

## PHASE RELATIONS IN THE SYSTEM $\text{PbO-CO}_2$ AND THE DECOMPOSITION OF CERUSSITE<sup>1</sup>

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### ABSTRACT

The decomposition of  $\text{PbCO}_3$  has been investigated by equilibrium methods over the range of 200 to 900° C. and 15 to 1400 bars  $\text{P}_{\text{CO}_2}$ . The four intermediate oxycarbonate phases are  $2\text{PbCO}_3 \cdot \text{PbO}$ ,  $\text{PbCO}_3 \cdot \text{PbO}$ ,  $\text{PbCO}_3 \cdot 2\text{PbO}$ , and  $4\text{PbCO}_3 \cdot 3\text{PbO}$ ; these have been characterized by optical and x-ray powder data. The P-T phase projection for the solid-vapor reactions in the system exhibits solid-vapor invariant points at 530° C. and 207 bars and at 570° C. and 380 bars. The liquidus temperature falls rapidly with increasing  $\text{CO}_2$  pressure and invariant points marking the intersection of SSV curves with the liquidus occur at 755° C. and 145 bars and at 670° C. and 1200 bars. Infrared spectra of the lead oxycarbonates have been obtained.

### INTRODUCTION

Although the stability relations of many of the common carbonate minerals have been studied in detail, some of the more complicated systems are not yet completely understood. One of these is cerussite. The  $\text{PbO-CO}_2$  system is complicated by the existence of a series of oxycarbonate compounds, intermediate in composition between  $\text{PbCO}_3$  and  $\text{PbO}$ . Very little information is available concerning the composition, structure or even the number of these compounds.

Previous work on the  $\text{PbO-CO}_2$  system has utilized dynamic methods, namely differential thermal analysis and thermogravimetric analysis, to study the decomposition of cerussite. Warne and Bayliss (1962) have made the most recent redetermination of the DTA pattern of cerussite. These authors give a complete discussion of the earlier literature which need not be repeated here.

A summary of the DTA and TGA results in the literature, is given in Fig. 1. The effects of non-equilibrium methods are clearly illustrated. Reactions conducted in  $\text{CO}_2$  are reasonably consistent at high temperatures but inconsistent at low temperatures as would be expected if the reactions were somewhat sluggish. Reactions conducted in air, in which the true vapor pressure of  $\text{CO}_2$  in the reaction vessel is not known, are almost completely inconsistent. There is also considerable uncertainty about the number and composition of compounds within the system.

In the study reported here, we have attempted to overcome these prob-

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lems by using equilibrium rather than dynamic methods and by using known pressures of CO<sub>2</sub>. In this way the equilibrium diagram can be obtained and the intermediate compounds characterized in some detail.

### EXPERIMENTAL METHODS

The phase projection for the system PbO-CO<sub>2</sub> was determined by reacting both PbO and PbCO<sub>3</sub> in individual open gold capsules to a common end product at high CO<sub>2</sub> pressures followed by quenching and examination of the products. The length of most runs was from 20 to 36 hours.

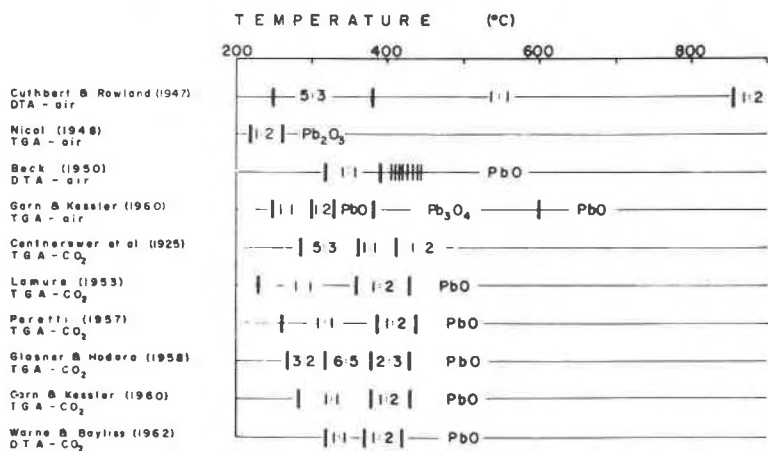


FIG. 1. Comparison of decomposition temperatures of lead oxycarbonates reported in the literature.

The high pressure "hydrothermal" apparatus used was similar to that described by Harker and Tuttle (1955). Measurements were made over the range of 200–900° C. and 15 to 1400 bars of CO<sub>2</sub>. Temperatures were measured by chromel-alumel thermocouples and should be accurate to  $\pm 5^\circ$  C. CO<sub>2</sub> was obtained from commercial tanks; pressure was measured by stainless steel bourdon tube gauges and should be accurate to  $\pm 5\%$ . To avoid the reduction of the lead compounds to metallic lead by traces of organic impurities the entire high pressure system was cleaned by a series of acetone flushings and evacuations.

Products of all runs were examined under the petrographic microscope and the phases determined by x-ray diffractometry. Precise x-ray powder data reported here were obtained by scanning glass slide mounts in a Norelco diffractometer using silicon metal as an internal standard.

Infra-red spectra were obtained on a Perkin-Elmer Model 21 Spec-

trophotometer equipped with KBr and NaCl prisms using the KBr disc technique.

