

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

**THE VAPOR PRESSURE OF AMMONIA.<sup>1</sup>**

By C. S. CRAGOE, C. H. MEYERS AND C. S. TAYLOR.

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**I. Introduction.**

The measurements presented in this paper form a portion of the work undertaken by the Bureau of Standards in the determination of the thermal properties of materials used as refrigerating media. The existing data on the vapor-pressure-temperature relation for ammonia are undoubtedly sufficiently accurate to meet the requirements of refrigeration engineering. The Clapeyron equation, however, offers a means of correlating the measurements of the latent heat of vaporization<sup>2</sup> with the data on specific volumes of saturated liquid and vapor (to be published shortly), provided the slope of the saturation line can be determined with sufficient accuracy. On account of the large errors which may be introduced into the calculated values of the slope by relatively small errors in the pressure or temperature, it appeared that existing data were deficient either in the range or the precision required.

The accuracy of any vapor-pressure measurements is determined in general by 4 factors, namely, (a) purity of the material; (b) certainty of equilibrium conditions; (c) precision of the pressure measuring instrument, and (d) temperature measurement and control.

(a) The extent to which factors (a) and (b) may affect the results of the vapor-pressure measurements will depend upon the methods used. Non-volatile impurities present in solution would affect measurements by the static method and also by the dynamic method if measurements were made of the temperature of the boiling liquid, while their effect on the temperature of the condensing vapor is relatively unimportant. Non-condensing gases have but little effect on measurements by the dynamic method, while in the static method a small amount of non-condensing gas may affect the measured pressure to an extent out of all proportion to the amount of gas present. It is worthy of note that the non-condensing gas does not notably affect the vapor pressure but causes the total pressure as measured by the static method to differ from the true vapor pressure.

(b) In measurements by the static method a very considerable lag in the attainment of equilibrium between the vapor and its liquid may be encountered even with a liquid well freed from impurities, especially if the liquid is not agitated. An example of this is furnished later. The presence of a small amount of permanent gas such as air greatly increases the lag in coming to pressure equilibrium. This was found to be the case

<sup>1</sup> Published by permission of the Director of the Bureau of Standards, Washington, D. C.

<sup>2</sup> Osborne and Van Dusen, **THIS JOURNAL**, 40, 14 (1918).

at low temperatures as illustrated in an attempt to measure the boiling point of a commercial sample of ammonia by the static method.

(c) The sensitivity of the pressure measuring instruments used in the present work was such as to permit readings of pressure to one part in 5000 or better, except for pressures below one atmosphere. Pressures below 5 atmospheres were measured with mercury manometers; pressures between 5 and 15 atmospheres with a mercury manometer and with a piston gage; pressures above 15 atmospheres with the piston gage only.

(d) Temperature control plays an important rôle in any vapor pressure measurement, particularly in the establishing of equilibrium. A change in the temperature of  $0.1^\circ$  in the case of ammonia is equivalent to a change in the vapor pressure of about 2 mm., 12 mm., and 40 mm. of mercury at  $-50^\circ$ ,  $0^\circ$ , and  $+50^\circ$ , respectively, or a percentage change in pressure of about 0.7, 0.4, and 0.25, respectively. The aim in the present experiments was to maintain temperatures constant to  $0.01^\circ$  or better for very long time intervals. Platinum resistance thermometers were employed for the temperature measurements and temperatures were read to thousandths of a degree.

## II. Previous Measurements.

The percentage deviations of the measurements of various observers from the results of the present work are shown in Fig. 1. The 4 curves also shown in this figure represent the deviations of values computed by

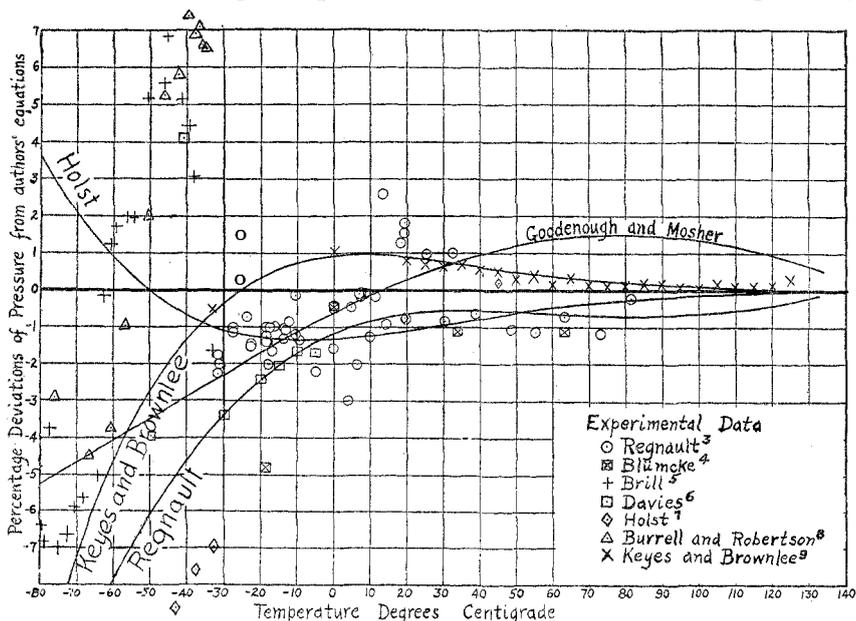


Fig. 1.—Comparison of measurements of the vapor pressure of ammonia. For references 3, 4, 5, 6, 7, 8, 9, see the next page.

Regnault, Goodenough and Mosher, Holst, and Keyes and Brownlee. A brief review of the previous measurements may be found in the complete paper.<sup>1</sup>

Various determinations of the normal boiling point of ammonia are given in Table I. Several of the earlier determinations were made by immersing a thermometer into liquid ammonia exposed to the air in an open vessel. It is now well known that liquid ammonia under these conditions will cool readily to nearly  $-40^{\circ}$ .

TABLE I.  
Determinations of the Normal Boiling Point of Ammonia.

Observer.	Date.	Degrees.	Remarks.
Bunsen(a).....	1839	$-33.4$	Observed $-33.7^{\circ}$ at 749.3 mm.
Loir & Drion(b).....	1860	$-35.7$	In an open vessel
Regnault.....	1862	$-37.9$	Observed $-38.1^{\circ}$ at 752 mm. in an open vessel
Regnault.....	1862	$-32.6$	Calculated from equation
Joannis(c).....	1893	$-38.3$	Probably in an open vessel
Ladenburg(d).....	..	$-35.0$	
Lange(d).....	..	$-33.7$	
Dickerson(e).....	..	$-33.0$	
De Forcrand(f).....	1903	$-32.5$	Vigorous boiling in an open vessel
Gibbs(g).....	1905	$-33.46$	
Brill.....	1906	$-33.0$	
Davies.....	1906	$-33.5$	Interpolated graphically from measurements by static method
Burrell & Robertson.....	1915	$-34.6$	
Keyes & Brownlee.....	1916	$-33.22$	
Bureau of Standards.....	1919	$-33.35$	

(a) *Pogg. Ann.*, **46**, 102 (1839).  
 (b) *Bull. soc. chim.*, **2**, 185 (1860).  
 (c) *Compt. rend.*, **115**, 822 (1892).  
 (d) Quoted in "Verflüssigtes Ammoniak als Lösungsmittel," by J. Bronn, Berlin, 1905.  
 (e) Quoted in "Liquid Air and Liquefaction of Gases," by T. O'Connor Sloane, London, 1900.  
 (f) *Ann. chim. phys.*, [7] **28**, 537 (1903).  
 (g) THIS JOURNAL, **27**, 858 (1905).

Keyes and Brownlee<sup>2</sup> have recently published the results of their measurements with an absolute piston gage between  $0^{\circ}$  and the critical tempera-

<sup>1</sup> Bur. Standards, *Bull.* 16 (to be published shortly).

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Mém. Inst. France*, **26**, 596 (1862).

<sup>4</sup> *Wied. Ann.*, **34**, 18 (1888).

<sup>5</sup> *Ann. Physik*, [4] **21**, 170 (1906).

<sup>6</sup> *Proc. Roy. Soc. (London)*, **78A**, 41 (1906-7).

<sup>7</sup> *Bull. Assoc. Intern. Froid*, **6**, No. 51 (1915).

<sup>8</sup> THIS JOURNAL, **37**, 2482 (1915).

<sup>9</sup> *Ibid.*, **40**, 25 (1918).

ture of ammonia. A special electrical contact method was employed to increase the sensitivity of the piston gage and to decrease the time necessary in making observations. The constant of the piston gage was determined by direct comparison with a mercury column. A 25-ohm platinum resistance thermometer was used in the temperature measurements. Considerable care was taken in the purification of the ammonia used and the difficulty of removing dissolved gases was particularly emphasized. The ammonia vapor was passed into dry ammonium nitrate which made it possible to keep the ammonia at ordinary temperatures at a moderate pressure. It is stated that dissolved gases could be very completely removed from this ammonium nitrate-ammonia solution. Rather sensitive preliminary tests made at this Bureau indicate that the dissolved gases cannot be removed with sufficient completeness by this method alone. The test used by Keyes and Brownlee for the absence of permanent gases was the complete collapsing of the vapor phase without rise in pressure. This may not be a very sensitive test due to the comparatively large solubility of gases in liquid ammonia. The attainment of equilibrium between the liquid and vapor required considerable time according to their experience. The lag appeared to be increased, it is stated, as the liquid was freed more perfectly from dissolved gases and was more pronounced at low temperatures. In our experience dissolved gases were found to increase greatly the lag in coming to equilibrium as illustrated later in the measurements near the boiling point of a commercial sample which was known to contain air. In the absence of dissolved gases the lags were not excessive in our experiments, except in the measurements at temperatures above about  $+25^{\circ}$ , which were due to thermal lags in the glass apparatus used.

