[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT OF DISSOCIATION OF CALCIUM CARBONATE AND THE ENTROPY OF CARBON DIOXIDE

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The thermal dissociation of calcium carbonate is one of the classical examples of a heterogeneous chemical equilibrium and, especially through the researches of Johnston[1] and of Smyth and Adams,[2] it may now be said to be, perhaps, the best known equilibrium of this kind. These observers have derived equations representing their dissociation-pressure measurements in a very satisfactory manner, but no attempt has been made so far at a complete thermodynamic treatment. This has been due to the fact that accurate thermochemical and specific-heat data have been lacking. It may be shown, however, that the specific-heat data now at hand are sufficiently accurate for the purpose, and by combining the results of the preceding paper[3] with regard to the heat of solution of calcite in hydrochloric acid, saturated with carbon dioxide, with a new determination of the heat of solution of calcium oxide under the same conditions, it has been possible to derive an accurate value for the heat of dissociation at room temperature. On the basis of these data a free-energy equation has been derived, which represents the dissociation-pressure measurements within limits of error and gives an independent value for the entropy of carbon dioxide which is in good agreement with previous values.

Experimental Part

The calorimetric arrangement was that described in the preceding paper, the only difference being that a different thermocouple was used. This was an 8-junction copper-constantan couple, made from a different kind of wire from the one used in the 20-junction couple.

The calcium oxide was obtained by igniting about 3 g. of calcite to constant weight in a platinum crucible.[4] The oxide was transferred directly from the crucible to the container tube, and the gold foil pasted on immediately with paraffin. The amount of oxide taken was determined by weighing the crucible again. The glass in the bottom of the tube had been made very thin, so that it could be punctured with the glass plunger.

As in the experiments with calcium carbonate, the acid was saturated with carbon dioxide before the run and the gas current continued all through the determination. The temperature of the calorimeter was adjusted in such a way that the final temperature was always 25° ± 0.1°.

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[1] Johnston, THIS JOURNAL, **32,** 938 (1910).

[2] Smyth and Adams, *ibid.*, **45,** 1167 (1923).

[3] Bäckström, *ibid.*, **47,** 2432 (1925).

[4] It has been shown by Gautier [*Compt. rend.*, **128,** 939 (1899)] that the temperature to which the oxide is heated has no influence on its heat of solution.

TABLE I

RESULTS

Oxide g.	Temp. rise °C.	Heat capacity, cal./deg.	Heat of soln. per mole, cal.
1.7399	1.7959	795.3	46,030
1.7551	1.8195	795.1	46,140
1.6984	1.7625	796.3	46,330
			Mean 46,170

As a weighted mean I shall take 46,200 cal. per mole. Thomsen[5] and Berthelot[6] found 46,030 and 46,060 cal., respectively. If it is taken into account that the concentration of the acid was lower in their determinations, the agreement is perfect.

In the preceding paper[3] the heat of solution of calcite under the same experimental conditions was found to be 3245 cal. per mole. This is the mean of two determinations made on 0.1 mole; a third determination using 0.03 mole, the same quantity as in the determinations on calcium oxide, gave 3290 cal. The difference is within the experimental error of the latter determination, but 3260 cal. will be taken as the final value. This value includes, however, a negative heat effect due to the fact that the carbon dioxide evolved must have become saturated with water vapor before leaving the calorimeter liquid. The heat of evaporation of water at 25° is 586 cal. per g. The saturation pressure above the solution at the reaction temperature was about 23 mm.; the heat effect per mole of carbonate dissolved is, therefore, $(23/737) \times 586 \times 18.02 = 330$ cal. Consequently, the heat of dissociation of calcite at 25° is found to be $46{,}200-3260-330 = 42{,}600 \pm 200$ cal. per mole. Thomsen's value is 42,520; Berthelot's, 43,300.[7]

