[Contribution from the Chemical Laboratory of the University of California]

THE THERMODYNAMIC PROPERTIES OF CALCITE AND ARAGONITE

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The present investigation was undertaken in the hope of obtaining an accurate test of the third law of thermodynamics by applying it to the transformation of aragonite into calcite. The specific heats of these substances have been determined by competent observers down to liquid-hydrogen temperatures, and the free energy of transition is known with considerable accuracy. This cannot, however, be said of the heat of transition. The transformation of aragonite into calcite cannot be made to proceed at room temperature with a speed sufficient for a calorimetric determination, and the heat of transition has to be obtained, therefore, by some indirect method such, for example, as the difference between the heats of solution of the two forms in an acid. Under such conditions a reliable result can be obtained only from measurements possessing a high degree of absolute accuracy.

An accurate redetermination of ΔH resulted in a value which differs even in order of magnitude from that obtained by Le Chatelier.[1] Together with the previously determined value[2] for ΔF, it furnishes a value for ΔS which should be accurate to $< \pm 0.2$ entropy units per mole. A calculation of the same quantity from the specific-heat curves reveals a discrepancy of 1.7 entropy units. An examination of the specific-heat data shows that this discrepancy can be accounted for only by assuming a systematic error in one of the curves and, indeed, reasons may be given for suspecting that the values for calcite at the lowest temperatures are high.

Experimental Part

In a determination of the heat of solution of a carbonate in an acid, the main difficulty lies in the fact that the carbon dioxide, which is formed in the reaction, is soluble in the acid. The reaction is not complete, therefore, until after equilibrium has been established between the gaseous and the liquid phase, which means that it takes more time than is ordinarily the case. Moreover, since the solubility changes rapidly with the temperature, it is necessary to regulate the temperature of the calorimeter in such a way that final temperature is the same in all cases. It seemed advisable to cut down the thermal leakage as far as possible by using a vacuum-jacketed calorimeter, and to control the temperature of its sur-

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[1] Le Chatelier, *Compt. rend.*, **116**, 390 (1893).

[2] Bäckström, *Meddel. Vetenskapsakad. Nobelinst.*, **5**, No. 11, **1921**; *Z. physik. Chem.*, **97**, 179 (1921).

roundings by submerging it in a stirred bath that could be heated to the desired temperature.

In every determination 10 g. of carbonate was dissolved in 800 cc. of *N* hydrochloric acid. The final temperature was always 25° ± 0.1°. Under these conditions about four times as much carbon dioxide is formed in the reaction as is needed for saturating the acid with the gas (0.1 mole against 0.0262 mole).[3]

The calorimeter was a jar-shaped Dewar vessel of 850cc. capacity, closed with a rubber stopper and fitted with a rotating stirrer. The heat capacity was obtained with the aid of an electric heater, and the temperatures were determined with copper-constantan thermocouples. All electrical measurements were made with a White double potentiometer, sensitive to 0.04 microvolt.

In calculating the warming correction, the thermal leakage was assumed to be proportional at every moment to the known temperature difference between calorimeter and bath. This must have been strictly true for the heat flow through the walls of the Dewar vessel and the stopper, and in order to make it at least approximately true also for the flow through the stirrer, the thermocouple, the lead wires of the heater and other parts of the apparatus that could not be totally submerged, special efforts were made to bring these into good thermal contact with the water of the bath.

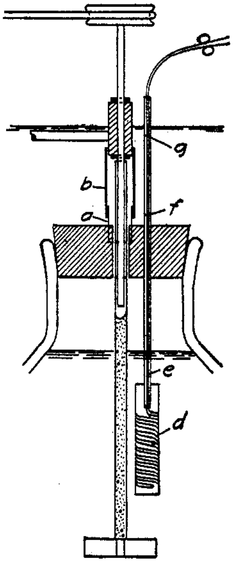

Fig. 1.—Stirring apparatus.

