TABLE VI

RELATIVE PARTIAL MOLAL HEAT CONTENT AND RELATIVE PARTIAL MOLAL SPECIFIC HEAT OF CADMIUM BROMIDE

m	$-\alpha$	β	$(\bar{L}_2)_{298.1}$	$(\bar{C}_p - \bar{C}_p^0)_{298.1}$
0.0005	1840	0.0226	169	13
.001	3612	.0402	− 44	24
.002	5060	.0558	− 98	33
.005	7020	.0775	−133	46
.007	7775	.0858	−147	51
.01	8583	.0941	−217	56
.02	9961	.1103	−160	66
.03	10813	.1200	−151	72
.05	11811	.1315	−124	78
.07	12560	.1398	−134	83
.1	13233	.1481	− 69	88
.2	14671	.1648	− 31	98
.5	16529	.1855	− 44	111
.7	17299	.1938	− 75	116
1.0	18075	.2021	−113	121
1.2	18533	.2067	−161	123
1.5	19046	.2118	−223	126
1.8	19413	.2151	−303	128

The author is pleased to acknowledge the kind assistance of Professor Herbert S. Harned.

Summary

1. Electromotive force measurements of the cell

Cd–Hg(2-phase)/CdBr₂(m)/AgBr–Ag

have been made at eight temperatures ranging from 5 to 40°. The molality of cadmium bromide was varied from 0.0004 to 1.8.

2. The standard potential of the cell has been evaluated on the assumption that CdBr$^+$ is the only ion aggregate present in appreciable quantities below 0.01 m. The constant for the dissociation of this intermediate ion appeared to have the following values: 0.006 ± 0.0003 at 5°, 0.0065 ± 0.0003 at 10, 15 and 20° and 0.007 ± 0.0003 at 25, 30, 35 and 40°.

3. The standard potential of the cadmium amalgam electrode from 5 to 40° has been determined, and a critical comparison with previous results has been made.

4. The stoichiometrical activity coefficients, relative partial molal heat content and relative partial molal specific heat of cadmium bromide in aqueous solution have been computed.

5. When incomplete dissociation effects are not taken into consideration, the La Mer, Gronwall and Greiff extension of the Debye–Hückel equation is inapplicable to cadmium bromide solutions more concentrated than 0.001 M.

The Solubility in Water of Carbon Dioxide at 50, 75 and 100°, at Pressures to 700 Atmospheres

BY R. WIEBE AND V. L. GADDY

The work presented here is a continuation of high pressure investigations of the properties of gases that are of importance to the fertilizer industry.[1] Sander[2] was the first to make an extended determination of the solubility of carbon dioxide in water under pressure. His results are valuable only in a qualitative sense, since his two sets differ from each other in many cases by more than 10%. Recently Zelvinskii[3] measured the solubility at several temperatures and in some cases to about 90 atm. We will discuss his work later in relation to our own.

Apparatus and Procedure.—The apparatus is shown in Fig. 1. Carbon dioxide from a tank was introduced into cylinder B through valve a.

This valve was then closed and the carbon dioxide compressed into C, D and E through valve b by means of hydraulic pressure on the mercury in A. Cylinders A and B were kept at 0° to facilitate compression. During runs, B was kept at a slightly higher pressure, serving as gas reservoir. D and E were enclosed in a thermostat, accurately controlled. The solubility bomb contained a closely-fitting, thin glass test-tube and had in the center a silver tube leading through the head. Both the head and surrounding valve parts were made of stainless steel. Samples of saturated water taken from E were expanded into buret system F where the water and gas were measured at barometric pressure and 25°.[4] Between the solubility apparatus and the gage a mercury–oil system was interposed to keep carbon dioxide from reaching the gage, as shown in the upper left-hand corner of

(1) For references to past work see Wiebe and Gaddy, THIS JOURNAL, **57**, 1487 (1935); **59**, 1984 (1937); **60**, 2300 (1938).

(2) Sander, Z. physik. Chem., **78**, 513 (1912).

(3) Zelvinskii, J. Chem. Ind. (U. S. S. R.), **14**, 1250 (1937); C. A., **32**, 852 (1938).

