Journal of Thermal Analysis, Vol. 46 (1996) 353-359

THERMODYNAMICS OF $CaCO_3$ PHASE TRANSITIONS

G. Wolf, J. Lerchner, H. Schmidt, H. Gamsjäger[1], *E. Königsberger*[1] *and P. Schmidt*[1]

Institut für Physikalische Chemie, TU Bergakademie Freiberg D-09596, Freiberg, Federal Republic of Germany
[1]Abteilung für Physikalische Chemie, Montanuniversität Leoben, Franz-Josef-Strasse 18, A-8700 Leoben, Austria

Abstract

Thermodynamic quantities of the aragonite → calcite transition, were evaluated using results of calorimetric investigations. (1) Dissolution enthalpies of the $CaCO_3$ polymorphs aragonite and calcite measured near room temperature with different calorimeter, (2) the enthalpy of the spontaneous phase transformation obtained by differential scanning calorimetry, (3) heat capacities and heat capacity differences determined with a heat flux calorimeter as well as previously determined, (4) *e.m.f.* data on Gibbs-energies of the phase transition were processed simultaneously with an optimization routine developed recently. The optimized data set (25°C) given below corresponds reasonably with CODATA recommendations, however, the precision has markedly improved.

$\Delta_{\mathrm{arag}}^{\mathrm{calc}}G^{*}/\mathrm{J\ mol^{-1}} = -840\pm20$
$\Delta_{\mathrm{arag}}^{\mathrm{calc}}H^{*}/\mathrm{J\ mol^{-1}} = 440\pm50$
$\Delta_{\mathrm{arag}}^{\mathrm{calc}}S^{*}/\mathrm{J\ mol^{-1}\ K^{-1}} = 4.3\pm0.2$
$\Delta_{\mathrm{arag}}^{\mathrm{calc}}C_p^{*}/\mathrm{J\ mol^{-1}\ K^{-1}} = 0.0\pm0.2$

Keywords: aqueous solutions, calcium carbonate polymorphs, dissolution reactions, phase transitions

Introduction

Although the $CaCO_3$ polymorphs, calcite, aragonite and vaterite, have been studied extensively [1], agreement is rather poor between phase transition enthalpies reported so far. A comprehensive study of $CaCO_3$ solubilities in CO_2–H_2O solutions between 0 and 90°C resulted in the respective *H*-, *S*- and *G*-functions [2], however, only the latter meet the standards of accuracy and precision desirable in the present context. Clearly *G*-functions are directly related to solubility constants, e.g. $\Delta_{\mathrm{arag}}^{\mathrm{calc}}G^{*} = RT\ln(K_{\mathrm{sp}}^{\mathrm{calc}}/K_{\mathrm{sp}}^{\mathrm{arag}})$, whereas *H*- and *S*-functions have to be deduced from the pertaining temperature derivatives, and thereby inevitably some accuracy is lost. When $\Delta_{\mathrm{arag}}^{\mathrm{calc}}S_{298}^{*}$ was obtained by a potentiometric method which essentially determined also the solubilities of arago-

0368–4466/96/ $ 5.00

John Wiley & Sons, Limited Chichester

nite and calcite relative to each other, the result agreed reasonably with calorimetric data [3]. On the other hand calorimetric measurements of $\Delta_{arag}^{calc}H^*$ in acidic solutions [4, 5] do not satisfactorily correspond with potentiometric data [3, 6], or the derivation from the temperature dependence of solubility functions [2]. The pertinent data are given in Table 1.

