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).

thermal expansion. If $V(t, P)$ is the volume of a given mass of nitrogen at $t°$ and P atm., then we will define κ the isothermal compression by (1)

$$\kappa = \frac{V(25, P) - V(25,1566)}{V(25, 1566)} \qquad (1)$$

and β the isobaric thermal expansion by (2)

$$\beta = \frac{V(t, P) - V(25, P)}{V(25, P)} \qquad (2)$$

Temperature Measurement.—Q was the cryostat described in I. A less sensitive method of temperature control was employed here; the heat input required to maintain constant temperature was actuated by a hydrogen–mercury thermoregulator and thyratron relay. This scheme produced temperature oscillations of period one minute, magnitude 0.25°. Cryostat temperature, t_2, was measured by the four junction copper–constantan thermocouple described in I. Temperature of B was thus known within 0.3° below 0°. For measurements of thermal expansion between 25° and higher temperatures, Q was a small oil-bath with stirring mechanism of the type described by Collins;[5] its temperature was controlled by a "Hytemco" resistance thermometer, A. C. bridge, amplifier, and phase shifting thyratron circuit as described elsewhere.[6] Bath temperature was read with a mercury-in-glass thermometer graduated in 0.5° and calibrated to 0.1° by the Bureau of Standards for all temperatures at which we used it. Proper emergent stem corrections were applied, so that the temperature of B at and above 25° was known within 0.1°.

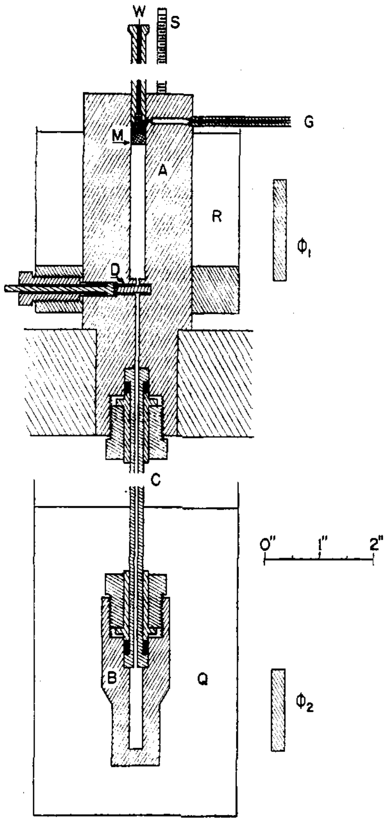

Fig. 1.—The apparatus.

Temperature t_1 of the unthermostated kerosene bath R surrounding the upper cylinder was measured with a copper constantan thermocouple touching the upper cylinder A. This thermocouple was compared with a calibrated mercury thermometer in the temperature range of interest. Its temperature drifted slowly with changes in room temperature from 22.5 to 27.5°. Temperature of the gas in the upper cylinder probably differed from that indicated by the thermocouple by less than 0.2° for the small rates of temperature change observed of the latter. All gas above liquid level in Q was supposed to have been at t_1; all below it, at t_2.

Pressure Measurement.—Details of pressure measuring equipment are given in I. Manganin resistance gage 2 was used to measure pressure in the experiments at low temperatures, and gage 5 was used in experiments above room temperature. Gage 2 was compared up to 6000 atm. with standard gage A, previously calibrated against the freezing pressure of mercury at 0°. Resistance change with pressure of gage 2 was proportional to that of the standard gage within a probable error of 0.16%. Unfortunately, both gage 2 and standard gage A were broken before they could be compared with the free piston gage. The comparison of gage 5 with standard gage B and with a free piston gage was described in I. Gages 2 and 5 had been wound from the same spool of American manganin and their values of α differed by only 0.14%. Gages A and B had been wound from the spool of German wire which Bridgman used in his original determination of the freezing pressure of mercury, and their values of α differed by only 0.01%. In view of this similarity in each pair of gages, we have supposed gages 2 and A to read the same pressure scale as gages 5 and B. We have therefore used eq. (4) of I to correct the pressure P_M read by gage 2 to the absolute pressure P. We estimate the maximum error in P thus calculated for gage 2 to be 0.3%.

Dimensions of Apparatus and Measurement of Volume. (a) Upper Cylinder.—The over-all length of the reamed hole in the upper cylinder was 8.5 cm., and its mean area at 1 atm. pressure, A_0, was 0.3462 cm.[2] The position of moving plug M in the cylinder was determined by observing the position of steel wire W relative to glass scale S with a vertical travelling microscope. Nominal sensitivity of the micrometer moving the latter was 0.0005 cm. The scale was ruled at 0.05-cm. intervals. Each ruling was compared with a standard meter bar ruled at 0.02-cm. intervals and checked at the U. S. Bureau of Standards. Positions of M were referred to a bench mark 1.63 cm. below the top of the cylinder. The working range of the plug was between the bench mark and a position 4.7 cm. lower. Total volume displaced was 1.63 cc. The clear-

---

(5) Collins, *Rev. Sci. Instruments*, **7**, 502 (1936).

