Thermodynamic Properties of Synthetic Otavite, $CdCO_3$(cr): Enthalpy Increment Measurements from 4.5 K to 350 K

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Enthalpy increments for cadmium carbonate were measured for temperatures from 4.5 K to 350 K with an adiabatic calorimeter. These measurements were used to compute the entropy, enthalpy relative to 0 K, and the heat capacity of cadmium carbonate. A small anomaly was observed for the sample in the temperature region from approximately 175 K to 265 K. Comparison of the calculated entropy for 298.15 K, 103.88 $J\cdot K^{-1}\cdot mol^{-1}$, is made with other previously published reference values to arrive at a more precise and consistent set of thermodynamic properties for otavite.

Introduction

The environmental fate of pollutants is controlled by both thermodynamic and kinetic properties. Despite the growing ability to mathematically and computationally process large simulations of soil and ground water chemistry, the quality of the simulations can be seriously compromised by poor quality thermodynamic and kinetic information. Examples of rather noxious materials for which dubious thermodynamic parameters exist are the precipitates formed when ground water containing transition metal ions and related “heavy metals” comes in contact with dissolved carbon dioxide and carbonate minerals, all of which are common in aquatic environments. In an attempt to ameliorate the problems caused by the incomplete and/or low-quality thermodynamic data in these models, many thermodynamic property data evaluations have been conducted. In general, even a good evaluation of poor empirical results cannot make the proverbial silk purse from the sow’s ear. The present paper provides new data on $CdCO_3$(cr), or by its mineral name, otavite. It also discusses and evaluates the thermodynamic properties of otavite. The revised values in this paper will improve the reliability of aqueous chemical models to represent processes involving cadmium in the environment and elsewhere.

In an excellent and exhaustive paper on the cadmium carbonate and water system, Stipp et al. (1993) tabulated values of the 298.15 K entropy for $CdCO_3$(cr) given in 17 different references, all of which were data evaluations. These 17 references yielded only four different values for the entropy of otavite; *i.e.* the same values were reported again and again. The four values and their first appearance were as follows: 105.5 $J\cdot K^{-1}\cdot mol^{-1}$, Kelley and Anderson (1935); 97.5 $J\cdot K^{-1}\cdot mol^{-1}$, Kelley and King (1961); 92.5 $J\cdot K^{-1}\cdot mol^{-1}$, Wagman et al. (1968); 106.3 $J\cdot K^{-1}\cdot mol^{-1}$, Sverjensky (1984). None of these values was based on low-temperature thermal properties; the values from Kelley and Anderson (1935) and Kelley and King (1961) were based on decomposition pressures of CO_2 over otavite. The Wagman et al. (1968, 1982) value will be discussed in more detail later. As Stipp et al. (1993) observed, all of the other data evaluations repeated the values from either the Kelley et al. sources or the Wagman et al. source, with the notable exception of Sverjensky (1984). Sverjensky compared thermodynamic values of other similar metal carbonates to estimate the entropy for $CdCO_3$(cr).

Stipp et al. (1993) also observed that the aqueous solubility that one would calculate from these different data evaluations ranged over nearly 4 orders of magnitude. This is a direct problem for the simulations. An error of 4 orders of magnitude in a calculated metal solubility (for example the difference between 10^{-5} $mol\cdot kg^{-1}$ and 10^{-9} $mol\cdot kg^{-1}$) can easily mean the difference between success and failure in a proposed remediation program or the difference between acceptable and unacceptable levels of water contamination.

Stipp et al. measured the solubility of cadmium carbonate at different temperatures and obtained the thermodynamic variables relating to the solution process after accounting for all hydrolysis reactions. Then they obtained the 298.15 K entropy of crystalline otavite through combination of their entropy of solution with the CODATA (Cox et al., 1989) entropies of aqueous cadmium and carbonate ions. Their value of the 298.15 K entropy of crystalline cadmium carbonate was 106 $J\cdot K^{-1}\cdot mol^{-1}$ with the conservative uncertainty estimate of 30 $J\cdot K^{-1}\cdot mol^{-1}$. Part of the large uncertainty estimate was due to difficulties that have recently been reported in obtaining reasonable agreement between the CODATA entropies of ions and measured properties of aqueous electrolytes (Archer, 1992b; Rard and Archer, 1995).

The present paper reports measured enthalpy increments for $CdCO_3$(cr) from 5 K to 350 K. From these values, and the assumption of no residual entropy at 0 K, the entropy of cadmium carbonate was determined.

Experimental Section

The cadmium carbonate used for the present measurements was obtained from Aldrich as 99.999% pure (metals basis). The ICP analysis performed by the manufacturer showed only Mo (2×10^{-6}) and Si (3×10^{-6}). The sample was used without further purification. The filling of the calorimeter and all handling of the samples were performed in an argon-filled drybox. The evacuation of the calorimeter was performed quickly so as not to remove CO_2 from the carbonate. Approximately 8 kPa (for 300 K) of helium was sealed in the calorimeter with the sample. The mass of cadmium carbonate used for the measurements was 6.2181 g and corresponded to approximately 25% of the

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[†] Certain commercial materials and suppliers are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by either the U.S. Government or the National Institute of Standards and Technology, nor does it imply that the equipment or materials identified are necessarily the best available for the purpose.

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internal volume of the calorimeter. The calorimetric apparatus has been described previously (Archer, 1995). The density and molecular mass of cadmium carbonate were taken to be 4.26 g·cm^{-3} and 172.419 g·mol^{-1}, respectively. The measured enthalpy increments of the filled calorimeter were converted into enthalpy increments for cadmium carbonate by subtraction of the enthalpy increments for the empty calorimeter and for the small differences in amounts of helium and vacuum grease between the empty and filled calorimeters. The enthalpy increments were corrected for the small systematic biases in the calorimetric system using the equations

$$\epsilon\Delta H_{\mathrm{m}} = -[\{(T_2 + T_1)/2\} - 100\ \mathrm{K}](0.00001\ \mathrm{K}^{-1})\Delta H_{\mathrm{m}} \qquad (T_1 > 100\ \mathrm{K}) \quad (1)$$

$$\epsilon\Delta H_{\mathrm{m}} = -0.0025\Delta H_{\mathrm{m}} \qquad (T_2 < 13.8\ \mathrm{K}) \quad (2)$$

where T_2 and T_1 are the larger and the smaller of the two temperatures for the enthalpy increment, respectively, and H_{m} is the correction added to the substance's enthalpy increment, ΔH_{m}. The origin of these corrections has been described previously (Archer, 1995).

