ESTIMATION OF PHYSICO-CHEMICAL PROPERTIES OF COAL SLAGS AND ASHES

K C MILLS
National Physical Laboratory, Teddington, Middx, TW11 OLW, UK.

1. INTRODUCTION.

Slags formed during the gasification of coal usually contain SiO_2, Al_2O_3, iron oxides, CaO, Na_2O and K_2O with minor amounts of various other oxides. A knowledge of the physico-chemical properties of these slags can improve the control of the process eg. the amount of flux required to bring the slag viscosity to a level suitable for tapping can be calculated from viscosity-composition relations. Physical property data for the coal slags can also improve process design by the development of reliable mathematical models of the process eg. thermal properties of the slags are needed for heat balance calculations. There is an appreciable variation in the compositions of slags formed from various coals and even from different batches of the same stock on occasions and these compositional variations can give rise to considerable differences in the physical properties. As the chemical analysis is frequently available on a routine basis it would be particularly desirable to have reliable models for the prediction of physico-chemical properties from their chemical composition. Furthermore such models would have the further advantage that they would eliminate the need for arduous interpolations on pseudo-ternary plots for slags which are really multicomponent and interactive systems.

The properties of slags are dependent not only upon chemical composition, but upon other factors also. The most pronounced deviations from addivity rules based on composition arise in the estimation of those properties which involve ionic transport such as electrical conductivity. However surface tension values estimated from additivity rules are frequently in error as bulk thermodynamic properties do not apply at surfaces. Furthermore, virtually all the physical properties of slags are, to some extent, dependent upon the structure of the slag (viz. the length of silicate chains,degree of crystallinity etc.) thus estimation procedures have to accommodate these structural factors, where possible.

There is only a limited amount of physical property data available for coal slags and consequently it has been necessary to examine a much broader range of silicates including magmatic liquids and those slags encountered in steelmaking, glassmaking and non-ferrous processes. Thus the models cited here should have a much wider range of application than coal gasification.

A critical evaluation of the extant physical property data has shown that virtually every physical property is markedly dependent upon the distribution of iron in the slag between FeO, Fe_2O_3 and free iron. Frequently these distributions are not reported and they can not be easily predicted as they are very dependent upon (i) the partial pressure of oxygen, p_{O_2} (1) (ii) temperature (1) T and (iii) the nature of the other oxides present, eg CaO, Na_2O and K_2O (1)(2)(3) increase the amount of Fe_2O_3 and SiO_2 increases the amount of FeO present. Even when the iron distributions are cited they are vulnerable to error owing to difficulties in chemical analysis and the possibility of some redistribution of the $Fe/Fe^{2+}/Fe^{3+}$ ratios during the quench. Nevertheless it is strongly recommended that all future physical property determinations on coal slags should be accompanied by chemical analysis for Fe(free), FeO and Fe_2O_3 on the quenched specimen as the surface tension, absorption coefficient, melting range etc. fluctuate dramatically with the iron distribution.

2. MODELS FOR ESTIMATING PHYSICO-CHEMICAL PROPERTIES.

2.1 Melting Range

Empirical rules have been formulated[4-6] for the estimation of melting range on the basis of the basicity of the slag or ash. However the various constants used in the calculations are applicable to very narrow compositional ranges and thus a large number of constants are required to represent the slags formed from different coals.

A more universal approach has been adopted recently by Gaye[7,8] who expressed, the dependency of liquidus temperature, T_{liq}, upon chemical composition as polynomial for each of the phases (or compounds) formed by the slag. The *maximum* calculated value of T_{liq} value for the various phases is the T_{liq} value. Good agreement was obtained between the calculated and experimental values for T_{liq} for the $SiO_2 + Al_2O_3 + MgO + FeO$ and the $SiO_2 + Al_2O_3 + MgO + CaO$ systems. However development of this model to cover the multicomponent coal slags could prove difficult.

A second model due to Gaye[9] would appear to offer more promise; it is based on the Kapoor-Frohberg model for the estimation of activities and assumes that both acidic and basic oxides are made up of symmetrical cells and that these interact to form assymmetrical cells. The activities of the various oxides calculated for quaternary slags with this model are in excellent agreement with those determined experimentally. Values of T_{liq} for a given composition can be derived by determining the temperature at which the solid phase formed has an activity of one. The model has been developed for systems based on seven components, SiO_2, Al_2O_3, CaO, MgO, FeO, Fe_2O_3 and MnO. The model will have to be enlarged to include Na_2O etc. before it can be used for the reliable estimation of T_{liq} of coal slags but it would seem to have considerable promise and has the decided advantage that it also produces activity data for the various component oxides.

