A Dynamic Method for Determining the Vapor Pressure of Carbon Dioxide at 0 °C

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The vapor pressure of carbon dioxide at 0 °C, or at 0.01 °C, has been used as a fixed point on the pressure scale. Comparisons between laboratories may be affected equally by pressure measurements, temperature measurements, and the purity (and possibly isotope composition) of the sample. A dynamic method for establishing this pressure is described, utilizing a device similar to those used to realize the sulfur and steam points on the International Practical Temperature Scale. Advantages of the method include rapid establishment of equilibrium conditions, and the automatic purification of the carbon dioxide. Results obtained indicate a sample-to-sample reproducibility better than one part in 25,000. The method is suggested as being suitable for general use in realizing the CO_2 point of the pressure scale. This experiment yielded a value for the vapor pressure at 0 °C of 3.48516 MN m^{-2} or 26,140.8 mm Hg; at the triple point of water, 0.01 °C, it was 3.48608 MN m^{-2} or 26,147.7 mm Hg.

Key Words: Carbon dioxide, fixed point, hypsometer, pressure standard, purification, vapor pressure.

1. Introduction

The use of fixed points in pressure calibration work, besides having possible direct application in measurement problems, also provides a valuable check on the stability of the pressure scale as determined by piston gages or mercury manometers. One such fixed point is the vapor pressure of carbon dioxide at 0 °C. Six careful determinations of the "CO_2 point" have been made in the last forty years [1, 2, 3, 4, 5, 6] [1]. All of these determinations used a static method in which a pressure vessel containing purified CO_2 was placed in a cryostat of known temperature. The pressure was then measured when the vapor-liquid mixture reached an equilibrium pressure. The results of these six determinations, given later in table 3, show a scatter with a range of about 5 parts in 10,000. The precision of the individual investigations, however, was in each case reported to be 1 part in 10,000 or better. This seems to indicate that the static method is subject to systematic errors which can go undetected even in very careful work. The static method of measuring vapor pressure faces several problems: While the experimenter may use elaborate procedures to obtain pure CO_2, the samples may be contaminated after filling the pressure vessel, as by leaching materials from the walls. It is difficult to eliminate temperature

gradients between the bath, the thermometer, and the interface between the liquid and vapor phases. A microscopic real or virtual leak, as by temperature fluctuations in the portions of the sample in parts of the apparatus outside the bath, will shift the temperature of the interface. Such corrections as those for gas head, capillarity and head corrections, in a mercury separator between the CO_2 vapor and the fluid used in the piston gage, may contribute susbtantial random and systematic errors. The object of the present work, therefore, is to develop an independent method of making the measurement which is less subject to systematic error. This method is suggested as being suitable for general use in interlaboratory comparisons.

2. Apparatus for the Dynamic Measurement of the Vapor Pressure of CO_2

2.1. General

The apparatus is patterned after the device used to reproduce two fixed points on the International Practical Temperature Scale — the boiling point of water and the boiling point of sulfur, and described in detail by Stimson [7]. It is similar to the "hypsometer" used by physical chemists. A schematic drawing of the CO_2 point boiler or hypsometer is shown in figure 1. In operation, liquid CO_2 in the bottom of the hypsometer
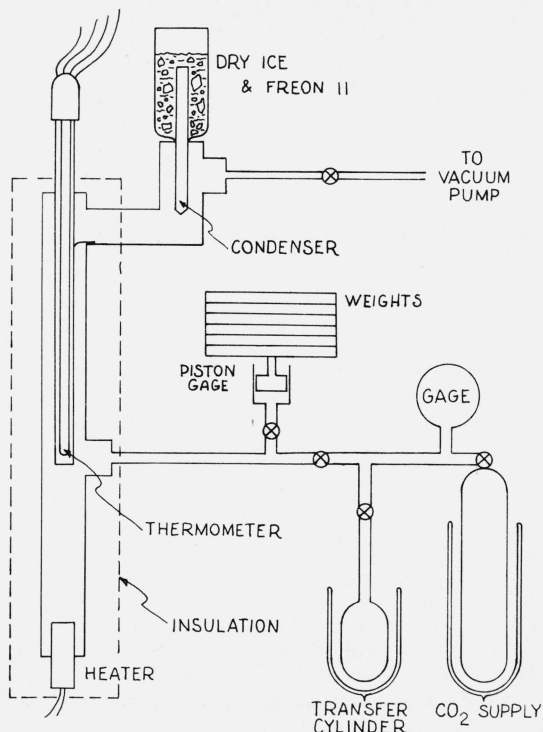
FIGURE 1. *Schematic diagram of apparatus.*

