has a density of 2.18. It is very probable that in addition to the effect of Wahl, we must regard the glass itself as in a varying state of transformation.

The problem of the phenomena of vaporization is a complicated one, and one which we do not particularly need to consider in this connection. It has been suggested that we probably have to do here with an irreversible reaction in the vapor phase.

With regard to the relation between black and red phosphorus we can offer only conjectures. It does seem pretty certain, however, that red and black cannot stand in the relation of ordinary monotropic solids. If they did bear this relation, the black must be the more stable form, because of its lower vapor pressure, and in this case we cannot understand the failure of the red to condense as black out of its vapor. The fact that the black apparently melts to the same liquid as the red is puzzling. It may be that the relations here are the same as in the vapor phase; that is, liquid black phosphorus may be unstable, and may transform itself irreversibly to liquid red as rapidly as it is formed.

Summary.

Two new modifications of phosphorus have been found. The first is a new modification of ordinary white phosphorus, possibly hexagonal, with a reversible transition point at atmospheric pressure at about —76.9°. The second modification, black phosphorus, is obtained irreversibly from white phosphorus at 12,000 kg. and 200°. A number of its physical constants have been determined; particularly striking are its high density, 2.691, and fair electrical conductivity. No attempt to transform either white or red to black phosphorus has been successful by any other method except that above. Finally, some conjectural explanations of the relations of the various modifications have been given.

THE JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERISTY.
No. 238.]

THE DISSOCIATION PRESSURES OF AMMONIUM- AND TETRAMETHYLAMMONIUM HALIDES AND OF PHOSPHONIUM IODIDE AND PHOSPHORUS PENTACHLORIDE.

BY ALEXANDER SMITH AND ROBERT PEYTON CALVERT.

Received May 8, 1914.

The dissociation pressures of the chloride, bromide, and iodide of ammonium and of phosphonium iodide have previously been measured. The methods used, and the results obtained are discussed below. The dissociation pressures of the chloride and iodide of tetramethylammonium, and of phosphorus pentachloride have not previously been determined. The present observations were made partly to supply data required for a study of the density and degrees of dissociation of the saturated vapors of these substances, in regard to which no previous measurements have been made.

The advantages and disadvantages of the various methods of measuring vapor or dissociation pressures have been considered critically by Smith and Menzies.[1] The method of confinement over mercury, in particular, is not applicable when, as in the present work, chemical action with the mercury occurs. In such cases, various dynamic methods have been employed. The most popular of these, Ramsay and Young's dynamic method,[2] however, presents especially grave irregularities when applied to cases of dissociating solids, in five of which, for example, the temperature of volatilization appeared to be independent of the pressure.[3]

The dissociation pressure of a solid may be measured by means of the spiral manometer of Ladenburg and Lehmann[4] or the dynamic[5] and static[6] isoteniscopes of Smith and Menzies. In the former method, as Smith and Menzies pointed out,[7] permanent distortion of the spiral may occur. Then too, the expansion of the glass makes the zero point change with the temperature, so that the trustworthiness of the measurements is considerably diminished unless the spiral is calibrated for each temperature.[8] The method of Smith and Menzies has been used successfully in difficult cases by Ruff,[9] Taylor and Hulett,[10] and Moles.[11]

The Apparatus.

The **isoteniscope** used in all our work, except that dealing with phosphorus pentachloride, was the *static*. The substance, the vapor or dissociation pressure of which is to be determined, is placed in the small bulb shown on the right (Fig. 1). The bend is filled with some substance which, at the temperature of the experiment, will melt to give a liquid suitable for confining the vapor. The isoteniscope is connected with a very large bottle for regulating the pressure. By the turning of the proper stopcock, this bottle can be put into communication, either with a similar vacuum bottle, with a compression pump (or the atmosphere), or with

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[1] "Studies in Vapor Pressure, III," This Journal, **32**, 1415 (1910).

[2] *J. Chem. Soc.*, **47**, 42; Ostwald-Luther, [3] 218.

[3] *Phil. Trans.*, **177**, 116 (1886).

[4] *Ber. physik. Ges.*, **4**, 20 (1906).

[5] This Journal, **32**, 1448 (1910).

[6] *Ibid.*, **32**, 1419 (1910).

[7] *Ibid.*, **32**, 1455 (1910).

[8] Preuner and Brockmöller, *Z. physik. Chem.*, 81, 129.

[9] *Z. anorg. Chem.*, **72**, 63.

[10] *J. phys. Chem.*, **17**, 565.

