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Succinic acid. Heat capacities and thermodynamic properties from 5 to 328 K. An efficient drying procedure

CECIL E. VANDERZEE

Department of Chemistry, University of Nebraska, Lincoln, Nebraska, 68508, U.S.A.

and

EDGAR F. WESTRUM, Jr.

Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48104, U.S.A.

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Heat capacities of succinic acid from 5 to 328 K were determined by adiabatic calorimetry. At 298.15 K, values of C_p, $S°$, $(H°-H°_0)/T$ and $(G°-H°_0)/T$ are 36.55, 39.99, 20.23, and −19.76 cal K^{-1} mol^{-1}. No thermal anomalies were detected except that from a trace of occluded water at 272 K, found to be (0.0030 ± 0.0005) per cent by analysis of the excess enthalpy absorption. Equilibration of pressed pellets for two days in a desiccator over Drierite proved to be an effective final drying technique.

1. Introduction

Apart from its interest to general and biological chemistry, succinic acid has long been of interest to thermochemists as a secondary standard substance in combustion calorimetry.[1] A critical analysis[2] of combustion studies on succinic acid dating back to 1924 shows that the results for $-\Delta E^\circ_c/M$ (corrected to 25 °C) cluster into two groups. The upper seven range from 3020.2 to 3020.57 cal g^{-1} while the lower five range from 3019.6 to 3019.9 cal g^{-1}.† Comparison of the experimental techniques indicates that the spread is due in part to differences in procedures for drying the substance.

In 1930, Parks and Huffman[3] measured the heat capacity of succinic acid from 90 to 290 K and computed the entropy by extrapolating its heat capacity below 90 K by analogy with similar organic compounds. In the vicinity of 272 K, they found a "hump" in the heat capacity, an anomaly with 41 cal mol^{-1} excess enthalpy absorption, but suggested no explanation. The only known phase transition in succinic acid crystals is that from monoclinic to triclinic at 137 °C.[4,5] It would be logical to attribute this observed anomaly to occluded water in the crystals, although the

† Throughout this paper, cal = 4.184 J and Torr = (101 325/760) N m^{-2}.

amount (0.4 per cent) seems unexpectedly high. Recently, one of us (C. E. V.) and Margret Månsson at the University of Lund found that it was very difficult, by grinding and heating cycles alone, to reduce the occluded water in succinic acid crystals below 0.02 per cent. In particular, pellets of succinic acid showed mass loss behavior after pelleting in striking coincidence with water content based on careful weight-buret titration assay of the succinic acid crystals. Because the solubility of succinic acid in water increases very rapidly with temperature, and the saturated solution boils at about 180 °C at 760 Torr,[6] it is quite likely that occluded water would be very difficult to remove from the crystals by heating.

The objectives of this study were to explore the heat capacity of thoroughly dried succinic acid from 5 to 325 K, to discover any thermal anomalies, and to obtain more reliable thermodynamic functions for the compound. It was also of interest to demonstrate that adiabatic calorimetry could detect occluded water to a level of about 0.001 per cent, and to confirm thereby that succinic acid could be dried by a rather simple procedure to a water content less than 0.004 per cent. Use of this drying procedure enhances the reliability of succinic acid as a standard substance, and indeed was included in the pellet handling techniques for some of the studies giving the larger values of $-\Delta E_c^\circ/M$. The procedure should be of utility not only for preparing samples for combustion calorimetry but in drying relatively soluble substances for other physicochemical purposes.

2. Experimental

CALORIMETRIC APPARATUS AND PROCEDURES

Measurements of the heat capacity from 5 to 328 K were made by adiabatic calorimetry, using the Mark II cryostat and automatic adiabatic shield control system described elsewhere.[7] The gold-plated copper calorimeter (laboratory designation W–42, capacity 93 cm^3) used in this study has horizontal radial vanes to facilitate thermal equilibration with the sample. The calorimetric sample (mass 86.724 g corrected from the apparent mass in air by use of a density of 1.562 g cm^{-3}) was enclosed with helium gas at 103 Torr, and its heat capacity was (85 $\pm$ 3) per cent of the total. Temperature measurements were made with a capsule-type strain-free platinum-resistance thermometer (laboratory designation A–5) located in the entrant well of the calorimeter. All measurements of mass, temperature, resistance, potential, and time are referred to standardizations and calibrations performed at the National Bureau of Standards.

