

Some Energy Relations in the Systems $\text{PbO-B}_2\text{O}_3$ and PbO-SiO_2

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Heats of solution of a series of glasses in the system $\text{PbO-B}_2\text{O}_3$ were measured in 2 *N* nitric acid with a simple vacuum-bottle calorimeter. Heats of solution of a series of glasses in the system PbO-SiO_2 , ranging in composition from 6 to 35 percent of SiO_2 , were measured in a mixture of HF and 2.5 *N* nitric acid with an electrically calibrated isothermal-jacket calorimeter. From these data, and heats of fusion available in the literature, calculations were made of the heats of reaction of the component oxides in either amorphous or crystalline states in forming glasses in these systems.

I. Introduction

The heat accompanying the glass-forming reactions is of interest to the physical chemist studying glass. Its significance lies in the fact that a knowledge of the energy changes accompanying glass formation should ultimately lead to a better understanding of the glassy state. The heat of glass formation is of practical importance, because it is one of the factors needed in evaluating the efficiency of glass-melting furnaces.

The direct measurement of the heat accompanying the reaction of components to form a glass is very difficult, if not impossible, because the reaction takes place at elevated temperatures and is often very sluggish. For this reason, indirect measurements were made by use of a heat-of-solution method. The reactants were dissolved in a suitable solvent and the heat of solution determined. The finished glass was dissolved in the same solvent in such an amount that its solution was identical with that resulting from the solution of the reactants. The difference between the heat of solution of the reactants and that of the finished glass was the desired heat of reaction. As the calorimetric procedure was conducted near room temperature, the heats of reaction so determined were at room temperature (approximately 25° C). The heats of reaction at elevated temperatures may be calculated from such data combined with the specific heats of the reactants and product over the desired temperature range.

II. The System $\text{PbO-B}_2\text{O}_3$

1. Preparation of Glasses

Two series of glasses were used in this study. The first was made specifically for heat-of-solution measurements; the second was made for another project, and portions remaining from that work were used to make additional heat-of-solution measurements. The two series were prepared in essentially the same manner, but details varied somewhat. Only the preparation of the first series will be described.

The raw materials used in melting the glasses were boric acid and PbO^1 of reagent quality. Fifty-gram batches were melted in platinum crucibles heated in an electric muffle to not less than 800° C. For melts high in B_2O_3 , temperatures as high as 950° C had to be used. During melting the glasses were homogenized by frequent stirring with a platinum wire mounted at the end of a long glass tube. For very fluid melts (those high in PbO), the mixing was aided by shaking the crucible and moving it with a swirling motion. When it appeared homogeneous the melt was quickly poured onto a clean steel plate. Each glass was ground to pass a No. 60 sieve, well-mixed and remelted.

Glasses containing more than 92 percent of PbO could not be obtained because of crystalliza-

¹ An X-ray pattern made by H. F. McMurdie indicated that this material was lithargite, the β or low-temperature form.

tion. Geller and Bunting [1]² obtained clear glasses containing as much as 94.5 percent of PbO, but they prepared much smaller quantities of material and used a more efficient quenching system.

2. Heat Treatment and Chemical Analysis

Most of the glasses were annealed by heating to 20°C or 30°C below their deformation temperatures [1] for an hour and then cooling very slowly. The heat of solution of a strained glass may be expected to be higher than that of the same glass after annealing. However, the method used was not sufficiently sensitive to detect this difference. Therefore, the remaining glasses were not annealed.

The glasses were analyzed for PbO. The PbO content was determined as the sulphate by several evaporations with HF and H₂SO₄ and heating at 500° to 550° C to constant weight.

3. Calorimetric Materials, Apparatus, and Procedure

A quantity of 2.00 *N* nitric acid was prepared from chemically pure acid and distilled water. About 500 g of analytical reagent grade ZnO was heated for 1 hour at 900° to 950° C, cooled, and ground to pass a No. 100 sieve and stored in a well-stoppered reagent jar. This material was used to determine the effective heat capacity of the vacuum-bottle calorimeter.

