[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY OF THE BUREAU OF SOILS]

THE COMPRESSIBILITY ISOTHERMS OF HYDROGEN, NITROGEN AND MIXTURES OF THESE GASES AT 0° AND PRESSURES TO 1000 ATMOSPHERES

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Direct synthetic ammonia processes now in use by the industries require mixtures of hydrogen and nitrogen at pressures ranging from 100 to 1000 atmospheres. Practical engineering design and scientific control of these processes demand complete data concerning the properties of the compressed gases.

Data have already been presented from this Laboratory concerning the vapor content of a compressed 3:1 hydrogen-nitrogen gas mixture in contact with liquid ammonia and with liquid water and also similar data for the pure gases in contact with liquid water.[1] This report deals with the compressibility and density of the same gases and of additional mixtures of hydrogen and nitrogen.

It has long been recognized that the gas law as defined by Boyle and Charles

$$pv = RT \tag{1}$$

fails to define the behavior of gases even under moderately increased pressure. However, in assembling the data reported in this paper it is assumed that at atmospheric pressure hydrogen and nitrogen and their mixtures conform to the law of the ideal gas. The deviation from the law at higher pressures or the "compressibility factor" is expressed as a ratio

$$(pv/p_0v_0)_T \tag{2}$$

where pv is the product of the pressure (atmospheres) times volume (liters) at pressure p, and p_0v_0 is the product of the pressure times volume at atmospheric pressure, p_0.

Measurement of and speculation regarding the deviations from the law of the ideal gas have provided a fertile field of investigation.[2] Mixed gases have, however, received little attention. Air has been frequently investigated but it presents no peculiar phenomena. Assuming the accuracy of Amagat's[3] results for nitrogen and for oxygen, the observed compressibility of air is within a maximum deviation of 0.4%, a linear function of the composition at pressures to 1000 atmospheres. Verschaffelt,[4] working

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[1] (a) Larson and Black, THIS JOURNAL, 47, 1015 (1925). (b) Bartlett, *ibid.*, 49, 65 (1927).

[2] For a bibliography of 700 references concerning this and closely allied subjects see *U. S. Bur. Standards Circ.*, No. 279, **1926**.

[3] Amagat, *Ann. chim. phys.*, [6] **29**, 68 (1893).

[4] Verschaffelt, *Comm. Phys. Lab. Leiden*, No. **47, 1899**.

at pressures below 100 atmospheres, found that mixtures of carbon dioxide and hydrogen do not conform to the additive pressure rule. Masson and Dolley[5] found wide deviation from the additive rule in their investigation of mixtures of argon-ethylene and oxygen-ethylene and a much smaller deviation in an argon-oxygen mixture. The deviation is largest when the two constituents are of highly different molecular dimensions and have widely different critical properties. These conclusions are supported by the recently published work of Verschoyle[6] on mixtures of nitrogen and hydrogen at pressures to 200 atmospheres. The results of the present investigation, which have been obtained independently and probably simultaneously with those of Verschoyle, support his findings but cover a much wider pressure range and deal with a larger number of gas mixtures. New phenomena are observed at high pressures.

While this study is primarily concerned with mixed gases, it is important to know the compressibility factors of pure hydrogen and pure nitrogen. An excellent critical résumé of all experimental data on these pure gases is furnished by Verschoyle.[6] He, however, considers as probably less reliable the classical work of Amagat[3] and the more recent work of Kohnstamm and Walstra[7] who alone have investigated the compressibility of these gases, at 15.4° and at 20°, in the important range from 200 to 1000 atmospheres. For the 0° isotherms of the pure gases, dependence must be placed on Amagat's experimental results or on values calculated from one of the numerous equations of state derived at lower pressures. In Table I are recorded pv/p_0v_0 values at 1000 atmospheres' pressure, calculated by several of the better known equations of state.

TABLE I

pv/p_0v_0 FROM VARIOUS EQUATIONS OF STATE OF NITROGEN AND HYDROGEN AT 1000 ATMOSPHERES AND 0°

Name	Amagat (obs.)	Van der Waals	Dieterici	Berthelot	Keyes	Verschoyle
N_2	(2.0685)	2.442	2.120	1.650	1.983	3.594
H_2	(1.7200)	2.090	2.130	1.645	1.640	1.794

As it is evident that such equations cannot be employed for quantitative calculations at high pressures, the determination of the compressibility of the pure gases is included in this investigation.

Method

A quantity of gas at known pressure and temperature is confined in a heavy steel pipet of known volume. This 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.

[5] Masson and Dolley, *Proc. Roy. Soc.*, **103A**, 524 (1923).

[6] Verschoyle, *ibid.*, **111A**, 552 (1926).

[7] Kohnstamm and Walstra, *Proc. Roy. Acad. Amsterdam*, **17**, 203 (1914).

Preparation and Purification of the Gases

Hydrogen was prepared by the electrolysis of a solution of potassium hydroxide. Nitrogen was obtained by the fractional distillation of liquid air. It was purchased on the market and was guaranteed by the manufacturers to contain less than 0.2% impurity. The most likely impurities are oxygen and small quantities of noble gases. All mixtures of hydrogen and nitrogen containing over 34% of hydrogen were made by burning hydrogen with air in the proper proportions. Lower hydrogen concentrations could not be obtained by this process because of the great heat generated in the burner, and on account of incomplete combustion of the oxygen. Mixtures of low hydrogen content were made by adding nitrogen in the proper proportions to some one of the hydrogen-nitrogen mixtures. No attempt was made to remove argon. Analyses were made by combustion with pure oxygen.