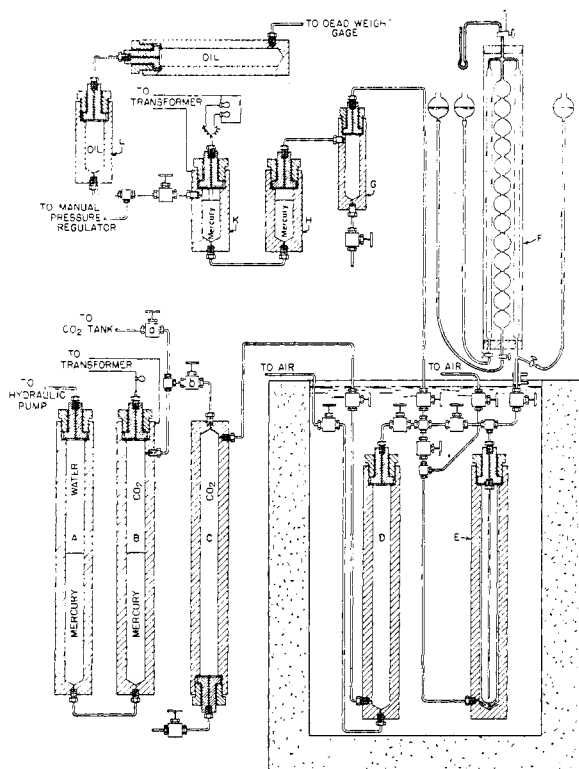(4) Wiebe and Gaddy, THIS JOURNAL, **55**, 947 (1933).

Fig. 1.

the drawing. The mercury levels in H and K were kept at the same height by means of a manual pressure regulator not shown in the drawing. Pressure balance was observed by means of the indicated electrical contact system. G and L were safety traps in case mercury should accidentally overflow from either H or K. Water was saturated with carbon dioxide in cylinder E and expanded into buret system F where the final measurement took place. Cylinders C and D were used as a capacity to keep the pressure fluctuations down to a minimum during sampling and also while saturating.

In spite of all precautions a slight amount of iron dissolved in the water. It was not immediately noticeable since the solution remained clear for an hour or so in an open beaker. Table I gives some of our analyses. The iron is probably

TABLE I

Temp., °C.	Total pressure	G. Fe/cc.
50	150	0.000007
75	300	.000035
75	400	.000025
100	25	.0000012
100	50	.000016
100	100	.000035
100	200	.000035

dissolved as a bicarbonate.[5] The bicarbonate concentration did not change at any one pressure after saturation was complete. Since at least two sets of from four to six samples were taken at several hours or sometimes days apart with no change, we concluded that no carbon dioxide was taken from the saturated solution. It was shown by Findlay and Creighton[6] that the solubility of carbon dioxide in a 0.24% ferric hydroxide solution was practically identical with that in pure water and, since our concentrations are far below that, we assume that the small amount of iron in our solution did not affect our determinations. The gas was analyzed by means of a Shepherd gas analysis apparatus,[7] the purity being 99.98% carbon dioxide.

Discussion of Results

The results expressed as the number of cc. of carbon dioxide (N. T. P.) contained in 1 g. of liquid water are given in Table II. In order to correct for the gas left in the water of the sample after expansion, 0.734 (Bunsen absorption coefficient = 0.758)[8] was added to the amount calculated from the gas phase. This value was obtained by multiplying the bunsen coefficient by $(760 - P_{H_2O})/(760 \cdot d_{H_2O})$ where P_{H_2O} and d_{H_2O} are the vapor pressure and density of water at 25°, the temperature of the buret.

TABLE II

Total pressure, atm.	Solubility of carbon dioxide in water cc. gas S. T. P. per g. of water		
	50°	75°	100°
25	9.71	6.815	5.365
50	17.246	12.590	10.179
75	22.534	17.044	14.289
100	25.628	20.61	17.67
125	26.77		
150	27.643	24.58	22.725
200	29.143	26.66	25.694
300	31.34	29.51	29.53
400	33.29	31.88	32.39
600	36.73		
700	38.34	37.59	38.50

In Fig. 2 we have plotted total presssure vs. cc. gas (S. T. P.) per g. of water. The lower the temperature the more abrupt a change occurs in the solubility in the range of 100 to 200 atm. This already had been observed by Sander[2] (p. 545). He called attention to the fact that the compressibility maxima for carbon dioxide for tempera-

(5) Müller and Henecka, Z. anorg. allgem. Chem., 181, 159 (1929).
(6) Findlay and Creighton, J. Chem. Soc., 97, 536 (1910).
(7) Shepherd, Bur. Standards J. Research, 6, 121 (1931).
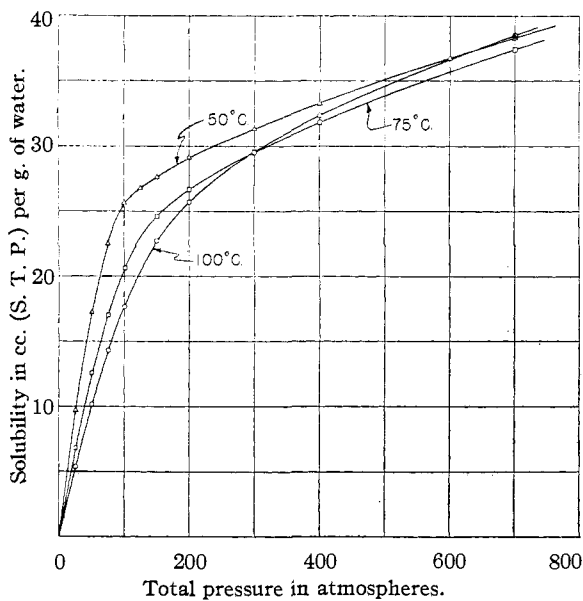(8) Geffcken, Z. physik. Chem., 49, 257 (1904).