Most of the heat-of-solution determinations were made with a simple vacuum-bottle calorimeter [2]. As can be seen (fig. 1), it consists of a wide-mouthed Thermos flask in a container of insulating material. Inserted through holes in the cork stopper are a two-bladed glass stirrer, a Beckmann thermometer, and a glass funnel through which the charge is introduced into the calorimeter. A paper disk marked with six equally spaced broad radial lines was glued to the top of the horizontal member of the friction drive, and a 3-neon bulb (not shown) was used to illuminate it. When the stirrer is operated at a speed of 600 rpm, the lines appear stationary. At higher speeds the lines appear to move in the same

² Figures in brackets indicate the literature references at the end of this paper.

direction as the stirrer, whereas at speeds lower than 600 rpm they appear to move in the reverse direction. A speed-adjusting screw permits the speed to be maintained approximately constant.

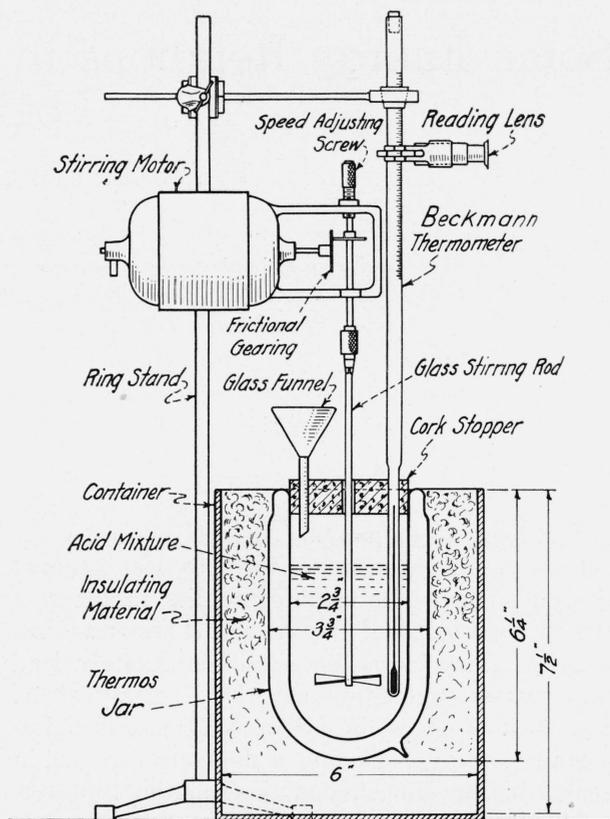


FIGURE 1. Vacuum-bottle calorimeter.

As ZnO was used to measure the heat capacity of the calorimeter, its heat of solution in 2.00 *N* HNO₃ was determined with an electrically calibrated calorimeter, which will be described later. As a check on the vacuum-bottle calorimeter, the heats of solution of crystalline PbO and of two PbO-B₂O₃ glasses were also determined with this apparatus.

4. Procedure and Calculations

The acid charge consisted of 425 ± 0.05 g of 2.00 *N* nitric acid. Its temperature was adjusted to 2 or 3 degrees below room temperature before introduction into the calorimeter, so that the initial temperature indicated by the Beckmann thermometer would be at the lower portion of its

scale. After the calorimeter was assembled a stirring period of not less than 10 minutes was allowed. The reading of the Beckmann thermometer was then recorded, the clock started, and the sample (powdered to pass a No. 100 sieve) introduced as uniformly as possible in not less than 1 minute or more than 2 minutes. Temperature readings were taken every 5 minutes until the rate of temperature change of the calorimeter was constant for at least three 5-minute intervals. Experiments showed that with a properly designed stirrer and an adequate stirring rate, complete solution was attained in 20 minutes, so that in general the total time of the experiment was 40 minutes, of which the last 20 were used as a rating period.

The calculation of the final temperature was made by extrapolating the constant rate of temperature change of the calorimeter during the rating period back to zero time. The "final" temperature so calculated minus the initial temperature of the calorimeter was taken as the temperature rise of the calorimeter caused solely by the energy evolved by the reaction of the sample with the acid. This corrected temperature rise of the calorimeter was converted to an energy change by multiplying it by the effective heat capacity of the calorimeter and its contents. The errors inherent in such a method of calculation are approximately the same in both heat-of-solution determinations and in the effective heat-capacity determinations and thus tend to compensate each other.

