Mechanism of Viscous Flow in Silicate Melt*

By Osamu HAIDA** and Toshihiko Emi**

Synopsis

Recent development in the theories of viscous flow in silicate melts is critically reviewed, with brief survey on the structure of the melts. Factors to be involved in a satisfactory modelistic theory are discussed, referring to existing models. Importance is stressed of cooperative nature of motion of flow species for viscous flow to occur in silicate melts.

I. Introduction

Recent review¹⁾ has indicated that the rate of many slag/metal reactions in metallurgical systems are controlled predominantly by mass transfer processes involved. Since the rate of mass transfer is usually slower in slag melts even with stirring, control of slag viscosity is of much practical importance to enhance the reactions in refining metals. Also, the viscosity of slag melts has been shown²⁾ to be one of factors determining surface quality of slabs and ingots cast under slags.

In contrast to abundant data and means available for controlling the viscosity, our understanding on the mechanism of viscous flow has been limited because of complicated structure of slag melts. However, recent advance in the knowledge on the ionic and polymeric constitution of the melts, combined with extensive investigation into the mechanism of viscous flow, are going to make it possible to reveal exact nature of viscous flow.

This article is intended to give present status of development in the mechanism of viscous flow with special reference to the structure of silicate melts.

II. Ionic Structure of Slag Melts

Random network model worked out by Zachariasen³⁾ and Warren⁴⁾ from X-ray diffraction analysis of amorphous silicates, and discrete anion model proposed by Bockris and his colleagues⁵⁻⁷⁾ on the basis of physical and kinetic properties of silicate melts, have long been two major pictures for the structure of silicate slag melts. Recently, marked advance in the modelistic theories of ionic structure of the slag melts has made it possible to explain thermodynamic quantities in terms of ionic species of the melts.

The activity, a , of metal oxide, MO, in ionic melts was given by Temkin¹⁾ as

$$a_{MO} = a_{M^{2+}} \cdot a_{O^{2-}} = N_{M^{2+}} \cdot N_{O^{2-}} \quad (1)$$

where N 's are cationic and anionic fractions. Equation (1) is obviously only approximate for multicomponent silicate melts, because ionic strength varies with wide variety of composition of the melts, supporting electrolyte is not existing in the melts, and hence equality

of the 2nd to 3rd terms in Eq. (1) is somewhat questionable. Nevertheless, this approximation has found extensive use in the following treatments.

In binary silicate melts, MO-SiO₂, one has

$$MO = M^{2+} + O^{2-} \quad (2)$$

and

$$O^{2-} + (\rightarrow Si-O-Si \leftarrow) = 2(\rightarrow Si-O^-) \quad (3)$$

or alternatively

$$O^{2-} + O^0 = 2O^- \quad (3')$$

It is customary to take only M^{2+} as cationic species and the rest, such as O^{2-} , SiO_4^{4-} , $Si_2O_7^{6-}$, and so forth, as anionic species. Then, $a_{M^{2+}}$, or $N_{M^{2+}}$, is unity and hence a_{MO} becomes equal to $N_{O^{2-}}$ in Eq. (1).

Here, the concept of activities of MO molecules and of charged oxygen seems unreasonable in view of the fact that the molecules are not existing in the melts and $a_{O^{2-}}$ cannot experimentally be determined. However, a_{MO} and $a_{O^{2-}}$ are convenient measures to deal respectively with slag formation reactions and with metallurgically important slag/metal reactions in which O^{2-} 's are involved. Derivation of these activities has, therefore, been one of the principal objects of the modelistic theories which can be divided into two categories.

The first approach is to avoid complications arising from explicit evaluation of the distribution of complex silicate anions, and to deal formally with equilibrium between oxygen ions (O^{2-}), doubly bonded oxygen atoms ($Si-O-Si$ as O^0), and singly bonded oxygen atoms ($Si-O^-$ as O^-): this was first attempted by Toop and Samis⁸⁾, then by Kapoor and Froberg.¹⁰⁾ The activities of the components of binary silicate melts (a_{MO} and a_{SiO_2}) and the free energy change of formation of the binary silicate melts (ΔG) were related in these theories to an equilibrium constant, $K = [O^{2-}] [O^0] / [O^-]^2$, and to the mole fraction, X , of SiO₂, by taking into account charge and mass balance of oxygen- and silicon-ions. The values of K were chosen to give best fit of calculated to observed values of ΔG (or a_{MO} and a_{SiO_2}), then $[O^{2-}]$, $[O^0]$, and $[O^-]$ were obtained subsequently as a function of X_{SiO_2} .

One more interesting contribution along this line of approach was made by Yokokawa and Niwa¹¹⁾ on the basis of a random network model. A quasi-lattice treatment was employed to evaluate partition function of silicate melts on the assumption that a melt containing n and m molecules of MO and SiO₂ is a

* Received September 5, 1974.

** Research Laboratories, Kawasaki Steel Corp., Kawasaki-cho 1, Chiba 280.

Fig. 1. Ternary plot of the proportions of singly bonded oxygen, silicon and doubly bonded oxygen in any discrete silicate anion⁹⁾

Fig. 2. Plot of the proportion of singly bonded oxygen atoms in the most probable or mean silicate anions present vs. the number of silicon atoms per ion for various values of X_{SiO_2} and K ⁹⁾

matrix consisting of $(n+2m)$ oxygen and sites for M and Si. The number of sites for Si is $(m+\frac{1}{2}n)$ only m of which are occupied. An oxygen atom was considered to face two vacant sites which are available for Si. Occupancy of 0, 1, or 2 vacant sites by Si corresponds to O^{2-} , O^- , or O^0 . After Si atoms were distributed among the vacant sites, positions of M^{2+} ions were automatically and uniquely determined depending on the geometrical and charge distributional factors. Here, the energy of modification or the energy of O^- relative to O^{2-} and O^0 is assumed constant (E_w), regardless of the composition of the melts. This means that the the enthalpy change of Eqs. (2) and (3) is equal to $2E_w$ (cal/bond). The partition func-

Fig. 3. Fraction of ion groups vs. composition curves calculated for PbO-SiO₂ melts at 1100°C ($K=1$)¹⁰⁾

tion thus evaluated yielded the values of ΔG , a_{MO} , and a_{SiO_2} . An advantage of the Yokokawa-Niwa model is that it could get rid of the Temkin equation which was introduced as an inevitable assumption in the Toop-Samis and Kapoor-Frohberg model.

Regarding the distribution of silicate anions, Toop and Samis⁹⁾ considered conceivable silicate anions, and gave graphical illustration of the proportions of tetrahedrally coordinated silicon, $\text{Si}^{(\text{IV})}$, O^- , and O^0 in any discrete silicate anion as shown in Fig. 1. This, combined with Fig. 2, served to estimate the distribution in the melts. In Fig. 2, 1 mole of MO-SiO_2 type melt (e.g., $K=0.005$) containing 0.63 moles of SiO_2 has anions in which average number of Si atoms is, as shown by dotted lines, about 9. Accordingly, anions existing would probably consist of double-ring anions containing 8 to 10 Si atoms/ion, i.e., $\text{Si}_8\text{O}_{20}^{8-}$ or $\text{Si}_{10}\text{O}_{25}^{10-}$ with some single ring anions, possibly $\text{Si}_3\text{O}_9^{6-}$ or $\text{Si}_5\text{O}_{15}^{10-}$, and some triple-ring anions, i.e., $\text{Si}_{12}\text{O}_{28}^{8-}$ to $\text{Si}_{15}\text{O}_{35}^{10-}$. The most probable number of these silicate anions present would be $0.07=(0.63/9)$ mole/mole of melt.

