RP538

THE VAPOR PRESSURE OF LIQUID AND SOLID CARBON DIOXIDE

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ABSTRACT

The vapor pressure of liquid carbon dioxide from the critical point (31.0° C.) to the triple point (−56.60° C.) and the vapor pressure of the solid from the triple point to the normal sublimation point (−78.515° C.) have been measured with an accuracy of 1 or 2 parts in 10,000. Equations have been obtained to represent these data, the average deviations from the equations being 1 part in 10,000 for the liquid and about 2 parts in 10,000 for the solid. The equation for the solid represents also the best work of other laboratories at and below −78° C.

The vapor-pressure equation for the solid has been correlated with calorimetric data from other laboratories.

Pressures and relative volumes have been observed along several isotherms in the critical region.

A set of tables of the vapor pressure and the rate of change of vapor pressure with temperature calculated from the equations are given.

CONTENTS

I. INTRODUCTION

The determination of the vapor pressure is one of a series of investigations on the thermodynamic properties of refrigerants conducted at the Bureau of Standards.

The measurements consisted of three sets made at different times. In 1919 and 1920 observations were made covering the range −55° to +31° C. The results of these observations were published[1] in 1926. These results have been recalculated and will be presented here together with the more recent observations.

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[1] Ref. Eng., vol. 13, p. 180, 1926.

In 1927 one of the original samples of CO_2 (used in the first series) was sent to the Massachusetts Institute of Technology where its vapor pressure at 0° C. was measured. In 1929 the vapor pressure of the same sample at 0° C. and at 25° C. was measured at this bureau.

In 1931 the vapor pressure of another of the original samples was measured in the range −50° to −79° C. No measurements below −79° C. have been made in the course of the work, but the published data have been reviewed critically and used in deriving an empirical equation for the vapor pressure of the solid over a wide temperature range.

II. PREPARATION OF SAMPLES

The liquid carbon dioxide used in these measurements was prepared by C. S. Taylor, formerly of the chemistry division of this bureau. Sodium bicarbonate and concentrated sulphuric acid which had been heated in order to expel traces of air were used for this purpose. The generating apparatus was very similar to that used and described by Bradley and Hale.[2] The flask *A* (fig. 1) was about half filled with sodium bicarbonate and sufficient distilled water was then added to form a thin paste. A dropping funnel *B* with its tip turned upward and a gas delivery tube were introduced through a rubber stopper which sealed the flask. The dropping funnel contained concentrated sulphuric acid, freshly boiled and cooled. The delivery tube was connected with the condenser *C*, traps, and drying train.

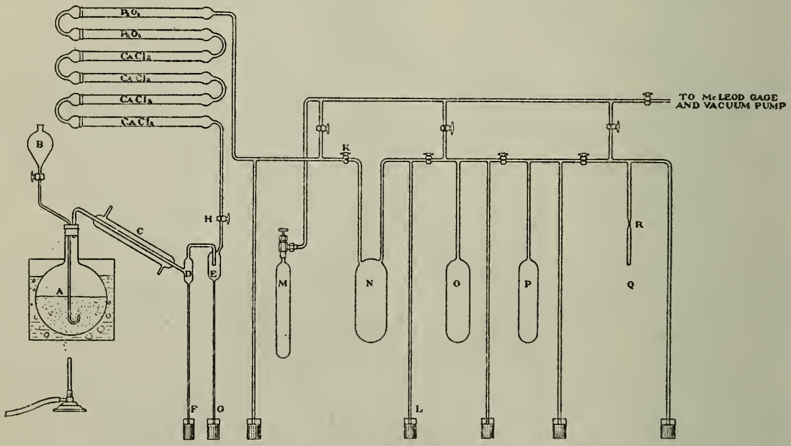

Figure 1.—*Apparatus for preparing samples*

The entire apparatus was evacuated to the vapor pressure of water, the flask was heated to approximately 100° C. by means of a water bath, and sulphuric acid admitted slowly into the flask. The flask and line were purged by discharging some carbon dioxide through the mercury seals *F* and *G* of traps *D* and *E*. Condensed water was also discharged through these mercury seals. After the entire system had been purged several times, the gas was allowed to flow through a

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[2] J. Am. Chem. Soc., vol. 30, 1090, 1908.

drying train containing $CaCl_2$ and sublimed P_2O_5, and finally frozen into bulb *N* by cooling with liquid air. When sufficient quantity of carbon dioxide had been collected in *N*, stopcock *K* was closed and the bulb connected to the vacuum pump, so that any gas not occluded in the crystals would be pumped out. The liquid air bath was then transferred to container *O* and after bulb *N* had warmed sufficiently so that gas was escaping freely through the mercury at *L*, the carbon dioxide was sublimed into container *O*. Gas not occluded in the crystals was then pumped out as before. The carbon dioxide was then distilled into a glass high-pressure container *M* fitted with a steel valve fastened to the glass by a method described elsewhere.[3]

After the carbon dioxide had warmed up and liquefied, the valve was opened slightly and the gas allowed to escape so rapidly that the remaining liquid was frozen by its own evaporation. The valve was then closed until liquid formed and the process repeated several times. The carbon dioxide was next sublimed into bulb *P*, the first and last portions being rejected. Then, as before, any gas not occluded in the crystals was pumped out. The carbon dioxide was sublimed back and forth between *O* and *P* eight times in all, and then sublimed into the apparatus sealed on at *Q*. While *Q* was still cooled with liquid air the vacuum pump was connected to it, and the apparatus sealed off at *R* by fusion.

As a test for purity 1,000 ml of the purified gas was dissolved in potassium-hydroxide solution in a pipette. From the fact that the residual bubble was microscopic and also from observations of the pressure when the sample was at liquid air temperature, together with a knowledge of the capacity of the sample container, it was estimated that the carbon dioxide contained less than 1 part in 1,000,000 by volume of noncondensing impurities.

III. DESCRIPTION OF APPARATUS AND METHOD

The samples used in this investigation were contained in three types of containers illustrated in Figure 2. Each of the containers of type 1 consisted of a glass U tube about 2.5 mm inside diameter, to which a valve was soldered.[4] These samples of carbon dioxide could be totally immersed in the constant temperature bath. Of the two such containers filled in 1919, one sample (designated by No. 1) is still intact (1932), the other (No. 2) failed by leakage through a soldered joint after one day of observations.

One container of type 3 was used. It consists of a glass bulb connected through glass tubing to a manometer (about 8 mm inside diameter and 1 m long) which was similarly soldered to a valve. During the observations the pressure was transmitted from the manometer on the container of this sample to the pressure gauge by an air pressure approximately equal to the carbon dioxide pressure. For the observations made in 1931 the constancy of this transmitting pressure was improved by attaching a container of about 1 liter capacity to the line and immersing the container in an ice bath. In order to avoid pressures which might rupture the glass when the sample

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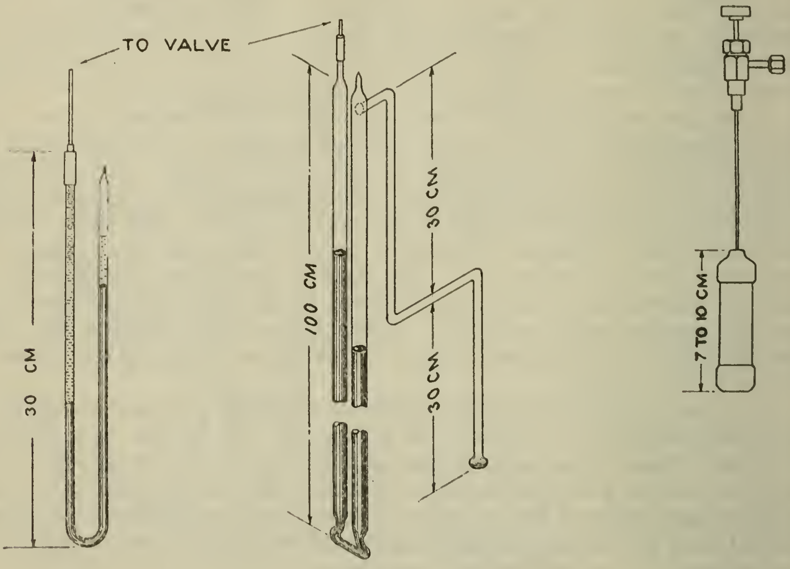
[3] McKelvy and Taylor, J. Am. Chem. Soc., vol. 42, p. 1364, 1920. Meyers, J. Am. Chem. Soc., vol. 45, p. 2135, 1923.

[4] See footnote 3.

was at room temperature, the amount of carbon dioxide used was sufficient only to produce liquid at temperatures below −20° C.

The containers of type A were of steel tinned inside and out.

The pressures were measured with dead-weight pressure gauges which are sensitive to better than 1 part in 10,000. These gauges, together with the calibration and method of use have been described in a previous paper.[5]



TYPE 1 TYPE 3 TYPE A

FIGURE 2.—*Containers for samples*

Temperatures were observed with platinum-resistance thermometers of the 4-lead potential terminal type, with strain-free windings inclosed in a tube.[6]

The Wheatstone bridges used both in the earlier observations[7] and in those[8] of 1931 have also been described in previous papers.

During the vapor-pressure measurements the carbon dioxide was maintained at a constant and uniform temperature in one of a number of stirred thermoregulated baths, the one chosen being determined by the temperature and the type of carbon-dioxide container. During the earlier observations the thermometer inserted near the carbon dioxide sample indicated no changes greater than 0.005° C. for periods of 20 minutes to 2 hours before the observation. The temperature differences between various parts of the baths were of the same order of magnitude. Some of the observations at 0° C. were made with the sample in an ice bath. The observations in 1931 were made with a bath[9] which could be controlled for a long time within 0.001° or 0.002° C. and which showed equally uniform temperature from place to place in the bath.

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[5] B. S. Jour. Research, vol. 6 (R. P. 324), p. 1061, 1931.
[6] B. S. Bull., vol. 6 (S124), p. 154, 1910. B. S. Sci. Papers, vol. 17 (S407), p. 49, 1922.
[7] B. S. Bull., vol. 11 (S241), p. 571, 1915.
[8] B. S. Bull., vol. 13 (S288), p. 547, 1917.
[9] B. S. Jour. Research, vol. 6 (RP284), p. 401, 1931.

To obtain correct results with the static method used, it is necessary that there be no temperature difference between the liquid or solid surface of the sample and the thermometer, a condition which can occur only when no condensation or evaporation is taking place. In order to reduce to a minimum the time required to attain such equilibrium within the sample, the apparatus was manipulated in such a way that equilibrium was reached through condensation of a portion of the sample. This precaution was found to be even more necessary for the solid than for the liquid, since the solid sometimes broke loose from the container and in consequence was in very poor thermal contact with its surroundings. Attainment of equilibrium has been discussed in detail in connection with the vapor pressure measurements of ammonia.[10]

IV. RESULTS OF VAPOR-PRESSURE MEASUREMENTS

The results of the observations on the vapor pressure of liquid carbon dioxide are given in Table 1. All the pressure measurements have been reduced to millimeters of mercury at 0° C. and at standard gravity ($g = 980.665$). The value of g (980.091) assumed for this laboratory is based on a determination made by the United States Coast and Geodetic Survey in 1910.[11] The thermometers have been calibrated in accordance with the specifications for the international temperature scale.[12]

The results obtained with samples in metal containers (Type A) and previously published [13] were given no weight in selecting the final values and have been omitted, because the conditions of observation were not conducive to accurate results, namely, (1) leaks in the valve packings were found at numerous times, and small leaks sufficient to lower the observed vapor pressure probably occurred undetected at other times; (2) the carbon dioxide may have acquired impurities in the connection between the metal container and the pressure gage, such as air not completely washed out of the tubing or wax dissolved from the valve packings.

In numerous cases the previously published data represented the mean of several readings which may be considered as separate observations, even though made successively at the same temperature, since for each reading the sample occupied a somewhat different volume. The values of temperature and pressure for these separate observations have been recalculated and are given in columns 3 and 4, respectively. A general increase of about 1 part in 5,000 over the previously published values of pressure is thus obtained.

Not all the measurements recorded can be considered as having the same weight. In some cases the greater number of readings and longer period of time covered insured that there was no drift in the observed values, and on some days the thermostat in the bath was operating better than on other days. Lack of space prevents the presentation of all these details for the reader's judgment in the matter, but in the review of the data an estimate was attempted of the relative merits

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[10] B. S. Bull., vol. 16 (S369), p. 1, 1920. Am. Soc. Ref. Eng. J., vol. 6, p. 307, 1920.
[11] B. S. Bull., vol. 8 (S171), p. 363, 1911.
[12] B. S. Jour. Research, vol 1 (R. P. 22), p. 635, 1928 .
[13] See footnote 1, p. 381.

of the observations. This estimate is recorded in column 5 of Table 1 where the number indicates the weight to be given to the observation when an average value is to be taken. It is believed that the values thus weighted yield slightly more probable averages than would be obtained from equally weighted observations. The values calculated from an equation (column 6, discussed in Sec. VIII of this paper) were not considered in making this estimate.