The arrangement by which the stirrer rod passes through the stopper while the apparatus is kept water-tight is shown in Fig. 1; *a* is a glass tube fitting into a slit in the rubber stopper; *b* is a piece of thick rubber tubing. The apparatus was submerged up to the point indicated, thus insuring that the metal parts of the stirrer were always at the temperature of the bath. A mixture of beeswax and rosin was used for making all connections between rubber and glass water-tight.

The electric heater *d* consisted of 36-gage constantan wire wound on glass tubing 1.1 cm. in diameter and insulated with paraffin. The 30-gage copper lead wires were taken out through Tube *e*, potential leads being connected just below the rubber stopper. Tube *e* was filled with paraffin between the points *f* and *g*. The resistance was 60 ohms, and the current used was 0.22 amp.

The energy measurements for the heat-capacity determinations were made by the same method and with the identical set-up used by Gibson and Giauque.[4]

During the heating period, current and e.m.f. were read at frequent intervals and the average was computed. The time of heating (generally 15 minutes) was measured with a calibrated stop watch.

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[3] Geffcken, *Z. physik. Chem.*, **49**, 273 (1904).

[4] Gibson and Giauque, THIS JOURNAL, **45**, 93 (1923).

The carbonate used in a determination was kept in a glass tube (7 cm. long and 2 cm. in diameter) which was closed at both ends with gold foil 0.025 mm. thick, cemented on with a melted mixture of beeswax and rosin. With the aid of two glass rods mounted in the rubber stopper, this tube was suspended vertically with the upper foil 1 cm. below the surface of the acid. The reaction was started by puncturing both foils with a sharp glass plunger, which was guided by a glass tube passing through the rubber stopper. This plunger was kept until used in a position such that its tip was a few millimeters from the upper foil. The gaseous carbon dioxide formed in the reaction passed through a long and winding glass tube before escaping into the air.

The 20-junction thermocouple used for measuring the temperature of the calorimeter had been made and calibrated by Dr. Bichowsky and Dr. Frost of this Laboratory. It was made from the same wire as the 4-junction couple of Eastman and Rodebush,[5] the e.m.f. of which was found by them to obey the equation: $E = 26672 - 2.2143\ T^{1.675}$. For 20 junctions this becomes: $E = 11.0715\ T^{1.675} - 133357.88$ (changing the second term slightly so that E becomes exactly zero for $T = 273.09°$ K.). This equation gives for the freezing point of mercury (—38.89°) —30256.5 microvolts, and for the transition point of $Na_2SO_4.10H_2O$ (32.383°) 27534.7 microvolts, while the observed values were —30242.7 and 27502.4, respectively. The final result would not be affected by small temperature errors introduced through use of the equation, since the heat capacity is determined experimentally, and the thermocouple is used, therefore, only for comparing two heat quantities directly. All determinations were made within a range of 5° so that the error from this source did not exceed 1 part in 10,000.

These calculations bring out a fact which does not seem to have been emphasized before, namely, that the method of determining the heat capacity experimentally has the added advantage of diminishing the effect of errors in the calibration of the thermocouple. Under these conditions it is even possible to use (within the restricted range of temperatures generally employed in calorimetry) the same equation for a set of thermocouples made from the same wire, without correcting for the minor deviations from the equation shown by the different couples. This is an advantage not only because it simplifies the calculations; it also relieves the rather embarrassing necessity of having to apply corrections to 0.1 microvolt that may be affected with systematic errors of several microvolts. The freezing point of mercury, which is one of the best thermometric fixed points is known only to 0.01°, that is, to about 8 microvolts on a 20-junction thermocouple. Yet if corrections are to be applied it is necessary —and theoretically correct—to compute them to 0.1 microvolt in order not to sacrifice anything in the real accuracy of the calorimetric determination.

The temperature of the bath was measured with either a 2- or an 8-junction thermocouple. These were calibrated against the 20-junction couple. When in use both thermocouples had their cold junctions in the same Dewar vessel with ice.

