Salts of the heavy metals in solution in liquid ammonia react with the soluble amides of the alkali metals to form amides, imides or nitrides of the former in a manner analogous to the formation of insoluble hydroxides and oxides in aqueous solutions.

Certain metallic salts undergo ammonolysis in liquid ammonia in a manner analogous to hydrolytic decomposition in water.

Many metallic salts, when in excess, react with soluble metallic amides to give ammono-basic salts after the manner of the formation of ordinary basic salts in water solutions.

The insoluble metallic amides, imides, and nitrides, as well as the ammono-basic salts, dissolve in liquid ammonia solutions of ammonium salts in a manner analogous to the solution of the corresponding oxygen compounds in aqueous acids.

Certain ammono-bases dissolve in excess of potassium amide solution in a manner analogous to the solution of certain metallic hydroxides in aqueous potassium hydroxide.

The following compounds have been prepared from liquid ammonia solutions:

Silver amide, $AgNH_2$.
Mercuric nitride, Hg_3N_2.
Ammono-basic mercuric iodide, Hg_2NI.
Ammono-basic mercuric bromide, Hg_2NBr.
Ammono-basic mercuric chloride, $HgNH_2Cl$.
Lead imide, $PbNH$.
Ammono-basic lead iodide, $Pb_2NI.NH_3$.
Bismuth nitride, BiN.

STANFORD UNIVERSITY, CALIFORNIA,
April, 1905.

THE BOILING-POINTS OF AMMONIA, METHYL AMINE, METHYL CHLORIDE AND SULPHUR DIOXIDE.

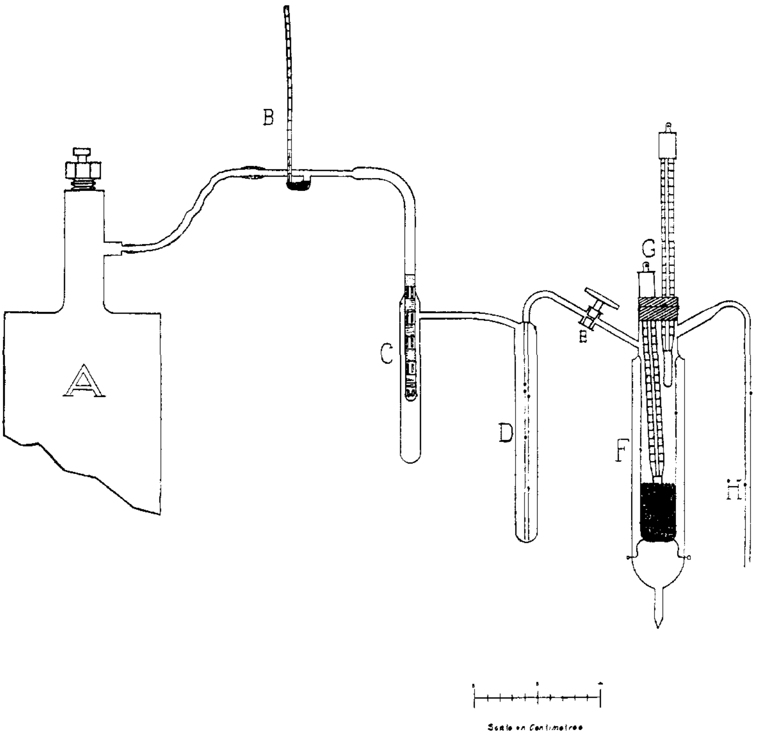
BY H. D. GIBBS.

Received May 1, 1905.

THE VALUES given in the literature for the boiling-points of a number of low-boiling liquids have been determined almost exclusively by means of measurements of the vapor-pressures, and as there is a great lack of agreement in the various results, the writer has undertaken a criticism and revision of the earlier work and a direct determination of the boiling-points. Improved methods for purifying the liquids, thermometers which have been compared with the normal thermometer of the Reichsanstalt, and a specially designed apparatus have been employed for the determinations.

Work which is being carried on in this laboratory makes the determination of the boiling-points of ammonia and methyl amine desirable, and as the apparatus was applicable for the determination of the values for methyl chloride and sulphur dioxide, their boiling-points lying in the same neighborhood and their literature showing the same lack of agreement, the work was extended to include them also.