The normal boiling point of ammonia was measured by Keyes and Brownlee by the static and also the dynamic method. The measurements by the static method were very discordant due to the admitted difficulty in maintaining a constant bath temperature. The results obtained are given in a table reduced to the temperature  $-33^{\circ}$ , which shows variations over a range of 40 mm. A direct determination was then made by the dynamic method, using a Beckman thermometer immersed in the liquid and a small heating coil to produce ebullition. The boiling point was observed to be a function of the heating current, varying from  $-33.13^{\circ}$  with no current to  $-33.70^{\circ}$  with 4 amperes. The most probable value of the normal boiling point by this method was chosen as  $-33.21^{\circ}$ .

The table containing all their experimental data reduced to integral degrees of temperature shows variations in the temperature interval  $0^{\circ}$  to  $50^{\circ}$  of about 0.5% in the individual measurements, made at a given temperature. At the higher pressures, the agreement is much better,

which indicates the unsuitability of their piston gage for measurements of low pressures. The deviations of the mean of the observations reduced to integral degrees of temperature are shown in Fig. 1. The curves marked Keyes and Brownlee represent the deviations of values computed by their empirical equation from the present author's equations.

### III. General Description of Apparatus and Method.

**Manometers.**—The manometers used in making the present measurements were of 3 types as shown in Fig. 2. The glass tubes used in each type were of 7 mm. i. d. and 1.5 mm. wall thickness. A calibrated metric scale etched on a strip of silvered plate glass was attached directly behind each manometer.

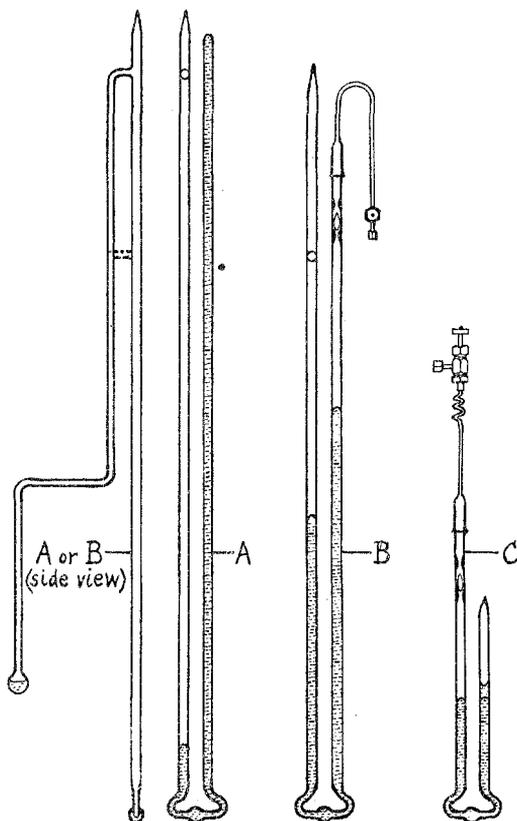


Fig. 2.—Hermetically sealed ammonia containers.

A calibrated metric scale etched on a strip of silvered plate glass was attached directly behind each manometer.

Type A consists of a glass U-tube containing mercury with one arm evacuated and sealed and the other arm connected to a bulb containing the liquid ammonia. The pressure in this type and also in Type B is transmitted from the liquid ammonia, contained in the small bulb and maintained at constant temperature, to the mercury manometer by means of superheated ammonia vapor. Type A was used in the measurements from  $-78^{\circ}$  to the normal boiling point.

Two manometers of the Type B were used in measuring pressures from slightly below the normal boiling point to that corresponding to  $+25^{\circ}$ . This type is similar to the former except that one arm is here attached, through a glass-steel joint and a short spiral coil of flexible copper tubing, to a brass needle valve. A small glass float fitting loosely at the bottom and ground at the top is also contained in this arm to act as a check valve to preserve the ammonia in case of a sudden release of the balancing pressure. Measurements near the normal boiling point

were made by opening the brass valve to atmospheric pressure. Manometer and barometer readings were then taken simultaneously. At the higher pressures a balance was obtained by admitting pressure from a cylinder of compressed air, connected by copper tubing to the brass valve. A steel bomb of about 3 liters capacity was inserted in the connecting line and immersed in a large insulated bath of liquid at room temperature to damp out, during any series of measurements, the effect of small change in room temperature on the pressure of this constant volume of air.

Two manometers of Type C were used to measure the higher pressures corresponding to temperatures above room temperature. In this case the liquid ammonia was enclosed in one arm of the manometer and the whole manometer immersed in a thermoregulated bath. Air pressure was used here, as before, to obtain a balance in pressure within a few cm. and manometer readings were taken through a window in the bath.

**Pressure Gages.**—An open mercury manometer was used to measure balancing pressures from one to fifteen atmospheres. This manometer will be described in detail elsewhere<sup>1</sup> and only a brief description will be given here. It consists of 5 glass U-tubes, each having a length equivalent to 3 atmospheres pressure. By a proper manipulation of valves the U-tubes may be connected in series or by-passed to measure any pressure from one to sixteen atmospheres. The pressure is transmitted between tubes by a liquid of known density, alcohol in the present case. Readings of the mercury levels in the various arms are made upon accurately calibrated metric scales of steel. A specially constructed and calibrated mercury thermometer with a bulb 2.4 meters in length is used to measure the average temperature of the mercury columns.

The piston gage used to measure the higher balancing pressures will also be described in detail elsewhere.<sup>2</sup> It was designed and constructed to measure pressures up to 100 atmospheres. The pressure measurements were made by weighing the force exerted against a rotating steel piston floating in oil. The piston has an area of about one sq. cm. A small mercury manometer, from which the pressure is transmitted to the piston by means of oil, serves to indicate when the piston is in equilibrium.

**Constant Temperature Baths.**—The thermoregulated bath used in the measurements below room temperature with manometers of Types A and B has been previously employed in the determination of specific and latent heats of ammonia and described in detail elsewhere.<sup>3</sup> It consists of a brass vessel, with two cylindrical vertical tubes connected at the bottom and near the top, filled with gasoline. The smaller tube

<sup>1</sup> Dickinson and Meyers, Bur. Standards, *Bull.* (to be published shortly).

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Osborne, Bur. Standards, *Bull.* 14, 145 (1917); *Sci. Paper* 301.

contains a screw propeller, electric heating coil, carbon dioxide cooling coil, and a thermostat coil filled with toluene. An oscillating contact in the thermostat head, previously described,<sup>1</sup> served to maintain the temperature constant to about one thousandth of a degree.

In the measurements above room temperature a large thermoregulated bath of about 100 liters capacity was used. This bath consists of half a wooden barrel filled with water and provided with a stirrer, heating coil, and thermostat. Evaporation to the room provided the necessary cooling and by the use of the oscillating contact in the thermostat head the temperature of the bath could be maintained remarkably constant for long periods of time.

**Thermometers.**—Platinum resistance thermometers of the 4-lead potential terminal type with strain-free winding previously described by Waidner and Burgess<sup>2</sup> were used in all the temperature measurements. The wheatstone bridge used in the observations of the platinum thermometer resistances has been previously described.<sup>3</sup>

#### IV. Purification of Samples and Description of Manometer Fillings.

The ammonia used in these measurements was prepared by methods to be described in detail in an independent paper. Only a brief description of the process of purification will, therefore, be given here.

A sample of synthetic ammonia (designated Sample K in a previous analysis),<sup>4</sup> which proved to be extremely pure except for a small amount of water and non-condensing gases, was transferred by distillation into a special small steel container which would hold about a kilogram. The first portion was distilled off and the middle portion distilled into a similar vessel containing a large quantity of metallic sodium, in the form of a fine wire, to remove any remaining traces of water. The ammonia remained in contact with the metallic sodium for about a week. During this interval the liquid was frequently shaken and the hydrogen blown off. The liquid was distilled into a high-pressure distillation apparatus, and fractionally distilled 8 times, rejecting the first and last fractions (about  $\frac{1}{10}$  the total volume of liquid) in each distillation. The rejected first fractions were removed through a mercury seal in such a way as to discard the non-condensing gas present. After the above treatment, which was all of a preliminary nature, the final product was distilled into a vacuum fractional distillation apparatus of glass and fractionally distilled at least 10 times under widely different conditions of temperature and pressure, the first and last portions being rejected in each case.

Since the accuracy of the physical measurements depends largely upon

<sup>1</sup> Sligh, *THIS JOURNAL*, 42, 60 (1920).

