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"Gaseous Metal Hydroxides at High Temperatures"*

Final Report for the Year
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Abstract

Transport of metals and metal oxides as gaseous metal hydroxides constitutes an important practical problem in the dispersion of metals to the environment. The objective of this study is to identify the gaseous metal hydroxide species that exist and determine their thermodynamic properties. The lead hydroxide system was the first system to be studied. Last year a transpiration apparatus was set up and preliminary studies were done on lead transport. This year improvements were made on the apparatus and ten additional transpiration runs were made. The data from runs made this year showed much less scatter than the earlier data. Flow rate conditions were determined at which saturation of the carrier gas steam was complete and diffusion of the volatile species was minimized. Assuming that the gaseous species is Pb(OH)_2 an equilibrium constant of 1.2×10^{-7} was found for the reaction: $\text{PbO(s)} + \text{H}_2\text{O(g)} = \text{Pb(OH)}_2\text{(g)}$ at 973°K . Using the above data the enthalpy of dissociation of $\text{Pb(OH)}_2\text{(g)}$ to Pb(g) and 2OH(g) at 298°K is 135 kcal/mole. Determination of the vapor species using the present apparatus appears to be impractical because of the small amount of lead transport that can be obtained. Alternative methods should be explored.

Introduction

The purpose of this study of gaseous metal hydroxides is to determine the molecular formulae of the hydroxide gaseous species that exist at high temperatures and to determine their thermodynamic properties where this is possible.

A number of cases of metal transport can be traced to the formation of a gaseous metal hydroxide that exists only at high temperatures. This mechanism could account for corrosion of metals by high pressure steam, the formation of some

ore bodies, and the dispersion of metals to the environment when water and a metal or metal oxide are in contact at a high temperature. Two specific areas of interest are the possible venting of hazardous fission products to the atmosphere as the result of underground nuclear testing and the problems associated with the storage of nuclear wastes where containment of radioactive wastes is essential.

The amount of information that is available on gaseous metal hydroxides is rather limited. This is surprising considering the extensive application of the data. Most of the known work has been summarized by Jackson (1).

The lead hydroxide system was chosen for the first investigation since possible dispersion of lead to the atmosphere from the venting of underground nuclear tests was an important consideration at the beginning of this study. In addition this system was a convenient one to study with the equipment available. This report covers work carried out during the second year of the investigation.

To investigate the lead hydroxide system, the transpiration method was used. Lead oxide in an aluminum oxide boat was placed in a heated Vycor tube and water vapor carried in a stream of oxygen gas was flowed over the heated oxide. Any lead that was transported was then collected in the cooler downstream portion of the apparatus. After each run the apparatus was partly disassembled and any lead deposited on the Vycor tube downstream from the heated zone was dissolved off the tube walls and analyzed. Since lead oxide (PbO) is quite involatile at the operating temperatures used, any transport of lead must be due to the formation of a volatile lead hydroxide or lead oxyhydroxide. Preliminary experiments carried out last year (2) indicated a detectable amount of lead was transported and assuming that the vapor species was $Pb(OH)_2$, a preliminary value of 137 kcal/mole was calculated for the enthalpy of dissociation of $Pb(OH)_2(g)$, to $Pb(g)$ and $2OH(g)$.

The results of last years work left two major points unresolved.

(1) Flow conditions needed to be determined where saturation of the transpiration gas stream with lead hydroxide vapor was assured and diffusion minimized.

(2) The vapor species needed to be determined.

This year's study resolved the first point. Additional transpiration runs showed what flow rates were needed to maintain equilibrium conditions. The second problem of the vapor species remains unresolved. With the present apparatus analytical techniques are not sensitive enough to permit determination of the vapor species.

Experimental

Commercial grade oxygen was used as a carrier gas. It was saturated with water vapor by flowing the gas through a sintered glass dispersion tube placed in the bottom of a one-liter flask filled with water and heated in a fluidized bed heater. The temperature of the water determined the vapor pressure of water in the carrier gas. The saturated gas stream was then led into a Vycor tube heated by a resistance furnace and passed over the lead oxide. Figure I shows the furnace and deposit tube where reaction and transport took place. After exiting from the deposit tube water was condensed out of the carrier gas in an ice cooled "U" tube and the gas volume was measured with a wet-test meter.

The apparatus and procedures followed are described in detail in last year's final report(2). No geometric modifications were made in the apparatus but considerable time and effort were put into making other significant improvements in the apparatus. A new low pressure regulator was installed and it greatly stabilized the flow of the oxygen carrier gas. Tap adjustments on the furnace increased the constant temperature ($\pm 2.0^{\circ}\text{C}$) zone of the furnace from 8.5 to 15.2 cm at

Figure I. Furnace and Deposit Tube

A - Furnace Tube
 B - Diffusion Barriers
 C - Sample
 D - Thermocouple

E - 19/38 Standard Taper Joint
 F - Deposit Tube
 G - Furnace Liner

680°C. Attempts to provide better temperature stability for the water saturator were unsuccessful. Simple regulation by manual adjustment of an autotransformer proved to be adequate. The whole transpiration apparatus was moved to a new air-conditioned laboratory. This move delayed operations somewhat but also provided more space and with more control over the room temperature, the flow and temperature control on the apparatus also improved.

Analytical procedures were modified somewhat to improve consistency of the results. After completing a run the deposit tube was removed and washed with 5 ml of hot concentrated hydrochloric acid followed by three washes of 5 ml of hot distilled water. The washings were collected and diluted to 50.0 ml with 6 N HCl. This procedure was repeated three times for each deposit tube to insure removal of all sublimate. For consistency the time the tube was washed with each solution was kept constant. The collected washings were then analyzed for lead content by atomic absorption spectrophotometric methods.