THE APPARATUS.



The liquids (ammonia, methyl amine, methyl chloride and sulphur dioxide) contained in steel or glass cylinders, *A*, are distilled into the tube *D*, and there condensed by a surrounding cooling-mixture, either ice-water or liquid ammonia, contained in a Dewar test-tube. During the process of distillation the gases are freed from any dust or material dissolved in the liquid, which might be carried along mechanically, by the filter *C*. This filter is composed of layers of carefully prepared asbestos fiber, separated to avoid too close packing, by bundles of fine glass rods or tubes. The asbestos layers are, however, so dense that the gases penetrate slowly and condense slowly and regularly in the tube *D*. The gas pressure during the distillation is indicated by the manometer *B*. The efficiency of this device was shown by the discoloration of the upper layer of asbestos fiber. The discoloration rarely extended to the second layer.

During the operation of filling the receptacle *D* the stop-cock *E* must be closed to retain the liquid. This stop-cock was carefully ground and no difficulty was experienced in holding liquid ammonia when the pressure, as shown by the manometer, was in the neighborhood of eight atmospheres. The vessel *F*, in which the liquids are boiled for the purpose of measuring their temperatures of ebullition, consists of an inner and outer tube sealed together, the space between being exhausted of air to provide a vacuum jacket for the inner tube. On opening the stop-cock *E* the tube *D* is emptied of its liquid contents into the boling tube *F*. That portion of the liquid which is vaporized in cooling *F* and during the boiling passes out through the tube *H*, at which point it is condensed in order to prevent loss of the liquid and contamination of the atmosphere of the room by introducing the tube *H* into a glass cylinder which is cooled by liquid ammonia or carbon dioxide in ether, contained in a Dewar test-tube of suitable size.

The liquid is made to boil in *F* by passing an electric current from a 110-volt alternating circuit through the platinum wires sealed into the bottom of the tube through the vacuum jacket. The bubbles of the boiling liquid are broken up by a deep layer of garnets. Thermometers, *G*, pass through a cork or rubber stopper which closes the inner tube tightly. All joints in the apparatus are made by sealing the glass tubes together, except where the steel cylinder is connected to the glass, at which point small lead tubing is used joined to the glass by sealing-wax.

During the boiling of the liquid the tube *F* is surrounded by a large empty Dewar test-tube to further provide against changes of temperature by absorption of heat from the outside. No difficulty is experienced in reading the thermometers through the four thicknesses of glass. A rather long focus lens is employed for this purpose.

The capacity of the inner tube of *F* is 8 cc. to cover the garnets, 66 cc. to the top of the vacuum-jacketed portion and 75 cc. to the opening of the outlet tube. With the thermometer in place the corresponding capacities are 8 cc., 61 cc. and 68 cc.

THE THERMOMETERS.

Four different thermometers were used in the various determinations: No. 21713 is a toluene thermometer graduated in fifths of a degree from —20° to —50° in a space of 10 cm. The total length of the thermometer is 20 cm. According to the certificate of the Reichsanstalt it requires no correction.

Number 21714 is a duplicate of the former, but according to the Reichsanstalt certificate accompanying it the readings of the thermometer at

$$\left.\begin{array}{r}-25^\circ\\-35^\circ\\-45^\circ\end{array}\right\}\text{ are }\left\{\begin{array}{l}0.1\\0.4\\0.3\end{array}\right\}\text{ degree too high.}$$

These thermometers are calibrated to the nearest tenth of a degree.

Number 3972 is a mercury thermometer graduated in half-degrees from —8° to +100° in a space of 25 cm. The total length of the thermometer is 34 cm. According to the accompanying certificate of the Reichsanstalt it requires no correction below 25° to the nearest tenth of a degree.

The fourth thermometer has not been standardized by the Reichsanstalt, but was corrected by careful comparison with the three above mentioned. It is a mercury thermometer, graduated in half-degrees from —42° to +54° in a space of 22 cm. The total length of the thermometer is 31 cm.

