[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICS, HARVARD UNIVERSITY]

Pressure, Volume, Temperature Properties of Nitrogen at High Density. I. Results Obtained with a Weight Piezometer

BY MANSON BENEDICT[1]

Introduction

To advance our knowledge of the properties of the liquid and gaseous states of aggregation it is desirable to have pressure–volume–temperature data on at least one substance over as wide a range of temperature and pressure as is experimentally feasible. Recent work of several investigators on nitrogen makes it the best known of all gases. In addition to the low pressure data summarized in the "International Critical Tables,"[2] Bartlett and co-workers[3] have completed their measurements up to 1000 atm. in the temperature range −70 to +400°, and Michels and co-workers[4] have finished their very precise measurements up to a density of 560 Amagat units in the temperature range 0–150°. Bridgman[5] has recently measured the course of the freezing curve for nitrogen up to 5800 atm., and obtained fragmentary *P–V–T* data for it between 3000 and 5800 atm. At Professor Bridgman's suggestion, the writer has undertaken the measurement of the density of nitrogen over the pressure and temperature range not covered by Bartlett and Michels up to 5800 atm. and between 200° and the temperatures at which the fluid phase freezes.

In order to conform to the usage of Amagat, Bartlett and Michels, the results of this research have been expressed in Amagat units. That is, the unit of pressure is the international atmosphere, the unit of temperature is the degree centigrade and the unit of density (specific volume) is the density (specific volume) of nitrogen at 0°C. and a pressure of 1 int. atm. Since the normal density of nitrogen is 1.2506 g./ml., the conversion factor from Amagat units of density to g./ml. is 1.2506 g./ml./A. u.

The presentation of results has been organized according to the experimental method used in the measurement of density. In this first paper, hereafter to be referred to as I, are described measurements of gas density by a gravimetric method. Gas was confined in a weight piezometer of known volume at measured temperature and pressure. The piezometer filled with gas was weighed, the gas was released and the empty piezometer was weighed again to determine the mass of gas confined. Gas density was measured in this way at −100, −125, −150 and −183° at pressures between 100 and 1250 atm., and at 0° C. and 1550 atm.

In the second paper of this series, hereafter to be referred to as II,[5a] change in gas density from the point at 0° and 1550 atm. to other temperatures between −175 and 200° and other pressures between 980 and 5800 atm. was determined by a piston displacement method. Gas was confined in two communicating vessels; the upper of these was kept at room temperature, and the lower could be maintained at any temperature of interest. A gas-tight piston fitted to the upper cylinder was used to adjust gas pressure and to measure its change of density from one temperature and pressure to others.

Experimental

Source of Nitrogen.—Nitrogen was the commercial compressed product obtained by the fractional distillation of liquid air. Our gas was from an especially pure lot certified by its manufacturers, the Air Reduction Co., to contain less than 0.2% by volume of total impurity.

The purity of the gas was checked by determining its normal density. Gas at approximately 760 mm. was admitted to a Pyrex bulb equipped with stopcock and ground joint. The bulb was kept at 0.00° in an ice-bath. Pressure registered on a mercury manometer was read to 0.02 mm. with a vertical comparator sliding on a brass scale. Proper corrections were applied to reduce the mercury height to mm. of mercury at 0° and standard gravity. The volume of the bulb had been found to be 529.79 ± 0.02 ml. at 0° by weighing the distilled water contained. Mass of gas contained by the bulb was determined by weighing it, first filled with gas and then evacuated, against a sealed glass counterpoise of approximately equal mass, area and displacement. All brass weights used in this research were corrected for air buoyancy. No correction was applied for the small and uncertain contraction of the bulb on evacuation. The reliability of this procedure for determining the normal density was checked by a determination on dry air, as shown in Table I.

The observed difference in normal density between our nitrogen and pure nitrogen, 0.0002 ± 0.0004 g./ml., would be caused by 0.1% O_2. The only effect such im-

---

[1] National Research Fellow in Chemistry, 1935-1936.

[2] "International Critical Tables," Vol. III, p. 17.

[3] Bartlett, Hetherington, Kvalnes and Tremearne, THIS JOURNAL, **52**, 1374 (1930).

[4] Michels, Wouters and de Boer, *Physica*, **3**, 585 (1936).

[5] Bridgman, *Proc. Am. Acad. Arts Sci.*, **70** (1) (1935).

[5a] Benedict, THIS JOURNAL, **59**, 2233 (1937).

TABLE I

NORMAL DENSITY OF THE NITROGEN USED

Material	Obsd.	Normal density, g./ml. "I.C.T."[6]
Dry air	1.2934	1.2930
Nitrogen	1.2504 1.2512	1.2506

purity can have on the density of the compressed gas is to make it uniformly high by 0.02%. Since this is well within the limit of error of our other measurements, no further purification of the gas was attempted.

Experimental Procedure.—Figure 1 is a schematic diagram of the apparatus. For a gas density determination it was first flushed out three times with gas at tank pressure. Then pressure was increased somewhat above the desired value by compressors beyond A. These were the conventional separator and intensifier described by Bridgman.[7] The compressors could be shut off by the valve B. C is a pressure chamber containing the manganin resistance pressure gage D. The left arm of the steel "T" F communicated with nickel piezometer P through calibrated nickel capillary R. P was cooled to the desired temperature and maintained there by the cryostat Q. Pressure was adjusted to the desired value as indicated by the resistance gage D. Weights corresponding to this pressure were placed on the piston gage I, and oil pressure was generated by the injector J until the weights floated. Valve K was opened and final adjustment of gas pressure was made so that mercury just made contact at both needle points of the mercury U block G. Necessary small adjustments of mercury volume were made with the small injector H. Then valve B was closed permanently. If conditions of temperature and pressure remained unchanged for fifteen minutes, the capillary was clamped by the vise at E. The capillary was next cut off between E and F without loss of gas from P, and the cut end was sealed with silver solder. E could then be removed and the piezometer and gas weighed against a nickel counterpoise of approximately equal mass and area until the weight was constant within 0.3 mg. The nickel capillary was cut with music wire cutters, and after all gas had escaped the piezometer was again weighed against the counterpoise; no metal was lost in this operation.

