Table V

Determination of the Cation Radius Ratio (M/R) for the Rhombohedral 1 Compounds

Compound	Radius of M^{+6}, Å.	Radius of R^{+3}, Å.	Radius ratio M/R
UO$_3$·3La$_2$O$_3$	0.80	1.06	0.75
CrO$_3$·3Y$_2$O$_3$[a]	0.52	0.89	0.58
WO$_3$·3Dy$_2$O$_3$	0.62	0.91	0.68
WO$_3$·3Gd$_2$O$_3$[a]	0.62	0.94	0.66
MoO$_3$·3Er$_2$O$_3$	0.615	0.88	0.70
MoO$_3$·3Y$_2$O$_3$	0.615	0.89	0.68
MoO$_3$·3Ho$_2$O$_3$[a]	0.615	0.89	0.68

[a] These hypothetical compounds do not form the rhombohedral 1 structure.

upon a critical ion size ratio. Using average cation radii values, the results given in Table V were obtained. It can be seen from these data that the rhomb 1 structure does not occur below a cation size ratio M/R of about 0.67.

By using the above criterion, it should be possible to predict the existence of other rhombohedral compounds of this type. For example, ReO$_3$ might be

expected to yield rhomb 1 structures with Y$_2$O$_3$ and the rare earth oxides. This expectation has been realized recently with the preparation of ReO$_3$·3Y$_2$O$_3$ by Grossman.[16] Other hexavalent metal oxides are somewhat rare, thereby limiting the further extension of this family.

Although there are many members of the rhomb 1 structure type, the compound 2UO$_3$·3Y$_2$O$_3$ is the only known example of the rhomb 2 structure having an oxygen-to-metal ratio of 15:8. In spite of the many ordered phases which have been found in the Pr–O, Tb–O, and Ce–O systems, no stable RO$_{1.875}$ composition has been reported. Furthermore, the metastable 2WO$_3$·3Y$_2$O$_3$ phase reported by Borchardt[2b] does not have the rhomb 2 structure.
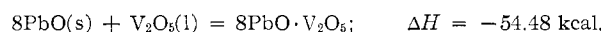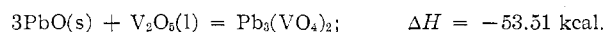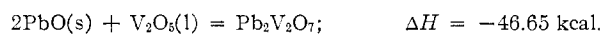
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A Calorimetric Study of the Lead(II) Oxide–Vanadium(V) Oxide System at 680°

By T. YOKOKAWA and O. J. KLEPPA

Calorimetric measurements have been carried out on the heat effects associated with solution of solid lead oxide in liquid vanadium pentoxide at 680°. Over the whole liquid range, which extends to a mole fraction of lead oxide $X_{PbO} > 0.6$, the molar heat of mixing may be represented by the expression $\Delta H^M = -18.42 (\pm 0.33) X_{PbO}$ kcal./mole. The significance of this result is discussed. Also measured were the heats of solution of the three solid lead vanadates in liquid vanadium pentoxide. By combination of these results with the corresponding heat of solution data for pure lead oxide, we derived the following values for the heat of formation of these compounds at 680°

$$2PbO(s) + V_2O_5(l) = Pb_2V_2O_7; \qquad \Delta H = -46.65 \text{ kcal.}$$

$$3PbO(s) + V_2O_5(l) = Pb_3(VO_4)_2; \qquad \Delta H = -53.51 \text{ kcal.}$$

$$8PbO(s) + V_2O_5(l) = 8PbO \cdot V_2O_5; \qquad \Delta H = -54.48 \text{ kcal.}$$

Finally, a direct method for the measurement of the heat of formation of Pb$_3$(VO$_4$)$_2$ from the solid oxides was explored. In this method a powdered mixture of lead oxide and vanadium pentoxide was dropped from room temperature into the calorimeter at 680°. In these experiments we obtained a value of -39.37 kcal./mole for the heat of formation of the lead vanadate at room temperature.