It was found to require the following corrections:

$$\left.\begin{array}{r}-6.3^\circ\\-24.2^\circ\\-33.6^\circ\end{array}\right\}\quad\left\{\begin{array}{l}0.4\\0.0\\0.0\end{array}\right\}\text{ too high.}$$

AMMONIA.

Review of the Literature.—Guyton[1] (1799) obtained liquid ammonia from a gas which he found to condense at a temperature of

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[1] *Ann. de Chim.*, **29**, 290.

—48.75°. His method of purification was very imperfect and an accurate determination of the boiling-point was not made.

R. Bunsen,[1] in 1839, from his determinations of the vapor-pressures of liquid ammonia at varying temperatures, calculates the boiling-point to be —33.7°, the barometer corrected to 0° and 749.3 mm. pressure. It is evident that he had very pure ammonia for reasons which will be mentioned later.

Michael Faraday's[2] (1844) determinations of the vapor-pressures at temperatures ranging from 0° to 85° F. place the boiling-point near —40° C. at one atmosphere pressure.

A. Loir and Ch. Drion,[3] in 1860, found that the temperature of liquid ammonia at ebullition at atmospheric pressure is —35.7°.

Regnault,[4] in 1860, and two years later with improved apparatus, determined the vapor-pressures at varying temperatures and from these measurements calculated the boiling-point to be —32.6° at 760 mm. pressure. To check this result a determination was also made with an alcohol thermometer immersed in ammonia contained in an open vessel, and as a result of this experiment the boiling-point is stated as —38.5° at 752 mm. pressure.

Raoul Pictet,[5] in 1885, determined the vapor-pressures of liquid ammonia between —30° and 50°.

He states that the boiling-point is very low, namely —33°.

Blümke,[6] in 1888, also made a parallel series of determinations.

M. W. Travers[7] (1901), in commenting upon the determinations of Pictet and Blümke, says that the results of Pictet when plotted by the method of Ramsay and Young[8] give a fairly straight line.

"The smoothed results place the boiling-point at 760 mm. at 236° absolute (—37° C.). The results obtained by Blümke appear to be less reliable."

On the next page Travers gives the boiling-point of liquid ammonia as 234.5° absolute (—38.5° C.).

A. Joannis[9] (1892), in his investigations of the properties of

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[1] *Pogg. Ann.*, **46**, 97 (1839).

[2] *Ann. chim. phys.* [3], **15**, 257 (1845); *Phil. Trans.*, **135**, 155 (1845).

[3] *Bull. Soc. Chim.* [Paris], 1860, p. 184.

[4] *Compt. Rend.*, **50**, 1072; *Jahresb.*, 1860, p. 40; *Ibid.*, 1863, p. 66; *Mem. de l'acad. des Sc. Inst. d. France*, **26**, 535 (1862).

[5] Nouvelles machines frigorique Genève, 1885; Arch. de Geneve, 1887; *Wied. Beibl.*, **11**, 629 (1887); *Arch. de Sc. Phys. et Nat.* [3], **13**, 212 (1885).

[6] *Wied. Ann.*, **34**, 10, 1888; *Jahresb.*, 1888, p. 152.

[7] "Study of Gases," p. 246.

[8] *Phil. Mag.*, **21**, 33 (1886).

[9] *Compt. Rend.*, **115**, 820 (1892).

some liquid ammonia solutions, states that the boiling-point is —38.2° at 764 mm. pressure.

Other statements concerning the boiling-point which cannot be traced to their sources are Dickerson,[1] —33°; Lange,[2] —33.7°, probably a copy of Bunsen's figures, and —33.5°.[3]

The statements in all of the text-books and larger work on chemistry, concerning the boiling-point of liquid ammonia, vary from the figures obtained by Bunsen, —33.7° at 749.3 mm., to those of Faraday, —40° at one atmosphere.

Criticisms of Some of the Earlier Methods and Results.—The vapor-pressure method for the determination of the boiling-points of liquids requires carefully purified material if results at all accurate are to be obtained. The presence of very small quantities of air, or other constituents which are more volatile than the liquid, greatly increases the vapor-pressure, while non-volatile impurities produce an opposite, but far less conspicuous effect. The high vapor-pressures, and consequently low boiling-points, as determined by Faraday, Pictet and Blümke are accounted for if one is permitted to assume the presence of air or other gases in their ammonia. From these considerations it appears that Bunsen had a very pure sample of ammonia.