is heated to the boiling point. The rising CO_2 vapor condenses on a "cold finger" and the condensate flows down a thermometer well where the liquid and the vapor come into equilibrium and are in good thermal contact with the thermometer. The pressure at the same level is measured with a gas-lubricated piston gage operating on CO_2 directly without the need for the mercury manometer-separator used in the previous determinations.

The advantages of the dynamic method over the static method can be seen at this point. The vapor-liquid interface in the hypsometer is relatively large and is being continually renewed. This should allow for an easier attainment of equilibrium. Furthermore, the upward flow of CO_2 vapor should tend to concentrate the permanent gas impurities at the top of the hypsometer, and the condensate flowing down the thermometer well should be free of the nonvolatile impurities which remain in the liquid at the bottom of the hypsometer. Since the pressure and temperature are measured at substantially the same level, and the temperature gradient is in a horizontal run of the connecting line, there is no head correction.

2.2. The Construction of the Hypsometer

The essential parts of the hypsometer were constructed using 1-in stainless steel tubing (type 304, $\frac{1}{32}$-in wall thickness) and compression tube fittings. The apparatus was designed with the intention that it should be possible for any reasonably well-equipped

laboratory to assemble it from commercially available parts.

The thermometer well was made with $\frac{3}{8}$-in stainless steel tubing and was designed to hold a standard platinum-resistance thermometer, 18 inches long. The space surrounding the lower end of the thermometer was filled with liquid (Freon)[2] to improve thermal contact with the thermometer well. Stainless steel wire, 0.010-in diam, was wound around the lower two-thirds of the well, the turns separated by about one diameter of the wire. This served to slow down the flow of liquid and to provide good thermal contact between the thermometer well and both phases of the CO_2. During preliminary studies, the temperature distribution was explored with thermocouples to verify that the thermometer well was out of contact with the walls and that the liquid CO_2 from the condenser flowed down the thermometer well.

A brass reentrant plug was machined to fit a compression union. The plug was bored so that a standard 110 V, 50 W soldering element would just fit inside. The space between the interior of the plug and the heater was filled with rosin to hold the heater in position and provide thermal contact. The reentrant part of the heater plug was wound tightly over its full length with type 304, 0.010-in diam, stainless steel wire to trap gas bubbles, thereby preventing superheating of the liquid CO_2. A column of about 1 in of packing composed of very small coils of wire was placed between Nichrome screens just above the heater to act as a radiation shield between the heater and the thermometer and to further promote uniform boiling. The packing above the liquid level serves as a short fractionating column.

The condenser consisted of a brass rod, $\frac{1}{2}$-in diam, extending about 6 in down into the hypsometer from a reducing union. A polyethylene bottle with its bottom cut off, was fitted on the upper portion of the brass rod. In operation, the condenser was cooled by filling the bottle with a mixture of Freon 11 and dry ice.

The hypsometer, insulated with about two inches of styrofoam, was placed in a 15-gal ice bath. The external connections to the supply cylinders and the piston gage were made with $\frac{1}{4}$-in copper tubing and standard flare fittings. The small transfer cylinder shown in figure 1 has a volume of about 1200 ml. The volume of the hypsometer itself was calculated to be roughly 400 ml.

2.3. The Temperature and Pressure Measurements

The platinum-resistance thermometer used was a four-lead thermometer constructed by C. H. Myers. Its resistance was measured with a Mueller temperature bridge. The bridge had been modified by adding a 0.00001 Ω dial and by adding a bridge power supply with provision for variation of the bridge current and

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[2] Certain commercial products are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products or equipment identified are necessarily the best available for the purpose.

for guarding both the power supply and the galvanometer. The bridge balance was determined using a galvanometer-phototube amplifier. The galvanometer had sufficient sensitivity, with a thermometer current of 1 mA, for interpolation to 1 $\mu\Omega$ using the 0.00001 Ω dial, if desired.