While under pressure traces of oxygen were removed from the gases containing hydrogen by the catalytic action of copper at 325°. Compressed nitrogen was freed from oxygen by copper at 450°. Water vapor was removed by means of an ice-cooled condenser following the deoxidizer. The hydrogen was further purified in a trap cooled with liquid air.

Apparatus

A complete description of the hydrogen burner, compressors, high-pressure gages, purification train and general high-pressure equipment in use at the Fixed Nitrogen Research Laboratory has recently been published.[8] For the discussion of the present problem it will be assumed that gas at any desired pressure, to 1000 atmospheres, is available at the shut-off valve A (Fig. 1).

The compressibility apparatus consists of two parts: (a) the high-pressure system containing the steel pipets connected in parallel but capable of independent use; (b) the low-pressure system in which the volume of the expanded gas is measured. Both systems are completely immersed in thermostatically controlled baths. The bath controlling the temperature of the high-pressure system is built for use through a range of temperatures. For the purpose of this investigation it was filled to the top with a mixture of water and finely crushed ice. The two pipets are of chrome vanadium steel. The insert in Fig. 1 shows the detail of construction. The chamber in which the compressed gas is confined is situated as near as possible to the center of the bath. The conduit from the pipets to the high-pressure manifold and to the capillary stopcock at G is of 1.5 × 4.5mm. steel tubing.

The bath, controlling the temperature of the low-pressure system, is provided with a heavy glass front through which all apparatus is visible and manometers may be read. As the expanded gas enters the bath, it passes through a capillary copper coil where it is brought to the temperature of the bath. It is then saturated with water vapor in the humidifiers and displaces an equal volume of moist gas into the buret through J. The open-end manometer, filled with a clear, heavy mineral oil, measures the differential

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[8] Ernst, Reed and Edwards, *Ind. Eng. Chem.*, **17**, 775 (1925). Ernst, *ibid.*, **18**, 664 (1926). Ref. 1 b.

pressure between that existing within the system and barometric pressure at the time of the experiment. The water-level gage is a convenience in determining the height of the water in the hydrostatic bottle. The mercury manometer and a 7-meter water manometer (not shown in the diagram) record the difference between total pressure within the hydrostatic bulb and barometric pressure. This pressure is regulated by a centrifugal vacuum-pressure pump attached at N. The needle valve at M is used as a fine control valve in adjusting pressure.

Calibration.—The thermometers, the manometers and the buret were calibrated by the usual methods. The dead-weight pressure gage is of extremely accurate construction. The diameter of the rotating piston is 0.4891 cm. and of the cylinder 0.4896 cm. The effective diameter is taken as 0.4893 ± 0.002 cm. All weights used with this gage were calibrated against an absolute standard.

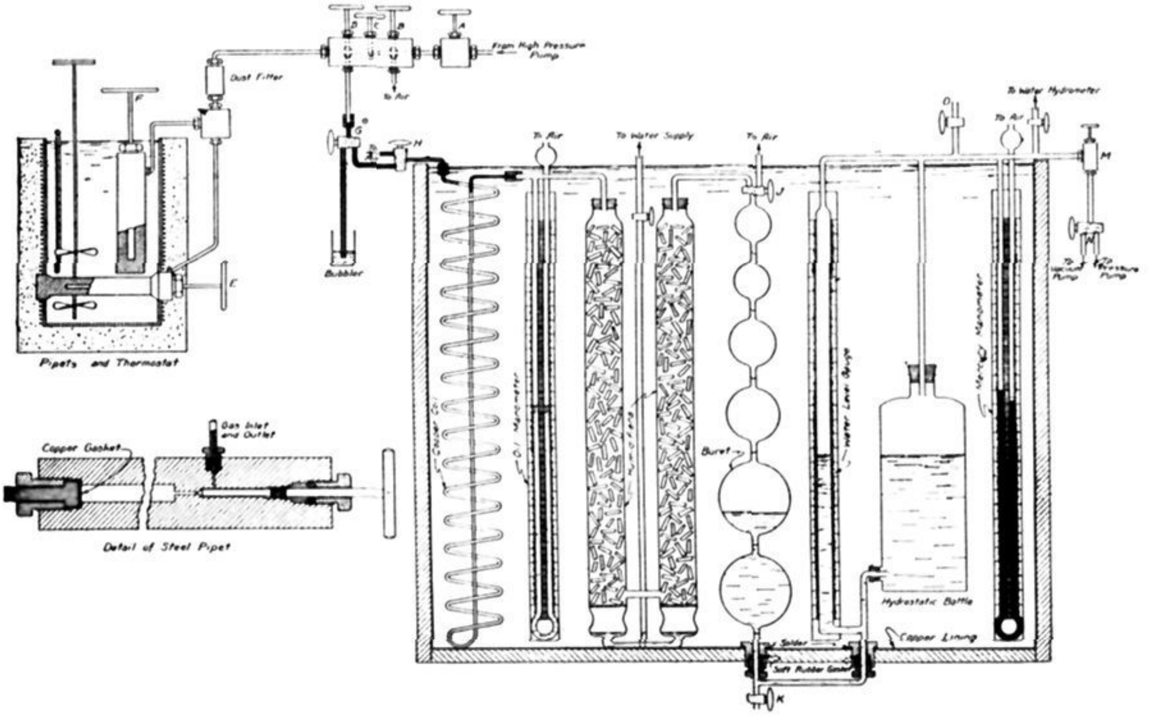

Fig. 1.—Apparatus used in the determination of the compressibility of gases.

The steel pipets are of two volume capacities, approximately 27.8 cc. and 2.38 cc., respectively. The larger pipet is employed at 50 and 100 atmospheres' pressure and the smaller at 100 to 1000 atmospheres' pressure. At 100 atmospheres' pressure expansions are made from both pipets and the size of the smaller pipet relative to the larger is established as the ratio of the volumes of expanded gas. This comparison is made at every change of gas composition. The larger pipet was calibrated with mercury for volume at 26.7° by the Bureau of Standards and later by this Laboratory. The two calibrations agreed to within 0.025%.