Observations have shown that liquid ammonia exposed to the air in an open vessel is almost certain to cool below the boiling-point, even if vigorously stirred, the supercooling readily going far enough to solidify mercury. The low results of Regnault are thus accounted for.

Purification of the Ammonia.—Sodium dissolves in liquid ammonia to form the well-known blue solution. On long standing, or quickly under the influence of platinum sponge or ferric oxide[4] there is generated from this blue solution, hydrogen and sodamide according to the equation

$$NH_3 + Na = NaNH_2 + H.$$

Any moisture which may be in the liquid ammonia is converted by the sodium into hydrogen and sodium hydroxide or by the sodium amide into ammonia and sodium hydroxide. The latter reaction is represented by the equation

$$NaNH_2 + H_2O = NaOH + NH_3.$$

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[1] "Liquid Air," by T. O'Connor Sloane, Ed., London, 1900.

[2] "Verflüsigtes Ammoniak als Lösungsmittel," by J. Bronn, p. 9.

[3] "Chemiker-Kalendar," 1905, p. 17.

[4] Franklin, This Journal, **27**, 820.

These reactions are made use of in drying the liquid ammonia.

Into a steel cylinder of about two liters capacity, a quantity of freshly cut sodium is placed, the screw caps are put in place and commercial liquid ammonia is siphoned in. The cylinder stood in this condition for several weeks before using. It is connected to the glass portion of the apparatus by means of small lead tubing and sealing-wax, as shown in the figure, and the ammonia is then ready to be distilled out of the steel cylinder through the filter *C* and condensed in the receptacle *D*.

The Boiling-Point Determination.—The toluene thermometers (Nos. 21713 and 21714) were put in place through a rubber stopper which was found to be practically not affected by the ammonia. First one thermometer was passed as far as possible through one hole in the stopper and into the garnets, the other thermometer being inserted only far enough to close the other hole. During the boiling of the liquid the positions of the thermometers were interchanged. Liquid ammonia was run into *F* until the inner tube was filled to the outlet tube which placed the entire toluene thread of the thermometer in the liquid. The current from an alternating incandescent circuit was passed through the platinum spiral, the regulating being done by means of lamp resistance.

The resistance of the spiral is 1.1 ohms. The energy consumed in boiling the liquid was from 18 to 40 watts. The higher energy expenditure boiled the liquid violently.

The thermometer was placed in position in the liquid and allowed to stand sometimes as long as an hour, then the current was turned on and the boiling continued until the thermometer became constant, which usually required only four or five minutes. Readings of the barometer and thermometer were then taken at intervals of about three minutes until it was evident that there was no variation. In some cases the boiling was continued for twenty-five minutes. The loss of liquid during this time was from 25 per cent. to 50 per cent. of the total, depending upon the rate of ebullition.

The relative positions of the thermometers were then changed and more liquid passed in to make up the loss by evaporation and the determination repeated.

The apparatus was then disconnected from the steel cylinder, the garnets removed and thoroughly cleaned, the tube *F* thoroughly cleaned and dried, the thermometers put in place and dry air drawn through the entire apparatus for at least three hours when the apparatus was ready for the next determination.

RESULTS.

Determination number.	Temperature of air.	Barometer reading.	Barometer corrected to 0.0°.	Thermometer number.	Thermometer reading.	Thermometer correction.	Thermometer reading corrected.	Boiling-point corrected to 760 mm.
I.	14.1	759.2	757.4[1]	21713	−33.60[2]	0.0	−33.60	−33.53
				21714	−33.25[3]	−0.35	−33.60	−33.53
				4	−33.55[4]	0.0	−33.55	−33.48
II.	16.8	757.9	755.7	21713	−33.44[5]	0.0	−33.44	−33.32
				21714	−33.20[6]	−0.34	−33.54	−33.42
				4	−33.60[7]	0.0	−33.60	−33.48
							Mean,	−33.46

No correction was necessary for capillarity in the form of barometer employed.

