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A Study of the Calcium Oxide–Water Vapor System by Means of the Transpiration Method

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The system of calcium oxide and water vapor was studied using the transpiration method. Under the conditions of a temperature range from 1678 to 2016 K and P_{H_2O} values from 1.2×10^{-2} to 4.7×10^{-1} atm, the predominant reaction in this system was found to be $CaO(s)+H_2O(g)=Ca(OH)_2(g)$. The standard Gibbs free energy of the reaction is given by this equation: $\Delta G_r^\circ=(61300\pm820)-(12.8\pm0.48)T$ (cal/mol) in the present temperature range. From the thermochemical cycle, the dissociation energy, $D_0^\circ(Ca\text{–}(OH)_2)$, was estimated to be 206.4 kcal/mol.

The volatility of alkaline-earth oxides is greatly increased by the presence of water vapor as a result of the formation of volatile hydroxide vapors by the following reactions:

$$MO(s) + H_2O(g) = M(OH)_2(g), \tag{1}$$

and:

$$MO(s) + \frac{1}{2}H_2O(g) = MOH(g) + \frac{1}{4}O_2, \tag{2}$$

where M is a Group IIa element. This has been shown to be true for BeO,[1–3] MgO,[4,5] and BaO.[6,7]

Although calcium oxide is one of the most important components in the ceramic industry, no systematic investigation of its vaporization behavior under various atmospheres had been made. Only a few investgators[8–11] have measured the dissociation energy, D_0°, for the $Ca(OH)_2(g)=Ca(g)+2OH(g)$ reaction using flamespectral measurements.

In the present study, the reaction of water vapor with solid calcium oxide was investigated by means of the transpiration method as part of a series of studies[5,7] of the effects of water vapor upon the vaporization of alkaline earth oxides. The vapor pressures of the gaseous $Ca(OH)_2$ formed according to Reaction 1 and the related thermodynamic properties were evaluated.

Experimental

Transpiration Apparatus. Figure 1 shows a schematic drawing of the reaction zone in the apparatus used in this study. The sample was placed in a reaction chamber, N (12 mm i.d. × 30 mm long), made of Pt/20% Rh alloy. The reaction chamber had a capillary, L (1 mm i.d. × 10 mm long), to prevent the vapor species formed in the chamber from back-diffusing and had a bottom with holes below which a Pt/Rh 20—40 themocouple, calibrated at the melting points of Pd and Pt (IPTS-68) and placed in a protective alumina tube was located.

The vaporized species were collected in a condenser, J, made of Pt/20% Rh alloy (3.4 mm i.d. × 300 mm long). The capillary, L, had a thorium oxide sleeve, M, in order to minimize the leakage of vapor species through the space between the condenser and the capillary and to prevent sticking with the condenser at high temperatures. The temperature of the reaction chamber was raised by the use of 6 rods of a $LaCrO_3$ heater up to 2016 K and then regulated with ± 3 °C.

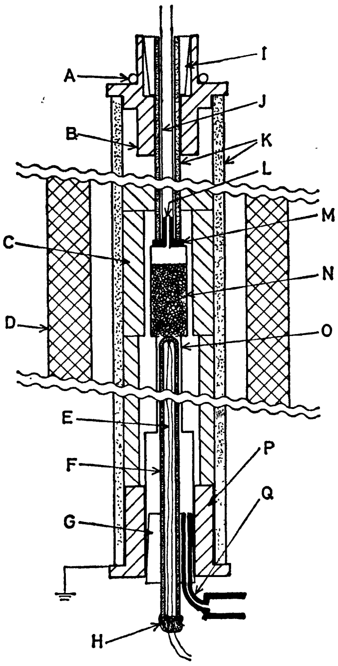

Fig. 1. Cross section of reaction zone in transpiration apparatus. A: cooling water, B: brass, C: alumina insulator, D: $LaCrO_3$ heater, E: Pt/Rh 20—40 thermocouple, F: alumina protective tube, G: Viton stopper, H: silicone seal, I: silicone stopper, J: condenser(Pt/20%Rh), K: alumina tube, L: capillary, M: thoria sleeve, N: reaction chamber and charge, O: reaction tube (Pt/20%Rh), P: brass, and Q: stainless steel.

