sity line at 556 cm^{-1} and a weaker line at 374 cm^{-1}. Since the polyethylene sample holder has a broad absorption between 600 and 900 cm^{-1} in the ir spectrum, the 650-cm^{-1} line reported by Miller and Baer could not be confirmed. Studies of $AsBr_3$ in H_2O could not be carried out since it is hydrolyzed much more readily than $AsCl_3$ and failed to show any solubility.

Two papers by Davies and Long[44] appeared subsequent to the conclusion of this study which show infrared and Raman evidence for $AsCl_3$ complexes in tri-*n*-butyl phosphate and chloro complexes in ether extracts of $AsCl_3$–HCl. It is interesting to note the absence of any As—O vibrational lines in the tributyl phosphate whereas the P═O frequency was shown to be quite sensitive. The depolarized Raman line observed by us near 345 cm^{-1} in alcohol solution accompanies the polarized line near 390 cm^{-1} and is not necessarily analogous to the line observed in tributyl phosphate by these authors. The existence of tetrachloroarsenites in ether extracts is significant since species with similar spectra are not found in aqueous medium and so tetrachloroarsenites cannot be present in water in appreciable concentration. The line reported by Davies and Long at 740 cm^{-1} in ether extracts from aqueous hydrochloric acid solution may represent an As–O vibration rather than an overtone of a line observed at 383 cm^{-1}. The assignment of the liquid $AsBr_3$ spectrum[44] differs slightly from ours in that, although we agree that there are overlapping bands at 272 and 287 cm^{-1}, we differ as to which is polarized and hence which is ν_1. Our assignment is based on analysis of Figure 2 by methods outlined above. Such analysis could not be performed on the spectrum reported by Davies and Long.

[44] J. E. D. Davies and D. A. Long, *J. Chem. Soc., A*, 1757, 1761 (1968).

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Thermochemistry of the Liquid System Lead Oxide–Silica at 900°

By T. ØSTVOLD and O. J. KLEPPA

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The partial enthalpies of liquid lead oxide and of solid silica (quartz) in lead–silicate melts have been measured calorimetrically at 900°. The partial enthalpies show a region of sharp dependence on composition near $N_{SiO_2} \simeq 0.35$. This is atrributed to the formation of the orthosilicate anion, SiO_4^{4-}. The enthalpy data show no evidence for the presence of any other simple silicate anion. The partial enthalpies are compared with available data on the partial excess free energies of mixing. The entropy data similarly are consistent with formation of the orthosilicate anion.

Introduction

In recent years there have been several different thermodynamic investigations of the liquid system $PbO–SiO_2$, based on emf and phase-equilibrium methods. The most recent studies known to the authors are that of Sridhar and Jeffes,[1] who made use of a formation cell

$$Pb(l)|PbO \text{ or } PbO–SiO_2|Pt;\ O_2(g)$$

and that of Kozuka and Samis,[2] who used a solid-electrolyte concentration cell of the type

$$Pb(l)|PbO(l)|ZrO_2 + CaO|PbO–SiO_2(l)|Pb(l)$$

The activities of PbO determined in these two studies do not differ very much. The values reported by Sridhar and Jeffes also agree very well with the earlier results of Richardson and Webb,[3] who measured the activities of PbO in $PbO–SiO_2$ melts on the basis of the oxygen content of liquid lead in equilibrium with lead–silicate mixtures. As a result of these earlier studies it would seem that the activities of PbO, say at 1000°, are known within reasonable limits of error. Since the activities of SiO_2 are related to those of PbO through the Gibbs–Duhem relation, we also have acceptable information on the activities of SiO_2.

In each of the quoted earlier studies, use is made of the temperature dependence of the activity to derive information on the partial enthalpy and entropy of the two components. It should come as no surprise to the critical reader that these derived enthalpy and entropy values differ a great deal from one study to the other (see, *e.g.*, Figures 7 and 8 of ref 1 and Figures 5 and 6 of ref 2). This represents the background for the present investigation, which was aimed at the direct measurement of the partial enthalpies of PbO and SiO_2 in $PbO–SiO_2$ melts at 900°. When our new enthalpy values are compared with the corresponding excess free energies (derived from the cited emf and equilibrium studies), we should obtain a more reliable picture of the behavior of the excess entropies.