The observed boiling-points at the observed barometric pressures (corrected to 0.0°) are calculated to 760 mm. pressure by means of the formula $\frac{dP}{PdT} = \frac{Q}{2T^2}$[8], in which P is the pressure in gram-centimeter units, T the absolute temperature and Q the molecular heat of volatilization of the liquid expressed in small calories. In the case in question *d*P and *d*T can be taken as the direct differences in pressure and temperature without introducing an appreciable error. By means of these calculations, we are enabled to compare the various results and determine the mean value. The heat of volatilization of liquid ammonia is taken as 330[9] small calories per gram.

Criticisms of the Results.—In the direct determination of the boiling-point of a liquid boiling below the temperature of the laboratory, the vapor must invariably become superheated, with

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[1] Ostwald-Luther: "Physiko-Chemische Messungen," 2nd Ed., p. 121.

[2] Constant for 18 minutes.

[3] During 8 minutes changed 0.02°.

[4] During 11 minutes changed 0.05°.

[5] During 9 minutes changed 0.04°.

[6] Constant for 7 minutes.

[7] During 7 minutes changed 0.05°.

[8] "Vorlesungen über Theoretische und Physikalische Chemie," by J. H. van't Hoff, Vol. I, p. 13 (1900).

[9] Franklin and Kraus: *Am. Chem. J.*, **21**, 8 (1899).

the result that a too high boiling-point is indicated if the thermometer is placed in the escaping vapor. Vigorous boiling and bright metallic protecting screens together with the vacuum jacket would minimize but probably not entirely eliminate this source of error. Hence the immersion of the thermometer in the liquid was resorted to. This method is, generally speaking, objectionable because of the superheating of the liquid, but this is avoided by the platinum wires sealed into the bottom of the tube and the garnets, the apparatus in this form being employed by Beckmann[1] for exact boiling-point determinations.

Another possible objection to this method is that the thermometer should show a higher reading when the bulb is deeply immersed in the liquid than when only slightly immersed (neglecting the exposed thread of the thermometer liquid), for the lower layers of the liquid are under greater pressure than the upper layers. Increase of pressure not only raises the boiling-point of the lower layers of the liquids but will also have an effect on the glass of the thermometer bulb. This latter is probably negligible and no variation could be noticed with the thermometers employed as the liquid boiled away, reducing the height of its column.

A more probable source of error when the toluene thermometers were employed, was the slowness of the running down and settling to place of the toluene. Every precaution was taken to avoid the introduction of error from this cause.

METHYL AMINE.

Review of the Literature.—E. D'Andreeff[2] (1859) states that the boiling-point of methyl amine is observed to be below 0° and calculated to be —8°.

A. W. Hofmann[3] (1889) determined the boiling-point of liquid methyl amine, employing for the purpose the apparatus described by Bannow,[4] which consisted of a flask of platinum foil 0.5 mm. thick, divided into two hemispheres 7.5 cm. in diameter and made tight at the flanged point of union with packing. In the throat of the upper hemisphere is a cork carrying a glass tube 1 cm. by 15 cm. which is surrounded by a glass mantle through which cold water could be run during the determination. The thermom-

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[1] *Z. physik. Chem.*, **4**, 593; **8**, 223; **15**, 661; **18**, 492; **21**, 245; **40**, 129 (1902).

[2] *Ann. chim. phys.* (3), **56**, 332.

[3] *Ber. chem. Ges.*, **22**, 699 (1889).

[4] "Die Chemische Industrie," 1886, p. 328.

eter passed through the inner tube a short distance below the cork and was for its whole length in the vapor of the boiling liquid. It was compared with the normal thermometer of the Reichsanstalt.

For each determination 100 cc. of the methyl amine were distilled over sodium: Barometer, 768.35; air temperature, 4.0°; duration of investigation, twenty-five minutes; boiling-point, —6.0° to —5.5°.

Criticisms.—It is evident that Hofmann's results are influenced by the fact that the temperature of the methyl amine vapor, in which the thermometer stood, is raised by the surrounding atmosphere, the temperature of which is stated to be 4.0°, that is, 10.0° above the boiling-point given for the liquid. Too high a value for the boiling-point would thus be expected.