The measurements in July, 1920, were made with special attention toward securing thermal equilibrium, the bath temperature being maintained constant within 0.005° C. for two or three hours at each of the temperatures 20°, 25°, 30°, and 31° C. Observations were made at −5° C. during the same month, but the pressure readings were erratic due evidently to partial freezing of the oil in the manometer. The trouble was so apparent that the data have been omitted. It is possible that the observation taken at 0° C. during the same month may also be slightly in error due to the same cause. This source of error has been avoided in all later measurements by substituting an oil with a lower pour point.

The accuracy of the observations taken in 1929 at 25° C. is impaired by a tendency of the bath temperature to drift. Although the temperature was kept constant within 0.005° C. by manual correction of this tendency, the observations should be given less weight than other observations.

The temperature of the bath used in 1931 for the range −50° to −79° C. was remarkably constant (0.001° or 0.002° C.), but the accuracy of the observations in March of that year was limited by uncertainty in observing the mercury surface in a manometer attached to the piston gage. The observations in April are more reliable, since they were made after removing the mercury from the manometer in question and allowing the transmitting air pressure to come directly in contact with the oil in the manometer. In addition, more care was taken to insure attainment of equilibrium.

TABLE 1.—*Measurements of the vapor pressure of liquid carbon dioxide*

Date	Sample No.	Observed temperature	Observed pressure	Weight of observations	Calculated pressure	Observed minus calculated—		
						Pressure		Temperature
		°C.	*mm*		*mm*	*mm*	*Parts in 100,000*	*0.001° C.*
June 2, 1920	3	−50.002	5,127.6	1	5,127.5	0.1	2	0
	3	−49.966	5,134.8	1	5,134.9	−.1	−2	0
	3	−45.011	6,246.8	1	6,247.2	−.4	−6	1
	3	−44.994	6,250.9	1	6,251.2	−.3	−5	1
	3	−44.982	6,253.3	1	6,254.2	−.9	−15	4
	3	−44.981	6,257.1	1	6,254.4	2.7	43	−11
May 29, 1920	3	−40.005	7,543.6	1	7,543.6	0	0	0
	3	−39.971	7,555.1	1	7,553.0	2.1	28	−8
May 28, 1920	3	−35.002	9,028.6	4	9,028.4	.2	2	−1
	3	−34.998	9,031.7	1	9,029.7	2.0	22	−6
	3	−34.996	9,029.9	1	9,030.3	−.4	−4	1
	3	−34.988	9,032.6	1	9,032.9	−.3	−3	1
	3	−30.005	10,716.8	1	10,716.7	.1	1	0
	3	−29.988	10,722.3	4	10,722.8	−.5	−5	1
	3	−29.982	10,722.1	1	10,725.0	−2.9	−29	8

TABLE 1.—*Measurements of the vapor pressure of liquid carbon dioxide*—Contd.

Date	Sample No.	Observed temperature	Observed pressure	Weight of observations	Calculated pressure	Observed minus calculated—		
						Pressure		Temperature
		°C.	*mm*		*mm*	*mm*	*Parts in 100,000*	*0.001°C.*
July 21, 1920	1	−.003	26,134.1	1	26,139.5	−5.4	−21	8
July 15, 1920	1	5.001	29,771.4	1	29,771.7	−.3	−1	0
	1	5.003	29,774.3	1	29,773.3	1.0	3	−1
July 17, 1920	1	9.995	33,759.4	4	33,759.1	.3	1	0
July 16, 1920	1	15.000	38,148.9	1	38,146.1	2.8	7	−3
	1	15.000	38,147.5	4	38,146.1	1.4	4	−2
July 14, 1920	1	19.999	42,961	4	42,958	3	8	−3
	1	20.000	42,960	2	42,959	1	3	−1
July 13, 1920	1	24.998	48,247	2	48,247	0	0	0
	1	24.999	48,250	2	48,248	2	5	−2
	1	25.001	48,248	4	48,251	−3	−6	3
May 13, 1920	1	29.986	54,054	1	54,069	−15	−28	12
May 12, 1920	1	29.987	54,060	1	54,070	−10	−18	8
May 13, 1920	1	29.988	54,058	4	54,071	−13	−24	10
May 12, 1920	1	29.990	54,061	1	54,074	−13	−24	10
	1	29.992	54,055	1	54,076	−21	−39	17
July 19, 1920	1	29.992	54,072	2	54,076	−4	−7	3
	1	29.993	54,073	4	54,078	−5	−9	4
May 12, 1920	1	29.995	54,074	2	54,080	−6	−11	5
May 11, 1920	1	30.021	54,099	1	54,112	−13	−24	10
May 18, 1920	1	30.799	55,078	2	55,076	2	4	−2
May 15, 1920	1	30.950	55,274	1	55,266	8	15	−7
May 13, 1920	1	30.988	55,316	1	55,312	4	7	−3
	1	30.989	55,319	1	55,313	6	11	−5
May 14, 1920	1	30.990	55,311	1	55,315	−4	−7	3
May 13, 1920	1	30.995	55,325	2	55,321	4	7	−3
July 19, 1920	1	30.999	55,325	4	55,326	−1	−2	1
	1	30.999	55,332	1	55,326	6	11	−5
	1	30.999	55,333	1	55,326	7	13	−6
May 15, 1920	1	31.003	55,344	1	55,331	13	24	−10
May 14, 1920	1	31.049	55,394	1	55,389	5	9	−4
May 17, 1920	1	31.050	55,391	1	55,390	1	2	−1
May 14, 1920	1	31.064	55,407	1	55,407	0	0	0
	1	31.069	55,412	1	55,414	−2	−4	2
May 19, 1920	2	31.081	55,440	1	55,429	11	20	−9
	2	31.081	55,436	1	55,429	7	13	−6
May 14, 1920	1	31.101	55,458	1	55,454	4	7	−3
Mar. 25, 1931	3	−56.476	3,905.4	1	3,906.5	−1.1	−28	6
Apr. 7, 1931	3	−56.434	3,913.4	4	3,913.6	−.2	−5	1
Mar. 24, 1931	3	−56.232	3,946.7	1	3,948.1	−1.4	−36	8
Apr. 6, 1931	3	−56.049	3,979.7	4	3,979.5	.2	5	−1
Mar. 24, 1931	3	−55.221	4,122.1	1	4,124.0	−1.9	−46	11
Mar. 26, 1931	3	−50.781	4,965.7	1	4,967.1	−1.4	−29	7
	3	−50.534	5,016.6	1	5,017.5	−.9	−18	4
Jan. 8, 1929	1	[1] 0	26,140.0	4	26,141.7	−1.7	−7	2
	1	[1] 0	26,139.9	4	26,141.7	−1.8	−7	3
Jan. 7, 1929	1	[1] 0	26,138.7	2	26,141.7	−3.0	−12	4
	1	[1] 0	26,139.0	4	26,141.7	−2.7	−10	4
Feb. 3, 1929	1	25.018	48,260	½	48,269	−9	−20	8
	1	25.026	48,269	½	48,278	−9	−18	8
	1	25.029	48,272	½	48,282	−10	−21	9
Jan. 31, 1929	1	25.116	48,378	½	48,378	0	0	0

[1] Observations on sample in ice bath.

All observations on the vapor pressure of the solid were made in 1931 on the one sample in a container of type 3. (Fig. 2.) The previous remarks in regard to the weighting and accuracy of observations on the liquid are applicable also to the solid. The results of these observations are given in Table 2 which is similar to Table 1.

TABLE 2.—*Measurements of the vapor pressure of solid carbon dioxide*

Date	Observed temperature	Observed pressure	Weight of observations	Calculated pressure	Observed minus calculated—		
					Pressure		Temperature
	°C.	*mm*		*mm*	*mm*	*Parts in 100,000*	*0.001 °C.*
Apr. 2, 1931	−78.797	[1] 742.44	4	742.57	−0.13	−17	2
	−78.796	742.53	2	742.63	−.10	−13	2
Mar. 24, 1931	−78.559	[1] 757.1	1	757.25	−.15	−20	2
	−78.551	757.9	1	757.73	.17	22	−3
Mar. 20, 1931	−78.506	[1] 760.5	1	760.53	−.03	−4	0
	−78.505	761.4	1	760.59	.8	105	−13
Apr. 3, 1931	−78.421	[1] 765.92	4	765.85	.07	9	−1
	−78.419	766.08	4	765.97	.11	13	−2
Mar. 20, 1931	−77.800	[2] 804.7	0	805.70	−1.0	−124	15
Mar. 25, 1931	−70.148	1,469.85	2	1,469.55	.35	24	−3
Mar. 24, 1931	−70.132	1,470.07	1	1,471.34	−1.27	−87	20
Mar. 20, 1931	−70.005	[2] 1,475.9	0	1,485.5	−9.6	−650	90
Apr. 2, 1931	−69.537	1,538.7	2	1,539.0	−.3	−20	3
Mar. 25, 1931	−60.265	3,017.2	1	3,016.7	.5	17	−2
Mar. 26, 1931	−60.222	3,024.8	2	3,025.8	−1.0	−33	4
Apr. 2, 1931	−60.134	3,044.74 [3] 3,044.64	2	3,044.4	.3	10	−1
Apr. 3, 1931	−59.851	3,104.46 [3] 3,104.39	2	3,105.2	−.8	−26	4
Mar. 25, 1931	−56.760	3,845.6	1	3,843.5	2.1	55	−8
Apr. 7, 1931	−56.655	3,871.94 [3] 3,871.86	2	3,871.1	.8	21	−3
Apr. 3, 1931	−56.653	3,871.00 [3] 3,870.80	4	3,871.6	−.7	−18	3
Apr. 6, 1931	−56.630	3,878.85 [3] 3,878.72	4	3,877.5	1.3	34	−5
Apr. 6, 1931	−56.629	3,878.69 [3] 3,878.56	2	3,877.8	0.8	21	−3

[1] This observation was made with the pressure gage disconnected and is therefore free from possible errors arising in the use of the piston gage, including the one mentioned in the following note.

[2] After the reading at −77.8 a leak from the container which held the transmitting air pressure was found. This observation is probably in error due to such leakage and no weight has been given to the result.

[3] This value was obtained with a 100-bar gage, the value immediately above was obtained with a 10-bar gage, the two gages being connected in parallel.

NOTE.—The uncertainty in reading the manometer on the sample container amounts to about 0.1 mm, but in some cases the values have been carried out to hundredths of a millimeter for purposes of comparison.

V. OBSERVATIONS AT THE TRIPLE POINT

All observations at the triple point were made on the one sample in the container of type 3. For the observations in 1920 of the pressure at the triple point, a glass tube about 7 cm in diameter closed at the lower end was partially immersed in a constant temperature bath at −52° C. The sample was lowered into the air space within this tube and sufficient carbon dioxide snow to freeze a portion of the sample was dropped into the tube. The liquid bath used in 1931 was under such excellent control that the sample was immersed directly in the bath. For the observations of April 7 the bath was adjusted to within a few hundredths of a degree of the triple point and observations taken continuously over a period of 1 hour and 40 minutes. During this period there was a gradual rise in pressure within the limits given in Table 3, which contains the observations of the triple point pressure. This rise in pressure may be attributed to one or both of two possible causes, namely (1) a small amount of impurity in the sample, and (2) the solid may have been entirely covered by a film of liquid in which temperature gradients would be caused by heat transfer to or from the sample. In such case the vapor pressure would correspond to the temperature of the liquid-vapor surface and the rise in pressure would be explained by assuming that the temperature of this surface increased about 0.004° C. in consequence of the fact that the observer increased the bath temperature about 0.04° C. during the observations. If the variation in pressure is caused by soluble impurities, the larger value of pressure would be more nearly correct; if caused by variable temperature gradients, the smaller value would be more nearly correct.

The weighted mean of the values given in Table 3 is 3,885.27 mm. The vapor pressure equations for the liquid and for the solid, equations (6) and (9), respectively, in section VIII of this paper, intersect at about 3,885.10 mm and −56.602° C. These data indicate with fair certainty that the triple point pressure and temperature are, respectively, 3,885.2 ± 0.4 mm and −56.602 ± 0.005° C.