A wet gas mixture, O_2–H_2O–Ar, was obtained by bubbling a dry O_2–Ar gas in water controlled about 10 degrees higher than desired temperature; it was then passed through a scerwed glass coil around which precisely thermostatted water was passed continuously to condense the oversaturated water vapor in the wet gas. This method has already been described in a preceding paper.[5] The partial pressure of the water vapor was determined from the weight increase in the P_2O_5 powder placed in a stream of the wet gas. The vapor pressure thus determined agreed with the saturated water vapor pressure at the temperature of the coil within ±2%. The water vapor pressure in the range from 1.2×10^{-2} to 4.7×10^{-1} atm was used in the experiments.

Sample. Powder of CaO from $CaCO_3$ with a 99.9% purity (supplied by Merck), fired at 1200 °C, was pressed and sintered at 2400 °C by means of H_2/O_2 flames and then crushed to particles of 15—30 mesh. The particles of CaO were used to fill about 80% of the reaction chamber, and

TABLE 1. IMPURITY CONTENT OF CaO USED IN THIS EXPERIMENT

Element	Content ppm	Element	Content ppm
Na	9	V	<1
Mg	116	Cr	144
Al	25	Fe	11
Si	38	Mn	<1
P	<1	Co	<1
S	23	Cu	1
K	5	Zn	2
Ti	<1		

These values were measured by means of a spark-source mass spectrograph.

a rid with the capillary was welded.

The impurities in the CaO specimens were analyzed by means of spark-ion-source mass spectrometry; the results are given in Table 1.

Procedure. The wet carrier gas, with a constant partial pressure of water vapor, was allowed to flow in a pipe leading the reaction tube. The pipe was heated to about 100 °C by means of a ribbon heater around it in order to keep the water vapor from condensing. The water vapor reacted with CaO in the reaction chamber at a constant temperature to form Ca-bearing hydroxide vapors. The carrier gas was saturated with vapors formed at an appropriate flow rate, and the vapors were transported into the condenser. The condenser was washed with a hot nitric-acid solution, and calcium in the solution was analyzed quantitatively using an atomic-absorption spectrophotometer.

The partial pressure of the volatile calcium hydroxide has been calculated from the amount of collected calcium. Assuming that each molecule of the volatile species contains one atom of calcium, and that the vapor is approximated to an ideal gas, the partial pressure at equilibrium is given by:

$$p(\mathrm{Ca(OH)}_{2x}) = n_v P/(n_c+n_v), \tag{3}$$

where n_c is the number of moles for the carrier gas; n_v, that for the sample vapor, and P, the total pressure, assumed here to be 1 atm.

Results and Discussion

Effect of Flow Rate on Vapor Pressure. Figure 2 shows the apparent vapor pressure of the assumed molecule, $\mathrm{Ca(OH)}_{2x}$, as a function of the flow rate at 1926 K and $p(H_2O)$ of 1.52×10^{-1} atm. A "plateau region" is seen in the range from 1.0 to 2.0 $\mathrm{cm^3/s}$. The decrease in the vapor pressure at the flow rate< 1.0 $\mathrm{cm^3/s}$ is thought to be due to vapor escaping from the space between the condenser and the capillary.

The "plateau region" for other temperatures and $p(H_2O)$ were obtained in a similar flow-rate region.

The output gas from the condenser was passed into a nitric solution, and the solution was subjected to the atomic-absorption analysis. Since no calcium was detected in the solution, the amount of Ca uncondensed in the condenser was considered negligible under the present experimental conditions.

Water-vapor Dependence. In addition to Eqs. 1 and 2, the following reactions must be considered under these conditions:

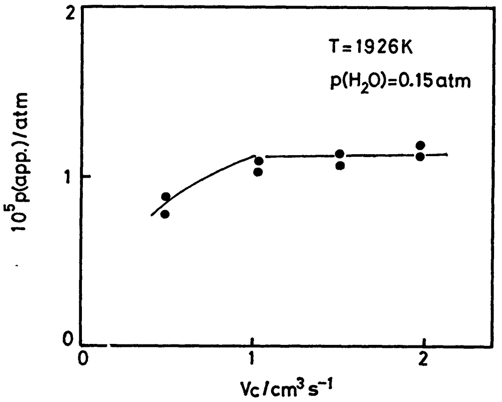

Fig. 2. Apparent vapor pressure, p(app.), *vs.* flow rate of carrier gas at T=1926 K and $p(H_2O)$=0.15 atm.

$$\mathrm{CaO(s)} = \mathrm{Ca(g)} + \frac{1}{2}O_2, \tag{4}$$

$$\mathrm{CaO(s)} = \mathrm{CaO(g)}. \tag{5}$$

Using the JANAF data,[12,14,15] the partial pressures of Ca(g) and CaO(g) at $p(O_2)$ of 0.5 atm are 2.8×10^{-16} and 4.8×10^{-14} atm at 1600 K, and 4.1×10^{-11} and 9.2×10^{-10} atm at 2000 K, respectively. On the other hand, the apparent vapor pressure is 1.1×10^{-5} atm at 1926 K, judging from Fig. 2. Hence, no correction was made for Reactions 4 and 5.

