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Enthalpy and Gibbs energy of formation of dolomite, $\text{CaMg}(\text{CO}_3)_2$,
at 298.15 K from HCl solution calorimetry¹

By

Bruce S. Hemingway² and Richard A. Robie³

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² U.S. Geological Survey, 959 National Center, Reston, VA 22092

³ 220 Meadow Lark Lane, Boalsburg, PA 16827

Abstract

The enthalpy of formation, $\Delta_f H^\circ$, of dolomite, $\text{CaMg}(\text{CO}_3)_2$, has been determined by hydrochloric acid solution calorimetry. For the reaction $\text{CaO}(\text{c}) + \text{MgO}(\text{c}) + 2\text{CO}_2(\text{g}) = \text{CaMg}(\text{CO}_3)_2(\text{c})$, $\Delta_f H^\circ = -300.9 \pm 0.5$ kJ. At 298.15 K and 1 bar pressure, the calculated enthalpy and Gibbs energy of formation from the elements are -2324.5 ± 1.1 and -2161.7 ± 1.1 kJ·mol⁻¹, respectively, and the ionic activity product for dolomite is $K_0 = 10^{-17.09 \pm 0.37}$. These values are in good agreement with values derived from other experimental data.

Introduction

Dolomite, $\text{CaMg}(\text{CO}_3)_2$, is an ordered double salt having a widespread geologic distribution. It is the most important phase involved in the Ca-Mg geochemistry of sea water and surface waters, and is a common participant in the thermal metamorphism of siliceous carbonate rocks. A knowledge of the Gibbs energy of formation, $\Delta_f G^\circ$, of dolomite is important for modelling many geologic processes.

Robie et al. (1978) provided a value for the enthalpy of formation of dolomite and listed the source as unpublished data. Their result has been used as a thermodynamic reference value or has been compared to results derived from phase equilibrium reactions by Holland and Powell (1990) and Berman (1988). Good agreement was found in both studies. However, the basis for their value has not been documented in the literature. In this study, we present the calorimetric data supporting the value selected by Robie et al. (1978).

Materials

The calorimetric reference phases selected for the reaction scheme to determine the enthalpy of formation of dolomite were CaO and MgO. The CaO sample was obtained by heating primary standard CaCO_3 (Mallinkrodt¹, C-65) at 1575 K in a platinum crucible for three hours. MgO was obtained from Johnson-Matthey as Specpure reagent MgO (J.M. 130). The MgO sample was heated in a platinum crucible at 1575 K for three hours to promote grain growth. Both samples were rapidly cooled and placed in a desiccator over fresh desiccant until used. The samples were portions of the material used by Hemingway and Robie (1973) in a study of some Ca- and Mg-carbonate minerals.

The dolomite, $\text{CaMg}(\text{CO}_3)_2$, sample was taken from a large, water-clear, single crystal from Binnental, Switzerland. The chemical analysis is given in Table 1. This material was a portion of the sample used by Stout and Robie (1963) for low-temperature heat-capacity measurements. The dolomite was ground in a Diamonite mortar and sieved using nylon screens to -100 +300 mesh. The powder was heated to 388 K for two hours, and cooled and stored in a desiccator until used.

¹ Any use of trade names in this report is for descriptive purposes only and does not constitute endorsement by the U. S. Geological Survey.

The hydrochloric acid (HCl) was special reagent obtained in five gallon lots from Fisher Scientific Company and certified to be 4.00 ± 0.01 M. The acid was a portion of that used by Hemingway and Robie (1973).

Apparatus and procedures

The vacuum-jacketed solution calorimeter used in this study has been described by Robie and Hemingway (1972). For this study, the calorimeter was operated sealed (i.e., under constant volume conditions). For each measurement (except CaO), the calorimeter was filled with a fresh batch of 950.0 grams of 4.00 M HCl. For the reaction involving CaO, a stoichiometric amount of MgO (with respect to the dolomite dissolution reaction) was dissolved in the 950.0 g of acid. The reactions involving CaO and dolomite corresponded to 0.020 mole with nominal weights of 1.211 g for CaO and 3.688 g for dolomite. Hemingway and Robie (1973) measured the enthalpy of solution of MgO under similar conditions (0.025 mol of MgO in 950.0 g HCl). Their values are used here.