[11] *An. Soc. Españ. di Fis. y Quim.*, **9**, 160 and 172.

the pressure gage. To make a determination of the vapor pressure, the isoteniscope is placed in a well stirred bath, maintained at the proper temperature, and the pressure is lowered until the substance in the bulb boils vigorously. Adhering air, moisture, and volatile impurities are thus carried out past the liquid seal in the bend. The pressure is then raised until the boiling stops and the level of the confining liquid becomes the same in both arms of the isoteniscope. The temperature of the bath and the pressure in the apparatus are then noted and recorded.

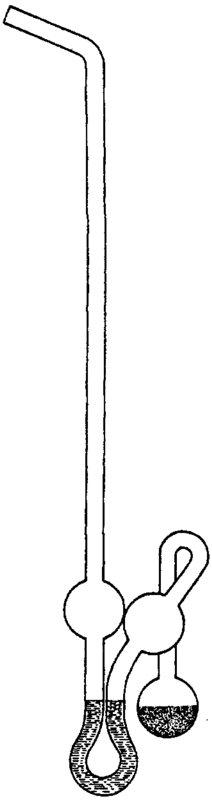

Fig. 1.—Static isoteniscope.

The **pressure gage,** a portion of which is shown in Fig. 2, was of the closed mercury-manometer type.[1] Each arm had a length of 2500 mm. and an internal diameter of 16 mm. The scale was engraved on silver inlaid in a heavy steel bar. It was graduated in mm. and calibrated, at 20°, against a standard meter. The carriage bearing the fine, horizontal reading line, ruled on glass, could be moved up or down on the stiff steel rod (diameter 20 mm.) which formed its support. A mirror, behind the glass tubes and extending the entire length of the gage, eliminated errors due to parallax in reading. Three thermometers were suspended at intervals along the gage. That they might show the same temperature lag as the mercury in the arms of the manometer, their bulbs were immersed in mercury

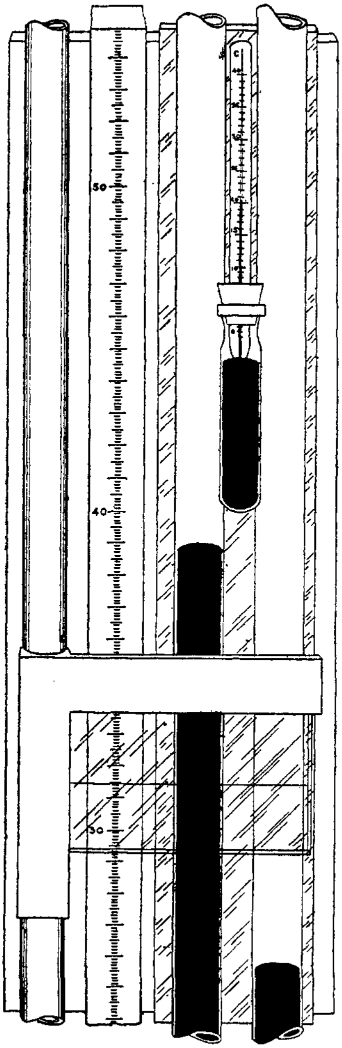

Fig. 2.—Pressure gage.

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[1] Before being erected, the gage was repeatedly exhausted to a pressure of 0.02 mm. Its reading was checked, at frequent intervals, against a standard barometer. In setting up the gage, care was taken to make the scale exactly vertical.

contained in small tubes (see figure). The mercury used in the gage was purified by spraying it eight times through a column of 8% nitric acid[1] and then by distilling it twice in a slow stream of air.[2] The pressures were reduced to 0° and the sea level at 45° latitude.

The **temperature** measurements were made with a resistance thermometer, of the Heräus type. The platinum coil is embedded in quartz. The leads are of gold and are uncompensated. This simple form of thermometer shows almost no temperature lag. In the calibration, which was repeated at frequent intervals, the procedure adopted by the Bureau of Standards[3] was used throughout. The standard resistances and bridge ratios were combined in the dial decade box of Leeds-Northrup. The coils were of manganin for which the temperature coefficient of resistance is low.[4]

The temperature scale is that based upon the ice point, steam point and sulfur boiling point, the latter being taken as 444.7° (constant volume nitrogen scale). The temperature error is less than ±0.2° at the highest readings.

The **liquids used in the heating bath,** and the temperatures at which each is suitable, are as follows: water, 0—70°; paraffin, 60—190°; fused sodium nitrite (10 parts), sodium nitrate (19 parts), and potassium nitrate (33 parts), 190–300°; eutectic mixture of nitrates of potassium and sodium (equimolar), 218–500°.

