from that proposed here. Berthelot exposed the entire reaction vessel for long periods and it is not surprising that no nitrates or nitrites were found, since both are decomposed photochemically.

Summary

1. The reaction of ammonia and oxygen in radiation from the zinc spark has been studied, and a chemical equation for the reaction has been derived from analyses of the products.

2. A reaction mechanism leading to the empirical equation is proposed and probable side reactions are considered; these are discussed in their relation to analytical results and to the form of the rate curve.

3. An empirical modification of Beer's law has been derived, which represents absorption by ammonia in the region of λ 2080.

4. The quantum yield in the reaction has been found variable, and reasons for the variation have been advanced.

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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 at Low Temperatures of the Alkaline Earth Carbonates[1]

BY C. TRAVIS ANDERSON[2]

In a previous paper from the Pacific Experiment Station of the United States Bureau of Mines the author presented low-temperature thermal data for some carbonates in the first periodic group. The present paper deals with the carbonates of calcium (calcite and aragonite), strontium and barium.

The method, apparatus and accuracy have been described previously.[3]

Materials

In Table I are shown the materials used. The −14 +35 mesh size of all the materials was prepared by simple crushing and separation by standard screens of selected, well-developed crystals. The finer sample of calcite was prepared by grinding in a mechanical agate mortar with frequent classification by means of an air elutriator, arranged as described by Roller.[4] The particle size of the final product was determined by microscopic means to average near 0.5 micron. It had a very low apparent density and was compressed into pellets at a pressure of about 2 tons per sq. in., so that an adequate amount of the material could be put into the calorimeter, and also to improve the thermal conductivity. The fairly dense pellets which were produced were again crushed to −14 +35 mesh size.

The calcite and aragonite were analyzed by thermal decomposition at 1000° in a slow stream of pure dry nitrogen, determining the carbon dioxide and water evolved, and loss in weight of the sample. Analysis of the coarse sample of calcite showed a carbon dioxide content of 43.959%, with an approximate correction to vacuum, against the theoretical content of 43.972%. Calculation from the carbon dioxide content of the fine material showed only 98.656% $CaCO_3$. No silica could be detected. Since the weight of carbon dioxide and water checked the loss in weight of the calcite during decomposition, the composition of the impurity was calculated to consist only of $Ca(OH)_2$ and H_2O, the actual figures being 0.726% $Ca(OH)_2$ and 0.618% H_2O. In correcting the specific heats the water was calculated as ice.[5]

Precise density determinations were made on the samples using carbon tetrachloride of high purity. The correction for the density of the fine materials was obtained by making a rough density determination on a sample of lime, hydrated with an amount of water corresponding to the analysis of the impurity.

The Specific Heats

The experimental results obtained for the two samples of calcite are presented in Table II, aragonite in Table III and strontianite and witherite in Tables IV and V, respectively. The data given as gram-calories (15° per gram formula

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(3) Anderson, THIS JOURNAL, **52**, 2296, 2712 (1930); **54**, 107 (1932); **55**, 3621 (1933).

(4) Roller, U. S. Bureau of Mines Tech. Paper 490 (1931).

(5) Anderson, THIS JOURNAL, **52**, 2712 (1930).

TABLE I

MATERIALS USED

Material	Source	Grain size	Sample, g.	Density	Density temp., °C.	Purity	Impurities corr. for
Calcite	Utah	−14 +35	159.4	2.7132	25.0	99.970%	None
Calcite	Utah	0.5 micron Compr. granules	116.6	2.6956 2.7236 corr.	25.0	98.656	0.726% $Ca(OH)_2$ 0.618 H_2O
Aragonite	Tolenas Springs, Cal.	−14 +35	184.6	2.930	24.0	99.9+	None
Strontianite	Hamm, Germany	−14 +35	227.7	3.736	25.0	93.0	7.0% $CaCO_3$ (aragonite)
Witherite	England	−14 +35	262.1	4.2865	24.0	99.9+	None

weight have been corrected for the impurities previously indicated. The calculations were made on the basis of Ca = 40.07, Sr = 87.63, Ba = 137.36, C = 12.00 and O = 16.00.