TABLE 3.—*Measurements of pressure at the triple point*

Date	Observed pressure		Weight of observation
	100-bar gage	10-bar gage	
	mm	*mm*	
June 3, 1920	3, 884. 1		1
	3, 886. 9		1
	3, 885. 4		2
	3, 886. 1		1
Apr. 6, 1931	3, 885. 05	3, 885. 09	2
	3, 885. 20	3, 885. 33	2
Apr. 7, 1931	3, 884. 68	3, 884. 77	2
	3, 885. 25	3, 885. 22	2

NOTE.—The uncertainty in reading the manometer on the sample container amounts to about 0.1 mm, but in some cases the values have been carried to hundredths of a millimeter for purposes of comparison.

VI. OBSERVATIONS AT THE CRITICAL POINT

Visual observations of the phenomena taking place in the sample at or near the critical point were made, but the critical temperature could not be fixed by this method much closer than about 0.1° C.

It may be noted that the critical point of a fluid is not a sharply defined point, such as the triple point, and can not be determined with the same degree of precision. No directly observable physical property exhibits a discontinuity at the critical point. The only discontinuities are those in the derivatives of certain quantities with respect to temperature or pressure, but such derivatives can not be directly observed. The exact critical temperature is therefore subject to considerable uncertainty, but the pressure-temperature relation in this region is definitely determinable. Near the critical point the compressibility of a fluid is very great, and appreciable differences in density therefore exist in a vertical column of the fluid. In this manner the action of gravity affects the observed phenomena, and the value chosen for the critical temperature will depend to some extent upon the interpretation of the observations.

When the bath containing the sample was warmed at the rate of about 0.002° C. per minute the meniscus gradually became fainter, and finally changed to a band about 1 or 2 mm wide which disappeared at 31.06° C. When the bath was cooled at the rate of about 0.006° per minute the band appeared at 31.02° C. When viewed with reflected light a gray fog was visible in the band, and through the temperature range 31.05° to 31.15° C. this fog was faintly visible throughout the sample.

In addition to these observations of the meniscus or band, the relative volumes occupied by samples Nos. 1 and 2 at various pressures were measured along several isotherms in the critical region. For these observations the sample was immersed in a bath maintained within a few thousandths of a degree centigrade of the constant temperature desired. The carbon dioxide was first expanded until it existed as a superheated vapor. Then the weight on the piston gage was increased by small increments. After time had been allowed for attainment of equilibrium subsequent to each increase in weight, the pressure and the length of the carbon dioxide column were observed. At some of the temperatures the length of tube occupied by the carbon dioxide was also observed at the beginning and at the end of condensation.

The diameter of the tube was assumed constant except for the end which had been tapered in the sealing off process. This tapered end was assumed to be a cone and one-third of its length was added to the length of the portion of uniform diameter. The observed lengths of sample No. 2 had to be multiplied by the factor 1.075 to make them comparable with those of No. 1. Since the uncorrected length was usually measured with an accuracy of not better than one-half millimeter, errors of 1 or 2 per cent in the measurement of relative volume may be expected.

These measurements are represented in Figure 3 where the pressure is plotted as ordinate and the corrected length of tube as abscissa. It is apparent that the shape of the isotherms can not be used as a criterion for determining the critical temperature within 0.2° or 0.3° C.

It was at first thought that since the temperature of disappearance of the band depended to some extent upon the illumination, the mean of the temperatures for disappearance and appearance of the band, 31.04° C., was at or slightly below the critical temperature. The observations of Kennedy and Meyers [14] on the same sample in which the meniscus was observed to be a sharply defined surface up to about 30.96° C. and to be a band of finite width above this temperature, as well as their observations on samples in capillary tubes, and further consideration of the matter leads to the belief that the critical temperature is very near 30.96° C.

It is believed that the band observed above this temperature is due to the rapid change of density and optical properties with pressure for the single phase which is enormously compressible in the

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[14] Ref. Eng., vol 15, p. 125, 1928.

critical region, and that this band would not be present if the sample were not in a gravitational field. Probably even a few hundredths of a degree below the critical temperature, the density of both the liquid and vapor at an infinitesimal distance from the meniscus differs appreciably from that in the remainder of the sample.

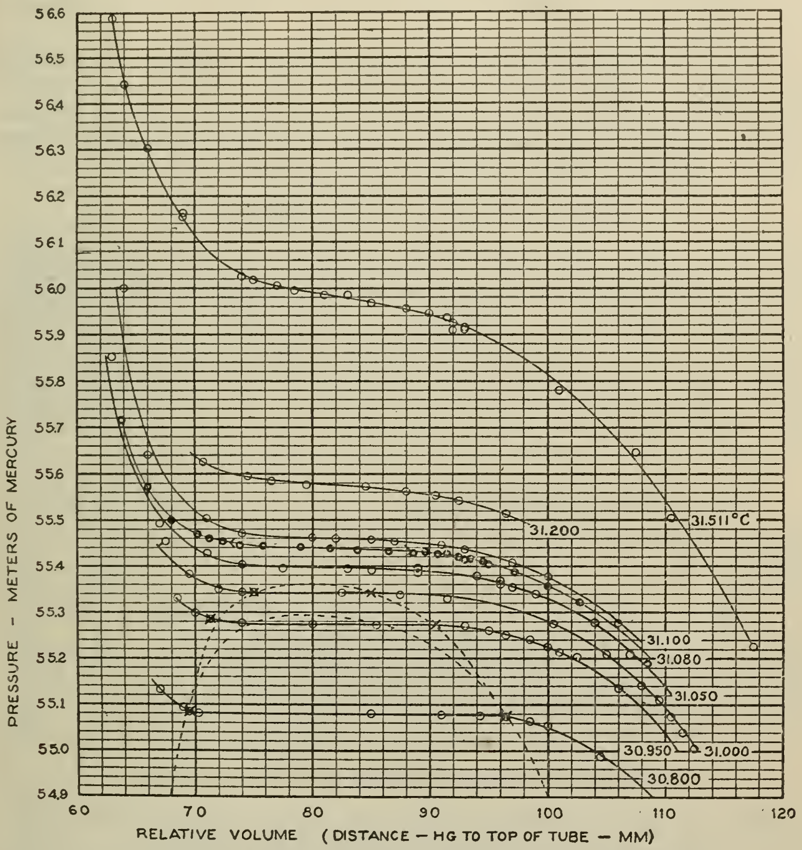

FIGURE 3.—*Isothermals for carbon dioxide in the critical region*

○ represents data on sample No. 1. ● represents data on sample No. 2. X point at which the carbon dioxide surface or band was either at the top or the bottom of the space. ⟨ ⟩ on the isotherm at 31.08° C. indicate that at volumes between these marks, fog was observed throughout the sample, while it could not be seen when the volume was outside these limits.

If this belief is correct the upper dotted curve in Figure 3 is not the true saturation curve, even though it was drawn approximately through the crosses which represent the average relative volume for the whole sample when the meniscus or band was either at the bottom or the top of the space occupied, but the lower dotted curve represents more nearly the state of the two phases under saturation conditions; that is, at the meniscus.

VII. MEASUREMENTS BY OTHER OBSERVERS

Measurements of vapor pressure by various observers are comparable only when both pressures and temperatures are expressed in units reducible to a common basis.

The pressure measurements quoted for comparison in the present paper were stated in units reducible to bars through multiplication by a constant factor.

Temperatures are given as reported by the authors, no attempt being made to take account of possible differences in temperature scales. With the exception of some data at the triple point, all temperatures tabulated in this paper differ from the international temperature scale by an amount less than the experimental error.

1. OBSERVATIONS AT THE TRIPLE POINT

The measurements of the triple point pressure, with the exception of those made by Faraday, who consistently observed high pressures for carbon dioxide, are practically in agreement with the present work. The observed temperatures are in agreement as well as can be expected considering the instruments used by the various observers. Table 4 shows the temperature and pressure observed at the triple point, the name of the author, and the reference to the publication. The results of this investigation are included for comparison.

Table 4.—*Data of various observers on carbon dioxide at the triple point*

Temperature	Pressure	Observer and reference
°C.	*Atmospheres*	
−57	5.31	Faraday, Trans. Roy. Soc., London, p. 155, 1845.
−56.7	5.1	Villard and Jarry, Compt. rend., vol. 120, p. 1413, 1895.
−56.24	5.10	Kuenen and Robson: Phil. Mag. (6) vol. 3, p. 149, 1902.
−56.4	5.11	Zeleny and Smith, Phys. Rev., vol. 24, p. 42, 1907; Phys. Zs., vol. 7, p. 667, 1906.
−56.60	5.112	Values from the present investigation.

2. OBSERVATIONS AT THE CRITICAL POINT

Table 5 gives a comparison with the present data of the results of various observers for carbon dioxide at the critical state.

Verschaffelt (1896) observed the capillary rise of the carbon dioxide in a glass tube a few tenths millimeter in diameter, at various temperatures up to 30° C. and extrapolated the data to a temperature at which the rise was zero. This he interpreted as the critical temperature.

Kuenen (1897) and Keesom (1903) observed the temperature at which the meniscus disappeared, and interpreted this as the critical temperature.

Von Wesendonck (1903) found that by repeated inversion of the vertical containing tube, a uniformly distributed fog was formed in the carbon dioxide in the temperature range 30.95° to 31.7° C. This fog remained indefinitely. Above 31.7° C. it decreased until at 32° C. it had entirely vanished.

Onnes and Fabius (1907) reported the critical temperature of carbon dioxide to be 30.985° C. The disappearance or the appearance of the meniscus with slow heating or cooling occurred at temperatures which differed by only 0.02° C. The carbon dioxide used by them was first purified until the molecular proportion of impurities was estimated to be less than 3 parts in 10,000, after which it was fractionally distilled and sublimed.

Bradley, Browne, and Hale (1908) used the method of preparing carbon dioxide which was followed in preparing material for the present investigation, with the exception that they used sulphuric acid in the first drier and did not sublime the carbon dioxide. They obtained material which contained 1 part in 30,000 or 40,000 of gases not absorbed in potassium hydroxide solution. They give the critical temperature as 31.26° C., the mean of the two temperatures at which the meniscus disappeared or appeared differing by 0.08° C.

Cardoso and Bell observed the critical temperature and pressure of two samples of carbon dioxide which had been purified first by passing through five flasks of sulphuric acid and a long tube of phosphorus pentoxide, and second by 10 sublimations. The critical constants for one sample were found to be 31.00° C. and 72.77 atmospheres, for the other 31.00° C. and 72.90 atmospheres. They used a closed end nitrogen manometer and a calibrated mercury-in-glass thermometer. They estimated the accuracy of their results as 0.1° C. and 0.1 atmosphere.

Table 5.—*Data of various observers on carbon dioxide at the critical point*

t_c	p_c	Observer and reference
°C.	*atmospheres*	
30.92	73	Andrews, Trans. Roy. Soc. London, vol. 159, II, p. 575, 1869.
31	--------	Hautefeuille and Cailletet, Compt. rend., vol. 92, p. 840, 1881.
31.9	77	Dewar, Phil. Mag., vol. 18, p. 210, 1884.
31.35	72.9	Amagat, Compt. rend., vol. 114, p. 1093, 1322, 1892.
31.40	--------	Chappuis, Compt. rend., vol. 118, p. 976, 1894.
31.7	--------	Villard, J. phys. (3), p. 441, 1894.
31.0	--------	Verschaffelt, Versl. Kon. Akad. Amst. p. 94, 1896; Comm. Leiden, No. 28.
31.1	73.26	Kuenen, Phil. Mag. (5), vol. 44, p. 179, 1897.
31.4	--------	De Heen, Bull. Acad. Roy. Belgique, vol. 31, pp. 147, 379, 1896.
30.95 to 31.7	--------	Von Wesenbonck, Verh. deutsch Phys. Ges., vol. 5, p. 238, 1903.
30.98	72.93	Keesom, Versl. Kon. Akad. Amst., pp. 391, 533, 616, 1903; Comm. Leiden No. 88, 1903
31.12	--------	Brinkmann, Brinkmann Diss. Amst., 1904.
30.985	--------	Onnes and Fabius, Versl. Kon. Akad. Amst., p. 44, 1907; Proc. Kon. Akad. Amst., vol. 10_{I}, p. 215, 1907–8; Comm. Leiden No. 98, 1907.
31.26	--------	Bradley, Browne, and Hale, Phys. Rev., vol. 26, p. 470, 1908.
31.10	73.00	Dorsman, Dorsman Diss. Amst., 1908.
31.00	72.85	Cordoso and Bell, J. chim. phys., vol. 10, p. 500, 1912.
30.97	--------	Hein, Zs. physik. chem., vol. 86, p. 385, 1913–14.
30.96	--------	Kennedy and Meyers, Ref. Eng., vol. 15, p. 125, 1928.

