with photographic attachments. A number of collisions have been observed visually during periods when the camera is not in use.

5. The method presented in this paper is being used to test experimentally the stability of atom nuclei. Such tests have not been made before. Rutherford's experiments, for example, reveal the disintegration of an extremely minute number of atoms to give long range hydrogen particles, but they do not show whether or not α- or any other short range particles are emitted. The difficulty of the present method lies in the small number of direct hits obtained. Less direct impacts are relatively numerous.

The remarkable feature of the present work is that in no case has any one of these oblique impacts effected a disintegration of the nucleus. Even more remarkable is the fact that the argon nucleus in Fig. 7 remains intact even under the sharp impact of a helium nucleus from Thorium C′ (α-particle) with a velocity of 25,000 or 30,000 times that of the swiftest rifle bullet, immediately before impact. This is evidenced by the fact that the visible tracks around the point of collision exhibit conservation of momentum. Fig. 1 illustrates the stability of an atom of air (nitrogen or oxygen) in exactly the same way except that the velocity of the α-particle just before impact is not quite so high.

It may be added that the photographs chosen for this paper have been selected altogether from the standpoint of the importance of the events they represent, even although they may not be so good as some of the others from the purely photographic viewpoint.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 152]

THE EQUATION OF STATE FOR PURE NITROGEN, GAS PHASE[1]

BY LEIGHTON B. SMITH AND ROBERT S. TAYLOR

Received June 25, 1923

Following the method of Keyes, pure nitrogen has been investigated by the isometric method. The theoretical work in connection with the equation of state[2,3,4,5] has made it appear highly probable that in the

---

[1] This investigation was undertaken by the Research Laboratory of Physical Chemistry at the request of the Bureau of Mines, working in coöperation with the War and Navy Departments. The Bureau of Mines as well as the Massachusetts Institute of Technology contributed liberally in funds needed to carry forward the work.

The present paper is the fourth published by this Laboratory presenting data required in perfecting the processes for the extraction of helium from natural gas.

[2] Phillips, (a) *J. Math. Phys., Mass. Inst. Techn.*, **1**, 42 (1921); (b) *Proc. Nat. Acad. Sci.*, **7**, 172 (1921).

[3] Keyes, THIS JOURNAL, **43**, 1452 (1921).

[4] Keyes, *J. Math. Phys., Mass. Inst. Techn.*, **1**, 89 (1922).

[5] Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917).

case of a fluid composed of molecules of invariable type, the pressure should vary linearly with the temperature at constant volume. The truth of this proposition involves the consequence that the potential energy of any given species of molecule or atom should be a function of the volume only. The derivative of the potential energy or the cohesive pressure, as it has come to be designated, may be directly evaluated for each constant volume setting employed in the isometric method. The form of function which represents the cohesive pressure as well as the volume correction term is known and indeed the constants of the equation of state may be easily evaluated directly from the isometric data.

The constants for the equation of state for atmospheric nitrogen based on the data of Amagat have been published by Keyes. Sufficient data, however, for pure nitrogen are not available and the purpose of the present work is to provide accurate data from which the fundamental constants for nitrogen may be deduced. Certain improvements in method and a greater accuracy in the volume control of the apparatus have been attained as a consequence of this study.

Preparation of Pure Nitrogen

The nitrogen was prepared by heating a mixture of ammonium sulfate and potassium nitrite in solution.

Fig. 1 illustrates the apparatus employed for generating and purifying the gas. The flask A was partially filled with a concentrated solution of ammonium sulfate and a solution of potassium nitrite was introduced from the separatory funnel, drop by drop. A safety tube and manometer B served to indicate the pressure and to relieve it, if it became excessive. The evolution of nitrogen was readily controlled by the heating and the rate at which the solution was admitted.

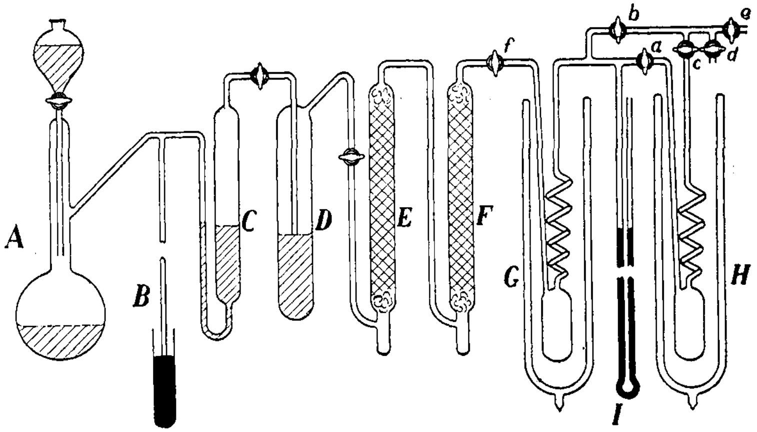

Fig. 1

The gas first passed through concd. sulfuric acid in the wash bottle C, then through a 20% solution of potassium hydroxide in D. E and F contained solid potassium hydroxide and phosphorus pentoxide, respectively. The gas was next passed through the bulb and spiral G immersed in liquid air which served to freeze and thus remove a large proportion of the impurities. From G the nitrogen passed to a similar arrangement at H which was immersed in liquid air through which hydrogen was bubbled. This so lowered the temperature of the liquid air that the nitrogen condensed to a liquid under a pressure of slightly more than 1 atmosphere. When a sufficient quantity of nitrogen had condensed in the bulb at H (about 20 cc.) the stopcocks a and f were closed and b and d opened, connecting G with the vacuum pump. G was now allowed to warm and the impurities that had condensed there were pumped away. The cock b was now closed and a opened for a short time, thus causing a portion of the liquid nitrogen to boil off and sweep out any fixed gaseous impurities in the vapor at H. The bulb and spiral at G were again cooled with liquid air through which hydrogen was then bubbled. The cock a was again opened and the bubbling of hydrogen at H stopped. As the temperature at H increased to that of liquid air boiling under 1 atmosphere pressure, the nitrogen slowly distilled from H and condensed at G. This process was stopped before all the liquid at H had disappeared and a was closed and C opened so that the residual nitrogen together with the impurities remaining in it were removed by the pump. This process of fractional distillation between G and H was repeated 5 times, and in each case the first and last fractions of distillate were discarded. The resulting liquid nitrogen was water-white and entirely free from particles of solid impurities. Finally, connection was made to the 6-liter Pyrex globe, which had previously been highly evacuated, and the nitrogen allowed to vaporize and fill the globe to somewhat over 1 atmosphere pressure.