TABLE II

HEAT CAPACITY PER GRAM-FORMULA WEIGHT OF CALCITE (COARSE)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
57.2	4.558	159.7	13.85	241.9	17.64
62.6	5.444	180.0	14.93	261.0	18.34
77.5	7.058	196.5	15.86	272.5	18.88
95.7	8.944	209.2	16.34	279.8	19.05
118.6	11.11	227.4	16.69	294.3	19.44
141.5	12.74				

HEAT CAPACITY PER GRAM-FORMULA WEIGHT OF CALCITE (FINE)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
57.0	4.637	131.3	12.09	233.7	17.32
61.6	5.505	148.5	13.29	254.1	18.39
73.5	6.611	168.3	14.54	272.1	19.06
84.4	8.164	192.4	15.82	287.5	19.49
111.5	10.46	207.7	16.50	296.5	19.79

TABLE III

HEAT CAPACITY PER GRAM-FORMULA WEIGHT OF ARAGONITE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.7	3.535	93.8	8.701	211.2	16.68
58.9	4.068	97.7	9.153	230.5	17.21
66.3	5.205	115.5	10.89	249.9	17.94
70.5	5.813	133.2	12.33	273.0	18.62
74.1	6.301	152.8	13.60	286.9	18.83
82.6	7.370	174.3	14.81	293.0	19.31
90.6	8.303	190.4	15.57		

TABLE IV

HEAT CAPACITY PER GRAM-FORMULA WEIGHT OF STRONTIANITE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.7	4.755	121.3	12.43	240.6	17.84
60.5	5.596	142.3	13.83	257.6	18.14
71.2	7.258	162.6	14.89	272.3	18.89
80.8	8.446	184.0	15.84	291.2	19.30
94.2	10.00	200.4	16.06		
105.4	11.12	218.8	17.16		

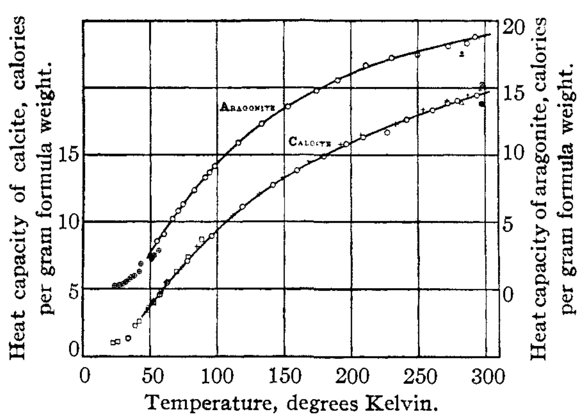
Figure 1 shows graphically a chart of the results obtained on the coarse and fine calcite and aragonite. It also has points representing the results

TABLE V

HEAT CAPACITY PER GRAM-FORMULA WEIGHT OF WITHERITE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.8	6.198	111.8	13.01	230.9	18.44
58.7	6.823	126.8	14.07	250.6	19.08
61.9	7.428	147.9	15.24	272.8	19.84
69.9	8.767	171.1	16.31	281.2	19.82
81.0	10.10	191.8	17.12	295.9	20.36
94.4	11.52	212.4	18.06		

of Nernst and Schwers[6] from 22 to 88°K. on calcite, and of several results near room temperature from the work of Brönsted[7] on both calcite and aragonite; of Nernst, Koref and Lindemann[8] on calcite; of Lindner[9] on calcite, and of Günther[10] on aragonite.



○, Anderson, coarse calcite and aragonite; +, Anderson, fine calcite; □, Nernst and Schwers; △, Brönsted; ●, Lindner; ☒, Nernst, Koref and Lindemann; ⊕, Günther.

Fig. 1.—The heat capacities of calcite and aragonite in calories per gram formula weight.

No previous low-temperature specific-heat measurements have been made on strontium or barium carbonates.

The results obtained for these two materials are shown graphically in Fig. 2.