The whole set-up was electrically shielded in the way recommended by White.[6]

[5] Eastman and Rodebush, THIS JOURNAL, **40**, 489 (1918).

[6] White, *ibid.*, **36**, 2011 (1914).

A calorimetric run was generally preceded by two heat-capacity determinations. The temperature of the bath was adjusted in such a way that at the end of the heating period or the reaction the temperature of the calorimeter was still slightly lower than that of the bath. This made the calculation of the warming correction more certain since the same constant could be used throughout for calculating the heat exchange between calorimeter and surroundings. With the calorimeter warmer than the surroundings the liquid commences to distil to the colder parts of the walls, and this raises the value of the constant. The formation of spray during the reaction undoubtedly caused distillation to take place in the other direction, but this was only after the end of the reaction when the temperature difference between calorimeter and bath was very small (approximately 0.1°), whence the effect on the warming correction must have been negligible.

During the reaction, the temperature rise was far from being linear. This was partly due to the fact that it was found necessary to regulate the speed of the reaction to prevent it from becoming too violent. For this purpose, after the reaction had been started by puncturing both gold foils with the glass rod, the rod was at first only raised sufficiently to leave the hole in the lower foil open. When, after a few minutes, the reaction had come almost to a standstill, the plunger was raised farther and the upper hole left open for a second. This was repeated several times until the reaction was almost complete, when both holes were left permanently open. During the reaction period temperature readings were made every minute. From these, and the readings of the temperature of the bath that were taken at greater intervals, the temperature integral was obtained on multiplication by the leakage modulus, giving that part of the warming correction which was due to thermal leakage.[7] Both the leakage modulus and the heat of stirring were obtained from observations of thermal head and rate of temperature change made during a preliminary period of approximately the same duration as the reaction period and similar observations during the preceding heat-capacity determinations. The corresponding observations made after the end of the reaction were not used for this purpose but only for ascertaining the end-point of the reaction and thus for fixing the final temperature. Only when the observed temperature gradient agreed with the value calculated from the known thermal head and the heat of stirring was the reaction considered complete. This precaution was taken because the reaction involved the attainment of equilibrium in the distribution of carbon dioxide between the liquid and the gaseous phase. This being in its last stages a comparatively slow process, the accompanying heat effect might easily have escaped detection.

The reaction period generally occupied 30 to 35 minutes. The warming

[7] This is essentially a method discussed by White, *Phys. Rev.*, 31, 546 (1910).

correction amounted to about 3% (0.017°). Approximately half of this was due to heat of stirring (about 1°/3000 per minute). To ensure constant rate of stirring the motor operating the stirrer was fed by a 100-volt motor-generator equipped with a volt regulator.

Preparation of Materials

The aragonite was prepared in the same way as the material used in the author's solubility measurements, by heating a solution[2] of calcium chloride and urea to 140°. The preparation was carried out in the inner tube of an autoclave, the necessary carbon dioxide pressure being obtained by the addition of solid carbon dioxide. As found previously, some calcite is always formed on the walls of the vessel. In an effort to avoid this, tubes made of different materials were tried (glass, porcelain, platinum, tin) but without success. The microscopic examination showed, however, that the percentage of calcite formed was too small to affect the results. The synthetic calcite was prepared by heating aragonite with an ammonium chloride solution to 200° for about 12 hours. The Iceland spar was the same sample that had been used for the solubility measurements.

Experimental Results

The experimental results are summarized in Table I. The values for the heat capacity are generally the mean of several determinations agreeing to about 0.1%. The heats of solution refer to a temperature of 25 ± 0.1° and are expressed in calories per mole.

TABLE I

	Temp. rise, °C.	Heat capacity Cal./deg.	Heat of solution cal.
Aragonite	0.5604	799.8	4485
Aragonite	.5568	800.5	4460
Aragonite	.5585	800.2	4472
Iceland spar	.5633	796.7[a]	4491
Synthetic calcite	.5612	799.0[a]	4487
Mixture	.5615	800.1	4496

[a] A smaller container tube was used in the experiments with calcite.