Results and Discussion

Ten transpiration runs were completed on the modified apparatus. The results of these runs are listed in Table I. Assuming that the vaporizing species is $Pb(OH)_2$, an equilibrium constant was calculated for each run. These are given in Table II and plotted as a function of carrier gas flow rate in Figure II. Data obtained from earlier runs at 973°K are also included in the figure.

Figure II shows that data obtained in runs 11-20 are much more consistent than the earlier data in that they show less scatter. The data obtained this year also give consistently lower equilibrium constants. If only the data for runs 11-20 is used a small but significant trend with oxygen flow can be observed. At lower flow rates equilibrium constants appear to be somewhat higher. This is in agreement with

Table I
Transpiration Run Data

Run No.	Temperature	Time	Oxygen Flow	Water Collected	Lead Found
11	973.7°K	1365min	31.82* ml/min	32.09*g	2.71ppm
12	973.7	983.5	57.02*	36.82*	0.88
13	975.5	1180	51.65	55.63	1.54
14	972.7	1373	49.27	54.42	1.24
15	976.3	1251	58.16	69.44	2.77
16	973.3	1192	29.60	34.35	2.02
17	973.3	1046	31.16	37.41	1.65
18	973.1	1076	34.19	30.96	4.74**
19	973.5	1060	27.28	24.58	1.66
20	972.1	1143	28.74	33.92	1.68

*A leak in the gas train downstream from the deposit-tube required estimation of these values. Errors in the estimate probably do not exceed

**Deposit tube accidentally contaminated with Pb. Data excluded from Figure II.

Table II
Equilibrium Constants for the Reaction:
 $\text{PbO}_{(s)} + \text{H}_2\text{O}_{(g)} = \text{Pb}(\text{OH})_{2(g)}$

Run	Pressure H_2O	Pressure $\text{Pb}(\text{OH})_2$	Kp
11	0.460 atm	1.69×10^{-7} atm	3.67×10^{-7}
12	0.435	0.452×10^{-7}	1.04×10^{-7}
13	0.508	0.612×10^{-7}	1.20×10^{-7}
14	0.485	0.480×10^{-7}	0.990×10^{-7}
15	0.521	0.904×10^{-7}	1.74×10^{-7}
16	0.527	1.35×10^{-7}	2.56×10^{-7}
17	0.567	1.09×10^{-7}	1.92×10^{-7}
18*	0.493	3.28×10^{-7}	6.65×10^{-7}
19	0.496	1.46×10^{-7}	2.94×10^{-7}
20	0.541	1.18×10^{-7}	2.18×10^{-7}

*Data point rejected. See Table I.

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Table II

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*Data point rejected. See Table I.

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Figure II Variation of Equilibrium Constant with Carrier Gas Flow at 973°K

other transpiration studies which show that at low flow rates, gaseous species can diffuse from the reaction zone to the deposit tube thus giving anomalously high equilibrium constants (3). At high flow rates the carrier gas does not become saturated with the vapor species and the equilibrium constant will decrease with flow rate. In the present set of experiments it does not appear that flow rates high enough to prevent saturation of the gas stream have been used. A representative curve for runs 11-20 is shown on Figure II and gives a plateau value of 1.2×10^{-7} for the equilibrium constant. The plateau value represents flow conditions where the transpiration gas stream is saturated and diffusion is at a minimum. This corresponds to a ΔH_{298}^0 value of 40.7 kcal/mole for the transpiration reaction given in Table II, an enthalpy of formation of -69.1 kcal/mole for $\text{Pb}(\text{OH})_2(\text{g})$ at 298°K, and an enthalpy of dissociation to $\text{Pb}(\text{g})$ and 2 $\text{OH}(\text{g})$ of 134.8 kcal/mole. The enthalpy of dissociation compares to a value 150 ± 15 kcal/mole estimated by Jackson (1).

Conclusion

The experimental work done this year established the magnitude of flow rates where equilibrium could be maintained in the carrier gas stream and diffusion effects were minimized. A few additional data points to determine the upper limit of flow rate where saturation of the gas stream is incomplete would be helpful for later work.

The major problem left to be solved is determination of the vapor species. Up to the present the vapor species has been assumed to be $\text{Pb}(\text{OH})_2$. While this assumption may not be unreasonable it is still an assumption unsubstantiated by any direct evidence. A paper dealing with hydrated gaseous lead ions (4) was reviewed but since the lifetime of such ions is very small in a flow system of the above design, it seems unlikely that cluster ions would be present. While it might be possible to relate the ion species to neutral species, I

am not aware of any studies in the literature where this has been done. Work on this approach was unproductive.

Using a transpiration apparatus the vapor species can be determined by observing the change in the amount of lead transported as the vapor pressure of water is changed. With the present apparatus runs of 18 hours at 973°K produced only 1-2 ppm lead in washings from the deposit tube. This is near the limit of present analytical methods. The amounts of lead could be increased by operation at a higher temperature, however the present apparatus is limited to a maximum of 1010°K because of the PbO-SiO_2 eutectic at this temperature. Thus lead transport can be increased only by changing materials of construction or by increased run times. With the present apparatus this approach does not seem to be very practical. Mass spectrometric determination of the vapor species would seem to be a more workable alternative.

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4. I. N. Tang and A. W. Castleman, Jr., J. Chem. Physics, 57, 3638 (1972).

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