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Structure Changes in the Molten Oxide System: Lead Oxide–Germanium Dioxide[1]

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An improved counterbalanced sphere viscometer was used to obtain viscosity and density information between 1000 and 1500° for molten PbO and a series of molten binary lead germanate compositions containing as much as 65 mole % PbO. This information has been used to explore the influence of divalent cations upon the structure of the molten GeO_2 network at 1300°. The viscosity and activation energy changes are indicative of a network bridging tendency for Pb(II). The molar volume, partial molar volume, and expansion coefficient deviations suggest that the coordination change previously reported for Ge(IV) in alkali germanate melts is not as pronounced in the presence of Pb(II). The addition of 20 to 50 mole % PbO to molten GeO_2 produces structure changes that differ from those previously reported for the addition of similar sized alkaline earth cations to SiO_2. These findings appear to be associated with the peculiar type of network bridging that can occur for Pb(II).

Introduction

Recent high-temperature viscosity[2] and density[3] results have suggested that there is a gradual change from tetrahedral to octahedral coordination for the germanium(IV) species with increase of alkali oxide content in binary alkali germanate melts at 1300°. The partial molar volume evidence shows that the maximum stability of octahedrally coordinated germanium(IV) at 1300° occurs for melts containing from 15 to 30 mole % Li_2O, Na_2O, K_2O, and Rb_2O. A rapid return to tetrahedral coordination appears to occur for germanium(IV) in these binary melts as the Na_2O, K_2O, and Rb_2O contents are increased above 30 mole %.

The presence of as little as 2 mole % alkali oxide was found to alter drastically the viscous flow parameters and expansion coefficient of molten GeO_2. The alteration of the molten GeO_2 network proceeds in a manner that is rather different from that observed for SiO_2. It was concluded that the "disturbed network–island–discrete anion" concept developed by Bockris and co-workers[4] is applicable only to those alkali germanate melts containing more than about 30 mole % M_2O.

Bockris and co-workers found that the structural phenomena observed for alkali silicate melts also occurred for alkaline earth silicates, but at compositions that were lower in silica content. The present study is an attempt to examine the possibility of a similar relationship for germanate melts that contain divalent cations. The absence of a miscibility gap, as well as reasonable liquidus temperatures (1000 to 1500°), led to the choice of the lead oxide–germania system.[5–7] These properties allow a comparison of physical properties for the univalent and divalent cation systems at the same temperature with respect to the melting point, and hence structure, of the network-forming oxide. This is necessary because the structures of molten GeO_2 and molten SiO_2 change slightly with temperature.[2–4] Bockris and co-workers were not able to obtain extensive experimental data for this condition at very low cation concentrations in the corresponding silicate systems.

Experimental

The improved high-temperature counterbalanced sphere viscometer–densitometer and measurement techniques have been described elsewhere.[8] The use of a linear variable differential transformer and recorder to determine the velocity of the suspended bob during vertical displacement has increased sensitivity and usefulness in the low-viscosity regions as well as overall ease of operation. All parts in contact with the melts were fabricated from Pt–40% Rh alloy while the supporting parts were formed from recrystallized alumina. Temperatures were measured as in the previous experiments with calibrated Pt–30% Rh *vs.* Pt–6% Rh thermocouples[9] and a Rubicon potentiometer (Model No. 2745).

Eagle Picher Company (Cincinnati 2, Ohio) Electronic Grade germania and Evans Lead Company (Charleston 25, West Virginia) litharge were used to prepare the 50-cc. glass samples. A spectrographic examination of the PbO showed 0.01 to 0.1% Bi_2O_3, 0.005 to 0.05% SiO_2, and under 0.01% alkali and alkaline earth contents. The individual glass samples were prepared from dried batch materials (GeO_2 at 1000° for 24 hr. and PbO at 100° for 24 hr.) that were melted in platinum crucibles. The melts were poured directly into the viscometer crucibles or platinum foil lined cavities and stored in desiccators until scheduled for a run.

A controlled-potential coulometric technique was used to determine the PbO content of each glass before and after high-temperature experimentation.[10] Complete reduction of the lead(II) in the dissolved glass sample, followed by removal of the lead from the mercury amalgam, indicated the absence of any

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[1] Presented before the Inorganic Chemistry Division at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 5, 1964.

