

THE BINARY SYSTEM CARBON DIOXIDE-WATER UNDER PRESSURE¹

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Data are presented for the binary system carbon dioxide-water between 12° and 100°C. and at pressures up to 700 atmospheres. It is shown that the composition of the phase rich in water above the critical temperature of carbon dioxide can be calculated quite accurately using the equation:

$$\frac{(d \ln N_2)_T}{(dP)} = \frac{V_2' - V_2}{RT}$$

Sharp minima are found in the composition-pressure isotherms for the phase rich in carbon dioxide.

The present discussion will deal with the equilibrium concentrations of the two phases of carbon dioxide in water (phase rich in water) and water in carbon dioxide (phase rich in carbon dioxide) as functions of pressure and temperature. Sander and others (13, 14, 17, 18) have investigated either one or the other phase. The data given in this article are those of Wiebe and Gaddy, except where specific reference is made to the work of others.

RESULTS

The composition of the phase rich in water (solubility of carbon dioxide in water) as a function of temperature and pressure is given in table 1. The composition *versus* temperature plot shown in figure 1 terminates abruptly at 12°C. above 25 atmospheres. Although several attempts were made to get data in the region above 25 atmospheres and below 12°C., only one series of measurements, at 10°C. and 150 atmospheres, was obtained. The formation of solid, presumably carbon dioxide hexahydrate, in the connecting pipe-lines made further measurements impossible in our appa-

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ratus. The fact that one series of measurements was obtained is very characteristic of the mode of formation of these gas hydrates (15). 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.

As indicated by the slopes of the solubility curves, the heat of solution changes sign at the higher pressures. The calorimetric data on the heat of solution of carbon dioxide gas in water at atmospheric pressure are as follows: Thompson (16), 5880 calories (18°); Berthelot (4), 5600 calories (18°); Adolph and Henderson (1), 4690 calories (22°).

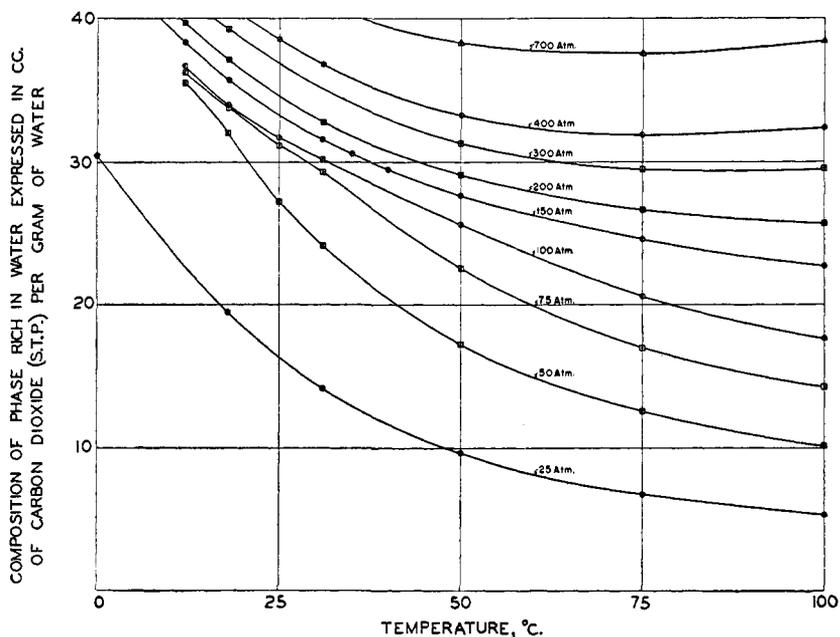


FIG. 1. Plot of composition against temperature

Approximate calculations of the heat of solution from solubility data at 1 atmosphere by means of the equation (6) which holds for ideal solutions,

$$\ln \frac{N'_2}{N_2} = \frac{\Delta H}{R} \left(\frac{T' - T}{TT'} \right) \quad (1)$$

where N'_2 and N_2 are the mole fractions of carbon dioxide at T' and T , respectively, give values similar to the ones above, depending on the temperature interval. For instance, a calculation using Bohr's data (5) for the interval from 0° to 25°C. will give a value of -5270 calories, while a similar one for 25° to 50°C. yields -4250 calories, giving an average of

-4760 calories. This value is close to the one obtained by Adolph and Henderson. The reversal of the trend from negative to positive values of the heat of solution may be explained if we assume that the change of the heat of solution with pressure is due solely to the change of heat content of carbon dioxide, and given by the relation is

$$\left(\frac{dH}{dP}\right)_T = \mu C_p \quad (2)$$

Burnett (6) determined μ experimentally at various temperatures up to 100 atmospheres, and Michels-Veraart (11) calculated the values of C_p .