Hein used the same method of preparing the carbon dioxide as Bradley, Browne, and Hale, but used apparatus entirely of glass, the only ground joint being in the stopcock in the dropping funnel. He estimated that the carbon dioxide contained not more than 1 part in 30,000 of air or other gas. The vapor of boiling propylchloride was used to maintain constant temperatures; and a calibrated thermometer divided in 0.1° C was used to measure temperatures.

The more accurate of the observations in Figure 5 indicate that the critical temperature is between 30.95° and 31.05° C. For practical purposes it probably will be sufficient to use 31.0° C. for which the corresponding calculated pressure (equation (6), Sec. VIII of this paper) is 72.80 atmospheres or 73.76 bars.

3. REVIEW OF VAPOR PRESSURE MEASUREMENTS

Onnes and Weber[15] measured the vapor pressure of the solid in the temperature range −183° to −135° C. A form of Knudsen's absolute manometer was used for the lower pressures.

A hot wire manometer which had a greater sensitivity than the Knudsen manometer was used for the higher pressures.

Their data on vapor pressure are precise to about 5 per cent or better at the lower temperatures and to a few tenths of a per cent at the higher temperatures.

The fact that their values at liquid air temperatures appear to be too high indicates that the samples contained traces of noncondensing impurities too small to be appreciable at the higher temperatures. This is confirmed by the fact that after the sample had warmed up and stood for a few days, the residual pressure at −200° C. increased from 0.007 to 0.016 microbars. A second series of measurements was corrected for this increase to make it comparable with the first.

Since boiling liquid baths of ethylene, methane, and oxygen were used, it is to be expected that the observed vapor pressure would be low because the thermometer can not be placed near the coldest part of the sample; that is, at the surface of the bath. In fact such is the case at the upper end of the temperature range where the measured pressure is relatively large (1,400 microbars), the observed values being about 1 per cent lower than the values calculated from equation (9), Section VIII of this paper, which are in agreement with calorimetric data and with vapor pressure measurements at higher temperatures. This discrepancy corresponds to about 0.07° C.

The thermal molecular pressure correction discussed in detail by Knudsen[16] becomes appreciable at temperatures below −140° C., and in the range −150° to −165° C. is uncertain.

Siemens[17] measured temperatures in the range −128° to −77° C. with a platinum resistance thermometer. The sample was in a container somewhat similar to the container (type 3) Figure 2 except that one side of the manometer was evacuated. The inside diameter of the manometer was 10 mm. The apparatus was evacuated through a side tube and carbon dioxide, generated from sodium bicarbonate and sulphuric acid, admitted to the apparatus. The carbon dioxide was purified by at least three sublimations. After each sublimation gaseous impurities were pumped out while the carbon dioxide was at liquid air temperature.

For the observations at temperatures within a few degrees of the normal sublimation point, the sample was placed in a bath which consisted of a thin mixture of carbon dioxide snow and alcohol rapidly stirred by a propeller. Air was admitted to the top of the bath so that the temperature was lowered below the sublimation point. Before a reading was to be taken the stirrer was stopped, thus allowing the solid

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[15] Comm. Phys. Lab. Univ. Leiden Nos. 137b and 137c, 1913; Proc. K. Akad. Wetensch. Amst., vol. 16_{I}, pp. 215 and 445, 1913.

[16] Ann. Physik (4), vol. 31, pp. 205 and 633, 1910, and (4), vol. 33, p. 1435, 1910.

[17] Ann. Physik (4), vol. 42, p. 871, 1913.

to settle with a consequent reduction in the evaporation and an increase in the temperature of the bath. Siemens believed that this expedient produced a bath warmer at the top. Although thermal conduction down the walls would tend to warm the bath from the top, yet the presence of air would accelerate the evaporation of carbon dioxide from solution, and it is a debatable question whether the surface of the bath was actually warmer than the remainder of the bath. Even if the attempt to make the top of the bath the warmest portion were successful, the temperature of the sample which is probably in poor thermal contact with the bath would lag considerably behind the rising bath temperature with consequent low observed pressures. The question of lag has been discussed in Section III of this paper.

For lower temperatures a large copper block was hung over liquid air in a Dewar flask. This block contained two wells filled with alcohol or pentane, in which the thermometer and the tube containing the sample of carbon dioxide were immersed. The sides and upper surface of this block were packed with insulating material. The temperature was controlled by raising or lowering the vessel containing the liquid air. Better observations are to be expected with this bath than with the former.

Henning [18] at the Physikalisch Technische Reichsanstalt measured the vapor pressure in the temperature range −81° to −78° C. For this purpose he used a bath [19] of petroleum ether in a silvered Dewar flask. The bath was cooled by a regulated stream of liquid air which was delivered to one side of a U tube, and, after evaporation, was expelled from the other side. This U tube, together with a screw propeller, was inclosed in a porcelain tube which had holes in its side at several different heights. The petroleum ether was drawn into the botton of the porcelain tube and forced past the U tube and out through the holes in the side of the porcelain tube. With only one exception the readings of the two platinum resistance thermometers used in the bath agreed within two or three hundredths degree.

The sample of carbon dioxide was contained in a glass apparatus only slightly different from that used by Siemens, the two arms of the manometer being separated and their open lower ends immersed in a dish of mercury. The manometer was read with a cathetometer readable to 0.01 mm. The sample of carbon dioxide was prepared by heating sodium bicarbonate and purified by numerous sublimations under reduced pressure.

Henning and Stock [20] measured the vapor pressure of carbon dioxide in the temperature range −110° to −80° C., with the aid of the same design of bath previously used by Henning. The thermometer of pure platinum used for these measurements had been carefully calibrated by comparison with a gas thermometer. The value given for the normal sublimation point is −78.52° C. The samples of carbon dioxide were obtained both from commercial tanks and by the heating of sodium bicarbonate previously evacuated. The samples from each source were purified by alternately subliming in liquid air and pumping off noncondensing gases with a vacuum pump three times for the first source and one for the second.

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[18] Ann. d. Phys. (4), vol. 43, p. 282, 1914.
[19] Zeits. fur Inst., vol. 33, p. 33, 1913.
[20] Zeits. fur Phys., vol. 4, p. 226, 1921.

The measurements at the Reichsanstalt were repeated by Heuse and Otto [21] in connection with a comparison between the international and the thermodynamic temperature scales. For the measurements at the normal sublimation point of carbon dioxide they used the same constant temperature bath previously used by Henning. The vapor pressure thermometer was improved over previous designs by the inclosure of the stem in a vaccuum jacket which extended from the portion at room temperature to near the end of the portion immersed in the bath. A bulb of about 1 cm^3 was left exposed to the bath. This insured that the bulb contained the coldest part of the sample, and consequently its temperature would correspond to the pressure measured. Two platinum resistance thermometers of the strain-free type were used as well as a helium gas thermometer which could at the normal sublimation point of carbon dixide be used either as a constant volume or constant pressure thermometer. The manometer was supplied with one fixed platinum point on the side connected to the gas thermometer and a series of fixed points on the other side so that the mercury could be adjusted on both sides of the manometer to optical contact with a pair of fixed points whose vertical distance had been measured. Their first series of measurements indicated the temperature of the normal sublimation point to be −78.483° and −78.523°, while the second series gave −78.471° and −78.509° C., respectively, on the thermodynamic and international scales.

Bridgeman [22] measured the vapor pressure of carbon dioxide at 0° C. Four piston gages were specially calibrated with an 8 m mercury column for this purpose. Groups of observations with these gages differed by only 1 part in 10,000. The process of purification is not described in detail, but the average difference observed for two samples is only 1 part in 40,000. The value given as a final mean (26,144.7 ± 1.0 mm) differs only about 1 part in 10,000 from the value (26,141.7 mm) calculated from equaton (6) and 2 parts in 10,000 from the mean of the observed values in this investigation.

Table 6 lists the vapor pressure observations which have been given weight in obtaining an equation for representing the vapor pressure as a function of temperature. The table gives also the corresponding values calculated from that equation, and the differences between the observed and calculated values.

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[21] Ann. Physik (ser. 5) vol. 9, p. 486, 1931; vol. 14, pp. 181 and 185, 1932.

[22] J. Am. Chem. Soc. vol. 49_1, p. 1174, 1927.

TABLE 6.—*Vapor pressure measurements by other observers*

Observed temperature	Observed pressure	Calculated pressure	$100\times\frac{p_{obs.}-p_{calc.}}{p_{calc.}}$	$\theta_{obs.}-\theta_{calc.}$
		ONNES AND WEBER		
° C.	*Microbars*	*Microbars*	*Per cent*	*° C.*
−183.0	0.008	0.005	58	−1.5
−179.60	.026	.019	36	−1.1
−175.37	.106	.087	22	−.6
−171.01	.404	.359	12	−.36
−168.83	.791	.699	13	−.37
−167.04	1.310	1.182	11	−.36
		WEBER		
−168.83	0.802	0.699	15	−0.47
−164.03	3.00	2.75	9.1	−.31
−163.19	3.76	3.45	9.0	−.32
−161.39	5.97	5.54	7.8	−.29
−159.72	8.80	8.49	3.7	−.15
−158.55	12.23	11.37	7.5	−.31
−155.00	27.96	26.58	5.2	−.22
[1] −151.46	47.88	58.90		
−152.46		47.27	1.3	−.06
−148.27	117.7	116.0	1.5	−.07
−145.44	205.0	205.4	−.2	.01
−143.07	323.8	325.0	−.4	.02
−140.63	509.6	512.0	−.5	.03
−138.69	720.0	726.0	−.8	.05
−136.78	1,001.8	1,013.7	−1.2	.07
−134.67	1,430.5	1,449.3	−1.3	.08
−129.29	5,257	3,431	54	−3.8
−129.28	5,263	3,436	54	−3.8
		HENNING		
	mm	*mm*		
−81.144	610.6	610.83	−0.04	0.005
−80.772	630.3	630.23	.01	−.001
−79.822	682.4	682.25	.02	−.002
−79.107	724.3	723.85	.06	−.007
−78.584	756.1	755.68	.06	−.007
−78.485	761.4	761.85	−.06	.007
		BRIDGEMAN		
0	26,144.7	26,141.7	0.01	−0.004
		SIEMENS		
−127.21	3.50	3.51	−0.3	0.02
−122.12	7.36	7.34	.3	−.02
−117.78	13.09	13.18	−.7	.05
−116.34	15.79	15.88	−.6	.04
−113.52	22.65	22.65	0	0
−110.57	32.19	32.37	−.6	.05
−106.64	50.39	50.96	−1.1	.10
−101.58	88.44	88.79	−.4	.04
−99.28	112.68	112.92	−.2	.02
−98.07	127.77	127.81	0	0
−95.03	172.9	173.12	−.1	.01
−92.66	217.1	217.72	−.3	.03
−89.89	283.1	282.40	.3	−.03
−87.59	348.9	348.39	.1	−.02
−87.10	364.1	364.08	0	0
−84.47	459.4	459.38	0	0
−82.61	538.4	539.39	−.2	.02
−81.87	573.2	574.47	−.2	.03
−80.86	622.7	625.60	−.5	.06
−80.05	667.1	669.43	−.3	.04
−79.60	692.1	694.94	−.4	.05
−79.06	723.0	726.67	−.5	.06
−78.47	759.7	762.77	−.4	.05
−77.39	830.1	832.99	−.3	.04

[1] This temperature appears to be in error by 1° C.

TABLE 6.—*Vapor pressure measurements by other observers*—Continued

HENNING AND STOCK

Observed temperature	Observed pressure	Calculated pressure	$100 \times \frac{p_{obs.} - p_{calc.}}{p_{calc.}}$	$\theta_{obs.} - \theta_{calc.}$
° *C.*	*Microbars* *mm*	*Microbars* *mm*	*Per cent*	° *C.*
−109. 74	35. 7	35. 70	0	0
−108. 73	40. 1	40. 18	−0. 2	0. 018
−98. 89	117. 7	117. 54	. 1	−. 013
−87. 91	350. 3	350. 60	−. 1	. 010
−108. 97	38. 9	39. 07	−. 4	. 036
−102. 96	76. 6	76. 50	. 1	−. 012
−95. 92	158. 7	158. 58	. 1	−. 009
−87. 91	338. 5	338. 47	0	−. 001
−80. 05	669. 9	669. 43	. 1	−. 008

HEUSE AND OTTO

−78. 523	760. 0	759. 45	0. 07	−0. 009
−78. 509	760. 0	760. 33	−. 04	. 005

References to papers not already discussed which contain data on the vapor pressure of carbon dioxide are listed below.[23] A few of these contain data on the solid, but have been given no weight in the determination of the constants in the empirical equation.