Formulae for the lead oxycarbonates were determined by gravimetric ignition. Pure oxycarbonate samples were placed in weighed platinum capsules, dried to constant weight, and then heated to constant weight at 650° C. in a nitrogen atmosphere. This yielded the per cent weight loss of CO<sub>2</sub> and from this value the ratio of PbCO<sub>3</sub> to PbO was calculated.

#### CHARACTERIZATION OF THE LEAD OXYCARBONATES

The lead oxycarbonates are white and possess indices of refraction greater than methylene iodide (1.736). CO<sub>2</sub> pressures of the order of 700

TABLE 1. WEIGHT LOSS ANALYSES

| Assigned Formula         | Preparation Conditions |         |         | % Weight Loss (actual) | % Weight Loss (theoretical) |
|--------------------------|------------------------|---------|---------|------------------------|-----------------------------|
|                          | P (psi)                | T (° C) | Time    |                        |                             |
| 2PbCO <sub>3</sub> ·PbO  | 5,000                  | 550     | week    | 11.69                  | 11.62                       |
|                          | 10,000                 | 585     | week    | 11.63                  |                             |
| PbCO <sub>3</sub> ·PbO   | 1,100                  | 465     | week    | 8.92                   | 8.97                        |
|                          | 1,100                  | 465     | 2 weeks | 8.91                   |                             |
| PbCO <sub>3</sub> ·2PbO  | 2,500                  | 625     | week    | 6.43                   | 6.16                        |
|                          | 8,200                  | 675     | 2 weeks | 6.28                   |                             |
| 4PbCO <sub>3</sub> ·3PbO | 15,000                 | 640     | week    | 10.10                  | 10.13                       |
|                          | 15,000                 | 635     | week    | 10.34                  |                             |
|                          | 14,000                 | 635     | week    | 9.97                   |                             |

bars were used to prepare samples for optical studies since lower pressure preparations tend to be poorly crystallized, appearing as cryptocrystalline aggregates.

The compositions of the lead oxycarbonates as determined by weight loss analysis are given in Table 1.

The lattice spacings are easily reproducible while intensities are at best rough approximations since these vary appreciably with the P-T conditions of formation. The results for all the compounds are presented in Table 2. The data in Table 2 for PbCO<sub>3</sub>·PbO and PbCO<sub>3</sub>·2PbO are in very poor agreement with the d-spacings obtained by Peretti (1957). Since Peretti obtained his materials at low pressures and temperatures, they are poorly crystallized as shown by the broadened peaks in his powder photographs. This may offer an explanation for the differences.

*2 PbCO<sub>3</sub>·PbO*. This compound possesses the highest degree of crystallinity of all the lead oxycarbonates. Optically, it is uniaxial negative and shows positive elongation. High pressure runs of relatively long duration, *i.e.* 700 bars for one week, showed an abundance of platy fragments. Many of these fragments showed partial or complete hexagonal outlines which yielded uniaxial optic axis interference figures thereby indicating a hexagonal compound with a well developed basal cleavage.

TABLE 2A. X-RAY POWDER DATA, 2PbCO<sub>3</sub>·PbO

| d     | I   | hkl      | d      | I  | hkl           |
|-------|-----|----------|--------|----|---------------|
| 6.948 | 10  | 002      | 1.408  | 1  | 304           |
| 4.625 | 10  | 100, 003 | 1.394  | 2  | 216           |
| 4.382 | 1   | 101      | 1.388  | 4  |               |
| 3.860 | 1   | 102      | 1.3111 | 2  | 222, 217      |
| 3.471 | 40  | 004      | 1.2825 | 6  | 306, 223, 310 |
| 3.271 | 65  | 103      | 1.2771 | 2  | 311           |
| 2.669 | 65  | 110      | 1.2362 | 1  | 313           |
| 2.379 | 2   | 105      | 1.2316 | 2  |               |
| 2.311 | 100 | 200, 006 | 1.2170 | 6  |               |
| 2.281 | 3   | 201      | 1.1563 | 15 | 400           |
| 2.115 | 1   | 114      | 1.1218 | 6  | 403           |
| 2.067 | 30  | 203, 106 | 1.1075 | 2  |               |
| 1.821 | 4   | 107      | 1.0612 | 6  | 320           |
| 1.747 | 15  | 210, 116 | 1.0398 | 4  |               |
| 1.734 | 10  | 211      | 1.0342 | 2  | 323           |
| 1.634 | 10  | 213      | 1.0316 | 2  |               |
| 1.560 | 1   | 214      | 0.9912 | 4  | 325           |
| 1.541 | 1   | 300      | 0.9692 | 5  |               |
| 1.504 | 2   | 302      | 0.9621 | 2  |               |
| 1.462 | 30  | 303      |        |    |               |

The compound was indexed on a hexagonal unit cell with parameters of  $a = 5.339 \text{ \AA}$  and  $c = 16.03 \text{ \AA}$ . Almost all the lines are accounted for using these parameters, but a few weak non-indexable reflections are present thereby suggesting that the compound possibly has a hexagonal subcell for a larger super-lattice. X-ray intensities also indicate a possible 100 cleavage. In both the h00 and 00l planes, the even numbered values of h and l are strong reflections while odd numbered values are very weak.

