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By H. C. Ko, N. Ahmad, and Y. A. Chang

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Heats of solution of calcium carbonate (calcite) and calcium oxide in hydrochloric acid were determined by solution calorimetry. Combination of these two heats yields a value of 42.643±0.024 kcal/mole for the enthalpy of calcination of calcite at 298.15 K. Literature data on $\Delta H^\circ_{298.15}$ of calcination of calcite were reviewed and compared. Thermodynamic properties for the calcination process were calculated from 298.15 to 1,500 K using Gibbs energy functions. This research was undertaken by the Bureau of Mines as an effort to provide thermodynamic data for the advancement of minerals technology, energy conservation, and environmental preservation.

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THERMODYNAMICS OF CALCINATION OF CALCITE

by

H. C. Ko,[1] N. Ahmad,[2] and Y. A. Chang[3]

ABSTRACT

Heats of solution of calcium carbonate (calcite) and calcium oxide in hydrochloric acid were determined by solution calorimetry. Combination of these two heats yields a value of 42.643±0.024 kcal/mole for the enthalpy of calcination of calcite at 298.15 K. Literature data on $\Delta H^\circ_{298.15}$ of calcination of calcite were reviewed and compared. Thermodynamic properties for the calcination process were calculated from 298.15 to 1,500 K using Gibbs energy functions. This research was undertaken by the Bureau of Mines as an effort to provide thermodynamic data for the advancement of minerals technology, energy conservation, and environmental preservation.

INTRODUCTION

Thermodynamic data were obtained for the calcination of calcite as part of the Bureau of Mines program to provide a scientific base for use in developing new technology and predicting the feasibility of new processes.

There are numerous data on the decomposition of calcite in the literature, but no calorimetric measurements were available for the enthalpy of calcination of calcite. In the course of this investigation, experimental heats of solution of calcite and calcium oxide (CaO) obtained by solution calorimetry were combined to yield the enthalpy of calcination of calcite at 298.15 K. Thermodynamic properties of the calcination reaction were calculated from 298.15 to 1,500 K by combining the calorimetric data with the values of Gibbs energy functions for the reactants and the products. The existing data for calcination were compiled, critically evaluated, and compared with the experimental results obtained in this investigation.

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MATERIALS

Calcium carbonate (calcite) has a rhombohedral structure isotypic with that of NaCl. The calcite used in these studies was obtained as Iceland spar from Mexico. X-ray diffraction analysis showed the primary constituent to be calcite with a trace of CaO. Chemical analysis showed 56.2 pct CaO, compared with 56.03 theoretical. Spectrographic analysis showed major impurities of 0.03 to 0.3 pct Al and 0.003 to 0.03 pct Si.

Calcium oxide was obtained by heating a commercially prepared calcium carbonate (Aldrich Chemical Co.,[4] 99.999 pct) in a platinum dish at 800° C for 17 hours. The sample was ground and further heated at 970° C for 4 hours. The sample was cooled in a desiccator inside a dry box with an argon atmosphere and transferred into a tightly sealed jar for storage. Analysis of this CaO sample, by converting it to $CaSO_4$, showed 99.99 pct CaO.

Hydrochloric acid, 4.360 molal ($HCl+12.731\ H_2O$), was used as the solvent. It was prepared from reagent-grade material, and analysis confirmed the composition as given.

APPARATUS AND PROCEDURE

The calcination process was studied using an isoperibol solution calorimeter. General description of the apparatus and procedure of this calorimeter was given elsewhere (25-26).[5] A modification was made so that gas could escape through a vent tube.

RESULTS AND DISCUSSION

The heat of solution of calcite was measured in 2,260 g of 4.360 molal HCl. Approximately 0.02 mole of the carbonate was used for each of eight determinations. The solvent was presaturated with CO_2 by bubbling CO_2 through the acid at a fixed flow rate for 1 hour. The presaturation was to ensure that all the CO_2 generated from the dissolution process went out of the solution. Correction was made for the heat of vaporization of water that accompanied the excaping CO_2. Heat of solution experiments were also carried out in the solvent that was presaturated with CO_2 for 1.5 hours. No appreciable discrepancy was observed in these two types of experiments.

The heat of solution of CaO was also measured using the same procedure for nine determinations. In about half of the experiments the solvent was not presaturated with CO_2. The values did not show significant differences from those experiments where the solvent was presaturated with CO_2.