(6) Benedict, *ibid.*, **8**, 252 (1937).

ance at each end of the cylinder was sufficient to avoid end effects in the stretch of the cylinder under pressure. Hence, eq. (5) of I can be used to estimate the increase of A_0 with pressure, provided ΔA and 0.3462 be substituted therein for ΔV_p and V. For steel

$E = 2.1 \times 10^6$ atm.
$\sigma = 0.3$, and
$r_1 = 2.54$ cm.
$r_2 = 0.332$ cm. so that
$A = 0.3462 + 4.2 \times 10^{-7} P_{\text{atm.}}$

The change of A with pressure may be in error by 20% because of uncertainty in the theory of the elastic distortion of thick-walled cylinders. The diameter of the reamed hole in A was determined at 0.5-cm. intervals over the working range by means of a special internal micrometer working on the principle of the star gage used to check the bore of guns.[7] The micrometer was checked against gage blocks with a probable error of 0.0003 cm. The reamed hole was circular within this tolerance and varied with elevation between 0.6621 and 0.6670 cm. At the end of the experiments the diameter was redetermined at one elevation and was found to have decreased by 0.0004 cm. Hence, no sensible permanent deformation of the upper cylinder took place. The irregularity in bore was allowed for by including the correction for it with the correction for errors in ruling of the glass scale. The largest correction for irregularity in bore corresponded to 0.010 cm. plug displacement. Errors in measurement of linear displacement and bore and in estimation of stretch produce an estimated maximum error of 0.3% in the volume displaced by the moving plug.

Volume contained by the connecting pipe and upper cylinder with M at the bench mark was determined with a gas buret as described in I. Volume contained by C was 0.151 ml., estimated from its length, 12″ (30.7 cm.) and its inside diameter, $^1/_{32}$″ (0.8 mm.). V_1, the volume contained by A with M at the bench mark and upper 9″ (23 cm.) of C, was 2.59 ± 0.005 ml. A rough estimate of this volume is required in correcting for variations of t_1 from 25°.

The volume of B was approximately 1.2 ml.

(b) Iron Blanks.—The iron blanks were cut from the block of Armco iron used by Bridgman[8] for measurements of its absolute compressibility. They were turned to right circular cylinders and polished. The length and diameter of each was measured by micrometer calipers checked against gage blocks. Their volumes at 25° and 1 atm. were $\phi_1^0 = 1.492 \pm 0.001$ ml. and $\phi_2^0 = 1.187 \pm 0.001$ ml. At centigrade temperature t_2 and pressure $P_{\text{atm.}}$ the volume of either blank, ϕ_{Pt}, was calculated from its volume at 25° and 0 atm., ϕ^0, by eq. (3).

$$\phi_{Pt} = \phi^0(1 - 6.05 \times 10^{-7}P + 2.5 \times 10^{-12}P^2 + 10^{-8}[35.4\,\theta + 20.6\,\theta^2 - 10.1\,\theta^3 + 3.5\,\theta^4])\quad \theta = 0.001\,(t_2 - 25) \qquad (3)$$

This equation is based on the "International Critical Tables"[9] formula for the linear expansion of iron above 0° and on Bridgman's value for the compressibility of iron at 30°. The change of compressibility with temperature is neglected. The "I. C. T." formula agrees well with Henning's[9] value for the mean linear expansion of iron between −190 and 20°. Use of eq. (3) to calculate the volume of iron under the conditions of these measurements probably introduces no error greater than 0.05%.

It is impossible to calculate the changes with pressure and temperature of the internal volume of the apparatus because of stretch in the packed connections. Also, 0.15 ml. of gas in connecting pipe C is exposed to an unknown temperature gradient. The effect of these two uncertainties was eliminated by the runs in which B was totally and A was partially filled with the iron blanks whose volume change with temperature and pressure was small and known with sufficient accuracy. Successful application of this method is based on the assumptions that the volume contained by the apparatus responds reproducibly to a given cycle of pressure and temperature changes, and that the temperature gradient in C is reasonably reproducible. If these conditions are fulfilled, the only volumes of nitrogen which enter the calculations of the compression and thermal expansion are those displaced by the moving plug in either run or replaced by the iron in the blank run.

(c) Possible Sources of Error.—There were a number of possible sources of error which needed consideration. Temperature gradient in C was made as definite as possible by maintaining thermostat liquid level constant within 1 cm. The four packed connections, shown black in

---

[7] See, for instance, W. H. Tschappat, "Ordnance and Gunnery," John Wiley and Sons, Inc., New York, 1917, p. 283.

[8] Bridgman, *Proc. Am. Acad. Arts Sci.*, **58**, 169 (1923); **70**, 312 (1935).

[9] "International Critical Tables," Vol. II, p. 460.

Fig. 1, were possible sources of erratic volume changes. Of them the two around the connecting pipe were lead and probably responded reproducibly to pressure and temperature change. The lower connection was broken each time ϕ_2 was put into or taken from the lower cylinder. Judging from the agreement of results for density change from 25° calculated from gas-filled runs made before and after a blank run, the volume of the lower cylinder could be satisfactorily reestablished within 0.3% each time this connection was made. However, some increase in volume of the apparatus gradually took place, because calculation of the compression by combining blank and gas-filled runs separated by many intermediate applications of pressure gave erratic results. This increase in volume was probably caused by extrusion of the soft rubber packing around the resistance gage electrode. Its effect was rendered unimportant by calculating the compression from consecutive blank and gas-filled runs at 25°. Change in the total volume of the upper cylinder between a blank and gas-filled run does not affect the thermal expansion calculated from them.

One troublesome source of volume change in the first three runs was gradual accumulation in the upper cylinder during a run of as much as 0.015 cc. of the soft rubber packing from around the moving plug. At the end of each run the packing was recovered and weighed and the observed positions of the moving plug were corrected for its presence by assuming that in a run in which n forward strokes of the piston were taken, one nth of the total volume of packing recovered was left within the cylinder after each stroke. After run 4, brass retaining rings were used on the moving plug, and the amount of packing accumulating was unimportant. Unless an audible leak had occurred, the apparent loss of gas during a run due to penetration of gas through the steel, slow leak, or permanent deformation of the apparatus never exceeded 0.005 cc. measured at 1566 atm. and 25°. Hence, only those runs in which an audible leak occurred were rejected.