Purification of the Methyl Amine.—Liquid methyl amine behaves toward metallic sodium in a manner analogous to that of liquid ammonia. The reaction producing the methyl sodamide,

$$CH_3.NH_2 + Na = CH_3.NHNa + H,$$

progresses much more slowly than the corresponding ammonia reaction[1].

Ten grams of freshly cut metallic sodium were placed in a steel cylinder of about 500 cc. capacity and methyl amine distilled in from a number of glass cylinders in which it was stored in the liquid condition. This methyl amine was a portion of a kilo purchased from Kahlbaum through the kindness of the trustees of the Bache Fund to whom acknowledgments are due. The steel cylinder was connected to the glass portion of the apparatus in the same manner as described under ammonia.

The Boiling-Point Determination.—The apparatus employed was identical with that used for the ammonia determination except that a different thermometer was used, and, as rubber is very quickly acted upon by methyl amine, the thermometers were supported by a cork stopper which closed the opening to the inner tube of *F*.

Thermometers number 3972 and 4 were used and the entire mercury threads of both thermometers were in the boiling liquid throughout each determination.

The same care was used in cleaning and drying the apparatus

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[1] Franklin and Kraus: *Am. Chem. J.*, **24**, 83 (1900).

before each determination as in the liquid ammonia determinations, and the boiling was conducted in the same manner.

The methyl amine vaporizing from the apparatus was carefully collected, in a tube cooled by liquid ammonia, for use in other investigations of its properties.

RESULTS.

Determination number.	Temperature of air.	Barometer reading.	Barometer corrected to 0.0°.	Thermometer number.	Thermometer reading.	Thermometer correction.	Thermometer reading corrected.
I.	13.6°	757.6	755.8	3972	—6.7[1]	0.0	—6.7
				4	—6.3[2]	—0.4	—6.7
II.	16.0°	757.6	755.5	3972	—6.7[3]	0.0	—6.7
				4	—6.3[4]	—0.4	—6.7
						Mean,	—6.7

The heat of volatilization of methyl amine not being known, the results cannot be reduced to standard conditions by the method employed for liquid ammonia.

METHYL CHLORIDE.

Review of the Literature.—Regnault[5] (1863), from determinations of the vapor-pressure, calculates the boiling-point to be——23.73° at 760 mm. pressure.

Berthelot[6] states the boiling-point as —21°.

Camille Vincent[7] (1877) obtained a colorless, mobile liquid, which boiled at —23° at 760 mm. pressure, by distillation of trimethyl amine hydrochloride.

Camille Vincent and Dalachanal[8] (1879) state, in their determination of the densities of methyl chloride, that the boiling-point is —23.7°.

Travers[9] says the boiling-point is —24°, but no authority is given for the statement.

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[1] Constant for 4 minutes.

[2] Constant for 4 minutes.

[3] Constant for 19 minutes while liquid was three-fourths boiled away.

[4] Constant for 15 minutes.

[5] *Jahresb.*, 1863, p. 70.

[6] Beilstein, 3rd Ed., Vol. **1**, p. 144.

[7] *Compt. Rend.*, **85**, 667; *Jahresb.*, 1877, p. 398.

[8] *Ann. chim. phys.* [5], **16**, 427; *Bull. Soc. Chim.*, **31**, 11.

[9] "Study of Gases," p. 54.

Purification of the Methyl Chloride.—The methyl chloride was prepared by the method of Groves[1] by passing dry hydrochloric acid into methyl alcohol, which contained dissolved zinc chloride. The methyl chloride was passed through a tower of potassium hydroxide in sticks, then through concentrated sulphuric acid and then condensed in glass cylinders cooled by a surrounding mixture of solid carbon dioxide dissolved in ether. It was thus partially, if not wholly, freed of hydrochloric acid and moisture.

From these cylinders, the methyl chloride was distilled and condensed in the receptacle *D*, the gas first passing through a purifying chain consisting of two tubes 25 cm. in length filled with soda-lime, two tubes of the same size containing phosphorus pentoxide, and the asbestos filter *C* with manometer which have been previously described.