Kapoor and Frohberg¹⁰⁾ noticed that only the following configurations of O^- and O^0 are possible around a Si atom, i.e., SiO_4^{4-} , SiO_3^{3-} , SiO_2^{2-} , SiO^{1-} , and SiO^0 , or more generally, SiO_4^{4-} , $(\text{Si}_n\text{O}_{3n+1})^{-2n-2}$, $(\text{SiO}_3)_n^{-2n}$, $(\text{Si}_2\text{O}_5)_n^{-2n}$, and $(\text{Si}_m\text{O}_{2m+1})_n^{-2n}$. Calculating the most probable distribution of the five configurations gave the distribution of complex silicate anions as a function of X_{SiO_2} . The result for PbO-SiO₂ melts is shown in Fig. 3.

The second approach, contrary to the foregoing models, deals explicitly with the distribution of discrete anions. Main contribution along this approach has been due to Masson and his colleagues.¹²⁻¹⁵⁾ It was assumed that self condensation of chains to yield ring structures or networks does not occur and that all O^- groups are chemically equivalent regardless of the size of the anions to which they are attached. Application of polymer theory to the following polycondensation reaction

was attempted firstly by considering that the equili-

equilibrium constants for reaction (4) are the same and independent of chain length, *i.e.*, monomeric SiO_4^{4-} 's are bifunctional¹²⁾:

$$K = K_{11} = \frac{N_{\text{Si}_2\text{O}_7} \cdot N_{\text{O}^{2-}}}{(N_{\text{SiO}_4})^2} = \dots\dots\dots$$

$$= k_{1n} = \frac{N_{\text{Si}_{n+1}\text{O}_{3n+4}} \cdot N_{\text{O}^{2-}}}{N_{\text{SiO}_4} \cdot N_{\text{Si}_n\text{O}_{3n+1}}} \dots\dots\dots(5)$$

Change of a_{MO} with X_{SiO_2} , and molecular weight distributions of silicate polyions for this linear chain model were calculated with the help of the Temkin equation to be

$$1/X_{\text{SiO}_2} = 2 + \frac{1}{1-a_{\text{MO}}} - \frac{1}{1+a_{\text{MO}}\left(\frac{1}{k}-1\right)} \dots\dots\dots(6)$$

$$N_{\text{Si}_n\text{O}_{3n+1}} = \left\{1 + \frac{a_{\text{MO}}}{k_{11}(1-a_{\text{MO}})}\right\}^{1-n}$$

$$\times \left\{\left(k_{11}/a_{\text{MO}}\right) + \frac{1}{1-a_{\text{MO}}}\right\}^{-1} \dots\dots\dots(7)$$

For multifunctional condensation, however, equal reactivity of functional groups as expressed in Eq. (5) for the bifunctional linear chain model fails, because the number of sites available for growth and degradation by reaction (4) varies with n . Calculating the variation of k_{1n} with n is equivalent to calculating the configurational aspect of the molecular size distribution in polyfunctional condensations. For tetrafunctional condensation of monomeric SiO_4^{4-} , Masson and his associates gave¹⁴⁾

$$1/X_{\text{SiO}_2} = 2 + \frac{1}{1-a_{\text{MO}}} - \frac{1}{1+a_{\text{MO}}\left(\frac{3}{k_{11}}-1\right)} \dots\dots\dots(8)$$

and

$$N_{\text{Si}_n\text{O}_{3n+1}} = \frac{(3n)!}{(2n+1)!n!} (1-a_{\text{MO}})$$

$$\times \left\{1 + \frac{3a_{\text{MO}}}{k_{11}(1-a_{\text{MO}})}\right\}^{1-n} \left\{1 + \frac{k_{11}(1-a_{\text{MO}})}{3a_{\text{MO}}}\right\}^{-(2n+1)}$$

$$\dots\dots\dots(9)$$

when intramolecular condensation is neglected. Since all chain configurations were allowed, this may be called all chain configuration model.

Comparison of experimental data with Eqs. (6) and (8) indicated that a_{MO} for CoO-SiO_2 ($k=2.0$) could be represented by Eq. (6), the linear chain model, whereas a_{MO} for SnO-SiO_2 ($k_{11}=2.55$), FeO-SiO_2 ($k_{11}=0.70$), MnO-SiO_2 ($k_{11}=0.25$), and PbO-SiO_2 ($k_{11}=0.196$) could be interpreted in terms of Eq. (8), the all chain configuration model. For CaO-SiO_2 ($k_{11}=0.0016$), it was not possible to distinguish experimentally between the theories. Assuming that CaO-SiO_2 undergoes all chain configurations, anion distribution was calculated which is shown in Fig. 4. The monomer, SiO_4^{4-} , is the most abundant species of silicate ions at all compositions and almost the sole species below $x_{\text{SiO}_2}=0.3$.

As pointed out by Masson¹⁴⁾, linear chain and all configuration models are valid below $x_{\text{SiO}_2}=0.5$. It should be reminded, too, that the two models disregarded the possibility of self-condensation, *i.e.*, ring ion formation which may take place in the silicate

melts.

The significance of k 's, which were taken to be adjustable parameters in the foregoing theories, was discussed by Masson¹²⁾ and Gaskell.¹⁶⁾ Also, extension of the above theories to ternary silicate melts was reviewed by Masson¹⁵⁾ and Yokokawa.¹⁷⁾

Further contribution to the second approach was made by Pretner¹⁸⁾ and more generally by Baes, Jr.¹⁹⁾ who took the intramolecular condensation reaction into account. Strain energy was assumed to arise when stoichiometry requires the formation of ring anions the member of which is less than six. Mixing of silicate anions was considered non-ideal, and the heat of mixing was assumed to originate from the contacts of O^{2-} with O^- . The entropy of mixing was expressed in terms of the volume fraction instead of ion fraction of polyions the former of which is more appropriate when large polyions are present in the mixture. The Baes model involved three adjustable parameters, and fitted observed activities well over the full composition range in LiF-BeF_2 , FeO- , MnO- , and PbO-SiO_2 systems. The distribution of complex anions was also derived, and the consequence was that the concentration in a given mixture of successive species with increasing number of Si or with increasing number of cross links fell logarithmically. As the composition was changed, however, the concentration of given species rised to a maximum and then fell.

An estimate of complex anions existing in quenched binary silicates was made by Yanagase and Sugino-hara²⁰⁾ from infrared absorption study. The locations of absorption peak in the IR spectra shifted continually with x_{SiO_2} for PbO-SiO_2 whereas the shift was discontinuous for $\text{Na}_2\text{O-}$, CaO- , BaO- , and ZnO-SiO_2 , suggesting the existence of SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$, $\text{Si}_n\text{O}_{3n}^{2n-}$, $\text{Si}_{2n}\text{O}_{5n}^{2n-}$ and/or $\text{Si}_{4n}\text{O}_{9n}^{2n-}$.

