The Heat Capacity of Potassium Sodium Tartrate Tetrahydrate from 15 to 340°K.[1]

By J. F. G. Hicks, Jr.,[2] and J. Gilbert Hooley[3]

The heat capacity of Rochelle salt ($KNaC_4H_4O_6 \cdot 4H_2O$) in the regions about the Curie points ($+24$ and $-18°$) is of interest in correlating the remarkable dielectric properties of this compound.[4]

The present investigation was carried out at the suggestion of Professor Hans Mueller and was designed to cover not only the temperature region -30 to $+30°$, but the entire range at our disposal. Mueller,[5] by means of his phenomenological theory of Rochelle salt behavior, was able to calculate approximately the change in heat capacity at the upper Curie point. His figure,[6] $\Delta c \sim 1.5 \times 10^5$ ergs/cc./degree~ 0.5 cal./mole/degree is rather too small to be positively shown by our measurements. The heat capacity of the salt at the upper Curie point where our experimental accuracy is 0.5%, is 92.5 cal./mole/degree. On the other hand, Kobeko and Nelidow[7] and Rusterholz[8] report a sharp discontinuity in the heat capacity–temperature curve at 26°. In both of these investigations the observed rise in heat capacity above the normal is about 5%.

Material.—The salt was of c. p. reagent quality and contained less than 0.01% impurities. It was allowed to stand, being mixed frequently, for two weeks at room temperature in a desiccator over 40 wt. per cent. sulfuric acid (vapor pressure 13.5 mm.) to ensure the presence of the single solid phase, $KNaC_4H_4O_6 \cdot 4H_2O$.[9] Subsequently, it was found that the material at our disposal did not require this treatment.

Analysis for water by loss of weight in vacuum ($\sim 10^{-4}$ mm. and 180 to 200°) showed 25.52 and 25.49%; theoretical, 25.54. For purposes of analysis, we were unable to drive off more than 3.8 of the 4 moles of water by heating in a drying oven at 130° for one week, but found that conditions under which the tartrates themselves exhibited incipient decomposition were necessary to remove the last bit of water.

Analysis for sodium plus potassium by ignition and conversion to the chlorides showed the sample to be 99.98 and 100.06% Rochelle salt.

A solution containing 20.0 g. of Rochelle salt per 100.0 ml. of solution gave $[\alpha]^{25}D +22.2°$ ml./gram decimeter.

All measurements were made on a single calorimeter loading of 88.760 g. *in vacuo*, or 0.31459 mole, the molecular weight of $KNaC_4H_4O_6 \cdot 4H_2O$ taken as 282.14.

Method.—The apparatus, method of measurement, and calorimeter all have been described in an earlier paper of this series.[10] The temperatures were measured by means of the platinum–rhodium resistance thermometer-heater having the laboratory designation R197. It had been calibrated previously against a helium gas thermometer,[11] and the ice-point resistance showed no appreciable departure from its calibration value.

In loading the calorimeter, special precautions were taken to avoid any decomposition arising from heating the salt above 40°.[12] The two ring seals of soft solder joining the monel lid to the monel collars of the calorimeter barrel[10] were made while the calorimeter and weighed contents were immersed to within 15 mm. of the top in ice and water. The solder was then flowed on as rapidly as possible. In this manner, a tight seal could be made without the salt ever attaining the temperature of 15°. However, the contents could not be recovered without decomposition. Prior to the above operation, several centimeters of thin-walled nickel–silver tubing had been sealed to the bottom of the empty calorimeter and the end of the tube closed. After soldering the lid to the barrel, the free end of the tube was opened, cemented to the vacuum line, the calorimeter and its contents cooled to 80°K., and exhausted. After several flushings with pure helium, sufficient helium was finally admitted to exert a pressure of one atmosphere at room temperature. The calorimeter was allowed to warm, the tube clipped and soldered, and the unit suspended in the apparatus.

The e. m. f.'s were read on an Eppley microvolt potentiometer having a range of one-ninth volt to one microvolt on the dials.

The calorie used in this work is defined equal to 4.1833 int. joules. The absolute temperature of the ice-point is assumed to be 273.19°.

Heat Capacity Measurements.—The data are presented in chronological order in Table I. Series I has been omitted because of the large error in reproducibility of these points. The inaccura-

(1) Low Temperature Studies, No. 4.

(2) Present address: Corning Glass Works, Corning, New York.

(3) Submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(4) For a review of recent work, see Staub, *Naturwissenschaften*, **23**, 728 (1935). Other substances behaving similarly are listed by Busch, *Helv. Phys. Acta*, **10**, 261 (1937).

(5) Mueller, *Phys. Rev.*, **47**, 175 (1935).

