incorrect interpretation of the observed pressure differences and (*b*) faulty estimation of the pressure readings corresponding to total decomposition. Warburg's data are slightly in error under (*a*), Wulf and Tolman's data rather more seriously in respect of (*b*), while Jahn's results are subject to very considerable errors under both heads.

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[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INCORPORATED]

THE DENSITIES OF COËXISTING LIQUID AND GASEOUS CARBON DIOXIDE AND THE SOLUBILITY OF WATER IN LIQUID CARBON DIOXIDE

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RECEIVED JULY 13, 1927 PUBLISHED NOVEMBER 5, 1927

At the usually prevailing temperatures liquid carbon dioxide is less dense than water and not miscible with it. Therefore, theoretically, the degree of dryness of liquid carbon dioxide which has been separated mechanically from liquid water depends only on the solubility of the water in the liquid carbon dioxide. Experiments have been performed in an attempt to determine this solubility.

The method chosen was to determine the density of gaseous carbon dioxide in the coëxisting state, both in the presence and absence of water. If water is appreciably soluble in liquid carbon dioxide, it should lower the vapor pressure and hence the density of the coëxisting gaseous carbon dioxide. It may be calculated by means of Raoult's law that a solubility of 0.1%[1] by weight of water in liquid carbon dioxide will cause a decrease in vapor pressure of about 0.25%. The averages of three sets of determinations of the density of saturated gaseous carbon dioxide at temperatures ranging from —5.8 to 22.9° in the absence of water were 0.08% lower than the averages of two sets of determinations made in the presence of liquid water. This difference is opposite in sign to what would be expected if there were any solubility and is attributed entirely to experimental error.[2] The results obtained may be interpreted to indicate that the solubility of water in liquid carbon dioxide is less than 0.05% by weight over the temperature range investigated.

Experimental Method and Data

For the present investigation there was chosen the sealed tube method

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[1] This is an upper limit of the solubility as suggested by experiments performed by Thomas Simon, *Z. ges. Kohlensäure Ind.*, **6**, 239 (1900), and similar preliminary experiments performed by the authors.

[2] The average deviation of the experimentally determined gas density from the value calculated from the equation best fitting the entire data is 0.7%. Thus, while the probable error of any single datum is about 0.6%, consideration of the entire data indicates that the calculated values are probably correct within ±0.1%.

of Young[3] which has not previously been used for carbon dioxide. In this method different weights of carbon dioxide are sealed into glass tubes of sufficient strength to withstand the pressures developed, and the volumes occupied by the gas and liquid determined. This determination requires only the measurement of the length occupied by either gas or liquid in a tube which has been previously calibrated for volume.

Now,

$$W = v_l d_l + v_g d_g \tag{1}$$

where W is the total weight of carbon dioxide, v_l, v_g, d_l and d_g are the volumes and densities of liquid and gaseous carbon dioxide, respectively. W may be obtained at the end of an experiment by determining the difference in weight of the tube full and empty. Since in Equation 1 there are two unknowns, d_l and d_g, it is necessary to make determinations on two tubes either of different total volumes or containing different total weights of carbon dioxide.

The experimental error of the method is largely one of reading length. As used by Young on many organic liquids, where lengths were read only to 0.1 mm., the errors under different conditions ranged from 0.5 to 6%.[4] Nevertheless his data[5] are apparently consistent to about 0.1%. In the present investigation lengths were read with a traveling microscope to 0.002 mm. Temperature was determined with a thermometer calibrated at the ice-point, 0°, and at the transition temperature of sodium sulfate decahydrate, 32.8°. On account of the great difference in density of the gas and liquid phases, correction was also made for the volume of the liquid meniscus,[6] which otherwise would be included with the gas volume. Corrections based on direct measurements were also applied to the volume of the tube for distortion introduced on sealing the ends of the tube. The reading of the length of tube filled by gas and liquid was in each case determined after the temperature was raised and again after it was lowered to the temperature of the experiment. The lengths so obtained agreed on the average to 0.020 mm. The arithmetical average of the two readings was used in the calculations. In order to facilitate reaching thermal equilibrium a small rod of permalloy was sealed in the tube for stirring the liquid. This stirring was accomplished by raising and lowering a small electromagnet around the tube. Calculations showed that the volume increase in the tube due to expansion caused by the maximum pressure developed within it would amount to only 0.02% of the total volume and hence no correction was made. Calculation also showed that changes in volume of the tube due to temperature changes are of the same order of magnitude and could also be neglected. Even with these corrections and precautions, analysis of the data obtained in three separate runs indicates that the average deviation of a single observation for the liquid density is ±0.1%, and since an error in determination of the liquid density introduces a larger error, opposite in sign, in the determination of the gas density, the average deviation of a single observation of gas density is greater, that is, 0.7%. Hence, to obtain a much higher

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[3] Young, *Trans. Chem. Soc.*, **59**, 37 (1891).