A method for the gas-chromatographic separation of silicate anions was first described by Lentz²¹⁾ who used a mixture of hexamethyldisiloxane, HCl , and water to prepare the trimethylsilyl derivatives according to

The trimethylsilyl derivatives of silicate anions under-

Fig. 4. Calculated ionic distributions for CaO-SiO_2 melts at 1600°C ¹⁴⁾

went resolution by gas-liquid partition chromatography. Sodium silicate solutions having Na/Si ratio of 4/1 to 0.6/1 were found to contain SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$, $\text{Si}_3\text{O}_{10}^{8-}$, $\text{Si}_4\text{O}_{12}^{8-}$, and poly-silicate structures. However, side-reactions were found to occur in his method. This difficulty was adequately eliminated from direct trimethylsilylation proposed by Goetz and Masson^{22,23} which was employed by Smith and Masson²⁴ to determine complex anions in quenched CoO-SiO_2 glass the composition of which was close to $\text{Co}_4\text{Si}_3\text{O}_{10}$. As in the above sodium silicate solutions, monomer, dimer, trimeric chain, and tetrameric ring were identified. The same species were also found in quenched lead orthosilicate glass.

Regarding the theories of ionic distribution so far presented, although considerable progress has been made, all suffer from insufficient steric consideration. On the other hand, IR-method and direct trimethylsilylation are promising but still inadequate because of poor resolution of absorption peaks and of modification of anions upon extraction, respectively.

The above discussions have dealt only with the distribution of silicate anions and oxygen ion in slag melts which do not contain amphoteric cations such as Fe^{3+} and Al^{3+} . The cations of basic and acidic oxides are known to occupy, respectively, octahedral and tetrahedral sites in the structure of corresponding oxides. However, the amphoteric cations can occupy both sites, *i.e.*, the coordination of oxygen ion, the activity of which determines slag-metal equilibria, around the amphoteric cations changes with the basicity, or more exactly, with the activity of oxygen ion of the slag melts. This is of particular metallurgical interest since Fe_2O_3 and Al_2O_3 function both as basic and acidic oxide depending on the basicity.

Theoretical model to account for the thermodynamic properties of melts consisting of amphoteric cations has been given for $\text{FeO-Fe}_2\text{O}_3$ melt by Takeuchi and Furukawa,²⁵ and more recently by Hagemark and Flood.²⁶ The two models, particularly the latter, reproduced experimental data satisfactorily. However, the coordination of Fe^{3+} and Al^{3+} in silicate melts has not yet been theoretically interpreted.

Optical absorption studies by Bates,²⁷ Kurkjian and Sigety,²⁸ and Ito and Goto²⁹ on quenched glasses indicated that Fe^{3+} in $\text{Na}_2\text{O-SiO}_2$ and $\text{Na}_2\text{O-P}_2\text{O}_5$ is in tetrahedral and octahedral sites, respectively. Tetrahedral coordination of Fe^{3+} in $\text{Na}_2\text{O-SiO}_2$ was confirmed also by Mössbauer Spectrometry carried out by Frischat,³⁰ Frischat and Tomandl,³¹ Pargamin,³² and Lupis.³³ In CaO-SiO_2 melts, Fe^{2+} and a portion of Fe^{3+} occupied tetrahedral sites, whereas the balance of Fe^{3+} was in octahedral sites. Behavior of Al^{3+} in CaO-SiO_2 melts was also studied by IR spectra.³⁴⁻³⁶ These data, if extended to slags with systematically changing compositions, will provide additional information on the structure of slags.

Action of fluorides is also important to control the viscosity of metallurgical slags. Formation of Si-F bond upon addition of fluorides to silicate melts according to

was suggested,³⁷ but not supported.^{36,38} Instead, fluorides are being considered to function only as a diluent of silicate melts. On the other hand, why addition of a few percents of fluorides yields marked decrease in the viscosity of neutral to acid slags is difficult to conceive on the basis of the latter mechanism. Function of fluorides in silicate and aluminate slags is open to a future investigation.

III. Viscous Flow of Silicate Melts

In iron- and steel-making practices, the viscosity of slag melts is usually maintained below a few poises to enhance mass transport of impurities being removed from metal phase in contact. For teeming practices, more viscous slags are employed to prevent physical entrainment of slags into molten metals and to provide glassy slag films on the surface of solidifying steel to give better surface.^{2,39} Comprehensive compilation of viscosity of slags of metallurgical importance is available elsewhere.⁴⁰

General features are that the viscosity decreases with increase of temperature and the ratio of network modifier to network former, reflecting distintegration of complex anion which (or agglomerate of which) constitutes a flow unit. Although major contribution to the viscosity of silicate melts comes from the distribution of polyions in the melts, interaction between polyions and surrounding cations was believed by Ito and Yanagase⁴¹ not to be neglected for PbO-SiO_2 melts. They found, as shown in Fig. 5, that when PbO in the melt was partially replaced by alkali oxide (M_2O) or alkali earth oxide (MO), the viscosity of the melts increased with increasing radii of M^+ or with decreasing radii of M^{2+} .

Temperature dependence of the viscosity, η , of slag melts can be expressed, within a narrow span of temperature, by an Arrhenius type equation at temperatures well above the glass transition point, T_g , as,

$$\eta = \eta_0 \exp(E_\eta/k_B T) \dots \dots \dots (11)$$

(where, k_B : the Boltzmann constant), which indicates the viscous flow to be a thermally activated process. On this basis, Eyring *et al.*⁴² derived an expression for the viscosity in terms of the theory of absolute reaction rates which will be discussed in section III, 1.

Semi-empirical interpretation of an observed cor-

Fig. 5. Viscosity of PbO-SiO_2 -Metal Oxide (MO or M_2O) melts plotted against radius of metal ion of the metal oxide (MO or M_2O)⁴²

Fig. 6. Observed value of log viscosity of standard glass No. 710 (SiO_2 70.5, Na_2O 8.7, K_2O 7.7, CaO 11.6) plotted against a function of temperature $4236/(T^\circ\text{C}-266)^{44)}$

Fig. 7. Arrhenius type to non-Arrhenius type transition of viscous flow as illustrated on a schematic phase diagram of one component system. T_g : glass transition temperature, T_m : melting temperature, T_A : Arrhenius temperature, G : Gibbs free energy

Fig. 8. Schematic illustration of non-Arrhenius behavior of viscosity

relation between E_η and melting point was attempted elsewhere⁴³⁾ for ionic melts.

However, the apparent activation energy, E_η , in Eq. (11) has been observed in many cases to increase with decreasing temperature if temperature span is considerably extended. The departure from Eq. (11) can be represented by

$$\eta = \eta_0 \exp [\text{const.}/(T - T_0)] \quad \text{.....(12)}$$

where, η_0 and T_0 are constants for a system. Equation (12) is known to cover wider variety of slag melts at

larger span of temperatures and hence larger span of viscosity, *e.g.*, 10^2 to 10^{13} poises for a silicate as shown in Fig. 6.⁴⁴⁾

The lowest temperature at which the experimental viscosity data follow the Arrhenius type equation was called after Davis and Matheson⁴⁵⁾ as Arrhenius temperature, T_A . Relation between T_g , T_A , and Arrhenius type or non-Arrhenius type behavior of viscosity is given schematically on a phase diagram, Fig. 7. Modelistic approaches to derive non-Arrhenius type viscosity expressions will be given in section III, 2 to 5 in which applications of the expressions to silicate melts will be also discussed.

