO % in cell

    (iv)    the slag composition is then converted to **mole fractions (given in column J)** and note the mean Molecular weight is given in cell H24- also that values of 1000 are used in cells H23 to prevent calculations involving 0/0.

    (v)     Values for (NBO/T) etc are calculated and ire displayed in cell N4 and Q is given in cell O4 and the corrected opt basicity is given in cell S4

## 5.2 Collected Worksheet

All the calculated values are reported on this worksheet. **No input data are needed on this worksheet**. Solid slag properties are reported in cells 5 to 19 with (i) glassy phase values between A and O and crystalline phase results between R and Z.
The calculated ( approximate) value of $T_g$ can be calculated by the following equation: In general, the estimated values will be within 50K of the true value but in some cases differences of 100 K could occur.

$$Tg(K)=1028-26X_{SiO2}+189.5X_{CaO}-95.626X_{Al2O3}-996X_{Na2O}-850X_{Li2O}+-598X_{K2O}-59760X_{MgO}+7034XCaF_2-6366X_{MnO}+3608X_{FeO} \tag{55}$$

Note the values of the constants for MgO, MnO and FeO were based on low concentrations and are unrealistic and thus should not be used when the mole fractions exceed >0.02

## 5.3 $C_p$ and Enthalpy Worksheet

**No data should be inputted into this worksheet**. The software performs calculations of $C_p$ and enthalpy $(H_T- H_{298})$ for *crystalline* slags, *glassy* (ie. *amorphous* slags)and *liquid* slags. The database is given in cells E27-E49-Q47-Q27. It should be noted that these values are given in cal mol$^{-1}$ and so should the data be modified or added to the inserted data should be converted to cal mol$^{-1}$= 4.184Jmol$^{-1}$.

### 5.3.1 Crystalline slag
The method has been described above in Section 4.2. The $C_p$ are calculated for various temperatures in columns N and O for units JK$^{-1}$kg$^{-1}$ and JK$^{-1}$mol$^{-1}$, respectively, and $(H_T- H_{298})$ values for units of kJkg$^{-1}$ and kJmol$^{-1}$, respectively, in columns Q and R.. The entropy of fusion $(\Delta S^{fus})$ was calculated from the partial molar entropies (Equn 23) and then $\Delta H^{fus}=T_{liq}* (\Delta S^{fus})$ where $T_{liq}$ is the inserted liquidus temperature.

### 5.3.2 Liquid slag
The $C_p$ for the liquid is calculated from the partial molar values of the individual slags $(\Sigma\ X_iC_{pi})$ see Equn 19 and $C_p$ for the liquid is assumed to be independent of temperature. Values of $C_p$ for the liquid are given for units of JK$^{-1}$kg$^{-1}$ and JK$^{-1}$mol$^{-1}$, respectively, in columns N 20-25 and O 20-25. and $(H_T- H_{298})$ values for units of kJkg$^{-1}$ and kJmol$^{-1}$, respectively, in columns Q 20-25 and R 20-25.

### 5.3.2 Glassy, amorphous slags
Glassy slags show a step-wise increase of 0.3 kJ K$^{-1}$kg$^{-1}$ at $T_g$. The basis of the calculation is that $(H_T-H_{298})$ value at $T_{liq}$ ( $=T^m$) for the liquid phase will be identical to that at obtained with the crystalline phase. We assume that for the range $(T^m-T_g)$ that Cp=a'+ b'T and it can be shown that

$$b'=2*\{(\ \Delta/(T_m-T_g)\ )\ -a'\ \}\ /\ (T^m+T_g) \tag{56}$$

where $\Delta=\ (H_{Tm}- H_{298})_{crys} -(H_{Tg}- H_{298})_{glass})$ and a' $=Cp_{scl\ Tg}$.The values of b' were determined (cell B 14) and Cp and $(H_T- H_{Tg})$ calculated for the $T_g-T_{liq}$ range.
- Tg will appear in E15 and E16 and other temperatures will appear between cells E8 and E14 and cells E16 and E19 and for the liquid in cells E22 to E25
- $T_{liq}= T^m$ will appear in E20
- The step-wise increase of 0.3 kJ K$^{-1}$kg$^{-1}$ which occurs at Tg  (when $C_p$= 1.1 kJ K$^{-1}$kg$^{-1}$ ) will be shown in E16
- The model assumes a linear increase in $C_p$ between $T_g$ and $T_{liq}$.
- All of the estimated values should lie within ± 5% of measured data and for many cases will lie within ± 2%.

### 5.3.3 Crystalline slags
Values of Cp and $(H_T-H_{298})$ are calculated using  Equns 19 to 24.

## 5.4 Density Worksheet

**No data should be inputted into this worksheet**

### 5.4.1 Liquid slags
The densities of liquid slags are calculated using the method outlined in Section 4.4 Table 3( –second model [42],which is essentially one of partial molar volumes but with molar volumes of $SiO_2$ and $Al_2O_3$ represented by equations. The densities are calculated for a reference temperature of 1773K and then adjusted for other temperatures by applying a temperature coefficient of  -0.01% K$^{-1}$ .