The present investigation is an extension of recent work by Holm and Kleppa[4] on the thermochemistry of the liquid system $PbO–B_2O_3$. As these authors did

[1] R. Sridhar and J. H. E. Jeffes, *Bull. Inst. Mining Met.*, **C76**, 43 (1967).

[2] Z. Kozuka and C. S. Samis, submitted for publication.

[3] F. D. Richardson and L. E. Webb, *Bull. Inst. Mining Met.*, **64**, 529 (1955).

[4] J. L. Holm and O. J. Kleppa, *Inorg. Chem.*, **6**, 645 (1967).

in the case of the lead borate system, we wish to explore possible evidence in the thermodynamic data for the formation of "complex" silicate species.

Experimental Procedures and Materials

The chemicals used in the present work were yellow lead(II) oxide (Baker Analyzed reagent), silicic acid (Mallinckrodt Analytical reagent), and pure crystalline quartz (200 mesh, from Lisbon, Md.). The silicic acid was heated to 1250° in air for 2–3 hr before it was mixed with the lead oxide to prepare the lead silicate melts.

All calorimetric experiments were performed at 900° in a single-unit microcalorimeter suitable for work-up to 1100°. Apart from its single (rather than twin) construction, this apparatus is similar to the one used by Hersh and Kleppa[5] at temperatures up to 800°. In the absence of a twin construction, the furnace surrounding the calorimeter is equipped with a very stable Leeds and Northrup proportional-temperature controller. The calorimeter assembly is heavily lagged with respect to the furnace so as to avoid as far as possible short-term drifts resulting from slight variations in the controlled temperature.

The temperature-sensing device of this calorimeter consists of a 54 + 54 junction Pt—Pt–13% Rh thermopile, the output of which is amplified by means of a Leeds and Northrup 9835-B dc amplifier and recorded on a Leeds and Northrup Type H-Azar recorder.

About 60 g of oxide melt was contained in an 80% gold–20% palladium crucible of about 17-mm diameter and 75-mm height. The lead oxide to be dissolved in the melt was kept in a very shallow platinum cup of about 10-mm diameter. This cup was attached, by means of three platinum wires, to a fused-silica tube which could be manipulated from outside the furnace system. The solution reaction was initiated by lowering the platinum cup into the melt. Stirring was accomplished by means of a platinum-covered silica plunger. The liquid PbO was displaced and brought to reaction by inserting the plunger into the platinum cup.

The quartz was added to the solvent in a similar manner, but in this case adequate stirring was achieved simply by moving the platinum cup up and down in the gold–palladium crucible. From two to six experiments were performed for each filling of the gold–palladium crucible. In each of the first three experiments 1–4 mmol of liquid PbO was added to the melt, while in the following experiments 1–2.5 mmol of SiO$_2$ (quartz) was used. Through each addition the mole fraction of lead oxide in the melt never changed by more than ±0.005.

Corrections were made for the heat effect associated with each set of stirrings. This heat effect is endothermic in character and is largely due to mass displacement in the vertical temperature gradient of the calorimeter. This gradient was about 0.1°/in. over about 7 in. When a plunger was used, the stirring correction was 10–50% of the total heat of reaction; without a plunger the correction was 10–20%.

The calibration of the calorimeter was carried out by dropping, from room temperature into the apparatus at 900°, small pieces of pure 2-mm Pt wire weighing a total of about 0.5 g. The evaluation of the resulting endothermic heat effect was based on Kelley's equation for the heat content of platinum.[6] No difference was found between calibrating into the platinum-covered plunger and calibrating directly into the lead–silicate melt. During its fall into the calorimeter, the platinum wire picked up some heat. The magnitude of this effect was determined in separate experiments, by carrying out calibrations with platinum wires of different diameters. Extrapolarion to zero surface area showed that, for 2-mm wires, this pickup of heat represented 3% of the heat content at 900°.

