

---

---

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

---

---

VOLUME 55

JANUARY, 1933

NUMBER 1

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, SERIAL NO. 284]

## The Normal Density of Ammonia

BY GERHARD DIETRICHSON, LOUIS J. BIRCHER AND JOHN J. O'BRIEN

### Introduction

The accompanying tabulation gives a summary of previous work in determining the density of ammonia at 0° and one atmosphere.

Blanchard and Pickering<sup>1</sup> in their review of the literature pertaining to gas densities conclude, in the case of ammonia, with the following statement: "The weight of a normal liter chosen is therefore 0.7710 with an uncertainty of two or three units in the last decimal place." This is exclusive of the results obtained by Leduc and of the most recent by Moles and Batuecas. In discussing the earlier work Moles and Batuecas<sup>2</sup> also state that they recalculated the data of Guye and Pintza, Perman and Davies and Scheuer. The resulting densities are shown in the column at the right.

The weight of a normal liter has also been calculated from the "compressibility" of ammonia,  $(\partial(pv)/\partial p)_T$ , using the equations

$$\begin{aligned} p_0 v_0 / p_1 v_1 &= 1 + \bar{\lambda} & d_n &= m/v_1 = \frac{M(1 + \bar{\lambda})}{RT_0} \\ p_0 v_0 &= m/M RT_0 \end{aligned}$$

where  $\bar{\lambda}$  is understood to be a mean value defined as  $\bar{\lambda} = \int_0^{1 \text{ atm.}} \lambda \, dp$ .<sup>1</sup> Beattie and Lawrence<sup>3</sup> using their own  $p$ - $v$ - $T$  data and the Beattie-Bridgeman equation of state

$$pv = RT + \beta/v + \gamma/v^2 + \delta/v^3$$

to obtain the  $p_1 v_1$  product, derive the value, 0.7706 g./l. On the other hand, the same form of equation applied to the data of Meyers and Jessup leads to a normal density of 0.7715 g./l.

The foregoing discloses considerable uncertainty as to the true normal density. In view of the elaborate precautions taken by the investigators in purifying ammonia from various sources, it seems certain that the irregularities are not traceable to impurities. It appears accordingly that the discrepancies must be attributed mainly to the experimental procedure adopted. All of the work up to the present has been done by either the

(1) Blanchard and Pickering, B. S. Sci. Paper No. 529, 1926.

(2) Moles and Batuecas, *Sitzb. Akad. Wiss. Wien*, **138**, 779 (1929).

(3) Beattie and Lawrence, *THIS JOURNAL*, **52**, 6 (1930).

## PREVIOUS WORK ON THE DENSITY OF AMMONIA

Name	Method	Source of NH <sub>3</sub>	No. of detns.	Density	Density as recalculated by Moles and Batuecas
Leduc (1898)	Balloon	Commercial		0.7720	
Guye and Pintza (1905)	Volumeter	Commercial	5	.77083 ( $\pm 0.0002$ )	0.7710
Perman and Davis (1906)	Volumeter	Commercial	4	.7717	
Perman and Davis (1906)	Volumeter	Commercial and (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	7	.77089 ( $\pm 0.0004$ )	
Perman and Davis (1906)	Balloon	NaNO <sub>2</sub> (reduced with Al + NaOH)	4	.77090 ( $\pm 0.0006$ )	.7714
Scheuer (1914)	Balloon	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	16	.7708 ( $\pm 0.00026$ )	.77093
McKelvey and Taylor <sup>a</sup> (1923)	Balloon and volumeter	Several sources	"Numerous"	.7713	
Meyers and Jessup <sup>a</sup> (1923)	Metal bombs	NH <sub>3</sub> prepared by McKelvey and Taylor	3	.7713 (max. var. 0.0013)	
Moles and Batuecas (1929)	Balloon	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	13	.77185	
Moles and Batuecas (1929)	Balloon	Synthetic	10	.77185	
Moles and Batuecas (1929)	Balloon	Mg <sub>3</sub> N <sub>2</sub>	8	.77200	
				.77190	
				Adsorption correction - .00020	
				<hr/>	
				.77170	

<sup>a</sup> Reported by Blanchard and Pickering.

"balloon" or the "volumeter" method. Neither of these would avoid definitely the adsorption effect expected with ammonia.

