

## Structure of Molten Oxides. II. A Density Study of Binary Germanates Containing Li<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O, and Rb<sub>2</sub>O

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## Structure of Molten Oxides. II. A Density Study of Binary Germanates Containing $\text{Li}_2\text{O}$ , $\text{Na}_2\text{O}$ , $\text{K}_2\text{O}$ , and $\text{Rb}_2\text{O}$

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(Received 29 July 1963)

An improved counterbalanced sphere viscometer–densitometer was used to obtain density information between 1050° to 1500°C for a series of binary germanate melts containing as much as 60 mole%  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{Rb}_2\text{O}$ . Densities and the expansion coefficient of molten  $\text{GeO}_2$  between 1100° to 1400°C were estimated from the binary data. The molar volume, expansion coefficient, partial molar volume and partial molar expansion deviations suggest a mode of network alteration that differs from that observed for silicate melts. This confirms the previously reported viscosity results for binary alkali germanate melts. It is suggested that a gradual change from tetrahedral to octahedral configuration occurs for  $\text{GeO}_2$  with the addition of alkali oxide. The maximum stability of octahedrally coordinated germanium at 1300°C appears to occur for melts containing from 15 to 30 mole%  $\text{M}_2\text{O}$ . A rapid return to tetrahedral configuration appears to take place for most germanate melts as the alkali oxide content is increased above 30 mole%. These alkali-rich germanate melts possess properties that are similar to those found for their silicate analogs. It is suggested that discrete anions also exist in these alkali rich germanate melts.

### I. INTRODUCTION

A RECENT paper described viscosity results obtained with an improved high-temperature counterbalanced-sphere viscometer<sup>1</sup> for molten  $\text{GeO}_2$  up to 1720°C and for a series of binary germanate melts containing as much as 30 mole %  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{Rb}_2\text{O}$ .<sup>2</sup> It was concluded that gross similarities exist between the viscous transport mechanisms of binary alkali germanate and silicate melts. However, differences of detail implied divergent modes of network alteration with the addition of a given amount of alkali oxide.

This paper presents density information obtained with the above instrument for binary germanate melts containing up to 60 mole %  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{Rb}_2\text{O}$ . Molar volume, expansion coefficient, partial molar quantities, and their deviations from ideality are discussed with respect to alteration of the molten three-dimensional  $\text{GeO}_2$  structure. These results are also compared with the available molten silicate information.<sup>3–7</sup>

### II. EXPERIMENTAL

The purity of the materials, methods of sample preparation, and analytical procedures have been previously described.<sup>2</sup> The counterbalanced sphere viscometer principle allows the determination of viscosity

and/or density for a given melt composition. The use of a linear variable differential transformer (LVDT) and recorder as the velocity determining devices have increased sensitivity and usefulness in the low-viscosity regions as well as over-all ease of operation.<sup>1</sup> 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. General data acquisition procedures were similar to those previously described.<sup>1,2</sup>

The use of a single 1.6-cc bob, as well as buoyancy values ( $\beta$ ) that are uncorrected for the positive effect of surface tension, can yield density values that possess the same degree of reliability as those calculated from data obtained for two different-size bobs.<sup>1</sup> This technique was used to calculate the experimental densities from

$$\rho_{\text{melt}} = \frac{\beta}{v_T} = \frac{\beta}{v_0(1+\alpha_m T)} = \frac{\beta}{(\beta_0/\rho_{\text{H}_2\text{O}})(1+\alpha_m T)}$$

$$= \frac{w - w_0'}{[(w - w'')/\rho_{\text{H}_2\text{O}}](1+\alpha_m T)}, \quad (1)$$

where  $w$  = weight of the bob in air at temperature as determined prior to immersion. The high-temperature air weight is usually a few milligrams less than the room-temperature value. This arises from the decreased density of air at elevated temperatures.  $w_0'$  is the equilibrium weight of the bob immersed in the melt;  $w''$ , the weight of the bob immersed in water;  $\alpha_m$ , the volume expansion coefficient of the bob; and  $\rho_{\text{H}_2\text{O}}$ , the density of water.

$w_0'$  values for melts of low viscosity were generally obtained by a direct weighing technique that involved the use of the LVDT recorder arrangement as a drift check.  $w_0'$  values for melts of higher viscosities were determined from the large scale plots of off balance versus bob velocity. Five to 10 weight–velocity points

<sup>1</sup> E. F. Riebling, *Rev. Sci. Instr.* **34**, 568 (1963).

<sup>2</sup> E. F. Riebling, *J. Chem. Phys.* **39**, 1889 (1963).

<sup>3</sup> H. Bloom and J. O'M. Bockris, in *Modern Aspects of Electrochemistry*, edited by J. O'M. Bockris (Academic Press, Inc., New York, 1959), Vol. 2, p. 160.

<sup>4</sup> J. D. Mackenzie, in *Modern Aspects of The Vitreous State*, edited by J. D. Mackenzie (Butterworth and Company, Ltd., Washington, D. C., 1960), p. 188.

<sup>5</sup> J. O'M. Bockris, J. W. Tomlinson, and J. L. White, *Trans. Faraday Soc.* **52**, 299 (1956).

<sup>6</sup> J. W. Tomlinson, M. S. R. Heynes, and J. O'M. Bockris, *Trans. Faraday Soc.* **54**, 1822 (1958).

<sup>7</sup> J. L. White, Ph.D. dissertation, University of California, 1955.

(each one duplicated) were taken for both ascending and descending conditions. The buoyancy uncertainty arising from the use of extrapolated ascending and descending data was of the order of  $\pm 2$  mg or  $\pm 0.05\%$  for a 5500-mg buoyancy. The large buoyancies encountered with germanate melts tend to minimize most of the experimental uncertainties involved in the use of Eq. (1).

Visual examination of the suspension wires and protection tube contents after each run revealed the absence of serious evaporation problems. The absence of significant composition changes was also confirmed by several postrun chemical analyses. The suspension assemblies were weighed (a) subsequent to dissolution of glass adhering to the bobs and (b) following immersion of the suspension wire in NaOH solutions. These procedures also revealed an absence of condensation on the suspension wire. The post run suspension assembly weights generally agreed with the prerun values to within normal weighing uncertainties.