Results and Discussion

In Table I we give a summary of the experimental results obtained in the course of the present work. It will be noted from the data listed in this table that our experiments covered the composition range from $N_{\mathrm{PbO}} = 1.00$ to about $N_{\mathrm{PbO}} = 0.50$. For lower concentrations of lead oxide the melt is too viscous for effective calorimetric work at 900°. According to the phase diagram for PbO–SiO$_2$ of Geller, Creamer, and Bunting[7] the liquidus on the silica-rich side is at about $N_{\mathrm{PbO}} = 0.37$ at 900°.

TABLE I

ENTHALPIES OF SOLUTION OF LIQUID LEAD OXIDE AND OF QUARTZ IN PbO–SiO$_2$ MELTS AT 900°

$N_{\mathrm{SiO_2}}$	$\Delta H_{\mathrm{PbO(l)}}/\Delta n_{\mathrm{PbO}}$,[a] kcal/mol	$N_{\mathrm{SiO_2}}$	$\Delta H_{\mathrm{SiO_2(s)}}/\Delta n_{\mathrm{SiO_2}}$,[a] kcal/mol
0.205	−0.12 (1)	0.054	−5.35 ± 0.1 (2)
0.249	−0.40 (1)	0.156	−4.80 ± 0.05 (3)
0.298	−0.55 ± 0.05 (2)	0.253	−3.75 ± 0.05 (3)
0.328	−0.95 ± 0.05 (2)	0.300	−3.05 ± 0.05 (3)
0.397	−1.30 ± 0.10 (3)	0.340	−2.10 ± 0.05 (4)
		0.400	−0.70 ± 0.05 (2)
0.447	−2.1 ± 0.30 (3)	0.446	<0
0.495	−2.7 ± 0.50 (3)	0.501	>0

[a] The quoted uncertainties represent the average deviation from the mean. The numbers in parentheses are the numbers of experiments performed.

The experimental quantities recorded in Table I are $\Delta H_{\mathrm{PbO}}/\Delta n_{\mathrm{PbO}}$ and $\Delta H_{\mathrm{SiO_2}}/\Delta n_{\mathrm{SiO_2}}$. Since the changes in the composition of the melt which result from the additions of lead oxide and silica are quite small (see above), these ratios may be considered to represent the relative partial molar enthalpies of the two components, $\Delta \bar{H}_{\mathrm{PbO(l)}}$ and $\Delta \bar{H}_{\mathrm{SiO_2(s)}}$.

Figures 1 and 2 are graphical representations of the dependence of $\Delta \bar{H}_{\mathrm{PbO}}$ and $\Delta \bar{H}_{\mathrm{SiO_2}}$ on composition. Note that the experimental precision achieved for the addition of SiO$_2$ to the melt on the whole is better than for PbO. This presumably is related to the larger stirring corrections associated with the lead oxide experiments. In drawing our "best curves" through the experimental points, we have taken into account the higher reliability of the results for SiO$_2$ and have determined the line for $\Delta \bar{H}_{\mathrm{PbO}}$ through a Gibbs–Duhem integration of the SiO$_2$ data. This integration was carried out by the trapezoidal method, starting out from the value of $\Delta \bar{H}_{\mathrm{PbO}} = 0$ at $N_{\mathrm{PbO}} = 1.00$. Within experimental error, the calculated curve for $\Delta \bar{H}_{\mathrm{PbO}}$ is consistent with all of the experimental points except for the point at $N_{\mathrm{PbO}} = 0.6$.

From the partial enthalpies of the two components, we have calculated the integral enthalpies of mixing, ΔH^{M}. These values, as well as the corresponding values of the enthalpy interaction parameter $\Delta H^{\mathrm{M}}/N(1 - N)$, are plotted against composition in Figure 3. Note that both ΔH^{M} and $\Delta H^{\mathrm{M}}/N(1 - N)$ exhibit fairly well-defined minima at or near $N_{\mathrm{SiO_2}} = 0.33$.

