COUPLED IONIC DIFFUSION IN

MULTICOMPONENT SILICATE GLASSES

COUPLED IONIC DIFFUSION IN MULTICOMPONENT SILICATE GLASSES

by

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SCOPE AND CONTENTS:

A phenomenological scheme for ionic diffusion in multicomponent silicates based on self diffusion data and the Nernst-Planck equation has been formulated which is capable of predicting the concentration profiles of mobile ions in a diffusion couple with or without a fixed silicate anion step discontinuity at the boundary. It is demonstrated that the diffusion potential appearing within this formalism is due entirely to a distribution of self-generated dipoles and equivalently, that the well-known contradiction between the electroneutrality constraint on real charges and the non-zero field predicted within the phenomenological formalism vanishes when it is recognized that the charge to be entered into Poisson's equation is the dipole charge.

The reported experimental diffusion profiles in $K_2O-SrO-SiO_2$ and $Na_2O-CaO-SiO_2$ glass couples have been compared with the predictions of the model and the agreement

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has been found to be good. Diffusion couples in the $K_2O-CaO-SiO_2$ system were investigated by microprobe analysis and the resulting concentration profiles were also found to be in good agreement with predictions. It has been demonstrated that while the quasi-binary (i.e., immobile silicate anions) approximation is satisfactory for the $K_2O-SrO-SiO_2$ system at low temperatures, it is unsatisfactory for all other systems considered at low and high temperatures.

An extension of the phenomenological scheme to glassmetal diffusion couples with interfacial electrochemical reactions is given in Appendix A.

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CHAPTER I

INTRODUCTION

This study of silicate glasses was undertaken to increase our understanding of the diffusion interactions and mechanisms, the structure of silicates and the control of technologically interesting processes such as slag-metal reactions, glass-metal junctions and ion-exchangers.

Despite their great theoretical and technological importance, studies of diffusion in silicates have not been as extensive nor as precise as those in metallic systems. While there exists a considerable amount of data on self or tracer diffusion in glasses for the ions H, Li, Na, K, Rb, Cs, Sr, Ca, O, Si, Pb and Al, these have not yet been widely used in the analysis of diffusion in multicomponent silicates. We note, however, that Cooper ^(1a) has pioneered in this direction by developing a phenomenological scheme ("the mobility model") in which the coefficients of the equations for multicomponent silicate diffusion are expressed in terms of the independently measured tracer diffusion coefficients of the mobile species. This model has been further developed by Varshneya and Cooper ^(1b). Lu and Jin ⁽²⁾ have used similar equations from irreversible

thermodynamics to analyze a particular example of diffusion in glasses.

It was anticipated that an extension of this approach would lead to better understanding of the diffusion potential and of the electrical coupling between the diffusive fluxes in a silicate system. From such understanding of diffusion processes in silicates, and with the considerable wealth of knowledge already existing in the literature on diffusion processes in metallic systems and on reaction kinetics, we predict that early inroads will be made into the complex and important problem of analysis of the kinetics of slag-metal and glass-metal systems.

CHAPTER II

THE STRUCTURE OF SILICATE MELTS - A LITERATURE REVIEW

2.1 Vitreous Silica

The study of the structure of vitreous silica, ${\rm SiO}_2$, is fundamental to the understanding of silicates since ${\rm SiO}_2$ is the basic constituent of the multicomponent silicates. The starting point in this study can be traced to Zachariasen's ⁽³⁾ postulate of a continuous random threedimensional network of ${\rm SiO}_4$ tetrahedra formed by union of these tetrahedra at their corners.

Each tetrahedron (Fig. 1) has four oxygen atoms at the corners covalently bonded to silicon at the centre. Each oxygen is thus on the average shared by two tetrahedra, with large interstices between networks. Bond energies (energies required for dissociation) of the Si-O bonds are about 105 k.cal/mole ⁽⁴⁾ so that there are very few thermally activated bond ruptures. A structure with such rigid bonds is consistent with high viscosities of silica melts, the enormous increase in the viscosities of silica melts during cooling and the difficulty of achieving crystallization at normal cooling rates.



O atom

Fig. 1: Two SiO₄ tetrahedra with a common oxygen bond

This random network model of fused silica has been supported by X-ray studies, notably those of Warren and Loring ^(5a), Warren ^(5b), Biscoe and Warren ^(5c) and Mackenzie and White ^(6a). These studies yield the following interatomic distances:

Si-O = 1.60
$$\pm$$
 0.05 A°
Si-Si = 3.0 \pm 0.05 A°
O-O = 2.65 \pm 0.05 A°
Mackenzie and White ^(6a)

with a distribution of the Si-O-Si bond angle between 120° and 180° and a maximum of the distribution at about 144°.

Many properties of vitreous silica calculated from the random network model are in agreement with experiment. For example, Bell and Dean (7) have shown that the spectrum of atomic vibrations as measured by infrared absorption, Raman emission and inelastic neutron scattering is consistent with the random network model. However, it has been suggested that rather than a completely random distribution of the tetrahedra, there may be some short range order over a few tetrahedra. This short range order is the basis of the "crystallite theory" (8) of silica in which very small crystalline regions are supposed to be connected by disordered materials. However, experiments imply that such ordered regions are not very large (generally less than 100 A° long) so the random network model of vitreous silica has been accepted by most workers in this field.

2.2 Silicate Melts

2.2.1 Comments on the various models

The Zachariasen random network model ⁽³⁾ of vitreous silica is fundamental to nearly all the models of silicate structure; indeed all these models consider the effect of metal oxide addition on the silica structure. Although there are inumerable theories and models of the silicate structure, we shall review only those that have been instrumental in furthering our understanding.

Nearly all the models are qualitative, and the few that attempt to be quantitative are based on weak assumptions which limit their applicability to narrow ranges of composition (e.g., Toop and Samis (17), and Masson (21)). All the models are speculative and no direct confirmation has been obtained with such techniques as X-ray diffraction and/or chromatography. The only supporting evidence is, therefore, indirect. The one feature of these melts which has been firmly established is their ionic nature. This has been achieved through measurements of electrical conductivity (9).

2.2.2 The random network model (3,4,6b)

Starting from the Zachariasen random network model of fused silica, the approach to silicate structure has been to consider the chemical effect of addition of a metal oxide. The addition of certain metal oxides (network modifiers) such as Na₂O to the fused pure silica is conjectured to result in a break-up (depolymerisation) of the 3-dimensional network by a bond rupture of the type:

(see also Fig. 2) with the metal ions located in the interstices of the network near the ionized (non-bridging) oxygen, forming dipoles (Na⁺ O⁻) whose moments depend on the cation radius. Myuller ⁽¹⁰⁾ postulates that the interaction of the M^+O^- dipoles thus formed leads to the formation of quadrupoles (Fig. 3) and structural groups of the form $SiO_{3/2}O^-$ Na⁺. The bond strengths between the dipoles, i.e., between the modifying cation and its associated oxygen (non-bridging oxygen) are much lower than between the Si and O, the bond between the former being ionic whereas the latter is mainly covalent.

Zachariasen ^(3,4,6b) divided all cations that participate in glass formation into three groups:

- Network formers, such as Si, B and P. These have coordination numbers 3 or 4.
- (2) Network modifiers, such as Na, K, Li, Sr, Cs, Ca and Ba which have coordination numbers of 6.







Fig. 3: Schematic depiction of a covalently bonded chain (-SiO_{4/2}O_{2/2})_n ..., cross-linked with neighbouring chains by associated dipoles M⁺O_{1/2}, in alkali silicate glasses. The dashed lines outline the structural units. (a) [M⁺₂O_{2/2}SiO_{4/2}]; (b) [SiO_{4/2}]; (c) [M⁺₂O_{2/2}] (after Myuller ⁽¹⁰⁾)

(3) Intermediates, such as Al, Pb, Fe, Ti, Mg and Zn with coordination numbers of 4 to 6. These can act in the same way as (1) or (2) depending on their concentration in the glass.

It has been shown by Ermolenko ⁽¹¹⁾ that a rigid classification of cations into network formers and modifiers is not possible since certain metals generally regarded as network modifiers (e.g., Ca, Ba and Cr) at low concentrations become network formers at high concentrations. We note also that H^+ also acts as a network modifier so that in fused silica containing H_2O (water) impurities depolymerisation reactions lead to the formation of (OH)⁻ anions.

The random network model assumes that the network splitting and the incorporation of the modifier cations into the interstices of the network take place in a completely random manner (Fig. 4). Thus as the metal oxide content of the silicate melt is increased the bond rupture continues statistically until at the orthosilicate composition, corresponding to 66 mole% metal oxide, the network is completely broken down and discrete $\operatorname{SiO}_4^{4-}$ anions exist with few free oxygen ions. This manifests itself as a lowering of the viscosity as the metal oxide content of the melt increases. Above 66 mole% metal oxide, the network concept loses its meaning since no network exists in the system; only the metal cations and the $\operatorname{SiO}_4^{4-}$ and O^{2-} anions can be imagined to exist.



Fig. 4: Randomly distributed modifier cations in a random 3-Dimensional network of an oxide glass

The entities existing at different metal oxide contents of the melt are summarized as follows:

Pure silica

- Continuous 3-D network of SiO_4 : tetrahedra with a small degree of thermal bond-breaking. 0-33 mole% metal oxide: Essentially a 3-D network of
 - SiO_A tetrahedra with the number of broken bonds equal to the number of added O atoms from M_2O ; end of 3-D boundary at 33%. "Infinite" 2-D sheets of SiO, 33 mole% metal oxide: tetrahedra; M⁺ ions and O⁻ ions between sheets. Region of sheets and some chains of tetrahedra.

33-50 mole% metal oxide:

50 mole% metal oxide: Chains of infinite length. 50-60 mole% metal oxide: Chains of decreasing length. sio_{4}^{4-} . 66 mole% metal oxide:

The structural changes envisaged above by this model are not all compatible with experimental results. For example, on the basis of this model, one would expect very large changes in the heat of activation for viscous flow in the composition range of 33 to 66 mole% metal oxide since the size and shape of the kinetic unit (the jumping entities)

is supposed to undergo a radical change - sheets are broken (12)into chains and discrete ions. Yet the observed change in the heat of activation over this range is only 25%. On the other hand while the observed change in the energy of activation between the composition 0-10% metal oxide is very dramatic (a change of about 200%), with an abrupt change around the 10% metal oxide (Fig. 5), the network model fails to predict such changes. Similar changes were also observed in other physical properties of binary silicate melts such as density and thermal expansivity (13,14) (Fig. 6). Thus it appears that the random network theory, while providing a good basis for an understanding of the fused silica structure, is only extendable to binary silicates containing less than about 10 mole% metal oxide.

The fact that one can visualise an infinite number of ways of linking together SiO_4 tetrahedra has led to a number of alternate models for the binary silicate melts. In most of these models the central theme concerns the arrangements of the SiO_4 tetrahedra which give predictions consistent with experimental results.

Fig. 5: The variation of the energy of activation for viscous flow in a binary Na₂O-SiO₂ melt as a function of the mole% Na₂O (after Bockris et al.⁽¹²⁾)



Fig. 6: The sharp change in the expansivity of binary silicate melts around the 10 mole% of M₂O composition: (Δ) K₂O-SiO₂; (Ο) Na₂O-SiO₂; (Π) Li₂O-SiO₂; (∇) SiO₂ (after Bockris et al. ⁽¹⁴⁾)

2.2.3 Discrete polyanion models

2.2.3.1 The Bockris, Mackenzie and Kitchener model (4,6b,12)

To explain the abrupt changes of the physical properties of silicates in the composition interval of 10-20 mole% metal oxide, Bockris et al. (4,6b,12) postulated the presence of discrete polyions such as $(Si_3O_9)^{6-}$ and $(Si_4O_{12})^{8-}$ in silicate melts in place of the 3-D network and infinite chains of the random network model. The existence of these anions was suggested by the fact that certain minerals such as wollastonite, CaSiO₃ and pyrophyllite, $Al_2Si_4O_{10}(OH)_2$ are known to contain $Si_6O_9^{6-}$ and $Si_4O_{12}^{8-}$.

Starting from the orthosilicate composition (66 mole% metal oxide), it is conjectured in this model that the reduction of the metal oxide content of the binary silicate melt leads to a series of polymerisations of the tetrahedral sio_4^{4-} monomers. For example, the dimer $si_2o_7^{6-}$ will be obtained by:

 $sio_4^{4-} + sio_4^{4-} \rightarrow {}^{3-}o_3si-O-sio_3^{3-} + o^{2-}$.

As the metal oxide content is progressively reduced, the next silicate entity after the dimer will be the trimer

$$^{3}\circ_{3}si-o-sio_{3}^{3-} + sio_{4}^{4-} \rightarrow ^{3}\circ_{3}si-o-si-o-sio_{3}^{3-} + o^{2-}$$

and so on, with polymers of the general formula $Si_n O_{3n+1}^{(2n+2)}$ appearing. This general formula for linear chains was noted to be inapplicable near 50 mole% metal oxide and below, since the formula diverges:

$$\frac{O}{Si} = 3$$
 when $\frac{3n+1}{n} = 3$

i.e., when $n \rightarrow \infty$,

which implies infinite chains at the exact composition, and becomes meaningless for <50 mole% metal oxide (i.e.,

$$\frac{3n+1}{n} < 3$$

for n an integer).

On the basis of experimental results, Bockris et al. conjectured that ring anions would be formed at about 50 mole% metal oxide by a linking up of network anion chains. Further structural changes between 50 and 30 mole% metal oxide could then be understood on the basis of these $\text{Si}_30_9^{6^-}$ and $\text{Si}_40_{12}^{8^-}$ ring systems. At 33 mole% metal oxide composition polymers $\text{Si}_60_{15}^{6^-}$ and $\text{Si}_80_{20}^{8^-}$, postulated as arising from dimerisation of the ring anions $\text{Si}_30_9^{6^-}$ and $\text{Si}_40_{12}^{8^-}$, were conjectured to exist. As the metal oxide content is then continuously reduced, further polymerisation of the rings is presumed; thus at 25 mole% metal oxide, the six-membered ring, having the formula $\text{Si}_9 \text{O}_{21}^{6-}$ and consisting of three rings polymerized together is generated.

Ring stability was expected to decrease with the increase of size corresponding to the increasing proportion of SiO₂. The silicate polyanions which correspond to compositions near the 10 mole% composition are so large that they become unstable and rearrangement to the random 3-D network of silica occurs with the physical properties of silicate melts undergoing abrupt changes.

The various silicate entities postulated by the model at different silicate compositions are illustrated in Fig. 7, and summarised as follows:

Pure silica

: Continuous 3-D networks of SiO₄ tetrahedra with some thermal bondbreaking and a fraction of SiO₂ molecules.

0-10 mole% metal oxide : A SiO₄ network with the number of broken bonds approximately equal to number of added O atoms (from the metal oxide), having a fraction of SiO₄ entities and radicals containing M⁺.
10-33 mole% metal oxide : Discrete silicate polyanions

based on a six-membered ring $Si_60_{15}^{6-}$.


33-55 mole% metal oxide : A mixture of discrete polyanions
based on
$$\text{Si}_30_9^{6-}$$
 and $\text{Si}_60_{15}^{6-}$ or
 $\text{Si}_40_{12}^{8-}$ and $\text{Si}_80_{20}^{8-}$.
55-66 mole% metal oxide : Chains of general form $\text{Si}_n0_{3n+1}^{(2n+2)-}$
such as $\text{Si}_20_7^{6-}$.
66-100 mole% metal oxide: Si_4^{4-} and 0^{2-} anions.

Although this model can rationalise the abrupt changes in the physical properties of silicate melts at 10 mole% metal oxide composition there is no known theoretical reason why a particular anion entity must exist at any composition (except perhaps the SiO_4^{4-} at the orthosilicate composition). Furthermore, the model cannot account for such phenomena as phase separation or the results of electron microscope studies ⁽¹⁵⁾ of the pores and extracts obtained by acid leaching* of alkali silicate glasses which showed extensive microheterogeneity of structure. The size of regions of heterogeneity ranged from 10 to over 1000 A°, and was found to depend on (1) heat

The leaching process is essentially an ion-exchange process, and involves the exchange of the alkali-metal ion by H⁺, thus:

 $-Si-O^{-}Na^{+} + H^{+} \rightarrow -Si-O^{-}H^{+} + Na^{+}$.

Thus sodium disilicate for example goes to disilicic acid $H_2Si_2O_5$.

treatment, (2) concentration of metal oxide, (3) field strength of the modifier cation, and (4) method of glass preparation.

Despite its weakness, the discrete-polyanion model of Bockris and co-workers was a major advance over the network model in providing a more consistent qualitative account of the observed changes in the physical properties of silicate melts; and indeed the silicate entities suggested are based on the results of the structural analyses of certain mineral silicates.

2.2.3.2 The Bockris, Tomlinson and White model - the "iceberg" model (4,6b,14)

To account for the microheterogeneity of structure and phase separation, Bockris et al. (4,6b,14) proposed that in the region of 12-33 mole% metal oxide, the discrete silicate polyanions based on a six-membered ring Si₆O⁶⁻₁₅ should predominate (as postulated in the discrete polyanion model of Bockris, Mackenzie and Kitchener) but with some frozen-in 3-D random network structure in the form of "icebergs" or "islets" with the composition of fused silica.

The "icebergs" were thought to be similar to clusters that occur in liquid water, and the submicroscopic networks were pictured as continually breaking down and reforming. Microphase regions (with the structure corresponding to that of 33 mole% metal oxide silicate melt) occur in the form of thin films separating the silica-rich icebergs, thus allowing for the possibility of phase separation of the liquid into two phases - one rich in SiO₂ and the other in the metal oxide.

This proposed model seems to be in line with Myuller's^(10,16) postulate that glass formation is analogous to the processes taking place when polar substances dissolve in nonpolar solvents: dipoles are drawn together by electrostatic forces and tend to unite with the formation of associated polar groups in a nonpolar medium, especially in the concentration range corresponding to 10-33 mole% metal oxide as considered by this model.

From 33 mole% metal oxide and above, the iceberg model becomes essentially identical with the model of Bockris, Mackenzie and Kitchener discussed earlier.

2.2.3.3 The Toop and Samis model (17a,17b)

Toop and Samis ⁽¹⁷⁾ made an attempt to determine the most probable number of discrete silicate anions in any binary silicate composition in terms of an equilibrium constant involving various forms of oxygen (singly bonded, doubly bonded and free oxygen) in the melt.

The basic assumption made by the authors was that any equilibrium polymerisation scheme should not involve

specific silicate ions, since the reaction via which equilibrium is established should be the same for all binary silicate compositions. They proposed that the equivalent reaction between all three forms of oxygen in the melt, i.e., bridging oxygen 0^{0} , non-bridging oxygen 0^{-} , and free oxygen ions 0^{2-} , given by Fincham and Richardson ⁽¹⁸⁾ as:

$$20^{-} \neq 0^{0} + 0^{2-}$$
 (2.1)

was the overall equivalent equilibrium reaction occuring when any silicate anions polymerise to form higher polymers plus oxygen ions. Therefore, according to them, the degree of polymerisation in silicate melts would be given by the equilibrium constant k for the reaction (2.1).

The equilibrium constant k from Eq. (2.1) was written as

$$k = \frac{(0^0) (0^{2^-})}{(0^-)^2}$$
(2.2)

and was shown to be characterized only by the cations present in the melt at a given temperature and to be a measure of the extent of polymerisation in a silicate melt. Table I gives the k values obtained for a number of binary melts.

From material and charge balances; (0^{2-}) , (0^{-}) and (0^{0}) were expressed in terms of moles of silica, N_{SiO_2} , and since for a given k Eq. (2.2) could be solved yielding the

TABLE I

VALUES OF EQUILIBRIUM POLYMERISATION CONSTANT & FOR VARIOUS BINARY SILICATES (AFTER TOOP AND SAMIS ⁽¹⁷⁾)

SYSTEM	k	TEMPERATURE		
		OF MILLI		
Cu20-Si02	0.35	1100°C		
FeO-SiO ₂	0.17	1600°C		
ZnO-SiO2	0.06	1300°C		
PbO-SiO2	0.04	1100°C		
CaO-SiO,	0.0017	1600°C		

number of free oxygen ions $(0^{2^{-}})$, doubly bonded oxygen atoms (0^{0}) and singly bonded oxygen atoms (0^{-}) per mole of binary silicate melts as a function of $N_{Si0_{2}}$, it was argued that the discrete silicate anions were not needed.

The reaction between silica and metal oxide in Eq. (2.1) can be rewritten as

$$0^{2-} + 0^{0} \rightarrow 20^{-}$$
 (2.3)

and the free energy change ${\rm \Delta G}^0$ as

$$\Delta G^0 = - RT \ln \frac{1}{k} = RT \ln k . \qquad (2.4)$$

Since the actual number of moles of oxygen ions which have reacted in the melt is 1/2 (0⁻), the free energy change per mole of liquid silicate formed in Eq. (2.3) is, in fact,

$$\Delta G^{\text{mix}} = \frac{(O^{-})}{2} \text{ RT In k}$$
(2.5)

Toop and Samis also derived the integral free energies of mixing from the Gibbs-Duhem equation and by fitting the calculated free energy curves to the experimentally determined curves, the values of k were obtained for a number of binary silicate melts. From a knowledge of (0^0) , (0^-) , (0^{2-}) and k, and using ternary phase diagrams, they arranged silicate anions in a complex polymerisation pattern assuming that Si is tetrahedrally coordinated with four oxygen atoms. Figure 8 gives their plot of the proportion of 0^- in the most probable silicate anions present in a binary melt. The following example based on Fig. 8 was given for a binary silicate melt (k = 0.005) containing 0.63 moles of SiO₂. The silicate anions present were proposed as consisting of double-ring anions containing 8 to 10 silicon atoms per ion, i.e., $Si_80_{20}^{8-}$ or $Si_{10}0_{25}^{10-}$ with some single-ring anions, possibly $Si_{12}0_{28}^{8-}$ to $Si_{15}0_{15}^{10-}$. The probable number of these silicate anions present was given as 0.07 mole/mole of slag.

The problem with this model is that it is essentially a curve fitting scheme, and its basic assumption that equilibrium reactions should be the same over the entire binary silicate compositions is hard to justify. However, it was one of the first attempts at predicting the fraction of the discrete anions in binary silicate melts.

2.2.3.4 The Flood and Knapp model (19)

In considering the usual depolymerisation reaction resulting from the addition of alkali oxides to silica, Flood and Knapp ⁽¹⁹⁾ showed that the activity data for PbO



Fig. 8: Plot of the proportion of single bonded oxygen atoms in the most probable or mean silicate anions present vs the number of silicon atoms per ion for various values of N_{SiO2} and k (after Toop and Samis ⁽¹⁷⁾)

determined by Richardson and Webb ⁽²⁰⁾ would agree with their calculated values for the activity of PbO if the PbO-SiO₂ melts behave as ideal mixtures of certain specific anionic species such as O^{2-} , SiO_4^{4-} , $(SiO_3)_3^{6-}$, $(SiO_{2.5})_6^{6-}$. The relative amounts of these anions were determined by considering the equilibria:

 $(\text{SiO}_{2.5})_{6}^{6-} + 90^{2-} \neq 2(\text{SiO}_{3})_{3}^{6-} + 60^{2-} \neq 6\text{SiO}_{4}^{4-}$. (2.6)

Unlike Toop and Samis ⁽¹⁷⁾, Flood and Knapp assumed that the equilibrium constant would be a function of concentration and so proposed three equilibrium constants, one for each of the composition ranges considered. In each of these composition ranges certain anions were assumed to predominate viz:

0-20 mole% SiO_2 : The predominant anions are supposed to be O^- and SiO_4^{4-} . 20-40 mole% SiO_2 : Anions are O^{2-} , $\text{Si}_3O_9^{6-}$, SiO_4^{4-} . 40-60 mole% SiO_2 : Anions are O^- , $\text{Si}_3O_9^{6-}$, $\text{Si}_6O_{15}^{6-}$ and SiO_4^{4-} .

They concluded, however, that the agreement obtained with activity data was only circumstantial proof of the silicate anions present.

This model is again a curve fitting scheme.

2.2.3.5 The Masson model (21)

Masson ⁽²¹⁾ considered a binary silicate melt of the type MO-SiO₂ in which the ratio of metallic oxide MO to silica is sufficiently high that depolymerisation may be regarded as complete and the silica is present exclusively as the simple tetrahedral SiO_4^{4-} monomers. With increase in silica content of the melt, a series of polymerisation reactions may be envisaged in which SiO_4^{4-} ions at first dimerise and then react further with higher members of the series thus formed to yield linear and branched polyionic chains with the elimination of oxygen at each step. Thus:

$$\sin \frac{4^{-}}{4} + \sin \frac{4^{-}}{4} = \sin_2 \frac{6^{-}}{7} + 0^{2^{-}} \dots k_{1,1}$$
(2.7a)

$$\sin \frac{4}{4} + \sin_2 \frac{6}{7} = \sin_3 \frac{6}{10} + 0^2 \dots k_{1,2}$$
(2.7b)

$$\sin^{4-}_4 + \sin_3 \circ^{8-}_{10} = \sin_4 \circ^{10-}_{13} + o^{2-} \dots k_{1,3}$$
 (2.7c)

etc.

Each polymerisation stage is characterized by an equilibrium constant $k_{1,1}$, $k_{1,2}$, $k_{1,3}$, ..., k_{1n} . Using ion fractions as approximations for activities the ion fraction of each series is expressed in terms of those of the lower numbers, viz:

$$N_{\text{Si}_{2}^{0}7} = k_{11} \frac{N_{\text{Si}_{4}}}{N_{2^{-}}} N_{\text{Si}_{4}}$$
(2.8)

$$N_{\text{Si}_{3}^{0}_{10}} = k_{12} \frac{N_{\text{Si}_{4}}}{N_{0}^{2-}} N_{\text{Si}_{2}^{0}_{7}}$$
(2.9)

$$N_{\text{Si}_{4}^{0}13} = k_{13} \frac{N_{\text{Si}_{4}}}{N_{0}^{2}} N_{\text{Si}_{3}^{0}10}$$
(2.10)

etc.

Masson then assumed (with Toop and Samis ⁽¹⁷⁾) that all the equilibrium constants are equal, i.e.,

$$k_{11} = k_{12} = k_{13} = \dots = k$$
 (2.11)

This sweeping assumption was justified by Masson from experience gained in the studies of polymerisation processes generally.

From these sets of equations Masson writes the sum of the ion fractions of silicate anions as

$$\Sigma N_{\text{silicate}} = N_{\text{SiO}_{4}} + N_{\text{Si}_{2}O_{7}} + N_{\text{Si}_{3}O_{10}} + \dots$$

$$= N_{\text{SiO}_{4}} + k \frac{N_{\text{SiO}_{4}}}{N_{\text{O}^{2-}}} (N_{\text{SiO}_{4}} + N_{\text{Si}_{2}O_{7}} + \dots)$$

$$= N_{\text{SiO}_{4}} + k \frac{N_{\text{SiO}_{4}}}{N_{\text{O}^{2-}}} \Sigma N_{\text{silicate}} . \quad (2.12)$$

Hence

$$\Sigma N_{\text{silicate}} = \frac{N_{\text{siO}_4}}{1 - k \frac{N_{\text{siO}_4}}{N_{\text{o}^{2-}}}} .$$
(2.12a)

Assuming that silicate and oxygen are the only anionic species in the melt, and adopting Temkin's definition of ion fraction, then

$$\Sigma N_{\text{silicate}} = 1 - N_{0^2}$$
(2.13)

so that from (2.12) and (2.13)

$$N_{SiO_4} = \frac{1 - N_{O^{2-}}}{1 + k(\frac{1}{N_{O^{2-}} - 1})}$$
(2.14)

giving N_{SiO_4} as a function of $N_{O^{2-}}$ if the value of k is known for the system. For k=0, SiO_4^{4-} is the only silicate species in the melt, and as k increases N_{SiO_4} decreases (if $N_{O^{2-}}$ is constant).