*PbCO<sub>3</sub>·PbO*. The stability field of this compound is well below the CO<sub>2</sub> pressures used to prepare the other lead oxycarbonates. Although runs of two weeks duration produced very few observable crystal fragments, the addition of water enhanced crystallinity to the point that optical exami-

TABLE 2B. X-RAY POWDER DATA,  $\text{PbCO}_3 \cdot \text{PbO}$ 

| <i>d</i> | <i>I</i> | <i>d</i>                              | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> |
|----------|----------|---------------------------------------|----------|----------|----------|----------|----------|
| 6.478    | 20       | 1.933                                 | 15       | 1.536    | 4        | 1.1963   | 8        |
| 4.135    | 30       | 1.910                                 | 35       | 1.499    | 6        | 1.1717   | 8        |
| 4.024    | 55       | 1.887                                 | 7 B      | 1.486    | 10       | 1.1567   | 3        |
| 3.449    | 2        | 1.841                                 | 3 B      | 1.467    | 10       | 1.1468   | 4        |
| 3.385    | 15       | 1.822                                 | 10       | 1.441    | 4        | 1.1414   | 6        |
| 3.223    | 100      | 1.811                                 | 9 B      | 1.423    | 6        | 1.1157   | 7        |
| 3.182    | 95       | 1.801                                 | 4 B      | 1.382    | 6        | 1.1005   | 6        |
| 2.935    | 30       | 1.750                                 | 15       | 1.370    | 3        | 1.0933   | 4        |
| 2.859    | 60       | 1.731                                 | 25       | 1.348    | 6        | 1.0793   | 2        |
| 2.737    | 4        | 1.720                                 | 15       | 1.3324   | 6        | 1.0700   | 4        |
| 2.652    | 20       | 1.694                                 | 15       | 1.3164   | 6        | 1.0623   | 7        |
| 2.568    | 40       | Remainder of peaks<br>generally broad |          | 1.3084   | 3        | 1.0502   | 5        |
| 2.498    | 6 B      |                                       |          | 1.2954   | 6        | 1.0372   | 4        |
| 2.471    | 4 B      | 1.667                                 | 7        | 1.2848   | 5        | 1.0243   | 4        |
| 2.328    | 20       | 1.654                                 | 15       | 1.2737   | 20       | 1.0147   | 4        |
| 2.288    | 30       | 1.632                                 | 7        | 1.2611   | 6        | 0.9881   | 4        |
| 2.253    | 35       | 1.619                                 | 6        | 1.2533   | 8        | 0.9769   | 5        |
| 2.183    | 35       | 1.608                                 | 6        | 1.2483   | 7        | 0.9666   | 4        |
| 2.160    | 15       | 1.597                                 | 30       | 1.2396   | 9        | 0.9539   | 3        |
| 2.063    | 15       | 1.580                                 | 15       | 1.2254   | 4        | 0.9410   | 4        |
| 2.013    | 25       | 1.558                                 | 4        | 1.1995   | 9        |          |          |

nation was possible. The compound is biaxial negative, orthorhombic, shows positive elongation and possesses a rather large  $2V$  estimated at  $60^\circ$ – $70^\circ$ . Pinacoidal and dome cleavages are present, the dome being preferred as indicated by a dominance of off-center acute bisectrix figures.

Diffraction peaks were rounded and often occurred as clusters of reflections whose resolution decreased at higher angles.

TABLE 2C. X-RAY POWDER DATA,  $\text{PbCO}_3 \cdot 2\text{PbO}$ 

| <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i>                              | <i>I</i> | <i>d</i> | <i>I</i> |
|----------|----------|----------|----------|---------------------------------------|----------|----------|----------|
| 7.070    | 4        | 2.776    | 100      | 1.790                                 | 20       | 1.434    | 5        |
| 5.553    | 15       | 2.659    | 2        | 1.759                                 | 15       | 1.418    | 2        |
| 4.566    | 4        | 2.427    | 2        | 1.714                                 | 10       | 1.386    | 5        |
| 4.457    | 9        | 2.368    | 3        | 1.696                                 | 5        | 1.2923   | 10       |
| 4.015    | 3        | 2.349    | 8        | Remainder of peaks<br>generally broad |          | 1.1837   | 2        |
| 3.598    | 2        | 2.280    | 7        |                                       |          | 1.1419   | 3        |
| 3.523    | 2        | 2.189    | 5        | 1.680                                 | 7        | 1.1220   | 3        |
| 3.005    | 55       | 2.048    | 15       | 1.640                                 | 9        | 1.1088   | 5        |
| 2.939    | 25       | 1.997    | 5        | 1.571                                 | 15       |          |          |
| 2.875    | 35       | 1.847    | 10       | 1.504                                 | 6        |          |          |

*PbCO<sub>3</sub>·2PbO*. Optical examination of this compound shows it to be biaxial, negative and orthorhombic with  $2V=50^{\circ}$ - $55^{\circ}$ . Crystals show three well defined pinacoidal cleavages and a platy habit. Occasional groups of fragments were observed which showed cleavages and habit, appearing as stacked rectangular plates.