2.2 Viscosity (η)

Several models have been reported for the estimation of viscosities (η) of silicate melts to cover the compositional ranges of glasses[10,11] steelmaking slags[12-14], *magmas*[15-18] and coal slags and ashes[19-24]. The temperature (T) dependence of the viscosity is expressed in the form of the Arrhenius relationship (equation 1)) or the Frenkel relationship (equation 2) which is sometimes known as the Weymann equation) where A and B are constants, E is the activation energy and R is the Gas Constant.

$$\eta = A \exp. (E/RT) \qquad 1)$$

$$\eta = AT \exp.(E/RT) \qquad 2)$$

Estimated viscosities have been calculated using these various models and the closest agreement with experimental values was obtained with the models due to Riboud *et al*[13] and Urbain *et al*[17,18]. These estimation procedures use the Frenkel relationship and thus their superiority may be largely due to the use of equation 2). The model due to Schobert which involves petrographic classification of the coal slag has not been checked and this procedure may provide reliable estimates of viscosity for coal slags but could not be applied to slags covering a wide range of composition. Thus effort in the present study was focussed predominantly on the Riboud and Urbain models.

Model due to Riboud et al[13]

The slag constituents are classified in five different categories in this model. The mole fractions (x) for those categories being given by

(i) $x("SiO_2") = x(SiO_2) + x(PO_{2.5} + x(TiO_2) + x(ZrO_2)$

(ii) $x("CaO") = x(CaO) + x(MgO) + x(FeO) + x(FeO_{1.5})$

(iii) $x(Al_2O_3)$

(iv) $x(CaF_2)$ and

(v) $x("Na_2O") = x(Na_2O) + x(K_2O)$.

The parameters A and B of equation 2) are calculated from the mole fraction of the five categories by using equations 3) and 4).

$$A = \exp(-19.81+1.73x("CaO")+5.82x(CaF_2)+7.02x(Na_2O)-33.76x(Al_2O_3)) \quad 3)$$

$$B = +31140-23896x("CaO")-46356x(CaF_2)-39159x("Na_2O")+68833x(Al_2O_3) \quad 4)$$

Subsequently, from the values of A and B it is possible to calculate the viscosity for the temperatures in question by use of equation 2).

Model due to Urbain et al[18]

In this model the parameters A and B are calculated by dividing the slag constituents into three categories (i) "glass formers", $x_G = x(SiO_2) + x(P_2O_5)$ (ii) "modifiers", $x_M = (CaO) + x(MgO) + x(Na_2O) + x(K_2O) + 3x(CaF_2) + x(FeO) + x(MnO) + 2x(TiO_2) + 2x(ZrO_2)$ (iii) "amphoterics", $x_A = x(Al_2O_3) + x(Fe_2O_3) + x(B_2O_3)$.

However we consider that Fe_2O_3 behaves more like a modifier than an amphoteric and in our revised programme $1.5\ x(FeO_{1.5})$ has been added to x_M and $x(Fe_2O_3)$ deducted from x_A. "Normalized" values x_G^* and x_M^* and x_A^* are obtained by dividing the mole fractions, x_G, x_M and x_A by the term $(1 + 2x(CaF_2) + 0.5\ x(FeO)_{1.5}) + x(TiO_2) + x(ZrO_2))$. Urbain proposed that the parameter B was influenced both by the ratio, $\beta = [x_M^*/(x_M^* + x_A^*)]$ and by x_G^*. The parameter B can be expressed in the form of equation (5) where B_1, B_2 and B_3 can be obtained by equation (6).

$$B = B_o + B_1\ x_G^* + B_2(x_G^*)^2 + B_3(x_G^*)^3 \quad 5)$$

$$B_i = a_i + b_i\beta + c_i\beta^2 \quad 6)$$

B_o, B_1, B_2 and B_3 can be calculated from the equations listed in Table 1 and these parameters are then introduced into equation 5) to calculate B. The parameter A can be calculated from B by equation 7) and the viscosity of the slag (in PaS) can then be determined using equation 8).

$$-\ln A = 0.2693\ B + 11.6725 \quad 7)$$

$$\eta = 0.1[AT \exp(10^3\ B/T)] \quad 8)$$

TABLE 1

$B_o = 13.8 + 39.9355\beta - 44.049\beta^2$

$B_1 = 30.481 - 117.1505\beta + 129.9978\beta^2$

$B_2 = -40.9429 + 234.0486\beta - 300.04\beta^2$

$B_3 = 60.7619 - 153.9276\beta + 211.1616\beta^2$

Modifications to the Urbain model

Urbain[18] has recently modified the model to calculate separate B values for different individual modifiers, CaO, MgO and MnO. The global B value for a slag containing all three oxides can be derived using equation 9)

$$B(\text{global}) = \frac{x(CaO)B(CaO) + x(MgO)B(MgO) + x(MnO)B(MnO)}{x(CaO) + x(MgO) + x(MnO)} \qquad 9)$$

Assessment of the viscosity models

These two models have been used to calculate the viscosities of slags with widely-varying compositions and it has been found that both give values which agree well with experiment.

The model of Urbain gives a slightly better fit than the Riboud model. The discrepancies between the experimental values and the predicted values are of the order of $\pm$ 30% which are of similar magnitude to the experimental uncertainties for viscosity measurements.