The experimental heats of solution of calcite and CaO are listed in table 1. A value of 257 cal/mole was taken as the heat correction for vaporization of water from the solvent. This value was derived from the vapor pressure and heat of vaporization of water taken from Gokcen (15).

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[4] Reference to a specific name is made for identification only and does not imply endorsement by the Bureau of Mines.

[5] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 1. - Heats of solution of calcite and CaO at 298.15 K, kcal/mole

Calcite (reaction 1):	CaO (reaction 2):
-4.932	-47.622
-4.967	-47.618
-4.976	-47.622
-5.020	-47.644
-4.993	-47.656
-5.000	-47.591
-4.973	-47.626
-5.005	-47.598
	-47.653
-4.983±0.019[1]	-47.626±0.015[1]

[1] Average.

The solution reactions are as follows:

$$CaCO_3(c,calcite) + 2H^+(sol) = Ca^{2+}(sol) + H_2O(sol) + CO_2(g) \quad (1)$$

$$\Delta H_1(298.15\ K) = -4.983 \pm 0.019\ kcal/mole$$

$$CaO(c) + 2H^+(sol) = Ca^{2+}(sol) + H_2O \quad (2)$$

$$\Delta H_2(298.15\ K) = -47.626 \pm 0.015\ kcal/mole.$$

The calcination of calcite is represented by

$$CaCO_3(c,calcite) = CaO(c) + CO_2(g) \quad (3)$$

for which

$$\Delta H_3 = \Delta H_1 - \Delta H_2 = 42.643 \pm 0.024\ kcal/mole$$

The thermal data for CaO, $CaCO_3$, and CO_2 from Pankratz (34), Robie (39), and JANAF Thermochemical Tables (12), respectively, are listed in table 2. Table 2 also lists our $\Delta H^\circ_{298.15}$ value and calculated thermal data for the calculation reaction. Table 3 lists the equilibrium data for the calcination reaction by various investigators. Their data were evaluated by the third-law method given below.

$$Gef \equiv \frac{G^\circ_T - H^\circ_{298.15}}{T} = \frac{H^\circ_T - H^\circ_{298.15}}{T} - S^\circ_T \quad (4)$$

$$\Delta G^\circ_T = T\Delta Gef + \Delta H^\circ_{298.15} \quad (5)$$

$$\Delta G^\circ_T = -RT\ \ell n\ K = -RT\ \ell n\ P_{CO_2} \quad (6)$$

TABLE 2. - Thermodynamic data for calcination of calcite, $CaCO_3$(c, calcite) = CaO(c) + CO_2(g)

($\Delta H^\circ_{298.15}$ = 42.643±0.024 kcal/mole)

T, K	cal/mole·K						$CaCO_3$ (calcite) = CaO + CO_2		
	CaO		$CaCO_3$ (calcite)		CO_2		$-\Delta Gef$,	ΔG°_T,	$-\log P_{CO_2}$
	S°	−Gef	S°	−Gef	S°	−Gef	cal/ mole·K	kcal/mole	atm
298.15	9.100	9.100	21.919	21.919	51.072	51.072	38.253	31.238	22.900
300	9.162	9.100	22.043	21.919	51.127	51.072	38.253	31.167	22.707
400	12.233	9.511	28.289	22.749	53.830	51.434	38.196	27.365	14.953
500	14.793	10.319	33.671	24.410	56.122	52.148	38.057	23.614	10.323
600	16.965	11.250	38.344	26.350	58.126	52.981	37.881	19.914	7.254
700	18.845	12.204	42.471	28.365	59.910	53.845	37.684	16.264	5.078
800	20.502	13.140	46.174	30.363	61.522	54.706	37.483	12.657	3.458
900	21.984	14.042	49.539	32.309	62.992	55.546	37.279	9.092	2.208
1,000	23.325	14.904	52.634	34.190	64.344	56.359	37.073	5.570	1.217
1,100	24.550	15.726	55.504	35.999	65.594	57.143	36.870	2.086	.414
1,200	25.679	16.509	58.186	37.737	66.756	57.896	36.668	−1.359	− .248
1,300	26.727	17.255	60.710	39.408	67.841	58.620	36.467	−4.764	− .801
1,400	27.705	17.967	63.099	41.016	68.859	59.315	36.266	−8.129	−1.269
1,500	28.623	18.647	65.369	42.564	69.817	59.984	36.067	−11.458	−1.670