TABLE 2D. X-RAY POWDER DATA, 4PbCO<sub>3</sub>·3PbO

| <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i>           | <i>I</i> |
|----------|----------|----------|----------|----------|----------|--------------------|----------|
| 7.115    | 7        | 2.466    | 2        | 1.732    | 5        | 1.3288             | 4        |
| 7.031    | 20       | 2.447    | 3        | 1.724    | 6        | Remainder of peaks |          |
| 6.992    | 20       | 2.361    | 5        | 1.722    | 9        | broad              |          |
| 6.190    | 7        | 2.338    | 3        | 1.718    | 9        | 1.3222             | 2 B      |
| 5.720    | 10       | 2.312    | 4        | 1.695    | 2        | 1.3184             | 2        |
| 5.173    | 7        | 2.267    | 20       | 1.686    | 3        | 1.3152             | 3        |
| 4.172    | 10       | 2.201    | 4        | 1.676    | 10       | 1.3093             | 3        |
| 4.620    | 3        | 2.194    | 4        | 1.662    | 15       | 1.3082             | 3        |
| 4.420    | 55       | 2.185    | 7        | 1.658    | 15       | 1.3039             | 3        |
| 3.822    | 6        | 2.154    | 20       | 1.652    | 15       | 1.3009             | 3        |
| 3.639    | 15       | 2.148    | 20       | 1.640    | 3        | 1.2604             | 3        |
| 3.539    | 15       | 2.140    | 15       | 1.625    | 6        | 1.2501             | 3        |
| 3.346    | 3        | 2.075    | 20       | 1.611    | 5        | 1.2475             | 4        |
| 3.285    | 50       | 2.070    | 20       | 1.605    | 3        | 1.2334             | 5        |
| 3.250    | 20       | 2.055    | 3        | 1.602    | 6        | 1.1812             | 2        |
| 3.236    | 20       | 2.024    | 6        | 1.548    | 6        | 1.1574             | 3        |
| 3.224    | 35       | 2.018    | 5        | 1.561    | 3 B      | 1.1558             | 4        |
| 2.994    | 100      | 1.993    | 3        | 1.543    | 2 B      | 1.1457             | 9        |
| 2.962    | 15       | 1.958    | 9        | 1.499    | 10       | 1.1254             | 2        |
| 2.862    | 50       | 1.952    | 10       | 1.495    | 20       | 1.1143             | 2        |
| 2.810    | 35       | 1.949    | 15       | 1.464    | 2        | 1.1065             | 3        |
| 2.670    | 10       | 1.919    | 2        | 1.459    | 4 B      | 1.1025             | 3        |
| 2.664    | 15       | 1.906    | 8 B      | 1.450    | 3        | 1.0834             | 7        |
| 2.647    | 7        | 1.871    | 7        | 1.437    | 3 B      | 1.0740             | 2        |
| 2.614    | 5        | 1.858    | 2        | 1.430    | 5        | 1.0564             | 3        |
| 2.599    | 10       | 1.852    | 3        | 1.396    | 4        | 0.9999             | 3        |
| 2.584    | 15       | 1.839    | 4 B      | 1.393    | 4 B      | 0.9971             | 3        |
| 2.553    | 8        | 1.769    | 25       | 1.384    | 5        | 0.9796             | 2        |
| 2.503    | 3        | 1.753    | 20       | 1.344    | 2        | 0.9441             | 2        |
| 2.493    | 3        |          |          |          |          |                    |          |

The x-ray data were not extended above  $2\theta=90^{\circ}$  since the few peaks which occurred above that angle were extremely broad and of very low intensity thus making accurate  $2\theta$  determination impossible.

*4PbCO<sub>3</sub>·3PbO*. This compound, stable at high P-T conditions, has never been reported in literature and is the most difficult to study of all the solid phases of the PbO-CO<sub>2</sub> system.

Optically, it is biaxial, negative and possesses a  $2V$  of  $50^\circ \pm 10^\circ$ . Probably its most distinctive optical feature is its irregular fracture as well as the fact that it appears to possess the highest relief and birefringence of all the lead oxycarbonates. Several cleavages were present which could not be determined and there appeared to be an absence of  $BxO$  figures. While it appeared that both parallel and inclined extinction were present, suggesting a monoclinic crystal, there is some question as to whether the former may not really be slightly inclined, but not sufficiently resolved under the microscope. The latter condition indicates a triclinic compound with interaxial angles close to  $90^\circ$ .

Inconsistent intensities were obtained when powder mounts were made by the usual method and a technique of sieving powder onto a thin film of vaseline had to be adopted to obtain consistent intensities from specimen to specimen. The notable feature of the diffractometer patterns of this compound are its clustered peaks. Many of the broad peaks are composed of two to four reflections.

#### SOLID-VAPOR REACTIONS

The construction of the P-T projection required only the accurate identification of the phases present in order to determine how far  $PbCO_3$  had decomposed and  $PbO$  carbonated. If both capsules had one phase (plus vapor) in common, that phase was the stable one under the P-T conditions of that particular run. Complete conversion was not necessary, only the direction was needed to place the equilibrium point on the projection. If both starting materials had two solid phases (plus vapor) in common, the P-T conditions were considered to lie on a univariant curve.

The stability fields of the solids and liquid phase of the system are represented in the P-T projection (Figure 2) from  $200^\circ$  to  $900^\circ$  C. and 15 to 1400 bars. All the solid-vapor univariant curves possess a characteristic positive slope while the liquidus slope is negative.