To determine the effective heat capacity of the calorimeter, a heat-of-solution experiment with ZnO as the sample was made. The known heat³ evolved by ZnO $[-256.9 + 0.1(T - 24)]$ cal/g, T = temperature in deg C—previously determined with an electrically calibrated calorimeter, when divided by the observed temperature rise yielded the heat capacity of the calorimeter. Since the isothermal heat of solution of ZnO varies with temperature, the value at the final temperature of the calibration was used. The effective heat capacity obtained was thus that of the calorimeter and the reactants, i. e., the ZnO and the

acid. For subsequent experiments with glasses or oxide mixtures, their heat capacities were substituted for that of the ZnO in the value obtained for the calibration.

The solid material introduced into the calorimeter was at room temperature, which was higher than the initial temperature of the calorimeter. Account was taken of the sensible heat thus carried into the apparatus. This heat is given by the formula $C_s(T_R - T_O)$, where C_s is the heat capacity of the solid, T_R is the temperature of the room, and T_O is the initial temperature of the calorimeter. In the determination of effective heat capacity, this amount of heat must be added to that developed by the reaction of the zinc oxide and acid to obtain the total heat input into the calorimeter. For the heat-of-solution measurements, this amount of heat must be deducted from the total heat measured to obtain the quantity solely due to the reaction of the sample with the acid.

5. Data and Discussion

Table 1 gives the data obtained, and figure 2 shows them in graphical form. As the heats of solution of the first two mixtures of PbO (crystal)

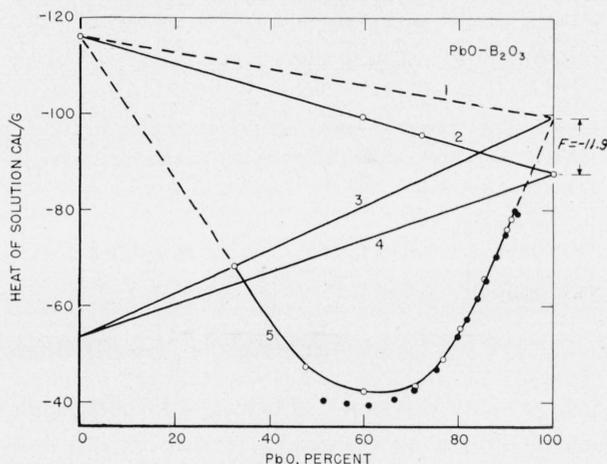


FIGURE 2. Heats of solution in the system PbO-B₂O₃.

Mixtures of PbO (gls) and B₂O₃ (gls) (curve 1); mixtures of PbO (c) and B₂O₃ (gls) (curve 2); mixtures of PbO (gls) and B₂O₃ (c) (curve 3); mixtures of PbO (c) and B₂O₃ (c) (curve 4); PbO-B₂O₃ glasses (curve 5). Open circles (except 0 percent of PbO) represent values obtained with 10-g samples; closed circles represent values obtained with samples of 18 to 25 g. The difference between the heat of solution of PbO (gls) and PbO (c), represented by F , is the heat of fusion of PbO at room temperature.

³ The calory defined as 4,1840 abs j is used in this paper. According to convention, heat evolved is negative.

TABLE 1. *Heats of solution in the system PbO-B₂O₃*

Substance	Vacuum-bottle calorimeter			Precision calorimeter		
	Percentage of PbO	Heat of solution ^{1,2,3}	Number of determinations	Approximate weight of sample	Heat of solution	Number of determinations
FIRST SERIES						
B ₂ O ₃ (c)-----	0.0	⁴ -53.5				
B ₂ O ₃ (gls)-----	.0	-116.1	1	2.25		
Glass-----	⁵ 32.3	-68.3	1	10		
Do-----	47.5	-47.3	2	10		
Do-----	59.9	-42.4	3	10		
Do-----	70.9	-43.5	1	10		
Do-----	76.8	-49.0	1	10		
Do-----	80.4	-55.5	5	10	-55.2	1
Do-----	85.4	-65.7	3	10		
Do-----	90.1	-76.1	4	10		
Do-----	91.1	-78.1	2	10		
Do-----	92.5				-79.3	1
Lithargite-----	100 (c)	-87.6	4	10	-87.7	2
Oxide mixtures:						
B ₂ O ₃ (gls)+PbO(c)	59.6	-99.5	1	10		
Do-----	72.1	-96.0	1	10		
SECOND SERIES						
Glass-----	51.3	-40.2	1	18		
Do-----	56.2	-39.8	2	18		
Do-----	61.0	-39.4	1	20		
Do-----	66.5	-40.6	1	20		
Do-----	70.7	-42.8	2	23		
Do-----	75.5	-47.1	1	20		
Do-----	79.9	-53.7	1	20		
Do-----	82.1	-57.4	2	25		
Do-----	84.1	-61.7	1	20		
Do-----	86.0	-65.5	2	25		
Do-----	88.0	-70.2	2	20		
Do-----	89.8	-74.9	2	20		
Do-----	91.9	-79.8	2	23		
Do-----	⁶ 100(gls)	-99.5				