The last value refers to a mixture of 50% synthetic calcite and 50% aragonite. Taking also this determination into account the mean values become for aragonite 4472, and for calcite 4495. This gives for the heat of transformation only about —20 cal. per mole as against —600 cal. found by Le Chatelier.

In order to test this rather surprising result by an independent method, the heats of solution were also determined in *N* hydrochloric acid that had previously been saturated with carbon dioxide. For this purpose carbon dioxide was passed through the liquid at a rate of about 25 cc. per minute for about 12 hours before the experiment was started, and this current was kept up also during the heat-capacity determinations and during the reaction. Before entering the calorimeter, the gas passed through a system of glass tubes and wash bottles containing water, immersed in the bath.

The heat effect of this current was therefore proportional to the temperature difference between calorimeter and bath, and the cooling correction could be calculated as before, the only difference being that the leakage modulus was raised by about 20%, from 0.00053° per minute per degree to 0.00064° when the current was exactly 25 cc. per minute. That after 12 hours of contact with carbon dioxide the calorimeter liquid was actually saturated with the gas, was shown by the absence of any special heat effect due to the process of solution.

The increase in temperature during the reaction causes some carbon dioxide to evaporate from the saturated solution. The attendant heat effect can be calculated from the solubility curve and amounts to 3.6 cal. per degree for 800 cc. of acid at 25°. By the method of passing carbon dioxide through the acid also during the heat-capacity determinations, this heat effect is, however, automatically included in the heat capacity, provided that a current of 25 cc. per minute is sufficient to keep the solution permanently in equilibrium with the gas. Even if this should not be the case, the error from this source is inappreciable. The results are given in Table II.

Table II

Results

	Temp. rise, °C.	Heat capacity Cal./deg.	Heat of solution cal.	Mean
Aragonite	0.3982	803.4	3201	3204
Aragonite	.3990	(803.3)	3207	
Synthetic calcite	.4060	801.3	3256	3245
Iceland spar	.4031	(801.3)	3233	

In Expts. 2 and 4 the saturation with carbon dioxide was carried out at the temperature at which the reaction was started (24.5°). In these cases the heat capacity was not determined experimentally but calculated on the basis of previous determinations.

The heat of transformation as obtained from these measurements is —40 cal. per mole. The agreement between the two values must be considered good and the mean, —30 cal., should not be in error by more than about 20 cal.

The difference between the two heats of solution determined should give the heat of solution of carbon dioxide. The determinations on calcite give $4495-3245 = 1250$ cal., those on aragonite $4472-3204 = 1268$ cal.; mean, 1259. According to Geffcken,[3] the "Ostwald solubility" for carbon dioxide in N hydrochloric acid at 25° is 0.799. The concentration is, therefore, $(0.799 \times 273 \times 737)/(22.4 \times 298 \times 760) = 0.0317$ mole per liter. The above value for the heat of solution is for 8 liters, which gives

1259/(8 × 0.0317) = 4965 cal. per mole, in excellent agreement with the value of about 4900 ± 100 cal., obtained from the solubility curve of Bohr and Bock.[8]

This good agreement is important since it shows that in the second series of measurements the acid was really saturated with carbon dioxide, as was assumed. In some older determinations of the same heat of solution made by von Kohner[9] this has probably not been the case. He obtained the very much higher value of 6570 ± 330 cal. per mole. His measurements were made under such conditions that the ratio of carbon dioxide in the saturated calorimeter liquid to calcium carbonate dissolved was about 1.1 moles of carbon dioxide per mole of calcium carbonate. The heat of solution of this amount of carbon dioxide is about 5500 cal. (corresponding to the value 1259 in the present determinations). In order to account for the discrepancy on this basis it is necessary, therefore, to assume that his calorimeter liquid was only about 40% saturated. Judging from the rather meager description of his experimental procedure this seems altogether possible.

