the final experiment, the solution was probably not saturated, since the amount of bromine left was very small.

TABLE V.—CONCENTRATION AND CONDUCTANCE OF SATURATED BROMINE SOLUTIONS

No.	Time (hours).	Equiv. conc.	Spec. cond. × 10^6.
2	70	0.506	7440
3*a*	1	0.465	4160
b	20	0.466	4160
4	2	0.440	2210
5	1	0.424	907
6	1	0.424	734
7*a*	1	0.411	726
b	6	0.425	805
8	2	0.411	728

The concentration decreases slightly, and the conductance greatly in the first five experiments, probably owing to the gradual removal of some impurity, such as hydrobromic acid or potassium bromide. The bromine appears, from the approximate constancy of the two series of results, to have been nearly pure in the last four experiments; and the following values are probably not greatly in error: solubility, 0.21 mol Br_2 per liter;[1] specific conductance, 727×10^{-6} reciprocal ohms.

If we assume that the conductance is solely due to the hydrobromic acid formed by the hydrolysis, $Br_2 + H_2O = H^+ + Br^- + HBrO$, then the concentration calculated for $(H^+) = (Br^-) = (HBrO)$ is 0.0017. This corresponds to 0.8 per cent. hydrolysis, and the calculated equilibrium constant is:

$$(H^+)(Br^-)(HBrO)/(Br_2) = 2.4 \times 10^{-8}.$$

This value differs very little from the geometric mean, 1.7×10^{-8}, of the hydrolysis constants of chlorine and iodine.

Summary.

From conductance and solubility measurements of iodine and of bromine in water, the hydrolysis constants $(H^+)(I^-)(HIO)/(I_2)$ and $(H^+)(Br^-)(HBrO)/(Br_2)$ are found to be 0.6×10^{-12} and 2.4×10^{-8}, respectively.

BOSTON, March, 1910.

THE THERMAL DISSOCIATION OF CALCIUM CARBONATE.

BY JOHN JOHNSTON.

Received June 16, 1910.

Measurements of the dissociation pressures of calcium carbonate have been made through a range of temperatures by Debray,[2] LeChatelier,[3]

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[1] This value agrees well with that determined by Winkler (Seidell, solubilities, page 67) 3.36 g. per 100 g. soln., or approximately 0.206 mol per liter.

[2] *Compt. rend.*, 64, 603 (1867).

[3] *Id.*, 102, 1243 (1886).

Brill,[1] Pott[2] and Zavriev.[3] Quite recently, E. H. Riesenfeld[4] has discussed the data of each of these authors. He concludes that, owing to errors in the measurement of pressure or of temperature, or of both, the data of the first three authors are altogether untrustworthy, and sets up an involved empirical formula to express the mean results of Zavriev and Pott. Pott made four series of measurements over the temperature range 600–900°; these, however, are by no means so concordant as might be wished, *e. g.*, for 892° he found pressures which varied from 593 mm. to 776 mm. Still, a curve drawn through the midst of his points coincides approximately with that which represents the results of Zavriev, which are relatively few in number but more concordant among themselves.

From the results of either author it follows that the dissociation point (*i. e.*, the temperature at which the pressure of carbon dioxide is one atmosphere) is close to 910°. This value was confirmed by special experiments made by Riesenfeld, who determined anew the temperature at which a loss of weight occurred when the carbonate was heated in an atmosphere of pure carbon dioxide. He showed, moreover, that the possibility of formation of solid solutions of calcium oxide in the carbonate and *vice versa* is practically excluded, while it was shown by Zavriev that no basic carbonate exists.

It has therefore now been definitely proved that the dissociation of calcium carbonate proceeds according to the scheme $CaCO_3 \rightleftarrows CaO + CO_2$, and to that scheme solely. The discrepancies in the results are thus to be attributed entirely either to errors in the measurement of the temperature of the substance, or to errors in the pressure, due either to the fact that equilibrium conditions had not been attained or to the presence of water vapor or of some other impurity capable of developing a pressure.[5]

The apparatus used by both Pott and Zavriev consisted essentially of a long porcelain tube closed at one end, connected to a manometer at the other. In this tube were placed quantities of substance weighing from 2–5 grams, and the thermoelement was embedded in the charge in such a way that the junction was in the hottest part of the furnace. Now Zavriev observed directly differences of more than 50° in the temperature at various points of somewhat larger charges contained in a boat 5 cm. in length; so it is not unreasonable to suppose that the temperature variations throughout the charge were still considerable in the actual measurements. This difficulty has been encountered in all accurate high tem-

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[1] *Z. anorg. Chem.*, 45, 275 (1905).