[2] E. F. Riebling, *J. Chem. Phys.*, **39**, 1889 (1963).

[3] E. F. Riebling, *ibid.*, **39**, 3022 (1963).

[4] H. Bloom and J. O'M. Bockris, "Molten Electrolytes" in "Modern Aspects of Electrochemistry," J. O'M. Bockris, Ed., Vol. I, Academic Press, New York, N. Y., 1959, pp. 219–261.

[5] E. I. Speranskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 162 (1959); see *Chem. Abstr.*, **53**, 11971*a* (1959).

[6] A. Lange and H. F. Hadamovsky, *Freiberger Forschungsh.*, **B58**, 47 (1961); see *Chem. Abstr.*, **56**, 15219*a* (1962).

[7] B. Phillips and M. G. Scroger, American Ceramic Society Meeting, Pittsburgh, Pa., May, 1963, paper No. 10-G-63.

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

[9] W. Obrowski and W. Prinz, *Arch. Eisenhuettenw.*, **33**, 1 (1962); see *Platinum Metals Rev.*, **6**, 96 (1962).

[10] P. R. Segatto, *J. Am. Ceram. Soc.*, **45**, 102 (1962).

lead(IV). This result was confirmed by the fact that the analyzed compositions generally agreed with the batch formulations to within about ±1%. Volatilization losses of PbO were minimized by gradually decreasing the maximum experimental temperature as the PbO content increased. The experimental temperatures were kept higher than the estimated liquidus temperatures in all cases.

Experimental procedures involving the suspension wires and 1.6-cc. bobs were similar to those discussed in detail in previous papers.[3,8]

Results

A reliable value of the density of molten PbO was required for the calculation of molar volume (v_M) and partial molar volume ($\bar{v}$) information. However, there is a disagreement between the literature values. Bockris and Mellors[11] reported a value of 7.44 g./cc. while Esin and Zyazev[12] subsequently reported a value of 7.00 g./cc. at 1000°. Both studies used a relatively crude electric probe technique. Esin and co-workers[13] recently used a maximum bubble pressure technique and reported a value of 8.00 g./cc. at 1000°.

The experimental value for the density of molten PbO at 1000° reported herein is 7.99 (±~0.5%) g./cc. A small (~0.6 cc.) bob was used for the pure PbO experiment. Small surface tension corrections were applied to these density data because of the greater relative effect of the H_2O and melt surface tensions on the smaller buoyancies encountered with this bob.[14] A small amount of crucible corrosion was found to have a negligible effect on the final results. The bob density and volume did not change significantly during the experiment. While some volatilization did occur, none of the PbO condensed on the suspension wire. The excellent agreement of the above density value with the most reliable literature value allowed its use for calculation of the ideal molar volumes of the binary lead germanate liquids.

The experimental viscosities obtained for the lead germanate melts were found to obey a log η *vs.* $1/T$ (°K.) relationship over the temperature ranges studied. The constants for the least-square viscosity equations are presented in Table I. Instrument limitations reduced the amount of useful viscosity information that could be acquired for the relatively fluid ($\eta < 2$ poise) liquids encountered for compositions containing more than 25 mole % PbO. The viscosity of a lead germanate melt at 1300° (Fig. 1) is about ten times greater than the value of a typical alkali germanate melt for the 0 to 12 mole % M_xO_y composition region. The viscosities for compositions containing more than 20 mole % PbO were generally as small as the values reported for the alkali germanates at these compositions.

TABLE I

VISCOSITY EQUATIONS FOR LEAD GERMANATE MELTS

$\log \eta = -a + b \times 10^4/T$ (°K.)