¹ 1 calory=4.1840 abs j.

² According to convention, heat evolved is negative.

³ In 2.00 N HNO₃.

⁴ Calculated. J. C. Southard, J. Am. Chem. Soc. 63, 3147 (1941).

⁵ Average composition of two immiscible glasses.

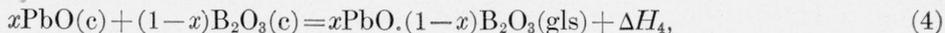
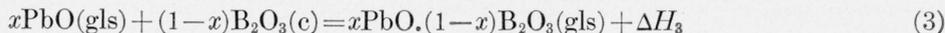
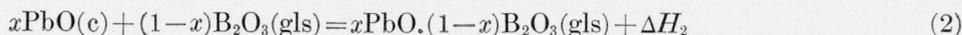
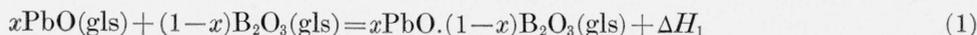
⁶ Extrapolated.

plus B₂O₃ (glass) tested fell on a straight line between the end members, no other determinations of oxide mixtures were made.

A curve (5, fig. 2) was fitted to the heats of solution of the first series of glasses. The heats of solution of the second series (solid circles in fig. 2) were somewhat lower than those of the first series because the amounts of sample dissolved in the latter were about twice as great as in the former, thus causing the final concentration to be different.

The heats of solution of glasses having high percentages of PbO seemed to be linear with the weight percent of PbO. The equation of a line was fitted by the method of least squares to the data obtained with the vacuum-bottle calorimeter on glasses containing more than 85 percent of PbO. The value at 100 percent of PbO obtained from the equation of this line was -99.5 cal/g. Since the average vacuum-bottle value of the heat of solution of PbO (c) was -87.6 cal/g, the heat of fusion of PbO (c) at room temperature calculated from these data is +11.9 cal/g.

The value for the heat of solution of B₂O₃ (c) was taken as -53.5 cal/g, the difference between the heat of solution of glassy B₂O₃ (-116.1 cal/g) and the heat of crystallization of B₂O₃ (c) at room temperature (-62.6 cal/g [3]). Straight lines were drawn between the values for the heats of solution of B₂O₃ (gls) and PbO (gls), curve 1; B₂O (gls) and PbO (c), curve 2; B₂O₃ (c) and PbO (gls), curve 3; and B₂O₃ (c), and PbO (c), curve 4. These lines represent the heats of solution of mixtures of the oxides. These data, together with the heats of solution of the glasses, enable a calculation to be made of the heats accompanying the following four reactions at approximately 25° C:



in which x and $(1-x)$ are the grams of the appropriate oxide necessary to make 1 g of glass and ΔH_1 , etc., the heats of glass formation, are variables dependent upon x . These calculations were made by subtracting the heats of solution of the glasses from those of the appropriate oxide mixtures on the assumption that the heat of solution of the mixtures is a linear function of the heats of solution of the component oxides. The results are shown graphically in figure 3. The two curves where PbO (gls) is one of the reactants are hypothetical, because glassy PbO at room temperature is as yet unknown. Table 2 gives values of heats of reaction at such intervals that linear interpolation may be used.

