Structure of Molten Oxides. I. Viscosity of GeO2, and Binary Germanates Containing Li2O, Na2O, K2O, and Rb2O

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and ν_9 with ν_6 will be superimposed on the actual changes in moments of inertia. The data show that the "average" value of

$$\left[\left(A'-\frac{B'+C'}{2}\right)-\left(A''-\frac{B''+C''}{2}\right)\right]$$

contributes substantially to the Q-branch frequencies. Since the discrepancies in fitting the measured Q-branch frequencies are nearly all less than the term

$$K'\left[\left(A'-\frac{B'+C'}{2}\right)-\left(A''-\frac{B''+C''}{2}\right)\right],$$

it is expected that the uncertainty in the parameters not determined graphically will be of comparable size. With these difficulties, only rough estimates of the Coriolis coupling constants can be given; they should lie in the ranges $0.85 < |\zeta_{7,8}| < 1.0$ and $0.06 < |\zeta_{7,9}| <$

0.22. The uncertainty in the band centers quoted is less than 4 cm⁻¹.

Although these parameters, by comparison to the accuracy of the experimental data, seem to be poorly determined, the addition of two more parameters having effects somewhat parallel to those already introduced would probably not reduce the uncertainties greatly. The added parameters would serve to complicate the theory and increase the parametric freedom.

ACKNOWLEDGMENTS

Structure of Molten Oxides. I. Viscosity of GeO₂, and Binary Germanates Containing Li₂O, Na₂O, K₂O, and Rb₂O

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An improved counterbalanced sphere viscometer was used to determine the viscosity of pure molten GeO₂ at temperatures from 1470° to 1720°C. This data agrees with the Kurkjian and Douglas data obtained below 1500°C. Activation energy and entropy calculations suggest a gradual thermal breakdown of molten GeO₂ compared to SiO₂.

Viscosity information was obtained at temperatures between 1000° and 1500°C for binary alkali germanate melts containing up to 32 mole % Li₂O, Na₂O, K₂O, and Rb₂O. Viscosity isotherms, activation energies, and activation entropies suggest gross similarities between the viscous flow mechanisms of binary alkali germanate and silicate melts. However, differences of detail imply divergent modes of network alteration with the addition of a given amount of alkali oxide.

I. INTRODUCTION

A NEW picture of the structure of molten binary silicates has been developed by Bockris and co-workers.[1,2] Their viscosity,[3-5] density,[6,7] and electrical

conductance[8-10] results provided indirect evidence for the presence of discrete silicate anions such as chains between 67 and 50 mole % M₂O, rings and polymerized rings between 50 and 33 mole % M₂O, islands or icebergs of silica between 33 and 10 mole % M₂O, and a damaged random network between 10 mole % M₂O and pure SiO₂.

Recent evidence[11-13] has suggested possible differences

[1] H. Bloom and J. O'M. Bockris, "Molten Electrolytes," in *Modern Aspects of Electrochemistry*, edited by J. O'M. Bockris (Academic Press Inc., New York, 1959), Vol. 2.

[2] J. D. Mackenzie, "Structure of Some Inorganic Glasses from High Temperature Studies", in *Modern Aspects of the Vitreous State*, edited by J. D. Mackenzie (Butterworth and Company, Washington, D. C., 1960).

[3] J. O'M. Bockris and D. C. Lowe, J. Sci. Instr. **30**, 403 (1953).

[4] J. O'M. Bockris and D. C. Lowe, Proc. Roy. Soc. (London) **A226**, 423 (1954).

[5] J. O'M. Bockris, J. D. Mackenzie, and J. A. Kitchener, Trans. Faraday Soc. **51**, 1734 (1955).

[6] J. O'M. Bockris, J. W. Tomlinson, and J. L. White, Trans. Faraday Soc. **52**, 299 (1956).

[7] J. W. Tomlinson, M. S. R. Heynes, and J. O'M. Bockris, Trans. Faraday Soc. **54**, 1822 (1958).

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[10] J. O'M. Bockris, J. A. Kitchener, S. Ignatowicz, and J. W. Tomlinson, Trans. Faraday Soc. **48**, 75 (1954).

[11] J. D. Mackenzie, J. Am. Ceram. Soc. **44**, 598 (1961).

[12] Ya. S. Bobovich and T. P. Tolub, Opt. i Spektroskopiya **12**, 489 (1962) [English transl. Opt. Spectry. **12**, 269 (1962)].