Professor F. G. Keyes proposed to the authors a number of years ago a modification of a method originally proposed and used by Maass and Russell<sup>4</sup> in determining the density of acetylene, methyl ether and hydrobromic acid and later by Cooper and Maass<sup>5</sup> in determining the density of carbon dioxide. The suggested modification provides a means of estimating quantitatively the adsorption effect on the container walls. The principle involved is that of measuring the temperature and pressure of the gas in a relatively large bulb of known volume, condensing it in a small bulb that can be sealed off and then weighing in the liquid form or under high pressure. This method obviously makes it possible to work with comparatively large amounts of material and only involves the weighing of very small bulbs with a corresponding decrease in total mass and surface area. It was assumed that the adsorption effect could be eliminated by bringing the gas down to varying final bulb pressures during the condensation process. According to the adsorption law,  $q = ap^{1/n}$ , the total amount adsorbed tends to approach a constant saturation value at relatively low pressures provided a true adsorption effect is involved.<sup>6</sup> The condensed liquid should, therefore, as the residual pressure is made progressively larger, represent material drawn from the gas phase only. By means of an approximate equation of state it is possible to calculate with exactness the small weight of gas corresponding to the residual pressure, exclusive of the adsorbed layer. This in turn when added to the weight of the gas that has been condensed would give the mass corresponding to the initial pressure. According to this procedure it becomes a matter, therefore, of determining the limiting minimum density with increasing residual pressures.

As the work progressed it was found that the method outlined above did not apparently serve to eliminate completely the adsorption effect. The authors feel, however, that this was finally accomplished by subjecting the ice-bath bulb to a thorough baking and pumping previous to the density determinations and by observing special care in removing the last traces of ammonia in the line before each condensation. The details as to this will be described more fully in a later section.

The present work was undertaken with the idea of obtaining density data at one, two-thirds and one-third of an atmosphere, also for corre-

(4) Maass and Russell, *THIS JOURNAL*, **40**, 1847 (1918).

(5) Cooper and Maass, *Can. J. Res.*, **2**, 388 (1930).

(6) Keyes [Keyes and Brownlee, "Thermodynamic Properties of Ammonia," John Wiley and Sons, New York, 1916, p. 21] has called attention to the fact that ammonia very likely absorbs in the adsorbed water layer rather than adsorbing to any extent. The amount of ammonia on the walls of the globe would therefore not be related to the pressure by the above formula but more in accordance with Henry's law. In any event, however, the method will indicate the part played by the walls in retaining gas. The final outcome of our work indicates that ammonia does not adsorb on water freed surfaces.

sponding pressures at higher temperatures. At this time only the results at one atmosphere and  $0^\circ$  are being reported. The preliminary densities at the lower pressures and  $0^\circ$  were used to obtain an equation of state needed in the computation of the residual amount of gas in the bulb.

### Experimental Method

The experimental work carried out divides itself into two distinct parts. The general arrangement of the apparatus for the first part, experiments Nos. 1-66, is shown in Fig. 1. That for the second, experiments Nos. 67-119, was similar except that the ice-bath and five-liter Pyrex bulb which it

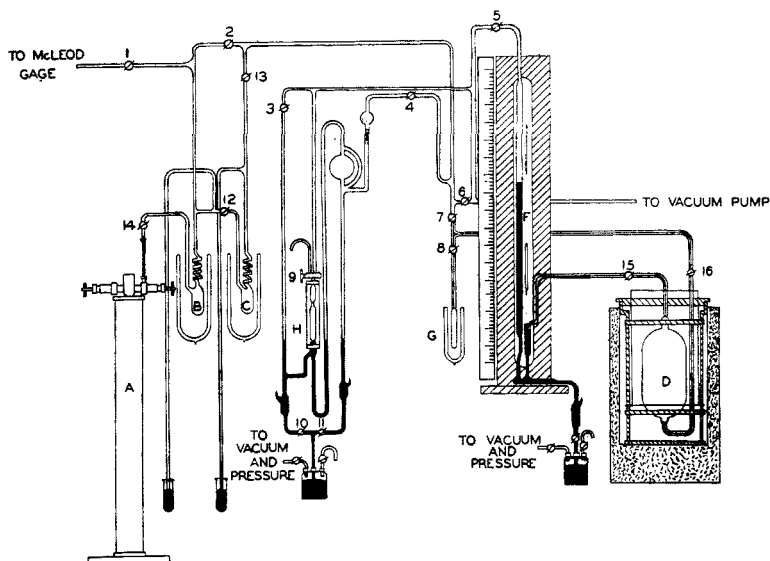


Fig. 1.—General arrangement of apparatus for gas density determinations.