(6) Mueller, *ibid.*, **45**, 736 (1934). This value is, of course, dependent upon the Lorentz factor. If this factor be three times as great as that assumed in the calculation, the change in heat capacity should have been detected.

(7) Kobeko and Nelidow, *Phys. Z. Sowjetunion*, **1**, 382 (1932).

(8) Rusterholz, *Helv. Phys. Acta*, **8**, 39 (1935).

(9) Lowry and Morgan, This Journal, **46**, 2192 (1924).

(10) Hicks, *ibid.*, **60**, 1000 (1938).

(11) Blue and Hicks, *ibid.*, **59**, 1962 (1937).

(12) Lowry and Morgan[9] and van Leeuwen, *Z. physik. Chem.*, **23**, 33 (1897), observed that the vapor pressures of Rochelle salt at lower temperatures were not reproducible, if at any previous time the salt had been held above 40°. Lowry and Morgan do not state the composition of the other solid phase in equilibrium with Rochelle salt and water vapor when reproducible vapor pressures are obtained.

cies were traced to a poor contact in one of the potentiometer dials and the defect was remedied before observations labelled Series II.

TABLE I

T, °K.	C_p in cal. mole^{-1} degree^{-1}	T, °K.	C_p in cal. mole^{-1} degree^{-1}	T, °K.	C_p in cal. mole^{-1} degree^{-1}
Series II		246.64	80.59	26.28	6.03
59.93	24.29	248.86	81.31	29.04	7.23
63.85	26.08	250.98	82.01	31.72	8.61
69.06	28.24	253.12	81.96	34.04	9.88
73.06	30.39	255.27	82.38	36.75	11.16
77.07	31.51	252.56	81.83	40.28	13.20
81.08	33.92	254.70	82.21	43.97	15.25
85.00	35.37	256.78	83.26	47.81	17.39
88.74	36.68	259.08	83.80	52.15	19.94
92.42	38.13	265.16	85.07	56.68	22.08
96.09	39.07	270.38	85.80	61.06	24.67
99.98	41.03	275.60	87.06	65.24	26.89
103.94	41.76	280.10	88.63	69.74	28.93
107.53	43.72	286.80	89.82	74.61	31.28
111.51	44.98	293.01	91.60	Series V	
115.97	46.70	296.48	92.23	244.19	79.58
120.47	48.06	298.72	92.98	246.32	80.17
125.05	48.91	300.94	92.40	248.54	80.83
130.04	50.22	Series III		251.08	81.44
134.19	51.73			252.06	81.73
139.22	53.34	246.13	78.73	254.23	82.33
144.22	54.54	245.76	80.37	256.34	82.73
149.29	56.25	248.32	80.57	258.39	83.07
155.67	57.81	250.91	81.50	258.62	83.56
161.33	59.49	253.45	82.01	261.30	83.60
167.20	61.42	255.89	82.56	263.71	84.90
173.04	62.91	258.32	83.92	Series VII	
178.84	64.73	263.60	84.56	244.73	80.36
184.89	66.02	267.35	84.96	300.11	93.07
187.11	66.75	287.90	89.96	303.72	94.20
192.96	68.08	292.74	91.63	307.41	95.16
201.10	69.96	295.70	91.72	311.00	95.59
210.54	72.45	298.15	92.59	314.49	96.80
217.36	73.79	299.90	93.43	317.94	98.97
223.66	75.55	302.15	91.79	321.35	100.76
229.89	77.13	Series IV		324.67	104.07
226.08	76.13			323.33	99.93
232.36	77.41	16.72	3.31	326.57	107.07
238.82	78.83	18.95	2.98	332.87	191.35
243.42	79.77	21.14	4.04	335.25	188.24
244.29	76.10	23.62	4.74		

Before Series II, the calorimeter was held for two weeks at 80°K. and between Series II and III, the calorimeter was cooled directly to hydrogen temperatures and was below 80°K. for about two days during the course of Series IV measurements. It was then allowed to warm up slowly over a period of four days to 245°K. where it was held for six days. Series V data were then taken. Following these runs the calorimeter was immediately cooled to 240°K. and held just below 250°K. for one week after which Series VI observations

were made. Thereafter, Series VII and the heat of transition were measured; these required three days. It is evident from the data that the variety of thermal treatments produced no effect on the heat capacity below 310°K.

The data of Table I are shown graphically in Fig. 1. The data of Series III and V are displaced, but all three curves are identical. The three dots are from Wilson's[13] work; his straight line is indistinguishable from that portion of our curve when the data are plotted on this scale. Figure 2 is a deviation plot with ordinate the observed heat capacity minus that calculated from the straight line, $C_p = 0.300T + 7.00$. The lengths of the vertical lines represent 0.5% of the total heat capacity at that temperature. The upper curve in Fig. 2 is the portion of the deviation curve from 240 to 300°K. replotted on a larger scale abscissa so that the experimental points can be distinguished.