Introduction

Thermodynamic and structural studies of oxidic melts are of very considerable scientific and technological interest. However, due to the high temperatures involved there have been many restrictions on the methods of measurements which have been applied. For example, we are unaware of any attempts so far at the study of oxidic melts by means of high-temperature reaction calorimetry. The only enthalpy of mixing data relating to mixed oxidic melts which may be found in the literature have been derived from the temperature dependence of the thermodynamic activity, as

measured by equilibrium methods. The significance which can be attributed to these enthalpy (and the related entropy) data leaves much to be desired.

In the present communication we describe a series of calorimetric measurements involving lead oxide and vanadium pentoxide carried out at 680°. At this temperature vanadium pentoxide is liquid (m.p. 672°) while lead oxide is solid (m.p. 890°). The liquid range at 680° extends from $X_{PbO} = 0$ to $X_{PbO} \gtrsim 0.6$.

In addition to our study of the formation of these melts from the two components, we have also measured the heats of solution in liquid vanadium pentoxide of

the three solid lead vanadates, $Pb_2V_2O_7$ (m.p. 725°), $Pb_3(VO_4)_2$, (m.p. 952°), and $8PbO \cdot V_2O_5$ (m.p. 794°). By comparing these results with the corresponding data for pure PbO when dissolved in V_2O_5, we have obtained the enthalpies of formation of these vanadates (from solid PbO and liquid V_2O_5) at 680°.

In a third series of measurements we have studied the heat of formation of solid $Pb_3(VO_4)_2$ by a direct combination method.

Experimental

Materials.—Vanadium pentoxide (Baker's Analyzed, >99.5% V_2O_5) was used without further purification or treatment after drying at 130°. Yellow lead oxide (Mallinckrodt analytical reagent) was melted and crystallized in a platinum crucible in order to obtain a dense material. The three lead vanadates, $Pb_2V_2O_7$, $Pb_3(VO_4)_2$, and $8PbO \cdot V_2O_5$, were prepared as follows. Mixtures of the two solid oxides in the appropriate stoichiometric ratio were melted in a platinum crucible and then poured into a cold platinum dish. The quenched samples were ground in a mortar and then annealed at suitable temperatures ($Pb_2V_2O_7$, 4 days at 600°; $Pb_3(VO_4)_2$, 1 week at 600°, then 1 day at 750°; $8PbO \cdot V_2O_5$, 1 week at 750°). The powdered samples of these compounds were examined by X-ray diffraction. The observed patterns showed that each compound contained no lines from the other compounds or from any of the pure oxides. The crystal structures of the compounds were not investigated further.

Experimental Procedures.—The experiments were performed in Calvét type microcalorimeters for work at temperatures up to about 800°. This equipment will be described elsewhere.[1] In previous work the high-temperature melts usually were contained in test tubes made from fused silica. However, since both lead oxide and vanadium pentoxide attack silica at the temperature of our measurements, a different container material was required. The details of the adopted experimental arrangement will most readily be understood by consulting Fig. 1.

The liquid vanadium pentoxide was contained in a gold crucible of 17 mm. o.d. and approximately 7 cm. length. The lead oxide or lead vanadate to be dissolved in the melt was maintained immediately above this crucible in a small gold foil dish. This was in turn supported by a fused silica tube, whose lower open end was slightly reduced in cross section so as to retain the dish.

After a thermal steady state was established in the calorimeter assembly, the closed-end stirrer, which was made from fused silica tubing and covered with a thin-walled gold sleeve, was pushed down so as to release the gold foil dish. In order to speed the dissolution of the sample, the melt was stirred a few times by moving the stirrer up and down.

The calorimeter was calibrated by the "gold drop" method, *i.e.*, by dropping small pieces of 2-mm. pure gold wire into the calorimeter from room temperature. The resulting heat effect was calculated from the heat content equation for gold given by Kelley.[2] A correction of about 1% was applied for the small heat pickup of the gold piece during the drop.[3] Another small correction (1.3%) was made because the gold pieces were retained inside the hollow stirrer and did not fall into the melt. The magnitudes of these corrections were determined in separate experiments.