A logarithmic plot of the equilibrium pressure of the volatile complex as a function of the partial pressure of water at a constant temperature and partial pressure of oxygen will indicate whether Reaction 1 or 2 occures.

Combining Reaction 1 with 2 yields the following equation for the CaO-H_2O-O_2 system:

$$\mathrm{CaO(s)} + xH_2O(g) = \mathrm{Ca(OH)}_{2x}(g) + \frac{1-x}{2}O_2. \tag{6}$$

The equilibrium constant, k_p for the above reaction is written as:

$$k_p = \frac{p(\mathrm{Ca(OH)}_{2x})p(O_2)^{(1-x)/2}}{a(\mathrm{CaO})p(H_2O)^x}. \tag{7}$$

Assuming $a(\mathrm{CaO})=1$, and taking the logarithms of both sides, we obtain:

$$\log p(\mathrm{Ca(OH)}_{2x}) = x\log p(H_2O) - \frac{(1-x)}{2}\log p(O_2) + \log k_p. \tag{8}$$

The value of x in Eq. 8 can be determined to ascertain the contribution of Reaction 1 or 2.

A series of measurements were made at 1678 to 2016 K and $p(O_2)$=0.5 atm with a varied water vapor pressure at atmospheric pressure; the results are shown in Fig. 3. The values of x were obtained from the slopes of a log $p(\mathrm{Ca(OH)}_{2x})$ versus log $p(H_2O)$ plot. The average value of x was 1.04±0.04, which was very close to unity. Considering the experimental errors, the value of x has been determined as unity. Therefore, the predominant reaction of water vapor with calcium oxide under these experimental conditions is:

$$\mathrm{CaO(s)} + H_2O(g) = \mathrm{Ca(OH)}_2(g). \tag{9}$$

TABLE 2. EQUILIBRIUM CONSTANT, k_p, FOR THE $CaO(s)+H_2O(g)=Ca(OH)_2(g)$ REACTION

T/K	No. of points	Time/h	Flow rate/cm^3 s^{-1}(STP)	$p(H_2O)$/atm	k_p	$-\Delta fef$/cal mol^{-1} K^{-1}	ΔH°_r(298 K)/kcal mol^{-1}
2016	7	1.00—12.5	1.50—1.62	5.87×10^{-2}— 4.33×10^{-1}	(1.39 ± 0.10) $\times10^{-4}$	13.549	62.90±0.30
1976	7	2.00—13.0	1.49—1.63	5.83×10^{2}— 4.00×10^{-1}	(1.05 ± 0.07) $\times10^{-4}$	13.566	62.78±0.26
1926	11	2.00—37.8	1.03—1.97	5.64×10^{-2}— 4.07×10^{-1}	(6.87 ± 0.85) $\times10^{-5}$	13.587	62.88±0.46
1829	8	3.00—45.3	1.51—1.57	2.59×10^{-2}— 3.65×10^{-1}	(3.21 ± 0.23) $\times10^{-5}$	13.627	62.53±0.27
1762	8	3.00—44.7	1.46—1.61	2.66×10^{-2}— 4.03×10^{-1}	(1.58 ± 0.12) $\times10^{-5}$	13.653	62.77±0.28
1678	6	5.00—89.2	1.46—1.61	2.66×10^{-2}— 3.90×10^{-1}	(6.50 ± 0.90) $\times10^{-6}$	13.687	62.94±0.32
	47						Av. 62.79±0.37

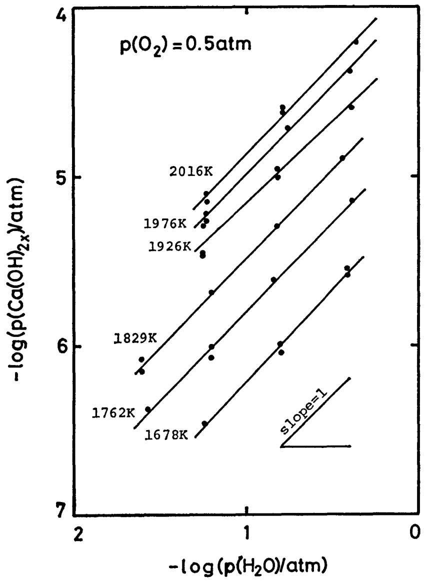

Fig. 3. Variation of log (vapor pressure of calcium bearing species) *vs.* log (partial pressure of water).