The validity of Eq. (12) was first revealed for silicate melts,^{46,47)} then for organic polymer melts⁴⁸⁾ and melts consisting of small molecules.^{49,50)} It is worth considering why Eq. (12) was found suitable for silicate melts as the first instance, since this seems to be relevant to the nature of the viscous flow of the silicate melts. Relation between $\log \eta$ and $1/T$ as given by Eq. (12) is shown in Fig. 8. $\log \eta$ is proportional to $1/T$ at $T \gg T_0$, whereas it diverges to infinity as T approaches to T_0 . Non-Arrhenius behavior can be recognized only when the value of $\Delta \log \eta$ exceeded the error of measurement at $T_i < T < T_j$. It is obvious from Fig. 8 that T_A , which is known to depend upon substances,⁴⁵⁾ varies with the accuracy of viscosity measurement as well as the span of temperatures employed for the measurements. Non-Arrhenius behavior as represented by Eq. (12) can be observed if the error of measurement is much smaller than $\Delta \log \eta$. This can be attained if the measurement is extended to a temperature sufficiently close down to T_0 . The measurement below melting point, T_m , is usually inhibited by crystallization of melt. However, silicate melts often retains vitreous state and hence make viscosity measurement possible even for supercooled liquid. This is behind why Eq. (12) has first been found for silicate melts.

Non-equilibrium statistical mechanics has been successful in describing the viscosity of rare gas liquids⁵¹⁾ and liquid metals⁵²⁾ in both of which flow unit can be regarded spherical. Many difficulties arise when this approach is extended to treat liquids in which flow unit is polyatomic. In fact, few attempts have been published for silicate melts along this line. In view of the theoretical importance, however, brief survey of this approach will be given in section III, 6.

1. Theory of Absolute Reaction Rates

Eyring and his co-workers⁴²⁾ applied the theory of absolute reaction rates to the problem of the viscosity of liquid. Two adjacent layers of molecules were considered in a liquid, and sliding motion of one layer with respect to the other under the influence of an applied force was assumed to involve the passage of a molecule from one equilibrium position to another such position in the same layer. The difference in the specific rate of the passage between forward direction, *i.e.*, direction of the force, and backward direction was evaluated to give

$$\eta = \frac{hN}{V} \cdot \frac{F}{F^*} \exp(\varepsilon_0/k_B T) \dots\dots\dots(13)$$

where, h is the Planck constant, V is the molar volume, N is the Avogadro number, F and F^* are the partition function, for unit volume, of the molecule in the initial and activated state, and ε_0 is the activation energy for the passage at 0 °K. Utilizing the identity

$$\frac{F}{F^*} \exp(\varepsilon_0/k_B T) = \exp(\Delta G^*/RT) \dots\dots\dots(14)$$

Eq. (14) turns into

$$\begin{aligned} \eta &= \frac{hN}{V} \exp(\Delta G^*/RT) \\ &= \left[\frac{hN}{V} \exp(-\Delta S^*/R) \right] \exp(\Delta H^*/RT) \dots\dots\dots(15) \end{aligned}$$

where, ΔG^* , ΔH^* , and ΔS^* are, respectively, the free energy, enthalpy, and entropy of activation. Equation (15) is equivalent to Eq. (11) for a narrow temperature span in which V , ΔS^* , and ΔH^* are practically constant.

Estimation of F and F^* in terms of a cell model of liquid yielded an alternative expression given by

$$\eta = \left(\frac{N}{V} \right)^{2/3} \frac{cRT}{\Delta E_{\text{vap}}} (2\pi m k_B T)^{1/2} \exp(\varepsilon_0/k_B T) \dots\dots(16)$$

where c is the packing number ($=2$ for cubic packing), m is the mass of molecule, and ΔE_{vap} is the molar energy of vaporization

These concepts were incorporated by Bockris and his colleagues^{53,54)} to discuss the mechanism of viscous flow of silicate melts. Assuming SiO_2 molecule to be the flow unit in pure fused silica, the free energy of activation in Eq. (15) was calculated from observed viscosity to be 90 kcal mol⁻¹. This was shown⁵³⁾ to be in good agreement with 87 kcal mol⁻¹ separately calculated from the empirical relationship⁵⁵⁾

$$\Delta G^* \cong \Delta E_{\text{vap}}/2.4 \dots\dots\dots(17)$$

where heat of vaporization, ΔE_{vap} , was roughly estimated as one half of the energy for breaking four Si-O bonds. The agreement was taken to be an evidence to support the assumption.

Bockris *et al.*⁵⁴⁾ subsequently showed that the addition of small amount of metal oxides to fused silica melts results in a marked decrease of E_η as shown in Fig. 9. The addition of metal oxides was considered to break Si-O bonds, introducing "weak points" into silica network. Also, Si-O bonds near the metal ion are weakened owing to the polarizing effect of cation. These contributions were thought to decrease the energy to form flow unit such as SiO_2 molecule or the entity

and hence decrease the activation energy of the viscous flow with the addition of metal oxides.

When the addition of metal oxides exceeded a critical value, *c.a.* 10mol% for alkali oxides or *c.a.* 20 mol% for alkaline earth oxides, three dimensional network of SiO_2 was believed to be broken into dis-

crete silicate anions, which constitute flow units in the melts. Further addition of the metal oxides were to make the size of the anions smaller. However, this effect had limited influence on E_η on the basis of Fig. 9.

It must be noted that straight forward application of Eyring's viscosity expression to silicate melts is obviously inadequate in that it fails to explain considerable departure of temperature dependence of the viscosity from Arrhenius behavior even if pre-exponential factor, which contains a temperature dependent $T^{3/2}$ terms, is taken into account. This clearly indicates that the activation energy for a silicate melt cannot be uniquely determined over a wide span of temperature.

2. Free Volume Theory

The above inadequacy stimulated the application of free volume theory to interpret the viscosity of silicate melts. Doolittle⁵⁶⁾ showed empirically that the viscosity can be related to the free volume of a liquid as

$$\eta = A_1 \exp(BV_0/V_f) \dots\dots\dots(18)$$

where, V_0 is close packed volume, V_f is the free volume, and A_1 and B are constants characteristic of the liquid.

Cohen and Turnbull⁵⁷⁾ provided solid theoretical foundation of Eq. (18). They assigned a free volume to each of the flow units in a hard sphere melt, and explicitly calculated the distribution of the free volume by maximizing the configurational entropy of the free volume at a given total free volume.

Resulting probability of finding a free volume, v , nearby was given by

$$P(v) = (\gamma/v_f) \exp(-\gamma v/v_f) \dots\dots\dots(19)$$

where, v_f is average free volume/flow unit, γ is a correction factor ($\frac{1}{2}$ to 1) for the overlapping between free volumes. Assuming that a minimum free volume, v^* , is needed for a jump of a flow unit to occur, jump probability, P_v , was calculated as

$$P_v = \int_{v^*}^{\infty} P(v) dv = \exp(-\gamma v^*/v_f) \dots\dots\dots(20)$$

The viscosity was assumed to be inversely proportional to the diffusional jump probability, and hence was given by

Fig. 9. Activation energy of viscous flow for $\text{M}_2\text{O}-\text{SiO}_2$ systems as a function of composition

$$\eta = A_2/P_v = A_2 \exp(\gamma v^*/v_f) \dots\dots\dots(21)$$

where temperature dependence of A_2 is usually regarded much less than that of the exponential term. Equation (21) is identical to Eq. (18). When a product of thermal expansion coefficient, α , and volume, V , is essentially constant for a melt over a temperature range in question, total free volume may be approximated by

$$V_f = \alpha V(T - T_0) \dots\dots\dots(22)$$

where, T_0 is a temperature at which V_f becomes zero. Then, one gets from Eqs. (21) and (22)

$$\eta = A_2 \exp\left(\frac{C}{T - T_0}\right), \quad C = N\gamma v^*/\alpha V \dots\dots\dots(23)$$

where, N is the number of flow units. Equation (23) is equivalent to Eq. (12), and reduces to an Arrhenius type equation at $T \gg T_0$.