Mole % PbO	a	b	T range, °C.
0.923	4.0580	1.2128	1350–1530
2.21	3.7884	1.0385	1200–1360
6.12	3.0864	0.8435	1130–1360
9.43	3.2306	0.8089	1160–1350
11.84	2.9843	0.6918	1120–1330
16.10	3.2844	0.6782	1110–1310
20.66	3.4728	0.6187	1060–1280

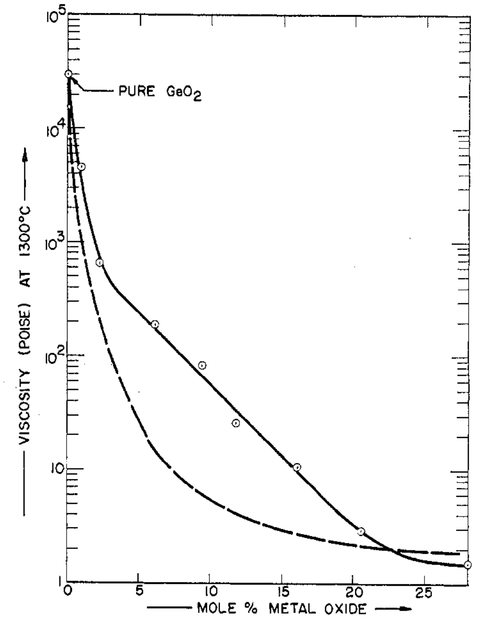

Fig. 1.—Viscosity at 1300° for lead germanate melts (———) compared with the values obtained for alkali germanate melts (- - - -).

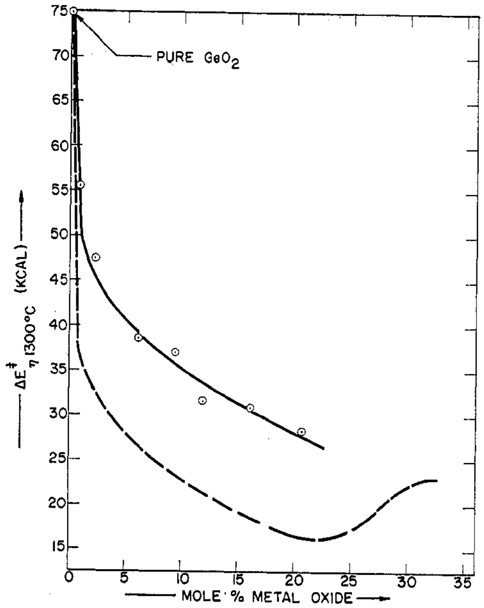

Fig. 2.—Activation energy of viscous flow for lead germanate melts (———) compared to the values obtained for potash germanate melts (- - - -).

The activation energies for viscous flow in these lead germanate melts (Fig. 2) are about 10 to 12 kcal./mole greater than the values for the corresponding potash germanate melts, and are about 25 kcal./mole less than

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[11] J. O'M. Bockris and G. W. Mellors, *J. Phys. Chem.*, **60**, 1321 (1956).

[12] O. A. Esin and V. L. Zyazev, *Zh. Neorgan. Khim.*, **3**, 1381 (1958).

[13] B. M. Lepinskikh, O. A. Esin, and G. A. Teterin, *ibid.*, **5**, 642 (1960); see *Russ. J. Inorg. Chem.*, **5**, 310 (1960).

[14] The methods discussed in ref. 8 show that surface tension corrections are unnecessary if one uses a 1.6-cc. bob to study the density of silicate, germanate, and borate and similar melts.

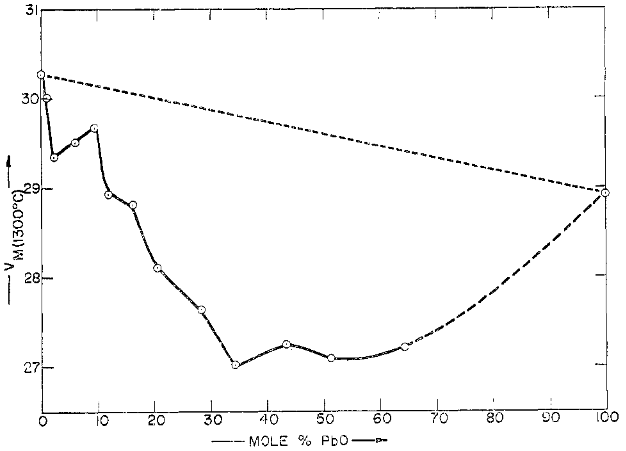

Fig. 3.—Molar volume isotherm (1300°) for lead germanate melts.

