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THE STABILITY OF SMITHSONITE [1]

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ABSTRACT

The P_{CO_2}-T curve for the reaction $ZnCO_3 \rightleftharpoons ZnO + CO_2$ has been determined experimentally up to 50,000 lbs/in.^{2} of CO_2. At 10,000, 30,000 and 50,000 lbs/in.^{2} the curve passes through 310, 410 and 460°C respectively.

INTRODUCTION

THE importance of zinc is evident from the fact that it ranks fourth in tonnage of metals produced in the U.S.A. The most important and widespread zinc ores are sphalerite (ZnS), smithsonite ($ZnCO_3$), hemimorphite ($(ZnOH)_2SiO_3$) and willemite (Zn_2SiO_4), and these four minerals may be associated with one another.

This paper describes the work carried out in order to determine the limits of stability of smithsonite and zincite, according to the equation $ZnCO_3 \rightleftharpoons ZnO + CO_2$, under varying pressures of CO_2 between 5,000 and 60,000 lbs/in.^{2}. Previous attempts to determine the variation in the temperature of dissociation of $ZnCO_3$ were made by Mehmet and Valensi (1) between 0 and 770 mm Hg, but at these low pressures it was not possible to obtain equilibrium.

EXPERIMENTATION AND RESULTS

All the experimental work was carried out in cold seal pressure vessels designed by Tuttle (2). The CO_2 was supplied to these vessels by way of a hydraulic jack pump and the pressure vessels were heated by means of movable furnaces with nichrome windings. The apparatus as a whole has been described previously (3). The pressures were controlled to ± 3 percent and the temperatures to $\pm 5°$ C.

In order to establish that the P_{CO_2}-T curve for the dissociation of $ZnCO_3$ is in fact the thermal equilibrium curve, it was necessary to make the reaction go both ways. Thus, in each of the experimental runs the starting materials consisted of both $ZnCO_3$ and ZnO ($+ CO_2$). The materials which were used are listed below:

1) Basic Zinc Carbonate (Baker's analytical reagent),
2) Natural Smithsonite from Kelly, New Mexico,
3) Neutral Zinc Carbonate,
4) Zinc Oxide (Baker's analytic reagent),
5) Zinc Oxide prepared by heating 1) above.

[1] Contribution No. 55-47 from the College of Mineral Industries, The Pennsylvania State University.

The CO_2 which was used was the Bone Dry grade of the Matheson Company, Inc., New Jersey (99.8% pure).

The natural smithsonite from Kelly was found to be less reactive than the other starting materials and, as its exact composition was not known,