2.3 Density (ρ)

Recently Keene[25] has reported that the density at 1673K of molten slags can be obtained within $\pm$ 5% using the equation 10)

$$\rho\ /gcm^{-3} = 2.46 + 8.018\ (\%\ FeO + \%\ Fe_2O_3 + \%\ MnO + \%\ NiO) \qquad 10)$$

An additive method for the estimation of densities (ρ) in slags has been widely used for some time[26,27]. In this method, the molar volume, V, can be obtained from equations 11) and 12) below, where M, x and $\bar{V}$ are the molecular weight, mole fraction and the partial molar volume, respectively, and 1, 2 and 3 denote the various oxide constituents of the slag.

$$V = M_1x_1 + M_2x_2 + M_3x_3 \qquad 11)$$

$$V = x_1\bar{V}_1 + x_2\bar{V}_2 + x_3\bar{V}_3 \qquad 12)$$

The partial molar volume is usually assumed to be equal to the molar volume of the pure component (V^o). Bottinga and Weill[28] produced a series of values of $\bar{V}$ for various oxides assuming a constant value for $\bar{V}(SiO_2)$ and it was claimed that good estimations of the density could be obtained for compositions containing between 40 and 80% SiO_2. Two more recent studies[29,30] also concluded that $\bar{V}$ (SiO_2) was independent of composition and have revised the $\bar{V}$ values for the various oxides. However it has been pointed out[31,32] that the density of the slag is also related to its structure. Silicate slags contain a mixture of chains, rings and basic silicate units, which are dependent upon the silica concentration and upon the nature of the cations present. Thus the densities of silicate slags estimated using a constant value for $\bar{V}(SiO_2)$ will be subject to error as the arrangement of these silicate chains varies with silica concentration.

Furthermore Grau and Masson[31] pointed out that for the series M_2O, M_2SiO_2 the partial molar volume of SiO_2 is not constant. They calculated a $\Delta\bar{V}$ term for the differences between any two members of the series and in this way calculated values were derived for the systems FeO + SiO_2, PbO + SiO_2, FeO + MnO + SiO_2 and FeO + CaO + SiO_2 for compositions in the range x_{SiO_2} = 0.5 to 1.0. However this method is not suitable for calculating densities of multicomponent systems.

Very recently, Bottinga et al[33] have presented a model in which the partial molar volumes of alumina-silicate liquids were considered to be composition-dependent.

New model for calculating the densities of slags

Slags containing SiO_2, Al_2O_3 and P_2O_5 consist of chains, rings and complexes which are dependent upon the amount and nature of the cations present. Thus it is necessary to make the partial molar volumes dependent upon composition for oxides of this type. If in a binary system, equation 12) were applicable and if $\bar{V}_i = V_i^o$ ie. $\bar{V}$ is independent of composition, then the curve of V as a function of composition will be that shown by the solid line in Figure 1a and the two $x_i\bar{V}_i$ contributions by the dotted lines. If we now consider a binary silicate system the molar volume (V) would have the form shown as a solid line in Figure 1b. It is reasonable to assume that $\bar{V}(M_xO)$ is independent of composition and would have the form of $x_1\bar{V}_1$ in Figure 1b. The parameter $x_2\bar{V}_2$ can be derived for SiO_2 by use of equation 13) below.

$$x_2\bar{V}_2 = V - x_1\bar{V}_1 \qquad 13)$$

Thus $x_2\bar{V}_2$ will have the form of the curve shown in Figure 1b.

It is possible to derive $x\bar{V}$ for SiO_2 in ternary and quaternary slags by using equation 14). Values for $x\bar{V}$ (SiO_2) have been derived using experimental density data for the systems, $FeO + SiO_2$, $CaO + SiO_2$, $MnO + SiO_2$, Na_2O+SiO_2, $K_2O + SiO_2$ and $CaO + FeO + SiO_2$ and are plotted against $x(SiO_2)$ in Figure 2. It can be seen from this figure that there is excellent agreement between the $x\bar{V}(SiO_2)$ calculated from different sources, with the exception of that for the $MnO + SiO_2$ system; however the reliability of the experimental data for this system, have been questioned previously. From this curve for $x\bar{V}(SiO_2)$ we can derive the relationship, $V(SiO_2) = 19.55 + 7.966.x(SiO_2)$. The recommended values for $\bar{V}$ for the various oxides at 1500°C are given in Table 2.

$$xV(SiO_2) = V - x_1\bar{V}_1 - x_2\bar{V}_2 - x_3\bar{V}_3 \qquad 14)$$

Values for $x\bar{V}$ (Al_2O_3) were determined in a similar manner by using experimental density data for the systems, $CaO + Al_2O_3$, $CaF_2 + Al_2O_3$, $CaF_2 + Al_2O_3$, $SiO_2 + Al_2O_3$, $MgO + CaO + Al_2O_3$ and $MnO + SiO_2 + Al_2O_3$. The xV (Al_2O_3) results are plotted in Figure 3 and the relationship $\bar{V}(Al_2O_3) = 28.31 + 32\,x(Al_2O_3) - 31.45\,x^2(Al_2O_3)$ was derived from this curve.