The steel used in these pipets has a composition similar to S346, S551 and S555, tested by the Bureau of Standards.[9]

The temperature coefficient of volume change was derived from an equation furnished by Smith and Taylor.[10] The numerical values of the constants are based on data of the Reichsanstalt.

$$V_t^{\mathrm{Fe}} = V_0\,(1 + 3.25 \times 10^{-5}t + 2.85 \times 10^{-8}t^2 - 1.65 \times 10^{-11}t^3) \qquad (3)$$

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[9] *Bur. Standards Sci. Papers*, No. 433, 1922.

[10] Smith and Taylor, THIS JOURNAL, **45**, 2113 (1923).

The volume change of the pipet due to internal pressure is not easily calculated for thick-walled cylinders. Fortunately, the effect is not large and until laboratory tests can be made, an expression derived from an equation presented by Love[11] for thin-walled cylinders is employed. It assumes a cylinder long in comparison with radius, and consequently neglects the uncertain end effects.

$$\Delta V = \frac{V_0}{E(r_2^2 - r_1^2)} [3(1 - 2\mu)(p_1 r_1^2 - p_2 r_2^2) + 2(1 + \mu)(p_1 - p_2) r_2^2] \qquad (4)$$

V is the inside volume of the cylinder, E the modulus of elasticity of steel (20.4×10^5 atm./cm.^{2}), r_2, r_1 the external and internal radii of the cylinder, p_1 and p_2 the external and internal pressures and μ Poisson's ratio (0.287).[12] In the larger of the pycnometers, r_1 is 0.7620 cm. and r_2 is 2.6492 cm. and the length of the chamber 15.24 cm. In the smaller pycnometer used at high pressures, r_1 is 0.2381 cm., r_2 is 1.7463 cm. and the length of the chamber 13.41 cm. The pressure-correction factor on the large pipet at 100 atmospheres is calculated to be 1.00014 and on the small pipet, at 1000 atmospheres, 1.00129. The change in volume due to the bulge at the end of the cylinder is calculated to be negligible in cylinders of these dimensions (a maximum of 6×10^{-7} cc. at 1000 atm.). Except for the uncertainty introduced by this method of computation of volume change with pressure, it is believed that the maximum errors in the average results presented in this paper lie between 0.1 and 0.2%.

Manipulation.—The high-pressure system is thoroughly flushed with the gas under investigation by filling with gas through A, closing A and releasing the gas through B. A stream of gas is also passed through the humidifier and bubbled through the confining liquid until it is thoroughly saturated. With B and D closed and C, E and F open, the pipets are filled by opening A. Pressure is maintained constant for about ten minutes. While the system is coming to temperature equilibrium, J is opened to the air and the buret filled to the stopcock J by pressure within the hydrostatic bottle. J is closed and O opened to release the pressure. H is opened to the air until the oil manometer indicates that atmospheric pressure has been attained in the humidifiers. E and F and then A are closed and B is opened to release most of the gas in the connecting tubes. C is closed to prevent any leakage of gas from the high-pressure side of the system and D opened through G to the bubbler. If F or E are not leaking, bubbling ceases almost immediately. Both sides of the stopcock system G, H are now at atmospheric pressure.[13] G and H are manipulated to connect the two systems. J is opened to the humidifiers and the confining liquid falls a short distance in the buret, leaving the system from F and E to the buret under reduced pressure, the magnitude of which is

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

[12] Holborn, Scheel and Henning, "Wärmetabellen," Friedrich Vieweg and Son, Braunschweig, 1919, p. 53.

[13] The gas in the conduit tube from E to H is not at controlled temperature. It is assumed that conditions before and after expansion are identical. The capacity is about 4 cc. A temperature change of 10° would cause a volume change of 0.15 cc. which is but 0.07% of the smallest volume measured (200 cc.).

measured by the height of the oil manometer. E or F is then opened with great care. Flow of the expanding gas is indicated by the fall of the liquid in the buret and by the change in level of the oil manometer. O is closed and by means of pressure in the hydrostatic bottle, the pressure within the system is again brought to atmospheric pressure. J is closed. The gas in the buret is equivalent in amount to the gas which expanded from the pipet.

Again, by regulating the pressure on the hydrostatic bottle, the liquid level is brought to one of the etched division points between the bulbs, and the readings of the various manometers are recorded.

Calculation of Results

The volume of the space between the stopcock J and each etched mark was determined by calibration. The pressure on the gas is the algebraic

TABLE II

TYPICAL DATA TABLE USED IN COMPRESSIBILITY INVESTIGATIONS[a]