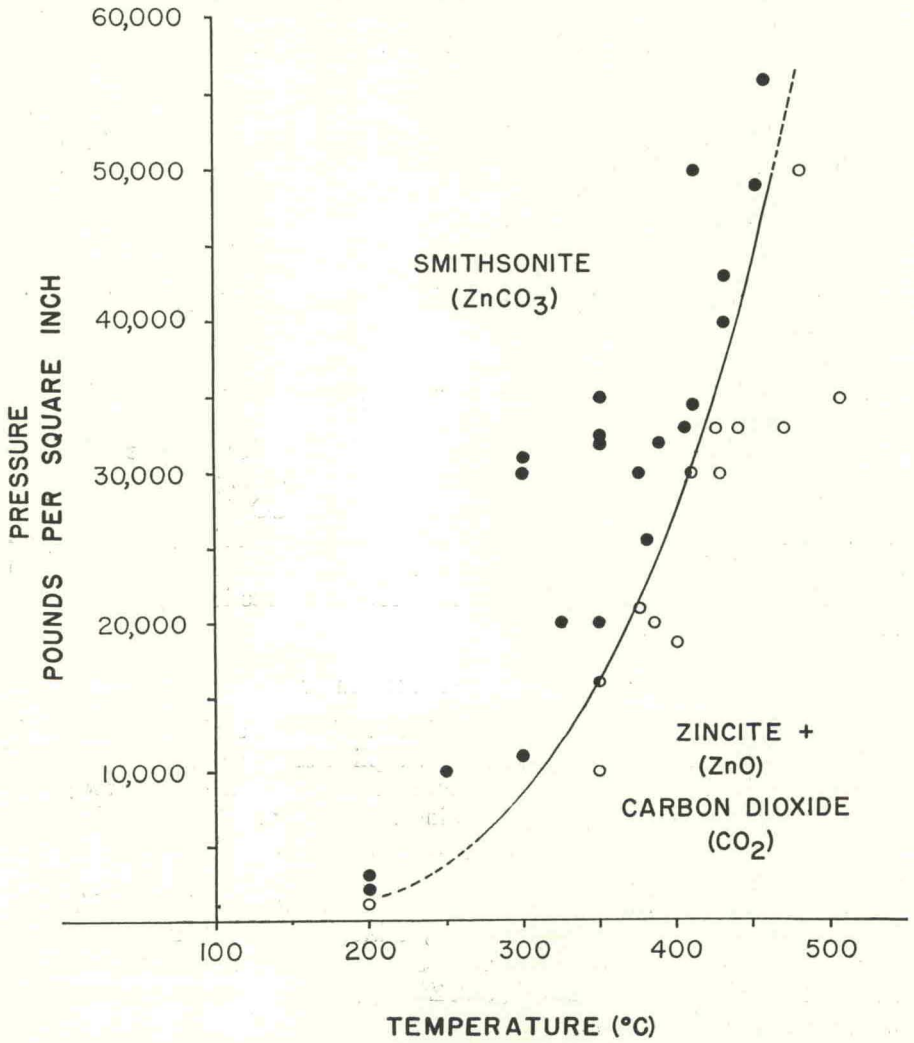

FIG. 1. Univariant pressure (CO_2)-temperature curve for the reaction: $ZnCO_3 \rightleftharpoons ZnO + CO_2$; $ZnCO_3$ stable = ●; $ZnO + CO_2$ stable = o.

it was soon discarded as unsuitable. The neutral zinc carbonate was made by placing an intimate mixture of zinc sulphate and sodium bicarbonate in a Morey bomb containing solid carbon dioxide. The bomb was then sealed and heated at 160° C for two days. After this treatment the product was

thoroughly washed, leaving very fine grained neutral zinc carbonate which was then dried and ready for use.

The starting materials were wrapped in gold foil and placed in the pressure vessel. On the high temperature side of the curve, the ZnO was stable and the $ZnCO_3$ decomposed. On the low temperature side, $ZnCO_3$ was stable and the ZnO combined with CO_2 to form carbonate. It was not necessary for the reaction to go to completion and the runs had to be made only for a sufficient length of time to show in which direction the reaction was going. For example, if at the end of a run it was found that $ZnCO_3$ had recrystallized but that ZnO showed small rims of $ZnCO_3$ then the P-T conditions of the run lay on the low-temperature side of the P-T curve. Likewise, only a small amount of $ZnCO_3$ had to decompose to indicate that a run was made on the high-temperature side of the curve. The products were identified with the aid of the X-ray spectrometer and the petrographic microscope.

The successful runs made to determine the P_{CO_2}-T curve for the reaction $ZnCO_3 \rightleftharpoons ZnO + CO_2$ are listed in Table 1 from which the curve in Figure 1 has been drawn. It was found that reaction was aided considerably when the starting materials were moistened with a little water to act as a flux. This procedure has been adopted with much success in similar experiments, e.g. during the study of the reaction $CaCO_3 + SiO_2 \rightleftharpoons CaSiO_3 + CO_2$(4). In Table 1, the runs in which the samples were dry are labeled 'd' and the ones in which they were moistened are labeled 'w'. Experiments 20 and 25, run on the low-temperature side of the curve under the same conditions of pressure and temperature and for approximately the same length of time, illustrate the effectiveness of having a little water present. In the former, the conversion of ZnO to $ZnCO_3$ is almost complete whereas in the latter, in which dry samples were used, only a very small trace of $ZnCO_3$ developed from one of the oxides.