The **bath vessel** was a two-liter Jena beaker, of the tall form, jacketed by a glass battery jar from which the bottom had been removed. The 2 cm. space between the beaker and the battery jar was closely packed with asbestos wool, two small windows being left on opposite sides and about midway between top and bottom. To increase the accuracy of leveling the liquid in the isoteniscope, a fine wire was stretched horizontally across the front window and an electric light was placed just behind the other. The brass stirrer consisted of four propellors attached to a vertical shaft driven by a high speed motor. The bath was heated by a vulcan burner. With a divided gas stream and screw clamps, the supply of gas could be so controlled as to keep the temperature constant for a considerable time, to within ± 0.1°, even above 400°

Ammonium Bromide.

Previous Determinations.—F. M. G. Johnson,[5] using the spiral manometer, has determined the dissociation pressures of three ammonium halides. In regard to his temperature measurements, the following points[6] should

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[1] Method of Hildebrand, This Journal, 31, 933 (1909).

[2] Method of Hulett and Minchin, *Physic. Rev.*, 21, 388 (1905).

[3] Waidner and Burgess, *Bull. Bur. Standards*, 6, 150 (1909).

[4] Ostwald-Luther, [3] 412.

[5] F. M. G. Johnson, *Z. physik. Chem.*, 65, 36-40 (1909).

[6] For a detailed discussion see Smith and Menzies, This Journal, 32, 1456 (1910).

be noted: (1) The heating bath, of air, was unstirred; (2) the dissociating substance and the glass spiral, in which the pressure was registered, were kept at different temperatures; (3) the temperatures were read by means of mercury thermometers, either of the ordinary type or nitrogen-filled. The untrustworthiness of mercury thermometers at high temperatures need not be pointed out; (4) no satisfactory provision was made for removing water vapor and gases adsorbed by, or adhering to the substances and the interior of the apparatus.

The Present Measurements.—The sample of ammonium bromide used by us was purified by recrystallization and then by sublimation. The confining liquid in the isoteniscope consisted of fused silver bromide, to which had been added ammonium bromide sufficient in amount to lower the melting point from 426° to 255°. This mixture was without visible action on the vapors formed by the dissociation.

After the raising of the pressure until the boiling of the ammonium bromide ceased, there was observed a slow, uniform increase in the pressure of the vapor. Thus at 388.9°, the pressure rose 650 mm. in ten minutes, 2 mm. in the following 10 minutes, and approximately 2 mm. in each of the succeeding ten-minute periods. The enormous difference in the rates of increase shows that there must be some secondary change. The slow increase may be due to a dissociation of hydrogen bromide (produced in the primary dissociation) and the removal of either the hydrogen or bromine by the confining liquid. Or, more probably, it may be due to the dissociation of ammonia. It is well known that the reaction $2NH_3 \rightleftarrows N_2 + 3H_2$ occurs as the temperature rises, and that at 327°, for example, the equilibrium, if reached, would leave over 90% by volume of the free elements[1]. In any case, the increase is very slow, and we have eliminated its effect altogether by correcting all pressure readings back to the time zero, at which the boiling out ceased. This is illustrated in the table below, which gives the readings in a preliminary experiment at 388.96°:

Time (min.)...	10	20	30	40	50		Zero
Pressure (mm.)	675.2	677.4	678.9	680.5	682.3	Mean	673.4
ΔP...........		2.2	1.5	1.6	1.8	1.8	(calc.)

The deviations in the value of ΔP from the mean (1.8 mm.) correspond to temperature differences of less than 0.03°, which is about the limit of accuracy in the temperature control. The size of the correction factor decreased as the temperature was lowered. For an entire series of pressures and temperatures the correction averaged 1.1 mm. That Johnson did not detect this increment of pressure is probably due to the fact that it is close to the limit of sensibility of the spiral manometer, said by him to be "of the order of 1 mm."

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[1] Haber and Van Oordt, *Z. anorg. Chem.*, **44**, 356 (1905).

The Results.—Two series of measurements were made. When the results were plotted on a large piece of cross-section paper, the points were found to lie closely along a smoothed curve. Three points on this curve (320°, 100.6 mm.; 370°, 404.8 mm.; and 397°, 806.9 mm.) were used to evaluate the constants in the Kirchhoff-Rankin-Dupré formula, $\log p = -A/T + B \log T + C$. This equation, with the constants introduced, becomes

$$\log p = -2056.541/T + 9.54014 \log T - 20.98468.$$

Since points calculated from the equation must lie exactly on a perfectly smooth curve, the irregularities in the individual pressures and temperatures observed can be shown by the magnitude of their deviations from the values found from the formula. Table I gives the observed pressures (Col. 1), those of the second series of measurements being distinguished by the asterisk; the observed temperatures (Col. 2); the temperatures calculated from the above formula (Col. 3); and the differences (Δ) between the observed and the calculated temperatures. The temperatures are given to the second decimal place, because in comparing the values, this figure is significant.

