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

The Heat Capacities of Sodium Carbonate and Bicarbonate and Silver Carbonate at Low Temperatures[1]

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The measurements described in this paper, which are a part of a series carried out in this Laboratory in a general program of determination of the thermal properties of important metallic carbonates, had a further incentive in the desire to compare the entropies so obtained with the corresponding figures from thermal decomposition. A discrepancy of several units still exists in the entropy of carbon dioxide as determined from equilibria, the third law, or spectroscopic data.

The method, apparatus and accuracy have been described in previous publications.[3] A new calorimeter with a gold wire resistance thermometer was constructed and used in the heat capacity determinations of the sodium bicarbonate. The heat capacity measurements with this new calorimeter are probably better than 1% at 55°K., as the gold wire resistance thermometer does not have the rapid diminishing resistance or the decrease of temperature coefficient that the copper wire resistance has at this low temperature. At higher temperatures the errors are probably substantially the same as with the copper wire resistance thermometer.

Materials

The sample of sodium carbonate used was Merck anhydrous C. P., and analysis showed the impurities to total less than 0.1%. A 91.4-g. sample was studied.

The sample of sodium bicarbonate was a product of Squibb. An analysis showed it to be better than 99.8% sodium bicarbonate, the impurities being about 0.1% each of water and sodium carbonate. No correction was made for these small impurities. The calorimeter was filled with 127.0 g.

The sample of silver carbonate was prepared in this Laboratory. Silver nitrate prepared from pure silver foil and C. P. nitric acid was recrystallized several times, dissolved in a large volume of water and a deficiency solution of sodium carbonate was added to precipitate the silver carbonate. Carbon dioxide was passed into the cold liquid for several hours in the dark, the liquid decanted and more water added. This was continued until no traces of sodium nitrate could be detected in the supernatant liquid. It was then filtered by suction, washed, dried over sulfuric acid and finally over phosphorus pentoxide. A conversion to metal indicated a purity of 99.96% silver carbonate.

Hydrogen was used as the conducting gas in the first series of measurements. It was found to have reacted with the silver carbonate. To remedy this difficulty helium was then used as the conducting gas, with 261.7 g. of silver carbonate.

The Specific Heats.—No previous low temperature measurements have been made on any of these carbonates. The results obtained in this

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(3) Anderson, THIS JOURNAL, **52**, 2296, 2712 (1930); **54**, 107 (1932).

Laboratory on the heat capacities of sodium carbonate, sodium bicarbonate and silver carbonate, expressed in gram calories (15°) per gram formula

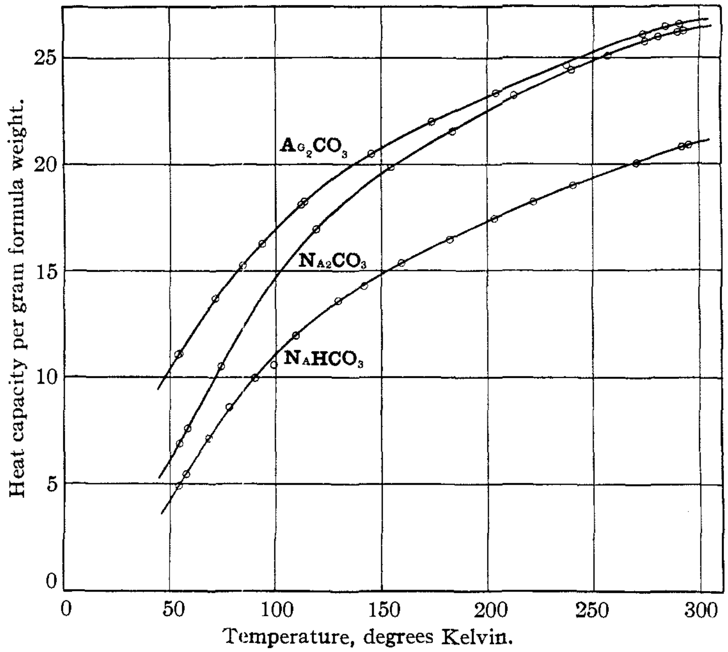

Fig. 1.—The heat capacities of sodium and silver carbonates and sodium bicarbonate, in calories per gram formula weights.

