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The Solubility of Carbon Dioxide in Water at Various Temperatures from 12 to 40° and at Pressures to 500 Atmospheres. Critical Phenomena*

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The present paper extends previous work on the solubility of carbon dioxide in water. The apparatus and procedure are essentially the same as described.[1]

Aside from the particular interest in the solubility data themselves, we were also interested in investigating a phenomenon we had noticed in our previous work but had not reported. It was found that during saturation at pressures exceeding 700 atm. there was some pressure above which the solubility of water in the gas phase increased tremendously. This was shown by the appearance of large amounts of water in the expanded gas. We had apparently reached the critical solution pressure for the carbon dioxide–water system.

Discussion of Results

The results on the solubility are given in Table I and are expressed as the number of cc. of carbon dioxide (S. T. P.) contained in 1 g. of water.

TABLE I

SOLUBILITY OF CARBON DIOXIDE IN WATER (cc. S. T. P. PER G. OF H_2O)

Total pressure in atm.	Temperatures, °C. 12	18	25	31.04	35	40
25		19.51		14.18	12.95	11.62
50	35.54	32.03	27.23	24.15	22.21	20.35
75	36.33	33.85	31.17	29.33	27.84	25.81
100	36.77	33.98	31.75	30.17	29.13	27.81
125						28.71
150	38.39	35.75		31.59	30.52	29.39
200	39.77	37.17		32.78	31.83	31.74
300	41.07	39.31				
400			38.62	36.78	35.73	34.87
500				38.67	37.99	36.73

In Fig. 1 the solubility is plotted *versus* temperature, our previous data having been included. For the most part the curves resemble those obtained for hydrogen, nitrogen, and helium[2] except that the minimum solubility occurs at higher temperatures, but there are decided differences in the low temperature range. The principal reason for this is undoubtedly the fact that we are dealing here with two liquid systems but other factors are also influential and will be discussed presently.

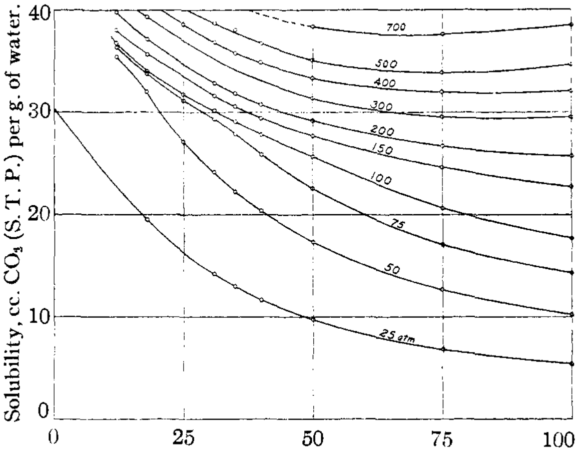

Fig. 1.

Although several attempts were made to get data at 10° above 50 atm. total pressure, only one series of measurements, at 150 atm., was obtained. When proceeding to check these values, a solid, presumably carbon dioxide hexahydrate, formed and the freezing of the liquid in the connecting lines made further measurements impossible. The fact that one series was obtained is very typical of the mode of formation of these gas hydrates.[3] A special technique, *e. g.*, sudden expansion, must often be used to initiate the formation of the hydrate, although once started it will form readily. At 12° we were able to get measurements up to 300 atm. but above this pressure, aside from solid formation, another difficulty was encountered, the disappearance of one phase, indicating complete miscibility. The compositions of the gas and liquid phases at 12° and 600 atm. were identical. We believe this to be true also for 500 atm. at the same temperature. At 18° similar conditions prevail.

In Fig. 2 we have attempted to portray qualitatively the probable course of the critical curve. With our present set-up it was not possible to determine accurately the change of the critical

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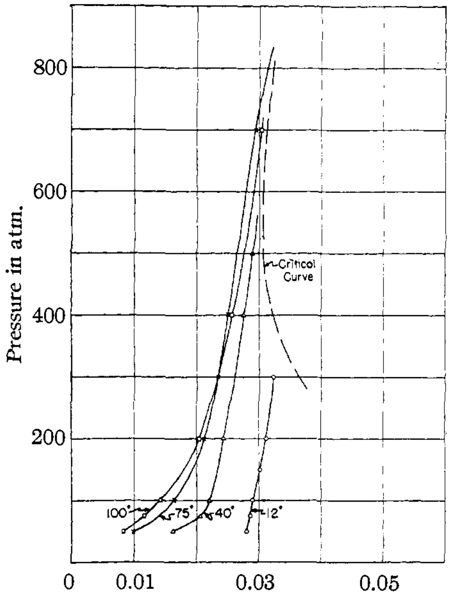
(1) Wiebe and Gaddy, THIS JOURNAL, **61**, 315 (1939).

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

(3) For a summary on gas hydrates with references, see W. Schroeder, *Sammlung Chem. und Chem. tech. Vorträge*, **29**, 1 (1927).

solution pressure with either temperature or composition. It will be seen that apparently there is a pressure maximum at about 75° and that both the 100 and 40° solubility curves will end at lower pressures than the 75° isotherm. It must be emphasized that we are basing our discussion on qualitative evidence only.



Mole fraction of CO_2 in water at various temperatures.

Fig. 2.

The dissociation pressure curve of the system hydrate–vapor–water saturated with carbon dioxide is shown in the lower left-hand corner of Fig. 3.[4] This curve ends in the critical decomposition point at 10° and 44.3 atm., the latter being practically the vapor pressure of pure carbon dioxide at that temperature. The critical decomposition point represents the invariant system consisting of hydrate, vapor, carbon dioxide saturated with water, and water saturated with carbon dioxide. When increasing the pressure the vapor phase disappears and the univariant system, hydrate, carbon dioxide saturated with water, and water saturated with carbon dioxide will continue to exist under certain temperature and pressure conditions.