The room-temperature bob volumes ( $v_0$ ) were determined by weighing (a), in air and (b), to a known depth in pure water before and after each run. No significant changes or trends were noted. The position at which the bob touched the melt surface was noted. A pointer attached to the movable pedestal of the viscometer allowed immersion of the bob and wire to the same depth at elevated temperatures. Bob-to-bottom distances at elevated temperatures were kept within the fixed limits employed during the viscosity calibration procedures. Periodic determinations of bob densities revealed good agreement with published values for the Pt-40% Rh alloy<sup>8</sup> as well as an absence of significant changes with prolonged use at elevated temperatures. The linear coefficient of expansion for the Pt-40% Rh alloy for temperatures up to 1500°C has been recently determined.<sup>9</sup> These data, the relationships given by White,<sup>10</sup> and the  $v_0$  values were used to calculate the bob volumes at temperature ( $v_T$ ). The use of two 1.6-cc calibrated bobs served to expedite the experimental work.

The total uncertainty in determining a  $v_T$  of about 1.68 cc amounted to approximately  $\pm 0.25\%$ . About 0.15% arose from  $v_0$  and 0.10% from high-temperature considerations. The total uncertainty compares favorably with the value given by Bockris *et al.* for their silicate melt studies.<sup>5</sup>

<sup>8</sup> R. B. Green, *Metals Handbook, Properties and Selection of Metals* (American Society for Metals, Novelty, Ohio, 1961), 8th ed., Vol. 1, p. 1191.

<sup>9</sup> H. E. Hagy of this laboratory used a sapphire dilatometer and obtained this equation:

$$\Delta L/L = 8.85 (T - 25) + 0.00176 (T - 25)^2,$$

where  $\Delta L/L$  is the change in length per unit length (ppm) and  $T$  is degrees Centigrade. The uncertainty in  $\Delta L/L$  amounted to about  $\pm 1\%$  for temperatures between 900° and 1500°C.

<sup>10</sup> J. L. White, *Physicochemical Measurements at High Temperatures*, edited by J. O'M. Bockris, J. L. White, and J. D. Mackenzie (Academic Press Inc., New York, 1959), pp. 344-345.

TABLE I. Density equations for alkali germanate melts.

Mole % M <sub>2</sub> O	$\rho = a - b \times 10^{-3} (T^\circ \text{K})$		T range (°C)
	a	b	
1.39 % Li <sub>2</sub> O	3.625	0.0763	1200-1450
2.48	3.677	0.0919	1150-1450
8.02	3.875	0.194	1100-1350
9.59	3.931	0.225	1100-1400
17.7	4.039	0.330	1100-1350
31.8	3.787	0.329	1100-1400
44.6	3.509	0.324	1250-1500
60.6	3.171	0.340	1200-1500
1.53% Na <sub>2</sub> O	3.685	0.102	1180-1450
4.29	3.866	0.187	1100-1400
7.79	4.017	0.270	1100-1400
12.8	4.160	0.388	1080-1400
21.7	4.003	0.409	1050-1350
29.9	3.682	0.354	1050-1300
37.6	3.484	0.325	1050-1350
47.0	3.383	0.345	1100-1400
54.6	3.297	0.373	1080-1350
0.84% K <sub>2</sub> O	3.636	0.0894	1200-1500
3.01	3.752	0.144	1100-1400
4.58	3.884	0.220	1100-1380
7.41	3.985	0.296	1050-1400
16.7	3.920	0.429	1080-1350
21.7	3.705	0.387	1050-1350
28.1	3.456	0.343	1100-1350
31.6	3.396	0.348	1050-1300
40.9	3.300	0.395	1090-1350
50.8	3.289	0.527	1100-1300
0.42% Rb <sub>2</sub> O	3.535	0.0367	1270-1510
2.34	3.740	0.117	1150-1450
6.34	4.086	0.276	1150-1460
9.24	4.298	0.406	1050-1400
17.2	4.308	0.506	1030-1300
28.0	3.995	0.409	1080-1350
39.1	4.180	0.545	1070-1310

Finally, several factors influenced the maximum temperature ranges employed for each composition. Buoyancy changes can be quite small for melts with small expansion coefficients. The melt expansivity [ $\alpha = 1/v(dv/dT)_P$ ] does not have to be zero in order

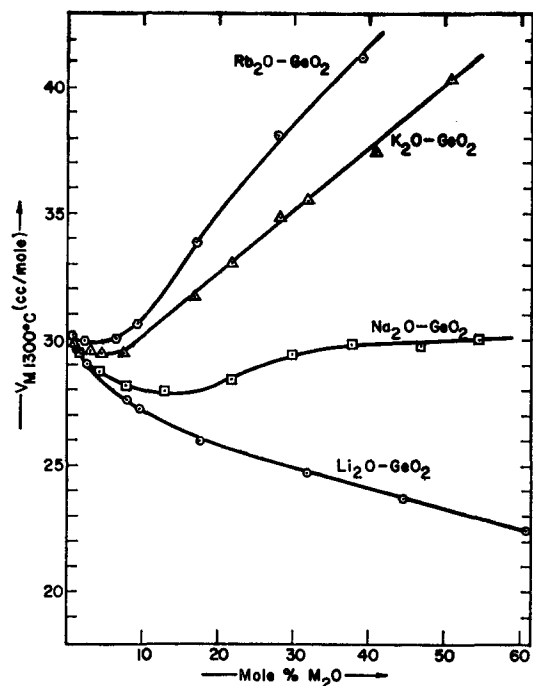


FIG. 1. Molar-volume isotherms (1300°C) for alkali germanate melts.

to have  $\Delta\beta=0$ . Actually,  $\beta$  can increase with temperature for melts with small  $\alpha$  values. These effects arise because the bob volume also increases with temperature [Eq. (1)]. A 300°C temperature spread is generally attempted for this type of density study. However, phase diagram (liquidus temperatures) and anticipated volatilization considerations can limit this value.

### III. RESULTS

All of the experimental density data were linearly dependent upon temperature. The least-square equations that present melt density as a function of temperature (K°) are given along with the experimental temperature ranges in Table I. The molar volume isotherms presented in Fig. 1 were calculated from Eqs. (2) and (3):

$$MW_{Av} = x_{\text{GeO}_2} MW_{\text{GeO}_2} + x_{\text{M}_2\text{O}} MW_{\text{M}_2\text{O}}, \quad (2)$$

where  $x$  is the mole fraction of each species.

$$v_M = \frac{MW_{Av}}{\rho \text{ (gm/cc)}}. \quad (3)$$

Deviations from ideality were calculated with Eq. (4):

$$\Delta v = v_{\text{ideal}} - v_{\text{exptl.}} \quad (4)$$

This requires a knowledge of  $v_{\text{GeO}_2}$  and  $v_{\text{M}_2\text{O}}$ :

$$v_{\text{ideal}} = x_{\text{GeO}_2} v_{\text{GeO}_2} + x_{\text{M}_2\text{O}} v_{\text{M}_2\text{O}}. \quad (5)$$