<sup>2</sup> Bur. Standards, *Bull.* 6, 154 (1910); *Sci. Paper* 124.

<sup>3</sup> Mueller, Bur. Standards, *Bull.* 11, 571 (1914); *Sci. Paper* 241.

<sup>4</sup> McKelvy and Taylor, *J. Am. Soc. Refrig. Eng.*, 3, No. 5, 45 (1917).

the purity of the ammonia used and especially upon having the amount of non-condensing gases reduced to a minimum, particular care was taken in the removal of these gases. The ammonia was, therefore, frozen with liquid air and the vapor then pumped off by means of a high vacuum pump. The ammonia was then allowed to warm up until it was entirely liquid and some of the vapor allowed to escape through the mercury seal. It was again frozen with liquid air and the vapor pumped off as before. This process was repeated several times. Finally the ammonia was frozen into small, flocculent crystals by its own evaporation, the resulting vapor being pumped off and discarded. During this series of operations samples were taken continuously and the amount of non-condensing gas determined by a method previously outlined,<sup>1</sup> to be described more in detail in a later paper.

The tests on the final samples of ammonia, used in filling the vapor pressure manometers, gave the following results: non-condensing gases in the vapor at  $+25^{\circ}$  and 760 mm. pressure, less than one part in 100,000 by volume; water, less than 0.003% by weight, which was practically the limit of sensitivity of the chemical test applied.

The vapor-pressure manometers were thoroughly cleaned with conc. nitric and sulfuric acids, and aqueous potassium hydroxide solution, and washed with distilled water. They were then sealed, one at a time, into the glass line of the vacuum distillation apparatus. A flask containing about 50 cc. of mercury, purified by the anode process and by distillation, was sealed into the connecting line in such a manner as to permit the mercury to be distilled into the manometers under a high vacuum. In one case, a manometer of Type B was heated to  $300^{\circ}$  in a specially constructed electric furnace, before filling with mercury, to drive off more completely any occluded gases. (The vapor-pressure measurements made with this manometer, designated B<sub>1</sub> in Table II, show no systematic difference, however, from those made with other manometers which were not given this treatment.) A portion of the purified ammonia was then distilled into each manometer, being frozen in finely divided crystals by means of liquid air. After a sufficient quantity had been distilled into the apparatus, the supply reservoir was cut off by closing an intervening stopcock and the vapor phase pumped off with the aid of a high vacuum pump. The manometers were finally sealed, with the vacuum pump still in operation.

#### V. Description of Preliminary Experiments.

In the preliminary experiments two phenomena were observed which determined to a large extent the procedure adopted in the final measurements. A brief discussion of them is, therefore, given here.

##### 1. Hysteresis in an Impure Sample.—In the early stages of this in-

<sup>1</sup> McKelvy and Taylor, *J. Am. Soc. Refrig. Eng.*, 3, No. 5, 34 (1917).

investigation an attempt was made to determine the boiling point of a commercial sample of ammonia by measurements of the vapor pressure near the normal boiling point, using the static method. The apparatus used in these measurements was similar to Type B (Fig. 2) except that the open end of the manometer tube was drawn down to a small capillary and sealed. When the liquid ammonia in the bulb had been cooled to within a few degrees of the normal boiling point, the glass tip of the capillary was broken off to admit atmospheric pressure. The pressure was then determined from readings of the manometer and the barometer.

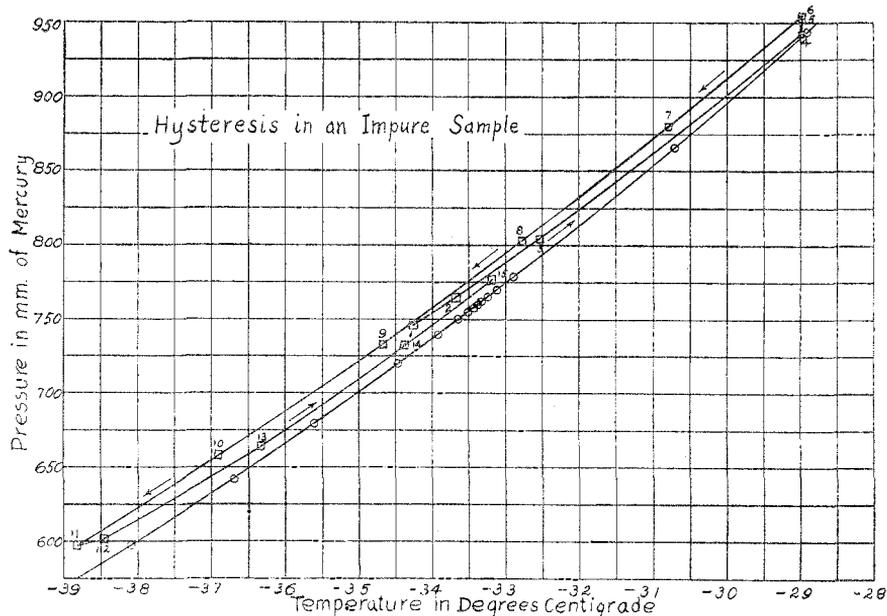


Fig. 3.—Comparison of measurements with a pure and impure sample.

Fig. 3 illustrates the results obtained with a commercial sample known to contain air as compared with those obtained with a thoroughly purified sample almost completely freed from dissolved gases. The observations taken with the commercial sample are numbered in the order in which they were made. No definite procedure was followed in these measurements to insure equilibrium. Observations were made about 5 or 10 minutes after the regulation of the bath at a constant temperature had been accomplished and consequently do not represent the system in equilibrium. The observations designated 4, 5 and 6 were made at a constant bath temperature; 4 soon after the bath temperature had been raised about 4 degrees, 5 after an interval of one hour, and 6 fifteen minutes later. The lower curve represents the vapor-pressure measurements with a pure sample, taken with a similar apparatus and procedure,

which show no evidence of hysteresis but lie consistently on a smooth curve. The occurrence of hysteresis, at least, with the type of apparatus here used, furnishes an excellent test of the presence of non-condensing gases even in very small quantities.

The phenomenon of hysteresis is undoubtedly associated with the presence of non-condensing gases in the ammonia, but whether the phenomenon observed is due primarily to changes in the amount of gas in solution in the liquid or to changes in the distribution of the gas between the saturated and superheated vapor has not been determined. While the observed pressures were always above those for pure ammonia, the phenomenon produced by the presence of non-condensing gas is evidently much more

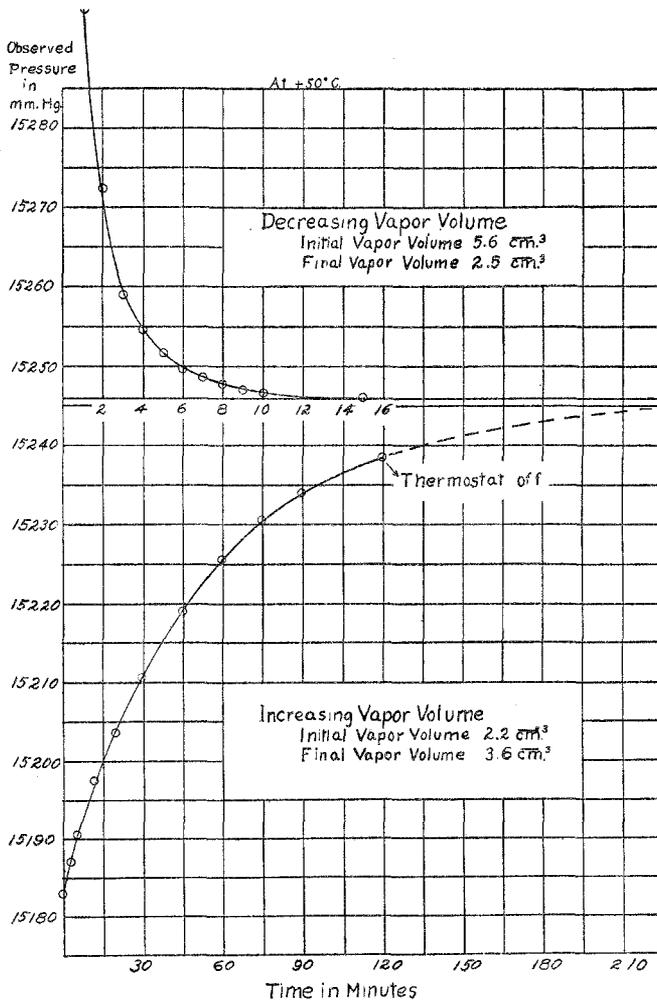


Fig. 4.—Time lag in coming to equilibrium at +50°.

complex than the mere increase of pressure by an approximately constant amount.

2. **Lag in Coming to Equilibrium.**—With a purified sample of ammonia well freed from dissolved gases no very great difficulty was encountered at temperatures below  $0^{\circ}$  in establishing equilibrium conditions, *i. e.*, constant pressure at a constant bath temperature. Non-condensing gases present, however, greatly increased the lag in coming to equilibrium as shown in the previous section. Equilibrium could be obtained at higher temperatures within a comparatively short time only when a certain procedure was followed.