[4] Ref. 3, p. 126.

[5] As summarized in *Proc. Roy. Soc. Dublin*, **12**, 374 (1910). It is not clear whether these data are original observations or interpolated values.

[6] "International Critical Tables," Vol. 1, pp. 72 and 73, 1926. For this purpose values of the surface tension of liquid carbon dioxide were obtained from the data given in the Landolt-Börnstein Tabellen, 5th edition, 1923.

degree of accuracy, a larger number of observations would be necessary at each temperature. It may be estimated, however, that mathematical analysis of the data of this investigation permits values of coëxisting liquid and gaseous carbon dioxide to be calculated with an accuracy of ±0.1% over the temperature range —5.8 to 22.9°.

The data obtained are given in Table I. For purposes of comparison there are included in this table values of d_l, d_g and $(d_l + d_g)/2$ calculated from the equations

$$d_l = 0.4683 + 0.001442(t_k - t) + 0.1318\sqrt[3]{(t_k - t)} \qquad (2)$$[7]

$$d_g = 0.4683 + 0.001442(t_k - t) - 0.1318\sqrt[3]{(t_k - t)} \qquad (3)$$

and

$$(d_l + d_g)/2 = 0.4683 + 0.001442(t_k - t) \qquad (4)$$

Table I

The Densities of Coëxisting Liquid and Gaseous Carbon Dioxide

	d_l			d_g			$(d_l + d_g)/2$		
t, °C.	Obs.	Calcd.	Calcd.-obs.	Obs.	Calcd.	Calcd.-obs.	Obs.	Calcd.	Calcd.-obs.
22.9	0.7422	0.7448	+0.0026	0.2163	0.2152	−0.0011	0.4793	0.4800	+0.0007
17.2	.8045	.8044	− .0001	.1721	.1720	− .0001	.4883	.4882	− .0001
15.2	.8216	.8216	.0000	.1607	.1606	− .0001	.4912	.4911	− .0001
11.2	.8547	.8535	− .0012	.1390	.1401	+ .0011	.4969	.4968	− .0001
6.2	.8878	.8886	+ .0008	.1217	.1196	− .0021	.5048	.5041	− .0007
1.2	.9198	.9201	+ .0003	.1029	.1025	− .0004	.5114	.5113	− .0001
−1.8	.9378	.9376	− .0002	.0940	.0936	− .0004	.5159	.5156	− .0003
−5.8	.9604	.9598	− .0006	.0803	.0828	+ .0025	.5204	.5213	+ .0009

For these calculations, t_k was assumed to be 31.0°[8] and the critical density, 0.4683, was obtained by plotting $(d_l + d_g)/2$ against t and extrapolating the straight line thus obtained to 31.0°. This method of obtaining the critical density, first suggested by Cailletet and Mathias,[9] is very convenient, since by averaging the densities the errors are minimized, due to the fact that in the method used too high a value of the density of either phase is necessarily accompanied by too low a value of the other phase. Since the liquid density is just as much greater as the gas density is lower than their average, the equation giving either as a function of temperature should be obtained by addition to or subtraction from the equation representing their average of an additional term. The agreement of the data with Equations 2, 3 and 4 showed that the data may be satisfactorily represented in this way.