Results

The measured enthalpy increments for cadmium carbonate are given in Table 1. Above 50 K, the measurements for this sample were expected to be uncertain by no more than 0.1 to 0.2%, dependent upon the particular temperature. These uncertainty values were based on the previous measurements of enthalpy increments for calorimetric reference materials (Archer, 1995), the present reproducibility, and the percentage of the total measured enthalpy increment that was due to the cadmium carbonate sample. Below 50 K, the results must be considered less accurate, partly due to limits in accuracy of platinum resistance thermometer temperature scales below 20 K and also due to a decreasing contribution of the sample's enthalpy to the total measured enthalpy increment. These uncertainties do not include contributions from low levels of impurities. The contribution of the cadmium carbonate to the total measured enthalpy increment was a maximum of 24% near 20 K. The sample contributed 10% of the total enthalpy increment for the lowest temperature measurement. For temperatures greater than 9 K, the contribution to the total measured enthalpy increment from the cadmium carbonate sample varied between 17% and 24%.

For convenience of discussion, the measured values in Table 1 were grouped in series. Each series contains the chronological succession of measurements in that series, and each series appears in its chronological order.

Measurements of the enthalpy increments were fitted by means of a least-squares representation using a cubic-spline method described previously (Archer, 1992a). Briefly, a function $f(T)$ was used, where

$$f(T) = [T(C^{\circ}_{\mathrm{p,m}}/C^{\circ}_{\mathrm{p}})^{-1/3} - bT]/T^{\circ} \quad (3)$$

and where T was temperature, T° was 1 K, $C^{\circ}_{\mathrm{p,m}}$ was the molar heat capacity, C°_{p} was 1 J·K^{-1}·mol^{-1}, and b was a constant arbitrarily chosen to be 0.2 for the present case. The function $f(T)$ of eq 3 was fitted with a cubic spline using polynomials of the form

$$f(T) = a_i(T - T_i)^3 + b_i(T - T_i)^2 + c_i(T - T_i) + d_i \quad (4)$$

where the subscript i referred to the polynomial that contained the specified value of T and spanned the temperature range T_i to T_{i+1}. A particular (T_i, d_i) pair is referred to as a "knot." A "natural spline" end condition (*i.e.* second derivative equal to 0) was imposed at the highest temperature knot. The end condition imposed at the lowest temperature knot was a value of $-b$ (-0.2) for the first derivative. This was equivalent to assuming that the Debye temperature was independent of temperature near 0 K. (For the purpose of calculation: $T_{i+1} > T > T_i$.) The calculated heat capacity was thus

$$C^{\circ}_{\mathrm{p,m}}/C^{\circ}_{\mathrm{p}} = \left(\frac{T}{T^{\circ}f(T) + bT}\right)^3 \quad (5)$$

Equation 5 was integrated numerically to obtain the enthalpy. The model was determined by fitting to the measured values with a nonlinear least-squares program. The estimated square root of the variance for the least-squares procedure was calculated from twice the irreproducibility for a full calorimeter determination and the percentage of the observed enthalpy due to the cadmium carbonate sample. These values, given as σ in Table 1, approximately corresponded to a 95% confidence interval rather than the square root of the variance.

An anomaly in the thermal functions that spanned the temperature range of approximately 175 K to 265 K was apparent in the thermal functions calculated from the enthalpy increments for this sample of cadmium carbonate. Calculated values of the heat capacity are shown as the solid line in Figure 1. A calculation of the heat capacity of cadmium carbonate without the anomaly was obtained from a representation of the enthalpy increments with the measurements from 175 K to 260 K removed. This calculation is shown in Figure 1 as a dashed line. For lack of any better name, the values that constitute the dashed curve will be referred to here as "lattice" values.

The anomaly was first detected from a representation of the results from series 1 through 5. The differences of the measured enthalpy increments (all series) from the "lattice" values are shown in Figure 2. Because of its small size and rather wide temperature range, further measurement series were made. In order to ensure that the effect seen in Figures 1 and 2 was not due to improper contact of the calorimeter with the adiabatic shield, the cryostat was disassembled, the calorimeter was rehung, the calorimeter leads were relocated and then the measurements in series 6 were made. These measurements agreed with the previous measurements within 0.1% of the enthalpy increment for the cadmium carbonate. (This corresponds to ~0.02% of the enthalpy increment for the addenda and the cadmium carbonate sample. This difference in the enthalpy determination of a laden calorimeter after removal and replacement was a bit larger than previous such exercises, but not alarmingly so.)

A test was also made to demonstrate whether the observed effect was due to a nonequilibration effect from a lower temperature. During series 6 the measurement sequence was paused after measurement of the 244.4 K → 247.7 K enthalpy increment (nominal temperatures). The calorimeter was held at 247.7 K for 5 h, and then the measurement sequence was resumed. The next, and subsequent, measurements showed no discontinuity with the earlier results. This indicated that the effect was not related to a nonequilibration error.

Series 7 was obtained after cooling the calorimeter to 238 K, which is near, but not below, the temperature of the maximum of the peak, holding for 0.67 h, and then commencing the measurement sequence. These measurements did not agree with the previous measurements but agreed instead with the "lattice" values. Series 10 was

