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**THE SYSTEM CALCIUM
PEROXIDE—CALCIUM
OXIDE—OXYGEN**

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The System Calcium Peroxide-
Calcium Oxide-Oxygen

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Abstract

The peroxidation of lime to calcium peroxide would be of interest as a method for the commercial manufacture of hydrogen peroxide if it could be caused to occur readily and in reasonable yield. The feasibility of this reaction, however, has been beclouded by uncertainties as ^{to} the equilibrium relationships involved. Previous data bearing on this question are analyzed here and some new experimental determinations are presented. The equilibrium characteristics of this system are still somewhat uncertain but it appears that, for example, 1525 psia oxygen pressure exists at equilibrium above calcium peroxide-calcium oxide at about 111°C. However, it was only possible to form traces of calcium peroxide from calcium oxide and oxygen.

The results indicate that the characteristics of this system are much less favorable for the peroxidation of lime than had been thought previously.

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The historical process for the manufacture of hydrogen peroxide, which accounts for but a small fraction of present day commercial production, involves the peroxidation of barium oxide in air at atmospheric pressure to form barium peroxide, followed by its reaction with an acid to yield hydrogen peroxide and a barium salt. An analogous process involving peroxidation of lime to calcium peroxide would provide an interesting method for commercial production of hydrogen peroxide, but attempts to carry out this particular peroxidation have generally given negative results. The reaction is represented by Equation 1.



The crux of the problem is the question of equilibrium in the system calcium peroxide-calcium oxide-oxygen. The system has been regarded as univariant, probably by analogy to barium peroxide-barium oxide and strontium peroxide-strontium oxide, in which systems the equilibrium pressure has been found to be independent of the gross composition of the solid present and dependent only on temperature. Two contradictory reports of the equilibrium of reaction 1 appear in the literature, one by Bergius (1) and the other by Blumenthal (2). However both sets of data have appeared highly questionable since calcium peroxide has been found to decompose under conditions under which these data would indicate it should be stable. Therefore it was felt desirable to re-examine this

question in order to lay a foundation for evaluation of the industrial potentiality of this peroxidation reaction.

Previous Investigations

Frederick von Bergius (1) placed samples of the solids in a closed system containing oxygen, and the pressure was allowed to come to "equilibrium" at a fixed temperature. Thus oxygen was intended to be added or removed from the gas phase by the formation or decomposition of the calcium peroxide. However, Bergius found this rate extremely slow and consequently, to increase the rate, dissolved the calcium peroxide and lime in a eutectic mixture of sodium and potassium hydroxide. "Equilibrium" pressure data were reported over a considerable temperature range for each charge studied, and the liquid phase was also analyzed for peroxide content. The results of Bergius' experimentation are plotted on Figure 1.*

* Bergius' results have been erroneously quoted in the International Critical Tables. Values were actually reported by Bergius in atmospheres, but were incorrectly assumed in the compilation of the Tables to be expressed in millimeters of mercury. Consequently they were incorrectly divided by 760 to convert to "atmospheres."

The validity of Bergius' results appears questionable from several viewpoints. Application of the gas law to the results of a typical run shows that the moles of gaseous oxygen present

remained essentially constant as the temperature and pressure were varied. This indicates that the pressure changes reported were due primarily to expansion and contraction of the oxygen rather than chemical reaction. Fischer and Plötze (3) also report that under the conditions of Bergius' experiment there is a 30% conversion of potassium hydroxide to potassium peroxide.



This would indicate that the peroxide which Bergius reported to be formed and which he believed to be calcium peroxide was probably actually potassium peroxide.

M. Blumenthal (2) attempted to determine the dissociation pressures of calcium peroxide at pressures in the vicinity of one atmosphere. Samples of lime and calcium peroxide were placed in a closed container and the "equilibrium" oxygen pressure was measured at each of several temperatures. This technique has been used by others with apparent success to determine the equilibrium oxygen pressures above barium peroxide-barium oxide and strontium peroxide-strontium oxide, but in both of these cases the equilibrium temperatures are much higher than in the calcium peroxide-calcium oxide system and reaction occurs much more rapidly. Blumenthal's report is rather sketchy and does not state the length of time which was allowed for equilibrium to be reached but it appears to be of the order of minutes or at the most, of a few hours. In a preliminary experiment by the present authors a sample of calcium

peroxide was placed in a leak-tight reactor at 143°C and the variation of pressure with time observed. Even after 69 hours, the pressure was still slowly rising and the final pressure attained after 333 hours was still far below the equilibrium pressure indicated by later experiments. Thus it appears highly doubtful that equilibrium was attained in Blumenthal's work. His results are also plotted on Figure 1.