The Specific-Heat Curves

The most reliable dissociation-pressure measurements lie within the range 700–900°. For calcium carbonate and calcium oxide the heat capacities have been determined up to about 750°. It is necessary, therefore, to extrapolate the specific-heat curves over a range of 150°. In the case of calcite this is made difficult by the shape of the curve. It was shown in the preceding paper that the heat-capacity data for temperatures higher than about 80° K. when plotted against log T, form a straight line represented by the equation, $C_p = 4.23 \log T - 6.55$. When this formula is used for extrapolating to higher temperatures, it soon gives values considerably above the Dulong-Petit value, and these high values cannot be accounted for on the basis of the difference between C_p and C_v, since a calculation of this difference from coefficient of expansion and compressi-

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[5] Thomsen, "Thermochemische Untersuchungen," vol. 3, p. 247.

[6] Berthelot, *Ann. chim. phys.*, [5] **4**, 531 (1875).

[7] Landolt-Börnstein, "Tabellen," Julius Springer, Berlin, **1923**.

bility at room temperature and using the rule of Lindemann and Magnus[8] for extrapolating to higher temperatures shows that even at these temperatures $C_p - C_v$ is negligible.[9] The graphical representation of the data shows, however, very definitely that it is impossible to draw a specific-heat curve that will not rise above the Dulong-Petit value. The above formula has, therefore, been used also for extrapolation.

The heat-capacity data for calcium oxide have been summarized in Table II. The values in Col. 4 have been read from a curve obtained by plotting C_p against log T. Mean specific heats were calculated by dividing the temperature interval into a number of equal parts, reading the corresponding values of C_p from the curve and integrating by Simpson's one-third rule. The values for temperatures up to 68.4° K. have been calculated from the formula, $\log C_p = 3.22 \log T - 4.003$, which is in good agreement with the requirements of the Debye equation. The entropy at 25° C., as obtained from the area under the curve, is 4.75 entropy units per mean gram atom.

TABLE II

MEAN ATOMIC HEAT OF CALCIUM OXIDE

Temp. °Abs.	C_p obs.	C_p calcd.	Observer Footnote No.	Temp. °C.	Temp. °Abs.	C_p obs.	C_p calcd.	Observer Footnote No.
28.2	0.055	0.046	10	—188.5 to —79.8	84.6–193.3	2.81	2.91	11
41.5	.128	.161	10	—77.9–0	195–273	4.48	4.60	11
51.6	.326	.326	10	23	296	5.10	5.12	12
60.1	.535	.532	10	1.5–100	274.6–373.1	5.33	5.28	13
68.4	.805	.805	10	18–100	291–373	5.28	5.33	14
85.2	1.572	1.40	10	18–319	291–592	5.65	5.65	14
89.3	1.698	1.53	10	16–556	289–829	5.81	5.80	15
				17–759	290–1032	5.89	5.90	15

This curve is of the type characterizing substances of Class 1.[16] When log Θ is taken as 2.145 and the constant a in the expression of Lindemann and Magnus ($C_p - C_v = aT^{3/2}$) as 2.0×10^{-5}, the agreement is within a few hundredths of a calorie over the whole range up to 700° K. Above this

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[8] Lindemann and Magnus, *Z. Elektrochem.*, **16**, 269 (1910).

[9] As a matter of fact, it is doubtful whether a calculation of this kind can be made for a crystal which does not belong to the regular system. Such a crystal, on being heated at constant volume, changes its shape, and the work involved in this process would have to be accounted for.

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

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

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

[13] Ewald, *Ann. Physik*, **44**, 1213 (1914).

[14] Magnus, "Habilitationsschrift," Tübingen, **1910**.

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

[16] Lewis and Gibson, THIS JOURNAL, **39**, 2554 (1917).

temperature the expression of Lindemann and Magnus seems to fail. With these values of the constants, I obtain from the table of Lewis and Gibson: $S_v = 4.75$; $S_p = 4.82$.