[13] A. O. Ivanov and K. S. Yevstropov, Dokl. Akad. Nauk S.S.S.R. **145**, 797 (1962).

of behavior between silicate and germanate compositions, once thought to be similar with respect to network and glass formation as well as structure. However, little, if any, precise structural information is available for molten germanates. Mackenzie determined the viscosity and electrical conductance of molten GeO_2 up to $1550°C$[14,15] while Kurkjian and Douglas studied the viscosity of molten GeO_2 and the system Na_2O-GeO_2 up to 15 mole %.[16] Their results for pure GeO_2 did not agree with one another.[11]

Binary alkali germanate systems offer greater liquid composition ranges for study than do their silicate counterparts. It is possible to obtain information for germanate melts containing small amounts of M_2O over a considerable temperature range below $1700°C$. This eliminates the need to extrapolate from higher M_2O compositions. Availability of structural information for germanate melts can allow a test of the scope of the discrete anion–iceberg concept for oxide melts. It can also serve to point out any differences of network forming ability between silica and germania.

This paper presents the results of a viscosity study of molten GeO_2 and binary alkali germanate melts containing as much as 30 mole % alkali oxide. Density information for molten germanate compositions containing as much as 60 mole % alkali oxide will be presented in a subsequent paper.

II. EXPERIMENTAL

The GeO_2 used for this study was the Electronic-Grade powder supplied by the Eagle Picher Company. The Li_2CO_3, Na_2CO_3, and K_2CO_3 powders were Baker reagent-grade analyzed materials. The Rb_2CO_3 was supplied by the Varlacoid Chemical Corporation. Spectrographic analysis of the Rb_2CO_3 indicated K_2O and Cs_2O to be the only impurities present in amounts greater than approximately 0.1 wt. %. Chemical analysis showed 1.25 wt. % K_2O and 0.05 wt. % Cs_2O. This was the purest Rb_2CO_3 available in pound quantities.

Pure GeO_2 glass slugs were prepared by two methods. In the first method, the powder was air dried at $1000°C$ for 24 h and subsequently melted at $1500°C$ for 5 h. This produced bubble-free samples with melting histories similar to Mackenzie's sample.[14,15] In the second method, the powder was vacuum dried for 16 h at $1000°C$, vacuum melted for 5 h at temperatures between $1100°$ to $1300°C$, and finally held under oil-pumped N_2 for 16 h at $1400°C$ before quenching.

Preparation of the binary alkali germanates involved an air drying of the alkali carbonates at $120°C$ for 24 h and an air drying of the GeO_2 at $1000°C$ for 24 h. Sample preparation usually involved starting with a large batch of 1 mole % M_2O composition.

Calculated amounts of alkali carbonate were periodically added to change composition following removal of enough melt to form the required 55-cc viscometer slugs. The melts were poured into viscometer crucibles or platinum foil lined cavities in an aluminum block and analytical samples obtained. All samples and filled crucibles were stored in dessicators.

The alkali contents were determined flame photometrically. Several samples analyzed after high-temperature experimentation showed no significant composition changes. Visual examination of the protection tube contents after each run revealed the absence of serious evaporation problems. The radiation shields and the temperature ranges employed served to curtail evaporation. CO_2 analysis, performed on most samples showed the residual CO_2 levels to be between 0 and 0.6 wt. %. These CO_2 levels usually contributed less than 0.5% uncertainty to the final alkali oxide composition calculations. This situation corresponds favorably with the CO_2 levels reported by Bockris and co-workers for their silica compositions.[6]