[2] Dissertation, Freiburg in B., 1905.

[3] *Compt. rend.*, 145, 428 (1907); *J. chim. phys.*, 7, 31 (1909).

[4] *J. chim. phys.*, 7, 561 (1909).

[5] Cf. J. Johnston, *Z. physik. Chem.*, 62, 336 (1908); H. Schottky, *Idem.*, 64, 432 (1908).

perature work, but its importance, and the magnitude of the error introduced thereby, have not yet been generally appreciated.[1] For accurate work it is of the highest importance that the temperature of the charge be as uniform as possible; for otherwise, since the carbon dioxide is in equilibrium with that calcium oxide which is at the *lowest* temperature, one cannot determine with any certainty the appropriate temperature corresponding to the pressure observed. In the author's experiments,[2] this difficulty was obviated by using charges of only about 0.1 gram, the total vapor space being not more than 5 cc.; this possesses the additional advantage that a transfer of a very small amount of carbon dioxide from the solid to the vapor phase suffices to bring the system into equilibrium, and consequently equilibrium conditions are established comparatively rapidly.

The apparatus used was a slight modification of an apparatus previously described by the author.[3] The substance was contained in a platinum tube 6 cm. in length, 6 mm. in external and 5 mm. in internal diameter, which was sealed directly on to a glass tube and thereby, through an adjustable mercury trap, connected to a mercury manometer, on which the pressures were read directly with the aid of a fine mirror scale divided in millimeters. After complete evacuation of the apparatus, the platinum tube was heated gently for some time in order to expel any water or other volatile impurity; by manipulation of the stopcocks the mercury was raised in the trap, thereby delimiting the vapor space. The platinum tube was enclosed almost entirely in a small vertical resistance furnace, and was well packed with asbestos at the mouth of the furnace. The temperature was in general increased step by step; in a few cases it was dropped some degrees with a corresponding drop in the pressure. In all cases the reading was taken only when at constant temperature the pressure had attained a constant value; at low pressures, this required an interval of some hours, but at the higher pressures half an hour usually sufficed.

The temperature of the charge was measured by means of a thermoelement the junction of which was welded on to the outside closed end of the platinum tube; elsewhere the thermoelement wires were insulated by small Marquardt tubes. The element used had previously been carefully calibrated at the melting points of zinc, silver and copper (418°,

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[1] Cf. Day and Sosman, *Am. J. Sci.*, 29, 99, 102 (1910); W. P. White, *Idem.*, 28, 335 (1909).

[2] To avoid possible misunderstanding, it may be stated that the measurements were completed in April, 1909; that at that time I had seen only the preliminary paper of Zavriev (*Compt. rend.*, 145, 428 (1907)), and was entirely unacquainted with the work of Pott; further, that Table 1 is a complete record of the measurements which I have made.

[3] *Z. physik. Chem.*, 62, 333, 335 (1908).

960°, and 1083° respectively), the electromotive forces being measured by the usual arrangement of potentiometer and galvanometer. After being welded on the element was compared several times with a previously calibrated standard element the junction of which was immersed in calcium carbonate inside the platinum tube, the other conditions being precisely those of the actual pressure measurement. By this means it was shown that the maximum variation in the temperature of the charge did not exceed 2° and that the difference between the temperature registered by the element welded outside and that of the standard element inside the tube was 2.5° at 400° and 5° at 900°,[1] the variation being practically linear. All the temperatures given have been corrected for this difference, and it is considered that they are certainly correct to within ±2°. Four series of observations were made; in two series, pure precipitated calcium carbonate alone was used, some carbon dioxide being driven off by the initial heating after evacuation; in the other two series, the substance taken was a mixture of the pure carbonate with pure freshly ignited oxide. All the observations are brought together and arranged in Table 1; p is the pressure in millimeters of mercury, t and T the centigrade and the absolute temperatures respectively. These points are all plotted on Fig. 1, from which it is evident that they all lie close to the graph of equation VIa. The derivation of this equation will now be given.

