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A THEORETICAL MODEL FOR IONIC MELTS AND ITS APPLICATION IN THE ESTIMATION OF SLAG VISCOSITIES

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Synopsis:

A theoretical model has been developed to calculate the viscosities in complex slag systems as well as in metallic melts. In the case of slag systems, a modified Temkin approach was adopted to represent the composition. The absolute reaction rate theory was employed to describe the viscous flow process. The model has been applied to some multicomponent systems. The calculated results indicate that the model can be successfully used in the estimation of the viscosities of melts at high temperatures.

Key words:

Viscosity, slag, ionic melt, modelling

Introduction:

An understanding of the mechanism of the metallurgical process phenomena and an optimization of the processes require access to accurate data of the physical properties of the systems involved. Among them, the most important property in the case of molten systems is viscosity , in view of its direct effect on the kinetic conditions of the processes. Although, the viscosity measurements that have been carried out in the case of slag systems are numerous, the data available in literature are still too few to meet the technological demands. This is particularly true in the case of complex slag systems, for which, experimental data are very often found to be available only for a few temperatures and cover small composition ranges. Process simulation models require extrapolation of the available viscosity data to relevant temperature and composition ranges. Carefully assessed viscosity data can be stored, with the help of a suitable theoretical model, as model parameters so that the values for relevant conditions can be calculated and even be retrieved on line.

Quite a few models have been developed to evaluate viscosities of pure liquids as well as solutions. These models could be classified into two categories, viz. models based on fundamental molecular approach and those that employ semi-theoretical procedure. The former type of theories are still under development and hardly meet the technological requirements of today. On the other hand, the semi-theoretical or empirical procedures seem to give somewhat satisfactory results [1-10]. Among such models for high temperature slag systems [6-10], the one proposed by McCauley and Apelian [6] is based on the Clausius-Clapeyron equation to describe the viscosity-temperature relationship for Newtonian liquids. These authors point out that the activation energy for viscous flow is a linear function of temperature only in a limited temperature range. They also found that the viscosity, in the case of casting fluxes, was strongly dependent on the ratio of the network forming ions to anions in the flux. Lanyi and Rosa [7], from their viscosity measurements of casting fluxes, suggested that at constant temperature, the flux viscosity was primarily dependent on the mole fractions of SiO_2 and Al_2O_3. Riboud et al [9] have made use of the relationship $\eta = T \cdot A \cdot \exp(B/T)$, where η = viscosity, T = temperature K, A and B are viscosity parameters both being functions of slag composition. A similar equation without the pre-exponent term was later proposed by Koyama et al. [10].

The present work aims at developing a self-consistent model, which enables, to a great extent, the computation of the viscosities of higher-order systems from simpler ones. A modified Temkin approach is employed to represent the composition.

Model:

Viscous flow in liquids can be regarded as a thermally activated rate process, in which an ion in the case of liquid slags or an atom in the case of metallic melts at a certain site in the liquid has to overcome an energy barrier to move to an adjacent vacant site. According to the absolute reaction rate theory proposed by Glasstone, Laidler and Eyring [11], the viscosity of viscous flow, η can be expressed by the following equation

$$\eta = \frac{hN}{V_m}\cdot\exp(\frac{\Delta G^*}{RT}) = \frac{hN\rho}{M}\cdot\exp(\frac{\Delta G^*}{RT}) \text{ -----(1)}$$

h: Planck's constant, N: Avagadro's number,
V_m: molar volume $=$(Density,ρ/Molecular weight M),
ΔG^*: Gibbs energy of activation per mole, calculated from experimental viscosity data using equation (1).

I. Unary system

For unary systems, equation (1) can be written as

$$\eta_i = \frac{hN\rho_i}{M_i}\cdot\exp(\frac{\Delta G_i^*}{RT}) \text{ ---------------------------------(2)}$$

The subscript denotes the pure liquid i. From the density of a pure liquid, usually expressed as a linear function of temperature, the pre-exponent term in equation (2) can be calculated. The Gibbs energy of activation of liquid i is described by the type of equation

$$\Delta G_i^* = a + bT + cT\ln T + \ldots\ldots \text{ ------------------------(3)}$$

Parameters a, b and c in equation (3) could be optimized from available experimental data. It has been found that in almost all the pure oxide systems, it was sufficient to use the first two or three terms on the right side of equation (3) in order to get a satisfactory description of the viscosity.

