Title
THE KINETICS and THERMODYNAMICS OF DECOMPOSITION OF BARIUM CARBONATE

Permalink
https://escholarship.org/uc/item/3xc3f1gx

Author
Basu, Tushar Kanti

Publication Date
1975-08-01
THE KINETICS AND THERMODYNAMICS OF 
DECOMPOSITION OF BARIUM CARBONATE

Tushar Kanti Basu and Alan W. Searcy

August 1975

Prepared for the U. S. Energy Research and 
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
THE KINETICS AND THERMODYNAMICS OF DECOMPOSITION OF BARIUM CARBONATE

Tushar Kánti Basu and Alan W. Searcy

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and Department of Materials Science and Engineering, College of Engineering; University of California, Berkeley, California 94720

ABSTRACT

The equilibrium vapor pressure of barium carbonate and the vacuum decomposition rates of the (001) face of its single crystal were measured by torsion-effusion and torsion-Langmuir techniques, respectively. The rate of the free surface decomposition reaction was constant for product layers up to about 1 mm thickness. The apparent activation enthalpy of decomposition for the reaction

\[ \text{BaCO}_3(s) = \text{BaO}(s) + \text{CO}_2(g) \]

is 225.9 KJ, which is less than the enthalpy of the equilibrium reaction, 251.1 KJ. The apparent activation entropy for the reaction is 53.5 J/deg. This entropy is also less than the entropy of the equilibrium reaction, 146.6 J/deg in the temperature range studied. These results prove that desorption of carbon dioxide cannot be rate limiting.

The ratio of the free surface decomposition pressure to the equilibrium decomposition pressure decreased in the temperature range of study from \(2.4 \times 10^{-4}\) at 1100°K to \(1.9 \times 10^{-4}\) at 1200°K.
To date the Langmuir method has been applied only to study the decomposition of calcite and the torsion-Langmuir method has been applied only to study the decomposition of barium sulfate. Barium carbonate has been chosen as a substance to further test the applicability of the torsion-Langmuir technique. Though many studies have been made of the kinetics of decomposition of calcite, no studies have been made of the decomposition of barium carbonate which at the temperature of our decomposition studies has the aragonite-type structure.

Thermodynamic data indicated that barium carbonate should decompose according to the equation

\[ \text{BaCO}_3(s) = \text{BaO}(s) + \text{CO}_2(g). \]

The equilibrium decomposition pressure was measured as part of the present study by the torsion-effusion technique in order to obtain thermodynamic data above a transition point at 1023°K.

**Experimental**

The torsion-effusion technique is a method for measuring directly the recoil force exerted by a vapor effusing into a vacuum from a small hole, and the torsion-Langmuir technique is a method for measuring the recoil force imparted to a sample surface by vaporizing molecules. In either method, vapor escapes through eccentrically placed orifices in a rigid structure which is suspended from a fine wire, thereby exerting forces which produce a torque on the wire. The individual torques resulting from effusion are additive. The vapor pressure can be calculated from the angle through which the cell is rotated by means of the formula

\[ P = 2\phi D/\Sigma q_i a_i f_i \]
where \( P \) is the vapor pressure to be measured, \( D \) is the torsion constant of the wire, \( q_i \) is the perpendicular distance from the cell center to the axis of an orifice \( i \), \( a_i \) is the area of the orifice, \( f_i \) is the force reduction factor due to finite orifice channel lengths,\(^{10,11}\) and \( \phi \) is the angle through which the cell is rotated.

The apparatus is essentially the same as the one described by R. T. Coyle.\(^{12,2}\)

Witherite (\( \text{BaCO}_3 \)) single crystals obtained from Hexham, England, were analyzed by the American Spectrographic Laboratories, Inc., which reported the following impurities as oxides of the elements: 3.0\% \( \text{Sr} \), 0.035 \( \text{Ca} \), 0.005 \( \text{Si} \), <0.001 \( \text{Mg} \), 0.001 \( \text{Al} \), <0.001 \( \text{Cu} \).