TABLE 1.—ACTUAL EXPERIMENTAL RESULTS.

t.	T.	p. in mm.	t.	T.	p. in mm.
587	860	1.0	749	1022	72
605	878	2.3	777	1050	105
631	904	4.0	786	1059	134
			788	1061	138
671	944	13.5	795	1068	150
673	946	14.5	800	1073	183
680	953	15.8	819	1092	235
682	955	16.7	830	1103	255
691	964	19.0	840	1112	311
701	974	23.0	842	1115	335
703	976	25.5	852	1125	381
711	984	32.7	857	1130	420
			871	1144	537
727	1000	44	876	1149	557
736	1009	54	881	1154	603
743	1016	60	883	1156	629
748	1021	70	891	1164	684
			894	1167	716

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[1] It was found that the absolute magnitude of these temperature differences varied within 1° or 2° with the depth of immersion of the platinum tube in the furnace and with the efficiency of the packing at the mouth of the furnace; this variation of the differences could; however, be rendered inappreciable by reproducing always the same conditions.

In a previous paper[1] it was shown that for a number of heterogeneous equilibria similar to that under consideration, the dissociation pressure is connected with the heat of reaction[2] ΔH by the equation

$$\log P = \frac{\Delta H}{4.576T} - \frac{I'}{4.576} \qquad \text{(I)}$$

I' being the so-called thermodynamically indeterminate constant; and that this relation holds within the limits of accuracy of our present knowledge of ΔH and of the other thermochemical quantities involved. The above simple relation is derived by neglecting all the higher terms; this is equivalent to the assumption that ΔH is independent of the temperature.

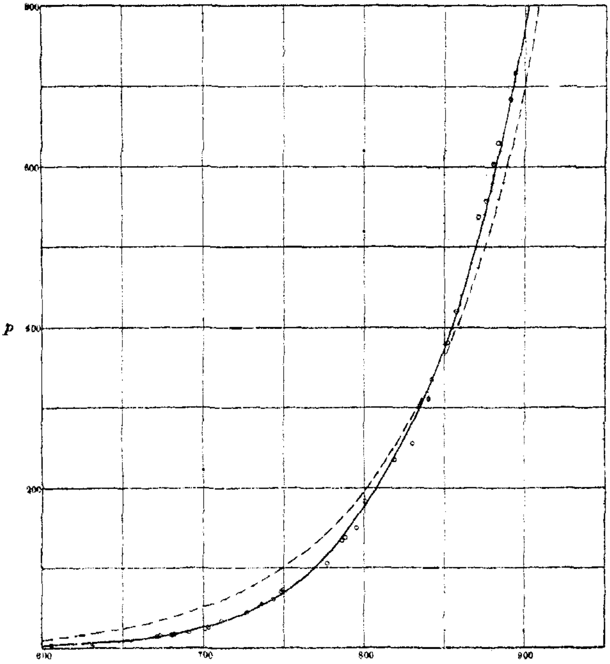

Fig. 1.—Experimental results on the dissociation pressure of $CaCO_3$. The full line is the graph of equation VI*a*; the broken line that of Riesenfeld's equation.

In the present case, our knowledge of the thermal quantities, though by no means satisfactory, is such that it is advisable to insert terms

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[1] This Journal, 30, 1357 (1908); *Z. physik. Chem.*, 65, 737 (1909).

[2] ΔH is the amount of heat *absorbed*, as ordinarily measured calorimetrically, when the reaction $RCO_3 = RO + CO_2$ takes place. In the former paper, the pressure was expressed throughout in atmospheres; in the present paper, p is expressed always in millimeters mercury; this is more convenient, and causes only a numerical difference in the value of I. It may be noted that $4.576 \log P = R \ln P$ where ln is the natural log, and R the gas constant.

which shall represent the change of ΔH with the temperature. Consequently, we write $\frac{d(\Delta H)}{dT} = \Delta C_p$ and assume $\frac{d(\Delta C_p)}{dT} = \alpha$ where α is a constant; ΔC_p is the change in heat capacity of the system when the reaction $CaCO_3 = CaO + CO_2$ takes place. Hence, by integrating, we obtain

$$\Delta H = \Delta H_0 + \Delta C_{p0} T + \tfrac{1}{2} \alpha T^2 \qquad \text{(II)}$$

and therefore equation (I) becomes[1]

$$-RT \ln p = \Delta H_0 - \Delta C_{p0} T \ln T - \tfrac{1}{2} \alpha T^2 + I T \qquad \text{(III)}$$