From (2.14), (2.8), (2.9) and (2.10), the ion fractions of the other silicate anions can be evaluated as functions of N $_{O^{2-}}$ if k is known. With k=1, Masson calculated the distributions for a number of silicate anionic species as shown in Fig. 9.

To apply the scheme outlined above, Masson sought to express the mole fraction of silica in terms of the ion



Fig. 9: Theoretical curves of (1) N_{SiO_4} , (2) $N_{Si_2O_7}$



Fig. 10: Ion fractions of (1) $\operatorname{SiO}_{4}^{4-}$, (2) $\operatorname{Si}_{2}\operatorname{O}_{7}^{6-}$, (3) $\operatorname{Si}_{3}\operatorname{O}_{10}^{8-}$, (4) $\operatorname{Si}_{4}\operatorname{O}_{13}^{10-}$, (5) $\operatorname{Si}_{5}\operatorname{O}_{16}^{12-}$ and (6) $\operatorname{Si}_{10}\operatorname{O}_{31}^{22-}$ plotted against mole fraction of SiO₂ for the system FeO-SiO₂ at 1530-1680°K (after Masson ^(21a))

fractions of the individual constituents as follows:

$$N_{SiO_2} = \frac{\text{moles SiO}_2 \text{ from silicates}}{(\text{moles MO + moles MO from silicates})}$$
$$= \frac{N_{SiO_4} + 2N_{Si_2O_7} + 3N_{Si_3O_{10}} + \cdots}{N_{O^{2-}} + 3N_{SiO_4} + 5N_{Si_2O_7} + \cdots}.$$
(2.15)

From (2.8), (2.9), (2.10) and (2.11)

$$N_{SiO_2} = \frac{1}{[3 - k + \frac{0^{2-}}{1 - N_0^2} + \frac{k(k - 1)}{(\frac{0^{2-}}{1 - N_0^2}) + k}]}$$
(2.16)

From Temkin's equation for the activity

$$a_{MO} = N_{M}^{2} + N_{O}^{2} -$$
 (2.17)

and for a binary system (N $_{M^{2+}}$ = 1), Eq. (2.16) becomes

$$N_{SiO_2} = 1 - N_{MO} = \frac{1}{[3 - k + \frac{a_{MO}}{1 - a_{MO}} + \frac{k(k-1)}{(\frac{a_{MO}}{1 - a_{MO}}) + k}]}$$
(2.18)

so that values of N $_{O^{2-}}$ can be translated to N $_{SiO_{2}}$. In addition k could be evaluated if the activity a_{MO} were known experimentally. Thus Masson obtained k values for a number of systems (Table IIa).

From experimental activities of FeO in the range $N_{FeO} \geq 0.55$ in the system FeO-SiO₂, Masson calculated the ion fractions of various silicate entities in the melt as plotted in Fig. 10. He notes that k determines the tendency towards polymerisation in binary silicate melts in line with the conclusions of Toop and Samis. Thus it was expected that the average chain length would be determined by the magnitudes of both the cation-silicate ion and cation-oxygen ion attractions.

The following limitations to the above model were outlined by Masson:

- (a) It is applicable only to binary silicates. Temkin's equation would be less applicable for ternaries where competition for different cations between oxygen and silicate anions will become significant.
- (b) Ring formation was not considered. It is thought that this will be especially favoured in systems with low k values where cation-silicate interaction is high and coiling of the polyanions may occur due to effective neutralization of the charged groups on the polymeric chains. For systems with a high value of k, the charged

TABLE IIa

VALUES OF k FOR VARIOUS BINARY SILICATE MELTS (AFTER MASSON ⁽²¹⁾)

SYSTEM	k
FeO-SiO ₂	1.4
MnO-SiO2	0.75
PbO-SiO2	0.2
CaO-SiO ₂	0.003

TABLE IIb

VARIATION OF k_{in} WITH n FOR VARIOUS BINARY SILICATE MELTS (AFTER MASSON ET AL. ⁽²¹⁾)

SYSTEM	^k ll	^k 12	^k 13	k ₁₄	k _{l∞}
SiO ₂ -CaO	0.0016	0.0021	0.0024	0.0026	0.0036
sio ₂ -PbO	0.196	0.261	0.299	0.324	0.441
SiO ₂ -MnO	0.25	0.33	0.38	0.41	0.56
SiO ₂ -FeO	0.70	0.93	1.07	1.16	1.575
SiO <mark>2</mark> -CoO	2.0	2.7	3.1	3.3	4.5
SiO ₂ -SnO	2.55	3.40	3.89	4.22	5.74

groups will exert a mutually repulsive effect, leading to a stiffening of the chains with a consequent lower probability of ring closure.

(c) The scheme is limited to the highly basic silicate melts (< 40 mole% SiO₂).

The most serious simplifying assumption in the above scheme is that of equal equilibrium constant (Eq. (2.11)). This sweeping assumption has now been removed by Masson and co-workers ^(21b,21c). Using multi-chain polymer theory they evaluated the "ideal" ionic distribution in binary silicate melts taking into account the variation of the equilibrium constant k_{in} with the chain length n. Noting that the calculation of "how k_{in} varies with n is equivalent to calculating the configurational aspect of the molecular size distribution in polyfunctional condensation", the authors obtained the following relation for k_{in}

$$\frac{k_{\text{in}}}{k_{11}} = \frac{(3n+1)(3n+2)}{2(2n+3)(n+1)}$$
(2.19)

enabling k_{in} to be calculated for any value of n if k_{11} is known. Values of k_{in} for some experimental systems as obtained by Masson et al. are given in Table IIb.

Masson's model is thought to represent the most comprehensive attempt at computing anion distributions in binary silicate melts. 2.2.3.6 The structure of super-cooled silicate melts

Mackenzie ⁽²²⁾ considered two structures that could result on cooling a silicate melt to glass:

- The melt could undergo a rather sudden polymerisation and rearrangement to give a random network structure.
- (2) Alternatively, the anions could be envisaged as
 "frozen-in" to preserve the melt structure in the solid state.

From kinetic considerations, Mackenzie argues, in agreement with the conclusions of McKinnis and Sutton ⁽²³⁾, that the anions present in the equilibrated melt will be preserved in the silicate glass so that (2) is favoured.

Therefore, although lacking direct or indirect evidence about the structure of silicate glasses, we will assume that the structure of molten silicates will be preserved on cooling to the rigid state.

2.3 Conclusions about Silicate Structure of Relevance to the Diffusion Process

The conclusions to be drawn about the structure of silicates with relevance to diffusion studies are (i) the concentrations of silicate anions are dependent on the concentration and chemical properties of the metal oxides in the glass. Thus, two glasses with different metal oxide concentrations in general have different anion concentrations or anion charge densities; (ii) by virtue of its size, the silicate anion will be nearly immobile relative to the cations, especially in the high silica range (> 66 mole% SiO, content) where structures consisting of large rings and long chains are expected; (iii) since the size and nature of the interstices or holes in the silicate structure are concentration dependent, the diffusion rate of the modifier cations (which are supposed to migrate via these interstices) will be concentration dependent. Self diffusivity data confirm this conclusion (see Chapter 3.2); (iv) the number of free oxygen ions 0^{2-} in the system will depend on the concentration of metal oxide in the glass, the temperature, and the prior history of the glass, and so will the diffusivity of the 0^{2-} ions; and (v) the number of (OH) anions will depend on the water content of the glass.

Factors (i) and (ii) will be major sources of diffusion interactions in system with concentration gradients such as diffusion couples or in two-phase systems such as metal/silicate systems, glass electrodes and silicate ionexchangers.

CHAPTER III

A REVIEW OF IONIC DIFFUSION IN SILICATES

3.1 Introduction

Ionic migration under a driving force (such as the gradient of the electrochemical potential), is generally accepted to be constituted by a series of ion jumps. Each ion is imagined to vibrate at its equilibrium position until upon acquiring the energy sufficient to surmount the barrier separating sites, it jumps into a neighbouring site. The various mechanisms whereby this jump process are accomplished in ionic crystals is described by a number of authors (see, for example, Manning (24) or Shewmon (25)). Ion jumps can be achieved by either:

- place exchange, i.e., an ion exchanges place directly
 (or via a ring mechanism) with its nearby neighbour;
- (2) some intrinsic-type defect in the system, e.g., Schottky defects (equal number of vacant anion and vacant cation lattice points, generally dominant in alkali halides) or Frenkel defects (interstitial ions with accompanying vacant sites, common in AgCl crystals); or
- (3) extrinsic vacancies, as in impure crystals of the type
 CdCl₂ + AgCl where each divalent Cd⁺⁺ impurity ion

replaces two univalent Ag⁺ ions in the lattice in order to maintain electrical neutrality, so that there is a vacant Ag⁺ lattice (cation vacancy with an effective negative charge). As a result of coulombic interactions, some of these vacancies are attracted to the divalent cations to form complexes.

Analyses of diffusion studies in ionic crystals and considerations of the activation energies required for ion jumps have led to the conclusion that vacancies (single vacancies, complexes and pairs) and interstitials (direct and indirect) are most likely involved in diffusion in ionic systems. The indirect interstitial (or the interstitialcy) occurs when one ion pushes a nearby ion into an interstitial position and takes occupancy of the vacated site.

In general it is found that ionic diffusion proceeds in such a way that the system remains electrically neutral.

3.2 Self-diffusivity Data for Silicates

Self diffusion is by definition diffusion in a chemically homogeneous material. This term has come to be applied to any diffusion measured with a radioactive tracer since the amount of main solute is generally so small that the composition change can be ignored. Self-diffusion coefficients are usually measured by placing an isotope on or in a chemically homogeneous material and subsequently analysing sections from the specimen after a diffusionanneal and comparing with the appropriate solution $^{(25)}$ of Fick's second equation to evaluate D_i (the self-diffusion coefficient).

There is a large amount of data in the literature for the self-diffusion coefficients of the ions Na, K, Li, H, O, Ca and Sr. Doremus ⁽²⁸⁾ has reviewed most of the data prior to and including 1962, and more recent material is available in Diffusion Data publications ⁽²⁹⁾. The data show that the self-diffusion coefficients are very strongly concentration dependent. For example, Evstropev ⁽³⁰⁾, and Evstropev and Pavlovskii ⁽³¹⁾ have measured D_{Na} , D_{K} and D_{Rb} in a series of binary silicate and germinate glasses and found that the values increase as the mole% Na₂O, K₂O and Rb₂O, respectively. The composition dependencies of D_{Na} and D_{K} in the system Na₂O-SiO₂ and K₂O-SiO₂, respectively, are shown in Figs. 11a and 11b. As can be seen the



Fig. lla: Variation of the self diffusivity of Na, D_{Na} with mole% Na₂O content of Na₂O-SiO₂ glasses



Fig. 11b: Variation of the self diffusivity of K, $\rm D_{K}$ with mole% $\rm K_{2}O$ content of $\rm K_{2}O-SiO_{2}$ glasses

dependencies are logarithmic within the range (0-30 mole%)alkali oxide) investigated. It has also been established that the self-diffusion coefficient of an alkali is lowered by the addition of another alkali oxide to the glass. An empirical equation relating the self-diffusivity D_i to concentration in ternary silicates based on such data is developed in Appendix B.

Thus it appears that the concentration dependence of D_i is much stronger in silicates than in metals, a fact which may be directly connected with the opening up of the structures of silicate systems by the addition of alkali oxides.

3.3 Proposed Mechanisms for Ionic Diffusion in Silicate Glasses

Diffusion in and through a system is intimately connected with the structure and defects of the system and with the nature of the diffusing species and other constituents. Because of the non-crystalline nature of silicate glasses and the dependence of the structure on concentration, it has not been easy to pinpoint the exact mechanism of ionic diffusion as has been the case in crystalline materials. Where there is general agreement that diffusion is by some type of defect, experimental results have not been unequivocal in support of one mechanism or the other.

At the outset we note that the introduction of the crystal concepts of Frenkel defects, vacancies, interstitials, etc., into amorphous systems such as silicate glasses is somewhat arbitrary but permissible as long as the meaning is clear.

Frischat $^{(32a)}$ investigated the diffusion of Na²² in a commercial silica glass with a hydroxyl content of 4×10^{-4} mole/litre prepared by fusion of natural quartz crystals and suggested that Na⁺ diffuses via an interstitialcy (indirect interstitial) mechanism. In another study involving measurement of D_{Na} in the Na₂O-K₂O-Al₂O₃-SiO₂ system, Frischat ^(32b) inferred from his results that analogously to the Frenkel pairs in the Ag^+ sublattice of AgBr, Na⁺ ions near $[SiO_{4/2}]$ tetrahedra must occupy energetically suitable sites in the glass. Complexes like Na⁺SiO_{4/2} and SiO_{3/2}O⁻ were considered as "interstitial" and "vacancy" sites. These complexes were considered to form by a dissociation process in the glass structure. By comparing the size of the correlation factor and sign of the entropy factor with those of crystalline materials, Frischat concluded that the interstitialcy is more probable than a vacancy mechanism. Barr et al. ⁽³⁴⁾ were also quoted by Frischat as reaching the same conclusion from measurements of the isotope effect of Na diffusion in glass.

Terai and Kitaoka $^{(35)}$ measured the self diffusion of Na in the Na₂O-SiO₂ system containing a variety of other oxides and showed that D_{Na} decreases as the effective radius of the added cation modifier increases. They found the results consistent with either a vacancy or an interstitialcy mechanism and noted that the mechanism was not influenced by the kind of divalent cation added.

Charles ⁽³⁶⁾ in treating self diffusion in silicate glasses in terms of formation, migration and ultimate annihilation of defects, postulated that there are a number of equivalent equilibrium positions (separated by energy barriers) for an alkali cation around each non-bridging oxygen ion. He considered the migration of an alkali ion through the glass to involve a reorientation around a non-bridging oxygen ion. This reorientation was considered to be accomplished by means of either a direct or an indirect rotation (see Fig. 12). A direct rotation involves a direct jump of an ion from one equivalent equilibrium site to another around a given oxygen ion; indirect rotation occurs when an alkali ion leaves an equivalent site of one oxygen ion to occupy a site of another, leaving behind two vacant equivalent sites (a defect) on the original oxygen ion, which a migrating ion may fill (an annihilation of defect). Thus ionic self diffusion was described as a series of polarisation events. The model was shown to be consistent with the conductivity data of soda-lime glass.

Charles' model appears to be the most comprehensive to date in that he considered the detailed migration process in the silicate structure, and was able to relate the ionic diffusion to the conductivity as well as relaxation processes in silicate glasses. However, it was outlined only in terms of the self diffusion process. The relation between the postulated orientational polarisation and interdiffusion in multicomponent systems was not pursued. In a later section, an attempt will be made to extend Charles' model with diffusion polarisation in self diffusion to interdiffusion in multicomponent silicate systems.



Fig. 12: Hypothetical conduction and polarisation events in an alkali silicate glass (after Charles ⁽³⁶⁾)

3.4 Observations of Diffusion in Multicomponent Silicate Glasses

Cooper and Varshneya (44) have investigated interdiffusion in the system K₂O-SIO-SiO₂ at 750°C in a couple with roughly equal SiO₂ concentrations on the two sides. Their observed concentration profiles represent normal counter-current flow of K and Sr. From these profiles, they calculated the interdiffusion coefficients for K and Sr.

In a later paper, Varshneya and Cooper ⁽¹⁾ measured the concentration profiles in glass diffusion couples of the system K_2O -SrO-SiO₂, some of which had substantial differences of SiO₂ concentration on the two sides. A typical observation is shown in Fig. 13 and demonstrates a form of up-hill diffusion. A large part of our contribution has to do with the interpretation of such phenomena.

Borom and Pask ⁽⁴⁵⁾ have studied the kinetics of interfacial reaction and diffusion processes in the ironsodium disilicate system in the 900-1100°C temperature range and have concluded that the process is limited by the interfacial reaction between iron and glass. The iron is incorporated inside the glass as ferrous iron Fe²⁺ and diffuses by exchange with Na⁺ ions in a constant silica framework. An activation energy for interdiffusion of 26.7 kcal. was obtained. Succev and Gorman ⁽⁴⁶⁾ have



Fig. 13: Concentration profiles of K_2^0 and Sr0 in K_2^0 -Sr0-Si0₂ glass couple showing uphill diffusion of Sr at the interface due to discontinuity in the nearly immobile anion concentration (result from Varshneya and Cooper ⁽⁴⁴⁾)

investigated the interdiffusion of Na and Ca in Na₂O-CaO-SiO₂ system in the range 880-1308°C, and concluded that with a nearly uniform Na₂O concentration, both the Na and Si are stationary while Ca diffuses with singly-bonded oxygens O⁻ to maintain electrical neutrality in the system.

The data of Cooper and Varshneya, Varshneya and Cooper and of Sucov and Gorman will be subjected to detailed analysis in a later section.

CHAPTER IV

PHENOMENOLOGICAL THEORY FOR DIFFUSION IN IONIC SYSTEMS

4.1 Introduction

The phenomenological basis for multicomponent diffusion was defined by Onsager ⁽³⁷⁾ using irreversible thermodynamics. Onsager showed that for near equilibrium situations, there is a linear dependence between the forces and fluxes viz:

$$J_{i} = \sum_{j=1}^{n} L_{ij} X_{i}$$
(4.1)

i = 1, 2, 3, ..., n

where J_i, X_i, L_{ij} are the fluxes (diffusion, electrical conduction, heat transport, chemical reaction, etc.), the driving force and the phenomenological coefficients respectively; and for independent fluxes and forces which generate the bilinear form of the entropy production rate per unit volume

$$T\sigma = \sum_{i=1}^{n} J_{i}X_{i}$$
(4.2)

reciprocal relations hold between the phenomenological coefficients, viz,

$$L_{ij} = L_{ji} \qquad (4.3)$$

From the second law of thermodynamics, which requires that the entropy production rate be positive, it follows that matrix L_{ij} must be positive definite, i.e.,

$$L_{ii} > 0$$
; $L_{ii}L_{ij} - L_{ij}L_{ji} > 0$; etc. (4.4)

For chemical diffusion of neutral components where n in Eq. (4.1) is the number of such components, the X_{i} are not independent, being related via the Gibbs-Duhem equation

$$\sum_{i=1}^{n} N_i X_i = 0$$

$$(4.5)$$

and accordingly the reciprocal relations, (4.3), need not apply.

For the interpretation of chemical diffusion experiments the fluxes must be defined with respect to a suitable frame of reference, of which the four most common ones are (1) solvent-fixed, (2) volume-fixed, (3) latticefixed, and (4) laboratory-fixed. The solvent-fixed frame is that relative to which the solvent flux is zero, i.e.,

$$J_{\text{solvent}} = 0 \quad . \tag{4.6}$$

Similarly the volume-fixed frame is that moving locally so that no net flow of volume occurs, i.e.,

$$\sum_{i=1}^{n} J_{i} \overline{V}_{i} = 0$$
(4.7)

where the \overline{V}_i are the partial molar volumes

$$\overline{\mathbf{v}}_{\mathbf{i}} = \left(\frac{\partial \mathbf{v}}{\partial \mathbf{N}_{\mathbf{i}}}\right)_{\mathbf{T},\mathbf{P},\mathbf{n}_{\mathbf{j}}},\dots$$
(4.8)

(3) and (4) are similarly defined. Any convenient reference frame can be chosen and a transformation exists for passing from one frame to another (38).

For diffusion in an n-component non-ionic system it has been shown ⁽³³⁾ that

$$T\sigma = -\sum_{i=1}^{n} J_{i} \frac{\partial \mu_{i}}{\partial x} .$$
 (4.9)

If we define our frame of reference as in (4.7) then this can be reduced to

$$T\sigma = \sum_{i=1}^{n-1} J_i \frac{\partial (\mu_i - \frac{\nabla_i}{\overline{\nabla}_n} \mu_n)}{\partial x}$$
(4.10)
which now has a bilinear form in terms of independent fluxes J, and forces

$$X_{i} = \frac{\partial (\mu_{i} - \frac{\overline{\nabla}_{i}}{\overline{\nabla}_{n}} \mu_{n})}{\partial x} . \qquad (4.11)$$

The μ_n 's can, of course, be eliminated via the Gibbs-Duhem equation. The relation between the fluxes and forces will have the form

$$J_{i} = \sum_{i=1}^{n-1} L_{ik} X_{k}$$

$$(4.12)$$

with the Onsager reciprocal relations (4.3) now valid.

$$L_{ik} = L_{ki} \qquad (4.3)$$

The validity of the Onsager reciprocal relations has been extensively investigated experimentally by Gosting and his group ⁽³⁹⁾ in Wisconsin using liquid electrolytes. Kirkaldy and his group ⁽⁴⁰⁾ at McMaster have amplified the physical basis of this relationship in multicomponent liquid electrolytes and metallic crystalline systems.

The phenomenological description of diffusion implied by Eq. (4.12) fully takes into account the cross effects of all other constituents of the system on the flux of any one species. Thus, the diffusion process in any multicomponent system, no matter how complex, can be completely characterised once the phenomenological coefficients are known as functions of temperature, concentration and pressure. Thus such phenomena as up-hill diffusion, i.e., diffusion of one component against its own concentration gradient or under a zero concentration gradient are natural outcomes dependent upon the magnitudes and signs of the L_{ij}'s.

The understanding of diffusion in ionic systems is complicated by the fact that the diffusing species are charged and there exist associations between species (i.e., complexes, pairs, etc.). Furthermore, analysis is inhibited by a lack of accurate thermodynamic data. It is, therefore, not surprising that work on these systems has not been as extensive as in non-ionic systems. Nonetheless, important simplifications have been recognised. The first of these derives from the fact that diffusion generally proceeds under the zero net electrical current condition, viz,

 $\Sigma z_{j}J_{j} = 0$. (4.13)

The second simplification, according to Schmalzried and Holt ⁽⁴¹⁾, arises from the fact that if the anion sublattice is fixed (and this is more or less the rule because of the large ionic sizes) then there will be no Kirkendall effect. Further simplification is made possible through the often

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valid assumption that the Onsager cross terms L_{ij} (i \neq j) are small relative to the diagonal terms L_{ii} .

Through kinetic arguments, Lane and Kirkaldy (40g), Howard and Lidiard (42) and a number of other authors (43)have related the coefficients L_{ij} to measurable parameters (such as activities, jump frequencies, and lattice spacings) in metallic and ionic crystals, thus making it possible to characterize the system.

4.2 Phenomenological Theory of Ionic Diffusion: The

Nernst-Planck Equation

For an n-component isothermal ionic system, Eq. (4.9) generalizes to ⁽³³⁾

$$T\sigma = -\sum_{j=1}^{n} J_{j} \cdot \{ \text{grad}(\mu_{j}) - z_{j} \vec{E} \} - \rho \frac{d\vec{P}}{dt} \cdot (\vec{E}_{eq} - \vec{E}) \qquad (4.14)$$

where \vec{E} is the electric field, \vec{P} is the polarisation (dipole moment per unit volume), ρ is density, (mass per unit volume), t is time and \vec{E}_{eq} is defined by ⁽³³⁾

$$\vec{E}_{eq} = \kappa^{-1} \vec{P}$$
(4.15)

where K is the electric susceptibility. If the dipoles are in equilibrium with the field \vec{E} ($\vec{E} = K^{-1} \vec{P}$) then

$$\vec{E} = \vec{E}_{eq}$$
(4.16)

and the contribution of dipole relaxation to σ vanishes. This limit also justifies omitting such terms from the flux-force relation since the relaxation force is $\vec{E}_{eq} - \vec{E}$. We can, therefore, write a flux-force relation of the form

$$\vec{J}_{i} = -\sum_{i=1}^{n} L_{ij}(grad(\mu_{j}) - z_{j}\vec{E}) . \qquad (4.17)$$

A rigorous treatment of this relation based on the Onsager reciprocal relations and leading to the definition of a diffusion potential is to be found in DeGroot and Mazur ⁽³³⁾ (p. 367 ff). We proceed here with sufficient knowledge of the mechanism to obviate a detailed calculation.

With Lane and Kirkaldy (40g), LeClaire (27b) and Ziebold and Cooper (91) we recognise that for condensed phases there exists a frame of reference for J_i in which all cross terms in the L_{ij} matrix are approximately zero. For substitutional metals, this has been recognized as the Kirkendall frame and for ionic liquid solutions the frame depends on relative ionic radii (or molar densities). Cooper has applied the same ideas to glasses as considered here, representing the fluxes in the laboratory frame by relations like

$$\mathbf{J}_{i} = -\mathbf{L}_{ii}(\operatorname{grad}(\mu_{i}) - \mathbf{z}_{i} \mathbf{J} \mathbf{\vec{E}}) + \rho_{i} \mathbf{\vec{u}}$$
(4.18)

where \vec{u} is a drift velocity depending on volume changes of mixing.

Although we recognise that the drift term \vec{u} , may be important in certain systems with large composition differences we do not regard it as significant to the analysis of the data treated herein. Accordingly we proceed with the simple relation in one dimensional form (x-coordinate):

$$J_{i} = -L_{ii} (\text{grad } \mu_{i} - z_{i} \neq E)$$
 (4.19)

$$= -L_{ii} \frac{RT}{C_i} \left(\frac{\partial C_i}{\partial x} + C_i \frac{\partial \ln \gamma_*}{\partial x} + z_i C_i \frac{\mathbf{J}}{RT} \frac{\partial \phi}{\partial x} \right)$$
(4.19a)

where γ_i , z_i , \mathcal{F} , and ϕ are the activity coefficient, valence, the Faraday constant and the electrostatic potential, respectively, and the electric field E is given by the electrostatic potential gradient, viz:

$$\mathbf{E} = -\frac{\partial \phi}{\partial \mathbf{x}} \quad . \tag{4.20}$$

Following Darken (50) and others, the mobilities L_{ii} can be related to the tracer diffusion coefficients D_i by

$$L_{ii} = \frac{D_i C_i}{RT} (1 + N_i \frac{\partial ln\gamma_i}{\partial N_i}) \Big|_{E=0}$$
(4.21)

or in Einstein's approximation

$$L_{ii} = \frac{D_i C_i}{RT}$$
(4.22)

where C_i are the ion concentrations, and R and T are the gas constant and absolute temperature, respectively. The approximation from Eqs. (4.21) to (4.22) implies that the activity coefficients γ_i vary slowly with N_i . In the same approximation and with D_i assumed independent of the field \vec{E} , then

$$D_{i} = -D_{i} \left[\frac{\partial C_{i}}{\partial x} + \frac{z_{i} \overline{J} C_{i}}{RT} \frac{\partial \phi}{\partial x}\right]$$
(4.23)

which is the well-known Nernst-Planck equation. All our subsequent analyses will be based on Eq. (4.23) for the fluxes of the mobile ions.