TABLE 1
Composition of water-rich phase

TOTAL PRESSURE IN ATMOS- PHERES	SOLUBILITY OF CARBON DIOXIDE IN WATER, IN CUBIC CENTIMETERS (AT S.T.P.) PER GRAM OF WATER									
	0°C.	12°C.	18°C.	25°C.	31.04°C.	35°C.	40°C.	50°C.	75°C.	100°C.
25	30.51*		19.51		14.18	12.95	11.62	9.71	6.82	5.37
50		35.54	32.03	27.23	24.15	22.21	20.35	17.25	12.59	10.18
75		36.33	33.85	31.17	29.33	27.84	25.81	22.53	17.04	14.29
100		36.77	33.98	31.75	30.17	29.13	27.81	25.63	20.61	17.67
125							28.71	26.77		
150		38.39	35.75		31.59	30.52	29.39	27.64	24.58	22.73
200		39.77	37.17		32.78	31.83	30.74	29.14	26.66	25.69
300		41.07	39.31					31.34	29.51	29.53
400				38.62	36.78	35.73	34.87	33.29	31.88	32.39
500				39.74	38.67	37.99	36.73			
600								36.73		
700								38.34	37.59	38.50

* Zelvinskiĭ (18).

Since $C_p - C_v$ must be rather large in the neighborhood of the critical region (9), we obtain for $\int_{50}^{100} \mu C_p dP$ at 75°C. approximately 500 calories, whereas the same value calculated from the corresponding heats of solution using equation 1 is in the neighborhood of 800 calories. Considering the assumptions made, this represents a fair check at least of the order of magnitude.

Figure 2 shows a plot of compositions vs. pressure. Using the equation (10)

$$\left(\frac{d \ln N_2}{dP}\right)_T = \frac{V'_2 - \bar{V}_2}{RT} \quad (3)$$

which holds, however, only for ideal solutions and where N_2 is the mole fraction of carbon dioxide in water and V'_2 and \bar{V}_2 are the molar volume

and partial molar volume of carbon dioxide in the phase rich in carbon dioxide and the phase rich in water, respectively, we may calculate the solubility of carbon dioxide from 40° to 100°C. with considerable accuracy. V'_2 was calculated from data of Deming and Deming,³ and \bar{V}_2 was taken to be equal at all pressures and temperatures to the molar volume of carbon dioxide in water at 0°C. and atmospheric pressure (2, 17,). Table 2 gives a comparison between calculated and experimental results.

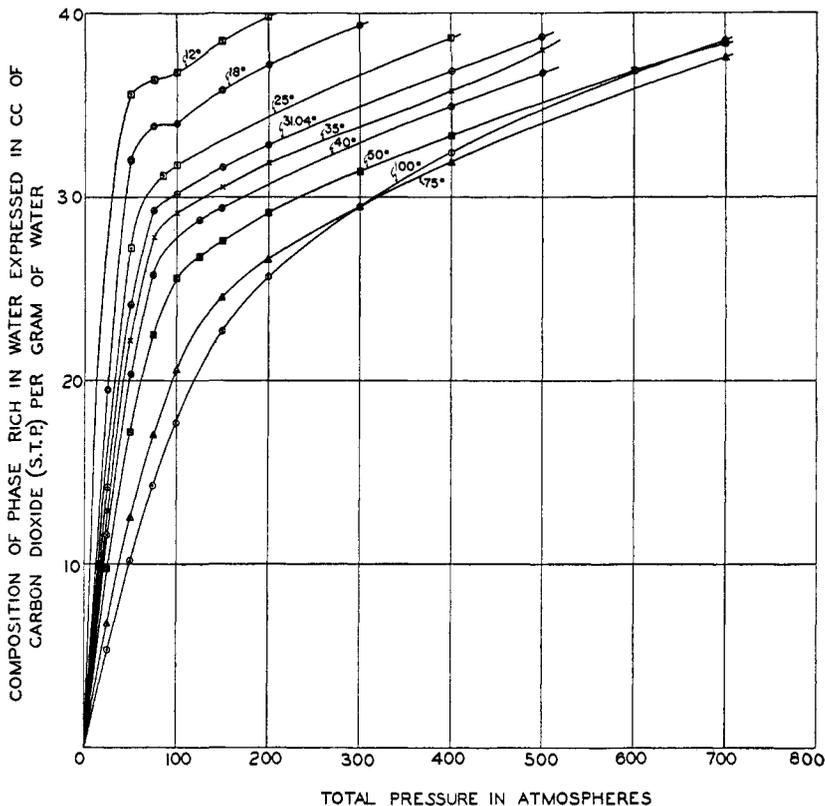


FIG. 2. Plot of composition against pressure

The composition of the phase rich in carbon dioxide as a function of pressure and temperature is given in table 3 and figure 3. For comparison we have plotted the 50°C. isotherm for water vapor in compressed hydrogen from the work of Bartlett (3). The very sudden reversal in the slopes of

³ Dr. and Mrs. Deming kindly gave us permission to use their unpublished data on carbon dioxide, calculated from the work of Michels, Bijl, and Michels (12).