TABLE I.—DISSOCIATION PRESSURES OF NH_4Br—OBSERVATIONS.

Press. Mm.	Temperature.			Press. Mm.	Temperature.		
	Obsd.	Calcd.	Δ.		Obsd.	Calcd.	Δ.
928.6*	402.87	402.68	+0.19	421.6	371.60	371.53	+0.07
789.3	396.21	396.17	+0.04	334.7	362.40	362.79	—0.39
792.3*	396.22	396.34	—0.12	329.9*	362.50	362.27	+0.23
662.2	389.01	389.10	—0.09	227.9	348.63	348.64	—0.01
661.9*	388.96	389.08	—0.12	131.3*	329.10	329.12	—0.02
533.9	380.50	380.61	—0.11	59.5*	303.25	302.78	+0.47
534.2*	380.57	380.65	—0.12				

The algebraic sum of the differences between the observed and the calculated temperatures is +0.02°, or close to zero, as it should be. The mean deviation of a single observation from the curve is 0.15°. The observations are therefore consistent. This deviation is within the limits of error of the absolute temperature measurements themselves (less than ±0.2°), so that the smoothed curve as a whole is probably correct to ±0.2°.

The dissociation pressures of ammonium bromide, for rounded temperatures, are given in Table II. The pressures in the second column (S. and C.) have been calculated from the formula; those in the third column (J.) have been read from a large curve plotted from the results of F. M. G. Johnson. This table shows, as do also the curves (Fig. 3), that the differences between our results and those of Johnson become large at the higher temperatures, at which a mercury thermometer is especially unreliable. At 394.6° this difference is 45 mm.

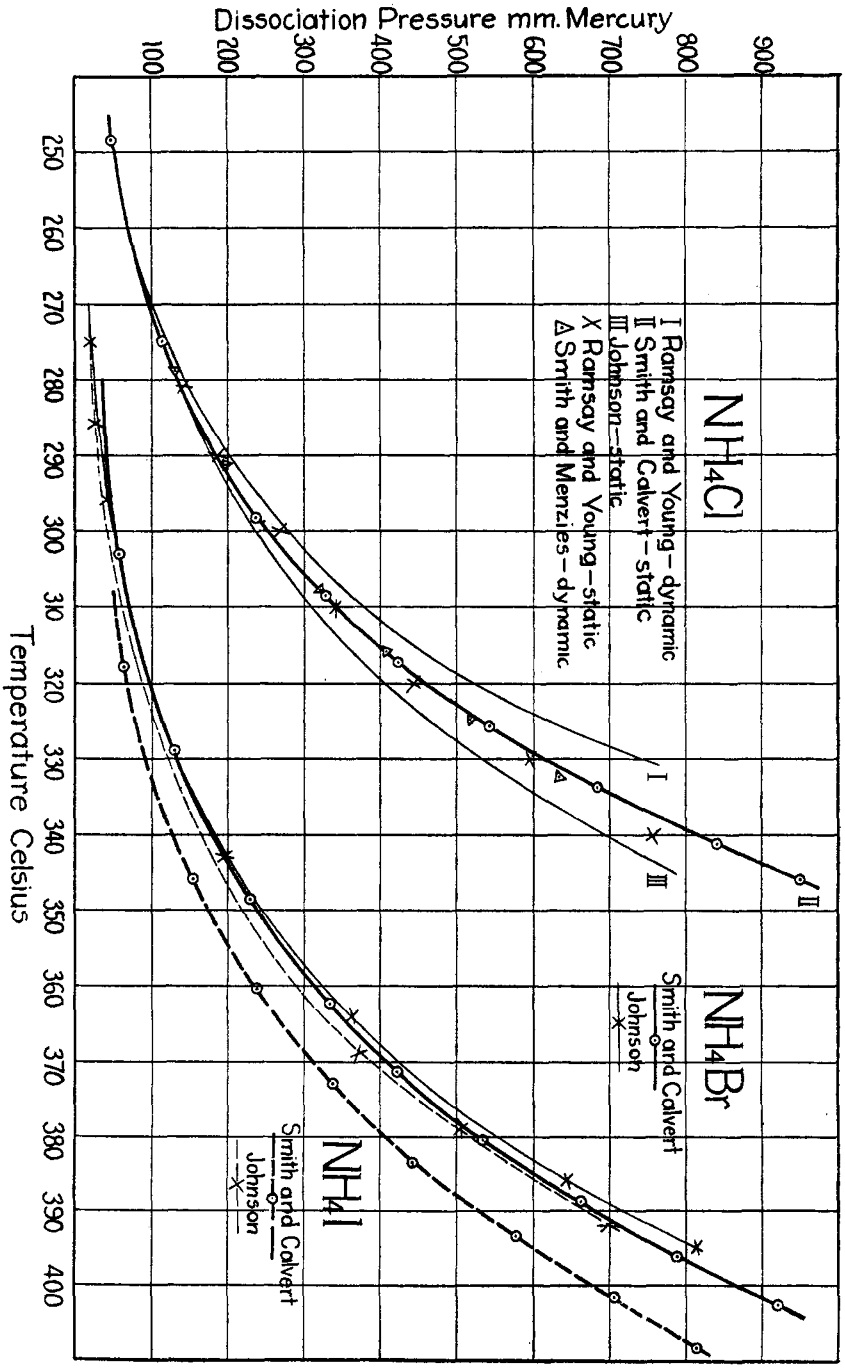
Dissociation Pressure mm. Mercury
100
200
300
400
500
600
700
800
900
Temperature Celsius
250
260
270
280
290
300
310
320
330
340
350
360
370
380
390
400
NH_4Cl
I Ramsay and Young–dynamic
II Smith and Calvert–static
III Johnson–static
X Ramsay and Young–static
△ Smith and Menzies–dynamic
I
II
III
NH_4Br
Smith and Calvert
Johnson
NH_4I
Smith and Calvert
Johnson