contained were replaced by the ice-bath and one-liter Jena glass bulb shown in Fig. 2. In making a determination the ice-bath, provided with a stirrer, was filled with chipped ice and distilled water. Following that the evacuated bulb was filled with ammonia from the storage bulb, C, to very nearly the desired pressure, *i. e.*, one, two-thirds or one-third of an atmosphere, allowance being made for the corrections to be applied. Upon closing stopcock No. 16 the line was pumped down to that point. It developed that this operation required much more time than was at first anticipated. After allowing for temperature equilibrium to be established, ordinarily about three hours, the initial pressure was read. The ammonia was then condensed into bulb G with liquid air to varying final pressures, 0.0 to 40 mm. A total of twelve to fifteen hours was allowed for the condensation in the case of a zero residual pressure. Stopcock No. 16 was always closed during the final pressure readings. The

last step consisted in sealing off the capillary extension of the bulb G while the latter was still immersed in liquid air. Necessarily before doing this the ammonia in the line down to stopcock No. 16 (5 l. bulb) and No. 17 (1 l. bulb) was condensed. During the early stages of the work a Toepler pump was used in testing for uncondensed ammonia after sealing off the bulb. This was subsequently found to be unnecessary. The details of weighing the bulbs, closed and open, will be discussed in a later section.

### Purification of Ammonia

Synthetic anhydrous ammonia was used throughout the work, that for experiments Nos. 37-119 having been kindly donated by the Barrett Company through the courtesy of Doctor J. M. Braham. The steel cylinder, A, containing freshly cut sodium, was partially filled with the liquid and allowed to stand for several days. The system having been previously evacuated, ammonia was condensed in B by means of liquid air and subjected to several fractionations, the end portions being always discarded. Furthermore, at the end of each distillation the solidified ammonia was pumped until the pressure became less than 0.001 mm. The portion remaining was stored in C, the bulb being kept immersed in liquid air.

As far as could be observed there was no occasion to question this method of purification. Water and non-condensing gases should, on the basis of McKelvey and Taylor's<sup>7</sup> work, be the principal impurities and the treatment described above ought to eliminate completely these or any other foreign substances likely to be present. That such was the case seems evident from the following considerations. It was noted on the one hand in making as many as fifteen successive density determinations from a given portion in the storage bulb, with practically all of the ammonia being used, that no differences in the results could be detected. This obviously would indicate that the material was uniform, *i. e.*, there were no lighter and heavier fractions. Also, it was found that there was no indication of a permanent pressure developing in the bulb used for measuring the volume of the gas, in spite of the fact that the bulb was not pumped between successive determinations in a

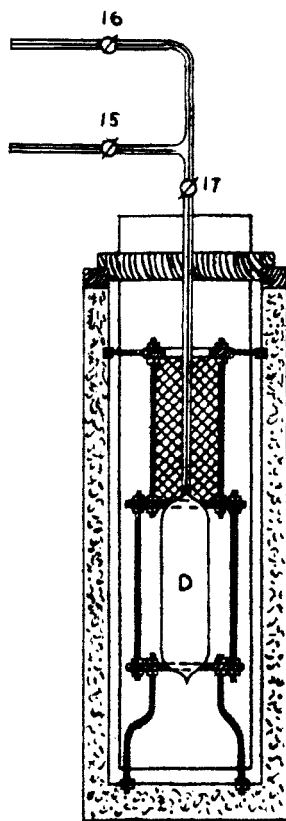


Fig. 2.—One-liter bulb and ice-bath.

(7) McKelvey and Taylor, B.S., Sci. Paper No. 465, 1923.

given series. Non-condensing gases, especially hydrogen, must therefore have been absent.