In the majority of the runs the basic zinc carbonate was found to be the most sensitive starting material. In run 15 for example (a relatively short run at only moderate pressure and fairly close to the P-T curve) it was the only starting material to react. On heating, the water from the hydroxide component was readily given off leaving $ZnCO_3 + ZnO$ (see run 18). Runs on the high-temperature side of the curve were indicated by an increase of ZnO at the expense of $ZnCO_3$, over and above that derived from $Zn(OH)_2$, while on the low temperature side of the curve, $ZnCO_3$ increased at the expense of the ZnO derived from the $Zn(OH)_2$. The relative amounts of $ZnCO_3$ and ZnO were estimated by a comparison of the intensities of the {211} $ZnCO_3$ peak and the $\{10\bar{1}1\}$ $\{10\bar{1}0\}$ and {0002} ZnO peaks of the X-ray powder diffraction patterns.

Of the two oxides which were used, one was frequently more reactive than the other, but as it was not possible to predict which would be the more reactive in a proposed run, both were usually put in together.

The products of runs 21 and 46 have been taken to indicate that the P-T conditions of these runs lie on the univariant curve because in them

TABLE 1

Run No.	Initial materials		Pressure $\times 10^{-3}$ lbs/in.^{2}	Temperature °C	Time hrs.	Products
54	*ZnO*	w	56	456	21	$ZnCO_3$ + ZnO
	Basic Zn Carb.	w	56	456	21	$ZnCO_3$
	$ZnCO_3$	w	56	456	21	$ZnCO_3$
	ZnO c.p.	w	56	456	21	ZnO
36	*ZnO*	w	50	410	18	$ZnCO_3$
	Basic Zn Carb.	w	50	410	18	$ZnCO_3$
	$ZnCO_3$	w	50	410	18	$ZnCO_3$
	ZnO c.p.	w	50	410	18	$ZnCO_3$
55	*ZnO*	d	50	480	24	ZnO
	Basic Zn Carb.	d	50	480	24	ZnO
	$ZnCO_3$	d	50	480	24	ZnO
	ZnO c.p.	d	50	480	24	ZnO
53	*ZnO*	w	49	450	38	$ZnCO_3$ + ZnO
	Basic Zn Carb.	w	49	450	38	$ZnCO_3$ + ZnO
	$ZnCO_3$	w	49	450	38	$ZnCO_3$
	ZnO c.p.	w	49	450	38	$ZnCO_3$
38	*ZnO*	d	40	430	85	ZnO + $ZnCO_3$
	Basic Zn Carb.	d	40	430	85	$ZnCO_3$
	$ZnCO_3$	d	40	430	85	$ZnCO_3$
	ZnO c.p.	d	40	430	85	ZnO
16	*ZnO*	w	35	350	32	$ZnCO_3$ + ZnO
	ZnO c.p.	w	35	350	32	$ZnCO_3$ + ZnO
8	$ZnCO_3$	d	35	505	21	ZnO
	ZnO c.p.	d	35	505	21	ZnO
41	*ZnO*	d	34.5	410	516	$ZnCO_3$
	Basic Zn Carb.	d	34.5	410	516	$ZnCO_3$ (+ ZnO)
	ZnO c.p.	d	34.5	410	516	ZnO + $ZnCO_3$
18	Basic Zn Carb.	d	33	390	0.25	$ZnCO_3$ + ZnO
7	Basic Zn Carb.	d	33	405	61	$ZnCO_3$ (+ ZnO)
13	Basic Zn Carb.	d	33	425	43	ZnO
	$ZnCO_3$	d	33	425	43	ZnO
	ZnO c.p.	d	33	425	43	ZnO
10	Basic Zn Carb.	d	33	440	16	ZnO
	$ZnCO_3$	d	33	440	16	ZnO
	ZnO c.p.	d	33	440	16	ZnO
9	Basic Zn Carb.	d	33	470	16	ZnO
	$ZnCO_3$	d	33	470	16	ZnO
	ZnO c.p.	d	33	470	16	ZnO
16	Basic Zn Carb.	w	32.3	350	32	$ZnCO_3$ (+ ZnO)
	$ZnCO_3$	w	32.3	350	32	$ZnCO_3$ (+ ZnO)
5	Basic Zn Carb.	d	32	350	22.5	$ZnCO_3$ (+ ZnO)
6	Basic Zn Carb.	d	32	390	17.5	$ZnCO_3$ (+ ZnO)
3	Basic Zn Carb.	d	31	300	16	$ZnCO_3$ (+ ZnO)
4	Basic Zn Carb.	d	30	300	29	$ZnCO_3$ (+ ZnO)
25	*ZnO*	d	30	375	26	ZnO (+ $ZnCO_3$)
	ZnO c.p.	d	30	375	26	ZnO
20	*ZnO*	w	30	375	25	$ZnCO_3$ (+ ZnO)
	Basic Zn Carb.	w	30	375	25	$ZnCO_3$
	$ZnCO_3$	w	30	375	25	$ZnCO_3$
	ZnO c.p.	w	30	375	25	$ZnCO_3$