Table 1. Enthalpy Increment Measurements for Cadmium Carbonate

T_1/K	T_2/K	$\Delta H_{\mathrm{m}}(T_1 \rightarrow T_2)/\mathrm{J{\cdot}mol^{-1}}$	σ^a	δ^b	T_1/K	T_2/K	$\Delta H_{\mathrm{m}}(T_1 \rightarrow T_2)/\mathrm{J{\cdot}mol^{-1}}$	σ^a	δ^b	T_1/K	T_2/K	$\Delta H_{\mathrm{m}}(T_1 \rightarrow T_2)/\mathrm{J{\cdot}mol^{-1}}$	σ^a	δ^b
Series 1														
10.2315	12.2418	0.7614	0.7	0.14	18.6772	21.0517	5.986	0.7	−0.59	28.4844	31.1375	19.511	0.50	−0.17
12.2793	14.3050	1.3722	0.7	0.30	21.0289	23.4615	8.520	0.5	0.06	31.1062	33.8412	24.366	0.25	−0.15
14.3082	16.4627	2.419	0.7	0.17	23.4326	25.9649	11.748	0.5	0.14	33.8105	36.6132	29.672	0.25	0.14
16.4406	18.7008	3.913	0.7	−0.49	25.9347	28.5153	15.316	0.5	0.07	36.5833	39.4141	34.857	0.25	0.28
Series 2														
5.8949	7.2914	0.0928	2.0	−0.29	17.2294	19.5184	4.568	0.70	−0.35	32.0493	34.7830	25.911	0.25	−0.08
7.3320	9.0945	0.2365	2.0	0.05	19.4931	21.8794	6.844	0.70	0.50	34.7534	37.5568	31.308	0.25	0.18
9.0786	10.9629	0.4843	2.0	0.07	21.8524	24.3281	9.592	0.50	0.00	37.5277	40.3939	36.902	0.25	0.02
10.9669	13.0107	0.9496	1.0	−1.64	24.2979	26.8547	12.973	0.50	0.08	40.3655	43.2744	42.557	0.25	−0.09
12.9990	15.0855	1.715	0.70	0.51	26.8235	29.4177	16.635	0.50	−0.08	43.2465	46.1927	48.404	0.25	−0.05
15.0752	17.2396	2.875	0.70	0.42	29.3867	32.0797	21.212	0.50	−0.27					
Series 3														
4.3870	5.5959	0.0290	15.0	−14.87	23.5714	26.0667	11.741	0.50	0.29	48.2183	51.2515	59.038	0.20	−0.20
5.7211	7.0588	0.0819	2.0	1.37	26.0383	28.6304	15.527	0.50	0.01	51.2257	54.2786	65.093	0.20	0.08
8.4975	10.4140	0.4022	2.0	−1.07	28.6008	31.2617	19.740	0.50	−0.22	54.2538	57.3413	71.332	0.20	0.06
10.3955	12.4098	0.8029	1.0	0.24	31.2321	33.9418	24.326	0.25	−0.14	57.3169	60.4223	77.272	0.20	0.14
12.4227	14.4196	1.3922	0.7	−0.16	33.9129	36.6977	29.641	0.25	0.14	60.3985	63.5404	83.483	0.20	−0.07
14.4079	16.6283	2.573	0.70	0.34	36.6691	39.5139	35.116	0.25	0.06	63.5167	66.6779	89.505	0.20	0.02
16.6191	18.8790	4.046	0.70	−0.34	39.4860	42.3718	40.688	0.25	0.07	66.6543	69.8298	95.284	0.20	0.03
18.8572	21.1745	6.014	0.70	0.09	42.3448	45.3029	46.996	0.20	0.02	69.8067	73.0051	101.269	0.20	0.03
21.1542	23.5975	8.688	0.50	−0.04	45.2766	48.2538	52.678	0.20	−0.01	72.9824	76.1958	106.925	0.20	0.01
Series 4														
39.8174	42.2860	34.943	0.20	−0.08	108.5789	111.8965	160.338	0.20	0.15	212.7348	217.6450	373.877	0.20	0.05
42.2567	45.2270	46.934	0.20	−0.20	111.8354	115.1321	162.676	0.20	−0.05	217.6113	222.5130	378.455	0.20	0.06
45.1981	48.1846	52.709	0.20	−0.01	115.1162	120.0021	248.368	0.20	0.24	222.4738	227.3912	384.986	0.20	0.12
48.1562	51.1731	58.696	0.20	−0.02	119.9840	124.8669	255.355	0.20	0.09	227.3505	232.2676	389.921	0.20	0.11
51.1452	54.2059	65.091	0.20	0.04	124.8470	129.7340	261.906	0.20	−0.26	232.2249	237.1424	394.671	0.20	0.09
54.1785	57.2733	71.242	0.20	−0.12	129.7132	134.6082	270.615	0.20	0.23	237.0981	242.0152	398.753	0.20	0.02
57.2466	60.3572	77.255	0.20	0.10	134.5861	139.4828	276.502	0.20	−0.13	241.9687	246.8748	401.411	0.20	0.01
60.3310	63.4783	83.759	0.20	0.22	139.4576	144.3595	284.005	0.20	0.10	246.8264	251.7428	405.125	0.20	0.07
63.4530	66.6195	89.535	0.20	0.00	144.3350	149.2516	291.214	0.20	0.06	251.6916	256.6152	408.517	0.20	0.14
66.5942	69.7731	95.294	0.20	0.03	149.2256	154.1357	297.187	0.20	0.06	256.5627	261.4758	410.239	0.20	0.05
69.7482	72.9496	101.261	0.20	0.02	154.1090	159.0212	303.900	0.20	0.17	261.4198	266.3231	412.358	0.20	−0.06
72.9251	76.1402	106.890	0.20	0.01	158.9944	163.9103	310.005	0.20	0.08	266.2581	271.1686	416.774	0.20	0.02
76.1117	79.3487	112.537	0.20	−0.16	163.8850	168.8079	316.279	0.20	−0.02	271.1010	276.0182	420.988	0.20	0.06
79.3191	82.5715	118.371	0.20	0.09	168.7818	173.7002	321.667	0.20	−0.14	275.9443	280.8603	423.920	0.20	−0.04
82.5440	85.7967	123.217	0.20	0.06	173.6736	178.5873	328.211	0.20	0.10	280.8007	285.7054	426.606	0.20	0.01
85.7695	89.0313	128.216	0.20	0.00	178.5591	183.4703	334.217	0.20	0.15	285.6426	290.5429	429.932	0.20	0.08
