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Powell, E.K.

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THE KINETICS AND THERMODYNAMICS OF DECOMPOSITION
OF DOLOMITE TO A METASTABLE SOLID PRODUCT

Elizabeth K. Powell and Alan W. Searcy

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Materials Science and Mineral
Engineering, University of California
Berkeley, CA 94720

ABSTRACT

The decomposition of dolomite, $\text{CaMg}(\text{CO}_3)_2$, in vacuum was studied by the torsion effusion and torsion Langmuir methods. Complete decomposition yields poorly crystalline MgO and CaO of high total surface area, but the decomposition product when the reaction is 50% complete does not give coherent x-ray scattering. Extrapolation of the effusion pressures to pressures for zero orifice area yields thermodynamic data that disagree with well established data for dolomite and its thermodynamically stable products. The data are consistent with the interpretation that dolomite and CO_2 are at equilibrium with a glass-like solid which has a free energy of formation of $(17,600 - 8.8T)$ cal from $1/2 \text{ CaO} + 1/2 \text{ MgO}$. From the torsion Langmuir data, the apparent activation enthalpy and entropy of decomposition to this product are calculated to be 46.5 kcal and 22.3 cal/degree per mole of CO_2 . The ratio of the free surface decomposition pressure to the metastable equilibrium pressure is 1×10^{-4} at 850°K. Earlier anomalously low pressures measured for decomposition of $\text{Mg}(\text{OH})_2$ are also consistent with the interpretation that the solid product was glass-like.

Dolomite, $\text{CaMg}(\text{CO}_3)_2$, has been studied extensively,¹⁻¹⁰ because of its mineralogical importance and its importance as an industrial raw material. Recently, dolomite has taken on added significance because the oxide mixture produced by its decomposition under controlled conditions has been shown to be a promising getter for sulfur oxides in stack gases.¹⁰

The solid products of dolomite decomposition depend upon the pressure of CO_2 . In differential thermal analyses (DTA) runs made at pressures less than 50 torr, the decomposition reaction is said to be

At CO_2 pressures greater than 50 torr, the decomposition occurs in two steps with the first step being

At higher temperatures, the CaCO_3 produced in reaction 2 decomposes. What were believed at the time of measurement to be equilibrium CO_2 pressures have been measured for both reaction 1 and reaction 2. The measurements for reaction 2 are well substantiated: Two separate sets of measurements^{6,7} are in fair agreement. Furthermore, the enthalpy of formation for dolomite which is calculated from CO_2 pressures for reaction 2 agrees within one or two kcal with enthalpies calculated¹¹ from each of two quite different kinds of measurements.

In contrast, the purported equilibrium measurements made by Mitchell⁸ for reaction 1 show a questionable temperature dependence. And if the experimental data are interpreted by a method that is insensitive to a temperature dependent error, they yield an enthalpy of formation of

dolomite that differs from the accepted enthalpy by about 12 kcal per mole.

It has appeared, therefore, that the measurements for reaction 1 were in error. But we here report torsion effusion^{12,13} measurements of CO₂ decomposition pressures for dolomite which are in general agreement with the pressures reported by Mitchell for reaction 1, and we show that both studies may yield valid measurement of a highly metastable equilibrium.

We also report and analyze measurements by the torsion-Langmuir¹³ method of the kinetics of decomposition of dolomite single crystals. The only previous measurement of the rate of isothermal decomposition of dolomite in vacuum was made with pellets.⁹

Theoretical Background

The torsion effusion technique¹³ is a method for measuring directly the recoil force of a vapor that effuses under Knudsen flow conditions into a vacuum through a small orifice in a cell containing the reactant. When the gas flux density through the orifice is much less than the gas flux density that can be generated by the decomposition reaction, the observed pressure, P_{obs} is the equilibrium pressure. If a step of the decomposition reaction is slow, the observed pressures will be less than the equilibrium pressures by amounts that depend on the orifice area. This area dependence is given by the Whitman-Motzfeld equation.¹⁴⁻¹⁶

$$P_{\text{eq}} = P_{\text{obs}} \left(1 + \frac{fa}{\alpha_v A} \right) \quad (3)$$

where a is the effusion orifice area, A is the effective vaporizing surface area, f is the force correction factor for a nonideal orifice,^{17,18} and α_v is a function of the reaction irreversibility.

