Summary

1. Electric moment data for a number of substituted phenols have been obtained by the method of the binary mixture. The dielectric constant and density data have been included.

2. The data have been discussed from the point of view of the stereochemistry of the oxygen atom.

3. It is shown that the dipole moment of a molecule can in general be calculated only provided the vectors characteristic of the groups be considered to be acting in *space*, for two reasons: (a) it is necessary to take into account the stereochemistry of the atoms forming the substituent group, and (b) it is necessary to take into account mutual attractions or repulsions between substituent groups unless they be separated by at least a distance equivalent to a chain of four carbon atoms, that is, by 5 Å.

4. Our knowledge is not at present sufficient to enable us to calculate with any degree of accuracy the electric moment of an "oxygen derivative."

MADISON, WISCONSIN

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE COMPRESSIBILITY ISOTHERMS OF HYDROGEN, NITROGEN AND A 3:1 MIXTURE OF THESE GASES AT TEMPERATURES OF −70, −50, −25 AND 20° AND AT PRESSURES TO 1000 ATMOSPHERES

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This investigation was undertaken to provide data supplementing the earlier results obtained in this Laboratory on the compressibility of hydrogen, nitrogen and a 3 : 1 mixture of these gases at temperatures between 0 and 400° and at pressures to 1000 atmospheres.[1] The new data cover the temperature range −70 to 20°. They should be useful in the design of condenser equipment for synthetic ammonia plants and should be of especial interest in the study of equations of state for real gases.

Compressibility data in this temperature range dealing with hydrogen and nitrogen are already available.[1,2] However, at temperatures below 0°

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[1] Bartlett, Cupples and Tremearne, THIS JOURNAL, **50**, 1275 (1928).

[2] (a) Natterer, *Pogg. Ann. Physik. Chem.*, **94**, 436 (1855); (b) Amagat, *Ann. chim. phys.*, [6] **29**, 68 (1893); (c) Witkowski, *Krakauer Anzeiger*, 305 (1905); (d) Kohnstamm and Walstra, *Proc. Roy. Acad. (Amsterdam)*, **17**, 203 (1914); (e) Schalkwijk, *Comm. Phys. Lab. Univ. Leiden*, No. 70; (f) Onnes, Crommelin and Smid, *ibid.*, No. 146b; (g) Holborn and Shultzer, *Ann. Physik*, **47**, 1089 (1915); (h) Smith and Taylor, THIS JOURNAL, **45**, 2107 (1923); (i) Smith and Taylor, *ibid.*, **48**, 3122 (1926); (j) Onnes and Penning, *Arch. Neerland. sci.*, IIIA, **6**, 277 (1923); (k) Crommelin and Swallow, *Comm. Phys. Lab. Univ. Leiden*, No. 172a (1924); (l) Onnes and van Urk, *ibid.*, No. 169d

investigations have been limited to pressures under 100 atmospheres. At 20° there have been reported only the data on hydrogen by Kohnstamm and Walstra at pressures to 1000 atmospheres, the data of Schalkwijk on hydrogen at pressures to 60 atmospheres, the data by Onnes, Crommelin and Smid on this same gas at pressures to 100 atmospheres, and the data by Verschoyle on hydrogen, nitrogen and their mixtures at pressures to 200 atmospheres. In the vicinity of 20° are to be found Amagat's data at 15–16° on both gases at pressures to 1000 atmospheres, Scott's data on hydrogen at pressures to 170 atmospheres and at 25°, and Bartlett's data on the 3:1 mixture of hydrogen and nitrogen at pressures to 1000 atmospheres and at 25°. At 0 and 50° extensive investigations on both gases have been conducted. The new results presented in this report will serve to round out the data at 20°.

Method.—As in previous work a quantity of gas at known pressure and temperature is confined in a heavy metal pipet of known capacity. The gas is allowed to expand into a gas buret maintained at constant temperature and the quantity of gas determined by measurement of a fixed volume at a measured pressure, not far above or below atmospheric pressure.