The tendency to crystallize when formed as above, with a moderate quench, was greatest for the lithia germania compositions. The soda germania samples generally formed glasses only out to about 10 mole % Na_2O, the potash germania compositions out to about 40 mole % K_2O, and the rubidia–germania compositions out through 50 mole % Rb_2O. However, an atmospheric moisture adsorption study indicated the higher K_2O
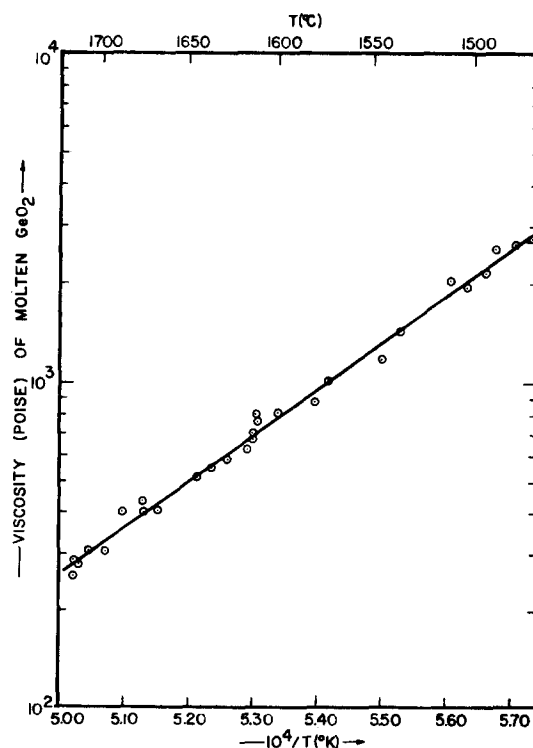

Fig. 1. Viscosity of molten GeO_2.

14 J. D. Mackenzie, J. Chem. Phys. 29, 605 (1958).
15 J. D. Mackenzie, J. Chem. Phys. 30, 1357 (1959).
16 C. R. Kurkjian and R. W. Douglas, Phys. Chem. Glasses 1, 19 (1960).

and Rb_2O content (>40 mole % K_2O and >25 mole % Rb_2O) glasses to be the least durable.

The improved counterbalanced sphere viscometer, its advantages, and its operating characteristics have been previously described in detail.[17] Basically, the use of a linear variable differential transformer (LVDT) and recorder as the velocity-determining device increased the sensitivity and usefulness in the low viscosity region as well as the over-all ease of operation. The crucibles, bobs, and suspension wires were constructed of Pt–40% Rh alloy. The protection tube and the rest of the high-temperature parts were fabricated from recrystallized alumina. Temperatures were measured with calibrated Pt–30% Rh vs Pt–6% Rh thermocouples. These materials allowed temperatures up to 1750°C to be obtained. Slight modifications included removal of the upper radiation shield disk and, in the case of the pure GeO_2 measurements, the addition of a small auxiliary heater in the cavity so created. Excessive evaporation of GeO_2 and condensation on the suspension wire, encountered only with the pure GeO_2 samples, were reduced considerably by these changes of design.

The molten samples were usually held for about three hours at temperature prior to the commencement of data acquisition. This tended to ensure complete fining (removal of bubbles). Data for each temperature was obtained only after the temperature drift had
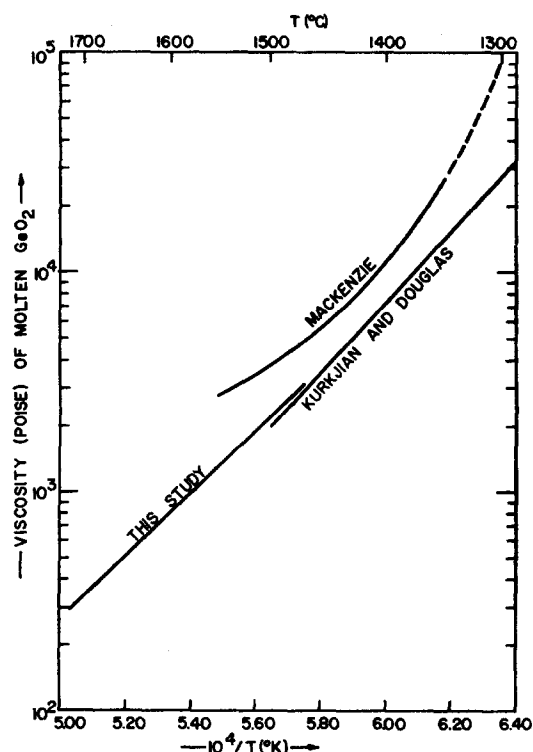

FIG. 2. Comparison of results for the viscosity of GeO_2.

[17] E. F. Riebling, Rev. Sci. Instr. **34**, 568 (1963).

TABLE I. Viscosity equations for GeO_2 and binary alkali germanates.