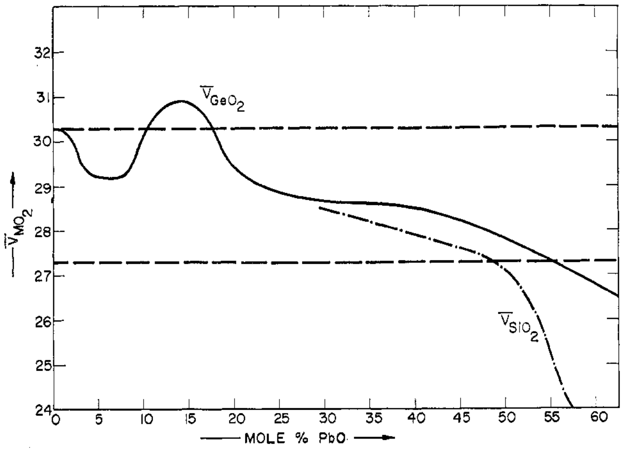

Fig. 4.—Partial molar volume function for GeO_2 as a function of composition (———) compared with the calculated values for SiO_2 (—·—·—·). Ideal values represented by (– – – –).

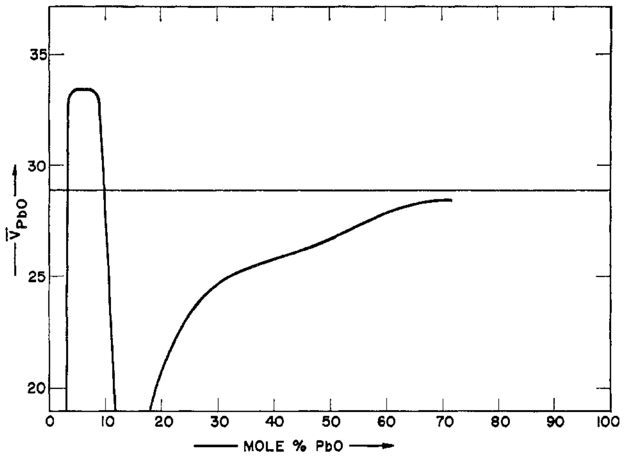

Fig. 5.—Partial molar volume function of PbO as a function of melt composition for the lead germanate system.

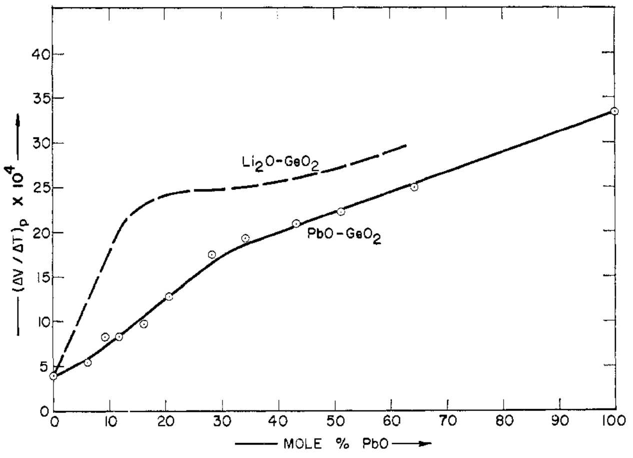

Fig. 6.—Expansion coefficient of lead germanate melts (———) compared to the values for the lithia germanate system (– – – –).

the values reported for the corresponding alkaline earth silicates (which were obtained at temperatures between 1600 and 1800°).[15]

The least-square density equations are presented in Table II. The small uncertainties (~0.3% total) in the buoyancy and volume terms of the density equations for data obtained with this instrument for germanate melts have been described previously.[3,8] Density data were taken, as previously, for increasing and decreasing temperature conditions and found to be highly reproducible. All of the density data were taken at relatively low viscosities (generally ≤ 1000 poises) where the counterbalanced sphere technique possesses its maximum sensitivity. The molar volumes at 1300° are shown in Fig. 3. The molar volume data were treated in a fashion similar to that previously described for the calculation of partial molar quantities.[3] The deviations from ideality (Δv) were calculated from $\Delta v = v_{\text{exptl}} - v_{\text{ideal}}$. They ranged from -2 to -8%. Plots of Δv *vs.* composition were used to calculate the partial molar functions shown in Fig. 4 and 5. The present value for the density of molten PbO has been used in conjunction with the available density data for melts in the lead silicate system[11] to calculate the $\bar{v}_{SiO_2}$ values shown for comparative purposes in Fig. 4.