TABLE 2

"PARTIAL PRESSURE" OF CO ₂ IN ATMOS- PHERES	MOLE FRACTION OF CARBON DIOXIDE IN WATER							
	40°C.		50°C.		75°C.		100°C.	
	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.
50	0.0162	0.0159	0.0138	0.0136	0.0102	0.0099	0.0083	0.0082
75	0.0205	0.0202	0.0179	0.0177	0.0137	0.0134	0.0116	0.0113
100	0.0220	0.0221	0.0203	0.0198	0.0164	0.0160	0.0142	0.0138
150	0.0232	0.0234	0.0219	0.0214	0.0195	0.0191	0.0181	0.0175
200	0.0243	0.0246	0.0230	0.0226	0.0211	0.0208	0.0204	0.0199
300		0.0266	0.0247	0.0247	0.0233	0.0234	0.0234	0.0230
400	0.0275	0.0285	0.0262	0.0266	0.0251	0.0257	0.0256	0.0256
700		0.0338	0.0301	0.0318	0.0294	0.0315	0.0303	0.0322

* Total pressure — vapor pressure of water corrected by means of Poynting's relation. (See Wiebe and Gaddy: J. Am. Chem. Soc. **55**, 947 (1933)). Table of values shown in table 2 in Wiebe and Gaddy (J. Am. Chem. Soc. **56**, 76 (1934)).

TABLE 3

Composition of the phase rich in carbon dioxide in equilibrium with the phase rich in water

TOTAL PRESSURE IN ATMOSPHERES	GRAMS OF WATER PER LITER OF EXPANDED GAS AT S.T.P.			
	25°C.	31.04°C. (critical temperature)	50°C.	75°C.
1	0.023	0.032	0.093	0.242
25	0.00132	0.00183	0.00498	0.00855
50	0.00104	0.00129	0.00308	
60			0.00287	
75			0.00281	
100	0.00267	0.00293	0.00361	0.00666
110				0.00652
125				0.00687
150	0.00289		0.00490	0.00768
200	0.00303	0.00338	0.00544	0.00910
300				
400		0.00383	0.00610	0.01060
450	0.00322			
475	0.00321			
500	0.00319	0.00386		
525		0.00382		
550		0.00384		
600			0.00637	0.01120
700			0.00644	0.01125

the curves is very striking. A consequence of this is that water dissolved in the phase rich in carbon dioxide changes from a "vapor" to a liquid. This may be qualitatively shown by means of the general equation for