Table 1 Phase transition enthalpies of $CaCO_3$ polymorphs (25°C)

Quantity	Observed value / kJ mol^{-1}	Method	Ref.
$\Delta_{arag}^{calc}H^*$	0.172±0.084	$\Delta_{sol}H$ (HCl soln.)	[4]
	0.176±0.084	$\Delta_{sol}H$ (HCl soln.)	[5]
	-0.270±0.095	$\Delta_{arag}^{calc}E$, $\Delta_{arag}^{calc}S^*$	[6, 16]
	-1.120±1.200	$\partial \ln (K_{sp}^{calc}/K_{sp}^{arag})/\partial T$	[2]
	0.540±0.060	$\partial(\Delta_{arag}^{calc}E/T)/\partial(1/T)$	[3]

In the present work it was attempted to determine reliable enthalpies of the aragonite → calcite transition by means of different dissolution techniques, differential scanning calorimetry as well as heat capacity measurements. Moreover, thermochemical and potentiometric data were simultaneously evaluated with the versatile Gibbs-energy minimizing program Chem-Sage [7] employing a previously developed optimization routine [8]. The results of this work and previous data on the $\Delta_{arag}^{calc}G^*$–T-function [3] were combined so as to calculate a consistent set of thermodynamic quantities.

Experimental methods

Apparatus

Two types of calorimeters were used to determine the enthalpies of dissolution:

– twinned calorimeters (designated as MBK1 and MBK2) with a metal block thermostat and Dewar reaction vessels (ca. 25 and 50 cm^3) in which the $CaCO_3$ polymorphs (ca. 50 and 100 mg) were dissolved.

– a modified LKB 8700 calorimeter (designated as LKB) where similar sample/solution ratios as with the MBKs can be employed.

The enthalpy of dissolution of potassium chloride was used as standard reference reaction for calibrating the calorimetric set-ups [9], its concentration and temperature dependence was described by a polynomial function recommended previously [10].

Dissolution reactions of $CaCO_3$ may have long reaction times. To process the output data of the calorimeters in these cases reliably, the heat exchange constant of the measuring system was determined by separate experiments [11].

The phase transition enthalpies of the $CaCO_3$ polymorphs at high temperatures were measured with a differential scanning calorimeter of the type DSC 111 from Setaram (France). The measurements were carried out in a CO_2-atmosphere (1 bar) with different heating rates (2 to 30 K min^{-1}).

For the measurements of the heat capacity and heat capacity differences of the $CaCO_3$ polymorphs a heat flux calorimeter of the type DAK1 (Russian) was modified. A very sensitive method to obtain heat capacity differences of solids was developed previously [12]. In the twin calorimeter two samples of nearly equal heat capacity were heated keeping the heater power exactly constant. During the period between the thermal equilibrium state (just when the heating was started) and the final stationary state the temperature differences, $\Delta T_{1,2}$, between both samples were measured as a function of time. The heat capacity difference is then proportional to

$$\int_0^t \Delta T_{1,2} dt.$$

Reagents

Reagent grade (p.a.) calcite was obtained from Merck. Aragonite was prepared by a well known technique [13]. Composition and structure of all samples were ascertained by chemical analyses and X-ray methods. $CaCO_3$ polymorphs selected for further investigation were pure phases of calcite and aragonite respectively. In the case of aragonite a natural product from Bilin (Czech Republic) was used also. The different aragonite samples were indistinguishable with respect to these thermochemical experiments.

Results

Attempts to determine reliable phase transition enthalpies of the $CaCO_3$ polymorphs by means of dissolution calorimetry in acidic media (0.7 mol kg^{-1} HCl saturated with NaCl, or 2.0 mol kg^{-1} $HClO_4$, 2.0 mol kg^{-1} NaCl saturated with CO_2) met with difficulties, because the results depend critically on the final state of carbon dioxide. Reactions (1) evolving gaseous carbon dioxide produce much less enthalpy than reactions (2) leading to dissolved carbon dioxide.

$$CaCO_3(\text{arag or calc}) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(aq) \quad (1)$$

$$CaCO_3(\text{arag or calc}) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(aq) + H_2O(aq) \quad (2)$$

Whether it was attempted to keep carbon dioxide in solution or in the gas phase the maximum experimental error could not be reduced below ±450 J mol^{-1}. Dissolution in aqueous alkaline EDTA-media (0.5 mol kg^{-1},

