[CONTRIBUTION FROM THE FERTILIZER RESEARCH DIVISION, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

Vapor Phase Composition of Carbon Dioxide–Water Mixtures at Various Temperatures and at Pressures to 700 Atmospheres

BY R. WIEBE[1] AND V. L. GADDY

The present paper completes the work on the binary system carbon dioxide–water and gives measurements of the composition of the phase rich in carbon dioxide. Pollitzer and Strebel[2] made a few measurements of the composition of this phase at 50 and 70° to 85 and 50 atmospheres, respectively. Their measurements at 50° agree for the most part with our low pressure values. At 70° no comparison was attempted since we had no data at that temperature, and interpolation in the low pressure region is too uncertain.

The apparatus was identical with that used in our solubility determinations.[3] After saturating the water in the apparatus with carbon dioxide at some specified pressure and temperature, samples were taken from the gas phase. In order to prevent spray formation, the upper portion of the bomb (phase rich in carbon dioxide) was filled with glass beads and a separate spray catcher was inserted between the solubility bomb and the expansion valve. During the sampling, gas passed continuously through the bomb to maintain a constant pressure. In other words when we decided to take a sample, the expanded gas was merely turned into the absorption train instead of being passed into the atmosphere. The absorption train was essentially that of Bartlett.[4] Ordinarily about 40 to 80 liters of gas (S. T. P.) were necessary to give a sufficient quantity of water for weighing. The rates of flow of the expanded gas were varied, but no change in composition of gas was detected, indicating that the gas was saturated and no spray was carried over.

Results

The data for the composition of the phase rich in carbon dioxide are given in Table I, and plotted in Fig. 1. It is interesting to note that in the lower pressure range, the composition trend is similar to that of water–hydrogen and water–nitrogen,[3] but somewhere between 50 and 110 atmospheres a sudden reversal takes place, and each isotherm goes through a minimum. Beyond this point the curves bear some resemblance to those giving the composition of the phase rich in water (solubility curves of carbon dioxide in water).[5]

TABLE I

COMPOSITION OF THE PHASE RICH IN CARBON DIOXIDE IN EQUILIBRIUM WITH THE PHASE RICH IN WATER (G. H_2O PER LITER OF EXPANDED GAS AT S. T. P.)

Total press., atm.	Temperatures, °C.			
	25	31.04 (crit. temp.)	50	75
1	0.023	0.032	0.093	0.242
25	.00132	.00183	.00498	.00855
50	.00104	.00129	.00308	
60			.00287	
75			.00281	
100	.00267	.00293	.00361	.00666
110				.00652
125				.00687
150	.00289		.00490	.00768
200	.00303	.00338	.00544	.00910
300				
400		.00383	.00610	.01060
450	.00322			
475	.00321			
500	.00319	.00386		
525		.00382		
550		.00384		
600			.00637	.01120
700			.00644	.01125

TABLE II

RATIO OF MOLE FRACTIONS N_2^1/N_2 OF WATER (N_2^1 MOLE FRACTION OF WATER IN PHASE RICH IN CARBON DIOXIDE AND N_2 MOLE FRACTION OF WATER IN PHASE POOR IN CARBON DIOXIDE)

Total press., atm.	Temperature, °C.			
	25	31.04	50	75
25		0.00226	0.00615	
50	0.00132	.00163	.00385	0.0106
100	.00336	.00370	.00449	.00834
200	.00382	.00428	.00686	.0113
400	.00407	.00484	.00770	.0132
500	.00405	.00489		
600			.00803	.0141
700			.00814	.0141

At all temperatures and at pressures somewhat beyond our highest experimental points (at 75°, *e. g.*, in the neighborhood of 1000 atm.) the water content of our expanded gas increased suddenly

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[2] Pollitzer and Strebel, *Z. physik. Chem.*, **110**, 768 (1924).

[3] R. Wiebe and V. L. Gaddy, THIS JOURNAL, **61**, 315 (1939).

[4] E. P. Bartlett, *ibid.*, **49**, 65 (1927).

[5] R. Wiebe and V. L. Gaddy, *ibid.*, **62**, 815 (1940).