$\log\eta = -a + b \times 10^4/T(°K)$		
Composition	a	b
100% GeO_2	4.7042	1.4230
1.39 mole % Li_2O	1.9284	0.3798
2.48 mole % Li_2O	2.2076	0.6635
8.02 mole % Li_2O	2.5097	0.5538
9.59 mole % Li_2O	2.6266	0.5308
17.7 mole % Li_2O	2.0847	0.3706
1.58 mole % Na_2O	2.4864	0.7578
4.29 mole % Na_2O	2.2316	0.5853
7.79 mole % Na_2O	2.6681	0.5652
29.9 mole % Na_2O	2.0346	0.3615
0.84 mole % K_2O	2.5511	0.8457
3.01 mole % K_2O	2.4406	0.6996
4.58 mole % K_2O	2.7606	0.6561
7.41 mole % K_2O	2.6739	0.5808
16.7 mole % K_2O	2.2693	0.4197
21.7 mole % K_2O	1.7482	0.3293
28.1 mole % K_2O	2.9401	0.5122
31.6 mole % K_2O	2.7849	0.4903
0.42 mole % Rb_2O	2.4287	0.9172
2.34 mole % Rb_2O	2.6039	0.7618
6.34 mole % Rb_2O	2.9397	0.6474
9.24 mole % Rb_2O	3.7150	0.7096
17.2 mole % Rb_2O	3.9434	0.6203
28.0 mole % Rb_2O	3.4357	0.5955

dropped to less than the 0.05°-to-0.10°C-per-minute level. This was necessary because it usually required about 15 to 30 min for data acquisition at each temperature.

III. RESULTS

Figure 1 shows the $1/T(°K)$ dependence of log viscosity for pure molten GeO_2. Results were obtained for four runs. The viscosity values obtained above 1550°C are the first reported for this high-temperature region. The average uncertainty for each point, due to the difference between the ascending and descending weight-vs-velocity slopes, varies from ±0.1% to to ±2% over the entire range. The mean standard deviation for the least-square equation (Table I) corresponds to about ±5% at the 250-P level and ±0.5% at the 2500-P level. The results of Mackenzie, as well as those of Kurkjian and Douglas, are shown for comparison in Fig. 2. Mackenzie's original incorrect results were revised with the instrument correction factor supplied in Ref. 15. The high-temperature viscosity results of the present study agree rather closely with
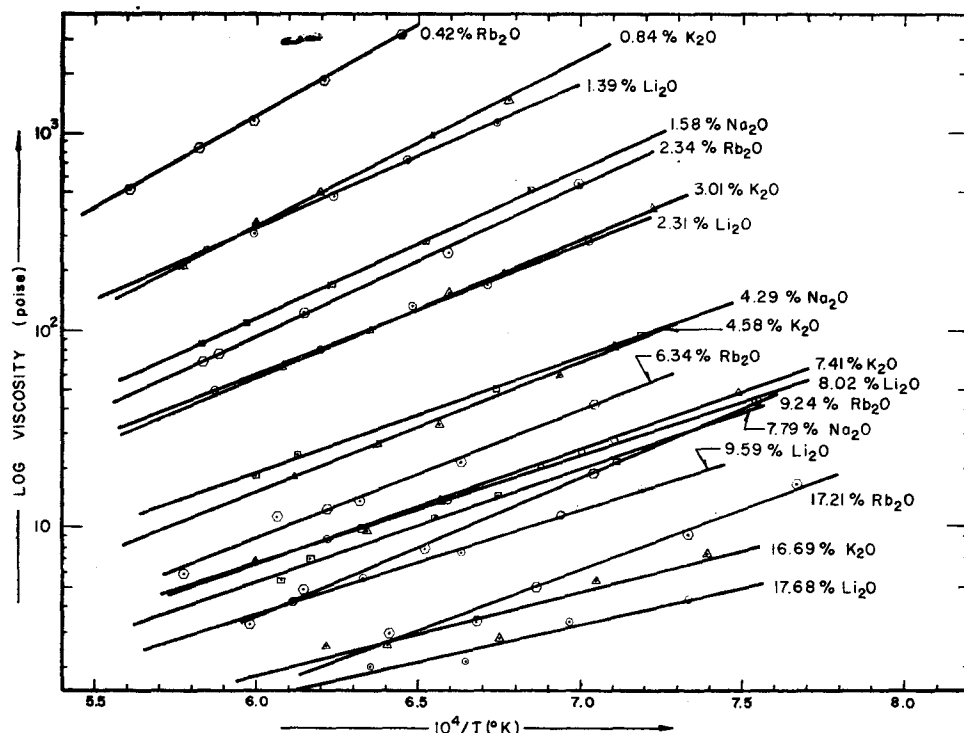
FIG. 3. Viscosity of binary alkali oxide germanate melts.

the low-temperature values obtained by Kurkjian and Douglas below 1500°C.