Preparation and Purification of the Gases.—The hydrogen was prepared by the electrolysis of a solution of sodium hydroxide. Analyses by a low pressure analytical method devised by Kvalnes[3] indicated a possible maximum nitrogen impurity of 0.06–0.09%. The nitrogen was a commercial product manufactured by the air liquefaction process. Analysis by a method devised by Leatherman and Bartlett[4] indicated a maximum inert gas content of 0.06–0.08%. No oxygen could be detected by the usual method of analysis. However, any traces of this gas were removed on finely divided copper (reduced copper oxide) under pressure at 400°. The 3:1 mixture of hydrogen and nitrogen was made by "cracking" pure anhydrous ammonia on a rugged ammonia catalyst at dull red heat. An analysis of the resulting gas showed 74.6 ± 0.1% of hydrogen and 25.4 ± 0.1% of nitrogen by volume. Both the hydrogen and the 3:1 mixture were purified under pressure from any possible traces of oxygen by passage over finely divided copper at 325°. All of the gases were subsequently dried by passage through a trap maintained at 0° with a mixture of ice and water and a second trap maintained at about −80° by means of a mixture of solid carbon dioxide and acetone.

Apparatus.—The apparatus used in this investigation has been described in an earlier report from this Laboratory.[5] For work at low temperatures it has been found expedient to shorten the head and valve stems of the two-valve high-pressure pipet and

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(1924); (m) Holborn and Otto, *Z. Physik,* **33,** 1 (1925); (n) Holborn and Otto, *ibid.,* **38,** 359 (1926); (o) Verschoyle, *Proc. Roy. Soc.* (London), **111A,** 552 (1926); (p) Bartlett, THIS JOURNAL, **49,** 687 (1927); (q) Bartlett, *ibid.,* **49,** 1955 (1927); (r) Scott, *Proc. Roy. Soc.* (London), **125A,** 330 (1929).

[3] A description of this method will eventually appear in a separate report.

[4] Leatherman and Bartlett, *Ind. Eng. Chem., Analytical Edition,* **1,** 223 (1929).

[5] For a diagrammatic drawing and description of the compression and purification systems, see Bartlett, THIS JOURNAL, **49,** 68 (1927). For description of the general arrangement of the expansion and measuring devices see Bartlett, Refs. 1 and 2. For description of the high pressure pipet see Bartlett, Cupples and Tremearne, Ref. 1.

to omit the heating unit and water-cooling system described in the earlier report. The pipet was of copper alloy instead of the steel hitherto used. The pipet bath was designed especially for maintaining temperatures between 0 and $-70°$ to within $\pm 0.03°$. Because of its unique yet simple construction a somewhat detailed description of this apparatus is presented.

A sectional diagram of the thermostat is given in Fig. 1. For simplicity of construction A and B are separate units. The boxes are ruggedly constructed of 1-inch lumber. The copper cans E are of 22-gage copper brazed to form one-piece water-tight units. These fit over the edges of the containing boxes and are nailed in place. The insulation material D is ground cork. Each unit is 30 cm. wide; the other dimensions are given in the figure.

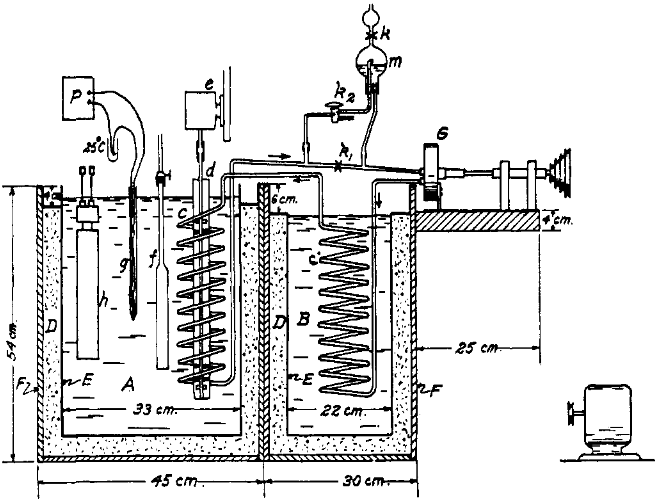

Fig. 1.—A low temperature thermostat.