Table II

Density Equations for Lead Germanate Melts

ρ (g./cc.) = $a - bT$ (°K.)

Mole % PbO	a	$b \times 10^3$	T range, °C.
0.923	3.521	. . .	1350–1530
2.21	3.644	. . .	1200–1360
6.12	3.899	0.06759	1130–1360
9.43	4.073	0.1093	1160–1350
11.84	4.292	0.1224	1120–1330
16.10	4.522	0.1446	1110–1310
20.66	4.925	0.2104	1060–1280
28.18	5.493	0.3168	1050–1230
34.28	5.904	0.3798	1010–1220
43.33	6.420	0.4413	1000–1240
51.20	6.917	0.5195	1020–1220
64.28	7.621	0.6125	1000–1220
100.0	9.152	0.9128	930–1120

The molar volume expansion coefficients $(\Delta v/\Delta T)_p$ for the lead germanate liquids can be considerably less than those observed for the alkali germanate systems (Fig. 6). The $(\Delta v/\Delta T)_p$ function at 10 mole % PbO is only 7.5×10^{-4}. This represents a relatively small change at this temperature and composition compared to the value for molten GeO_2 ($\sim 3.9 \times 10^{-4}$).

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

Discussion

Viscosity Measurements.—Bockris and co-workers reported that the flow mechanism changes for alkaline earth silicate melts occur at about 20 mole % MO compared to about 10 mole % M_2O for the alkali silicate melts.[15] This phenomenon was associated with the bridging tendency of the divalent cations. These ions can be less effective in collapsing a molten network such as SiO_2. Several comparisons will be made between the effect of the Pb^{+2} ion (r = 1.20 Å.) and the effect of the K^+ ion (r = 1.33 Å.) in an effort to isolate the effect of charge.

The initial viscosity decrease associated with the addition of PbO occurs in the same rather low metal oxide concentration range that was observed for the alkali germanate systems (Fig. 1). However, the rate of viscosity decrease with the addition of network modifier is less severe for Pb^{+2} than for K^+. This is apparently related to the corresponding decrease of the activation energy for viscous flow. Thus, a value of 35 kcal./mole has been found for ΔE_η^* at the 10 mole % PbO composition. This is about one-half of the value for pure molten GeO_2 at 1300°. The corresponding ΔE_η^* value occurs for a K_2O content of about 1.5 mole %. It would appear that a change in flow mechanism occurs in these lead germanate melts at slightly higher concentrations of network modifier for PbO than for the alkali oxides.

Values of ΔS_η^* calculated (as previously discussed[2]) for lead germanate melts containing 1, 3, 10, and 15 mole % PbO are $+1.0$, -1.8, -3.5, and -3.0 cal. mole^{-1} deg.$^{-1}$ (the value for pure molten GeO_2 at 1300° is $+10.0$ cal. mole^{-1} deg.$^{-1}$). The ΔS_η^* values for the corresponding potassium germanate melts are -6.2, -6.5, -6.0, and -7.0 cal. mole^{-1} deg.$^{-1}$, respectively.[2] The more positive character of the entropies encountered with the lead(II) species is suggestive of a tendency toward network bridging, as is the fact that the initial decrease of ΔS_η^* with composition is less sharp for the lead(II) species. However, the interpretation of the ΔS_η^* results remains qualitative because of the approximations involved in deriving the equation in the above form.

Molar Volume and Partial Molar Volumes.—The addition of PbO to molten GeO_2 at 1300° produces an initial volume decrease that results in a small v_M minimum at 2 mole % PbO and a slight v_M maximum at about 10 mole % PbO. The v_M minimum amounts to about -3% of $v°_{GeO_2}$. Similar v_M minima occur for the alkali germanate melts where the extent and composition are proportional to I (the cation–oxygen attraction) for Na^+, K^+, and Rb^+ ions.