	Expansion 31		Expansion 32		Expansion 33	
	Reduced press.	Increased press.	Reduced press.	Increased press.	Reduced press.	Increased press.
Date	6/9/26					
Absolute pressure, atm.	800.0					
Barometric press., corr.	750.4	750.3	750.4	750.3	750.3	750.3
Temp. of high-pressure system	0.0	...	...	...	...	...
Temp. of low-pressure system	25.0	...	...	...	...	...
Vapor pressure of water, mm. of Hg, 25°.	23.5	...	...	...	...	...
Mercury manometer (top), mm.	480.5	378.6	480.4	378.6	480.4	379.0
Mercury manometer (bottom), mm.	165.6	261.0	165.8	260.8	165.9	260.3
Height of mercury manometer, mm.	314.9	117.6	314.6	117.8	314.5	118.7
Corr. mercury manometer (0°), mm.	−313.5	117.1	−313.2	117.3	−313.1	118.2
Water manometer (top), mm.	5385	4050	5385	4049	5389	4060
Water manometer (bottom), mm.	1105	2439	1108	2441	1109	2536
Height of water manometer, mm	4280	1611	4277	1608	4280	1624
Temp. of water manometer, °C	32.5	32.0	31.5	35.5	35.0	35.0
Height of water manometer, mm. of Hg, 0°.	−313.2	117.9	−313.0	117.6	−312.9	118.8
Water col. (buret), mm.	129.0	284.0	129.0	284.0	129.0	284.0
Water col. (water-level tube), mm.	219.0	154.0	219.0	154.0	219.0	154.0
Height of water col., mm.	−90.0	130.0	−90.0	130.0	−90.0	130.0
Height of water col., mm. of Hg, 0°	− 6.6	9.6	− 6.6	9.6	− 6.6	9.6
Corr. for capillarity, mm. of Hg	0.3	...	...	...	...	...
Total press. on gas in buret (mercury manometer, mm. of Hg)	420.2	834.6	420.6	834.9	420.7	835.8
Total press. on gas in buret (water manometer, mm. of Hg)	420.4	835.4	420.7	835.1	420.9	836.4
Av. press. on gas			420.6	835.3		
Vol. of gas in buret, cc			2077.6	1047.4		
Vol. of gas, 760 mm., 0°, cc			1053.3	1054.5		
Vol. of gas in pipet, cc			2.4	2.4		
Total vol. of expanded gas (760 mm., 0°), cc.			1055.7	1056.9[b]		
Av. vol. of expanded gas (760 mm., 0° = p_0v_0), cc.				1056.5		
Value of pv (2.3758 × 800)				1900.6		
pv/p_0v_0				1.7985		

[a] Data in this table are for pure nitrogen at 0° and at 800 atmospheres' pressure.

[b] As the increased pressure readings can be made with the same actual error limit as the reduced pressure reading, the proportional degree of accuracy is greater. Increased pressure readings are, therefore, given twice the weight in calculating average results.

sum of the following. (1) The corrected barometric pressure in millimeters of mercury. (2) The differential pressure indicated by the mercury manometer corrected to 0° (or) the differential pressure indicated by the water manometer corrected to millimeters of mercury at 0°. The average of the two manometer readings is used in calculations. (3) The differential pressure due to the difference in height of liquid in the buret and in the water-level gage, corrected to millimeters of mercury at 0°.

When calculating the volume of dry gas, the vapor pressure of water at the temperature of the bath is subtracted from the total pressure. Capillarity at the constricted points in the measuring bulbs requires a positive pressure correction of 0.3 mm. of mercury.

When possible the quantity of gas is measured under both increased and reduced pressure, thus giving a check on the results. The value of p_0v_0 is calculated from the formula

$$p_0v_0 = (p/760)(273.1/T)V \tag{5}$$

where p is the corrected pressure on the gas in the buret, T the temperature of buret bath and V the volume of gas in the buret. Data for a single point on one curve (Table II) will suffice to make clear the method used in recording data and calculating results. The average results from 2 to 10 separate expansions are used in calculating each of the eighty compressibility factors given in Table IV.

Experimental Results

Table III records the compressibility factors, pv/p_0v_0, observed for pure hydrogen and pure nitrogen and, for purposes of comparison, any corresponding data furnished by Amagat,[3] Holborn,[14] Onnes,[15] Witkowski,[16] Smith and Taylor[10] and Verschoyle.[6]

TABLE III

THE COMPRESSIBILITY FACTORS, pv/p_0v_0, FOR HYDROGEN AND NITROGEN AT 0.0°

Hydrogen

At 0° and 1 atm. pressure $p_0v_0 = 1$

Press., atm.	Bartlett	Amagat	Holborn	Witkowski	Verschoyle	Smith and Taylor	Onnes
50	1.0331	....	1.0311	1.0309	1.0311	....	....
100	1.0660	1.0690	1.0640	....	1.0637	....	....
200	1.1312	1.1380	1.1328[a]	....	1.1313	....	....
300	1.2038	1.2090	....	....	....	....	....
400	1.2768	1.2830	....	....	....	....	....
600	1.4213	1.4315	....	....	....	....	....
800	1.5671	1.5775	....	....	....	....	....
1000	1.7107	1.7200	....	....	....	....	....

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[14] Holborn, *Ann. Physik*, **63**, 674 (1920).

[15] Onnes, *Comm. Phys. Lab. Leiden*, No. 169D (1924).

[16] Witkowski, *Krahauer Anzeiger*, 305 (1905).

TABLE III (*Concluded*)

Nitrogen

Press., atm.	Bartlett	Amagat	Holborn	Witkowski	Verschoyle	Smith and Taylor	Onnes
50	0.9839	....	0.9852	....	0.9840	0.9835[b]	0.9846
100	.9840	0.9910	.9856	....	.9842	.9830	.9784[a]
200	1.0330	1.0390	1.0331[a]	....	1.0346	1.0340[a]	0.9943[a]
300	1.1332	1.1360	....	....	....	....	....
400	1.2540	1.2570	....	....	....	....	....
600	1.5211	1.5260	....	....	....	....	....
800	1.7985	1.7980	....	....	....	....	....
1000	2.0659	2.0685	....	....	....	....	....

[a] Extrapolated results.

[b] Recalculated from corrected data furnished by F. G. Keyes.