Fig. 4 shows that only a few minutes were required to establish equilibrium when a slightly excessive balancing pressure was used which produced a decrease in the vapor volume and condensation of the vapor. This procedure was finally adopted in all the vapor-pressure measurements. Much greater lags were observed when too small a balancing pressure was used so that the vapor volume was increasing which necessitated evaporation of the liquid. The lower curve shown in this figure was determined by first obtaining equilibrium conditions and then decreasing the balancing pressure a small amount with the bath maintained at a constant temperature. This curve indicates that equilibrium would have been reached only after some hours. A similar phenomenon was observed when the bath temperature was raised and the balancing pressure maintained constant.

Fig. 5 shows qualitatively the variation at different temperatures of

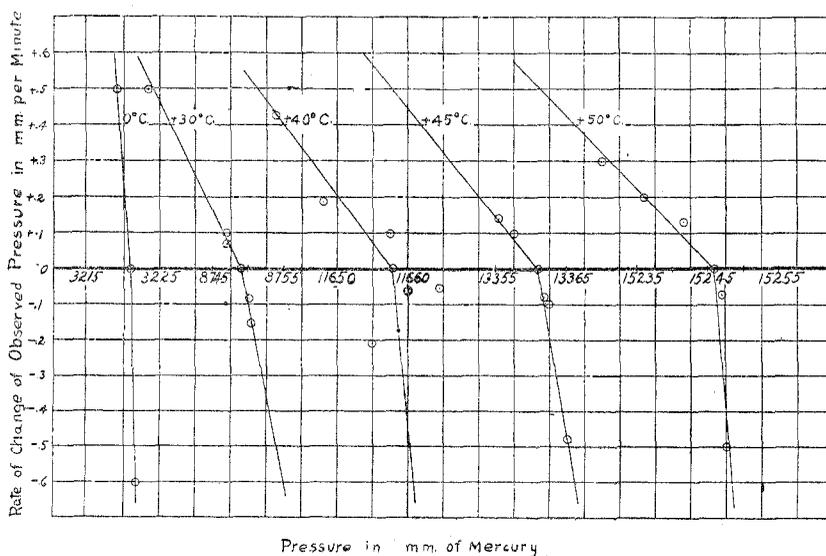


Fig. 5.—Preliminary measurements showing effect of non-equilibrium.

the observed vapor pressure with the rate of change of vapor volume which corresponds in this case with the rate of change of observed total pressure. The lag is evidently much greater with increasing vapor volume or positive rate of change of observed pressure and apparently increases with temperature and vapor density.

A simple calculation of the time required to transmit, through the glass walls, sufficient heat to the surface of the liquid ammonia in order to vaporate the requisite amount of liquid to saturate the increased vapor space indicates that lags of this magnitude are to be expected. This time is obviously greater at the higher temperatures here employed since the vapor density increases very rapidly (for example, it is 5 times as great at  $+50^{\circ}$  as at  $0^{\circ}$ ) thus necessitating the evaporation of a greater quantity of liquid and, therefore, a greater amount of heat transfer. The correct order of magnitude of the time required to reach equilibrium upon decreasing the vapor volume may be obtained by a similar calculation. The comparatively large surface available for condensation with this procedure decreases to a great extent the lags in coming to pressure or thermal equilibrium. Doubtless agitation or stirring of the liquid would tend to reduce very materially these lags. With a metal container they would also be reduced due to the larger thermal conductivity of metal as compared with glass.

All of the preliminary measurements, most of which are shown in Fig. 5, have been discarded and no weight given to them in the final result. They were purposely made under very poor conditions to determine the most advantageous procedure to secure equilibrium and also to study the magnitude of the error produced in the pressure measurement.

#### VI. Measurements by the Static Method.

**Measurements below  $-55^{\circ}$ .**—Measurements of the vapor pressure were made at 3 temperatures below  $-55^{\circ}$ , the lower limit of the thermo-regulated gasoline bath with carbon dioxide refrigeration. The constant temperatures employed in these measurements were obtained at the freezing point of commercial chloroform, the triple point of ammonia and the temperature of a mixture of solid carbon dioxide and gasoline at atmospheric pressure.

The bulb containing the liquid ammonia of the manometer (Type A) and a platinum resistance thermometer were immersed in a double-walled glass tube, partially filled with commercial chloroform. The glass tube and contents were placed in a bath of gasoline which was cooled by adding solid carbon dioxide. No provision was made to prevent the condensation in the tube of moisture from the atmosphere since only a constant temperature was desired. Stirring of the chloroform was produced mechanically and readings taken when the temperature became constant, that is, during the process of freezing.

Several determinations, which will be published later, of the freezing point of pure ammonia under its own vapor pressure (the triple point) have been made in a special apparatus provided with a resistance thermometer and a stirrer operated from the outside by a magnet. Measurements of vapor pressure at this point were made with a small mercury manometer attached to this apparatus and readings taken with a cathetometer. Meniscus corrections were applied to the manometer readings.

The manometer of Type A was used in the vapor-pressure measurements with a carbon dioxide-gasoline slush bath. The temperature of the slush bath was measured in the first experiment with a platinum resistance thermometer and in another experiment with a carbon dioxide vapor-pressure thermometer.

**Measurements above  $-55^{\circ}$ .**—Manometers of Types A and B were used in the measurements from  $-55^{\circ}$  to the normal boiling point of ammonia. Two manometers of Type B were used in the majority of the measurements between the normal boiling point and room temperature. The measurements made with the first filling of these manometers are designated  $B_1$  and  $B_3$ , while those made with the second filling are designated  $B_2$  and  $B_4$ . In each experiment approximate pressure equilibrium was obtained by producing condensation of the vapor and a series of 4 or 5 readings, which served as a test of the equilibrium prevailing during the experiment, was taken to constitute one measurement of the vapor pressure.

In a few experiments 2 manometers (designated  $B_4 B_2$ ) were used at the same time, that is, with the same bath and the same balancing pressure. The pressures measured on these manometers were identical under these conditions.

**Meniscus Depression.**—The heights of the menisci in the manometer tubes were not measured consistently throughout these experiments. The heights on the ammonia side of the manometers were observed, however, to be very uniform (about 1.5 mm.) while those in the opposite arms were somewhat flatter. Assuming, in the extreme case, one meniscus entirely flat and the other 1.5 mm. in height, the maximum error introduced would be about 0.8 mm. in the 7 mm. tubes used, according to the data of Mendelejeff and Gutkowski.<sup>1</sup> Since the heights in one arm of the manometers were observed to be slightly greater than the other, a uniform correction of  $-0.3$  mm. has been applied to all the observed pressures.

**Unit of Pressure.**—All of the pressure measurements were reduced to mm. of mercury at  $0^{\circ}$  and standard gravity ( $g = 980.665$ ).<sup>2</sup> The value

<sup>1</sup> Landolt and Börnstein, *Tabellen*, 1912, p. 34.

<sup>2</sup> This value was adopted by the International Committee on Weights and Measures in 1901 (*Travaux et Mémoires du Bur. Int.*, third general conference, 1902, p. 66.

of  $g$  in this laboratory is 980.091 based on a direct determination made by the Coast and Geodetic Survey in 1910.<sup>1</sup>

**Temperature Scale.**—The platinum resistance thermometers used in all the temperature measurements were calibrated in ice, steam and sulfur vapor (444.6° taken as the normal boiling point of sulfur). The constants determined by this calibration are:

Thermometer.	$R_0$ .	$R_{100} - R_0$ .	$\delta$ .
C <sub>21</sub> .....	25.5440	9.9958	1.491
C <sub>22</sub> .....	25.5484	9.9876	1.495
C <sub>23</sub> .....	25.5345	9.9865	1.488

Using the Callendar equation  $t = \frac{R_t - R_0}{R_{100} - R_0} 100 + \delta \left( \frac{t}{100} - 1 \right) \frac{t}{100}$ , as an interpolation equation, the temperature scale so defined represents the centigrade thermodynamic scale in the interval  $-40^\circ$  to  $+450^\circ$  to the accuracy with which that scale is at present known. The scale defined by the resistance thermometer of pure platinum has been adopted as the standard working scale of the Bureau of Standards for use in the interval  $-40^\circ$  to  $+450^\circ$ . Temperatures between  $0^\circ$  and  $+100^\circ$  may be measured on this scale with a precision of a few thousandths of a degree. Below  $-40^\circ$  temperatures determined by the above equation are consistently lower than those determined with a gas thermometer. By direct comparison of several resistance thermometers of very pure platinum with a constant volume hydrogen thermometer, Henning<sup>2</sup> found that the following corrections were necessary to reduce to the gas scale the temperatures determined with these thermometers, by means of the Callendar equation:  $+0.01^\circ$ ,  $+0.06^\circ$ , and  $+0.16^\circ$  at  $220^\circ$ ,  $200^\circ$  and  $180^\circ$  A., respectively. The temperature measurements below  $-40^\circ$  C. in this work have accordingly been corrected by interpolation between these corrections.