The addition of less than 2 mole % PbO produces no significant change in the $\bar{v}_{GeO_2}$ function (Fig. 4). However, the addition of more than 2 mole % PbO produces a $\bar{v}_{GeO_2}$ minimum that amounts to only -1 cc. at about 6 mole % PbO. Apparently, only a few per cent of the germanium(IV) atoms are able to change from tetrahedral to octahedral configuration before a restraining influence alters the pattern of events.

The $\bar{v}_{PbO}$ function (Fig. 5) shows a positive maximum between the 4 and 8 mole % PbO compositions. This would be expected to occur because of the more efficient packing of oxygens around some of the germanium(IV) species. Thus, the coordination number of Pb^{+2} could decrease from eight to perhaps seven or six during the formation of octahedrally coordinated germanium(IV) species. The less efficient packing of oxygens around the Pb^{+2} ions could produce the observed $\bar{v}_{PbO}$ increase.

The aforementioned sequence of events has a relatively narrow composition range of stability at rather low PbO concentrations. It is herein suggested that the appearance of lead(II) in a network bridging capacity at about 10 mole % PbO is responsible for this limitation. A given divalent cation could commence bridging activity at lower concentrations in molten GeO_2 compared to SiO_2 because the field strength (or cation–oxygen attraction) of Ge^{+4} is only about 70% of the value for Si^{+4}. The Pb^{+2} ion should be better able to compete with Ge^{+4} than with Si^{+4} for the available oxygens at a given composition.

The $\bar{v}_{GeO_2}$ increase to the more normal tetrahedral value in the 9 to 18 mole % PbO region could thus be a result of an incorporation of lead(II) within the molten GeO_2 network. However, this raises the question of whether O–Pb–O or PbO_4 pyramids (with the lead atom at the apex as in the tetragonal form of crystalline PbO[16]) act as the network bridging units.

Bray, *et al.*,[17] have reported nuclear magnetic resonance evidence that supports the formation of bridging PbO_4 pyramids in lead borate glasses. The tetragonal form of PbO is more dense (v_M is about 4.5 cc. less at 25°) than the orthorhombic form and involves the previously mentioned pyramids (four O–Pb–O angles of 75° and two of 188°) bound in layers. It is interesting to note that the pyramids in the tetragonal form share oxygen–oxygen edges.

Now, the $\bar{v}_{GeO_2}$ increase in the 9 to 18 mole % PbO region is associated with rather small $\bar{v}_{PbO}$ values that slowly increase as the PbO concentration is increased above 18 mole % PbO. The negative $\bar{v}_{PbO}$ deviations for the 9 to 18 mole % PbO region of the lead germanate system are much greater than those that were observed[18] for $\bar{v}_{BaO}$ in the barium silicate system ($r_{Pb^{+2}} \sim r_{Ba^{+2}}$).[19] In connection with these structure changes, a recent X-ray study by Ingri and Lundgren[20] has shown that the crystalline compound $Na_4Ge_9O_{20}$ consists of Ge_4O_{16} groups (each containing four octahedra that share three common edges) joined at their corners

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[16] A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford University Press, London, 1962, pp. 476–477.

[17] P. J. Bray, M. Leventhal, and H. O. Hooper, *Phys. Chem. Glasses*, **4**, 47 (1963).

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

[19] It is difficult to compare data for $\bar{v}_{PbO}$ in germanate melts containing less than 25 mole % PbO with the corresponding silicate system as no data have been reported for this region of the latter system.

[20] N. Ingri and G. Lundgren, *Acta Chem. Scand.*, **17**, 617 (1963).

by GeO_4 tetrahedra to form chains that are in turn connected by GeO_4 spirals.[21]

It is now suggested that the substitution of more than a few of the GeO_4 tetrahedra by PbO_4 pyramids (if a structural condition similar to that observed in crystalline germanates exists in the corresponding liquids) can place a significant amount of bond angle strain on a given GeO_6 species. In an attempt to share two oxygens (or an edge) of a GeO_6 octahedron, as do the PbO_4 pyramids in tetrahedral PbO, a PbO_4 pyramid could significantly alter the stability of an octahedral GeO_6 species and force it to return to the tetrahedral GeO_4 configuration. The previously mentioned O–Pb–O edge angle of 75° would not readily lend itself to edge sharing with GeO_6 octahedra where the O–Ge–O edge angle is 90°.