$v_{\text{M}_2\text{O}}$  values for  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  at several temperatures between 1100° and 1400°C were calcu-

lated from the data given by White<sup>7</sup> and later developed by Tilton.<sup>11</sup> Corresponding values for  $\text{Rb}_2\text{O}$  were obtained from an extrapolation of a linear plot of  $v_{\text{M}_2\text{O}}$  vs  $(r_+ + r_-)^3$  for the three lighter alkali oxides.  $v_{\text{GeO}_2}$  was obtained indirectly by extrapolating the smooth density curves for the alkali germanate melts back to zero mole %  $\text{M}_2\text{O}$ .<sup>12</sup> The density vs composition isotherms exhibit maxima for compositions between 5 to 15 mole %  $\text{M}_2\text{O}$ . However, it is possible to obtain reasonable extrapolations because of the number of data obtained for compositions rich in  $\text{GeO}_2$ . This procedure produced values of 3.465 g/cc ( $v=30.19$  cc) at 1100°C, 3.456 g/cc ( $v=30.27$  cc) at 1300°C and 3.452 g/cc ( $v=30.30$  cc) at 1400°C for the density of pure molten  $\text{GeO}_2$ .

Figure 2, drawn on a large scale, more clearly shows the presence of molar volume isotherm minima for  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{Rb}_2\text{O}$  germanate melts rich in  $\text{GeO}_2$ . This type of behavior was not observed for binary alkali silicate melts.

The  $\Delta v$  curves shown in Fig. 3 are indicative of considerable fluctuations for the negative deviations from ideality. They occur for all four systems studied. The negative deviations found for silicate systems varied more regularly with composition. Plots for additional temperatures were similar.

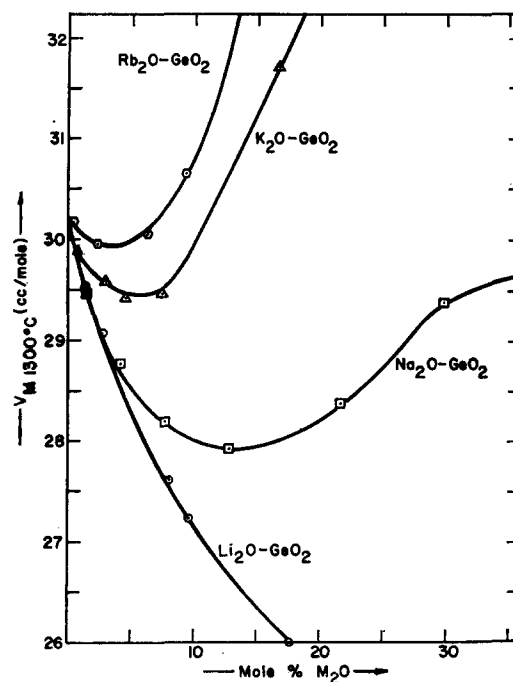


FIG. 2. Large-scale plot of molar volume isotherms (1300°C) for  $\text{GeO}_2$  rich alkali germanate melts.

<sup>11</sup> L. W. Tilton, J. Am. Ceram. Soc. **43**, 9 (1960).

<sup>12</sup> Attempts to determine the density of pure molten  $\text{GeO}_2$  at temperatures between 1500° and 1700°C were unsuccessful because condensation of  $\text{GeO}_2$  on the suspension wire (primarily above 1600°C) and rather high viscosities served to reduce the sensitivity of the counterbalanced sphere technique.

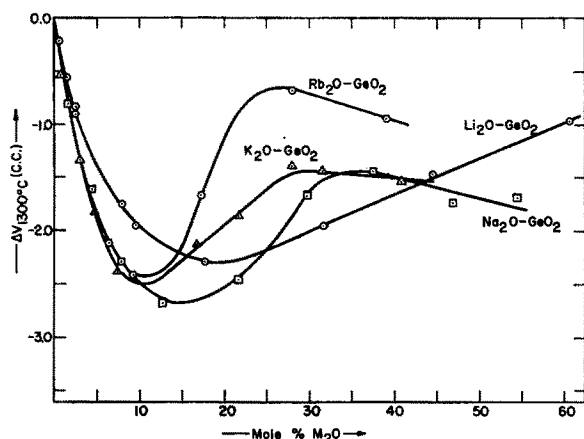


FIG. 3. Molar-volume deviations from ideality ( $\Delta v$ ) for alkali germanate melts at 1300°C.

Figure 4 compares the present molar volume expansion coefficients  $(dv/dT)_P$  for binary alkali germanate melts with the available information for the corresponding silicate systems. The molar volume expansion coefficients are well suited for theoretical comparisons because they are extensive properties that refer to a specific number of atoms. The addition of even small amounts of alkali oxide to  $\text{GeO}_2$  causes a significant increase of the expansion functions. Plots of germanate melt expansivities,  $\alpha = 1/v(dv/dT)$ , versus composition were similar to the  $(dv/dT)_P$  isotherms.

Partial molar quantities were obtained from large scale smooth curve plots of  $\Delta v$  versus composition that were similar to those shown in Fig. 3. The graphical "method of intercepts"<sup>13</sup> and a mirror technique<sup>14</sup> were particularly valuable for rapidly determining tangents

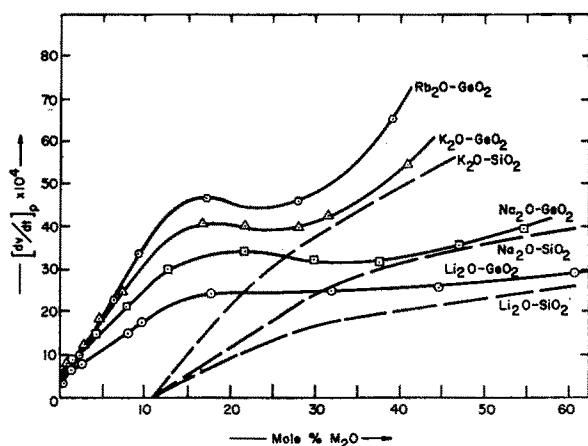


FIG. 4. Molar-volume expansion coefficients for alkali germanate melts (—) compared to the alkali silicate melt values (---) reported by Bockris *et al.*

<sup>13</sup> G. N. Lewis and M. Randall, *Thermodynamics*, revised by K. S. Pitzer and L. Brewer (McGraw-Hill Book Company, Inc., New York, 1961), 2nd ed., pp. 207–208.

<sup>14</sup> M. Latshaw, J. Am. Chem. Soc. **47**, 793 (1925).