The coils C, C′ and connections to the pump G are of 0.63-cm. copper tubing, each coil being about 3 meters in length. Acetone is used in the coil system. The rate of flow is determined by the proper choice of the pulley used on the shaft of the pump and by the proper adjustment of the stopcocks k_1 and k_2. The by-pass through the 500-cc. flask m is for the purpose of adding acetone and for observing the rate of flow. The pump was designed and built at this Laboratory; however, any of the regular water-circulating pumps should prove satisfactory.

Unit A, in which the temperature is maintained constant, contains a stirrer d driven by an overhead motor, an immersion knife heater f, a copper–constantan thermocouple g, and the high pressure pipet h. The bath liquid is acetone, which is kept in vigorous agitation. The heater is operated from a remote control switch located conveniently near the potentiometer by which the temperature of the bath is determined.

To operate the thermostat, unit B is filled with a mixture of solid carbon dioxide and acetone, while the acetone in unit A is brought to approximately the desired temperature by adding solid carbon dioxide. The rate of flow of acetone through the coils is adjusted until the liquid in A tends toward a temperature slightly below that desired. The operator at the potentiometer then regulates the current through the knife heater to maintain the temperature constant. When the acetone in A is comparatively dry and vigorously agitated, very little attention is needed for accurate control of temperature, once the proper flow of acetone in the coils is attained.

The acetone rapidly condenses water from the atmosphere at temperatures below 0°, and at −70° in a humid atmosphere will condense enough water in four or five days to render the mixture too viscous for adequate stirring. When this condition is evidenced by fluctuations in the potentiometer readings a new supply of dry acetone is placed in the thermostat.

The thermostat arrangement described possesses a flexibility that is highly advantageous when the apparatus in the thermostat is of a fixed nature and it is desired to work at two or more temperatures within a short period of time. A twenty-five degree change in temperature is effected in from ten to twenty minutes, while a fifty degree change is made in from twenty to thirty minutes, providing the temperature is not below −50°. A somewhat longer time proportionately is required to lower the temperature from −50 to −70°.

Calibration.—All volume, temperature and pressure measuring devices employed in this investigation were carefully calibrated. The low temperatures were measured by means of a copper-constantan thermocouple calibrated at 100, 50, 25, 0 and −25° against standard thermometers.

Pipet calibrations were carried out by the methods described in earlier reports.[1] The measurements to 150 atmospheres were, in general, made in a pipet of 20-cc. capacity. At this pressure a direct comparison of size was made at each temperature with a pipet of about 4.1-cc. capacity and the PV measurements at higher pressures were conducted with the smaller pipet.

The effect of temperature and pressure on the pipet volume depends upon the physical properties of the metal used. Analysis showed the copper alloy pipets to be of the following composition

Copper	65.00%	Iron	2.60%	Manganese	5.03%
Zinc	21.69%	Aluminum	5.72%	Lead	(Trace)

The Bureau of Standards[6] reports the ultimate tensile strength of a single sample of this material to be 129,000 pounds per sq. inch and Young's Modulus (E) to be approximately 16,000,000 pounds per sq. inch. The linear coefficient of thermal expansion determined by the interferometer is 1.90×10^{-5} from −51 to 20° and 1.97×10^{-5} from 20 to 263°.[7] The elongation under load is known to be so small at the temperature used in this investigation that its effect may be neglected.