Fig. 3.

Table II.—Dissociation Pressures of NH_4Br at Rounded Temperatures.

Temp.	Pressure. S. & C.	Pressure. J.	Temp.	Pressure. S. & C.	Pressure. J.
300	55.0	56	380	525.5	548
320	100.6	101	390	677.5	718
340	178.8	180	394.6	**760.0**	805
360	310.4	316	400	868.4	
370	404.8	421	403	935.1	

Ammonium Iodide.

The Present Measurements.—A c. p. ammonium iodide was purified by recrystallization and dried by heating *in vacuo* at 100°. It was not resublimed because, at high temperatures, it is decomposed by moist air with the formation of free iodine. Sublimation of a substance to be used in the isoteniscope is really unnecessary. The repeated boiling out, before each reading, removes the volatile matter; non-volatile matter does not affect the vapor pressure of the solid, unless contained in solid solution.

The confining liquid was fused silver iodide (m. p. 530°)[1] to which had been added an equal weight of ammonium iodide. The mixture froze at 260°.

In the heated vapor of ammonium iodide the following changes occur:

$$NH_4I \rightleftarrows NH_3 + HI$$
$$2HI \rightleftarrows H_2 + I_2$$
$$2NH_3 \rightleftarrows 3H_2 + N_2$$

The hydrogen iodide[2] and ammonia dissociate very slowly. Since we desired to measure the pressure due to ammonium iodide and its primary dissociation products only, we have eliminated the effect of the slow, uniform increase in pressure produced by the secondary changes. The data below, taken from a preliminary observation at 346°, will show the method. The time is expressed in minutes after the boiling out ceased.

Time (min.)	10	20	30	40	50	60	70
Pressure (mm.)	164.1	165.2	166.1	166.5	166.7	167.2	167.6
ΔP		1.1	0.9	0.4	0.2	0.5	0.4

The mean value of ΔP is 0.6, and the pressure at zero time, therefore, 163.5 mm.

As was to be expected, the correction factor became larger at the higher temperatures, at which slight traces of free iodine could be detected in the isoteniscope. Johnson observed a rise in pressure of 10 mm. per hour at 357°. Although he worked rapidly, the accumulation of free iodine

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[1] Landolt and Börnstein, *Tabellen*, [4] 229.

[2] At 350° and 380 mm. pressure, hydrogen iodide is dissociated to the extent of 4% after 24 hours' time. Bodenstein, *Z. physik. Chem.*, **13**, 117 (1894).

in the spiral during an entire series of pressure and temperature readings must have been considerable.

The Results.—From the final temperature-pressure readings a large, smooth curve was constructed. A Kirchhoff-Rankin-Dupré formula, for this curve, was calculated from the following fundamental points; 340°, 130.3 mm.; 380°, 407.3 mm.; 400°, 675.2 mm. The equation, with the constants evaluated, is

$$\log p = -7714.591/T - 10.04345 \log T + 42.69560.$$

Table III gives, for each pressure, the temperature observed, the temperature calculated from the formula, and the difference (Δ) between the two values. In two cases only does the difference exceed 0.14°.

TABLE III.—DISSOCIATION PRESSURES OF NH_4I—OBSERVATIONS.