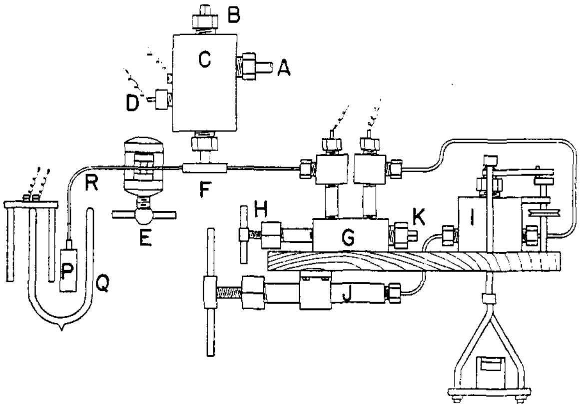

Fig. 1.—Apparatus assembly.

Closing off the capillary under pressure requires further comment. Before gas pressure was generated, the nickel capillary had been annealed at a bright red heat at the point where it was to be clamped. Figure 2 will make clear the method of closure. Two hardened steel dies, C and C′, aligned on opposite sides of the capillary by the steel guide, B, were pressed together between the vise jaws, A and A′. This flattened the capillary and sealed the hole in it against passage of gas. Successful closure depends mainly on the shape of the faces of the dies. The dies finally adopted had the following characteristics: They compressed the capillary over 1/4″ (6.4 mm.) of its length. When in contact they left a rectangular opening whose width was the diameter of the capillary and whose area was about 80% of the area of the metal in a section of the capillary. Too deep an opening would result in leakage; too wide or too shallow an opening would result in excessive deformation of the capillary, weakening it and causing it to burst under gas pressure upon release of the clamp. Leakage of gas from either cause was always tested for with soap suds. As finally perfected, this technique for closing the capillary under pressure was employed twenty-three times in succession without leakage of gas.

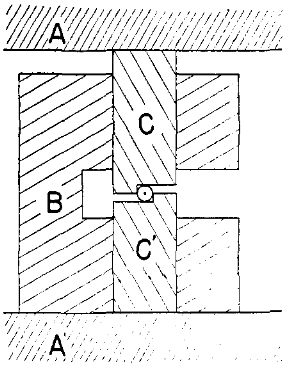

Fig. 2.—Method of clamping capillary.

In silver soldering the cut end of the capillary, two procedures were used. At densities of nitrogen below 550 A. u. the cut end was simply closed by a drop of silver solder. Gas at this density exerts a pressure of about 1600 atm. at 25°. At densities higher than 550 A. u. the higher pressures generated when the gas was warmed to 25° in the balance case would either stretch or burst the piezometer; hence, a different method of sealing the cut end was required. A polished nickel weighing tube (G, Fig. 3), kindly furnished us by Professor G. Dietrichson of M. I. T., was silver soldered over the end of the cut capillary so that when the clamp was released the pressure of nitrogen would be reduced to less than 200 atm. without loss of gas.

Production and Measurement of Constant Temperature.—0.0° was produced in a felt-covered iron container filled with finely chopped ice and distilled water.

Temperatures of −100, −125 and −150° were produced in the stirred bath of liquefied propane described by Bridgman.[5] For the present work better thermostatic control was necessary. This was attained as follows: liquid air was aspirated through the cooling coil at a constant rate to produce a temperature decrease,

---

(6) "International Critical Tables," Vol. 1, p. 102.

(7) P. W. Bridgman, "The Physics of High Pressures," The Macmillan Co., New York, 1931, Chap. II.

if uncompensated, of about 0.5° per minute. Sufficient electrical energy to maintain a constant bath temperature was supplied to a coil of nichrome wire placed in the propane next to the cooling coil. The energy input was regulated by means of a "Hytemco" resistance thermometer and a thyratron temperature control circuit described elsewhere.[8] Bath temperature varied less than 0.1° in fifteen minutes, the time required to ensure temperature equilibrium with the piezometer contents. Exploration with the thermocouple described below disclosed no temperature variation greater than 0.1° throughout the useful space of the cryostat.

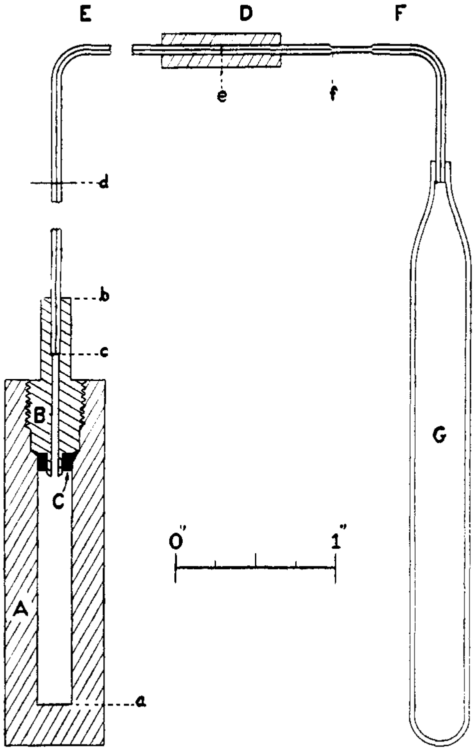

Fig. 3.—Detail of piezometer ready for weighing: A, B, C, piezometer; E, F, capillary tubing; D, connecting sleeve; G, expansion tube.