Volume hysteresis with respect to pressure change was reproducible and, in the extreme pressure range, amounted to 0.012 cc. Since observations customarily were made on decreasing pressure only, it was important to establish that the hysteresis was not in the bore of the upper cylinder or in the iron blanks. If it occurred elsewhere, it was of no importance since it was reproducible. Accordingly, blank and gas-filled isotherms were run at 25° on both increasing and decreasing pressures. The average difference in the volume observed at ten pressures increasing from 1566 to 5800 atm. from the volume observed at the same pressures in reverse order was +0.06%. The difference is within the probable error of volume measurement.

Reduction of Data.—The primary data from a single loading of gas consisted of a set of points at each of which were measured y, the distance of M below the bench mark; t_1, the temperature of the upper cylinder; t_2, the temperature of the lower cylinder; and P, the pressure, each calculated from the calibration of the appropriate measuring instrument. The data had to be taken quickly because of the short life of gas-tight packing at high pressure. In the time available t_2 was not brought exactly to the even temperature desired, but differed from it on the average by 0.5°, and P differed from the desired pressure by 5 atm., on the average. If β' be $1/V(\partial V/\partial t)_P$ for nitrogen at 25° and P atm., δy, the correction to be added to y for the departure of t_1 from 25° was calculated by (4). β' was calculated from the eq. of state (12), to be given later.

$$\delta y = \beta'(V_1/A_0 - y)(t_1 - 25) \qquad (4)$$

y was next corrected to the value it would have had at the desired value of P by interpolation between adjacent points with respect to log P, on which y was roughly linearly dependent. Finally, y was corrected to the value it would have had at the desired value of t_2 by linear interpolation between adjacent temperatures. It is to be noted that these adjustments preserve any error in y and do not smooth it.

The isothermal compression was calculated from corresponding positions of the moving plug in a blank and a gas-filled run at 25° as follows: In the gas-filled run, suppose the moving plug is initially Y_{00} cm. below the bench mark at 1566 atm. and after a specific cycle of pressure changes suppose it is Y_{P_0} cm. below at P. Then suppose the internal volume of the apparatus reduced in the blank run by the addition of iron having a volume ϕ_0 at 1566 atm. and ϕ_P at P and 25°. Suppose the piston position in the blank run is y_{00} at 1566 atm. before the same cycle of pressure changes and y_{P_0} at P after it. Let A_0 and A_P be the internal areas of the upper cylinder and

U_0 and U_P the total internal volumes of the apparatus (with $y = 0$) at 1566 and P atm. respectively. We can express the conservation of gas by

$$(U_0 - A_0Y_{00})/V(25, 1566) = (U_P - A_PY_{P_0})/V(25, P) \tag{5}$$

in the gas-filled run and

$$(U_0 - \phi_0 - A_0y_{00})/V(25, 1566) = (U_P - \phi_P - A_Py_{P_0})/V(25, P)$$

in the blank run. The unknown volumes U_0 and U_P may be eliminated

$$\frac{V(25, P)}{V(25, 1566)} = \kappa + 1 = \frac{\phi_P + A_P(y_{P_0} - Y_{P_0})}{\phi_0 + A_0(y_{00} - Y_{00})} \tag{6}$$

The equation for calculating the thermal expansion, β, from positions of the moving plug in gas-filled and blank runs is derived analogously. In the gas-filled run after a given cycle of pressure changes, suppose the moving plug is at Y_{P_0} when B is at 25° and pressure is P. After a further cycle of pressure and temperature changes, suppose the plug is at Y_{Pt} when B is at t_2° and the pressure is again P. Then suppose iron blank ϕ_2 is placed in the lower cylinder and the cycle of pressure and temperature change is repeated, yielding corresponding plug positions y_{P_0} and y_{Pt}.. If the volume of the iron blank is ϕ_{P_0} at P and 25° and ϕ_{Pt} at P and t_2, we obtain for β

$$\frac{V(t, P)}{V(25, P)} = \beta + 1 = \frac{\phi_{Pt}}{\phi_{P_0} + A_P(y_{P_0} + Y_{Pt} - y_{Pt} - Y_{P_0})} \tag{7}$$

$V(t, P)/V(25, 1566)$ was not calculated directly from blank and gas-filled runs because corresponding runs were sometimes separated by several applications of pressure or by necessary repairs to the upper cylinder. Each of these would introduce possible volume changes in the upper cylinder and consequent uncertainties in the calculation of isothermal compression, though not in the calculation of isobaric thermal expansion.

Results

The Measurements.—Three series of measurements were required to cover the temperature and pressure range discussed in this paper.

They are summarized in Table I. Runs B1a, B4a and 10a were made without repacking anything after the preceding runs. Otherwise, the moving plug was repacked after each run and the connection at the lower end of C was broken when necessary to insert or remove ϕ_2. The electrode of the resistance gage was repacked after runs 4 and 5. Between B1 and B1a about one-third of the gas originally present in the apparatus was released.