One would expect the lead silicate Δv values to lie between those observed for the strontium silicate and barium silicate systems if these same Δv deviations were strictly related to cationic volume. The Δv values calculated from the Bockris and Mellor density data for the lead silicate system in the 20 to 50 mole % MO region, as well as the Δv values reported herein for the same composition region of the lead germanate system, decrease with addition of MO to values that are less than one-half of the Δv values observed for the alkaline earth silicate melts by Bockris, *et al.* Thus, the total structural rearrangement that occurs with the addition of *relatively large* amounts of PbO in both of these systems does not involve as large a decrease of total v_M as with similar size alkaline earth cations. This difference could be associated with the unusual oxygen packing (pyramidal) that can occur with lead(II).

The gradual occurrence of pyramidal PbO_4 bridges, instead of simple O–Pb–O bridges, could involve $\bar{v}_{PbO}$ values that were less than anticipated from a consideration of molten alkaline earth silicate compositions for this composition region (20 to 50 mole % PbO). Actually, there is an absence, for $\bar{v}_{PbO}$ in both the lead germanate and lead silicate systems, of the $\bar{v}_{MO}$ maxima that were observed at about 40 to 50 mole % BaO and SrO by Bockris, *et al.*,[18] for the silicate systems. They suggested that the M^{+2} experienced a less efficient packing arrangement that was similar to the Block and Levin "A" arrangement[22] (where two network modifier cations bond to the same oxygen of a given tetrahedron). It can be concluded that the absence of this maximum for the present system (and its silicate analog) suggests the retention of a more efficient oxygen packing around the lead(II) species. This packing could be similar to the Block and Levin "B" type coordination where the network modifier bonds to two oxygens of the same tetrahedron (edge sharing). This supports the PbO_4 pyramidal bridging unit and edge sharing that have been postulated for these high per cent PbO germanate melts.

Expansion Coefficients.—The expansion coefficient data for lead germanate melts (Fig. 6) are indicative of an initial GeO_2 network alteration that is similar to, but not as pronounced as, that observed for the addition of alkali cations to molten GeO_2.[3] In addition, the change of composition dependence for $(\Delta v/\Delta T)_p$ occurs at about 30 mole % PbO compared to about 15 mole % M_2O for all of the alkali germanate systems. The expansion coefficient at a given lead germanate composition is not proportional to $1/I$ in the same fashion as it is for the alkali germanate melts. The $(\Delta v/\Delta T)_p$ value for a lead germanate melt containing less than about 25 mole % PbO is about one-half the value predicted from the alkali data. However, for the 30 to 50 mole % PbO region, $(\Delta v/\Delta T)_p$ is close to the value predicted from the alkali germanate data.

The above phenomena can be taken as further evidence that the first 25 mole % PbO that is added to molten GeO_2 at 1300° does not produce the same sequence of structural changes that were observed for the alkali germanate melts.[3] The same is apparently true for a comparison with the results that are available for the 25 to 50 mole % PbO (or BaO) silicate systems.[11,18]

It can be concluded that the addition of as much as 25 mole % PbO to molten GeO_2 at 1300° produces a tighter packing arrangement than would otherwise be predicted on the basis of field strength and simple bridging arguments for a divalent cation. It is suggested that the unusual bridging encountered with lead(II) could be partially responsible for the observed phenomena.

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[21] There is now experimental evidence for octahedrally coordinated germanium atoms in the liquid (ref. 3), in the glass [A. O. Ivanov and K. S. Yevstropov, *Dokl. Akad. Nauk SSSR*, **145**, 797 (1962); M. K. Murthy and J. Aguayo, American Ceramic Society Meeting, Pittsburgh, Pa., April 28, 1963, paper No. 9-G-63], and in the crystalline state for alkali germanate compositions containing about 20 mole % Na_2O.

[22] S. Block and E. M. Levin, *J. Am. Ceram. Soc.*, **40**, 95 (1957).