It is interesting to note that Eq. (23) is valid for monoatomic liquids.⁵⁸⁾ Since Eq. (23) gives marked increase in viscosity at $T \cong T_0$, monoatomic liquids should also exhibit viscosity of about 10^{13} poises⁴⁷⁾ for transition from supercooled to glassy state provided that crystallization is prevented. The existence of glassy state for monoatomic liquids has long been in question,⁵⁹⁾ but recent observation of glassy state for simple liquids such as H_2O ,⁶⁰⁾ $CHCl_3$,⁶¹⁾ CCl_4 ,⁶²⁾ and *etc.* may suggest the existence of glassy state for monoatomic liquids.

From the above discussions, existence of glassy state for highly basic silicate melts could be predicted because symmetric SiO_4^{4-} coordinated by much smaller cations can be regarded monoatomic constituent of the melts. Then, it is of much theoretical interest to examine the validity of Eq. (23) for supercooled highly basic silicate melts.

The validity of Eq. (21) was examined by Kumar⁶³⁾ for fused boric oxide, alkali borates, barium borate, and alkali silicates. If flow units in these melts were assumed to be of spherical symmetry and to move at kinetic velocity of gas, Eq. (21) becomes, after some manipulation, to be

$$\log \eta/T^{1/2} = \log A'_2 + \gamma v^*/v_f \dots\dots\dots(24)$$

$$A'_2 = 1/3 \cdot (mk_s/3\pi ga^2)^{1/2} \dots\dots\dots(25)$$

where, m and a are mass and diameter of the flow unit, and g is a steric factor. Plot of $\log \eta/T^{1/2}$ against $1/v_f$ showed straight lines which confirmed the validity of Eq. (24) for these melts. The slope and intercept of these lines gave $\log A'_2$ and γv^* , respectively. Decrease of γv^* with increasing alkali oxide concentration was found for alkali borates, as shown in Fig. 10, indicating the disintegration of anions. Major flow species in alkali silicate melts was estimated to be SiO_4^{4-} and/or $Si_2O_7^{6-}$ on the basis of the value thus obtained for γv^* which was 4 to 7 folds of the size of O^{2-} . This compares with the Masson theory which predicted that most abundant silicate anion in alkali silicate melts in the vicinity of meta-silicate composition is SiO_4^{4-} . Also, the value of A'_2 theore-

Fig. 10. Composition *vs.* number of oxygen atoms in a flow unit in $M_2O-B_2O_3$ systems with assumed γ of 0.9: 1; $Li_2O-B_2O_3$, 2; $Na_2O-B_2O_3$, 3; $K_2O-B_2O_3$.⁶²⁾

tically calculated by use of Eq. (25) was in good agreement with those experimentally obtained. Exceptions were for barium borates and vitreous silica for both of which observed A'_2 was much larger.

Difficulties involved in the above theory are that the value of T_0 cannot uniquely be determined by the theory (T_0 is an adjustable parameter, instead) and that $d \ln \eta / dT$ becomes zero at constant volume in contrast to experimental observation.

3. Hybrid Theory

Foregoing difficulties were to some extent resolved by Macedo and Litovitz,⁶⁴⁾ who introduced another probability, P_e , of attaining sufficient energy to surmount the energy barrier before a jump of a flow unit to occur, and worked out a hybrid equation combining aspects of both the Eyring and Cohen and Turnbull theories. Resulting expression is

$$\eta = A_3/P_v P_e = A'_3 \exp(E_v^*/RT + \lambda V_0/V_f) \dots\dots\dots(26)$$

where, E_v^* is the activation energy for jumping. This reduces to the Cohen-Turnbull equation when $V_0/V_f \gg E_v^*/RT$, and to an Arrhenius type equation with some contribution of free volume retained (when $T \gg T_0$) or without that (when $\alpha \cong 0$, thus $V_f = \text{const.}$).

They were able to reproduce observed η *vs* T relationship for GeO_2 -, SiO_2 -, silicate-, and borate-melts with sufficient accuracy by choosing appropriate values for A'_3 , α , V , V_0 , and E_v^* . In many cases, V_0 's thus chosen were found to be consistent with the volume of closest-packing. The values of α 's thus obtained for SiO_2 and $Na_2O \cdot CaO \cdot SiO_2$ glass were close to those correspondingly estimated from experimental observation. Also, concentration dependence of η of $Na_2O-B_2O_3$ melts was explained by taking $1/E_v^*$ to be equal to $x_{Na_2O}/E_v^* Na_2O$ plus $x_{B_2O_3}/E_v^* B_2O_3$. Derivation of the Macedo-Litovitz equation on the basis of statistical mechanics was carried out by Chung.⁶⁵⁾ In the Macedo-Litovitz equation, V_0 may depend upon temperature and pressure as it was so for borosilicate glass.⁶⁶⁾ If so, use of such hybrid equation lacks its original meaning. The value of T_0 cannot uniquely be determined, too.

4. Cooperative Motion Theory

It is not easy to conceive the significance of activated jumping for some silicate melts in which a flow

unit (complex anion) is fairly large, forming long chain or network. In reality, motion of a flow unit should involve for viscous flow to occur cooperative motion of surrounding flow units.

This was first taken into account by Adam and Gibbs.⁶⁷⁾ They considered a macroscopic system to be an isobaric-isothermal ensemble of N_s independent, equivalent, and distinguishable subsystems composed of z molecular segments (flow units) each. Upon a sufficient fluctuation in energy, the subsystem can cooperatively rearrange into another configuration independently of its environment. Among N_s subsystems, n_s were allowed a cooperative rearrangement and $N_s - n_s$ were in states not allowing a transition. Denoting the Gibbs free energy for the former and the latter to be G' and G and the difference to be $z\Delta\mu$, the cooperative transition probability, P , was given by

$$P = A_4 n_s / N_s = A_4 \exp [-(G' - G) / k_B T] \\ = A_4 \exp (-z\Delta\mu / k_B T) \quad \dots\dots\dots(27)$$

where A_4 is a constant. The average transition probability, $\bar{P}$, which is inversely proportional to η , was given by the summation of P over subsystems the size of which is larger than z^* :

$$1/\eta \propto \bar{P} = \sum_{z=z^*}^{\infty} A_4 [\exp (-\Delta\mu / k_B T)]^z \\ = A_4' \exp (-z^* \Delta\mu / k_B T) \quad \dots\dots\dots(28)$$

Here, z^* is a critical lower limit to the size of cooperative regions that can yield nonzero transition probability. If the macroscopic system consisted of 1 mole of segments, the configurational entropy of the macroscopic system (S_c) was given by $N_s s_c$ where s_c is the configurational entropy of a subsystem of z segments. Noting that s_c and critical value of which are given by

$$s_c = k_B \ln (P_c)^{z/N_A}, \\ s_c^* = k_B \ln (P_c)^{z^*/N_A} \quad \dots\dots\dots(29)$$

where P_c^{1/N_A} is average number of configurations and N_A is the Avogadro number, one obtains z^* to be equal to $N_A s_c^* / S_c$. This z^* was inserted into Eq. (28) to give

$$\eta = A_4' \exp [(\Delta\mu s_c^* / k_B)(1/T S_c)] \quad \dots\dots\dots(30)$$

where the first term in the square bracket is a constant.