TABLE 2. Heats of glass formation at room temperatures (approximately 25° C) from oxides in the system PbO-B₂O₃

Product (glass) percentage of PbO	Reactants			
	PbO(gls)+B ₂ O ₃ (gls)	PbO(c)+B ₂ O ₃ (gls)	PbO(gls)+B ₂ O ₃ (c)	PbO(c)+B ₂ O ₃ (c)
	Heat of reaction, cal/g of product ^{1 2}			
	ΔH_1	ΔH_2	ΔH_3	ΔH_4
0	0	0	³ +62.6	³ +62.6
5	(-6.6)	(-6.0)	(+52.9)	(+53.5)
10	(-13.1)	(-11.9)	(+43.2)	(+44.4)
15	(-19.7)	(-17.9)	(+33.5)	(+35.3)
20	(-26.2)	(-23.8)	(+23.9)	(+26.3)
25	(-32.8)	(-29.9)	(+14.1)	(+17.1)
30	-39.4	-35.9	+4.4	+8.0
35	-46.0	-41.8	-5.3	-1.1
40	-52.7	-48.9	-15.1	-10.3
45	-58.8	-53.5	-24.4	-19.0
50	-62.3	-57.3	-31.0	-25.0
55	-63.7	-57.1	-35.5	-29.0
60	-63.7	-56.6	-38.7	-31.6
65	-63.2	-55.5	-41.3	-33.6
70	-61.2	-52.9	-42.4	-34.1
75	-56.9	-47.9	-41.2	-32.3
80	-48.3	-38.8	-35.8	-27.3
85	-36.9	-26.8	-27.5	-18.4
90	-25.4	-14.6	-19.1	-9.4
95	-12.7	-1.4	-9.6	+0.7
100	0	+11.9	0	+11.9

¹ 1 calory = 4.1840 abs *j*.

² According to convention, heat evolved is negative.

³ J. C. Southard, J. Am. Chem. Soc. **63**, 3147 (1941).

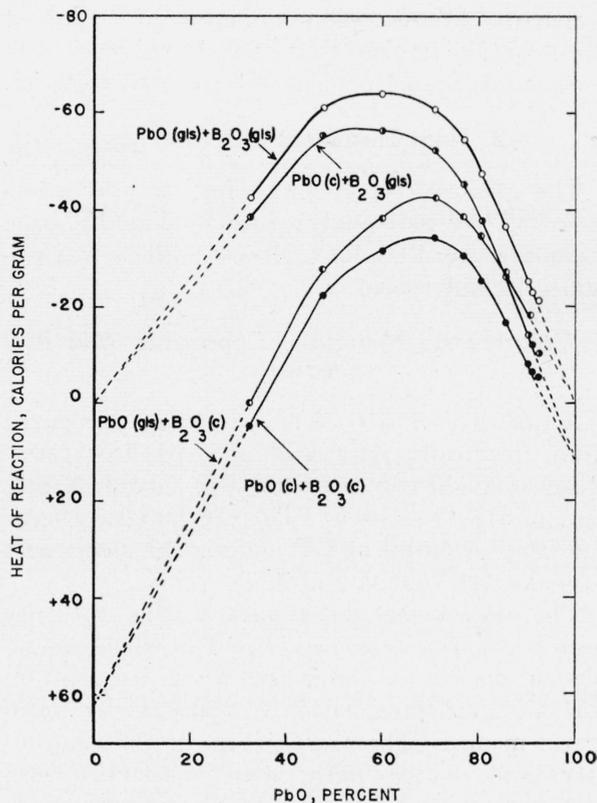


FIGURE 3. Heats of reaction to form glasses in the system PbO-B₂O₃.

III. The System PbO-SiO₂

1. Preparation of Glasses

The glasses investigated were prepared by melting, in platinum crucibles, the requisite amounts of PbO and SiO₂. The weights of the melts ranged between 300 and 500 g. They were stirred with a platinum rod and when they seemed homogeneous were poured into iron molds. Glasses containing more than 35 percent of SiO₂ could not be conveniently melted in the apparatus available. Melts containing less than 13 percent of SiO₂ crystallized when poured into molds. In order to prepare glasses containing less than 13 percent of silica, small portions of the crystallized compositions were melted in platinum crucibles and poured into ice water. In this manner glasses containing as little as 6 percent of SiO₂ were

prepared. Microscopic examination of the lowest silica-containing glass thus quenched showed it to contain less than 1 percent of crystalline material.