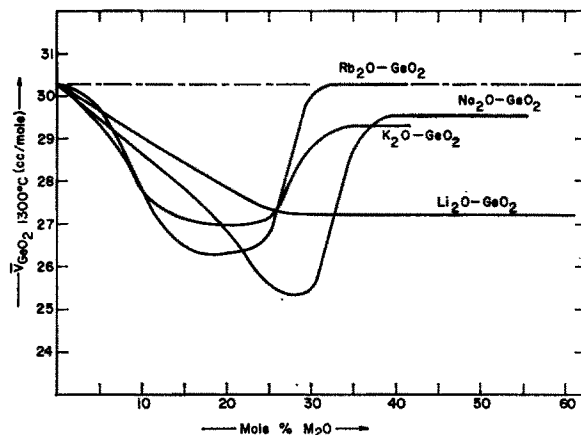


FIG. 5. Partial molar volume of  $\text{GeO}_2$  as a function of composition at 1300°C.

to the smooth curves. The Gibbs-Duhem equation<sup>15</sup> expresses the interdependence of the  $\bar{v}_{\text{GeO}_2}$  and  $\bar{v}_{\text{M}_2\text{O}}$  values thus obtained. The  $\bar{v}$  values are superior to the  $\Delta v$  values for structural interpretative purposes because they are more independent of any uncertainties involved in choosing the ideal  $v_{\text{M}_2\text{O}}$  and  $v_{\text{GeO}_2}$  values.

The  $\bar{v}_{\text{GeO}_2}$  and  $\bar{v}_{\text{M}_2\text{O}}$  curves are shown as functions of composition at 1300°C in Figs. 5 and 6, respectively. The sharp  $\bar{v}_{\text{GeO}_2}$  minimum at 28 mole %  $\text{Na}_2\text{O}$  and the broad  $\bar{v}_{\text{GeO}_2}$  minima at 20 mole %  $\text{K}_2\text{O}$  and 18 mole %  $\text{Rb}_2\text{O}$  represent considerable negative devia-

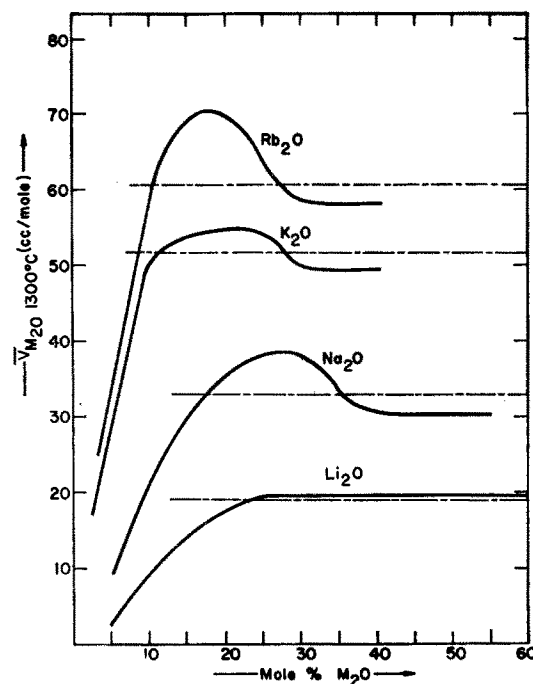


FIG. 6. Partial molar volumes of the alkali oxides as functions of composition at 1300°C.

<sup>15</sup> I. M. Klotz, *Chemical Thermodynamics* (Prentice-Hall, Inc., New York, 1950), p. 191.

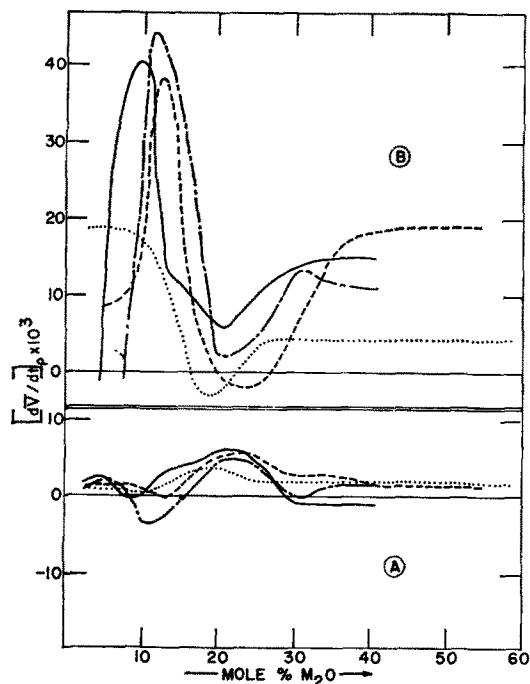


FIG. 7. Partial molar expansion coefficients for  $\text{GeO}_2$  (A) and the alkali oxides (B).  $\text{Li}_2\text{O}-\text{GeO}_2$ , ....;  $\text{Na}_2\text{O}-\text{GeO}_2$ , ----;  $\text{K}_2\text{O}-\text{GeO}_2$ , -.-.-;  $\text{Rb}_2\text{O}-\text{GeO}_2$ , —.

tions (about 3.5 to 5.0 cc). The positive  $\bar{v}_{\text{M}_2\text{O}}$  deviations amount to +6 cc at 28 mole %  $\text{Na}_2\text{O}$ , +3 cc at 24 mole %  $\text{K}_2\text{O}$ , and +10 cc at 18 mole %  $\text{Rb}_2\text{O}$ . None of these irregularities were reported for the corresponding molten silicates.

Knowledge of the temperature dependence of  $\bar{v}_{\text{GeO}_2}$  and  $\bar{v}_{\text{M}_2\text{O}}$  allowed calculation of the partial molar expansion coefficients for  $\text{GeO}_2$  and the alkali oxides. The composition dependence of  $(d\bar{v}_{\text{GeO}_2}/dT)_P$  and  $(d\bar{v}_{\text{M}_2\text{O}}/dT)_P$  are depicted in Figs. 7(A) and 7(B), respectively. Significant features of these curves are (a), the slight broad  $(d\bar{v}_{\text{GeO}_2}/dT)_P$  maxima that coincide with the rather extensive  $(d\bar{v}_{\text{M}_2\text{O}}/dT)_P$  minima between 18 and 25 mole %  $\text{M}_2\text{O}$  and (b), the general similarity to alkali silicate behavior for compositions containing more than 30 mole %  $\text{M}_2\text{O}$ .

