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Transpiration Study of the Reaction of Water Vapor with Barium Oxide

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Barium oxide has been found to react with water vapor at temperatures from 1443 to 1593 K to form gaseous $Ba(OH)_2$ according to the reaction; $BaO(s)+H_2O(g)\rightarrow Ba(OH)_2(g)$. The standard free energy of formation is given by the equation, $\Delta G_T^\circ = 49400-16.6\ T$ (cal/mol) in the present temperature range. From the thermodynamic cycle the bond energy between barium and two hydroxyl groups has been found to be 196.8 kcal/mol.

The volatility of the alkaline earth oxides is greatly increased by the presence of water vapor due to the formation of volatile hydroxide vapors which result from the following reactions;

$$MO(s) + H_2O(g) \rightarrow M(OH)_2(g) \qquad (1)$$

$$MO(s) + 1/2H_2O(g) \rightarrow M(OH)(g) + 1/4O_2 \qquad (2)$$

where M is a Group IIa element. This has been verified for BeO,[1-3] MgO,[4,5] and BaO.[6] Stafford and Berkowitz[6] studied the $BaO-H_2O$ system mass-spectrometrically and found that dihydroxide vapor $Ba(OH)_2$, predominanted at temperatures between 1485 and 1785 K under a water pressure above 4×10^{-5} atm. The bond energy for $Ba(OH)_2$ was given by 206.3 kcal/mol. Mass-spectrometry is, however, often accompanied by errors due to the uncertainty of the relative cross section for ionization and the relative efficiency of the secondary-electron multiplier. Consequently it is necessary to confirm the value by other methods.

In the present study, the reaction of water vapor with solid barium oxide has been investigated by the transpiration method as a series of studies on the effects of water vapor upon the vaporization of alkaline earth oxides. The vapor pressures of gaseous $Ba(OH)_2$ formed according to Reaction 1 and the related thermodynamic properties have been evaluated.

Experimental

Transpiration Apparatus. Figure 1 shows a schematic drawing of the reaction zone in the apparatus used in this study. Approximately 2 g of sample was loaded into a Pt/20%Rh boat lined with magnesia. The vaporized species were collected in a condenser made of Pt/20%Rh alloy. The condenser had a capillary (0.7 mm i.d.×6 mm long) at one end. All other structual components except for those described above were made of alumina. Barium oxide reacts with alumina to form three barium aluminates, *i.e.*, $BaO\cdot6Al_2O_3$, $BaO\cdot Al_2O_3$ and $3BaO\cdot Al_2O_3$, but the partial pressure of BaO(g) over these compounds is very small.[7,8] Therefore, it has been assumed that the formation of the barium aluminates has no effect on the equilibrium relation of the gas phase containing the barium bearing gaseous species. Temperatures were measured with a Pt/13%Rh thermocouple and regulated within ±1 °C.

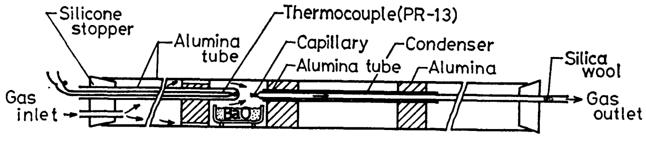

Fig. 1. Cross section of reaction zone in transpiration apparatus.

A wet gas mixture, Ar/H_2O, was obtained by passing argon gas three times through a water reservoir, the temperature of which was accurately controlled. The partial pressure of water vapor was determined from the weight increase of P_2O_5 placed in a stream of the wet gas.

Procedure. The argon carrier gas used was passed through the water reservoir described above and saturated with water vapor after passage through a KOH-column to remove carbon dioxide contained as an impurity, and then into the charge room at a given temperature. The water vapor reacted with BaO to form Ba-bearing hydroxide vapors. The carrier gas was saturated with vapors formed in the charge room at an appropriate flow rate and the vapors formed were transported by the carrier gas to the condenser. The condensate was removed into concentrated nitric acid solution and the barium in the solution was analyzed by chelatometry using EDTA and cresolphthalene complexon. The estimated analytical error is less than ±0.6% by weight of Ba.

The partial pressure of the volatile barium hydroxide compound has been calculated from the amount of collected barium, assuming that each molecule of the volatile species contains one atom of barium and that the vapor approximated to an ideal gas. Therefore, it follows that partial pressure at equilibrium is given by

$$p(Ba(OH)_{2x}) = n_v P/(n_c+n_v) \qquad (3)$$

where n_c is the number of mole for the carrier gas, n_v for the sample vapor, and P the total pressure.