2. Heat Treatment and Analysis

The glasses were given no further heat treatment. They were analyzed for PbO in the same manner as the PbO-B₂O₃ glasses. Silica was obtained by difference.

3. Calorimetric Materials, Apparatus, and Procedure

A quantity of 2.50 *N* nitric acid was prepared from chemically pure acid and distilled water. Reagent quality hydrofluoric acid (about 48 percent of HF) was used. The calorimetric charge consisted of 50 ml of HF and enough nitric acid to make 648.5 ± 0.05 g of mixed acids.

The calorimeter (fig. 4) used in this work has been previously described [4]. The whole assembly was placed in a water bath whose temperature was kept constant within $\pm 0.005^\circ$ C by automatic means. The temperature of the calorimeter and water bath were measured with platinum-encased platinum resistance thermometers whose resistances were determined with Mueller temperature bridges.

The Regnault-Pfaundler formula [5] was used in calculating the temperature rise obtained and to guard against arithmetical errors, the temperature rise was also calculated by the second Geophysical Laboratory formula [5], by using the value of the thermal-leakage modulus obtained by the former method.

The effective heat capacity of the calorimeter and contents was measured by introducing a measured amount of electrical energy and measuring the resultant temperature rise.

4. Data and Discussion

Table 3 gives the data obtained, and figure 5 shows them in graphical form. The equation of a straight line was fitted by the method of least squares to the values of heats of solution of compositions containing less than 17 percent of silica. The value at 0 percent of silica (100 percent of PbO) obtained from the equation of this line was -99.2 cal/g. As the value for the heat of solution of PbO (c) was -89.4 cal/g, the heat of

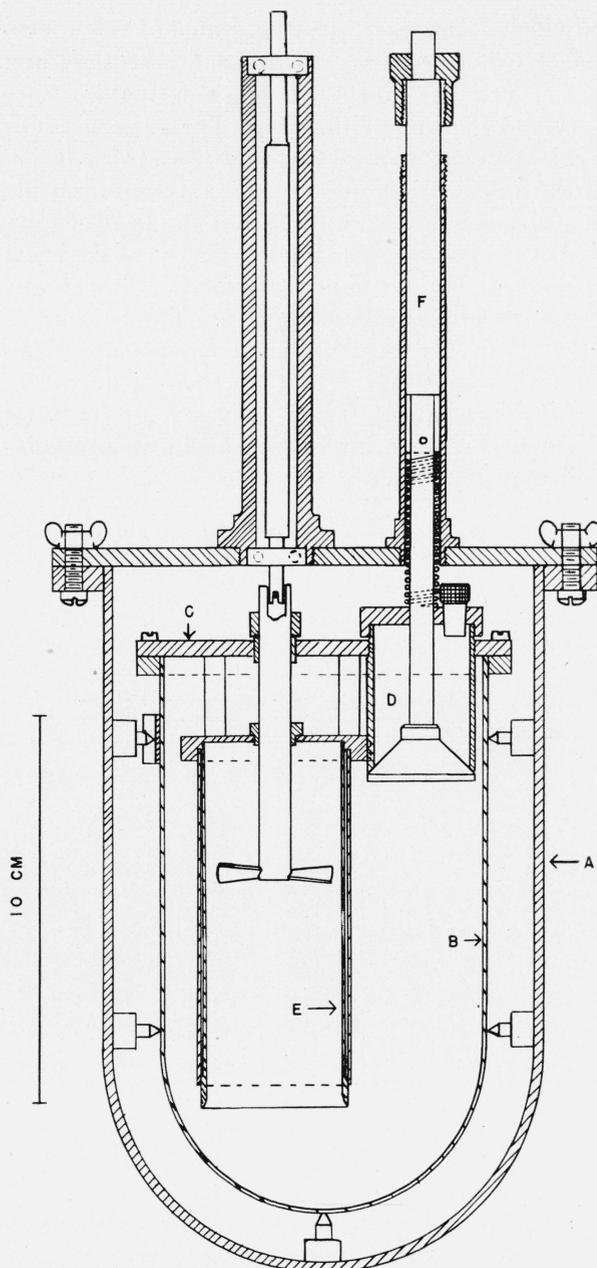


FIGURE 4. Heat-of-solution calorimeter.