**Results.**—The results of all the measurements by the static method, except the preliminary measurements previously referred to as having been rejected, are given in Table II, which gives the date of the experiment, the sample used, the observed temperatures and pressures, and the deviations in mm. of mercury of the observed values from the empirical equations, given in Section IX.

It may be noted from the following table of results that 4 values of the vapor pressure of ammonia may be obtained which are independent of the temperature scale employed. These are at the temperature of (1) the melting point of ice; (2) the freezing point of pure mercury; (3) the triple point of ammonia; and (4) the normal sublimation point of carbon dioxide. The corresponding vapor pressures of ammonia observed at these

<sup>1</sup> Bur. Standards, *Bull.* 6, 363 (1912); *Sci. Paper* 171.

<sup>2</sup> *Ann. Physik*, [4] 40, 653 (1913).

TABLE II.  
Measurements of Vapor Pressure of Ammonia by the Static Method.

Date.	Sample.	Obs. temp. deg.	Pres. obs. by manom- eter mm. mercury.	Deviations from equa- tion mm. mercury.	Date.	Sample	Obs. temp. deg.	Obs. pres. by manom- eter mm. mercury.	Deviations from equa- tion mm. mercury.
June 25, '19	A	-78.44	42.2	-0.6	May 10, '19	B <sub>4</sub>	-25.019	1136.6	+0.4
June 25, '19	A	-78.45	42.8	+0.1	Apr. 15, '19	B <sub>2</sub>	-25.018	1136.3	0.0
July 26, '19	Special	-77.70	44.9	-0.4	Apr. 16, '19	B <sub>2</sub>	-25.005	1137.0	+0.1
June 26, '19	A	-64.50	121.2	0.0	Mar. 15, '19	B <sub>1</sub>	-22.812	1257.3	-0.1
June 25, '19	A	-64.27	122.8	-0.3	Mar. 15, '19	B <sub>1</sub>	-22.782	1259.2	+0.1
Mar. 14, '19	B <sub>1</sub>	-53.036	256.3	+0.9	May 6, '19	B <sub>4</sub>	-20.012	1426.3	+0.2
Nov. 22, '18	A	-51.760	276.6	+0.7	May 7, '19	B <sub>2</sub>	-20.008	1426.9	+0.6
Nov. 30, '18	A	-51.603	278.9	+0.3					
Mar. 15, '19	B <sub>1</sub>	-50.717	294.5	+0.7	Apr. 16, '19	B <sub>2</sub>	-20.005	1426.6	+0.1
Mar. 18, '19	B <sub>3</sub>	-50.717	294.4	+0.6	Apr. 15, '19	B <sub>2</sub>	-20.004	1426.2	-0.4
Mar. 14, '19	B <sub>1</sub>	-48.495	335.2	+0.3	May 2, '19	B <sub>4</sub>	-20.002	1427.3	+0.6
Nov. 30, '18	A	-48.172	341.9	+0.6	May 2, '19	B <sub>4</sub>	-15.046	1769.8	+0.8
Nov. 22, '18	A	-47.781	349.5	+0.4	May 7, '19	B <sub>2</sub>	-15.025	1770.9	+0.3
Nov. 22, '18	A	-47.620	352.3	-0.1	Apr. 16, '19	B <sub>2</sub>	-15.020	1770.9	0.0
Nov. 26, '18	A	-45.946	388.3	+0.5	Apr. 17, '19	B <sub>2</sub>	-15.003	1772.5	+0.3
Nov. 30, '18	A	-44.597	419.0	+0.5	May 6, '19	B <sub>4</sub>	-15.002	1772.6	+0.3
Nov. 22, '18	A	-44.270	426.2	0.0	May 6, '19	B <sub>4</sub>	-10.024	2179.9	+0.6
Nov. 22, '18	A	-44.169	428.6	0.0	May 7, '19	B <sub>2</sub>	-10.020	2179.8	+0.2
Mar. 14, '19	B <sub>1</sub>	-44.059	431.9	+0.7	May 2, '19	B <sub>4</sub>	-10.010	2181.4	+0.9
Mar. 15, '19	B <sub>1</sub>	-44.034	432.4	+0.6	Apr. 16, '19	B <sub>2</sub>	-10.009	2180.7	+0.1
Mar. 18, '19	B <sub>3</sub>	-43.937	434.3	+0.1	Apr. 15, '19	B <sub>2</sub>	-9.999	2180.5	-0.9
Nov. 30, '18	A	-43.423	446.9	+0.1	Apr. 16, '19	B <sub>2</sub>	-5.061	2654.1	-1.1
Nov. 26, '18	A	-42.476	471.2	+0.5	May 3, '19	B <sub>4</sub>	-5.021	2659.8	+0.4
Nov. 22, '18	A	-40.274	530.6	+0.2	Apr. 17, '19	B <sub>2</sub>	-5.016	2659.7	-0.2
Nov. 22, '18	A	-40.240	531.8	+0.5	May 6, '19	B <sub>4</sub>	-5.014	2660.2	+0.1
Mar. 14, '19	B <sub>1</sub>	-38.875	572.0	+0.5	May 7, '19	B <sub>2</sub>	-5.010	2660.3	-0.2
Nov. 30, '18	A	-38.873	571.6	0.0	May 3, '19	B <sub>4</sub>	-5.005	2661.7	+0.7
Dec. 3, '18	A	-38.873	571.3	-0.3	Apr. 17, '19	B <sub>2</sub>	-0.003	3220.7	-0.1
Dec. 3, '18	A	-38.873	571.9	+0.3	Apr. 15, '19	B <sub>2</sub>	0.000	3220.5	-0.3
Dec. 2, '18	A	-38.872	571.7	+0.1	Apr. 16, '19	B <sub>2</sub>	0.000	3220.8	0.0
Nov. 30, '18	A	-38.872	571.8	+0.2	Apr. 17, '19	B <sub>2</sub>	0.000	3220.7	-0.1
Nov. 29, '18	A	-38.872	571.7	+0.1	May 3, '19	B <sub>4</sub>	0.000	3220.4	-0.4
Mar. 18, '19	B <sub>3</sub>	-38.872	571.6	0.0	May 6, '19	B <sub>4</sub>	0.000	3221.2	+0.4
Nov. 29, '18	A	-38.872	571.7	+0.1	May 7, '19	B <sub>4</sub>	0.000	3220.8	0.0
Nov. 29, '18	A	-38.870	571.9	+0.2	May 7, '19	B <sub>4</sub>	0.000	3221.2	+0.4
					May 14, '19	B <sub>4</sub>	+5.022	3871.5	+0.4

Mar. 15, '19	B <sub>1</sub>	-38.867	572.0	+0.2
Nov. 29, '18	A	-38.866	571.7	-0.1
Mar. 15, '19	B <sub>1</sub>	-38.865	572.1	+0.3
Mar. 17, '19	A	-38.861	571.8	-0.1
Nov. 26, '18	A	-37.643	610.2	+0.4
Nov. 30, '18	A	-36.781	637.9	+0.1
Nov. 22, '18	A	-36.667	641.2	-0.4
Nov. 22, '18	A	-36.645	642.5	+0.2
Mar. 28, '19	C <sub>2</sub>	-36.616	643.6	+0.3
Dec. 2, '18	A	-36.605	643.5	-0.2
Nov. 30, '18	A	-35.476	682.5	+0.2
Nov. 26, '18	A	-34.907	702.8	+0.4
Nov. 26, '18	A	-34.119	731.1	+0.1
Nov. 30, '18	A	-33.746	745.1	+0.2
Nov. 23, '18	A	-33.389	758.7	+0.3
May 2, '19	B <sub>4</sub>	-33.369	760.2	+0.1
Apr. 15, '19	B <sub>2</sub>	-33.368	759.3	+0.1
May 5, '19	B <sub>4</sub>	-33.363	760.1	+0.7
Apr. 17, '19	B <sub>2</sub>	-33.362	760.0	+0.5
Mar. 28, '19	C <sub>2</sub>	-33.361	760.1	+0.6
Mar. 28, '19	C <sub>2</sub>	-33.354	760.1	+0.4
Mar. 18, '19	B <sub>3</sub>	-33.314	761.6	+0.3
Nov. 22, '18	A	-33.305	761.2	-0.4
Nov. 22, '18	A	-33.297	761.3	-0.6
Nov. 22, '18	A	-33.283	762.2	-0.3
Mar. 15, '19	B <sub>1</sub>	-33.270	763.4	+0.4
Nov. 30, '18	A	-33.257	763.4	-0.1
Nov. 30, '18	A	-33.250	763.7	0.0
Dec. 3, '18	A	-33.244	763.6	-0.4
Mar. 17, '19	A	-33.243	764.3	+0.3
Mar. 15, '19	B <sub>1</sub>	-33.241	764.5	+0.4
Mar. 14, '19	B <sub>1</sub>	-33.123	768.9	+0.3
Mar. 28, '19	C <sub>2</sub>	-30.451	877.4	-0.2
Apr. 16, '19	B <sub>2</sub>	-30.081	893.3	+0.1
May 2, '19	B <sub>4</sub>	-30.038	895.8	+0.8
May 10, '19	B <sub>4</sub>	-30.011	897.1	+0.9
Apr. 17, '19	B <sub>2</sub>	-30.004	896.9	+0.4
Apr. 16, '19	B <sub>2</sub>	-29.913	900.7	+0.2
Mar. 18, '19	B <sub>3</sub>	-25.059	1134.2	+0.1
Mar. 15, '19	B <sub>1</sub>	-25.050	1134.7	+0.1
May 2, '19	B <sub>4</sub>	-25.035	1136.0	+0.6