Some of the more accurate measurements on the liquid are compared with the results given in this paper in Figure 4. The dotted curve indicates the percentage error corresponding to an error of 0.5° C. The zero line has been drawn sufficiently wide to include all the observations on samples in glass used in the present investigation.

The results of Jenkin and Pye shown in Figure 4 are unique in being the only measurement of the vapor pressure of carbon dioxide by the dynamic method.

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[23] List of references on the vapor pressure of carbon dioxide.

Observer	Reference
Faraday	Trans. Roy. Soc., London, p. 155, 1845; Faraday's Researches in Chemistry and Physics (Univ. London Press, 1859).
Regnault	Relation des Experiences, vol. 2, p. 618, 1862 (Mem. Acad. Sci. Paris, vol. 26).
Andrews	Trans. Roy. Soc. London, vol. 159, II, p. 575, 1869; Scientific Papers of Thomas Andrews (MacMillan & Co. 1889).
Andrews	Phil. Mag. (5), vol. 1, p. 78, 1876; Ann. chim. phys. (5), vol. 8, p. 555, 1876.
Pictet	Arch. sci. phys. Nat. Geneve, vol. 61, p. 91, 1878; Ann. chim. phys. (5), vol. 13, p. 212, 1878.
Amagat	Ann. chim. phys. (6), vol. 29, p. 136, 1893; J. phys. (3), vol. 1, p. 288, 1892; Compt. rend., vol. 114, pp. 1093 and 1322, 1892.
Villard and Jarry	Compt. rend., vol. 120, p. 1413, 1895.
Villard	Ann. chim. phys. (7), vol. 10, p. 387, 1897.
Kuenen	Phil. Mag. (5), vol. 44, p. 179, 1897.
duBois and Wills	Verh. d. Ges., vol. 1, p. 168, 1899.
Holborn	Ann. Physik, vol. 6, p. 253, 1901.
Kuenen and Robson	Phil. Mag. (6), vol. 3, p. 149, 1902.
Lange	Z. ang. Chem., vol. 16, p. 514, 1903.
Keesom	Comm. Phys. Lab. Univ. Leiden No. 88, 1903; Proc. Kon. Akad. Amst., vol. 6, II, p. 565, 1904.
Zeleny and Smith	Phys. Zts., vol. 7, p. 667, 1906; Phys. Rev., vol. 24, p. 42, 1907.
Zeleny and Zeleny	Phys. Zts., vol. 7, p. 716, 1906; Phys. Rev., vol. 23, p. 308, 1906.
Nernst (published by Falck)	Phys. Zts., vol. 9, p. 435, 1908.
Jenkin and Pye	Trans. Roy. Soc. London, vol. 213, p. 67, 1913.
Keyes Townshend and Young	Jour. Math. and Phys., vol. 1, p. 243, 1922.

VIII. EMPIRICAL REPRESENTATION OF THE DATA

1. LIQUID CARBON DIOXIDE

For the representation of vapor pressure, an equation of the form

$$\log \frac{p}{p_0} = \frac{\theta-\theta_0}{\theta}\left\{A - B\,\frac{\theta-\theta_0}{\theta_0} + C\left(\frac{\theta-\theta_0}{\theta_0}\right)^2\right\} \qquad (1)$$

has been used by Cragoe,[24] where p and p_0 are, respectively, the observed pressure and the pressure at some standard temperature and θ and θ_0 are the corresponding absolute temperatures. In order to represent the measurements of the vapor pressure of liquid carbon dioxide within the limits of accuracy of the observations, it was necessary to add two terms involving higher powers of $\frac{\theta-\theta_0}{\theta_0}$.

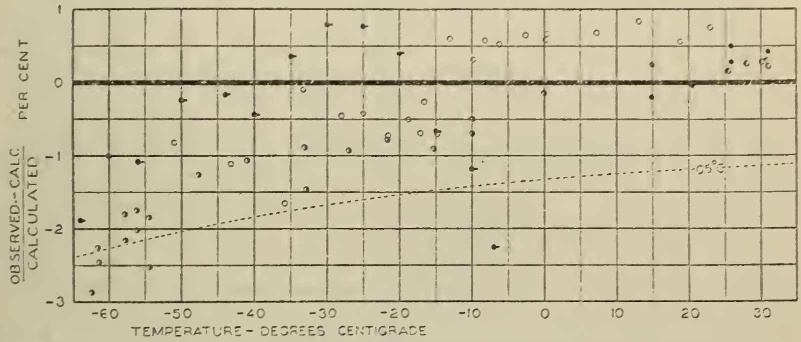

FIGURE 4.—*Comparison of the measurements on liquid by various observers*

The dotted curve shows the deviation in per cent of the pressure corresponding to an error of 0.5° C. The points shown are:
- ● Kuenen.
- ◑ Kuenen and Robson.
- ◐ Keesom.
- ► Zeleny and Smith.
- ○ Jenkin and Pye.

With the addition of these two terms, the choice of θ_0 as 0° C., and an algebraic transformation, the equation

$$\log p = 1.542235 + \frac{1}{273.10+t}\,(3.136105\,t + 0.000578554\,t^2 + 2.77120\,t^3\,10^{-5} + 3.19406\,t^4\,10^{-7} + 3.17316\,t^5\,10^{-9}) \qquad (2)$$

was obtained, t is the temperature in degrees centigrade on the international scale, and p is the pressure in bars.

Another equation has been obtained through graphical representation of the data. The values of $\theta \log p$ obtained from the observa-

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[24] Int. Critical Tables, vol. 3, p. 228, McGraw Hill Book Co.

tions are approximately a linear function of temperature as may be deduced from the fact that the well-known equation

$$\log p = a - \frac{b}{\theta} \tag{3}$$

where a and b are constants, is a fair approximation. Consequently, $\theta\ (a - \log\ p)$ has an almost constant value. This quantity was plotted as ordinate with the square of the absolute temperature as abscissa. The points plotted lay on a curve which had a point of inflection and a form approximately that of a cubic. When a value of a was chosen such that the slope of the curve was zero at the point of inflection as in Figure 5, the curve was symmetrical about the point of inflection within the accuracy of the data. The position of the point of inflection was determined with sufficient accuracy by plotting on separate large semitransparent sheets of paper the points on the opposite sides of the point of inflection and superimposing the two parts of the curve thus formed.

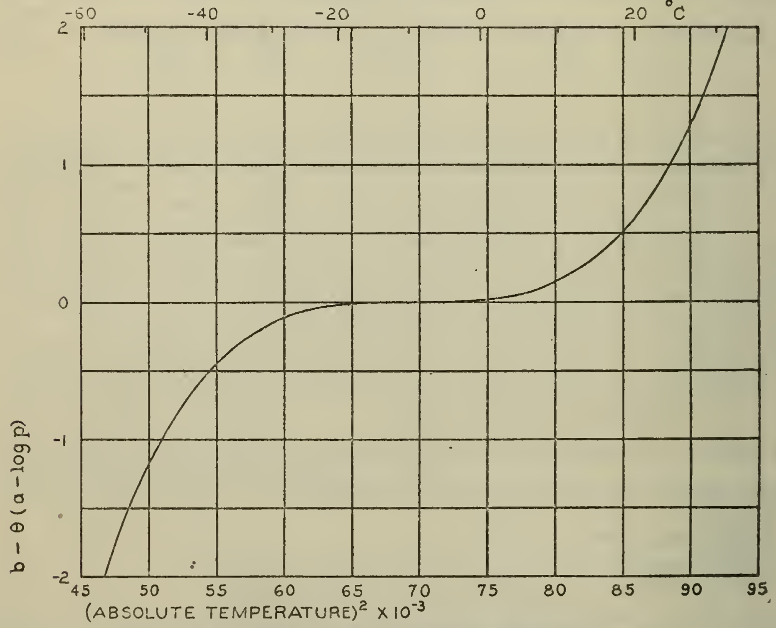

Figure 5.—*Term subtracted from b in equation (6).*

It was found that the equation

$$\theta(a - \log p) = b - c(\theta^2 - \theta_1^2)^3 \tag{4}$$

where c is a constant and θ_1 is the temperature at the point of inflection, represented the data within about 1 part in 2,000, but that a consistent deviation from the observed values still existed, the curve in Figure 5 being steeper at the extremities than would be indicated by equation (4). This led to the use of the equation

$$\theta(a-\log p)=b-my(10^{ny^2}-1) \tag{5}$$

or

$$\log_{10}p=a-\frac{1}{\theta}\{b-my(10^{ny^2}-1)\} \tag{6}$$

where for liquid carbon dioxide with p in bars

$a=4.674193$
$b=855.352$
$m=1.131\times10^{-4}$
$n=4.7\times10^{-10}$
$y=\theta^2-\theta_1^2$
$\theta_1^2=69{,}700$ $(\theta_1=264.01)$

The term which has been added to equation (3) is relatively small (0.3 per cent of b or less for liquid carbon dixoide), and the use of a table of squares, a table of logarithms, and a slide rule yields values of this term with sufficient accuracy for calculating the vapor pressure of liquid carbon dioxide to 1 part in 10,000.

The pressures in the sixth column of Table 1 were calculated from equation (6) using the values given for the constants. The differences between observed and calculated pressures in millimeters, in parts in 100,000, and in thousandths of a degree centigrade are given, respectively, in the last three columns of the table. There is no apparent consistent variation in these differences with temperature. The reproducibility of pressure measurements on a given day indicates that an appreciable part of the differences for different days may be due to small irregularities in the behavior of the Wheatstone bridge used, especially for the measurements at the higher temperatures.

Differentiation of equation (6) gives

$$\frac{0.4343}{p}\frac{dp}{d\theta}=\frac{1}{\theta^2}[b-my(10^{ny^2}-1)]+2m[10^{ny^2}(4.605\,ny^2+1)-1] \tag{7}$$

The values of pressure and of $dp/d\theta$ for liquid carbon dioxide given in the appendix to this paper have been calculated from equations (6) and (7), using the constants already given.

Figure 6 gives an intercomparison between values calculated from equations (2) and (6), and groups of observed values. The upper part of the figure shows deviations from equation (2) and the lower part shows deviations from equation (6). The cross represents the mean of observations made on sample No. 1 at 0° C. at the Massachusetts Institute of Technology. The solid black circle at 0° C. represents the mean of the observations by Bridgeman.[25] The point is shown in this figure since the accuracy of his results and the agreement with this investigation are better than can be indicated on the more compressed scale used for other observations in Figure 4. The remaining circles represent observations made at this bureau. The point at −55° C. which is omitted in the upper part of the figure, represents only a single observation; its percentage deviation is rela-

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[25] See footnote 22, p. 396.

tively large, but corresponds to an error of only 0.011° C. in the temperature. Each of the other circles represents the mean of several observations. The values for plotting these points were obtained by dividing the values in the eighth column of Table 1 into groups covering small temperature ranges and taking a mean of the values in each group, weighted as indicated in the fifth column of the table. The figure shows that both equations represent the data almost equally well, although near the critical temperature equation (6) appears to be slightly better. This equation probably represents the vapor pressure of the samples observed within 1 or 2 parts in 10,000. The values of $dp/d\theta$ calculated from the two equations differ by less than 1 part in 1,500 in the temperature range −56° to 25° C.; but at 31° C., equation (6) yields the larger value by 0.5 per cent. No exact estimate can be made of the accuracy of the values of $dp/d\theta$ calculated from equation (6), but it seems fairly certain that the accuracy is better than 1 part in 1,000 except near the critical temperature and that the error does not exceed 0.5 per cent at that point. This accuracy is considered ample for use in the Clapeyron-Clausius relation

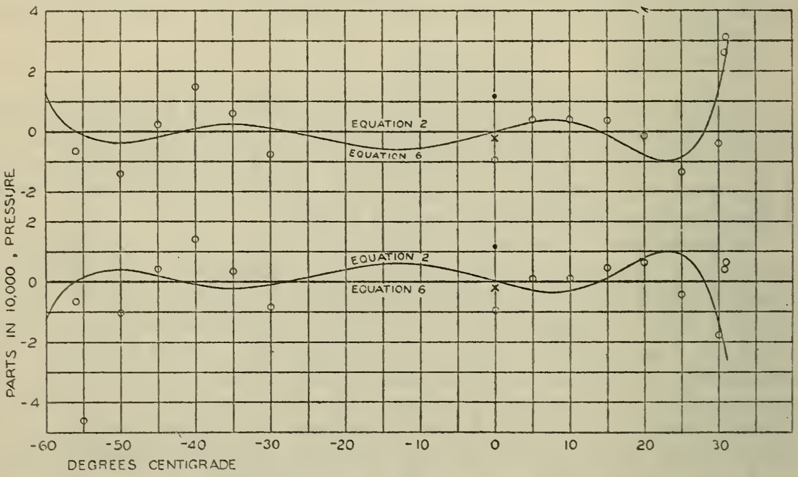

FIGURE 6.—*Intercomparison of equations (2) and (6) and observed values*

× represents mean of observations at 0° C. on sample No. 1 by Massachusetts Institute of Technology. ○ mean of observations at this bureau. Point at −55° C., is a single observation and is omitted in the upper part of the figure. ● mean of measurements by O. C. Bridgeman

$$L/\theta=(V-v)dp/d\theta \tag{8}$$

since the latent heat and difference between the specific volumes of the vapor and liquid approach zero as a limit at the critical temperature.