The following reactions are found to occur within the range of this study:

1.  $3PbCO_3 \leftrightarrow [2PbCO_3 \cdot PbO] + CO_2$
2.  $2[2PbCO_3 \cdot PbO] \leftrightarrow 3[PbCO_3 \cdot PbO] + CO_2$
3.  $3[PbCO_3 \cdot PbO] \leftrightarrow 2[PbCO_3 \cdot 2PbO] + CO_2$
4.  $[PbCO_3 \cdot 2PbO] \leftrightarrow 3PbO + CO_2$
5.  $PbO \leftrightarrow Liquid$
6.  $[PbCO_3 \cdot 2PbO] \leftrightarrow Liquid$
7.  $[2PbCO_3 \cdot PbO] \leftrightarrow [PbCO_3 \cdot 2PbO] + CO_2$
8.  $7[2PbCO_3 \cdot PbO] \leftrightarrow 3[4PbCO_3 \cdot 3PbO] + 2CO_2$
9.  $3[4PbCO_3 \cdot 3PbO] \leftrightarrow 7[PbCO_3 \cdot 2PbO] + 5CO_2$
10.  $[4PbCO_3 \cdot 3PbO] \leftrightarrow Liquid$

From 17 to 145 bars the reaction sequence with increasing temperature is  $1 \leftrightarrow 2 \leftrightarrow 3 \leftrightarrow 4 \leftrightarrow 5$ , the univariant curve for reaction 5 being estimated.

The lowest pressure invariant point occurs at 755° C. and 145 bars where 1:2, PbO, liquid and vapor coexist. At 530° C. and 207 bars there is a second invariant point at which 2:1, 1:1 and 1:2 coexist with vapor. Between these invariant point pressures, the reaction sequence with increasing temperature is 1↔2↔3↔6. The third invariant point occurs at 570° C. and 380 bars where 2:1, 1:2 and 4:3 coexist with vapor and at

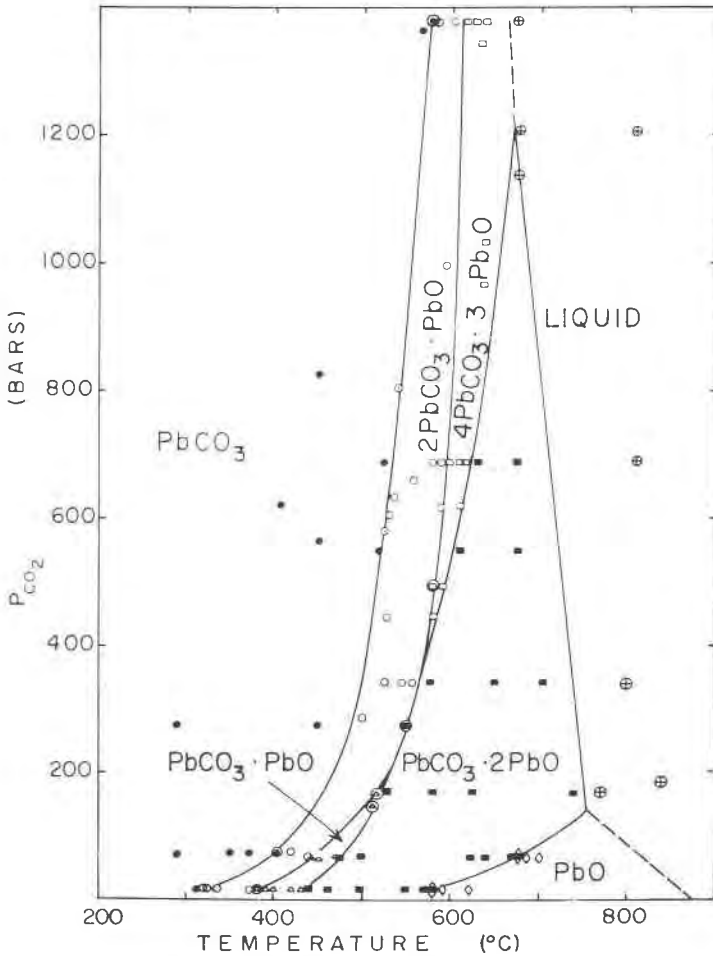


FIG. 2. P-T phase projection for the system PbO-CO<sub>2</sub>. Univariant curves are based on the critical runs shown.

- PbCO<sub>3</sub>
- 2PbCO<sub>3</sub>·PbO
- 4PbCO<sub>3</sub>·3PbO
- △ PbCO<sub>3</sub>·PbO
- PbCO<sub>3</sub>·2PbO
- ◇ PbO
- ⊗ Liquid



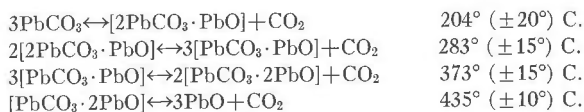
pressures between 207 and 380 bars the reaction sequence is  $1 \leftrightarrow 7 \leftrightarrow 6$ . A fourth invariant point occurs at  $670^\circ \text{C}$ . and 1200 bars at which 1:2, 4:3 and liquid coexist with vapor. The reaction sequence at pressures between 380 and 1200 bars occurs as  $1 \leftrightarrow 8 \leftrightarrow 9 \leftrightarrow 6$ . At pressures above the last invariant point, the reaction sequence is  $1 \leftrightarrow 8 \leftrightarrow 10$ , the univariant curve of reaction 10 being estimated.

The liquidus curve of reaction 6 was located by the physical appearance of the sample. When melting occurred, the sample underwent a large apparent volume change and appeared as a small lump molded to the capsule bottom. The negative slope of the curve implies that the vapor is increasingly soluble in the liquid with increasing pressure.