### Details of Procedure

(a) **Volume.**—As explained in the preceding section, two different bulbs were used for the volume measurements. The calibration of the five-liter Pyrex bulb was carried out by first filling it, at the ice-point temperature, with recently boiled, distilled water to fixed marks on the connecting capillaries. The water was weighed by draining it off into glass-stoppered flasks, the usual air buoyancy and calibration corrections being applied. That adhering to the walls was subsequently pumped out and collected in a liquid air trap that could be disconnected and weighed. Four independent determinations of the bulb volume were made before use and a second series of three a year and a half later. The deviation in all of these determinations was not greater than one part in 50,000. The "stretch" of the bulb was determined and found to be 0.480 ml. per atmosphere. After connecting the calibrated bulb to the manometer and loading apparatus the volume of the exposed parts was 2.27 ml. Allowance was made for the temperature difference of the latter in estimating the effective volume of the bulb when filled with ammonia. The total volume included that of the bulb and the capillaries, through the bore of stopcock No. 16 (Fig. 1) and to a fixed mercury level in the short arm of the manometer.

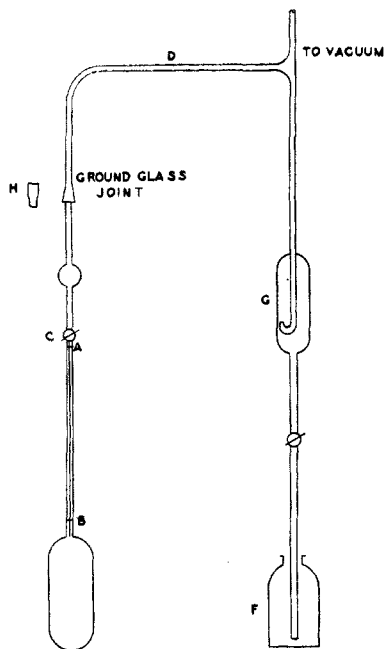
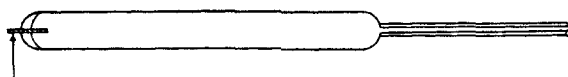


Fig. 3a.—One-liter bulb as set up for calibration.

The one-liter bulb was annealed in a tube furnace at 300° before being calibrated. It was then set up as shown, exclusive of the ice-bath, in Fig. 3a. Before introducing water the bulb was evacuated and weighed with the ground-glass cap, H. Special precautions were taken to exclude air while the bulb was being filled with water. The reservoir above the stopcock served to allow for expansion upon removal from the ice-bath. Before being weighed the bulb and its contents were brought to room temperature. The net volume of the bulb and connecting capillary, including the bore of the stopcock plug, as obtained in five determinations was 1030.56 ( $\pm 0.01$ ) ml. The "dead space" was in this case only 0.3 ml. with a correspondingly smaller correction for the exposed portion. The "stretch" of the bulb was found to be 0.087 ml. per atmosphere.



Platinum tube  
Outside diameter 1.00 mm., wall thickness 0.05 mm.

Fig. 3b.—Condensing bulb.

(b) **Temperature.**—No direct measurements of the ice-bath temperatures were made. However, baths made up in a similar manner, with chipped ice and distilled

water, have been tested very thoroughly in this Laboratory by J. M. Gaines, Jr., by means of platinum resistance thermometers and found to be constant within  $0.003^\circ$  or  $0.000$  ( $\pm 0.003$ )  $^\circ\text{C}$ .

(c) **Pressure.**—The same manometer was used throughout all of the work. A great deal of time was devoted to improving the conditions under which the readings were made, especially as regards temperature control and illumination. In the following paragraph there is given a description of the manometer in its final form.

The glass tube of the mercury manometer, F (Fig. 1), had an internal diameter of 17 mm. and was placed in a heavy cast bronze case provided with a plate glass front and a frosted glass back. The sides were covered with felt. The bronze case was placed on a large slate slab, and a cabinet, the interior of which was painted black, built around it. The door on the front of the cabinet was provided with slots through which the observations could be made. Two different cathetometers, both of them Geneva instruments, were available for measuring the pressures. The first of these which was used in experiments Nos. 1–26 carried a silver scale on the column. The second cathetometer was one that had been made with a special device for clamping the telescopes rigidly in position and proved to be a very satisfactory instrument. This cathetometer did not have an attached metal scale, the readings being made on a glass standard meter bar that was set up at the left of the brass case. The scale on the meter bar was ruled in millimeters with a diamond chip by the Société Gènevoise d'Instruments de Physique. It was calibrated at Berne, Switzerland.