May 15, '19	B <sub>4</sub>	5.022	3870.3	-0.8
May 16, '19	B <sub>4</sub> B <sub>2</sub>	4.974	3864.3	-0.1
May 16, '19	B <sub>4</sub> B <sub>2</sub>	9.994	4610.9	-0.3
May 15, '19	B <sub>4</sub>	10.021	4615.4	-0.1
May 14, '19	B <sub>4</sub>	10.035	4618.3	+0.6
May 16, '19	B <sub>4</sub> B <sub>2</sub>	15.008	5463.3	-0.5
May 15, '19	B <sub>4</sub>	15.159	5491.3	0.0
May 15, '19	B <sub>4</sub>	20.018	6432.5	+0.2
May 16, '19	B <sub>4</sub> B <sub>2</sub>	20.020	6432.2	-0.5
May 15, '19	B <sub>4</sub>	25.016	7525.1	+0.8
May 17, '19	B <sub>4</sub> B <sub>2</sub>	25.176	7561.9	+0.4

			Pres. obs. by piston gage, mm. mercury.	
Mar. 22, '19	C <sub>2</sub>	15.120	5485.5	+1.5
Mar. 26, '19	C <sub>2</sub>	19.999	6427.4	-1.0
Mar. 26, '19	C <sub>2</sub>	24.981	7515.1	-1.2
Mar. 26, '19	C <sub>2</sub>	25.081	7538.4	-0.7
May 19, '19	C <sub>1</sub>	29.936	8735.9	+3.5
Apr. 1, '19	C <sub>2</sub>	30.002	8749.8	+0.2
Apr. 1, '19	C <sub>2</sub>	35.058	10137.0	-4.4
May 20, '19	C <sub>1</sub>	35.022	10133.3	+2.5
May 23, '19	C <sub>1</sub>	39.928	11637.8	+3.0
May 23, '19	C <sub>1</sub>	39.928	11636.6	+1.8
May 20, '19	C <sub>1</sub>	39.995	11661.5	+5.0
Mar. 31, '19	C <sub>2</sub>	44.919	13332.7	+0.5
Apr. 2, '19	C <sub>2</sub>	44.965	13348.7	0.0
May 20, '19	C <sub>1</sub>	45.071	13388.9	+2.3
May 23, '19	C <sub>1</sub>	50.036	15262.3	+2.6
Mar. 31, '19	C <sub>2</sub>	50.083	15274.1	-4.2
May 20, '19	C <sub>1</sub>	50.117	15293.0	+1.2
May 24, '19	C <sub>1</sub>	55.004	17327.0	+2.1
May 27, '19	C <sub>1</sub>	60.057	19632.1	-1.5
May 27, '19	C <sub>1</sub>	60.062	19635.6	-0.4
May 27, '19	C <sub>1</sub>	60.062	19639.1	+3.1
May 27, '19	C <sub>1</sub>	60.060	19632.4	-2.7
May 27, '19	C <sub>1</sub>	60.066	19638.1	+0.2
May 27, '19	C <sub>1</sub>	65.051	22136.7	+1.6
May 27, '19	C <sub>1</sub>	65.059	22139.6	+0.3
May 27, '19	C <sub>1</sub>	65.063	22140.1	-1.2
May 28, '19	C <sub>1</sub>	70.011	24843.5	-4.6
May 28, '19	C <sub>1</sub>	70.011	24842.6	-5.5

temperatures are (1) 3220.8 mm., the mean of 7 experiments; (2) 571.8 mm., the mean of 14 experiments in which the bulb containing ammonia was immersed in freezing mercury; (3) 44.9 mm., the mean of 2 experiments with the 3 phases solid, liquid, and vapor present; and (4) 42.2 mm., the mean of 2 experiments with sub-cooled liquid ammonia.

The mean of the seventeen observations taken within  $0.1^\circ$  of the normal boiling point of ammonia with 6 different samples and corrected to 760 mm. pressure gives the value  $-33.354^\circ$ .

### VII. Determination of the Normal Boiling Point by the Dynamic Method.

In order to check the measurements of the normal boiling point of ammonia by the static method, a direct determination was undertaken by the dynamic method, analogous to the ordinary method of measuring steam points.

The apparatus used consisted of 2 concentric tubes of pyrex glass cemented together to form a double-walled vessel as shown in Fig. 6.

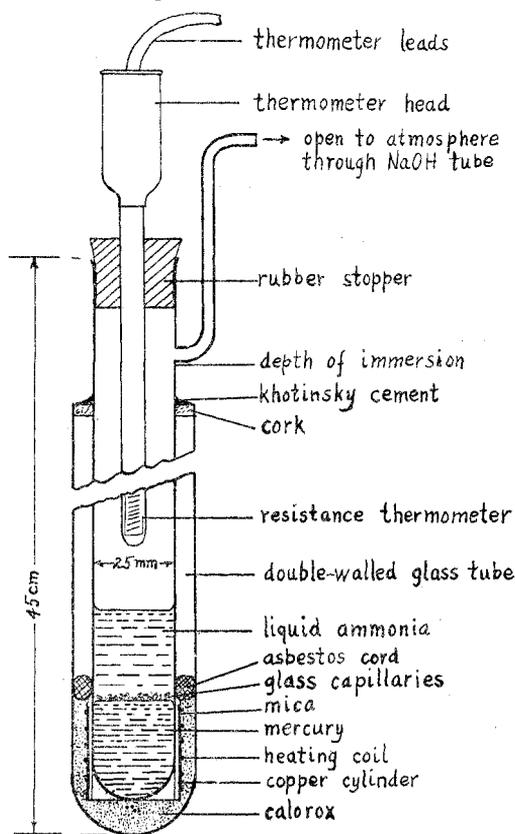


Fig. 6.—Boiling point apparatus.

About 20 cc. of pure mercury and a large number of small glass capillaries were placed in the bottom of the inner tube to promote uniform boiling. A rubber stopper in the open end served to hold the platinum resistance thermometer in place and allowed it to be moved up and down. After a thorough cleaning the apparatus was placed in a thermoregulated bath, evacuated and cooled below the normal boiling point of ammonia. Commercial ammonia of high purity contained in a small cylinder was then distilled into the apparatus through sodium hydroxide in a drying tube. Chemical tests made upon this commercial sample indicated less than 0.01% of solid impurities (residue on evaporation) 0.01% volatile carbon compounds and 0.03% of water.

TABLE III.

Determination of the Normal Boiling Point by the Dynamic Method.

Date.	Bath. temp. degrees.	Heating current. Amp.	Height of therm. above liquid in cm.	Depth of liquid in cm.	Bar. Rdg. reduced to 0° & sp. gr.	Temps. obs.	Normal boiling point.
Aug. 15, '19. ....	-48	1.0	10	5	749.87	-33.589	-33.322(a)
	-48	1.0	10	5	749.87	-33.602	-33.335(a)
	-48	1.0	10	5	749.82	-33.612	-33.343(a)
	-48	1.0	10	5	749.82	-33.615	-33.346(a)
Aug. 19, '19. ....	-40	1.0	7	4	750.65	-33.593	-33.346
	-40	1.0	3	4	750.60	-33.594	-33.345
	-40	1.0	11	4	750.55	-33.594	-33.344
	-40	1.0	15	4	750.50	-33.594	-33.343
	-40	1.0	2	9	750.27	-33.583	-33.327
	-40	1.0	10	9	750.27	-33.583	-33.327
	-40	1.0	(therm. immersed)		750.20	-33.541	-33.283(b)
	-40	1.0	5	9	750.14	-33.595	-33.335
	-38	0.9	5	9	750.08	-33.614	-33.352
	-38	0.9	10	9	750.08	-33.612	-33.350
	-42	1.1	10	9	750.08	-33.610	-33.348
	-42	1.1	10	9	750.08	-33.611	-33.349
	-49	1.1	10	9	750.39	-33.592	-33.339
-49	1.1	5	9	750.39	-33.594	-33.341	

Mean = -33.341

(a) Very irregular boiling—observations taken without the addition of mercury.

(b) Not included in mean.

The results of observations which were taken under various experimental conditions, are shown in Table III. The thermometer was placed at different heights above the boiling liquid as the test of a sufficiently high condensation line to produce uniform temperature. In one instance the bulb of the resistance thermometer was completely immersed in the boiling liquid and a rise in temperature of about  $0.05^\circ$  was observed. The mean of 17 observations corrected to temperatures corresponding to 760 mm. pressure gives the value  $-33.341^\circ$  for the normal boiling point.