Since the values obtained in the presence of excess water agree with the

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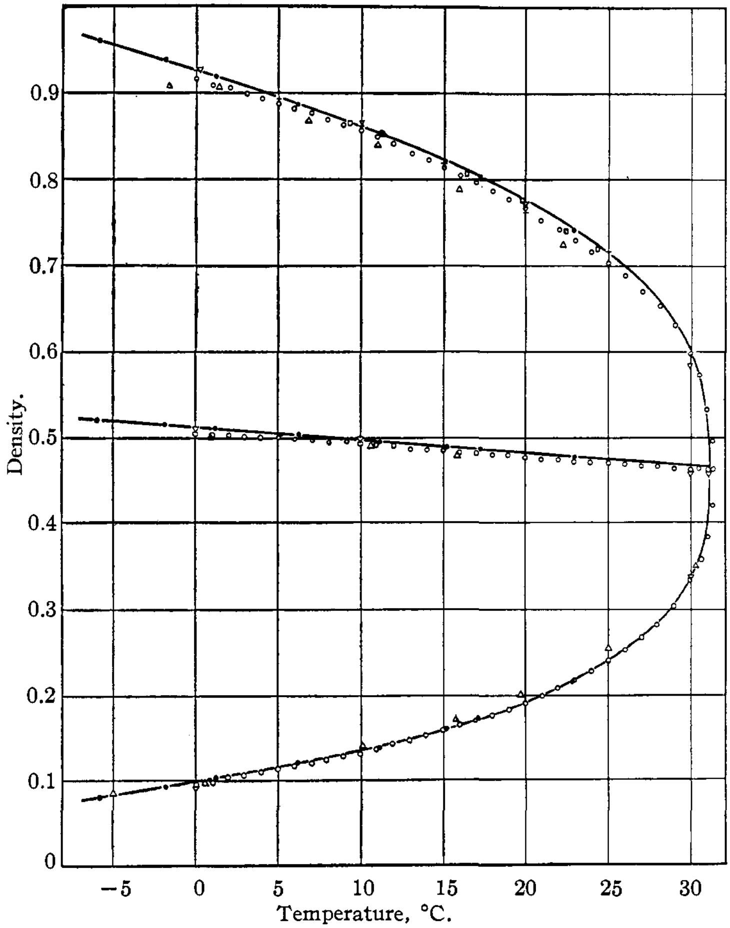
[7] Attention might be called to the fact that for all materials for which the data are available the densities of the coëxisting gaseous and liquid phase are less or greater, respectively, than their average densities at any temperature, within about 100° of their critical temperature, by a quantity $a\sqrt[n]{t_k - t}$, where $n = 3.000$.

A theoretical discussion of this relationship is given by S. Sugden, *J. Chem. Soc.*, **1927**, p. 1780 ($n = 10/3$).

[8] Landolt-Börnstein Tabellen, 5th edition, **1923**.

[9] Cailletet and Mathias, *Compt. rend.*, **102**, 1202 (1886).

values given in Table I within the experimental error, they will not be separately tabulated. It should be stated that at about 4° the water in the tube appeared to freeze and offered considerable resistance to passage of the stirrer. According to W. Hempel and J. Seidel[10] carbon dioxide forms a hydrate, $CO_2.9H_2O$, which melts at 8° and 43 atmospheres. It seems probable that, due to supercooling, the hydrate did not form at the melting point in our experiments.



△ Cailletet and Mathias; ○ Amagat; □ Behn; + Jenkin; ● Lowry and Erickson; ▽ Keyes and Kenny.

Fig. 1.—The densities of coëxisting liquid and gaseous carbon dioxide.

The data obtained in this investigation are plotted in Fig. 1. For

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[10] Hempel and Seidel, *Ber.*, **31**, 2997 (1898). (See also P. Villard, *Compt. rend.*, **119**, 368 (1894) who describes the hydrate as $CO_2.6H_2O$.)

purposes of comparison with other recorded data there are also plotted the results of previous investigators. The curves are drawn to fit Equations 2, 3 and 4. In Table II there is presented a summary of the interpolated values at 5° intervals from —5° to the critical temperature for all observers except Andréeff,[11] whose points are undoubtedly in considerable error. The values of density given by F. G. Keyes and A. W. Kenny,[12] although not original data, are also included in the figure and in Table II.

TABLE II

INTERPOLATED VALUES OF THE DENSITIES OF COËXISTING LIQUID AND GASEOUS CARBON DIOXIDE AT TEMPERATURES FROM —5 TO 31°

Density[a]