In Fig. 4 is shown the construction of the short arm of the manometer as suggested by F. G. Keyes. The fine glass tip served as a fixed mark to which the mercury level was brought while making readings. The mercury surface was illuminated with diffused light coming through the frosted plate glass and a slit in a semicircular brass plate surrounding the rear half of the glass tube. The electric light bulb could be moved up and down by means of an overhead pulley. It was found possible in this way to illuminate the mercury surface so as to get a sharply defined meniscus. The long arm of the manometer was provided with a movable brass plate and a lighting arrangement similar to the one just described. In the case of the glass scale the best results were obtained by illumination from the rear. The lights for this purpose were supported from the same bars that carried the bulbs for the mercury columns. After having made the necessary initial adjustments it was therefore possible to swing the cathetometer telescope directly from the mercury meniscus at any level to the illuminated glass scale. In doing this the spirit levels on the telescopes were always checked.

The temperature within the brass case was determined by means of two calibrated thermometers that could be read to  $0.01^\circ$ . Ordinarily the temperature variations were considerably less than  $0.1^\circ$  during a given set of readings.

The vernier box of each telescope carried a circular head with a scale divided into one hundred divisions that could be estimated to tenths. When the cathetometer was at a distance of twenty-four inches from the manometer and the glass scale one millimeter on the latter corresponded to about a hundred and forty divisions. The following procedure was adopted in making observations. Five settings on the meniscus were first made in succession and the mean of these calculated. The telescopes were then

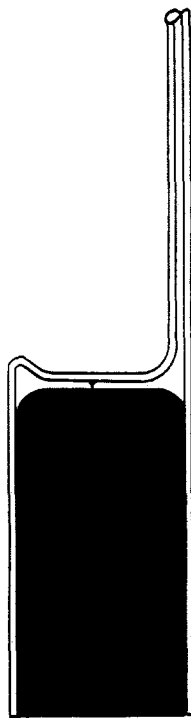


Fig. 4.—Short arm of manometer.

swung over to the glass scale and two settings made on each of the millimeter divisions within which the meniscus level fell. By interpolation the fractional part of a millimeter was computed to the third place. Ordinarily eighteen sets of these observations were made on each mercury column, corresponding therefore to as many independent

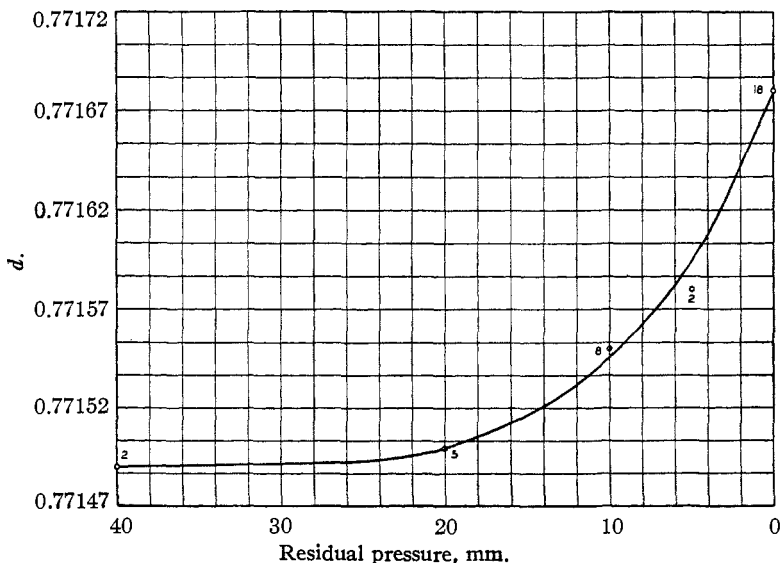


Fig. 5.

pressure determinations. The thermometers were read at the beginning and end of each set of three observations and a correction applied to the mean of these. As a precaution to guard against any lag the mercury columns were lowered at these same intervals and new settings made. By way of illustrating the degree of reproducibility the resultant six mean values for the last experiment, No. 119, as obtained in pairs by three observers, are tabulated, temperature corrections having been applied.

	760.243
	760.231
	760.253
	760.255
	760.257
	760.246
Av.	760.248
Meniscus corr.	+0.006
Level corr.	+0.030
Gravity corr.	-0.207
Final corr. press.	760.077 ( $\pm 0.01$ )

A correction for the difference in curvature of the two mercury surfaces was made by using the equation developed by Lohnstein.<sup>8</sup> Since the short arm of the manometer and the one-liter bulb were not at the same level, there was a positive correction at one atmosphere of 0.03 mm.