There are few experimental data for the density of phosphate slags, $x\bar{V}(P_2O_5)$ values were derived from data for the systems $CaO - FeO - P_2O_5$ and $Na_2O - P_2O_5$. A constant value of $\bar{V} = 65.7\ cm^3\ mol^{-1}$ was obtained from the selected linear relationship.

TABLE 2

Recommended values for the partial molar volumes, $\bar{V}$, of various slag constituents at 1500°C

SiO_2	$19.55 + 7.966\,x(SiO_2)$	FeO	15.8	K_2O	51.8
Al_2O_3	$28.31 + 32\,x(Al_2O_3) - 31.45\,x^2(Al_2O_3)$	Fe_2O_3	38.4	CaF_2	31.3
CaO	20.7	MnO	15.6	P_2O_5	65.7
MgO	16.1	Na_2O	33	TiO_2	24

Units of $\bar{V} = cm^3\ mol^{-1} = 10^{-6}\ m^3\ mol^{-1}$

In order to provide a temperature coefficient, the temperature dependencies of

the molar volumes (dV/dT) of many slag systems were examined and a mean value of 0.01% K^{-1} was adopted.

Assessment of density models.

An analysis of the uncertainties associated with the estimated of densities with this model has not been completed yet. However on the basis of those values obtained so far the standard deviation of the factor '[(ρest-ρexpt/ρexpt] is between 1 and 2% and less than that recorded vary the method due to Bottinga et al[33]. The experimental uncertainties associated with density measurements for slags are i.e. ± 2%.

2.4 Surface tension (γ)

Methods for estimating the surface tension of slags based on the addition of the partial molar contributions ($\bar{\gamma}$) of the individual constituents have been reported by Appen[34] by Boni and Derge[35] and by Popel[36]. All these methods make use of equation 13a where 1,2,3 etc denote the various slag constituents.

$$\gamma = x_1\bar{\gamma}_1 + x_2\bar{\gamma}_2 + x_3\bar{\gamma}_3 + \ldots\ldots \qquad 13a)$$

Values of $\bar{\gamma}_i$ are often taken to be the surface tension of the pure components, γ_i^o, and have also been obtained by reiterative procedures. Figure 4a shows a typical plot of γ as a function of x for a binary slag and the individual $x_i\bar{\gamma}_i$ contributions have been included These methods work well for certain slag mixtures but break down when surface-active constituents, such as P_2O_5, are present. Surface active components migrate preferentially to the surface and cause a sharp decrease in the surface tension and only very small concentrations are required to cause an appreciable decrease in γ if the constituent is concentrated in the surface layer. Thus some unreported or undetected impurity could have a marked effect on the surface tension of the slag and consequently produce an apparent error in the value estimated by the model. In this aspect surface tension differs from all the other physical properties which are essentially bulk properties.

Model for calculating the surface tension of slags

Figure 4a shows the surface tension of two slag constituents which are not surface active. For a binary mixture with one surface active component the surface tension-composition relationship will have the form of that shown in Figure 4b where 2 denotes the surface-active constituent. If we assume that $x\bar{\gamma}$ for component 1 is unaffected then the term $\gamma_2 x_2$, the partial molar contribution of the surface active material, can be calculated by equation 14a below. The term $(x_2\bar{\gamma}_2)$ can similarly be calculated for ternary and quaternary systems providing there is only one surface active component. The compositional dependence of the $(x_2\bar{\gamma}_2)$ term is shown in

$$x_2\bar{\gamma}_2 = \gamma - x_1\bar{\gamma}_1 \qquad 14a)$$

Figure 4b and it should be noted that as $x_2 \rightarrow 1$ then $x_2\bar{\gamma}_2 \rightarrow \gamma_2^o$. Values of $(x\bar{\gamma})$ for various surface active materials derived from experimental surface tension data are shown in Figures 5a. It is possible to deal with the compositional dependence of these $(x\bar{\gamma})$ values by considering two curves viz. one operating up to the point N and the other representing values of x where x > N. The partial surface tension for non-surface active constituents is shown in Table 3 and the equations for calculating $\bar{\gamma}$ for surface active components and values of N are given in Table 4. There is a considerable discrepancy in the $x_2\bar{\gamma}_2 - (x_2)$ relationships for B_2O_3 obtained from experimental data on two different systems,

consequently a mean value has been adopted until further data become available.

TABLE 3
Partial molar surface tension, $\bar{\gamma}$, at 1500 °C
for different slag constituents

Oxide	SiO_2	CaO	Al_2O_3	MgO	FeO	MnO	TiO_2
$\bar{\gamma}$/mNm^{-1}	260	625	655	635	645	645	360