Section	Volume, ml. at S. T. P.	Length, cm.
ab	1.0778	
bc	0.0185	0.96
ce	.0100	21.95
cd(calcd.)	.0041	9.0
cf	.0161 ±	
ef	.0009 ±	1.8 ±

Temperature was measured by a four-junction, copper–constantan thermocouple whose cold junctions were exposed directly to the propane 12 cm. below its surface and within 5 mm. of the piezometer. Crushed ice and distilled water in a Dewar vessel was used for a reference temperature.

The e. m. f. of the thermocouple was measured to 1 μv. by a calibrated Leeds and Northrup Type K potentiometer; 1 μv. corresponds to 0.015° in the least sensitive range of the thermocouple. The thermocouple was calibrated against boiling nitrogen, boiling oxygen, subliming carbon dioxide, freezing mercury and, in a water-bath, against a calibrated thermometer at 25°. Precautions were taken at each calibration point to ensure a knowledge of its temperature to 0.05°. At each point the thermocouple could be moved 2 cm. without changing the e. m. f. more than 2 μv. In calibrating the thermocouple and using it for temperature measurement, the same portion of wire was exposed to the principal thermal gradient.

TABLE II

RESULTS OF THERMOCOUPLE CALIBRATIONS

Point	Month	E obsd., μv.	Temp., °C.	ΔE obsd., μv.	ΔE calcd., μv.
N_2	8/35	−22,284	−195.65	−398	−405
	1/37	−22,290	−195.65	−404	
O_2	8/35	−21,400	−182.78	−382	−383
	12/36	−21,419	−182.84	−397	
	1/37	−21,400	−182.72	−386	
CO_2	8/35	−11,012	− 78.30	−156	−161
	2/37	−11,030	− 78.43	−159	
Hg	9/35	− 5,782	− 38.87	− 78	− 75
	8/35	+ 3,952	+ 24.68	+ 48	+ 40

The results of all calibrations are given in Table II and can be expressed by the equation

$$\Delta E(\text{calcd.}) = -32 \times 10^{-8}E^2(\text{obsd.}) + 111 \times 10^{-4}E(\text{obsd.}) \quad (1)$$

ΔE is the difference E(obsd.) − $4E$(standard), where the standard e. m. f.'s are taken from Adams'[9] values. All e. m. f.'s are in microvolts. From the internal agreement of the various calibrations the maximum uncertainty in the temperature measured in this way is estimated to be 0.1° between 25 and −183°. The maximum uncertainty in the actual temperature of the piezometer is estimated to be 0.2°.

−183° was produced for density measurements in the same manner as for thermocouple calibration, in a bath of boiling oxygen.

Measurement of Pressure. (a) **Dead Weight Piston Gage.**— Gas pressure below 1000 atm. was measured with the M. I. T.-type dead

---

[8] Benedict, *Rev. Sci. Instruments*, **8**, 252 (1937).

[9] "International Critical Tables," Vol. I, p. 58.

weight piston gage. We are greatly indebted to Professors Keyes and Beattie of that institution who kindly lent us this instrument. The particular piston and cylinder combination used had the M. I. T. serial number 49; its calibrations have been described by Beattie and Bridgeman.[10] The constant of the piston gage was taken as 4.140 mm. per g. of brass in air. This result is based on Bridgeman's[11] value 34.4009 atm. for the vapor pressure of carbon dioxide at 0°. The gage constant given above has been extrapolated with respect to time from the last calibration made in 1931, and is probably correct to 0.1% up to 1500 atm. The mercury U-block (G, Fig. 1) has been described by Keyes.[12] 0.25 watt neon glowers in series with 1 megohm and 110 v. were used to detect contact.

The piston gage was sensitive to 2 g. or 0.01 atm. over the entire range of pressure. The weights and accessories loading the piston were calibrated by comparison against standards of the Research Laboratory of Physical Chemistry at M. I. T. If W is the total mass of brass in air loading the piston, P the pressure in int. atm. is given by

$$P = W\frac{4.140}{760}\,[1 + 2.2{\cdot}10^{-5}(30 - t)]\;\frac{980.397}{980.665} + B \qquad (2)$$

In this equation 2.2×10^{-5} is twice the coefficient of linear expansion of steel, t is the room temperature in °C., 30 is the temperature at which the gage was calibrated, 980.397 is the acceleration of gravity at the laboratory, 980.665 is the standard acceleration of gravity, and B is the barometric pressure in int. atm. In use with the apparatus of Fig. 1, no correction was applied for heads of oil, mercury or nitrogen, since the maximum effect of their respective lengths of 0, 0.0, and 30 cm. is 0.02 atm.

(b) **Manganin Resistance Gage.**—Gas pressure in excess of 980 atm. was measured with manganin resistance gage 5 of the type used by Bridgman.[5] The gage consisted of a 150 ohm coil of #40 double silk covered manganin wire of recent American manufacture obtained from Driver Harris and Co. The wire was wound non-inductively on a lacquered brass core. One end was soldered to a hardened steel electrode leading out of the pressure chamber through gas tight and electrically insulating packing of the type described by Bridgman.[7] The other end of the wire was soldered to a spring terminal piece which was forced firmly against the interior of the steel pressure chamber when the packing around the electrode was compressed. The connections to the coil were tested by short circuiting it at the ends of the manganin wire and exposing it to 6000 atm. gas pressure. The short circuited coil and connections showed a resistance change equivalent to −1.5 atm. in 6000 atm. Before use the coil had been seasoned by baking for a week at 140° and then by exposure to 11,000 atm. kerosene pressure.

The resistance of the coil was measured on a Carey Foster bridge. A 150-ohm coil identical in all particulars with the gage coil, sealed in brass and placed in an oil-bath surrounding the pressure chamber, was used for a compensating coil. Change in resistance of the gage coil with pressure was measured with the slide wire of the bridge. This could be estimated to 0.1 mm. Two slide wires were used; on the one employed below 1000 atm. 0.1 mm. corresponded to 0.5 atm.; on the one used for higher pressure, to 1.8 atm.