A very different approach was employed for the measurement of the heat of formation of solid $Pb_3(VO_4)_2$ by the direct combination method. In this case a powdered mixture of the two oxides (−150 mesh) in the 3:1 ratio was dried at 180°, after which a sample of about 1 g. was weighed into a cylindrical gold capsule of 5-mm. diameter. This capsule was capped with a gold lid and then dropped into the calorimeter at 680° from room temperature (25°). The reaction appeared to be completed in a

(1) O. J. Kleppa, to be published.
(2) K. K. Kelley, U. S. Bureau of Mines Bulletin 584 (1960).
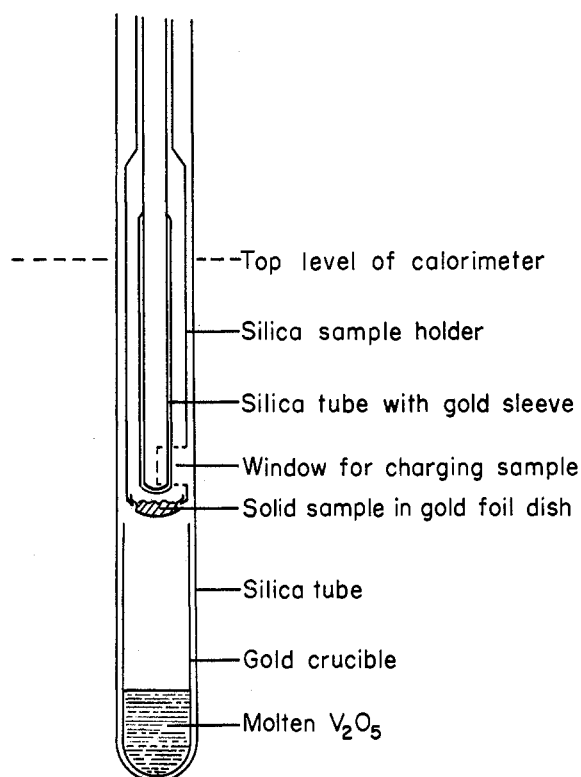(3) L. S. Hersh, to be published.

Fig. 1.—Experimental arrangement in the calorimeter.

time shorter than the time required for the calorimeter to return to the initial steady state (less than 1 hr.).

In a consecutive experiment the same capsule, containing the vanadate formed in the previous experiment, was again dropped into the calorimeter from room temperature. The difference in the two observed heat effects is the enthalpy of formation of the considered sample at room temperature.

The key problem in the use of this method is whether the reaction between PbO and V_2O_5 at 680° is complete. We did not look into this problem in great detail. However, we did examine the reaction product by X-ray diffraction and found only Pb_3-$(VO_4)_2$ lines. Also, the heat of formation actually obtained (see below) indicates a complete or near-complete reaction.

Results and Discussion

PbO(s) + V_2O_5(l) Mixing.—The actually observed enthalpies of reaction, ΔH_{obsd}, as well as the molar enthalpies of mixing, ΔH^M, obtained in twelve separate experiments at mole fractions of lead oxide, X_{PbO}, ranging from 0.0249 to 0.606 are recorded in Table I. The last column in this table gives the ratio $\Delta H^M/X_{PbO}$. It will be noted that this ratio, the molar heat of solution of lead oxide in vanadium pentoxide, appears to be very nearly constant over the whole concentration range. The mean value is −18.42 kcal./mole, with a standard deviation of 0.33 kcal., or somewhat less than 2%. We shall have use for this quantity below.