The measurements of Series VI are listed in Table II and plotted in Fig. 3. They represent relative total heat capacities of the full calorimeter in the neighborhood of the lower Curie temperature. Each heating period was made through approximately a 0.3° interval with the shield sur-

TABLE II

T, °K.	Cal. degree^{-1}
Series VI	
249.18	55.16
249.63	55.01
250.07	54.83
250.50	55.09
250.97	54.89
251.42	55.10
251.85	54.75
252.29	55.36
252.78	54.48
253.17	55.39
253.60	55.34
254.05	55.18
254.50	55.17
254.98	55.41
255.40	54.98
256.07	55.59
256.82	55.54
257.28	55.61
257.71	55.67
258.15	55.15
258.59	55.58
259.04	55.77
259.48	55.35

TABLE III

T, °K.	C_p in cal. mole^{-1} degree^{-1}
15	1.50
20	3.40
25	5.47
30	7.71
35	10.30
40	12.96
45	15.70
50	18.56
60	24.17
70	29.08
80	33.40
90	37.17
100	40.71
120	47.36
140	53.56
160	59.47
180	64.92
200	69.77
220	74.54
240	79.10
260	83.57
280	88.30
300	93.00
310	95.86
320	99.96

(13) A. J. C. Wilson, Doctor's Dissertation, M. I. T. Physics Department, 1938.

rounding the calorimeter maintained within ±0.2° of the calorimeter and the temperature of both rising at the same rate. The calorimeter temperature was measured by means of the attached thermocouple, the resistance thermometer not being used as such in these measurements. The data fall on a straight line within experimental error.
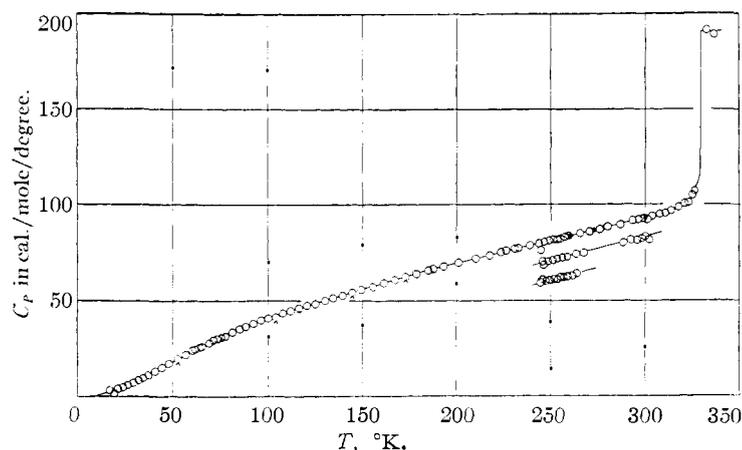
Fig. 1.—O, this research; ●, Wilson's curve.

Our data in their final form cannot be interpreted as suggesting a small anomaly at the lower Curie point as was stated previously.[14] The two low points around 245°K. and those two around 300°K. cannot be accounted for, but repeat determinations in these regions have fallen on the curve. Within experimental error, no discontinuities in the heat capacity–temperature curve are apparent at either the upper or lower Curie points. The accuracy of measurement is about that reported earlier with this apparatus,[10] viz., 0.3% from 40°K. to room temperature and correspondingly lower outside this region.

Table III lists molal heat capacities at even temperatures as read from the smoothed deviation curve reproduced in Fig. 3.

Heat of Transition.—The transition (presumably decomposition into the mixed hydrated tartrates and their saturated solution) occurs sharply at 328.78°K. (55.6°C.) ±0.05°. A single measurement of the heat of transition yielded 10,218 cal. per mole absorbed. Because

of the rapidly increasing slope of the curve just below 328.8°K., the method of arriving at 10,218 cal. per mole is somewhat arbitrary. However, 10,820 cal. is the measured amount of heat required to raise one mole of Rochelle salt from 328.14 to 331.62°K. In the absence of check determinations, it is difficult to assign a probable error to this figure, but it is believed to be good to ±20 cal.

Two and one-half hours were required to heat the calorimeter through the transition and during that period the maximum variation of the calorimeter thermocouple was 0.15°. At each end of the heating period, the calorimeter surface was 0.15° hotter than at the middle of this period; while during the middle two-thirds of the transition, the thermocouple did not vary by more than 0.02°.