#### IV. DISCUSSION

##### A. Density of $\text{GeO}_2$

An expansivity ( $\alpha$ ) of  $1.2 \times 10^{-5}$  can be calculated for pure molten  $\text{GeO}_2$  at  $1300^\circ\text{C}$  if one uses the density values obtained from extrapolations of the binary alkali germanate data. This value agrees closely with the average value of  $1.4 (\pm 0.4) \times 10^{-5}$  obtained from direct extrapolations of the binary melt expansivity data. Therefore, it would appear that pure molten  $\text{GeO}_2$  possesses an expansion coefficient of  $3.9 (\pm 1.3) \times 10^{-4}$  for a temperature that is  $200^\circ\text{C}$  above its melting point. This value is larger than the corresponding

value ( $\sim$ zero) for  $\text{SiO}_2$  at the same temperature. This agrees qualitatively with low-temperature expansion data for  $\text{GeO}_2$  and  $\text{SiO}_2$  glasses.<sup>16</sup> However, liquids generally possess larger expansion coefficients than their respective solids.  $\text{SiO}_2$  at  $1300^\circ\text{C}$  has not yet melted. Thus, a more valid comparison would involve comparable  $T > T_{\text{mp}}$  values.

Bacon, Hasapis, and Wholley<sup>17</sup> used a tungsten-equipped counterbalanced-sphere viscometer to measure the viscosity of pure  $\text{SiO}_2$  at temperatures between  $1900^\circ$  to  $2300^\circ\text{C}$ . One can calculate an expansion coefficient of about  $27 \times 10^{-4}$  between  $1900^\circ$  and  $2100^\circ\text{C}$  and a value of about  $85 \times 10^{-4}$  between  $2100^\circ$  and  $2300^\circ\text{C}$  from the few density values that they also reported.

This analysis suggests that molten  $\text{SiO}_2$  possesses a much larger expansion coefficient than  $\text{GeO}_2$  for a given  $T > T_{\text{mp}}$ . Bacon *et al.* obtained their density data for a relatively low expansion compound at viscosities between  $5 \times 10^4$  and  $6 \times 10^5$  P. The experimental uncertainties and the low sensitivity for buoyancy changes, involved in the use of the counterbalanced sphere technique for these extreme conditions, do not strengthen the  $\text{SiO}_2$  density data and conclusions. More precise density data for molten  $\text{SiO}_2$  will be required before a valid comparison can be performed.

##### B. Molar Volumes

One mole of molten  $\text{GeO}_2$  has now been found to occupy about 11% more volume than one mole of  $\text{SiO}_2$  at  $1300^\circ\text{C}$ . This larger volume for  $\text{GeO}_2$  could arise partially from the longer Ge-O distance and larger Ge-O-Ge angle<sup>16</sup> compared to that of  $\text{SiO}_2$ . These parameters can produce larger interstitial spaces for the three-dimensional  $\text{GeO}_2$  lattice compared to  $\text{SiO}_2$ .

The molar volume minima shown in Fig. 2 appear to represent lattice perturbations caused by the presence of cation-oxygen attractive forces  $\{I \sim z/(r_+ + r_-)^2\}$  within the open spaces. The mole %  $\text{M}_2\text{O}$  at the minimum and the  $\Delta v'$  at the minimum (where  $\Delta v' = v_{\text{GeO}_2} - v_{\text{exptl}}$ ) are linear functions of  $I$  at all temperatures for  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Rb}^+$ . They are not linear functions of  $r_+^3$ . Thus, the molten  $\text{GeO}_2$  lattice appears to be distorted to only a small extent by the relatively large  $\text{Rb}^+$  ions, compared to  $\text{K}^+$  and  $\text{Na}^+$ , before further addition of alkali institutes the anticipated molar volume increase (because  $v_{\text{Rb}_2\text{O}} > v_{\text{GeO}_2}$ ).

Molar volume minima are not noted for lithia germanate melts because  $v_{\text{Li}_2\text{O}} < v_{\text{GeO}_2}$  at  $1300^\circ\text{C}$ . Addition of  $\text{Li}_2\text{O}$  to molten  $\text{GeO}_2$  at  $1300^\circ\text{C}$  would be expected to decrease the molar volumes of these mixtures below the 30.3 cc value for  $\text{GeO}_2$ .

<sup>16</sup> C. R. Kurkjian and R. W. Douglas, *Phys. Chem. Glasses* **1**, 19 (1960).

<sup>17</sup> J. F. Bacon, A. A. Hasapis and J. W. Wholley, Jr., *Phys. Chem. Glasses* **1**, 91 (1960).

The linear dependence of molar volume upon cation volume (Fig. 8) suggests a similarity of environment for the cations that form linear portions of each isocomposition line. Strict dependence of  $v_M$  upon  $r_+^3$  alone should result in (a), complete linearity and (b), a single point of intersection for all isocomposition lines. Intersection is caused by the previously mentioned  $v_M$  decrease associated with  $\text{Li}_2\text{O}$ . The presence of several intersection points and the resultant negative deviation for compositions containing more than 20 mole %  $\text{Li}_2\text{O}$  tend to discount a simple cation volume-dependent model for these melts. This conclusion is supported by the absence of linear isocomposition relationships for  $v_M$  vs  $I$ , for  $\Delta v$  vs  $r_+^3$ , and for  $\Delta v$  vs  $I$ . The extensive  $\Delta v$  minima in the 10 to 25 mole %  $\text{M}_2\text{O}$  region (Fig. 3) are a manifestation of a rather complicated molar volume formulation for the 0 to 30 mole %  $\text{M}_2\text{O}$  region.

Bockris *et al.*<sup>6</sup> presented positive  $v$  and  $\Delta v$  associations with  $r_+^3$  at 40 mole %  $\text{M}_2\text{O}$  for silicate melts. They concluded that cation-oxygen attraction was not important in determining the molar volume of these alkali and alkaline-earth silicate melts. It was suggested that the  $\text{K}^+$  and  $\text{Ba}^{++}$  exceptions for the dependence of  $\Delta v$  upon  $r_+^3$  were caused by structural rearrangements involving volume increases. While they obtained very little information for the 0 to 15 mole %  $\text{M}_2\text{O}$  region, the trends of their  $v_M$  and  $\Delta v$  vs composition lines do not indicate anything approaching the germanate behavior reported in this paper.

Generally, there appear to be significant differences

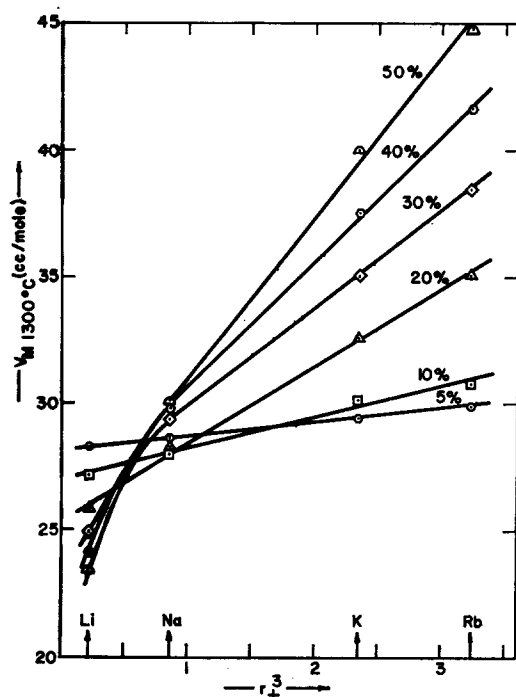


FIG. 8. Isocomposition (mole %  $\text{M}_2\text{O}$ ) plots of melt molar volume at  $1300^\circ\text{C}$  versus alkali cation radius cubed.