The Pressure Gage

The gage was that employed by Keyes, Smith and Joubert[6] in the work on the equation of state for methane gas phase and was of about 1 cm. in diameter.

It was calibrated against an open top mercury column about 9 meters high. A platinum needle in the short arm of the column for electrical contact with the surface of the mercury was used for detecting the equilibrium of the column. Temperature control of the column was obtained by enclosing it in a channel-shaped support closed on the front side by adjustable pieces of cardboard. The electrical system for detecting equilibrium of the gage consisted of a telephone with an audion bulb in circuit as indicated in Fig. 2. This device made possible the use of very feeble currents in the contact circuit, thus avoiding emulsification of the oil at the surface of the mercury and so insuring very sharp make and break. This emulsification of the mercury and oil is of very great importance in the compressibility measurements as it amounts to removing a small quantity of mercury from the piezometer portion of the system and thus changing its volume.

The length of the mercury column was measured on a steel tape, stretched by a load of 7 kg., which had been calibrated under the same stretching load by comparison with a standard meter compared at the United States Bureau of Standards. The complete data for the calibration of the gage have been published in the paper of Keyes, Smith and Joubert. The mean value of the constant is 1.0255 mm./g.

The Compressibility Apparatus and Method of Loading the Piezometer

The general apparatus is shown in Fig. 2, which is a further development of the apparatus used by Keyes and Felsing.[7]

---

[6] Keyes, Smith and Joubert, *J. Math. Phys., Mass. Inst. Techn.*, **1**, 195 (1922).

[7] Keyes and Felsing, THIS JOURNAL, **41**, 589 (1919).

The floating pressure piston with scale pan and motor for oscillating the piston is represented at J, L and K. The oil injector I serves to adjust the height of the floating piston and to compensate for leak of oil around the floating piston. The steel block C contains a stopcock V for exhausting and an insulated needle D for indicating the mercury level. This contact serves to detect equilibrium of the load on the piston and the pressure exerted by the material in the piezometer. For example, if too great a weight is on the piston the mercury will be depressed, and if too small a weight it will rise and make contact; 1 g. suffices, as a rule, to make or break the contact. A shut-off is provided for closing the piezometer B from the entire apparatus while connection is made from the block C to the mercury volume-displacement piston apparatus G submerged in a constant temperature bath F, whose contents are stirred by means of the motor and propeller apparatus Q. The nut H serves to force the piston into the mercury, driving it through fine steel tubing of small bore into the piezometer. The advance of the piston is indicated by 100 divisions engraved on the under portion of the nut. Whole turns are counted by a "cyclometer" not shown in the drawing. It is possible with the 16mm. piston driven by a screw with 7.1 threads per cm. to estimate 0.001 turn of the nut, corresponding to about 0.00028 cc. The packing of the piston which moves into the cylinder G consists of cotton fabric heated in ceresin wax to 160°, and hard rubber forced into place by means of a steel ring driven by a screw cap.[8] The packing is perfectly tight over long

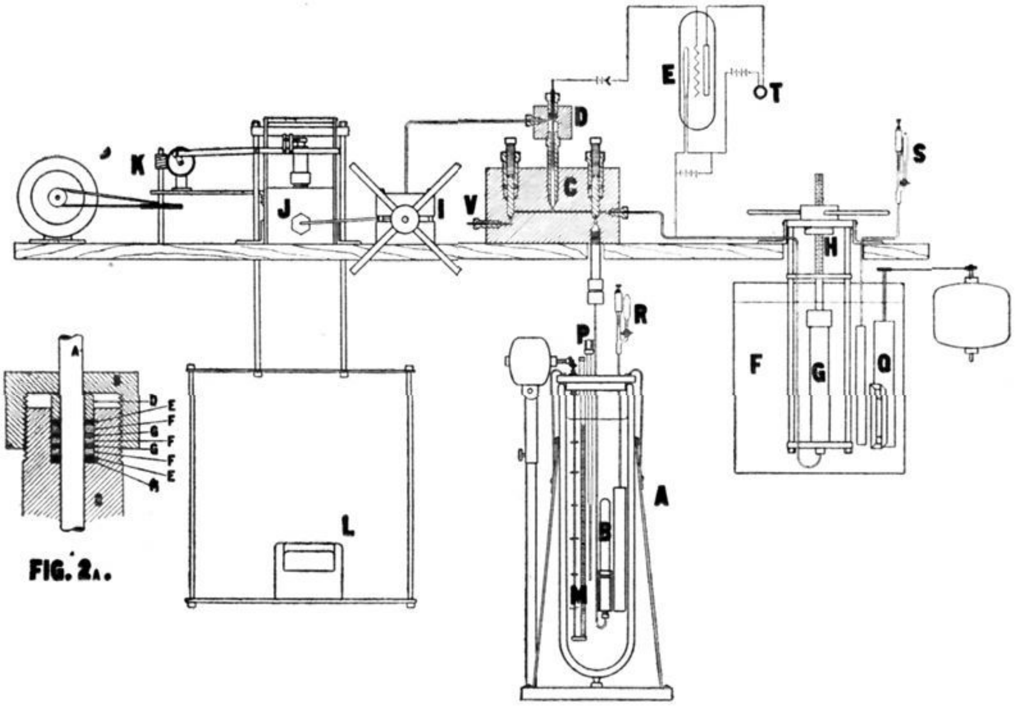

Fig. 2

---

[8] The diagram, Fig. 2A, shows the method of applying the packing to the piston in the mercury volume injector. The piston is represented by A and the nut driving the packing at B through pressure on the steel ring D. At the bottom of the packing gland is a steel ring H which also is a snug fit to the piston. E, E indicate hard rubber rings and F,F,F the cotton fabric (such as unbleached cotton) impregnated quickly with ceresin wax at 160°. G,G are rings of soft steel. The annular width of the packing gland is about 3 mm. and the depth for moderate pressures (500 atm.) about 3 to 4 cm. The hard rubber ring protects the waxed packing from the kerosene of the bath and serves to wipe the piston as it moves backward and forward, thus minimizing the removal of wax. This latter objective is not as satisfactorily accomplished as desirable, but no better method of wiping the piston has been applied.

periods of use after having been seasoned by exposing it to several hundred atmospheres with successive tightenings of the driving nut. A similar packing is used on the stopcocks of the block C.