### 5.4.2 Solid slags
*Crystalline slags:* Slags with crystalline phases have a higher density than glassy, amorphous slags and will show a marked change in density at $T_{liq}$. 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 9x $10^{-6}$ $K^{-1}$. This is crude because α depends on Q.

*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 at $T_{liq}$ ($V^m$) for the liquid is calculated by:

$$V_T = V_{Tg} + (T-T_g)\{(V^m - V_{Tg}) /(T_{liq}-T_g)\} \tag{56}$$

Most estimated liquid densities lie within ± 2% but values obtained for slags containing constituents for which the parameters (used in the calculation) are not been well-defined could be subject to higher uncertainties.

### 5.4 Surface tension worksheet

**No data should be inputted into this worksheet**
Surface tension values are calculated (Method 1)using the partial molar method [86] outlined above in Section 4.7.3 and Equn 45 and Figure 25.

$$\gamma= \Sigma\ X_1\ \gamma_1 + X_2\ \gamma_2 + X_3\ \gamma_3 +\quad . \ . \tag{45}$$

- The calculated surface tensions using an average dγ/dT =-0.15 will appear in cells M4 to M9 and are denoted as "a" *ie*. Method1a or 2a
- Values calculated using a dγ/dT obtained by dγ/dT= $\Sigma$ $X_1$(dγ/dT)$_1$ + $X_2$(dγ/dT)$_2$ + . . . are given in cell O24 and the surface tension values calculated with this γ/dT are given in cells N4 to N9 (note I have been unable to establish dγ/dT for some components) These values are denoted b *ie*.Method1b or 2b.

The uncertainty in the estimated values is ca. ±10% the model tends to underestimate the surface tension when the slag contains more than one surfactant t eg, $B_2O_3$.This is because there will be competition for surface sites between the various surfactants.

Consequently, Method 2 was devised to address this problem. It was assumed that (i) surfactants to occupy the surface would be in the hierarchy of lowest surface tension $B_2O_3$> $K_2O$>$Na_2O$>$CaF_2$> $Fe_2O_3$>$Cr_2O_3$ and (ii) that surface saturation occurred at N=0.12. The contributions were calculated from the various oxides until N=0.12 was attained.Above N=0.12 all contributions were taken as positive contributions ,$X_i$ $\gamma_I$, for the remaining surfactants *ie*. they were not present in the surface layer and thus contributed normally in the bulk.The values from this method are preferred.

### 5.6 Viscosity Worksheet

**No data should be inputted into this worksheet.** The viscosity worksheet contains several models. The chemical composition and $T^{liq}$ are shown on this sheet –**do not insert values here** <span style="color:red">**Always ensure these values are changed on the Composition worksheet or the calculations will get corrupted.**</span>
**The $T^{liq}$ value inserted on the composition worksheet will appear on Viscosity- cell D19 and temperatures of interest will appear automatically in cells D20- D25 and cells D3 to D8; L38 toR38 and T39 to T45.**

### 5.6.1 Procedures
1. 1. Insert (i) slag composition (cells B4 to B23) and (ii) $T_{liq}$ (cell B28) in Composition worksheet
2. $T_{liq}$ will appear in cell D19 and insert other temperatures of interest in cells **D20 to D25**
3. These temperatures will appear automatically in cells (D3 to D8-Riboud) (J19 to J25- Opt. Bas) and (L38- R38 and T39- T45 for Iida model) –do not insert temperatures into any cells but **D20 to D25 as it may corrupt the software.**
4. Calculated viscosity values will appear in the following cells:
-Riboud model G3 to G8 and H3 to H8
-Optical basicity model:K19-K25 and L19 to L25

-MLL model  E19 to E25 and F19 to F25
-Iida model  Y39-Y45 and Z 39-Y45  and (Forsbacka a, b, c values) AB 39-AB 45 and AC 39-AC 45
**Note: the values for units Pas and dPas do not always appear in the same order**

### 5.6.1 Riboud model
This model is simple and is applicable to a wide range of slags. The model divides the slag constituents
into 5 different categories; additional slag constituents are covered here 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%)

$X_{"SiO2"} = X_{SiO2} + X_{P2O5} + X_{TiO2} + X_{ZrO2}$

$X_{"CaO"} = X_{CaO} + X_{MgO} + X_{FeO} + X_{Fe2O3} + \{ X_{MnO} + X_{NiO} + X_{CrO} + X_{ZnO} + X_{Cr2O3} \}$