In their earlier work on PbO–B$_2$O$_3$ Holm and Kleppa

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(5) L. S. Hersh and O. J. Kleppa, *J. Chem. Phys.*, **42**, 1309 (1965).

(6) K. K. Kelley, U. S. Bureau of Mines Bulletin No. 584, U. S. Government Printing Office, Washington, D. C., 1960.

(7) R. F. Geller, A. S. Creamer, and E. N. Bunting, *J. Res. Natl. Bur. Std.*, **13**, 237 (1934).

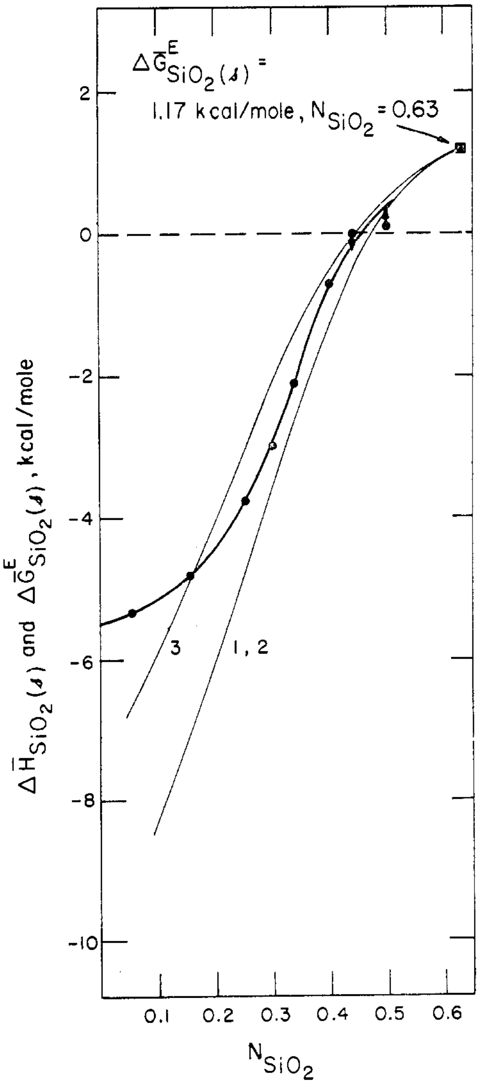

Figure 1.—Partial excess Gibbs free energies of SiO_2 (tridymite) and relative partial enthalpies of SiO_2 (quartz) in lead-silicate melts: ●, $\Delta\bar{H}_{SiO_2}$, this work, 900°, 1, $\Delta\bar{G}^E_{SiO_2}$, Richardson and Webb,[3] 1000°; 2, $\Delta\bar{G}^E_{SiO_2}$, Sridhar and Jeffes,[1] 1000°; 3, $\Delta\bar{G}^E_{SiO_2}$, Kozuka and Samis,[2] 1000°.

noted a sharp dependence of the partial enthalpy on composition in two rather narrow concentration regions, $N_{B_2O_3}$ = 0.16–0.20 and $N_{B_2O_3}$ = 0.55–0.60. They suggested that this behavior might be related to acid–base reactions of the type

$$O^{2-} + B_2O_3 = \text{borate-1 anion}$$

$$\text{borate-1} + B_2O_3 = \text{borate-2 anion}$$

The location of the two sharp changes in partial enthalpy was attributed to the essential "completion" of these two acid–base steps at the two compositions in question.

In their discussion of the possible anionic species in lead silicate melts Flood and Knapp[8] suggested that in the highly basic region (0–20 mol % SiO_2) the only silicate species present is the SiO_4^{4-} anion. In support of this they cited the activity data of Richardson and Webb, as well as the phase diagram data of Geller, *et al.*