Although no attempts were made to study reaction kinetics, x-ray identification of the runs indicated the solid-vapor reaction to be rather sluggish, complete conversion requiring a week's duration.

Runs were plotted on a  $\text{CO}_2$  pressure (log scale) versus reciprocal temperature diagram and the resulting curves extrapolated to one bar  $\text{CO}_2$  in order to compare the results of this study with those previously reported. The plot and literature values are shown in Fig. 3 where, at one atmosphere, the horizontal lines represent the temperature ranges reported in the literature for the various reactions while the vertical marks along these lines indicate individual data. The reactions represented by four of the authors are the successive formation of the 1:1, 1:2 and  $\text{PbO}$  compounds while Glasner and Hodara (1958) indicate two reactions to occur within the reported formation temperature range of the 1:1 compound. Centnerswer's work was not included since it is wrong insofar as the reaction sequence is concerned.

The results of this study when extrapolated suggest the following reactions and their respective temperatures at one atmosphere  $\text{CO}_2$ :



The first reaction has never been reported while the last three reactions are in close agreement to Garn and Kessler (1960) who reported  $283^\circ$ ,  $380^\circ$  and  $430^\circ \text{C}$ . respectively.

The extrapolated reaction temperatures are estimated to be accurate to  $\pm 20^\circ \text{C}$ . From the large range of reaction temperatures, it would appear that equilibrium was not attained in the previous studies. The decrease of temperature ranges with increasing temperature points to the non-equilibrium conditions especially prevalent at lower temperatures where reactions are naturally more sluggish. Even at elevated P-T condi-

tions complete conversion of starting materials generally required a week, thus, one can hardly hope to obtain equilibrium in a DTA or TGA study at one atmosphere CO<sub>2</sub>.

The above discussion points to the reason why the formation of 2 PbCO<sub>3</sub>·PbO has never been reported. The wide range of reported formation temperatures of PbCO<sub>3</sub>·PbO results from the formation of both

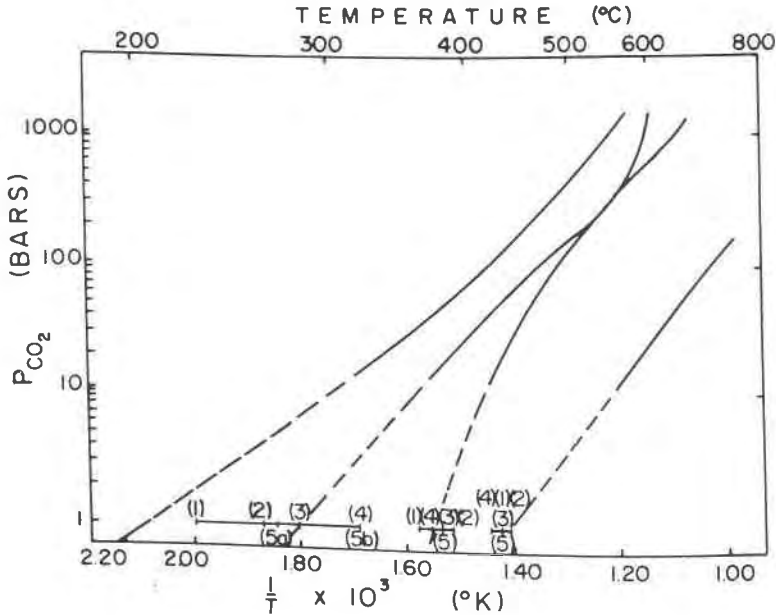


FIG. 3. CO<sub>2</sub> pressure versus reciprocal temperature plot extrapolated to one bar CO<sub>2</sub> for comparison with literature values by: (1) Lamure (1953), (2) Peretti (1957), (3) Garn and Kessler (1960), (4) Warne and Bayliss (1962), and (5) Glasner and Hodara (1958).

compounds since at low temperatures the two reactions overlap one another and appear as one reaction on DTA or TGA apparatus. In only one case (Glasner and Hodara, 1958) has the literature reported two reactions within the above mentioned temperature range, and as one would expect, the recorded temperatures are considerably higher than those suggested by this study.

It would not be meaningful to extrapolate the curves of Fig. 3 to the CO<sub>2</sub> pressure in air (approximately 0.0035 bars) in order to attempt an interpretation of the literature results since it is impossible to predict the composition of the ambient atmosphere surrounding the sample once the decomposition has begun. However, one can be relatively certain that

$\text{PbCO}_3 \cdot 2\text{PbO}$  does not exist in equilibrium with air on the basis of the converging slopes of the third and fourth curves from the left in Fig. 3.

### INFRARED ABSORPTION SPECTRA

There has been much interest lately in relating infrared vibrational frequencies to the structural arrangement of ionic solids. In the case of

TABLE 3. INFRARED ABSORPTION SPECTRA IN NaCl REGION RESULTING FROM INTERNAL VIBRATIONS OF THE CARBONATE ION  
(Frequency in Reciprocal Centimeters)

|                                    | ( $\nu_1$ ) | ( $\nu_2$ ) | ( $\nu_3$ )    | ( $\nu_4$ )                  |
|------------------------------------|-------------|-------------|----------------|------------------------------|
| $\text{PbCO}_3$                    | 1049        | 837         | (1425)<br>1393 | (688)<br>677<br>(668)        |
| $2\text{PbCO}_3 \cdot \text{PbO}$  |             | 827         | 1389           | 697<br>688<br>675<br>(668)   |
| $\text{PbCO}_3 \cdot \text{PbO}$   | 1048        | 840         | 1422<br>1366   | (689)<br>681<br>(670)        |
| $\text{PbCO}_3 \cdot 2\text{PbO}$  |             | 842<br>835  | 1350<br>1276   | 692<br>669<br>(651)          |
| $4\text{PbCO}_3 \cdot 3\text{PbO}$ |             | 828         | 1383<br>1314   | 696<br>685<br>(673)<br>(669) |

carbonates, the bands are subdivided into a high frequency group arising from the internal vibrations of the carbonate ion and a low frequency group arising from lattice vibrations.