The formula weights used in the calculations are based on the 1985 atomic weights scale (Mills et al., 1988). The values are CaO 56.077, MgO 40.304, and $\text{CaMg}(\text{CO}_3)_2$ 184.401 $\text{g}\cdot\text{mol}^{-1}$. The densities used to correct the observed weights for buoyancy were CaO 3.345, MgO 3.584, $\text{CaMg}(\text{CO}_3)_2$ 2.866, and 4.00 M HCl 1.0658 $\text{g}\cdot\text{cm}^{-3}$. The internal volume of the calorimeter is 950 cm^3 , and that of the internal sample holder is 3.6 cm^3 . The vapor space above the solution after reaction is 62.8 cm^3 .

Experimental results

It should be noted that the measurements reported here were made immediately following those made by Hemingway and Robie (1973). The second author had planned to expand upon his dissertation (Robie, 1957) as was done by Goldsmith and Newton (1969), and to provide an analysis of equilibria involving dolomite similar to that provided by Holland and Powell (1990) or Berman (1988), but did not have an opportunity to do so before he retired. Thus no degradation of the solvent or samples occurred as a consequence of a time delay.

The reaction scheme used to determine the enthalpy of formation of dolomite is listed in Table 2. The experimental values are given in Table 3.

Reaction 1 (Table 2) is written as though all of the CO_2 released in the dissolution reaction for dolomite escapes to the gas phase. However, about 93 per cent of the CO_2 dissolves in the acid. To obtain the enthalpy of Reaction 1, it is necessary to correct the observed enthalpy of solution for the heat effect of that portion of the CO_2 that remained in solution. This correction is discussed in detail by Hemingway and Robie (1973). The observed enthalpy of solution of dolomite is -460.22 ± 0.56 $\text{J}\cdot\text{g}^{-1}$ at 300.15 K. Correction for the CO_2 dissolved in the acid and correction to CO_2 at its standard state of 1 bar pressure yields -255.29 ± 1.90 $\text{J}\cdot\text{g}^{-1}$ at 300.15 K.

Reactions 2 and 3 are the dissolution of MgO and CaO. The heat effect of both of these reactions are dependent upon both particle size and

crystallinity of the material used. It has been shown in several studies (e.g., Taylor and Wells, 1938, Livey et al., 1957, and Natarajan et al., 1969) that preparation of MgO and CaO through decomposition reactions results in well crystallized material only when high temperature annealing is used. Table 4 shows the increase in the enthalpy of solution of MgO samples prepared at lower temperatures by decomposition of Mg(OH)₂ as compared to similar samples prepared at higher temperatures. The properties of the MgO and CaO samples used as reference phases must be nearly the same as those of the material upon which the enthalpy of formation of MgO and CaO are based or a systematic error will result. The results of Natarajan et al. (1969) suggest that our preparation of CaO and MgO should eliminate such systematic errors.

Four measurements of the enthalpy of solution of calcium oxide were made in 950.0 g of 4.00 *N* HCl in which 0.806 g of MgO had been dissolved previously. This was necessary for the reaction stoichiometry and because Hemingway and Robie (1973, Figure 1) had shown that the enthalpy of solution of CaO varied with the amount of MgO dissolved in the solution. Our result for the enthalpy of reaction 2 at 300.15 K is -197.74 ± 0.34 kJ·mol⁻¹.

The enthalpy of solution values for MgO are taken from Hemingway and Robie (1973). Their results were corrected to 300.15 K using $d\Delta H/dT = 84$ J·mol⁻¹·K⁻¹. The selected value is -150.30 ± 0.08 kJ·mol⁻¹.