If the difference in the heat capacity between equilibrium liquid state and glassy state of silicates (ΔC_p) is assumed constant over the temperature range in question, one has

$$S_c(T) - S_c(T_2) = \int_{T_2}^T [\Delta C_p(T) / T] dT \\ = \Delta C_p \ln (T / T_2) \quad \dots\dots\dots(31)$$

Further, if T_2 is chosen to make $S_c(T_2)$ to be zero and $(T - T_2)$ is sufficiently smaller than T_2 , one gets $T S_c(T) = \Delta C_p (T - T_2)$ from which and Eq. (30) the following results:

$$\eta = A_4'' \exp \{(\Delta\mu s_c^* / k_B)[1/\Delta C_p(T - T_2)]\} \quad \dots\dots\dots(32)$$

Adam and Gibbs⁶⁷⁾ determined the values of $\Delta\mu s_c^* / k_B$ and T_g / T_2 for various liquids from experiments. The

latter value was in good agreement with T_g / T_2 of 1.3 which was separately obtained by calorimetry using the following relation:

$$S_c(T_g) = [S_c(\text{glass}) - S_c(\text{crystal})]_{T=0} \\ = \int_{T_2}^{T_g} (\Delta C_p / T) dT \quad \dots\dots\dots(33)$$

Also, the value of $\Delta\mu$ was consistent with estimated potential barriers. Ambiguities in the physical significance of T_0 and E_v^* involved in the Macedo-Litovitz equation have been resolved by the concept of rearrangement of segments. However, the validity of this theory has not yet fully tested for silicate melts. In order to get an equation of the type of Eq. (12), which covers wide span of temperatures, approximations made for going from Eq. (30) to (32) are obviously insufficient. Thus, it is not clear for silicate melts whether or not Eq. (30) yields a type of Eq. (12) covering temperature much higher than T_2 . Further development to obtaining reliable expression for S_c is awaited.

5. Environmental Relaxation Theory

The importance of the cooperative nature of motion in the mechanism of viscous flow was also revealed by Macedo and his colleagues in a different way. Macedo and Napolitano⁶⁶⁾ compared observed with calculated viscosities of B_2O_3 melts over the range of 10^2 to 10^{14} poises and found that all foregoing theories are inadequate to account for the observed data as shown in Fig. 11. Apparent activation energy, E_{app} , calculated from the data as $R d \ln \eta / d(1/T)$ is reproduced in Fig. 12. E_{app} was constant below 320°C and above 800°C whereas it increased in between with decreasing temperature. This corresponded to the deviation of viscosity from an Arrhenius behavior. All foregoing theories were so far not aware of, and hence incapable to explain the Arrhenius type behavior at the lower temperatures. In this connection, Tauc, Litovitz, and Macedo⁶⁸⁾ measured velocity and absorption of ultrasonic wave in B_2O_3 melts, and determined the distribution, $g(\tau)$, of relaxation time, τ , the results being depicted in Fig. 13. The distribution was insensitive to temperature above 800°C , but it became broader with decreasing temperature. These observation indicate that the departure from the Arrhenius type behavior of viscosity at 320 to 800°C may be attributable to the broadening of $g(\tau)$ with decreasing temperature. Regarding this, Simmons and Macedo⁶⁹⁾ proposed environmental relaxation model for the viscous flow of liquids. They considered that in a liquid there is distribution of relaxation time which is determined by the structure of liquid within a radius r_0 around a flowing species (structural relaxation range). With decreasing temperature, local structure of liquid becomes more orderly, and the size of the orderly structure or "micro-structure" was expressed by another radius λ (correlation length). Temperature dependence of λ yields three temperature regions, as shown in Fig. 14, with respect to the relative magnitude of λ to r_0 . At higher temperatures, local struc-

ture within r_0 does not change markedly irrespective of the location of the center of r_0 in the liquid because $r_0 \gg \lambda$. Consequently, $g(\tau)$ gets sharper. Small change in λ caused by temperature change does not affect $g(\tau)$ much since $r_0 \gg \lambda$ and dr_0/dT was assumed negligibly small. At medium temperatures, the local structures, *i.e.*, number of configurations, change markedly depending upon the choice of location of the structural relaxation range because at these temperatures $r_0 \cong \lambda$. This makes $g(\tau)$ quite sensitive to temperature. At lower temperatures where $r_0 \ll \lambda$, the location of r_0 will be mostly within the orderly structure, the "microstructure", and has little influence on the local structure, and hence the Arrhenius type dependence of viscosity on temperature results. This qualitatively explains the features of viscosity of B_2O_3 melts. Although lack of detailed knowledge on the size of the microstructure of silicate melts makes it impossible to quantitatively deduce viscosity expression from this model, it was successfully applied by Simmons, Mills, and Napolitano⁷⁰⁾ to interpret the anomaly in the viscosity of two sodium-borosilicate glasses caused by concentration fluctuation nearby critical point for phase separation at which λ , as given to be the radius of one separated phase in the other matrix phase, was available as a function of temperature. The values of r_0 for the two glasses, $7Na_2O \cdot 23B_2O_3 \cdot 70SiO_2$ and $4Na_2O \cdot 13B_2O_3 \cdot 2Al_2O_3 \cdot 81SiO_2$, were found to be 57 and 58 Å, respectively.

6. Non-equilibrium Statiscomechanical Treatment

Statistical mechanics of non-equilibrium state has

Fig. 11. Deviations between the observed log viscosity values and those calculated from the least-squares fit to several models for B_2O_3 glasses⁶⁵⁾
A; Fulcher, B; WLF, C; Rec, Rec and Eyring, D; Macedo and Litovitz, and E; Adam and Gibbs

been developed by Rice and Kirkwood⁷¹⁾ to express short range force contribution to the viscosity of dense fluid in terms of local equilibrium pair correlation function, $g_0^{(2)}(r_{12})$, and intermolecular potential, $u(r_{12})$, as

$$\eta_{RK} = \frac{m}{30\zeta} (N/V)^2 \int r_{12}^2 \left(u'' + \frac{4}{r_{12}} u' \right) g_0^{(2)}(r_{12}) d^3 r_{12} \dots (34)$$

where m is the mass of a molecule, N is the number of molecules, V is the volume, and the friction coefficient ζ is obtained from the mean frictional force as

$$\zeta^2 = (mN/3V) \int \nabla_{r_{12}}^2 u(r_{12}) g_0^{(2)}(r_{12}) d^3 r_{12} \dots (35)$$

Fig. 12. Plot of apparent activation energies *vs.* temperature for B_2O_3 glass⁶⁵⁾

Fig. 13. Observed relaxation time spectrum and activation energy distribution for B_2O_3 glass⁶⁵⁾

Fig. 14. Schematic illustration of the size of "micro-structure" (r_0) relative to that of "structural relaxation range" (λ) at different temperatures ($T_I > T_{II} > T_{III}$)⁶⁹⁾

For a melt constituting of cations and complex anions for which interionic potentials and spacial correlation functions are unavailable, straightforward application of the above small step diffusion formulation is extremely difficult. To resolve this, Nozaki and Shimoji⁷²⁾ noticed that largest contribution to the value of the integration in Eqs. (34) and (35) arises at r_{12} very close to the first peak, $r_{12}=a$, on $g_0^{(2)}(r_{12})$. This was introduced in Eqs. (34) and (35) to get a simplified version,

$$\eta = na^2\zeta/10, \quad n: N/V \quad \dots\dots\dots(36)$$

to describe the viscosity observed for $\text{Na}+\text{NH}_3$ and $\text{NH}_4\text{I}+\text{NH}_3$ systems. Eliminated in Eq. (30) were $u(r_{12})$ and $g_0^{(2)}(r_{12})$ which are usually unavailable for polyatomic liquids. Also neglected was a term

$$\eta^* = (m/15\zeta)(N/V)^2 \int r_{12}u'(r_{12})g_0^{(2)}(r_{12})d^3r_{12} \quad \dots(37)$$

which is too small, $\cong 2 \times 10^{-5}$ poises for NH_3 at -30°C , to be reserved in Eq. (34).