For the heat capacity of carbon dioxide Lewis and Randall[17] have given the formula, $C_p = 7.0 + 0.0071\ T - 0.00000186\ T^2$, summarizing the measurements of Holborn and Austin[18] and Holborn and Henning,[19] made by the flow method. Quite recently, however, Dixon and Greenwood[20] have proposed a very different formula, $C_p = 7.9 + 0.0031\ T$, based on measurements of the velocity of sound in carbon dioxide at temperatures up to 600°. Both of these formulas will be considered.

Table III gives the molar heat capacities at constant pressure for calcite, calcium oxide and carbon dioxide for a number of temperatures. The values in Col. 4 have been obtained from the formula of Lewis and Randall, those in Col. 5 from that of Dixon and Greenwood. Cols. 6 and 8 give the corresponding values for the difference, $\Delta = C_{CaCO_3} - (C_{CaO} + C_{CO_2})$. The figures in Cols. 7 and 9 have been calculated from the formulas $\Delta = 0.12 + 1.1525 \times 10^{-2}t - 4.13 \times 10^{-6}t^2$ and $\Delta = 0.17 + 1.4525 \times 10^{-2}t - 6.03 \times 10^{-4}t^2$, respectively. They agree with the values in Cols. 6 and 8, respectively, to less than 0.1 cal. per degree over the whole range. When absolute temperatures are introduced, these formulas become $\Delta = -3.34 + 1.378 \times 10^{-2}T - 4.13 \times 10^{-6}T^2$ and $\Delta = -4.25 + 1.782 \times 10^{-2}T - 6.03 \times 10^{-6}T^2$.

TABLE III

COLLECTED HEAT-CAPACITY DATA

Temp. °C. 1	Calcite 2	CaO 3	L. and R. 4	D. and G. 5	Δ_1 obs. 6	Δ_1 calcd. 7	Δ_2 obs. 8	Δ_2 calcd. 9
0	18.78	9.95	8.80	8.75	0.03	0.12	0.08	0.17
100	21.64	11.02	9.39	9.06	1.23	1.23	1.56	1.56
200	23.83	11.56	9.94	9.37	2.33	2.26	2.90	2.83
300	25.59	11.86	10.46	9.68	3.27	3.21	4.05	3.98
400	27.06	12.00	10.94	9.99	4.12	4.07	5.07	5.02
500	28.34	12.12	11.38	10.30	4.84	4.84	5.92	5.92
600	29.45	12.20	11.78	10.61	5.47	5.55	6.64	6.71
700	30.45	12.23	12.15	10.92	6.07	6.16	7.30	7.38
800	31.35	12.26	12.48	11.23	6.61	6.70	7.86	7.95
900	32.17	12.28	12.77	11.54	7.12	7.15	8.35	8.35
1000	32.92	12.30	13.03	11.85	7.59	7.52	8.77	8.67

With $\Delta H_{298} = 42{,}600$ and $d\Delta H/dT = 3.34 - 1.378 \times 10^{-2}T + 4.13 \times 10^{-6}T$ the dissociation-pressure equation becomes $\log p = -9212.4/T + 1.6797 \log T - 1.5048 \times 10^{-3}T + 0.1503 \times 10^{-6}T^2 + I$.

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[17] Lewis and Randall, THIS JOURNAL, **34,** 1128 (1912).

[18] Holborn and Austin, *Sitzb. Akad. Wiss. Berlin,* **1905,** 175.

[19] Holborn and Henning, *Ann. Physik,* **23,** 809 (1907).

[20] Dixon and Greenwood, *Proc. Roy. Soc.*, **105A,** 199 (1924).

Table IV gives the values of I that are obtained when this equation is applied to the experimental results of Johnston and of Smyth and Adams.