4.3 The System of Coupled Diffusion Equations

4.3.1 Quasi-binary Ionic Systems (Fixed Anion Solvent)

For a system of n ionic species, the flux of each diffusing species is described by Eq. (4.23). To eliminate the as yet unknown quantity $\partial\phi/\partial x$ (= - E) from (4.23), we must introduce a final assumption viz, that the net real electrical current in the system is zero, i.e.,

$$\sum_{i=1}^{n} z_i J_i = -J_r \approx 0$$
 (4.24)

This assumption which for an initially neutral system implies electrical neutrality at all times, has become traditional for ionic diffusion and has generally been borne out by experimental results. One may consider it to be the result of the system's "tendency to instantaneously minimize the electrostatic energy through minimization of the net accumulation of charge (47)". It is sufficient that $|J_r|$ be small relative to each of the $|z_i J_i|$.

Applying this condition to the flux equations (4.23),

$$\sum_{i=1}^{n} z_{i} D_{i} \left(\frac{\partial C_{i}}{\partial x} + \frac{z_{i} \mathcal{F} C_{i}}{RT} \frac{\partial \phi}{\partial x} \right) = 0$$
 (4.24a)

we obtain the electric field E (the so-called diffusionpotential) as

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$$-\frac{\partial \phi}{\partial x} = E = \frac{RT}{3} \frac{\sum_{j=1}^{n} D_j z_j^2}{\sum_{j=1}^{n} D_j z_j^2 C_j} . \qquad (4.25)$$

Substituting (4.25) in (4.23) we obtain the following coupled diffusion equations:

$$J_{i} = \frac{-\begin{pmatrix} n \\ j=1 \end{pmatrix} (C_{j}z_{j}^{2}) - D_{i}C_{i}z_{i}^{2}}{n} D_{i} \frac{\partial C_{i}}{\partial x} + \frac{\begin{pmatrix} n \\ j\neq i \end{pmatrix} (D_{j}z_{i}z_{j}^{2}) (D_{j}z_{i}z_{j}^{2})}{n} \frac{\partial C_{j}}{\partial x} \cdot (4.26)$$

For a quasi-binary system with two mobile ions 1 and 2 in a fixed anion solvent (a special case of ternary system), the flux equations from the general expression (4.26) are

$$J_{1} = -D_{11} \frac{\partial C_{1}}{\partial x} - D_{12} \frac{\partial C_{2}}{\partial x}$$

$$J_{2} = -D_{21} \frac{\partial C_{1}}{\partial x} - D_{22} \frac{\partial C_{2}}{\partial x}$$
(4.27)

where

$$D_{11} = \frac{D_1 D_2 z_2^2 C_2}{D_1 z_1^2 C_1 + D_2 z_2^2 C_2} , \quad D_{12} = -\frac{z_2}{z_1} D_{22}$$

$$D_{22} = \frac{D_1 D_2 z_1^2 C_1}{D_1 z_1^2 C_1 + D_2 z_2^2 C_2} , \quad D_{21} = -\frac{z_1}{z_2} D_{11}$$
(4.28)

and the internal electric field is

$$E = \frac{RT}{\mathcal{F}} \frac{(D_1 z_1 \frac{\partial C_1}{\partial x} + D_2 z_2 \frac{\partial C_2}{\partial x})}{(D_1 z_1^2 C_1 + D_2 z_2^2 C_2)} .$$
(4.29)

A set of coupled diffusion equations analogous to Eq. (4.27) has also been formulated by Dorward ⁽⁵¹⁾, and by Hu and Schmidt ⁽⁵²⁾ for application to diffusion of two species in semiconductors, and also by Cooper ^(1a) and Varshneya and Cooper ^(1b) for application to glasses. The latter's equations are more general than those developed here, as noted previously.

The combination of (4.27) with the law of conservation of mass in the following expressions:

$$\frac{\partial C_{i}}{\partial t} + \frac{\partial J_{i}}{\partial x} = 0$$
(4.30)

i = 1, 2, ..., n

yield the Fick-type non-linear partial differential equations:

$$\frac{\partial C_{1}}{\partial t} = \frac{\partial}{\partial x} \left(D_{11} \frac{\partial C_{1}}{\partial x} \right) + \frac{\partial}{\partial x} \left(D_{12} \frac{\partial C_{2}}{\partial x} \right)$$
(4.31a)

$$\frac{\partial C_2}{\partial t} = \frac{\partial}{\partial x} \left(D_{21} \frac{\partial C_1}{\partial x} \right) + \frac{\partial}{\partial x} \left(D_{22} \frac{\partial C_2}{\partial x} \right)$$
(4.31b)

which can be uniquely solved numerically subject to the appropriate initial and boundary conditions on C_1 and C_2 , e.g.,

$$C_{i}(x_{+}, 0) = C_{i}(+\infty, t) = C_{i0}$$

 $C_{i}(x_{-}, 0) = C_{i}(-\infty, t) = C_{i1}$

(4.32)

and provided we know the values of the self-diffusion coefficients D₁ and D₂. Thus D₁ and D₂ are the only two independent parameters required for describing the diffusion process.

4.3.2 Comparison with Helfferich's Formulation

It is important to note that the application of the zero net electrical current condition to an initially neutral system must imply a zero net real charge density for all times. That is to say

$$\sum_{i=1}^{n} z_{i}C_{i} = 0 .$$
 (4.33)

We specify real charges as distinct from polarisation charges which arise from permanent or induced dipoles.

In formulating the equations for ionic diffusion in quasi-binary systems, previous workers have usually applied both forms of the electroneutrality condition in Eqs. (4.24) and (4.33). In applying (4.33) the anion concentration is assumed constant everywhere so that the first derivative of (4.33) becomes

$$z_1 \frac{\partial C_1}{\partial x} + z_2 \frac{\partial C_2}{\partial x} = 0 \quad . \tag{4.34}$$

Equation (4.34) is then used to simplify the flux equations (4.27) to

$$J_{1} = - (D_{11} + D_{22}) \frac{\partial C_{1}}{\partial x}$$

$$J_{2} = - (D_{11} + D_{22}) \frac{\partial C_{2}}{\partial x}$$
(4.35)

and the internal field in (4.29) as

$$E' = \frac{RT}{3} \frac{z_1 (D_1 - D_2)}{(D_1 z_1^2 C_1 + D_2 z_2^2 C_2)} \frac{\partial C_1}{\partial x}$$
(4.36)

Equations (4.35) and (4.36) are due to Helfferich (53).

It is evident that our present formulation in Eqs. (4.27) is more general for it does not require the anion concentration to be constant everywhere. As has been discussed at length in reference (47) the first derivative of Eq. (4.33) for a quasi-binary system is

$$z_{1} \frac{\partial C_{1}}{\partial x} + z_{2} \frac{\partial C_{2}}{\partial x} + z_{a} \frac{\partial C_{a}}{\partial x} = 0$$
 (4.37)

which for the case where the anion concentration contains a step at the origin of value ΔC_a , becomes

$$z_{1} \frac{\partial C_{1}}{\partial x} + z_{2} \frac{\partial C_{2}}{\partial x} + z_{a} \Delta C_{a} \delta(x) = 0$$
 (4.38)

where $\delta(x)$ is the Dirac δ function. In such a case, Eqs. (4.35) are not valid at the origin, whereas (4.27) are valid everywhere including the origin. We emphasize that for some special systems, e.g., infinite diffusion couples with a uniform anion concentration throughout, or semi-infinite systems where the concentrations are fixed at one surface (e.g., glass/salt solution, ion-exchangers) Helfferich's equations (4.35) are quite valid. This indeed has been verified by a number of workers in ion-exchange kinetics.

4.3.3 Ternary Ionic Systems (Mobile Anion Solvent)

For a ternary ionic system in which the two solutes 1 and 2 as well as the anion solvent a are diffusing, the flux equations from the general expression (4.26) are

$$J_{1} = -(D_{1}D_{2}z_{2}^{2}C_{2}+D_{1}D_{a}z_{a}^{2}C_{a})\frac{\partial C_{1}}{\partial x} + D_{1}D_{2}z_{1}z_{2}C_{1}\frac{\partial C_{2}}{\partial x} + D_{1}D_{a}z_{1}z_{a}C_{1}\frac{\partial C_{a}}{\partial x}$$
(4.39a)

$$J_{2} = -D_{1}D_{2}z_{1}z_{2}C_{2} \frac{\partial C_{1}}{\partial x} - (D_{1}D_{2}z_{1}^{2}C_{1} + D_{2}D_{a}z_{a}^{2}C_{a})\frac{\partial C_{2}}{\partial x} + D_{2}D_{a}z_{2}z_{a}C_{2} \frac{\partial C_{a}}{\partial x}$$

$$(4.39b)$$

$$J_{a} = -(z_{1}J_{1} + z_{2}J_{2})/z_{a}$$

$$(4.39c)$$

and the internal electric field is

$$E = \frac{RT}{\cancel{3}} \frac{(D_1 z_1 \frac{\partial C_1}{\partial x} + D_2 z_2 \frac{\partial C_2}{\partial x} + D_a z_a \frac{\partial C_a}{\partial x})}{(D_1 z_1^2 C_1 + D_2 z_2^2 C_2 + D_a z_a^2 C_a)} \quad .$$
(4.40)

Since we no longer have a step discontinuity of the anion concentration at the interface, we can apply the l^{st} derivative of the neutrality condition of zero real charge in the form of Eq. (4.37) to the flux equations (4.39) and eliminate $\partial C_a/\partial x$ thus reducing the 3×3 matrix to the following 2×2 matrix:

$$J_{1} = -D'_{11} \frac{\partial C_{1}}{\partial x} - D'_{12} \frac{\partial C_{2}}{\partial x}$$

$$J_{2} = -D'_{21} \frac{\partial C_{1}}{\partial x} - D'_{22} \frac{\partial C_{2}}{\partial x}$$
(4.41)

and similarly the field can be expressed as

$$E = \frac{RT}{\exists} \frac{\left[(D_1 - D_a) z_1 \frac{\partial C_1}{\partial x} + (D_2 - D_a) z_2 \frac{\partial C_2}{\partial x} \right]}{(D_1 z_1^2 C_1 + D_2 z_2^2 C_2 + D_a z_a^2 C_a)}$$
(4.42)

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where

$$D_{11} = \frac{(D_1 D_a z_1^2 C_1 + D_1 D_2 z_2^2 C_2 + D_1 D_a z_a^2 C_a)}{(D_1 z_1^2 C_1 + D_2 z_2^2 C_2 + D_a z_a^2 C_a)}$$
(4.43a)

$$D'_{12} = \frac{(D_1 D_a - D_1 D_2) z_1 z_2 C_1}{(D_1 z_1^2 C_1 + D_2 z_2^2 C_2 + D_a z_a^2 C_a)}$$
(4.43b)

$$D'_{21} = \frac{(D_2 D_a - D_1 D_2) z_1 z_2 C_2}{(D_1 z_1^2 C_1 + D_2 z_2^2 C_2 + D_a z_a^2 C_a)}$$
(4.43c)

$$D'_{22} = \frac{(D_1 D_2 z_1^2 C_1 + D_2 D_a z_2^2 C_2 + D_2 D_a z_a^2 C_a)}{(D_1 z_1^2 C_1 + D_2 z_2^2 C_2 + D_a z_a^2 C_a)} \quad .$$
(4.43d)

Notice that the determinant of the |D| matrix is nonzero. Note also, that with $D_a = 0$, the above set of equations (4.41) - (4.43) reduce to those for the quasibinary systems (4.27) - (4.29).

The combination of (4.41) with the law of conservation of mass (4.30) yields the Fick-type non-linear partial differential equations:

$$\frac{\partial C_{1}}{\partial t} = \frac{\partial}{\partial x} \left(D_{11}' \frac{\partial C_{1}}{\partial x} \right) + \frac{\partial}{\partial x} \left(D_{12}' \frac{\partial C_{2}}{\partial x} \right)$$
(4.44a)
$$\frac{\partial C_{2}}{\partial t} = \frac{\partial}{\partial x} \left(D_{21}' \frac{\partial C_{1}}{\partial x} \right) + \frac{\partial}{\partial x} \left(D_{22}' \frac{\partial C_{2}}{\partial x} \right)$$
(4.44b)

A major practical difficulty in accounting for the anion motion is the fact that there are different forms of anionic species: OH^- , O^{2-} , SiO_4^{4-} , $Si_2O_7^{6-}$, $Si_8O_{20}^{8-}$, etc. (as discussed in Chapter II), each with its own diffusion coefficient. Thus although we know the total anion charge density z_aC_a, from (4.33), we do not know the individual concentrations nor their distribution probabilities to enable us to calculate their diffusion fluxes. As a first approximation, we assume that one anionic species predominates and that it has the same charge as oxygen, i.e., $z_{a} = -2$. As a matter of fact, the choice of z value is not critical as can be seen from the manner it enters into the diffusion equations (z_a goes into the Eqs. (4.43) as a product $D_{a}z_{a}^{2}C_{a}$, where the anion diffusion coefficient D_a is generally such that $D_1 >> D_2 >> D_a$). Implicit in this is the admission that the theory as formulated is not sensitive enough to enable a determination of the particular anionic species diffusing.

4.4 The Analytic (Approximate) Solution of the Coupled Diffusion Equations (4.31)

For infinite and semi-infinite systems we can transform Eqs. (4.31) (or (4.44)) from partial to ordinary differential equations by the substitutions

$$C_{i} = C_{i}(\lambda) , \quad \lambda = x/t^{1/2}$$
(4.45)

to obtain

$$-\frac{1}{2}\lambda \frac{d^{2}C_{1}}{d\lambda^{2}} = \frac{d}{d\lambda}\left(D_{11}\frac{dC_{1}}{d\lambda}\right) + \frac{d}{d\lambda}\left(D_{12}\frac{dC_{2}}{d\lambda}\right)$$

$$-\frac{1}{2}\lambda \frac{d^{2}C_{2}}{d\lambda^{2}} = \frac{d}{d\lambda}\left(D_{21}\frac{dC_{1}}{d\lambda}\right) + \frac{d}{d\lambda}\left(D_{22}\frac{dC_{2}}{d\lambda}\right)$$
(4.46)

and since the initial and boundary conditions (4.32) can be expressed in terms of λ , i.e.,

$$C_{i}(\lambda = +\infty) = C_{i}^{0}$$

$$(4.32a)$$

$$C_{i}(\lambda = -\infty) = C_{2}^{1}$$

the parametric solutions are unique ^(40a).

Analytic solutions of (4.46) for the case where the D_{ij} are constants have been independently worked out by Fujita and Gosting ^(39b) and by Kirkaldy ⁽⁵⁴⁾. In the

present case, however, the D_{ij} by definition (4.28) or (4.43) are strong functions of C_i so that (4.46) are non-linear and we must in general seek numerical solutions.

Before undertaking numerical solution it is worthwhile to gain some insight into the nature of Eqs. (4.46) by linearising them through use of average values of the D_{ij} and seeking analytic solutions. We expect that for systems lying within a not too large composition range, the use of average values of D_{ij} will lead to good approximate solutions. The analytic solutions of (4.46) with constant D_{ij} 's are ^(39b,54)

$$C_1 = a \operatorname{erf}(\frac{\lambda}{2u^{1/2}}) + b \operatorname{erf}(\frac{\lambda}{2v^{1/2}}) + g$$
 (4.47a)

$$C_2 = d \operatorname{erf}(\frac{\lambda}{2u^{1/2}}) + e \operatorname{erf}(\frac{\lambda}{2v^{1/2}}) + f$$
 (4.47b)

where the eigenvalues are

$$u, v = \frac{1}{2} (D_{11} + D_{22}) \pm [(D_{11} + D_{22})^{2} - 4(D_{11}D_{22} - D_{21}D_{12})]^{1/2} . \qquad (4.48)$$

From the definitions of D_{ij} for the case of quasi-binary systems (4.28)

$$D_{11}D_{22} - D_{12}D_{21} = 0$$

(4.49)

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and, therefore,

$$u = D_{11} + D_{22}$$
, $v = 0$ (4.48a)

and the coefficients in (4.47) are found to be

$$a = \frac{z_2^2 \overline{C}_2 (C_{10} - C_{11}) - z_1 z_2 \overline{C}_1 (C_{20} - C_{21})}{2 (z_1^2 \overline{C}_1 + z_2^2 \overline{C}_2)}$$
(4.50)

$$b = \frac{z_1^2 \overline{C}_1 (C_{10} - C_{11}) + z_1 z_2 \overline{C}_1 (C_{20} - C_{21})}{2(z_1^2 \overline{C}_1 + z_2^2 \overline{C}_2)}$$
(4.51)

$$g = \overline{C}_1 = \frac{1}{2} (C_{10} + C_{11})$$
 (4.52)

$$d = \frac{z_1^2 \overline{C}_1 (C_{20} - C_{21}) - z_1 z_2 \overline{C}_2 (C_{10} - C_{11})}{2 (z_1^2 \overline{C}_1 - z_2^2 \overline{C}_2)}$$
(4.53)

$$e = \frac{z_2^2 \overline{C}_2 (C_{20} - C_{21}) + z_1 z_2 \overline{C}_2 (C_{10} - C_{11})}{2 (z_1^2 \overline{C}_1 + z_2^2 \overline{C}_2)}$$
(4.54)

$$f = \overline{C}_2 = \frac{1}{2} (C_{20} + C_{21})$$
 (4.55)

4.5 Discontinuity of Concentration Profiles at the Interface

The vanishing of the D matrix (Eq. (4.49)) implies that the concentration profiles of C_1 and C_2 will in general have step discontinuities at the origin of magnitudes 2b and 2e, respectively. These discontinuities arise solely from the fixed anion step discontinuity and the necessity of maintaining neutrality of real charges throughout the system.

If the anion moves appreciably, the system must be treated as a ternary and the ionic diffusion of the species are described by Eqs. (4.41) - (4.44). From the definitions of D_{ij} 's in Eqs. (4.43),

$$D_{11}'D_{22}' - D_{12}'D_{21}' = \frac{[D_1D_a(z_1^2C_1 + z_a^2C_a) + D_1D_2z_2^2C_2]}{(D_1z_1^2C_1 + D_2z_2^2C_2 + D_az_a^2C_a)^2}$$

× $[D_1 D_2 z_1^2 C_1 + D_2 D_a (z_2^2 C_2 + z_a^2 C_a)]$

$$-\frac{(D_1 D_a - D_1 D_2) (D_2 D_a - D_1 D_2) z_1^2 z_2^2 C_1 C_2}{(D_1 z_1^2 C_1 + D_2 z_2^2 C_2 + D_a z_a^2 C_a)^2}$$
(4.56)

≠ 0

(4.56)

which is clearly not zero and hence the eigenvalues, u and v, by definition (4.48) are both non-zero, i.e., $u \neq 0$, $v \neq 0$. This implies a relaxation of the discontinuities in

 C_1 and C_2 , which is expected since the anion step discontinuity relaxes through the anion motion.

4.6 Relative Directionality of the Diffusion Fluxes

The flux equations (4.27) can be written in the form

$$J_{1} = \frac{-D_{1}D_{2}z_{2}}{(D_{1}z_{1}^{2}C_{1} + D_{2}z_{2}^{2}C_{2})} \{z_{2}C_{2} \frac{\partial C_{1}}{\partial x} - z_{1}C_{1} \frac{\partial C_{2}}{\partial x}\}$$
(4.57)

$$J_{2} = \frac{D_{1}D_{2}z_{1}}{(D_{1}z_{1}^{2}C_{1} + D_{2}z_{2}^{2}C_{2})} \{z_{2}C_{2} \frac{\partial C_{1}}{\partial x} - z_{1}C_{1} \frac{\partial C_{2}}{\partial x}\}$$
(4.58)
$$= -\frac{z_{1}}{z_{2}}J_{1} .$$
(4.58a)

From the analytic solutions presented earlier, (4.47) - (4.55), the fluxes (4.57) and (4.58) above can be written as

$$J_{1} = -A[z_{2}^{2}\overline{C}_{2}(C_{10}-C_{11}) - z_{1}z_{2}\overline{C}_{1}(C_{20}-C_{21})]$$
(4.59)

$$J_2 = -\frac{z_1}{z_2} J_1$$
 (4.60)

where A is a positive coefficient. In this form, it is clear that the relative directionality of counter-ion flow is independent of the relative magnitude of the diffusion coefficients of the ions, and is thus strictly controllable through control of the initial conditions on the system. This fact is quite contrary to earlier concepts ⁽⁴⁴⁾ that the counter-ion flow direction is determined by the most



Fig. 14b: Predicted reversal of the diffusion directions in glass couple of Fig. 14a following a change in initial conditions to $C_{10}=36.0$, $C_{20}=15.0$, $C_{11}=28.0$, $C_{21}=9.0$

mobile ion. Thus with the appropriate choice of \overline{C}_1 , \overline{C}_2 , $(C_{10}-C_{11})$, $(C_{20}-C_{21})$ and the valences z_1 and z_2 (independent of the knowledge of the self diffusivities) we can control the flow directions. The reversal of flow directions by alteration in the magnitudes of the above parameters are shown in Figs. 14a and 14b for a hypothetical system. This control over flow directions of the ions has potential technological applications, such as in ion-exchangers.

4.7 The State
$$J_1 = J_2 \approx 0$$
 (Transient Equilibrium)

The flux equations for quasi-binary systems (4.27) predict that for finite systems, the cation distributions approach stationary profiles with respect to the sustained anion profile defined by (Fig. 15)

$$J_{1} = -\frac{z_{2}}{z_{1}} J_{2} = 0 \quad . \tag{4.61}$$

From (4.57) or (4.58) this becomes

$$z_2 C_2 \frac{\partial C_1}{\partial x} - z_1 C_1 \frac{\partial C_2}{\partial x} = 0$$
(4.62)

and upon integration to the final (f) state yields

$$z_{2}^{\ln}\left(\frac{c_{11}^{f}}{c_{10}^{f}}\right) = z_{1}^{\ln}\left(\frac{c_{21}^{f}}{c_{20}^{f}}\right) \qquad (4.63)$$

Alternatively (4.62) can be approximated directly to

$$z_2 \overline{C}_2 (C_{10}^f - C_{11}^f) = z_1 \overline{C}_1 (C_{20}^f - C_{21}^f)$$
 (4.64)

Thus the state defined by (4.61) is described by (4.63) or (4.64) along with the constraints (mass and charge conservations):

 $C_{11} + C_{10} = C_{11}^{f} + C_{10}^{f}$ (4.65)



 $C_2^{b0} = 15.0$, to the transient state: $C_1^{af} = 25.53$, $C_2^{af} = 8.23$, $C_1^{bf} = 34.42$, $C_2^{bf} = 15.79$

$$c_{21} + c_{20} = c_{21}^{f} + c_{20}^{f}$$
 (4.66)

$$z_1 C_{11}^{f} + z_2 C_{21}^{f} + z_a C_a = 0$$
 (4.67)

Alternatively the state $J_i = 0$ could have been prepared from time zero (compare Eqs. (4.59) and (4.64)) by judicious choice of concentrations.

This state for glass-like materials, defined by a stationary unbalanced anion distribution and a resulting vanishing of the cation fluxes, is analogous to that observed by Kirkaldy and Purdy ^(40e) in metallic systems, and identified by them as a "transient" equilibrium. We note that in this "transient equilibrium" state for ionic materials such as glasses, the gradient of the electrochemical potential vanishes while the chemical potential gradient remains non-zero. The latter quantity is balanced by the internal field due to the stationary unbalanced anion distribution. That is to say

$$\frac{\partial \overline{\mu}_{i}}{\partial x} = \left(\frac{\partial \mu_{i}}{\partial x} - z_{i} E\right) = 0$$
(4.68)

while

$$\frac{\partial \mu_i}{\partial x} = z_i E \neq 0 . \qquad (4.69)$$

The final stable equilibrium state is only realised with the vanishing of the electrochemical potential gradient, chemical potential gradient, and the internal field, i.e.,

$$\frac{\partial \mu_{i}}{\partial x} = z_{i} E = 0 \quad . \tag{4.70}$$

CHAPTER V

NATURE OF THE DIFFUSION POTENTIAL*

5.1 Introduction

Numerous authors ^(56,57) have commented upon the contradiction between the existence of a diffusion potential (4.25) and the assumed condition that a diffusing system is everywhere neutral (zero net electrical current, Eq. (4.24), implies zero net charge density (4.33)) and yet has no applied external field. This seems to follow from Poisson's equation for a neutral system:

div
$$\vec{E} = \frac{\rho}{\varepsilon_0} = 0$$
 (5.1)

where in mks units, the permittivity of free space $\varepsilon_0 = 8.85 \times 10^{-12}$ farad/m, ρ is the charge density in coulombs/m³ and the field \vec{E} has the dimension volts/m. For an infinite diffusion couple, Eq. (5.1) has the solution:

$$\vec{E} = 0$$
 . (5.2)

* Paraphrased from an unpublished manuscript due to Professor J. S. Kirkaldy.

Actually, there is no contradiction as has been noted recently ⁽⁴⁷⁾, since the charge which is properly entered into the Poisson's equation must include both the real charge $(\rho = \Sigma z_i C_i)$ as well as the dipole charge ρ' ⁽⁵⁵⁾, i.e.,

div
$$\vec{E} = \frac{\rho + \rho'}{\varepsilon_0}$$
 (5.3)
= $\frac{\rho'}{\varepsilon_0}$ (5.3a)

when $\rho = 0$. That is to say, the diffusion potential must be associated with a distribution of dipoles in the diffusion zone, and keeping in mind that

 $\rho' = -\operatorname{div} \vec{P} \tag{5.4}$

the polarisation \vec{P} (dipole moment per unit volume) must be given by

$$\vec{P} = -\epsilon_0 \vec{E} \quad . \tag{5.5}$$

We can say alternatively that under these diffusion conditions the electric displacement

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} = 0 \quad . \tag{5.6}$$

If the charge on each of the dipoles is q, with displacement \vec{d} (a vector, pointing along the direction of the dipole moment) between the equal and opposite charges, the polarisation \vec{P} is by definition

$$\vec{P} = \frac{N}{V} q \vec{d}$$
 (5.7)

or alternatively as

$$\vec{P} = \frac{N}{V} \alpha \vec{E}$$
 (5.7a)

where N/V is the number of dipoles (effective or quasiparticles) per unit volume and α is the polarisability of the quasi-particles. Since from (5.7a) the polarisability of the quasi-particles is negative, we conclude that a quasi-particle interpretation of the diffusion polarisation may not be too fruitful.