## VIII. Form of Empirical Equations.

Numerous empirical equations of widely different forms have been proposed in the past century to represent vapor pressures as a function of temperature. Attempts have been made to establish this functional relationship upon a semi-rational basis by introducing approximations into the Clapeyron equation and then integrating. The Rankine-Dupré formula

$$\log p = A + B/\theta + C \log \theta$$

was deduced in this manner and found to represent the experimental re-

sults for a large number of substances with a fair degree of approximation. Similarly Nernst deduced an equation of the form

$$\log p = A + B/\theta + C \log \theta + D\theta$$

which represents very accurately pressure measurements within a limited region, particularly in the region below the normal boiling point. Quite recently Brunelli<sup>1</sup> has gone one step farther and proposed an empirical equation of the form

$$\log p = A + B/\theta + C \log \theta + D\theta + E\theta^2. \quad (1)$$

He has evaluated the constants in this equation for water and compared the calculated values of vapor pressure with those determined by experiment which are more accurately known perhaps than for any other substance. The agreement throughout the range from 0° to the critical temperature is remarkably good. A similar empirical equation of the form

$$\log p = A + B/\theta + C\theta + D\theta^2 + E\theta^3 \quad (2)$$

has been used by Keyes and Brownlee to represent their experimental results on ammonia.

Equations of the form (1) and (2) were found to represent very closely the results of the present experimental work and also Cardoso and Giltay's<sup>2</sup> determination of the critical data. An equation of the form

$$\log p = A + B/\theta + C/\theta^2 + D/\theta^3$$

was tried but did not represent the data satisfactorily.

### IX. Discussion of Results.

The results of the measurements may be expressed equally well by means of either of the following empirical equations:

$$\log_{10} p = 30.256818 - \frac{1914.9569}{\theta} - 8.4598324 \log_{10} \theta + 2.39309 \times 10^{-3} \theta + 2.955214 \times 10^{-6} \theta^2$$

and

$$\log_{10} p = 12.465400 - \frac{1648.6068}{\theta} - 0.01638646 \theta + 2.403276 \times 10^{-5} \theta^2 - 1.168708 \times 10^{-8} \theta^3$$

which were made to agree with Cardoso and Giltay's critical data,  $p_c = 85348$  mm. and  $\theta_c = 132.9^\circ$ . In these equations  $p$  and  $\theta$  are expressed in mm. of mercury and degrees absolute, respectively ( $^\circ$  abs. =  $^\circ$  C. + 273.1).

The deviations of the individual measurements in mm. of mercury from values computed by these equations are shown in Table II. In the 122 measurements made with the single manometers and the open

<sup>1</sup> *Nuovo Cimento*, 14, 57 (1917).

<sup>2</sup> *Arch. sci. phys. nat. Genève*, 34, 20 (1912).

mercury manometer in the interval from  $-78^{\circ}$  to  $+25^{\circ}$ , inclusive, the maximum deviation is 1.1 mm. and the average deviation is 0.3 mm., which is within the limit of error of actual pressure observation. In the 28 measurements made in the interval  $+15^{\circ}$  to  $+70^{\circ}$ , inclusive, with the piston gage, the maximum deviation is 5.5 mm., at the highest temperature, and the average deviation is 2.1 mm. or on the average about 2 parts in 10,000 in the pressure. This agreement is very satisfactory when consideration is given to the precision of the piston gage and also to the effect of temperature on the pressure, for example, an error of  $0.01^{\circ}$  in the temperature is equivalent in this range to from 2 to 6 mm. in the pressure.

The majority of the measurements except those below the normal boiling point were purposely taken at approximately  $5^{\circ}$  intervals, within  $0.1^{\circ}$ . The rate of change of vapor pressure with temperatures computed from the above equations was used to correct the individual measurements to the integral degrees. The means of these corrected measurements are given in Table IV and compared with the calculated values. The deviations, expressed in degrees C. indicate the good agreement between observed and calculated values.

TABLE IV.

Deviations of Mean Observed Pressures from Authors Equations in Degrees.

$t$	No. of obs.	Mean $p_{\text{calc.}}$	$t_{\text{calc.}}$	$t-t_{\text{calc.}}$ in $0.001^{\circ}$	$t$	No. of obs.	Mean $p_{\text{calc.}}$	$t_{\text{calc.}}$	$t-t_{\text{calc.}}$ in $0.001^{\circ}$
-78.0	3	44.00	-78.076	+76	+ 5	3	3867.9	+ 4.999	+ 1
-64.0	2	125.29	-64.016	+16	10	3	4612.1	10.000	0
-51.0	4	289.43	-50.966	-34	15	3	5462.6	14.999	+ 1
-48.0	4	345.03	-47.983	-17	20	3	6428.2	19.998	+ 2
-44.0	7	432.98	-43.987	-13	25	4	7520.5	25.000	0
-40.0	2	538.58	-39.990	-10	30	2	8750.9	30.007	- 7
-38.870	14	571.77	-38.867	- 3	35	2	10123.5	35.003	+ 3
-33.354	17	760.00	-33.347	- 7	40	3	11661.4	40.010	-10
-30.0	6	897.2	-29.989	-11	45	3	13362.3	45.003	- 3
-25.0	6	1137.4	-24.995	- 5	50	3	15245.4	50.000	0
-20.0	5	1427.0	-19.997	- 3	55	1	17325.3	55.005	- 5
-15.0	5	1772.8	-14.995	- 5	60	5	19606.1	59.999	+ 1
-10.0	5	2181.6	- 9.998	- 2	65	3	22108.5	65.000	0
- 5.0	6	2661.5	- 5.000	0	70	2	24836.8	69.991	+ 9
0	8	3220.8	0.000	0					

The remarkable reproducibility of the observed pressures at the normal boiling point and at the ice point ( $0^{\circ}$ ) on different days and with various samples seems to preclude the possibility of any systematic error due to the sample, which was not obscured by errors of measurement or, in other words, that the material was of a high degree of purity. The agreement between the pressures observed by means of the open mercury manometer and the piston gage in the interval within which they overlap

indicates that no appreciable systematic error resulted from the use of the latter. Additional confirmation of this is furnished in the careful calibration of the piston gage against the open mercury manometer.

The slope of the vapor-pressure temperature curve for ammonia is expressed equally well by the differentiation of either of the above equations as follows:

$$\frac{dp}{d\theta} = 2.30258 \frac{p}{\theta} \left( \frac{1914.9569}{\theta} - 8.4598324 \log_{10} e - 2.39309 \times 10^{-3} \theta + 5.910428 \times 10^{-6} \theta^2 \right)$$

and

$$\frac{dp}{d\theta} = 2.30258 \frac{p}{\theta} \left( \frac{1648.6068}{\theta} - 0.01638646 \theta + 4.806552 \times 10^{-5} \theta^2 - 3.506124 \times 10^{-8} \theta^3 \right)$$

where  $dp/d\theta$  and  $p$  are in mm. of mercury and  $\theta$  in degrees absolute, ( $^{\circ}\text{abs.} = ^{\circ}\text{C.} + 273.1$ ).

The estimated errors in the values of  $dp/d\theta$  thus obtained are, from consideration of Table IV, about one part in 200 in the range  $-80^{\circ}$  to  $-50^{\circ}$ , one part in 500 in the range  $-50^{\circ}$  to  $-30^{\circ}$  and one part in 1000 in the range  $-30^{\circ}$  to  $+70^{\circ}$ .

The results of the measurements of the normal boiling point by the static method, which give a mean value of  $-33.354^{\circ}$ , are in fair agreement with the measurements by the dynamic method whose mean is  $-33.341^{\circ}$ . The normal boiling point of ammonia is, therefore, taken as  $-33.35^{\circ}$ .

The present work has been carried out with very pure samples of ammonia. The question immediately arises in the practical application of the results as to how much the results would be affected by the impurities commonly found in commercial samples. The normal boiling point found by the dynamic method, in which the temperature of the condensing vapor is measured, would be very little affected by these impurities while a satisfactory determination by the static method with commercial samples is practically impossible. This illustrates the fact that the results obtained in measurements with impure materials may depend more upon the method chosen than upon the purity and that refined physical measurements should be attempted only with the purest materials. The impurities present in commercial materials may prevent the engineers being able to utilize fully the accuracy of the physical data, yet the data for pure material are at least as likely to be representative of a given commercial sample as data on impure material. As shown in the normal boiling point determinations, the properties of commercial samples under proper conditions may differ very slightly from those of a pure material.

In conclusion, the authors wish to acknowledge their indebtedness to Dr. C. W. Waidner, E. F. Mueller and E. C. McKelvy, of this Bureau, for many valuable suggestions during the progress of this investigation.

### X. Summary.

A detailed description is given of the apparatus and method employed in the present measurements throughout the temperature interval  $-78^{\circ}$  to  $+70^{\circ}$ .

Seven samples of thoroughly purified ammonia were used. Special tests showed less than one part in 100,000 by volume of non-condensing gases present, and less than 0.01% by weight of other impurities. The methods of purification and filling of manometers are briefly described.

The phenomenon of hysteresis was observed near the normal boiling point of ammonia with a commercial sample containing a small amount of air, which indicated the necessity of very complete removal of dissolved gases for any accurate measurements of vapor pressure by the static method. Lags in coming to equilibrium were encountered and studied in order to determine the most advantageous procedure in establishing equilibrium.