Bridgman[13] has compared a manganin resistance gage, made from wire manufactured in Germany probably before 1900, with a piston gage sensitive to 10 atm. up to 13,000 atm. He found their indicated pressures proportional within the sensitivity of his measurements. He proposed the use of the freezing pressure of mercury at 0° as the sole calibration point necessary for the manganin resistance gage, and he found the pressure at this point to be 7395[14] atm. on the scale of his piston gage. Then P_M, the pressure on the manganin scale, may be calculated from the resistance R_P of the manganin resistance gage by eq. (3).

$$P_M = \frac{\alpha}{R_0}(R_P - R_0);\quad \alpha = \frac{7395R_0}{R_{Hg} - R_0} \qquad (3)$$

Here R_{Hg} is the resistance of the gage at the freezing pressure of mercury at 0°, R_0 is its resistance at zero pressure.

The constant α of resistance gage 5 was determined by comparison with another resistance gage B of the original German manganin at pressures between 1000 and 10,000 atm. Each gage read the same pressure scale within a probable error of 0.07%. The difference in manganin of the two gages therefore does not appear to be significant. α for gage B was determined by

---

[10] Beattie and Bridgeman, *Ann. Physik*, [5] **12**, 827 (1932).

[11] Bridgeman, THIS JOURNAL, **49**, 1174 (1927).

[12] Keyes, *Proc. Am. Acad. Arts Sci.*, **68** (12), 505 (1933).

[13] Bridgman, *ibid.*, **47**, 321 (1911).

[14] Bridgman, *ibid.*, **47**, 347 (1911).

calibration against freezing mercury. In order to study the deviation of P_M from P, the absolute pressure, gages 5 and B were each compared with the piston gage over the pressure range accessible to the latter. The results are given in Table III. The column $P - P_M$ (calcd.) was calculated from eq. (4).

$$P - P_M = 0.011\, P_M \log 7395/P_M \qquad (4)$$

Equation (4) is based on the assumptions (1) that the freezing pressure of mercury is 7395 atm. absolute pressure, and (2) that no differences between P and P_M much greater than 10 atm. are to be expected between 1500 and 7400 atm. In the absence of a comparison at high pressures of the manganin resistance gage and a piston gage more sensitive than 10 atm., we will use eq. (4) to express the difference between the pressure scales. Without correction the maximum error of the manganin gage predicted by eq. (4) would be 13 atm. at 2500 atm. The maximum possible error in absolute pressure calculated by eq. (3) and (4) is estimated to be 0.2% up to 2000 atm. and 0.3% from 2000 to 7400 atm.

TABLE III

COMPARISON OF MANGANIN RESISTANCE GAGES WITH PISTON GAGE

P, atm.	$P - P_M$ gage B, atm.	$P - P_M$ gage 5, atm.	$P - P_M$ calcd, atm.
100		1 ± 1	2
230		3 ± 1	4
360		4 ± 0	5
500	6 ± 1	6 ± 1	6
620		7 ± 0	7
740		8 ± 1	8
860		9 ± 1	9
1000	8 ± 2	11 ± 3	10
1500	12 ± 0		12

Measurement of Densities.—All densities reported in this paper were determined in the weight piezometer P of Fig. 1, illustrated in detail in Fig. 3. The body of the piezometer A and the closure piece B were turned from pure nickel, and all interior surfaces were highly polished. Pressure tight closure was effected by heating the assembled piezometer upside down in an atmosphere of hydrogen at 1200°. The copper washer C melted and welded A and B together. After welding, the nickel was very soft; its elastic limit was raised by stretching the piezometer under a gas pressure of 2200 atm. The stretching also gave a test for tightness against gas pressure. In subsequent measurements the internal pressure never exceeded 1800 atm.; this pressure produced no further permanent deformation of the piezometer. When proved tight the exterior of the piezometer was polished and the threads sealed against external moisture with glyptal.

The volume contained by the piezometer between the points a and b, Fig. 3, was determined by weighing the water contained. The water for this purpose was deaerated by the method of Keyes[12] and distilled into the bottle *in vacuo*. After each filling, absence of air in the piezometer was checked as follows: a glass capillary and rubber connector filled with boiled water were attached at D. Piezometer and capillary were placed in a vacuum chamber, and pressure was reduced to 150 mm. If the meniscus in the capillary displaced less than 0.0002 cm.^{3} during pressure reduction, air was assumed absent. The slight difference of volume before and after measurements as given in Table IV is probably without significance.

TABLE IV

VOLUME CONTAINED BY PIEZOMETER

Date	5/36	1/37
Vol. at 0° and 1 atm., ml.	1.0781 1.0782 1.0778	1.0770
Average vol., ml.	1.0778 ± 0.0004	

The volume contained by the piezometer at temperatures other than 0° was estimated by the formula given in the International Critical Tables[15] for the coefficient of linear expansion of nickel between 0° and $t°$ with the following results

Temperature, °C	−100	−125	−150	−183
Dec. in vol. from 0°, ΔV_t, ml.	0.0035	0.0043	0.0050	0.0059

ΔV_t is probably accurate to 0.0001 ml.

The stretch of the piezometer with pressure was estimated from the equation given by Love,[16] which holds strictly for long, narrow, thin-walled cylinders. This equation when applied to such a cylindrical vessel under P internal pressure and 0 external pressure takes the form

$$\Delta V_P = \frac{VP}{E(r_0^2 - r_1^2)} [3(1 - 2\sigma)r^2_1 + 2r^2_0(1 + \sigma)] \qquad (5)$$

ΔV_P is the increase in internal volume, V is the internal volume of the cylinder at 0 pressure, E is Young's modulus in the same units as P, σ is Poisson's ratio, and r_0 and r_1 are, respectively,

---

(15) "International Critical Tables," Vol. II, p. 461.