SAMPLE PREPARATION

Reagent grade succinic acid (J. T. Baker Analyzed, Lot No. 34139) was recrystallized four times from distilled water. In the last stage of purification, the hot solution was filtered through a sintered glass funnel before the crystal crop was grown and collected. The crystals were rinsed with cold, filtered, distilled water and given a preliminary drying 24 h in a desiccator over Drierite. They were then dried for 1 h at 80 °C, cooled, and ground in an agate mortar to 25 to 100 mesh. The crystals were then dried 20 h at 102 °C, 2 h at 112 °C, 3 h at 118 °C, and stored in a desiccator over Drierite.

A week later, the succinic acid was pressed into 1 cm diameter pellets, weighing about 2 g, as for combustion calorimetry. The loss in mass of selected pellets was followed with a Mettler microbalance. The typical mass loss pattern is shown in table 1. The pellets reached equilibrium in 24 h, and showed mass losses of 430 p.p.m., which is attributed to loss of solvent (H_2O) from the porous pellet. To establish that the pellets were near equilibrium dryness, some pellets which had dried for 48 h in the desiccator were crushed in a mortar to coarse fragments and repelleted within 10 min. The typical mass loss pattern on repelleting is shown in table 2, showing a new mass

TABLE 1. Typical mass loss pattern of succinic acid after pelleting[a]

Age of pellet	p.p.m. mass loss	Age of pellet	p.p.m. mass loss
0	—	45.3 h[b]	364
3 min	ref. point	57.7 h[b]	363
4 min	20	58.7 h[b]	359
6 min	31	59.7 h[b]	354
9 min	67	60.7 h[b]	359
23 min	161	61.7 h[b]	362
32 min	197	Estimated total	
14.6 h	327	p.p.m. mass loss: 430	
17.5 h	330		

[a] Prior to pelleting, the material was dried for 1 h at 80 °C, crushed to about 25 to 100 mesh, then dried for 20 h at 102 °C, 2 h at 112 °C, 3 h at 118 to 120 °C. Unless otherwise noted, the samples were stored in the balance case at 45 per cent relative humidity of the ambient air between weighings.

[b] Stored in desiccator over Drierite in period prior to weighing.

TABLE 2. Typical mass loss of succinic acid after repelleting previously pelleted acid dried to equilibrium[a]

Age of pellet	p.p.m. mass loss	Age of pellet	p.p.m. mass loss
0	—	8.5 h[b]	25
3 min	0	21.5 h[b]	40
10 min	2	24.2 h[b]	40
34 min	3	31.5 h[b]	40
1.5 h	6	46 h[b]	40
2.5 h	10	76 h[b,c]	40
3.5 h	11		

[a] Pellets were dried for 48 h in a desiccator over Drierite, then crushed in a mortar to coarse fragments and repelleted within 10 min.

[b] Stored in desiccator over Drierite in period prior to weighing.

[c] Mass gain of dried pellet in air (45 per cent relative humidity) was 5 p.p.m. after 2 h.

loss of only 40 p.p.m. and a new equilibrium again after 24 h. The implications are that over 90 per cent of the occluded solvent was removed after the first pelleting process.

The calorimetric sample was prepared by taking pellets which had been stored for 48 to 72 h in the desiccator, breaking them into coarse fragments, and loading the material within a few hours into the calorimeter. A small amount of further drying may have occurred between the time of preparation and loading into the calorimeter, as well as during evacuation of the calorimeter at 300 K for 30 min under high vacuum prior to adding helium gas and sealing the gold-gasketed closure.

3. Results

THERMODYNAMIC PROPERTIES

The experimental heat capacity values at the mean temperature of each determination are presented in table 3 in chronological order. Temperature increments for individual runs in a series may usually be estimated from adjacent temperatures. The results are shown in figure 1 as a function of temperature, with the region around 272 K considerably enlarged. These results have been adjusted for curvature, and the probable error is estimated at about 5 per cent at 5 K, decreasing to 1 per cent at 10 K, and to less than 0.1 per cent above 25 K. The results are stated in terms of the defined