Most of the viscosity results obtained for the molten alkali germanate compositions are presented in Fig. 3. The scatter of points about the least-square line for each composition is small, increasing slightly at viscosities below the 5- to 10-P level. The constants for the least-square equations are presented in Table I. Phase-diagram considerations and instrument limitations reduced the amount of useful viscosity information that could be acquired for the relatively fluid germanate compositions containing more than 32 mole % M_2O.

Figure 4 depicts viscosity as a function of composition at constant temperature (1300°C). The addition of alkali oxide decreases the viscosity rather drastically. Additions of M_2O greater than 15 mole % M_2O do not result in a further significant reduction of viscosity. There is a similarity of effect for all four alkali cations.

The activation energy for viscous flow ($\Delta E_\eta^\ddagger$) is given as a function of composition in Fig. 5. A definite change of slope occurs for all four alkali cations at approximately 2 mole % M_2O with a subsequent leveling off beyond about 5 mole % M_2O. There is an apparent difference between Rb_2O and K_2O, Na_2O, and Li_2O as a group between 10 and 20 mole % M_2O. Beyond this region there is an apparent inverse relationship between the cation oxygen attraction I[$I = Z/(r_+ + r_-)^2$], where $Z =$ cation charge, $r_+ =$ cation radius, $r_- =$ oxygen radius.

Figure 6 shows that there is an entropy of activation

($\Delta S_\eta^\ddagger$) minimum at 1 to 2 mole % M_2O that is approximately related to I. The minimum is less pronounced for the larger ions. There is an apparent
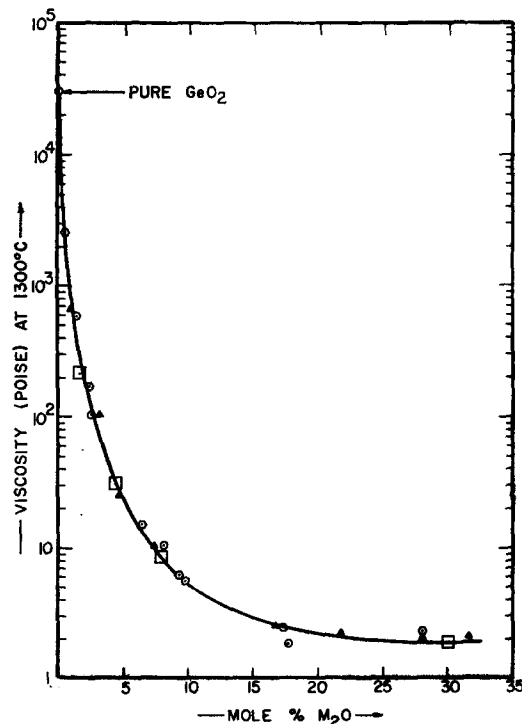

FIG. 4. Viscosity isotherm for 1300°C as a function of composition. Li_2O. ⊙; Na_2O, ▫; K_2O, △; Rb_2O, hexagon.

difference in behavior between Rb_2O and Li_2O, Na_2O, and K_2O as a group at compositions between 8 to 18 mole % M_2O. The entropy values were calculated with an assumed activated complex molar volume of 30 cc. Assumption of a simple GeO_2 flow species for compositions containing more than 2 mole % M_2O is not justified because of the large decrease of $\Delta E_\eta{}^{\ddagger}$. An ion-pair species involving alkali cations, such as the type suggested by Bockris,[5] appears to be more reasonable. The volume of this species would not differ appreciably from the value for a simple GeO_2 unit.

IV. DISCUSSION

A. Pure Molten GeO_2

Mackenzie, who used a counterbalanced sphere technique[14,15] reported a value of 3 650 P for the viscosity of molten GeO_2 at 1500°C. Subsequent work by Kurkjian and Douglas, with a rotating-cylinder viscometer,[16] yielded a value of 1 800 P at the same temperature. The viscosity equation for GeO_2 that is presented in Table I yields a value of 2 098 P for the viscosity at 1500°C. Significant points concerning this rather close agreement with the Kurkjian and Douglas data include:

(a) Two different types of instruments, used in two different temperature regions, yield viscosities and activation energies that are in close agreement ($\Delta E_\eta{}^{\ddagger} \sim$ 70±5 kcal).