	Liquid						Gaseous			
t, °C.	C&M	A	B	J	K&K	L&E	C&M	A	K&K	L&E
31.0	0.459[b]	0.536[c]	...	...	0.4597	0.4683	0.396[b]	0.392[c]	0.4597	0.4683
30.0	.556[b]	.598	0.598	...	.5841	.6016	.355	.334	.3370	.3380
25.0	.685[b]	.703	.711	0.717	.7015	.7165	.254	.240	.2391	.2375
20.0	.755	.766	.772	.761	.7698	.7784	.203	.190	.1883	.1910
15.0	.807	.814	.819	.819	.8228	.8236	.167	.158	.1518	.1594
10.0	.848	.856	.860	.861	.8636	.8626	.139	.133	.1323	.1350
5.0	.883	.888	.893	.894	.8980	.8966	.117	.114	.1090	.1154
0.0	.913	.914	.925	.925	.9268	.9273	.099	.096	.0958	.0993
−5.0	.938	...	.954	...	.9551	.9556	.084	...	.0825	.0854

[a] C&M, Cailletet and Mathias;[9] A, Amagat;[13] B, Behn;[14] J, Jenkin;[15] K&K, Keyes and Kenny;[12] L&E, Lowry and Erickson.

[b] Extrapolated according to formula given by Cailletet and Mathias.

[c] According to Amagat's data, $t_k = 31.35$ and $d_l = d_g = 0.464$.

Consideration of the data given in Table II shows in general that there is quite satisfactory agreement among the observers. It is evident, however, that the equations used by Keyes and Kenny give values of density considerably too low for the liquid phase at the higher temperatures and for the gas phase at the lower temperatures.

Summary

The densities of coëxistent liquid and gaseous carbon dioxide have been measured and it has been shown that they can be satisfactorily represented by equations involving the first and one-third powers of the temperature on the critical scale over a temperature range from —5.8 to 22.9°. A comparison of the data of other observers with these data has shown them to be in substantial agreement. The data indicate that the critical density of carbon dioxide is 0.4683, which may be compared with the value 0.464 of Amagat and 0.4597, as judged by Keyes and Kenny, from analysis of earlier data.

[11] Andréeff, *Ann.*, **110**, 1 (1859).

[12] Keyes and Kenny, *J. Am. Soc. Refrig. Eng.*, **3**, 48 (1916).

[13] Amagat, *Compt. rend.*, **114**, 1093 (1892).

[14] Behn, *Ann. Physik*, [4] **3**, 733 (1900).

[15] Jenkin, *Proc. Roy. Soc.* (*London*), **98**, 170 (1920).

It has been shown that the density of saturated carbon dioxide vapor is the same in the presence or absence of water within the experimental error. Assuming applicability of Raoult's law and direct proportionality between vapor pressure and vapor density, it may be calculated that the solubility of water in liquid carbon dioxide is less than about 0.05% by weight over the temperature range of this investigation. Attention has been called to qualitative evidence of the formation of a solid hydrate of carbon dioxide at about 4°.

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THE SYSTEM POTASSIUM CARBONATE, SODIUM CARBONATE AND WATER AT 40° AND THE TRIHYDRATE OF SODIUM CARBONATE

BY J. W. BAIN

RECEIVED JULY 29, 1927 PUBLISHED NOVEMBER 5, 1927

An investigation of this system has been proceeding in this Laboratory for a number of years and brief statements of progress have appeared elsewhere.[1] The excellent investigations of Hill and Miller[2] have thrown a flood of light upon the various phases which exist between 20 and 40° and have explained some of the difficulties encountered in the work here; conflicting results which were met with early in our study have focused attention on the isotherm of 40°. This communication gives additional data which had escaped the notice of previous investigators.

At the outset of our work a number of determinations confirmed the accuracy of the results of Osaka[3] and of Kremann and Zitek[4] regarding the composition of the saturated solution; the residues were not analyzed and the existence of the double salt $K_2CO_3.Na_2CO_3.12H_2O$ was assumed, instead of the solid solution $(K_2Na_2)CO_3.6H_2O$ found by Hill and Miller. In order to be well beyond the transition point of the supposed double salt, the temperature of 40° was selected for the next isotherm. An inspection of the solubility curves for potassium and sodium carbonates showed that there was only a slight variation in solubility in both cases with a change of temperature of several degrees, and for this reason an ordinary thermometer divided to single degrees was considered sufficiently accurate to show the temperature of the bath; this choice gave much trouble subsequently.

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[1] (a) Bain and Oliver, *Trans. Roy. Soc. Canada*, **10**, III, 65–66 (1916); (b) Bain, **18**, III, 273–274 (1924).

[2] Hill and Miller, THIS JOURNAL, **49**, 669 (1927).

[3] Osaka, *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, **3**, 51 (1911).

[4] Kremann and Zitek, *Monatsh.*, **30**, 323 (1909).