In order to derive numerical values of the coefficients in equation (III) from the thermal data available, it is necessary to proceed in the following somewhat roundabout manner: The mean of the concordant values for the heat of reaction obtained by Thomsen and by de Forcrand is 42900 cal.; *i. e.*, $\Delta H = 42900$ when $T = 300°$. Now, by making a least square solution for all the experimental data comprised between $T = 1000°$ and $T = 1167°$ on the assumption that the equation $\log p = a/T + b$ holds (*i. e.*, on the assumption that within the above temperature range ΔH is fairly constant), we obtain the equation

$$\log p = -8419/T + 10.071 \qquad \text{(I}a\text{)}$$

Hence at the mean temperature, say $T = 1100$, we have, by comparison with equation (I),

$$\Delta H = 8419 \times 4.576 = 38500 \text{ cal.}$$

By substitution of these pairs of values in equation (II) and elimination of ΔH_0, the equation

$$5.5 = -\Delta C_{p0} - 700\, \alpha \qquad \text{(IV)}$$

results; this can be solved by combining it with some recent results on the specific heats of calcium carbonate and oxide. Lindemann,[2] namely, found that the specific heat, at the ordinary temperature, of $CaCO_3$ was 0.2027; and that of CaO was 0.1821. Hence, the values of C_p (the molecular heat capacity) are 20.3 and 10.2 respectively. When $T = 300°$, C_p for CO_2, as deduced from the work of Holborn and Henning, is 9.0; hence

$$\Delta C_p = 9.0 + 10.2 - 20.3 = -1.1 \text{ when } T = 300.$$

This statement is equivalent to the equation

$$-1.1 = \Delta C_{p0} + 300\, \alpha \qquad \text{(V)}$$

from which, by combination with (IV), we obtain

$$\alpha = -0.011$$
$$\Delta C_{p0} = 2.2$$

and hence from II, $\Delta H_0 = 42700$.

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[1] Cf. Haber, "Thermodynamics of Technical Gas Reactions," pp. 26, etc.; Johnston, *Loc. cit.*, p. 1358.

[2] Nernst, Koref, and Lindemann, *Sitzungsber. Akad. Wiss., Berlin*, **1910**, 247.

Inserting these values, equation III becomes

$$-RT \ln p = 42700 - 2.2\, T \ln T + 0.0055\, T^2 + I\, T$$

which may be written in a form more convenient for calculation,

$$\log p = -9340/T + 1.1 \log T - 0.0012\, T - I''. \qquad \text{(VI)}$$

When the corresponding values of p and T are substituted in equation (VI), concordant values of I'' are obtained, the mean of which is -8.882. Finally, therefore, as the equation which represents p (expressed in mm. mercury) as a function of T (the absolute temperature) we have

$$\log p = -9340/T + 1.1 \log T - 0.0012\, T + 8.882. \qquad \text{(VI}a\text{)}$$

This equation reproduces the observations over the whole range within the probable error of experiment;[1] and since its form is theoretically the most satisfactory, consistent with present knowledge, it may be used with some confidence for extrapolation. By means of equation VI*a* the equilibrium pressures have been calculated for a number of temperatures (centigrade); the results are presented in Table II. The dissociation point is 898°.

These results are considered to be better than any of the existing data on the subject because of the superior accuracy with which the temperature of the dissociating substance was determined. For the sake of comparison, however, results interpolated graphically from the experimental data of Zavriev and of Pott are included in Table II.

TABLE II.—EQUILIBRIUM PRESSURES (IN MM.) FOR $CaCO_3$ AT ROUND TEMPERATURES.

		Interpolated from the data of	
t.	Calc. by equation VI*a*.	Zavriev.	Pott.
500	0.11	...	...
550	0.57	...	...
600	2.35	..	...
650	8.2	...	...
700	25.3	43	53
750	68	95	101
800	168	197	195
850	373	381	350
900	773	697	667
950	1490	...	...
1000	2710	...	...

From the data of these authors, Riesenfeld deduced the mean values at five temperatures—700°, 750°, 800°, 850° and 900°;[2] and on the basis of these results, with the aid of the Nernst formula for heterogeneous equilibria, arrived at the equation[3]

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[1] Equation I*a* fits the data from $T = 1000$ to $T = 1167$ almost as well as equation VI*a*; but, on account of the fact that ΔH actually does vary with the temperature, it is not satisfactory as an extrapolation formula.

[2] The values are close to the arithmetic means of columns 2 and 3, Table II.