Table 2 Experimental data for ΔH of aragonite and calcite dissolution

Substance or reaction	Method	θ / °C	ΔH / kJ mol^{-1}	Calorimeter
calcite	HCl–NaCl soln.	25	–31.54±0.20	LKB
aragonite	HCl–NaCl soln.	25	–31.44±0.50	LKB
arag. → calc.		25	0.10±0.54	
calcite	HCl–NaCl soln., CO_2	25	–18.24±0.08	MBK
aragonite	HCl–NaCl soln., CO_2	25	–18.03±0.45	MBK
arag. → calc.		25	0.21±0.46	
calcite	EDTA soln.	40	–32.66±0.10	MBK
aragonite	EDTA soln.	40	–32.61±0.15	MBK
arag. → calc.		40	0.05±0.18	

$pH=10.3$) led to a better defined final state than dissolution in acids. Measurements near room temperature with different calorimeters and dissolution conditions by different investigators were carried out in our laboratories and resulted in $\Delta^{calc}_{arag}H^*_{298}$-values with a maximum experimental uncertainty of ±200 J mol^{-1}. Typical results are collected in Table 2.

High temperature $\Delta^{calc}_{arag}H^*$ was studied by DSC in a CO_2-atmosphere at varying heating rates. The DSC measurements were carried out using a SETARAM DSC 111. Natural and synthetic aragonites resulted in $\Delta^{calc}_{arag}H^*=403\pm8$ J mol^{-1}. With rising heating rates (2 to 25 K min^{-1}) the onset temperature increased from

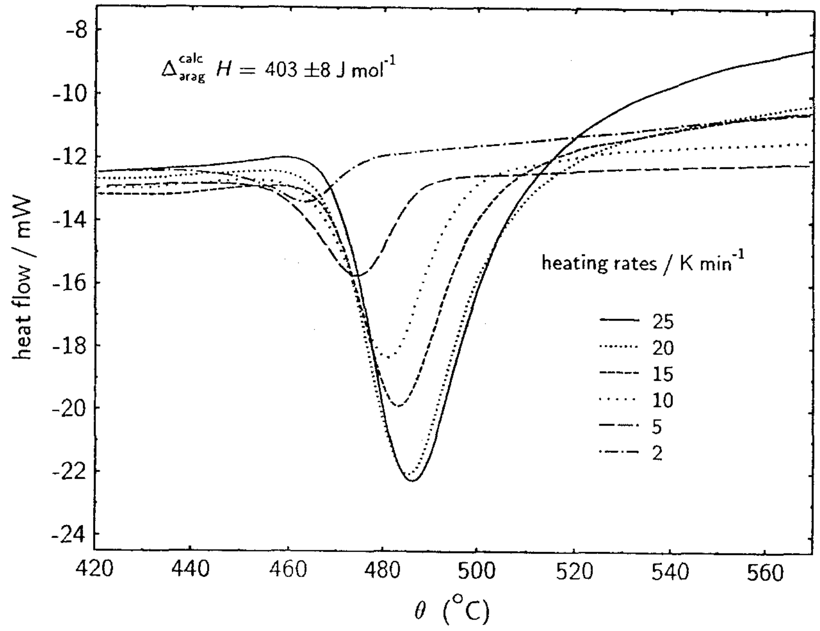

Fig. 1 DSC-curves of aragonite

448 to 469°C, see Fig. 1. It turned out that $\Delta^{\mathrm{calc}}_{\mathrm{arag}}H^*$ did not significantly change with varying onset temperatures; this indicates a small difference in the heat capacities of the carbonate phases.