A, outer jacket; B, reaction vessel; C, cover of reaction vessel; D, valve for introduction of sample; E, heater coil; F, rod for opening valve.

fusion of PbO (c), at room temperature, calculated from these data is $+9.8$ cal/g.

The concentration of HF used for the glasses was not sufficient to produce an adequate rate of solution of vitreous silica. A somewhat roundabout method of obtaining its heat of solution in the desired concentration of HF was therefore

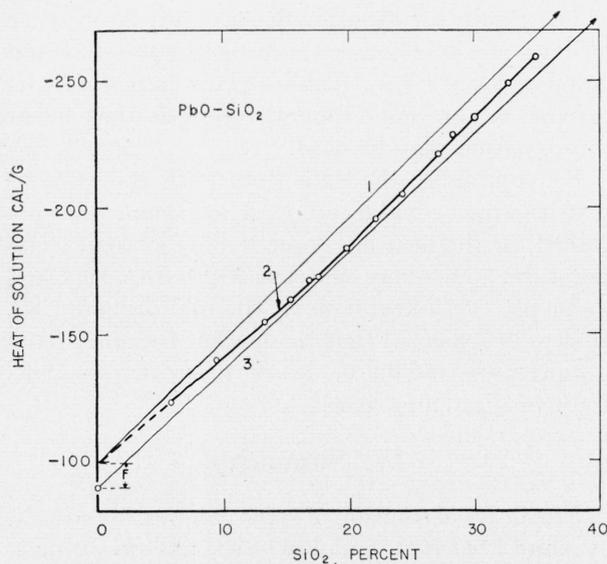


FIGURE 5. Heat of solution in the system PbO-SiO₂.

Mixtures of PbO (gls) and SiO₂ (gls) (curve 1); PbO-SiO₂ glasses (curve 2); mixtures of PbO (c) and SiO₂ (c). The difference between the heat of solution of PbO (gls) and PbO (c) (curve 3), represented by *F*, is the heat of fusion of PbO at room temperature.

adopted. The heats of solution of silica gel and vitreous silica were determined in a high-HF concentration. The difference between these two values when corrected for the heat of dilution caused by the water contained in the gel is the energy difference between these two forms of silica and therefore independent of the solution in which it was measured. This difference was then added algebraically to the heat of solution of silica gel in the lower concentration of HF, such heat being calculated to the ignited weight of the gel and corrected for the heat of dilution caused by the water in the gel. The necessary heats of dilution were measured in separate experiments. The heat of solution of quartz was calculated by subtracting -36.8 calories (the value obtained by Mulert

[6] for the difference in heat content of amorphous silica and quartz at room temperature) from the heat of solution of vitreous silica.

TABLE 3. Heats of solution in the system PbO-SiO₂

Substance	Percentage of SiO ₂	Heat of solution ^{1,2}	Number of determinations	Approximate weight of sample
50 ml HF+sufficient 2.5 (N) HNO ₃ to make 648.5 g				
		<i>cal/g</i>		<i>g</i>
PbO (c).....	0.0	-89.4	2	7
PbO (gls).....	³ 0.0	-99.2	-----	-----
Glasses.....	5.9	-123.2	2	7
Do.....	9.4	-139.8	2	7
Do.....	13.2	-154.7	2	7
Do.....	15.3	-163.5	2	7
Do.....	16.8	-171.4	2	5
Do.....	17.5	-172.6	2	7
Do.....	19.8	-183.7	2	7
Do.....	22.1	-195.4	2	7
Do.....	24.3	-205.2	2	7
Do.....	27.1	-221.1	2	7
Do.....	28.3	-229.4	2	7
Do.....	30.0	-235.6	9	7
Do.....	32.7	-248.8	2	7
Do.....	34.9	-259.3	2	7
Silica gel.....	100.0	⁴ -591.7	2	3
H ₂ O.....	0.0	-0.9	1	0.5
SiO ₂ (gls).....	100.0	⁵ -592.4	-----	-----
SiO ₂ (quartz).....	100.0	⁶ -555.6	-----	-----
250 ml HF+sufficient 2.5 (N) HNO ₃ to make 648.5 g				
Silica gel.....	100.0	⁴ -593.7	2	3.0
SiO ₂ (gls).....	100.0	-592.9	2	2.5
H ₂ O.....	0	-11.0	1	0.5

¹ 1 calory=4.1840 abs j.