The gravity correction was made by taking  $g_0 = 980.665$  cm./sec.<sup>2</sup> and  $g_1 = 980.398$  cm./sec.<sup>2</sup>, the constant of gravity in Room 4-458 at M. I. T. The value 980.665 cm./sec.<sup>2</sup> is that adopted by the "International Critical Tables" and by Blanchard and Pickering in their review of the literature relating to gas densities.

(d) **Mass.**—As in the case of the pressures, much time was devoted to developing

(8) Lohnstein, *Ann. Physik*, **33**, 296 (1910).



the technique of obtaining the weight of the ammonia. For that reason the procedure will be discussed in some detail.

(1) **Condensing Bulbs.**—Necessarily an important step in connection with the weighing was that of devising a form of bulb that could be opened without any loss of glass. In experiments Nos. 1-79, 100, 102, 104, 106, 108 and 110 the Pyrex bulb was of the simple form illustrated in Fig. 1. This type was opened by first freezing the ammonia with liquid air in the capillary end. Upon removal from the liquid air a cloth was wrapped around the cooled portion and a fine flame applied at the other end. In view of the high vacuum existing the glass caved in upon melting and in doing so the particles of blown glass were carried along into the bulb. Following this the capillary end was again immersed in liquid air and the ammonia allowed to evaporate as the liquid air gradually disappeared. There was a tendency for the bulbs to crack unless they were handled in this manner. Before weighing the empty bulb it was put in a tube that could be evacuated in order to replace the remaining ammonia vapors with air.

The above type of bulb proved in the end not to be entirely satisfactory. In some unexplained way they did apparently undergo slight changes in mass while being opened. They were accordingly abandoned in favor of a modification proposed by F. G. Keyes and illustrated in Fig. 3b. It had previously been found by Keyes and Kraus that platinum tubes of a high degree of purity and sufficiently thin walled could be sealed directly into Pyrex glass in such a way as to hold a vacuum at liquid air temperatures on the one hand and also to stand the vapor pressure of liquid ammonia at room temperature, approximately ten atmospheres. The outer end of the platinum tube was closed by welding with a fine flame. The bulbs were opened by puncturing the platinum tube with a small needle. Density data obtained with these bulbs showed, when other disturbing factors had been eliminated, a high degree of consistency.

(2) **Balances and Methods of Weighing.**—Considerable difficulty was experienced in determining the weight of the bulbs with the degree of accuracy desired, *i. e.*, 0.01 mg.<sup>9</sup> However, with the right kind of a balance and with due regard to the necessary air buoyancy correction involved this was definitely accomplished.

Four different balances were used, the last being a special fifty gram load, semi-micro balance with a sensitivity (displacement of the rest-point) of approximately thirteen scale divisions. The notched beam was divided into a hundred divisions and carried a one milligram rider. Both the substitution and the transposition methods were used in making the weighings. The latter seemed on the whole to give more consistent results. The weights, Class M, had been calibrated by the Bureau of Standards. A counterpoise in the form of an open bulb was always placed on the scale pan with the weights. The size of this was such that its mass would be a little less than that of the empty bulb being weighed. The scale pans were fitted with aluminum wire supports by means of which the bulbs could be kept in a vertical position. This was necessary especially in weighing the sealed bulbs with their liquid contents. The rest points were determined by taking three readings to the right and two to the left. In all cases the weight to the nearest milligram was obtained by placing the proper fractional weights on the pan. With the first three balances the fractional part of a milligram was in turn computed from the rest-point, no rider being required. In the case of the special semi-micro balance referred to above the rider was used for the tenths and the rest-points for hundredths of a milligram. No-load rest-points were obviously not needed in either the substitution or the transposition method.

The procedure adopted consisted in making a total of sixteen weighings, usually only four on any one day. In doing this the temperature within the balance case, the barometric pressure and the humidity were recorded at regular intervals. An elaborate

(9) The authors are indebted to Mr. A. T. Pienkowsky of the Bureau of Standards for valuable suggestions in connection with the weighing.

set of tables was made up to simplify the work involved in obtaining the air densities. Since 1 cc. of air under ordinary conditions weighs approximately 1.2 mg. it was necessary to know the net volume displaced to within 0.01 cc. in making the air buoyancy correction. The volumes of the sealed bulbs were determined by means of hydrostatic weighings, whereas those of the open bulbs and the weights were calculated from the known densities of Pyrex glass, platinum, bronze and aluminum.