ZnO c.p. = Zinc Oxide (Baker's analytical reagent).
Basic Zn Carb. = Basic Zinc Carbonate ($mZnCO_3.nZn(OH)_2$, Baker's analytical reagent).
ZnO = Zinc Oxide prepared by heating the Basic Zinc Carbonate at atmospheric pressure.
$ZnCO_3$ = Zinc Carbonate prepared from Zinc Sulfate and Sodium Bicarbonate under a pressure of CO_2.
(+ $ZnCO_3$) or (+ ZnO) = Zinc Carbonate or Zinc Oxide occurring in very small amounts in the products.

TABLE 1—*Continued*

Run No.	Initial materials	Pressure $\times 10^{-3}$ lbs/in.^{2}	Temperature °C	Time hrs.	Products
21	*ZnO* w	30	410	28	ZnO (+ $ZnCO_3$)
	Basic Zn Carb. w	30	410	28	ZnO + $ZnCO_3$
	$ZnCO_3$ w	30	410	28	ZnO
	ZnO c.p. w	30	410	28	$ZnCO_3$ + ZnO
23	*ZnO* d	30	427	25	ZnO
	Basic Zn Carb. d	30	427	25	ZnO
	$ZnCO_3$ d	30	427	25	ZnO
	ZnO c.p. d	30	427	25	ZnO
43	*ZnO* d	23.5	380	128	ZnO (+ $ZnCO_3$)
	Basic Zn Carb. d	23.5	380	128	$ZnCO_3$ (+ ZnO)
	$ZnCO_3$ d	23.5	380	128	$ZnCO_3$
	ZnO c.p. d	23.5	380	128	ZnO
15	*ZnO* d	21	375	26.5	ZnO
	Basic Zn Carb. d	21	375	26.5	ZnO
	$ZnCO_3$ d	21	375	26.5	$ZnCO_3$
	ZnO c.p. d	21	375	26.5	ZnO
19	*ZnO* w	20	325	17	$ZnCO_3$ (+ ZnO)
	Basic Zn Carb. w	20	325	17	$ZnCO_3$
	$ZnCO_3$ w	20	325	17	$ZnCO_3$
	ZnO c.p. w	20	325	17	$ZnCO_3$ + ZnO
24	*ZnO* w	20	350	25	$ZnCO_3$ + ZnO
	Basic Zn Carb. w	20	350	25	$ZnCO_3$ + ZnO
	$ZnCO_3$ w	20	350	25	$ZnCO_3$
	ZnO c.p. w	20	350	25	$ZnCO_3$
52	*ZnO* d	20	385	78	ZnO
	Basic Zn Carb. d	20	385	78	ZnO
	$ZnCO_3$ d	20	385	78	ZnO
	ZnO c.p. d	20	385	78	ZnO
2	Basic Zn Carb. d	18.7	400	17	ZnO
	ZnO c.p. d	18.7	400	17	ZnO
46	*ZnO* d	16	350	105.5	ZnO + $ZnCO_3$
	Basic Zn Carb. d	16	350	105.5	ZnO + $ZnCO_3$
	$ZnCO_3$ d	16	350	105.5	$ZnCO_3$
	ZnO c.p. d	16	350	105.5	ZnO
17	*ZnO* w	11	300	59.5	ZnO
	Basic Zn Carb. w	11	300	59.5	ZnO
	$ZnCO_3$ w	11	300	59.5	$ZnCO_3$
	ZnO c.p. w	11	300	59.5	ZnO
26	*ZnO* w	11	300	131	ZnO + $ZnCO_3$
	Basic Zn Carb. w	11	300	131	$ZnCO_3$
	$ZnCO_3$ w	11	300	131	$ZnCO_3$
	ZnO c.p. w	11	300	131	$ZnCO_3$
22	*ZnO* w	10	250	168	$ZnCO_3$
	Basic Zn Carb. w	10	250	168	$ZnCO_3$
	$ZnCO_3$ w	10	250	168	$ZnCO_3$
	ZnO c.p. w	10	250	168	$ZnCO_3$
11	*ZnO* w	10	350	94	ZnO
	Basic Zn Carb. w	10	350	94	ZnO (+ $ZnCO_3$)
	$ZnCO_3$ w	10	350	94	ZnO
	ZnO c.p. w	10	350	94	ZnO
45	*ZnO* d	3	200	640	ZnO + $ZnCO_3$
	ZnO d	2	200	337	ZnO (+ $ZnCO_3$)
	ZnO d	1	200	1222	ZnO

