and concentrations of o.1 M potassium and sodium hydroxides is increased by the addition of neutral salts.

3. Tables for the increase of the hydrogen-ion activity of hydrochloric acid solutions, and the hydroxyl-ion activity of potassium and sodium hydroxide solutions containing neutral salts have been appended.

4. The evidence thus far obtained in the acid–salt system indicates that the increase in activity of the hydrogen ion in the acid differs little for the different salts used in these experiments. This does not appear to hold in the hydroxide–salt system.

5. Calculations made by the Planck formula for liquid potential lend confirmation to the experimental results.

6. The experimental fact that sodium bromide produces the same effect on the hydrogen-ion activity of hydrochoric acid solutions as does sodium chloride has been proved to be in accord with the law of mass action. This is also true of similar cases in the hydroxide–salt systems.

7. If the interpretation of the experimental results as given above is correct, then, in a solution of o.1 M hydrochloric acid, the hydrogen-ion concentration has been increased from o.092 to o.1765 M by the presence of 3 M potassium chloride. This points to the conclusion that the solution acts as if it were contracting, or that the volume of solvent has decreased.

PHILADELPHIA, PA.

THE VAPOR PRESSURES OF ACETYLENE, AMMONIA AND ISOBUTANE AT TEMPERATURES BELOW THEIR NORMAL BOILING POINTS.[1]

BY G. A. BURRELL AND I. W. ROBERTSON.

In this report are shown the vapor pressures of acetylene, ammonia, and isobutane at temperatures below their normal boiling points. The method of procedure is the same as that detailed in previous communications to THIS JOURNAL by the authors.[2] The thermometers were calibrated at two additional points, other than those used by the authors in previous work. These points are the melting points of mercury and ice. Henning[3] gives for the melting point of mercury, —38.89°. In calibrating thermometers against this point, the authors carefully purified mercury by the method of Hulett.[4] About 15 cc. of mercury were placed in a test tube and immersed in the gasoline bath[5] maintained at a

[1] Published by permission of the Director of the Bureau of Mines.

[2] THIS JOURNAL, **37**, 1893 (1915).

[3] *Ann. Phys.*, **43**, 294 (1913).

[4] *Phys. Rev.*, **34**, 307 (1911).

[5] See THIS JOURNAL, **37**, 1893 (1915) (Fig. 1).

temperature of a few degrees below the melting point of the mercury. The bath temperature was next allowed to rise slowly. At the melting point the temperature, of course, became stationary until all of the mercury had melted. Next the mercury was again distilled and the operation repeated with the same results. In the two carefully conducted trials with each thermometer, No. 707 was found to register —38.4 and —38.5°, while No. 504 in the same calibrations read —36.5 and —36.6°. From the values so found, the thermometers were corrected according to the melting point found by Henning.

Preparation of Gases.—Acetylene was prepared by the action of water on calcium carbide. The evolved gas was passed through caustic potash solution and then dried over phosphorus pentoxide. Next it was repeatedly fractionated at the temperature of liquid air to remove air and other gases of high vapor pressure at that temperature and finally fractionated several times at a temperature of —120° to —110°, thereby distilling the acetylene from water vapor or other gases whose vapor pressure is prac-
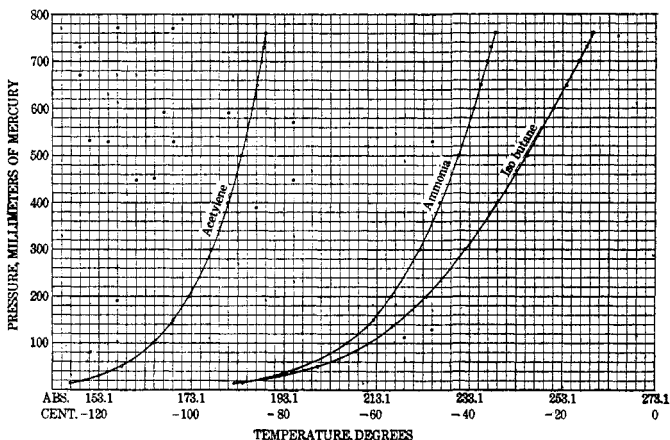

Fig. 1.—Temperature plotted against pressure.

tically nil at that temperature. During the course of the vapor-pressure measurements, part of the acetylene was allowed to evaporate away at different times and the observations were repeated with the remaining portions of the gas. After each introduction of fresh portions of gas into the vapor-pressure bulb, fractionation was performed at the temperature of liquid air to make sure that atmospheric air had not been trapped in the transfer. The above precautions were taken in all the vapor-pressure measurements.