II. High-order system

In view of the ionic nature of slag systems, the liquid slag is described by a modified Temkin approach [12], which consider the mixing of cations and anions within each of their subgroupings. The ionic solution can be represented by the formula

$$(C1,C2,...Ci,...Cn)_P(A1,A2,...Aj,...Am)_Q$$

where P and Q are the coefficients determined by stoichiometric considerations. C1, C2, Ci,..., Cn represent different cations, and A1, A2, Aj,..., Am different anions. The ionic fraction of cation Ci within the cation grouping is defined as

$$y_{Ci} = \frac{N_{Ci}}{\sum N_C} \text{ -----------------------------(4)}$$

In equation (4), N represents the number of the ions and the summation covers all the cations in the system. In a similar way the ionic fraction of anion Aj within the anion grouping is defined as

$$y_{Aj} = \frac{N_{Aj}}{\sum N_A} \text{ -----------------------------(5)}$$

It is to be pointed out that the values of P and Q vary with composition so that the electrical charge neutrality of the system is maintained. Furthermore, at the terminal composition corresponding to one of the pure compounds, $Ci_{vi}Aj_{vj}$, the stoichiometric coefficients will be $p = vi$, and $Q = vj$.

In view of the presence of complex and polymeric ions, most of the slag models have to consider each of the ionic species present in the solution. This complication is avoided in the present model by considering the disintegration of complex ions to basic entities. For example, $[SiO_4]^{-4}$ ion could be considered to consist of Si^{+4} and 4 O^{-2}. The model representation in such a case may not be in agreement with the physical description of the ionic melt. However, the deviations from reality are compensated mathematically in the model.

In the use of equation (1), the molecular weight of the complex slag can be calculated by the equation

$$M = \sum X_{ij} \cdot M_{ij} \text{ ----------------------------- } (6)$$

where, X_{ij} represents the mole fraction of the component $Ci_{vi}Aj_{vj}$ in the solution, and M_{ij} is the molecular weight of the same. In a similar way, the density of the solution may be estimated, as a first approximation, by the relationship,

$$\rho = \sum X_{ij} \cdot \rho_{ij} \text{ ----------------------------- } (7)$$

ρ_{ij} is the density of the pure component $Ci_{vi}Aj_{vj}$ in liquid state.

The Gibbs energy of activation is expressed, in analogy with integral molar Gibbs energies of solutions as

$$\Delta G^* = \sum \sum y_i y_j \Delta G^*_{ij} - K \cdot T + \Delta^E G^* \text{ ------- } (8)$$

The first term on the right hand side of the above equation represents the "linear" variation of the Gibbs energy of activation from the pure components in the absence of interaction between different components. In this term, i and j denote cation grouping and anion grouping respectively; ΔG_{ij}^* is the Gibbs energy of activation of pure component $Ci_{vi}Aj_{vj}$ in liquid state.

The second term $K \cdot T$ has been introduced in order to take into account the effect of compositional variations on non-linear behaviour. The general expression for K used in the present work is

$$K = -R(P\sum y_i \cdot \ln y_i + Q\sum y_j \cdot \ln y_j) \text{ ---------- } (9)$$

which is identical with Temkin's expression for ideal entropy of mixing in ionic melts.

The third term in equation (8) represents the part due to the mutual interaction between different species. This term is expressed as

$$\Delta^E G^* = (\sum\sum\sum y_{i1} y_{i2} y_j L_{i1,i2(j)} + \sum\sum\sum y_{j1} y_{j2} y_i L_{j1,j2(i)}) +$$

$$(\sum\sum\sum\sum y_{i1} y_{i2} y_{i3} y_j L_{i1,i2,i3(j)} + \sum\sum\sum\sum y_{j1} y_{j2} y_{j3} y_i L_{j1,j2,j3(i)}) + \dots \quad (10)$$

The first two terms in equation (10) represent the binary interactions between different species. The product in the first three-power summation stands for the interaction of different cations Ci1 and Ci2 when anion Aj is present. Similarly, The product under the second three-power summation represents the interaction of different anions Aj1 and Aj2 when cation Ci is present. The L parameters can be expressed as

$$L_{i1,i2(j)} = {}^{0}L + {}^{1}L(\, y_{i1} - y_{i2}\,) + {}^{2}L(\, y_{i1} - y_{i2}\,)^2 \text{-------------}(11)$$

and

$$L_{j1,j2(i)} = {}^{0}L + {}^{1}L(\, y_{j1} - y_{j2}\,) + {}^{2}L(\, y_{j1} - y_{j2}\,)^2 \text{-------------}(11')$$

with

$${}^{k}L = {}^{k}L_1 + {}^{k}L_2T \text{-------------------}(12)$$

where k stands for 0, 1 or 2.