weight, are shown graphically in Fig. 1. The experimental determinations of heat capacities for these carbonates are given in Tables I, II and III,

TABLE I

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF SODIUM CARBONATE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.60	6.878	154.6	19.88	256.7	25.12
58.43	7.579	183.6	21.56	292.1	26.29
74.23	10.53	212.6	23.24	274.1	25.81
119.2	16.96	239.7	24.43	280.2	26.01
				289.3	26.24

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF SODIUM BICARBONATE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.17	4.923	109.4	11.90	221.8	18.25
57.54	5.438	129.8	13.60	240.6	19.00
68.65	7.225	142.0	14.28	270.7	20.06
77.86	8.591	159.4	15.37	291.8	20.79
90.07	9.953	182.3	16.46	295.1	20.89
99.07	10.57	203.4	17.45		

TABLE III

HEAT CAPACITIES PER GRAM FORMULA WEIGHT OF SILVER CARBONATE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
53.51	11.06	93.57	16.28	204.2	23.39
54.46	11.10	112.0	18.12	237.4	24.65
71.57	13.71	113.7	18.25	272.9	26.16
84.25	15.26	145.2	20.52	283.7	26.50
93.53	16.28	173.9	22.03	290.4	26.62

respectively. In changing joules to calories the factor 1/4.184[4] was used. The calculations were made on the basis of Na = 22.997, C = 12.00, O = 16.00, H = 1.008, and Ag = 107.88.

Calculation of Entropies.—The entropies were calculated by the usual method of plotting the heat capacity against the logarithm of the temperature. The heat capacity curves were extrapolated to the absolute zero by means of combination of Debye and Einstein functions. The Debye functions used had the following parameters (Θ): for Na_2CO_3, 137.6; $NaHCO_3$, 209.5; and Ag_2CO_3, 96.2.

The following combinations of Debye and Einstein functions were found to fit the specific heat curves per formula weights of these carbonates.

$$C_{Na_2CO_3} = D\,(138)/T + 2E\,(266)/T + 2D\,(737)/T$$
$$C_{NaHCO_3} = D\,(210)/T + 2E\,(292)/T + 2D\,(1601)/T$$
$$C_{Ag_2CO_3} = D\,(96)/T + 2E\,(172)/T + 2E\,(497)/T$$

The Na_2CO_3 combination fits the experimental heat capacity curve up to 200°K., the $NaHCO_3$ combination to 225° and the Ag_2CO_3 to about 160°. The results of the entropy calculations are given in Table IV.

TABLE IV

ENTROPY DATA

	Na_2CO_3	$NaHCO_3$	Ag_2CO_3
Extrap. (0–56.2) °K.	4.10	2.19	7.86
Graph. (56.2–298.1) °K.	28.40	22.20	32.13
$S°_{298}$ graphical	32.5 ± 0.6	24.4 ± 0.4	40.0 ± 0.9
$S°_{298}$ calcd. from functions	33.0	24.4	40.5

The related thermal data will not be mentioned at the present time, but will be fully discussed in a separate paper after the completion of this series of experiments.

Summary

The heat capacities of sodium carbonate, sodium bicarbonate and silver carbonate from about 55 to 300°K. have been determined and their corresponding entropies calculated as 32.5, 24.4 and 40.0, respectively.

BERKELEY, CALIFORNIA RECEIVED MAY 22, 1933
PUBLISHED SEPTEMBER 5, 1933

(4) "International Critical Tables," Vol. I, p. 24. 4.185 abs. joules = 1 cal. = 4.1837 Int. joules.