Love's formula[8]

$$\Delta V = \frac{V_0}{E(r_2^2 - r_1^2)}\, 3(1 - 2\mu)(P_1r_1^2 - P_2r_2^2) + 2(1 + \mu)(P_1 - P_2)r_2^2$$

was employed to determine change in volume ΔV with change in total pressure $(P_1 - P_2)$. r_1 and r_2 are the internal and external radii of the pipet and P_1 and P_2 are the internal and external pressures.[9] The value

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[6] Courtesy of L. B. Tuckerman, Bureau of Standards.

[7] Courtesy of G. W. Merritt, Bureau of Standards.

[8] Love, "Mathematical Theory of Elasticity," Cambridge University Press, **1920**, p. 141.

[9] It has been called to the attention of one of the authors that in his earlier papers he has incorrectly defined P_1 and P_2. This was an oversight in proof-reading. It does not affect the accuracy of data presented in these papers. See THIS JOURNAL, **49**, 691 (1927), and **50**, 1277 (1928).

of Poisson's ratio μ for this alloy is still under investigation but it is believed to be approximately 0.30, and this value was used in the calculations. Supporting evidence for this value of μ has been independently and subsequently procured. First a pipet was calibrated with hydrogen at 100 and at 800 atmospheres and its size at the two pressures calculated by the use of PV data for hydrogen which had been determined in a steel pipet. The actual change in volume between these pressures amounted to 0.19%, while that calculated by the formula was 0.17%. In a similar manner the pipet was calibrated with nitrogen at 200 and at 1000 atmospheres. The observed change in volume was 0.20% and the calculated change 0.19%. This agreement is well within the limit of accuracy of the experimental work.

In the calculation of change in volume of the pipet with change in temperature it was assumed that the average cubical coefficient of expansion is three times the average linear coefficient of expansion of the metal for the same temperature range.[10] Data for more refined calculation of the magnitude of this change are not available. However, it is known that when a calculation of this type is made for steel, the difference between volume changes calculated by this simple method and by the use of an equation of the type[11]

$$V_t = V_0 (1 + at + bt^2 - ct^3)$$

differ by so little as to be well within the limits of accuracy of the present experimental work.

Experimental Results

The data obtained in this investigation are presented in the form of Amagat units, that is, the unit gas mass is the mass of 1 liter at 1 atmosphere pressure and 0°. At this pressure and temperature PV is unity.

In addition to the new data the tables also include results obtained by other investigators in so far as they cover approximately the same pressure and temperature ranges. Interpolations and short extrapolations have been necessary in some cases to make these scattered data strictly comparable. This is especially true in calculating Holborn's PV data at 20, -25 and $-70°$ from his observed data at 50, 0, -50 and $-100°$; and in calculating Amagat's data at 20° from his observed results at 0 and 15–16°. Where the PV–T relationships are not approximately linear, graphical methods of interpolation were employed. In Tables I, II and III are recorded the observed PV values for hydrogen, nitrogen and a 3 : 1 mixture of these gases. In the case of the 3 : 1 mixture the reported PV values were calculated from the observed values obtained with a 74.6–25.4% mixture. Interpolations over the short percentage range seemed

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[10] Lucke and Flather, "Textbook of Engineering Thermodynamics," McGraw-Hill Book Co., Inc., New York, **1915**, p. 299.

[11] Keyes, Joubert and Smith, *J. Math. Phys., Mass. Inst. Tech.*, **1**, 191 (1922).

TABLE I

THE COMPRESSIBILITY FACTORS, PV FOR HYDROGEN (PV = 1 AT 1 ATM. AND 0°)