2. SOLID CARBON DIOXIDE

Over the temperature range within which accurate vapor pressure data have been obtained for solid carbon dioxide the results can be represented in bars by the equation

$$\log p=6.92804-\frac{1}{\theta}[1{,}347.00-1.167\ (\theta^2-35{,}450)^3 10^{-12}] \tag{9}$$

The calculated pressures in the fifth column of Table 2 as well as the values of pressure and of $dp/d\theta$ for solid carbon dioxide given in the appendix to this paper have been calculated from equation (9). The differences between the pressures observed in this investigation and the calculated pressures are given in the last three columns of Table 2.

These differences are represented graphically in Figure 7 with the exception of two values observed March 20, 1931, which are discarded

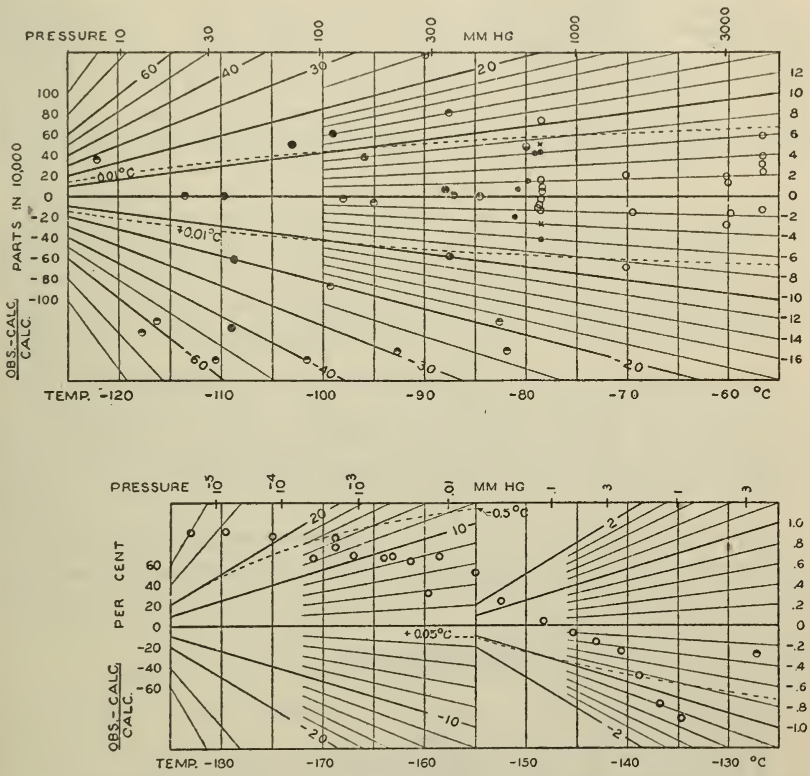

FIGURE 7.—*Comparison of observed pressures with equation (9)*

The dotted curves show the deviation in pressure corresponding to the indicated error in temperature. The points shown are:

- ○ this investigation (upper chart).
- • Henning, Ann. Physik (ser. 4), vol. 43, p. 282, 1914.
- ● Henning and Stock, Zs. Phys., vol. 4, p. 226, 1921.
- ◓ Siemens, Ann. Physik (ser. 4), vol. 42, p. 871, 1913.
- ○ Weber, Leiden Comm. No. 137c, 1913 (lower chart).
- ○ Onnes and Weber, Leiden Comm. No. 137b, 1913 (lower chart).
- × Heuse and Otto, Ann. Physik (ser. 5), vol. 9, p. 486, 1931, and vol. 14, pp. 181 and 185, 1932.

(see footnote to Table 2). The coordinates have been chosen to give as nearly as possible a uniform dispersion of the points throughout the temperature range. The dotted lines indicate the errors in temperature corresponding to percentage errors in the pressure while the scale of pressures at the top makes possible an estimate of the absolute value of the pressure differences. These points form four groups covering small temperature intervals in the temperature range −56.6° to −80° C. If the mean of the points in each group, weighted as indicated in Table 2, is taken, the maximum deviation from the equation for these means is 2 parts in 10,000.

It will be seen that these observed values and equation (9) are both in excellent agreement with the work at the Reichsanstalt. There is also good agreement at the lower temperatures with the observations of Siemens, but his observations near the normal sublimation point are so low as to be off the scale used in the figure. This discrepancy is discussed in part 3 of Section VII of this paper.

The observations of Onnes and Weber are very precise except for their value at −129° C. which is far off the scale used. From Figure 7 alone, one might conclude that the equation did not actually represent the vapor pressure below −100° C., but it is shown in Section IX of this paper that the equation is in much better agreement with pressures calculated with the aid of calorimetric data than are the observed values.

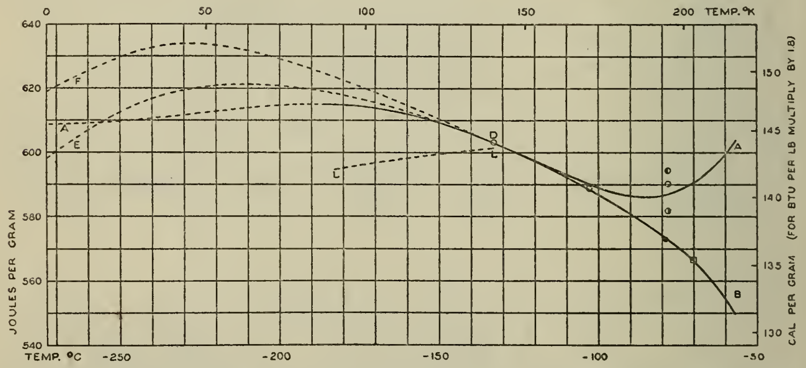

Figure 8.—*Correlation of vapor pressure data with latent heat of sublimation*

AA, values of $\frac{R\theta^2}{p}\frac{dp}{d\theta}$ from equation (9).
LL, same from equation given by Weber.
BDE and *BDF*, possible values for latent heat of sublimation.
□ calculated latent heat from *AA* and volumetric measurements of Maass and Mennie.
Observed latent heats are as follows:

○ Eucken and Donath.
● Maass and Barnes.
◐ Behn, Ann. Physik (4), vol. 1, p. 270, 1900.
◒ Andrews, J. Am. Chem. Soc., vol. 47, p. 1597, 1925.
◑ Favre, Compt. rend., vol. 39, p. 729, 1854; Liebig's Ann., vol. 92, p. 194, 1854.

(Other references given in the text.)

IX. CORRELATION OF THE VAPOR PRESSURE DATA WITH CALORIMETRIC DATA

It is desirable to correlate calorimetric data with the vapor pressure and to use this correlation as an aid in estimating the accuracy of the calculated values of the vapor pressure particularly at the lower temperatures where the percentage accuracy of the vapor pressure measurements is relatively poor.

From the exact Clapeyron-Clausius relation (see equation (8)) and the approximation, $V-v=\frac{R\theta}{p}$, which is sufficiently accurate at the lower temperatures, one obtains

$$L=\frac{R\theta^2}{p}dp/d\theta \qquad (10)$$

Values of $\frac{R\theta^2}{p}\,dp/d\theta$ for the solid were calculated from equation (9), plotted in Figure 8 as ordinates with temperature as abscissa, and represented by the curve *AA*.

Of the various observed values of latent heat represented in the figure, the two by Eucken and Donath [26] are probably the most accurate. The agreement between the various data presented in the figure confirms the claim of those authors for an accuracy of 0.1 or 0.2 per cent. The point at −133.1° C. coincides with the curve *AA*, while the point at −103.1° C. is slightly below the curve *AA* in consequence of the fact that $V-v$ departs from $\frac{R\theta}{p}$ at the higher temperatures. It is to be noted that the value for the latent heat at −133.1° C. published by Eucken and Donath is 0.2 per cent smaller than the mean of their observed values which is given in Figure 8.

The square at −70° C. represents a value of latent heat calculated from equation (8) using the value of $dp/d\theta$ obtained in the present investigation and an extrapolation to the saturation pressure of the value obtained by Maass and Mennie [27] for the specific volume of the vapor at about one atmosphere. This extrapolation was based on the assumption that at constant temperature PV varies linearly with the density.

The curve from *B* to *D* was drawn approximately through the three points under discussion. It is in agreement with the observation of the latent heat at the normal sublimation point by Maass and Barnes,[28] and except near the triple point, with the values chosen by Plank and Kuprianoff [29] in their correlation of the properties of carbon dioxide.

At temperatures lower than −133.1° C., the latent heat may be calculated from Eucken and Donath's observed value at that temperature and an integration of specific heat data. For carbon dioxide at these low temperatures the equation

$$C_{p_{\text{gas}}}-C_{p_{\text{solid}}}=dL/d\theta \tag{11}$$

is a very close approximation to the exact thermodynamic relation

$$C_{p_{\text{gas}}}-C_{p_{\text{solid}}}=dL/d\theta-L/\theta+\theta\left[\left(\frac{\delta v}{\delta\theta}\right)_{p_{\text{gas}}}-\left(\frac{\delta v}{\delta\theta}\right)_{p_{\text{solid}}}\right]dp/d\theta. \tag{12}$$

For the purpose of this integration Eucken's [30] determinations of the specific heat at constant pressure for the solid were used. In the temperature range above −170° C. these observations can be represented by the equation

$$\begin{aligned}C_{p_{\text{solid}}}&=0.60+0.0033\theta,\text{j/g°C.}\\&=0.143+0.00079\theta,\text{cal/g°C., or Btu/lb°F.}\end{aligned} \tag{13}$$

Below this temperature integration was performed by choosing from a graph, the average differences between the specific heat for the gas and for the solid over a limited temperature range and multiplying

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[26] Z. phys. Chem., vol. 124, p. 181, 1926.
[27] Proc. Roy. Soc., London, Ser. A. vol. 110, p. 198, 1926.
[28] Proc. Roy. Soc., London, Ser. A, vol. 111, p. 224, 1926.
[29] Beiheft Z. ges. Kälte-Ind. Reihe 1, Heft 1, 1929.
[30] Verhand, Deutschen phys. Gesell., vol. 18, p. 4, 1916.

by the temperature increment. Although the values of specific heat published by Maass and Barnes[31] differ somewhat from those by Eucken, it appears that a correction should be applied to their data especially at the higher temperatures for evaporation of part of the sample when warmed, since the solid did not fill the container entirely. Although the information available was insufficient for determining this correction accurately, it appears that the correction is of the proper magnitude to bring the two sets of data into substantial agreement.

The specific heat of the vapor is not well established at low temperatures by experimental values, the observed value at the lowest temperature being 0.768 joules per gram per °C., at 1 atmosphere and −75° C. by Heuse.[32]

Theoretical considerations have led various authors to believe that C_p for carbon dioxide vapor approaches $3.5R$ or 0.662 joules per gram per °C. as a limit at absolute zero. A graph of the available data plotted with specific heat and temperature as coordinates indicates that if this is the limit approached, $C_{p_{\text{gas}}}$ below −130° C. may for our purpose be considered equal to the limiting value. With this assumption

$$\int (C_{p_{\text{gas}}} - C_{p_{\text{solid}}}) d\theta$$

is represented by the curve DE in Figure 8.

The graph of experimental data mentioned does not determine the limiting value for $C_{p_{\text{gas}}}$. If, as is believed for hydrogen, the limit is $2.5R$, a smooth curve through the experimental data near saturation and through $2.5R$ at absolute zero is, to a first approximation, represented by assuming $C_{p_{\text{gas}}}$ equal to $0.473+7.5\times,10^{-6},\theta^2$. This assumption leads to the curve DF in Figure 8.