$X_{"Al2O3"} = X_{"Al2O3"} + \{ X_{"B2O3"} \}$

$X_{CaF2}$

$X_{"Na2O"} = X_{Na2O} + X_{K2O} + \{ X_{Li2O} \}$

The temperature dependence is expressed using the Weymann equation:

$$\eta(dPas) = A \; T \; exp \; (B/T)$$

$$A = exp \; ( \; -19.81 + 1.73 X_{"CaO"} + 5.82 X_{CaF2} + 7.02 \; X_{"Na2O"} - 35.76 X_{Al2O3} \qquad (57)$$

$$B = 31140 - 23896 \; X_{"CaO"} - 46356 \; X_{CaF2} - 39159 \; X_{"Na2O"} + 68833 \; X_{"Al2O3"} \qquad (58)$$

### 5.6.2 Optical basicity (Λ) model
Mills and Sridhar [83] reported a simple model using the optical basicity (Λ) to represent both the
structure and cationic effects, which was applicable to a wide range of slags. The optical basicity was
corrected ($\Lambda_{corr}$) for charge balancing necessary for $Al_2O_3$ going into the silicate network; this was done
by deducting X $_{Al2O3}$ from the mole fraction of the network breaker ($X_{NB}$) with the largest Λ value. Here
the deduction was made from $X_{NB}$ for all cations (*ie* assumes the charge balancing is equally shared by all
cations).Values used for the various constituents are given in Table 5. Note for $CaF_2$ n is taken as 1.

*Table 5: Optical basicity values used in calculation a value of Λ =0.61 was assumed for $ZrO_2$.*

| $K_2O$ | $Na_2O$ | BaO | SrO | $Li_2O$ | CaO | MgO | $Al_2O_3$ | $TiO_2$ | $SiO_2$ | $B_2O_3$ | $Fe_2O_3$ | $Cr_2O_3$ | FeO | NiO | MnO | CrO | $CaF_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.4 | 1.15 | 1.15 | 1.1 | 1.0 | 1.0 | 0.78 | 0.60 | 0.61 | 0.48 | 0.42 | 0.75 | 0.75 | 1.0 | 1.0 | 1.9 | 1.0 | 1.2 |

$$\Lambda = \Sigma \; X_i n_i \Lambda_i \; / \; \Sigma \; X_i n_i \qquad (59)$$

Where i= slag constituent eg. CaO ;n= number of O eg 3 for $Al_2O_3$.
After correction of Λ the viscosity was calculated via Equns 60-62

$$ln \; (B/1000) = -1.77 + 2.88/ \; \Lambda_{corr.} \qquad (60)$$

$$ln \; A = -232.69(\Lambda_{corr})2 + 357.32 \; \Lambda_{corr} - 144.17 \qquad (61)$$

$$\eta(Pas) = A.exp \; (B/T) \qquad (62)$$

This model was found not to perform very well and the calculated values do not appear on the Collected
worksheet

### 5.6.3 Iida model
The model [79,80] is based on  using the basicity index ($B_i$) to represent structure:

$$\eta(Pas) = A \; \eta_0 \; exp \; (E/Bi) \qquad (63)$$

where A =pre-exponential term, E=activation energy; $\eta_0$ =hypothetical viscosity for each slag constituent
(*i*) ; the parameters A, E and $\eta_0$ are all given as  functions of temperature.

$$A= 1.029-2.078 \times 10^{-3}T +1.05 \times 10^{-6}T^2. \tag{64}$$

$$E= 28.46- 2.884 \times 10^{-2}T+ 4.0 \times 10^{-6}T^2. \tag{65}$$

$$\eta_0= \Sigma\ \eta_0\ X_{SiO2} + \eta_0\ X_{CaO} + \eta_0\ X_{Al2O3} + \eta_0\ X_{MgO} + . \tag{66}$$

$$\eta_0= 1.8 \times 10^{-7}\ \{ (M_iT_i^m)^{0.5}\ \exp (H_i /R^*T)\} / \{V_m\}_i^{0.6667} \exp(H_i /RT)\}\ . \tag{67}$$

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 (1) *acidic* ($SiO_2$, $ZrO_2$, $TiO_2$) denoted by A  (2) *basic* (CaO, MgO, $Na_2O$, $K_2O$ $Li_2O$,FeO, MnO, CrO, $CaF_2$ etc  denoted B and (3) amphoteric $Al_2O_3$, $B_2O_3$, $Fe_2O_3$, $Cr_2O_3$.The basicity index  Bi is calculated by

$$B_i= \Sigma\ (\alpha_i.\%i)\ _B/ \Sigma\ (\alpha_i.\%i)_A \tag{68}$$

where $\alpha_i$.=constant for each constituent expressing its relative basicity and %i =mass %.