5.2 Interpretation of the Diffusion Potential

We here seek a physical interpretation of the polarisation within the solutions of the diffusion equations. For simplicity, we consider an infinite diffusion couple for which the anion concentration is uniform (Section 4.3.2). In this case the approximate solution (constant D_{ij}) giving the concentration C_1 is obtained from Eqs. (4.47) - (4.55) as

$$C_{l} = a \operatorname{erf} \frac{x}{2\sqrt{ut}} + g \tag{5.8}$$

where

$$u = D_{11} + D_{22} \tag{4.48a}$$

and a and g are given by (4.50) and (4.52). Since from (4.20) and (4.36),

$$-\frac{\partial \phi}{\partial x} = E = \frac{RT}{3} \frac{z_1 (D_1 - D_2)}{(D_1 z_1^2 C_1 + D_2 z_2^2 C_2)} \frac{\partial C_1}{\partial x}$$
(5.9)

it follows on integration of (5.9) (introducing average values of C_1 and C_2 in the denominator) that

$$\phi = -k_1 C_1 + k_2 \tag{5.10}$$

where

$$k_{1} = \frac{RT}{\cancel{3}} \frac{z_{1}(D_{1} - D_{2})}{(D_{1}z_{1}^{2}\overline{C}_{1} + D_{2}z_{2}^{2}\overline{C}_{2})}$$
(5.11)

and k_2 is an arbitrary constant of integration. Furthermore, in view of this (5.10), and of Eqs. (5.4), (5.5) and (5.8), we can easily prove that ϕ , E, P and ρ ' as well as C₁ all satisfy Fick's second equation, viz,

$$\frac{\partial ()}{\partial t} = \frac{\partial^2 ()}{\partial x^2}$$
(5.12)

and corresponding to the solutions of (5.12) we have from (5.8) and (5.9)

$$P = -\epsilon_{0}E = -\epsilon_{0} \frac{RT}{J} \frac{z_{1}(D_{1} - D_{2})}{(D_{1}z_{1}^{2}\overline{C}_{1} + D_{2}z_{2}^{2}\overline{C}_{2})} \frac{a}{\sqrt{\pi ut}} e_{xp}^{-\frac{x^{2}}{4ut}}$$
(5.13)

and from (5.4)

$$\rho' = -\frac{1}{\varepsilon_0} \frac{RT}{f} \frac{z_1(D_1 - D_2)}{(D_1 z_1^2 \overline{C}_1 + D_2 z_2^2 \overline{C}_2)} \frac{ax}{\sqrt{4\pi u^3 t^3}} e^{-\frac{x^2}{4ut}} . \quad (5.14)$$

It is particularly to be noted that P and ρ' depend not on the dielectric properties of the medium (ε_0 is the value for free space) but on its diffusive properties. Figures 16 (a, b, c, and d) show schematic representations of the solutions for C_1 , ϕ , P and ρ' for time t > 0.



- (C) Schematic representation of the Polarisation (dipole moment per unit volume) in an infinite glass diffusion couple at t > 0
- (d) Schematic representation of the dipole charge density in an infinite glass diffusion couple at t > 0

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While C_1 and ϕ have derived from initial conditions which are step functions, P derives from an initial condition which is proportional to a Dirac δ -function and δ' derives from an initial condition which is proportional to the derivative of δ , δ' . Recognising the limit of the continuum description at the order of one lattice parameter, the initial condition $\rho' \propto \delta'$ must have a finite representation as in Fig. 17a and P $\propto \delta$ must have the representation as in Fig. 17b. That is to say, the initial condition for ρ' must be a simple dipole with a displacement roughly equal to the lattice parameter d, and an initial dipole moment per unit volume (P) corresponding to this dipole. Making this attribution we can write

$$qd = -A \int Pdx$$
 (5.15)

where the q is the charge and A the interface area of the diffusion couple, and the polarisation P is given by (5.13). Noting that the Dirac δ -function

$$\delta(\mathbf{x}) = \lim_{t \to 0} \frac{1}{2\sqrt{\pi u t}} \exp^{-\frac{\mathbf{x}^2}{4u t}}$$
(5.16)

we obtain the initial charge per unit area (from the integration* of (5.15) at $t \rightarrow 0$), as

 $\int f(x) \delta(x) dx = f(0) \quad .$

*

Since



(a) Schematic representation of the initial dipole charge at the interface of a diffusion couple arising from charge separation due to unequal mobilities of the diffusing ions

t.WW



(a') The interface can be considered a charged parallel plate condenser of charge density ρ'



(b) Schematic representation of the initial dipole moment per unit volume at the interface of a diffusion couple
$$\frac{q}{A} = \frac{2RT}{\frac{1}{2}d} \frac{\varepsilon_0^{az_1(D_1 - D_2)}}{(D_1 z_1^2 \overline{C}_1 + D_2 z_2^2 \overline{C}_2)} .$$
(5.17)

From the definition of a in Eq. (4.50), we have

$$\frac{q}{A} = \frac{2RT}{\exists d} \frac{\varepsilon_0 (D_1 - D_2) z_1 [z_2^2 \overline{C}_2 (C_{10} - C_{11}) - z_1 z_2 \overline{C}_1 (C_{20} - C_{21})]}{2 (D_1 z_1^2 \overline{C}_1 + D_2 z_2^2 \overline{C}_2) (z_1^2 \overline{C}_1 + z_2^2 \overline{C}_2)}$$
(5.18)

$$=\frac{2RT\varepsilon_{0}F}{\exists d}$$
 (5.18a)

where

$$\mathbf{F} = \frac{(D_1 - D_2) z_1 [z_2^2 \overline{C}_2 (C_{10} - C_{11}) - z_1 z_2 \overline{C}_1 (C_{20} - C_{21})]}{2 (D_1 z_1^2 \overline{C}_1 + D_2 z_2^2 \overline{C}_2) (z_1^2 \overline{C}_1 + z_2^2 \overline{C}_2)} \quad . \quad (5.19)$$

The maximum value of |F| will be obtained when $D_1 >> D_2$ (or vice versa), $z_1 = 1$ and $z_2C_{20} = 0 = z_1C_{11}$ leading to

 $|\mathbf{F}| \leq 1 \quad . \tag{5.20}$

The maximum initial charge per unit area, therefore, is

$$\frac{q}{A} = \frac{2RT}{d} \varepsilon_0 \qquad (5.21)$$

The origin of this initial dipole is not hard to fathom. Consider the moment of contact of a couple for which $D_1 >> D_2$. Because of its high mobility, cation component 1 will at the instant of contact penetrate the junction towards the left at a much higher rate than component 2 will penetrate towards the right, thus producing an initial dipole on the time average which is represented by Fig. 17a. Consequently at $t \rightarrow 0$, the system can be considered equivalent to a charged parallel plate condenser. Now the zero net real electric current condition does not allow this initial charge separation to become cumulative beyond one lattice parameter, which is to say that cations 1 will not have completed a permanent jump until appropriate numbers of cations 2 have done so as well. Yet the time average positioning of the two charges during this interchange represents a dipole with a moment of unique sign.

Upon careful reflection it is apparent that the same argument holds for motion in a non-infinite gradient (t > 0) as well as for the step-function (t = 0) under the zero net real electric current condition, and that the total dipole strength (effective number of dipoles) must be independent of the concentration distribution (i.e., of time). That is to say, it does not matter whether the concentration difference is sharp or distributed for a couple distribution can always be thought of as an infinite series of thin couples each with a small step. This conservation law for total dipoles is clearly exhibited in the fact that both the polarisation P and the dipole charge satisfy Fick's second equation (5.12). That is, both the dipole moment per

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unit volume and the number of initial dipoles diffuse as though conserved (c.f. relations (5.13) and (5.14), and Figs. 16c and 16d).

This argument could be rephrased in terms of diffusion models such as described by Charles ⁽³⁶⁾ in Fig. 13. Dipole configurations as in Fig. 13 due, for example, to cations 2 jumping to the right will have mirror image configurations due to cations 1 jumping to the left. However, because of different jump rates of 1 and 2, the concentrations of the two configurations will on the time average be different thus generating a dipole moment.

An estimate of the maximum value of the initial dipole charges associated with the diffusion potential is given in the following section.

5.3 The Effect of a Discontinuity in Anion Concentration

The generalization of the discussion to systems with anion concentration discontinuities at the interface (b,e \neq 0 in Eq. (4.47)) is trivial, for the discontinuities in C₁ and C₂ so generated, lead through (4.29) and (5.1) to the superposition of a stationary δ -function on P and a stationary δ' -function on ρ' which can represent nothing more nor less than a superposed permanent dipole at the initial interface. Of course, if the anion were to diffuse as considered in Chapter 4.3.3, leading to the field in (4.42), this dipole would also migrate in a conservative manner.

With an anion concentration discontinuity at the interface, the extra term in E, over and above the value given by (5.9) or (5.13), which we shall call E_1 , is obtained from (4.29) and (4.27) as

$$E_{1} = \frac{RT}{\underbrace{\ddagger (D_{1}z_{1}^{2}C_{1} + D_{2}z_{2}^{2}C_{2})}_{\sqrt{\pi u t}}} \left\{ \frac{\underbrace{D_{2}(z_{2}d + z_{1}a)}_{\sqrt{\pi u t}} - \frac{x^{2}}{4ut}}{\sqrt{\pi u t}} + \frac{\underbrace{(D_{1}z_{1}b + D_{2}z_{2}e)}_{\sqrt{\pi v t}}}{\sqrt{\pi v t}} - \frac{x^{2}}{exp^{4vt}} \right\}.$$

Since $v \rightarrow 0$ for all t (Eq. (4.48))

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(5.22)

$$E_{1} = \frac{RT}{\mathcal{F}(D_{1}z_{1}^{2}\overline{C}_{1}+D_{2}z_{2}^{2}\overline{C}_{2})} \left\{ \frac{D_{2}(z_{2}d+z_{1}a)}{\sqrt{\pi u t}} - \frac{x^{2}}{4ut} + 2(D_{1}z_{1}b+D_{2}z_{2}e)\delta(x) \right\} .$$
(5.23)

From the definitions of a, b, d, and e in Eqs. (4.50) to (4.54)

$$D_2(z_2d + z_1a) = 0 (5.24)$$

and

$$\frac{(D_{1}z_{1}^{b} + D_{2}z_{2}^{e})}{(D_{1}z_{1}^{2}\overline{C}_{1} + D_{2}z_{2}^{2}\overline{C}_{2})} = \frac{z_{1}(C_{10}-C_{11}) + z_{2}(C_{20}-C_{21})}{(z_{1}^{2}\overline{C}_{1} + z_{2}^{2}\overline{C}_{2})}$$
(5.25)

so that E₁ becomes

$$E_{1} = \frac{RT}{\neq} \frac{\left[z_{1}^{(C_{10}-C_{11})} + z_{2}^{(C_{20}-C_{21})}\right]}{(z_{1}^{2}\overline{c}_{1} + z_{2}^{2}\overline{c}_{2})} \delta(x)$$
(5.26)

which as expected is independent of the kinetic parameters of the system.

The superimposed permanent polarisation P_1 implied by (5.26) and (5.5) is

$$P_{1} = -\frac{RT}{\cancel{F}} \epsilon_{0} \frac{\left[z_{1}^{(C_{10}-C_{11}^{0} + z_{2}^{(C_{20}-C_{21}^{0})}\right]}}{(z_{1}^{2}\overline{c}_{1} + z_{2}^{2}\overline{c}_{2}^{0})} \delta(x) \qquad (5.27)$$

and the corresponding dipole charge density $(\rho')_1$ is

$$(\rho')_{1} = \frac{RT\varepsilon_{0}}{f} \frac{[z_{1}(C_{10}-C_{11}) + z_{2}(C_{20}-C_{21})]}{(z_{1}^{2}\overline{C}_{1} + z_{2}^{2}\overline{C}_{2})} .$$
(5.28)

If we attribute this to a dipole with a negative displacement equal in magnitude to one lattice parameter d, then the charge per unit area at t \rightarrow 0 will be given from (5.15) and (5.27) by

$$\frac{q}{A} = \frac{2RT}{f} \frac{\varepsilon_0}{d} \frac{\left[z_1^{(C_{10}-C_{11})} + z_2^{(C_{20}-C_{21})}\right]}{2(z_1^2 \overline{C}_1 + z_2^2 \overline{C}_2)}$$

$$= \frac{2RT}{f} \frac{\varepsilon_0}{d} F_1$$
(5.29)

where

$$F_{1} = \frac{z_{1}(C_{10}-C_{11}) + z_{2}(C_{20}-C_{21})}{2(z_{1}^{2}\overline{C}_{1} + z_{2}^{2}\overline{C}_{2})} .$$
(5.31)

 $|F_1|$ as defined by (5.31) will generally lie between 0 and unity, its maximum possible value of unity depends on an initial state of the system which has pure silica (SiO₂), on one side.

Comparison of relations (5.19) and (5.31) shows that the maximum attainable magnitude of the initial dipole charge due to the diffusion potential is equal to the maximum attainable magnitude of the permanent interface dipole charge associated with an anion discontinuity. Of course, the two maximum values do not occur for the same boundary and initial conditions. Indeed the two maxima are mutually exclusive, for when there is a maximum in the initial dipole charge due to the diffusion potential there can be no anion discontinuity and its associated dipole charge is zero. On the other hand, when the dipole charge associated with an anion discontinuity has its maximum value, there can be no diffusion of cations (since $C_{11} = C_{21} = 0$ and $z_1 = z_2 = 1$ in (5.31)) and the kinetic dipoles do not appear. We conjecture, therefore, that the total initial dipole charge for all initial conditions must have a charge

$$\frac{q}{A} \leq \frac{2RT\varepsilon_0}{d} \qquad (5.32)$$

Assuming the extremes of |F| = 1 or $|F_1| = 1$, we now seek an order of magnitude estimate for the maximum possible dipole charge associated with either the initial dipole due to the diffusion potential or with the permanent dipole associated with an anion discontinuity. Consider a typical soda-lime glass at 727°C:

2RT = 4000 k cal/mole = 4000 × 4.18 joules/mole

 $\varepsilon_0 = 8.85 \times 10^{-12}$ Farads/m = 8.85×10^{-14} Farads/cm = 96,500 coulombs/mole . Taking d to be the average separation of non-bridging oxygen atoms and adopting the value of 5.5 A° given by Charles (36), we have

$$\frac{q}{A} = \frac{2 \times 4000 \times 4.18 \times 8.85 \times 10^{-14}}{76,500 \times 5.5 \times 10^{-8}}$$
$$= 5.6 \times 10^{-7} \text{ coulombs/cm}^2 . \qquad (5.33)$$

If we were to attribute these dipoles to particles with one electronic charge, $e = 1.6 \times 10^{-19}$ coulombs, then the effective number of particles n per unit area involved in the polarisation will be

$$\frac{n}{A} = \frac{5.6 \times 10^{-7}}{1.6 \times 10^{-19}} \sqrt[5]{4} \times 10^{12} \text{ particles}$$

With a lattice parameter of 5.5 A°, the total number of particles contained on a unit area is

$$\frac{1}{(5.5 \times 10^{-8})^2} \simeq 4 \times 10^{14} / \text{cm}^2$$

Thus the fraction of interface sites contributing to the polarisation is about 1/100 or 1%. Of course, this is the maximum possible value, the practical value being in general much less than this.

We have already noted that the dipole configurations at the instant of contact of the two halves of the couple give the interface the essential characteristics of a charged parallel plate condenser. Thus from Gauss' theorem ⁽⁵⁸⁾, the field E between the plates is

$$E = \frac{\sigma}{\varepsilon_0} = \frac{1}{\varepsilon_0} \frac{q}{A} \quad \text{volts/cm}$$
(5.34)

and from (5.33) at the instant of contact it is

$$E = \frac{5.6 \times 10^{-7}}{8.85 \times 10^{-14}} ~~^{\circ}_{\sim} ~6 \times 10^{6} ~\text{volts/cm}$$

Furthermore the potential difference

$$V = -\int_{0}^{d} Edx = \frac{q}{A} \frac{d}{\varepsilon_{0}} \quad volts = 0.3 \text{ volt} \quad . \tag{5.35}$$

This value is of the same order of magnitude as the 0.06 volt obtained by Hafemann (56) for liquid junction potentials.

We would emphasize that the principles expounded in this section are applicable to diffusion processes in all ionic systems for which the zero net electrical current condition is valid, e.g., ionic crystals, glasses, zeolites, ion exchange resins and many semiconductor arrangements. The diffusion potential, or its associated field is to be uniquely associated with a self-generated distribution of electric dipoles, given to a first approximation by solutions of the Nernst-Planck equation under the zero net electric current condition. This interpretation removes the apparent contradiction between the existence of a diffusion potential and the electroneutrality condition as applied to the real charges.

CHAPTER VI

EXPERIMENTAL TEST OF THE PHENOMENOLOGICAL SCHEME

6.1 Introduction

Two sets of coupled diffusion equations have been formulated in Chapter IV; one for a quasi-binary system (fixed anion solvent), Eq. (4.27), and the other for true ternary systems (all 3 components diffusing), Eq. (4.41). We note that the question as to whether a system can be approximated as a quasi-binary will depend on the relative magnitudes of the cationic diffusion coefficients D_1 and D_2 with respect to that of the anion. For systems in which

 $D_{1}, D_{2} >> D_{a}$ (6.1)

we anticipate that the quasi-binary approximation will satisfactorily describe the diffusion configuration. However, when (6.1) is not true, as would for example be the case at high temperatures (when depolymerisation of the silicate anions leading to smaller and more mobile silicate anion units (Chapter II) becomes appreciable) and all ions have comparable D_i, the system must be considered as a ternary and the more general formulation applied. Systems in which one of the cations (cation 2 for example) has a diffusion coefficient nearly comparable to the anion value, i.e.,

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$$D_1 >> D_2 \sim D_a$$
 (6.2)

must similarly be treated as a ternary.

We can firmly entrench our formulation by successfully testing it against experiments. The published works of Cooper and Varshneya ^(44a), Varshneya and Cooper ^(44b) and Sucov and Gorman ⁽⁴⁵⁾ provide us with the appropriate data.

6.2 Numerical Solution of the Coupled Diffusion Equations

As remarked earlier, the approximate analytic solutions obtained by using average D_{ij} in the flux equations (4.31) or (4.44), are only valid for systems lying within a narrow composition range. For more precise solutions to (4.31) or (4.44) we must use numerical techniques ⁽²⁶⁾.

We note that the boundary conditions in Eq. (4.32) imply

$$\lim_{x \to \infty} \frac{\partial C_i}{\partial x} = 0 \quad . \tag{6.3}$$

Thus we solve (4.31) or (4.44) numerically subject to appropriate initial conditions and boundary conditions (6.3) when we have an infinite system. For finite systems, (6.3) can be simply modified to

$$\frac{\partial C_{i}}{\partial x} = 0 \quad \text{at} \quad x = \pm x_{0}$$
 (6.4)

where x₀ is the coordinate of the boundaries.

An outline of the computer program together with a listing of the program is given in Appendix C.

6.3 Choice of Concentration Units

The concentration units used in the diffusion equations must be in amount per unit volume. Thus compositions given in molar or weight percentages (as given by the microprobe) must be transformed to moles or weight per unit volume. Glass densities as a function of composition (needed for the conversion) are, however, not generally known. In the absence of such data we must seek an approximation. If the range of composition within any one diffusion couple is relatively small then we invoke the assumption that the silica (SiO2) lattice is volume invariant with respect to basic oxide additions and introduce the units of mole% cations/mole% SiO, into our diffusion equations. This is equivalent to using total ion fraction (number of ionic species i/total number of ions in the system) and assuming that the total number of ions per molar volume is invariant.

6.4 Application to the Published Data

6.4.1 The K20-Sr0-Si02 system

Varshneya and Cooper ⁽⁵⁹⁾ have determined the self diffusion coefficients of K and Sr in the system $K_2O-SrO-SiO_2$ over the temperature range 530 to 830°C and obtained the following rate equations for D_K and D_{Sr} :

$$D_{K} = 36.5 \exp[-(48,000 \pm 2,400)/RT]$$
 (6.5)

$$D_{Sr} = 0.17 \exp[-(42,700 \pm 2,400)/RT]$$
 (6.6)

When required D_a was estimated by trial and inspection of the experimental curves near the origin.

Cooper and Varshneya ^(44a) measured the distribution profiles of K⁺ and Sr²⁺ (as K₂O and SrO) in a glass couple of the initial composition given in Table III after a diffusion anneal of 8.37 hrs at 750°C. Using the values of $D_{\rm K}$ and $D_{\rm Sr}$ obtained by Varshneya and Cooper ⁽⁵⁹⁾, Eqs. (6.5) and (6.6), we have predicted the concentration profiles of K₂O and SrO in this glass couple for (1) the quasi-binary approximation and (2) the complete ternary formulation, Eqs. (4.31) and (4.44), respectively, following the computation procedure described in Appendix C. The predicted concentration profiles and the experimental results of Cooper and Varshneya are compared in Figs. 18a and 18b.



Fig. 18a: Observed and predicted concentration profiles of K and Sr in a K₂O-SrO-SiO₂ glass after 8.37 hr at 750°C (prediction based on the quasibinary approximation)

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TABLE III

TERMINAL CHEMICAL COMPOSITION OF THE GLASS COUPLE STUDIED BY COOPER AND AND VARSHNEYA (44a)

OXIDE	WT 8		MOI	E8
к ₂ 0	19.7	23.1	14.9	17.3
Sr0	20.0	15.5	13.7	10.6
SiO2	60.3	61.4	71.4	71.7

TABLE IV

TERMINAL CHEMICAL COMPOSITIONS OF THE GLASS COUPLES STUDIED BY VARSHNEYA AND COOPER ^(44b)

COUPLE	OXIDE	W	[8	MOI	LE%
	к ₂ 0	22.8	19.8	17.1	14.9
A	SrO	15.6	20.0	10.7	13.7
	sio ₂	61.3	60.5	72.2	71.4
	к ₂ 0	20.1	23.0	15.0	17.5
В	SrO	17.0	18.4	11.5	12.7
	sio ₂	63.1	58.5	73.6	69.8
			10.15		
	^K 2 ⁰	22.8	18.12	1/.1	13.5
C	SrO	15.6	18.0	10.7	12.1
	SiO2	61.3	64.1	72.2	74.4



Fig. 19a: Observed and predicted concentration profiles of K and Sr in a K₂O-SrO-SiO₂ glass after 3.7 hr at 737°C (prediction based on the quasi-binary approximation)











*

Fig. 20b: ... (prediction based on ternary formulation) $D_a = 2 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$



Fig. 21a: Observed and predicted concentration profiles of K and Sr in a K₂O-SrO-SiO₂ glass couple after 4.55 hr at 798°C (prediction based on quasi-binary approximation)



Fig. 21b: ... (prediction based on ternary formulation) $D_a = 1 \times 10^{-12} \text{ cm}^2 \text{ sec}^{-1}$

In a second and more extensive investigation of cation diffusion in $K_2^{O-SiO-SiO}_2$ glasses, Varshneya and Cooper ^(1b) have measured the concentration profiles of K and Sr in glass couples A, B and C (Table IV) subjected to the following heat treatments: 3.7 hours at 737°C, 7.9 hours at 708°C and 4.55 hours at 798°C respectively. The recorded K_2^O and SrO concentrations were subject to analytical errors of ±0.1 wt% and ±0.2 wt%, respectively.

Using the values of D_K and D_{Sr} calculated at the test temperatures from Eqs. (6.5) and (6.6), (and the indicated estimate for D_a for the full ternary calculation) the concentration profiles for each of the couples have been computed. The predicted profiles are plotted in Figs. 19, 20 and 21 together with the experimental results of Varshneya and Cooper.

6.4.2 Na₂O-CaO-SiO₂ system

Self-diffusion coefficients for Na have been extensively measured and reported $^{(29)}$. From a survey of these, the values of D_{Na} in Table V have been adopted for this system. The values for D_{Ca} on the other hand are not accurately known for the temperature range of interest in this system. From the limited data $^{(29)}$ we have adopted the values shown in Table V as reasonable estimates for D_{Ca} at the experimental temperatures of interest.

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TABLE V

DIFFUSIVITY DATA FOR Na⁺, Ca²⁺ AND ANION

IN SILICATE GLASS

ION SELF-DIFFUSION COEFFICIENT

Anion	2	×	10 ⁻¹³	cm ²	sec ⁻¹	(705°C)
Anion	5	×	10 ⁻¹³	cm ²	sec-1	750°C
Anion	1	×	10 ⁻¹²	cm^2	sec1	800°C
				13	308°C	
Na ⁺			5 ×	10-5	5 cm ²	sec-1
Ca ²⁺			7 ×	10-8	³ cm ²	sec ⁻¹
Anion			l ×	10-9	cm^2	sec-1

TABLE VI

TERMINAL CHEMICAL COMPOSITION OF THE SODA-LIME GLASS USED BY SUCOV AND GORMAN (46)

OXIDE	MOLE %		
Na ₂ 0	15.3	15.2	
CaO	14.9	12.0	
SiO2	69.8	72.8	

Sucov and Gorman (46) investigated the interdiffusion of Ca²⁺ and Na⁺ in a soda-lime glass couple (Table VI) after a 90 min diffusion-anneal at 1308°C. The two sides of their couple had nearly the same Na₂O, but a substantial difference in CaO. The authors measured only the Ca concentration since their microprobe was not capable of analyzing for Na.

Using the adopted values of D_{Na} , D_{Ca} and D_{a} we have predicted the concentration profiles for Ca and Na and compared them with the data in Figs. 22a and 22b.



Fig. 22a: Observed and predicted concentration profiles of Ca in a Na₂O-CaO-SiO₂ glass after 90 min at 1308°C (prediction based on quasi-binary approximation)





6.5 Discussion

The agreement between the predicted and experimental values for the K₂O-SrO-SiO₂ system at 708°C, 737°C and 750°C are seen in Figs. 18-20 to be quite good. As anticipated, because of the relative magnitudes of D_K, D_{Sr} and D_a at these moderately low temperatures, the quasi-binary approximation and the full ternary treatment lead to similar predictions. It is apparent that within the usual analytical errors the quasi-binary approximation is an adequate prediction. The agreement between the predicted and experimental values for the K₂O-SiO-SiO₂ system at 798°C is reasonable in the quasi-binary approximation, Fig. 21a, but is appreciably better in the ternary formulation. In the Na₂O-CaO-SiO₂ system at 1308°C, the quasi-binary approximation fails badly while the agreement between the ternary prediction and experiment is good. At this high temperature, it is apparent that the quasi-binary assumption is unreasonable both from structural and kinetic considerations, and D is no longer negligible.

CHAPTER VII

EXPERIMENTAL TECHNIQUES AND PROCEDURES FOR THE

K20-CaO-SiO2 SYSTEM

7.1 Couple Design

In designing (i.e., choosing the various compositions) of our diffusion couples the following factors were taken into account:

- (a) The softening point of silicate glasses decreases (in general) with the SiO₂ content.
- (b) It was desirable to carry out the diffusion anneal for the couples in the rigid state (to avoid any uncertainties with the location of the interface), and yet work at not too low temperatures (relatively short annealing times).

(c) The assumption that 'the structure of silicate glasses is the "frozen-in" structure of the melt' is more valid in the high SiO₂ range because the large silicate anions (and the corresponding high viscosity of the melt) make polymerisation on cooling unlikely.

(d) The approximate analytical solutions to the diffusion equations given in Chapter 4.3 are more correct the smaller the composition range involved.

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Thus we chose our glass compositions in the high ${\rm SiO}_2$ range (at least 65 mole% ${\rm SiO}_2$), and within a composition range of about ±10 mole% for the oxides in the glass. Furthermore, since the major source of interaction is expected to be from the discontinuity in the anion concentration (resulting from different ${\rm SiO}_2$ content of the two halves of the couple) we chose seven glass compositions, three of which were separated by 10 mole% step in ${\rm SiO}_2$ content at 5 mole% intervals, with two pairs having the same ${\rm SiO}_2$ content. The metal oxide contents of the glasses were then varied so that uphill as well as downhill interdiffusion profiles would be exhibited.

The system $Na_2O-K_2O-SiO_2$ was originally to be investigated because more information is available for the diffusion coefficients of Na and K, but since the Cameca probe at McMaster was not equipped to detect Na, this system was discarded; Ca was substituted for Na and the system $K_2O-CaO-SiO_2$ studied.