In the torsion Langmuir method,¹³ the pressure of gases which escape from a free surface into vacuum is measured. If all steps of the reaction are rapid compared to desorption, Langmuir and effusion pressures will be equal. However, if a step of the reaction is slow, the Langmuir pressure may be much lower than the effusion pressure and comparison of the two pressures as functions of temperature gives a measure of the irreversibility of the reaction.^{19,20}

EXPERIMENTAL

The effusion cells of 99.5% purity alumina are shown schematically in Fig. 1(a) and 1(b). Two identical cells are placed in a graphite cell holder, with the orifices facing in opposite directions, as seen in Fig. 1(c). Cells are protected from reaction with the graphite holder by molybdenum foil. The cell holder is pinned to an alumina support rod which extends out of the hot zone of the furnace. The rod is suspended by a Pt-Ni ribbon of cross section .0127mm by .127mm. A mirror which is attached to the alumina rod is used to reflect a collimated light source through a window in the water cooled vacuum chamber onto a translucent scale mounted outside. The resistance furnace with tungsten heating elements is surrounded by a tantalum heat shield. Tantalum shields are placed above the furnace to reduce heating of the torsion wire. The vacuum is maintained at 2×10^{-5} torr by an oil diffusion pump and a liquid nitrogen cold trap.

The recoil of the vapor that escapes from an orifice causes the torsion wire to twist, resulting in a deflection of the light beam on the scale. The entire suspension assembly is rotated by means of a gear system until the light beam is again centered at the zero point on the

scale. This rotation is measured by the numerical change of a counter coupled to the gearing system.

The vapor pressure of the decomposition reaction is then determined from

$$P = \frac{2\phi D}{q_1 a_1 f_1 + q_2 a_2 f_2}$$

where ϕ is the angle of rotation in radians, D is the torsion constant, q is the moment arm of the orifice, a is the orifice area, and f is the force reduction factor.

Experimental Preparation

A dolomite single crystal from Pomplona, Spain was used for the Langmuir study and for some of the effusion measurements. A polycrystalline sample of Natividad, California dolomite was used for additional effusion studies. Spectrographic analysis by American Spectrographic Laboratories are summarized in Table I. Values are reported as weight % oxides of the elements, with Ca and Mg to the nearest 5%.

For the effusion studies, crystals were ground. Grinding for times on the order of hours has been shown to produce a decrease in temperature of the dolomite decomposition endotherm in DTA studies.⁵ For this reason, crystals were ground for the minimum time necessary to produce fine powder, about 1 minute for 10 grams of sample. X-ray diffraction patterns of the powders matched those for dolomite in the ASTM Powder Diffraction Files. The weight loss that resulted from complete decomposition of the Pomplona dolomite was 48%, compared with the theoretical value of 47.7% for stoichiometric dolomite.

Langmuir samples were prepared by cleaving the crystals into slices approximately 1 mm thick along the natural cleavage (1011) planes. Sections were selected which had parallel faces. A crystal section was placed on the cell support disc, and the cell lid pressed tightly over it. Proper fit of the lid is vital in preventing leakage of gases around the orifice edges. In many cases leakage did occur, as verified by visual observation of crystal decomposition in areas other than that defined by the orifice. In such cases data were discarded. At temperatures above 900°K, leakage occurred no matter how tight the fit. This fact greatly limited the temperature range of study. Slow heating to the experimental temperature was necessary to prevent the crystal from cracking.

System Calibration

The furnace was calibrated by placing a dummy cell holder containing a thermocouple at a position in the furnace where the cell temperature was constant to $\pm 2^{\circ}\text{C}$ over a distance of 2 cm, and where the sample cell would be located during experimental runs. A reference thermocouple was placed 6 mm below the cell. The temperature difference between the cell and the reference thermocouple was recorded as a function of temperature.

The torsion constant of the ribbon was determined in the temperature range of study, while carrying approximately the same weight as during experimentation. The weight was a stainless steel disc with known moment of inertia. The period of oscillation for the system were measured with and without the disc. Periods were taken as the average time of several oscillations in order to minimize start and stop errors. The torsion constant was remeasured periodically during the course of experimentation,

and was found to vary less than 1.5%.

Cell orifice areas and moment arm lengths were measured with a comparitor. Several measurements were made for each orifice, and the results were averaged. Diameters and lengths of effusion channels are given in Table II.