² By convention, heat evolved is negative.

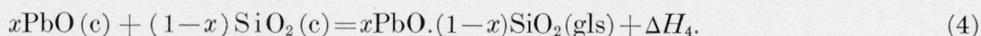
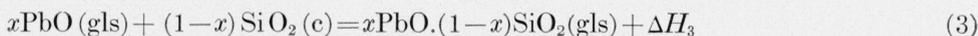
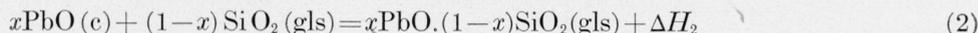
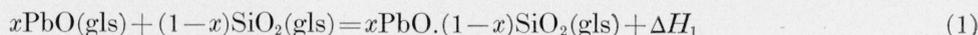
³ Extrapolated.

⁴ Calculation made on the basis of ignited weight.

⁵ Calculated.

⁶ O. Mulert, Z. anorg. Chem. **75**, 198 (1912).

With these data and the previously outlined methods, calculations were made of the heats accompanying the following reactions at approximately 25° C:



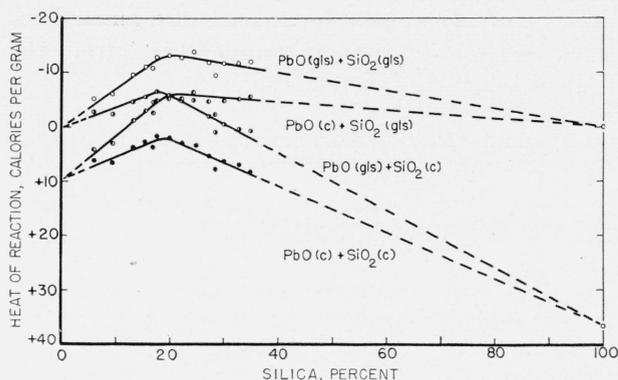


FIGURE 6. Heats of reaction to form glasses in the system PbO-SiO₂

TABLE 4. Heats of glass formation at room temperatures (approximately 25° C) from oxides in the system PbO-SiO₂

Product (glass) percentage of SiO ₂	Reactants			
	PbO(gls)+ SiO ₂ (gls)	PbO(c)+ SiO ₂ (gls)	PbO(gls)+ SiO ₂ (c)	PbO(c)+ SiO ₂ (c)
	HEAT OF REACTION, CAL/G OF PRODUCT ^{1,2}			
	ΔH ₁	ΔH ₂	ΔH ₃	ΔH ₄
0	0	9.8	0	9.8
5	-3.6	5.7	-1.7	7.6
10	-7.6	1.7	-3.4	5.4
15	-10.6	-2.2	-5.1	3.3
20	-12.7	-4.9	-6.0	2.5
25	-12.3	-5.0	-3.1	4.2
30	-11.8	-4.9	-0.7	6.1
35	-11.2	-4.8	1.7	8.0
100	0	0	36.8	36.8

¹ 1 calory=4.1840 abs j.

² According to convention, heat evolved is negative.

³ O. Mulert Z. anorg. Chem. **75**, 198 (1912).

The results are shown in figure 6. In the absence of data, straight lines were drawn between 35 and 100 percent of silica. Table 4 gives values of heats of reaction at small enough intervals that linear interpolation may be used.

By combining the data from both the systems investigated, a value of +2.4 kcal/mole was obtained for the heat of fusion of PbO at room temperature. This may be compared with a reported value of +2.75 kcal/mole at the melting point [7]. It is to be expected that the heat of fusion at room temperature should be lower than at 1,163° K, the melting temperature.

IV. Summary

The heats of solution of some compositions in the systems PbO-B₂O₃ and PbO-SiO₂ have been measured. From these data and from values of heats of fusion available in the literature, heats of reaction of appropriate oxides to form glasses in these systems have been calculated.

V. References

- [1] R. F. Geller and E. N. Bunting, J. Research NBS **18**, 585 (1937) RP995.
- [2] W. Lerch, Eng. News-Record **113**, 523 (1934).
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