TABLE 3. Heat capacity of succinic acid

$\frac{T}{\mathrm{K}}$	$\frac{C_p}{\mathrm{cal\ K^{-1}\ mol^{-1}}}$	$\frac{T}{\mathrm{K}}$	$\frac{C_p}{\mathrm{cal\ K^{-1}\ mol^{-1}}}$	$\frac{T}{\mathrm{K}}$	$\frac{C_p}{\mathrm{cal\ K^{-1}\ mol^{-1}}}$	$\frac{T}{\mathrm{K}}$	$\frac{C_p}{\mathrm{cal\ K^{-1}\ mol^{-1}}}$
Series I		40.87	6.307	171.34	23.65	265.18	33.06
5.17	0.026	44.74	7.227	180.87	24.58	267.18	33.27
5.57	0.035	48.66	8.128	190.10	25.46	269.16	33.44
6.06	0.043	53.22	9.120	199.04	26.31	271.14	33.70
6.63	0.054	57.87	10.066	207.73	27.18	273.10	33.94
7.20	0.072	62.46	10.968	216.19	28.04	275.05	34.10
7.77	0.086	68.09	11.954			277.00	34.29
8.41	0.116	75.06	13.055	Series III		278.93	34.49
9.19	0.160	82.73	14.224	211.14	27.49		
10.03	0.209	90.87	15.310	222.45	28.64	Series V	
10.91	0.261			235.91	30.01	239.35	30.36
11.89	0.328	Series II		248.92	31.36	246.68	31.13
12.84	0.414	72.45	12.656	259.18	32.44	253.84	31.88
13.81	0.513	77.92	13.504	266.79	33.22	260.87	32.65
14.85	0.632	83.69	14.362	272.79	33.92	265.29	33.05
16.09	0.789	89.68	15.164	278.66	34.47	267.16	33.26
17.53	1.001	95.31	15.841	286.24	35.27	269.02	33.47
19.30	1.293	100.69	16.457	294.42	36.14	270.87	33.72
21.30	1.665	107.04	17.171	303.42	37.13	272.71	33.94
23.35	2.084	115.27	18.06	313.11	38.21	274.54	34.04
25.45	2.544	124.69	19.05	322.85	39.30	276.37	34.25
27.89	3.109	134.27	20.02			278.18	34.42
30.75	3.801	143.71	20.96	Series IV		281.33	34.76
33.86	4.576	153.06	21.88	261.17	32.63		
37.14	5.397	162.07	22.75	263.18	32.84		

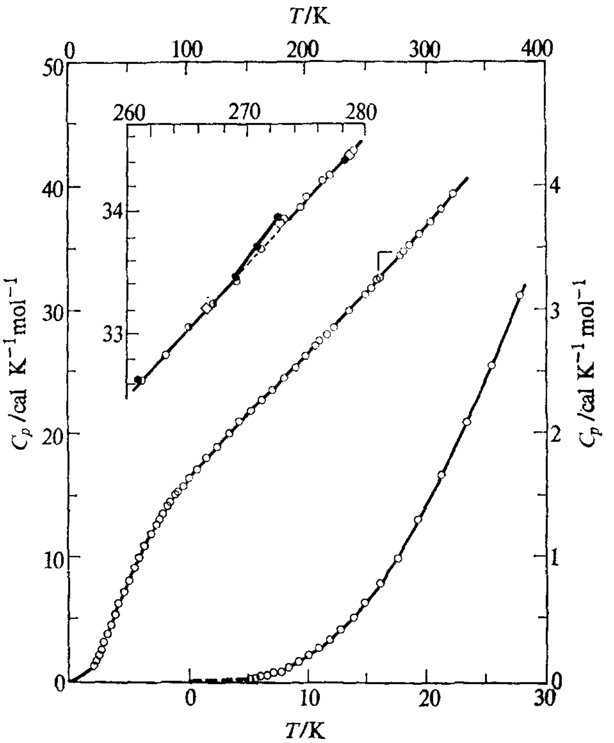

FIGURE 1. Experimental values for the heat capacity of succinic acid. The ice-point region has been enlarged in the inset.

thermochemical calorie (cal = 4.184 J), an ice point of 273.15 K, and a molar mass of 118.090 g mol^{-1} for succinic acid. Table 4 presents smoothed heat capacities and associated thermodynamic functions obtained by digital data processing of the experimental results. The estimated errors in the functions are less than 0.1 per cent above 70 K. Below 5 K, the heat capacities were extrapolated by means of the Debye T^3 limiting law. Nuclear spin and isotopic mixing contributions have been omitted from the entropy and Gibbs function.

4. Discussion

The heat capacities in table 3 are in excellent agreement with those of Parks and Huffman[(3)] except in the region from 240 to 276 K. In that region, we find no "hump" such as Parks and Huffman[(3)] observed, but only a very slight excess enthalpy absorption around 272 K, as shown in figure 1. The mean excess enthalpy absorption from series III, IV, and V was found to be (0.29 ± 0.05) cal mol^{-1} of succinic acid. Attributing this to melting of water at the eutectic temperature (272.6 K), we calculate (0.0030 ± 0.0005) per cent occluded water in the succinic acid sample used in this investigation. This amount is in striking agreement with that attributed to mass loss upon repelleting dried pelleted material (table 2).