Another strong argument in favor of the present value was furnished by a determination in which the ratio of carbon dioxide to calcium carbonate was 3.3 times as high as in the other determinations. Under these conditions a systematic error due to incomplete saturation or supersaturation would evidently cause a correspondingly larger error in the molar heat of solution. The agreement shows that this source of error has been successfully eliminated. The heat of solution per mole was 3290 cal., as against 3245 found previously. The agreement is all that can be expected in view of the very small temperature rise.

One more determination was made, namely, on 10 g. of Iceland spar that had been ground in an agate mortar for two hours. The molar heat of solution was 3306 cal., as against 3245 found previously.

It has long been known that the free energy of a substance, as measured by its solubility, increases as the size of the particles decreases. The limiting size, below which the effect begins to be noticeable, was found for three different substances studied by Hulett[10] to be about 2 microns. The corresponding effect on the heat content has, however, apparently never been investigated. In some experiments with Iceland spar the author[2] found an increase in solubility of about 13% when it was ground, corresponding to an increase in free energy of 200 cal. per mole. The increase in heat content of 60 cal. per mole found in the present experiment seems to be decidedly outside the bounds of experimental errors. It cannot have been due to increased adsorption of gases caused by the increase in

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[8] Landolt-Börnstein, "Tabellen," Julius Springer, Berlin, **1912**, 597.

[9] v. Kohner, *Dissertation*, Berlin, **1914**.

[10] Hulett, *Z. physik. Chem.*, **37**, 385 (1901).

surface, since this would have lowered the heat of solution instead of raising it. A microscopic examination showed that the particles varied in size from < 0.5 micron to about 12 microns, with the larger sizes predominant.

The Specific-Heat Curves

Existing specific-heat data for calcite and aragonite have been arranged in Tables III and IV. The mean atomic heats were plotted against the

TABLE III

MEAN ATOMIC HEAT OF CALCITE

Temp. °Abs.	C_p obs.	C_p calcd.	Observer Footnote No.	Temp. °C.	Temp. °Abs.	C_p obs.	C_p calcd.	Observer Footnote No.
22.3	0.199	0.152	11	—191.2 to				
				—81.3	81.9–191.8	2.41	2.43	12
26.2	.220	.208	11	—78–0	195–273	3.45	3.46	12
33.4	.319	.336	11	10	283	3.78	3.82	13
38.8	.450	.450	11	25	298	4.05	3.915	14
41.7	.519	.518	11	25	298	3.76	3.915	15
52.5	.813	.813	11	58	331	4.16	4.11	15
57.8	.968	.984	11	75	348	4.27	4.20	15
63.7	1.110	1.09	11	125	398	4.31	4.45	15
69.3	1.260	1.24	11	175	448	4.42	4.66	15
78.0	1.460	1.46	11	225	498	4.62	4.86	15
88.2	1.737	1.68	11	275	548	5.09	5.04	15
				17–356	290–629	4.72	4.67	16
				18–754	291–1027	5.27	5.27	17

TABLE IV

MEAN ATOMIC HEAT OF ARAGONITE

Temp. °Abs.	C_p obs.	C_p calcd.	Observer Footnote No.	Temp. °C.	Temp. °Abs.	C_p obs.	C_p calcd.	Observer Footnote No.
23.3	0.046	0.039	18		50.5	0.446	0.44	18
26.8	.056	.060	18		52.6	0.500	0.49	18
29.7	.073	.085	18		56.2	.566	.575	18
31.9	.104	.107	18	10	283	3.800	3.86	13
34.1	.138	.133	18	30	303	4.06	3.96	19
35.9	.169	.157	18	50	323	4.13	4.05	15
38.6	.193	.200	18	58	331	4.17	4.085	19
41.7	.256	.256	18	150	423	4.36	4.375	15
47.7	.370	.385	18	250	523	4.56	4.59	15

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[11] Nernst and Schwers, *Sitzb. Akad. Wiss. Berlin*, **1914**, 355.

