

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

THE SURFACE TENSION OF LIQUID CARBON DIOXIDE

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RECEIVED JUNE 4, 1927

PUBLISHED NOVEMBER 5, 1927

Interest in the question of solubility led the author a few years ago to inquire whether liquids which exist only under very high pressures behave in the same manner towards solutes as those with which we are most familiar. The answer to this inquiry was not easy to obtain from the literature because of the small amount of quantitative work which has been done on such liquids. It seemed worth while, therefore, to attempt to determine some of the important properties of a liquid of this type and, if possible, to fit it into the solubility theory of Hildebrand.¹ As carbon dioxide exists as a liquid at ordinary temperatures only under very high pressures and under these conditions is but slightly removed from its critical temperature, it may well be used for determinations of this kind.

One of the most useful properties of a liquid, which can be used for calculating its internal pressure and therefore its position in a solubility table, is its surface tension. Although a few surface tension measurements have been made on liquid carbon dioxide² it cannot be said that these values are reliable enough or extensive enough to be used as a basis for such a calculation. The work described in this paper was carried out in an attempt to obtain enough data to predict some of the solubility relations of this compound. Later, if possible, these results will be checked against some actual solubility determinations.

On account of the extremely high vapor pressure of carbon dioxide at ordinary temperatures, the capillary tube method is the only one that can be readily applied to the solution of this problem. The pressure of its saturated vapor at 20° is about 56 atmospheres and therefore the apparatus must be designed for strength, which will, of course, render it difficult to apply all the refinements which are usually applied to measurements of this kind.³

Preparation of Tubes

Capillary tubes were made by drawing down ordinary soft glass tubes to a diameter of about 0.2 to 0.5 mm. Selected pieces from a very large number of these tubes were inspected with a microscope for uniformity of bore and circular cross section. The tubes which passed this inspection were then placed in carefully cleaned Pyrex glass tubes of 1 cm. internal diameter which had been sealed at one end. They were fitted with small platinum wires placed in such a way that the capillary was held firmly in the center of the tube. The Pyrex tubes were then constricted just above the end of the

¹ Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York City, 1924.

² Verschaffelt, *Verhandel, Akad. Wetenschappen Amsterdam*, **4**, 74 (1895).

³ Richards and Coombs, *THIS JOURNAL*, **37**, 1656 (1915).

capillary to facilitate the final sealing. The tubes when finished were about 15 cm. in length.

The carbon dioxide used for filling the Pyrex tubes as well as that used for making the freezing mixtures was furnished through the courtesy of the Carbo Chemical Company of Salt Lake City. The analysis of the gas from the top of the cylinder showed it to be 99.8% carbon dioxide; this value increased somewhat as the gas was drawn from the cylinder. There was no evidence of oil but there was a small amount of water vapor in the gas. A long drying tube filled with calcium chloride was connected at one end with the carbon dioxide cylinder and at the other with the Pyrex tube containing the capillary. These connections were made with small copper tubing and the joint between the copper tube and the glass tube was made with de Khotinsky cement. The glass tube was placed in a freezing mixture of carbon dioxide snow and ether and the liquid carbon dioxide distilled from the standard carbon dioxide cylinder into it. The freezing mixture was easily kept at -100° by reducing the pressure of the carbon dioxide above it with a vacuum pump. After the glass tube had been purged several times with carbon dioxide to remove all of the air, it was partly filled with liquid and allowed to stand until the carbon dioxide had frozen to a transparent mass. It was then sealed in an oxy-gas flame at the constriction and the contents were allowed to melt.

Eight tubes were prepared in the above manner and used for several months without breaking. This was quite remarkable as several tubes of much thicker sodium glass exploded in the preliminary trials.

Temperature Control

Fig. 1 is a drawing of the thermostat in which the tubes were placed for measurement. *A* is an inverted standard 20-lb. carbon dioxide cylinder containing the liquid carbon dioxide. It was connected through the needle valve *B* with the coil of copper tubing placed in the unsilvered vacuum tube *C*. This vacuum tube was about 9 cm. in diameter by about 30 cm. high. It was