TABLE 4
Values of $x_i\bar{\gamma}_i$ at 500°C for surface-active constituents

Slag Constituent	$x_i\bar{\gamma}_i$ for x < N	N	$x_i\bar{\gamma}_i$ for x > N
Fe_2O_3	$-3.7 - 2972\,x + 14312\,x^2$	0.125	$-216.2 + 516.2\,x$
Na_2O	$0.8 - 1388\,x - 6723\,x^2$	0.115	$-115.9 + 412.9\,x$
K_2O	$0.8 - 1388\,x - 6723\,x^2$	0.115	$-94.5 + 254.5\,x$
P_2O_5	$-5.2 - 3454\,x + 22178\,x^2$	0.12	$-142.5 + 167.5\,x$
B_2O_3	$-5.2 - 3454\,x + 22178\,x^2$	0.10	$-155.3 + 265.3\,x$
Cr_2O_3	$- 1248\,x + 8735\,x^2$	0.05	$-84.2 + 884.2\,x$
CaF_2	$-2 - 934\,x + 4769\,x^2$	0.13	$-92.5 + 382.5\,x$
S	$-0.8 - 3540\,x + 55220\,x^2$	0.04	$-70.8 + 420.8\,x$

The reported values of $(d\gamma/dT)$ for various slag systems were examined and a mean value of -0.15 mN m^{-1} K^{-1} was applied as a temperature coefficient.

Assessment of the model

The standard deviation of the factor $[(\gamma_{est} - \gamma_{expt})/\gamma_{expt}]$ was ca. $\pm$ 10%. Undoubtedly much of the uncertainty arises from experimental errors, where the effect of unreported surface active impurities and the nature of the gaseous atmosphere could have a marked effect on the value of surface tension.

Another major source of error is the amount of Fe_2O_3 present in the slag, this investigation has shown clearly that Fe_2O_3 is very surface active. Few investigators cite the (Fe^{3+}/Fe^{2+}) ratio which in turn is dependent upon, (i) p_{O_2} (ii) T and (iii) the nature and amount of other oxides present and furthermore the ratio, when quoted, is vulnerable to error. Thus the problem arises if a decrease in γ is recorded when Na_2O is added to the slag, is this decrease due to a increase in Fe_2O_3 content or due to the surface activity? In this investigation attempts were made to compensate γ for an increase in Fe_2O_3 content but the effects of basic oxides on the Fe distribution are not well documented and some error may ensue.

A major unresolved problem concerns the situation where the slag contains more than one surface active component. It is possible that there is some competition for sites on the surface and hence the decrease in γ would not be as sharp as that calculated from the summation of $(x_A\bar{\gamma}_A + x_B\bar{\gamma}_B)$ where A and B denote surface active constituents. In this case the model may overestimate the decrease in γ. There are no extant data to confirm this possibility, we have, however, considered $(Na_2O + K_2O)$ as one contribution in the model.

2.5 Thermal Properties

The computation of the thermal losses in the converter by conductive and radiative processes requires knowledge of the following thermal properties, heat capacity, enthalpy, thermal conductivity, absorption coefficient and emissivity.

2.5.1 Heat capacity C_p and enthalpy $(H_T - H_{298})$ of slags

When a silicate liquid is cooled the structure of the solid formed is dependent upon the cooling rate and the thermal history of the sample. Consider a liquid at a temperature corresponding to the point C in Figure 6, a rapid quench will produce a glass and the enthalpy evolved will follow the path CLGA. By contrast, a very slow cooling rate will result in the formation of a crystalline slag, the enthalpy evolution following the path CL DB. It will be noted from Figure 6 that $(H_T - H_{298})_{cryst} = (H_T - H_{298})_{glass} + \Delta H^{vit}$, where ΔH_{vit} is enthalpy of the endothermic transformation of (crystal $\longrightarrow$ glass). The C_p values for the various phases can be summarized as:

$$C_p(\text{crystal}) \simeq C_p(\text{glass}) < C_p\ (\text{supercooled liquid}) \simeq C_p\ (\text{liquid})$$

It can be seen from Figure 6 that at the glass temperature (T_{gl}) there is a sudden increase in C_p (ΔC_p^{gl}) as the glass transforms into a supercooled liquid. Drop calorimetry studies on the glass phase at temperatures between T_{gl} and T_{liq} will produce progressively more crystallization as T_{liq} is approached and consequently the $(H_T - H_{298})$ - T relationship will be similar to that depicted by the dots in Figure 6 and not the path, AGLC; the magnitude of the apparent enthalpy of fusion (ΔH^{fus}) will be dependent upon the fraction of the sample crystallized during annealing at temperatures between T_{gl} and T_{liq}. The C_p values for the liquid and supercooled liquids have been reported to be constant and independent of temperature[37]. It follows from the triangle GEL in Figure 6 that $\Delta C_p^{gl}(T_{liq} - T_{gl}) = \Delta H^{fus}$. Thus it is possible to estimate the enthalpy of a slag with a glassy structure from estimates of C_p(glass) C_p(liq) and T_{gl}. However the estimation of T_{gl} is difficult as it can vary between ~ 700 and 1100 K and the various estimation rules suggested are known to be prone to appreciable errors[38]. Inspection of literature data[38,39] indicates that the glass transformation occurs when C_p attains a value of ca. 1.1 J $K^{-1}g^{-1}$; this rule has been used in the development of the following model for the estimation of $(H_T - H_{298})$ and C_p of slags with a glassy structure.