[12] Koref, *Ann. Physik*, **36**, 49 (1911).

[13] Brönsted, *Z. Elektrochem.*, **18**, 714 (1912).

[14] Nernst, Koref and Lindemann, *Sitzb. Akad. Wiss. Berlin*, **1910**, 247.

[15] Lindner, *Sitzb. Physik, med. Soc. Erlangen*, **34**, 217 (1902).

[16] Magnus, "Habilitationsschrift," Tübingen, 1910.

[17] Magnus, *Physik. Z.*, **14**, 5 (1913).

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

[19] Landolt-Börnstein, "Tabellen."

logarithm of the temperature and smooth curves drawn through the points. The curve for calcite has a rather unusual shape, being a straight line from about 78° K. to the highest temperatures for which measurements exist. The equation of this line is $C_p = 4.23 \log T - 6.55$. For the mean of the atomic heat over a temperature interval $T_2 - T_1$ this gives

$$\frac{1}{T_2 - T_1}\int_{T_1}^{T_2} C_p \, dT = \frac{4.23\ (T_2 \log T_2 - T_1 \log T_1)}{T_2 - T_1} - 8.387$$

The values given in Col. 4 for temperatures higher than 78° K. have been calculated from these formulas. Of the other values in this column those for temperatures between 78° and 57.8° K. have been obtained from the curve, while for lower temperatures they have been calculated from the formula $\log C_p = 1.96 \log T - 3.461$, obtained by plotting $\log C_p$ against $\log T$. The agreement shows that the specific heat drops off much more slowly at low temperatures than required by the Debye equation, the exponent being 1.96 instead of 3. This is remarkable in view of the fact that the curve for aragonite is in good agreement with this equation, the corresponding formula being in this case $\log C_p = 3.25 \log T - 5.857$. The values in Table IV, Col. 4, up to $T = 41.7°$ have been calculated from this formula; the rest were obtained from the curve.

There are no direct determinations for aragonite between 56° and 282° K. The existing measurements are, however, so consistent and define a curve of so slight a curvature, that the uncertainty caused by this fact is very small. Table V gives for a number of round temperatures the mean atomic heat of aragonite as obtained from the curve.

Table V

T °K.	50	75	100	125	150	175	200	250	300
C_p	0.43	1.06	1.68	2.19	2.61	2.96	3.24	3.66	3.95

The curves for calcite and aragonite do not satisfy the requirements of either of Lewis and Gibson's two classes of specific-heat curves.[20] In determining the areas under the curves, Simpson's one-third rule[21] was found to be very useful. In the case of calcite the extrapolation to the absolute zero is made uncertain through the fact that Debye's equation is not obeyed. The possible error from this source is, however, small. Extrapolating with the aid of the empirical exponent 1.96, the following formula is obtained for the entropy per mean gram atom, valid at temperatures higher than 78° K.: $S_T = 4.870 (\log T)^2 - 15.082 \log T + 11.962$. This gives for the entropy at 25° C., 4.46 cal. per degree. If, instead, the exponent required by the Debye equation, namely 3, is used for extrapolating below the lowest experimental point, the above value for

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[20] Lewis and Gibson, This Journal, 39, 2554 (1917).

[21] See, for instance, Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green and Co.

the entropy is lowered by about 0.03 cal. per degree. The entropy of aragonite at 25° C., as obtained from the curve, is 3.98 cal. per degree per mean gram atom.

Discussion of Results

We now have three independent values for the entropy change in the transformation of aragonite into calcite.