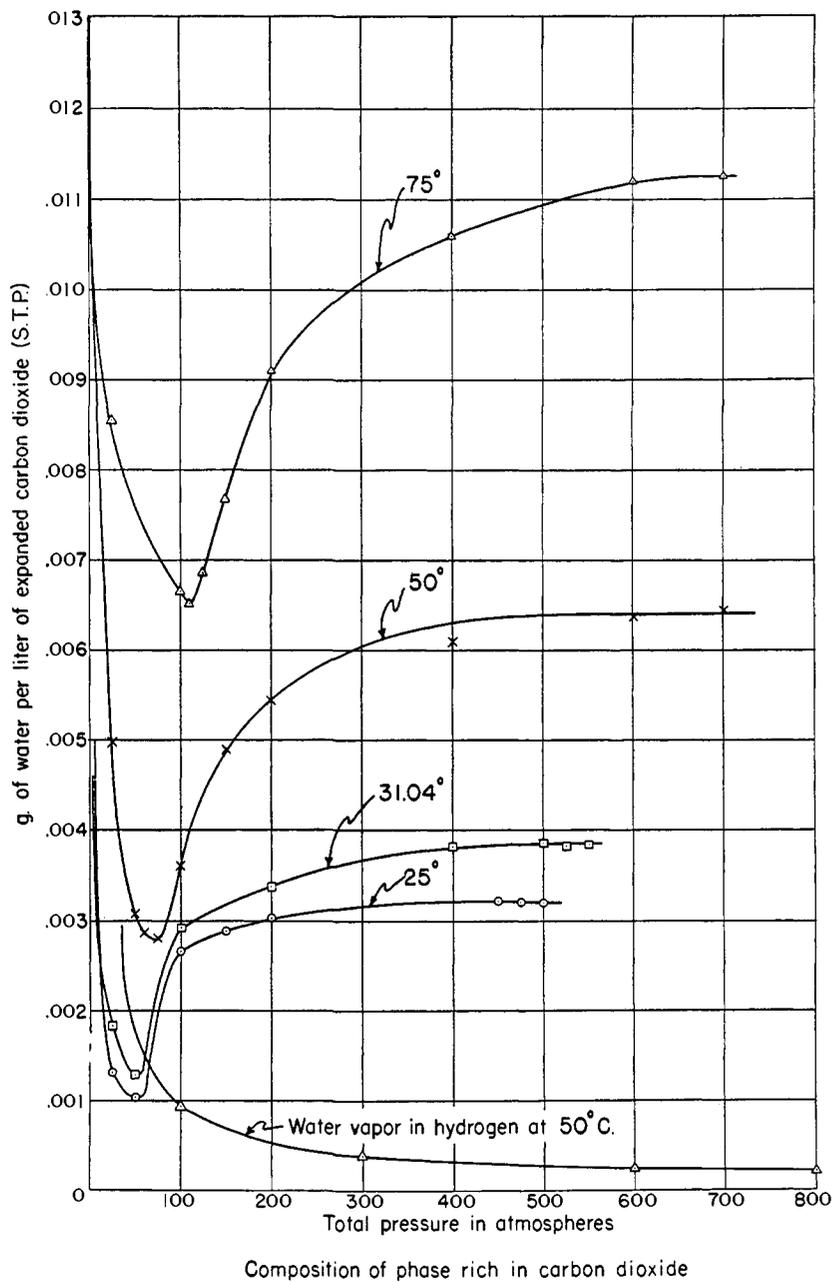


FIG. 3. Composition of the phase rich in carbon dioxide as a function of pressure and temperature

each component of a binary isothermal system with two phases in equilibrium (16):

$$\bar{V}'_1 - \bar{V}_1 = \left(\frac{d\bar{F}'_1}{dN_1} \right)_P \frac{dN_1}{dP} - \left(\frac{d\bar{F}'_1}{dN'_1} \right)_P \frac{dN'_1}{dP} \quad (4)$$

where \bar{V}_1 and \bar{V}'_1 are the partial molar volumes of water in the phases rich in water and rich in carbon dioxide, respectively. From the data we know that dN'_1/dP changes from negative to positive, dN_1/dP is positive but approaching some small value or zero, and $d\bar{F}_1/dN_1$ and $d\bar{F}'_1/dN_1$ are both positive. The left-hand factor of equation 4, $\bar{V}'_1 - \bar{V}_1$, therefore diminishes; in other words, the partial molar volumes of water in the two phases may become practically equal.

At various pressures beyond the ones given in the paper, depending on the temperature, a very sudden increase in the water content of the phase rich in carbon dioxide was noted. The exact composition could not be determined in the apparatus used, and the significance has never been definitely determined. It may have been due to some experimental factor, or it may be a critical mixing phenomenon.

REFERENCES

- (1) ADOLPH, E. F., AND HENDERSON, L. J.: J. Biol. Chem. **50**, 463 (1932).
- (2) ÅNGSTROM, K.: Wied. Ann. **33**, 223 (1888).
- (3) BARTLETT, E. P.: J. Am. Chem. Soc. **49**, 65 (1937).
- (4) BERTHELOT, M.: Ann. chim. phys. [4] **30**, 456 (1873).
- (5) BOHR AND BOCK: Wied. Ann. **44**, 318 (1891).
- (6) BURNETT, E. S.: University of Wisconsin Bull. **9**, No. 6 (1926).
- (7) See, e.g., DEMING, W. E., AND SHUPE, L. E.: Phys. Rev. **37**, 638 (1931); calculation of $C_p - C_v$ for nitrogen at -70°C .
- (8) LEWIS, G. N., AND RANDALL, M.: *Thermodynamics and the Free Energy of Chemical Substances*, p. 229. McGraw-Hill Book Company, Inc., New York (1923).
- (9) Reference 8, p. 228.
- (10) Reference 8, Chapter 18.
- (11) MICHELS-VERAART, C. A. M.: Some Physical Properties of Carbon Dioxide. Dissertation, Amsterdam, 1937.
- (12) MICHELS, A., BIJL, A., AND MICHELS, MRS.: Proc. Roy. Soc. (London) **A160**, 376 (1937).
- (13) POLLITZER, F., AND STREBEL, E.: Z. physik. Chem. **110**, 768 (1924).
- (14) SANDER, W.: Z. physik. Chem. **78**, 513 (1912).
- (15) SCHROEDER, W.: Sammlung Chem. und Chem. Tech. Vorträge. **29**, 1 (1927).
- (16) THOMSEN, J.: *Thermochemische Untersuchungen*, Vol. IV. Barth, Leipzig (1882).
- (17) WIEBE, R., AND GADDY, V. L.: J. Am. Chem. Soc. **61**, 315 (1939); **62**, 815 (1940); **63**, 475 (1941).
- (18) ZELVINSKIĬ, Y. D.: J. Chem. Ind. (U. S. S. R.) **14**, 1250 (1937); Chem. Abstracts **32**, 852 (1938).