The constant temperature bath represented at A, Fig. 2, consists of a Pyrex Dewar tube 6.6 cm. in inside diameter and 40 cm. in length. The disposition of the platinum thermometer, stirrer, heater and mercury in the steel regulator is evident from the figure. For the bath fluid a high-boiling light oil sufficed for the range 50° to 200°, while an ice-bath served to maintain the piezometer at 0°. The cover of the bath is of asbestos wood and carries the bearing for the stirrer and binding posts for the electrical connections of the heater. The Dewar tube bath here represented is very convenient and has been employed to 330°. It possesses obvious advantages due to its permitting a view of the interior at all times, and the heat insulation is excellent. The Dewar tube, however, requires prolonged heating at 450° during exhaustion. Recent tubes silvered in such a manner as to leave a clear strip 2 cm. to 5 cm. in width parallel to the long axis have greater heat-insulating properties, at the same time permitting a view of the interior. The silver will not peel, once it has been slowly and thoroughly baked out during exhaustion.

The piezometer is represented in detail at A, Fig. 3. It was made in one piece from cold rolled steel, the lower end being spun shut and welded with the oxy-acetylene flame. A left-hand thread was cut on the outer portion, where it screwed into the top piece E surrounded by a cooling coil of copper B. The latter piece carried a screw driver F passing through a packing gland and sealed with mercury. The piezometer was locked by means of the plug D, which had a 0.75 mm. hole drilled throughout its length. The locking of the piezometer was secured by the compression of the gold washer C against a seat in the piezometer by means of the screw D. The purpose of the cooling coil about E was to preserve the packing gland during the exhaustion of the bomb at 350°.

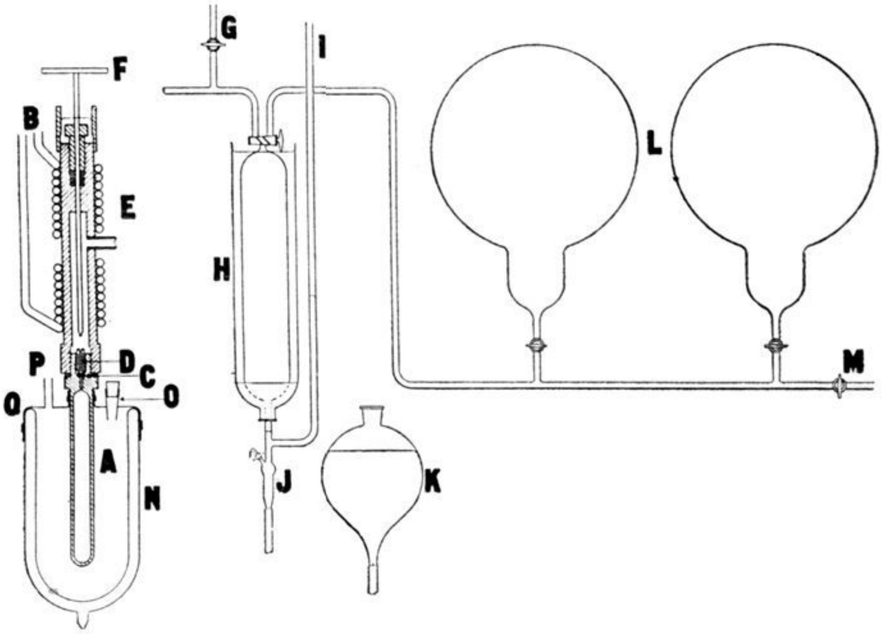

Fig. 3

Nitrogen is, of course, above its critical temperature at ordinary temperatures, and it was necessary to place in the piezometer sufficient nitrogen to give a range of volumes per gram from 5 to 23 cc. over the temperature range 0° to 200°. The capacity of the piezometer was 13.3143 cc. at 0° to the under surface of the gold disk. The quantity of nitrogen employed was about 0.51 g., corresponding to about 410 cc. at N.T.P. and producing about 40 atmospheres pressure in the piezometer at ordinary temperatures.

The procedure of loading consisted in first exhausting the buret H connected by means of the 2-way stopcock with the piezometer, the latter being, of course, heated to drive off adsorbed matter. Nitrogen was then permitted to expand into H from the holders L and, when temperature equilibrium had been established, the pressure was read on the mercury column I. The buret was of the constant volume type, with the lower buret mark engraved on a tube of the same diameter as the manometric tube, thereby avoiding corrections for capillary depression. The nitrogen in the buret was transferred to the piezometer by cooling the latter in liquid air and raising the mercury reservoir K, thus liquefying the nitrogen in the piezometer. The vapor pressure of nitrogen at the temperature of liquid air is rather high, so the air was boiled under reduced pressure. For this purpose the Dewar tube containing the liquid air was provided with a spun cap of german silver Q that had an opening for the piezometer and tubes O and P for introducing liquid air and for connection with the vacuum pump. O could be closed with a rubber stopper. The cap was made fast to the Dewar tube and the piezometer by means of soft rubber tape and rubber cement. The air was boiled under a vacuum of 5 or 6 mm. of mercury which made it possible to liquefy the nitrogen under a pressure of 20 or 30 cm. The piezometer was then locked by screwing down the screw D by means of the screw driver F. The nitrogen remaining in the leads and in E above the gold disk was removed by means of a Toepler pump and the volume measured at a known temperature and pressure. To obtain the true mass requires the equation of state for nitrogen, or it suffices for the accuracy obtainable[9] to employ the weight of a liter at N.T.P.

The weight of a liter of pure nitrogen was taken as 1.2507 g., or the volume of a gram is 799.55 cc. as given by Moles.[10] Holborn and Otto[11] found for their nitrogen 1.2509 g., in fairly good agreement with the above. Later in this paper further reference to the matter of the weight of a liter of pure nitrogen will be made.

---

[9] The gas is measured in the buret H, Fig. 3, under other conditions of temperature and pressure than N.T.P., under which the liter is measured. Strictly, one should know the compressibility and coefficient of expansion of the gas to obtain the true weight of the quantity actually measured. The use of the perfect-gas laws with the measured weight per liter leads to no appreciable error, however, in the case of nitrogen, as was proved when the constants of the equation of state were obtained. It will be shown in the present paper that the weight of a liter of nitrogen calculated by the equation of state agrees very well with the experimental determination of Moles.

[10] Moles, *J. chim. phys.*, **19**, 283 (1922).

[11] Holborn and Otto, *Z. Physik*, **10**, 367 (1922).