The distillation of the methyl chloride through the purifying apparatus to the condensing tube *D* is carried on slowly so as to insure complete purification; in fact, the phosphorus pentoxide tubes and the filter *C* were packed so tightly that the distillation could not progress rapidly.

The Boiling-Point Determination.—Thermometers 21713, 21714 and 4 were employed and the determination was carried out in exactly the same manner as described under ammonia.

RESULTS.

Determination number.	Temperature of air.	Barometer reading.	Barometer corrected to 0.0°.	Thermometer number.	Thermometer reading.	Thermometer correction.	Thermometer reading corrected.	Boiling-point corrected to 760 mm.
I.	16.85	760.2	758.0	21713	−24.05[2]	0.0	−24.05	−23.98
				21714	−24.1[3]	−0.1	−24.20	−24.13
				4	−24.2[4]	0.0	−24.2	−24.13
II.	18.1	760.5	758.1	21713	−24.15[5]	0.0	−24.15	−24.09
				21714	−24.10[6]	−0.1	−24.20	−24.14
				4	−24.1[7]	0.0	−24.1	−24.04
							Mean,	−24.09

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[1] *J. Chem. Soc.*, 1874, p. 641; *Ann. Chem.* (Liebig), **174**, 378.

[2] During 5 minutes varied 0.05°.

[3] During 4 minutes varied 0.05°.

[4] Constant for 6 minutes.

[5] During 6 minutes varied 0.05°.

[6] Constant for 4 minutes.

[7] Constant for 8 minutes.

The heat of volatilization of methyl chloride is taken as 96.9[1] small calories per gram.

SULPHUR DIOXIDE.

Review of the Literature.—R. Bunsen[2] (1839), by determinations of the vapor-pressures at several different temperatures, places the boiling-point at —10.5°; barometer, 744 mm. corrected to 0°.

Michael Faraday[3] (1845), by measurements of the vapor-pressure, finds the boiling-point to be —10° at one atmosphere pressure.

Pierre[4] (1847) determined the boiling-point as —8° at 759.18 mm. pressure.

Ch. Drion[5] (1859) states the boiling-point to be —8°.

E. D. Andreeff[6] (1859) gives the boiling-point as —10.3° at 741 mm.; —9.9° at 754 mm.

Regnault[7] (1860) gives the vapor-pressure as 762.49 mm. at —10°, and later, in 1863,[8] by measurements of the vapor-pressures, he determined the boiling-point to be —10°.08 at 760 mm. pressure.

Pierre[9] (1873), by boiling the liquid in 25- or 30-gram portions, found the boiling-point to be —8°.

R. Pictet[10] (1877) found the boiling-point to be —10° at one atmosphere pressure by the vapor-pressure method.

A. Blümcke[11] (1888), by determinations of the vapor-pressure, finds the boiling-point to be —10° at 1.01 atmospheres pressure.

Purification of the Sulphur Dioxide.—The commercial sample of the sulphur dioxide was distilled from a steel cylinder through two phosphorus pentoxide tubes, each 25 cm. long, through the filter *C*, and condensed in the tube *D*. The distillation was carried on slowly, the tube *D* being cooled by liquid ammonia.

The Boiling-Point Determination.—Thermometer number 4 was the only one available for this determination which was otherwise carried out as previously described for the other liquids.

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[1] Chappius: *Ann. chim. phys.* [6], **15**, 517 (1888).

[2] Pogg. *Ann.*, **46**, 97 (1839).

[3] *Ann. chim. phys.* [3], **15**, 257 (1845); *Phil. Trans.*, **135**, 155 (1845).

[4] *Ann. chim. phys.* [3], **21**, 336; *Jahresb.*, 1847, p. 63.

[5] *Ann. chim. phys.* [3], **56**, 5; *Jahresb.*, 1859, p. 18.

[6] *Ann. Chim. Pharm.*, **110**, 1; *Ann. chim phys* [3], **56**, 317; *Jahresb.*, 1859, p. 19

[7] *Compt. Rend.*, **50**, 1072 (1860): *Jahresb.*, 1860, p. 41.