This was the original Iida model. Subsequently, he modified [79,80] it to account for the amphoterics where their basicity changed according to the temperature. This was done through the modified basiciy index ( $B_i^j$) particularly for $Al_2O_3$ which was done through back-calculation from experimental viscosity data (Equn ). 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 eg $CaO+MgO+Al_2O_3+SiO_2$ and then expressed by:

$$( B_i^j)= \{\Sigma\ (\alpha_i.\%i)_B\ + (\alpha_i.\%i)\ _{Fe2O3}\ + (\alpha_i.\%i)\ _{BCr2O3}\ \} / \{\Sigma\ (\alpha_i.\%i)_A + \Sigma\ (\alpha_i.*\ \%i)\ _{Al2O3}\ \} \tag{69}$$

$$\alpha_i.*= aBi +b \%_{Al2O3} + c \tag{70}$$

The model becomes extremely complicated and confusing to predict unknown viscosities because $\alpha_i.*$values are determined for each system/family and there is no general overall value for $\alpha_i*$ *eg* one can calculate it from a,b and c values for $CaO+MgO+Al_2O_3+SiO_2$ but other a, b, c values (leading to a different $\alpha_i.*_{Al2O3}$) 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.

Calculated viscosity values are given for the selected temperatures in cells E19-E25 and F19-F25.. Forsbacka [81,82] gives different a,b,c values for the $CaO+MgO+Al_2O_3+SiO_2$  system values calculated with this are given in cells AB 39-AB45 and AC39-AC45. Values due to Forsbacka were used for CrO and $Cr_2O_3$.

### 5.6.4 Urbain model
This model divides the various slag constituents into :
Glass formers     $X_G= X_{SiO2}$
Network modifiers: $X_M= X_{CaO} + X_{MgO} + X_{CaF2} + X_{FeO} + X_{CaO} + X_{MnO} + X_{CrO} + X_{NiO} + X_{Na2O} + X_{K2O} + X_{Li2O} +2\ X_{TiO2} + X_{ZrO2}$
Amphoterics:    $X_A= X_{Al2O3} + X_{B2O3} + X_{Fe2O3}\ X_{Cr2O3}$

Here it has been assumed that $Fe_2O_3$ and $Cr_2O_3$ behave as network breakers than amphoterics so they have been allocated so that the fraction (f) behaving as network modifiers f=0.6.
Urbain works predominantly on a basis of $M_xO$ so this creates extra ions and it is necessary to normalise $X_G$ $X_M$ and $X_A$ by dividing by the term $(1+0.5\ X_{FeO1.5}+ X_{TiO2} + X_{ZrO2}+ X_{CaF2})$ to give $X_G*$ $X_M*$ and $X_A*$
The model assumes the Weymann relation

$$\eta(dPas) =A\ T\ \exp (B/T) \tag{71}$$

Urbain [95] found that A and B were linked through the equation

$$-\ln A = 0.29B + 11.57 \qquad (72)$$

The B value must be calculated via the equations

$$\alpha^* = X_M / (X_M + X_A) \qquad (73)$$

$$B_i = a_i + b_i\alpha + c_i\alpha^2 \qquad (74)$$

Where subscript i can be 0, 1, 2 or 3 and a, b and c are given constants for each case eg 0, 1, 2 3

$$B = B_o + B_1 X_{SiO2} + B_2 X^2_{SiO2} + B_3 X^3_{SiO2} \qquad (75)$$

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. Here X"MnO" = represents $X_{MnO}$ + $X_{FeO}$ + $X_{NiO}$ + $X_{CrO}$ +0.6( $X_{Fe2O3}$ + $X_{Cr2O3}$ ) and the global B ($B_{global}$) is given by

$$B_{global} = (X_{MnO} B_{MnO} + B_{CaO} X_{CaO} + B_{MgO} X_{MgO)} / (X_{MnO} + X_{CaO} + X_{MgO}) \qquad (76)$$

The values calculated with this software are in good agreement with the values cited by Urbain [95]

### 5.6.5 Mills, Lang and Li (MLL )model
A new model for estimating viscosity was prepared for this course. It assumed an Arrhenius relation for the viscosity.

$$\eta(dPas) = A \exp (B/T) \qquad (77)$$

Values for ln A and B were determined for binary and ternary slag systems and values were derived for both -ln A and B which were then plotted against $Q^{corr}$. The plots revealed a linear correlations between both B and ln A with Q between Q= 0 and 3.5 with small, systematic deviations from the curve for individual cations $eg.Li^+$. These deviations were then plotted against $X_{MxO}$ $eg$ $X_{Li2O}$.The resulting equations are given by:

$$\ln A = -6.0 - 1.15Q_{slag} + 8.085 X_{Na2O+K2O} - 9.67 X^2_{Na2O+K2O} + (15.1 X_{Li2O} - 17.97 X^2_{Li2O}) + 1.14 X_{FeO} - 20 X_{Cr2O3}. -44.2 X_{CaF2} + 220 X^2_{CaF2} \qquad (78)$$

$$B = -10000 - 4500 Q_{slag} - 21000 X_{Na2O+K2O} + 18050 X^2_{Na2O+K2O} - 35666 X_{Li2O} + 36000 X^2_{Li2O} - 6050 X_{FeO} - 17500 X_{CaF2.} \qquad (79)$$

However, the model did not perform well and consistently over-estimated the viscosities qnd so it has not been cited in the "Collected data". Details of the model are given in Appendix 2. Further work will be carried out to determine the reasons for the poor performance.