In those cases where the complexity of the ions strongly affect the viscosity, the high-order interactions are introduced. The high-order interaction terms are given in the second pair of parentheses in equation (10). In the same way as binary interactions, while the product under the first four-power summation represents the three-cation interaction when anion Aj is present, the product under the second four-power summation denotes the three-anion interaction when cation Ci is present. The L parameters are expressed as

$$L_{i1,i2,i3(j)} = {}^{0}L + \sum {}^{1}L_m y_m + \sum {}^{2}L_m y_m^2 \text{---------}(13)$$

$$m = i1,\ i2$$

and

$$L_{j1,j2,j3(i)} = {}^{0}L + \sum {}^{1}L_n y_n + \sum {}^{2}L_n y_n^2 \text{---------}(13')$$

$$n = j1,\ j2$$

with

$${}^{k}L_m = {}^{k}L_{m,1} + {}^{k}L_{m,2}T + [\ {}^{k}L_{m,3}T\ln T] \text{-------------------}(14)$$

and

$${}^{k}L_n = {}^{k}L_{n,1} + {}^{k}L_{n,2}T + [\ {}^{k}L_{n,3}T\ln T] \text{-------------------}(14')$$

The logarithmic term in brackets in equations (14) as well as (14') are to be used when the temperature range is very large.

Application

The model has been applied to various systems from unary to quaternary slags. In general, the experimental data can be very well fitted by the present model. Figure 1 presents the calculated iso-viscosity curves in the CaO-SiO$_2$ system using the experimental data reported by Urbain et al [13] and Bockris et al [14].

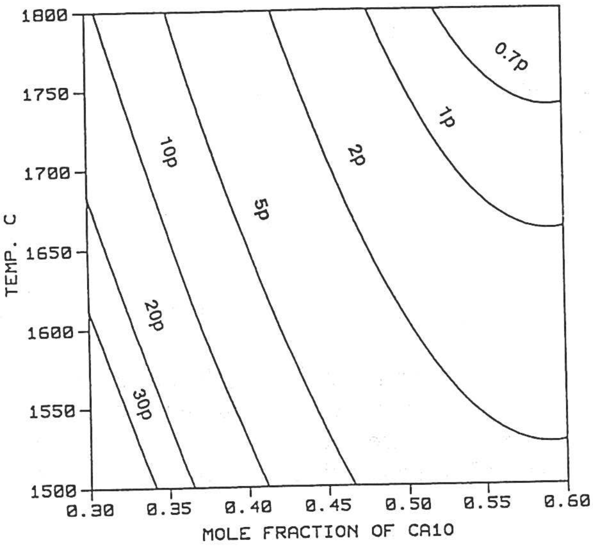

Figure 1 The calculated iso-viscosity curves in the CaO-SiO$_2$ system

Figure 2 shows the viscosity as a function of temperature in the Al$_2$O$_3$-CaO-SiO$_2$ system at a given composition of $X_{Al2O3}=0.05$ and $X_{CaO}=0.25$. This system was assessed in the present work using the experimental data obtained by Machin et al [15] as well as Kozakevitch [16] in the temperature range 1423-2273 K. But the experimental values in the temperature range 1523-1723 K have been excluded in the model calculation. The viscosity values calculated using the model are compared with the reported experimental data [15] at 1623 K in Table I. The good agreement between the two sets of values demonstrates the reliability of the present model in the interpolation of the viscosity data.

The values for viscosity in the case of the quaternary system Al_2O_3-CaO-MgO-SiO_2 have been reported by Jakubeiner et al [17]. These values have been treated using the model in the present work. The iso-viscosity curves in the system for the section $X_{Al2O3}=0.06$ and $T=1673$ K are presented in Figure 3. The variation of the viscosity with the mole fraction of CaO at 1773 K, $X_{Al2O3}=0.10$ and $X_{MgO}=0.30$ has been shown in Figure 4. These figures illustrate the potentialities of the present model.