89.0040	92.2823	133.419	0.20	−0.05	183.4383	188.3483	340.196	0.20	0.16	290.4775	295.3820	434.083	0.20	0.17
92.2548	95.5389	138.192	0.20	0.00	188.3149	193.2274	345.985	0.20	0.06	295.3163	300.2199	437.128	0.20	0.10
95.5101	98.8020	142.969	0.20	0.07	193.1923	198.1162	352.675	0.20	0.06	300.1518	305.0467	439.774	0.20	0.09
98.7731	102.0644	146.791	0.20	−0.17	198.0773	203.0051	358.501	0.20	−0.01	304.9683	309.8781	444.560	0.20	0.09
102.0356	105.3316	151.686	0.20	0.24	202.9607	207.8806	363.860	0.20	0.08	309.7949	314.6955	447.328	0.20	0.12
105.3025	108.6079	155.947	0.20	0.17	207.8170	212.7674	371.582	0.20	0.07					
Series 5														
78.5360	81.9309	122.231	0.20	−0.06	157.6556	161.5077	241.400	0.20	0.21	237.5169	241.3483	310.467	0.20	−0.04
81.9297	85.6443	139.808	0.20	−0.12	161.4802	165.3142	243.741	0.20	0.10	241.2996	245.1390	313.378	0.20	−0.04
85.6406	89.3736	146.621	0.20	−0.20	165.2879	169.1170	246.947	0.20	0.02	245.0886	248.9296	315.586	0.20	0.05
89.3681	93.1106	153.179	0.20	−0.10	169.0895	172.9350	251.442	0.20	−0.08	248.8767	252.7144	317.115	0.20	0.15
93.1030	96.8689	160.175	0.20	0.02	172.9062	176.7469	255.178	0.20	0.06	252.6639	256.5002	318.140	0.20	0.03
96.8602	100.6354	166.005	0.20	−0.12	176.7163	180.5497	258.798	0.20	0.23	256.4474	260.2865	320.368	0.20	0.10
100.6244	104.4145	172.369	0.20	0.01	180.5222	184.3562	262.037	0.20	0.06	260.2323	264.0674	321.755	0.20	0.00
104.4024	108.1971	177.880	0.20	0.02	184.3272	188.1614	265.757	0.20	0.07	264.0111	267.8484	324.337	0.20	0.08
108.1840	111.9772	182.858	0.20	0.00	188.1316	191.9706	269.703	0.20	0.07	267.7908	271.6251	326.088	0.20	0.05
111.9626	115.7707	188.225	0.20	−0.14	191.9395	195.7794	273.472	0.20	0.10	271.5591	275.3982	327.831	0.20	−0.19
115.7549	119.5674	193.682	0.20	0.11	195.7482	199.5873	276.679	0.20	0.00	275.3432	279.1651	329.425	0.20	0.11
119.5503	123.3787	198.987	0.20	0.04	199.5552	203.3851	279.536	0.20	0.02	279.1068	282.9394	332.164	0.20	0.02
123.3607	127.1842	203.180	0.20	0.03	203.3531	207.1885	283.469	0.20	0.06	282.8785	286.7147	334.646	0.20	0.05
127.1651	130.9908	207.710	0.20	0.06	207.1549	210.9962	287.202	0.20	0.04	286.6509	290.4848	336.519	0.20	0.05
130.9709	134.8051	212.261	0.20	−0.01	210.9588	214.7876	289.570	0.20	0.05	290.4179	294.2563	338.966	0.20	0.04
134.7820	138.6256	216.843	0.20	−0.05	214.7492	218.5846	293.875	0.20	0.25	294.1871	298.0222	341.264	0.20	0.19
138.6012	142.4376	220.523	0.20	−0.04	218.5454	222.3902	297.340	0.20	0.11	297.9531	301.7904	343.620	0.20	0.21
142.4123	146.2451	224.325	0.20	−0.02	222.3493	226.1838	299.540	0.20	0.08	301.7211	305.5462	344.019	0.20	0.03
146.2183	150.0548	228.732	0.20	0.11	226.1411	229.9841	303.304	0.20	0.09	305.4753	309.3004	346.489	0.20	0.14
150.0299	153.8679	232.401	0.20	−0.01	229.9362	233.7767	306.013	0.20	0.06	309.2271	313.0521	348.173	0.20	0.02
153.8419	157.6839	236.617	0.20	0.06	233.7280	237.5602	308.251	0.20	0.07	312.9761	316.8054	350.903	0.20	0.09
Series 6														
90.4891	94.2854	157.251	0.20	−0.07	154.9875	158.8316	237.572	0.20	−0.07	218.4016	221.6940	253.826	0.20	−0.09
94.2757	98.0395	161.681	0.20	−0.10	158.8074	162.6430	240.671	0.20	−0.13	221.6516	224.9406	255.826	0.20	−0.09
98.0274	101.8038	167.724	0.20	−0.15	162.6171	166.4595	244.981	0.20	−0.07	224.8965	228.1972	258.982	0.20	−0.09
101.7912	105.5849	174.647	0.20	0.28	166.4332	170.2713	248.371	0.20	−0.10	228.1518	231.4538	261.450	0.20	−0.04
105.5710	109.3698	179.586	0.20	−0.02	170.2439	174.0796	251.146	0.20	−0.38	231.4064	234.7046	263.272	0.20	−0.06
109.3527	113.1488	184.426	0.20	−0.05	174.0480	177.8930	256.059	0.20	−0.13	234.6548	237.9545	265.687	0.20	0.02
113.1301	116.9464	190.571	0.20	0.10	177.8627	181.4860	244.751	0.20	−0.10	237.8998	241.1973	267.357	0.20	−0.01
116.9286	120.7385	194.768	0.20	0.00	181.4543	185.2996	263.558	0.20	−0.01	241.1451	244.4408	268.917	0.20	0.00
120.7217	124.5410	199.691	0.20	−0.06	185.2644	189.1086	267.301	0.20	0.05	244.3762	247.6885	271.583	0.20	−0.03