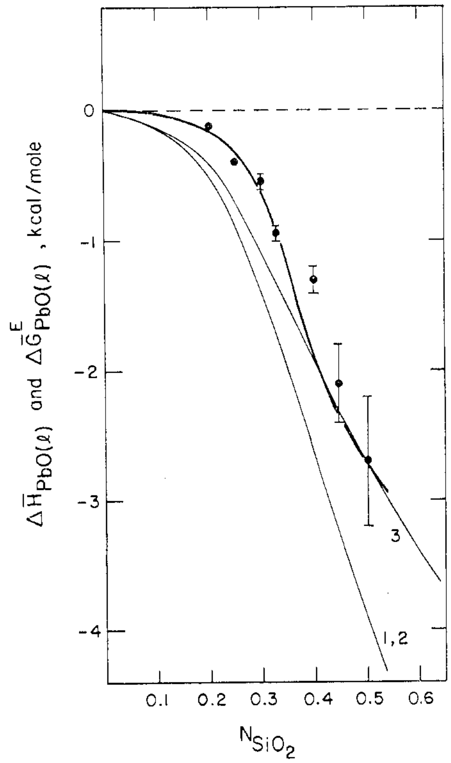

Figure 2.—Partial excess Gibbs free energies and relative partial enthalpies of PbO(l) in lead silicate melts: ●, $\Delta\bar{H}_{PbO}$, this work, 900°; ———, $\Delta\bar{H}_{PbO}$, from Gibbs–Duhem integration of $\Delta\bar{H}_{SiO_2}$; 1, $\Delta\bar{G}^E_{PbO}$, Richardson and Webb,[3] 1000°; 2, $\Delta\bar{G}^E_{PbO}$, Sridhar and Jeffes,[1] 1000°; 3, $\Delta\bar{G}^E_{PbO}$, Kozuka and Samis,[2] 1000°

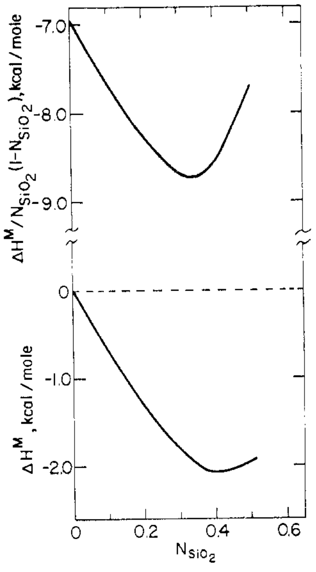

Figure 3.—Enthalpies of mixing (ΔH^M) and enthalpy of mixing interaction parameters ($\Delta H^M/N_{SiO_2}(1 - N_{SiO_2})$ in the liquid mixtures of PbO and SiO_2 at 900°.

The new enthalpy data reported in the present work are consistent with this view. Thus the relative partial enthalpies of PbO range from 0 at N_{PbO} = 1.0 to about −150 cal/mol at N_{PbO} = 0.8. However, as the silica content is raised above 20%, the partial enthalpy of PbO becomes significantly more negative. The partial enthalpy curves exhibit their sharpest dependence on composition in the vicinity of $N_{SiO_2} \simeq 0.35$.

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(8) H. Flood and W. J. Knapp, *J. Am. Ceram. Soc.*, **46** [2], 61 (1963).

This is very near the composition at which the reaction $2O^{2-} + SiO_2 = SiO_4^{4-}$ would have reached its "end point."

On the other hand, we can find no evidence in the enthalpy data for any other simple silicate anion such as, *e.g.*, the metasilicate anion $(SiO_3)_3^{6-}$, which was also postulated by Flood and Knapp. In fact our enthalpy data, as well as the comparable data previously reported for the lead borate melts, raise serious doubts about any attempt to describe these complex oxidic melts in terms of an "ideal" mixture of two anionic species which are associated with a common cation. While this approximation may have some merit when one of the two anions is present in moderate concentration in a "matrix" consisting largely of the other anion (*e.g.*, SiO_4^{4-} in O^{2-} up to $N_{SiO_2} \simeq 0.2$), it is likely to be too crude in the more general case.