TABLE IV

VALUES OF I

DATA OF JOHNSTON

T	p Mm.	I	T	p Mm.	I	T	p Mm.	I
860.1	1.0	6.964	1000.1	44	7.172	1103.1	255	7.124
878.1	2.3	7.114	1009.1	54	7.182	1112.1	311	7.148
904.1	4.0	7.064	1016.1	60	7.168	1115.1	335	7.159
944.1	13.5	7.178	1021.1	70	7.193	1125.1	381	7.147
946.1	14.5	7.189	1022.1	72	7.197	1130.1	420	7.155
953.1	15.8	7.158	1050.1	105	7.127	1144.1	537	7.170
955.1	16.7	7.163	1059.1	134	7.170	1149.1	557	7.153
964.1	19.0	7.133	1061.1	138	7.167	1154.1	603	7.155
974.1	23.0	7.123	1068.1	150	7.150	1156.1	629	7.161
976.1	25.5	7.149	1073.1	183	7.199	1164.1	684	7.147
984.1	32.7	7.185	1092.1	235	7.168	1167.1	716	7.148
			DATA OF SMYTH AND ADAMS					
1115.4	343.0	7.167	1179.6	875.0	7.159	1430.8	14,202	7.136
1126.0	398.6	7.160	1210.1	1350	7.166	1499.4	26,093	7.144
1127.6	404.1	7.156	1210.1	1340	7.163	1499.3	26,093	7.145
1142.0	510.9	7.162	1322.4	4894	7.140	1514.0	29,718	7.150
1177.4	879.0	7.174	1355.6	6758	7.128	1512.0	30,579	7.169

The Free-Energy Equation

The mean from Johnston's determinations (excluding the first three) is 7.161, while the values of Smyth and Adams fort emperatures up to 1210° K. give 7.1635. Their values for higher temperatures are too far outside the range of the specific-heat data to be used for testing the equation, but apparently the formula represents also these determinations within limits of error. They were made by the method of heating curves, which is liable to give slightly low results. The authors consider their determination of the eutectic point ($T = 1513 \pm 1°$, $p = 30{,}000 \pm 300$ mm.) the most accurate of their high-temperature values. With $I = 7.162$, which may be taken as the final mean, the formula gives $30{,}300 \pm 250$ mm.

When p is expressed in atmospheres, I becomes 4.281; hence, the free-energy equation for the reaction $CaCO_3 = CaO + CO_2$ is $\Delta F = 42{,}180 - 3.34T \, ln \, T + 6.89 \times 10^{-3}T^2 - 0.688 \times 10^{-6}T^3 - 19.601T$; $\Delta F_{298} = 31{,}258$; $\Delta S_{298} = 38.05$.

The dissociation-pressure equation that is obtained when the specific heat of carbon dioxide is assumed to obey the Dixon-Greenwood formula instead of that of Lewis and Randall is not in agreement with the measurements; there is a definite trend in the values for the integration constant. It may, however, be of interest to calculate ΔS_{298} also on this assumption, since it gives an idea of the accuracy of the above value. The formulas

$\Delta C_p = 3.34 - 1.378 \times 10^{-2}T + 4.13 \times 10^{-6}T^2$ and $\Delta C_p = 4.25 - 1.782 \times 10^{-2}T + 6.03 \times 10^{-6}T^2$, when used for extrapolating ΔH_{298} to the temperature at which $\Delta F = 0$, namely, the dissociation point 1169.1° K. give 38,870 and 38,074 cal. per mole, respectively. The corresponding values for ΔS at this temperature are 33.25 and 32.57 cal. per degree, that is, they differ by 0.68 entropy unit. When, however, these values for ΔS are referred to 298.1°, using the same equations for ΔC_p, the resulting values (38.05 and 38.43, respectively) differ by only 0.4 entropy unit. Analogous calculations show that the error of ±200 cal. in ΔH_{298} corresponds to only ±0.2 entropy unit in ΔS_{298}, and that an error in the dissociation temperature of 2° would make an uncertainty in ΔS of 0.06 entropy unit.