The high partial pressure of oxygen in the carrier gas would suppress the formation of gaseous CaOH and lead to a value of x close to unity.

Vapor Pressure of $Ca(OH)_2(g)$ and Related Thermodynamic Values. The vapor pressures of gaseous $Ca(OH)_2$ and the equilibrium constant, k_p, have been calculated from the amount of calcium collected; the results are given in Table 2 and illustrated graphically in Fig. 4. The values of k_p for Reaction 9, obtained from the JANAF data[12–15] are also shown in Fig. 4. The results of this work differ from those of the JANAF data by 20%.

The solid line in Fig. 4, obtained from a least-square treatment for the data of 47 points, corresponds to the expression:

$$\log k_p = (2.80\pm0.10) - (13400\pm180)/T \ (1678-2016\ \mathrm{K}). \tag{10}$$

Hence, the standard Gibbs energy for Reaction 9 is given by:

$$\Delta G^\circ_r = (61300\pm820) - (12.8\pm0.48)T. \tag{11}$$

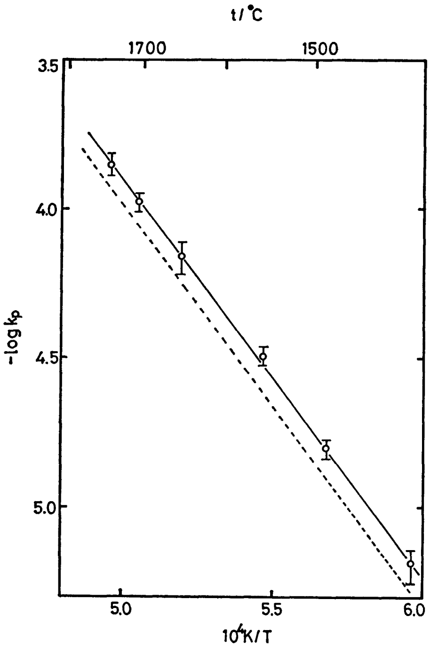

Fig. 4. Plot of equilibrium constant k_p for the reaction $CaO(s)+H_2O(g)=Ca(OH)_2(g)$ *vs.* reciprocal temperature.

——: This work, ----: JANAF data.

This gives:

$$\Delta H^\circ_r(1850\ \mathrm{K}) = 61.3\pm0.8\ \mathrm{kcal/mol}, \tag{12}$$

and:

$$\Delta S^\circ_r(1850\ \mathrm{K}) = 12.8\pm0.5\ \mathrm{cal/mol\ K}, \tag{13}$$

Using the changes of heat capacity, ΔC_p, for Reaction 9 obtained from the JANAF data, Eqs. 12 and 13 lead to:

$$\Delta H^\circ_r(298\ \mathrm{K}) = 62.6\pm0.8\ \mathrm{kcal/mol}, \tag{14}$$

and:

$$\Delta S^\circ_r(298\ \mathrm{K}) = 13.9\pm0.5\ \mathrm{cal/mol\ K}. \tag{15}$$

This entropy change at 298 K coincides with the value, 14.0±2.0 cal/mol K, obtained from the JANAF data.

From the free-energy functions, *fef*, of CaO(s),[14] $H_2O(g)$,[12] and $Ca(OH)_2(g)$[15] and the following relationship:

$$\Delta H_r^\circ(298\text{ K}) = -RT\ln k_p - T\Delta fef, \qquad (16)$$

the ΔH_r° (298 K) was calculated for each k_p; the results are given in the last column of Table 2. The average value of the ΔH_r° (298 K) values obtained by a third-law treatment, 62.8±0.4 kcal/mol, agrees well with the second-law treated value (Eq. 14); this indicates the high reliability of this work.