The piston gage used in the measurements was one of the two NBS controlled-clearance, air-lubricated piston gages. These piston gages are regarded as primary pressure standards between 1 and 35 atm and

are described briefly by Lloyd and Johnson [8]. The controlled-clearance piston gage, in general, is discussed by Johnson and Newhall [9].

A sectional view of the piston gage is shown in figure 2. The piston, 1 in in diameter, is made from Carboloy. The weights used were 50-, 10-, and 1-lb stainless steel weights. Their masses were known to about 1 ppm (part per million). At the pressure of the CO_2 point, the sensitivity of the piston gage had been previously observed to be about 1 ppm.
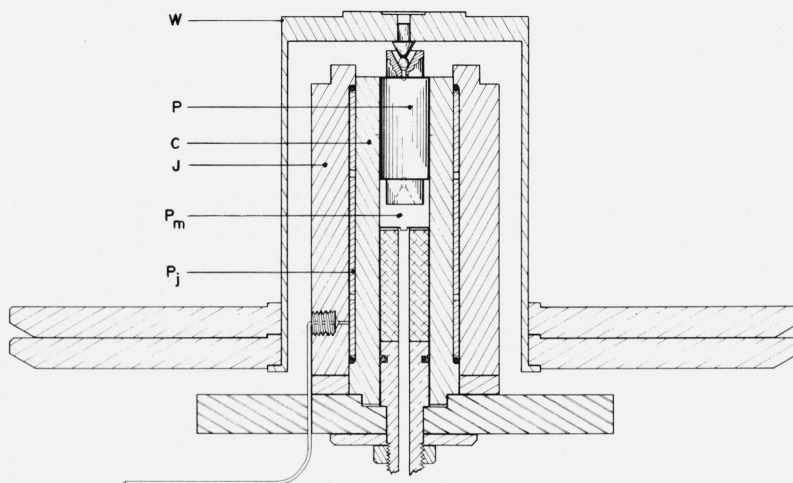

FIGURE 2. *Controlled-clearance piston gage.*
W. Weights; P, Piston; C, Cylinder; J, Jacket; P_m, Pressure to be measured; P_j, Jacket Pressure, adjusted to control clearance between piston and cylinder.

The uncertainties of the measurement are believed not to exceed the following:

	Systematic	Random
	Parts per million	
Piston gage parameters	30	
Mass and density of weights		
Piston area		
Elastic deformation		
Estimate of clearance	3	
Thermal expansion of piston	17	
Atmospheric pressure		3
Air density		1
Local gravity		
Temperature measurements—Hypsometer		
Thermometer self-heating		1
Bridge balance		5
Change of contact resistance		3
Measurements with triple-point cell		
Realization of triple point	5	
Bridge balance		3
Change of contact resistance		3
Total systematic error	55	
Resultant random error		8

Here the systematic errors are those which apply to all measurements made with this combination of

instruments, and are not reduced by replication of the experiment. The random errors are those which are believed to be independent of each other and of the systematic errors; they are combined as the square root of the sum of the squares. The total uncertainty would be about 56 ppm, or about 1.5 mm Hg.

3. Experimental Procedure

3.1. Purification and Filling

One of the features desired for a fixed point procedure is that reproducible results be obtainable with material which is readily obtainable, and any necessary purification be done by methods within the resources of the ordinary standards or research laboratory. The pressure to be realized from the fixed point should be insensitive to residual impurities in the range covered by the procedure.