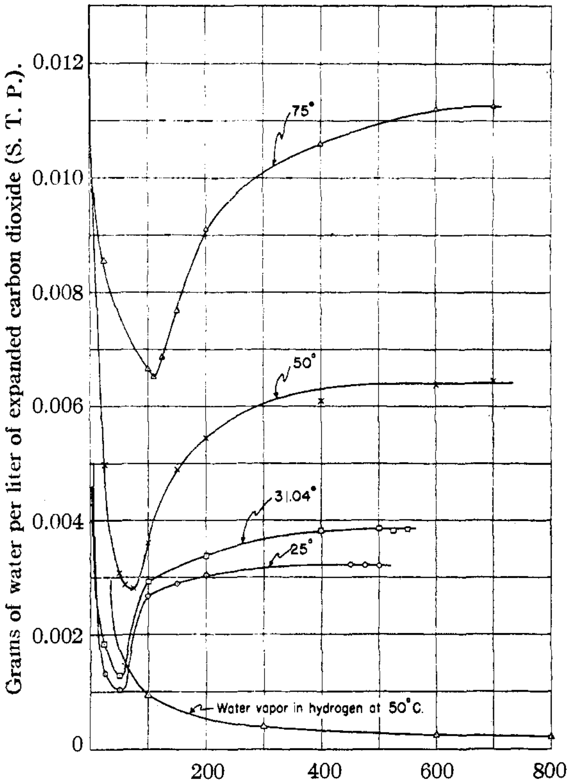

Fig. 1.—Composition of phase rich in carbon dioxide.

to such an extent as to show condensed liquid in the outlet tube, indicating supersaturation at "room temperature" and atmospheric pressure. This represented a jump from, *e. g.*, 0.00319 g. of water per liter of expanded gas to far more than 0.023 g. (approximate saturation value at 25°) in a pressure range of only five atmospheres. Since our set-up was not designed for compositions beyond that of saturated gas at approximately one atmosphere and possibly 25°, we could not determine the actual water content.

In our last paper[5] we explained this as being a possible critical mixing of the two phases. It is conceivable that the sudden increase in water content of the expanded gas (from the phase rich in carbon dioxide) could have been due to the effect of accidentally introduced minute quantities of soap (used for leak testing) on the surface tension of water. D. L. Katz[6] suggested a reversal of the phases or a possibility of a relatively uniform suspension, but since the sample of the phase rich in water taken near this point still indicated normal composition, neither of his explanations seems applicable. Whether these are critical mixing points at which complete miscibility takes place is still an open question. Unfortunately, the work was discontinued before we were able to secure unequivocal results in this region.

The somewhat weird behavior of water in the phase rich in carbon dioxide is readily explained. The general equation for each component of a binary isothermal system with two phases in equilibrium is given by Lewis and Randall[7]

$$\left(\frac{d\overline{F}_2}{dP}\right)_{N_2} dP + \left(\frac{d\overline{F}_2}{dN_2}\right)_P dN_2 = \left(\frac{d\overline{F}_2^1}{dP}\right)_{N_2^1} dP + \left(\frac{d\overline{F}_2^1}{dN^1}\right)_P dN_2^1 \quad (1)$$

where $\overline{F}_2$ and $\overline{F}_2^1$ are the partial molal free energies of water in the phases rich in water and rich in carbon dioxide, respectively, and N_2 and N_2^1 the corresponding mole fractions. Substituting and transposing, we obtain

$$\overline{V}^1 - \overline{V}_2 = \left(\frac{d\overline{F}_2}{dN_2}\right)_P \frac{dN_2}{dP} - \left(\frac{d\overline{F}^1}{dN_2^1}\right)_P \frac{dN_2^1}{dP} \quad (2)$$

where $\overline{V}_2$ and $\overline{V}_2^1$ are the partial molal volumes of water in the phases rich in water and rich in carbon dioxide, respectively. From Fig. 1, it will be seen that dN_2^1/dP changes from negative through zero to positive and finally approaches zero again; $d\overline{F}_2/dN_2$ and $d\overline{F}_2^1/dN_2^1$ are both positive and previous work has shown that dN_2/dP is also positive though approaching zero. The left hand factor of equation (2) $\overline{V}_2 - \overline{V}_2$ therefore becomes smaller. The physical meaning of this is that as the partial molal volumes of water approach each other, the change of solubility of water in carbon dioxide becomes smaller and approaches practically a constant value. This is true in the present work.

We might add that application of Poynting's equation[8]

$$dP_A/dP_B = V_B/V_A$$

where P_AV_A and P_BV_B are the pressures and molal volumes of one component, to water is hardly admissible in this case since carbon dioxide exerts a very large influence on water and cannot be treated as an "indifferent gas." In one of our previous publications[9] we have given the effect of pressure on the vapor pressure of water assuming an indifferent gas. In Table II the ratios of the mole fractions of water in the two phases have been

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[6] D. L. Katz, This Journal, **62**, 1629 (1940).