Table 3 Heat capacities of aragonite and calcite

Substance or reaction	C_p^* / J mol^{-1} this work	C_p^* / J mol^{-1} [14–16]	θ / °C
calcite	83.68±1.10	83.86	30
aragonite	83.26±1.10	82.22	30
arag. → calc.	0.0±0.2		30
calcite	88.52±2.20	88.66	80
aragonite	88.47±2.00	87.79	80
arag. → calc.	0.0±0.2		80
calcite	95.82±1.20	93.31	130
aragonite	94.28±1.30	92.73	130
arag. → calc.	0.6±0.2		130

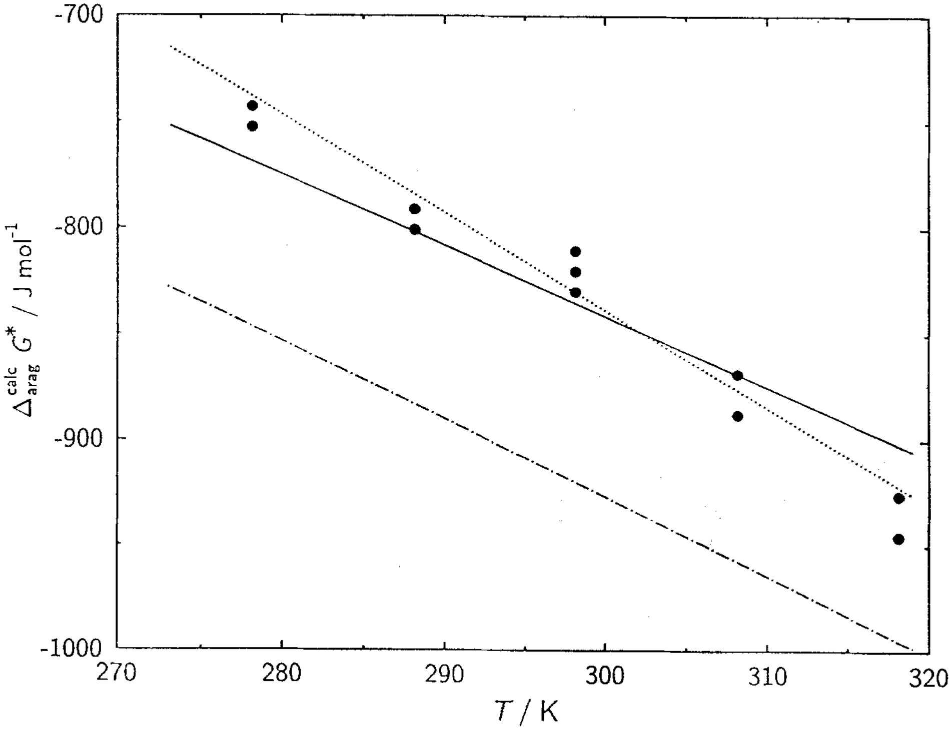

Fig. 2 ΔG^*-function of aragonite → calcite transition: • Experimental data [3], dotted line: linear regression, dashed-dot line: CODATA recommendations [18], full line: optimization, this work

Heat capacities and heat capacity differences of calcium carbonate polymorphs were obtained using a heat flux calorimeter. A high sensitivity method was developed to determine the small differences between the heat capacities of calcite and aragonite [12]. Although the C_p^*-values of these compounds found at 30, 80 and 130°C agreed within the experimental errors with the values given in Refs [14–16], it is proposed to rely for optimization purposes on the directly measured $\Delta_{\mathrm{arag}}^{\mathrm{calc}}C_p^*$-values [17], which were found to be negligible within a comparatively small error range of ± 0.2 J mol^{-1}. Typical results are collected in Table 3.

Discussion

For computational purposes the Gibbs-energy minimizer Chem-Sage was employed [7]. All experimental data determined in this work $\Delta_{\mathrm{arag}}^{\mathrm{calc}}H^*$, $\Delta_{\mathrm{arag}}^{\mathrm{calc}}C_p^*$ together with $\Delta_{\mathrm{arag}}^{\mathrm{calc}}G^*$ published previously [3] were processed with a recently developed optimization routine [8]. As shown in Fig. 2 the optimized G-function runs almost parallel to that recommended by CODATA [18]. The linear regression through the potentiometric data pairs is somewhat steeper leading to a higher entropy of aragonite → calcite transition. However, the deviations between optimized straight line and that obtained potentiometrically are always less than ± 20 J mol^{-1} or ± 0.1 mV.