TABLE I

PRESSURE AND TEMPERATURE RANGE OF RUNS

Run	Iron blanks	Mang. gage	Pressure Range	Order of isotherms, ° C.
1	..	2	1550	25 0 −125 −100 −75 −45 25
B1	ϕ_2		to	25
B1a	ϕ_2		5850	25
B2	$\phi_1 + \phi_2$		atm.	25 0 −125 −100 −75 −45 25
2	..			25 0 −125 −100 −75 −45 25
3	..	2	980	25 0 −175 −150 −125
B3	$\phi_1 + \phi_2$		to	−100 −75 −45 25
4	..		3400	25
5	..		atm.	as in 3 and B3
8	..	5	1250	25
B4	$\phi_1 + \phi_2$		to	25 50 100 150 25
B4a	$\phi_1 + \phi_2$		5850	25 200 25
B5	$\phi_1 + \phi_2$		atm.	25 150 100 50 25
9	..			25
10	..			25 150 100 50 25
10a	..			25 200 25
11	..			25 50 100 150 25

The 25° Isotherm.—To minimize the influence of the gradual volume change in the packing around the resistance gage electrode, the isothermal compression at 25° was calculated from consecutive 25° isotherms only. The isothermal compression calculated from all possible consecutive 25° isotherms was averaged and represented by eq. (8).

$$\kappa + 1 = V(25, P)/V(25, 1566) = 1.8666x - 1.6079x^2 + 0.9165x^3;\ x = \sqrt[3]{1000/P} \tag{8}$$

Eight independent combinations of consecutive runs were used in calculating $\kappa + 1$; the deviation plot for 25° in Fig. 2 illustrates the scattering at the individual points. The root mean square deviation of the averaged observed volumes from the calculated volumes at 25° was 0.04%. The root mean square deviation of the individual observed volumes from the averaged observed volumes was 0.27%.

Reference to Table I will show that about as many gas-filled runs precede the associated blank run as follow it. This should disclose the magnitude of systematic error due to gradual increase in volume contained by the apparatus. Table I will show also the variety of blank runs used to eliminate the unknown volumes and stretch of the apparatus. The agreement of the various results for the compression indicates the degree of trustworthiness of this method. In the different combinations of blank and gas-filled runs, the area of the upper cylinder and the volumes of the iron blanks enter the calculation of the compression with differing weights; in an extreme instance, runs B1 and B1a, the volume of ϕ_1 and ϕ_2 do not enter eq. (6) at all. Hence, it is reasonable to take the root mean square error of the 25°

isotherm, namely 0.27%, as a measure of the magnitude of all errors in volume measurement. These include errors in volumes of the iron blanks, in their compressibility, in the bore and stretch of the upper cylinder or displacement of the moving plug, in the reproducibility of the volume of the lower cylinder after breaking the connection between it and the pipe, and in permeability of the apparatus to gas and adsorption of gas by it.

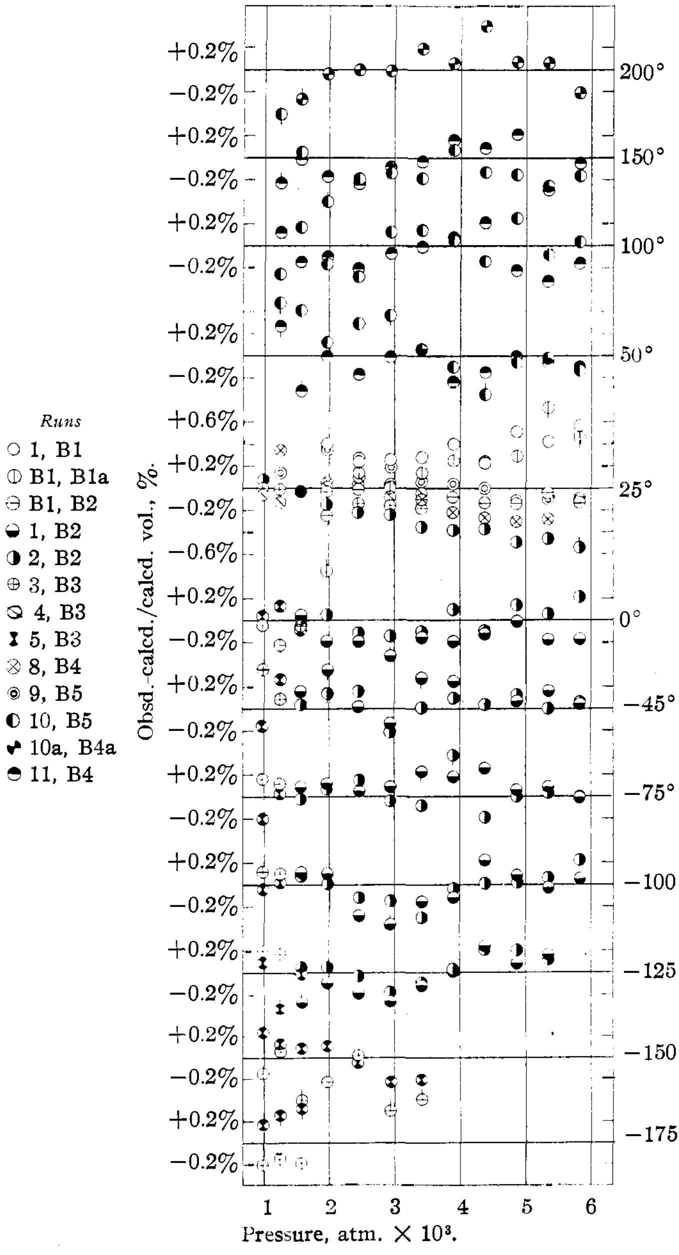

Fig. 2.—Dev. plot of individual observed volumes.