The crystals were cut with a diamond saw along the (001) plane in order to obtain 1 mm thick wafers. Powdered barium carbonate of 99.9\% purity was obtained from Mallinckrodt Chemical Works, St. Louis, Mo., for use in the equilibrium studies.

Two cylindrical alumina cells (99.5 purity) were mounted with their cylindrical axes horizontal in a light weight graphite cell holder. Molybdenum foil between cells and the cell holder prevented reaction between the graphite and alumina. The alumina cells were designed so that they could be used interchangeably for torsion-effusion and torsion-Langmuir studies. The torsion constant of the wire was 0.7219 dyne-cm-rad\(^{-1}\). The moment arms were both 1.04 cm. Orifice and collimating geometries for the Knudsen cells and Langmuir cells are given in Table I.

A region of the furnace was found in which a vertical displacement of the cell of \( \pm 2.0 \) cm gave a constant temperature to within 1.5°K, then the temperature inside a dummy graphite cell was measured to
calibrate a second thermocouple placed 6 mm below the cell holder.

The cell assembly was suspended from a 1.5 mil diameter tungsten wire. The torsion constant of the wire was determined from its period of oscillation when it supported a brass disc with known moment of inertia. The constant was checked repeatedly to insure that it remained unchanged to within 5%. The apparatus was calibrated with sodium chloride for which the equilibrium vapor pressure is well known.

Two independent effusion runs were made with barium carbonate powder and two Langmuir runs were made with (001) faces of barium carbonate single crystals as free vaporizing surfaces. In all cases, the pressures were measured at temperatures above a phase transformation at 1023°K. The low temperature crystallographic modification (witherite) is orthorhombic and the high temperature phase is hexagonal (aragonite-type). 9

At the beginning of each run, the cells were heated at about 1100°K until the ambient pressure in the furnace fell to $5 \times 10^{-5}$ torr or less. Usually that pressure was reached in one to one and one-half hours. In any particular run from 10 to 16 points were taken with at least 15 minutes being allowed after each temperature change in order to ensure that equilibrium was reached. The effusion measurements were corrected by the force-correction factor for finite channel lengths, 10 but factors were not used for the torsion-Langmuir measurements; because the evaporation coefficient is low, the condensation coefficient of molecules returned to the surface after collision with a wall should also be low, 6 and these molecules should eventually escape.

The barium oxide that formed in Langmuir runs was examined by X-ray diffraction for possible metastable modifications. A scanning electron
microscope and optical microscope both were used to examine the various surfaces before and after partial decomposition had taken place.

RESULTS

Two torsion effusion measurements of sodium chloride yielded by least square analysis $\Delta H_v^0 = 243.5 \pm 3.3$ KJ, $\Delta S_v^0 = 171.5 \pm 2.9$ J/deg, and $\Delta H_v^0 = 238.5 \pm 2.8$ KJ, $\Delta S_v^0 = 162.7 \pm 2.9$ J/deg for the standard molar heats and entropies of vaporization. The combined data give $\Delta H_v^0 = 240.2 \pm 2.9$ KJ, and $\Delta S_v^0 = 164.8 \pm 2.9$ KJ. The accepted values (13) at the midpoint of the temperature range over which this work was conducted are $\Delta H_v^0 = 231.8$ KJ and $\Delta S_v^0 = 153.9$ J/deg.

Figure 1 shows the results obtained for barium carbonate decomposition with two different orifice geometries. Several preliminary runs made with a 2 mil wire agree, except for greater scatter, with the data obtained with the 1-1/2 mil wire as long as the orifice geometry was constant. There was, however, a marked trend in observed pressures with effusion orifice size; higher pressures were obtained with smaller orifices. Equilibrium dissociation pressures were calculated from the effusion data by means of the Whitman-Motzfeld equation

$$ P_{eq} = P_m (1 + \frac{f_\alpha}{\alpha A}) $$

where $P_m$ is the measured effusion pressure, $\alpha$ is the decomposition pressure coefficient, and $A$ is the effective vaporizing surface area. From the slopes and intercepts of the calculated equilibrium curve (Fig. 2) the standard molar heats and entropies of dissociation to barium oxide and carbon dioxide gas were calculated to be $256.5 \pm 7.5$ KJ
and $153.6 \pm 5$ J/deg, respectively.