Table 1 (Continued)

T_1/K	T_2/K	ΔH_m $(T_1 \rightarrow T_2)$/ J·mol^{-1}	σ^a	δ^b	T_1/K	T_2/K	ΔH_m $(T_1 \rightarrow T_2)$/ J·mol^{-1}	σ^a	δ^b	T_1/K	T_2/K	ΔH_m $(T_1 \rightarrow T_2)$/ J·mol^{-1}	σ^a	δ^b
Series 6														
124.5229	128.3448	204.002	0.20	−0.18	189.0750	192.9197	270.538	0.20	−0.11	247.3730	250.9628	295.214	0.20	−0.14
128.3247	132.1488	209.164	0.20	0.18	192.8843	196.7324	274.307	0.20	−0.13	250.9030	254.2095	273.359	0.20	−0.02
132.1289	135.9540	212.960	0.20	−0.04	196.6959	200.5280	277.062	0.20	0.01	254.1477	257.4544	274.437	0.20	−0.06
135.9352	139.7577	216.747	0.20	−0.11	200.4916	204.3297	280.498	0.20	−0.16	257.3842	260.6962	276.273	0.20	−0.05
139.7394	143.5723	221.281	0.20	−0.14	204.2940	208.1379	284.208	0.20	−0.20	260.6176	263.9464	279.055	0.20	−0.10
143.5534	147.3878	225.378	0.20	−0.11	208.1007	211.9317	286.961	0.20	−0.06	263.8833	267.7328	324.882	0.20	−0.04
147.3665	151.1986	229.131	0.20	−0.11	211.8940	215.1800	248.627	0.20	−0.10	267.6673	271.5007	325.639	0.20	−0.05
151.1764	155.0109	233.058	0.20	−0.13	215.1444	218.4421	251.890	0.20	−0.10	271.4320	275.2713	327.433	0.20	−0.29
Series 7														
238.2706	242.1034	307.322	U	−1.24	264.7399	268.5752	323.667	U	−0.20	291.1092	294.9557	340.411	U	0.14
242.0557	245.8890	309.543	U	−1.23	268.5119	272.3435	325.685	U	−0.13	294.8638	298.7168	341.630	U	−0.28
245.8395	249.6667	311.813	U	−0.89	272.2776	276.1146	327.347	U	−0.40	298.6204	302.4726	343.930	U	−0.20
249.6156	253.4572	315.347	U	−0.60	276.0461	279.8783	330.157	U	−0.06	302.3697	306.2193	346.322	U	−0.05
253.4050	257.2415	317.108	U	−0.40	279.8066	283.6547	333.712	U	−0.03	306.1122	309.9784	350.095	U	0.00
257.1861	261.0236	319.884	U	−0.13	283.5802	287.4261	335.503	U	−0.06	309.8672	313.7273	351.479	U	−0.05
260.9671	264.8004	321.563	U	−0.14	287.3486	291.1985	338.104	U	−0.01	313.6323	317.4506	349.530	U	−0.12
Series 8														
309.2018	314.4032	472.833	0.20	−0.22	324.3254	329.3942	472.377	0.20	−0.12	339.3444	343.9202	437.006	0.20	0.05
314.2949	319.3436	462.558	0.20	−0.24	329.3423	334.4011	475.379	0.20	−0.07	343.8461	348.4153	440.062	0.20	0.21
319.3097	324.3682	467.506	0.20	−0.16	334.3415	339.4116	480.490	0.20	0.00					
Series 9														
304.8441	310.0177	467.559	0.20	−0.10	320.0352	325.0918	468.520	0.20	−0.03	334.9855	339.9420	469.824	0.20	−0.07
309.9998	315.0496	459.786	0.20	−0.17	325.0553	330.1217	472.812	0.20	−0.10	339.8789	344.9599	485.418	0.20	−0.04
315.0232	320.0693	463.506	0.20	−0.10	330.0738	335.0349	466.544	0.20	−0.11	344.8883	349.9574	489.196	0.20	0.22
Series 10														
209.7600	214.1461	329.975	0.20	−0.20	239.0203	242.8583	311.947	0.20	−0.04	265.4789	269.3212	325.426	0.20	0.03
214.1130	218.4807	332.982	0.20	−0.14	242.8100	246.6427	313.501	0.20	−0.07	269.2504	273.0951	327.819	0.20	0.06
218.4459	222.8158	337.556	0.20	−0.05	246.5920	250.4241	315.207	0.20	−0.04	273.0200	276.8655	328.828	0.20	−0.30
222.7758	227.1497	341.920	0.20	−0.04	250.3718	254.2031	316.952	0.20	0.08	276.7862	280.6278	331.621	0.20	0.01
227.1085	231.4878	346.578	0.20	0.04	254.1486	257.9776	318.126	0.20	0.01	280.5310	284.4049	336.642	0.20	0.05
231.4444	235.2723	305.827	0.20	−0.05	257.9208	261.7527	320.164	0.20	−0.02					
235.2284	239.0671	309.259	0.20	−0.12	261.6937	265.5403	323.277	0.20	−0.08					

σ is the percentage uncertainty assigned to the observation for the purposes of the least squares calculation. A "U" indicates that observation was not included in the least-squares calculation. ^{b} δ is the percentage difference of the calculated enthalpy increment from that observed.

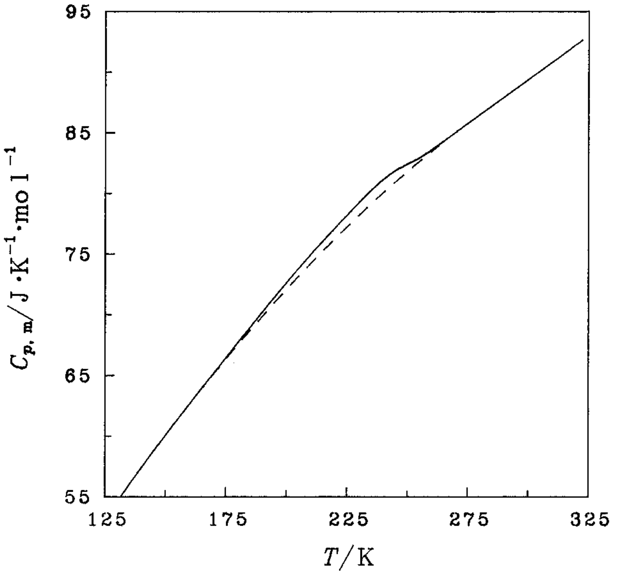

Figure 1. Heat capacity of cadmium carbonate. The solid line was calculated from the least-squares representation of the measured enthalpy increments of all series except series 7. The dashed line was calculated from a representation that excluded the measured values from 175 to 265 K. Values corresponding to the dashed line were labeled in the text as "lattice" values.

obtained after cooling the calorimeter to 210 K, which is below the temperature of the maximum of the peak, holding for 0.67 h, and then commencing measurements. Measurements in series 10 followed the previously determined anomaly (series 4−6).

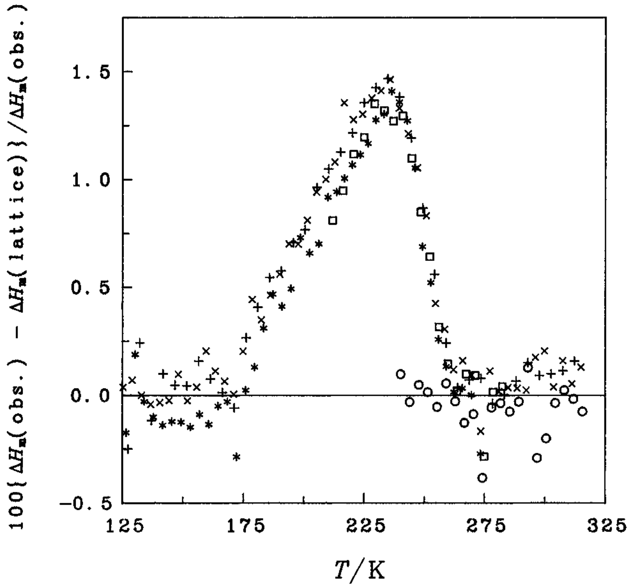

Figure 2. The difference of the measured enthalpy increments from the so-called "lattice" values. The symbols are: (+) series 4, (×) series 5, (*) series 6, (○) series 7, and (□), series 10.