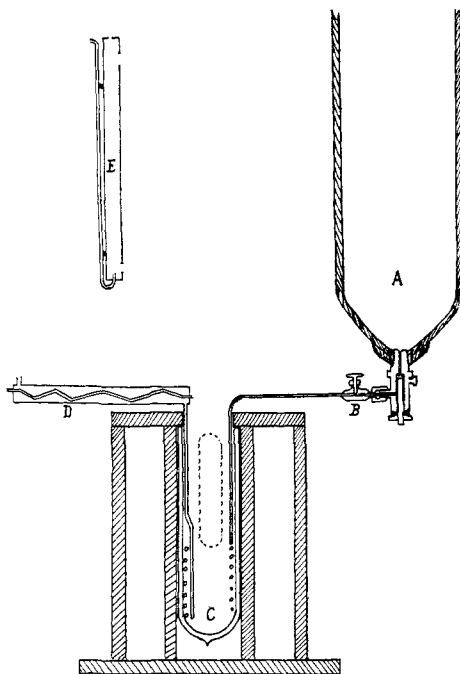


Fig. 1.

placed in a wooden box in which it just fitted. This box was then placed in a larger one, leaving a space of about two inches all around which was then packed with mineral wool. Two windows, indicated in the drawing by the dotted lines, were placed opposite each other in order to make it possible to observe the contents of the tube. The bath liquid was alcohol and this was kept in constant agitation by means of the brass pump *E*. This pump was essentially an air-lift pump and the com-

pressed air, which had been pre-cooled, forced the alcohol up the tube and forced it out at the top of the bath. The cooling of the air took place in the apparatus marked *D*, which in this case was a coiled glass tube around which the escaping carbon dioxide from the bath was allowed to pass. With this apparatus it was possible to lower the temperature of the bath to -50° and with close attention to keep it constant to within $\pm 0.2^{\circ}$. The temperature was changed by manipulating the needle valve *B*, and as one temperature was not needed longer than about three hours at a time this did not prove to be very troublesome.

Temperatures were measured with a pentane thermometer which had been calibrated by the Bureau of Standards and was checked again just before this work was started. The freezing points of water and mercury and the sublimation temperature of solid carbon dioxide were taken as the fixed points.

The capillary rise of the carbon dioxide was measured with a cathetometer. It so happened that the micrometer screw of this cathetometer was long enough to measure the greatest height of the liquid without making necessary any other adjustments of the instrument. Four tubes were used at each temperature and at least five readings of the cathetometer were made on each tube, the observed heights h_0 given in Table II being the average of these readings.

At each temperature where readings were taken the height of the meniscus in the capillary tube was measured with a meter stick. This was done to determine the point at which the capillary should be cut for measuring its diameter. This point was very nearly constant for all temperatures, in no case varying more than 5 mm. The capillary was cut at the average of these heights, each piece set in a paraffin block, the cut ends colored with drawing ink and the diameter measured with a microscope fitted with a micrometer attachment with movable cross hairs. One graduation mark on this micrometer screw head was equal to 0.0006 mm. but probably the error of setting the cross hairs was great enough so that the individual measurements were not accurate to within ± 0.005 mm. Five measurements were made on each piece of the capillary in each of two directions, which were at right angles to each other, and the average of these twenty measurements was taken as the inner diameter of the tube.

Calculations

The observed height h_0 was corrected for the quantity of liquid in the meniscus by means of the equation $h_1 = h_0 + r/3$, where h_1 is the corrected height and r the radius of the capillary. Although this equation is not exact, it was found by Richards and Carver⁴ to apply with sufficient accuracy where the value of r is small, as it is in this case.

⁴ Richards and Carver, *THIS JOURNAL*, **43**, 828 (1921).

The surface tension was calculated by means of the equation $\gamma = \frac{1}{2} r h g (D - d)$, where γ is the surface tension in dynes per centimeter, g the acceleration due to gravity, which at Salt Lake City is 979.8 cm./sec.²; D is the density of the liquid carbon dioxide, and d the density of the saturated vapor. The values for these gas densities between 0° and the critical temperature (31.35°) were taken from Amagat's table.⁵ By plotting the values for the density of liquid carbon dioxide obtained by Behn⁶ and those obtained by Jenkin⁷ on large scale cross-section paper, a curve was obtained which served very well to indicate the liquid densities down to -60°. The values obtained by Amagat above 0° gave a satisfactory agreement with those read from this curve. The only determinations we have of the density of the saturated vapor of carbon dioxide below 0° were made by Cailletet and Mathias.⁸ We have in addition to these determinations some calculated values by Jenkin⁹ and some extrapolated values calculated by Mollier by means of Amagat's values above 0°. ¹⁰ On account of the general acceptance of Amagat's values above 0°, it seemed best to make a new extrapolation of his curve to temperatures below zero in order to obtain the data necessary for making the surface tension calculations. This extrapolation was carried out by first plotting the experimental values of Amagat against the temperature and drawing the curve. The equation of this curve was found to be $Td = 1.936 P^n$, which can be readily derived from the gas laws if we keep in mind that in the case of an actual gas $P^n V = K$.¹¹ In this equation, d is the density of the saturated vapor, T the temperature in degrees absolute, 1.936 is a constant, P is the vapor pressure in atmospheres and the exponent n is equal to $0.737 + 0.0048t$, where t is the temperature in degrees centigrade. The values for P for the vapor pressure of liquid carbon dioxide were taken from the tables in Landolt-Börnstein.¹² Table I shows the agreement between the densities calculated by means of this equation and the observed experimental results.