These calculations illustrate how the very nature of the entropy function favors an accurate result in a calculation of standard entropies from high-temperature, free-energy data. Errors in ΔH and ΔF have less influence on the final result, the higher the temperature at which the free-energy measurements were made; the relative effect of errors in the heat-capacity data is smaller at the higher temperatures, where the uncertainty is generally larger.

The Entropy of Carbon Dioxide

In the preceding paper[3] the entropy of calcite, as obtained from its specific-heat curve, was found to be 22.3 entropy units per mole at 25° C. A different value was obtained from the specific-heat curve of aragonite and the entropy of transition, 19.9 + 0.74 = 20.64, and reasons were given why more confidence should be placed in this latter value. When combined with the entropy of calcium oxide (9.5) and the entropy of dissociation (38.05) these values give 50.85 and 49.2, respectively, for the entropy of carbon dioxide. Calculations of the same quantity from other sources give satisfactory agreement with the latter value, which is another argument in favor of the lower value for the entropy of calcite. When the entropies of graphite and carbon monoxide are taken as 1.3 and 45.55 cal. per degree, respectively,[10] the free-energy equation for the reaction, $C + CO_2 = 2CO$[21] gives $S_{298} = 48.5$ for carbon dioxide. Similarly the value 48.3 is obtained from the free-energy equation for the reaction, $CO + {}^1/{}_2O_2 = CO_2$, taking the entropy of oxygen as 48.0 entropy units per mole. In the absence of reliable, low-temperature, specific-heat data for carbon dioxide[22] these two calculations are probably the most direct that can be made from other sources.

Summary

A new value for the heat of dissociation of calcium carbonate has been obtained by combining a determination of the heat of solution of calcium

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[21] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 569.

[22] See the discussion of Eucken's data in Lewis and Gibson, Ref. 10.

oxide in hydrochloric acid with the measurements for the corresponding quantity for calcite that were presented in the preceding paper. On the basis of this value a free-energy equation for the reaction, $CaCO_3 = CaO + CO_2$, has been derived, which represents the dissociation-pressure measurements within limits of error and yields a value for the entropy of carbon dioxide, which is in good agreement with values obtained from other sources.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY AND THE JEFFERSON PHYSICAL LABORATORY OF HARVARD UNIVERSITY]

THE CONSTRICTED MERCURY ARC AS A SOURCE OF LIGHT FOR PHOTOCHEMICAL WORK

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Any adequate study of reactions having very low photochemical yields, of the reciprocity law and of kindred problems requires very great light intensities produced simultaneously with a high degree of spectral resolution. Dissatisfied with the compromises between these objectives found unavoidable with the usual types of mercury-vapor lamp, we have previously designed and investigated two special lamps.[2,3] The relative intensities of fifteen sets of lines were measured up to extreme conditions of pressure, voltage gradient, current density and constriction of the luminous column.

These researches showed that a constricted arc between two mercury surfaces, confined in a water-cooled quartz tube of 2-mm. internal and 7-mm. external diameter, 38 mm. long with its ends open to the atmosphere, could most nearly meet our requirements.

Our monochromator has been described elsewhere[2] in detail. Fig. 1 gives wave-length energy curves for a constricted arc running on 3 amperes and 90 volts, taken with the monochromator used as a spectro-radiometer, and shows the degree of resolution obtained when the entrance slit was 0.1 mm. wide, and when it was ten times that width. It should be noted that in taking the upper curve, 140 ohms' resistance was introduced in series with the galvanometer and thermopile, so that 1.0cm. deflection corresponded to 1.50 microwatts per sq. mm. at the exit slit, whereas in the lower curve 0.36 microwatt was the corresponding figure. It appears that with the 1mm. entrance and exit slits as commonly used in our instrument, as much (approximately) monochromatic radiation of λ366 was transmitted as was received of *total radiation* from the same arc through

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[1] National Research Fellow in Physics.

[2] Harrison and Forbes, *J. Optical Soc. Am.*, **10**, 1 (1925).

[3] Forbes and Harrison, *ibid.*, **11**, 99 (1925).