Fig. 2.—Solubility of carbon dioxide in water.

tures from 50 to 100° lie between 100 and 200 atm. and that beyond this point the gas phase assumes the property of a liquid, i. e., being only slightly compressible. He mentioned that the mutual solubility of liquids in liquid is affected by pressure to only a slight extent. This will appear obvious later in the discussion of equation 3. Figure 3 shows most clearly the complete reversal of the solubility trend at 700 atm. The minimum is also shown at 400 atm. but at this pressure the solubility at 100° is still lower than the corresponding value at 50°. Minima have been observed in previous work[9] for nitrogen, hydrogen and helium.

The general equation for a binary isothermal system with two phases in equilibrium is given by[10]

$$\left[\frac{d\overline{F}_1}{dP}\right]_{N_1} dP + \left[\frac{d\overline{F}_1}{dN_1}\right]_P dN_1 = \left[\frac{d\overline{F}_1^1}{dP}\right]_{N_1^1} dP + \left[\frac{d F_1^1}{d N_1^1}\right]_P d \quad (1)$$

where $\overline{F}_1$ and $\overline{F}_1^1$ are the partial molal free energies of constituent 1 in the liquid and gas phases, respectively. This equation may be changed into a more convenient form

$$\overline{V}_1 dP + RT \left[\frac{d \ln f_1}{d \ln N_1}\right]_P \frac{dN_1}{N_1} =$$
$$\overline{V}_1^1 dP + RT \left[\frac{d \ln f_1^1}{d \ln N_1^1}\right]_P \frac{dN_1^1}{N_1^1} \quad (2)$$

(9) Wiebe, Gaddy and Heins, THIS JOURNAL, **55**, 947 (1933); Wiebe and Gaddy, ibid., **56**, 76 (1934); **57**, 847 (1935).

(10) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, Chapter 18.

where $\overline{V}$'s and f's are the partial molal volumes and fugacities of component 1 in the two phases. Since we are dealing here with a dilute solution of carbon dioxide in water and a small concentration of water in the gas phase we may write equation 2 as follows

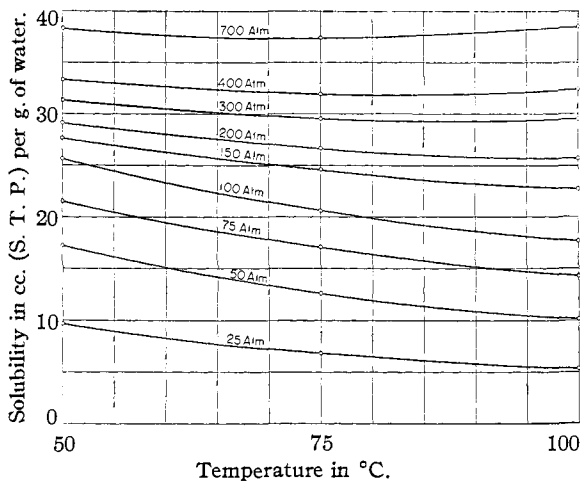$$d \ln N_1 = \frac{\overline{V}_1^1 - \overline{V}_1}{RT} dP \quad (3)$$

Fig. 3.—Solubility of carbon dioxide in water.

This equation would strictly apply only to infinitely dilute solutions but we shall use it to calculate the solubilities of carbon dioxide in water at 75 and 100°.[11] The molal volume of carbon dioxide in water at 0° and atmospheric pressure according to Ångström is 28.9 cc./mole.[12] In our calculations,[13] we assumed $V = \overline{V}$ for both phases. In the liquid phase we also assumed $\overline{V}$ independent of pressure and equal to 29 cc./mole. Our reference point was the value at 25 atm.