In Table 4 the respective results are compared numerically with the thermodynamic data recommended by the CODATA compilation [18]. It turns out that optimized and CODATA values agree within markedly reduced mean errors.

Table 4 Aragonite → calcite transition at 25°C

Quantity	CODATA [18]	This work
$\Delta_{\mathrm{arag}}^{\mathrm{calc}}G^*$/J mol^{-1}	-920 ± 1410	-840 ± 20
$\Delta_{\mathrm{arag}}^{\mathrm{calc}}H^*$/J mol^{-1}	190 ± 1490	440 ± 50
$\Delta_{\mathrm{arag}}^{\mathrm{calc}}S^*$/J mol^{-1} K^{-1}	3.72 ± 0.30	4.3 ± 0.2
$\Delta_{\mathrm{arag}}^{\mathrm{calc}}C_p^*$/J mol^{-1} K^{-1}	1.15 ± 0.43	0.0 ± 0.2

Work on thermodynamic quantities of the vaterite→calcite phase transition is still under progress, discrepancies between the $\Delta_{\mathrm{vat}}^{\mathrm{calc}}G^*$-, $\Delta_{\mathrm{vat}}^{\mathrm{calc}}H^*$- and $\Delta_{\mathrm{vat}}^{\mathrm{calc}}S^*$-values obtained by the methods described and those listed in the CODATA compilation [18] have been recognized.

* * *

Financial support by the Deutsche Forschungsgemeinschaft (DFG) and the Austrian Science Foundation (FWF) is gratefully acknowledged (Project 8120)

References

1 W. D. Carlson, R. J. Reeder, editor, Carbonates: Mineralogy and Chemistry; Reviews in Mineralogy, Vol. 11, Chapter 6, Mineralogical Society of America, 1983, p. 191–225.
2 L. N. Plummer and E. Busenberg, Geochim. Cosmochim. Acta, 46 (1982) 1011.
3 E. Königsberger, J. Bugajski and H. Gamsjäger, Geochim. Cosmochim. Acta, 53 (1989) 2807.
4 H. L. J. Bäckström, J. Amer. Chem. Soc., 47 (1925) 2432.
5 W. A. Roth and P. Chall, Z. Elektrochem. Soc., 34 (1928) 185.
6 P. A. Rock and A. Z. Gordon, J. Amer. Chem. Soc., 98 (1976) 2364.
7 G. Eriksson and K. Hack, Metall. Trans. B, 21 B (1990) 1013.
8 E. Königsberger and G. Eriksson, CALPHAD, 1994 (submitted for publication).
9 C. Günther, R. Pfestorf, M. Rother, R. Zimmermann, G. Wolf and V. Schröter, J. Thermal Anal., 33 (1988) 359.
10 V. Vacek and V. Pekárek, Chemicky Prumysl, 4 (1982) 178.
11 G. Wolf, Proc. 3rd Polish Conf. on Calorimetry, 1984, p. 47.
12 G. Wolf, Proc 4th Polish Conf. on Calorimetry, 1986.
13 F. Lippmann, Fortschr. Mineral., 38 (1960) 156.
14 K. Kobayashi, Sci. Rep. Tohoku University Series 1, 35 (1951) 103.
15 K. Kobayashi, Sci. Rep. Tohoku University Series 1, 35 (1951) 111.
16 L. A. K. Staveley and R. G. Linford, J. Chem. Thermodynamics, 1 (1969) 1.
17 G. Wolf and H. Schmidt, to be published.
18. CODATA Task Group, in D. Garvin, V. B. Parker and H. J. White, Jr., editors, CODATA Series on Thermodynamic Properties, Hemisphere Publishing Corporation, Washington-New York-London, 1987.