An integration of the function represented by the curve DF gives values for vapor pressure about 15, 3, and 0.3 per cent smaller at −190°, −170°, and −150° C., respectively, than those obtained from equation (9). The corresponding differences between values obtained from integration of the function represented by DE and those from equation (9) are about one-third as great. The curve BDE probably gives as good an estimate of the latent heat of sublimation as can be made from the available data.

Weber and Onnes[33] have shown that their measurements in the range −180° to −130° C. are very well represented by the equation

$$\log p = \frac{6007.9}{4.571}\,\frac{1}{\theta} + 1.75 \log \theta - \frac{0.009008}{4.571}\,\theta + 3.1700 \tag{15}$$

Values of $\frac{R\theta^3}{p} dp/d\theta$ calculated from this equation are represented by the dotted curve LL. It is apparent that their observations are not in agreement with calorimetric data.

From this correlation of the data it appears that the vapor pressures calculated from equation (9), although considerably smaller at very low temperatures than the observed pressures, are not too small but may be slightly too large.

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[31] See footnote 28, p. 405.
[32] Ann. Physik (4), vol. 59, p. 86, 1919.
[33] See footnote 15, p. 394.

It is to be noted that under conditions such as occur in the present case where the percentage accuracy of the observed vapor pressures decreases with decreasing temperature, the vapor pressure equation gives the quantity $\frac{1}{p}dp/d\theta$ with greater percentage accuracy than it does the quantity $dp/d\theta$ or even the vapor pressure itself. For example, two equations which gave at −130° C. the same vapor pressures and the same values for $\frac{R\theta^2}{p}dp_2/d\theta$, yielded at −190° C. vapor pressures differing by 15 per cent and values of $\frac{R\theta^2}{p}dp/d\theta$ differing by only 3 per cent.

X. CONCLUSIONS

The vapor pressure of liquid and solid carbon dioxide has been measured at this bureau in the range 31° to −79° C. The average deviation of the weighted observations from values calculated from an equation is 1.0 part in 10,000 for the liquid and 2.4 parts in 10,000 for the solid. These average deviations correspond to about 0.004° C. for both liquid and solid. The value of the vapor pressure at 0° C. calculated from the equation for the liquid is only 1 part in 10,000 less than that observed by O. C. Bridgeman.

The measurements near the normal sublimation point (−78.514° C.) are in agreement with those at the Reichsanstalt. The equation for the solid has been designed to represent also the measurements at temperatures below −79° C. by Henning and Stock, Siemens, and Onnes and Weber.

The values of vapor pressure given in the Appendix to this paper are considered accurate within 1 or 2 parts in 10,000 in the range 31° to −80° C., 1 part in 1,000 in the range −80° to −100° C., 1 per cent in the range −100° to −140° C., and about 20 per cent in the range −140° to −190° C.

The triple point pressure and temperature are 3,885.2 ± 0.4 mm and −56,602 ± 0.005° C., respectively.

The critical point temperature is considered to be between 30.95° and 31.05° C. For practical purposes the temperature may be assumed to be 31.00° C. for which the corresponding pressure is 73.76 bars (72.80 atmospheres or 55,330 mm).

Observations of pressure and relative volumes along several isotherms in the neighborhood of the critical point are given.

The values of $dp/d\theta$ in the Appendix obtained through differentiation of the vapor pressure equations for the liquid and the solids are considered accurate within 1 part in 1,000 in the range 25° to −100° C., and within about 0.5 per cent near the critical point. The differentiation of the vapor pressure equation for the solid leads to results which together with volumetric data from other laboratories make possible, through the Clapeyron-Clausius relation, a better estimate of latent heat of sublimation than has hitherto been made from such data. Such estimate is in agreement with the latent heat observed by Eucken and Donath. A graph (fig. 8) showing the relation between the latent heat and temperature is given. Values from the curve *BDE* of this graph are considered to represent the latent heat of sublimation within 1 per cent down to liquid air temperatures and within 2 or 3 parts in 1,000 in the range −80° to −150° C.

XI. ACKNOWLEDGMENTS

Acknowledgement is made to C. S. Taylor, who prepared and purified the carbon dioxide; to D. O. Burger for assistance in taking the observations in 1931.

XII. APPENDIX

The values in the following tables have been calculated from equations (6) and (9) given in the text or from their differential equations. The temperatures recorded have been corrected to the international temperature scale. The term "bar" is used in accordance with the usage now internationally accepted; that is, to indicate a pressure of 1,000,000 dynes per square centimeter or 0.96784 normal atmospheres. The term microbar is used to indicate a pressure of one dyne per square centimeter.

The error caused by linear interpolation between the pressure given every degree may be appreciable especially for the solid, but linear interpolation between the logarithms of these pressures will rarely introduce an error greater than a unit in the last decimal place given in the tables.

Table 7.—*Vapor pressure of solid carbon dioxide*

[In lbs. per in.^{2}, reduced to g=32.1740 ft. per sec.^{2}]

°F.	0	1	2	3	4	5	6	7	8	9
−210	0.022	0.020	0.018	0.016	0.015	0.014	0.012	0.011	0.010	0.009
−200	.053	.049	.045	.041	.038	.034	.031	.029	.026	.024
−190	.120	.111	.103	.095	.087	.080	.074	.068	.063	.058
−180	.255	.237	.220	.204	.190	.176	.163	.151	.140	.129
−170	.513	.480	.448	.419	.391	.364	.339	.316	.295	.274
−160	.984	.924	.867	.813	.763	.715	.670	.627	.587	.549
−150	1.804	1.701	1.603	1.511	1.423	1.339	1.260	1.186	1.115	1.048
−140	3.18	3.01	2.85	2.69	2.54	2.40	2.27	2.15	2.03	1.91
−130	5.40	5.13	4.87	4.62	4.39	4.16	3.95	3.74	3.54	3.36
−120	8.90	8.48	8.07	7.69	7.32	6.96	6.62	6.30	5.98	5.69
−110	14.25	13.61	13.00	12.40	11.84	11.30	10.78	10.28	9.80	9.34
−100	22.24	21.30	20.39	19.51	18.67	17.86	17.08	16.33	15.61	14.92
− 90	33.95	32.57	31.25	29.97	28.74	27.55	26.41	25.31	24.24	23.22
− 80	50.81	48.84	46.94	45.11	43.34	41.63	39.98	38.39	36.85	35.37
− 70	74.79	72.01	69.31	66.71	64.19	61.76	59.42	57.15	54.97	52.85

Triple point, −69.88° F.; 75.13 lbs./in.^{2}

Table 8.—*Vapor pressure of liquid carbon dioxide*

[In lbs. per in.^{2}, reduced to g=32.1740 ft. per sec.^{2}]

°F.	0	1	2	3	4	5	6	7	8	9
−60	94.75	92.61	90.51	88.44	86.40	84.40	82.43	80.50	78.61	76.74
−50	118.28	115.75	113.26	110.81	108.40	106.03	103.70	101.41	99.15	96.94
−40	145.90	142.94	140.02	137.15	134.33	131.55	128.81	126.12	123.46	120.85
−30	178.02	174.59	171.21	167.88	164.60	161.37	158.18	155.04	151.95	148.90
−20	215.09	211.15	207.26	203.42	199.64	195.91	192.23	188.60	185.03	181.50
−10	257.6	253.1	248.6	244.2	239.9	235.6	231.4	227.2	223.1	219.1
− 0	305.9	300.8	295.7	290.7	285.8	281.0	276.2	271.4	266.7	262.1
0	305.9	311.0	316.3	321.6	326.9	332.4	337.9	343.4	349.1	354.8
10	360.5	366.3	372.2	378.2	384.3	390.4	396.6	402.8	409.1	415.5
20	422.0	428.5	435.1	441.8	448.6	455.4	462.4	469.3	476.4	483.6
30	490.8	498.1	505.5	513.0	520.5	528.1	535.8	543.6	551.5	559.5
40	567.5	575.7	583.9	592.2	600.6	609.1	617.7	626.3	635.1	643.9
50	652.9	661.9	671.0	680.2	689.6	699.0	708.5	718.1	727.8	737.6
60	747.5	757.6	767.7	777.9	788.2	798.7	809.2	819.9	830.7	841.5
70	852.6	863.7	874.9	886.3	897.8	909.4	921.1	933.0	945.0	957.1
80	969.4	981.8	994.3	1,007.0	1,019.8	1,032.7	1,045.9	1,059.1	----------	----------

Critical point, 87.8° F.; 1,069.9 lbs./in.^{2}
Triple point, −69.88° F.; 75.13 lbs./in.^{2}

Table 9.—*Vapor pressure of solid carbon dioxide*

[Mercury column, density=13.5951 g/cm³]

[g=980.665]

PRESSURE IN MICRONS OF MERCURY

° C.	0	1	2	3	4	5	6	7	8	9
−180	0.013	0.008	0.006	0.004	0.003	0.0017	0.0011	0.0007	0.0005	0.0003
−170	.37	.27	.20	.14	.10	.074	.052	.037	.026	.018
−160	5.9	4.6	3.6	2.7	2.1	1.58	1.19	.90	.67	.50
−150	60.5	48.8	39.2	31.4	25.1	19.9	15.8	12.4	9.8	7.6
−140	431	359	298	247	204	168	138	113	92	75

PRESSURE IN mm OF MERCURY

° C.	0	1	2	3	4	5	6	7	8	9
−130	2.31	1.97	1.68	1.43	1.22	1.03	0.87	0.73	0.61	0.51
−120	9.81	8.57	7.46	6.49	5.63	4.88	4.22	3.64	3.13	2.69
−110	34.63	30.76	27.27	24.14	21.34	18.83	16.58	14.58	12.80	11.22
−100	104.81	94.40	84.91	76.27	68.43	61.30	54.84	48.99	43.71	38.94
−90	279.5	254.7	231.8	210.8	191.4	173.6	157.3	142.4	128.7	116.2
−80	672.2	618.3	568.2	521.7	478.5	438.6	401.6	367.4	335.7	306.5
−70	1,486.1	1,377.3	1,275.6	1,180.5	1,091.7	1,008.9	931.7	859.7	792.7	730.3
−60	3,073.1	2,865.1	2,669.7	2,486.3	2,314.2	2,152.8	2,001.5	1,859.7	1,726.9	1,602.5
−50	---------	---------	---------	---------	---------	---------	---------	3,780.9	3,530.2	3,294.6

Triple point, −56.602±0.005° C.; 3885.2±0.4 mm.

Table 10.—*Vapor pressure of liquid carbon dioxide*

[Millimeters of mercury, density=13.5951 g/cm³]

[g=980.665]

° C.	0	1	2	3	4	5	6	7	8	9
−50	5,127.8	4,922.7	4,723.9	4,531.1	4,344.3	4,163.2	3,987.9	[1]3,818.2	[1]3,653.9	[1]3,495.0
−40	7,545	7,271	7,005	6,746	6,494	6,250	6,012	5,781	5,557	5,339
−30	10,718	10,363	10,017	9,679	9,350	9,029	8,716	8,412	8,115	7,826
−20	14,781	14,331	13,891	13,461	13,040	12,630	12,229	11,838	11,455	11,082
−10	19,872	19,312	18,764	18,228	17,703	17,189	16,686	16,194	15,712	15,241
−0	26,142	25,457	24,786	24,127	23,482	22,849	22,229	21,622	21,026	20,443
0	26,142	26,840	27,552	28,277	29,017	29,771	30,539	31,323	32,121	32,934
10	33,763	34,607	35,467	36,343	37,236	38,146	39,073	40,017	40,980	41,960
20	42,959	43,977	45,014	46,072	47,150	48,250	49,370	50,514	51,680	52,871
30	54,086	55,327	---------	---------	---------	---------	---------	---------	---------	---------

[1] Undercooled liquid.

Critical temperature=31.0° C.
Triple point, −56.602±0.005° C.; 3885.2±0.4 mm.