A calculation showed the anomaly was not due to water impurity in the form of adsorbed water in the sample or the presence of some hydrate in the sample. This calculation was as follows: The total enthalpy under the anomaly peak was approximately 2 J. The enthalpy for transfer of 1 mol of water from a hydrate to the gas phase is approximately 60 kJ·mol^{-1} (300 K). The observed enthalpy

Table 2. Least-Squares Estimated Knot Positions

T_i/K	d_i	T_i/K	d_i
0	16.6951	180	8.16546
10	13.8345	200	7.93592
16	11.5601	230	7.54560
23	10.1031	245	7.41743
30	9.34579	255	7.47136
40	8.79299	265	7.43376
60	8.38749	300	7.09748
100	8.21596	380	5.64801
150	8.30544		

of the anomaly thus would have corresponded to vaporization of 3.3 × 10^{-5} mol of water from the sample. The resultant vapor pressure in the calorimeter vessel due to this amount of water at 250 K would have been 0.15 bar and was thus not thermodynamically likely, as this pressure would have been significantly greater than the sublimation pressure of ice. Since transfer of the supposed adsorbed water impurity to the gas phase was not possible, the supposed water would have to have been transferred to the ice phase and not to vapor. The smaller enthalpy for transfer to the solid phase, as compared to the transfer to the gas phase, resulted in calculating an impurity of 2.2 10^{-4} mol of water. This ice phase would necessarily melt as the calorimeter passed through 273.16 K, requiring an additional 2 J in those enthalpy increments in order to complete the melting process. This 2 J would be in addition to the 12 J to 15 J measured for those particular enthalpy increments for the cadmium carbonate sample, creating an error of 13% to 17% in those increments. No such error was observed. Thus, the attribution of the anomaly to adsorbed water or the existence of a small amount of a hydrate was not physically realistic. This rationale does not exclude the possibility that the observed anomaly was due to a very small amount of aqueous solution contained in inclusions.

The fact that measurements followed the “lattice” curve if the sample was not cooled too far through the maximum of the anomaly would seem to obviate the possibility that the anomaly was due to any particular small, volatile impurity.

Representation of the experimental results over the full range of temperature and including the anomaly required 17 variable values for the knot positions. The final knot positions are given in Table 2. The number of digits given in Table 2 should be sufficient for calculation of thermodynamic properties and were not meant to be representative of any statistical assessment. The root-mean-square difference of the measurements, for temperatures above 50 K, from the model was 0.11% for all measurement series except series 7. The differences of all of these measured values from the fitted model are shown in Figure 3. Calculated thermodynamic properties of cadmium carbonate are given in Table 3. Also given in Table 3, within parentheses, are the “lattice” values calculated from the fitted equation used to generate Figure 2. The difference in the 298.15 K entropy due to the anomaly was only 0.26 J·K^{-1}·mol^{-1}, or 0.25%. Thus, it has little impact on the calculation of the Gibbs energy of reaction for reactions involving crystalline cadmium carbonate.

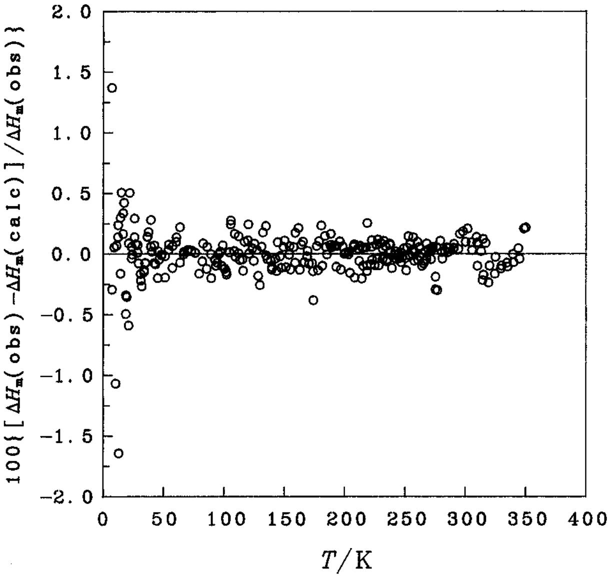

Figure 3. Differences of the measured enthalpy increments from the fitted model, in percent, for all measurements except series 7.

Table 3. Thermodynamic Properties of Cadmium Carbonate Calculated from Eqs 4 and 5

T/K	$C_{p,m}$/J·K^{-1}·mol^{-1}	$H_m(T) - H_m(0\ K)$/ kJ·mol^{-1}	S_m/J·K^{-1}·mol^{-1}
5	0.0279	0.000	0.009
10	0.2519	0.001	0.079
15	1.021	0.003	0.301
20	2.582	0.012	0.791
25	4.776	0.030	1.592
30	7.471	0.061	2.695
40	13.514	0.165	5.662
50	19.663	0.331	9.341
60	25.490	0.557	13.447
70	30.925	0.840	17.790
80	35.918	1.174	22.250
90	40.443	1.557	26.747
100	44.516	1.982	31.222
110	48.178	2.446	35.640
120	51.49	2.944	39.976
130	54.53	3.475	44.220
140	57.36	4.034	48.366
150	60.05	4.621	52.415
160	62.64	5.235	56.374
170	65.18	5.874	60.248
180	67.70 (67.55)	6.538 (6.537)	64.045 (64.033)
190	70.20 (69.87)	7.228 (7.224)	67.772 (67.748)
200	72.63 (72.10)	7.942 (7.934)	71.435 (71.389)
210	74.95 (74.23)	8.680 (8.666)	75.04 (74.96)
220	77.15 (76.27)	9.441 (9.419)	78.57 (78.46)
230	79.25 (78.22)	10.223 (10.191)	82.05 (81.89)
235	80.26 (79.16)	10.622 (10.585)	83.76 (83.59)
240	81.16 (80.07)	11.025 (10.983)	85.46 (85.26)
250	82.43 (81.82)	11.844 (11.792)	88.81 (88.57)
260	83.59 (83.46)	12.673 (12.619)	92.06 (91.81)
270	85.05 (85.01)	13.517 (13.461)	95.24 (94.99)
280	86.49	14.374 (14.319)	98.36 (98.10)
290	87.94	15.247 (15.191)	101.42 (101.17)
298.15	89.11	15.968 (15.912)	103.88 (103.62)
300	89.38	16.133 (16.077)	104.43 (104.17)
310	90.84	17.034 (16.978)	107.38 (107.12)
320	92.30	17.950 (17.894)	110.29 (110.03)
330	93.8	18.880 (18.824)	113.15 (112.90)
340	95.2	19.825 (19.769)	115.97 (115.72)
350	96.7	20.785 (20.729)	118.75 (118.50)