The C_p for glass, liquid and supercooled liquid phases can be estimated from the slag composition using partial molar heat capacities ($\bar{C}_p$) as shown in equation 15).

$$C_p = x_1\bar{C}_{p_1} + x_2\bar{C}_{p_2} + x_3\bar{C}_{p_3} + x_4\bar{C}_{p_4} \ldots \qquad 15)$$

For most materials the temperature dependence of C_p is usually expressed the form given by equation 16) where a, b and c are constants

$$C_p = a + bT - c\,T^{-2} \qquad 16)$$

The enthalpy at T relative to 298 K (25 °C) is obtained from equation 17) for the glass phase

$$(H_T - H_{298}) = \int_{298}^{T} Cp = a(T-298) + \frac{b}{2}(T^2 - 298^2) + \frac{C}{T} - \frac{C}{298} \qquad 17)$$

Values of a, b and c for the various slag components are given in Table 5 and it should be noted that the P_2O_5 and S in the slag were calculated as CaP_2O_6 and $CaSO_4$, respectively. The amount of CaO used in the calculation of $x\bar{C}_p$ (CaO) should be adjusted by the relationship x(CaO) = x(CaO ,total) - x(P_2O_5) - x(S) to account for the CaO in CaP_2O_6 and $CaSO_4$. The model also takes into account the presence of free iron in the slag.

TABLE 5

Slag Component	M	$\bar{C}_p$(glass)/calK^{-1}mol^{-1}=a+bT -c/T^2 a	b.10^3	c.10^5	$\bar{C}_p$(liq) cal K^{-1}mol^{-1}
SiO_2	60.09	13.38	3.68	3.45	20.79
CaO	56.08	11.67	1.08	1.56	19.3
Al_2O_3	101.96	27.49	2.82	8.4	35
MgO	40.31	10.18	1.78	1.48	21.6
K_2O	94.2	15.7	5.4	0	17.7
Na_2O	61.98	15.7	5.4	0	22
TiO_2	79.9	17.97	0.28	4.35	26.7
MnO	70.94	11.11	1.94	0.88	19.1
FeO	71.85	11.66	2.0	0.67	18.3
Fe_2O_3	159.7	23.49	18.6	3.55	45.7
Fe	55.85	3.04	7.58	-0.6	10.5
P_2O_5	141.91	43.63	11.1	10.86	58
CaF_2	78.08	14.3	7.28	-0.47	23
SO_3	80.06	16.78	23.6	0	42

1 cal = 4.184 J; T in K

The values of $\bar{C}_p$ for the liquid and supercooled liquid given in Table 5 are those reported by Carmichael et al[40] except $\bar{C}_p$ values for Al_2O_3 and Fe_2O_3, where other values have been preferred.

Thus ($H_T - H_{298}$) values for a liquid slag at temperature T can be estimated by determining T_{gl} (ie temperature at which C_p = 1.1 J K^{-1} g^{-1}) and calculating ($H_{T_{gl}} - H_{298}$) from equation (17) and ($H_T - H_{T_{gl}}$) from C_p(liq).(T-T_{gl}).

Values of C_p(glass) obtained with this model lie within 2% of the experimental values and the C_p(liq) values also appear to agree with experimental data; values of ΔC_p at T_{gl} calculated using the model lie within the range of experimental values[38,39] of 0.15 to 0.30 J K^{-1} g^{-1}. One major uncertainly would appear to lie in the calculation of T_{gl}, however it can be shown that an error in T_{gl} of 100 K would only produce an error of ca. 1% in the value of ($H_{1900} - H_{298}$) for the slag. The most serious source of error would thus appear to arise through crystallization of the sample during quenching, as few data are available for ΔH^{vit}, the magnitude of errors arising from this source have not been evaluated.

2.5.2 Heat transfer in slags

Heat is transferred through slags by a variety of mechanisms which include convection, radiation and various thermal conduction processes, viz. thermal ("phonon") conductivity, (k_c), electronic conductivity (k_{el}) and radiation conductivity (k_R). Methods for estimating the various physical properties involved in these processes are considered below.

2.5.3 Thermal conductivity (k)

Heat is transferred by phonons which are quanta of energy associated with each mode of vibration in the sample. Scattering of the phonons causes a decrease in the thermal conductivity and thus the conductivity is sensitive to the structure of the slag and consequently those factors affecting structure such as the basicity. Despite this structure dependence, estimation rules based on the additivity principle (equation 18)) have been proposed[41,42]. Other models have been developed which relate k to the volume concentration of the oxides in the

glass[43] and a third approach[44] relates the thermal resistance (1/k) to $x_i m_i$ where m_i is the effectiveness of modifier of component i in scattering phonons.

$$k \doteq (\%i)k_i + (\%j)k_j + \ldots\ldots \qquad 18)$$

However in coal slags there is frequently an appreciable degree of crystallization and the thermal conductivity value varies with the thermal history of the sample[45], and consequently rules developed for glasses may not apply well for coal slags. Recent work carried out on a large number of silicate slags[46] indicated that the thermal diffusivity, a, ($a=k/C_p.\rho$) of various slags was independent of both composition and temperature in the range (500-1300 K) with a(glass) = $4.5(\pm 0.5)\times10^{-7}$ m^2s^{-1} ; a(cryst) = 6×10^{-7} m^2s^{-1} and a(liq) $\cong$ a(glass). These data are consistent with values reported for coal slags[45] and steelmaking slags[47]. However, the values reported by Nauman et al[48] indicate that at high FeO contents (> 20%) both k and a increase with increasing FeO content ($k = 0.8 + 1.7\times10^{-2}$(% FeO) $Wm^{-1}K^{-1}$).