(16) A. E. H. Love, "Mathematical Theory of Elasticity," Cambridge University Press, London, 1927, p. 145.

the external and internal radii of the cylinder. In the present instance

$r_0 = {}^5/_{16}''$ $\sigma^{17} = 0.33$
$r_1 = {}^7/_{64}''$ $E^{17} = 2.1 \times 10^6$ atm.

Hence, $\Delta V_P/P = 1.6 \times 10^{-6}$ ml./atm. In the absence of data on E and σ at low temperatures, this expression is assumed to hold at −100° to −183° as well as at 0°. In view of this questionable assumption and the uncertainty in the applicability of (5) to a thick-walled cylinder, ΔV_P is estimated to be uncertain by 25%, or 0.0006 ml. at the highest pressure.

The piezometer was connected to the pressure gages by about 25 cm. of cold drawn seamless nickel tubing, 1.6 mm. o. d. and 0.25 mm. i. d. The internal volumes of 40-cm. lengths of tubing cut consecutively from a longer portion were determined by weighing the mercury contained. The results showed that its cross section varied less than 0.00002 sq. cm. per 40 cm. of length. Connections to the capillary were made with silver solder. In fact, nickel was chosen for piezometer and capillary because of the ease with which strong tight joints could be made on it with silver solder.

The volumes involved in calculating gas density are illustrated in Fig. 3. The volume contained by E below the cryostat level, V_{cd}, was assumed to be

$$V_{\text{cd}} = V_{\text{ce}}(\text{cd}/\text{ce}) \qquad (6)$$

The total volume contained by capillaries E and F up to the beginning of the clamped portion f and by the nickel sleeve D, V_{cf}, was determined by waxing the point C to a capillary gas buret. V_{cf} was inferred from the change in pressure of the air in the buret when a known volume of the air was forced into the capillary. Three determinations for a particular capillary F gave $V_{\text{cf}} = 0.0161 \pm 0.0002$ ml. At each gas density determination F was replaced, and the new capillary necessarily had slightly different internal and external diameters and a slightly different length ef. The small correction to V_{cf} for variation in dimensions of D was calculated in the obvious manner, and never exceeded 0.0008 ml. The two volumes required in calculating gas density are the volume at cryostat temperature V_1, and the volume at room temperature V_2. $V_1 = V_{\text{ab}} - V_{\text{bc}} + V_{\text{cd}} = 1.0634$ ml., and $V_2 = V_{\text{cf}} - V_{\text{cd}} \pm$ small correction to $D = 0.0120$ ml. ± small correction.

If W be the weight of gas confined in the piezometer up to the point f, d_1 the density at cryostat temperature t and pressure P, and d_2 the density at 25° and P

$$d_1 = \frac{W - V_2d_2 + 0.0012}{V_1 - \Delta V_t + \Delta V_p} \qquad (7)$$

d_2 was obtained from the recent work of Michels[4] and collaborators.

Air buoyancy corrections on the piezometer assembly were inappreciable since allowance was made for residual gas in piezometer and nickel expansion tube G, Fig. 3. The expansion tube contained 4 ml. of extraneous air in the "full" weighing and 4 ml. of residual nitrogen in the "empty" weighing, each at 1 atm. pressure. The difference of 0.1 mg. between their weights was neglected. However, the piezometer contained 1.07 ml. of residual nitrogen in the "empty" weighing; the correction of +1.2 mg. for it appears in equation (7).

Discussion of Errors.—In eq. (7) the maximum error anticipated in W is 0.6 mg. The separate uncertainties in V_2, V_1, ΔV_t and ΔV_P introduced a total maximum error in d_1 of about 0.08% at low pressures and 0.12% at high pressures. The effect of these errors and those previously estimated in temperature and pressure may be expressed most concisely by their total effect on the measured density. The maximum error anticipated in each individual density determination of this paper is 2.0 A. u. The basis for this estimate will be clear from Table V, which gives the effect of errors in mass, volume, temperature and pressure on the two extreme densities.

TABLE V

EFFECT OF ERRORS ON EXTREME DENSITIES

Temperature. °C.	−100		−183	
Pressure, atm.	99.90		1252	
Density, A. u.	221.9		749.5	
	Max. error	Effect on density, A. u.	Max. error	Effect on density, A. u.
Mass, mg.	0.6	0.5	0.6	0.5
Volume	.08%	.2	.12%	.9
Temperature	.2° C.	.9	.05°C.	.1
Pressure	.02 atm.	.0	3 atm.	.2
Normal density of gas	.04%	.1	0.04%	.3
Total error in density, A. u.		1.7		2.0

Since all data given in the next paper are referred to the density at 1550 atm. and 0°, greater accuracy was sought here. It was attained by making five determinations of this point. Thereby errors in weighing and V_2 were largely elimi-

---

(17) "International Critical Tables," Vol. II, p. 480.

nated. With allowance for probable errors in V_1, pressure scale and normal density, the net probable error in this reference density was 0.09%.

Results

The results of density determinations on nitrogen with the weight piezometer are summarized in Table VI. Correction of each entry to nominal temperature was made with a rough estimate of change in density with temperature taken from the data themselves; the corrected results have not been smoothed. At 0° the densities were corrected to 1550 atm. by using 0.11 A. u./atm. for $(\partial d/\partial P)_T$; this value was obtained from the high pressure data to be given in the next paper. Points for which the expansion tube was used are denoted by an asterisk.