[3] P is in atmospheres. It may be noted that the coefficient of the first term on

$$\log P = -9300/T + 1.75 \log T + 0.011{,}916\ T - 0.000{,}020{,}323\ T^2 + 0.000{,}000{,}008{,}2446\ T^3 + 3.2.$$

The graph of this equation over the experimental range is drawn as a broken line in Fig. 1, which shows that from about 800–900° the results from both equations are not very different. It is otherwise at other temperatures, and the discrepancy becomes especially noticeable at higher temperatures; at 1500°, Riesenfeld's equation leads to a value of 6,790,000 atmospheres, whereas equation VI*a* gives 151 atmospheres. In order to bring out the difference between the two formulas and the consequent uncertainty of extrapolation, Fig. 2 has been constructed by drawing the graphs of both equations for a range of temperature extending from 400–1500° C. This was accomplished by plotting the values of log *p* (in mm.) against those of $10^6/T$;[1] that part of either curve

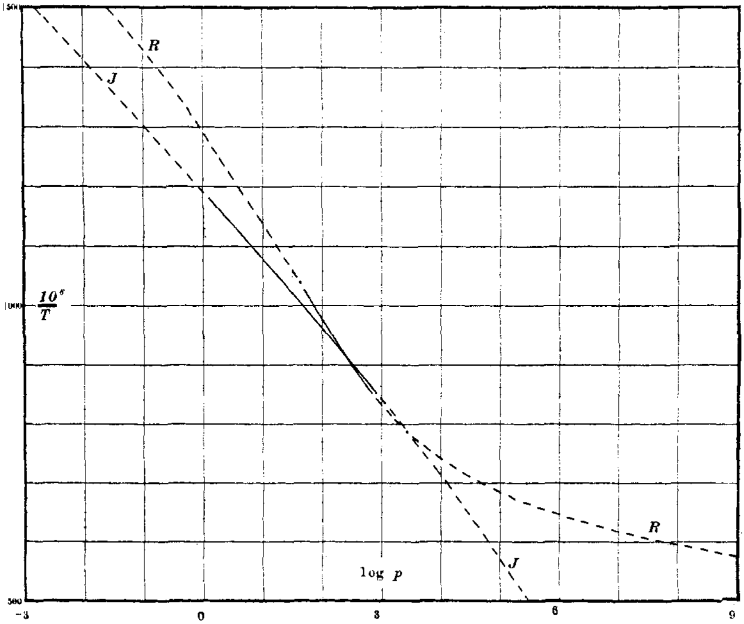

Fig. 2.—Graphs of Riesenfeld's equation (RR) and of equation VI*a* (JJ): the portions extrapolated are represented by broken lines.

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the right-hand side is derived from the heat of reaction at room temperature, and is the only coefficient to which a direct physical interpretation can be given; that of the second term and the constant are taken from Nernst; the other three coefficients were chosen so as to fit the pressure data.

[1] Plotting with these coördinates possesses the advantages: that the graph of equations such as VI is nearly a straight line, and is absolutely a straight line so long as ΔH is independent of T; that the value of ΔH at any point can be readily derived from the slope of the curve at that point.

based on direct experiment is drawn full, while the extrapolated portions are represented by broken lines. Comment is unnecessary.

Summary.

In preceding measurements of the equilibrium pressure of the reaction $CaCO_3 \rightleftarrows CaO + CO_2$, the errors have been due mainly to a lack of definiteness in the temperature of the reacting system; in the author's experiments this difficulty has been obviated by the use of a very small quantity (0.1 gram) of material, by which means the extreme temperature variation throughout the charge did not exceed 2°. This necessitated the use of a form of apparatus in which the vapor space was always small; this, and the mode of measuring the temperature accurately, are described in the paper. It is considered that the uncertainty in the temperature is not greater than ±2°.

The results of four separate series of measurements can be well reproduced by the equation

$$\log p = \frac{-9340}{T} + 1.1 \log T - 0.0012\, T + 8.882$$

where p is the equilibrium pressure (expressed in millimeters of mercury) at the absolute temperature T. The pressure reaches one atmosphere at 898° C. Two of the numerical coefficients of the above equation are derived from the heat of reaction and the heat capacities of the components; the form of the equation is consistent with our present theoretical knowledge; consequently, in spite of the somewhat unsatisfactory character of the thermal data, the equation may be used with some confidence for extrapolation. The above equation represents the experimental results much better than the formula proposed by Riesenfeld, and derived from the approximation formula of Nernst; values extrapolated by means of the latter diverge from, and are inherently less probable than, those derived from the former, especially at temperatures above 1000°.

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ON THE CONDUCTIVITY OF SOME CONCENTRATED AQUEOUS SOLUTIONS AT ZERO.

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As a preliminary step to an investigation of the conductivities of certain salts in mixed solutions of water and ammonia, some measurements were made of the conductivity of potassium iodide in concentrated aqueous solutions, which gave unexpected values. Further investigation confirmed these results, and the measurements were extended to potassium bromide, sodium nitrate, ammonium nitrate, silver nitrate, and copper