Torsion-Langmuir measurements for the (001) face are shown in Fig. 2. Least square analysis of the combined data yields for the apparent enthalpy and apparent entropy of decomposition $230.1 \pm 6.7$ KJ and $58.6 \pm 3.7$ J/deg.

The heats and entropies measured for barium carbonate decomposition with either equilibrium or free surface vaporization techniques should be corrected by the amounts necessary to bring heat and entropies measured for sodium chloride under nearly identical experimental conditions into exact agreement with the accepted values for sodium chloride. The corrections were made by multiplying measured torsion-effusion and torsion-Langmuir carbon dioxide pressures by the ratio of accepted sodium chloride pressures to measured sodium chloride pressures at two different temperatures. The corrections in pressures were 5% or less in the range of study. From the slopes and intercepts of the resulting new curves of log $P$ vs $1/T$, corrected heats and entropies were calculated.

The corrected molar values are:

Torsion-effusion: $\Delta H_d^0 = 252.1 \pm 7.5$ KJ
$\Delta S_d^0 = 146.6 \pm 5.0$ J/deg.

Torsion-Langmuir: $\Delta H_d^* = 225.9 \pm 6.7$ KJ
$\Delta S_d^* = 53.5 \pm 2.9$ J/deg.

Extrapolation of equilibrium pressures obtained from room temperature calorimetric and heat capacity data in (9) to the same experimental range of this work gives $\Delta H_d^0 = 257.7$ KJ and $\Delta S_d^0 = 156.5$ J/deg if the unknown heat and entropy of the crystallographic transition at 1023°K are
neglected. The two sets of equilibrium data are consistent with an assumed heat of transition of 6 KJ/mole, a reasonable value, but the uncertainty is of the order of 9 KJ.

X-ray diffraction studies on the surface of Langmuir specimens showed the layer of stable crystalline barium oxide which is formed on decomposition is in its normal structure (NaCl-type) with the crystallites randomly oriented relative to the carbonate surface. X-ray patterns also showed that the undecomposed portion of the carbonate was reconverted from the high temperature modification to a single crystal of the orthorhombic modification after heating. The surfaces after vaporization were examined with the scanning electron microscope. Pores were observed to be about 1 μ in diameter. These pores result because the decomposition of witherite, which has a molal volume of 44.5 cm$^3$, yields barium oxide for which the molal volume is 26.8 cm$^3$.

DISCUSSION

Two aspects of the kinetic data are of special interest: the dependence of the decomposition rates on time of heating at constant temperatures and the dependence of the rate on temperature.

The rate of decomposition of barium carbonate at a fixed temperature proved to be independent of the quantity of carbon dioxide evolved until at least 80% of the barium carbonate had decomposed. This means that the rate was unaffected by barium oxide product layers up to some 1 mm in thickness.

As stated earlier, most of the pores through the oxide layer are of 10$^{-3}$ mm/$^*$ diameter. Dushman$^{15}$ provides an equation which predicts for Knudsen flow the fraction $K$ of molecules which, having entered one end of a
cylindrical channel of length, \( l \), and radius, \( a \), will escape from the other end of the channel rather than return to the initial vapor source:

\[
K = \frac{1}{1 + \frac{3}{8} \left( \frac{l}{a} \right)}
\]  

(2)

According to Eq. (2), the vaporization flux should decrease with increasing product layer thickness. For an oxide layer 1 mm thick and with pores of about \( 10^{-3} \) mm radius, the expected rate of escape of carbon dioxide should be reduced by a factor of about 1000 below the initial rate if the carbonate surface acts as an equilibrium source.