Equation of State.—To facilitate interpolation and differentiation of the low temperature data and to correlate with the results of other investigations in neighboring pressure and temperature ranges, an equation of state was fitted to all P–V–T data available in the temperature range −45 to −208° and in the density range 210 to 750 A. u. The data thus treated include Bartlett's[3] isotherms at −50 and −70°; four points at the high pressure end of Holborn and Otto's isotherms[18] at −100 and −130°; a number of points at the high pressure end of Onnes and van Urk's[19] isotherms at −131.27, −141.53, −144.46 and −146.32°; the density of liquid nitrogen[20] under its vapor pressure between −208.36° and the critical point at −147.13°;[21] points at pressures above 980 atm. given in the following paper in this series (II) at −45, −70, −100, −125, −150 and −175°; and the low temperature points of Table VI. The equation finally adopted was

$$PV = A + \beta d \qquad (8)$$
$$\beta = p + qd + rd^4 + (T/100)(s + td + ud^2) + (100/T)v + (100/T)^3 d^3 w\, 10^{-xd^2}$$

A is the ideal gas term; in Amagat units $A = 1.00046\ T/T_0$. T is the absolute temperature and T_0 is the absolute temperature of the ice-point, here assumed to be 273.20°K. P is the pressure in atm., V is the volume in A. u. and $10^3 d$ is the density in A. u. The numerical values of the constants are

$p = -1.66453$ $s = 0.67617$ $v = -1.21342$
$q = -1.35938$ $t = 0.91512$ $w = 107.03$
$r = 11.3200$ $u = 2.06932$ $x = 6.975$

The form chosen for the equation of state was dictated by the following considerations. Despite the necessity for using nine constants, the equation can be integrated or differentiated easily with respect to T or d. In the neighborhood of the critical point it is impossible to represent the density or volume as a single-valued analytic function of the pressure and temperature. Hence, it was necessary to use the less convenient representation of the pressure as an explicit function of the temperature and density. Michels[22] has found that the "virial" form of the equation of

TABLE VI

RESULTS OF DENSITY DETERMINATIONS WITH WEIGHT PIEZOMETER

Temperature, 0.0°; nominal pressure, 1550 atm.

Date	Pressure, atm.	Density, A. u.	Density corrected to nominal pressure, A. u.
5/5/36	1558	558.6	557.7
5/6/36	1555	559.1	558.6
5/6/36	1563	559.8	558.4
6/1/36	1550	558.7	558.7
1/17/37	1556	559.7	559.0*
		Average	558.5 ± 0.3

Temp., °C.	Pressure atm.	Density, A. u.	Density corrected to nominal temp., A. u.	Density from eq. of state, A. u.
		Nominal Temperature, −100.0°		
− 99.9	99.90	221.5	221.9	223.0
−100.2	149.94	318.2	317.4	318.2
− 99.9	202.02	374.4	374.7	376.7
−100.2	299.85	440.8	440.3	440.6
−100.1	399.73	480.4	480.2*	481.3
− 99.9	699.85	555.6	555.8*	554.7
		Nominal Temperature, −125.0°		
−124.8	99.89	332.1	(333.2)	351.3
−125.1	149.92	420.2	419.8	420.6
−124.8	201.90	460.8	461.4	459.3
−124.9	399.73	535.3	535.5*	535.7
−124.8	699.85	596.1	596.4*	596.1
		Nominal Temperature, −150.0°		
−150.4	99.90	495.9	493.3	493.0
−149.8	200.00	538.6	539.2*	540.3
−150.0	399.77	593.2	593.2*	592.5
−149.7	699.82	639.3	639.9*	639.7
		Nominal Temperature, −183.0°		
−182.9	99.90	619.7	620.1*	619.6
−183.1	202.15	640.5	640.2*	639.4
−183.1	399.73	671.6	671.4*	670.2
−182.7	699.87	703.2	703.8*	703.8
−182.8	1252	749.1	749.5*	747.7

---

[18] Holborn and Otto, *Z. Physik*, **30**, 320 (1924).

[19] Onnes and van Urk, Comm. Phys. Lab. Leiden, 169d.

[20] Mathias, Onnes and Crommelin, *Proc. Acad. Sci. Amsterdam*, **17**, 953 (1915).

[21] Onnes, Dorsman and Holst, *ibid.*, **17**, 950 (1915).

[22] Michels, de Gruyter and Niesen, *Physica*, **3**, 346 (1936).

state in which PV was represented as a polynomial in the density failed to represent the isotherms of carbon dioxide and ethylene in the critical region. The same difficulty was encountered in the critical region of nitrogen; hence, the exponential term was required to represent this critical anomaly. Michels[22] found for carbon oxide and ethylene that $(\partial^2P/\partial T^2)_V$, which is negative at high temperatures over the entire density range, becomes positive near the critical density and temperature. This is true for nitrogen also. The exponential term, which has an appreciable value only near the critical point, also gives $(\partial^2P/\partial T^2)_V$ the required positive values in this region.

The numerical constants were determined as follows: $(pV-A)/d$ was plotted against d for each isotherm. $(pV - A)/d$ was read from the curves at even values of d and plotted against T. v, w, and x were selected by trial so that $(pV-A)/d - (100/T)v - (100/T)^3d^3w\ 10^{-xd^2}$ was roughly a linear function of T at each density. With the approximate value of x thus chosen, the constants p, q, r, s, t, u, v and w were determined from the original points by the method of least squares. Each observed pressure was given a weight proportional to d^{-6}. Since a fixed error in d affects P by an amount roughly proportional to d^3, giving these weights to P is roughly equivalent to assuming a fixed error in d over the entire density and temperature range. Finally, in order to obtain better values of w and x, the logarithm of $(T^3/10^6d^3)\{(pV - A)/d - [p + qd + rd^4 + (T/100)(s + td + ud^2) + (100/T)v]\}$ was plotted against d^2 for the points in the critical region, and final values of log w and x were determined from the straight line drawn through the points. Since the exponential term is small except in the critical region, this procedure improved the fit there without altering it much away from that region.