TABLE III

"Partial pressure" of CO_2, atm.	Mole fraction of CO_2 in water			
	75°		100°	
	Exptl.	Calcd.	Exptl.	Calcd.
50	0.0102	0.0099	0.0083	0.0082
75	.0137	.0134	.0116	.0113
100	.0164	.0160	.0142	.0138
150	.0195	.0191	.0181	.0175
200	.0211	.0208	.0204	.0199
300	.0233	.0234	.0234	.0230
400	.0251	.0257	.0256	.0256
700	.0294	.0315	.0303	.0322

(11) Similar calculations were made by Michels, Gerver and Bijl, Physica, **3**, 797 (1936); Krichevsky and Kasarnovsky, THIS JOURNAL, **57**, 2168 (1935).

(12) Ångström, Wied. Ann., **33**, 223 (1888).

(13) Dr. and Mrs. W. E. Deming kindly gave us permission to use their unpublished data on carbon dioxide calculated from the work of Michels, Bijl and Mrs. C. Michels, Proc. Roy. Soc. (London), **A160**, 376 (1937).

It should be noted that the pressures in Table III are "partial pressures" of carbon dioxide and not total pressure and the experimental data are slightly different from those of Table II. In making this correction we have taken into account the change of vapor pressure of water with total pressure.[14] The agreement is quite remarkable and falls down only at 700 atm. The weak point, assuming for the moment that formula (3) will represent the true course of solubility, is how to select the partial molal volume for the liquid, since usually only values at one atmosphere and one temperature are known. In our case we adjusted the value of $\bar{V}$ until we got a reasonable fit. It clearly shows that even though of interest, a prediction based on such a calculation would be uncertain. Equation 3 brings out the fact mentioned previously that when the gas phase assumes the characteristics of a liquid, the change in $\bar{V}_1^1 - \bar{V}$ will be small and consequently the solubility will be affected by pressure only slightly. Zelvinskii's results[3] were expressed in cc. gas (S. T. P.) per cc. of water. The volume of water was taken at room temperature which we suppose was 20° and we believe he used "partial pressures." In order to compare our low pressure results with those of Zelvinskii we have made the corresponding changes and the two sets are given in Table IV. The agreement is poorer the higher the pressure. At 100° Zelvinskii admits that he could not get reproducible results above 60 atmospheres. In the other instances

(14) See Table II in Wiebe and Gaddy, THIS JOURNAL, **56**, 76 (1934).

TABLE IV

"Partial pressure" of CO_2, atm.	Solubility[a] 50°		Solubility[a] 75°		Solubility[a] 100°	
	Our values	Zelvinskii's equation 3	Our values	Zelvinskii's equation 4	Our values	Zelvinskii's equation 5
25	9.74	9.65	6.90	7.10	5.57	5.57
50	17.25	17.35	12.65	12.99	10.35	10.75
75	22.52	23.10	17.09	17.67	14.42	15.51
100	25.62	26.90	20.62	21.14	17.78	19.88

[a] Solubility expressed in cc. gas (S. T. P.) per cc. of water, the latter at 20°.

his experimental fluctuations would explain the discrepancies. He was handicapped in not having a piston gage but had to resort to a roundabout intermittent compressibility measurement to calculate his pressure, using a Bourdon gage in the meantime. Zelvinskii obviously could not anticipate the sudden change in the solubility curve beyond 100 atm. and his equations therefore cannot be used for extrapolation.

We want to thank Mrs. W. E. Deming for helping us in our calculations.

Conclusion

An apparatus for measuring the solubility of carbon dioxide in water has been described.

The solubility of carbon dioxide in water has been measured at 50, 75 and 100° from 25 to 700 atm.

A calculation of the solubilities was made at 75 and 100°, according to the theory of dilute solutions, and agreement was obtained.

Carbon dioxide, like nitrogen, hydrogen and helium, shows a minimum of solubility, though only in the higher pressure range.

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The Rate of Formation and the Dissociation of Calcium Hydride

BY WARREN C. JOHNSON, MORRIS F. STUBBS, ALBERT E. SIDWELL AND ALPHONSE PECHUKAS

A survey of the literature shows a wide variation in the results obtained by several investigators who have studied the reaction between hydrogen and calcium.[1] Although there is no question that a definite compound is formed between these elements, there is considerable uncertainty regarding the conditions for combination. This situation may be attributed to several factors among which are: (1) the variations in the purity

(1) See Remy-Genneté, *Ann. chim.*, [10] **19**, 353 (1933), for earlier references.

of the calcium and of the hydrogen, (2) the form and surface area of the metal and (3) the presence or absence of a film of oxygen or nitrogen or both on the surface.

Metallic calcium which has been exposed to air does not react appreciably with hydrogen at room temperature; but when it is purified by distillation and maintained in a vacuum, it will react slowly with hydrogen at a temperature as low as 0°.[1] Hüttig[1] has observed that calcium is exceedingly active when it is obtained from a liquid ammonia