Using the JANAF data, the ΔH_r° (298 K) obtained by the 3rd-law treatment leads to:

$$\Delta H_r^\circ(0\text{ K}) = 63.1 \pm 0.4\text{ kcal/mol}. \qquad (17)$$

Dissociation Energy of Ca(OH)$_2$(g). The dissociation energy of $Ca(OH)_2(g)$ into 2OH(g) and Ca(g), $D_0^\circ(Ca\text{-}(OH)_2)$, has been estimated using the following thermochemical cycle:

$$\begin{tikzcd}
Ca(OH)_2(g) \arrow[r, "D^\circ"] & Ca(g) & +\ 2OH(g) \\
CaO(s) + H_2O(g) \arrow[u, "\Delta H_r^\circ"] & Ca(s) \arrow[u, "\Delta H_s^\circ"] \arrow[l, "\Delta H_f^\circ"'] & +\ \frac{1}{2}O_2 + H_2O(g) \arrow[u, "\Delta H_f^\circ"]
\end{tikzcd} \qquad (18)$$

whereby:

$$D_0^\circ(Ca\text{-}(OH)_2) = -\Delta H_{r,0}^\circ(Ca(OH)_2) - \Delta H_{f,0}^\circ(CaO) + \Delta H_{s,0}^\circ(Ca) + 2\Delta H_{f,0}^\circ(OH), \qquad (19)$$

where $\Delta H_{r,0}^\circ(Ca(OH)_2)$ represents the heat of reaction for Reaction 9; $\Delta H_{f,0}^\circ(CaO)$, the heat of formation for CaO(s); $\Delta H_{s,0}^\circ(Ca)$, the heat of sublimation for Ca(s), and $\Delta H_{f,0}^\circ(OH)$, the heat of formation for OH(g) from $H_2O(g)$ and O_2. The values required were 63.12±0.4 (Eq. 17), −150.99±0.21,[14] 42.74±0.3,[12] and 37.90±0.04[12] kcal/mol at 0 K, respectively. The substitution of these values into Eq. 19 gives the value of $D_0^\circ(Ca-(OH)_2)$. This result is shown in Table 3, along with the literature values.[8–11]

This value is in very good agreement with the JANAF table's recommended value (No. 1 in Table 3). From the D_0° thus obtained, we calculated $\Delta H_{f,0}^\circ(Ca(OH)_2, g) = -145.0 \pm 1.0$ kcal/mol.

TABLE 3. DISSOCIATION ENERGY OF $Ca(OH)_2(g)$

No.	Method	$D_0^\circ(Ca\text{-}(OH)_2)$ / kcal mol^{-1}	Ref.
1	Flame photometry	205.6[a),b),c)]	8
2	Flame photometry	207.6[a),b)]	9
3	Flame photometry	210.4[b)]	10
4	Flame photometry	207.8	11
5	Transpiration	206.4	This work

a) Recalculated from Refs. 8 and 9 by Cotton and Jenkins. b) Treated with current JANAF data. c) JANAF table's recommended value.

References

1) L. I. Grossweiner and F. L. Seifer, *J. Am. Chem. Soc.*, **74**, 2701 (1952).

2) W. A. Young, *J. Phys. Chem.*, **64**, 1003 (1960).

3) T. B. Douglas, *J. Res. Natl. Bur. Stdn.*, **76A**, 511 (1972).

4) C. A. Alexander, J. S. Ogden, and A. Levy, *J. Chem. Phys.*, **39**, 3057 (1963).

5) E. Maeda, T. Sasamoto, and T. Sata, *Yogyo Kyokai Shi*, **86**, 461 (1978).

6) F. E. Stafford and J. Berkowitz, *J. Chem. Phys.*, **40**, 2963 (1964).

7) T. Sasamoto, K. Mizushima, and T. Sata, *Bull. Chem. Soc. Jpn.*, **52**, 2127 (1979).

8) V. G. Ryabova and V. L. Gurvich, *Teplofiz. Vys. Temp.*, **3**, 318 (1965).

9) K. Schofield and T. M. Sugden, *Trans. Faraday Soc.*, **62**, 566 (1966).

10) D. H. Cotton and D. R. Jenkins, *Trans. Faraday Soc.*, **64**, 2988 (1968).

11) E. M. Starovoitov, V. G. Ryaboba, L. V. Gurvich, A. N. Khitrov, I. I. Nazarenko, and A. V. Belyaev, *Teplofiz. Vys. Temp.*, **15**, 909 (1977).

12) D. R. Stull and H. Prophet, "JANAF Thermochemical Tables," Dow Chemical Co. (1970).

13) M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud, and L. C. Walker, *J. Phys, Chem. Ref. Data*, **3**, 443 (1974).

14) M. W. Chase, J. L. Curnutt, H. Prophet, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data*, **4**, 62 (1975).

15) M. W. Chase, Jr., J. L. Curnutt, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data*, **7**, 882, 883 (1978).