Table IV summarizes the observed compressibility factors of pure hydrogen, pure nitrogen and eight mixtures of these gases. These data appear as full-line curves on a pressure-compressibility factor-composition

TABLE IV

OBSERVED (o) AND CALCULATED (c) COMPRESSIBILITY FACTORS (pv/p_0v_0) AND OBSERVED DENSITY (d) FOR HYDROGEN, NITROGEN AND THEIR MIXTURES

0° and 1 atm., $p_0v_0 = 1$ Density expressed in g. per liter

Press., atm.	H_2, % N_2 %	100 0	88.5 11.5	75.4 24.6	55.1 44.9	45.9 54.1	34.1 65.9	26.0 74.0	13.7 86.3	6.1 93.9	0 100
1	o	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	c	....	....	....	....	....	....	....	....	....	....
	d	0.0898	0.2233	0.3753	0.6111	0.7179	0.8548	0.9489	1.0917	1.1799	1.2507
50	o	1.0331	1.0312	1.0257	1.0193	1.0167	1.0094	1.0044	0.9951	0.9898	0.9839
	c	1.0327	1.0306	1.0275	1.0201	1.0159	1.0094	1.0042	.9951	.9887	.9831
	d	4.3461	10.827	18.295	29.976	35.305	42.341	47.237	54.854	59.603	63.558
100	o	1.0660	1.0616	1.0571	1.0454	1.0392	1.0274	1.0195	1.0036	0.9942	0.9840
	c	1.0649	1.0624	1.0575	1.0456	1.0385	1.0276	1.0190	1.0040	.9937	.9847
	d	8.4240	21.034	35.503	58.456	69.082	83.200	93.075	108.78	118.68	127.10
200	o	1.1312	1.1225[a]	1.1216	1.1094	1.0990	1.0862	1.0735	1.0557	1.0445	1.0330
	c	1.1314	1.1298	1.1249	1.1101	1.1014	1.0875	1.0765	1.0578	1.0450	1.0338
	d	15.876	39.786	66.922	110.17	130.65	157.39	176.79	206.82	225.93	242.15
300	o	1.2038	1.2014	1.1978	1.1932	1.1814	1.1704	1.1628	1.1494	1.1409	1.1332
	c	1.2063	1.2031	1.1988	1.1882	1.1832	1.1735	1.1653	1.1502	1.1391	1.1279
	d	22.379	55.760	93.997	153.65	182.30	219.10	244.81	284.94	310.26	331.10
400	o	1.2768	1.2781	1.2811	1.2841	1.2790	1.2701	1.2669	1.2613	1.2602	1.2540
	c	1.2765	1.2786	1.2810	1.2813	1.2767	1.2708	1.2667	1.2606	1.2568	1.2538
	d	28.132	69.885	117.18	190.36	224.52	269.21	299.60	346.21	374.51	398.95
600	o	1.4213	1.4369	1.4514	1.4760	1.4806	1.4904	1.4969	1.5097	1.5171	1.5211
	c	1.4214	1.4356	1.4528	1.4780	1.4841	1.4928	1.4994	1.5106	1.5182	1.5248
	d	37.909	93.242	155.15	248.41	290.92	344.12	380.35	433.87	466.64	493.34
800	o	1.5671	1.5929	1.6240	1.6761	1.6883	1.7158	1.7321	1.7642	1.7794	1.7985
	c	1.5663	1.5926	1.6246	1.6748	1.6914	1.7147	1.7320	1.7606	1.7796	1.7957
	d	45.842	112.15	184.88	291.68	340.18	398.55	438.27	495.05	530.47	556.33
1000	o	1.7107	1.7510	1.7952	1.8737	1.9003	1.9348	1.9632	2.0141	2.0401	2.0659
	c	1.7112	1.7497	1.7965	1.8715	1.8988	1.9367	1.9647	2.0107	2.0411	2.0667
	d	52.493	127.53	209.06	326.15	377.78	441.80	483.34	542.03	578.35	605.40

[a] This result appears to be about 0.5% low. No adequate explanation can be given. It was the average result of five independent, closely checking experiments.

diagram (Fig. 2). In Table IV are also included the corresponding values calculated from empirical equations of state derived from our observed data (Equations 6–12) and the observed density of each gas or gas mixture. The latter values are calculated by Equation 16.

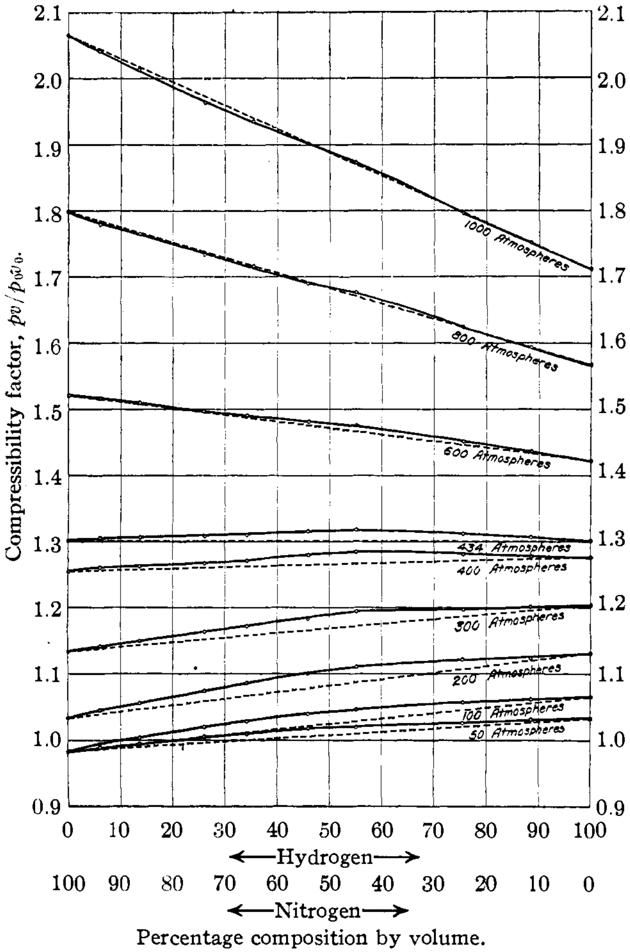

Fig. 2.—Composition, pressure and pressure-volume relationships of nitrogen-hydrogen gas mixtures at 1–1000 atmospheres and 0.0°. — — — — — Calculated from the additive law. ———— Observed.