Other Temperatures.—At temperatures other than 25° the thermal expansion β was calculated from corresponding blank and gas-filled runs by means of eq. (7). These observed thermal expansions were combined with the mean observed values of κ to convert them to isobaric volume change relative to the volume at 25° and 1566 atm. That is

$$\beta(1 + \kappa) = [V(t, P) - V(25, P)]/V(25, 1566) \quad (9)$$

Eq. (10) was fitted to the mean observed value of $\beta(1 + \kappa)$ by the method of least squares,

$$\begin{aligned}\beta(\kappa + 1) = x[0.0003176(T - T') - \\ 2.4911(1/\sqrt{T} - 1/\sqrt{T'})] + \\ x^2[-0.0010315(T - T')] + \\ x^3[0.0031237(T - T') + 4.4620(1/\sqrt{T} - \\ 1/\sqrt{T'}) - 3.2661(1/T - 1/T')] \quad (10)\end{aligned}$$

$$x = \sqrt[3]{1000/P};\ T = t + 273.2;\ T' = 298.2\text{°K}.$$

The deviations of the observed volume changes from those calculated by eq. (10) are illustrated by the deviation plots of Fig. 2 for temperatures other than 25°. The root mean square deviation of the average observed volume changes from those calculated by (10) was 0.14% of the total volume and the root mean square deviation of the individual observed volumes from their average was 0.17%. 0.17% is a measure of the effect of errors of observation, fluctuations in temperature gradient in C, and erratic volume changes taking place in the apparatus during a run.

In order to express $V(t, P)$ in Amagat units, eq. (8) was substituted for $(1 + \kappa)$ in eq. (10); from this $V(0°, 1550)/V(25, 1566) = 0.9669$. In I $V(0°, 1550)$ was found to be 1/558.5 A. u. Hence

$$V(25°, 1566) = 0.0018518 \text{ A. u.} \quad (11)$$

With this datum, mean observed values of $(1 + \beta)(1 + \kappa)$ were converted to density in Amagat units in Table II. The average probable error in these densities is estimated to be 0.24% from the average root mean square errors in $(1 + \kappa)$ and $(1 + \beta)(1 + \kappa)$, 0.27 and 0.17%, respectively, and the probable error in $V(0, 1566)$, 0.09%. The probable error at temperatures near 25° and pressures near 1566 atm. is less than at points further removed.

Equation of State.—By combining eqs. (8), (10) and (11) the equation of state (12) was obtained. This equation is

$$10^3V = (3.54842 + 0.0005881T - 4.6131/\sqrt{T})x - (2.40797 + 0.0019102T)x^2 + (-0.48596 + 0.0057846T + 8.2630/\sqrt{T} - 6.0483/T)x^3 \qquad (12)$$

$$x = \sqrt[3]{1000/P};\ T = t(^\circ\text{C.}) + 273.2$$

valid over the temperature range −175 to +200° and the pressure range 980–5800 atm. V is volume in Amagat units, and P is in atmospheres.

TABLE II

MEAN OBSERVED DENSITIES OF NITROGEN IN AMAGAT UNITS

Temp., °C. Press., atm.	−175	−150	−125	−100	−75	−45	0	25	50	100	150	200
981	713.3	672.2	631.8	596.2	563.1	526.1	479.3	456.1				
1250	732.7	695.1	661.2	627.7	597.5	563.9	521.4	499.4	477.4	443.5	411.7	
1566	754.2	721.5	688.9	658.1	631.1	600.5	560.5	540.0	520.7	486.6	456.3	429.5
1955		744.6	714.9	687.5	662.3	633.8	598.3	578.9	560.7	529.3	501.0	473.9
2442	F	768.7	742.3	718.2	693.3	668.2	635.4	616.9	600.0	571.4	543.8	517.8
2927	R	794.1	767.1	744.1	720.8	698.6	666.8	648.9	632.2	604.4	579.2	554.8
3413	E	813.7	787.5	766.4	743.8	721.1	692.6	676.1	661.0	633.5	609.6	584.9
3898	E		805.1	784.7	762.5	742.1	714.7	699.5	686.6	658.7	634.3	612.5
4382	Z		821.3	801.5	784.2	763.0	736.1	721.0	709.0	681.6	659.0	634.8
4866	E		838.1	818.8	800.7	780.3	753.5	740.1	727.2	702.4	679.8	658.6
5351	S		852.4	833.8	815.7	796.0	771.0	757.2	744.7	722.1	700.7	678.1
5835				847.5	831.4	811.9	785.0	773.6	762.1	738.5	717.4	698.2

Discussion of Results

The deviation plot, Fig. 3, illustrates the agreement between the *P–V–T* data of this paper, summarized by eq. (12), and all other existent data for nitrogen above 1000 atm. The disagreement of 0.5% with Bartlett's[10] points at 1000 atm. and −50 and −70° has been mentioned in I. It will be seen that this disagreement persists up to 25°, but at higher temperatures the agreement is satisfactory. The present data differ from those of Amagat[11] and of Michels[12] in that nitrogen appears to be 2% more compressible, but the agreement of the volumes at all but six of the points is within 0.3%, our estimated probable error. Bridgman's[3] results at 68° differ from eq. (12) by about 1%, on the average, and he finds nitrogen about 12% less compressible; this discrepancy is probably within his rather large experimental error. His points at lower temperatures[4] are not shown because they were based on his 68° isotherm and show the same general trend with pressure. Basset and Dupinay's[13] volumes at 16° are seen to be about 3% smaller than those of any other investigator.

