show that the deviations from the ideal solution decrease with increasing concentrations of urea.

The slope of the curve for that portion of it which may be represented by a straight line (AB), is −757.58, with the intercept at 0.002464 on the $1/T$ axis. This corresponds to a heat of fusion[4] of 3470 (approx.) and a melting point of 132.7°.

The values obtained by Shnidman and Sunier in the neighborhood of 70° are appreciably higher than those obtained here. While it is true that the tendency of our method would be in the direction of low results, despite precautions taken against loss of water, the values obtained are in good agreement with those of Pinck and Kelly.[3] Furthermore, it is clear that the curve of Shnidman and Sunier cannot continue as a straight line if it is to terminate in the melting point of urea. There must be a change in slope and curvature.

(4) For perfect solutions the differential heat of solution is equivalent to the heat of fusion; Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 229.

From the fact that Shnidman and Sunier agree well with Pinck and Kelly up to 50° (except for the 20° point) and from the nature of the curve obtained in this work, it is probable that in the neighborhood of 70° the values of Shnidman and Sunier are high and those obtained here somewhat low. The true curve should probably show a gradual transition from the one curve to the other in this region as indicated in Fig. 1.

Summary

1. The solubility of urea in water between 70° and the melting point of urea (132.7°) has been determined by the synthetic method.

2. The results when plotted on a log N *vs.* $1/T$ basis show that the urea–water solutions appear ideal when the mole fraction of urea is greater than approximately 0.6.

3. The heat of fusion of urea is calculated to be 3470 cal./mole.

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[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, AT THE UNIVERSITY OF CALIFORNIA]

The Heat Capacities of Magnesium, Zinc, Lead, Manganese and Iron Carbonates at Low Temperatures[1]

BY C. TRAVIS ANDERSON[2]

This report on the carbonates of magnesium, zinc, lead, manganese and iron supplements earlier publications[3] relative to the carbonates of the first periodic group and the alkaline earth group.

The method, apparatus and accuracy have been described previously.[4]

Materials.—In Table I are shown the materials used. All the samples were crushed and screened to −14 +35 mesh. Carbon tetrachloride was used in determining the densities of the carbonates by the precise method described in a previous paper.[3b]

The Specific Heats.—The experimental results obtained for the magnesium, zinc, lead, manganese and iron carbonates are shown in Tables II, III, IV, V and VI, respectively. The data, given in gram calories (15°) per gram formula weight, have been corrected for the impurities as previously indicated. The calculations were made on the basis of Mg, 24.32; Zn, 65.37; Pb, 207.20; Mn, 54.93; Fe, 55.84; C, 12.00; and O, 16.00.

No previous low temperature measurements have been made on any of these carbonates. The results obtained in this investigation on the heat capacities of magnesite, smithsonite and cerussite are shown graphically in Fig. 1. Figure 2 gives the graphic representations of the heat capacities of rhodochrosite and siderite.

Calculation of Entropies.—The conventional method was used in calculating the entropies. The experimental heat capacity curves coincided at low temperatures with Debye functions having the following parameters (Θ): for magnesite, 354; smithsonite, 243; cerussite, 90; rhodochrosite, 223; and siderite 179. Combinations of Debye and Einstein functions were made to fit

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(3) (a) Anderson, THIS JOURNAL, **55**, 3621 (1933); (b) **56**, 340 (1934).

(4) Anderson, *ibid.*, **52**, 2296, 2712 (1930); **54**, 107 (1932); **55**, 3621 (1933).

TABLE I

MATERIALS USED

Material	Source	Sample, g.	Density	Density temp., °C.	Purity, %	Impurities	Impurities corrected for
Magnesite ($MgCO_3$)	Snarum, Norway	173.5	2.9798	21.4	89.7	9.0% $CaCO_3$ 1.3% $FeCO_3$	Calcite Siderite
Smithsonite ($ZnCO_3$)	Marion Co., Ark.	284.5	4.3476	23.2	99.8	0.1% SiO_2 .1% $FeCO_3$	None
Cerussite ($PbCO_3$)		360.5	6.5329	22.1	100.2 on conversion to molybdate	None	None
Rhodochrosite ($MnCO_3$)		223.2	3.6333	21.4	97.8	0.1% SiO_2 .1% $FeCO_3$ 2.0% $CaCO_3$	Calcite
Siderite ($FeCO_3$)	Germany	228.5	3.8507	20.7	88.29	1.90% $CaCO_3$ 5.19% $MnCO_3$ 4.62% $MgCO_3$	Calcite Rhodochrosite Magnesite

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF MAGNESITE

T, °K.	C_p	T, °K.	C_p
56.3	1.584	160.3	11.25
60.7	1.998	184.0	12.75
69.6	2.797	201.3	13.92
83.9	4.199	229.2	15.23
107.6	6.647	250.8	16.42
121.6	7.971	273.5	17.36
140.7	9.768	291.6	17.91

TABLE III

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF SMITHSONITE

T, °K.	C_p	T, °K.	C_p
58.7	3.611	141.8	11.85
61.4	3.957	158.4	12.95
64.1	4.271	182.0	14.29
77.1	5.725	200.1	15.28
80.2	6.045	218.5	16.20
85.0	6.622	229.3	16.60
88.2	6.994	241.0	17.16
91.2	7.305	264.4	18.05
93.0	7.489	276.9	18.45
107.8	8.974	277.2	18.46
122.9	10.37	288.7	18.82
132.2	11.12	294.7	18.96
135.0	11.49	298.8	19.16