The Torsion effusion and Torsion Langmuir methods yield directly pressures as functions of temperature, but the level of systematic error in measurements is difficult to estimate. Accordingly, the vapor pressures of NaCl and Bi and the rates of vaporization of NaCl single crystal slices were measured and used for calibration. Ewing and Stern²¹ reported that Langmuir pressures are 0.74 times the equilibrium (effusion) pressures in our experimental range, but they found that increasing by a factor of 3 the surface area of NaCl that vaporizes through a fixed projected area did not increase their flux. This result shows that their measured Langmuir fluxes were the maximum possible fluxes, i.e. equilibrium fluxes and that the apparent difference that they found must be a consequence of a small systematic error.²²

Results for sodium chloride are shown in Fig. 2. In this plot of $\log P$ vs. $1/T$, by the second law method the slope yields the enthalpy for the reaction ΔH° , and the intercept determines the standard entropy ΔS° , since

$$-\ln P = \frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R}$$

where R is the gas constant. Measured enthalpies correspond closely to accepted JANAF values, but accepted total NaCl pressures average about 0.85 times our measured pressures. For Bi accepted pressures are about

0.70 times our measured values, as seen in Fig. 3. Accordingly, measured dolomite pressures were multiplied by a factor of 0.81 to correct for systematic errors. The measured Langmuir pressures for NaCl are very close to the equilibrium pressures, as expected in light of Ewing and Stern's finding that Langmuir fluxes are independent of sample area. Dolomite crystals could be decomposed very little (0.1 mm) before leakage at the orifice edge became sufficient to cause apparent decomposition rates to increase. Until then, rates were time independent. This result indicates that neither heat transport nor CO_2 transport through the growing layers of solid reaction product is rate limiting under our conditions of study.

At the lower end of the temperature range at least one hour was required to attain a steady pressure reading, and at the upper end only a half hour was necessary. Data were taken by alternately raising and lowering the temperature to reduce the chances of systematic error in pressure observations. Effusion measurements were corrected by the force correction factors for a nonideal orifice, but these factors were not used for the torsion Langmuir measurements: because the free surface vaporization flux is much lower than the flux corresponding to the equilibrium data, we know the decomposition is highly irreversible. Accordingly, molecules reflected from the channel walls to the reactant surface are unlikely to react to form dolomite.

RESULTS

In SEM pictures, the solid product of dolomite decomposition appeared to occupy the same volume as the dolomite.

From the molar volumes of dolomite and product oxides we calculate that the product has a porosity of 56%. Pores through the product oxide were

not visible with SEM examination, perhaps because they were too small to resolve or perhaps because of reaction with water vapor and CO_2 during handling and mounting of the specimen.

X-ray powder patterns obtained with Cu K_α radiation are presented in Fig. 4. The upper pattern shows the sharp peaks of the starting material, and the lower, for fully decomposed dolomite, shows broad CaO and MgO peaks. The positions of peaks of the pure binary oxides are marked. The BET surface area measured for the oxide products of fully decomposed dolomite was $21 \text{ m}^2/\text{g}$.

The CO_2 pressures, corrected as described above for the small systematic errors in NaCl and Bi pressure determinations, are summarized in Table III and Fig. 5. The measured effusion pressures showed a dependence on orifice area. The extrapolated line above the effusion plots of Fig. 4 is made by use of the Whitman-Motzfeld equation (equation 3).

Apparent enthalpies and entropies were calculated from each of the plots of $\log P$ vs. $1/T$ shown in Fig. 4, as follows:

	$\Delta H(\text{Kcal/mole})$	$\Delta S(\text{cal/deg-mole})$
0.02cm dia.	52.9 ± 0.7	47.4 ± 0.8
0.04cm dia.	53.3 ± 0.6	45.9 ± 0.8
0.04cm dia. low Fe	50.8 ± 0.4	42.9 ± 0.5
0.04cm dia combined	52.0 ± 0.5	44.2 ± 0.7
Whitman-Motzfeld extrapolation	52.5 ± 1.3	47.6 ± 1.6
0.30cm dia. Langmuir	46.5 ± 0.1	22.3 ± 1.4

Possible interpretations of these quantities are presented below.

DISCUSSION

Figure 6 shows the equilibrium pressures measured for decomposition of dolomite to CaCO_3 and MgO reported by Graf and Goldsmith⁷ and by Haul and Markus⁶ (Reaction 2) and also shows the much lower decomposition pressures measured by Mitchell⁸ and by us. Our CO_2 pressure at 800°K is only about 10^{-3} times the pressure calculated from the well established thermodynamic data to $1/2 \text{CaO(s)} + 1/2 \text{MgO(s)} + \text{CO}_2\text{(g)}$ (Reaction 1). It is certain, therefore, that the pressures which we calculate by means of the Whitman-Motzfeld extrapolation are not equilibrium decomposition pressures for that reaction. In this respect, our findings for dolomite decomposition are similar to findings reported in 1958 for the reaction

Kay and Gregory²³ showed that the Whitman-Motzfeld extrapolation yielded for reaction 3 what they termed pseudoequilibrium pressures which were only about 3×10^{-4} times the known equilibrium H_2O pressures for the reaction at 500°K . We suggest, however, that Mitchell, Kay and Gregory, and we may have obtained true equilibrium pressures for decomposition to metastable solid reaction products.