Richards and Coombs showed that a considerable error is introduced when a capillary tube is set in a narrow outer jacket. They found that in the case of water the outside tube must be greater than 38 mm. in order to make this correction negligible. From the experience the author has had using large quantities of liquid carbon dioxide in glass tubes it seemed quite unsafe to use an outer jacket larger than 1 cm. in internal

⁵ Amagat, *Ann. chim. phys.*, [6] 29, 68 (1893).

⁶ Behn, *Ann. Physik*, [4] 3, 733 (1900).

⁷ Jenkin, *Proc. Roy. Soc. (London)*, 98A, 170 (1920).

⁸ Cailletet and Mathias, *J. Phys.*, [2] 5, 549 (1886).

⁹ Jenkin, *Trans. Roy. Soc. (London)*, 213A, 67 (1914).

¹⁰ Mollier, *Z. ges. Kalte-Ind.*, Nos. 4 and 5, 66 and 85 (1895).

¹¹ Leinweber, *Z. Ver. deut. Ing.*, 60, 363-6 (1916).

¹² Landolt-Börnstein-Roth-Scheel, "Physikalisch-Chemische Tabellen," p. 1342.

TABLE I
CALCULATED AND OBSERVED VALUES FOR THE DENSITY OF THE SATURATED VAPOR OF
CARBON DIOXIDE FROM 25 TO -29.8°

Temp., $^{\circ}\text{C.}$	Density, obs.	Observer	Density, calcd.	Dif.
25	0.240	Amagat	0.227	-0.013
20	.190	Amagat	.190	.000
15	.158	Amagat	.159	+ .001
10	.133	Amagat	.134	+ .001
5	.114	Amagat	.113	- .001
0	.096	Amagat	.096	.000
-12	.069	Cailletet	.067	- .002
-21.8	.052	Cailletet	.049	- .003
-29.8	.035	Cailletet	.032	- .003

diameter. It became necessary, therefore, to apply a correction to each reading for the capillary effect of the outside tube. The internal diameter of the eight outer jackets used averaged 0.96 cm., with a variation of only 0.01 cm. All of the capillary tubes had an outside diameter of 0.1 cm. The effect of this capillary was to decrease the diameter of the outside tube, so this value was subtracted from 0.96, giving 0.43 as the value of the radius of the outside jacket. The corrections were calculated by means of the equation $h = h_1 r / 0.43$, where h is the correction to be added to the observed height, h_1 the observed height and r the radius of the capillary. While the correction for each tube is indicated in the table, only the average of these values at each temperature was added to the observed height.

The results of these measurements and calculations are tabulated in Table II.

TABLE II
SURFACE TENSION MEASUREMENTS OF LIQUID CARBON DIOXIDE

Temp., $^{\circ}\text{C.}$	Tube no.	Obs. height, h_0 , cm.	Corr. height, h_1 , cm.	Correc- tion for capillary effect of outer jacket, cm.	Corr. height, h_2 , cm.	Density of liquid D	Density of vapor d	$D - d$	Surface tension γ , dynes per cm.	Ave- rage value of γ
25	1	0.133	0.139	0.006	0.145	0.703	0.240	0.463	0.59	(not averaged)
	2	.141	.147	.006	.153	.703	.240	.463	.69	
	3	.178	.182	.006	.188	.703	.240	.463	.59	
20	1	.252	.258	.011	.269	.766	.190	.576	1.37	1.37
	2	.242	.248	.011	.259	.766	.190	.576	1.44	
	3	.317	.321	.010	.332	.766	.190	.576	1.30	
	4	.199	.206	.011	.217	.766	.190	.576	1.37	
15	1	.345	.351	.015	.365	.814	.158	.656	2.12	2.09
	2	.316	.322	.015	.336	.814	.158	.656	2.14	
	3	.434	.438	.014	.452	.814	.158	.656	2.02	
	4	.269	.276	.014	.290	.814	.158	.656	2.10	
10	1	.444	.450	.019	.468	.856	.133	.723	3.00	2.94
	2	.394	.400	.018	.418	.856	.133	.723	2.93	
	3	.554	.558	.018	.576	.856	.133	.723	2.84	
	4	.340	.347	.018	.365	.856	.133	.723	2.91	