Pressure	Observer	20°	−25°	−50°	−70°
0		1.0719	0.9073	0.8159	0.7428
1		1.0732	.9085	.8170	.7438
25	Bartlett	....	.9230	.8307	.7566
	Schalkwijk	1.0887	...	...	...
	Verschoyle	1.0889	...	...	...
	Holborn	1.0889	.9224	.8303	.7560
	Witkowski	1.0885[a]	.9240	.8330	.7580
50	Bartlett	....	.9384	.8447	.7703
	Schalkwijk	1.1049	...	...	...
	Verschoyle	1.1053	...	...	...
	Holborn	1.1048	.9374	.8447	.7695
	Witkowski	1.1049[a]	.9382	.8450	.7710
75	Bartlett	1.1215[a]	.9540	.8598	.7852
	Schalwijk	1.1214	...	...	...
	Verschoyle	1.1218	...	...	...
	Onnes	1.1223	...	...	...
	Holborn	1.1217	.9546	.8597	.7842
100	Bartlett	1.1391	.9706	.8756	.8003
	Schalkwijk	1.1382	...	...	...
	Verschoyle	1.1383	...	...	...
	Onnes	1.1402	...	...	...
	Holborn	1.1384	.9695	.8754	.7980
	Amagat	1.1464 1.1385[a]	...	...	...
125	Bartlett	1.1558	.9867	.8922	.8155
	Verschoyle	1.1550 1.1560[a]	...	...	...
150	Bartlett	1.1731	1.0034	.9082	.8306
	Verschoyle	1.1717	...	...	...
	Amagat	1.1804 1.1735[a]	...	...	...
200	Bartlett	1.2079	1.0383	.9411	.8640
	Verschoyle	1.2054	...	...	...
	Amagat	1.2154 1.2094[a]	...	...	..
300	Bartlett	1.2799	1.1093	1.0112	.9340
	Amagat	1.2858 1.2817[a]	...	...	...
400	Bartlett	1.3511	1.1808	1.0832	1.0075
	Amagat	1.3578 1.3545[a]	...	...	...
500	Bartlett	1.4240	1.2542	1.1568	1.0804
	Amagat	1.4320 1.4274[a]	...	...	...
600	Bartlett	1.4958	1.3272	1.2301	1.1555
	Amagat	1.5057 1.5006[a]	...	...	...
800	Bartlett	1.6391	1.4717	1.3755	1.3018
	Amagat	1.6504 1.6450[a]	...	...	...
1000	Bartlett	1.7795	1.6139	1.5185	1.4443
	Amagat	1.7923 1.7885[a]	...	...	...

[a] Values by Kohnstamm and Walstra.

TABLE II

THE COMPRESSIBILITY FACTORS, PV, FOR NITROGEN

$PV = 1$ at 1 atmosphere and 0°

Pressure	Observer	20°	−25°	−50°	−70°
0		1.0738	0.9090	0.8174	0.7441
1		1.0735	.9082	.8162	.7432
25	Bartlett	....	...	...	...
	Verschoyle	1.0685	...	...	...
	Onnes	1.0689	...	...	...
	Holborn	1.0695	.8910	.7900	.7044
50	Bartlett	....	...	...	.6747
	Verschoyle	1.0667	...	...	...
	Onnes	1.0668	.8780	.7680	...
	Holborn	1.0672	.8780	.7672	.6680
	Smith and Taylor	1.0646	...	...	...
75	Bartlett	....	.8700	...	.6503
	Verschoyle	1.0685	...	...	...
	Onnes	....	...	...	...
	Holborn	1.0694	.8714	.7502	.6448
	Smith and Taylor	1.0644	...	...	...
100	Bartlett	1.0745	.8676	.7438	.6362
	Verschoyle	1.0737	...	...	...
	Holborn	1.0766	.8677	.7407	.6290
	Amagat	1.0796	...	...	...
	Smith and Taylor	1.0693	...	...	...
125	Bartlett	1.0836	.8738	.7433	.6340
	Verschoyle	1.0825	...	...	...
	Smith and Taylor	1.0784	...	...	...
150	Bartlett	1.0963	.8817	.7514	.6430
	Verschoyle	1.0947	...	...	...
	Smith and Taylor	1.0906	...	...	...
200	Bartlett	1.1320	.9151	.7854	.6823
	Verschoyle	1.1297	...	...	...
	Amagat	1.1332	...	...	...
300	Bartlett	1.2293	1.0179	.8986	.8053
	Amagat	1.2290	...	...	...
400	Bartlett	1.3467	1.1445	1.0334	.9477
	Amagat	1.3468	...	...	...
500	Bartlett	....	1.2798	1.1748	1.0914
	Amagat	1.4761	...	...	...
600	Bartlett	1.6098	1.4186	1.3159	1.2331
	Amagat	1.6115	...	...	...
800	Bartlett	1.8817	1.6958	1.5928	1.5111
	Amagat	1.8822	...	...	...
1000	Bartlett	2.1481	1.9600	1.8573	1.7783
	Amagat	2.1527	...	...	...