The transition temperature has been reported by others to lie between 54 and 59°.[15]

Discussion.—The disagreement of our data with those of the European workers, and the excellent accord with Wilson's[13] work, have already been reported.[14] However, at 22°, the data of this research agree well with those of Kobeko and Nelidow[7] but are 11% lower than those of Ruster-
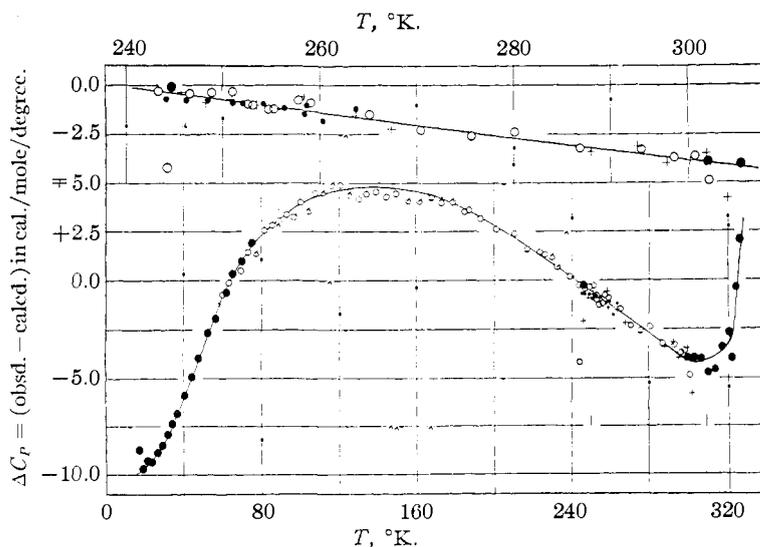
Fig. 2.—O, Series II; +, Series III; ●, Series IV and VII; ◉, Series V.

holz;[8] while our values and Wilson's[13] agree within 0.3% over the temperature interval covered by Wilson. We believe that if any discontinuities

(14) Wilson, Hicks and Hooley, *Phys. Rev.*, **54**, 87 (1938).

(15) "I. C. T.," Vol. III, p. 374.

in specific heat exist below the melting point and above 15°K., they are less than 0.5%, about ten times less than the one reported by Kobeko and Nelidow and Rusterholz[8] at the upper Curie temperature. We are unable to reconcile the previous data with our own.

Fig. 3.—Series VI.

Additional determinations of the heat capacity between 310 and 328°K. with a wide variation in the thermal treatment of the sample would settle the question of whether or not the large slope is a characteristic of the pure salt or due to its slow decomposition. The work of Lowry and Morgan[9] and others[16] indicates decomposition, while Mueller[6] found that a Rochelle salt crystal could be annealed for several hours at 45° without impairing its "Seignette electric" properties. Because of the possibility of decomposition, the present sample was heated without repetition of measurements from 310 to 340°K. Our apparatus is not well suited to repeated loadings and maintaining the calorimeter at constant temperature in this region for periods of many hours. It is therefore not improbable that our curve between 310 and 328°K. is dependent upon the history of the sample.

A complete study of the ternary system sodium tartrate, potassium tartrate, water with special emphasis on the Rochelle salt composition would be desirable. Although it is stated in the "International Critical Tables"[16] that the transition at *ca.* 54° consists in the decomposition into sodium and potassium tartrates, both present as the dihydrates, we infer from the vapor pressure measurements undertaken by Lowry and Morgan[9]
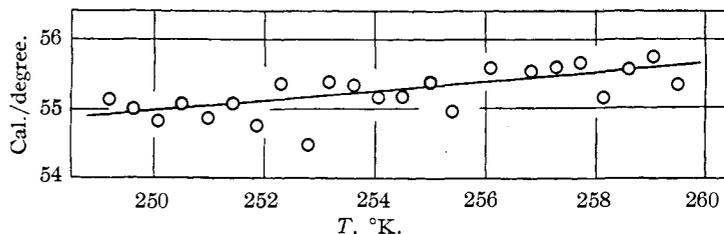
that $K_2C_4H_4O_6 \cdot {}^1\!/_2H_2O$ is the potassium salt to be expected.

It would be of interest to measure the heat capacities of other "Seignette electric" substances such as $NH_4H_2AsO_4$ and KH_2PO_4[14] to discover whether a marked gradual rise occurs just above the upper Curie point. In these cases no complications rising from decomposition would be encountered. It is also possible that the change in heat capacity of these salts at their Curie points would be a larger percentage of the total and therefore more susceptible to detection.

Summary

The heat capacity of Rochelle salt from 15 to 340°K. has been measured. A single measurement of the heat of transition at 328.78°K. (55.6°C.) has been made. The transition is sharp. No discontinuous changes in heat capacity were observed at the Curie points. The observations at the upper Curie point are in conflict with those reported by Kobeko and Nelidow and Rusterholz. The desirability of further investigations on Rochelle salt and other "Seignette electric" compounds has been pointed out.