Accordingly commercial carbon dioxide in 20-lb cylinders was used in this experiment. The cylinder of CO_2 was set in an insulated container and the lower half cooled with dry ice until the pressure in the cylinder had fallen to the triple point. In the meantime the apparatus, at room temperature, was evacuated to a pressure of about 1 mm Hg, and then

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rinsed by a flow of gas drawn from the top of the supply cylinder. During this time the supply pressure dropped to just above the atmospheric pressure, so that most of the CO_2 was in the solid form. The apparatus was again evacuated. The transfer cylinder was cooled below the temperature of the supply tank, and filled with CO_2. About 12 hr were required. Then the transfer cylinder was warmed to room temperature and the apparatus filled to a pressure of about 60 bars. Most of the permanent gas impurities were believed removed from the supply tank and the apparatus during the rinsing.

During the preliminary operations, the apparatus was filled several times, and the carbon dioxide in the supply tank was melted and frozen three times. While a small amount of permanent gas may have been entrapped in the CO_2 crystals in the first freezing, this would be released on melting, and removed on the next cycle. By the time the apparatus was filled for the first run, the CO_2 must have been quite free of permanent gas impurities. Most of the condensible impurities were retained in the supply cylinder during the sublimation. The content of water vapor, which might be particularly troublesome, is greatly reduced by sublimation, since at $-78\ °C$ the ratio of the vapor pressure of water to that of carbon dioxide is about 1 to 10^6, as compared with about 1 to 5700 at $0\ °C$.

3.2. Vapor Pressure Measurements

These were performed as follows: Ice was packed into the bath around the hypsometer, dry ice and Freon 11 (monofluoro-trichloromethane, used because it is nontoxic, nonflammable, and does not foam if dry ice is added rapidly) was put into the condenser, and the heater power adjusted until the hypsometer temperature was approximately 0 °C. This power, about 40 W, was such that the CO_2 was vaporized at a rate on the order of $1/2$ liter per hour. This was sufficient to provide a thin layer of condensed liquid flowing over the entire external surface of the thermometer well. Several hours were allowed to establish a steady state. The piston gage was leveled, and the pressure in the jacket set at the optimum value as determined from the calibration curves of the gage. The weights corresponding to a desired pressure were placed on the piston, and the piston and weight assembly then rotated by hand. The valve connecting the piston and the hypsometer was opened. The heater power was increased slightly until the piston gage lifted and was in a "floating" condition; that is, until the vapor pressure of the CO_2 equaled that determined by the piston gage. While the piston gage was floating, the temperature at the bottom of the thermometer well was determined with the platinum resistance thermometer. It was found necessary to make small adjustments in heater power to maintain the piston gage in a floating condition during the 20 to 30 min required for making a series of normal and reversed readings with the thermometer bridge. By removing a 1-lb weight from the piston gage, the above process could be repeated at another pressure.

In this manner, the temperatures corresponding to four different vapor pressures near the ice point were determined.

The other four sets of vapor pressure measurements were made to determine the effect of varying the CO_2 flow rate within the hypsometer and to investigate the effect of using unpurified CO_2.

For these runs, a fresh cylinder of commerical CO_2 was used. This gas had been produced by the decomposition of limestone. The supplier's estimate of the impurity content was as follows:

Nitrogen	0.1%
Oxygen	.03%
Argon	.001%
Water	.002% or less
Oil	.0004%, approx.

Runs 2 and 3 were made with gas drawn from this supply cylinder at room temperature with no purification of any kind.

For run 2 the measurements were made at the same flow rate as for run 1. For run 3, the area of the cold finger in contact with the cooling mixture was reduced. The heater power, and the flow of liquid were reduced by approximately a factor of ten. The reduced flow was maintained for run 4 but the unpurified CO_2 was discarded and the hypsometer refilled with CO_2 sublimed from the supply cylinder in the manner described above. Finally, for run 5 the sublimed CO_2 was used with the full cooling power and flow rate.

The piston gage temperature and the atmospheric pressure were recorded before and after each vapor pressure measurement, and the platinum-resistance thermometer was calibrated before and after each set of measurements, using a water triple-point cell prepared in the standard manner. The data reduction procedure for the piston gage was that given by Cross [10]. The vapor pressure at 0 °C was found for each of the five sets of measurements by fitting the pressure to a quadratic equation in the temperature using the OMNITAB least squares solution [11].