It is known that if the solid product of a given decomposition reaction is metastable, i.e. of higher chemical activity than the stable solid product, the equilibrium pressure of the gaseous product must be lower than its pressure when the stable solid product is formed.^{24,20} The complete decomposition of our dolomite gave crystalline MgO and CaO , but when the sample was as much as 50% decomposed no x-ray pattern was yet observable. The solid produced during our pressure measurements,

therefore, was amorphous and must have had a higher activity than the crystalline products of reaction 1. Mitchell's pressures were measured in a static system, but they only became constant at the reported values after he had repeatedly pumped off CO_2 gas. Because our extrapolated pressures agree reasonably well with his, it appears probable that he obtained the same amorphous solid that was present during our effusion pressure measurements. The fact that he was able to approach the same constant CO_2 pressures from higher and lower initial pressures is good evidence that those constant pressures were equilibrium pressures.

The standard free energy of decomposition of CaCO_3 ²⁵ near 800°K is $\Delta G^\circ = (40,200 - 35.6T)$ cal and for MgCO_3 ²⁶ is $(26,600 - 39.4T)$ cal. The standard free energy of formation of dolomite from CaCO_3 and MgCO_3 is $(-2,900 + 0.8 T)$ cal.¹¹ From these quantities we calculate that if a metastable MgO-CaO solid phase is in equilibrium with dolomite at our observed decomposition pressures, that phase must have a free energy of formation from $1/2 \text{MgO(s)}$ and $1/2 \text{CaO(s)}$ of $(17,600 - 8.8T)$ cal.

Giauque²⁴ showed that when crystalline MgO is produced by Mg(OH)_2 decomposition in static systems the surface free energy is surprisingly high, about $(900 - 0.2T)$ cal per mole. But this value is too low by more than a factor of ten to explain the low pressures measured for dolomite or Mg(OH)_2 decomposition.

The high apparent entropy of formation of our amorphous product suggests that it is a glassy material. Because formation of the stable crystalline oxides from dolomite would require collapse of the solid products of reaction to a volume only about one-half that of the parent dolomite and because the reaction occurs at only about one-fourth the

temperatures at which the constituent oxides melt, where mobility of the ions must be very low, a glass could well be produced.

If we assume that dolomite decomposes by the reaction

where the glass is assumed to be an ideal supercooled solution of the liquid oxides, we calculate, using the estimated heats and entropies of fusion for MgO and CaO in the JANAF tables, that the free energy of formation from $1/2 \text{ CaO}(\text{s}) + 1/2 \text{ MgO}(\text{s})$ would be $(18,800-7.4T)$ cal in close agreement with $(17,600-8.8T)$ cal from our interpretation of the effusion data.

Kay and Gregory did not report x-ray data for the MgO produced in their effusion study of $\text{Mg}(\text{OH})_2$ decomposition. That oxide was probably also amorphous. The estimated entropy of fusion of MgO and its melting point give for the free energy of formation of liquid MgO from solid MgO $\Delta G = (18,600-6.0T)$ cal compared to $\Delta G = (11,400-6.7T)$ cal calculated for formation of the oxide product from MgO in the effusion measurements. Here the supercooled liquid model gives only fair agreement with the experimental enthalpy, but gives good agreement with the experimental entropy.

It is well known that amorphous or poorly crystalline phases are often produced in decomposition reactions,²⁷ but apparently no one before has reported evidence that decomposition reaction products may have such high heats of formation compared to the stable reaction products as would be required if we are correct in suggesting that metastable equilibria have been measured for these two systems. Meschi and Searcy have initiated

calorimetric measurements to test our interpretation.

The apparent activation enthalpies calculated from the temperature dependence of the pressures measured by the torsion-Langmuir method in this study are slightly lower than the apparent enthalpies measured by Britton et al,⁹ who decomposed pellets of dolomite in vacuum. Their apparent enthalpies ranged from 49.9 kcal to 55.6 kcal. Such results are consistent with our expectation that the escape of CO₂ from the interior of their pressed, polycrystalline samples would lead to apparent enthalpies that are intermediate between apparent enthalpies measured with a single crystal and enthalpies measured in effusion experiments.