Table 11.—*Vapor pressure of solid carbon dioxide*

[In absolute units]

PRESSURE IN MICROBARS

° C.	0	1	2	3	4	5	6	7	8	9
−180	0.017	0.011	0.008	0.005	0.003	0.002	0.0015	0.0010	0.0006	0.0004
−170	.49	.36	.26	.19	.14	.10	.07	.05	.03	.02
−160	7.9	6.1	4.7	3.6	2.8	2.10	1.59	1.19	.89	.66
−150	81	65	52	42	33	26.6	21.0	16.6	13.0	10.2
−140	574	478	398	329	272	224	184	150	123	100

PRESSURE IN BARS

° C.	0	1	2	3	4	5	6	7	8	9
−130	0.00308	0.00263	0.00225	0.00191	0.00162	0.00137	0.00116	0.00098	0.00082	0.00069
−120	.01311	.01145	.00997	.00868	.00753	.00652	.00564	.00486	.00419	.00359
−110	.04620	.04104	.03639	.03222	.02849	.02514	.02215	.01948	.01710	.01499
−100	.1397	.1258	.1132	.1017	.0912	.0817	.0731	.0653	.0583	.0519
−90	.3727	.3396	.3091	.2810	.2552	.2315	.2098	.1898	.1716	.1549
−80	.8962	.8243	.7575	.6955	.6380	.5847	.5354	.4898	.4476	.4086
−70	1.9813	1.8362	1.7006	1.5739	1.4555	1.3451	1.2422	1.1462	1.0568	.9736
−60	4.0971	3.8198	3.5593	3.3148	3.0854	2.8701	2.6684	2.4794	2.3023	2.1365
−50	---------	---------	---------	---------	---------	---------	---------	5.0408	4.7066	4.3924

Triple point, −56.602±0.005° C.; 5.1798±0.0005 bars.

TABLE 12.—*Vapor pressure of liquid carbon dioxide*

[In bars]

° C.	0	1	2	3	4	5	6	7	8	9
−50	6.836	6.563	6.298	6.041	5.792	5.551	5.317	[1] 5.091	[1] 4.872	[1] 4.660
−40	10.059	9.694	9.339	8.994	8.659	8.332	8.015	7.707	7.408	7.118
−30	14.290	13.817	13.355	12.905	12.466	12.038	11.621	11.215	10.819	10.434
−20	19.706	19.106	18.519	17.946	17.386	16.839	16.304	15.782	15.273	14.775
−10	26.494	25.748	25.017	24.302	23.602	22.916	22.246	21.590	20.948	20.320
−0	34.853	33.940	33.045	32.167	31.306	30.463	29.637	28.827	28.033	27.255
0	34.853	35.783	36.732	37.700	38.686	39.691	40.716	41.760	42.824	43.908
10	45.013	46.139	47.286	48.454	49.645	50.857	52.093	53.352	54.635	55.942
20	57.27	58.63	60.01	61.42	62.86	64.33	65.82	67.35	68.90	70.49
30	72.11	73.76	---------	---------	---------	---------	---------	---------	---------	---------

[1] Undercooled liquid.

Critical temperature = 31.0° C.
Triple point, −56.602±0.005° C.; 5.1798±0.0005 bars.

TABLE 13.—*Vapor pressure of solid carbon dioxide*

[In kg/cm², g = 980.665]

° C.	0	1	2	3	4	5	6	7	8	9
−140	0.00059	0.00049	0.00040	0.00034	0.00028	0.00023	0.00019	0.00015	0.00012	0.00010
−130	.00313	.00268	.00229	.00195	.00165	.00140	.00118	.00100	.00084	.00070
−120	.01334	.01165	.01015	.00883	.00766	.00664	.00574	.00495	.00426	.00366
−110	.04708	.04181	.03707	.03282	.02901	.02560	.02255	.01983	.01741	.01525
−100	.14249	.12833	.11543	.10370	.09302	.08334	.07456	.06661	.05942	.05293
−90	.3800	.3463	.3152	.2865	.2602	.2360	.2139	.1936	.1750	.1580
−80	.9139	.8405	.7724	.7092	.6506	.5963	.5460	.4994	.4564	.4167
−70	2.0204	1.8724	1.7341	1.6049	1.4843	1.3716	1.2667	1.1688	1.0776	.9928
−60	4.1779	3.8951	3.6295	3.3802	3.1462	2.9267	2.7210	2.5283	2.3477	2.1786
−50	---------	---------	---------	---------	---------	---------	---------	5.1402	4.7994	4.4790

Triple point, −56.602±0.005° C.; 5.2818 kg/cm².

TABLE 14.—*Vapor pressure of liquid carbon dioxide*

[In kg/cm², g = 980.665]

° C.	0	1	2	3	4	5	6	7	8	9
−50	6.9713	6.6925	6.4222	6.1601	5.9061	5.6600	5.4216	[1] 5.1909	[1] 4.9675	[1] 4.7515
−40	10.257	9.885	9.524	9.172	8.829	8.497	8.174	7.860	7.555	7.259
−30	14.572	14.089	13.618	13.159	12.711	12.275	11.850	11.436	11.032	10.640
−20	20.095	19.483	18.885	18.300	17.729	17.171	16.625	16.093	15.574	15.067
−10	27.016	26.255	25.510	24.781	24.069	23.368	22.684	22.015	21.361	20.721
−0	35.540	34.609	33.696	32.801	31.924	31.064	30.221	29.395	28.585	27.793
0	35.540	36.489	37.457	38.443	39.449	40.474	41.519	42.583	43.668	44.774
10	45.900	47.048	48.218	49.409	50.623	51.860	53.120	54.404	55.712	57.045
20	58.403	59.787	61.198	62.635	64.101	65.595	67.120	68.674	70.260	71.878
30	73.531	75.217	---------	---------	---------	---------	---------	---------	---------	---------

[1] Undercooled liquid.

Critical temperature = 31° C. Triple point, −56.602±0.005° C.; 5.2819 kg/cm².

TABLE 15.—*Vapor pressure of solid carbon dioxide*

[Density of mercury=13.5951, g=980.665]

[Temperatures in °C. below zero for even millimeters of mercury]

mm	0	1	2	3	4	5	6	7	8	9
400	86.045	86.016	85.988	85.960	85.932	85.904	85.876	85.848	85.821	85.794
410	85.766	85.738	85.710	85.683	85.656	85.628	85.601	85.574	85.547	85.520
420	85.493	85.466	85.439	85.412	85.385	85.358	85.331	85.304	85.278	85.251
430	85.225	85.198	85.172	85.146	85.120	85.094	85.067	85.041	85.015	84.989
440	84.963	84.937	84.911	84.885	84.860	84.834	84.809	84.783	84.757	84.731
450	84.706	84.681	84.656	84.630	84.605	84.580	84.555	84.530	84.505	84.480
460	84.455	84.430	84.405	84.380	84.355	84.330	84.306	84.281	84.257	84.232
470	84.207	84.183	84.159	84.134	84.110	84.086	84.062	84.037	84.013	83.989
480	83.965	83.941	83.917	83.893	83.869	83.846	83.822	83.798	83.774	83.750
490	83.727	83.703	83.680	83.656	83.633	83.609	83.586	83.562	83.539	83.516
500	83.493	83.470	83.447	83.424	83.401	83.378	83.355	83.332	83.309	83.286
510	83.263	83.240	83.218	83.195	83.172	83.149	83.127	83.104	83.082	83.059
520	83.037	83.015	82.993	82.970	82.948	82.926	82.904	82.881	82.859	82.837
530	82.815	82.793	82.771	82.749	82.727	82.706	82.684	82.662	82.640	82.618
540	82.597	82.575	82.554	82.532	82.510	82.489	82.467	82.446	82.425	82.403
550	82.382	82.360	82.339	82.318	82.297	82.275	82.254	82.233	82.212	82.191
560	82.170	82.149	82.128	82.107	82.087	82.066	82.045	82.024	82.004	81.983
570	81.962	81.941	81.921	81.900	81.880	81.859	81.839	81.818	81.798	81.777
580	81.757	81.737	81.716	81.696	81.676	81.655	81.635	81.615	81.595	81.575
590	81.555	81.535	81.515	81.495	81.475	81.455	81.435	81.416	81.396	81.376
600	81.356	81.337	81.317	81.297	81.277	81.258	81.238	81.219	81.199	81.180
610	81.160	81.140	81.121	81.102	81.083	81.064	81.044	81.025	81.005	80.986
620	80.967	80.948	80.928	80.909	80.890	80.871	80.852	80.833	80.814	80.795
630	80.776	80.757	80.739	80.720	80.701	80.682	80.663	80.645	80.626	80.607
640	80.588	80.570	80.551	80.533	80.514	80.496	80.477	80.459	80.440	80.422
650	80.403	80.385	80.367	80.348	80.330	80.311	80.293	80.275	80.257	80.239
660	80.220	80.202	80.184	80.166	80.148	80.130	80.112	80.094	80.076	80.058
670	80.040	80.022	80.004	79.986	79.968	79.950	79.933	79.915	79.897	79.879
680	79.862	79.844	79.826	79.809	79.791	79.774	79.756	79.738	79.721	79.703
690	79.686	79.668	79.651	79.634	79.616	79.599	79.581	79.564	79.547	79.530
700	79.512	79.495	79.478	79.461	79.444	79.426	79.409	79.392	79.375	79.358
710	79.341	79.324	79.307	79.290	79.273	79.256	79.239	79.222	79.205	79.189
720	79.172	79.155	79.138	79.121	79.104	79.088	79.071	79.054	79.038	79.021
730	79.004	78.988	78.971	78.955	78.938	78.921	78.905	78.889	78.872	78.856
740	78.839	78.823	78.806	78.790	78.774	78.757	78.741	78.725	78.708	78.692
750	78.676	78.660	78.643	78.627	78.611	78.595	78.579	78.563	78.547	78.530
760	78.514	78.498	78.482	78.467	78.451	78.435	78.419	78.403	78.387	78.371
770	78.355	78.339	78.323	78.308	78.292	78.276	78.260	78.244	78.229	78.213
780	78.197	78.182	78.166	78.150	78.135	78.119	78.104	78.088	78.072	78.057
790	78.041	78.026	78.010	77.995	77.979	77.964	77.949	77.933	77.918	77.902
800	77.887	77.871	77.856	77.841	77.826	77.811	77.795	77.780	77.765	77.750
810	77.735	77.719	77.704	77.689	77.674	77.659	77.644	77.629	77.614	77.599
820	77.584	77.569	77.554	77.539	77.524	77.509	77.494	77.479	77.464	77.449

TABLE 16.—*Rate of change of vapor pressure with temperature for solid carbon dioxide*

[In bars per ° C.]

° C.	0	1	2	3	4	5	6	7	8	9
−130	0.000478	0.000415	0.000359	0.000310	0.000267	0.000230	0.000197	0.000169	0.000144	0.000122
−120	.001764	.001562	.001380	.001217	.001071	.000941	.000825	.000722	.000631	.000550
−110	.005444	.004898	.004400	.003948	.003536	.003162	.002822	.002516	.002239	.001990
−100	.01453	.01325	.01206	.01097	.00997	.00904	.00819	.00741	.00670	.00604
−90	.03450	.03179	.02926	.02691	.02472	.02269	.02080	.01905	.01742	.01592
−80	.07461	.06931	.06435	.05970	.05534	.05126	.04744	.04386	.04053	.03741
−70	.1500	.1403	.1311	.1224	.1143	.1066	.0994	.0926	.0862	.0802
−60	.2861	.2687	.2523	.2367	.2221	.2083	.1953	.1830	.1713	.1604
−50	--------	--------	--------	--------	--------	--------	--------	.3446	.3240	.3045

$pd/d\theta$ at triple point (−56.602° C.)=0.3533 bars per ° C.

TABLE 17.—*Rate of change of vapor pressure with temperature for liquid carbon dioxide*

[In bars per ° C.]

° C.	0	1	2	3	4	5	6	7	8	9
−50	0.2775	0.2692	0.2610	0.2530	0.2452	0.2375	0.2300	0.2226	[1] 0.2154	[1] 0.2083
−40	.3698	.3598	.3500	.3404	.3309	.3216	.3124	.3034	.2946	.2860
−30	.4793	.4676	.4560	.4446	.4334	.4224	.4115	.4008	.3903	.3800
−20	.6070	.5934	.5800	.5667	.5537	.5408	.5282	.5157	.5034	.4913
−10	.7538	.7382	.7228	.7077	.6927	.6779	.6633	.6490	.6348	.6208
−0	.9218	.9039	.8863	.8690	.8518	.8350	.8183	.8019	.7856	.7696
0	.9218	.9399	.9582	.9768	.9957	1.0148	1.0343	1.0540	1.0741	1.0944
10	1.115	1.136	1.158	1.180	1.202	1.224	1.247	1.271	1.295	1.319
20	1.344	1.370	1.397	1.424	1.451	1.480	1.509	1.540	1.571	1.603
30	1.637	1.672	--------	--------	--------	--------	--------	--------	--------	--------

[1] Undercooled liquid.

Critical temperature=31.0° C.
$dp/d\theta$ at triple point (−56.602° C.)=0.2256 bars per ° C.

WASHINGTON, December 15, 1932.