4. Results

The experimental data are shown in table 1. For each observation the temperature value is the mean of five to ten readings made while the pressure was under the control of the piston gage. The residuals are the deviations of these observations from the smooth quadratic curve.

Two parameters of the quadratic fits for the five runs, i.e., the pressures at 0 °C and the slopes, are summarized in tables 2 and 3. In these tables the standard deviations represent the precision of the pressure at 0 °C for each run, as calculated from the residuals of table 1.

Table 2 compares the results with three samples of CO_2. Run 2, made with gas containing more than 0.13 percent impurities agreed quite closely with runs 1 and 5, made with gas which was relatively pure.

TABLE 1. *The experimental results*

T(°C)*	P (bars)	P (mmHg)	Residuals (mmHg)
Run No. 1, sublimed CO₂, normal flow			
0.21511	35.0515	26290.8	−0.1
.11991	34.9633	26224.6	+0.2
.02516	34.8751	26158.5	−0.2
−.07146	34.7868	26092.3	+0.1
Run No. 2, CO₂ not purified, normal flow			
0.21422	35.0488	26288.8	+0.1
.11923	34.9609	26222.8	−0.1
.02404	34.8732	26157.1	−0.1
−.07094	34.7862	26091.8	−0.2
−.16632	34.7000	26027.1	+0.5
−.26131	34.6126	25961.6	−0.2
Run No. 3, CO₂ not purified, reduced flow			
0.12189	34.9644	26225.4	0.0
.02739	34.8774	26160.2	+0.1
−.06769	34.7899	26094.6	0.0
−.16297	34.7027	26029.2	0.0
−.25875	34.6154	25963.7	0.0
Run No. 4, sublimed CO₂, reduced flow			
0.20062	35.0353	26278.7	−0.4
.00995	34.8583	26145.9	+1.8
−.08011	34.7705	26080.0	−1.0
−.17460	34.6831	26014.5	−1.2
−.27284	34.5958	25949.0	C.8
Run No. 5, sublimed CO₂, normal flow			
0.20486	35.0398	26282.0	−0.2
.11046	34.9526	26216.6	−0.2
.01577	34.8654	26151.2	0.0
−.07942	34.7778	26085.6	0.0
−.17450	34.6904	26020.0	0.0
−.27077	34.6022	25953.8	0.0
.01596	34.8658	26151.5	+0.1
.20595	35.0414	26283.2	+0.2

*Means of five to ten temperature observations at each pressure.

TABLE 2. *Observed values for the vapor pressure of carbon dioxide at 0 °C*

Run No.	Pressure (bars)	(mmHg)	Std. dev. of pres. (mmHg)	Slope (mmHg/ °C)	Std. dev. of slope (mmHg/ °C)
1	34.8523	26141.4	0.24	689.7	3.1
2	34.8514	26140.7	0.21	687.9	0.9
5	34.8510	26140.4	0.09	690.9	0.4
Mean	34.8516	26140.8		689.5	

TABLE 3. *Test at reduced flow rates*

Run No.	Pressure (bars)	(mmHg)	Std. dev. of pres. (mmHg)	Slope (mmHg/ °C)	Std. dev. of slope (mmHg/ °C)
3	34.8520	26141.2	0.04	689.5	0.4
4	34.8466	26137.1	1.24	701.3	5.5

Table 3 shows the effect of reducing the CO₂ flow rate by a factor of ten. Run 4 was relatively erratic and gave a low mean pressure, compatible with intermit-

tent coverage of the well with liquid. Since operation at this reduced flow rate is not to be recommended, both runs 3 and 4 were excluded from the result to be reported.

These results are compared with those of other authors in table 4. Much of the previous work was reported in mm Hg (the conventional mm Hg is the pressure corresponding to the height of a fluid of density 13.5951 g/cm², under normal gravity, 9.80665 m/sec²). The value, 26,132.2 reported by Roebuck and Cram was given in terms of the value 13.5955 for the density of mercury; here it has been adjusted to the conventional mm Hg. Michels et al., and Greig and Dadson reported the value at the triple point of water; the numbers in parentheses were calculated from the reported value and slope.