### 5.7 Thermal conductivity worksheet
**Liquid slags**
Three methods are given for estimating the thermal conductivity of liquid slags. Experimental data [87-93] for thermal conductivity used here were limited to those using line source techniques because other techniques may yield values containing a large contribution from radiation conductivity

### 5.7.1 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 $k^m$ [87-93 ] were correlated with Riboud calculations of ln $\eta^m$; the data showed some scatter because of (i) uncertainties in the calculated ln $\eta^m$ values(ii) experimental uncertainties associated

with $\ln k^m$ and (iii) sensitivities of both $\eta^m$ and $k^m$ in the region around $T_{liq}$ and the uncertainties in $T_{liq}$ itself. The following relation was obtained.

$$\ln k^m = -2.178 + 0.282 . \ln \eta^m \qquad (80)$$

### 5.7.2 Method 2 - relation to both Q and ln $\eta^m$

This method is similar to Method 1 in that it uses a relation between $\ln \eta^m$ and $\ln k^m$. The data shown in Figure 32b (derived with the MLL method) can be expressed as an exponential relation.

$$\eta^m = 0.165 \exp (Q / 0.817) \qquad (81)$$

Then $\ln k^m$ can be calculated using the equation

$$\ln k^m = -1.8755 - 0.0893 (\ln \eta^m) + 0.0352 (\ln \eta^m)^2 . \qquad (82)$$

*The values of km obtained are only valid 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 (eg 45% CaO+10%SiO$_2$ +45%Al$_2$O$_3$ which would will show a high Q value but in actual fact, is largely made up of calcium aluminates and will relatively low l$\eta^m$;and $k^m$ values).*

### 5.7.3 Method 3 - relation with Q

Te relation between $\ln k^m$ and Q is shown in Figure 32a and it can be seen that it has similarities to the equation between $\ln \eta^m$ and Q (Figure 32b, Equn ). 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:

$$\ln k^m = -1.914 + 0.00037 \exp (Q/0.402) \qquad (83)$$

*This equation should not be used out of range ie  Q>3.2 or Q<2*

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

$$\ln k_T (liq) = A \exp (B/T) \qquad (84)$$

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

$$dk/dT = 0.0005 \exp (0.5551Q) \qquad (85)$$

*but should be used with caution.*

*Solid slags*
The experimental data for $\ln k_{298}$ and $\ln k_{Tg}$ show appreciable scatter when plotted vs Q (Figure 33) but they do show k increasing with increasing Q. The data were assumed to follow an exponential relation like that for $\ln k^m$ (Equn 83, Figure 32a).It was noted that the experimental data for solid, $Li_2O$-containing slags were significantly higher than the curve values and so the correction for $Li_2O$ was added to the exponential relation:

$$\ln k_{298} = -0.424 + 0.00002 \exp(Q / 0.299) + 3.2.X_{Li2O} \qquad (86)$$

$$\ln k_{Tg} = -0.435 + 0.00005 \exp(Q / 0.332) + 3.0 X_{Li2O} \qquad (87)$$

*This equation should not be used out of range ie  Q>3.3 or Q<2*

Values can be calculated at other temperatures by linear interpolation between 298 K and Tg 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, Eqn 37 but there were too few data to establish the necessary constants). ***This procedure should only be accepted for slags in the range Q= 2 to 3.3.***

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

### Crystalline slags

Nishioka et al. [94] report k values for crystalline slags are between 1.5 and 2.5 times higher than that for the glassy slag and are remain independent of temperature (Figure 31). Thus it has been assumed that $k_{cryst} = 2k_{glass}$ and is independent of temperature from 298 to 1000K

## 5.8 Electrical conductivity worksheet

The electrical conductivities have been estimated using recent papers by Zhang and Chou [58, 59] both of which involve using the relation between conductivity and viscosity.

### 5.8.1 Method 1

Chou and Zhang [58, 59] proposed a relation for slags containing $CaO, MgO, Al_2O_3$ and $SiO_2$.

$$\ln k = (-0.08 - \ln \eta)/1.18 \tag{88}$$

Zhang calculated values of ln k using this equation and parameters to calculate the viscosity. These are not generally available so $\ln \eta$ values were calculated using the Riboud, Iida and Urbain models.