The loaded piezometer is connected with a piece of hexagonal steel carrying a steel tubing of 0.75 mm. bore locking against an annealed aluminum washer, and placed inverted in the constant-temperature bath. Referring again to Fig. 2, the piezometer with its steel tube may then be connected with the block C and the steel lead exhausted through V to the gold washer serving to confine the nitrogen in the piezometer. After closing the stopcock in block C at V, mercury may be run in by screwing in the piston of the mercury volume-injector G. It is to be added that a plug replaced the oil lead from I in D during the exhaustion and the oil lead was replaced after filling the block and lead with mercury. The oil lead having been connected, mercury is brought to the needle point by manipulating the oil injector I and volume injector G. By this means a zero setting may be obtained at a definite pressure corresponding to the position of the mercury which is in contact with the gold disk closing the piezometer. After the zero setting is obtained the pressure is increased to several hundred atmospheres and in about 24 hours the gold disk, weakened by amalgamation with the mercury, is punctured, bringing the mercury into contact with the nitrogen. By means of the mercury injector G a setting may be made for a chosen specific volume of nitrogen and a series of pressures and temperatures observed.

It is necessary to know expansion of the mercury with the temperature as well as its compressibility[12] while the stretch of the steel piezometer and apparatus may be obtained by separate blank measurements. For the true expansivity with temperature of the steel piezometer, the data of the Reichsanstalt were correlated as a function of the temperature as follows.

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

The equation for the volume of mercury as a function of the temperature, as given by Callendar and Moss, was employed.

$$V_t^{Hg} = V_0 (1 + 1.80555 \times 10^{-4}\, t + 1.2444 \times 10^{-8}\, t^2 + 2.539 \times 10^{-11}\, t^3)$$

The shifting of the temperature requires, for preserving constancy of the nitrogen volume, a resetting of the mercury injector G to compensate

---

[12] The compressibility of mercury is a function of both pressure and temperature. Thus Bridgman gives the compressibility at 1 atmosphere as 3.80×10^{-6} at 0° and 3.95×10^{-6} at 22°. The decrease of the compressibility with pressure is given as about 3% for the first thousand atmospheres. The effect of increase in pressure may be neglected in the present work since 400 atmospheres was not exceeded. The temperature effect on the stretch of the piezometer is determined as the sum of that due to the compressibility of the mercury contained in the piezometer and the stretch of the piezometer itself. These direct measurements failed to disclose any pronounced effect on the combined mercury compressibility and piezometer stretch because of the small amount of mercury (13.3 cc.) contained in the piezometer and the smallness of the temperature coefficient of stretch of the piezometer. The value 3.9×10^{-6} was assumed for the mercury compressibility independent of the temperature. The total stretch of the piezometer amounted to 9.73×10^{-5} cc. per atm.

for the combined increase in volume of the mercury in the piezometer and the dilation of the piezometer with temperature and pressure. The method of making this computation is obvious, when the stretch of the piezometer and apparatus with pressure and the expansion of the piezometer and mercury with temperature are known.

The Experimental Data

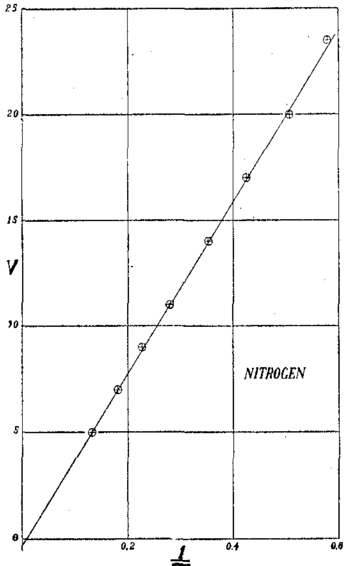

Fig. 4

The data were taken first at 50°, continued to 100°, 150° and 200°, and the observations at 0° were made last, using a Dewar tube filled with ice. In Table I will be found the absolute temperatures and pressures for the fixed volumes beginning with 23 cc. per g. of nitrogen. A linear equation is given with each volume which has been used to calculate the pressures recorded under each observed pressure.

The equation of state gives, for the tangent of the pressure-temperature lines at constant volume, the expression $R/(v-\delta)$. The magnitude of R per mole is known with tolerable accuracy,[13] being 82.058 cc., atm. per degree C., per mole. The molecular weight of nitrogen has been taken as 28.02. The value of R per g. of nitrogen is, therefore, 2.92855.

From the equations for the isometrics the constants for the cohesive pressure term $\Phi = A/(v-l)^2$ may be derived. The constant of the linear equation for each volume is equal to Φ for that volume. These values were calculated over to $1/\sqrt{\Phi}$ and plotted against v giving a straight line as shown in Fig. 4. When we represent this by an equation of the form $V = a + \frac{b}{\sqrt{\Phi}}$, we see

Table I

Observed Pressure Represented as a Linear Function of the Temperature at Constant Volume

Volume Cc.	0°	49.98°	100°	152.34°	200°	Pressure
			$p = 0.136096T-2.9794$			
23	34.175	41.012	47.812	54.930	61.380	Obs.
	34.193	40.896	47.804	54.927	61.413	Calc.
			$p = 0.157963T-3.8947$			
20	39.251	47.141	55.088	63.322	70.839	Obs.
	39.251	47.146	55.048	63.315	70.844	Calc.

---

[13] Keyes, *J. Am. Soc. Refrig. Eng.*, **8**, 505 (1922).

			$p = 0.188830T - 5.5225$			
17	46.054	55.503	65.021	74.809	83.766	Obs.
	46.054	55.492	64.938	74.821	83.821	Calc.
			$p = 0.233740T - 8.0190$			
14	55.835	67.470	79.281	91.443	102.545	Obs.
	55.824	67.507	79.199	91.433	102.573	Calc.
			$p = 0.306481T - 12.7333$			
11	70.979	86.290	101.698	117.676	132.197	Obs.
	70.977	86.297	101.627	117.668	132.275	Calc.
			$p = 0.388372T - 19.3732$			
9	86.707	106.130	125.564	145.765	163.911	Obs.
	86.705	106.118	125.544	145.871	164.381	Calc.
			$p = 0.521857T - 30.4779$			
7	111.962	138.263	164.401	191.614	216.152	Obs.
	112.060	138.145	164.248	191.562	216.434	Calc.
			$p = 0.798581T - 57.9004$			
5	160.224	200.153	240.052	281.956	319.534	Obs.
	160.220	200.137	240.082	281.880	319.940	Calc.

that $l = -a$ and $A = b^2$. In Table II are listed the observed Φ's and those calculated from the equation $\Phi = \frac{1623.6}{(v + 0.2954)^2}$.