Ammonia was prepared by distilling the gas from C. P. ammonia water.

Isobutane was prepared by the action of isobutyl iodide on a zinc-copper couple.

Both the ammonia and isobutane were purified by repeated distillations at low temperatures.

Table I shows the observed and the calculated vapor pressures for the three gases.

TABLE I.—CALCULATED AND OBSERVED VAPOR PRESSURES.

Acetylene.			Isobutane.			Ammonia.		
Temp. ° Abs. Av. of two.	Pressure. Mm. Hg. Obs.	Calc.	Temp. ° Abs. Av. of two.	Pressure, Mm. Hg. Obs.	Calc.	Temp. ° Abs. Av. of two.	Pressure. Mm. Hg. Obs.	Calc.
189.1	760	760	259.7	760	760	238.5	760	760
188.6	730	731	258.2	730	731	237.7	730	730
188.0	700	700	256.6	700	694	236.8	700	699
187.2	650	658	254.0	650	651	235.4	650	648
186.1	600	606	251.1	600	598	233.8	600	595
183.6	500	499	245.4	500	500	230.7	500	501
180.8	400	400	239.0	400	400	226.8	400	400
177.3	300	300	232.0	300	305	222.4	300	306
172.5	200	199	211.7	100	115	216.3	200	205
169.1	150	147	200.4	50	58	212.3	150	154
164.9	100	99	192.2	30	32	206.5	100	100
158.0	50	53	182.4	15	15	197.0	50	45
153.2	30	30	174.7	7	7.4	191.0	30	26
147.0	15	15	166.9	3	3.5	184.2	15	14
138.5	6	5.2	158.3	1	1	176.4	7	5.4
132.5	2.5	2.3				171.9	4	3.1
129.9	1	1.58				159.8	1	0.6

Calculation of Vapor Pressures.—The vapor pressures were calculated, using the Nernst equation.

$$\text{Log } P = \frac{\lambda_0}{4.571T} + 1.75 \log T - \frac{\epsilon}{4.571} T + C.$$

Table II shows the values of P at three different temperatures that were taken to find the constants in the Nernst equation.

TABLE II.

Acetylene.		Isobutane.		Ammonia.	
$T°$.	P.	$T°$.	P.	$T°$.	P.
189.1	760	259.7	760	238.5	760
177.3	300	245.4	500	226.8	400
147.0	15	182.4	15	206.5	100

The equations of the curves are

For acetylene, $\log P = -\dfrac{957.21}{T} + 1.75 \log T - 0.001511T + 3.6728.$

For isobutane, $\log P = -\dfrac{1632.661}{T} + 1.75 \log T - 0.0158873T + 9.06814.$

For ammonia, $\log P = -\dfrac{1951.72}{T} + 1.75 \log T - 0.015525 T + 10.6063.$

The straight line curves shown at Fig. 2 were drawn according to an equation which was derived by the method of least squares and which represents the average of all the points.

For ammonia the equation is $\log P = -\dfrac{1371.86}{T} + 8.64.$

For acetylene, $\log P = -\dfrac{1127.09}{T} + 8.84.$

For isobutane, $\log P = -\dfrac{1056.25}{T} + 6.98.$

The heats of evaporation may be calculated from the integrated form of the Clausius-Clapeyron equation

$$\ln P = -\frac{Q}{RT} + \text{const.}$$

Using the values 1371.86, 1127.09 and 1056.25 in this equation, one obtains as the average heats of evaporation over the temperature range studied, in calories per gram-molecule

For ammonia: $Q = (1371.86 \times 4.571) = 6271$ colories
For acetylene: $Q = (1127.09 \times 4.571) = 5152$ calories
For isobutane: $Q = (1056.25 \times 4.571) = 4828$ calories

Brill[1] has determined saturated vapor pressures for ammonia between —80.0° and —33.0°. His results are shown in Table III, along with those of the authors of this paper. The latter were taken from the curve shown at Fig. 1 (drawn to larger scale than shown in Fig. 1).