[8] *Ann. chim. phys.* [3], **15**, 134; *Jahresb.*, 1863, p. 70.

[9] *Compt. Rend.*, **76**, 214.

[10] *Ann. Phys. and Chem. Beibl.* (Wiedemann), 1887, **11**, 629; *Arch. de Sc. Phys. Nat.* [3], **13**, 212 (1885).

[11] *Wied. Ann.*, **34**, 10 (1888); *Jahresb.*, 1888, p. 152.

The boiling was carried on for one hour and six minutes, the liquid almost boiling away in this time, the variation in temperature during this time being 0.13°, namely, —9.60 to —9.73°.

RESULTS.

Determination number.	Temperature of air.	Barometer reading.	Barometer corrected to 0.0°.	Thermometer number.	Thermometer reading.	Thermometer correction.	Thermometer reading corrected.	Boiling-point corrected to 760 mm.
I.	19.1	763.4	760.90	4	—9.73[1]	—0.33	—10.06	—10.09

The value for the heat of volatilization of sulphur dioxide is taken as 91.7[2] small calories per gram.

These results are open to the same criticisms as those for ammonia, and in addition it is to be regretted that the objection may also be made that the thermometer was not compared with the normal thermometer of the Reichsanstalt.

SUMMARY.

(1) The literature of the boiling-points of ammonia, methyl amine, methyl chloride, and sulphur dioxide, has been collected and the various results criticized.

(2) The boiling-points of these liquids have been redetermined, improved apparatus, method of working and means for purifying the liquids, having been employed.

(3) As a result of the work the boiling-point of ammonia is found to be —33.46° at 760 mm.

(4) The boiling-point of methyl amine is found to be —6.7° at 755.67 mm. No value for the heat of volatilization of the liquid is available for calculating the value at 760 mm.

(5) The boiling-point of methyl chloride is found to be —24.09° at 760 mm.

(6) The boiling-point of sulphur dioxide is found to be —10.09 at 760 mm.

This work was undertaken at the suggestion of Professor E. C. Franklin, of Stanford University, carried to completion under his

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[1] During 34 minutes the boiling-point changed 0.01° and the liquid almost completely boiled away.

[2] Chappius: *Ann. chim. phys.* [6], **15**, 513; *Compt. Rend.*, **104**, 897 (1897).

kindly advice and assistance, and I wish to express my grateful thanks to him and acknowledge the many favors shown me.

STANFORD UNIVERSITY,
January 31, 1905.

Note.—The methods employed for the purification of the ammonia used in these experiments precludes the possibility of the presence of objectionable quantities of impurities other than possibly pyridine and its homologues. Tests for pyridine, by the method of H. Ost[1] failed to show more than traces of that substance in the liquid, which was not so highly purified as that used for the boiling-point determinations.

Franklin and Kraus[2] have shown the boiling-point elevation constant of ammonia to be 3.4, a value smaller than that of any other known liquid, whence it follows that nearly 3 per cent. of pyridine by weight must be present to produce a change in the boiling-point of the solvent of 0.1 degree. Since tests have shown that nothing approaching such a quantity was present, the conclusion is justified that the value given in this paper for the boiling-point of liquid ammonia can not be appreciably in error from the presence of impurities in the ammonia used.

I am indebted to Dr. William A. Noyes for the suggestion that tests for pyridine be made.

H. D. GIBBS.

FOOD LABORATORY,
SAN FRANCISCO, CALIFORNIA,
June 12, 1905.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, DEPARTMENT O
AGRICULTURE, NO. 58. SENT BY H. W. WILEY.]

CHEMICAL GLASSWARE.

BY PERCY H. WALKER.

Received April 28, 1905.

It is unnecessary to call the attention of the analytical chemist to the fact that all glass is more or less soluble in water and in various solutions. He simply accepts the fact and when working with the greatest care avoids, as far as possible, the use of glass. Of really greater practical importance than the difference in solu-

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[1] "Commercial Organic Analysis," Allen, Vol. III, Part II, p. 104.

[2] *Amer. Chem. J.*, **20**, 846 (1898).