Press. Mm.	Temperature. Obsd.	Temperature. Calcd.	Δ.	Press. Mm.	Temperature. Obsd.	Temperature. Calcd.	Δ.
830.3	408.54	408.63	+0.09	335.6	372.69	372.73	+0.04
704.6	401.74	401.77	+0.03	238.0	360.33	360.34	+0.01
699.3	401.38	401.43	+0.05	153.3	345.93	345.35	—0.58
576.5	393.63	393.57	—0.06	156.1	345.79	345.93	+0.14
452.9	384.06	384.07	+0.01	64.0	317.80	318.05	+0.25
339.3	372.99	373.13	+0.14			Algebraic sum	+0.12

The equilibrium pressures for ammonium iodide, at rounded temperatures, are given in Table IV. The pressures in the second column (S. & C.) have been calculated from the formula; those in the third column (J.) have been read from a large curve plotted from the data of F. M. G. Johnson.[1]

TABLE IV.—DISSOCIATION PRESSURES OF NH_4I AT ROUNDED TEMPERATURES.

Temp.	Pressure. S. & C.	Pressure. J.	Temp.	Pressure. S. & C.	Pressure. J.
310	48.5	67	380	407.3	512
330	95.0	127	390	527.0	662
350	176.3	219	400	675.2	...
360	235.7	291	404.9	**760.0**	...
370	311.5	384	410	857.0	...

As seen from the table, and also from the curve (Fig. 3), the pressures found by Johnson are much higher than those found by us for the same temperatures. This difference is 18 mm. at 310° and 135 mm. at 390°. As stated above, the pressures given by Johnson probably include considerable partial pressures of hydrogen and iodine produced by the dissociation of hydrogen iodide, especially at the higher temperatures.

Ammonium Chloride.

Previous Determinations.—The dissociation pressures of ammonium chloride have been determined by a number of investigators but with

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[1] Since the pressure-temperature points of Johnson are rather irregular, we have smoothed the curve as indicated in the small figure in his dissertation (Breslau, 1908).

only fair agreement between the results. The spiral manometer, as used by F. M. G. Johnson,[1] has been described and discussed under ammonium bromide, above.

Ramsay and Young have measured the dissociation pressures by two widely different methods. In the dynamic method,[2] a thermometer was inserted into a hole bored in a block of solid ammonium chloride. Then the block, with the thermometer, was placed in a combustion tube heated to about 30° above the probable temperature of sublimation for ammonium chloride. The pressure in the combustion tube could be varied at will. When the thermometer reading became constant, it was considered that the surrounding solid was at the sublimation point for that particular pressure. In the static method[3] of Ramsay and Young, ammonium chloride was heated and the vapors confined over mercury. The hydrogen chloride produced in the dissociation reacted with the mercury at a rate which necessitated a rather large correction for the change of pressure with time. Another source of uncertainty lay in the slow diffusion of the mercury vapor into the vaporization chamber. The authors ascribe to thermometric errors the differences in the values found by the two methods. At the highest temperatures, this difference amounts to 100 mm.

Smith and Menzies[4] have determined the dissociation pressures of ammonium chloride by the dynamic isoteniscope, alkali nitrates being used as the confining liquid. The vapors acted chemically on the fused nitrates, and the production of a gas made impossible the adjustment of the pressure until the bubbling entirely ceased. Their experiments were intended especially to show the value of the isoteniscope even when used under unfavorable conditions.

The Present Measurements.—The measurements were repeated, partly for the purpose of using the *static* isoteniscope with this substance, partly because results covering a wider range of temperature were desired, and partly in order that the pressures and vapor densities (the latter to be determined subsequently) might be correlated by using identical samples of ammonium chloride and thermometers calibrated in exactly the same manner.

For most of the readings, the confining liquid here used was a fused mixture of silver chloride and ammonium chloride, in approximately equal parts by weight. This liquid froze at 290°. At 275°, the liquid employed was recrystallized bismuth; at 249°, it was Kahlbaum's tin. Oxidation of these metals was prevented by displacing the air in the appa-

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[1] *Z. physik. Chem.*, **61**, 458 (1908).

[2] Ramsay and Young, *Phil. Trans.*, **177**, 96 (1886). This method had been used previously by Horsmann, *Ber.*, **2**, 137 (1869).

[3] Ramsay and Young, *Phil. Trans.*, **177**, 86 (1886).

[4] THIS JOURNAL, **32**, 1457 (1910).

ratus at the beginning with illuminating gas. All pressures were read ten minutes after the "boiling out" had been stopped and were corrected to the time zero by subtracting the uniform increment of pressure found for succeeding ten-minute intervals. The correction factors averaged less than 1 mm.