Other clues as to the equilibrium in the system can be obtained from the results of various attempts which have been made to prepare calcium peroxide by reacting calcium oxide and oxygen, or from knowledge of the conditions under which calcium peroxide has been found to decompose. Riesenfeld and Nottebohm (6) found varying degrees of calcium peroxide decomposition at each of a number of combinations of temperature and pressure between 238 and 305°C and 118 and 190 atmospheres pressure. Four attempts were made to form calcium peroxide from a calcium oxide produced by decomposition of calcium peroxide, but without success. The experimental conditions are shown on Figure 1. From the present results, the conditions at the two higher temperatures studied are unfavorable for peroxide formation. Their tests at the two lower temperatures were for 15 and 20 hours, which may have been insufficient to allow significant peroxide formation. More recently, Hart and Smith (5) prepared samples of calcium oxide from various sources such as calcium carbonate, calcium peroxide, and calcium hydroxide and subjected them in a high pressure bomb to oxygen at various

pressures and temperatures. In no case was any calcium peroxide formed. In each run, a sample of calcium peroxide was also subjected to the same experimental conditions, with the results shown in Table 1.

It is seen that at all the temperatures except 65°C., decomposition of calcium peroxide occurred. (Comparison of runs 2 and 3 shows that significant decomposition would also have occurred in run 2 if the time of the experiment had been longer). Therefore it appears that under each set of conditions represented by runs 2 through 7, calcium oxide is stable but not calcium peroxide, which is consistent with the conclusions of the present work. Each of these sets of experimental conditions is located on Figure 1. In all but one of these experiments, calcium peroxide decomposed under conditions which an extension of the Blumenthal data would predict to be stable conditions for calcium peroxide. The run at 65°C. was too short to be significant and is not shown on the Figure 1; however the data reported in the present paper indicate that calcium peroxide should be stable at this temperature and 100 atmospheres pressure.

The actual formation of calcium peroxide from calcium oxide and oxygen has only been reported once, other than in the present work. M. Blumenthal stated that a sample of calcium oxide prepared by decomposition of calcium peroxide and retaining 0.12-0.13% active oxygen, yielded 1.65% active oxygen after heating for

Table 1

Heating of Calcium Peroxide, Results of Hart and Smith (5)

Run No.	Temp. (°C)	Pressure (psia)	Time (hr)	%CaO ₂ decomposed
1	65	1470	4	nil
2	180	1470	5	nil
3	170	1470	28	10%
4	250	1617	30	all
5	360	1470	2	all
6	150	5145	8	10%
7	250	5145	8	all

3 days at 90°C and atmospheric pressure. A sample of calcium oxide prepared by calcination of calcium nitrate gave negative results under similar conditions. A second sample yielded 1.53% CaO_2 after being heated in 1 atmosphere of oxygen at 75 and 40°C. The presence of peroxide was determined in these cases by titration with permanganate. These points are located in Figure 1.

EXPERIMENTAL

Bergius and Blumenthal each attempted to measure the equilibrium conditions by placing samples of lime and calcium peroxide in a closed reactor and allowing the oxygen pressure to adjust itself to a constant value under fixed temperature conditions.

Theoretically the dissociation pressure is reached by either forming peroxide from the lime or by decomposing the peroxide. In practice, however, this method is not suitable for use here since the rates of the reactions are extremely slow. This provides two difficulties; first, the time required to reach equilibrium is long and there is considerable uncertainty as to when, or if, equilibrium has been reached. The second difficulty is in maintaining the system absolutely leakproof for the long periods of time involved. The time factor required may be a matter of weeks when it is attempted to form the peroxide from lime.

For the present studies, a series of tests were made at each of four different oxygen pressures. In each series, samples of calcium peroxide of known initial composition were subjected to

the fixed oxygen pressure for a fixed length of time, but at different temperatures. Each sample was then analyzed and the composition determined. The dissociation temperature at the oxygen pressure studied is taken to be the lowest temperature at which decomposition was observed. By making the time of each test sufficiently long, in principle this point can be determined with considerable accuracy. In practice, the time required may be so long that the method becomes unsuitable. The equilibrium was also approached from the other side by forming small amounts of calcium peroxide from lime and oxygen.