The essential constancy of the ratio $\Delta H^M/X_{PbO}$ up to $X_{PbO} \backsim 0.6$ is of very considerable interest. It indicates that, at least so far as the heat of mixing is concerned, pure V_2O_5 and a melt of composition $(PbO)_{0.6}$-$(V_2O_5)_{0.4}$ represents a nearly ideal liquid mixture. This in turn suggests that the exothermic chemical reaction which occurs when lead oxide is dissolved in vanadium pentoxide probably has the same general
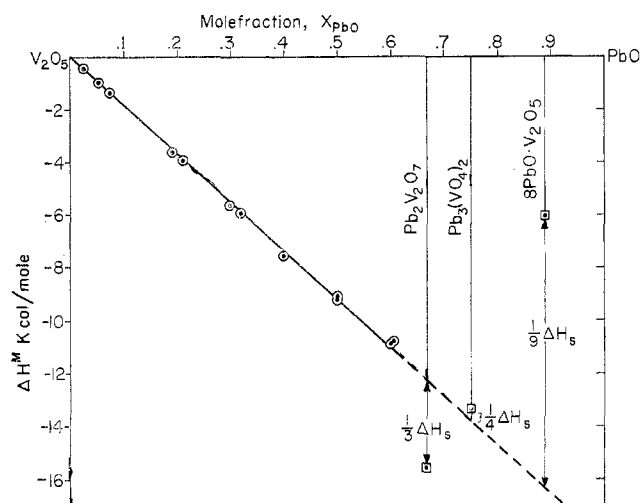
Fig. 2.—Heat of mixing of $PbO(s)$–$V_2O_5(l)$ and heats of formation of three solid vanadates from oxides at $680°$.
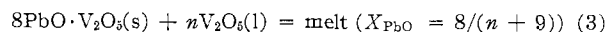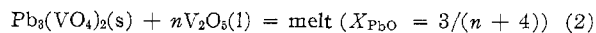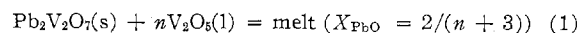
TABLE I

HEATS OF MIXING OF $PbO(s)$–$V_2O_5(l)$

Mole fraction of PbO, X_{PbO}	$-\Delta H_{obsd}$, cal.	$-\Delta H^M$, kcal./mole	$-\Delta H^M/X_{PbO}$, kcal./mole
0.0249	27.46	0.455	18.27
0.0532	23.38	0.959	18.03
0.0734	35.73	1.362	18.56
0.192	109.4	3.647	18.99
0.210	127.1	3.913	18.63
0.301	91.14	5.640	18.74
0.321	183.9	5.959	18.56
0.401	207.1	7.542	18.81
0.500	200.8	9.203	18.41
0.501	248.3	9.095	18.15
0.602	246.8	10.899	18.10
0.606	269.5	10.799	17.82

Av.: 18.42 ± 0.33 (s.d.)

character over the whole of the considered composition range. Of course, the calorimetric results do not permit a positive identification of the reaction products. However, it seems likely that the dissolution reaction involves the formation of one (or possibly both) of the anionic species $V_2O_7^{-4}$ and VO_4^{-3} (or polymeric species of the same composition). In pure form these species correspond to mole fractions of lead oxide larger than 0.6. On the other hand, the calorimetric data give no indication of the existence in this melt of the metavanadate ion, VO_3^- (or of its polymer). Thus, there appears to be full correspondence between the considered melts and the solid lead vanadate phases. According to the published phase diagram for PbO–V_2O_5,[4] there exists no solid lead metavanadate, only the three phases, pyrovanadate ($Pb_2V_2O_7$), orthovanadate (Pb_3-$(VO_4)_2$), and the more complex compound $8PbO\cdot V_2O_5$. It should be noted that in their apparent simplicity the liquid lead oxide–vanadium pentoxide mixtures appear to differ, e.g., from the corresponding lead silicate melts, for which Flood and Knapp[5] on the basis of
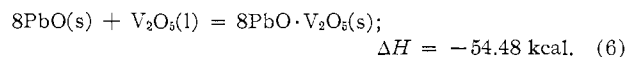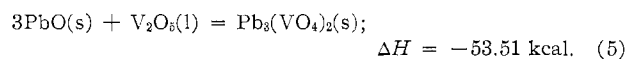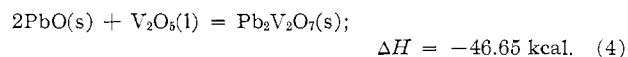
(4) E. M. Levin, H. F. McMurdie, and F. P. Hall, "Phase Diagrams for Ceramists," The American Ceramic Society, Columbus, Ohio, 1956, p. 59.
(5) H. Flood and W. J. Knapp, *J. Am. Ceram. Soc.*, **46**, 61 (1963).

equilibrium data recently have postulated the existence of several different anionic species.