Entropies of Mixing.—We have included in Figures 1 and 2 plots of the partial excess free energies referred to pure liquid PbO and pure SiO_2 (quartz), respectively.[9] These excess free energies have been taken from the cited studies of Richardson and Webb, Sridhar and Jeffes, and Kozuka and Samis. A comparison of the excess free energies with the corresponding enthalpy data provides the most reliable information on the partial excess entropies. These new entropy curves are presented in Figures 4 and 5. Note that in calculating the excess entropies for SiO_2 we have referred both heat and excess free energies to undercooled, liquid SiO_2. For this purpose we have set the enthalpy of fusion of SiO_2 (quartz) at 900° equal to 1.55 kcal/mol (Holm and Kleppa[10]) and assumed this value to be independent of temperature between 900° and the (metastable) melting point of quartz, 1423°. We have adopted the published excess free energies at 1000° and assumed that our own partial enthalpies are independent of temperature between 900 and 1000°.

We remarked above that the activities reported in the various emf and equilibrium studies appeared to be known within "reasonable limits of error." This statement perhaps should be modified in the light of Figures 4 and 5, which bring out the rather striking difference between the excess entropies calculated from the results of Richardson and Webb and of Sridhar and Jeffes, on the one hand, and those of Kozuka and Samis, on the other. Only in two important respects do we find full agreement among these studies: (1) they show positive excess entropies for PbO of comparable magnitude when the silica contents are below about 15%; (2) all of the excess entropy curves exhibit characteristic S-shaped forms with a transition region between $N_{SiO_2} = 0.3$ and $N_{SiO_2} = 0.4$. We believe that these two features of the excess entropy curves can be accounted for in a semiquantitative manner on the basis of the following considerations.

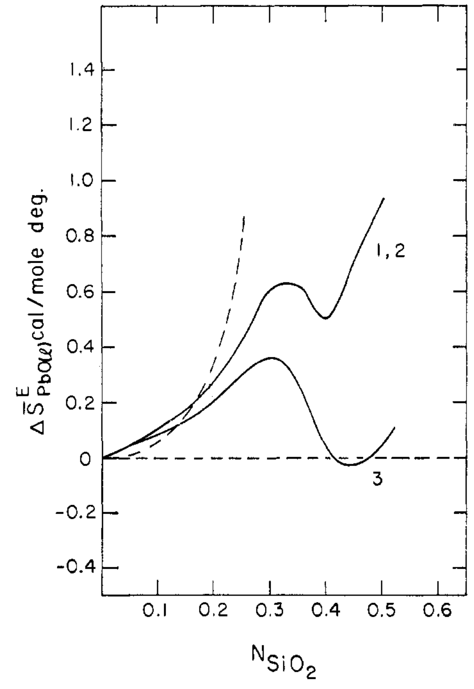

Figure 4.—Excess partial entropies of PbO(l) in lead–silicate melts ($\Delta\bar{S}^E_{PbO(l)}$): ------ Flood and Knapp[8] model; from activity data of (1) Richardson and Webb,[3] (2) Sridhar and Jeffes,[1] and (3) Kozuka and Samis,[2] combined with enthalpy data from the present work.

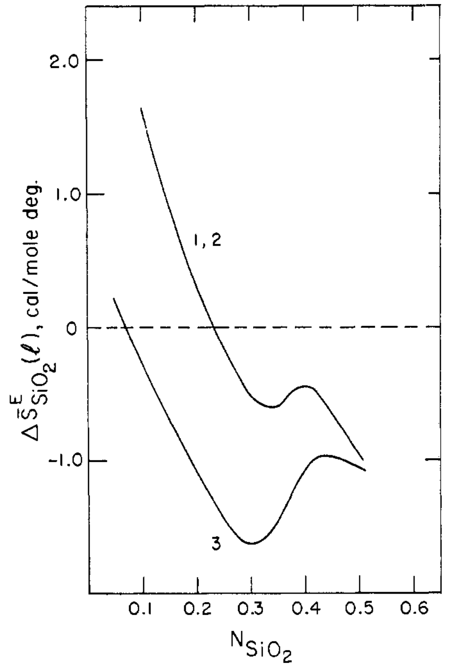

Figure 5.—Excess partial entropies of SiO_2 (undercooled liquid) in lead–silicate melts ($\Delta\bar{S}^E_{SiO_2(l)}$) from activity data of (1) Richardson and Webb,[3] (2) Sridhar and Jeffes,[1] and (3) Kozuka and Samis,[2] combined with enthalpy data from the present work.