The normal boiling point of ammonia was determined by the static and also the dynamic method, the mean of the results by the two methods being  $-33.35^{\circ}$ .

Two empirical equations were found to represent closely the results in the temperature range covered experimentally and also the latest determination of the critical data for ammonia. The results of 122 measurements in the interval  $-78^{\circ}$  to  $+25^{\circ}$  made with direct observations of mercury columns agree with the empirical equations within one mm. of mercury. The results of 28 measurements in the interval  $+15^{\circ}$  to  $+70^{\circ}$  made with an accurately calibrated piston gage agree with the empirical equations within about 3 mm. of mercury.

As a final result the vapor pressure of ammonia is expressed in the range  $-80^{\circ}$  to  $+70^{\circ}$  by either of the following equations:

$$\log_{10} p = 30.256818 - \frac{1914.9569}{\theta} - 8.4598324 \log_{10} \theta + 2.39309 \times 10^{-3} \theta + 2.955214 \times 10^{-8} \theta^2.$$

$$\log_{10} p = 12.465400 - \frac{1648.6068}{\theta} - 0.01638646 \theta + 2.403276 \times 10^{-5} \theta^2 - 1.168708 \times 10^{-8} \theta^3.$$

where  $p$  is expressed in mm. of mercury and  $\theta$  in degrees absolute, ( $^{\circ}$  abs. =  $^{\circ}$  C. + 273.1). The slope of the vapor pressure-temperature curve is obtained by differentiation of either of the above equations.

## APPENDIX I.

Degrees C.	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Vapor Pressure of Ammonia (mm. Mercury at 0° and g = 980.665).										
-80	37.6									
-70	81.9	76.1	70.6	65.5	60.6	56.1	51.9	48.0	44.3	40.8
-60	164.2	153.7	143.7	134.3	125.4	117.1	109.2	101.8	94.7	88.1
-50	306.6	288.8	272.0	255.9	240.7	226.2	212.5	199.4	187.0	175.3
-40	538.3	510.1	483.1	457.3	432.7	409.1	386.6	365.2	344.7	325.2
-30	896.7	853.9	812.8	773.3	735.4	699.0	664.1	630.6	598.5	567.8
-20	1426.8	1364.6	1304.6	1246.8	1191.0	1137.2	1085.3	1035.4	987.4	941.2
-10	2181.4	2094.2	2009.7	1928.0	1848.9	1772.4	1698.5	1627.0	1557.9	1491.2
0	3221.0	3102.2	2987.0	2875.2	2766.7	2661.5	2559.4	2460.4	2364.5	2271.5
+ 0	3221.0	3343.0	3468.5	3598.0	3731.0	3868.0	4009.0	4153.5	4302.5	4455.0
10	4612.0	4773.5	4939.0	5109.0	5283.5	5462.5	5646.0	5834.5	6027.5	6225.5
20	6428.5	6636.5	6849.5	7068.0	7291.5	7520.5	7755.0	7995.0	8240.5	8492.0
30	8749.0	9012.0	9281.0	9556.0	9837.0	10124.0	10418.0	10718.0	11025.0	11338.0
40	11658.0	11985.0	12318.0	12659.0	13006.0	13361.0	13723.0	14092.0	14469.0	14853.0
50	15245.0	15645.0	16052.0	16467.0	16891.0	17323.0	17763.0	18211.0	18667.0	19132.0
60	19606.0	20089.0	20580.0	21080.0	21589.0	22108.0	22636.0	23173.0	23720.0	24276.0
70	24842.0									

## Atmospheres (1 atmos. = 760 mm. Mercury).

-80	0.0495									
-70	0.1078	0.1001	0.0929	0.0861	0.0797	0.0738	0.0683	0.0631	0.0582	0.0537
-60	0.2161	0.2022	0.1891	0.1767	0.1651	0.1541	0.1437	0.1339	0.1246	0.1159
-50	0.4034	0.3800	0.3578	0.3367	0.3167	0.2977	0.2796	0.2624	0.2461	0.2307
-40	0.7083	0.6712	0.6357	0.6017	0.5693	0.5383	0.5087	0.4805	0.4536	0.4279
-30	1.1799	1.1236	1.0695	1.0175	0.9676	0.9197	0.8738	0.8297	0.7875	0.7471
-20	1.8774	1.7956	1.7166	1.6405	1.5671	1.4963	1.4281	1.3624	1.2992	1.2384
-10	2.8703	2.7555	2.6443	2.5368	2.4328	2.3322	2.2349	2.1408	2.0499	1.9621
0	4.2380	4.0818	3.9303	3.7832	3.6405	3.5020	3.3677	3.2375	3.1112	2.9888
+ 0	4.2380	4.3985	4.5640	4.7340	4.9090	5.0895	5.2750	5.4655	5.6610	5.8620
10	6.0685	6.2805	6.4985	6.7225	6.9520	7.1875	7.4290	7.6770	7.9310	8.1915
20	8.4585	8.7320	9.0125	9.3000	9.5940	9.8955	10.2040	10.5195	10.8430	11.1735
30	11.512	11.858	12.212	12.574	12.943	13.321	13.708	14.103	14.507	14.919
40	15.339	15.770	16.209	16.656	17.113	17.580	18.056	18.542	19.038	19.543
50	20.059	20.585	21.121	21.667	22.224	22.793	23.372	23.962	24.562	25.174
60	25.797	26.432	27.079	27.737	28.407	29.089	29.784	30.491	31.211	31.942
70	32.687									

## APPENDIX II.

Rate of Change of Vapor Pressure with Temperature ( $dp/d\theta$ ) mm. Mercury per Degree.

Degrees C.	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
-80	3.08	..	..	..	..	..	..	..	..	..
-70	6.02	5.66	5.31	4.98	4.66	4.36	4.08	3.81	3.55	3.31
-60	10.81	10.23	9.67	9.14	8.63	8.14	7.67	7.22	6.80	6.40
-50	18.15	17.28	16.44	15.63	14.85	14.10	13.38	12.70	12.05	11.42
-40	28.82	27.58	26.38	25.22	24.10	23.02	21.98	20.97	20.00	19.06
-30	43.61	41.92	40.28	38.69	37.15	35.65	34.20	32.79	31.42	30.10
-20	63.29	61.08	58.93	56.83	54.78	52.78	50.84	48.95	47.12	45.34
-10	88.64	85.83	83.08	80.40	77.78	75.21	72.70	70.26	67.88	65.56
0	120.35	116.90	113.49	110.14	106.86	103.66	100.53	97.46	94.45	91.51

## APPENDIX II (continued).

Degrees C.	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
+ 0	120.35	123.90	127.55	131.25	135.00	138.80	142.70	146.70	150.75	154.90
10	159.10	163.40	167.75	172.20	176.70	181.30	186.00	190.75	195.45	200.50
20	205.50	210.55	215.70	220.95	226.30	231.70	237.20	242.80	248.50	254.25
30	260.1	266.0	272.0	278.1	284.3	290.6	297.0	303.5	310.0	316.6
40	323.3	330.1	337.0	344.0	351.1	358.3	365.6	373.0	380.5	388.1
50	395.8	403.6	411.4	419.4	427.5	435.7	444.0	452.3	460.8	469.4
60	478.1	486.9	495.8	504.8	513.9	523.1	532.4	541.8	551.3	561.0
70	570.8	..	..	..	..	..	..	..	..	..

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

REPRODUCIBLE LIQUID JUNCTION POTENTIALS: THE FLOWING JUNCTION.<sup>1</sup>

BY ARTHUR B. LAMB AND ALFRED T. LARSON.

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The potentials of liquid junctions in voltaic cells are sources of perplexity in measurements of the electromotive force of cells and of the single potentials of electrodes, not only because they evade direct observation, complete elimination, or a rigorous calculation, but because they are also a frequent source of considerable experimental uncertainty. It has been particularly difficult to secure reproducible liquid junction potentials when the ions on the two sides of the junction have marked differences in mobility. Uncertainties in such junctions frequently amount to several millivolts.<sup>2</sup>

We have recently been engaged upon a study of the Thomson effect in electrolytes, which involved the precise measurement of the electromotive force of cells containing 2 or more liquid junctions. This has led us to a study of the reproducibility of such junction potentials and ultimately to the development of a type of junction, which, even under unfavorable conditions, that is, with ions of marked differences in mobility, gives electromotive forces reproducible to 0.01 of a millivolt.

In this study we followed 2 procedures: first, we constructed cells similar to those of Chanoz<sup>3</sup> containing 2 identical but oppositely directed liquid junctions, and 2 identical electrodes, for example:



Such a cell should give a constant zero potential. If it does not, and the

<sup>1</sup> This investigation was completed in December, 1915; an account of it was presented before the Harvard-Technology Physical-Chemical Club in February, 1916.

<sup>2</sup> Chanoz, *Ann. Univ. Lyon*, Nouv. Ser., 1, 1906, 18; Cumming, *Trans. Faraday Soc.*, 9, 174 (1913); Lewis, Brighton and Sebastian, *THIS JOURNAL*, 39, 2253 (1917).

<sup>3</sup> *Loc. cit.*