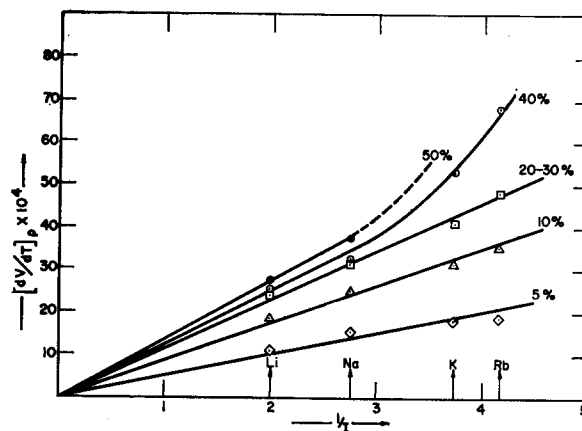


FIG. 9. Isocomposition (mole %  $\text{M}_2\text{O}$ ) plots of melt expansion coefficient versus  $1/I$ , where  $I$  = cation-oxygen attraction.

between molten germanates and silicates. All of the molar volume evidence for alkali germanate melts suggests that an extensive structural rearrangement accompanies the addition of alkali oxide. This rearrangement produces considerable volume decreases that are not related to cation volume and/or cation-oxygen attraction in a simple fashion.

### C. Expansion Coefficients

The composition dependence of the expansion functions (Fig. 4) can best be discussed in terms of three composition regions. These regions are 0 to 10 mole %  $\text{M}_2\text{O}$ , 10 to 30 mole %  $\text{M}_2\text{O}$ , and 30 to 60 mole %  $\text{M}_2\text{O}$ .

The sharp thermal expansion increase associated with the presence of small amounts of alkali oxide distinguishes  $\text{GeO}_2$  from  $\text{SiO}_2$ . Larger interstitial spaces in  $\text{GeO}_2$  would provide Ge-O-Ge surroundings that could involve different alkali cation distortions than their smaller Si-O-Si counterparts. The dependence of  $(dv/dT)_P$  on  $1/I$  for germanate melts in this composition region (Fig. 9) supports this model. These distortions involving the  $\text{GeO}_2$  lattice and alkali cations coincide with the previously discussed molar volume deviations.

The evidence does not support an initial change from a continuous three-dimensional network (involving strongly directional Ge-O bonds) to a structure in which expansion arises mostly from the nondirectional ionic bonds between cations and anionic germanate aggregates. This would force adoption of a germanate model at 1 mole %  $\text{M}_2\text{O}$  that was similar to that proposed for molten silicates at 12 mole %  $\text{M}_2\text{O}$ . Bockris *et al.*<sup>5</sup> constructed physical models to show that each ionic link can be surrounded by a cage of 14 Si-O-Si bridges at 12 mole %  $\text{M}_2\text{O}$ . Addition of further alkali supposedly eliminated the three-dimensional network and induced silica "island" formation. Adoption of this model for molten germanates containing 1 mole %  $\text{M}_2\text{O}$  cannot be accepted because 1 mole

TABLE II. Density parameters for the various forms of  $\text{GeO}_2$ .

	Density (g/cc)	Molar volume (cc)	Expansion coefficient $\alpha_t \times 10^{-7}$	Temperature range
Liquid at 1100°C	3.465 <sup>a</sup>	30.19	...	...
Glass at 1100°C	...	29.29 <sup>a</sup>	...	...
Glass	3.660 <sup>b,c</sup>	28.58	75 <sup>e</sup>	25–400°C
High-temperature quartz form	4.703 <sup>b,d</sup>	22.24	95 <sup>f</sup>	25–500°C
Low-temperature rutile form	6.239 <sup>b,d</sup>	16.77	85 <sup>g</sup>	400–800°C

<sup>a</sup> This study.<sup>b</sup> Room-temperature values.<sup>c</sup> J. D. Mackenzie, *J. Am. Ceram. Soc.* **42**, 310 (1959).<sup>d</sup> *Handbook of Chemistry and Physics*, edited by C. D. Hodgman *et al.* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1962), 44th ed., pp. 578–579.<sup>e</sup> Extrapolated value.<sup>f</sup> M. K. Murthy, *J. Am. Ceram. Soc.* **45**, 616 (1962).<sup>g</sup> J. F. Sarver, *J. Am. Ceram. Soc.* **46**, 195 (1963).

%  $\text{M}_2\text{O}$  cannot possibly eliminate the three-dimensional bonding in  $\text{GeO}_2$ . There are not enough alkali ions to allow all of the germanium atoms to take part in the formation of this particular type of “cage” structure.

Finally, if the low alkali content germanate melts simply possessed looser versions of their silicate analogs, one would expect an expansion of about  $4 \times 10^{-4}$  between zero and 10 mole %  $\text{M}_2\text{O}$ . This has not been observed (Fig. 4).

The experimental evidence (Fig. 4) suggests the presence of forces that restrict thermal expansion between 10 and 30 mole %  $\text{M}_2\text{O}$ . These forces apparently modify the factors responsible for the previously discussed rapid  $(dv/dT)_P$  rises. They also coincide with the start of a return to more normal molar volume deviations (Figs. 2 and 3). It would appear that these  $(dv/dT)_P$  “plateaus” are the result of an interplay between two structure determining parameters.

The similarity of expansion coefficients for germanate and silicate melts containing between 30 and 60 mole %  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  is indicative of the general picture developed for this silicate composition region by Bockris *et al.*<sup>3</sup> These similarities are discussed in more detail later in this paper.

#### D. Partial Molar Volumes

The addition of alkali oxide to molten  $\text{GeO}_2$  produces significant contractions in the effective volume (or  $\bar{v}_{\text{GeO}_2}$ , the partial molar volume) occupied by one mole of  $\text{GeO}_2$  in these mixtures (Fig. 5). This shrinkage amounts to as much as 5.0 cc, out of a 30.3-cc molar volume, for  $\text{GeO}_2$  in a melt containing 28 mole %  $\text{Na}_2\text{O}$ .