The true entropy that should be used in thermodynamic calculations depends on whether the anomaly arises from the real behavior of cadmium carbonate or from an impurity artifact in the measured cadmium carbonate sample. In the former case, the appropriate value would be that calculated from the parameters of Table 2, for example, 103.88 J·K^{-1}·mol^{-1} for 298.15 K. In the latter case, the appropriate value would be that from the so-called “lattice values” with a somewhat larger uncertainty, for example 103.62 J·K^{-1}·mol^{-1} for 298.15 K. The assumed uncertainty of the latter value would be expected to be larger than that assumed for the former value.

Cadmium carbonate loses carbon dioxide to form the oxide. Measurements of the pressure of carbon dioxide in equilibrium with cadmium carbonate constitute the decomposition studies mentioned in the Introduction. The pressure of carbon dioxide in equilibrium with cadmium carbonate at various temperatures may be calculated. This calculation gives the following pressure–temperature equilibrium pairs: 300 K, 1×10^{-4} Pa; 400 K, 1.5 Pa; 500 K, 920 Pa; and 600 K, 61.7 kPa. These pressures indicate that thermal measurements for temperatures greater than 400 K would have little meaning without correction for the enthalpy of decomposition. This may explain the absence of high-temperature thermal measurements in the literature. For the largest temperature obtained in this study, approximately 350 K, the equilibrium pressure would be calculated to be 0.03 Pa (3×10^{-7} bar). Thus, it was not expected that the decomposition reaction had any significant effect on the present measurements.

Discussion

The 298.15 K entropy determined here, 103.88 J·K^{-1}·mol^{-1} was in much better agreement with the value that Stipp et al. (1993) obtained from their measurements, namely, (106 ± 30) J·K^{-1}·mol^{-1}, especially when one considers the uncertainty estimate they attached to the value. As stated before, that large uncertainty value, in part, represented past difficulties experienced with CODATA Key Values for Thermodynamics (Archer 1992b; Rard and Archer, 1995). The difference of these two values, 2.1 J·K^{-1}·mol^{-1}, was smaller than Cox et al.'s (1989) combined uncertainties for the Cd^{2+} and CO_3^{2-} aqueous ions used in Stipp et al.'s calculation. In other words, all of the difference between the value from Stipp et al. and the present value could be due to the uncertainty in the CODATA Key Values. The present value was also in reasonably good agreement with the reference value given by Sverjensky (1984), 106.3 J·K^{-1}·mol^{-1}. However, the present value is more accurate than either of these two values. Of the previous reference values obtained from measurements of thermodynamic properties of cadmium carbonate or of reactions involving cadmium carbonate, the most accurate value also happened to be the earliest, that from Kelley and Anderson (1935), 105.4 J·K^{-1}·mol^{-1}. The subsequent value given by Kelley and King (1961), (97.5 ± 2.5) $^{-1}$·mol^{-1}, was lower than the present value by significantly more than the estimated uncertainty. The value of 92.5 J·K^{-1}·mol^{-1}, first given by Wagman et al. in 1968, is 11.4 J·K^{-1}·mol^{-1} lower than the present value. Because the value from Wagman et al. (1968, 1982), commonly known as an NBS Tables value, is both extraordinarily different from the present value and is widely used, further inspection as to its source and its probable uncertainty, neither of which were published by Wagman et al., seemed reasonable. This examination is presented next.

As mentioned above, the NBS Tables (Wagman et al. 1968, 1982) value for the entropy of $CdCO_3$(cr), 92.5 $^{-1}$·mol^{-1}, was significantly different, 5 to 14%, from the other values that Stipp et al. (1993) found in the literature (other than those that were exactly the same and either stated as or were presumably taken from the NBS Tables) and because its source was undocumented, this value is considered in more detail here. The origin of the NBS Tables value was found in handwritten notes at the National Institute of Standards and Technology (NIST), the successor to the NBS. Their value was obtained as follows: The potential given by Saegusa (1950) for the electrochemical cell

$$\mathrm{Cd(Hg)|CdCO_3(cr)|K_2CO_3(aq),\ KHCO_3(aq)|Ag_2CO_3(cr)|Ag} \quad (6)$$

was used to obtain a Gibbs energy of formation of $CdCO_3$(cr) of −669.4 kJ·mol^{-1}. Thomsen (1886) measured the enthalpy of reaction for

$$\mathrm{CdSO_4\ (800\ mol\ of\ H_2O) + Na_2CO_3\ (800\ mol\ of\ H_2O) = Na_2SO_4\ (1600\ mol\ of\ H_2O) + CdCO_3(cr)} \quad (7)$$

The enthalpy of reaction obtained by Thomsen, $\Delta_r H_m$ = −1.55 kJ·mol^{-1}, was for 291.15 K. In order to adjust this value to 298.15 K, Wagman et al. took the value for the heat capacity change for reaction 7 to be −125 J·K^{-1}·mol^{-1}. The enthalpies of formation for $CdSO_4$ (800 mol of H_2O), Na_2CO_3 (800 mol of H_2O), and Na_2SO_4 (1600 mol of H_2O) were listed on the notes as (−979.884, −1157.09, and −1388.67) kJ·mol^{-1}, respectively. Using these values they calculated the enthalpy of formation of $CdCO_3$(cr) to be −750.6 kJ·mol^{-1}. They then calculated the entropy of formation of $CdCO_3$(cr) by the appropriate manipulation of the enthalpy and Gibbs energy of formation. This value of the entropy of formation was combined with the entropies of the elements to obtain their value of the entropy of $CdCO_3$(cr), 92.5 J·K^{-1}·mol^{-1}.

Even at first glance, the heat capacity change for reaction 7 taken by Wagman et al. (1968, 1982) appeared incorrect. The heat capacity of the $CdCO_3$ precipitate must be positive, and none of the aqueous ionic species would be expected to have positive heat capacities at high dilution. Thus the heat capacity change for reaction 7 must be *positive*, not negative.