7.2 Materials and Reagents

The K_2O and CaO were added in the form of carbonates. The carbonates K_2CO_3 and $CaCO_3$ powder were Fisher certified grade. The lot analyses reported on the label of each reagent are given in Appendix \bigcirc . The SiO₂ also supplied by Fisher was in the form of floated SiO₂ powder (of about 240 mesh). The analysis of this silica powder could not be obtained from Fisher but it was expected that major impurities would be Al, Mg, Ca, Fe and possibly Na and K. Chemical analyses of the glasses (Appendix E) showed these impurities to be at negligibly low concentrations.

7.3 Apparatus

7.3.1 Glass Melting Furnace

A Harrop muffle furnace heated by means of 4 pairs of silicon carbide resistors, and having a maximum temperature capability of about 1550°C, was used for the glass melting. A 3/4" diameter hole was drilled through the furnace roof via which a stirring rod could be lowered into the melt. The stirring rod consisted of a 0.2" diameter by 4" solid Pt-40% Rh rod attached to the end of a 1/4" I.D. × 27" mullite tube. The mullite end of the rod was screwed on to a pulley system with a differential gear which was coupled to a motor, thus allowing the stirring speed to be varied if desired. This stirring arrangement was mounted vertically on the insulated furnace roof.

7.3.2 Furnace for Stress-relieving of the Prepared Glasses

A horizontally mounted Kanthal wound, resistance furnace was used for stress-relieving of the prepared glasses. A mullite tube 2 1/2" O.D. × 2 1/4" I.D. × 30" long open at both ends was wound over a length of 12" with Kanthal wire. The tube was aligned centrally within a bank of insulating bricks. A pair of polaroid lenses were positioned (held with clamps and support) at the two open ends of the furnace tube (one lens at each end), and a 40 watt light bulb was positioned about 3" from one of the polaroid lenses. This arrangement was used to test for internal stresses.

7.3.3 Furnace for the Diffusion-anneal

A vertically mounted Kanthal REH tube element furnace was used for the diffusion runs. The tube element, REH 7-60 type capable of up to 2100 watts, measuring $3.85" \text{ O.D.} \times 2.76" \text{ I.D.} \times 19.70"$ long, supplied by Ferro Enamels Ltd. of Oakville, was inserted in a protecting ceramic tube. The inside diameter of the protecting tube was about 0.5" less than that of the outside diameter of the tube element, and the space inbetween was filled with coarse grained Al_2O_3 powder as recommended by the suppliers to allow for the expansion and contraction of the strip element and to ensure that neither the strip nor the ceramic insulating parts were exposed to mechanical stresses. The encased tube element was then centred in a brick-lined furnace of casing measuring 13" \times 13" base and 21" high.

A mullite tube 2 1/2" O.D. \times 2 1/4" I.D. \times 30" long was used as the working tube of the furnace, and was placed inside and concentric with the tube element so that about 4 1/2" length of the mullite tube was exposed at each end of the insulating box. The windings of the tube elements were led via a pair of reinforced Kanthal strips on the furnace top to a 220 volt A.C. main supply through a powerstat, a Wheelco on-off temperature controller (with a 120 volt A.C. main supply) connected to a relay (mercury plunger type) and an ammeter.

The furnace tube was fitted at each end with watercooled brass caps. The lower brass cap had a centrally located opening with swagelock 1/4" diameter to allow a thermocouple protection sheath carrying the thermocouple for monitoring the specimen temperature, into the working area of the furnace.

A temperature control thermocouple (Chromel-Alumel) was inserted to come to rest at the side of the tube element through a hole drilled through the insulating box, bricks and ceramic protecting tube.

7.3.4 Crucible Assembly

A Pt-10% Rh dish measuring 1 11/16" base diameter to 2" diameter at the open top, and 3/4" deep was used to hold the diffusion-couples during diffusion anneals. The inside of the Pt-dish was divided into 4 compartments using thin platinum foils so that up to 4 diffusion couples could be done in one single run. Three Pt wires were attached to the dish through three small holes drilled concentrically at the mid-side, thereby enabling the dish to be raised or lowered into the furnace by means of the wires. The Pt-10% Rh dish
was positioned in the furnace on a mullite tube (1 1/2" O.D. by 18" long) which rested inside the lower water-cooled brass cap. The thermocouple sheath containing the thermocouple for monitoring the specimen temperature was introduced into the furnace through the central opening in the lower watercooled brass cap, and was positioned such that its upper end comes to rest at the base of the platinum dish.

7.3.5 Temperature Measurement and Control

All the temperature monitoring and control were by means of Chromel-Alumel thermocouples. The temperature control thermocouple positioned as described in 7.3.3 was connected to the on-off Wheelco controller. From the thermocouple for monitoring the specimen temperature, readings at regular intervals showed that the furnace temperatures were controlled to within ±2°C in the range 700 - 750°C. The temperature profile of the furnace was determined at 700°C and is shown in Fig. 28. The hot zone of the furnace extended over a length of about 3" and it is located at a distance of about 17" to 20" from the lower end of the furnace. Since the platinum dish was short (7.3.4) and the temperature profile provided a hot zone of about 3" length (Section 7.3.6), it is inferred that the quoted specimen temperatures are accurate to with ±2°C.

7.4 Procedure

7.4.1 Glass Melting

For each glass composition in Table VII, measured amounts of K₂CO₃, CaCO₃ and SiO₂ powder, calculated to give the desired nominal composition and totalling approximately 500 gm mixture, were weighed out into a plastic bottle. This was put into the ball mill and left to homogenize for about 6 hours. The mixture was then ready for melting. A 200 c.c. capacity Pt-10% Rh crucible was used for the glass melting. Each glass composition was melted twice, first at 1450°C and then at 1490°C. No special furnace atmosphere was needed since glasses are relatively inert at ordinary furnace atmospheres.

The 500 gm mixture was divided into four approximately equal portions. The melting was carried out in stages (at 1450°C): the first portion was melted, then the next portion was added into the molten pool and put back into the furnace to melt before the next portion was added, and so on until all the 500 gm mixture was molten in the crucible. The molten glass was then held in the furnace for 4 hours at 1450°C. A glass disc 1" diameter by 1/4" thick was cast from the melt and the rest of the melt quenched by pouring it inside a cold graphite mould and directing a jet of cold air blast onto it causing the glass to shatter.

The pieces of the shattered glass were crushed overnight in the ball mill using 3/4" high purity high

TABLE VII

NOMINAL AND ANALYSED CHEMICAL COMPOSITIONS OF THE SILICATE GLASSES STUDIED

GLASS	NOMINAL			COMPOSITION			ANALYSED COMPOSITION					
	М	IOLE %			WT%			MOLE%			WT%	
	SiO ₂	к ₂ 0	Ca0	SiO2	к20	CaO	SiO2	к20	CaO	SiO2	^к 2 ⁰	CaO
A	75	15	10	69.5	21.8 2,18	8.7	74.56	15.40	10.07	69.0	22.3	8.7
В	70	15	15	65.1	21.9	13.0	70.00	15.02	14.98	65.1	21.9	13.0
С	67	20	13	60.6	28.4	11.0	66.49	20.57	12.94	60.0	29.1	10.9
D	74	17	9	67.9	24.4	7.7	73.84	17.04	9.12	66.7	24.5	7.8
Е	70	20	10	63.2	28.3	8.4	69.20	20.69	10.12	62.3	29.2	8.5
F	70	16	14	64.7	23.2	12.1	70.00	15.71	14.25	64.8	22.8	12.3
G	67	21	12	60.3	29.7	10.1	66.5	21.26	12.29	59.8	30.0	10.3

density Alumina grinding balls in a 0.30 gallon capacity procelain jar.

The melting sequence was again repeated (in order to ensure homogeneity of the finished glass), this time at 1490°C, and the meltwas stirred intermittently for 20 minutes in every hour using the stirring rod described in Chapter 7.3.1, for a total of 8 hours. The glass melt was then cast into two preheated (500°C) graphite moulds; one measuring 7 cm \times 6 cm \times 3 cm and the other 2.5 cm diameter by 1 cm deep, and immediately put into a small muffle furnace at 550°C. The furnace was then turned off and allowed to cool down to room temperature. The temperature of 550°C was determined as described in 7.4.2 to be the annealing temperature of the glasses.

This melting sequence was adopted for all the seven glass compositions prepared.

7.4.2 Determination of the Annealing Temperatures of the Glasses

The small pre-cast glass discs were used for determining the annealing temperatures of the glasses. The furnace assembly described in Chapter 7.3.2 was used.

The light source was switched on, and with the polaroid lens nearest to the light source fixed and clamped

in position, the polaroid lens at the far end of the furnace was rotated till all the transmitted light was cut off. The lenses are now in crossed positions, and the second lens was clamped. The glass disc was mounted in a small graphite holder and pushed into the hot zone of the furnace. Because of the stresses in the glass disc, some light was transmitted through the second lens. By varying the furnace temperature and heating the disc for some time at each temperature, the annealing temperature was determined as that at which all transmitted light was cut off. The annealing temperature for all the glasses was determined to be about 550°C.

7.4.3 Chemical Analyses of the Prepared Glasses

Using the diamond wheel, 1/8" thick slices were cut off from all the six sides of the glass blocks, to eliminate any possible differences in composition between the glass surface and the bulk. Small pieces were sectioned from the block and crushed for chemical analyses.

The wet gravimetric technique was used for SiO_2 while Atomic Absorption spectrophotometry was used for K_2O and CaO and other trace elements such as Al, Mg, Na, Fe, Ti, Sr and Ni. Details of the analytical procedures are outlined in Appendix E.

The resulting analyses (see Table VII) were in each case quite close to the nominal measured composition, which

implied that the losses due to evaporation during melting were small. The low level of the trace elements (in wt%: 0.15% Al, 0.08% Na, <0.08% Mg, <0.05% Fe, Ni, Ti and Sr) indicated that there was very little pick-up of these elements during the melting and crushing stages, and also that the SiO₂ powder whose analyses was not supplied by Fisher was of high purity.

7.4.4 Couple Preparation

The glass blocks were cut into small pieces $1/2" \times 1/4" \times 1/4"$, and the mating surfaces polished down from coarse SiC grit to 0.05µ on Linde γ -alumina, thoroughly washed with acetone and dried. Two such prepared glass pieces of the desired compositions formed a couple. Each couple was formed by placing one prepared glass piece on top of the other with the two polished surfaces, and clamping them together with a Pt wire to ensure that they remained in contact while being lowered into the furnace for diffusionanneal.

It was established that when such a prepared couple was put into a furnace at 725°C, diffusion-welding was achieved in under 10 minutes. This was not surprising since the softening temperature of these glasses is in this temperature range, and the glass surfaces were probably smooth. Accordingly, for the diffusion runs of 200 - 300 hours, the time errors due to welding, start-up and shut-down were negligible.

7.4.5 Diffusion Anneal

The couples were placed in the Pt-dish (two couples in the dish for each run) and lowered into the furnace for the diffusion-anneal (Section 7.3.3). The dish was positioned on the mullite stool (Section 7.3.4) and the diffusion-annealing was timed from this moment. Temperature readings were taken every half hour, and the variations were within ±2°C. After annealing for the desired time, the Pt-dish was lowered to the base end of the furnace by opening the brass cap at the lower end of the furnace working tube and withdrawing the mullite stool on which the Pt-dish sat. This base end of the furnace was at about 100°C. The Pt-dish was left in this cold zone for about 15 minutes before it was taken out of the furnace and allowed to cool to room temperature. This procedure was necessary in order to avoid subjecting the glass couples to excessive thermal shocks.

The softening temperature of these glasses, ~750°C, put an upper limit on the temperatures for the diffusionanneal. A lower limit was set by the low diffusivity of Ca. Prior tests and rough theoretical calculations indicated that carrying the diffusion-anneals at temperatures of 600°C and lower would require periods of over 6 weeks to yield measurable penetration depths. Consequently temperatures for diffusion-anneals were confined to the narrow range of 700 - 750°C at intervals of approximately 25°C, viz: 702°C, 723°C, and 749°C.

7.4.6 Sample Preparations for Microprobe Analyses

On cooling down, the diffusion couples were each mounted in a 1" diameter cold mounting resin. After hardening, they were ground on SiC abrasives (grinding off at least 1/10" to ensure the elimination of any surface curvatures on the previous polished surfaces) and polished down to 0.05μ using Linde γ -alumina, washed profusely with alcohol and dried.

Knoop microhardness indentations were made on the diffusion interface of each couple to ensure easy location of the interface during microprobe analysis. Colour differences between the two halves of the couple and the presence in some couples of air bubbles at the interface aided in locating the interface during the indentation.

A fairly thick (~ 300 A°) conducting layer of carbon was deposited on the surface of the polished couples. The couples were then stored in a dessicator ready for the microprobe analyses.

7.4.7 Microprobe Analyses

7.4.7.1 Introduction - special problems with microprobe analyses of alkali silicate glasses

The electron microprobe analysis of alkali silicate glasses calls for special techniques and critical settings of the operating parameters, because (1) the specimens are poor conductors and (2) with spot beams, the resultant characteristic intensities of the elements are generally time-dependent - a phenomenon usually referred to as the Lineweaver effect ⁽⁸²⁾. The details of this phenomenon are briefly described in Appendix F. These problems are overcome by (i) coating the specimen surface with a conducting material, (ii) working with relatively low beam voltages \sim 15 kV, low specimen currents \sim 0.02 μ A, and (iii) using line scans to obtain beams about 100 to 150 μ m long so that the spot beam does not impinge on one spot for too long a time.

7.4.7.2 Microprobe analyses with the Cameca microprobe

The initial part of the microprobe analyses was carried out on an Acton (CAMECA MS-64) microprobe. This instrument has 4 spectrometers with a take-off angle of 18°. Three of these spectrometers (no. I with Quartz 1010, nc. II with Quartz 1011, and no. III with Mica, crystals) are currently in use and thus K, Ca and Si intensities could be measured simultaneously with spectrometers I, II and III. With this microprobe it was established that using a beam voltage of 15 kV and sample currents of \leq 0.02 µA, no Lineweaver effect would be observed on specimens that have been coated with films of Al or C, provided the microprobe was operated on a line mode at 60 cps in order to obtain effectively a line beam about 100 µm long. However, because of the low take-off angle of this microprobe (which implied severe absorption for the detected X-rays) the X-ray intensities obtained with such small specimen currents were very weak. Consequently the count statistics were poor, and the resulting data showed very wide scatter (Figs. 23). Counting for longer times (> 200 secs) in order to accumulate more counts was not possible because of the Lineweaver effect.

It was realised that some increase in counts could be achieved by changing the crystals, e.g., replacing the two quartz crystals with LiF crystals, and replacing Mica with ADP. On the other hand, a much greater improvement could be obtained by increasing the take-off angle of the spectrometers. Therefore, the use of this microprobe was abandoned and subsequent analyses were carried out using an ARL microprobe in the Geology Department, University of Toronto.

7.4.7.3 Microprobe analyses of the couples on the ARL microprobe

The ARL microprobe has 3 fully focusing monochromators, with take-off angle of 52.5°, and a choice of two crystals for each spectrometer, making it possible to measure the X-ray intensities of the three elements K, Ca and Si, simultaneously.

A beam voltage of 15 kV and a specimen current of .02 μ A, using a line scan to obtain a beam measuring approximately 150 μ m long and 2 μ m wide ensured counting times of over 50 secs without any Lineweaver effect (7.4.7.1). The scalers were automatically controlled via a current digitizer and control scaler (rather than via the timer) which automatically stopped the scalers after a preset charge (electron current) had passed down the column. The preset current operating condition corrects for any small drifts due to beam current or lens instability. Preset charge was always chosen so that the counting times were generally about 50 secs.

The ends of the diffusion couples were used as standards. In each case the specimen was oriented so that the line beam was parallel to the diffusion interface and counts were taken on one end (designated X) of the couple, then point-counting in steps of 10 μ m (using a motor) over the diffusion zone. Counts were then taken at the end of the couple (designated Y) as a second standard. The standardization was repeated on a fresh area on end X, giving a second calibration at this end, and thus affording another means of checking for pronounced drift. Starting from a fresh zone, a second scan across the diffusion zone was carried out with standardization at the ends.

Digital outputs of the X-ray intensities in terms of counts were automatically printed as well as punched on cards using a typewriter and cardpuncher coupled to the scaler.

A total of 6 diffusion couples (Table VIII) were analysed.

7.4.8 Corrections to the Microprobe Data

A computer programme, the EMPADR VII, developed by J. Rucklidge and E. L. Gasparirini ⁽⁸⁸⁾ for microprobe data correction was used for reducing the microprobe data to concentrations. The EMPADR, designed mainly for oxides and silicates, is based on the correction procedure recommended by Sweatman and Long ⁽⁸⁹⁾.

Microprobe data for the peak and background counts of the standards and specimens are supplied to the programme in the same form and order that they are generated from the microprobe read-out and the programme corrects for backgrounds, Atomic number factor, Absorption factor and characteristic fluorescence factor. Details of the EMPADR VII and the correction procedure can be found in the references given. The basic equation for data correction is



Absorption	Characteristic
factor	fluorescence
	factor

where the subscripts refer to standard and sample, respectively. UIN is the measured concentration given by the ratio of the counts on the sample and standard after dead time correction and background subtraction. All other parameters are fully defined in the references and will not be reproduced here.

Concentrations in wt% are printed out for the elements K, Ca and Si as well as for their stochiometric oxides. In most cases the total oxide wt% was always within 100 ± 0.7%. Any set outside this range (an indication of considerable drift) was discarded. Independent of this EMPADR VII computer correction procedure, conversion from X-ray counts to concentrations was made by making only background corrections and assuming linearity between the X-ray counts and concentrations, that is, neglecting the three correction factors in Eq. (7.1) since we are only working over a fairly narrow concentration range. There was close agreement between the two approaches, with appreciably less scatter in curves obtained by the linear interpolation approach. This latter was accepted because of the uncertainties in the correction factors in the former. Linear interpolation has also been adopted by Cooper and Varshneya ⁽⁴⁴⁾ and by Varshneya and Cooper ^(1b).

CHAPTER VIII

RESULTS

8.1 Experimental

The resulting experimental concentration profiles of K_2O and CaO in each of the couples examined are given in Figs. 23 to 27. In some cases, profiles of independent analyses of a couple have been plotted (Figs. 24a and 24b, 25a and 25b, and 26a and 26b), giving an indication of the reproducibility of the results. Figures 23a and 23b represent some early results obtained with the Cameca microprobe. The low count rates on this microprobe are reflected by the wide range of scatter in the results. The standard deviations in this case were $\pm 4\%$, $\pm 4\%$ and $\pm 2\%$ for K_2O , CaO and SiO concentrations respectively.

Figures 24 to 27 represent the data obtained with the ARL microprobe. Standard deviations in these are $\pm 0.50\%$ for K₂O, $\pm 1.5\%$ for CaO and $\pm 0.60\%$ for SiO₂.

8.2 Prediction of the Results

From the self-diffusion coefficients reported by Varshneya and Cooper $^{(59)}$ and Tochon $^{(60)}$ good interpolations for D_K at 705°C and 723°C have been made (Table IX). Similarly, from Frischat $^{(61)}$, King and Koros $^{(62)}$ and Towers and Chipman $^{(63)}$ the estimates of D_{Ca} given in Table IX have been adopted. These self-diffusion coefficients D_K, D_{Ca} and those of the anion D_a, specified on the figures were used to predict the concentration profiles following the computation procedure previously outlined. Computations were carried out for each of the diffusion couples using (1) the quasi-binary approximation (Section 4.3.1) and (2) ternary formulation (Section 4.3.3). The results are shown in Figs. 23 to 27 for comparison with experiment.

For couple A/C (Fig. 26) we note first that this couple has a rather large concentration difference between the two halves 00 mole% difference in metal oxide. Now it was noted in Section 3.2 that the diffusion coefficients of the modifier cations, especially Na and K, are very sensitive to alkali oxide concentration, exhibiting an exponential dependence on the oxide concentration. Similarly, the self diffusion data for Ca obtained by Frischat ⁽⁶¹⁾ demonstrated this sensitivity to the CaO concentration. This suggests that the diffusion coefficients used in the flux equations

TABLE IX

DIFFUSIVITY DATA FOR K, Ca AND ANION IN SILICATE GLASSES

COUPLE	SELF-DI	SELF-DIFFUSION COEFFICIENT						
		CM ² SEC ⁻¹						
	D _K	D _{Ca}	Da					
в/С	3×10 ⁻⁸	2×10 ⁻¹²	2×10 ⁻¹³	702°C				
A/D	2×10 ⁻⁸	2×10 ⁻¹²	2×10 ⁻¹³	702°C				
A/C	3×10 ⁻⁸	2×10 ⁻¹²	2×10 ⁻¹³	702°C				
B/D	5×10 ⁻⁸	4×10 ⁻¹²	4×10 ⁻¹³	723°C				
F/G	3×10 ⁻⁸	2×10 ⁻¹²	2×10 ⁻¹³	705°C				

(4.23) should contain this dependence whenever we are working over a rather wide range of concentration (say > 6 mole%). Accordingly we have evaluated the profiles for couple A/C using different values of the selfdiffusivities for each half of the couple. For the right hand side of the couple an upward adjustment of the values of D_K and D_{Ca} were made ($D_K = 8 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ and $D_{Ca} = 2 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$) to obtain a satisfactorily good fit to the experimental data as shown in Fig. 26d. These increases in D_K and D_{Ca} are consistent with the increases expected from the empirical equation given in Appendix B relating D_i to concentration.



Fig. 23a: Observed and predicted concentration profiles of K and Ca in a K₂O-CaO-SiO₂ glass couple, F/G, after 300 hr at 705°C (prediction based on quasi-binary approximation)



Fig. 23b: ... (prediction based on ternary formulation)



Fig. 24a: Observed and predicted concentration profiles
of K and Ca in a K₂O-CaO-SiO₂ glass couple,
B/D, after 200 hr at 723°C (prediction based
on quasi-binary approximation)



Fig. 24b: Observed and predicted concentration profiles
of K and Ca in a K₂O-CaO-SiO₂ glass couple,
B/D, after 200 hr at 723°C (prediction based
on quasi-binary approximation)







Fig. 25a: Observed and predicted concentration profiles of K and Ca in a K₂O-CaO-SiO₂ glass couple, B/C, after 300 hr at 702°C (prediction based on quasi-binary approximation)



Fig. 25b: Observed and predicted concentration profiles of K and Ca in a K₂O-CaO-SiO₂ glass couple, B/C, after 300 hr at 702°C (prediction based on quasi-binary approximation)







Fig. 26a: Observed and predicted concentration profiles of K and Ca in a K₂O-CaO-SiO₂ glass couple, A/C, after 300 hr at 702°C (prediction based on quasi-binary approximation)



Fig. 26b:

Observed and predicted concentration profiles of K and Ca in a K₂O-CaO-SiO₂ glass couple, A/C, after 300 hr at 702°C (prediction based on quasi-binary approximation)







Fig. 26d:

... (prediction based on ternary formulation (variable diffusivities) L.H.S.: $D_{K} = 3 \times 10^{-8}$ cm² sec⁻¹, $D_{Ca} = 2 \times 10^{-12}$ cm² sec⁻¹, $D_{a} = 4 \times 10^{-13}$ cm² sec⁻¹; R.H.S.: $D_{K} = 8 \times 10^{-8}$ cm² sec⁻¹, $D_{Ca} = 2 \times 10^{-11}$ cm² sec⁻¹, $D_{a} = 4 \times 10^{-13}$ cm² sec⁻¹



Fig. 27a: Observed and predicted concentration profiles
of K and Ca in a K₂O-CaO-SiO₂ glass couple,
A/D, after 300 hr at 702°C (prediction based
on quasi-binary approximation)





CHAPTER IX

CONCLUDING REMARKS

The zero net real current condition is the major assumption behind the theory used herein. This assumption, which can be traced back to Planck ⁽⁶⁴⁾, enabled us to eliminate the diffusion potential from the Nernst-Planck equation to produce a soluble diffusion equation. We have noted that the imposition of this condition on an initially electrically neutral system of necessity ensures that the system remains electrically neutral with no real charge accumulation, i.e., $\Sigma z_i J_i = 0$ implies $\Sigma z_i C_i = 0$. An argument for the existence of electrical neutrality was advanced by Guggenheim (65) who examined the consequence of a very slight departure from neutrality. He considered a sphere of radius 1 cm in vacuo with an excess of 10⁻¹⁰ moles of an ionic species (far too small to be detected chemically) with valence +1 accumulated at the surface of the system, and showed the electrical potential to be about 10⁷ volts - a potential that would result in a high voltage breakdown of the system! Such considerations and the results of many experiments strongly support the zero current assumption.

It is apparent from the above considerations that the strongest diffusion interactions which occur in the ionic

systems under consideration must be intimately connected with the necessity that diffusing ions of unequal mobilities migrate to sustain the electrical neutrality. This was the basis on which we neglected all the Onsager cross coefficients, drift velocities and variations of activity coefficients. The satisfactory agreement between our theory and the experiments validates such a formulation for small concentration differences.

The salient features of this electrical interaction or coupling among the diffusive fluxes as embodied in the theory have been sufficiently demonstrated, and we now recapitulate these. Fixed silicate anion step discontinuities, or more generally a very slow silicate anion penetration, results in a large uphill diffusion of cations (whose step is proportional to the anion concentration difference between the two halves of the couple) of the type shown in Figs. 18, 21, 23, 24 and 25. This interaction is of electrical origin and arises from the need for the system to maintain neutrality.

For finite systems, with a relatively immobile silicate anion concentration discontinuity at the interface, a metastable state characterised by $J_i \approx 0$, $\partial \overline{\mu}_i / \partial x = 0$, with $\partial \mu_i / \partial x = z_i \in \neq 0$, Eqs. (4.68) and (4.69) is approached. This is not a true equilibrium state, and with Kirkaldy and Purdy ^(40e) we label it as "transient equilibrium". True

equilibrium is only approached as the anion migrates towards uniformity, leading finally to $\partial \mu_i / \partial x = z_i E = 0$.

The relative directionality of the diffusion fluxes depends only upon the initial conditions as demonstrated in Chapter 4.6, and is independent of the relative magnitudes of the self diffusion coefficients of the ions. It is envisaged that knowledge of this fact could aid in the control of some technologically interesting processes such as ion-exchangers.

The nature of the diffusion potential, which has been discussed at length by many workers in this field, has been shown to be associated with a distribution of dipoles within the diffusion zone. Recognition of this dipole characteristic of the diffusion potential and the fact that it is the associated dipole charge which must be entered into Poisson's equation to generate the diffusion potential, removes an apparent classical contradiction.

Figures 23a, 24a, 24b, 25a, 25b, 26a, 26b and 27a show for the K_2 O-CaO-SiO₂ system, the comparison between experiments and predictions based on the quasi-binary approximation. Comparisons with the ternary formulation are given in Figs. 23b, 24c, 25c, 26c, 26d and 27b.

The figures show that the quasi-binary approximation is barely adequate for a system in which D_a is not negligible compared to D_{Ca} ($D_{Ca}/D_a \sim 10$). On the other hand, the agreement between experiments and the predictions based on the ternary formulation is good except for Fig. 26c in which constant self diffusivities were assumed for couple A/C with large concentration difference on both halves of the couple. Good agreement is obtained for this couple by using different self diffusivities for the two halves of the couple as is shown in Fig. 26d.