2.5.4 Absorption coefficient (α)

Radiation conductivity (k_R) can be the predominant mode of heat transfer through semi-transport media like glasses and the magnitude of k_R is determined largely by the optical properties such as the absorption coefficient (α) and the refractive index (n). The value of k_R increases as the slag thickness (d) is increased until a critical point is attained, above this point k_R remains constant and independent of thickness. Above this critical point the slag is said to be "optically thick, this condition applies when $\alpha d > 3.5$ and values of k_R can be calculated using equation 19), where σ is the Stefan-Boltzmann constant.

$$k_R = \frac{16\, n^2 T^3 \sigma}{3\,\alpha} \qquad 19)$$

No formulae exist for the calculation of k_R for optically thin conditions. The absorption coefficient (α) is markedly dependent upon the amounts of Fe^{2+} and Mn^{2+} present in the slag[49]; levels for FeO < 5% the following relationship can be applied, $\alpha(cm^{-1}) = 11(\%FeO)$. Temperature appears to have little effect on the absorption coefficient of glasses but the absorption coefficients of magmas have been reported to increase with increasing temperature[50,51]. Crystallization of the slag will result in a large increase in the absorption (or extinction) coefficient which could reduce k_R to virtually zero.

The importance of radiation conduction in heat transfer through coal slags can readily be demonstrated, for a slag with an appreciable FeO content (7%) Fine et al[47] recorded $\alpha \cong 50$ cm^{-1} at 298 K using this value and equation 19), a value of $k_R = 0.9$ $Wm^{-1}K^{-1}$ can be calculated for 1873 K. As $k_c \cong 1.5$ $Wm^{-1}K^{-1}$ it can be seen that about 40% of the heat is transferred by radiation conduction.

2.5.5 Emissivity (ε)

The emissivity (ε) of a semi-transparent medium, is a bulk property cf. ε(metal) which is solely dependent upon the surface. In the basis of the spectral and total normal emissivity data reported for coal and metallurgical slags the value $\varepsilon = 0.8 \pm 0.1$ can be adopted for coal slags in the range (1100 - 1900 K).

CONCLUSIONS

1) Estimation procedures based on the chemical composition of the slag have now been developed for the prediction of viscosity, surface tension, density and heat capacity.
2) The accuracy of these estimation routines for some physical properties (eg viscosity, surface tension) can be improved when more reliable experimental data become available.
3) The distribution of iron in the slag betwen free Fe, FeO and Fe_2O_3 has a pronounced effect of virtually all the physical properties and it is recommended that experimental data for the properties of the slag should always be accompanied by values for the distribution of iron.
4) The development of models for the prediction of some physical properties (thermal conductivities, absorption coefficient) is restricted by the limited amount of experimental data available.

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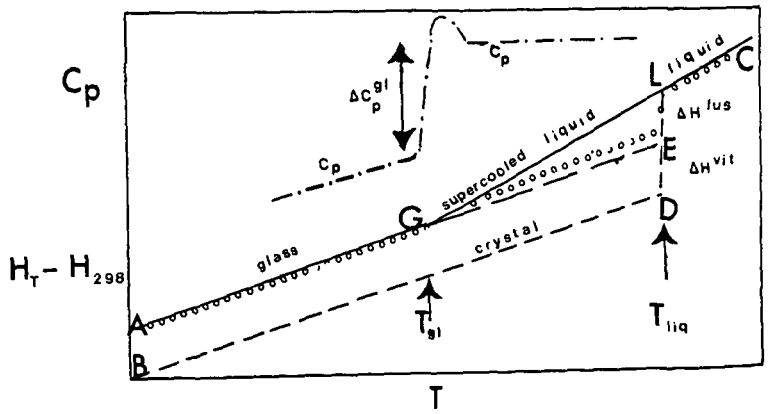
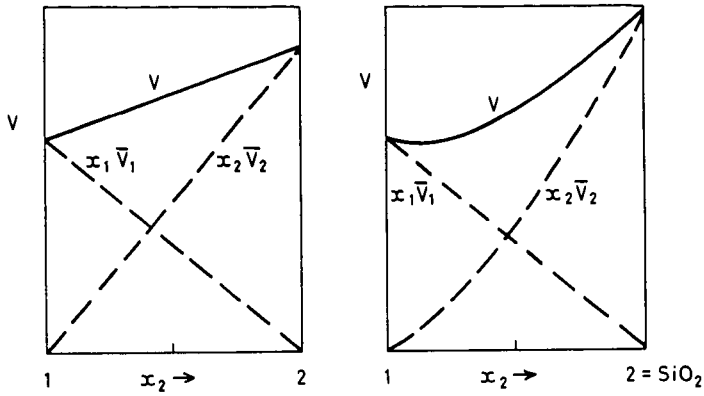
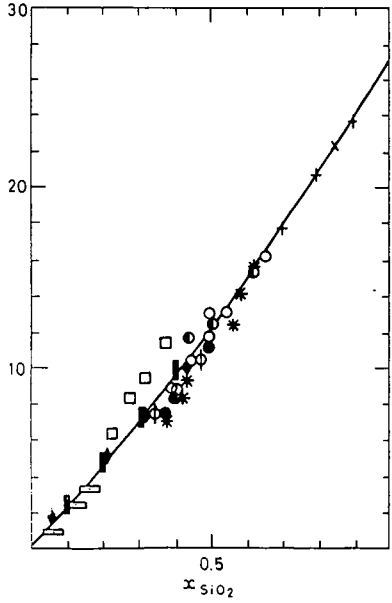