TABLE II

COHESIVE PRESSURE DEDUCED FROM INTERCEPTS OF STRAIGHT-LINE EQUATIONS COMPARED WITH COHESIVE PRESSURE CALCULATED BY MEANS OF THE EQUATIONS

$$\Phi = \frac{1623.6}{(v + 0.2954)^2} \text{ (Eq. a), and } \Phi = \frac{1623.3}{v^2} e^{-\frac{0.5732}{v}} \text{ (Eq. b)}$$

Volume Cc.	Φ	Φ Calc. from Eq. a	Φ Calc. from Eq. b
23	2.979	2.992	2.993
20	3.895	3.942	3.944
17	5.523	5.428	5.431
14	8.019	7.945	7.950
11	12.733	12.726	12.735
9	19.373	18.791	18.804
7	30.478	30.506	30.524
5	57.900	57.901	57.900

To complete the equation of state it remains to obtain the constants for the δ equation. δ was calculated for each observed pressure from the relation $\delta = v - \frac{RT}{p + \Phi}$. The values for each volume were averaged and the mean values $\log \delta$ were plotted against $1/v$. The plot is reproduced in Fig. 5, showing that nitrogen follows the function $\delta = \beta e^{-\alpha/v}$.

The complete equation of state for nitrogen is, therefore,

$$p = \frac{2.92855}{v - \delta} T - \frac{1623.6}{(v + 0.2945)^2}, \quad \log_{10} \delta = 0.18683 - \frac{0.3113}{v} \qquad (1)$$

TABLE III

VALUES OF δ FOR INDIVIDUAL TEMPERATURES CALCULATED FROM OBSERVED PRESSURES AND THE VALUE OF Φ GIVEN BY THE EQUATION $\Phi = \frac{1623.63}{(v + 0.2954)^2}$

Volume Cc.	0°	49.98°	100°	152.34°	200°	δ Mean	δ Calc.
23	1.4781	1.4958	1.4908	1.4876	1.4749	1.4854	1.490
20	1.4807	1.4758	1.4881	1.4754	1.4711	1.4782	1.483
17	1.4624	1.4698	1.4886	1.4705	1.4652	1.4753	1.474
14	1.4584	1.4524	1.4721	1.4629	1.4594	1.4610	1.461
11	1.4438	1.4432	1.4499	1.4446	1.4324	1.4428	1.441
9	1.4178	1.4250	1.4301	1.4279	1.4160	1.4234	1.420
7	1.3854	1.3931	1.3934	1.3902	1.3824	1.3888	1.388
5	1.3328	1.3320	1.3324	1.3336	1.3289	1.3319	1.332

In Table IV will be found the pressures calculated by means of Equation 1 for comparison with the observed values.

TABLE IV

NITROGEN ISOMETRICS

Sp. vol.		0.0° 273.14° Press. atm.	49.98° 323.12° Press. atm.	100.00° 373.14° Press. atm.	152.34° 425.48° Press. atm.	200.00° 473.14° Press. atm.
23	Obs.	34.175	41.012	47.812	54.930	61.380
	Calc.	34.196	41.000	47.810	54.936	61.425
20	Obs.	39.251	47.141	55.088	63.322	70.839
	Calc.	39.256	47.198	55.072	63.350	70.887
17	Obs.	46.054	55.503	65.021	74.809	83.766
	Calc.	46.092	55.520	64.955	74.827	83.817
14	Obs.	55.835	67.470	79.281	91.443	102.545
	Calc.	55.848	67.521	79.204	91.428	102.559
11	Obs.	70.979	86.290	101.698	117.676	132.197
	Calc.	70.955	86.267	101.591	117.626	132.228
9	Obs.	86.707	106.130	125.564	145.765	163.911
	Calc.	86.737	106.047	125.372	145.594	164.008
7	Obs.	111.962	138.263	164.401	191.614	216.152
	Calc.	112.029	138.110	164.212	191.525	216.396
5	Obs.	160.224	200.153	240.052	281.956	319.534
	Calc.	160.175	200.080	240.016	281.804	319.856

$$p = \frac{RT}{v - \delta} - \frac{1623.63}{(v + 0.2954)^2} \text{ where } \log \delta = 0.18683 - \frac{0.3113}{v}$$

$R = 2.92855$ $\beta = 1.5376$ and $\alpha = 0.7169$

It seems probable that the true form of the cohesive-pressure equation is $\frac{A'}{v^2}e^{-l'/v}$ where A' and l' are constants of similar significance to the constants in the form $A/(v + l)^2$. In the gas phase it is difficult to distinguish between the two forms. Thus $\frac{A'}{v^2}e^{-l'/v}$ for large volumes becomes, with sufficient accuracy, equal to $\frac{A'}{v^2}\left(1 - \frac{l'}{v}\right) = \frac{A'}{v^2\left(1 + \frac{l'}{2v}\right)^2} \equiv \frac{A}{(v + l)^2}$.

Hence, for the gas phase $A = A'$ and $2l = l'$. In order to determine the constants of this exponential form, one takes logarithms of both sides,

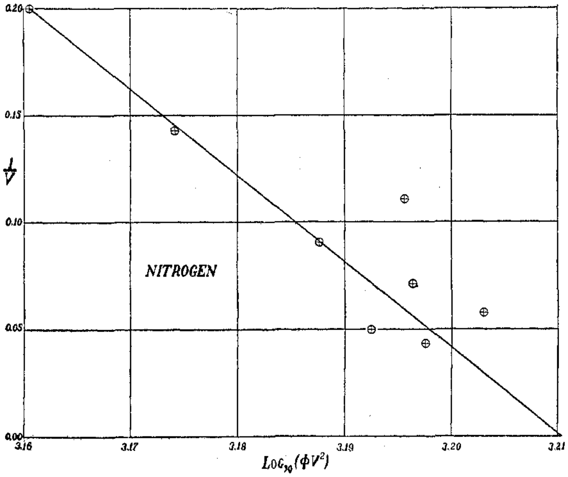

Fig. 4a

whence one gets $\log \Phi = \log \frac{A}{v^2} - \frac{l'}{v}$. Hence, a plot of $\log \Phi v^2$ against $1/v$ should give a straight line. Fig. 4a shows that a straight line is all that the assemblage of points will justify. Giving most weight to the high-pressure points, since they always serve to locate the constants better than low-pressure data, one obtains the following constants: $A = 1623.3$, and $l = 0.2866$. This is an excellent check and shows that the two forms are interchangeable as far as the present data go. The equation is $\log \Phi = \log \frac{1623.3}{v^2} - \frac{0.2489}{v}$. In Table II are also given the values of Φ calculated from this second form.