1. ΔF as previously determined by the author is about —190 cal. per mole at 25° C. With $\Delta H = 30$ this gives $\Delta S = 220/298 = 0.74$ cal. per degree.
2. $\mathrm{d}\Delta F/\mathrm{d}T$ as determined by the author is —2.9 cal. per degree; ΔS consequently is 2.9.
3. The third law gives $4.46-3.98 = 0.48$ cal. per degree per mean gram atom, or 2.4 per mole.[2]

The first of these values should be correct to < 0.2 cal. per degree. The second rests on solubility measurements at 25° and 35°, that is, over a very small temperature range. Moreover, in the case of calcite it was found impossible to reach equilibrium from both sides, so that the equilibrium values had to be obtained by interpolation; and the fact, brought out only in the last experiment performed, that the reaction velocity decreases with the time of contact between crystals and solution, makes this interpolation rather doubtful. It seems possible, therefore, that this value may be wrong by as much as 2.2 cal. per degree. A value of $\mathrm{d}\Delta F/\mathrm{d}T$ of 0.7 cal. per degree would mean that the ratio of the activity products should be practically independent of the temperature. This conclusion is supported by solubility measurements at higher temperatures made by other observers even though, for reasons pointed out by the author,[22] their evidence cannot be considered conclusive.

The third value should be correct to 0.5 entropy unit, provided that there is no systematic error in the specific-heat curves. At higher temperatures the heat capacities of the two substances are not very different. At 100° K. the entropy difference is practically the same as at 298°. The values are 1.28 and 0.83 respectively; that is, $\Delta S = 0.45$ cal. per degree as against 0.48 at 298°. This centers attention on the low-temperature measurements. The fact that Günther's values for aragonite meet the requirements of the Debye equation makes it seem likely that they are correct. On the basis of the third law it appears probable, therefore, that a systematic error has caused the measurements of the specific heat of calcite at low temperatures to give too high results. Additional evidence, pointing in this direction, will be given in the following paper.[23]

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[22] See the review of the literature given in the author's paper in *Z. physik. Chem.*, Ref. 2.

[23] Bäckström, THIS JOURNAL, **47**, 2443 (1925).

The Transition Point

The author has previously calculated[2] the transition temperature, obtaining a value of —43° C. This calculation was based on Le Chatelier's value for the heat of transition and must, therefore, now be rejected. The transition point must be situated at a temperature very near to the absolute zero. The discrepancy which the application of the third law has revealed between the determinations of the specific heats at low temperatures and the other thermodynamic data, makes a calculation of the exact value of the transition point impossible for the present.

This does not, however, affect the conclusion drawn previously[2] that pure aragonite is never the stable form under geological conditions. The pressure necessary to make aragonite the stable phase depends only on the change in free energy and the change in volume involved in the transition. When $\Delta F = -190$ cal. and $\Delta V = -2.75$ cc. per mole, this pressure is found to be 2900 atmospheres. In the greatest depths of the sea the pressure is only about 1000 atmospheres, and in the deeper strata of the earth's crust the increase in pressure is not sufficient to outweigh the increase in the free energy of transition caused by the increase in temperature.

The writer wishes to acknowledge his indebtedness to Drs. F. R. von Bichowsky and W. F. Giauque for valuable advice and assistance in connection with the present work.

Summary

The heats of solution of calcite and aragonite in N hydrochloric acid have been determined under two different sets of conditions, in pure acid and in acid saturated with carbon dioxide. From these determinations ΔH_{298} for the transformation of aragonite into calcite is found to be 30 ± 20 cal. per mole. When $\Delta F_{298} = -190$ cal., this gives $\Delta S_{298} = 0.74$ entropy unit per mole, a figure which is estimated to be accurate to at least 0.2 entropy unit.

The third law of thermodynamics gives for the entropies of calcite and aragonite under standard conditions 22.3 and 19.9 entropy units per mole, respectively; that is, ΔS as obtained from this source is 2.4 entropy units. The discrepancy is too large to be explained in any other way than by assuming a systematic error in one of the specific-heat curves. The low temperature data for aragonite are in agreement with the Debye equation, while for calcite this is not the case. This may be taken as an indication that the error, if any, is to be sought in the low-temperature measurements for calcite.

The heat content of calcite was found to be raised measurably when the substance was finely pulverized.

The paper also contains a discussion of some points in connection with the calibration of thermocouples for use in calorimetric work.

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