The fact that our torsion Langmuir pressures are some 4 orders of magnitude lower than our effusion measurements indicates that some step of the decomposition to the metastable solid product of our effusion studies is irreversible. In endothermic decomposition reactions, it is commonly assumed that the rate limiting step is a surface step in which the activated complex is the adsorbed solid or gaseous product.²⁷ Searcy and Beruto²⁰ recently showed, however, that when the decomposition flux in vacuum is lower than the flux effusing from a Knudsen cell, other steps may be rate limiting, such as diffusion of the solid or gaseous reaction component in the reactant phase, or transfer of the oxide product at the reaction-product interface.

The observation that the apparent activation enthalpy is lower than the enthalpy of the metastable equilibrium reaction shows that desorption of CO₂ cannot be rate limiting. But from the measured rates of decomposition in vacuum alone we cannot further identify the irreversible step.

It has recently been shown that the dependence of decomposition rates on product gas pressure must depend on whether the slowest step of the process is one for the chemical component that forms the gaseous or the solid reaction product.²⁸ Accordingly, the effect of CO₂ pressure on the rate of dolomite decomposition will be investigated under conditions that yield the metastable solid reaction product.

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Table I. Spectrographic Analysis of Dolomite Samples

	<u>Natividad Dolomite</u>	<u>Pamplona Dolomite</u>
Mg	20. %	20. %
Ca	30.	35.
Si	0.2	0.03
Al	.05	.025
Fe	.07	.7
Pb	.015	<.003
Mn	.015	.08
Sr	.003	.04
Ba	<.001	.006
Cu	<.001	<.001
Ag	<.001	<.001
Na	<0.05	<0.05
K	<0.75	<0.75
Ni	<.001	<.001
Ti	.002	-
Zr	.01	-

Table II. Effusion Orifice Geometries

Cell	<u>Orifice Diameters</u>			<u>Channel Lengths</u>		
	(1)	(cm)	(2)	(1)	(cm)	(2)
Knudsen Cell						
1	0.020		0.021	0.0800		0.0826
2	0.040		0.042	0.0839		0.0834
Langmuir Cell						
3	0.2954		0.2954	0.0684		0.0792

Table III. Dolomite Decomposition Data

Orifice Diameter		Temperature (°K)	Pressure (Atm)
0.2mm			
Run 1	1	850	5.85×10^{-4}
	2	842	4.07×10^{-4}
	3	859	7.02×10^{-4}
Run 2	1	805	9.32×10^{-5}
	2	828	2.57×10^{-4}
	3	849	5.39×10^{-4}
	4	814	1.52×10^{-4}
	5	843	4.31×10^{-4}
	6	863	8.51×10^{-4}
	7	885	1.73×10^{-3}
	8	770	1.94×10^{-5}
	9	789	4.83×10^{-5}
	10	833	2.86×10^{-4}
	11	800	7.37×10^{-5}
0.4mm			
Run 1	1	853	2.19×10^{-4}
Run 2	1	785	1.52×10^{-5}
	2	827	8.91×10^{-5}
	3	879	6.06×10^{-4}
	4	847	1.93×10^{-4}
	5	827	9.96×10^{-6}
0.4mm	1	753	4.25×10^{-6}
Natividad	2	821	6.85×10^{-5}
Dolomite	3	881	6.00×10^{-4}
	4	853	2.16×10^{-4}
	5	801	3.06×10^{-5}
3.0mm Langmuir			
Run 1	1	850	8.08×10^{-8}
	2	871	1.57×10^{-7}
	3	861	1.17×10^{-7}
	4	881	2.28×10^{-7}
	5	876	1.76×10^{-7}
	6	856	1.30×10^{-7}
Run 2	1	824	3.90×10^{-8}
	2	838	5.69×10^{-8}
	3	851	8.34×10^{-8}
	4	874	1.73×10^{-7}
	5	868	1.34×10^{-7}
	6	884	2.44×10^{-7}
	7	900	4.24×10^{-7}
	8	890	3.01×10^{-7}

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FIGURE CAPTIONS

- Fig. 1. Torsion cells and holder.
- Fig. 2. NaCl calibration.
- Fig. 3. Bismuth calibration.
- Fig. 4. Equilibrium and free surface pressures from dolomite decomposition as a function of temperature.
- Fig. 5. X-ray diffraction patterns of dolomite and its decomposition products. (Cu K α radiation).
- Fig. 6. Dolomite decomposition pressures to stable and metastable products.

XBL 775-5534

Fig. 1.

XBL 775-5532

Fig. 2.

XBL 775-5533

Fig. 3.

XBL 775-5535

Fig. 4.

Pamplona Dolomite before Decomposition (TC=1000)

Fully Decomposed Powder, 580°C in Vacuum (TC=300)

XBL 775-5531

Fig. 5.

XBL777-5731

Fig. 6.

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TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720