Sample. Guaranteed reagent-grade BaO with a 99.9% purity (supplied by Rare Metallic Co., Ltd.) was used. In order to stop dispersion of the fine particles in the carrier gas, the BaO was sintered at 1300 °C prior to use. The compacted sample was kept in a desiccator filled with pure argon to avoid reaction with water and carbon dioxide.

Results and Discussion

Effect of Flow Rate on Vapor Pressure. To determine the conditions for equilibrium a series of measurements was made at 1593 K with varying flow rates. Figure 2 illustrates the apparent vapor pressure of the assumed molecule, $Ba(OH)_{2x}$, calculated from Eq. 3 as a function of the flow rate. As can be seen from Fig. 2, the vapor pressures obtained are approximately constant in the range 1.3 up to 2.5 cm^3/s.

The decrease in vapor pressure, *i.e.*, $<1.2\ cm^3/s$, is thought due to escaping vapor from the space between the condenser and the support (alumina tube).

Water Vapor Dependence. A plot of the logarithm of the equilibrium pressure of the volatile complex as a function of the logarithm of the partial pressure

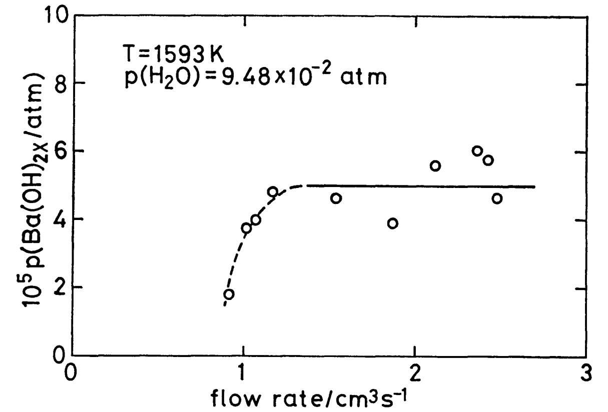

Fig. 2. Vapor pressure *vs.* the flow rate of carrier gas at T=1593 K and $p(H_2O)$=0.0948 atm.

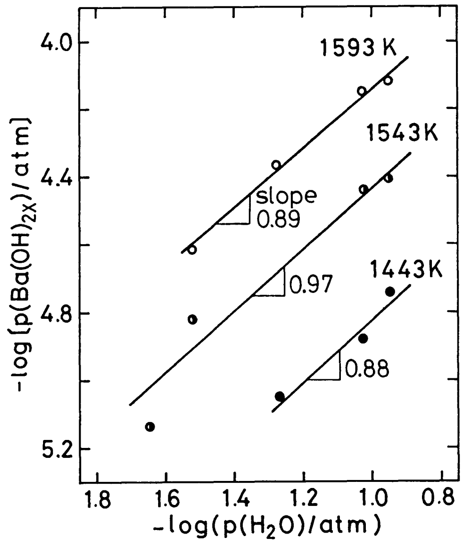

Fig. 3. Variation of log(vapor pressure of barium bearing species) *vs.* log(partial pressure of water).

of water at constant temperature and partial pressure of oxygen will indicate whether Reaction 1 or 2 occurs (this includes the correct value of x in $Ba(OH)_{2x}$) as outlined below.

Combining Reaction 1 with 2 yields the following equation for the BaO–H$_2$O system,

$$BaO(s) + xH_2O(g) \rightarrow Ba(OH)_{2x}(g) + \frac{(1-x)}{2}O_2(g) \quad (4)$$

The equilibrium constant k_p for the above reaction may be written as

$$k_p = \frac{p(Ba(OH)_{2x})\cdot p(O_2)^{(1-x)/2}}{a(BaO)\cdot p(H_2O)^x} \quad (5)$$

Assuming $a(BaO)=1$ and taking logarithms of both sides;

$$\log p(Ba(OH)_{2x}) = x\log p(H_2O) - \frac{(1-x)}{2}\log p(O_2) + \log k_p \quad (6)$$

From Eq. 6 the value of x can be determined, *i.e.*, the contribution of Reactions 1 and 2 to Reaction 4.

No correction need be made for the partial pressure of BaO(g) since this is equal to only 3.54×10^{-7} atm at 1593 K, the highest temperature used in these measurements.