Equation (12) follows the trends of the *P–V–T* data sufficiently well to permit its use in evaluating derivatives of V with respect to T and P (estimated accurate to 2%), and in extrapolating the volume somewhat beyond the measured temperature and pressure range. Several interesting consequences of eq. (12) may be noted.

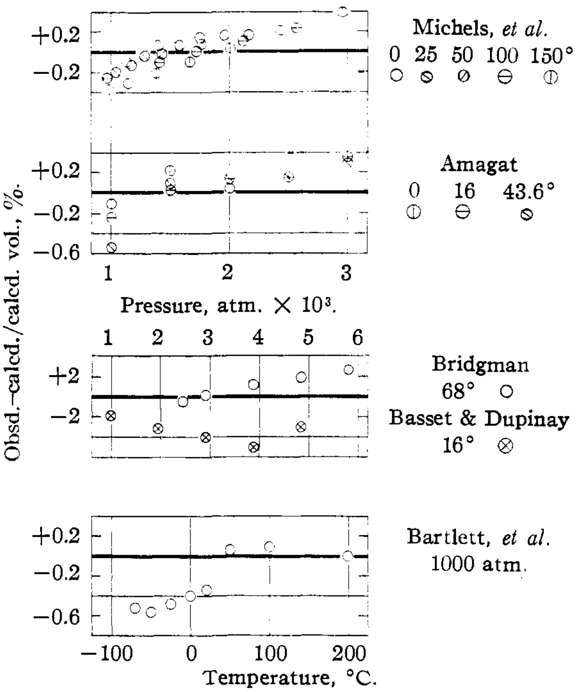

Fig. 3.—Dev. plot for others' obs. volumes.

Isobars of V against T have positive curvature below about 1800 atm. and negative above that pressure. This is illustrated in Fig. 4 which shows the isobars calculated from (12) at even thousands of atmospheres. Since $(\partial C_P/\partial P)_T =$

---

(10) Bartlett, *et al.*, THIS JOURNAL, **49**, 687, 1955 (1927); **52**, 374 (1930).

(11) "International Critical Tables," Vol. III, p. 17.

(12) Michels, Wouters and de Boer, *Physica*, **3**, 585 (1936).

(13) Basset and Dupinay, *Compt. rend.*, **191**, 1295 (1931).

$-T(\partial^2 V/\partial T^2)_P$, C_P will have a minimum at each temperature where the isobars have no curvature. The pressures at which C_P is a minimum are given in Table III.

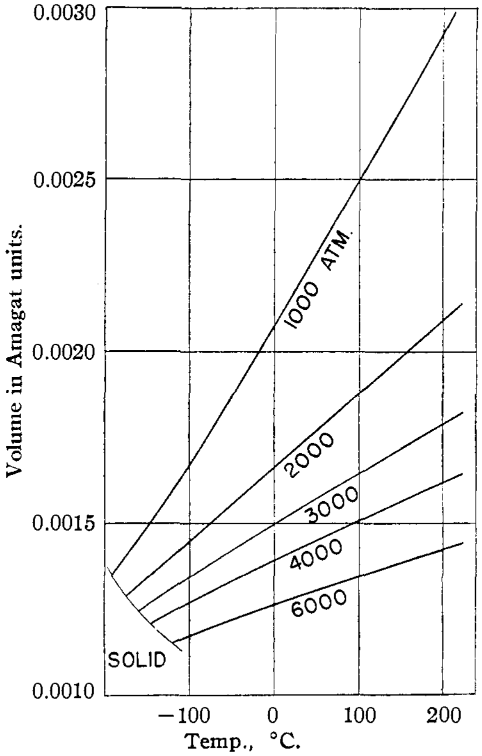

Fig. 4.—Isobars of nitrogen.

Equation (12) has also been used to calculate temperatures and pressures at the inversion points for the Joule free expansion effect at which the "internal pressure," $(\partial U/\partial V)_T = 0$ and the energy U is a minimum. When $(\partial U/\partial V)_T = 0$, $T(\partial V/\partial T)_P + P(\partial V/\partial P)_T = 0$. The coördinates of the Joule inversion curve at several temperatures are also given in Table III. Density on this curve runs from 600.9 A. u. at 200° to 807.7 A. u. at −150°. This is in qualitative agreement with the findings of Michel, Wouters, and de Boer;[14] at 150° their curve for $(\partial U/\partial P)_T$ extrapolates to 0 at about 600 A. u.

TABLE III

INVERSION POINTS FOR $(\partial U/\partial V)_T$ AND $(\partial C_P/\partial P)_T$

Temp., °C.	Pressure (atm.) at which $(\partial U/\partial V)_T = 0$	$(\partial C_P/\partial P)_T = 0$
200	3675	2082
100	3634	2048
0	3562	1985
−100	3412	1884
−150	3325	1794
−175		1725

It will be noted that eq. (12) predicts that V will approach zero as the pressure increases indefinitely. This is opposed to the van der Waals model of the molecule as a rigid attracting sphere, but is consistent with the contemporary notion of the existence of a finite potential energy for every intermolecular distance.

Some properties of nitrogen at 30° above 1000 atm. are compared with those of an ideal gas in Fig. 5. Each dimensionless quantity shown there equals 1 for an ideal gas. Although PV/RT increases seven fold over its ideal value, $(\partial V/\partial T)_P P/R$ and $-(\partial V/\partial P)_T P^2/RT$ remain much nearer unity.