The observed  $\bar{v}_{\text{GeO}_2}$  deviations are of the order of magnitude expected if the oxygens in these molten mixtures adopt octahedral instead of tetrahedral configuration around significant numbers of germanium atoms. Table II shows that the molar volume of the rutile form of  $\text{GeO}_2$  is 5.47 cc less than the molar

volume of the quartz form in crystals at room temperature. A radius ratio of about 0.41 allows either a tetrahedral or octahedral configuration for  $\text{GeO}_2$  (Fig. 10).<sup>18</sup> The octahedral configuration occupies a smaller volume because it involves a more efficient packing of oxygens around each germanium atom.

The transition from the low-temperature rutile form to the high-temperature hexagonal form of  $\text{GeO}_2$  occurs just about 100°C below the melting point of 1115°C. Small amounts of  $\text{Li}_2\text{CO}_3$  (~1%) and  $\text{KCl}$  (~5%) will promote the rather sluggish transformation from the metastable hexagonal form ( $CN=4$ ) to the rutile form ( $CN=6$ ) at temperatures between 750° and 900°C.<sup>19</sup> While this is a solid-state phenomenon, it is significant that the transformation occurs in the presence of alkali cations. Ivanov and Yevstropov have obtained a refractive index maximum for germanate glasses containing about 15 mole %  $\text{Na}_2\text{O}$ .<sup>20</sup> They suggested that the addition of alkali oxide to  $\text{GeO}_2$  produced a change of coordination number from 4 to 6 for germanium. This refractive index maximum has

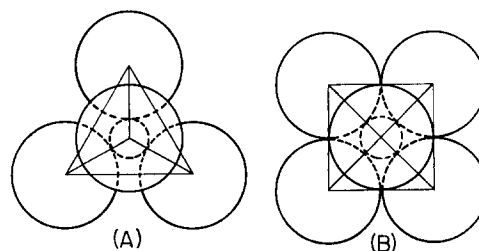


FIG. 10. Tetrahedral configuration (A) and octahedral configuration (B) of  $\text{GeO}_2$ . Assumed  $r_{\text{Ge}} = 0.53 \text{ \AA}$ , and  $r_{\text{O}} = 1.40 \text{ \AA}$ .

<sup>18</sup> L. Pauling, *The Nature of The Chemical Bond* (Cornell University Press, Ithaca, New York, 1948), 2nd ed., Chap. X.

<sup>19</sup> Y. Kotera and M. Yonemura, *Trans. Faraday Soc.* **59**, 147 (1963).

<sup>20</sup> A. O. Ivanov and K. S. Yevstropov, *Dokl. Akad. Nauk S.S.S.R.* **145**, 797 (1962).



been subsequently reported for about 23 mole %  $\text{Na}_2\text{O}$  by Aguayo and Murthy.<sup>21</sup>

The gradual decrease of  $\bar{v}_{\text{GeO}_2}$  with increase of alkali oxide content suggests that equilibria exist between octahedrally and tetrahedrally coordinated germanium atoms at each composition and temperature. It would appear that octahedrally coordinated germanium is present in the largest amount for melts containing between 10 to 25 mole %  $\text{Rb}_2\text{O}$  and  $\text{K}_2\text{O}$ , 15 to 32 mole %  $\text{Na}_2\text{O}$ , and more than 20 mole %  $\text{Li}_2\text{O}$ . Germanium appears to retain significant amounts of octahedral configuration for all melts between 20 to 65 mole %  $\text{Li}_2\text{O}$ .

Additional support for these postulates can be found in the positive inflections noted for  $\bar{v}_{\text{M}_2\text{O}}$  of the three larger cations in Fig. 6. These positive deviations show the same sequence of composition regions observed for the  $\bar{v}_{\text{GeO}_2}$  contractions in Fig. 5. The more efficient packing of oxygens around each germanium is apparently accompanied by a slightly more voluminous packing of oxygens around each cation. It is possible that the increased number of close-packed oxygens around germanium causes a partial shift to a structure similar to the *A*-type coordination proposed by Block and Levin for alkali cations in silicate melts.<sup>22</sup>

Apparently, the coordination increase observed for germanium is not accompanied by a measurable coordination decrease for lithium. This could be a result of the rather high cation-oxygen attraction exhibited by  $\text{Li}^+$ .

The partial molar volume deviations observed for binary alkali germanate melts can be interpreted in terms of the onset and subsequent disappearance (except for  $\text{Li}^+$  containing melts) of significant amounts of octahedrally coordinated germanium atoms. The additional information for glasses and crystals is in general support of these high-temperature findings and postulates.

### E. Partial Molar Expansion Coefficients

The partial molar expansion coefficient functions for  $\text{GeO}_2$  and the alkali oxides (Fig. 7) show that most of the initial  $(d\bar{v}/dT)_P$  increase observed between 0 to 10 mole %  $\text{M}_2\text{O}$  is associated with the alkali oxide. However, these trends are almost but not quite reversed for melt compositions between 10 to 30 mole %  $\text{M}_2\text{O}$ . These changes contrast rather sharply with the silicate-

type behavior observed for compositions containing more than about 30 mole %  $\text{M}_2\text{O}$ . The expansion of these latter melts is apparently again associated with the alkali cations rather than with their germania rich environments.

It is entirely possible that a partial molar expansion coefficient increase can accompany the partial molar volume decrease for the germania portion of these mixtures during the postulated increase of coordination number from 4 to 6. Figure 10 shows that each oxygen just touches four other oxygens for the octahedral arrangement. The more efficient packing of oxygens in an octahedral arrangement around each germanium atom decreases the oxygen-to-oxygen distance and thereby increases the anion-anion repulsive forces.<sup>18</sup> This strained structure could stabilize itself by increasing the Ge-O distances slightly. A somewhat looser structure would thereby arise because of the decreased vibration frequencies. Sclar and co-workers have recently shown that the 4 to 6 transformation produces a 23 % increase for the wavelength of the main Ge-O or Si-O vibration absorption band in the infrared region for both the  $\text{GeO}_2$  and  $\text{SiO}_2$  crystalline polymorphs.<sup>23</sup>

Associated with the  $(d\bar{v}_{\text{GeO}_2}/dT)_P$  changes are the  $(d\bar{v}_{\text{M}_2\text{O}}/dT)_P$  minima between 10 to 30 mole %  $\text{M}_2\text{O}$ . A decreased coordination number for each alkali cation (less efficient oxygen packing) would result in a decrease of the oxygen-oxygen repulsive forces and a decrease of the M-O distances (increased vibration frequencies). The corresponding partial molar volume ( $\bar{v}_{\text{M}_2\text{O}}$ ) increase could thus be accompanied by an expansion decrease  $(d\bar{v}_{\text{M}_2\text{O}}/dT)_P$  for the  $\text{M}_2\text{O}$  portion of these molten mixtures. The fact that  $(d\bar{v}_{\text{Li}_2\text{O}}/dT)_P$  is not much larger than  $(d\bar{v}_{\text{GeO}_2}/dT)_P$  for compositions between 30 and 60 mole %  $\text{Li}_2\text{O}$  also supports the contention that some of the germanium atoms in these lithia melts continue to possess a coordination number of 6.