Apparatus

The equipment for high pressure work consisted of a reaction chamber, equipped with a pressure gage, to which oxygen was passed from a cylinder equipped with an oxygen pressure regulator.. The reaction chamber, which was $3/4$ " in inside diameter and $6\ 5/8$ " long, was constructed from a steel tube, sealed at one end and fitted with a suitable closure at the other. The reactor was held in a horizontal position in a low temperature oven, and samples of calcium peroxide were placed in the bomb in platinum boats. The temperature of the reactor was measured by a thermocouple on the outside of the bomb, which had been calibrated against boiling water. It is estimated that temperatures were measured within 1°C .

It was found that needle valves were unsatisfactory for holding the oxygen pressures for long periods of time. Thus at high

pressures, about 1000 psia, a check valve was used; at about 100 psia, a standard oxygen regulator maintained a constant pressure in spite of small leaks. The pressure gages were of the Bourdon type, and were calibrated against a deadweight tester. For studies at atmospheric pressure, samples were supported in a desiccator through which a stream of dry oxygen was passed.

Oxygen from a commercial cylinder, reported to be not less than 99.5% pure was passed through soda-lime and phosphorus pentoxide, in succession, to remove any carbon dioxide or water which might be present. A boat containing phosphorus pentoxide was also placed in the reaction vessel.

All samples of calcium peroxide studied were dried in an oxygen atmosphere at room temperature over phosphorus pentoxide for a minimum duration of a month. Previous work has established that this will remove all water of hydration which may be present. One sample studied was a commercial product which had approximately the following analysis; before drying.

CaO ₂	55 - 60%
CaO	15 - 20%
CaCO ₃	7 - 8%
Ca(OH) ₂	12 - 13%
H ₂ O	1 - 1 1/2%

Other, purer, samples of calcium peroxide were prepared by mixing 90% aqueous hydrogen peroxide with a saturated solution of calcium chloride and adding ammonium chloride to precipitate calcium peroxide. The product was washed and then dried over phosphorus pentoxide at room temperature for a minimum of one month. After drying, the solid contained 90 - 95% calcium peroxide. The remainder was assumed to be calcium hydroxide. Decomposition of calcium peroxide during the drying was found to be negligible.

In each run the bomb was first flushed with oxygen, and after the run was completed, the bomb was allowed to cool before releasing the oxygen. The sample of calcium peroxide was analyzed immediately after removal from the reaction vessel.

Each sample weighed about 0.25-0.35 grams and was spread out in a thin layer of about 1 mm thick. The calcium peroxide consisted of agglomerates varying in the general range of 0.1 to 1 mm in diameter.

The procedure for analysing the calcium peroxide was to add about 0.3 grams of calcium peroxide to 50 ml. of water, added slowly to avoid the heat of hydration of the lime. This was dissolved by the addition of dilute hydrochloric acid and then titrated with 0.1 N potassium permanganate solution. Blanks were carried out with equal samples of lime.

RESULTS

Studies were made at oxygen pressures of 1525, 1000, 115 and 14.7 psia, with the results given in Tables 2-5. The studies at 1000, 1525, and 115 psia were made with commercial grade calcium peroxide which averaged about 60% CaO_2 initially. Those at 14.7 psia were made with the high purity calcium peroxide. Additional tests were also made at 1000 and 115 psia to see if the same results would be obtained with the two different samples.

Table 2

Studies at 1525 psia. Time Duration, 24 hours

Temp. (°C)	% of original CaO_2 decomposed
103	0
108	0
110	0
113	35
123	97
128	99+
130	99+

Table 4
(Cont.)

High Purity Calcium Peroxide

Temp (°C)	% of calcium peroxide decomposed
95°0	0
99	1.05

Table 5

Studies at 14.7 psia. Time Duration, two weeks.
High Purity Calcium Peroxide

Temp (°C)	% of calcium peroxide
58	0
61	0
65	0.6%
72	4.9%
76	3% (one week only)
78	5.8%

The formation of calcium peroxide from calcium oxide was attempted under two different experimental conditions, using the same equipment. A sample of reagent grade calcium oxide was found to contain 0.3% calcium peroxide, by solution in acid followed by titration with standardized potassium permanganate solution, after being held at 115 psia and a temperature of 87-89°0 for a period of 28 days. Several titrations were made of the final product, as well as of the starting material, in order to establish definitely the presence of peroxide. Three other samples

of calcium oxide were prepared by calcination of calcium carbonate, calcium acetate, and calcium peroxide, respectively. After 6 days at 735 psia and 100°C, each of these samples contained from 0.14 to 0.17% calcium peroxide. These points are shown on Figure 1.