Using Hess' law, we calculate the enthalpy of formation of dolomite at 300.15 K as $\Delta_f H = -\Delta_1 H + \Delta_2 H + \Delta_3 H = -300.94 \pm 0.49$ kJ·mol⁻¹. The correction to 298.15 K is obtained from Kirchoff's relation $d\Delta H/dT = \Delta C_p^\circ = C_p^\circ(\text{dolomite}) - [C_p^\circ(\text{CaO}) + C_p^\circ(\text{MgO}) + 2C_p^\circ(\text{CO}_2)]$ where C_p° is the heat capacity at constant pressure. At 298.15 K, the heat capacities (Robie et al., 1978) for CaO, MgO, CO₂, and dolomite are 42.12, 37.78, 37.13 and 157.53 J·mol⁻¹·K⁻¹, respectively, and the correction is 3.37 J·K⁻¹ or 7 J. Using the enthalpies of formation of the oxide reference phases (Robie et al., 1978), we calculate the enthalpy of formation of dolomite from the elements as -2324.5 ± 1.1 kJ·mol⁻¹. Combining this value with the entropies of the elements (Robie et al., 1978), we calculate the Gibbs energy of formation of dolomite as -2161.7 ± 1.1 kJ·mol⁻¹. From this value, we may calculate the ion activity product of dolomite as $K_b = 10^{-17.09 \pm 0.37}$, and note that it is in reasonable agreement with several of the more recent values listed in Table 5 that are derived from solubility studies, particularly those based upon studies of ground water (Barnes and Back, 1964, and Hsu, 1964) and sea water (Kramer, 1959).

Discussion

Holland and Powell (1990) and Berman (1988) used the enthalpy of formation of dolomite, -2324.5 ± 1.5 kJ·mol⁻¹, reported by Robie et al. (1978, unpublished data) as a calorimetric constraint in their analyses of the thermodynamic data for minerals in the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂. Good agreement was found between that value and values derived from phase equilibrium experiments (less than 1.2 kJ·mol⁻¹ of difference). The results presented here provide the derivation of the calorimetric value.

Recently, Chai and Navrotsky (1993) have determined the enthalpy of formation of dolomite from calcite and magnesite using high-temperature molten salt calorimetry. Their result, $-11.1 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}$, is substantially more negative than equivalent values calculated from the results of Berman (1988), $-4.8 \text{ kJ}\cdot\text{mol}^{-1}$; Holland and Powell (1990), $-5.5 \text{ kJ}\cdot\text{mol}^{-1}$; Navrotsky and Capobianco (1987), $-6.0 \text{ kJ}\cdot\text{mol}^{-1}$; and Robie et al. (1978), $-3.8 \text{ kJ}\cdot\text{mol}^{-1}$. Their value is in good agreement with the value calculated from Helgeson et al. (1978), $-10.2 \text{ kJ}\cdot\text{mol}^{-1}$. The results reported by Navrotsky and Capobianco (1987) and Robie et al. (1978) are based on dissolution measurements in aqueous acid solvents at temperatures near room temperature. The results reported by Holland and Powell (1990), Berman (1988) and Helgeson et al. (1978) are based on an analysis of phase equilibrium data.

It is somewhat difficult to analyze the differences in these studies because the values used for the reference phases vary by 2.2 kJ in the case of MgCO_3 and by 1.4 kJ for CaCO_3 . Two of the studies, Helgeson et al. (1978) and Chai and Navrotsky (1993) yield nearly identical results of $-2330.0 \pm 3 \text{ kJ}\cdot\text{mol}^{-1}$ for the enthalpy of formation of dolomite from the elements at 298.15 K. Values calculated from the remaining four studies vary from -2324.5 to $-2326.5 \text{ kJ}\cdot\text{mol}^{-1}$ with $-2325.5 \pm 3 \text{ kJ}\cdot\text{mol}^{-1}$ a good average for the set. Considering the fact that Berman (1988) and Holland and Powell (1990) used an improved method of analysis in comparison to the pioneering effort of Helgeson et al. (1978), their results are preferred. Also, since Hemingway (1991) has raised questions regarding the use of molten salt calorimeters for the study of phases that liberate a volatile phase on dissolution, the aqueous acid solution calorimetric values are preferred. However, corrections for and potential systematic errors arising from the liberation CO_2 gas in both types of calorimetric reaction experiments are a problem.

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Table 1. Analysis of dolomite from
Binnental, Switzerland.