### 5.8.2 Method 2

Zhang et al reported that the following equations for $M_2O$- $SiO_2$ (where $M_2O$= $Na_2O$ etc) and MO-$SiO_2$ (eg CaO) systems (Figure 21)

$M_2O$- $SiO_2$:  $\qquad\qquad\qquad$ $\ln k = (.02 - \ln \eta)/ 2.87$ $\qquad\qquad\qquad\qquad$ (89)

MO- $SiO_2$ $\qquad\qquad\qquad\qquad$ $\ln k = (0.15 - \ln \eta)/1.1$ $\qquad\qquad\qquad\qquad$ (90)

This was attributed to the fact that there are twice as many $Na^+$ ions as $Ca^{2+}$ for equivalent compositions. The model calculates the ratio of $2 \Sigma X_{M+} / \Sigma (2 X_{M+} + X_{M2+} \ 0.667 \ X_{M3+} + 0.5 X_{M4+})$ and adjusts Equn for $X_{M+}$ ions present in the slag. **This method should be used when the slag contains $M^+$ ions eg. $Na^+$, $K^+$ or $Li^+$.**

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## Methods of determining structure

The various methods of determining structure are summarised in Table 1. For further details the reader should consult other sources [9-12]

*Table 1: Methods used to obtain structural information on melts*

| Method | Measurement | Structural information obtained |
|---|---|---|
| **Diffraction** X-ray, Neutron, Electron | rdf | 1. Bond lengths 2. Co-ordination Numbers 3. Inter-tetrahedral angles T-O-T 4. Overall intermediate structure 5. Local O co-ordination around large cations |
| **Spectroscopy** Raman, Infra-red Ultra- Violet | | 1. Bond lengths 2. Bond angles 3. Identification and concentrations of various anionic units |
| Nuclear Magnetic Resonance (NMR) | Chemical shift | 1. Bond lengths 2. Bond angles 3. Identification and concentrations of various anionic units |
| Mossbauer | Isomer shift | 1. Valence state 2.Co-ordination of environment; identification and concentration of $Fe^{3+}$ with 4- and 6- fold co-ordination. |
| | Quadrupole splitting | 1. Distortion of O   olyhedron 2. Oxidation state $Fe^{2+}$ or $Fe^{3+}$ 3. Co-ordination of $Fe^{3+}$ (4- or 6- fold) |
| X-ray absorption spectroscopy | EXAFS XANES | 1. Bond lengths 2. Bond angles 3. Co-ordination of specific atoms or ions |
| X-ray emission (ESCA or XPS) ESR spectroscopy | $K_\alpha$: $K_\beta$ | 1. Co-ordination of specific atoms or ions 2. Changes in valence state |
| Luminescence spectroscopy | | Co-ordination of $Mn^{2+}$, $Fe^{3+}$, $Ti^{3+}$ or S ($S^{2-}$ or $SO_4^{2-}$) |
| Chromatography | | Distribution of chain lengths of different polymeric units |
| **Property measurement** | Density, Molar volume | Packing and co-ordination |
| | Molar refractivity | Concentrations of $N^{Oo}$; $N^{O-}$; $N^{O2-}$ |
| | Viscosity | 1. Activation energies related to bond strength 2. Effect of cations on structure. |
| | Enthalpy of mixing, or solution | 1. Measure of bond strength     2. Effect of different cations including structural ordering |
| | Electrical / Thermal conductivity | 1. Indication of amount of ionic and electronic conduction 2. Information on whether fluorides form Si-F bonds |
| **Molecular dynamics (MD)** | Calculations | 1. Bond strengths 2. T-O-T angles 3. Co-ordination ( e.g. Al is 4- fold in $Na_2O+Al_2O_3 +SiO_2$ slags) |
| **Thermodynamic modelling** | Calculations |  Concentration of various anionic polymeric units in melt |

**APPENDIX 2**

*Details of MLL model*

*Underlying principles of model*

The model is based on the fact that the viscosity is largely controlled by polymeric structure of the liquid slag. It uses the parameter Q (=4-NBO/T) to represent the structure. The temperature dependence for the liquid is expressed by the Arrhenius equation ($\eta$(dPas)= A exp (B/T)) where T is in K. The terms, ln A and B are represented as functions of Q and small corrections are made to these relationships between ln A and Q and B and Q . These equations were derived from experimental viscosity- temperature data for binary and ternary silicates (Figures A2-1 and A2-2 ). The parameter Q does not differentiate between different cations and their effect on the structure and on the viscosity. Consequently, small corrections to the basic equation are made to account for the effect of individual cation effects on the viscosity (see Table A2-1).