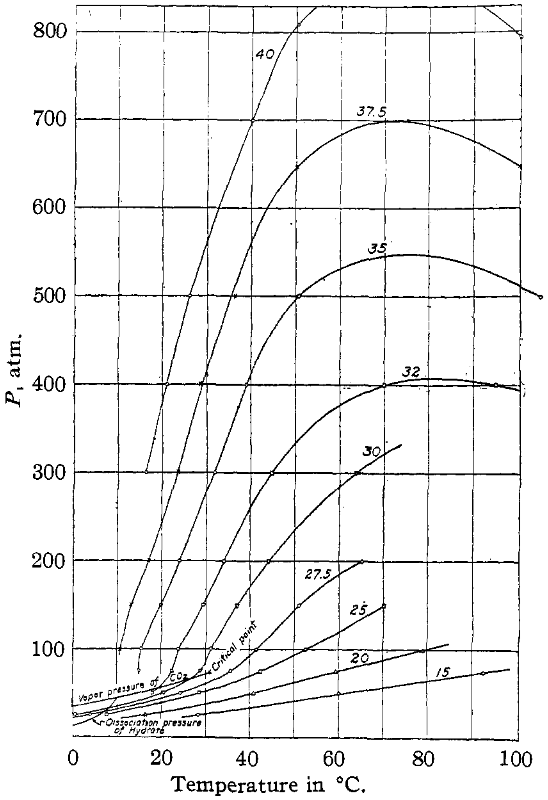


Fig. 3.—Composition expressed as cc. of CO_2 (S. T. P.) per g. of water.

We found evidence of this univariant system at 10 and 12°, *i. e.*, increase of pressure raises the temperature of coexistence of the three phases. At the point of complete miscibility (possibly 500 atm.), even at 12° no solid was detected, though the possibility of its existence is not excluded. We believe that the curve bounding the region of complete miscibility roughly follows the course of the curves of constant composition, at least in the low temperature range (see data in Table II). Our deduction is based on the fact that we encounter complete miscibility when-

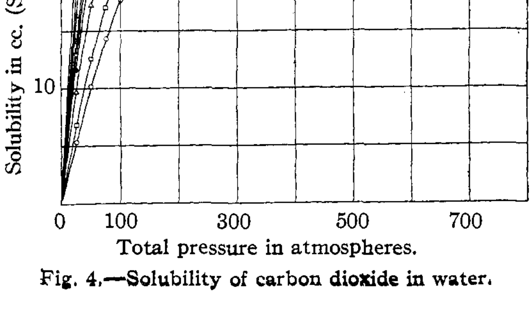


Fig. 4.—Solubility of carbon dioxide in water.

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[4] Data taken from "I. C. T.," Vol. VIII, p. 244.

TABLE II

TEMPERATURES AT CONSTANT COMPOSITION EXPRESSED IN CC. OF CO_2 (S. T. P.) PER G. OF WATER

Total press. in atm.	Composition (cc. of CO_2 (S. T. P.) per g. of water) 10	15	20	25	27.5	30	32	35	37.5	40
25	48.1	28.4	16.5	7.7	4	0.6				
50	102.4	60.0	40.9	28.6	24.3	20.6	18.0			
75		92.5	59.4	42.5	35.8	29.0	22.5			
100			79.2	52.6	41.6	31.3	24.0		10.8	
150				70.2	51.0	37.1	29.5		13.1	
200					65.3	44.2	34.1		17.1	11.6
300						63.7	44.7	16.2	23.5	16.2
400							72, 95	21.0	28.5	21
500								50.7, 104	36.3	26
646									50, 100	
700									75	40
789										100
818										50

ever we try to obtain values higher than about 40 cc. of carbon dioxide (S. T. P.) per gram of water. We have mentioned the likelihood of a possible pressure maximum at 75° in connection with the discussion of Fig. 2.

Figure 4 shows solubility isotherms that illustrate particularly the change of state of carbon dioxide from gas to liquid. At the lower temperatures this amounts to almost a discontinuity. In Table III we have made a few additional calculations by means of the approximate formula derived previously[1]

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

where $\overline{V}_1^1$ and $\overline{V}_1$ are the partial molal volumes of carbon dioxide in the vapor and liquid phases, respectively; and N_1 the mole fraction of carbon dioxide in the liquid phase. The agreement between calculated and observed values is good and only breaks down at about 400 and 700 atm. at 40° and 50°, respectively.

TABLE III

MOLE FRACTION OF CARBON DIOXIDE IN WATER

Pressure of CO_2 atm.	40° Exp.	40° Calcd.	50° Exp.	50° Calcd.
50	0.0162	0.0159	0.0138	0.0136
75	.0205	.0202	.0179	.0177
100	.0220	.0221	.0203	.0198
125	.0227	.0228	.0212	.0207
150	.0232	.0234	.0219	.0214
200	.0243	.0246	.0230	.0226
300		.0266	.0247	.0247
400	.0275	.0285	.0262	.0266
500	.0289	.0304		.0284
700		.0338	.0301	.0318

Summary

The solubility of carbon dioxide in water has been determined at 12, 18, 25, 31.04, and 40° and at pressures to 500 atmospheres.

Evidence of complete miscibility was found particularly in the low temperature range and an attempt was made to portray qualitatively the course of the critical curve.

Solid carbon dioxide hexahydrate was discovered at 10° at all pressures above 50 atm. and at 12° between 300 and 500 atm.

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