TABLE 3. - Literature data for calcination of calcite

Source	Year	Temperature range, K	$\Delta H^\circ_{298.15}$, kcal/mole
Debray (11)..............	1867	1,133-1,313	47.738±1.101
Le Chatelier (28)........	1887	883-1,138	39.467± .970
Pott (36)................	1905	820-1,240	41.007±2.181
Brill (9)................	1905	473-1,343	40.494
Riesenfeld (38)..........	1907	973-1,173	42.438± .670
Zavrieff (53)............	1009	633-1,199	41.116±3.580
Johnston (23)............	1910	860-1,167	42.874± .175
Kohner (27)..............	1914	787-1,006	42.203± .301
Hedvall (19).............	1916	1,191	43.699
Mitchell (33)............	1923	876-1,169	46.552±2.213
Smyth and Adams (42).....	1923	1,115-1,612	42.927± .043
Andrussow (1)............	1925	779-1,175	42.335± .110
Dutoit (13)..............	1927	980-1,131	42.890± .137
Whiting and Turner (52)..	1930	773-1,175	43.150
Tamaru (47)..............	1931	887-1,164	42.447± .028
Matsui (31)..............	1933	1,026-1,154	42.304± .105
Matsui (30)..............	1933	909-1,153	42.118± .167
Southard and Royster (43)	1936	1,048-1,173	42.829± .031
Hill and Winter (21).....	1956	722-1,177	42.779± .127
Mauras (32)..............	1959	915-1,104	43.874± .244
Baker (3)................	1962	1,175-1,487	43.404± .171
Hills (22)...............	1967	953-1,171	43.102± .125
Verdonk (50).............	1975	914-1,169	42.809± .070
Criado and Morales (10)..	1978	673-1,250	43.357± .041
Selected value......			42.748± .389

In these equations, G_T° is the standard Gibbs energy at temperature T, Gef is the Gibbs energy function defined by equation 4, $H_{298.15}^\circ$ is the standard enthalpy at 298.15 K, and Δ represents the change in these quantities. In this case Δ refers to the change in the calcination reaction. The equilibrium constant K for the reaction is identical with the equilibrium pressure of CO_2, and R is the gas constant, 1.98717 cal/mole•K.

The data listed in table 3 were obtained by static vapor pressure, weight loss technique, and static and dynamic thermogravimetric methods. Treatment of their data using equations 5 and 6 coupled with the values of ΔGef for the calcination reaction listed in table 2, yielded values of $\Delta H_{298.15}^\circ$. Each $\Delta H_{298.15}^\circ$ value in table 3 is then the average value of $\Delta H_{298.15}^\circ$ values obtained by the third-law method for all the data points within the temperature range listed for each investigation.

The data of Debray (11), Le Chatelier (28), Pott (36), Brill (9), Zavrieff (53), Hedvall (19), Mitchell (33), and Mauras (32) were rejected for one or more of the following reasons: (1) the scattering of data was rather large, (2) the calculated $\Delta H_{298.15}^\circ$ values showed a trend with temperature, and (3) the single data point was not considered reliable. The selected $\Delta H_{298.15}^\circ$ value, as given in table 3, was based on the data of the other investigators.

In carrying out the third-law method evaluation, the data obtained by Backstrom (2), Balarew and Lukowa (4), Beck (5), Bito, Aoyama, and Matsui (6-7), Bito and Matsui (8), Friedrich (14), Gokhale (16), Gruver (17), Haul and Heystek (18), Herzfeld (20), Matsui and Bito (29), Rao, Yoganarasimhan, and Lewis (37), Rowland and Lewis (40), Saito (41), Speros and Woodhouse (44), Sweeney (46), Thomasson and Cunningham (48), and Vaidya and Nicholson (49) were not considered, since it is believed that these data do not correspond to equilibrium conditions.

Our experimental $\Delta H_{298.15}^\circ$ value of 42.643±0.024 kcal/mole is in fair agreement with the selected value listed in table 3. It is in excellent agreement with values of various compilers listed in table 4. We use our value for $\Delta H_{298.15}^\circ$ and the values of ΔGef for reaction 3 to obtain the values of ΔG_T and log P_{CO_2}. The results are listed in table 2.

TABLE 4. - Values of $\Delta H_{298.15}^\circ$ for calcination of calcite from different compilers

Source	Year	$\Delta H_{298.15}^\circ$, kcal/mole
Kelley and Anderson (24).............	1935	42.665
Stern and Weise (45)..................	1969	42.610
Wagman (35, 51).......................	1971	42.620
Robie, Hemingway, and Fisher (39).....	1978	42.727

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