DISCUSSION

At the two higher pressures studied, the results show an abrupt initiation of substantial calcium peroxide decomposition as the temperature was raised in successive experiments over a few degree interval. From these data the equilibrium temperature may be taken with considerable confidence as $111^{\circ} \pm 2^{\circ}\text{C}$ at 1525 psia and $106 \pm 2^{\circ}\text{C}$ at 1000 psia. These points are shown on Figure 1. At the two lower pressures studied, no such abrupt decomposition was initiated over a short temperature range. Under these conditions the reaction is so slow that it is doubtful that the minimum temperature at which decomposition was observed in each case truly represents an equilibrium temperature.

A check on the accuracy of equilibrium values may be provided by the van't Hoff equation,

$$\frac{d \ln K}{d(1/T)} = \frac{\Delta H}{R} \quad (3)$$

For the case here the equilibrium constant of the reaction, in the form written in equation 1, is simply the oxygen pressure. If the enthalpy change on reaction is constant over the temperature

range studied, a plot of oxygen pressure versus the reciprocal of the absolute temperature should be a straight line, the slope of which equals $\Delta H/R$.

Two determinations of the heat of formation of calcium peroxide have been reported in the literature. An early value was that of M. deForcrand (4) who quoted a heat of the peroxidation reaction of 5.43 kilocalories per mole or -10.86 kilocalories if expressed as the enthalpy change for the reaction as written in Equation 1. From the values for the heat of formation of calcium peroxide and of calcium oxide given in the Thermodynamic Tables of the U.S. Bureau of Standards, the enthalpy change of reaction 1 is -11.2 kilocalories. Their figure for calcium peroxide is from deForcrand. A second determination was made very recently by Vedenev, Kazarnovskaya, and Kazarnovskii (7) who reported the enthalpy of formation of calcium peroxide to be -155.77 kcal/mole. Combining this with the accepted value of -151.9 kcal/mole for calcium oxide gives -7.8 kcal as the enthalpy change of reaction 1, which is a reasonably fair check with the deForcrand value. The equilibrium curve calculated from the van't Hoff equation using the more recent enthalpy data and drawn through the equilibrium points at 1000 and 1525 psia is shown in Figure 1. Extrapolation indicates that the equilibrium temperature at atmospheric pressure would be about -5°C.

These conclusions must be reconciled with the fact that small amounts of calcium peroxide have been formed from calcium oxide and oxygen by both Blumenthal and in the present work under conditions in which calcium peroxide would be expected to be unstable if the system were strictly univariant.

Although in the equivalent reactions involving barium peroxide or strontium peroxide, the systems do appear to be univariant, it appears quite possible that this may not be strictly true here. Since the calcium oxide is quite porous and has a ^{high} surface area, the formation of the small quantities of calcium peroxide found here and by Blumenthal might be attributed to reaction of oxygen with surface molecules whose activity was far different than those comprising the bulk of the mass; in other words, that oxygen might be "chemisorbed" onto the surface to form peroxide-type structures. However, in a gross sense, the system could still be univariant.

To provide a further check on the validity of the equilibrium temperatures determined, a sample of the high purity calcium peroxide containing initially 91.6% CaO_2 was held at 1000 psia and 103.5°C. for 7 days instead of the 24 hours used in other studies at this pressure. The equilibrium temperature has been taken as $106 \pm 2^\circ\text{C}$. for this pressure. At the end of this time, 1.7% of the peroxide initially present had decomposed. This slight degree of reaction might likewise be attributed to a difference in activity between matter on the surface and in the bulk.

Another source of difficulty may be associated with the fact that some quantity of calcium hydroxide is always present in any calcium peroxide studied, whereas none is present when it is attempted to approach the equilibrium from the other side by reaction of calcium oxide and oxygen. The presence of traces of water vapor can cause significant decomposition of calcium peroxide. For example, a sample of calcium peroxide supported in a desiccator over phosphorus pentoxide at 49°C. lost 5% of its peroxygen content when oxygen from a commercial cylinder was slowly passed over it for 9 days. On repeating the experiment but with previous drying of the inlet oxygen with phosphorus pentoxide, no decomposition occurred.

It is apparent from the above that the solid phase appears to be rather complex, and that the equilibrium characteristics of the system are still in considerable doubt, particularly since no substantial amounts of calcium peroxide have yet been formed from calcium oxide and oxygen.

However, from the practical point of view, the results of the present study definitely indicate that the equilibrium relationships in this system are much less favorable for the peroxidation of lime than had been thought previously. It appears that the best chance of obtaining substantial conversion of lime to calcium peroxide would probably be at pressures of at least several hundred atmospheres, at a temperature of about 100°C., under

which conditions the reaction rate might still be extremely slow, even if highly subdivided lime were used.

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