The infrared spectrum and the allowed vibrations of the carbonate ion have been discussed by Herzberg (1945). The only infrared spectrum previously reported for the carbonate containing compounds in this system is that of  $\text{PbCO}_3$ . The  $\text{PbCO}_3$  spectrum obtained in this study disagrees with that of Miller and Wilkins (1952) but agrees with the recent literature of Huang and Kerr (1960) Miller *et al.* (1960), Weir and Lippincott (1961) and Adler and Kerr (1963a).

The notations assigned to the various vibrations in Table 3 correspond

to those used by Herzberg. The free carbonate ion has six fundamental vibrations of which two are nondegenerate and two are doubly degenerate, giving rise to four expected vibration frequencies. The totally symmetric stretching frequency ( $\nu_1$ ) and the out of plane bending frequency ( $\nu_2$ ) are nondegenerate while the asymmetrical stretching and planar bending frequencies,  $\nu_3$  and  $\nu_4$  respectively, are doubly degenerate. The spectra of the carbonate containing solids in the PbO-CO<sub>2</sub> system are so similar to the spectrum of the free carbonate ion given by Herzberg that an unequivocal assignment of the internal vibrations can easily be made.

It is apparent from Fig. 4, that more than four fundamental vibrations appear in the absorption spectrum of the lead carbonates. Most of the bands are split into several components. Such a splitting can result from any of three causes:

- (a) Removal of degeneracy of the vibration due to a low symmetry environment.
- (b) The existence of carbonate ions in two or more non-equivalent sites in the structure.
- (c) Coupling of the fundamental with a low frequency lattice vibration.

The removal of degeneracy occurs in many internal vibration spectra in solids. Adler and Kerr (1963b) have discussed the doubling of bands that occurs when carbonate ions occur in non-equivalent sites.

The symmetric stretching frequency ( $\nu_1$ ) of the free ion is infrared forbidden. This frequency appears as a weak band in both PbCO<sub>3</sub> and PbCO<sub>3</sub>·PbO spectra near 1050 cm<sup>-1</sup> indicating that some breakdown of the selection rules does take place. For this mode to appear, the ion must undergo a change in dipole moment during the vibration. The effective molecular symmetry must be lowered from  $D_{3h}$  to  $C_{3v}$  or lower.

The out-of-plane bending frequency gives rise to only one absorption peak which is present in all the spectra in the neighborhood of 830 to 840 cm<sup>-1</sup>. The unique doublet which occurs at this frequency in the PbCO<sub>3</sub>·2PbO spectrum cannot be due to a simple removal of degeneracy and must be explained as an interaction of the out-of-plane bending frequency with the lattice or to the carbonate ion being located in two distinctly different lattice sites.

The asymmetrical stretching frequency ( $\nu_3$ ) occurs in the neighborhood of 1300 to 1400 cm<sup>-1</sup> and is the strongest band in all these carbonate spectra. In the case of 2PbCO<sub>3</sub>·PbO only a single band appears. This is not surprising since this compound possesses the highest symmetry of the solid compounds in this system. The other spectra all show splitting of this absorption band implying that two-fold degeneracy has been removed in the lower symmetry lattices.

The same removal of degeneracy occurs in the case of the planar bending frequency ( $\nu_4$ ) which occurs in the frequency range of 650 to 690 cm<sup>-1</sup>.