For the $K_2^{O-SrO-SiO_2}$ system in which the anion self diffusivity, D_a is negligible compared to those of the cations K and Sr at low temperatures, (e.g., $D_K^{D_a} > 10^5$ and $D_{Sr}^{D_a} > 10^3$) at temperatures below 750°C, the quasi-binary approximation, $D_a \approx 0$ (Eqs. (4.27) - (4.31)) is satisfactory. However, at high temperatures where D_a becomes large and all the diffusivities approach to within two orders of magnitude of each other, the system must be considered as a true ternary as described by Eqs. (4.39) to (4.44). This is demonstrated by the K_2O -SrO-SiO₂ system at 798°C and the Na₂O-CaO-SiO₂ system investigated by Sucov and Gorman at 1308°C.

In considering the complete ternary formulation it was noted that since D_a is the smallest self diffusion coefficient, the form of the D_{ij}'s in the coupled flux equations ensured that any errors arising from an improper choice of the diffusing anion would be well within the usual microprobe errors. This was also the basis for admitting
that the present experimental techniques are incapable of identifying the actual diffusing anions.

Diffusivity data for OH^- and O^{2-} anions are known, and kinetic considerations indicate that

$$D_{OH} > D_{O} > D_{SiO_4} > D_{Si_2O_7} > \dots \text{ etc.}$$

It is conceivable that a comparison between accurately measured diffusion profiles and predictions based on the values of D_{OH}, D_O and D_{silicate anion} in turn could be carried out to identify the most mobile anion. It is likely, however, that more than one anion will be diffusing significantly so diffusion experiments alone would not be definitive.

TABLE VIII

#206 COUPLE A/C

(i)	(i	i)	DISTANCE
Ca0	к ₂ 0	CaO	к ₂ 0	TYMEDER
IN WT%	IN WT%	IN WT%	IN WT%	(MICRONS)
10.99	29.45	10.9	29.11	130
10.77	29.17	11.02	29.36	120
10.64	29.01	11.05	29.21	110
10.90	29.12	11.13	28.91	100
10.95	28.83	10.9	28.81	90
10.73	28.74	10.8	28.52	80
11.18	28.60	11.24	28.41	70
11.30	28.60	11.05	28.20	60
11.32	28.20	11.24	28.00	50
10.84	27.81	11.15	27.76	40
10.96	28.14	11.43	27.54	30
10.53	27.95	10.8	27.34	20
9.92	27.90	10.2	27.28	10
8.79	27.59	9.23	26.86	0
7.79	25.95	8.18	25.75	-10
7.83	24.94	7.72	24.34	-20
8.37	23.48	8.28	22.84	-30
8.69	22.93	8.65	22.67	-40

#206 COUPLE A/C

	(i	_)		(ii)	DI	STANCE
	Ca0	к ₂ 0	Ca	aO	к ₂ 0	ТМТ	FROM
I	N WT%	IN WT%	IN V	VT8 :	IN WT%	(MI	CRONS)
	8.75	22.66	8	.82	22.67		-50
	8.86	22.26	8	.85	22.60		-60
	8.65	22.41	8	.39	22.50		-70
	8.48	22.46	8	.39	22.54		-80
	8.80	22.34	8	.50	22.54		-90
	8.75	22.34	8	.65	22.45		-100
	8.69	22.21	8	.60	22.40		-110
	8.76	22.21	8	.67	22.30		-120
	8.62	22.24	× ×				-130

#403 COUPLE B/D

(i)			(1	DISTANCE	
	Ca0	к ₂ 0	CaO	к20	FROM
I	N WT%	IN WT%	IN WT%	IN WT%	(MICRONS)
		04 5		04 F	100
	1.15	24.5	/ 1.8	24.5	-120
	7.84	24.5	7.8	24.5	-110
	7.75	24.6	7.69	24.56	-100
	7.92	24.4	7.89	24.43	-90
	7.67	24.5	7.84	24.27	-80
	8.15	24.5	7.57	24.35	-70
	8.12	24.36	7.61	24.28	-60
	7.96	24.14	7.66	24.20	-50
	8.20	24.32	7.87	24.10	-40
	7.98	24.27	8.29	24.03	-30
	8.49	24.29	9.38	23.28	-20
	9.47	24.03	10.69	23.0	-10
	10.64	23.66	12.24	22.93	0
	11.93	23.03	12.83	22.81	10
	12.71	22.67	12.93	22.35	20
	12.78	22.41	12.89	22.42	30
	12.90	22.36	13.14	22.32	40
	13.0	22.15	12.93	22.29	50

#403 COUPLE B/D

(i)			(i.	DISTANCE	
	CaO	к ₂ о	CaO	к20	FROM INTERFACE
1 1	IN WT%	IN WT%	IN WT%	IN WT%	(MICRONS)
	12 0	22.20	12.02	22.20	C 0
	13.0	22.20	12.93	22.29	60
	13.0	22.09	13.18	22.07	70
	13.09	21.82	12.98	22.07	80
	13.01	21.82	12.98	21.91	90
	13.05	22.0	13.20	21.9	100
	13.07	21.9	13.24	21.91	110
	13.00	21.78	12.84	21.94	120
	13.04	21.9	12.93	21.9	130

#	2	0	5	7/	D
π	4	U	2	n/	L

#203 B/C

,		(:	i)	(i	i)	DISTANCE
CaO	к20	CaO	к ₂ 0	CaO	K ₂ O	FROM
IN WT%	IN WT%	IN WT8	IN WT%	IN WT%	IN WT%	(MICRONS)
7.7	24.5	10.9	28.97			-115
7.73	24.5	10.86	29.19			-105
7.66	24.54	11.0	29.35	10.95	29.1	-95
7.89	24.55	11.0	29.23	10.97	29.25	-85
7.65	24.36	11.08	28.84	10.95	28.91	-75
7.81	24.25	11.17	28.96	11.14	28.93	-65
7.82	24.44	11.0	28.68	11.21	28.69	-55
7.84	24.15	11.2	28.60	11.31	28.43	-45
7.94	23.97	11.0	28.53	11.22	28.34	-35
7.85	23.90	11.2	28.20	11.22	28.11	-25
8.17	23.68	11.41	28.13	11.34	27.97	-15
8.19	23.32	11.63	27.93	11.52	27.15	-5
8.28	23.08	11.54	27.51	11.85	27.23	5

#205 A/D

#203 B/C

,			(i)		(ii)	DISTANCE
CaO	к ₂ 0	Ca	о к ₂ 0	CaO	K ₂ O	FROM
IN WT%	IN WT%	IN W	T% IN WT%	IN WT%	IN WT%	(MICRONS)
8.64	22.93	11.	39 27.02	11.85	26.98	15
8.54	22.93	11.	51 26.40	11.35	26.38	25
8.92	22.92	. 11.	61 25.15	11.70	24.84	35
8.60	22.67	11.	57 24.24	11.87	24.04	45
8.82	22.51	11.	78 23.64	12.11	23.08	55
8.72	22.52	12.	52 22.67	12.59	22.40	65
8.66	22.41	12.	84 22.15	13.14	21.86	75
9.0	22.25	13.	33 22.12	12.82	21.86	85
8.7	22.34	13.	03 21.88	13.16	21.81	95
8.73	22.48	13.	0 21.8	13.06	22.08	105
8.7	22.22	12.	84 22.05	12.79	21.98	115
8.75	22.22	13.	28 22.0	12.79	22.13	125
8.6	22.23	12.	83 22.10	13.16	22.0	135
8.7	22.38	13.	0 21.9	13.0	21.9	145





APPENDIX A

COUPLED DIFFUSION AND REACTION IN

METALLIC-IONIC COUPLES (SYSTEMS)

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APPENDIX A

COUPLED DIFFUSION AND REACTION IN METALLIC-IONIC COUPLES (SYSTEMS)

A.1 Introduction

Ionic-metallic systems such as glass-metal joints, slag-metal and alloy-salt systems, etc., are of great interest to scientists and engineers. For example, process metallurgists are interested in smelting and refining processes involving slag-metal systems, while the physical chemists are sometimes interested in salt processing for the removal of fission products from liquid metal fuels ⁽⁶⁶⁾.

These ionic-metallic systems consist of two immiscible phases with the possibility of a third phase (gas phase) if gaseous products are formed from the reactions, e.g., CO, CO_2 or SO_2 in slag-metal systems. Being immiscible, and since no species can exist in the same molecular form in both phases, all reactions occur at the boundary between the two phases. The processes occurring in the system can, therefore, be considered to consist of the following sequential steps: (1) mass transport in the metal phase to or from the phase boundary, (2) mass transport in the slag phase to or from the phase boundary and (3) a number of parallel coupled anodic and cathodic reactions of the type

$$M_{i} \neq M_{i}^{z_{i}} + z_{i}e$$

at the boundary.

The mass transport generally consists of atomic diffusion and convection (natural and forced) so that the mass transport equation must be written to account for atomic diffusion as well as convective mass transport in the form ⁽⁶⁷⁾

$$J_{i} = -D_{i} \frac{\partial \overline{\mu}_{i}}{\partial x} + C_{i} v_{x} - E \frac{\partial C_{i}}{\partial x}$$
(A.2)

where the first, second and third terms in Eq. (A.2) are for atomic diffusion, convective flow and eddy diffusion, respectively. v_x is the x-component of the convective flow velocity, and E is the coefficient of eddy diffusion. The relative importance of the last two terms in comparison with atomic diffusion will depend on the fluid mechanical properties of the system. In most systems, mechanical stirring would eliminate any concentration gradient in the bulk, while maintaining some concentration gradient near the interface provided the interface remains undisturbed. Consequently atomic diffusion is generally thought to be always operative within the so-called "boundary layer" (67,68). The "boundary layer" refers to the film of liquid near the interface, estimated to vary from 0.005 - 0.03 cm (depending of the fluid mechanical state of the system), in which

(A.1)



Fig. 29: Concentration profile in the boundary layer next to the slag-metal interface. The effective thickness of the boundary layer is marked out as δ_j

concentration gradients are considered to exist but beyond which a uniform bulk composition is maintained by turbulent or convective flow (see Fig. 29). The thickness of the boundary layer is defined by ⁽⁶⁷⁾:

$$\delta_{j} = \frac{C_{j(\text{bulk})} - C_{j}(x=0)}{\binom{\partial C_{j}}{(\frac{\partial J}{\partial x})_{x=0}}}$$
(A.3)

where the interface is at x = 0.

At low temperatures in glass-metal systems when both phases are rigid, all mass transport will generally be by atomic diffusion. In any ionic-metallic system under consideration, however, proper analysis requires a good knowledge of the transport processes as well as the chemical kinetics of the interfacial reactions.

Because of the immiscibility of the two phases and from the sequential steps outlined above, the entire process in the system could be considered as a problem of transport within two phases, with one of the boundary conditions determined by the chemical reaction rate at the interface. This viewpoint will be adopted in the following theoretical consideration of the problem. Indeed, the important point to note is that these ionic-metallic systems are generally multicomponent with 2, 3 or more processes occurring simultaneously, each of which consists of at least three of the sequential steps outlined above and with all the chemical reactions coupled through the electrical term. This implies that the exact form of coupling must be understood in order that experiments be properly designed and resulting data be meaningfully interpreted.

A.2 Literature Review

To date we are not aware of any quantitative work [except the brief work of Borom and Pask (45) already discussed in Chapter 3.4] on the overall (diffusion + chemical reaction) kinetics of glass-metal systems. We note that in the related area of slag-metal kinetics, some work has been carried out in one form or another. In most of the experimental work on slag-metal kinetics only individual reactions, especially those of S, P, C or Si, have been studied while the accompanying side reactions are usually neglected. In a few of them, however, the effect of the side reactions, i.e., the coupling between the side reactions and those under investigation, have been studied but a convincing interpretation of the data has been lacking. For example, it has been reported (74,80,81) that phosphorous removal from molten iron is aided by high slag basicity and high oxygen content of the metal while sulphur removal is aided by high slag basicity and low oxygen content of the metal, generally achieved by the addition of deoxidizing agents, e.g., Si, Mn, Al and Ti. A good account and references to all these works can be found in The Making, Shaping and Treating of Steel by United States Steel (69), and The Physical Chemistry of Steelmaking (70a).

Using an induction-heated carbon crucible containing calcium-alumino-silicate slag and carbon saturated iron

brought together in the liquid state and stirred by rotation of the crucible against a stationary paddle, Ramachandran, King and Grant ⁽⁷⁵⁾ have shown that sulphur transfer in slag-metal systems proceeds in such a way that the system remains electrically neutral, i.e., the net current is zero. They obtained the rate of sulphur transfer in terms of other elements from metal to slag as

$$2n_{S} = 2n_{Fe} + 2n_{Mn} + 3n_{A1} + 4n_{Si} + 2n_{C}$$
(A.4)

where the rate of transfer of each species is given in n_i moles/sec. The sign of n is positive for transfer from metal to slag, and negative for slag to metal. Equation (A.4) indicated that these slag-metal reactions are coupled, but owing to the apparent complexity of the system the coupling between simultaneous reactions could not be formulated by any simple explicit expression. King and Ramachandran⁽⁷⁵⁾ later showed that sulphur transfer in slag-metal systems is electrochemical in nature rather than occurring by direct collisions among reactants.

Derge and Birchenall ⁽⁷³⁾ studied the equilibrium exchange rate of radioactive tracer iron Fe⁵⁵, between iron and iron-silicate slag. They noted that first order kinetics formulation for homogeneous systems was adequate and obtained at 1600°C the value of the specific rate constant k, for the

exchange as 0.006, which was expressed so as to be independent of the units used. This contribution of Derge and Birchenall is the only work that we are aware of on the determination of this very important parameter.

In one of the first thorough analyses of the kinetics of slag-metal systems, Wagner (70b) has considered the slagmetal phase boundary reactions to consist of simultaneous anodic and cathodic reactions occurring randomly over the interface in a manner very similar to the corrosion of a homogeneous surface. The main difference between the latter and a slag-metal system is that two liquid phases are involved so that sites of anodic and cathodic reaction fluctuate with time and location. Wagner expressed the reaction rate in a Butler-Volmer type expression (76) for current density giving the current carried by a species in terms of the potential difference across the slag-metal interface, viz:

$$J_{i} = k_{i}C_{i}^{*} \exp[(1-\alpha_{i})z_{i}EF/RT]$$

 $- k_{i}C_{i}^{*} \exp[-\alpha_{i}z_{i}EF/RT]$ (A.5)

where E is the electropotential difference across the interface, k_i and k_i^{\prime} are the rate constants for anodic and cathodic processes respectively for component i, C_i^{\star} and $C_i^{\prime \star}$ are the interfacial concentrations of component i in metal to be oxidized anodically and that of ions to be reduced cathodically, α_i is the charge transfer coefficient whose value lies between zero and unity. With this equation, Wagner considered a number of specific reactions occurring in steelmaking systems - such as sulphur transfer, silica reduction and CO evolution.

Lu ⁽⁷⁷⁾ has applied the irreversible thermodynamic approach to slag-metal reactions to examine the coupling between simultaneous reactions. He showed that the resulting kinetic equations in which the reaction rate of each species is expressed in terms of the electrochemical affinity is equivalent to the Butler-Volmer type expression used by Wagner. The theoretical implications of Lu's analysis appear consistent with the experimental results of Ramachandran et al.⁽⁷⁵⁾ and Kawai ⁽⁷¹⁾. However, the theory was not quantified due to the complicated nature of the computation involved.

No attempt has yet been made to quantitatively analyse the overall rate processes occurring in these systems, i.e., to treat the three sequential steps (diffusion-reaction-diffusion) as a combined process.

A.3 Phenomenological Rate Equations for Coupled Reactions at Glass-Metal Interface

A.3.1 The Scheme and Fundamental Assumptions

In thermodynamic and kinetic studies of metallic phases, adequate representations of these systems are achieved by considering them to consist of neutral atoms. On the other hand, glasses, slags or molten salts must be treated as consisting of ions. Therefore, the interfacial reactions between a truly metallic phase and a truly ionic phase must be of the form

$$M_{i} \stackrel{z}{\leftarrow} M_{i}^{z_{i}} + z_{i}^{e}$$
(A.1)

where M_i are the atomic species in the metallic phase, M_i^{2i} are the ions in the ionic phase having valence z_i and e is the electronic charge.

With respect to the glass-metal system under consideration we, therefore, make the following assumptions:

- (1) The glass is truly ionic with no electronic conduction [all the electrons as written in Eq. (A.1) exist only in the metal], and similarly the metal or alloy phase is completely metallic.
- (2) Following from (1), therefore, all reactions take place only at the glass-metal interface.
- (3) The interfacial reactions proceed in such a way that the

net electric current is zero. This is an experimentally verified fact (75).

- (4) All the reactions as written in (A.1) are of first order.
- (5) We neglect any charge separation at time t = 0. That is, we assume that the system is initially neutral everywhere including the interface which from basic electrochemistry is known to contain dipole layers.
- (6) Although we are not aware of any equilibrium studies of glass-metal systems, we assume that glass-metal equilibria exist. This assumption is also implicit in the work of Borom and Pask ⁽⁴⁵⁾.

A.3.2 Formulation of the Reaction Rate Expressions A.3.2.1 The linear flux-force expression for reactions

Following Wagner ^(70b), it is now accepted that slag-metal displacement, oxidation and reduction reactions* occur by a combination of electrochemical cathodic and anodic reactions of the form

* Displacement or exchange reaction for the case
z₁ = z₂ giving

 $[M_1] + (M_2^{2_1}) \ddagger (M_1^{2_1}) + [M_2]$.

Oxidation and reduction reaction for the case $z_1 + z_2 = 0$ giving

 $[M_1] + [M_2] \stackrel{2}{\leftarrow} (M_1^{z_1}) + (M_2^{z_2})$

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(A.1)

$$M_{i} \stackrel{2}{\leftarrow} M_{i}^{z_{i}} + z_{i}^{e}$$

i = 1, 2, ..., n.

Based on the mass action law, the reaction rates for (A.1) are:

$$\omega_{i} = k_{i}a_{M_{i}} - k_{i}a_{e}^{z_{i}} \qquad (A.6)$$

where a_i 's are the activities or the effective concentrations in the reaction zone at the phase boundary, and we note that these interfacial quantities cannot be measured directly. k_i and k'_i are the individual forward and backward rate constants respectively. These rate constants are analogous to the self diffusion coefficients encountered in diffusion studies, and can be determined by means of exchange reactions involving radioactive isotopes as was attempted by Derge and Birchenall ⁽⁷³⁾.

We now put Eq. (A.6) in an alternative form as

$$\omega_{i} = k_{i}a_{M_{i}}(1 - \frac{k_{i}a_{z_{i}}a_{e}^{z_{i}}}{k_{i}a_{M_{i}}})$$

(A.7)

(from now on we represent $M_i^{z_i}$ by M_i^{\prime}).

By definition, the equilibrium constant K_e is given by the ratio of the forward and backward rate constants, i.e.,

$$K_{e} = \frac{k_{i}}{k_{i}} \quad . \tag{A.8}$$

Also,

$$\ln K_{e} = \frac{\Delta \mu_{i}^{\circ}}{RT}$$
(A.9)

where

 $\Delta \mu_{i}^{\circ} = \Sigma \ \mu_{r}^{\circ} - \Sigma \ \mu_{p}^{\circ}$

is the difference in the standard state chemical potentials between the reactants and products.

The affinity (78) A, of a reaction is defined as the difference between the chemical potentials of the reactants and products, so the electrochemical affinity \overline{A} is

$$\overline{A} = \Sigma \overline{\mu}_{\text{reactants}} - \Sigma \overline{\mu}_{\text{products}}$$
(A.10)

where the electrochemical potential $\overline{\mu}_i$ is defined as

$$\overline{\mu}_{i} = \mu_{i}^{\circ} + RT \ln a_{i} + z_{i} \phi \qquad (A.11)$$

so that

$$\frac{k_{i}^{\prime}}{k_{i}} \frac{a_{M_{i}}a_{e}^{Z_{i}}}{a_{M_{i}}} = \exp\left(-\frac{\overline{A}_{i}}{RT}\right) , \qquad (A.12)$$

therefore, the reaction rate ω_i in (A.7) can be written as

$$\omega_{i} = k_{i} a_{M_{i}} \left[1 - \exp\left(-\frac{\overline{A}_{i}}{RT}\right)\right]$$
(A.13)

i = 1, 2, ..., n .

Lu (77) has shown that Eqs. (A.13) are equivalent to the Butler-Volmer expressions (A.5) for the current density. Both equations, however, have very little practical use for the study of multicomponent systems because of the complex mathematical relations among the simultaneous rate expressions. The simplified forms of (A.5) and (A.13) obtained by linearization of the exponential terms have been examined by Lu (77) who concluded that although both expressions are equivalent in the exact forms, only (A.13) retains the essential characteristics of the reaction on linearization.

The condition for simplifying (A.13) by linearization is that the system is not too far from equilibrium, i.e., that

$$\left| \frac{\overline{A}_{i}}{\overline{RT}} \right| << 1$$

(A.14)

From a Taylor series expansion

$$\exp\left(-\frac{\overline{A}_{i}}{RT}\right) = 1 - \frac{\overline{A}_{i}}{RT} + \frac{1}{2!} \left(\frac{\overline{A}_{i}}{RT}\right)^{2} - \frac{1}{3!} \left(\frac{\overline{A}_{i}}{RT}\right)^{3}$$
(A.15)

so that for (A.14)

$$\exp\left(-\frac{\overline{A}_{i}}{RT}\right) \simeq 1 - \frac{\overline{A}_{i}}{RT}$$
 (A.16)

and (A.13) becomes

$$\omega_{i} = k_{i} a_{M_{i}} \frac{\overline{A}_{i}}{RT} . \qquad (A.17)$$

To be consistent with assumption (A.14), $a_{M_{i}}$ in the above expression (A.17) may be replaced by the equilibrium value $a_{M_{i}}^{e}$, in the final state. Therefore, Eq. (A.17) may be written as

$$\omega_{i} = k_{i} a_{M_{i}}^{e} \frac{\overline{A}_{i}}{RT} , \qquad (A.18)$$

i.e.,

$$\omega_{i} = \omega_{i}^{\circ} \frac{\overline{A}_{i}}{RT}$$
(A.19)

where ω_i° may be identified as the equilibrium exchange rate. Defining a phenomenological constant ℓ_i given by

$$\lambda_{i} = \frac{\omega_{i}^{\circ}}{RT} = \frac{k_{i} a_{M_{i}}^{e}}{RT}$$
(A.20)

we can in general write our rate expressions as

$$\omega_{i} = \ell_{i} \Lambda_{i} \tag{A.21}$$

a special form of a linear flux-force relation of Onsager with all the cross coefficients ignored. The inequality (A.14) seems at first sight to be a very serious limitation on the applicability of the linear phenomenological equation (A.19). However, when the affinity of a given chemical reaction is large, so that (A.14) is not satisfied, the reaction may often be split into a certain number of elementary steps each having an affinity sufficiently small to justify the application of the linear phenomenological laws ⁽⁷⁹⁾. For example, if

$$\overline{A}_{i} = \sum_{j} \overline{A}_{ij}$$
(A.22)

where the index j indicates the individual elementary steps in the ith reaction, the new condition for the validity of the linear phenomenological equation will be

$$\frac{|\overline{A}_{ij}|}{RT} << 1 \quad \text{for all j's}$$
 (A.23)

even though

$$\frac{\left|\bar{A}_{i}\right|}{RT} >> 1 \quad . \tag{A.24}$$

In cases where both (A.23) as well as (A.24) are satisfied, Eq. (A.17) rather than (A.18) should be used.

It should be remembered that Eq. (A.23) is the central restriction on the applicability of the present work. We are reminded, however, that there always exists a region near equilibrium where the linear relationship represents a good approximation.

We now apply (A.21) to a number of systems.

A.3.2.2 Coupled rate expressions for binary systems

For binary systems with the following two electrodic reactions:

$$M_{1} \stackrel{*}{\leftarrow} M_{1}^{z_{1}} + z_{1} e \qquad (A.25a)$$

$$M_{2} \stackrel{*}{\leftarrow} M_{2}^{z_{2}} + z_{2} e \qquad (A.25b)$$

The reaction rates are:

 $\omega_1 = \ell_1 \overline{A}_1 \tag{A.26a}$

$$\omega_2 = \ell_2 \overline{A}_2 \quad . \tag{A.26b}$$

From the definition of affinity in (A.10),

$$\overline{A}_{1} = \xi_{1} + RT \ln\left(\frac{a_{M_{1}}}{a_{M_{1}}}\right) - z_{1} \Delta \phi \qquad (A.27)$$

where

$$\xi_{1} = \mu_{M_{1}}^{\circ} - \mu_{M_{1}}^{\circ} - z_{1}^{\mu} e$$
 (A.28)

and $\Delta \varphi \, (\varphi_{_{\mathbf{S}}} \, - \, \varphi_{_{\mathbf{M}}})$ is the potential difference between metal and slag.

Since slag-metal reactions maintain zero net electric current condition, we can eliminate $\Delta\phi$ in (A.27) by constraining (A.26) appropriately via the zero net current condition,

$$\sum_{i=1}^{N} z_i \omega_i = 0 , \qquad (A.29)$$

i.e.,

$$z_{1}\ell_{1}[\xi_{1} + RT \ell_{n}(\frac{a_{M_{1}}}{a_{M_{1}'}}) - z_{1} \Delta \phi] + z_{2}\ell_{2}[\xi_{2} + RT \ell_{n}(\frac{a_{M_{2}}}{a_{M_{2}'}}) - z_{2} \Delta \phi] = 0$$
 (A.30)

so that

$$\Delta \phi = \{z_1 \ell_1 \xi_1 + z_2 \ell_2 \xi_2 + RT(z_1 \ell_1 \ell_n \frac{a_{M_1}}{a_{M_1'}} + z_2 \ell_2 \ell_n \frac{a_{M_2}}{a_{M_2'}})\} / (z_1^2 \ell_1 + z_2^2 \ell_2)$$
(A.31)

Putting (A.31) into (A.26a) and (A.26b) gives

$$\omega_{1} = \frac{\ell_{1}}{(z_{1}^{2}\ell_{1} + z_{2}^{2}\ell_{2})} \{ (\xi_{1} + RT\ell n \ \frac{a_{M_{1}}}{a_{M_{1}'}}) (z_{1}^{2}\ell_{1} + z_{2}^{2}\ell_{2}) \\ - z_{1}(z_{1}\ell_{1}\xi_{1} + z_{2}\ell_{2}\xi_{2} + z_{1}\ell_{1}RT\ell n \ \frac{a_{M_{1}}}{a_{M_{1}'}} + z_{2}\ell_{2}RT\ell n \ \frac{a_{M_{2}}}{a_{M_{2}'}}) \} ,$$

$$\omega_{1} = \frac{\ell_{1}\ell_{2}z_{2}}{(z_{1}^{2}\ell_{1}+z_{2}^{2}\ell_{2})} (z_{2}\xi_{1}-z_{1}\xi_{2}+z_{2}RT\ell n \frac{a_{M_{1}}}{a_{M_{2}'}} - z_{1}RT\ell n \frac{a_{M_{2}}}{a_{M_{2}'}}) .$$
(A.33)

From (A.9) and definition of ξ_i in (A.28)

$$\omega_{1} = B_{12} \left[- \ln K_{12} + \ln \left(\frac{a_{M_{1}}}{a_{M_{1}}} \right)^{z_{2}} \left(\frac{a_{M_{2}}}{a_{M_{2}}} \right)^{z_{1}} \right]$$
(A.34)

with

$$\omega_2 = -\frac{z_1}{z_2} \omega_1$$
 (A.35)

where K_{12} is the equilibrium constant for the net reaction (from (A.25a) and (A.25b)):

$$z_{2}^{M_{1}} + z_{1}^{M_{2}} \rightarrow z_{2}^{M_{1}} + z_{1}^{M_{2}}$$
 (A.36)

and is defined by

$$RT \ln k_{12} = - (z_2 \xi_1 - z_1 \xi_2)$$
 (A.37)

and B12 in (A.34) is given by

$$B_{12} = \frac{z_2^{k_1 k_2 a_{M_1}^{e} a_{M_2}^{e}}}{z_1^{2} k_1 a_{M_1}^{e} + z_2^{2} k_2 a_{M_2}^{e}}$$
 (A.38)

Notice that the chemical potential of the electrons has cancelled out. This follows from the neutrality condition of zero net current which leads to the overall reaction as given in (A.36).