TABLE III

THE COMPRESSIBILITY FACTORS, PV, FOR A 3:1 MIXTURE OF HYDROGEN AND NITROGEN

$PV = 1$ at 1 atm. pressure and 0°

Pressure	Observer	20°[a]	−25°	−50°	−70°
0		1.0724	0.9077	0.8163	0.7431
1		1.0733	.9084	.8168	.7435
25	Bartlett	....	.9187	.8254	.7510
50	Bartlett	1.1029	.9320	.8367	.7597
	Verschoyle	1.1024	...	...	...
75	Bartlett	....	.9449	.8484	.7704
100	Bartlett	1.1351	.9597	.8618	.7820
	Verschoyle	1.1335	....	....	....
125	Bartlett	....	.9760	.8753	.7951
150	Bartlett	....	.9909	.8903	.8096
200	Bartlett	1.2014	1.0265	.9259	.8433
	Verschoyle	1.2037	...	...	...
300	Bartlett	1.2808	1.1025	1.0007	.9185
400	Bartlett	1.3622	1.1831	1.0837	1.0023
500	Bartlett	....	1.2679	1.1696	1.0901
600	Bartlett	1.5327	1.3547	1.2570	1.1776
800	Bartlett	1.7042	1.5277	1.4309	1.3536
1000	Bartlett	1.8729	1.6986	1.6028	1.5269

[a] Our data in this column are calculated from observed results at 0 and 25°.

justified because of the fact that the PV factor of a mixture of hydrogen and nitrogen is approximately a linear function of the gas composition. The PV values at 1 atmosphere pressure are calculated from the volume–temperature coefficients of the several gases at this pressure.[12]

Discussion of Results

The values shown in the tables represent the mean result of from two to ten independent experiments. Temperature and pressure are easily controlled to within 0.1%. The exact volume of the high pressure pipet is the most difficult factor to determine accurately. However, the data were taken immediately after a careful calibration of the pipet with nitrogen and directly before a second closely agreeing calibration with hydrogen. Experimental evidence from investigations of the compressibility of hydrogen containing 0.9% nitrogen and 5.6% nitrogen proved that the presence of 0.09% of nitrogen can affect the compressibility of pure hydrogen by not more than 1 part in 5000. While no experimental data are available that show the effect of small traces of argon on the compressibility of nitrogen, it is believed that this effect is also so small as to be less than the possible experimental error. The maximum error in the recorded data should not exceed 0.2%.

In the pressure and temperature ranges in which the new data may be

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[12] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, **3**, 6 (1928).

compared with earlier data by other investigators, the agreement is satisfactory. An exception is in non-agreement of the new data for nitrogen at −70° with results interpolated from Holborn's data at −50 and −100°. Here the deviation reaches a maximum of 1.14%.