(6) Nernst and Schwers, *Sitzb. Akad. Wiss. Berlin*, 355 (1914).

(7) Brönsted, *Z. Elektrochem.*, **18**, 714 (1912).

(8) Nernst, Koref and Lindemann, *Sitzb. Akad. Wiss. Berlin*, 247 (1910).

(9) Lindner, *Sitzb. Physik. Med. Soc. Erlangen*, **34**, 217 (1902).

(10) Günther, *Ann. Physik*, [4] **51**, 828 (1916).

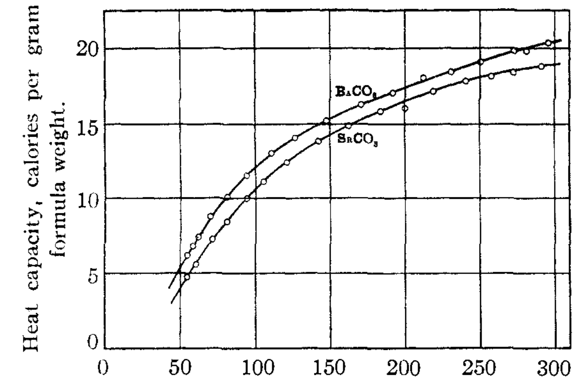


Fig. 2.—The heat capacities of strontianite and witherite in calories per gram formula weight.

Calculation of Entropies

The entropies of the carbonates were determined by the usual graphical method of integrating the expression $S^\circ_{298.1} = \int_0^{298.1} C_p \mathrm{d} \ln T$. The experimental curves coincided at low temperatures with Debye functions having the following parameter (Θ); for calcite, 180; aragonite, 244; strontianite, 210; and witherite, 148. Table VI gives the results of the entropy calculations.

TABLE VI

ENTROPIES FROM EXPERIMENTAL DATA

	Calcite (coarse)	Calcite (fine)	Aragonite	Strontianite	Witherite
Extrap. (0–56.2)°K.	2.42	2.42	1.51	2.11	3.59
Graph. (56.2–298.1)°K.	19.82	19.98	19.67	21.10	23.16
Direct $S^\circ_{298.1}$ (E. U.)	22.24 ± 0.4	22.40	21.18 ± 0.3	23.21 ± 0.4	26.75 ± 0.5
Function sum $S^\circ_{298.1}$	22.13		21.26	22.99	26.84

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

$$C_{\text{calcite}} = D\left(\frac{180}{T}\right) + 2E\left(\frac{370}{T}\right) + 2E\left(\frac{1210}{T}\right)$$

$$C_{\text{aragonite}} = D\left(\frac{244}{T}\right) + 2E\left(\frac{342}{T}\right) + 2D\left(\frac{1897}{T}\right)$$

$$C_{\text{strontianite}} = D\left(\frac{210}{T}\right) + 2E\left(\frac{304}{T}\right) + 2E\left(\frac{1344}{T}\right)$$

$$C_{\text{witherite}} = D\left(\frac{148}{T}\right) + 2E\left(\frac{274}{T}\right) + 2D\left(\frac{1730}{T}\right)$$

The two sets of data on calcite are so close together that no attempt has been made to reproduce separate curves for the fine and coarse material. The results are experimentally identical at the lower range, but the fine material shows a slight progressive increase of specific heat in the upper range. This apparent observed increase due to fine sizing is not necessarily a real property of the calcite. The maximum errors of the calorimeter appear in the upper range, and in exaggerated cases of bad cooling rates have been shown by other work to lie in the neighborhood of 2%, while the normal uncertainty is probably near 1% in this range. The fine material was a much poorer heat conductor than the coarse, even after the compression, and the correction due to impurities may be uncertain. The accuracy of determination on fine and coarse calcite cannot be claimed to be better than the observed differences.

The related thermal data on these carbonates will not be discussed at the present time, but will be included in a separate paper to be presented after this series of experiments on carbonates is completed.

Summary

The heat capacities of coarse and fine calcite, aragonite, strontianite, and witherite, from about 55 to 300°K., have been determined and their corresponding entropies calculated.

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