TABLE VII

COMPARISON OF PRESSURES OBSERVED IN OTHER WORK WITH PRESSURES CALCULATED BY EQUATION (8)

Temp., °C.	Density, A. u.	Pressure obsd.	(Int. atm.) obsd. − calcd.	ΔD, A. u.
Bartlett, Hetherington, Kvalnes and Tremearne[3]				
−50	254.7	200.00	−0.27	0.2
	333.8	300.00	−.30	.2
	387.1	400.00	−.56	.3
	425.6	500.00	−.08	.0
	456.0	600.00	−.28	.1
	502.3	800.00	−1.86	.4
	538.4	1000.00	−12.08	1.9
−70	232.9	150.00	0.73	−1.0
	293.1	200.00	.50	−0.5
	372.4	300.00	−.73	.5
	422.1	400.00	−.79	.3
	458.1	500.00	−1.35	.5
	486.6	600.00	−3.24	.8
	529.4	800.00	−4.79	.9
	562.3	1000.00	−9.41	1.5
Holborn and Otto[18]				
−100	214.46	96.246	−0.240	0.5
	219.53	98.193	−.325	.8
−130	281.45	65.974	−.507	2.7
	289.01	67.409	−.517	2.8
Onnes and van Urk[19]				
−131.27	240.8	58.31	0.42	−2.4
−141.53	231.2	41.68	.01	−0.2
	288.7	44.25	−.20	3.2
	347.2	50.25	−.05	0.5
−144.46	238.6	37.47	.04	−1.8
	299.4	38.79	.00	0.0
	348.8	42.19	.19	−1.9
−146.32	256.6	34.47	−.18	60
	294.3	34.675	−.15	24
	318.4	35.135	−.11	4.0
	344.5	36.49	.05	−1.0
Onnes, Dorsman and Holst[21]				
−147.13	248.49	33.490	0.116	−92
Mathias, Onnes and Crommelin[20]				
−148.08	344.7	31.37[23]	−0.30	15
−148.61	359.9	30.63[23]	−.32	6
−149.75	383.5	29.06[23]	.22	−0.7
−153.65	426.1	24.08[23]	.87	−1.1
−161.20	485.1	16.11[23]	1.16	−1.3
−173.73	553.1	7.31[23]	0.36	−0.2
−182.51	594.0	3.72[23]	−7.11	2.2
−195.09	642.7	1.08[23]	−7.30	1.6
−200.03	660.5	0.587[23]	−2.99	0.6
−205.45	679.2	0.266[23]	6.09	−1.0
−208.36	689.0	0.069[23]	14.16	−2.0
Benedict II				
−45	526.1	981	13	−2.0
	600.5	1566	−13	1.3
	668.2	2442	−5	0.3
	721.1	3413	8	−.4
−75	563.1	981	10	−1.5
	631.1	1566	−1	0.1
	693.3	2442	32	−2.0
	743.8	3413	26	−1.2
−100	596.2	981	13	−1.7
	658.1	1566	7	−0.6
	718.2	2442	11	−.7
	766.4	3413	−11	.6
−125	631.8	981	16	−1.9
	688.9	1566	−7	0.5
	742.3	2442	31	−1.7
−150	672.2	981	−1	0.1
	721.5	1566	−17	1.4
−175	713.3	981	4	−0.4
	754.2	1566	21	−1.5

The equation represents all except one of the

---

[23] These vapor pressures were calculated from the equation given by Mathias, Crommelin and Annes, Leiden Comm. 162a.

points of Table VI within the estimated maximum error of 2.0 A. u. The point at 100 atm. and −125° is grossly in error and was neglected in determining the constants. Table VII shows the degree of success with which equation (8) represents P–V–T data from other sources.

The average percentage deviation of the observed from the calculated pressures is 0.55%. In figuring this average, the points representing densities of the boiling liquid below −150° were excluded, because the percentage deviation of the pressure is a poor criterion of fit in this region; here the pressures are low and the liquid is relatively incompressible, so that a small error in the density makes an enormous percentage error in the pressure. The last column of Table VII, Δ_D, is a better criterion for these points. Δ_D is the deviation, observed minus calculated density, corresponding to the deviation in the pressure tabulated in the preceding column.

We may summarize the results of Table VII as follows. The equation fits Bartlett's two isotherms satisfactorily. At only three points are the deviations in density greater than 0.2%, his estimated maximum error. Holborn and Otto's measured pressures are lower than those calculated by the equation. This is caused by a difference of their data from those of Onnes and van Urk and Table VI. The difference amounts to about 0.75 atm. at −100° and 0.9 atm. at −130°. The data of Onnes and van Urk are represented satisfactorily by the equation. The deviations of the critical pressure and the three highest vapor pressures are no greater than the irregularities in Crommelin's[24] vapor pressure data. The boiling liquid densities below −150° are represented with an average deviation of 0.22%.

Above 980 atm. the pressure deviations become larger. However, since the gas is much less compressible at high pressures, no deviation corresponds to an error of more than 0.4% in the density. This is about the precision expected in II. Nevertheless, the deviations at 981 atm. average +10 atm. This is due to a discrepancy of about 20 atm., or about 0.5% in the density, between Bartlett's points and those of II at 981 atm.

Joule–Thomson Inversion Curve.—Equation (8) reproduces the change of P with d and T with sufficient exactness for evaluation of the derivatives $(\partial P/\partial T)_V$ and $(\partial P/\partial V)_T$ within an estimated precision of 2%. It therefore should be possible to use it to evaluate such observable heat data as specific heats or Joule–Thomson coefficients in the temperature and pressure range for which it is valid. Roebuck and Osterberg[25] have determined the J.–T. coefficient for nitrogen down to −165° and up to 200 atm. In Table VIII are compared their parameters for the J.–T. inversion curve with those calculated from eq. (8) and the condition that at an inversion point $T(\partial P/\partial T)_d = d(\partial P/\partial d)_T$.