Temperature and Deviation from the Law of the Ideal Gas

A convenient method of picturing the extent to which a gas under high pressure deviates from the law of the ideal gas is to plot the ratio

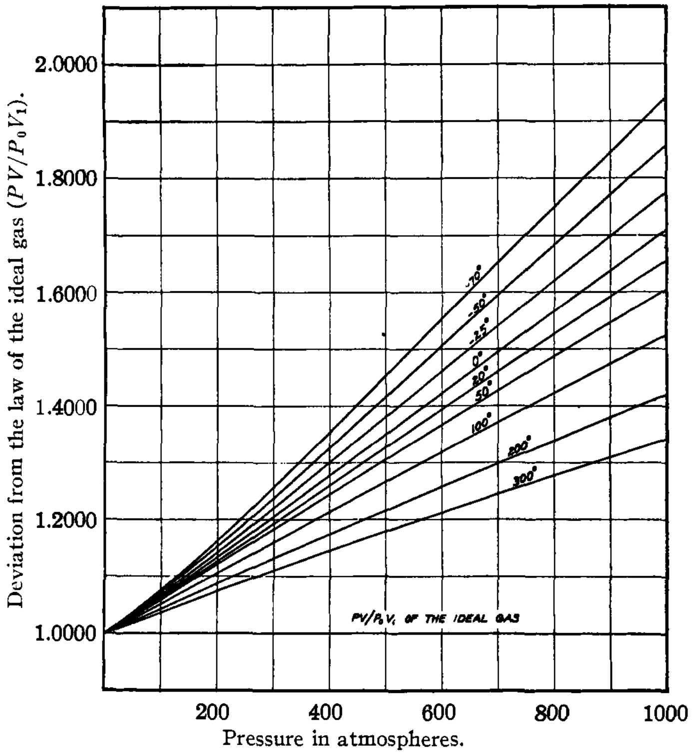

Fig. 2.—Pressure and pressure–volume product for hydrogen.

$(PV/P_0V_1)_T$ against pressure. The PV factor at any temperature T may be taken directly from the tables; the P_0V_1 factor is the PV factor at zero pressure and at the same temperature, T. It is therefore to be found as the first item in each column of the table. This results in bringing all the PV–P isotherms to a common origin. For the ideal gas the ratio $(PV/P_0V_1)_T$ is equal to unity. Figures 2, 3 and 4 show the deviations for hydrogen, nitrogen and the 3 : 1 mixture, respectively. In these diagrams are also included the results of previous work in this Laboratory[1] on these gases at 0° and higher temperatures. Especially interesting is the point at about 380 atmospheres' pressure where nitrogen exhibits approximately the same deviation at all temperatures from −70 to 100°. Obviously such a phenomenon cannot continue through an indefinite range of temperature, for the deviation pressure curve must approach with increasing temperature the horizontal line where the ratio $(PV/P_0V_1)_T$ is