Oxide	Weight per cent	Ideal
CaO	30.77	30.41
MgO	21.54	21.86
CO ₂	47.38	47.73
MnO	0.10	
FeO	0.008	
SrO	0.017	
Total	99.82	

Table 2. Reaction scheme for dolomite.

Reaction	$\Delta_r H^\circ$ kJ·mol ⁻¹
1. CaMg(CO ₃) ₂ (c) + [178HCl + 2276H ₂ O](aq) = [CaCl ₂ + MgCl ₂ + 174HCl + 2278H ₂ O](aq) + 2CO ₂ (g)	-47.08 ±0.35
2. MgO(c) + [178HCl + 2276H ₂ O](aq) = [MgCl ₂ + 176HCl + 2277H ₂ O](aq)	-150.30 ±0.08
3. CaO(c) + [MgCl ₂ + 176HCl + 2277H ₂ O](aq) = [CaCl ₂ + MgCl ₂ + 174HCl + 2278H ₂ O](aq)	-197.72 ±0.34
4. CaO(c) + MgO(c) + 2CO ₂ (g) = CaMg(CO ₃) ₂	-300.94 ±0.49

* enthalpy of reaction at 300.15 K

Table 3. Experimental enthalpies of solution for dolomite, CaO and MgO in 4.00 *N* HCl at 300.15 K.

Sample mass	Temperature change corrected for	Mean solution temperature	Heat capacities initial	Heat capacities final	Enthalpy of solution
g	K	K	J	J	J·g ⁻¹
Dolomite					
3.6877	0.4684	299.56	3644.3	3648.5	-463.22
3.6890	0.4651	300.08	3644.8	3640.5	-459.29
3.6900	0.4676	300.92	3657.4	3653.4	-463.29
3.6918	0.4818	301.09	3489.4	3484.0	-455.06
Calcium Oxide					
1.1209	1.0858	299.11	3644.1	3644.1	-3529.8
1.1214	1.0823	299.65	3639.0	3649.2	-3516.9
1.1213	1.0832	300.60	3649.4	3658.3	-3529.5
1.1210	1.0831	300.02	3654.4	3646.5	-3527.0

	Magnesium Oxide*				
1.0085	1.0288	303.42	3651.2	3644.1	-3721.0
1.0084	1.0293	303.71	3649.9	3645.7	-3723.7
1.0086	1.0296	303.47	3648.1	3645.4	-3722.8
1.0087	1.0307	303.63	3649.3	3643.5	-3726.0

* data taken from Hemingway and Robie (1973)

Table 4. Variations in the enthalpy of solution of MgO prepared from Mg(OH)₂ at different temperatures in acid of the same composition and at the same temperature.

Method	Enthalpy of Reference solution kJ·mol ⁻¹	
Heated at 723 K for 2.5 hours	-153.43 ±0.29	Taylor and Wells (1938) ^a
Heated at 1723 K for 2.5 hours	-149.45 ±0.13	Taylor and Wells (1938) ^a
Heated at 653 K for 2 hours	-156.69	Livey et al. (1957) ^b
Heated at 1653 K for 1.75 hours	-151.46	Livey et al. (1957) ^b
Heated at 623 K for 200 hours	-142.72	Natarajan et al. (1969) ^c
Heated at 1223 K for 3 hours	-138.03	Natarajan et al. (1969) ^c
^a 640 g of 2.08 M HCl at 298 K		
^b 1057 g of 5.1 N HCl at 298 K		
^c 0.1 N HCl at 308 K		

Table 5. Ion activity product values for dolomite at 298.15 K.

Reference	Ion activity product $\times 10^{17}$
Halla and Ritter (1935)	3.0
Yanat'eva (1954)	6.58×10^{-2}
Kramer (1959)	1.5
Garrels, Thompson, and Seiver (1960)	4.7×10^{-3}
Van Tassel (1962, referenced in Barnes and Back, 1964)	2.5
Hsu (1964)	2.0
Barnes and Back (1964)	0.5 - 3.0
Siebert and Hostetler (1970)	0.4
This study	0.81