A.3.2.3 Coupled rate expressions for ternary systems

Following similar steps as in the derivation of (A.34), the general rate expressions for an n-reaction system may be derived as,

$$\omega_{i} = \sum_{j=1}^{N} B_{ij} \left[-\ln K_{ij} + \ln \left(\frac{a_{M_{i}}}{a_{M_{i}}}\right)^{z_{j}} \left(\frac{a_{M_{j}}}{a_{M_{j}}}\right)^{z_{i}}\right]$$
(A.39)

where

$$B_{ij} = \frac{z_{j}^{k} i^{k} j^{a} M_{i}^{a} M_{j}}{\sum_{\substack{\Sigma \\ s=1}}^{N} z_{s}^{2} k_{s}^{a} M_{s}^{e}}$$
(A.40)

with

$$\frac{B_{ij}}{z_j} = \frac{B_{ji}}{z_i}$$
(A.41)

and K_{ij} are the equilibrium constants for the pair-reactions:

$$z_j^{M_i^{\prime}} + z_i^{M_j} \rightarrow z_i^{M_j^{\prime}} + z_j^{M_i}$$
 (A.42)

and represent an aspect of pair correlations in these electrochemical reactions. These pair equilibrium constants are defined by

$$RTlnK_{ij} = - (z_j\xi_i - z_i\xi_j)$$
(A.43)

with

$$\ln K_{ij} = -\ln K_{ji} \qquad (A.44)$$

From Eq. (A.39), it is clear that since B_{ij} 's are positive quantities, the sign and magnitudes of each ω_i will depend not only on its own driving force but also on the relative magnitudes of all the terms in the brackets in this equation, i.e., on the affinities of all the reactions. This is one important aspect of coupling and derives from the electrochemical nature of the system.

For a 3-reaction system involving 3 simultaneous half-cell reactions:

$$M_{1} \neq M_{1}^{z_{1}} + z_{1}e$$

$$M_{2} \neq M_{2}^{z_{2}} + z_{2}e$$

$$M_{3} \neq M_{3}^{z_{3}} + z_{3}e$$

[We define an n-reaction system as that in which there are reactions involving n-species.] The reactions are:

$$\omega_1 = B_{12} \left[- \ln K_{12} / Q_{12} \right] + B_{13} \left[- \ln K_{13} / Q_{13} \right]$$
(A.46)

$$\omega_2 = B_{21} \left[- \ln K_{21} / Q_{21} \right] + B_{23} \left[- \ln K_{23} / Q_{23} \right]$$
(A.47)

$$\omega_3 = B_{31} \left[- \ln K_{31} / Q_{31} \right] + B_{32} \left[- \ln K_{32} / Q_{32} \right]$$
(A.48)

where B_{12} , B_{21} , B_{13} , B_{23} , B_{31} and B_{32} are as defined in (A.40). The pair equilibrium constants K_{12} , K_{21} , K_{13} , K_{23} and K_{32} are as defined in (A.43) and (A.44) above, and Q_{12} , Q_{21} , Q_{13} , Q_{31} , Q_{23} and Q_{32} are given by

$$Q_{ij} = \left(\frac{a_{M_{i}}}{a_{M_{i}}}\right)^{z_{j}} \left(\frac{a_{M_{j}}}{a_{M_{j}}}\right)^{z_{i}}$$
 (A.49)

(A.45)

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and

$$\ln Q_{ij} = -\ln Q_{ji} \qquad (A.50)$$

Notice that rate expressions (A.46) - (A.48) satisfy the neutrality condition of zero net current. Also, from the definitions of B_{ij} , K_{ij} and Q_{ij} , we can rewrite (A.46) - (A.48) as

$$\omega_{1} = B_{12} [- \ln K_{12} / Q_{12}] + B_{13} [- \ln K_{13} / Q_{13}]$$
(A.51)

$$\omega_2 = \frac{z_1}{z_2} B_{12} [\ln K_{12} / Q_{12}] + B_{23} [-\ln K_{23} / Q_{23}]$$
(A.52)

$$\omega_3 = \frac{z_1}{z_3} B_{13} [\ln K_{13}/Q_{13}] + \frac{z_2}{z_3} B_{23} [\ln K_{23}/Q_{23}] \quad . \tag{A.53}$$

A.3.3 Analysis of the Reaction Rate ExpressionsA.3.3.1 Parameters required to describe the rate processes

in a system

From the rate expressions (A.39), it is clear that all the rates are uniquely defined, and no adjustable parameters need to be introduced. All that are required are the individual forward reaction rate constants k_i and the equilibrium concentrations C_i^e or activities a_i^e , in other words, the forward (or backward) reaction rate at equilibrium, as well as the pair equilibrium constants K_{ij} . The equilibrium constant K_{ij} and the rate constants k_i can be measured by means of isotope exchange techniques. The values of C_i^e or a_i^e will depend on the system so the need for this parameter to predict the process might prove awkward, unless equilibration experiments were carried out beforehand. However, it must be recalled that the instantaneous activities were replaced by the equilibrium values during the linearisation of the rate expressions in Section A.3.2.1 on the assumption that the state under consideration is near equilibrium. Consequently if the equilibrium concentrations or activity values are not readily available, it seems reasonable to replace $a_{M_i}^e$ by a_{M_i} .

Since the rate expressions are unique, one requires knowledge of the independently measurable individual rate constants k_i and the pair equilibrium constants K_{ij} only.

A.3.3.2 Reversal of a chemical reaction

Lu ⁽⁷⁷⁾ has defined the reversal of a chemical reaction as the change in sign of ω_i from positive to negative or vice-versa. The necessary (but not sufficient) condition for this is that ω_i vanish. The necessary and sufficient conditions for this phenomenon are that (1) ω_i vanish, and (2) ω_j (i \neq j) remain finite. Note that a 2reaction system (by virtue of the neutrality condition) cannot satisfy the above conditions, and hence the reversal phenomenon cannot take place in these systems.

We now investigate the possibility of having a reversal of the chemical reactions in a 3-reaction system. Let us suppose that ω_1 vanishes and investigate whether ω_2 and ω_3 can still remain finite. From Eq. (A.46) and the simplifying assumption

$$z_1 = z_2 = z_3$$
 (A.54)

which is not very crucial to our present investigation, we obtain the following cases:

(i) $\omega_1 = 0$ as a result of:

$$K_{12} = Q_{12}$$
 and $K_{13} = Q_{13}$. (A.55)

By definitions (A.43) and (A.54)

$$K_{23} = K_{13}/K_{12} {.} {(A.56)}$$

Also from (A.49) and (A.54)

$$Q_{23} = Q_{13}/Q_{12}$$
 (A.57)

Hence,

$$K_{23} = Q_{23}$$
 (A.58)

It follows, therefore, from the rate expressions, that $\omega^{}_2$ and $\omega^{}_3$ must also vanish, i.e.,

$$\omega_1 = \omega_2 = \omega_3 = 0 \tag{A.59}$$

for the case stated in (A.55). (ii) $\omega_1 = 0$ as a result of:

$$B_{12}[-\ln(K_{12}/Q_{12})] = B_{13}[\ln K_{13}/Q_{13}] .$$
 (A.60)

From (A.47), (A.56) and (A.57) we have

$$\omega_2 = B_{12} \ln K_{12} / Q_{12} + B_{23} [- \ln K_{13} / Q_{13} + \ln K_{12} / Q_{12}]$$
(A.61)

$$= (B_{12} + B_{23}) \ln K_{12} / Q_{12} - B_{23} \ln K_{13} / Q_{13}$$
 (A.61a)

Substituting (A.60) for lnK_{12}/Q_{12} in (A.61a), we have

$$\omega_2 = - \left[1 + \frac{B_{23}}{B_{12}} + \frac{B_{23}}{B_{13}}\right] B_{13} \ln K_{13} / Q_{13} \quad . \tag{A.62}$$

Since in general,

 $K_{13}/Q_{13} \neq 1$ and $B_{13} \neq 0$
we see that even if ω_1 vanishes via condition (ii), ω_2 (and hence ω_3) will remain non-zero as long as the quantities in the brackets of (A.62) do not sum to zero. That this sum is non-zero at least for the particular case $z_1 = z_2 = z_3$ under consideration, follows from the definition of the B_{ij} 's.

Thus we expect that reversal of a chemical reaction will in general take place if and only if the system does not reach the state

> $K_{ij}/Q_{ij} = 1$ i,j = 1, 2, ..., n

We note that Lu ⁽⁷⁷⁾ has shown for an n-reaction of finite size, that every reaction could reverse its direction as many as n-l times before its completion. In addition, he has predicted that with an arbitrary initial non-equilibrium state, the concentrations of reactants and products do not change monotonously towards the final state but oscillate about the final state with decreasing amplitude.

(A.63)

A.4 Analysis of Glass-Metal Kinetics

A.4.1 Basic Equations

The equation describing the kinetics of glass-metal (or slag-metal) systems are (1) the flux equations for diffusion in the glass phase, (2) the reaction flux at the interface and (3) the flux equations for diffusion in the metal phase.

To illustrate the analysis of the kinetics of glassmetal systems we consider a quasi-binary silicate glass in contact with a binary metal alloy. The equations describing diffusion in the glass phase and those for reactions at the interface have already been formulated in Chapter 4 and in Section A.3 respectively. For diffusion in the metal phase we have the usual Fick's law. Since we are dealing with a two phase system we use the simple Helfferich formulation (Section 4.3.2) in which the zero net charge condition is explicitly applied. For a quasi-binary silicate glass containing two mobile cations 1 and 2 and a fixed anion 3, the flux equations for the cations are given as in (4.35) (superscript s is used to denote the glass phase), i.e.,

$$J_{1}^{s} = - (D_{11} + D_{22}) \frac{\partial C_{1}^{s}}{\partial x} = - \widetilde{D} \frac{\partial C_{1}^{s}}{\partial x}$$
 (4.35a)

$$J_{2}^{s} = - (D_{11} + D_{22}) \frac{\partial C_{2}^{s}}{\partial x} = - \tilde{D} \frac{\partial C_{2}^{s}}{\partial x}$$
 (4.35b)

where C_{i}^{s} are defined in amount/unit volume and the mass balances give

$$\frac{\partial C_{1}^{s}}{\partial x} = \frac{\partial}{\partial x} (\tilde{D} \ \frac{\partial C_{1}^{s}}{\partial x})$$
(A.64a)
$$\frac{\partial C_{2}^{s}}{\partial x} = \frac{\partial}{\partial x} (\tilde{D} \ \frac{\partial C_{2}^{s}}{\partial x})$$
(A.64b)

From the neutrality condition:

$$z_1 C_1^s + z_2 C_2^s = - z_3 C_3 = constant$$
 (A.65)

For the metal phase with species 1 and 2, we have

$$J_{1}^{m} = -D \frac{\partial C_{1}^{m}}{\partial x}$$
(A.66)

where D is the chemical diffusion coefficient defined by (Darken (90))

$$D = D_1 N_2 + D_2 N_1$$
 (A.67)

where D_1 and D_2 are the self diffusivities of 1 and 2, respectively and N_1 and N_2 are the atom or mole fractions. The Fick's second equation from mass balance is

$$\frac{\partial C_1^m}{\partial t} = \frac{\partial}{\partial x} \left(D \; \frac{\partial C_1^m}{\partial x} \right) \quad . \tag{A.68}$$

If we assume that the molar volume of the metal alloy is essentially independent of concentration in the range under consideration, then

$$C_1^m + C_2^m = constant$$
 (A.69)

where C_1^m is in moles by unit volume.

To describe the kinetics, we solve Eqs. (A.64) and (A.65) for the glass phase, and Eqs. (A.68) and (A.69) for the metal phase subject to the following boundary conditions: at the interface, we have continuity of flux, since there are no sources or sinks, i.e.,

$$J_{1}^{m} = \omega_{1} = J_{1}^{s}$$
 (A.70a)

$$J_2^m = \omega_2 = J_2^s$$
 (A.70b)

which represents two independent relations,

$$J_{1}^{m} = \omega_{1}$$

$$J_{1}^{s} = J_{1}^{m}$$
(A.71)

since

$$z_1 J_1^{s} + z_2 J_2^{s} = 0$$

(4.24)

and in the number fixed frame:

$$J_1^m + J_2^m = 0$$
 . (A.72)

Equations (A.65) and (A.69) also apply at the interface which with (A.71) uniquely determine the interface concentrations.

At the metal end of an infinite couple we could have $C_i^m = C_{i0}^m$ at $x = -\infty$ or some finite location and at the glass end, $C_i^s = C_{i0}^s$ at $x = +\infty$ or some finite location. Thus one can completely solve Eqs. (A.64) and (A.65) for the glass phase, and (A.68) and (A.69) for the metal phase, subject to the continuity relations (A.71) and appropriate boundary conditions.

For consistency, both flux expressions for diffusion and for reaction in the continuity expressions (A.71) must be expressed in the same concentration units. The correct concentration units in the diffusion formalism are amount/unit volume whereas those for activities are mol. fraction. Therefore, care must be exercised to ensure that the same concentrations used in an expression are reduced to the same units. It is apparent that from the concentration units indicated, the densities of both phases will enter into the continuity expressions.

A.4.2 Limiting Cases

For finite systems such as are encountered in process metallurgy (steelmaking, non-ferrous refining, etc.), considerable simplification can be introduced into the problem of solving the equations if either diffusion or reaction is very fast relative to the other. In such a case, it is assumed that the slow step is the rate-determining one and that all other steps are virtually at equilibrium. Wagner ^(71b) has treated at some length the two possible limiting cases: (1) transport-control, and (2) reactioncontrol!

Transport-control is that limiting case where the reactions at the interface are proceeding so fast relative to transport of species in the bulk that the interface is considered to be virtually at equilibrium, and the rate of the process is determined by the transport of one or more of the reacting species to and from the interface. A naive way of looking at, or of picturing this situation is to imagine the reaction as being so fast that as soon as any reacting species is brought to the interface, it is immediately reacted, and so for all intents and purposes, the interface can be considered to be at equilibrium. Strictly speaking, however, we must note that the interface is never truly at the equilibrium concentration except when the system is at equilibrium (at $t \rightarrow \infty$). Under conditions prevailing in steelmaking systems, the temperatures are sufficiently high that interfacial chemical reactions are rapid enough that the overall rate of a reaction is not governed by chemical kinetics, but by how rapidly the participating species can be brought together. Consequently steelmaking kinetics are usually considered as transport-controlled processes. Empirically, it is well known that stirring or increased turbulence in steelmaking systems greatly speed up the kinetics.

Chemical-reaction control is referred to as that limiting case in which the transport of species in the bulk is very fast relative to the chemical reaction rate. In this case the concentration gradients in bulk phases of finite extent are insignificant and the overall rate of the process is determined essentially by the rate of the phaseboundary reaction.

A.4.3 Solutions of the Rate Expressions for Glass-Metal Binary Systems

The continuity expressions at the glass-metal interface (Eq. (A.71)) can be written fully as

$$D \frac{\partial^{2} C_{1}^{m}}{\partial x^{2}} = B_{12} [- \ln K_{12} + \ln Q_{12}]$$

$$D \frac{\partial^{2} C_{1}^{m}}{\partial x^{2}} = \tilde{D} \frac{\partial C_{1}^{s}}{\partial x^{2}}$$
(A.71a)

where B_{12} is defined in (A.38). A key problem in the numerical solution of the rate expressions has to do with the choice of concentration units. The concentration units in B_{12} and Q_{12} are in mole fractions whereas those in C_1^m and C_1^s are in moles/unit volume. For practical purposes it may be more convenient to express them all in mole fractions and so write (A.71a) as

$$D \frac{\partial^{2} C_{1}^{m}}{\partial x^{2}} = \frac{B_{12}}{\rho_{m}} \left[- \ln K_{12} + \ln Q_{12} \right]$$

$$D \frac{\partial^{2} C_{1}^{m}}{\partial x^{2}} = \frac{\rho_{s}}{\rho_{m}} \widetilde{D} \frac{\partial C_{1}^{s}}{\partial x^{2}}$$
(A.71b)

where $\rho_{\rm m}$ and $\rho_{\rm s}$ are the molar densities of metal and glass phase respectively and $C_1^{\rm m}$ and $C_1^{\rm s}$ are now in mole (or atom) fractions. For present purpose, we take $\rho_{\rm s} = \rho_{\rm m}$.

Values of the specific rate constants k_1 and k_2 and the interfacial equilibrium activities a_1^e and a_2^e are still unavailable for any interesting system. Therefore, for the purpose of solving the overall kinetic expressions (A.64), (A.68) and (A.71), we lump all these quantities in the single coefficient B_{12} . We thus consider B_{12} as a "lumped" rate constant analogous to the chemical diffusion coefficient defined by Darken in (A.67), and solve the kinetic expressions for different values of B_{12} .

Because of the non-linear nature of the diffusion equations (A.64) and (A.68) and the time-dependent form of the interface boundary conditions, analytic solutions do not exist. Therefore, we seek numerical solutions and as before we use the finite difference method. The boundary conditions at the ends of the system are similar to those defined in Eq. (6.4).

An outline of the computer program is given in Appendix G.

Solutions were sought for glass-metal systems A, B, C and D with the following initial state: glass phase concentration; $C_1^S = 0.35$, $C_2^S = 0.25$ with $z_1 = z_2 = 1$, and $z_3C_3^S = -0.60$ and metal phase; $C_1^m = 0.70$, $C_2^m = 0.30$ and equilibrium constant $K_{12} = .40$, having different values of self diffusion coefficients D_1^m , D_2^m , D_1^S and D_2^S and "lumped" rate constant B_{12} as indicated in Table A.I.

		,			
SYSTEM	D ^m CM ² SEC ¹	D_2^m CM ² SEC ⁻¹	D ^S CM ² SEC ⁻¹	D ^s CM ² SEC ⁻¹	^B 12 ^{/p} m CM/SEC-
А	10 ⁻⁵	10 ⁻⁵	10 ⁻⁵	10 ⁻⁵	10 ⁻⁴
В	10 ⁻⁷	10 ⁻⁷	10 ⁻⁷	10 ⁻⁷	10 ⁻⁴
С	10 ⁻⁶	10 ⁻⁶	10 ⁻⁸	10 ⁻⁸	10 ⁻⁵
D	10 ⁻⁵	10 ⁻⁵	10 ⁻⁵	10 ⁻⁵	10-7

TABLE A.I

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A.5 Results

The concentration profiles generated by Eqs. (A.64) and (A.69) with (A.71) for system A (Table X), after the following reactions times: 10 sec, 20 sec, 40 sec and 60 sec, are given in Figs. 30a-d. The thickness of the system (consisting of equal glass and metal thicknesses) was 0.04 cm. The concentration quotients Q_{12} (Eq. (A.49)) obtained at each time interval were as follows: 0.6779, 0.5834, 0.4886 and 0.4407, respectively.

Profiles for system B of thickness ± 0.01 cm are plotted in Figs. 31a and 31b, for 30 sec and 5 min reaction times, respectively. The following concentration quotients Q_{12} were obtained in this system at the corresponding time intervals:

(i)	30 sec,	$Q_{12} =$	0.4149;
(ii)	l min ,	Q ₁₂ =	0.4109;
(iii)	2 min ,	Q ₁₂ =	0.4076;
(iv)	4 min ,	Q ₁₂ =	0.4036.

The profiles for system C are plotted in Fig. 32, and the series for system D are shown in Figs. 33a-f. Q_{12} for system D were as follows:

(i)	15 min,	Q ₁₂ =	1.6096;
(ii)	30 min,	Q ₁₂ =	1.554;
(iii)	l hr ,	Q ₁₂ =	1.467;

(iv) 2 hr , $Q_{12} = 1.321$; (v) 4 hr , $Q_{12} = 1.083$; (vi) 8 hr , $Q_{12} = 0.8045$.



Fig. 30a&b: Predicted concentration profiles in system A after 10 sec and 20 sec



Fig. 30c&d: Predicted concentration profiles in system A after 40 sec and 60 sec



Fig. 31a&b: Predicted concentration profiles in system B after 30 sec and 5 min



















A.6 Discussion

The profiles (Figs. 30 - 33) illustrate the various forms of concentration profiles encountered in two-phase kinetics which were briefly discussed in Section A.4.2, viz; mixed control, diffusion control and reaction control. The concentration profiles for system A, Fig. 30, suggest a mixed control kinetics. The system goes toward equilibrium as can be inferred from the Q_{12} values at different times. This is the more common kinetic behaviour of many systems at moderate temperatures where the reaction rates and the diffusion kinetics are of the same order of magnitude and neither exhibits a controlling influence on the overall process.

System B on the other hand, shows clearly a diffusion control process. Within the first 30 sec, the interface is virtually at equilibrium: $Q_{12} = 0.415$, K = 0.4; while the diffusion rate is so slow that the bulk phases are still at the initial state. Note that as indicated earlier, the interface will be at complete equilibrium when the whole system approaches to equilibrium. For all intents and practical purposes the interface can be considered to be at a local equilibrium from the onset of reaction. One may not distinguish $Q_{12} = .415$ and $Q_{12} = 0.40 = K$, by noticing the difference in actual observation.

System C (Fig. 32) exhibits diffusion control in the glass. While diffusion in the metal phase can keep pace with

the fast reaction rate with local equilibrium at interface as before, the glass phase diffusion is very slow and hence controls the overall kinetics.

Reaction control is demonstrated by system D (Fig. 33). The diffusion rate is relatively fast compared to the reaction rate, leading to a practically zero concentration gradient in the bulk.

These concentration profiles, Figs. 30 - 33, illustrating the various rate controlling limits (diffusion, reaction and mixed) have been intuitively known by workers in heterogeneous chemical kinetics for some time now, but have never been formulated on the basis of one single set of equations for glass-metal or slag-metal systems. The ability of our formulation to generate these different controlling cases, depending only on the relative magnitudes of the kinetic parameters D; and k; (in the present case D; and B_{ij}) is extremely gratifying. And indeed this is indicative of not only the consistency of our formulation but also of its potential utility. Again we may draw attention to the fact that systems are all uniquely defined by our model, only the kinetic parameters D, and k, are required to completely characterise a system, and no adjustable parameters are required.

Finally we may again point out the following serious limitations of the model:

- (1) Assumption (5) in Section A.1, which neglects any charge separation at the glass-metal interface at time t = 0, could be open to dispute since it is well known from electrochemistry (though not in any simple quantitative way) that this may not indeed be the case; and
- (2) the linearisation (A.23) of the exponential term in Eq. (A.13) restricts the applicability of the above formulation to the linear range. At the same time, we note that nearly all practical phenomenological laws, Fick's law for diffusion, Ohm's law for electricity, etc., are all of this form.

APPENDIX B

AN EMPIRICAL EQUATION RELATING ALKALI ION SELF DIFFUSIVITY TO COMPOSITION IN SILICATE GLASSES

Cation self diffusivities D_i in glasses have been shown to be very sensitive to the composition of silicates. Figures 11a and 11b drawn from the data of Evstropev ⁽³⁰⁾, and Evstropev and Pavlovskii ⁽³¹⁾ show that D_K and D_{Na} increase exponentially with mole% K_2^0 and mole% Na_2^0 , respectively, in the range 10 - 30 mole%.

More recently Terai et al. (35) have carried out comprehensive experiments on the variation of D_{Na} for the addition of a number of alkali oxides in soda-silica based glass using radioactive tracer techniques. They showed that D_{Na} increased exponentially as the mole% of Na₂O increased, but decreased on the introduction of Li₂O, K₂O, CaO, ZnO, BaO, SrO or CdO into the binary silicate glass. The decrease in D_{Na} was related to the effective radius and the polarising power of the additional divalent cation.

From the data of the above groups of workers, we have deduced the following empirical relation for the concentration dependence of the self diffusivity D_M of a cation in a silicate glass containing MO and other oxides:

$$D_{M} = A \exp(2.3 \alpha C_{eff})$$
(B.1)

where α is the slope of the plot of the self diffusivity of ion M against MO in binary silicate such as in Figs. 11. A is a temperature dependent parameter and

$$C_{eff} = MO \left(1 - \sum_{R=1}^{n} f_{R} \frac{N_{R}O}{MO}\right)$$
(B.2)

is the effective concentration of MO, the summation being taken over all the oxides N_R^O , other than MO and silica, (the absolute value in (B.2) ensures a non-negative concentration); f is a measure of the retardation of the motion of ion M by the presence of other ions $N_R^{}$, and depends on the field strengths*, i.e., the polarising powers of $N_R^{}$.

* A measure of the field strength is the force needed to separate the displace a cation of radius r_R , valence z_R from its non-bridging oxygen, and as a first approximation, f_R per mole is given by

$$f_R \gtrsim \frac{z_R z_0 e^2}{(r_R + r_0)^2} N_0$$

where N_{O} is the Avogadro's number, e the electronic charge, the subscripts R and O refer to cation and oxygen, respectively.

The following values of f_R have been empirically deduced from data of Terai et al. ⁽³⁵⁾, Evstropev and Pavlovskii ⁽³¹⁾ and Towers and Chipman ⁽⁶³⁾: $f_{Na} \gtrsim f_K \gtrsim 1/3$; $f_{Ca} \gtrsim f_{Sr} \gtrsim 2/3$; for most other divalent cations f $\gtrsim 1$. There is an uncertainty about the value of f_{A1} ; it varies from 4 to 1 depending on the Al₂O₃ content of the glass, and this seems to be related to the "intermediate" role of Al in the silicate structure (see Chapter 2.2.2).

If D_M^a and D_M^b represent the self diffusivities of cation M in glass compositions (a) and (b), respectively, then from Eq. (B.1) we can write

$$D_{M}^{a} = A \exp(2.3 \frac{r}{20} C_{eff}^{a})$$
 (B.3)

$$D_{M}^{b} = A \exp(2.3 \frac{r}{20} C_{eff}^{b})$$
 (B.4)

$$D_{M}^{a} = D_{M}^{b} \exp[2.3 \frac{r}{20} (C_{eff}^{a} - C_{eff}^{b})]$$
 (B.5)

Therefore, if D_M^b is known from some previous independent measurement, D_M^a can be calculated from relation (B.5). Using Eq. (B.5) and the values of f_R given above, we were able to correlate the data by Terai et al. in the ternary sodasilicate glass with those of Evstropev in binary silicate (see Fig. 34).