(b) Both sets of data give viscosity values that are quite a bit smaller, at a given temperature, than the value reported by Mackenzie.
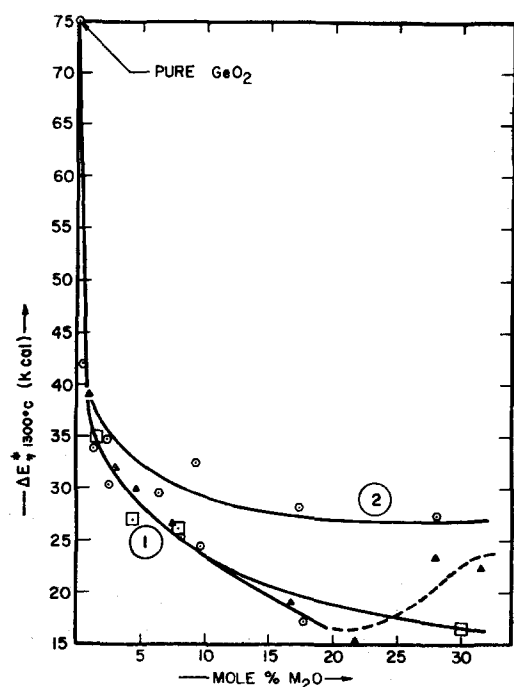
FIG. 6. $\Delta S\eta{}^{\ddagger}$ as a function of composition: 1. Li_2O, ⊙; 2. Na_2O, ▢, K_2O, △; 3. Rb_2O, hexagon.

The possibility that alkali and alkaline-earth contamination could be responsible for the lower values herein reported was spectroscopically examined. Li_2O and Na_2O were either not detectable or less than 0.001 wt. % before, and 0.0001 to 0.001 wt. % after, a given run, while K_2O was either not detectable or less than 0.001 wt. % before, and 0.001 to 0.1 wt. % after, a given run. MgO was the chief alkaline-earth impurity and was generally between 0.001 to 0.01 wt. % before and after a given run. SiO_2 was generally 0.001 to 0.1 wt. % before, and 0.01 to 0.1 wt. % after; Al_2O_3 was generally 0.001 to 0.01 wt. % before, and 0.005 to 0.05 wt. % after; and B_2O_3 was generally 0.001 to 0.01 before and after a given run.

Mackenzie reported 0.1 % of Ca, and less than 0.001 % of Na, Si, and Mg at the conclusion of his experiments,[14,15] while Kurkjian and Douglas reported approximately 0.01 mole % Na_2O and K_2O (these correspond to 0.006 wt. % Na_2O and 0.01 wt. % K_2O) before a run for their Johnson Matthey and Company, Ltd., and General Electric Company, Ltd., 99.95 % GeO_2 samples.[16] Thus, the GeO_2 used for this study was of a purity level comparable to the materials reported by the previous workers.

The possibility that water was responsible for the difference between this data and Mackenzie's results was examined. No significant difference between the viscosity data obtained for the air-dried GeO_2 powder and the data obtained for the vacuum-dried material was observed. There is very little difference between the Kurkjian and Douglas data, obtained in a pure,

FIG. 5. $\Delta E\eta{}^{\ddagger}$ as a function of composition. 1. Li_2O, ⊙; Na_2O, ▢; K_2O, △. 2. Rb_2O, hexagon.

dry O_2 atmosphere, and the present results obtained in an air atmosphere.