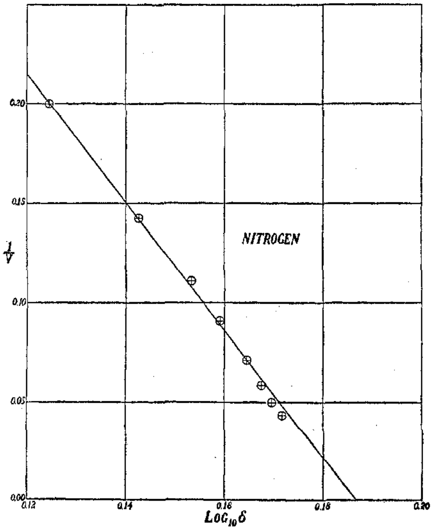

Fig. 5

Weight of a Liter of Nitrogen at Normal Temperature and Pressure

Moles has most recently measured the normal density of nitrogen[10] obtaining 1.2506 g. per liter as the mean of four volumetric determinations in good agreement with the mean value

1.2507 of 29 determinations by four authors using two different experimental methods with nitrogen produced by eight different reactions. Holborn and Otto[11] as a test of the purity of their nitrogen determined the weight of a liter to be 1.2509 g. The equation of state gives 779.40 cc. as the volume of 1 g. at 0° and 1 atm. pressure. The reciprocal of this multiplied by 1000 gives 1.2509 as the weight of 1 liter at N.T.P.

Equation of State for Atmospheric Nitrogen from Measurements by Amagat

Amagat[14] has measured the isotherms for gaseous atmospheric nitrogen. The data are divided into two series, the first set extending over a range of pressure from 100 to 1000 atmospheres and from 0.0° to 199.5°. The second series covers the range of pressures from 1000 to 3000 atmospheres and from 0.0° to 43.6°. The volumes given are relative to the capacity of a manometric tube and are not absolute. Keyes[15] has derived an equation from the low-pressure measurements which he gives as

$$p = \frac{2.9138}{v - \delta}T - \frac{1587.2}{(v - 0.007)^2}, \quad \log \delta = 0.2200 - \frac{0.284}{v}$$

He assumes the composition of atmospheric nitrogen to be 1.66% argon and 98.34% nitrogen by weight. The apparent molecular weight is taken as 28.163. The volume of 1 g. is taken as 795.12 cc.

Rayleigh,[16] Regnault, Von Jolly and Leduc have determined the weight of a liter of atmospheric nitrogen. Regnault's value was corrected by Crafts for contraction of the globe and Von Jolly's was corrected by Rayleigh. Rayleigh's and Leduc's values are the latest available and are in best agreement. The mean of their values, 1.25714 g., was assumed as the best figure for the weight of a liter. This gives 795.46 cc. as the volume of 1 g.

Two methods are available for determining the apparent molecular weight. From the weight of a liter of argon, 1.78094,[17] the weight of a liter of pure nitrogen[10] 1.2507 and the weight of a liter of atmospheric nitrogen, the composition of atmospheric nitrogen may be calculated. This method, which is not very accurate, gives 1.21% of argon.

Guye[18] gives the percentage by volume of oxygen in air as 20.94 and the weight of 1 liter of air as 1.2928 g. Keyes[13] gives 699.77 cc. as the best value for the volume of 1 g. of oxygen. Therefore, we obtain 23.147% oxygen by weight. Moureu and Lepape[19] give the percentage of argon in air as 1.29 by weight. From this, the composition of atmospheric

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

[15] Keyes, THIS JOURNAL, **42**, 54 (1920).

[16] Rayleigh, "Scientific Papers," Vol. IV, 51 (1893), or *Proc. Roy. Soc.*, **53**, 134 (1893).

[17] Watson, *J. Chem. Soc.*, **97**, 833 (1910).

[18] Guye, *J. chim. phys.*, [4] **15**, 570 (1917).

[19] Moureu and Lepape, *Ann. chim.*, [9] 4, **5**, 4 (1915).

nitrogen is 1.679% argon and 98.321% nitrogen by weight. This gives for the apparent molecular weight $\dfrac{1}{\dfrac{0.01679}{39.88}+\dfrac{0.98321}{28.020}} = 28.161$ using the accepted values of 39.88 and 28.020 for the molecular weights of argon and pure nitrogen. The gas constant R per gram is, therefore, 82.058/28.161 = 2.9139, which coincides with that obtained by Keyes.

TABLE V

AMAGAT'S HIGH PRESSURE ISOMETRICS

Vol. actual cc./g.	Vol. A units	0° Press. atm.	16.0° Press. atm.	43.6° Press. atm.	16.0° Press. calc. from st. line eqs.	Eq. used
1.647	0.00207	1000	1088	1239	1087.7	1
1.548	.001946	1200	1298	1474	1300.6	2
1.443	.0018135	1500	1613	1812	1614.5	3
1.364	.0017145	1800	1937	2168	1935.0	4
1.323	.0016635	2000	2150	2401	2147.2	5
1.260	.0015835	2400	2572	2858	2568.1	6
1.213	.0015250	2800	2990	..	....	7

1. $p = 5.482\,T - 497.36$
2. $p = 6.284\,T - 516.4$
3. $p = 7.156\,T - 454.6$
4. $p = 8.440\,T - 505.3$
5. $p = 9.197\,T - 512.1$
6. $p = 10.505\,T - 469.3$
7. $p = 11.875\,T - 443.5$

Amagat's series for 1000 to 3000 atmospheres extends over a very short temperature range. Table V gives his constant volume values and also the actual volumes in cc. per g. as obtained by multiplying his relative volumes by 795.5. Straight-line equations were passed through the points at 0.0° and 43.6° and are given below Table V. In Col. 6, Table V are given the pressures at 16.0° calculated from the corresponding constant-volume equations. These show that, within Amagat's limits of accuracy, p is a linear function of T at constant volume up to 3000 atmospheres.

In Fig. 6 the line represents the plot of log δ, as calculated from Keyes' equation, against $1/v$. The points represent the observed values obtained from Amagat's high-pressure series. The fact that all of the observed points fall upon one side of the line indicates that Amagat's low-pressure series is not entirely concordant with his high-pressure series.