A detailed discussion of the  $(d\bar{v}_{\text{M}_2\text{O}}/dT)_P$  deviations with the cation-oxygen attraction I is not completely justified because the partial molar expansion coefficients are second-order differentials. They possess a lower degree of accuracy than  $(d\bar{v}/dT)_P$ .

### F. 30-to-60-Mole % $\text{M}_2\text{O}$ Region

The general trends of the density derived properties for germanate melts containing more than 30 mole %  $\text{M}_2\text{O}$  are similar to those reported by Bockris *et al.*<sup>3,5</sup> for the corresponding silicate melts. They postulated the formation of discrete silicate ring and chain anions for this composition region. Evidence such as that given in Figs. 4, 8, and 9 suggests that discrete anions are also capable of formation in germanate melts that are rich in alkali oxide.

The formation of discrete germanate ring anions

<sup>21</sup> J. Aguayo and M. K. Murthy, Paper No. 9-G-63, American Ceramic Society Meeting, Pittsburgh, Pennsylvania, April 1963.

<sup>22</sup> S. Block and E. M. Levin, *J. Am. Ceram. Soc.* **40**, 95, 113 (1957); **41**, 49 (1958). They suggest that the coordination adopted by a given cation is related to its electrostatic bond strength ( $z/CN$ ). Alkali cations supposedly adopt the *B* type of coordination in silicate and borate melts because their bond strengths are less than  $\frac{1}{2}$  ( $\text{Rb}^+$ ,  $CN=12$ ;  $\text{K}^+$ ,  $CN=8$ ;  $\text{Na}^+$  and  $\text{Li}^+$ ,  $CN=6$ ). *B*-type coordination involves coordination to two oxygens of a given tetrahedron and is superior in packing efficiency to the *A*-type coordination that involves the coordination of two cations around a given oxygen in a tetrahedron.

<sup>23</sup> C. B. Sclar, L. C. Carrison, and C. M. Schwartz, *Science* **138**, 525 (1962).

could also explain the rather sharp  $\bar{\nu}_{\text{GeO}_2}$  and  $(d\bar{\nu}/dT)_P$  changes that occur at about 30 mole %  $\text{M}_2\text{O}$ . Large oxygen-oxygen repulsions, arising from (a), their octahedral configuration around the germanium atoms and (b), the packing of these octahedra in relatively small rings, could make the octahedral arrangement unstable with respect to the tetrahedral configuration for germanium in these postulated ring anions for melts between 30 and 50 mole %  $\text{M}_2\text{O}$  (except possibly for  $\text{Li}_2\text{O}$ ).

Lazarev and Tenisheva have recently reported chain<sup>24,25</sup> and ring<sup>26</sup> anions for alkali and alkaline earth metagermanate crystals. Their infrared data suggested (a) tetrahedral coordination for the germanium atoms and (b) pyroxene like chains of tetrahedra for  $\text{Na}_2\text{GeO}_3$  and  $\text{Li}_2\text{GeO}_3$ . They also suggested the presence of  $\text{Ge}_3\text{O}_9^{6-}$  rings in the high-temperature form of  $\text{SrGeO}_3$  and chains, similar to those found in  $\text{CaGeO}_3$ , for the low-temperature form of  $\text{SrGeO}_3$ . This evidence tends to support the above conclusion that octahedrally coordinated germanium atoms are unstable with respect to the tetrahedral configuration for most germanate melts containing more than 30 mole %  $\text{M}_2\text{O}$ .

## V. CONCLUSIONS

(A) It was previously suggested that gross similarities exist between the viscous transport mechanisms of binary alkali germanate and silicate melts. The differences of detail implied divergent modes of network alteration with the addition of a given amount of alkali oxide.<sup>2</sup> The present work confirms the viscosity findings and provides a detailed model for the structure of binary germanate melts containing as much as 60 mole %  $\text{M}_2\text{O}$ .

(B) Alteration of the molten  $\text{GeO}_2$  lattice proceeds

in a manner that is rather different from that observed for  $\text{SiO}_2$ . Germania is drastically altered by the presence of even small amounts of alkali oxide. The  $v_M$ ,  $(dv/dT)_P$ ,  $\bar{\nu}$ , and  $(d\bar{\nu}/dT)_P$  evidence suggests a gradual coordination number change from 4 to 6 for germanium. This is apparently followed by a rather sharp return to tetrahedral configuration for melts containing more alkali oxide.

(C) The maximum stabilities of octahedrally coordinated germanium atoms at 1300° occur between 15 and 25 mole %  $\text{K}_2\text{O}$  and  $\text{Rb}_2\text{O}$  and between 25 and 30 mole %  $\text{Na}_2\text{O}$ . Octahedrally coordinated germanium atoms appear to occur in all melts containing more than 25 mole %  $\text{Li}_2\text{O}$ .

(D) Cation-oxygen attraction forces appear to be associated with the extent of the deviations observed for each particular composition, especially in the 0-to-30-mole %  $\text{M}_2\text{O}$  region. Cation volumes appear to play a general magnitude determining role for each property over the entire 0-to-60-mole % region studied.

(E) Compositions containing more than 30 mole %  $\text{M}_2\text{O}$  behave in a fashion similar to comparable silicate melts. It is concluded that the anion types proposed for the silicate systems<sup>3,7</sup> also occur in the germanate melts studied.

(F) The "discrete anion-island-disturbed network" concept developed by Bockris *et al.*<sup>3</sup> for silicate melts cannot explain all of the molten germanate results. This concept can explain the structure of the more ionic germanate melts that occur between 1-2 and 2-1 compositions.

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<sup>24</sup> A. N. Lazarev and T. F. Tenisheva, Opt. i Spektroskopiya **10**, 79 (1961) [English transl. Opt. Spectry. **10**, 37 (1961)].

<sup>25</sup> A. N. Lazarev and T. F. Tenisheva, Opt. i Spektroskopiya **11**, 584 (1961) [English transl. Opt. Spectry. **11**, 316 (1961)].

<sup>26</sup> A. N. Lazarev, Opt. i Spektroskopiya **12**, 60 (1962) [English transl. Opt. Spectry. **12**, 28 (1962)].