The friction coefficient can also be connected with the self-diffusivity, D , by the Einstein relation:

$$D = KT/\zeta \quad \dots\dots\dots(38)$$

If the flow species can be regarded as hard spheres of diameter σ and the first peak on $g_0^{(2)}(r_{12})$ appears at $r_{12}=\sigma$, the number density of flow species can be expressed as

$$1/n = V/N \cong \pi\sigma^3/6\xi \quad \dots\dots\dots(39)$$

where, ξ is the packing factor. Substituting Eq. (39) into Eq. (36) gives

$$\eta_{NS} = 3\zeta\xi/5\pi\sigma \quad \dots\dots\dots(40)$$

When soft potential is operating between the flow species,

$$1/n \cong \pi a^3/6 \quad \dots\dots\dots(41)$$

is a reasonable approximation for which the viscosity becomes

$$\eta_{NS}' = 3\zeta\xi^{1/3}/5\pi a \quad \dots\dots\dots(42)$$

This approach was applied by Ejima and Shimoji⁷³⁾ to theoretically evaluate the viscosity of silicate melts. With values of ζ and a derived respectively from the self-diffusivity of Si (as a constituent of flowing species) and from surface tension of corresponding melt, the viscosity of CaO-SiO_2 melt (1:1) was estimated to be about 1 poise which favorably compared with experimental observation, 3.9 poises.

IV. Concluding Remarks

Foregoing modelistic theories for viscous flow can be classified in two categories. One is based upon the concept that viscous flow takes place by jumping of spherical flow units into neighbouring holes. The Eyring, Cohen-Turnbull, and Macedo-Litovitz model belong to this category. The other, to which the Adam-Gibbs and the Simmons-Macedo model belong, explicitly considers the cooperative motion of surroundings of flow units for viscous flow to occur.

Since silicate melts have been shown to be mixtures of silicate anions of varying size some of which are not spherical, applicability of the models in the former category are limited in principle only to a highly basic composition at which spherical anions, mostly SiO_4^{4-} , are abundant. For silicate melts other than this composition, it becomes difficult to conceive a specific anion to be a flow unit, and hence parameters involved in viscosity expressions of the models in the former category lose their original significance. In this context, the models in the latter category are more comprehensive to cover wide variety of compositions. The Adam-Gibbs theory, however, is not yet satisfactory in view of the fact that experimental determination of S_c is a tedious work and also the significance of S_c is obscure particularly at temperatures much higher than T_g . Also, Simmons-Macedo model is insufficient because no explicit expression in terms of the microstructure is as yet worked out for total viscosity.

Local fluctuation of liquid structure leads to presuming the distribution with respect to a certain parameter s of relaxation process involved in viscous flow. If the relaxation is regarded as a thermally activated process, then mean transition probability, $W(T)$, can be expressed by

$$W(T) = \int_s a(s) \cdot f(s) \cdot \exp(-E(s)/RT) ds \quad \dots\dots(43)$$

where, $a(s)$ is a factor to correlate the relaxation process to viscosity, $f(s)$ is the distribution function, and $E(s)$ is the activation energy. In the Macedo-Litovitz hybrid theory, which includes an Arrhenius type and a free volume type expression, s , $a(s)$, and $E(s)$ correspond to the free volume v , jump distance, and E_v^* , respectively, but dependence of E_v^* on v is neglected. In the Adam-Gibbs cooperative motion theory, s and $E(s)$ correspond to z and $z\Delta\mu$, respectively. Temperature dependence of $a(s)$ is included via that of z^* , the cut off number of segments. In this theory, however, a term, $f(s)$, is missing. In the Simmons-Macedo environmental relaxation model, s is equivalent to the local liquid structure within a radius r_0 . Unfortunately, however, no formulation of $a(s)$, $f(s)$, and $E(s)$ is given explicitly.

Hard sphere version of non-equilibrium statistico-mechanical description of viscosity falls within the same criticism as given to the modelistic theories in the former category. Namely, the version is applicable in its nature only to a melt of high basicity at which one may assume that the relaxation time for rotational motion is much shorter than translational one of flow units to which tentative mean radius may be assigned. Extension of nonequilibrium statistico-mechanical approach to acid rich region seems to be impracticable, if not totally impossible.

Possibility of occurrence of viscosity anomaly as a result of cluster formation was recently discussed by Ikeda, Tamura, Shiraishi, and Saito⁷⁴⁾ for FeO-SiO_2 melts. Influence of short range ordering on viscosity

together with the mechanism of viscous flow of melts with acidic composition offer challenging topics to be explored in the near future.