Table I A Comparison of the calculated viscosity values with the experimental data for the Al_2O_3-CaO-SiO_2 System

T (K)	X_{Al2O3}	X_{CaO}	Viscosity η (p) (Calculated)	ln(η) (Calculated)	ln(η) (experimental)
1623	.91416e-01	.44321e+00	.35542e+02	1.55	1.52
1623	.12500e+00	.39772e+00	.58659e+02	1.77	1.80
1623	.16035e+00	.34985e+00	.11797e+02	2.07	2.12
1623	.91754e-01	.38925e+00	.63541e+02	1.80	1.76
1623	.12548e+00	.34220e+00	.12691e+03	2.10	2.10
1623	.59893e-01	.38112e+00	.68172e+02	1.83	1.78
1623	.92096e-01	.33488e+00	.13804e+03	2.14	2.08
1623	.12596e+00	.28626e+00	.36628e+03	2.56	2.49
1623	.60111e-01	.32787e+00	.14870e+03	2.17	2.10
1623	.92440e-01	.28011e+00	.38771e+03	2.59	2.59
1623	.12644e+00	.22988e+00	.14335e+04	3.16	3.10
1623	.60331e-01	.27422e+00	.40559e+03	2.61	2.66
1623	.92786e-01	.22493e+00	.14595e+04	3.16	3.29
1623	.12693e+00	.17308e+00	.71451e+04	3.85	3.81
1623	.93135e-01	.16933e+00	.73278e+04	3.86	3.99
1623	.12742e+00	.11583e+00	.38196e+05	4.58	4.67

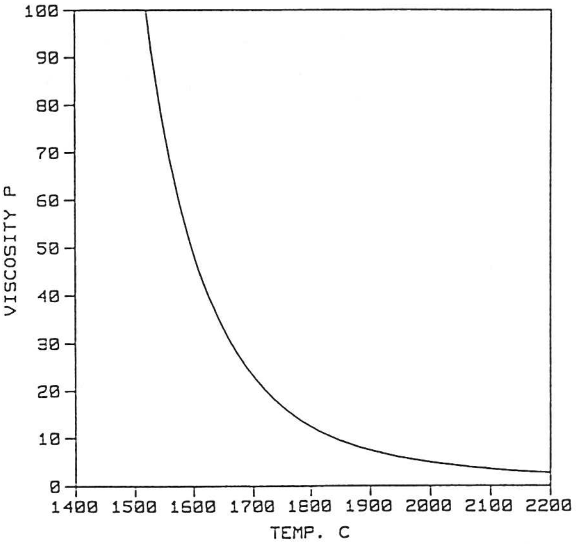

Figure 2 The calculated viscosity as a function of temperature in the Al_2O_3-CaO-SiO_2 system, $X_{Al2O3}=0.05$ and $X_{CaO}=0.25$

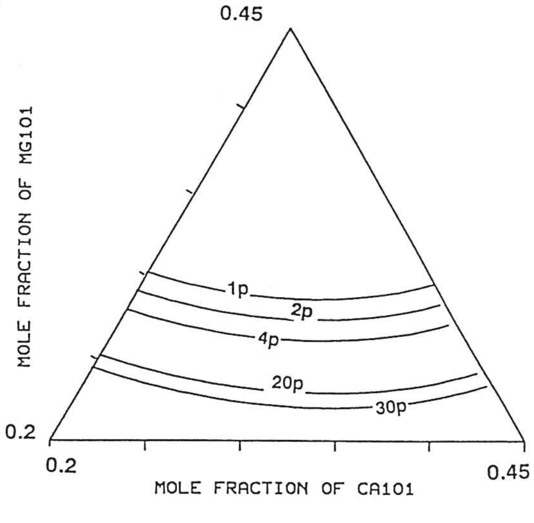

Figure 3 The calculated iso-viscosity curves in the Al_2O_3-CaO-MgO-SiO_2 system at $T=1673$ K and $X_{Al2O3}=0.06$

Discussion

The good agreement between the calculated results and the experimental data shown in Table I indicates that the present model can be used to interpolate or extrapolate the experimental viscosity data. This would be very helpful in reducing the heavy experimental work and the cost of the same. Even in the case of higher order systems, where no experimental data is available, the viscosity could be predicted, with certain amount of accuracy, by the present model using the information from the corresponding lower-order systems.