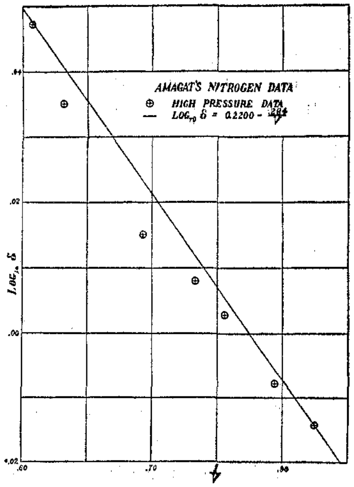

Fig. 6

Comparison of the Recent Work of Holborn and Otto with the Equation of State for Nitrogen

Holborn and Otto[11] have recently measured the products of $p \times v$ for oxygen, nitrogen and helium. They represent their data by equations of the form $pv = f(p)$ and $pv = f\,1/v$. For the second form they give equations representing the 0°, 50° and 100° isotherms for nitrogen, which when converted to v in cc. per g. and p in atmospheres are as follows:

$$pv = (pv)_0\left(1 - \frac{0.4563032}{v} + \frac{2.92858}{v^2}\right) \text{ at } 0.0° \qquad (2)$$

$$pv = (pv)_0\left(1 - \frac{0.0262332}{v} + \frac{3.06343}{v^2}\right) \text{ at } 50.0° \qquad (3)$$

$$pv = (pv)_0\left(1 + \frac{0.279970}{v} + \frac{3.18418}{v^2}\right) \text{ at } 100.0° \qquad (4)$$

From the equation of state,

$$pv = RT\frac{v}{v - \delta} - A\frac{v}{(v + l)^2}$$

Expanding this in the form of a series gives

$$pv = RT\,v\left(\frac{1}{v} + \frac{\delta}{v^2} + \frac{\delta^2}{v^3} + \frac{\delta^3}{v^4} + \ldots\right) - Av\left(\frac{1}{v^2} - \frac{2l}{v^3} + \frac{3l^2}{v^4}\ldots\ldots\right)$$

but

$$\delta = \beta e^{-\alpha/v} = \beta\left(1 - \frac{\alpha}{v} + \frac{\alpha^2}{2v^2} - \frac{\alpha^3}{6v^3} + \ldots\right)$$

Neglecting all terms of higher order than $1/v^2$ there is obtained

$$pv = RT\left[1 + \frac{1}{v}\left(\beta - \frac{A}{RT}\right) + \frac{1}{v^2}\left(\beta^2 - \alpha\beta + \frac{2Al}{RT}\right)\right] \qquad (5)$$

Since $(pv)_0 = RT$, Equation 5 is seen to be, at constant temperature, of the same form as Equations 2, 3 and 4. Substituting in (5) the constants of the equation of state for 0.0°, 50.0° and 100.0° one obtains the following equations for comparison with those of Holborn and Otto.

$$pv = (pv)_0\left(1 - \frac{0.49227}{v} + \frac{2.45735}{v^2}\right) \text{ at } 0.0° \qquad (6)$$

$$(pv)_0 = RT = 799.890$$

$$pv = (pv)_0\left(1 - \frac{0.17819}{v} + \frac{2.27236}{v^2}\right) \text{ at } 50.0° \qquad (7)$$

$$(pv)_0 = 946.317$$

$$pv = (pv)_0\left(1 + \frac{0.05172}{v} + \frac{2.13694}{v^2}\right) \text{ at } 100.0° \qquad (8)$$

$$(pv)_0 = RT = 1092.745$$

For comparison purposes there are given in Table VI, values of pressures in atmospheres and corresponding volumes in cc. per g. at 0°, 50° and 100° from determinations by Holborn and Otto. These values for volume were converted from the arbitrary units by multiplying the latter by the factor 607.43 which is that given by the equation of state when $p = 1$ meter $= 1.31579$ atm. and T is 273.135 abs.

TABLE VI

PRESSURES AND VOLUMES COMPUTED FROM EQUATIONS BY HOLBORN AND OTTO

Press. meters of Hg	Press. atm.	Volumes (cc. per g.)		
		0°	50°	100°
10	13.158	60.449	71.930	83.266
30	39.474	19.993	24.022	27.951
50	65.789	11.943	14.477	16.920
70	92.105	8.532	10.418	12.214

From the equation of state pressures were calculated corresponding to the volumes given in Table VI.

These values are listed in Table VII.

TABLE VII

PRESSURES FROM EQUATION OF STATE USING VOLUMES AND TEMPERATURES FROM TABLE VI

0°		50°		100°	
v	p	v	p	v	p
60.449	13.134	71.930	13.128	83.266	13.135
19.993	39.270	24.022	39.257	27.951	39.275
11.943	65.376	14.477	65.275	16.920	65.268
8.532	91.533	10.418	91.203	12.214	91.142

The pressures resulting from the present work corresponding to the volumes and temperatures given by Holborn and Otto are seen to be lower at about 90 atm. by 0.6%. It will be pointed out subsequently that until the "pure" nitrogen chemically prepared had been fractionated to remove traces of nitric oxide the higher pressures were obtained.

In Table VII of Holborn and Otto's paper are given values of the pv product at 0°, 50° and 100° for various constant densities. The values of 5, 15, 25, 35, 45 and 55 in their arbitrary units were chosen. Multiplying the pv products by the density gives the pressures in meters. Converting the densities to cc. per g. and the pressures to atmospheres, as explained above, the values contained in Table VIII were obtained.

TABLE VIII

PRESSURES AT CONSTANT VOLUME FROM HOLBORN AND OTTO

$\frac{1}{v}$ (arb. units)	v (cc. per g.)	Pressures (atm.)		
		0°	50°	100°
5	121.486	6.564	7.789	9.010
15	40.495	19.596	23.383	27.149
25	24.297	32.535	39.025	45.493
35	17.355	45.416	54.760	64.096
45	13.498	58.261	70.639	83.021
55	11.044	71.105	86.727	102.303

The above values of pressure are plotted against the absolute temperature as shown in Fig. 7. These constant volume lines are straight to within what is believed to be the accuracy of Holborn and Otto's results.

From Equation 5 we see that the coefficient of $1/v$ in the pv product equation is equal to $\beta - \frac{A}{RT}$. Taking the coefficients of $1/v$ in Equations 2, 3 and 4 of Holborn and Otto and solving simultaneously for A we obtain the 3 values 2223.2, 2162.4 and 2197.5, of which the mean is 2194.4. Substituting this mean value of A we obtain for β the 3 values 2.287, 2.293 and 2.288, of which the mean is 2.289.