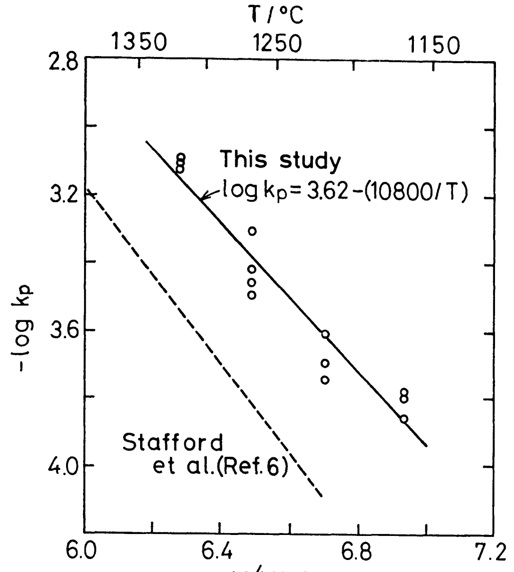

Fig. 4. Plot of equilibrium constant for the reaction $BaO(s)+H_2O(g)=Ba(OH)_2(g)$ *versus* reciprocal temperature.

A series of measurements were made at 1443 to 1593 K with a varied vapor pressure of water at atmospheric pressure passing over the barium oxide, and the results of which are given in Table 1 are shown graphically in Fig. 3. The values of x obtained from the slopes of a $\log p(Ba(OH)_{2x})$ *versus* $\log p(H_2O)$ plot were 0.88, 0.97, and 0.89 at 1443, 1543, and 1593 K, respectively. The average value was 0.91 which was very close to unity. Considering the mass-spectrometric results of Stafford and Berkowitz,[6] the reaction form of the alkaline earth oxides with water vapor[1-6] and flame-experiment data,[9,10] the value of x has been determined as unity. Therefore the predominant reaction of water vapor with barium oxide under these conditions ($p(H_2O)$=0.022—0.112 atm) is:

$$BaO(s) + H_2O(g) \rightarrow Ba(OH)_2(g) \quad (7)$$

The selection of oxygen as the carrier gas would suppress the formation of gaseous Ba(OH) and lead to a value of x move close to unity. No examination in an oxidizing atmosphere was conducted, however, because normal barium oxide oxidizes at relatively low temperature to the per-oxide BaO$_2$.

The decomposition temperature of $Ba(OH)_2(s)$ is 408 °C, and hence no solid $Ba(OH)_2$ exists at the present temperature.

Vapor Pressure of Ba(OH)$_2$(g) and Related Thermodynamic Values. The vapor pressures of gaseous $Ba(OH)_2$ and equilibrium constant k_p have been calculated from the amount of collected barium and the results are given in Table 1 and illustrated graphically in Fig. 4. The linear relationship obtained from a least squares treatment of the data corresponds to the expression,

$$\log k_p = -(10800\pm860)/T + 3.62\pm0.56 \quad (8)$$

and hence, the standard Gibbs energy for Reaction

TABLE 1. EQUILIBRIUM CONSTANT k_p FOR THE REACTION
$BaO(s) + H_2O(g) \rightarrow Ba(OH)_2(g)$

No.	T K	Time h	Flow rate $cm^3\,s^{-1}$	$p(H_2O)$ atm	Collected Ba $mg\,h^{-1}$	$p(Ba(OH)_2)$ atm	k_p	$-\Delta fef$ [a)] $cal\,mol^{-1}\,K^{-1}$	ΔH°_0 $kcal\,mol^{-1}$
1	1443	14.33	1.59	5.36×10^{-2}	0.312	8.91×10^{-6}	1.66×10^{-4}	54.56	53.78
2	1443	16.67	1.63	9.48×10^{-2}	0.475	1.32×10^{-5}	1.39×10^{-4}	54.56	53.26
3	1443	16.67	1.66	1.12×10^{-1}	0.661	1.80×10^{-5}	1.60×10^{-4}	54.56	53.71
4	1493	14.38	1.56	5.36×10^{-2}	0.335	9.76×10^{-6}	1.82×10^{-4}	51.88	51.93
5	1493	4.08	1.63	9.48×10^{-2}	0.843	2.34×10^{-5}	2.47×10^{-4}	51.88	52.82
6	1493	12.67	1.72	1.12×10^{-1}	0.869	2.28×10^{-5}	2.03×10^{-4}	51.88	52.24
7	1543	17.58	1.46	2.29×10^{-2}	0.235	7.31×10^{-6}	3.20×10^{-4}	49.49	51.71
8	1543	15.67	1.58	3.03×10^{-2}	0.527	1.51×10^{-5}	4.99×10^{-4}	49.49	53.06
9	1543	6.83	1.69	9.48×10^{-2}	1.359	3.64×10^{-5}	3.84×10^{-4}	49.49	52.26
10	1543	10.42	1.60	1.12×10^{-1}	1.387	3.91×10^{-5}	$3{\cdot}48\times10^{-4}$	49.49	51.95
11	1593	6.17	1.47	3.03×10^{-2}	0.781	2.41×10^{-5}	7.96×10^{-4}	47.01	52.31
12	1593	5.83	1.60	5.36×10^{-2}	1.534	4.35×10^{-5}	8.14×10^{-4}	47.01	52.38
13	1593	22.42	1.63	9.48×10^{-2}	2.563	7.12×10^{-5}	7.51×10^{-4}	47.01	52.12
14	1593	5.83	1.54	1.12×10^{-1}	2.595	7.62×10^{-5}	6.78×10^{-4}	47.01	51.80
									Av 52.52±0.69