REFERENCES

- 1) T. Emi: The Slag-Metal Reactions from Electrochemical Viewpoint, to be published in "Electrochemistry", ed. J.O'M. Bockris, Butterworths, London, (1975). Y. Kawai and K. Mori: *Trans. ISIJ*, **13** (1973), 303.
- 2) T. Emi, H. Nakato, K. Suzuki, Y. Iida, and T. Ueda: *Tetsu-to-Hagane*, **60** (1974), 981.
- 3) W. H. Zachariasen: *J. Amer. Chem. Soc.*, **54** (1964), 3842.
- 4) B. E. Warren: *J. Amer. Chem. Soc.*, **19** (1936), 202.
- 5) J. O'M. Bockris, J. A. Kitchener, S. Ignatowicz, and J. W. Tomlinson: *Trans. Faraday Soc.*, **48** (1952), 75.
- 6) J. O'M. Bockris, J. W. Tomlinson, and J. L. White: *Trans. Faraday Soc.*, **52** (1956), 299.
- 7) J. W. Tomlinson, M. S. R. Heynes, and J. O'M. Bockris: *Trans. Faraday Soc.*, **54** (1958), 1822.
- 8) M. Temkin: *Zur. Fiz. Khim*, **20** (1946), 105.
- 9) G. W. Toop and C. S. Samis: *Trans. Met. Soc. AIME*, **224** (1962), 878.
- 10) M. L. Kapoor and M. Froberg: *Arch. Eisenhüttenw.*, **41** (1970), 1035.
- 11) T. Yokokawa and K. Niwa: *Trans. JIM*, **10** (1969), 3.
- 12) C. R. Masson: *Proc. Roy. Soc.*, **A287** (1965), 201.
- 13) C. R. Masson: *J. Amer. Ceram. Soc.*, **51** (1968), 134.
- 14) S. G. Whiteway, I. B. Smith, and C. R. Masson: *Can. J. Chem.*, **48** (1970), 34, 202, 1456; I. B. Smith and C. R. Masson: *Can. J. Chem.*, **49** (1971), 684.
- 15) C. R. Masson: *JISI*, **11** (1972), 89.
- 16) D. R. Gaskell: *Met. Trans.*, **4** (1973), 185.
- 17) T. Yokokawa: *Bull. Japan Inst. Met.*, **13** (1974), 3.
- 18) B. Pretnar: *Ber. Busengesell. Phys. Chem.*, **72** (1968), 773.
- 19) C. F. Baes, Jr.: *J. Solid State Chem.*, **1** (1970), 159.
- 20) T. Yanagase and Y. Suginoara: *Trans. JIM*, **11** (1970), 400.
- 21) C. W. Lentz: *Inorg. Chem.*, **3** (1964), 574.
- 22) J. Götz and C. R. Masson: *J. Chem. Soc.*, **A** (1970), 2683.
- 23) J. Götz and C. R. Masson: *J. Chem. Soc.*, **A** (1971), 686.
- 24) I. B. Smith and C. R. Masson: *Can. J. Chem.*, **49** (1971), 683.
- 25) S. Takeuchi and K. Furukawa: *Phys. Chem. Process Metall.*, Interscience, New York, (1961), 245.
- 26) H. Flood and K. Hagemark: *Acta Chem. Scand.*, **15** (1961), 1624.
- 27) T. Bates: *Mod. Aspects of the Vitreous State*, Ch. 5, 2, Butterworths, London, (1962).
- 28) C. R. Kurkjian and E. A. Sigety: *Phys. Chem. Glasses*, **9** (1968), 73.
- 29) T. Ito and K. Goto: *Tetsu-to-Hagane*, **60** (1974), 184.
- 30) G. H. Frischat: *Glastech. Ber.*, **42** (1969), 182.
- 31) G. H. Frischat and G. Tomandl: *Glastech. Ber.*, **44** (1971), 173.
- 32) L. Pargamin: Ph. D. Thesis, Carnegie-Mellon Univ., (1971).
- 33) C. H. P. Lupis: *Met. Trans.*, **3** (1972), 2093.
- 34) D. E. Day and G. E. Rindone: *J. Amer. Ceram. Soc.*, **45** (1962), 489.
- 35) Y. Suginoara and T. Yanagase: *J. JIM*, **31** (1967), 1229.
- 36) Y. Suginoara and T. Yanagase: *J. JIM*, **33** (1969), 290, 443.
- 37) D. Kumar, R. G. Ward and D. J. Williams: *Discuss. Faraday Soc.*, **32** (1961), 147.
- 38) A. Mitchell: *Trans. Faraday Soc.*, **63** (1967), 1408.
- 39) R. Sato: *Bull. Japan Inst. Metals*, **12** (1973), 391.
- 40) Y. Matsumura and Y. Shiraishi: *Handbook of the Physical Properties of Molten Iron and Slags*, Ch. 2, 54, ed. T. Saito (Iron and Steel Inst. Japan), (1972).
- 41) H. Ito and T. Yanagase: *Trans. JIM*, **1** (1960), 116.
- 42) S. Glasstone, K. J. Laidler, and H. Eyring: *The Theory of Rate Processes*, McGraw-Hill, New York, (1941).
- 43) T. Emi and J. O'M. Bockris: *J. Phys. Chem.*, **74** (1970), 154.
- 44) A. Napolitano and E. G. Howkins: *J. Res. Natl. Bur. Std.*, **68A** (1964), 439.
- 45) D. B. Davies and A. J. Matheson: *J. Chem. Phys.*, **45** (1966), 1000.
- 46) G. S. Fulcher: *J. Amer. Ceram. Soc.*, **8** (1925), 339.
- 47) G. Tammann and W. Hesse: *Z. anorg. allgem. Chem.*, **156** (1926), 245.
- 48) M. L. Williams, R. F. Landel, and J. D. Ferry: *J. Am. Chem. Soc.*, **77** (1955), 3701.
- 49) O. G. Lewis: *J. Chem. Phys.*, **43** (1965), 2693.
- 50) A. J. Barlow, J. Lamb, A. J. Matheson: *Proc. Roy. Soc.*, **A292** (1966), 322.
A. J. Barlow, J. Lamb, A. J. Matheson, P. R. K. L. Padmini, and J. Richter: *Proc. Roy. Soc.*, **A298** (1967), 467.
A. J. Barlow, A. Erginsav, and J. Lamb: *Proc. Roy. Soc.*, **A298** (1967), 481.
- 51) S. A. Rice and P. Gray: *The Statistical Mechanics of Simple Liquids*, Intersci. Pub., New York, (1965).
- 52) M. Shimoji: *Adv. Phys.*, **16** (1967), 705.
- 53) J. O'M. Bockris and D. L. Lowe: *Proc. Roy. Soc.*, **226A** (1954), 423.
- 54) J. O'M. Bockris and J. D. Mackenzie, and J. A. Kitchener: *Trans. Faraday Soc.*, **51** (1955), 1734.
- 55) R. Powell, W. Roseveare and H. Eyring: *Ind. Eng. Chem.*, **33** (1941), 430.
- 56) A. K. Doolittle: *J. Appl. Phys.*, **22** (1951), 1471; **23** (1952), 231.
- 57) M. H. Cohen and D. Turnbull: *J. Chem. Phys.*, **31** (1959), 1164.
- 58) M. H. Cohen and D. Turnbull: *Nature*, **203** (1964), 964.
- 59) C. A. Angell: *J. Amer. Ceram. Soc.*, **51** (1968), 117.
- 60) M. Sugisaki, H. Suga, and S. Seki: *Bull. Chem. Soc. Japan*, **41** (1968), 2591.
- 61) O. Haida, H. Suga, and S. Seki: *Thermochimica Acta*, **3** (1972), 177.
- 62) O. Haida: Doctoral Thesis, Osaka Univ., (1973).
- 63) S. Kumar: *Phys. Chem. Glasses*, **4** (1963), 106.
- 64) P. B. Macedo and T. A. Litovitz: *J. Chem. Phys.*, **42** (1965), 245.
- 65) H. S. Chung: *J. Chem. Phys.*, **44** (1966), 1362.
- 66) P. B. Macedo and A. Napolitano: *J. Chem. Phys.*, **49** (1968), 1887.
- 67) G. Adam and J. H. Gibbs: *J. Chem. Phys.*, **43** (1965), 139.
- 68) J. Tauke, T. A. Litovitz, and P. B. Macedo: *J. Amer. Ceram. Soc.*, **51** (1968), 158.
- 69) J. H. Simons and P. B. Macedo: *J. Chem. Phys.*, **54** (1971), 1325; *J. Res. Natl. Bur. Std.*, **75A** (1971), 175.
- 70) J. H. Simons, A. Mills, and A. Napolitano: *J. Non-Cryst. Solids*, **14** (1974), 302.
- 71) S. A. Rice and J. G. Kirkwood: *J. Chem. Phys.*, **31** (1959), 901.
- 72) T. Nozaki and M. Shimoji: *Trans. Faraday Soc.*, **65** (1969), 1489.
- 73) A. Ejima and M. Shimoji: *Trans. Faraday Soc.*, **66** (1970), 99.
- 74) K. Ikeda, A. Tamura, Y. Shiraishi, and K. Saito: *Bull. Res. Inst. Min. Dress. Met. Tohoku Univ.*, **29** (1973), 24.