The following tabulation serves as an illustration of the degree of reproducibility obtained in making a series of weighings. The values given represent the mean, experiment No. 119, of each set of four weighings, after having been reduced to vacuum.

	Closed bulb	Open bulb
	2.243679	1.448758
	2.243673	1.448751
	2.243674	1.448747
	2.243677	1.448736
	<hr/>	<hr/>
Av.	2.243676	1.448748
Calibration corr.	+0.000054	+0.000069
Final corr. wt.	2.243730 ( $\pm 0.00001$ )	1.448817 ( $\pm 0.00001$ )

(3) **Residual Gas.**—The equation of state used in calculating the weight of the residual ammonia, in those experiments where the final pressure was not zero, was obtained by assuming first the general equation

$$pv = RT_0 + (RT_0\alpha)p + (RT_0\beta)p^2$$

This was in turn put in the form

$$(pv)_1 = A + Bp_1 + Cp_1^2$$

$$(pv)_2 = A + Bp_2 + Cp_2^2$$

$$(pv)_3 = A + Bp_3 + Cp_3^2$$

In evaluating the constants the following approximate values were taken for the density of ammonia

$$1 \text{ atm.} \quad 0.77160 \text{ g./l.}$$

$$\frac{2}{3} \text{ atm.} \quad 0.51189 \text{ g./l.}$$

$$\frac{1}{3} \text{ atm.} \quad 0.25470 \text{ g./l.}$$

By means of these densities the  $pv$  products per gram at the different pressures were calculated and a final equation of state for  $0^\circ$  obtained

$$pv = 1316.19 - 21.675p + 1.485p^2$$

$p$  being expressed in atmospheres and  $v$  in cc. For the purpose of calculation the equation was put in the form

$$\text{wt. of residual ammonia} = \frac{\text{vol. of bulb}}{(1316.19/p) + 1.485p - 21.675}$$

### Experimental Data and Discussion of Results

Altogether 119 density determinations were made, 88 at one atmosphere and 23 at lower pressures. The remaining eight were lost.

In Table I are presented the results with the five-liter Pyrex bulb at one atmosphere. It is to be noted that the density decreased from an average of 0.77168 at the lowest residual pressure to an average of 0.77149 at the highest. As will readily be seen from the accompanying curve, the latter seemed to represent a definitely limiting value. By way of confirmation it was decided to make a number of determinations with a bulb that had been baked and evacuated in order to remove the last traces of adsorbed water. It was thought that this would result in the complete elimination of any adsorption effects with ammonia and thus constant density data should be obtained regardless of the residual pressure. This proved in the end to be the case. However, before obtaining consistent results it became necessary to devise a new type of condensation bulb and also to observe additional precautions in avoiding adsorption effects in the line.

TABLE I  
DENSITIES DETERMINED WITH 5-LITER PYREX BULB

Expt.	Approx. res. press., mm.	Density g./l.	Average	Expt.	Approx. res. press., mm.	Density g./l.	Average
4	0.0	0.77167		11	5.0	0.77163	
5	.0	154		21	5.0	153	0.77158
6	.0	169		1	10.0	141	
8	.0	176		7	10.0	166	
9	.0	177		27	10.0	162	
12	.0	174		36	10.0	157	
22	.0	161		40	10.0	143	
28	.0	190		43	10.0	163	
29	.0	134		55	10.0	153	
37	.0	185		56	10.0	157	.77155
39	.0	177		42	20.0	146	
41	.0	175		52	20.0	145	
44	.0	169		53	20.0	152	
45	.0	153		61	20.0	153	
46	.0	158		62	20.0	156	.77150
47	.0	164		50	40.0	153	
48	.0	164		51	40.0	144	.77149
49	.0	168	0.77168				

In Table II will be found a summary of the results with the one-liter bulb. Experiments 67-79 were made with the first form of condensation bulb. The mean density values for the different residual pressures agreed very well. Nevertheless, the differences between individual determinations were greater than the accuracy of the measurements involved would lead one to expect. This led to some questioning of the method of opening the bulbs and it was accordingly decided to try the kind illustrated in Fig. 3b. The first two experiments, Nos. 80-81, agreed remarkably well. However, the next series, Nos. 82-92, was far

less satisfactory. In the first place the densities were higher and furthermore they varied considerably. Five additional experiments, Nos. 94-98, all at zero residual pressure, were likewise such as to leave one in doubt.