a) Estimated a manner similar to that of Stafford and Berkowitz.[6)]

7 is given by,

$$\Delta G^\circ_{\mathrm{r}} = (49400\pm3900) - (16.6\pm2.6)T \qquad (9)$$

This gives,

$$\Delta H^\circ_{\mathrm{r}}(1500\,\mathrm{K}) = 49.4\pm3.9\ \mathrm{kcal/mol} \qquad (10)$$

$$\Delta S^\circ_{\mathrm{r}}(1500\,\mathrm{K}) = 16.6\pm2.6\ \mathrm{cal/mol\,K} \qquad (11)$$

Using the $\Delta G^\circ_{\mathrm{r}}$ obtained and the JANAF data,[11)] the changes in Gibbs energy, enthalpy and entropy for the following formation reaction,

$$Ba(g) + H_2(g) + O_2 = Ba(OH)_2(g) \qquad (12)$$

are as follows;

$$\begin{aligned}\Delta G^\circ_{\mathrm{f}}(Ba(OH)_2,\ (g)) &= \Delta G^\circ_{\mathrm{r}} + \Delta G^\circ_{\mathrm{f}}(BaO,\ (s)) + \Delta G^\circ_{\mathrm{f}}(H_2O,\ (g))\\ &= 242400\pm4500 - (54.8\pm3.4)T \qquad (13)\end{aligned}$$

and

$$\Delta H^\circ_{\mathrm{f}}(Ba(OH)_2,\ (g),\ 1500\,\mathrm{K}) = 242.4\pm4.5\ \mathrm{kcal/mol} \qquad (14)$$

$$\Delta S^\circ(Ba(OH)_2,\ (g),\ 1500\,\mathrm{K}) = 114.5\pm3.4\ \mathrm{cal/mol} \qquad (15)$$

The decomposition energy of $Ba(OH)_2(g)$ into two hydroxyl radicals and Ba vapor, $D^\circ_0(Ba\text{–}(OH)_2)$, has been estimated using the following thermochemical cycle;

$$\begin{tikzcd}
Ba(OH)_2(g) \arrow[r, "D^\circ"] & Ba(g) & +\ 2(OH)(g) \\
BaO(s) + H_2O(g) \arrow[u, "\Delta H^\circ_{\mathrm{r}}"'] & Ba(s) \arrow[l, "\Delta H^\circ_{\mathrm{f}}"'] \arrow[u, "\Delta H^\circ_{\mathrm{s}}"'] & +\ \overbrace{\tfrac{1}{2}O_2 + H_2O(g)} \arrow[u, "\Delta H^\circ_{\mathrm{f}}"']
\end{tikzcd} \qquad (16)$$

whereby,

$$\begin{aligned}D^\circ_0(Ba\text{–}(OH)_2) = &-\Delta H^\circ_{\mathrm{r},0}(Ba(OH)_2)\\ &-\Delta H^\circ_{\mathrm{f},0}(BaO) + \Delta H^\circ_{\mathrm{s},0}(Ba) + 2\Delta H^\circ_{\mathrm{f},0}(OH) \qquad (17)\end{aligned}$$

where $\Delta H^\circ_{\mathrm{r},0}(Ba(OH)_2)$ represents the heat of reaction for the Reaction 7, $\Delta H^\circ_{\mathrm{f},0}(BaO)$ the heat of formation for BaO(s), $\Delta H^\circ_{\mathrm{s},0}$ (Ba) the heat of sublimation for Ba(s) and $\Delta H^\circ_{\mathrm{f},0}(OH)$ the heat of formation for OH(g) from $H_2O(g)$ and O_2. The values required were 52.52 (last column in Table 1), -130.696,[12)] 42.971,[13)] and 37.84[11)] kcal/mol at 0 K, respectively. Substitution of these values into Eq. 17 gives the value 196.8 kcal/mol as the value of $D^\circ_0(Ba\text{–}(OH)_2)$. This value differs from that of Stafford and Berkowitz[6)] by 4.6%.

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