Table V records the compressibility factors of mixtures containing 25, 50 and 75% of hydrogen taken from the smoothed curves of Fig. 2, for purposes of comparison with Verschoyle's results at pressures to 200 atmospheres. Together with the data for pure hydrogen and pure nitrogen, these data are plotted in a pressure-volume–pressure diagram in

Fig. 3. Other members of this family of curves are omitted from the diagram in order to prevent over-crowding.

TABLE V

COMPRESSIBILITY FACTORS, pv/p_0v_0, FOR MIXTURES OF HYDROGEN AND NITROGEN

0° and 1 atm. pressure; $p_0v_0 = 1$

Press., atm.	25:75, H_2:N_2 Bartlett	Verschoyle	50:50, H_2:N_2 Bartlett	Verschoyle	75:25, H_2:N_2 Bartlett	Verschoyle
50	1.0030	1.0035	1.0178	1.0172	1.0250	1.0276
100	1.0180	1.0186	1.0420	1.0420	1.0560	1.0570
200	1.0720	1.0760	1.1040	1.1062	1.1205	1.1244
300	1.1615	....	1.1880	....	1.1980	....
400	1.2660	....	1.2820	....	1.2815	....
600	1.4980	....	1.4800	....	1.4520	....
800	1.7360	....	1.6855	....	1.6245	....
1000	1.9670	....	1.8910	....	1.7980	....

Discussion of Results

Results of this investigation on pure hydrogen agree with those of Holborn and Verschoyle to 200 atmospheres with a maximum deviation of 0.22%. Through the entire pressure range results lie consistently below Amagat's values with a maximum deviation of 0.71% at 800 atmospheres.

The present data on nitrogen agree remarkably well with the data given by Verschoyle to 100 atm., while at 200 atm. the differences amount to only 0.15%. Moreover, the average of both of these sets of data agree with the results obtained for the same substance by Holborn,[14] by Onnes[15] and by Smith and Taylor[10] to within 0.14%. Each investigator used either nitrogen of approximately the same degree of purity or containing small traces of impurity which have little effect on compressibility.

The deviation of the results obtained in this investigation from those of Amagat may be due to differences in the pressure gages or to a difference in gas composition. The fact that results on both hydrogen and nitrogen at pressures to 200 atm. are 0.5 to 0.7% below Amagat's values supports the former hypothesis. At pressures of 800 to 1000 atm., however, the two investigations on nitrogen give closely agreeing compressibility factors. Amagat's "atmospheric nitrogen" contained 1.18 volume % of argon and 0.25 volume % of other noble gases.[17] Nitrogen used in this Laboratory, manufactured by the fractional distillation of liquid air, is probably quite free from argon. Holborn and Schultze's[18] data for argon at pressures extending to 100 atm. indicate that this substance is more compressible than nitrogen. It would be anticipated, therefore, that at low pressures Amagat's results would be lower than results obtained with pure nitrogen. In reality, however, little can be foretold as to the compressibility of mixed gases. The agreement between the results of the two investigations at

[17] Schloesing, *Compt. rend.*, **121**, 605 (1895).

[18] Holborn and Schultze, *Ann. Physik*, **47**, 1089 (1915).

high pressure forms an interesting commentary on the remarkably accurate work of Amagat, the pioneer in this field of investigation.

The compressibility factor of a mixture of hydrogen and nitrogen (Table IV, Fig. 2) is not a linear function of the composition of gas. On the diagram the factors for the "ideal"[19] mixtures are shown as broken-line curves and the observed points are connected by full lines. At 434 atm. pressure,

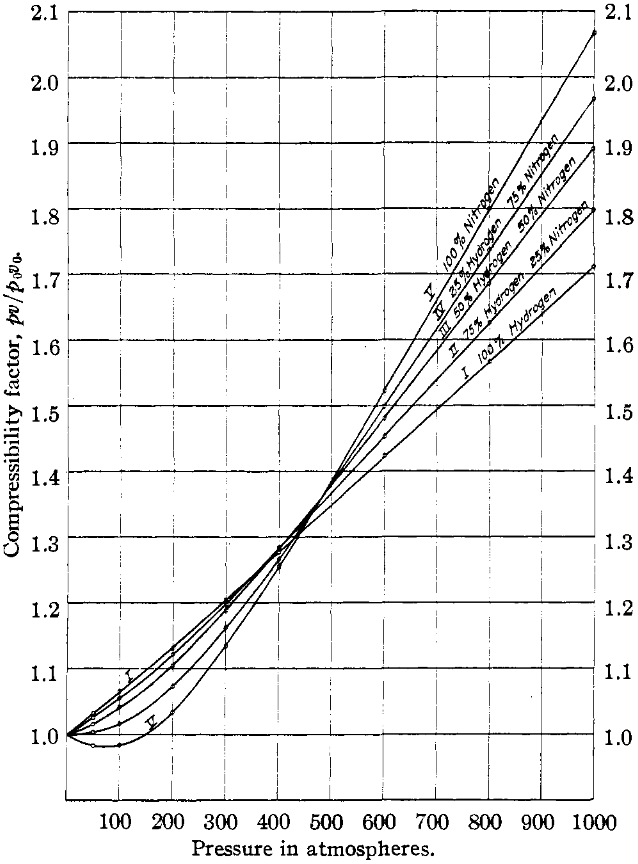

Fig. 3.—The relation of pressure to the pressure-volume product of nitrogen, hydrogen and their mixtures at 1–1000 atmospheres and 0.0°.

hydrogen and nitrogen and therefore all "ideal" mixtures of these gases have the same compressibility factor. At pressures to 600 atm., the deviation from the additive law is positive at all pressures investigated, with a maximum of 1.90% at about 60% of hydrogen, and at 200 atm. pressure.