TABLE II (Concluded)

Temp., °C.	Tube no.	Obs. height, h_0 , cm.	Corr. height, h_1 , cm.	Correc- tion for capillary effect of outer jacket, h_2 , cm.	Corr. height, h_2 , cm.	Density of liquid D	Density of vapor d	$D - d$	Surface tension γ , dynes per cm.	Ave- rage value of γ
5	1	.526	.532	.022	.554	.888	.114	.774	3.80	3.75
	2	.487	.493	.023	.515	.888	.114	.774	3.86	
	3	.662	.666	.022	.688	.888	.114	.774	3.63	
	4	.403	.410	.021	.432	.888	.114	.774	3.69	
0	1	.610	.616	.026	.642	.914	.096	.818	4.66	4.62
	2	.570	.576	.027	.602	.914	.096	.818	4.77	
	3	.767	.771	.025	.797	.914	.096	.818	4.44	
	4	.480	.487	.025	.513	.914	.096	.818	4.62	
- 6	1	.716	.722	.030	.752	.960	.080	.880	5.87	5.79
	3	.919	.923	.030	.953	.960	.080	.880	5.71	
-11.3	5	1.540	1.543	.033	1.577	.987	.067	.920	6.54	6.81
	6	1.071	1.075	.034	1.109	.987	.067	.920	6.80	
	7	0.861	0.867	.034	.901	.987	.067	.920	6.90	
	8	.913	.919	.034	.953	.987	.067	.920	7.00	
-21.7	5	1.934	1.937	.041	1.979	1.037	.049	.988	8.81	9.05
	6	1.285	1.289	.041	1.331	1.037	.049	.988	8.76	
	7	1.083	1.089	.043	1.111	1.037	.049	.988	9.30	
	8	1.135	1.141	.042	1.183	1.037	.049	.988	9.33	
-32.3	5	2.276	2.279	.049	2.328	1.084	.036	1.048	11.00	11.25
	6	1.603	1.607	.051	1.656	1.084	.036	1.048	11.50	
	7	1.247	1.253	.049	1.302	1.084	.036	1.048	11.36	
	8	1.277	1.283	.048	1.332	1.084	.036	1.048	11.14	
-42.7	5	2.734	2.737	.059	2.795	1.126	.027	1.099	13.84	13.88
	6	1.844	1.848	.058	1.906	1.126	.027	1.099	13.95	
	7	1.468	1.474	.058	1.532	1.126	.027	1.099	14.02	
	8	1.497	1.503	.057	1.561	1.126	.027	1.099	13.70	
-52.2	5	3.070	3.073	.066	3.139	1.168	.019	1.149	16.25	16.54
	6	2.096	2.100	.066	2.166	1.168	.019	1.149	16.58	
	7	1.676	1.682	.066	1.748	1.168	.019	1.149	16.72	
	8	1.740	1.746	.065	1.812	1.168	.019	1.149	16.62	

Internal Diameter of Capillary Tubes

Tube no.	1	2	3	4	5	6	7	8
Diameter, cm.	0.0363	0.0397	0.0278	0.0450	0.0184	0.0272	0.0341	0.0326

Discussion of Results

It is interesting to apply the above results to the equation of de Block¹³ which he writes in the following form, $\gamma = K(t_c - t)^n$; where t_c is the critical temperature of the liquid; γ is the surface tension at the temperature t in degrees centigrade; $K = \gamma_0/(t)^n$; γ_0 is the surface tension at 0° ; and the exponent n is approximately 1.2 for all non-polar liquids. The average value for n , which is not exactly constant over the range of temperatures used, is 1.24 for carbon dioxide. In order to get this value for n it is necessary to take 4.68 for the surface tension at 0° instead of 4.62 as given in Table II. This is justified by the fact that 4.68 at 0° falls exactly on the surface-tension curve made by plotting the above values on cross-section paper; also if we do not include the lowest value obtained at 0° in our average we get a value of 4.68 dynes per centimeter.

¹³ De Block, *Bull. sci. acad. roy. Belg.*, [5] 11, 292-300, 353-60 (1925).

We can now rewrite the de Block equation so that in the case of carbon dioxide it becomes $\gamma = .0653(31.35 - t)^{1.24}$. Table III shows the agreement between the observed and calculated values for the surface tension at various temperatures. The calculated values were obtained from the above equation. The values of n in the second column were obtained by substituting the experimental surface-tension values in the de Block equation and solving for n .