TABLE VIII

JOULE–THOMSON INVERSION PARAMETERS

Temp., °C.	d (eq. 8), A. u.	p (eq. 8), atm.	p (r & o), atm.
−167.0	532.5	31.3	20
−162.4	525.0	57.6	60
−156.5	515.7	89.1	100
−148.0	502.7	130.1	140
−134.7	483.3	185.6	180
−117.2	459.0	245.1	220
− 96.4	431.4	299.2	260
− 68.7	396.5	348.7	300

Roebuck and Osterberg's measured pressures agree with those calculated from eq. (8) within 11 atm. up to 200 atm.; this is within the precision with which the inversion pressure can be inferred from their experimental data. Above 200 atm. the divergence is larger but is not serious, since the last three points were obtained by extrapolation beyond their highest measured pressure at 200 atm. The manner in which eq. (8) reproduces the J.–T. inversion curve is evidence for the reliability of the P–V–T data on which it is based and gives assurance of the accuracy of other heat data calculated from it. More extensive tables of these will be given in a later paper.

Acknowledgment.—The writer wishes to thank the National Research Council for Fellowship Aid, and Professor T. Lyman for providing facilities in the Research Laboratory of Physics of Harvard University for carrying out the experimental work. He is especially grateful to Professor P. W. Bridgman for many criticisms and suggestions, for his generous loan of much of the apparatus used in this work, and for his friendly guidance.

Summary

1. A simple gravimetric method for determining gas density has been described.

2. The density of nitrogen has been determined at pressures from 100 to 1250 atm. and at temperatures from −100 to −183°.

---

[24] Crommelin, *Proc. Acad. Sci. Amsterdam*, **17**, 959 (1915).

[25] Roebuck and Osterberg, *Phys. Rev.*, **48**, 450 (1935).

3. An equation of state has been fitted to the data of this paper and to all other available data on nitrogen between −45 and −208° at densities from 210 to 750 Amagat units.

4. The Joule–Thomson inversion curve for nitrogen has been calculated from the equation of state and found to agree with the experimental curve of Roebuck and Osterberg.

5. The density of nitrogen at 0° and 1550 atm. has been determined as a reference datum for further work at higher pressures.

CAMBRIDGE, MASS. RECEIVED JULY 26, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICS, HARVARD UNIVERSITY]

Pressure, Volume, Temperature Properties of Nitrogen at High Density. II. Results Obtained by a Piston Displacement Method

BY MANSON BENEDICT[1]

Introduction

The first paper[2] of this series, hereafter to be referred to as I, described a gravimetric method for determining the density of nitrogen most suitable at densities greater than 200 A. u. (Amagat units) and pressures less than 1550 atm. Density at 1550 atm. and 0° was determined with special care for use as reference point for measurements at higher pressure. The present paper describes a piston displacement method for determining density, relative to this reference point, at pressures between 1000 and 6000 atm. and temperatures between −175 and +200°. In 1923 Bridgman[3] used this general method with kerosene as a pressure transmitting fluid to determine the isothermal compressions of five gases at pressures up to 15,000 atm. and at temperatures around 65°. The extreme pressure range there studied yielded much valuable information, but inevitably diminished the precision attainable, principally because of erratic volume changes in the pressure chamber. More recently he[4] designed an apparatus employing the gas itself as pressure transmitting fluid and used it to determine the freezing curves of nitrogen and argon. At the same time he determined the thermal expansion at constant pressure of these gases from 68° to lower temperatures at several points in the pressure range 3000–6000 atm. These recent data and the less precise earlier isothermal data served to outline roughly the $P-V-T$ surface of these gases at high pressures. At Professor Bridgman's suggestion the writer undertook a more complete study of the $P-V-T$ properties of nitrogen with the same apparatus. Isothermal compression, as well as isobaric thermal expansion, has been determined, so that dependence on the earlier isothermal data has been avoided. Though the pressure range was limited to 6000 atm., it was possible to extend the temperature range and to attain results estimated accurate to 0.3% on the density.

Experimental

Survey of Method.—A diagram of the apparatus is shown in Fig. 1. Bridgman's[4] paper describes its construction in detail. Paper I describes the nitrogen used and experimental procedure not explicitly mentioned here.

The apparatus consisted essentially of three parts, the upper cylinder A in which the gas was compressed at 25° and its volume change measured, the lower cylinder B, exposed to any temperature to be studied, and the connecting pipe C. For each loading of gas the moving plug M was brought to the top of the upper cylinder and nitrogen precompressed to 900 atm. or more was admitted at G. Pressure of gas in A was indicated by resistance of the manganin gage D. With gas in A, B, and C at the reference temperature, 25°, the gas-tight moving plug M was advanced by the piston until it had isolated this gas from the precompressors and compressed it to the reference pressure, 1566 atm. With A at 25° and B, successively, at each temperature to be studied, the displacement of M required to produce each pressure of interest was determined. At the conclusion of a specific cycle of pressure and temperature changes, a blank run was made to eliminate from consideration the unknown total volume of A, B, and C and their incalculable stretch with pressure. In this blank run, iron blanks ϕ_1 and ϕ_2 were placed in A and B, respectively, and the new positions of M required for the same cycle of pressure and temperature changes were determined. Then it was possible to express the ratio of the volume of gas at any temperature and pressure studied to its volume at 25° and 1566 atm. in terms of the positions of M observed in the blank and gas-filled runs, the area of A, and the known volumes of ϕ_1 and ϕ_2.

Terminology.—The two properties of the gas most directly obtainable from the observed positions of the moving plug are the isothermal compression and isobaric

---

[1] National Research Fellow in Chemistry, 1935–1936.

[2] Benedict, THIS JOURNAL, **59**, 2224 (1937).

[3] Bridgman, *Proc. Am. Acad. Arts Sci.*, **59**, 173 (1924).

[4] Bridgman, *ibid.*, **70**, 1 (1935).