[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, Chapter 18.

[8] Poynting, *Phil. Mag.*, (4) **12**, 32 (1881); also Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 183.

[9] R. Wiebe and V. L. Gaddy, This Journal, **56**, 76 (1934) (see Table II).

calculated. Incidental to our work we obtained a value for the composition of the water phase at 500 atmospheres and 25° as follows: 39.74 cc. of carbon dioxide (S. T. P.) per g. of water.

Summary

The composition of the phase rich in carbon dioxide, here called "vapor phase," was determined at 25°, 31.04° (critical temperature), 50° and 75° up to 700 atmospheres.

The behavior of carbon dioxide–water mixtures was discussed in connection with the general thermodynamic equation of binary mixtures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

The Alkyls of the Third Group Elements. I. Vapor Phase Studies of the Alkyls of Aluminum, Gallium and Indium[1]

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The alkyls of boron, aluminum, gallium and indium present some interesting questions of configuration and bonding. The atoms of each of these elements possess three valence electrons and can form three single covalent bonds to alkyl groups, thus building up a sextet of electrons. There is then the possibility of the central atom accepting another pair of electrons to complete an octet, which would account for the strong tendency of these alkyls to coördinate with many donor substances. Because neither the carbon nor the hydrogen atoms in the alkyls have unshared electron pairs to donate, association is not to be expected.

Stock and Zeidler[3] have shown by vapor density measurements that boron trimethyl and triethyl are monomeric in the vapor phase. There is some evidence for the association of aluminum trimethyl and triethyl,[4] although the reports of various investigators do not agree. Krause and Toonder,[5] and Brandt[6] report vapor density data for gallium trimethyl which show definitely that it is not associated in the vapor. There have been no vapor density measurements made on gallium triethyl, but cryoscopic studies[7] of solutions in benzene gave molecular weights approaching that of the dimer. The only alkyl of indium which has been prepared is indium trimethyl,[8] which melts at the surprisingly high temperature of 89°. This suggests association, and cryoscopic measurements indicated association to the tetramer in benzene. No vapor density data have been available.

Because of the lack of data on the vapor densities of gallium triethyl and indium trimethyl, and because of the unsatisfactory and conflicting reports on the properties of aluminum trimethyl and triethyl, which were investigated at an early date when refined techniques for handling these very reactive substances were not available, the present study has been undertaken. Vapor pressure and density measurements on these alkyls have been made over wide temperature ranges in order to establish the types of molecules present in their vapors. Thermal constants have been calculated.

Apparatus and Methods.—Since these alkyls react vigorously with oxygen and moisture, being spontaneously inflammable in air, they were prepared, purified and handled in nitrogen or in an all-glass evacuated apparatus.[9] Vapor pressure and density measurements were made in an all-glass cell of the "sickle" type, as described in a previous paper.[10] Nitrogen, rather than air, was used to balance the pressures of the samples in order to eliminate the danger of explosion, should the glass diaphragm break. Samples and cells were chosen of such sizes that saturation vapor pressure data at lower temperatures and vapor density data over higher temperature ranges could be obtained for the same sample. Readings were made both as the sample was progressively heated and then cooled, to make sure that the data represented equilibrium values and that irreversible decomposition had not occurred. In all cases duplicate runs were made and the data in the table for each alkyl summarize two such runs which showed good agreement.

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Detroit meeting, September, 1940.

[2] Present address: Research Laboratory, General Electric Co., Schenectady, N. Y.

[3] Stock and Zeidler, *Ber.*, **54**, 531 (1921).

[4] Buckton and Odling, *Ann. chim. phys.*, [4] **4**, 492 (1865); Louise and Roux, *Compt. rend.*, **106**, 602 (1888); **106**, 73 (1888); **117**, 600 (1888); Quincke, *Ber.*, **22**, 551 (1889).

[5] Krause and Toonder, *Proc. Natl. Acad. Sci. U. S.*, **19**, 292 (1933).

[6] Brandt, Thesis, Cornell University (1932).

[7] Dennis and Patnode, THIS JOURNAL, **54**, 182 (1932).

[8] Dennis, Work, Rochow and Chamot, *ibid.*, **56**, 1047 (1934).

[9] Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1043 (1926).

[10] Laubengayer and Schirmer, THIS JOURNAL, **62**, 1578 (1940).