Although the equation correlates the cation self diffusivities reasonably well for the systems tested,



Fig. 34: Variation of the self diffusion coefficient of Na with the effective concentration of Na_2^0 expressed as mole% | $(Na_2^0 - \Sigma f_R^N R^0)$ |

attention must be drawn to its limitations:

- The empirical fit was based on a rather limited set of data.
- (2) The necessary introduction of an absolute value into the expression for the effective concentration C_{eff} to avoid negative concentration values suggests that the expression needs modification.
- (3) The thermodynamic meaning of C_{eff} is not clear.

APPENDIX C

NUMERICAL SOLUTION OF THE DIFFUSION EQUATIONS BY FINITE DIFFERENCE METHOD

To solve Eqs. (4.31) by the finite difference method we divide the range in x and t into intervals Δx and Δt , respectively, and denote by C(I,J-1), C(I,J), C(I,J+1) the concentrations at time I Δt at the points $(J-1)\Delta x$, $J\Delta x$, $(J+1)\Delta x$, respectively, and by C(I+1,J) the concentration at time $(I+1)\Delta t$ and point $J\Delta x$. We then replace all the derivatives in (4.31) by finite difference approximations using a Taylor series expansion so that (4.31a) becomes:

$$C_{1}(I+1,J) = C_{1}(I,J) + \frac{\Delta t}{(\Delta x)^{2}} \{ (D_{11}(J+1) - D_{11}(J)) \\ \times (C_{1}(I,J+1) - C_{1}(I,J)) + D_{11}(J) \\ \times (C_{1}(I,J+1) - 2C_{1}(I,J) + C_{1}(I,J-1)) \\ - \frac{z_{2}}{z_{1}} (D_{22}(J+1) - D_{22}(J)) (C_{2}(I,J+1)) \\ - C_{2}(I,J)) - \frac{z_{2}}{z_{1}} D_{22}(J) (C_{2}(I,J+1)) \\ - 2C_{2}(I,J) + C_{2}(I,J-1)) \} .$$

(C.1)

The equation for C_2 is obtained by exchanging subscripts. This will be designated as Eq. (C.2).

By Taylor expansion at the boundaries about the intervals Δx , $2\Delta x$, condition (6.4) becomes:

$$C_{1}(I+1,1) = \left(4C_{1}(I+1,2) - C_{1}(I+1,3)\right)/3$$

$$C_{2}(I+1,1) = \left(4C_{2}(I+1,2) - C_{2}(I+1,3)\right)/3$$

$$C_{1}(I+1,M) = \left(4C_{1}(I+1,M-1) - C_{1}(I+1,M-2)\right)/3$$

$$C_{2}(I+1,M) = \left(4C_{2}(I+1,M-1) - C_{2}(I+1,M-2)\right)/3 \quad . \quad (C.3)$$

For infinite systems, M is chosen large enough that diffusion does not reach points $\pm M\Delta x$ during time t. For finite couples, points $\pm M\Delta x = x_0$ are the actual ends of the couple.

Using (C.1), (C.2) and (C.3) the computations were carried out at intervals of Δx over the range of given x and this was repeated in steps of Δt to the given t. Before each step of Δt , D_{11} and D_{22} are first calculated from previous concentrations obtained at time I. To minimize errors entering into the approximations above and to obtain accurate results, proper choices of magnitudes for Δx and Δt are required, particularly at the early stages of the diffusion when a discontinuity exists at the interface. All our solutions for infinite couples rapidly converged to a parabolic penetration behavior, thus establishing the stability of the finite difference methodology. Their stability was established via successively finer subdivisions and checking the convergence using the h²-extrapolation ⁽²⁶⁾.

All calculations were carried out on a CDC 6400 model digital computer at the McMaster University Data Processing and Computation Center. A listing of the programme is given below.

```
HWLD, T500.
FTN.
160.
          6400 END OF RECORD
                                                                       227
      PROGRAM TST (INPUT, OUTPUT, TAPES=INPUT, TAPE6=OUTPUT)
  NUMERICAL SOLUTION OF THE QUASI-BINARY DIFFUSION EQUATIONS BY FINITE DIFFRNO
C
    EXPERIMENTAL DATA FOR COUPLE B/C AT
                                               700 C
C
      DIMENSION C1(2,240), C2(2,240), X(240), D11(240), D22(240),
         (3(2,310), W1(2,310), W2(2,310), SUMW(310), IST(3), DFLD(310)
                    PARAMETERS
      READ
            COMMON
C
      RFAD
            (5,10) C1P, C2P, C1N, C2N
                     Z1,
                         Z2, D1,
                                    D2
      RFAD(5, 11)
      RFAD
           (5,12) K, N,M,LIMIT, DELT, DELX
                 4F10.4
   10 FORMAT
               (
                          )
             ( 2F4.0, 2F12.3
   11 FORMAT
                                  )
   12 FORMAT
             ( 4110. F10.1. F10.4 )
      STATE THE INITIAL CONDITIONS FOR THE COUPLE
C
      KN = K - 1
      KP = K + 1
   98 DO 200 J=1,KN,1
      (1(1,J)=(1N)
      (2(1, J) = (2N)
  200 CONTINUE
      C1(1,K) = (C1P + C1N)/2.
      C2(1,K) = (C2P + C2N)/2.
   99 DO 700 J=KP,M,1
      (1(1,J)=C1P)
      (2(1, J)=C2P
  700 CONTINUE
      X(1) = 0.
      DO 600 J=2.M
  600
      X(J) = DFLX * FLOAT(J-1)
      ISTART = 200
      IDELT = 200
      CONST = DELT /(DELX *DELX )
      772 = 72/71
      ZZ1 = Z1/Z2
      DD1 = D1 \times Z1 \times Z1
      DD2 = D2 \times Z2 \times Z2
      DN1 = D1*D2*Z2*Z2
      DN2 = D1*D2*Z1*Z1
  900 DO 1000 I=ISTART, LIMIT, IDELT
      T = FLOAT(I)
      DO 102
               J=1,M
      CK = DD1*C1(1,J) + DD2*C2(1,J)
      D11(J) = DN1*C2(1,J) / CK
      D_{22}(J) = D_{2*}(1,J) / CK
  102 CONTINUE
  100 DO 101 J=2.N
                              CONST
                                          )*((D11(J+1)-D11(J))*(C1(1,J+1)
      C1(2,J) = C1(1,J) + (
                -C1(1,J)+D11(J)*(C1(1,J+1)-2*C1(1,J)+C1(1,J-1))
     1
               -(7Z2)*((D22(J+1) -D22(J))*(C2(1,J+1) -C2(1,J)))
     2
                -( ZZ2 )*(D22(J))*(C2(1,J+1) -2.*C2(1,J)+C2(1,J-1))
     2
                                         )*((D_{2}(J_{+1})-D_{2}(J))*(C_{2}(1,J_{+1})))
      (2(2, J) = (2(1, J) + (
                              CONST
                -C2(1,J)+D22(J)*(C2(1,J+1)-2*C2(1,J)+C2(1,J-1))
     1
                -( ZZ1 )*((D11(J+1)-D11(J))*(C1(1,J+1)-C1(1,J)))
     2
                --( ZZ1 )*(D11(J))*(C1(1,J+1)-2.*C1(1,J)+C1(1,J-1)))
     2
  101 CONTINUE
      STATE THE BOUNDARY CONDITIONS FOR THE COUPLE
C
```

```
C1(2,1)=(4.*C1(2,2)-C1(2,3))/3.
      (2(2,1)=(4,*(2(2,2)-(2(2,3))/3))
      C1(2,M)=(4.*C1(2,M-1)-C1(2,M-2))/3.
      (2(2,M)=(4,*(2(2,M-1)-(2(2,M-2)))/3)
                                                                         228
  110 DO 105 J=1.M
      (1(1,J)=(1(2,J))
      (2(1,J)=(2(2,J))
  105 CONTINUE
 1000 CONTINUE
      DO \ 604 \ J = 1.M
      (3(2,J) = 100 - (2(2,J) - (1(2,J)/2))
  604 CONTINUE
      M1 = 94.2
      M2 = 56.08
      M3 = 60.08
      DO 605 J=1,M
      SUMW(J) = (C1(2,J)*M1)/2 + C2(2,J)*M2+C3(2,J)*M3
  605 CONTINUE
      DO \ 606 \ J = 1.00
      W1(2,J) = (C1(2,J)*M1)/(2.*SUMW(J))
  606 CONTINUE
      DO 607 J=1.M
      W_2(2,J) = (C_2(2,J) * M_2) / SUMW(J)
  607 CONTINUE
   CALCULATION OF THE INTERNAL FIELD FROM THE DIFFUSION POTENTIAL EXPRESSION
C
      DO 72 J = 2.N
      P_1 = Z_1 * D_1 * (C_1(2, J+1) - C_1(2, J-1)) / (2.* DELX)
      P_2 = Z_2 * D_2 * (C_2(2, J+1) - C_2(2, J-1)) / (2. * DELX)
      P3 = Z1 * Z1 * D1 * C1(2, J)
      P4 = Z_{2} \times Z_{2} \times D_{2} \times C_{2} (2, J)
      DFLD(J) = -0.085 * (P1 + P2) / (P3 + P4)
      CONTINUE
   72
  500 WRITE (6, 202)
                             T
  202 FORMAT (1H1, 10H TIME = , F8.0 , 6H SEC. /
                                                             DFLD(J)
          85H C1(2,J) C2(2,J) DISTANCE(CM)
     1
                     D22(J)
                                       )
          D11(J)
     2
      DO 204 J= 2.N
      WRITE (6,405) C1(2,J), C2(2,J), X(J), DFLD(J), D11(J), D22(J)
  204 CONTINUE
      DO \ 608 \ J = 2.00
      WRITE (6,405) W1(2,J), W2(2,J), X(J), DFLD(J), D11(J), D22(J)
  608 CONTINUE
  405 FORMAT (1H- , 4F12.4 , 2E17.9 )
      JJ = JJ + 1
 1001 STOP
      FND
      6400 END OF RECORD
                                   12.94
              14.98
                        41.14.
   30.04
                            2.E-12
                3.F-8
      2.
  1.
                                               200.
                                                          5.E-4
                                   1080000
                 120
                             121
        61
           END OF FILE
```

CD TOT 0110

APPENDIX D

LOT ANALYSES OF REAGENTS USED IN GLASS MAKING

K₂CO₃ Anhydrous powder (Fisher Certified) Lot Analysis Reported on Label

Insoluble Matter	` •••	0.010 %
Loss on Heating (285°C)	•••	1.0 %
Chloride (Cl)	(Limit about	0.003 %)
Nitrogen Compounds (as N)	•••	0.001 %
Phosphate (PO ₄)	•••	0.001 %
Silica (SiO ₂)	•••	0.005 %
Sulphur Compounds (as SO_4)	•••	0.004 %
Ammonium Hydroxide ppt	•••	0.010 %
Calcoim and Magnesium ppt	•••	0.010 %
Arsenic		0.0001%
Heavy Metals (Pb)	• • •	0.0005%
Fe	•••	0.0005%
Na	•••	0.020 %

CaCO₃ powder (Fisher Certified)

Lot Analysis Reported on Label

Insoluble	in Dilute	HC1	• • •		0.010	00
Ammonium,	Hydroxide	ppt	•••		0.010	8
Alkalinit	Y			Pass	Test	

Chloride (Cl)	• • •	0.001	00
Oxidizing Subs (as NO ₃)	•••	0.005	99
Sulphate (SO ₄)	•••	0.010	99
NH ₄	•••	0.003	010
Ba	•••	0.005	00
Heavy Metals (as Pb)	•••	0.001	00
Fe	• • •	0.002	olo
Mg	•••	0.02	00
K	•••	0.01	olo
Na	•••	0.10	8
Sr	• • •	0.10	00

SiO₂ supplied by Fisher
Lot No. 710344
Floated SiO₂ powder (∿ 240 mesh)
Analyses could not be obtained from Fisher.

APPENDIX E

ANALYSES OF SILICATE GLASSES FOR SiO₂, K₂O, AND CaO AND SOME TRACE ELEMENTS

I GRAVIMETRIC ANALYSES FOR SiO2

About 0.25 gm glass powder (\sim 200 mesh) was very accurately weighed (to the 5th decimal place) in a platinum crucible, and approximately 4 gm of Na2CO3 was added to the powder. The mixture was intimately mixed inside the crucible using a glass rod; and then fused on a Bunsen flame for about 1/2 hour. On cooling, the platinum containing the fused glass cake was immersed in a beaker containing 200 ml of 50% HCl. The cake dissolved in the acid, and after about 10 minutes the crucible was rinsed thoroughly. The contents of the beaker were evaporated to dryness overnight on a warm hot plate. Then the residue in the beaker was dissolved in 200 ml of 50% HCl and filtered through a 544 paper (Hardened Ashless paper). The residue on the filter paper contained the SiO2. The dehydration and filtration process was repeated once again on the filtrate, and the two residues (now containing almost all the SiO₂) were combined, ignited in a platinum crucible and weighed. This weighed residue was then treated with HF, evaporated to dryness and reweighed. The difference in weight gave the weight of SiO2.

The final crust left on the platinum crucible was dissolved in 50% HCl and added to the filtrate obtained after the second dehydration process. This filtrate was used for the analyses of K, Ca and traces of Si and other important trace elements using the Atomic Absorption Analyser.

II ANALYSES OF K, Ca AND Si USING ATOMIC ABSORPTION

The filtrate obtained after the SiO₂ analyses was poured into a 500 ml volumetric flask and the flask filled up with deionised distilled water. The flask was shaken to ensure homogeneity. The solution was then diluted to 5000 ml by pipetting 10 ml from the 500 ml flask and diluting to 100 ml with deionised distilled water.

To take account of absorption and interference effects which Ca may have on K and vice versa, standards were made by mixing K, and Ca standards prepared from ultra high purity KCl and CaCO₃, respectively. These standards were made from 2.5 ppm to 10 ppm (of K, and Ca), at intervals of 2.5 ppm.

Using these standards, calibration curves were drawn for both elements, and used to determine the K and Ca contents of the sample solution.

Blanks were carried in each case and the results obtained corrected accordingly. Analysis for each glass
sample was repeated four times and the averages taken. It was found that the Atomic Absorption was not sensitive enough to pick up Si from the filtrate which may have held up to 2% SiO₂.

The range of errors for each element were

Si0₂ ± 1%

 K_2O , CaO $\sim \pm 2\%$.

In addition to Ca, K and Si, a number of trace elements Fe, Al, Na, Mg, Ti, Ni and Sr were checked for. The concentrations of the latter were found to be quite low; typically 0.15 wt% Al, 0.08 wt% Na, Mg and Fe and < 0.05 wt% Ti, Ni and Sr.

APPENDIX F

LINEWEAVER PHENOMENON AND THE INSTABILITY OF ALKALI

SILICATE GLASSES UNDER ELECTRON BOMBARDMENT

Lineweaver ⁽⁸²⁾ first observed that electron bombardment of alkali silicate glasses (in the 10 - 27 kV range) caused evolution of oxygen from the glasses. The out gassing from most glasses fitted the empirical equation ⁽⁸²⁾

$$Q = Q_{m}[1 - \exp(-t/K)]$$
 (F.1)

where Q is the sum of oxygen evolved in time t, and Q_{∞} the maximum amount of oxygen expected from a sample bombardment for long times. The oxygen release mechanism was proposed by Lineweaver as follows: The high energy electrons entering the glass dissipate their energy by ionization and excitation of the atoms of the glass structure and finally come to rest at some depth (proportional to their energy, e.g., 2.7 μ at 20 keV for Corning 7740) within the glass producing a net negative space charge. The resulting electrostatic field inside the glass layer moves the alkali ions towards the negative charge, and the non-bridging oxygens away from this layer of negative charge towards the surface. With electron bombardment, therefore, there is a net diffusion of alkali ions from the surface layers towards the interior of the glass specimen and of oxygen ions towards the conductive surface coatings to which they lose their electrons and evaporate into the vacuum system as O_2 molecules. The loss of oxygen leads to a measurable shrinkage of the glass in the bombarded area, and the mass of glass affected, M, by electron bombardment on an area A cm² is given by

$$= A \frac{V_p^2}{\beta}$$
 (F.2)

where V_p is the electron energy (in volts) after passing through the conductive coating on the glass surface, and β is a constant describing the absorption of electrons by the material. For pyrex glass β was found to be $6.2 \times 10^{-11} V^2 g^{-1} cm^2$.

Μ

Varshneya, Cooper and Cable (83) observed that the characteristic intensities in a $K_2O-SrO-SiO_2$ glass were time dependent; Sr counts remained fairly constant while Si counts increased and K decreased. This phenomenon was explained in terms of the Lineweaver mechanism outlined above. Borom and Hanneman (84) have come to similar conclusions noting that the compositional changes during electron bombardment on glass surfaces are accompanied by severe electron-beam induced cratering damage. The importance of heat flow problems involved in these low thermal conductivity samples

(even with conducting coatings) have been noted by a number of workers ^(85,86,87).

Implicit in the Lineweaver mechanism is the existence of an "incubation period" or "delay time" from the start of electron bombardment before the onset of out gassing and the migration of cations away from the bombarded zone, as was later observed by Vassamillet and Caldwell ⁽⁸⁷⁾. The authors proposed that ion movement in glasses during electron bombardment must depend on the temperature of the volume irradiated, and that there exists a critical temperature (which depends on the glass composition) for an alkali ion diffusion from the irradiated zone. The length of the incubation time and the rate of decay of the X-ray intensities are now known to depend strongly on the beam voltage, current, beam size and the thickness of the conducting coating on the glass surface.

APPENDIX G

NUMERICAL SOLUTION OF THE GLASS-METAL KINETICS

BY FINITE DIFFERENCE METHOD

The procedure is similar to that adopted in the solution of diffusion equations for glass diffusion couples. The partial differential equations (A.64) and (A.68) and the continuity equations (A.71) defining the interface concentration were replaced by the finite difference approximations as described in Appendix C so that the continuity expression of Eq. (A.71a) becomes

$$C_{1}^{m}(I+\Delta t,L) = C_{1}^{m}(I,L-1) + \frac{B \cdot \Delta x}{D_{1}^{m}}$$

$$\times [- \ln K + z^{2} \ln \frac{C_{1}^{m}(I,L)}{C_{1}^{N}(I,L)}$$

$$+ z l \ln \frac{C_{2}^{N}(I,L)}{C_{2}^{m}(I,L)}] . \qquad (G.1)$$

Similarly for the (A.71b) which we designate as Eq. (G.2). The finite difference forms of Eqs. (A.68) and (A.64) describing diffusion in the metal and slag phase respectively are given in the program listing attached below.

In solving the above equations, we first establish the interface concentrations at time $I+\Delta t$ using (G.1) before

solving the diffusion expressions for both phases; and then repeating the process till the end of the diffusion period.

In this solution, Δx and Δt have to be chosen so as to ensure two stability conditions: first Δx is taken sufficiently small that Eq. (G.1) does not lead to a negative concentration (or a concentration greater than unity). From experience it was found that

$$B \cdot \frac{\Delta x}{D} \le 10^{-2} \tag{G.3}$$

ensured stability. This is stability condition no. 1. Secondly, Δx and Δt have to be chosen as described in Appendix F for the diffusion equations. Explicitly this condition is such that (see Crank)

$$D \frac{\Delta t}{x} \leq \frac{1}{3} \qquad (G.4)$$

For systems with very fast reactions and low diffusivities (limiting case of diffusion-control), condition (G.3) generally leads to a very small Δx , and thus a very small Δt . In these cases, long computing times are involved.

```
HWLD, T1000.
FTN.
                                                                      239
LGO.
        6400 END OF RECORD
1
      PROGRAM TST (INPUT, OUTPUT, TAPE5=INPUT, TAPE6=OUTPUT)
   NUMERICAL SOLUTION OF DIFFUSION EQUATIONS FOR A GLASS/METAL COUPLE BY FNIT D
C
      DIMENSION CIM(2,220), C2M(2,220), C1N(2,220), C2N(2,220), XX(500),
       DDM(220), DNN(220)
     1
    READ IN SYSTEM PARAMETERS
C
                                   600000
                                               1.E-3
                                                         5.E-5
C
       201
                 400
                            401
                                  1.E-8
                                                       1.E-5
                                             1.E-8
                                                                 .4
C 1.
             1.E-6
                        1.E-6
      1.
              .30 .70 .30
                                               .25
                                                    .35 .25
                                                                   -.60
                                    .35
C
     .70
      READ(5,12) L,N,NN,LIMIT,DELT,DELX
      READ(5,11) Z1,Z2,D1M,D2M,D1N,D2N,ORTK,FQK
      READ(5,10) CM1M, CM2M, C1M(1,L), C2M(1,L), CN1N, CN2N, C1N(1,L), C2N(1,L)
         ,ZC3
     1
   12 FORMAT
             (4I10,E10.4,E10.4)
   11 FORMAT (2F4.0, 5E10.3, F10.5)
   10 FORMAT(2F10.4,2F5.4,2F10.4,2F5.4,F10.4)
C STATE INITIAL CONDITIONS FOR THE SYSTEM
      LM = L-1
      LN = L+1
      DO 20 J = 1.1M
      C1M(1,J) = CM1M
      C2M(1,J) = CM2M
   20 CONTINUE
      DO 21 J = LN, NN
      CIN(1,J) = CNIN
      (2N(1,J)) = CN2N
   21 CONTINUE
      XX(1) = 0,
      DO 22 J = 2 NN
   22 \times (J) = DELX + FLOAT(J-1)
      MP = 500
      ISTART = 1
     IDELT = 1
      CONST = DELT/(DELX*DELX)
      ZZ1 = Z1 + Z1
      ZZ2 = Z2*Z2
      DN = D1N*D2N
      DZ1 = D1N*Z1
      DZ2 = D2N*Z2
   WE NOW START COMPUTING THE CONCENTRATION DISTRIBUTION FOR BOTH PHASES
C
   24 DO 1000 II = ISTART , LIMIT , IDELT
      T = FLOAT(II)
      DO 31 J = 1,L
      DDM(J) = D1M*C2M(1,J) + D2M*C1M(1,J)
   31 CONTINUE
      DO 51 J = L \cdot NN
      DNN(J) + DN*(ZZ1*C1N(1,J)+ZZ2*C2N(1,J))/(DZ1*C1N(1,J)+DZ2*C2N(1,J))
   51 CONTINUE
      BM = ORTK*DELX/DDM(L)
      BN = ORTK*DELX/DNN(L)
      CIM(2,L) = CIM(1,L-1) - BM*(-ALOG(EQK) + Z2*ALOG(CIM(1,L)))
     1 C1N(1,L)) + Z1*ALOG(C2N(1,L)/C2M(1,L)))
      C2M(2,L) = 1.0 - C1M(2,L)
      C1N(2,L) = C1N(1,L+1) + BN*(-ALOG(EQK) + Z2*ALOG(C1M(1,L)))
       C1N(1,L) + Z1*ALOG(C2N(1,L)/C2M(1,L))
     1
      (2N(2,L) = - (ZC3 + Z1*C1N(2,L))/Z2
```

```
C1M(1,L) = C1M(2,L)
                      C2M(1,L) = C2M(2,L)
                                                                                                                                                                                                                                                     240
                      CIN(1,L) = CIN(2,L)
                      (2N(1,L) = C2N(2,L))
           COMPUTE METAL PHASE CONCENTRATION DISTRIBUTION
C
                      DO 30 J=2.LM
                      C1M(2,J) = C1M(1,J) + CONST*((DDM(J+1) - DDM(J))*(C1M(1,J+1) - DDM(J))*(C1M(1,J+1)) - DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(DDM(J))*(D
                         C1M(1,J) + DDM(J)*(C1M(1,J+1) -2.*C1M(1,J) + C1M(1,J-1)))
                   1
            30 CONTINUE
           COMPUTE CONCENTRATIONS AT THE METAL END OF THE SYSTEMI.E AT J=1 USNG DC/DX=0
C
                      C_{1M(2,1)} = (4.*C_{1M(2,2)}-C_{1M(2,3)})/3.
                      DO 32 J = 1.LM
                      (2M(2,J) = 1.0 - CIM(2,J))
            32 CONTINUE
           COMPUTE GLASS PHASE CONCENTRATION DISTRIBUTION
C
                      DO 50 J=LN,N
                      C1N(2,J) = C1N(1,J) + CONST*((DNN(J+1) - DNN(J))*(C1N(1,J+1) - DNN(J))*(C1N(1,J+1)) - DNN(J))*(DNN(J))*(DNN(J+1)) + DNN(J))*(DNN(J+1)) + DNN(J)) + DNN(
                   2 \text{ CIN}(1,J) + \text{DNN}(J) * (\text{CIN}(1,J+1) - 2 * \text{CIN}(1,J) + \text{CIN}(1,J-1)))
            50 CONTINUE
           COMPUTE CONCENTRATION AT GLASS END OF THE SYSTEM USING DC/DX=0.
C
                      C1N(2,NN) = (4.*C1N(2,NN-1) - C1N(2,NN-2))/3.
C CALCULATE THE CONCENTRATION VALUES OF THE SECOND COMPONENT IN THE GLSS PHASE
                      DO 52 J=LN,NN
                      (2N(2,J)) = -(ZC3 + Z1 * C1N(2,J))/Z2
           52 CONTINUE
                      DO 60 J = 1, LM
                      C1M(1,J) = C1M(2,J)
                      C2M(1,J) = C2M(2,J)
           60 CONTINUE
                      DO 61 J = LN,NN
                      C1N(1,J) = C1N(2,J)
                      (2N(1,J) = C2N(2,J))
           61 CONTINUE
                      IF ( II .NE. MP ) GO TO 1000
           90 WRITE
                                             (6,91) T
           91 FORMAT
                                               (1H1 , 10H
                                                                                                   TIME = , F8.0,6H SEC. /
                                                                                                                                              DISTANCE(CM)
                                                                                                                                                                                                      )
                   1 42H
                                                       C1(2.J)
                                                                                                   (2(2,J)
                      DO \ 100 \ J = 1.1
                      WRITE (6,300) C1M(2,J), C2M(2,J), XX(J)
        300 FORMAT (1H- , 3F12.8)
        100 CONTINUE
                      WRITE
                                             (6, 92)
           92 FORMAT (1H- , 28H
                                                                                                                                                  (2N(2,J))
                                                                                              C1N(2,J)
                      DO 200 J = L NN
                                                                                C1N(2,J), C2N(2,J), XX(J)
                      WRITE (6,300)
        200 CONTINUE
                      MP = MP + 500
    1000 CONTINUE
    1001 STOP
                      END
                             6400 END OF RECORD
                                                              400
                                                                                                401
                                                                                                                            600000
                                                                                                                                                                     1.E-3
                                                                                                                                                                                                          5.F-5
                          201
                                                                                     1.E-6
                                                                                                                         1.E-8
                                                                                                                                                              1.E-8
                                                                                                                                                                                                  1.E-5
                                                                                                                                                                                                                                   .4
       1.
                      1.
                                                1.E-6
                   .70
                                                        •30 •70 •30
                                                                                                                                .35
                                                                                                                                                                     •25
                                                                                                                                                                                       .35
                                                                                                                                                                                                          .25
                                                                                                                                                                                                                                           -.60
                                        END OF FILE
```

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