Holborn and Otto prepared nitrogen from sodium nitrite and purified it by passing it through alkaline pyrogallol and over glowing copper. It is known that alkaline pyrogallol is likely to introduce carbon monoxide and Smyth and Roberts[20] have shown that unless the temperature of the copper is kept below 600° the copper oxide will decompose and introduce oxygen. Also, copper will not reduce oxides of nitrogen unless the temperature is fairly high. The good agreement between the weight of a liter as determined by Holborn and Otto and the accepted value does not necessarily indicate great purity of the gas since, in the first place, the weight of a liter is very difficult to obtain and second, since the molecular weight of carbon monoxide is essentially the same as that of nitrogen and since nitric oxide has only a slightly greater molecular weight, the pressure of appreciable quantities of these gases would not greatly affect the weight of a liter, but would affect the magnitude of the A and β constants greatly. Previous to the work on the equation of state of pure nitrogen as given in this paper an equation was determined for a sample of gas purified by the

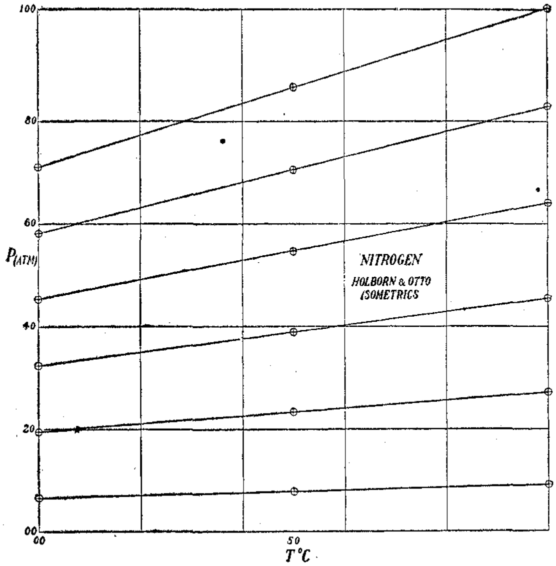

Fig. 7

---

[20] Smyth and Roberts, THIS JOURNAL, 42, 2582 (1920).

usual chemical methods. An A constant of about 1860 was obtained, which lies much nearer the value obtained above from Holborn and Otto's work. Subsequently it was found that when this sample of nitrogen was condensed, suspended solid impurities were observed in the liquid. After 5 fractional distillations a perfectly water-white liquid was obtained that was undoubtedly pure. This procedure was used in preparing the gas for the measurements upon which the equation of state was based. Since the impurities mentioned as likely to be present in nitrogen, purified by chemical means, are all less perfect gases than nitrogen, their presence in small amounts would tend to increase the magnitude of the constants.

Compressibility Coefficients

Maverick,[21] both alone and in collaboration with Batuecas, has made measurements on the compressibility coefficients at 1 atmosphere and 0°. Those made by Maverick alone seem to be more consistent than the others. His λ is defined as equal to $-\frac{1}{(pv)_{760}}\left(\frac{\partial(pv)}{\partial p}\right)_T$.

His average value and those of other observers at 0° are Maverick, 0.00044; Chappuis,[22] 0.00043; Leduc and Sacerdote,[23] 0.00038; Rayleigh,[24] 0.00056. Maverick's values for nitrogen prepared from urea were discarded because of impurities in the gas so prepared.

From Equations 2, 3 and 4 of Holborn and Otto values of λ are obtained as follows: 0°, 0.000561; 50°, 0.000023; 100°, —0.000360.

From Equations 6, 7 and 8 derived by the equation of state the following are obtained: 0°, 0.000608; 50°, 0.000216; 100°, —0.000071.

Owing to the extreme accuracy with which an observer must work in order to obtain any percentage accuracy for this coefficient, the agreement is about as good as can be expected. Keyes[4] has worked over the values for compressibility coefficients of Chappuis, Leduc and Sacerdote, and Rayleigh, comparing them with values obtained from the equation of state for atmospheric nitrogen.

In conclusion it is desired to thank Professor F. G. Keyes for his valuable suggestions and assistance, without which this work could not have been carried out.

Summary

1. The p, v, T relationship of pure gaseous nitrogen has been studied by the isometric method over the range of temperatures from 0° to 200° and 30 to 330 atmospheres' pressure. The Keyes equation represented

---

[21] Maverick, *Thesis*, University of Geneva, No. 708, Jan., **1923** (to be published soon in *J. chim. phys.* and *Chim. Helvetica Acta*).

[22] Chappuis, *Trav. mem. bur. intern.*, **13**, 66 (1903).

[23] Leduc, *Ann. chim. phys.*, [7] **15** (1899); *Compt. rend.*, **123**, 743 (1896); **125**, 297 (1897); **148**, 407 (1909).

[24] Rayleigh, *Proc. Roy. Soc.*, **73**, 153 (1904); *Z. physik. Chem.*, **37**, 713 (1901).

the data within the experimental limits of error. This equation obtained is, $p_{\text{atm.}} = \frac{2.92855\ T}{v - \delta} - \frac{1623.63}{(v + 0.2954)^2}$ where $\log \delta = 0.18683 - \frac{0.3113}{v}$.

2. The weight of a liter of nitrogen at N.T.P. was calculated from the equation of state to be 1.2509 g. as compared with the generally accepted value of 1.2507 g.

3. The compressibility coefficient at 0° was calculated and found to be 0.00061 as compared with 0.00056 from Holborn and Otto's equation and the work of Rayleigh, and 0.00043 and 0.00044 from Chappuis and Maverick, respectively.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 154]

THE MELTING POINT OF ICE ON THE ABSOLUTE TEMPERATURE SCALE

BY LEIGHTON B. SMITH AND ROBERT S. TAYLOR

Received June 25, 1923

Chappuis,[1] Day and Clement,[2] Holborn and Henning[3] and Eumorfopoulos[4] have made measurements on the expansion coefficients from 0° to 100° both for the constant volume and the constant pressure thermometers. Keyes[5] calculated ϵ, the expansion coefficient for a perfect gas, using the data of the above-mentioned workers and the equation of state which he based on Amagat's data for atmospheric nitrogen. Since then Henning,[6] and Henning and Heuse[7] have done some work on expansion coefficients for nitrogen and some other gases. It is, therefore, thought worth while to review the above data using the new equation of state of nitrogen[8] and also the method of obtaining ϵ using the equation of state, since this has never been given in detail before.

Instead of using a constant-pressure thermometer, a constant-π thermometer will be considered where π is defined by the equation $\pi\omega = RT$. From the Keyes equation of state $\omega = v - \delta$ or, for low pressures $\omega = v - \beta$ and $\pi = p + A/(v + l)^2$, which reduces at low pressures to the form, $\pi = p + (A/v^2)$.

[1] Chappuis, *Trav. mem. bur. intern.*, **6**, 59 (1888) and **13**, 66 (1903).

[2] Day and Clement, *Am. J. Sci.*, **26**, 405 (1908).

[3] Holborn and Henning, *Ann. Physik*, **35**, 761 (1911).

[4] Eumorfopoulos, *Proc. Roy. Soc. London*, **90A**, 189–203 (1914).

[5] Keyes, THIS JOURNAL, **42**, 54 (1920).

[6] Henning, *Z. Physik*, **5**, 264 (1921).

[7] Henning and Heuse, *ibid.*, **5**, 285 (1921).

[8] Smith and Taylor, THIS JOURNAL, **45**, 2115 (1923).