$$\ln A = -6.0 - 1.15Q_{slag} + 15.1X_{Na2O+K2O} - 18\,X^2_{Na2O+K2O} + (15.1X_{Li2O} - 17.97X^2_{Li2O}) + 1.14X_{FeO} - 20X_{Cr2O3}. \quad (A1)$$

$$B = -10000 - 4500Q_{slag} - 35700\,X_{Na2O+K2O} + 36000\,X^2_{Na2O+K2O} - 35666X_{Li2O} + 36000X^2_{Li2O} - 6050\,X_{FeO}. \quad (A2)$$
where $X_{M+}$= mole fractions of $Na_2O$, $Li_2O$ and $K_2O$
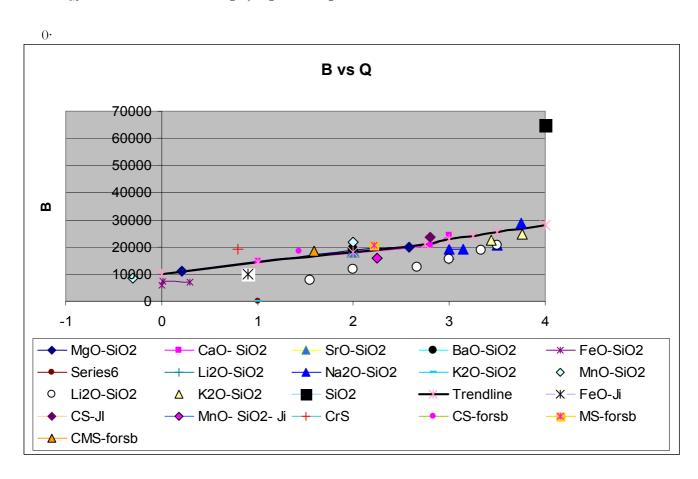


*Figure A2.1: The parameter B as a function of Q for binary silicates*

The model is valid for silicate slags in the range, Q=0 to 4,(ie. equivalent to range of 2CaO. $SiO_2$ to $SiO_2$). Some slags used in metallurgical processes will not be covered eg. some BOS slag compositions and FeO –rich fayalite (2FeO.$SiO_2$) slags used in copper production.
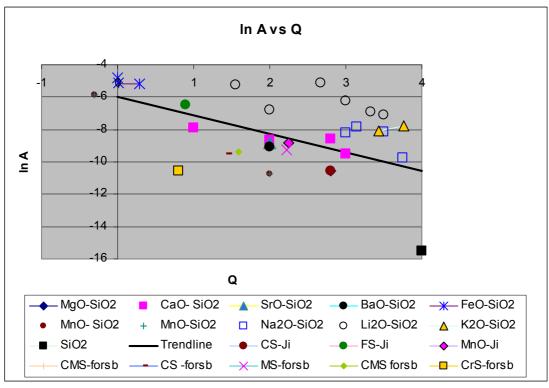
S – 49

*Figure A2.2 The parameter lnA as a function of Q for binary silicates.*

### Mould fluxes:

$$\ln A = -6.0 - 1.15 Q_{slag} + 8.085\, X_{Na2O+K2O} - 9.67\, X^2_{Na2O+K2O} + (15.1 X_{Li2O} - 17.97 X^2_{Li2O}) + 1.14 X_{FeO} - 20 X_{Cr2O3}.$$
$$-44.2 X_{CaF2} + 220\, X^2_{CaF2} \qquad\qquad (A2-3)$$

$$B = -10000 - 4500 Q_{slag} - 21000\, X_{Na2O+K2O} + 18050\, X^2_{Na2O+K2O} - 35666 X_{Li2O} + 36000 X^2_{Li2O} - 6050\, X_{FeO} - 17500\, X_{CaF2.} \qquad\qquad (A2-4)$$