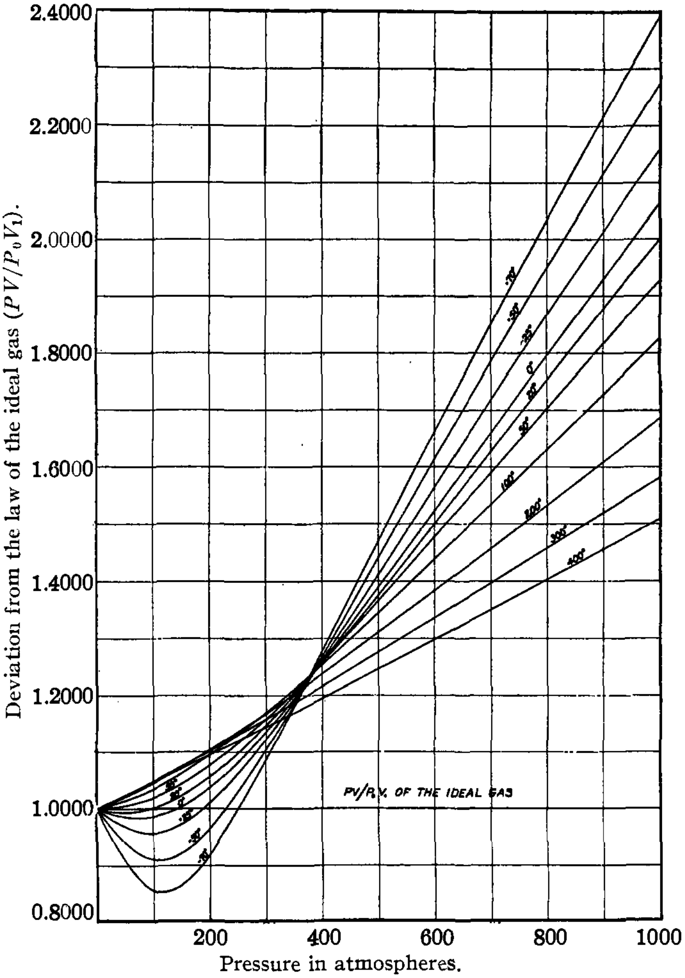

Fig. 3.—Pressure and pressure-volume product for nitrogen.

unity. At 200° and higher temperatures the deviation curves "fan out" toward the ideal gas isotherm. It is apparent, in the light of experimental data, that the general statement "a gas more nearly conforms to the law of the ideal gas with increasing temperature," must be modified somewhat, for in the case of nitrogen and of any other gas that exhibits a similar dip in the deviation-pressure curve, there are pressures and temperatures at which the deviation increases with temperature to a well-defined maximum. The methods by which the PV data in Tables I, II and III may be used in the solving of practical pressure–volume–temperature problems of laboratory or plant were presented in an earlier report.[1]

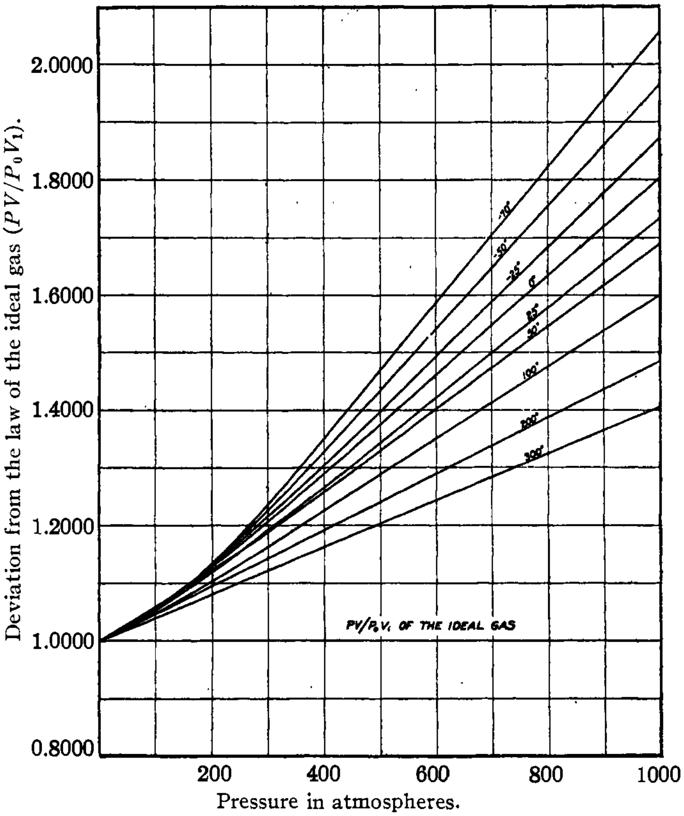

Fig. 4.—Pressure and pressure–volume product of a 3:1 hydrogen–nitrogen mixture.

The authors wish to express appreciation to the staff of the Fixed Nitrogen Research Laboratory for their interest and for their efficient help in paving the way to the successful conclusion of this investigation.

Summary

The compressibility isotherms of hydrogen, nitrogen and a 3:1 mixture of these gases each at 20, −25, −50 and −70° have been presented. In the case of nitrogen, a curious phenomenon appears at about 380 atmospheres' pressure where the deviation from the law of the ideal gas is nearly constant through the temperature range −70 to +100°.

WASHINGTON, D. C.