The close agreement of these viscosity results with the Kurkjian and Douglas data can be taken as evidence that the activation energy for viscous flow for molten GeO_2 is fairly constant over the temperature range 1000° to 1700°C.[18] The slight decrease of $\Delta E_\eta^{\ddagger}$ with temperature is much smaller than the decrease originally reported by Mackenzie for temperatures below 1550°C. These results are indicative of the fact that the apparent breakdown of the GeO_2 network at higher temperatures is not as pronounced as Mackenzie originally suggested.[14,15] They are more in line with subsequent suggestions (based on the work of Kurkjian and Douglas) that GeO_2 may possess an anomalous flow behavior when compared to silica.[11]

Calculation of the entropy of activation for viscous flow can be accomplished with the rate equation

$$\eta_{(P)} = [(Nh/V)\exp(-\Delta S_\eta^{\ddagger}/R)]\exp(\Delta H_\eta^{\ddagger}/RT) \quad (1)$$

if the volume of the flow species in the activated state can be estimated. The fact that the activation energy ($\sim$70 kcal) is close to the estimated Ge–O bond strength ($\sim$100 kcal) suggests the possibility that bond breaking could be involved in the flow mechanism. If this were the case, the simplest flow species could be GeO_2 as postulated by Mackenzie.[14,15] A volume of 30 cc ($\sim V_M$ for GeO_2) yields an entropy of -0.8 cal/degree mole at 1600°C. This is smaller than either Mackenzie's values[14,15] or a value of approximately 10 cal/deg mole (at 1300°C) that can be calculated from the Kurkjian and Douglas data.[16]

If there is a real difference of slope between the Kurkjian and Douglas data and the results presented in this paper, then the possibility exists that $\Delta S_\eta^{\ddagger}$ does become slightly less positive at higher temperatures. This supports the previous conclusion, based on the present $\Delta E_\eta^{\ddagger}$ value of 65.1 kcal, that the thermal disruption of the GeO_2 network is a rather gradual affair.

B. Binary Alkali Germanate Melts

The viscosity behavior of alkali germanate melts is generally similar to that previously reported for alkali silicate melts.[5] In addition, the present soda–germania results agree with the previously reported study of soda–germania melts containing as much as 15 mole % Na_2O.[16] The addition of alkali decreases the viscosity, activation energy, and activation entropy. However, close examination of the data reveals several significant differences of detail.

1. Viscosity Isotherms

The leveling off of the viscosity-vs-composition isotherm beyond about 15 mole % M_2O (Fig. 4) represents a departure from the behavior of corresponding silicate melts. The viscosity of molten silicates continues to decrease significantly with the addition of alkali beyond the 20 mole % region. This is indicative of the fact that the changes of structure for molten silicates containing more than 20 mole % M_2O may be more pronounced than they are with molten germanates in the same composition region.

The viscosity at 1300°C decreases by a factor of 10^4 from 3×10^4 P for pure GeO_2 to 3 P for 14 mole % alkali oxide. A comparable example for silica at 1200°C indicates a viscosity decrease of about 10^{10} from a value of $\sim 10^{13}$ P for pure silica to 2.24×10^3 P for 16.9 mole % K_2O. It can be concluded that a given amount of alkali oxide creates a much larger perturbation within the silica network at 1300°C than within the germania network at the same temperature. This difference between germanates and silicates could be associated with the fact that the melting point of germania is 600°C lower than that of silica.[19]

Germania and silica have similar viscosities ($\sim 10^6$ P) at their respective melting points (1115° and 1710°C).[2] However, the alkali–germania viscosity isotherm is at a temperature that is several hundred degrees above the melting point of germania where the network structure could be quite a bit looser than in the silicate cases. If it were possible to measure the viscosity of alkali germanates at about 500°C, one might find an order-of-magnitude viscosity difference that was similar to the silica case (10^{10} P).

There is a similarity of effect for the viscosity of all four cations within the 0 to 30 mole % M_2O composition region in the germanate systems. Unfortunately, there is not enough molten silicate data for compositions containing less than 15 mole % M_2O to allow a valid comparison.

2. Activation Energies for Viscous Flow

A definite change of slope for the activation energy of viscous flow occurs at about 2 mole % alkali oxide for all four cations (Fig. 5). The change of slope is sharper than for the alkali silicates. This difference could be apparent rather than real because little information is available for silicates containing less than 15 mole % alkali oxide. The germanate $\Delta E_\eta^{\ddagger}$ values are about one-half of the corresponding silicate

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[18] W. A. Plummer, E. H. Fontana, and H. E. Hagy of this laboratory have recently determined the viscosity of GeO_2 over a considerable temperature range below 1500°C. Their results are in substantial agreement with this conclusion.