there has been no detectable growth either of carbonate or of oxide from the basic zinc carbonate. The other products of run 21 provide rather conflicting evidence: the oxides have formed carbonate and the zinc carbonate has formed oxide. These results are probably due to small tempera-

ture changes and gradients which are effective in causing phase changes in runs so close to the P-T curve.

The formation of ZnO from $ZnCO_3$ in run 16 and from the basic zinc carbonate in run 17 is not easy to explain but may be due to the P-T conditions momentarily entering the field of zincite + carbon dioxide during the initial heating. Once zincite has crystallized it would probably be sufficiently coarse grained, especially if moisture were present initially, to make it difficult for it to revert to carbonate. A comparison of runs 17 and 26 show that, even with a little moisture present, long runs are necessary to determine which phases are stable at low pressures and temperatures when these are close to the P-T curve.

As is usually the case with P-T curves of this nature, it is possible to draw a variety of different curves between the experimentally determined critical points. In the present study it is considered that the most accurate part of the curve is that which lies between 15,000 and 35,000 lbs/in.^{2}. From the slope of the curve at 20,000 lbs/in.^{2} and 368° C and from Kennedy's tables for the P-V-T relations in CO_2 (5) it is estimated that the approximate value for the enthalpy of the reaction under these P-T conditions is 10.8 kcals/mole.

DISCUSSION OF RESULTS

The P-T curve for the dissociation of smithsonite lies at lower temperatures than any other P_{CO_2}-T curve determined at such elevated pressures. Between 10,000 and 40,000 lbs/in.^{2} it lies approximately 400° C below the corresponding P-T curve for the dissociation of magnesite (3) and approximately 350° C below the curve for the reaction: calcite + quartz $\rightleftharpoons$ wollastonite + carbon dioxide (4).

It is perhaps surprising that zincite is not a more common mineral in view of the low temperatures of dissociation of smithsonite. It is to be expected that even under high pressures of CO_2 a low grade of metamorphism would be sufficient to drive off the CO_2 from the smithsonite. In the presence of sufficient silica, however, willemite would be expected to form instead of zincite, or, with sufficient water pressure, hemimorphite would be produced.

A low temperature of formation has always been suggested for smithsonite on the basis of its paragenesis. It is commonly associated with other low temperature minerals, such as hemimorphite, goethite, limonite, siderite and cerussite, and it is frequently said to have developed by the alteration of sulfides by meteoric waters, e.g., $ZnS + H_2CO_3 \rightleftharpoons ZnCO_3 + H_2S$. It is possible that smithsonite and zincite could be formed in a variety of ways in the earth's crust: by primary crystallization, hydrothermal alteration or metamorphism. However, no matter what reactions are involved, provided the phases are pure and crystallized in equilibrium, the presence of smithsonite or zincite indicates on which side of the P-T curve the conditions of formation lay.

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