The Results.—Table V contains: the observed pressures (Col. 1), those of series 2 being marked with an asterisk; the observed temperatures (Col. 2); the temperatures calculated (Col. 3) from the equation for the smoothed curve, $\log p = -1920.357/T + 9.778609 \log T - 21.21708$; and the differences (Δ) between observed and calculated temperatures (Col. 4). The vapor-pressure formula given above is based on the following points: 280°, 135.0 mm.; 312°, 362.4 mm.; 338°, 764.8 mm.

TABLE V.—DISSOCIATION PRESSURES OF NH_4Cl—OBSERVATIONS.

Press. Mm.	Temperature.			Press. Mm.	Temperature.		
	Obsd.	Calcd.	Δ.		Obsd.	Calcd.	Δ.
949.6	345.91	345.86	+0.05	422.9*	317.35	317.26	+0.09
949.5*	345.96	345.84	+0.12	326.7	308.45	308.53	—0.08
840.8	341.35	341.43	—0.08	325.8*	308.37	308.43	—0.06
826.7*	340.90	340.82	+0.08	238.5	298.16	298.15	+0.01
711.5*	335.41	335.43	—0.02	238.1*	298.11	298.08	+0.03
684.4	334.08	334.04	+0.04	114.2	275.00	274.85	+0.15
544.2	325.85	325.95	—0.10	113.8*	275.15	274.75	+0.40
546.6*	325.82	326.09	—0.27	49.5	248.46	249.99	
424.1	317.27	317.35	—0.08		Algebraic sum		+0.30

It will be seen that the differences between observed and calculated temperatures are greater than 0.1° for only five of the seventeen observations. At the lowest temperature there is a large deviation (1.53°) which corresponds to a pressure difference of 2.6 mm. Much more weight is here to be given to the calculated than to the observed temperature, since the tin, used as confining liquid at this one temperature only, reacted with the vapor. The dissociation pressures, for rounded temperatures, are tabulated below[1] (Table VI).

TABLE VI.—DISSOCIATION PRESSURES OF NH_4Cl AT ROUNDED TEMPERATURES.

Temp.	Press.	Temp.	Press.
250	49.5	320	458.1
270	97.5	330	610.6
280	135.0	337.8	**760.0**
290	185.3	340	808.2
300	252.5	345	927.6
310	341.3	350	1063.0

These results and those of other observers are plotted in Fig. 3. The prediction[2] that, on account of lack of time for the attainment of full dis-

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[1] For the dissociation pressures found, by other observers, for rounded temperatures, see Smith and Menzies, THIS JOURNAL, **32**, 1458 (1910).

[2] Smits and Scheffer, *Z. physik. Chem.*, **65**, 70 (1908).

sociation, pressures found by the dynamic method would be very much lower than those determined by the static method has not been realized. That the pressures by the dynamic methods would be slightly lower is obvious, since the substance, which is boiling slowly, must be cooled somewhat below the temperature of the surrounding bath. The pressures (dynamic) of Smith and Menzies[1] are, on the average, lower than are those found by us (static) by 7.5 mm.

Tetramethylammonium Chloride.

Previous Observations.—Practically nothing is known of the temperatures at which the tetraalkyl-ammonium salts sublime. This may be due to the fact that, before the submerged bulblet was described,[2] the organic chemist had no convenient method for the accurate determination of the boiling point of a non-fusing solid.

With regard to tetramethylammonium chloride, Lawson and Collie[3] state that it "decomposes above 360°," yielding trimethylamine and methyl chloride. The reaction is similar to that for the dissociation of an ammonium halide.

$$N(CH_3)_4Cl \rightleftarrows N(CH_3)_3 + CH_3Cl.$$

Wagner[4] says that tetramethylammonium chloride "begins to decompose at 230° and volatilizes rapidly at 280°." Our results show the equilibrium pressure at the lower of these temperatures to be nearly one atmosphere.

The Present Measurements.—The confining liquid was mercury, which had been carefully purified by spraying several times through dilute nitric acid and then distilling twice. During the period of 45 minutes, which was the average time required to obtain equilibrium, the mercury vapor was able to diffuse back to the surface of the subliming solid. Thus the total pressure observed was the sum of the partial pressures of mercury and of tetramethylammonium chloride. At each temperature, the corresponding vapor pressure of mercury has therefore been subtracted from the observed pressure. The pressure to be subtracted varied, according to the temperature, from 11.0 to 43.1 mm., and was obtained by linear interpolation from the final table of Smith and Menzies.[5]

The tetramethylammonium chloride was purified by recrystallization from alcohol. It was dried, for a day, at 100° and then pulverized.

A difficulty arose in the very slow rate at which the system solid–vapor reached equilibrium. At 245°, for example, the pressure reached only 182 mm. during the first hour, although the equilibrium pressure for this

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[1] Smith and Menzies' temperatures, based on the scale S. B. P. = 445.0° have been reduced, for the purpose of this comparison, to the scale S. B. P. = 444.7°.