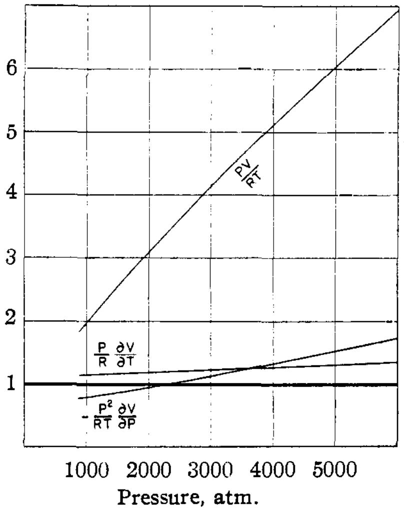

Fig. 5.—Comparison with ideal gas at 30°.

An interesting consequence of the trend of $(\partial V/\partial T)_P$ with increasing pressure is that $\int(\partial S/\partial P)_T dP = -\int(\partial V/\partial T)_P dP$ decreases without limit, and at sufficiently high pressure S, the entropy, would become negative, in violation of the third law of thermodynamics. This paradoxical situation is relieved by the fact that nitrogen freezes at very high pressures, and the properties of the solid phase presumably will not allow S to become negative. For instance, at 0° nitrogen freezes at about 20,000 atm.; at this pressure the entropy has decreased from its value of 45.2 cal./°C. mole at 1 atm.[15] to 21.3 cal./°C. mole.

It was possible to determine the freezing pressures of nitrogen at −125, −150, and −175°. These were 5708, 3673, and 1930 atm., respectively. The agreement with Bridgman's[4] freezing pressures is shown in Fig. 6. The freezing curve there plotted is

$$P_{\text{atm.}} = 20{,}621 + 150.14t + 0.24736t^2 \qquad (13)$$

---

(14) Michels, Wouters and de Boer, *Physica*, **3**, 597 (1936).

(15) Johnston and Davis, THIS JOURNAL, **56**, 271 (1934).

which fits the points with a root mean square error of 9 atm. and a maximum error of 14 atm. Equation (14) of the type proposed by Simon[16] fits the

$$P_{\text{atm.}} = -1607 + 0.99474T^{1.78152} \qquad (14)$$

data with the same root mean square error but is less convenient to use. At 0° the freezing pressures calculated by these two equations are: eq. (13) 20,621 atm.; eq. (14) 20,188 atm.

The volume of the fluid phase along the freezing curve was determined from eq. (13) and by extrapolation with eq. (12) and is illustrated in the volume curve of Fig. 6. The curve is consistent with the volume at the triple point[17] extrapolated from the liquid volumes of Mathias, Onnes and Crommelin.[18] The volume curve does not show the sharp inflection found in it by Bridgman.[4] The anomalous course of his curve is probably due to erroneous volumes at the oxygen and nitrogen boiling temperatures.

The equation of state found in I for the low pressure data can also be used for extrapolation to the freezing volumes. Freezing volumes calculated thus are plotted on Fig. 6. The radius of the circles is 0.1% of the volume. The two equations agree within 0.3% along the freezing curve above 1000 atm. This is about the precision to be expected in extrapolation over the range in question, and illustrates the degree of consistency of the two equations in the low temperature, high pressure region. It may be well to emphasize here that both of these equations were developed empirically to represent as well as possible the observed *P-V-T* properties of nitrogen in two limited pressure and temperature ranges. Long extrapolation with them involves all the risks usual in such procedure. This is particularly true of eq. (12) of this paper at low pressures and high temperatures, where it fails to satisfy the condition that lim $(V-RT/P)$ remain finite as either $1/P$ or T increases indefinitely. Equation (8) of I is satisfactory in this respect.

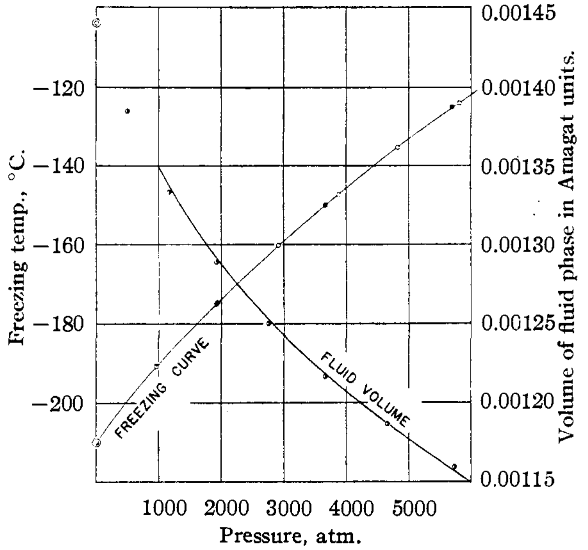

Fig. 6.—Freezing curve of nitrogen.

Freezing curve, eq. (13): ◉, triple point, Cath; ○, freezing pressure, Bridgman; ●, freezing pressure, this paper.

Fluid volume curve, eqs. (13) and (12): ◉, triple point volume, M., O. and C.; ◑, eq. (13) and Paper I (8).

Velocity of Sound.—It is hoped that the velocity of sound in nitrogen at high pressures will soon be determined in this Laboratory. Such measurements will serve as a valuable check on the *P-V-T* data of this paper. For purposes of this comparison and for its own interest, *u*, the velocity of sound in nitrogen at 30° between 1000 and 6000 atm. has been calculated from eqs. (12) and (14) and a value of 6.09 cal./°C. mole for C_V at 30° and 2000 atm. If V is the volume in cc./g. and P is the pressure in dynes/sq. cm.

$$u(\text{cm./sec.}) = V\sqrt{-(\partial P/\partial V)_T C_P/C_V} \qquad (14)$$

V, C_P, C_V and u at 30° are given in Table IV. The theoretical values at 1 atm. are given for comparison. The velocities are probably accurate to 2%.