TABLE IV

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF CERUSSITE

T, °K.	C_p	T, °K.	C_p
53.6	8.180	151.2	16.15
57.3	8.532	166.4	16.72
75.0	10.90	170.9	16.92
90.0	12.42	183.2	17.23
109.6	13.85	193.5	17.58
129.0	15.04	199.2	17.84
134.9	15.33	209.4	18.21
136.6	15.46	209.4	18.22
147.0	15.94	219.2	18.55
226.6	18.67	266.2	20.17
230.9	18.81	279.3	20.40
237.3	18.99	284.2	20.50
241.4	19.26	288.8	20.65
256.1	19.81	293.6	20.80

TABLE V

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF RHODOCHROSITE

T, °K.	C_p	T, °K.	C_p
55.3	3.462	168.9	14.02
58.4	4.044	185.8	14.79
75.6	5.834	194.0	15.35
83.2	6.835	203.8	15.82
95.4	8.164	220.2	16.52
105.8	9.225	248.3	17.68
115.0	10.14	252.0	17.55
125.5	11.04	254.6	17.74
140.6	12.19	262.0	18.27
154.2	13.11	289.4	19.19
162.0	13.59	296.8	19.43

TABLE VI

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF SIDERITE

T, °K.	C_p	T, °K.	C_p
54.1	4.117	154.5	13.64
57.6	4.660	184.0	15.15
67.4	5.714	211.9	16.59
72.5	6.382	240.4	17.83
90.8	8.489	286.0	19.34
108.4	10.38	296.3	19.57
131.8	12.14		

the experimental heat curves per formula weights of these carbonates. All the curves were fitted, using five functions, a Debye, two Einstein and the last two either Debye or Einstein. The last two functions on all the carbonates did not fit as well as most of the other materials which have been worked on in this Laboratory; the curves generally fell in between a Debye and an Einstein

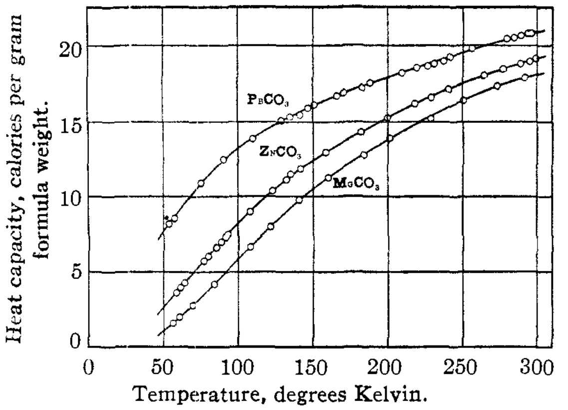

Fig. 1.—The heat capacities of magnesite, smithsonite and cerussite in calories per gram formula weight.

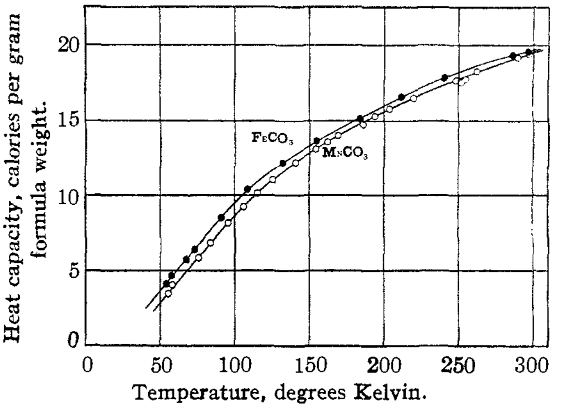

Fig. 2.—The heat capacities of rhodochrosite and siderite in calories per gram formula weight.

TABLE VII

ENTROPY DATA

	Magnesite	Smithsonite	Cerussite	Rhodochrosite	Siderite
Extrap. (0–56.2) °K.	0.57	1.45	6.45	1.65	2.33
Graph. (56.2–298.1) °K.	15.17	18.25	24.82	18.87	19.92
$S°_{298}$ graphical	**15.7** ± 0.2	**19.7** ± 0.3	**31.3** ± 0.8	**20.5** ± 0.3	**22.2** ± 0.4
$S°_{298}$ calcd. from functions	15.8	19.6	31.4	20.3	21.7

function. The following combinations were found to fit the specific heat curves to about 200°.

$$C_{\text{magnesite}} = \mathrm{D}\,\frac{(354)}{T} + 2E\,\frac{(468)}{T} + 2D\,\frac{(1994)}{T}$$

$$C_{\text{smithsonite}} = D\,\frac{(243)}{T} + 2E\,\frac{(393)}{T} + 2E\,\frac{(1279)}{T}$$

$$C_{\text{cerussite}} = D\,\frac{(89)}{T} + 2E\,\frac{(241)}{T} + 2D\,\frac{(1692)}{T}$$

$$C_{\text{rhodochrosite}} = D\,\frac{(223)}{T} + 2E\,\frac{(388)}{T} + 2D\,\frac{(2018)}{T}$$

$$C_{\text{siderite}} = D\,\frac{(179)}{T} + 2E\,\frac{(370)}{T} + 2D\,\frac{(2315)}{T}$$

The results of the entropy calculations, from the experimental heat capacity data and the function sums, are given in Table VII.

No related thermal data in connection with these carbonates will be discussed at present. A separate paper will be prepared shortly at this Laboratory to deal with the correlative data presented in this and two previous series of experiments dealing with metallic carbonates.

Summary

The heat capacities of magnesium carbonate (magnesite), zinc carbonate (smithsonite), lead carbonate (cerussite), manganese carbonate (rhodochrosite), and iron carbonate (siderite) from about 55 to 300°K. have been measured and their corresponding entropies determined as 15.7, 19.7, 31.3, 20.5 and 22.2, respectively.

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