According to the model of Flood and Knapp, the solutions of SiO_2 in PbO in the high PbO range consist of Pb^{2+}, O^{2-}, and SiO_4^{4-} ions. If every SiO_2 introduced into the melt were to remove two O^{2-} ions, we

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[9] Some of the cited free energy values for SiO_2 actually are referred to tridymite as the standard state at 1000°. Since the free energy difference between quartz and tridymite is very small at this temperature, it has been neglected in the present work: C. Hummel and H. E. Schwiete, *Glastech. Ber.*, **32**, 327 (1959).

[10] J. L. Holm and O. J. Kleppa, *Geochim. Cosmochim. Acta*, **31**, 2289 (1967).

would, in a system formed by mixing n^0_{PbO} moles of PbO and $n^0_{\mathrm{SiO_2}}$ moles of SiO_2, have

$$X_{\mathrm{PbO}} = \frac{n_{\mathrm{PbO}}}{n_{\mathrm{PbO}} + n_{\mathrm{Pb_2SiO_4}}} = \frac{n^0_{\mathrm{PbO}} - 2n^0_{\mathrm{SiO_2}}}{n^0_{\mathrm{PbO}} - n^0_{\mathrm{SiO_2}}}$$

Here n is the number of moles and X_{PbO} is the "effective" mole fraction of PbO at the composition N_{PbO} ($N_{\mathrm{PbO}} + N_{\mathrm{SiO_2}} = 1$). On this model then

$$\Delta\bar{S}^{\mathrm{E}}_{\mathrm{PbO}} = -R \ln X_{\mathrm{PbO}} + R \ln N_{\mathrm{PbO}} = -R \ln \frac{X_{\mathrm{PbO}}}{N_{\mathrm{PbO}}}$$

We have, in Figure 4, plotted this "theoretical" partial excess entropy curve for PbO for low to moderate mole fractions of silica. It seems that the experimental excess entropies of PbO are reasonably consistent with this model for silica contents up to 15–20%. On the other hand, obvious discrepancies are found at higher silica contents. This point is perhaps even better illustrated by Figure 6, which gives a comparison of the experimental *integral* entropies of mixing (derived from the partials in Figures 4 and 5) with values calculated for two idealized models given below.

(1) **Random Mixing of SiO_2 and PbO (or of Si^{4+} and Pb^{2+}).**—This is the usual "ideal" entropy curve, which forms the basis for our calculation of the partial excess entropies referred to above.

(2) **Random Mixing of PbO and Pb_2SiO_4 ($N_{\mathrm{SiO_2}} <$ 0.33) and of Pb_2SiO_4 and SiO_2 ($N_{\mathrm{SiO_2}} >$ 0.33).**—If the SiO_4^{4-} anion were assumed to be completely *undissociated* ($K = 0$), this model would give rise to an entropy of mixing curve which consists of two separate positive parts which join with a sharp cusp at $N_{\mathrm{SiO_2}} = 0.33$. The calculation of the two curves marked $K = 0$ in Figure 6 offers no difficulties. For example, a mixture which contains 0.5 mol of PbO and 0.5 mol of Pb_2SiO_4 will have an ideal integral entropy of mixing of 1.38 cal/deg mol of PbO–Pb_2SiO_4. However, in the binary system PbO–SiO_2 this mixture has a mole fraction $N_{\mathrm{SiO_2}}$ of 0.25 and an ideal entropy of mixing for $K = 0$ of $1.38/2 = 0.69$ cal/deg mol of PbO–SiO_2.