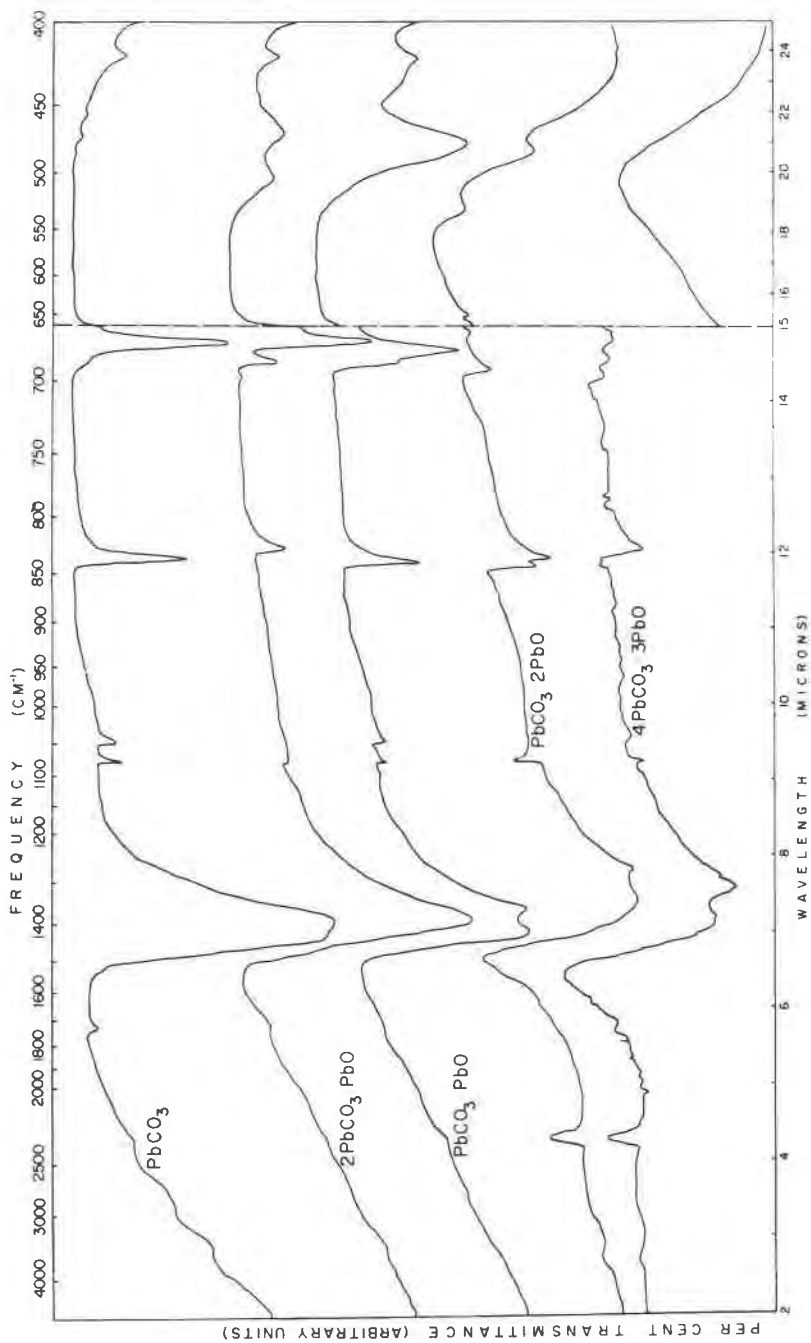


FIG. 4. Infrared absorption spectra of lead carbonate and the lead oxycarbonates. The spectra from 2–15 microns were obtained with NaCl optics; from 15–25 microns with KBr optics.

A series of bands also appear at longer wavelengths in the KBr region of the spectrum. Only two of these, the band at 420 cm<sup>-1</sup> in PbCO<sub>3</sub>·2PbO and the band (only half resolved within the limitations of the available instrument) at 390 to 400 cm<sup>-1</sup> in 4PbCO<sub>3</sub>·3PbO appear from their intensity to be true lattice vibrations. The other weaker bands are likely overtones and combination bands of lower-lying lattice modes.

#### THERMODYNAMICS OF THE SOLID-VAPOR REACTIONS

A relatively small amount of thermodynamic data have been published concerning solid-vapor reactions of the type encountered in this system. For this reason as well as to supply additional information regarding the PbO-CO<sub>2</sub> system, fundamental thermodynamic quantities of reactions

TABLE 4. CHANGES OF FREE ENERGY, ENTHALPY, AND ENTROPY OF REACTION AT 100 BARS

| Reaction   | Temperature<br>(° K.) | Fugacity<br>(bars) | ΔF<br>kcal<br>mole | ΔH<br>kcal<br>mole | ΔS<br>cal<br>mole |
|--|-----------------------|--------------------|--------------------|--------------------|-------------------|
| 3PbCO <sub>2</sub> ↔ 2PbCO <sub>3</sub> ·PbO + CO <sub>2</sub>           | 693                   | 103.5              | -6.39 (± 0.08)     | 17.2 (± 1.3)       | 15.5 (± 1.6)      |
| 2[PbCO <sub>3</sub> ·PbO] ↔ 3[PbCO <sub>3</sub> ·PbO] + CO <sub>2</sub>  | 743                   | 104.3              | -6.86 (± 0.08)     | 17.0 (± 1.3)       | 13.6 (± 1.6)      |
| 3[PbCO <sub>3</sub> ·PbO] ↔ 2[PbCO <sub>3</sub> ·2PbO] + CO <sub>2</sub> | 763                   | 104.7              | -7.05 (± 0.08)     | 26.6 (± 2.8)       | 25.6 (± 3.6)      |
| PbCO <sub>3</sub> ·2PbO ↔ 3PbO + CO <sub>2</sub>                         | 980                   | 107.0              | -9.10 (± 0.08)     | 23.8 (± 1.4)       | 15.0 (± 1.3)      |

have been calculated, namely changes of free energy, enthalpy, and entropy at 100 bars pressure.

In order to calculate thermodynamic quantities for the reactions, a plot of fugacity (Majumdar and Roy, 1956) versus reciprocal temperature was constructed. From this plot both the change of free energy of reaction (ΔF) and heat of reaction (ΔH) could be calculated and from these two quantities the entropy change of reaction (ΔS) in accordance with the following equations:

$$\Delta F = -2.303RT \log f$$

$$\Delta H = \frac{2.303R(\log f_2/f_1)}{1/T_1 - 1/T_2}$$

$$\Delta S = -\frac{\Delta F - \Delta H}{T}$$

The results of the calculations are given in Table 4.

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