TABLE II  
DENSITIES DETERMINED WITH ONE-LITER JENA GLASS BULB (BAKED)

Expt.	Approx. res. press., mm.	Density, g./l.	Average	Expt.	Approx. res. press., mm.	Density g./l.	Average
67 <sup>a</sup>	0.0	0.771305		94 <sup>a</sup>	0.0	0.771584	
68	.0	1301		95	.0	1454	
69	.0	1387		96	.0	1469	
70	.0	1349	0.771281	97	.0	1450	
71	10.0	1425		98	.0	1435	0.771478
78	10.0	1227					
79	10.0	1336	.771269	99	.0	1457	
72	20.0	1336		101	.0	1332	
74	20.0	1234		103	.0	1366	
75	20.0	1200	.771197	105	.0	1337	
73	40.0	1320		107	.0	1357	
76	40.0	1378		109	.0	1377	.771371
77	40.0	1243	.771254	100	.0	1484	
				102	.0	1091	
80 <sup>b</sup>	0.0	1307		104	.0	.769988	
81	.0	1308	.771248	106	.0	.771404	
				108	.0	1298	
89	.0	1448		110	.0	1508	.771129
90	.0	1476	.771402				
82	10.0	1379		111	.0	1311	
85	10.0	1425		112	.0	1332	
88	10.0	1478		113	.0	1236	
93	10.0	1407	.771362	114	.0	1305	
83	20.0	1515		115	.0	1293	.771297
86	20.0	1693					
91	20.0	1402	.771477	116	.0	1262	
84	40.0	1359		117	.0	1273	
87	40.0	1466					
92	40.0	1372	.771339	118	.0	1239	
				119	.0	1262	.771259

<sup>a</sup> Indicates stages at which the bulb was baked. <sup>b</sup> The remaining experiments with the exception of Nos. 100, 102, 104, 106, 108 and 110 were made with the type of condensation bulb shown in Fig. 3b.

In view of the above discrepancies it seemed advisable to obtain some comparative data with the two types of condensation bulbs. In the next series, therefore, Nos. 99-110, they were alternated. As in the case of the other series, the same sample of ammonia was used throughout. After having made the first experiment, No. 99, there were reasons for believing that the variable results might be due to slight traces of adsorbed ammonia in the line that had not been removed by evacuating before the

condensation process was started. Up to this point the pumping had been continued for comparatively short periods, ordinarily about an hour, or at least until a McLeod gage gave no indication of any pressure. Beginning with No. 100 the line was pumped somewhat longer with consequent lower densities and also a much higher degree of consistency, *i. e.*, with the new style of bulb. The six determinations, Nos. 100, 102, 104, 106, 108 and 110, made with the first type showed conclusively that the weight of the glass could not have remained constant.

In the next five experiments the line was pumped even longer than in the preceding series, six to eight hours. The results showed a still further decrease in density. In order to determine if the limit of the adsorption effect had been reached, two additional experiments, Nos. 116-117, were made in which dry air was admitted from time to time while the line was being evacuated over a period of fifteen hours. Also, as a further check, in the next two experiments Nos. 118-119, the ammonia was removed by condensing it with liquid air in a second bulb that could be shut off with a stopcock during the subsequent condensation from the one-liter bulb. Since the maximum deviation of the four determinations was slightly less than four parts in seventy-five thousand, it was concluded that the adsorption effect had finally been eliminated and the average of these was accepted as the density of ammonia at 0°.

The authors realize that in selecting the last four values for determining the final mean density of ammonia no weight is given to the previous determinations. The gradual development of the method with consequent elimination of disturbing factors would seem, however, fully to justify this procedure.

**Acknowledgment.**—The authors wish to express their appreciation to Professor F. G. Keyes at whose suggestion this research was undertaken. His continued interest and helpfulness contributed much to the progress of the work. They are also greatly indebted to C. W. Orleman, Charles Rubin and Stanley L. Witcher, who assisted in the work with the one-liter bulb, especially in developing the technique of weighing.

### Summary

A precision method for the determination of gas densities has been developed. An important feature of it is that it makes possible the definite elimination of adsorption effects. Also, the method readily lends itself to use over a wide range of temperatures.

On the basis of the data presented, the normal density of ammonia is considered to be 0.77126 ( $\pm 0.00001$ ).

CAMBRIDGE, MASSACHUSETTS

RECEIVED MAY 20, 1932  
PUBLISHED JANUARY 11, 1933