Using values for $C_{p,\phi}°$ for Na^+(aq), Cd^{2+}(aq), SO_4^{2-}(aq) (Horvath, 1985), and CO_3^{2-}(aq) (Peiper and Pitzer, 1982) and the present value of $C_{p,m}$ for $CdCO_3$(cr), the heat capacity change for the precipitation reaction was calculated to be approximately 460 J·K^{-1}·mol^{-1}. This changed the enthalpy of the precipitation reaction (298.15 K) from the −2.43 kJ·mol^{-1} calculated by Wagman et al. to +1.67 kJ·mol^{-1}. (Stipp et al. obtained +0.74 kJ·mol^{-1} for the enthalpy of the reaction $Cd^{2+}(aq) + CO_3^{2-}(aq) = CdCO_3(cr)$ for 298.15 K from their solubility measurements at different temperatures. The value recalculated here, +1.67 kJ·mol^{-1}, was in better agreement with the value obtained by Stipp et al. than was the value in the Wagman et al. handwritten notes, −2.43 kJ·mol^{-1}. Several reasons why one would not be surprised that agreement was not still better than this, 1.67 kJ·mol^{-1} vs 0.74 kJ·mol^{-1}, are given below.) Next, using the values of the enthalpies of formation for the aqueous ionic species found on the Wagman et al. notes, the enthalpy of formation of $CdCO_3$(cr) was calculated as −746.63 kJ·mol^{-1}, 4 kJ·mol^{-1} different from the value they reported, and the molar entropy of $CdCO_3$(cr) was then calculated to be 106.3 J·K^{-1}·mol^{-1}. This value, calculated in the same way as Wagman et al. (1968, 1982) calculated it, with the exception that the correct sign and a reasonable approximation for the heat capacity change for reaction 7 was used, is in much better agreement with the other values. Thus, the large difference of the Wagman et al. value from other values appeared to have originated in either incorrect assumptions regarding the numerical sign of the heat capacities of ionic solutes in dilute solutions or, perhaps, simply an error in addition.

The good agreement of the value recalculated in the preceding paragraph with the present value and with the value given by Stipp et al. (1993) was considered somewhat fortuitous for the following reasons. Thomsen (1882–1886) did not report pH control for his solutions and so correction for the enthalpic contributions due to changes in hydrolysis reactions could not be made. Also, the precipitate may have contained hydrated $CdCO_3$(cr). In other words, the precipitated phase might not have been the equilibrium anhydrous phase. The equilibration time for precipitated phases to achieve their final state can be quite long, and this enthalpy change would have been difficult to recover from the solution calorimeter's drift rate after the initial mixing enthalpy. The estimate of the heat capacity change for reaction 7 was obtained with standard state, 298.15 K, heat capacities. The true value of the integrated heat capacity change for reaction 7 would have been a bit different for finite concentration and for temperatures less than 298.15 K. (The true value for the 298.15 K heat capacity change for reaction 7 probably would have been smaller than 460 $J \cdot K^{-1} \cdot mol^{-1}$ but would have remained positive. The smaller value would come from the heat capacity contributions from both the hydrolysis (Na_2CO_3) and ion-pairing ($CdSO_4$) reactions to the molar heat capacities of the reactant species.) Finally, there is the observation that the enthalpies of formation of some of the species of reaction 7, given in Wagman et al.'s handwritten notes, do not match the values published by Wagman et al. (1982).

Literature Cited

Archer, D. G. Thermodynamic Properties of the NaCl + H_2O System. I. Thermodynamic Properties of NaCl(cr). *J. Phys. Chem. Ref. Data* **1992a**, *21*, 1−21.

Archer, D. G. Thermodynamic Properties of the NaCl + H_2O System. II. Thermodynamic Properties of NaCl(aq), $NaCl \cdot 2H_2O$(cr) and Phase Equilibria. *J. Phys. Chem. Ref. Data* **1992b**, *21*, 793−829.

Archer, D. G. Enthalpy Increment Measurements from 4.5 to 318 K for Bismuth(cr). Thermodynamic Properties from 0 K to the Melting Point. *J. Chem. Eng. Data* **1995**, *40*, 1015−1024.

Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: Washington, DC, 1989.

Horvath, A. L. *Handbook of Aqueous Electrolyte Solutions*; J. Wiley: New York, 1985.

Kelley, K. K.; Anderson, C. T. Contributions to the Data on Theoretical Metallurgy. IV. Metal Carbonates. *U.S. Bur. Mines Bull.* **1935**, No. 384.

Kelley, K. K.; King, E. G. Contributions to the Data on Theoretical Metallurgy. XIV. Entropies of the Elements and Inorganic Compounds. *U.S. Bur. Mines Bull.* **1961**, No. 592.

Peiper, J. C.; Pitzer, K. S. Thermodynamics of aqueous carbonate solutions including mixtures of sodium carbonate, bicarbonate, and chloride. *J. Chem. Thermodynam.* **1982**, *14*, 613−638.

Rard, J. A.; Archer, D. G. Isopiestic Investigation of the Osmotic and Activity Coefficients of Aqueous NaBr and the Solubility of $NaBr \cdot 2H_2O$(cr) at 298.15 K: Thermodynamic Properties of the NaBr + H_2O System over Wide Ranges of Temperature and Pressure. *J. Chem. Eng. Data* **1995**, *40*, 170−185.

Saegusa, F. Thermodynamic Studies on Carbonates. Part I. Thermodynamic Studies of Cadmium, Zinc, Lead, Mercurous and Thallous Carbonates. *Sci. Rep. Tohoku Univ. I Ser.* **1950**, *34*, 55−65.

Stipp, S. L. S.; Parks, G. A.; Nordstrom, D. K.; Leckie, J. O. Solubility-product Constant and Thermodynamic Properties for Synthetic Otavite, $CdCO_3$(s), and Aqueous Association Constants for the Cd(II)-CO_2-H_2O System. *Geochim. Cosmochim. Acta* **1993**, *57*, 2699−2713.

Sverjensky, D. A. Prediction of Gibbs free energies of calcite-type carbonates and the equilibrium distributions of trace elements between carbonates and aqueous solutions. *Geochim. Cosmochim. Acta* **1984**, *48*, 1127−1134.

Thomsen, J. *Thermochemische Untersuchungen*;J. Barth Verlag: Leipzig, 1882−1886.

Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm, R. H. Selected Values of Chemical Thermodynamic Properties. Tables for the First Thirty-Four Elements in the Standard Order of Arrangement. *NBS Tech. Note* **1968**, No. 270-3.

Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

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