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[19] An "ideal" mixture in the sense that the properties of the mixture may be calculated, by the additive rule of Leduc, from the properties of the pure components.

This deviation drops to 0.78% at 50 atm. and to 0.20% at 1000 atm. A mixture containing 25% of hydrogen shows a positive deviation to 400 atm., an "inversion point" or 0.0% deviation at 600 atm., and a negative deviation of 0.55% at 1000 atm. pressure.

The values in Table V show that at pressures up to 100 atm., the results of this investigation on mixed gases agree with those of Verschoyle[6] to within 0.10%. At 200 atm. Verschoyle's results are higher by a maximum of 0.37%. Two hundred atm. pressure is, however, near the upper limit of pressure employed by Verschoyle and near the lower limit of pressure employed in this investigation.

The phenomena observed in connection with the compressibility of mixtures of nitrogen and hydrogen seem to be of the same nature as those observed by Masson and Dolley.[5] The magnitude of the deviation is similar to that observed in an argon-oxygen mixture and very much less than that for either argon-ethylene or oxygen-ethylene mixtures which show a maximum of 8% at 125 atm. Moreover, deviation in the case of a hydrogen-nitrogen mixture is positive in the 125-atm. range in which the deviation of an argon-oxygen mixture is negative. In this respect the mixture is similar to the carbon dioxide-hydrogen mixture investigated by Verschaffelt.[4] The "inversion point" observed by Masson and Dolley for a single mixture of argon and ethylene finds its counterpart in the inversion points observed for mixtures of nitrogen and hydrogen.

Equations of State and Working Formulas

While the mass of experimental data presented in this paper offers material for testing the more theoretical type of equations of state in which attractive forces and molecular magnitudes are determining factors[20] this report will deal only with the purely empirical type of equation in use by Onnes[15] and others

$$pv/p_0v_0 = A + Bp + Cp^2 + Dp^3 \qquad (6)$$

where p is the pressure.

Inspection of the curves of Fig. 3 shows that at pressures to 350 atm. the third-power term must be utilized, while at pressures from 350 to 1000 atm., the curve is practically linear and requires but the first two terms of the equation. For this reason, constants for the two pressure ranges will be derived separately. The method of least squares has been employed in determining the numerical values of the constants.

The Pressure Range 1 to 350 Atmospheres

The compressibility factor of nitrogen or hydrogen and a mixture of these gases may be calculated with a maximum deviation of 0.5% (with

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[20] Fifty-six equations of state have been assembled and published by Partington and Schilling ["The Specific Heat of Gases," D. Van Nostrand Co., **1924**].

one exception mentioned in Table IV) from observed values by expressing B, C and D in terms of gas composition. A is the pv/p_0v_0 at the hypothetical zero pressure and differs from 1 by less than 0.06% under the conditions of this investigation. These values are given in the form of a graph in Fig. 4. They may be mathematically derived by the use of

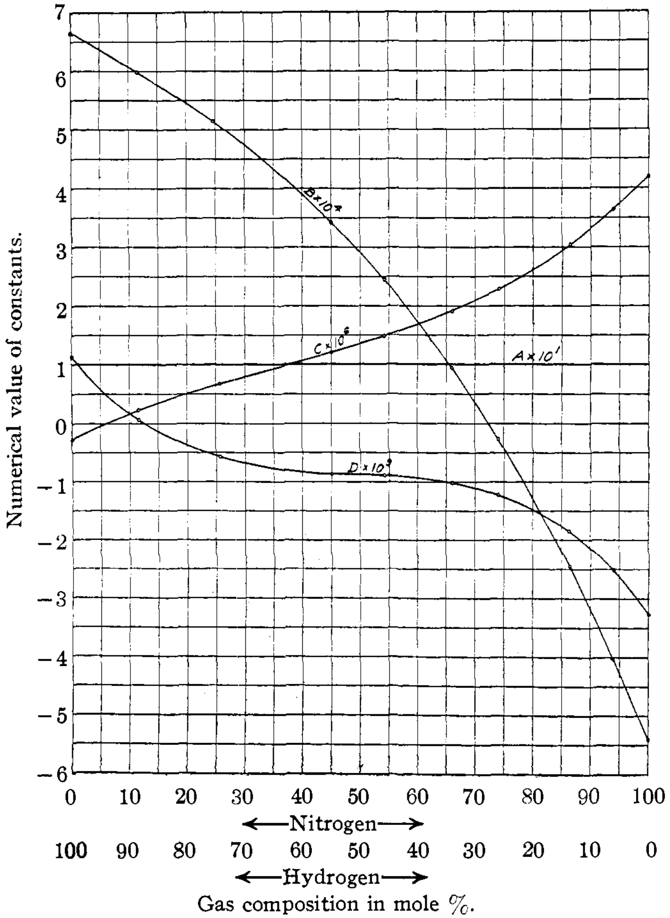

Fig. 4.—Numerical values of constants for use in calculation of compressibility factors of nitrogen, hydrogen and their mixtures to 400 atmospheres' pressure at 0°; $pv/p_0v_0 = A + Bp + Cp^2 + Dp^3$.