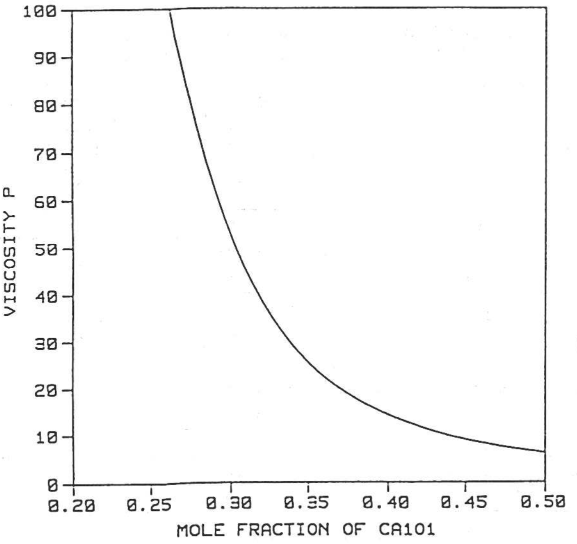

Figure 4 The calculated viscosity as a function of mole fraction of CaO in the Al_2O_3-CaO-MgO-SiO_2 system, T=1773 K, $X_{Al2O3}=0.10$ and $X_{MgO}=0.30$

The model has been developed in such way that both cation and anion groupings can accommodate a number of ionic species. However, at the present stage, the model has only been applied to systems with only one species, viz. O^{-2} ion, in the anion grouping. This is mainly due to the lack of the experimental data. It is hoped that the model can be tested for slags with more than one anion species, e.g. slags containing both oxides and fluorides, using the experimental results that are being generated in the department of Theoretical Metallurgy, KTH.

The model is also intended to introduce complex ions, such as SiO_4^{-4}, $Si_2O_7^{-6}$, as well as neutral species in the various ion groupings. However this would require the calculation of the y values using thermodynamic information. By using mole fractions instead of y terms in the representation of the composition, the model has been successfully employed for metallic melts.

Summary

A theoretical model has been developed to calculate the viscosities of melts at high temperatures. The viscous flow in liquid is described by the equation, $\eta = A\exp(\Delta G^*/RT)$. The Gibbs energy of activation, ΔG^* is considered to be a function of temperature as well as composition of the melt. In the case of slag systems, the composition is expressed by a modified Temkin approach. The model has been applied successfully to various systems from unary to quaternary slags.

Reference

1. P.K.Katti and M.M.Chaudhri: J. Chem. Eng. Data. 9(1964), p.442
2. R.Kalidas and G.S.Laddha: J. Chem. Eng. Data. 9(1964), p.142
3. S.C.Saxena: Chem. Phys. Letters, 19(1973), p.32
4. L.Grunberg and A.H.Nissan: Nature, 164(1949), p.799
5. A.S.Teja and P.Rice: Chem. Eng. Sci., 36(1981), p.7
6. W.L.McCauley and D.Apelian: Second International Symposium on Metallurgical Slags and Fluxes, p.924
7. M.D.Lanyi and C.J.Rosa: Metall. Trans. B,12B(1981), p.287
8. W.L.McCauley and D.Apelian: Canadian Metall. Quarterly, 20(1981), p.247
9. P.V.Riboud, Y.Roux, L.-D.Lucas and H.Gaye: (IRSID, Maizières-lès-Metz, Fr.), Fachber. Hüttenprax. Metallweiterverarb., 19(1981), p.859 (Eng.)
10. K.Koyama, Y.Nagano and T.Nakano: Design for chemical and physical properties of continuous casting powders, Nippon steel technical report No.34, July 1987
11. S.Glasstone, K.J.Laidler and H.Eyring: The Theory of Rate Process, McGraw-Hill, New York, 1941
12. M.Temkin: Acta Phys-Chim. 20(1945), p.411
13. G.Urbain, Y.Bottinga and P.Richet: Geochim. Cosmochim. Acta, 46(1982), p.1061
14. J.O.M.Bockris and D.C.Lowe: Proc. Royal Soc., London, Ser.A226(1954), p.423
15. J.S.Machin, T.B.Yee and D.C.Hanna: J. Am. Ceram. Soc., 35(1952), p.322
16. P.Kozakevitch: Rev. Metall., Paris, 57(1960), p.149
17. N.M.Jakubeiner, V.G.Nancinskij and L.A.Panjusin: Stal in Deutsch 8(1968), p.648