VAPOR PRESSURES OF AMMONIA AS DETERMINED BY BRILL AND BY BURRELL AND ROBERTSON.

Temp. ° C.	Pressure. Mm. Hg.		Temp. ° C.	Pressure, Mm. Hg.	
	Brill.	Burrell and Robertson.		Brill.	Burrell and Robertson.
—80.0	35.2	37	—59.5	172.4	166
—79.0	38.0	45	—56.5	210.0	209
—77.6	44.1	45	—54.4	239.5	239
—75.1	51.8	53	—50.7	309.3	305
—72.7	62.5	65	—46.2	403.5	400
—70.4	74.9	76	—45.0	437.1	430
—68.3	87.5	88	—41.5	521.9	526
—64.4	116.0	117	—39.8	568.2	580
—62.8	136.0	132	—38.2	610.4	630
—60.8	157.6	151	—33.0	761.0	...

Brill's pressure measurements were performed by the statical method. His temperatures were measured with an iron-constantan thermocouple checked against a pentane thermometer calibrated at the physical-technical institute. The agreement between his work and that of the authors is fairly good, except at temperatures near the normal boiling point. His

---

[1] "Vapor Pressures of Liquid Ammonia," *Ann. Physik*, **21**, 170 (1906).

value, 33.0° C., is 1.6° higher than ours.   The authors of this report note one possible error in his work.   As a check on the accuracy of his temperature measurements he calibrated his apparatus against the melting point of pure chloroform, assuming this to be 63.1°.   Recent measurements by Henning, place it at 63.7°.[1]
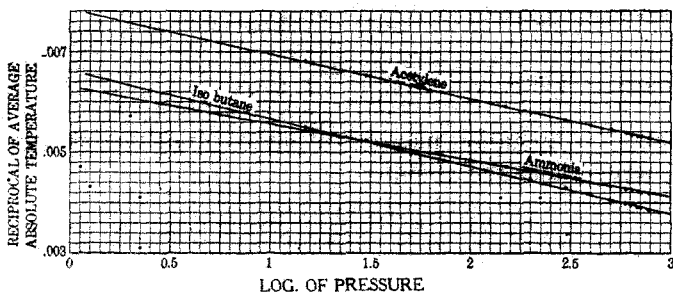

Fig. 2.—Log. of pressure plotted against reciprocal of absolute temperature.

Brill's work on ammonia is the only work on vapor pressures of gases at low temperatures that covers an extensive range for a gas that the authors also have worked on.   We extended the observations 20° lower than Brill.

PITTSBURGH. PA.

THE ACTION OF THIONYL CHLORIDE ON SULFIDES.

By H. B. NORTH AND C. B. CONOVER.

Investigation of the action of thionyl chloride on inorganic substances has been confined almost entirely to its deportment toward metals, metalloids and oxides.   The action of the reagent on these has been quite exhaustively studied by North and Hageman and described in THIS JOURNAL.[2]   Letting M represent a divalent metal of metalloid, reaction follows the general equation

$$3M + 4SOCl_2 = 3MCl_2 + 2SO_2 + S_2Cl_2.$$

With oxides, reaction takes place according to the following:

$$MO + SOCl_2 = MCl_2 + SO_2$$
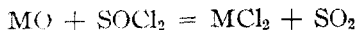
In the case of metals or metalloids having more than one compound with chlorine, the lower chloride is usually, but not always, produced if the metal is in excess.   Likewise the higher chloride is formed when the metal is treated with a large excess of the reagent.

The chief difference in the two reactions given above is that with metals

[1] Ann. Physik, 43, 294 (1913).

[2] THIS JOURNAL, 34, 890 (1912); 35, 352 (1913); 35, 543 (1913).