[19] The heat of fusion and the entropy of fusion for GeO_2 are larger than the corresponding values for SiO_2. The magnitudes of the melting energies for GeO_2 are similar to those reported for other refractory type oxides by O. Kubaschewski and E. L. Evans in *Metallurgical Thermochemistry* (Pergamon Press, Inc., New York, 1958). This suggests a possible difference in melting phenomena between GeO_2 and SiO_2.

values at about the same temperature. This might again be due to the fact that the germanate data is for temperatures that are several hundred degrees above the melting point of GeO_2. If the $\Delta E_\eta^\ddagger$ values were temperature-dependent over large temperature ranges, then similarities could exist between the two systems. It is also possible that the structural changes in binary germanate melts containing less than 15 mole % M_2O are rather different than those previously postulated for similar binary silicate melts.

There is no apparent relationship between I (the ion–oxygen attraction) and $\Delta E_\eta^\ddagger$ for the Li_2O, Na_2O, and K_2O germanates at compositions up to 18 mole % M_2O. For germanate melts containing 30 mole % M_2O, the experimental activation energy for viscous flow is apparently related to I in an inverse fashion (Fig. 5). The fact that $\Delta E_\eta^\ddagger$ for germanate melts containing more than about 8 mole % Rb_2O is larger than that experienced by melts containing Li_2O, Na_2O, and K_2O may stem from steric or packing effects ($r_{Rb+} > r_{Li+, Na+, K+}$). This could be associated with the number of large cations present at these higher mole percentage M_2O compositions. While Bockris found no relationship at 15 and 20 mole % M_2O for the silicates, his group did report inverse relationships at 33, 40, and 45 mole % M_2O.[4] There is no data available for the rubidia–silicate melts.

3. Activation Entropies for Viscous Flow

Interpretation of the entropy of activation results remains qualitative because of the approximations involved in deriving the rate equations and the volume of the activated species. The $\Delta S_\eta^\ddagger$ minima that occur at about 1 to 2 mole % M_2O are apparently related to I, the ion-oxygen attraction function (Fig. 6) because the $\Delta S_\eta^\ddagger$ minima is most pronounced for Li^+ and least pronounced for Rb^+. If a negative $\Delta E_\eta^\ddagger$ corresponds to an unfavorable configuration for the activated state during viscous flow, as has been postulated for molten silicates, then it would appear that molten germanates involving Li^+ ions have the least favorable activated complex configuration for viscous flow within the 1 to 2 mole % M_2O region. The high charge density of the small Li^+ ion could be responsible for this restrictive or ordering effect in the activated complex. Rb_2O would correspondingly present the most favorable activated complex configuration of the four ions studied.

The magnitudes of the negative $\Delta S_\eta^\ddagger$ values herein reported for the molten germanates are similar to those reported for molten alkali silicates at compositions greater than 15 mole % M_2O.[5] Bockris and co-workers

did not present enough data at lower alkali compositions to draw comparisons similar to those presented above for germanate melts.

The apparent difference in activation entropy behavior between Rb^+ and the three smaller cations becomes even more pronounced at compositions between 8 to 18 mole % M_2O. It would again appear that Rb^+ is the least offensive ion with respect to an unfavorable activated complex configuration.

The observed relationship between $\Delta S_\eta^\ddagger$ and the cation–oxygen attraction tends to support the proposed ion-pair type of activated complex flow species for compositions containing more than 2 mole % M_2O. The cations can be thought of as playing a role in the mechanism of viscous flow, especially for compositions containing more than 2 mole % M_2O.

4. Conclusions

To conclude, the over-all flow mechanisms for molten germanates and silicates appear to be of a similar nature. However, the differences of detail discussed above are indicative of distinctive differences between germanate and silicate melt structures of similar composition at 1300°C.

The viscosity, $\Delta E_\eta^\ddagger$, and $\Delta S_\eta^\ddagger$ evidence suggests that the flow mechanism of GeO_2 is considerably altered with the addition of as little as 1 to 2 mole % alkali oxide. The pattern of these property changes with the addition of alkali oxide is indicative of a significant disruption of the polymeric GeO_2 solvent at rather low alkali concentrations. This is in apparent contrast to silicate melts where the limited amount of data makes it difficult to decide whether the flow mechanism changes occur at 2 or 12 mole % alkali oxide.

Addition of large amounts of alkali oxide tend to accentuate the individual cation behavioral differences rather than introduce further gross changes of flow properties. Melt structural changes occurring with the addition of alkali oxide to GeO_2 will be discussed in greater detail in a subsequent paper that will be concerned with density measurements.