Dissolution of Lead Vanadates in V_2O_5.—In these cases the dissolution reactions may formally be written as in eq. 1–3. In our experiments the mole fraction
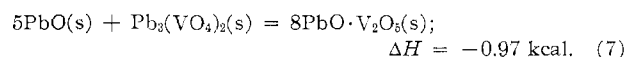
$$Pb_2V_2O_7(s) + nV_2O_5(l) = melt \ (X_{PbO} = 2/(n + 3)) \quad (1)$$

$$Pb_3(VO_4)_2(s) + nV_2O_5(l) = melt \ (X_{PbO} = 3/(n + 4)) \quad (2)$$

$$8PbO\cdot V_2O_5(s) + nV_2O_5(l) = melt \ (X_{PbO} = 8/(n + 9)) \quad (3)$$

of lead oxide falls between 0.06 and 0.10. Let us designate the heat effect (per mole of compound) associated with each of these reactions as ΔH_s. We showed above that the corresponding enthalpy changes for the dissolution of 2, 3, and 8 moles of pure, solid PbO in V_2O_5 to form the corresponding melts are $\Delta H_1 = -2 \times 18.42$, $\Delta H_2 = -3 \times 18.42$, and $\Delta H_3 = -8 \times 18.42$ kcal., essentially independent of the final composition of the melt. Accordingly, the molar enthalpies of formation of the considered lead vanadates, from solid PbO and liquid V_2O_5 at $680°$, are $\Delta H_1 - \Delta H_s$ for Pb_2-V_2O_7, $\Delta H_2 - \Delta H_s$ for $Pb_3(VO_4)_2$, and $\Delta H_3 - \Delta H_s$ for $8PbO\cdot V_2O_5$.

We record in Table II the actual experimental data obtained for the dissolution of the three lead vanadates in liquid vanadium pentoxide. The corresponding molar enthalpies of formation, valid at $680°$, calculated according to the given reactions, are

$$2PbO(s) + V_2O_5(l) = Pb_2V_2O_7(s);$$
$$\Delta H = -46.65 \text{ kcal.} \quad (4)$$

$$3PbO(s) + V_2O_5(l) = Pb_3(VO_4)_2(s);$$
$$\Delta H = -53.51 \text{ kcal.} \quad (5)$$

$$8PbO(s) + V_2O_5(l) = 8PbO\cdot V_2O_5(s);$$
$$\Delta H = -54.48 \text{ kcal.} \quad (6)$$

Note that combination of (5) and (6) gives

$$5PbO(s) + Pb_3(VO_4)_2(s) = 8PbO\cdot V_2O_5(s);$$
$$\Delta H = -0.97 \text{ kcal.} \quad (7)$$

Thus, from the point of view of the enthalpy the compound $8PbO\cdot V_2O_5$ has a relatively low stability.

In Fig. 2 we present a summary of all the enthalpy of mixing and formation data discussed so far. In order to be able to compare the data for the solid compounds directly with those for the melts, we have recalculated the results for the solid phases so that they apply for a total of one mole of lead oxide plus vanadium oxide.

This graph permits a rough estimate to be made of the heat of fusion of the compound $Pb_2V_2O_7$. By linear extrapolation of the data on liquid mixtures to $X_{PbO} = 0.667$ we estimate a heat of mixing at this composition of about -12.3 kcal./mole. The corresponding value for the solid phase of the same composition is $-46.65/3 = -15.55$ kcal. Thus the heat of fusion of $^1/_3Pb_2V_2O_7$ is about 3.25 kcal., i.e., 9.75 kcal./mole. Note that the extrapolation of the data for the liquid is somewhat doubtful. A significant curvature in the ΔH^M vs. X curve beyond $X = 0.6$ would tend to give a somewhat higher heat of fusion.

We have found no earlier data in the literature on the heat of formation of the complex compound $8PbO\cdot V_2O_5$. However, for $Pb_2V_2O_7$ and $Pb_3(VO_4)_2$ there