*Table A2-1: Details of effects of different cations*

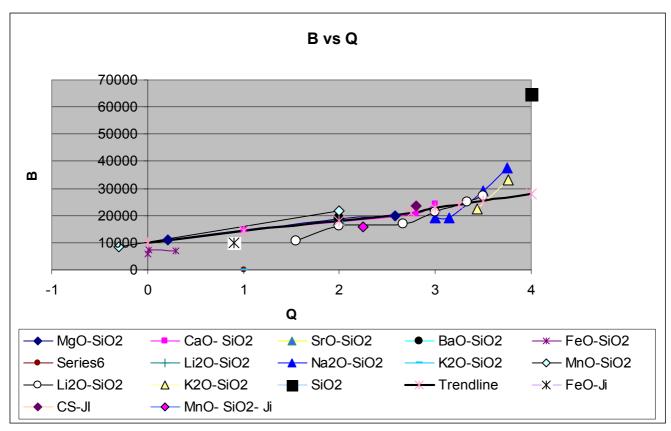| Constituent | Observation | Cause, Remedy |
|---|---|---|
| $Na_2O$, $K_2O$, $Li_2O$ | $M^+$ ions do not bond two chains together like $Ca^{2+}$- consistent deviations from B and ln A vs Q | Small corrections to equns of lnA and B vs Q involving $X_{M+} = \Sigma X_{Na2O} + X_{K2O} + X_{Li2O}$ |
| FeO | Found to give consistent deviations from lnA and B vs Q relations | Small corrections made to lnA and B vs Q equns |
| $Fe_2O_3$ | Experimental ln A and B values used to determine Q and f. Mean values of f=0.55; f=0.67-0.086Q | Calculates Q using f=0.55 then recalculates Q using f= 0.67 -0.086Q |
| $Cr_2O_3$ | Experimental B values used to determine Q and f. Mean values of f=0.45; f=0.73-0.113 Q Experimental ln A values consistently more negative can not be used for f | Calculates Q using f=0.45 then recalculates Q using f= 0.73 -0.113Q<br><br>Correction to ln A value ;-20$X_{Cr2O3}$ |
| $B_2O_3$ | Exhibits mixture of 3- and 4- coordination in borates and boro-silicates. Additions (<5%) to mould fluxes reduce viscosity and $_{Tliq}$ | **Program not suitable for high concentrations** Taken as a network breaker in low concentrations |
| MnO | Some of B values reported for high-MnO slags [**??**] show departure from B vsQ relations | No corrections made to relation |
| $TiO_2$ $ZrO_2$ | $TiO_2$ reported to reduce viscosity [ **???**]- acts as network breaker –assumed $ZrO_2$-identical | $TiO_2$ and $ZrO_2$ taken as network breakers |
| $CaF_2$ | $F^-$ reported to bond with $Ca^{2+}$ -leaving more-polymerised slag | $CaF_2$ ignored in calculation of Q- special calculations needed for slags containing F |

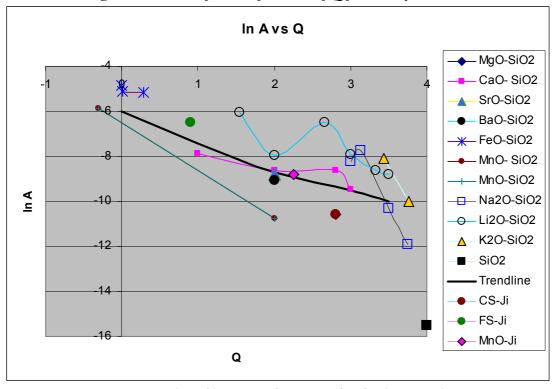*Figure A2-3 Plot of B as a function of Q for binary silicates*



*Figure A2-4. Plot of ln A as a function of Q for binary silicates*

There is some dispersion of the data in the range Q=3.5 to 4. It should be noted that Q=4 is the equivalent of pure $SiO_2$ which would cause an upward move to a higher B and a downward move to a more negative ln A value. However, other slags with compositions where the mole fraction of network breaker exactly charge balances the mole fraction of $Al_2O_3$ (eg $mX_{CaO} + mX_{Al2O3} + (1-2m)X_{SiO2}$) also have Q=4. These latter cases can be seen as a mixture of $SiO_2$ and CaO $Al_2O_3$ and the deviation from the linearity decreases with increasing "m" ie decreasing $X_{SiO2}$. It should also be pointed out that these slags with Q=4 tend to have high $T_{liq}$ and viscosity measurements are frequently restricted to temperature ranges of <100K which

leads to lnA and B values with much higher uncertainties. The linear relationship has been adopted for the the range Q=3.5 to 4 but uncertainties in calculated viscosities will be larger than in the range Q =0 to 3.5. The software will calculate Q for the specified composition using Equns A2.5 to A2.8 where f=fraction of $Fe_2O_3$ or $Cr_2O_3$ acting as a network breaker (6-fold coordination).

$NBO= 2\{ X_{CaO}+ X_{MgO}+ X_{Na2O}+ X_{K2O}+ X_{Li2O}+ X_{FeO}+ X_{MnO}+ X_{CrO}+ X_{NiO}+2X_{TiO2}+ 2X_{ZrO2}+3 f_1X_{Fe2O3}+$
$3f_2X_{Cr2O3} - X_{Al2O3}- X_{B2O3}- (1- f_1)X_{Fe2O3}-(1- f_2)X_{Cr2O3} \}$ (A2-5)

$T' = \{ X_{SiO2}+ 2X_{Al2O3} +2X_{B2O3}+2(1- f_1)X_{Fe2O3}+2(1- f_2)X_{Cr2O3}\}$ (A2-6)

$$NBO/T= NBO / T'$$ (A2-7)
$$Q= 4- (NBO/T)$$ (A2-8)

***Use of Model***

1. Insert $T_{liq}$ and appropriate temperatures into cell (Composition  B28 and Viscosity B19) and cells (Viscosity –B19-B25  ) respectively.
2. The program will calculate Q  (cell B20) ln A (cell) and B and the viscosity (dPAs) (cellB21) and ln viscosity (dPas) (cell B22 )