Table IV

Velocity of Sound in N_2 at 30°

Pressure, atm.	Volume, cc./g.	C_P cal./mole ° C.	C_V cal./mole ° C.	u, meters/sec.
1		6.96	4.97	354.8
1000	1.7569	9.05	5.80	831
1500	1.5136	8.99	5.92	1019
2000	1.3810	8.98	6.09[19]	1170
3000	1.2301	9.01	6.41	1393
4000	1.1402	9.08	6.69	1560
5000	1.0774	9.17	6.93	1697
6000	1.0295	9.27	7.14	1811

Summary

1. A piston displacement method for measuring the change in volume of gases has been described.

2. The method has been used to determine the specific volume of nitrogen from 980 to 5800 atm. and from −175 to +200°. The

---

(16) Simon, Ruhemann and Edwards, *Z. physik. Chem.*, **B6**, 331 (1930).

(17) Cath, *Proc. Acad. Sci. Amsterdam*, **21**, 656 (1919).

(18) Mathias, Onnes and Crommelin, *ibid.*, **17**, 953 (1915).

(19) Obtained by interpolation in Michels[11] table for C_V.

estimated probable error in the volumes is 0.24%.

3. An equation of state has been fitted to these volumes with a root mean square error of 0.14%.

4. Bridgman's freezing curve for nitrogen has been checked and represented by a quadratic equation.

5. Various consequences of the equation of state have been discussed and some derived thermal data have been obtained from it. Of these the velocity of sound should prove useful as a check on the P–V–T data.

CAMBRIDGE, MASS. RECEIVED JULY 26, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

The Transition Temperature of Gypsum to Anhydrite

BY ARTHUR E. HILL

The temperature of the transition of gypsum to anhydrite, $CaSO_4 \cdot 2H_2O \rightleftarrows CaSO_4 + 2H_2O$, was set at 63.5° by van't Hoff[1] and his co-workers, in the course of their epoch-making researches upon the Stassfurt salt deposits. The temperature was arrived at by indirect vapor tension measurements and the application of thermodynamic reasoning; as pointed out by D'Ans,[2] the determination was accompanied by great difficulties because of the marked slowness of the system in coming to equilibrium. The given temperature has been quite generally accepted and quoted, and has of course considerable significance geologically. Partridge and White,[3] who determined the solubility of anhydrite at temperatures of 100° and upward, pointed out that their curve, if extrapolated below 100° to meet a solubility figure for anhydrite at 33° by Haddon and Brown[4] (the only figure then extant for a temperature below 100°), indicated a transition temperature as low as 38–39° for the two salts. A later figure by Roller[5] was also found to fit in with this hypothesis. Hara[6] and his co-workers obtained figures for four temperatures between 40 and 100°, using natural anhydrite and approaching equilibrium from undersaturation, which indicate a transition temperature with gypsum at about 37.5°. In the study of the system $CaSO_4$–K_2SO_4–H_2O in this Laboratory,[7] anhydrite was found by solubility measurements to be stable with respect to gypsum at 60° at all concentrations of potassium sulfate about 1%; in an investigation as yet unpublished we have found the same to be true at 50° in the presence of sodium sulfate, which would prove that the transition temperature is lower than van't Hoff thought, if it could be demonstrated that the anhydrite still remained the stable form as the concentration of the added salt approached zero. Quite recently D'Ans and Hoefer[8] have found that the transition temperature gypsum–anhydrite is lowered to 25° by a concentration of phosphoric acid of 83 g. per 100 g. of water, while at 83° anhydrite is stable with respect to gypsum at all concentrations of phosphoric acid; by use of analogies as to depression of transition points by a third component they argue that their results are in accord with van't Hoff's belief that the transition is at 63.5°.

That none of the investigations cited above carries complete conviction, from van't Hoff's publication down to the latest, is because in no one of the measurements, either of vapor tension or of solubility, has any evidence been adduced that the system studied was at equilibrium or anywhere near it, other than that a considerable time was allowed to elapse before measurements were made; since it is known that anhydrite–water systems at lower temperatures may remain undersaturated or supersaturated for months one has no criterion for deciding which if any of the experiments cited is correct. It has been my endeavor to conduct a few solubility experiments in which equilibrium was reached from two directions and which could therefore place the solubility curve of anhydrite definitely either above or below that of gypsum in the temperature range 66–40° and thereby fix the transition tempera-

---

(1) Van't Hoff, *et al.*, *Z. physik. Chem.*, **45**, 257 (1903); also, van't Hoff, "Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen," Leipzig, 1912, p. 183, where the temperature is given as 66°.

(2) D'Ans, "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen," Verlagsgesellschaft für Ackerbau, Berlin, 1933, p. 5.

(3) Partridge and White, THIS JOURNAL, **51**, 360 (1929).

(4) Haddon and Brown, *J. Soc. Chem. Ind.*, **43**, 11 (1924).

(5) Roller, *J. Phys. Chem.*, **35**, 1132 (1931).

(6) Hara, *et al.*, *J. Soc. Chem. Ind. Japan*, **34**, suppl. binding 284 (1931); *J. Chem. Soc. Japan*, **55**, 1051 (1934).

(7) Hill, THIS JOURNAL, **56**, 1071 (1934).

(8) D'Ans and Hoefer, *Angew. Chem.*, **50**, 101 (1937).