TABLE II

HEATS OF SOLUTION OF LEAD VANADATES IN $V_2O_5(l)$

mmoles of compd.	ΔH_{obsd}, cal.	ΔH, kcal./mole
	$Pb_2V_2O_7$	
2.386	24.52	10.28
2.226	22.02	9.89
1.718	16.14	9.39
1.661	15.84	9.54
1.553	15.42	9.93
	Av.:	9.81
	$Pb_3(VO_4)_2$	
1.564	−3.32	−2.12
0.980	−1.55	−1.58
1.254	−1.77	−1.41
1.179	−1.94	−1.65
0.994	−1.74	−1.75
0.103	−2.04	−1.98
	Av.:	−1.75
	$8PbO \cdot V_2O_5$	
0.3053	−29.10	−95.32
0.4060	−37.49	−92.34
0.4701	−43.48	−92.49
0.3627	−32.85	−90.57
0.4862	−45.54	−93.67
	Av.:	−92.88

exists a very recent study by Kelley, Adami, and King,[6] who determined the heat of formation at 30° by means of acid solution calorimetry. According to these authors the reaction $2PbO(s) + V_2O_5(s) = Pb_2V_2O_7(s)$ is associated with an enthalpy change of −34.45 ± 0.25 kcal./mole. When our own result for this compound, −46.65 kcal./mole, is corrected for the heat of fusion of V_2O_5, 15.56 kcal./mole, we obtain for the same formation reaction at 680° the corresponding value −31.09 kcal./mole.

Similarly, for the reaction $3PbO(s) + V_2O_5(s) = Pb_3(VO_4)_2(s)$ at 30° Kelley, *et al.*, give $\Delta H = -39.82 \pm 0.29$ kcal./mole. From our results above, corrected for the heat of fusion of V_2O_5, we obtain $\Delta H = -37.95$ kcal./mole, valid at 680°.

Precise heat content data are not available for the compounds considered here. Therefore, it is not possible to correct the high-temperature data to room temperature. Even so, it seems unlikely that such a correction would completely remove the discrepancy between Kelley's data and our own. We have no satisfactory explanation for this discrepancy. Since Kelley's work was carried out using well-established methods and at room temperature, while our own study is in the nature of an exploration and was carried out at high temperature, we consider Kelley's data to

(6) K. K. Kelley, L. H. Adami, and E. G. King, Bureau of Mines Report 6197, U. S. Dept. of the Interior, 1963.

be somewhat more reliable. Nevertheless, our results are good enough to suggest that in the future high-temperature solution calorimetry may become a very valuable tool for the study of solid oxidic phases. Further investigations in this area are being planned.

Direct Formation of $Pb_3(VO_4)_2$.—In Table III we present the results of four pairs of experiments involving the direct combination of $3PbO + V_2O_5$ to form $Pb_3(VO_4)_2$. Note that the difference between the observed enthalpy changes, ΔH_1 and ΔH_2, represents the heat of formation of the sample of compound formed. The over-all mean of the four sets of experiments is −39.0 kcal./mole. If the last, apparently low, result is disregarded, the mean becomes −39.37 kcal./mole of $Pb_3(VO_4)_2$. These values should be compared with that of Kelley, *et al.*,[6] which was −39.80 ± 0.29 kcal./mole. When one takes into account the unusual simplicity of the direct combination method, our results must be considered to be remarkably good. We propose to explore further the usefulness of this method in work on other oxidic systems.

TABLE III

DIRECT COMBINATION OF $3PbO + V_2O_5$ TO FORM $Pb_3(VO_4)_2$

$Pb_3(VO_4)_2$, mmoles	ΔH_1 (25 to 680°) capsule + powders, cal.	ΔH_2 (25 to 680°) capsule + compd., cal.	$-\Delta H_f^{25°}$, kcal./mole
1.0710	75.25	117.22	39.19
1.0762	74.85	117.64	39.76
1.1569	79.87	125.17	39.16
1.1149	81.13	123.35	37.87

Finally, we want to stress that we do not claim to be the originators of the adopted direct combination method. A very similar method was used 25 years ago by Kubaschewski and Walter[7] in a study of the heats of formation of certain intermetallic compounds. A related method, which involved the use of a very simple heating calorimeter, was applied by Tammann[8] in an exploration of the reaction between acidic oxides $(MoO_3, WO_3, V_2O_5,$ etc.) and basic oxides $(MgO, CaO, PbO,$ etc.). This made possible crude determinations of the heats of formation of a number of oxidic combinations, notably those involving MoO_3 and WO_3 with basic oxides.

(7) O. Kubaschewski and A. Walter, *Z. Elektrochem.*, **45**, 630 (1939).
(8) G. Tammann, *Z. anorg. allgem. Chem.*, **149**, 21 (1925).