But barium carbonate clearly does not act as an equilibrium source of carbon dioxide when the decomposition is carried out in vacuum because the measured flux is only about \( 2 \times 10^{-4} \) times the flux which is obtained from an equilibrium source—the flux corresponding to the Whitman-Motzfeld extrapolated pressure.

The low activation enthalpy and entropies found for barium carbonate decomposition must reflect a markedly different rate limiting process from that which characterizes calcium carbonate decomposition. \(^1\) Calcium carbonate, in the form of calcite single crystals, was found to decompose in vacuum by a process for which the apparent activation enthalpy is greater than the enthalpy of the equilibrium decomposition reaction and the apparent enthalpy is approximately equal to the equilibrium value. Furthermore, a thin layer of a metastable form of calcium oxide was shown to be the direct product of the decomposition of calcite while no such metastable product could be detected in the present study. Both the metastable oxide and the stable outer oxide layer were, unlike the barium
oxide from barium carbonate decomposition, preferentially oriented relative to the underlying carbonate.

It has been shown for vaporization reactions that desorption cannot be rate limiting when the apparent activation enthalpies measured in free surface vaporization are substantially less than the enthalpies of the equilibrium vaporization reaction.\(^6\) Exactly the same arguments apply for a decomposition reaction. The apparent activation enthalpy measures the difference between the enthalpy content of the activated complex in a reaction and the reactant. Unless that difference is at least as large as the enthalpy difference between reaction products and reactants, the activated complex cannot have acquired the minimum enthalpy content necessary for desorption plus formation of the solid reaction product to take place.

We can conclude that in barium carbonate decomposition some step other than desorption of carbon dioxide limits the reaction rate, while for calcium carbonate decomposition one possible interpretation\(^{16}\) is that equilibrium is maintained between the carbonate and the metastable oxide product layer and that desorption of carbon dioxide at the maximum rate possible for that metastable equilibrium determines the reaction rate.

The very low decomposition pressure coefficient for barium carbonate can account for the fact that the substantial reduction in carbon dioxide flux predicted by Dushman's relation to result from the porous oxide layer is not observed. Searcy and Beruto\(^{16}\) have derived an expression that shows that for an irreversible decomposition reaction a porous layer will measurably reduce the rate only when the ratio \(a/l\) for
the pores becomes as small as the value of the decomposition pressure coefficient, $\alpha$. In this study $\alpha$ was smaller than estimated minimum values of $a/\ell$.

ACKNOWLEDGMENTS

We are indebted to Dr. D. Meschi, Dr. A. Büchler and Dr. D. Beruto and Dr. P. Mohazzabi for their valuable comments and advice.

This work was supported by the U. S. Energy Research and Development Administration.
REFERENCES

27. P. Mohazzabi and A. W. Searcy, unpublished work, Univ. of Calif.
Table I. Orifice and collimator

<table>
<thead>
<tr>
<th>Cell</th>
<th>Hole diameter (1) cm</th>
<th>(2) cm</th>
<th>Lid thickness (1) cm</th>
<th>(2) cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Knudsen cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.0820</td>
<td>0.0830</td>
<td>0.0863</td>
<td>0.0880</td>
</tr>
<tr>
<td>2</td>
<td>0.1002</td>
<td>0.1001</td>
<td>0.0787</td>
<td>0.0840</td>
</tr>
<tr>
<td>Langmuir cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.2954</td>
<td>0.2954</td>
<td>0.0792</td>
<td>0.0797</td>
</tr>
</tbody>
</table>
Figure Captions

Fig. 1. Equilibrium pressure of barium carbonate. Dashed line is the equilibrium pressure calculated by means of the Whitman-Motzfeld extrapolation.

Fig. 2. Langmuir pressures from decomposition of barium carbonate single crystals.
Fig. 1

MOTZFELD EXTRAPOLATION.

ORIFICE DIAM.

△ 0.8 mm

○ 1.0 mm

LEAST SQUARE FIT

10^{-5} - 10^{-4}

1/T °K x 10^4

9.0 9.1 9.2 9.3 9.4 9.5 9.6 9.7

XBL742-5646

Fig. 1
Fig. 2
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.