TABLE III

SHOWING THE AGREEMENT BETWEEN THE OBSERVED AND CALCULATED VALUES FOR THE SURFACE TENSION OF LIQUID CARBON DIOXIDE

Temp., °C.	n	γ , obs.	γ , calcd.	Diff.
20	1.21	1.37	1.33	-0.04
10	1.21	2.94	2.90	-.04
5	1.27	3.75	3.77	+.02
- 6	1.21	5.79	5.81	+.02
-11.3	1.22	6.81	6.85	+.04
-21.7	1.25	9.05	8.99	-.06
-32.3	1.24	11.25	11.26	+.01
-42.7	1.26	13.88	13.59	-.29
-52.2	1.29	16.54	15.77	-.77

There are several ways of treating surface tension measurements to determine the internal pressure of a liquid.¹⁴ Perhaps one of the most convenient methods in this case is to calculate its total energy of surface formation E_σ by means of the Thomson equation, $E_\sigma = \gamma - Td\gamma/dT$. At 20° E_σ becomes 61.9 when $d\gamma/dT$ is taken over the whole temperature range studied. This places carbon dioxide with carbon tetrachloride, toluene and chloroform in the Hildebrand series and indicates that it should behave as a solvent much as these liquids do. This cannot be confirmed by experimental evidence, as no measurements have been made on the solubility of these substances in liquid carbon dioxide. We know, however, that carbon dioxide in the solid state is readily soluble in ethyl ether¹⁵ and must have, therefore, nearly the same internal pressure. As ethyl ether is only slightly removed from these compounds in the internal pressure series, we may safely assume that they would behave in much the same manner towards carbon dioxide.

The author expects to treat this question of solubility more fully in a later communication.

The author wishes to acknowledge with gratitude the suggestions which Dr. J. H. Hildebrand made at the beginning of this work.

Summary

1. An equation has been derived for calculating the density of the saturated vapor of carbon dioxide from 25 to 0°. This equation gives

¹⁴ Ref. 1, p. 111.

¹⁵ Thiel and Schulte, *Z. physik. Chem.*, **96**, 312 (1920).

values which agree very well with the observed densities over this range. Use was made of this equation to calculate densities down to -52.2° .

2. Surface-tension measurements of liquid carbon dioxide have been made from 25 to -52.2° .

3. The equation of de Block when put into the form $\gamma = .0653(31.35 - t)^{1.24}$ was found to fit the experimental results for the surface tension of carbon dioxide very well except at lower temperatures.

4. From its total energy of surface formation it was found that carbon dioxide had an internal pressure about the same as carbon tetrachloride, toluene and chloroform.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

THE EFFECT OF IRON AND OXYGEN ON THE ELECTRICAL CONDUCTIVITY OF COPPER¹

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RECEIVED JUNE 16, 1927

PUBLISHED NOVEMBER 5, 1927

The electrical conductivity of dilute solid solutions of metallic elements in copper has been the subject of many investigations. The data presented treat the binary systems of copper and practically every metal which may occur as an impurity in commercial copper, namely, silver, gold, zinc, cadmium, aluminum, tin, phosphorus, arsenic, antimony, iron, cobalt and nickel.² Unfortunately much discordance is evident in the published results.

In illustration, the solute element iron may be considered. Addicks³ in his pioneer work upon the impurities of copper attempted to evaluate the effect of the 0.002 to 0.005% of iron present in electrolytic copper. From measurements upon alloys of 0.042, 0.046 and 0.068% of iron and upon pure copper, he interpolated for intermediate iron concentrations and concluded that the conductivity was lowered at the rate of 140% of the International Standard value for each 1% of iron present.

Hanson and Ford⁴ at the National Physical Laboratory in England, under Rosenhain's direction, have recently repeated Addicks' work, extending the data to higher iron concentrations. Using the observed conductivity of an alloy of 0.2% of iron, they project a curve to pure copper and suggest a lowering in conductivity at the rate of 235% for 1% of iron.

¹ A thesis for the degree of Doctor of Philosophy, presented to the Graduate Faculty of the University of Pennsylvania.

² Guertler, "Handbuch der Metallographie," Berlin, 1925; *Circular No. 73, Copper*, U. S. Bureau of Standards, 1922.

³ Addicks, *Trans. Am. Inst. Min. Eng.*, **36**, 18 (1906).

⁴ Hanson and Ford, *J. Inst. Metals*, **32**, 335 (1924).