TABLE VI

VALUES OF CONSTANTS IN EQUATION OF TYPE 7 FROM OBSERVED DATA

Constant	*a*	*b*	*c*	*d*
B	$+6.645 \times 10^{-4}$	-5.413×10^{-6}	-1.547×10^{-8}	-5.093×10^{-10}
C	-2.659×10^{-7}	$+5.045 \times 10^{-8}$	-6.596×10^{-10}	$+6.017 \times 10^{-12}$
D	$+1.1431 \times 10^{-9}$	-1.1773×10^{-10}	$+2.3461 \times 10^{-12}$	-1.6041×10^{-14}

the constants in Table VI from the type expression

$$B = a + bx + cx^2 + dx^3 \tag{7}$$

where x is the mole % of nitrogen in the mixture.

The Pressure Range 350 to 1000 Atmospheres

In a similar manner the compressibility factor of hydrogen or nitrogen or any of their mixtures in the higher pressure range may be computed from the expression[21]

$$pv/p_0v_0 = A + B(p - 400) \tag{8}$$

(a) For mole percentages (x) of nitrogen less than 40

$$A = 1.2765 + (1.828 \times 10^{-4})x \tag{9}$$

$$B = (7.246 \times 10^{-4}) + (5.092 \times 10^{-6})x + (1.531 \times 10^{-8})x^2 \tag{10}$$

(b) When x equals 40 or is greater than 40

$$A = 1.2538 + (4.981 \times 10^{-4})(100 - x) \tag{11}$$

$$1/B = (1.3021 \times 10^3) - (6.948)x + (1.308 \times 10^{-2})x^2 \tag{12}$$

Throughout this pressure range, calculated and observed results differ by a maximum of 0.27%.

Practical application of the data given in this report may be illustrated as follows. (a) The volume occupied by a known gas mass at any pressure may be calculated from the expression

$$\left[v_p = \frac{v_0}{p} \cdot \left(\frac{pv}{p_0v_0}\right)_p\right]_T \tag{13}$$

where v_p is the volume of compressed gas at pressure p and temperature T, v_0 the volume of the gas at atmospheric pressure and temperature T, p the total pressure and $(pv/p_0v_0)_p$, the compressibility factor of the gas at p and T. (b) The pressure exerted by a known gas mass at any given volume may be determined directly from the equation of state for the gas

$$\left[p = \frac{(p_0v_0)\ (A + Bp + Cp^2\ldots\ldots)}{v}\right]_T \tag{14}$$

where v is the given volume. However, in cases where the equation of state involves the third power of pressure, solution of the problem is simplified by employing a graphical method. In the expression

$$pV/p_0v_0 = f(p) \tag{15}$$

let V be the desired volume of the compressed gas. By assuming different values for (p) a series of values are obtained for pV/p_0v_0. These are plotted against pressure on a pressure-compressibility factor diagram (see Fig. 3) for a gas of the same composition. The pressure exerted by the gas is the pressure indicated at the intersection of the curves. (c) The density of any gas at any desired pressure may be calculated from the expression

$$\left[d_p = d_0p \cdot \left(\frac{p_0v_0}{pv}\right)_p\right]_T \tag{16}$$

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[21] Data from 400 to 1000 atm. pressure were used in calculating the numerical values of the constants of Equation 8.

where d_p is the density of the gas at pressure p and temperature T, and d_0 is the density of the gas at atmospheric pressure and at temperature T.

I wish to express my appreciation to the entire staff of the Fixed Nitrogen Research Laboratory for unstinted coöperation in solving the many problems involved in this investigation. I am especially indebted to Dr. J. A. Almquist for counsel and advice, to Dr. H. L. Cupples for assistance in the tedious mathematical computations and to my assistant, Mr. T. H. Tremearne, for his untiring and efficient help.

Summary

The compressibility factors at 0° for pure hydrogen, pure nitrogen and eight mixtures of these gases have been determined through a pressure range of 1000 atmospheres.

The compressibility factor of a mixture of the two gases is not a linear function of its composition. A maximum positive deviation of 1.9% was observed in a mixture containing 60% of hydrogen at 200 atmospheres pressure. A maximum negative deviation of 0.55% appears in a mixture containing 25% of hydrogen at 1000 atmospheres' pressure.

The densities of pure nitrogen, pure hydrogen and eight mixtures of these gases at nine pressures have been calculated. Densities range from 0.08982 g. per liter for pure hydrogen at 1 atmosphere to 605.4 g. per liter for pure nitrogen at 1000 atmospheres' pressure.

Empirical equations relating gas composition and compressibility have been derived and certain working formulas presented.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY OF NEW YORK UNIVERSITY]

THE DIRECT OXIDATION OF LITHIUM IODIDE

BY JOHN P. SIMMONS AND CHARLES F. PICKETT

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Many anhydrous inorganic halides, when heated in a current of oxygen, have been observed to undergo change, resulting in the formation of metallic oxides and the liberation of free halogen.[1] Potassium chloride, bromide and iodide, when heated in a stream of air or oxygen to a temperature of about 500° form, respectively, traces of chlorate, bromate and iodate simultaneously with the liberation of small amounts of free halogen.[2] In the investigations mentioned above, the experiments have apparently been but qualitative in nature, no data being given as to the amount of oxide, oxygenated salt formed, or of the halogen evolved.

[1] Schulze, *J. prakt. Chem.*, [2] **21**, 407 (1880).

[2] (a) Berthelot, *Bull. soc. chim.*, [2] **28**, 495 (1877). (b) Pettersson, *Z. anal. Chem.*, **9**, 362 (1870). (c) Schindler, *Mag. Pharm.*, **31**, **33** (1830). (d) Potilitzin, *Ber.*, **12**, **695** (1879).