It is tempting to interpret the differences between the various measurements as indicating differences in the pressure scales of the laboratories. Thus, O. C. Bridgeman included data from ten piston gages, with calibrations made at the Massachusetts Institute of Technology from 1911 to 1926, and Meyers and Van Dusen included data gathered at the National Bureau of Standards between 1919 and 1931. But a close reading of the latter paper shows that more is involved.

TABLE 4. *Determinations of the CO₂ point to date*

Investigator	Year	Bars 0.00 °C	Millimeters of mercury 0.00 °C	Millimeters of mercury 0.01 °C	Reference
Bridgeman	1927	34.8567	26,144.7		[1]
Meyers and Van Dusen	1933				[2]
Equation			26,141.7		
MIT measurements			26,141.2		
NBS measurements		34.8498	26,139.5		
Roebuck and Cram	1933	34.8411	26,133.0		[3]
Michels, et al.	1950	(34.8467)	(26,137.2)	26,144.0	[4]
Edmister, et al.	1964	34.8499	26,139.6		[5]
Greig and Dadson	1966	(34.8472)	(26,137.6)	26,144.5	[6]
This paper	1966	34.8516	26,140.8	26,147.7	—

Three values taken from the paper of Meyers and Van Dusen are shown in the table. The first is from an equation which was chosen to represent the vapor pressure of the liquid over the full range from the triple point to the critical point. The form of this equation is largely determined by observations made during 1920 on two samples prepared the previous year. The second was measured during 1927 at MIT on NBS sample No. 1. The numerical value was not stated in the paper, but the point is plotted on the graph in which Meyers and Van Dusen compared the equation and their experimental results. The third value was observed during 1929 at the NBS on the same sample. It will be seen that the measurements at MIT on the NBS and MIT samples differ by twice as much as the measurements by the two laboratories on the NBS sample, and that the difference between the two laboratories was less than the estimated systematic errors (0.01% for the NBS) in the pressure measurements.

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The difficulties of realizing a temperature of 0.000 °C in an ice bath are substantial. The ice point is defined at the temperature of melting pure ice in contact with water which is saturated with air. Pure water is in equilibrium with pure ice at atmospheric pressure and a temperature of 0.003 °C. This temperature difference corresponds to 2.1 mm of mercury at the CO_2 point. Since freshly melted ice is free of air, the conditions of the definition are hard to realize. The investigators both at MIT and the NBS were fully aware of these difficulties and it is probable that their temperatures did not differ by more than 0.0005 °C.

Apparently, at least part of the difference between the values published by the two laboratories must be charged to the preparation of the samples of carbon dioxide. Both laboratories took elaborate precautions to avoid chemical contamination. The gas was obtained by decomposition of sodium bicarbonate, dried with P_2O_5, and then sublimed five to eight times. In addition, at the NBS, the liquid was cooled by evaporation several times to obtain the solid. While substantial amounts of chemical contaminants seem unlikely, the possibility of isotope separation cannot be ruled out.

Recent determinations of the CO_2 point, including those made in Europe [4, 6], are lower than this measurement by an amount which slightly exceeds the sum of the uncertainties estimated by the various authors. This difference may be systematic as between the static and dynamic methods. However, one point with regard to the gas-lubricated piston gage should be mentioned. Carbon dioxide cools substantially on expansion. If this cooling reduces the temperature of the piston significantly, the effective area would be decreased and the apparent pressure increased. Estimates based on the Joule-Thompson coefficient and thermal conductivity of CO_2, the rate of leak, and the clearance indicate that this effect would not exceed 0.1 deg in temperature or 2 ppm in the pressure. This point could be verified by operation of the piston gage with helium, which has a positive Joule-Thompson coefficient.

5. Conclusions

In the use of the vapor pressure of CO_2 as a means of calibration, at least three factors are of comparable importance, i.e., pressure measurement, temperature measurement, and preparation of the sample.

Measurement of the vapor pressure of CO_2 by the dynamic method appears to be insensitive to impurities, at least at the level found in commerically available CO_2 in gas cylinders. The use of a gas-lubricated piston gage eliminates the need of fluid or diaphragm separators with the associated possible systematic errors.

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