Figure 6 Cp and $(H_T - H_{298})$ for glassy and crystalline phases of a slag; O, indicates typical drop calorimetry results.



Figures 1a The molar volume of binary slag system as a function of composition and 1b. showing the individual $x_i\bar{V}_i$ contributions.



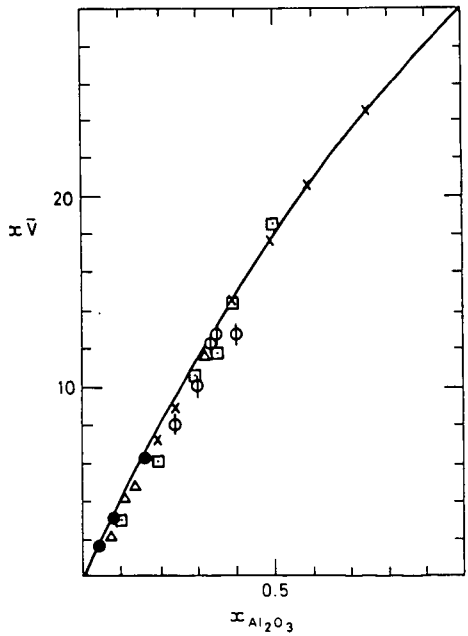


Figure 2. $x\bar{V}(SiO_2)$ as a function of $x(SiO_2)$

Figure 3. $x\bar{V}(Al_2O_3)$ as a function of $x(Al_2O_3)$

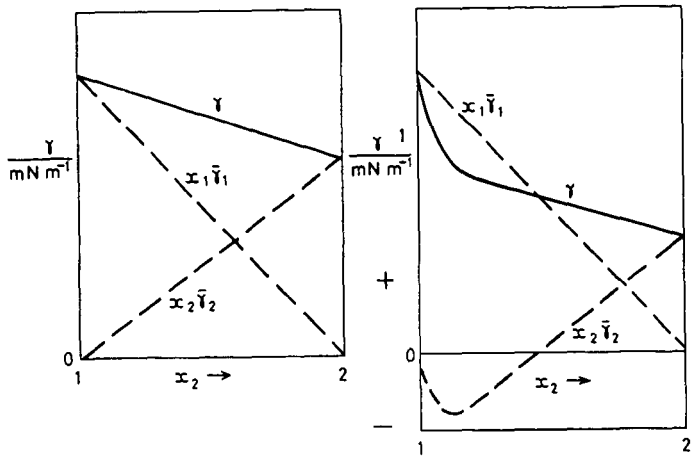


Figure 4a. The compositional dependence of , $x_1\bar{\gamma}_1$ and $x_2\bar{\gamma}_2$ for a binary slag system with non-surface active constituents

Figure 4b. with one surface active constituent (2).

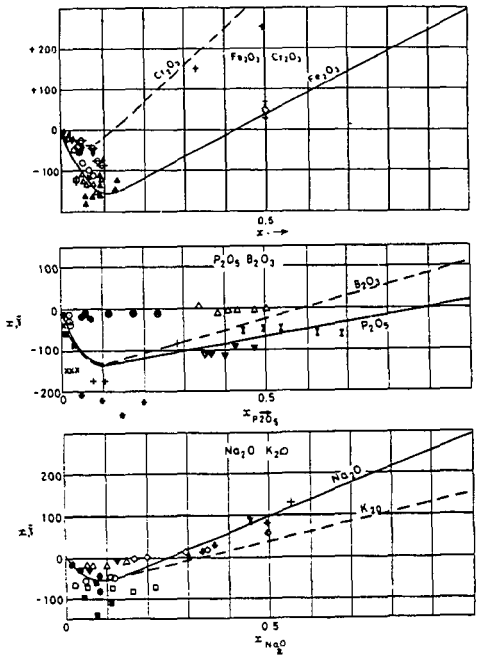


Figure 5 The compositional dependence of $x_i\bar{\gamma}_i$ for various surface-active constituents.