TABLE 4. Thermodynamic functions of succinic acid

$\frac{T}{K}$	$\frac{C_p}{\text{cal K}^{-1}\text{ mol}^{-1}}$	$\frac{S^\circ}{\text{cal K}^{-1}\text{ mol}^{-1}}$	$\frac{H^\circ - H^\circ_0}{\text{cal mol}^{-1}}$	$\frac{-(G^\circ - H^\circ_0)/T}{\text{cal K}^{-1}\text{ mol}^{-1}}$
5	0.024	0.008	0.03	0.002
10	0.194	0.064	0.48	0.016
15	0.649	0.218	2.46	0.054
20	1.419	0.503	7.50	0.128
25	2.444	0.926	17.07	0.243
30	3.616	1.474	32.18	0.401
35	4.864	2.124	53.36	0.600
40	6.090	2.855	80.78	0.835
45	7.289	3.642	114.26	1.103
50	8.424	4.469	153.57	1.398
60	10.489	6.192	248.4	2.052
70	12.277	7.946	362.4	2.769
80	13.821	9.689	493.1	3.525
90	15.175	11.397	638.2	4.306
100	16.391	13.060	796.1	5.098
110	17.51	14.675	965.7	5.896
120	18.57	16.245	1146.2	6.693
130	19.60	17.772	1337.1	7.487
140	20.60	19.261	1538.1	8.275
150	21.58	20.716	1748.9	9.056
160	22.55	22.139	1970	9.839
170	23.51	23.535	2200	10.595
180	24.48	24.907	2440	11.352
190	25.44	26.256	2689	12.101
200	26.41	27.585	2949	12.842
210	27.40	28.898	3218	13.575
220	28.40	30.195	3497	14.301
230	29.41	31.480	3786	15.020
240	30.44	32.753	4085	15.733
250	31.47	34.017	4395	16.439
260	32.51	35.27	4714	17.14
270	33.56	36.52	5045	17.83
280	34.61	37.76	5386	18.52
290	35.67	38.99	5737	19.21
300	36.75	40.22	6099	19.89
310	37.86	41.44	6472	20.56
320	38.98	42.66	6856	21.23
273.15	33.89	36.91	5151	18.05
298.15	36.55	39.99	6031	19.76

This investigation demonstrates that accurate heat capacity measurements can indeed detect (and determine) occluded solvent in crystals at a level of a few parts in 10^5, down to a few parts per million. It further demonstrates the effectiveness of the "pellet-drying" technique for removing residual solvent without the hazards of contamination associated with successive cycles of grinding and drying by heating. A plausible explanation of the pellet-drying behavior is that the shearing stresses in pelleting break up the vacuoles of occluded solvent, permitting it to escape from the pellet by capillarity. It may be worth noting that pellets made of the thoroughly dried material are not quite as coherent as those from the original crystals.

No symptoms of other thermal anomalies were detectable over the temperature range 5 to 328 K. At no time during the crystallizing or drying of the sample was the temperature above 120 °C, well below the known transition at 137 °C, so there should have been no remnants of the high-temperature form present in our sample.

Parks and Huffman[(3)] reported 42.0 cal K^{-1} mol^{-1} for the entropy of succinic acid at 298.15 K, in contrast to our value of 39.99 cal K^{-1} mol^{-1}. The difference results from their long extrapolation below 90 K, and suggests that similar errors may exist in the results for other compounds which they reported.[(3)]

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Note added in proof. The mass loss behavior of pelleted material was the subject of considerable discussion between Keffler, L. J. P. (a) *Rec. Trav. Chim. Pays-Bas* **1930**, 49, 428; (b) *Bull. Soc. Chim. Belg.* **1933**, 42, 609, and Beckers, M. (a) *Bull. Soc. Chim. Belg.* **1931**, 40, 518; (b) **1931**, 40, 571; (c) **1933**, 42, 621. Keffler attributed the phenomenon to loss of electric charge induced by pelleting. Beckers gave experimental evidence that the mass loss was due to escape of volatile material (solvent) from the pellet, observed the phenomenon for both salicylic and succinic acids, and used the pellet drying procedure in his combustion studies.