Actually the SiO_4^{4-} ion clearly is dissociated to some extent according to a reaction such as $SiO_4^{4-} = 2O^{2-} +$ "SiO_2." We have in Figure 6 given our estimates of the entropy contributions which would result near $N_{\mathrm{SiO_2}} = 0.33$ for two assumed rather small values of the dissociation constant for this reaction. These estimates are based on the following arguments. The effect of the dissociation of SiO_4^{4-} clearly is to reduce the sharpness of the cusp at $N_{\mathrm{SiO_2}} = 0.33$ and to replace it by a more rounded curve. While we do not know how to calculate this curve in detail, a very rough estimate of the entropy of mixing at $N_{\mathrm{SiO_2}} = 0.33$ can be obtained by considering the concentrations of SiO_4^{4-}, O^{2-}, and "SiO_2" which are present in equilibrium for a given small value of K. In our estimates we arbitrarily assumed a random mixture of these three entities. This is a reasonable assumption for O^{2-} and SiO_4^{4-}, but cannot easily be justified for "SiO_2."

It is apparent from the experimental entropy of mixing curves given in Figure 6 that these two curves do not show any well-developed cusp near $N_{\mathrm{SiO_2}} = 0.33$. However, there are small dips in the curves near this composition. This gives rise to the already noted S-shaped form of the partial excess entropy curves between $N_{\mathrm{SiO_2}} = 0.3$ and $N_{\mathrm{SiO_2}} = 0.4$. This behavior implies that the dissociation constant of the SiO_4^{4-} anion in this melt at 1000° should be larger than 4×10^{-3}, *i.e.*, the largest value of K for which we considered it justified to make a quantitative estimate of the entropy of disorder resulting from the dissociation process. Actually, from the activity data referred to above we find that the dissociation constant of SiO_4^{4-} at $N_{\mathrm{SiO_2}} = 0.33$ is of the order of 10^{-2} at 1000°.

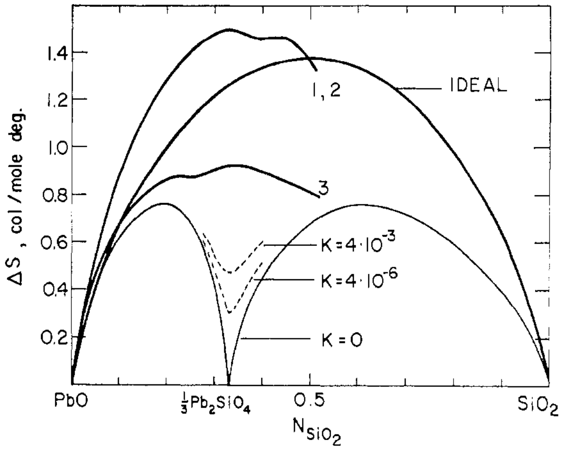

Figure 6.—Integral entropies of mixing of PbO(l) and SiO_2 (undercooled liquid) (ΔS) from activity data of (1) Richardson and Webb,[3] (2) Sridhar and Jeffes,[1] and (3) Kozuka and Samis,[2] combined with enthalpy data from present work. Ideal: random mixing of SiO_2 and PbO. $K = 0$: random mixing of PbO and Pb_2SiO_4 ($N_{\mathrm{SiO_2}} < 0.33$) and of Pb_2SiO_4 and SiO_2 ($N_{\mathrm{SiO_2}} > 0.33$); no dissociation of the SiO_4^{4-} ion. $K > 0$: random mixing of O^{2-}, "SiO_2," and SiO_4^{4-}.

In closing the present discussion we want to take note of the fact that the experimental entropy of mixing curves given in Figure 6 differ greatly with respect to the absolute magnitude of the entropy of mixing. While our own work offers no clear guidance for selecting one equilibrium study in preference to any other, we note that the entropy curve which results from a combination of the free energy data of Kozuka and Samis with our own enthalpy data (curve 3) intuitively seems more reasonable than the others (curves 1 and 2). If our physical picture of the PbO–SiO_2 melts is correct, we might expect the experimental entropy of mixing to be intermediate between the ideal entropy of mixing curve and the curve for $K = 0$. On the other hand, since we have no solid basis for estimating the magnitude of the nonconfigurational contributions to the entropy of mixing, we are not prepared to argue strongly for curve 3 in preference to curves 1 and 2.

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