[2] Smith and Menzies, THIS JOURNAL, 32, 897 (1910).

[3] *J. Chem. Soc.*, 53, 624 (1888).

[4] *Z. Krystall. Min.*, 43, 179 (1907).

[5] THIS JOURNAL, 32, 1447 (1910); *Ann. Physik*, [4] 33, 988.

temperature is more than 760 mm. Two methods of producing equilibrium in a shorter time present themselves: first, the use of a suitable catalyzer and, second, the heating of the substance to a high temperature in order to obtain a large pressure of the dissociation products and then cooling until recombination begins to occur. The second procedure[1] was adopted. It is illustrated by the following, typical set of readings which was obtained in one of the preliminary experiments:

Temp.	Press.	Δ P (per 10 min.) Mm.	Change.
228.7°	660.5	+11.0	Dissociation
228.2°	662.5	+ 2.6	Dissociation
227.8°	661.0	— 0.2	Combination
227.85°	661.0		Equilibrium

At lower temperatures the dissociation was even slower than in the foregoing example, and the individual readings are therefore probably less accurate than are those obtained with the simple halides. It is estimated, however, that the temperatures (absolute) read from the smoothed curve (Fig. 4) are accurate to less than ±0.4°.

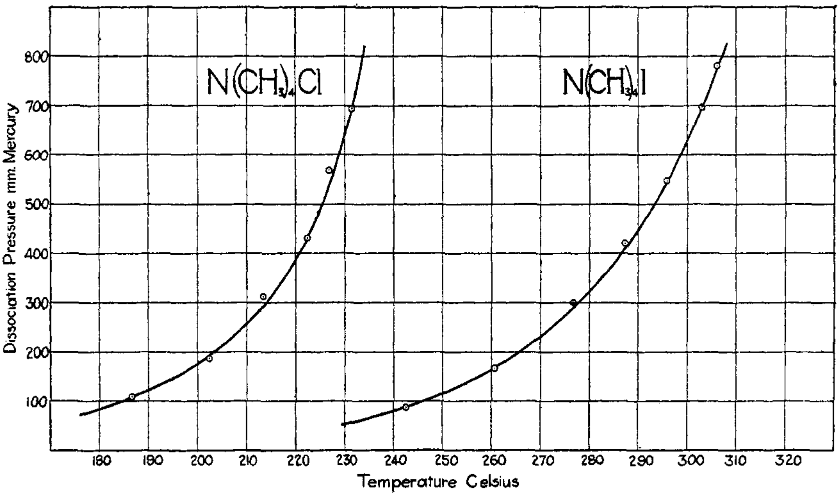

Fig. 4.

The Results.—Table VII shows, for each pressure, the temperature observed, the temperature calculated from the Kirchhoff-Rankin-Dupré formula, and the differences (Δ). The formula is based on the following points on the curve: 190°, 119.4 mm.; 220°, 398.0 mm.; 230°, 641.8 mm. The equation, with the constants introduced, is

$$\log p = 23649.7/T + 132.316 \log T - 401.3121.$$

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[1] This method has been used by us in earlier, unpublished experiments, on the dissociation of mercuric oxide. It has since been described by Taylor and Hulett, *J. Phys. Chem.*, 17, 571 (1913).

Table VII.—Dissociation Pressures of $N(CH_3)_4Cl$—Observations

Press.	Temperature.			Press.	Temperature.		
Mm.	Obsd.	Calcd.	Δ.	Mm.	Obsd.	Calcd.	Δ.
690	231.5	231.5	0.0	312	213.3	214.4	—1.1
567	227.1	227.4	—0.3	187	202.4	202.3	+0.1
430	222.5	221.6	+0.9	108	186.6	186.8	—0.2

The mean deviation of the observed points from the smooth curve represented by the equation is 0.4°. Readings from the curve (or calculations from the equation), relatively to one another, should therefore be accurate to within ±0.2°.

The equilibrium pressures, calculated from the formula, for rounded temperatures, are as follows:

Temp............	190°	200°	210°	220°	225°	230°	233.3°
Pressure (mm.)...	120	171	256	399	504	643	**760**

Tetramethylammonium Iodide.

Lawson and Collie[1] state that "decomposition" of tetramethylammonium iodide occurs "at a temperature not much short of a low red heat." According to Wagner,[2] "decomposition begins" at 230°.

The Present Measurements.—The dissociation pressures were determined by means of the static isoteniscope, with the eutectic mixture of the nitrates of sodium and potassium for confining liquid. The tetramethylammonium iodide was purified by recrystallization from water. Its vapors had no action on the molten nitrates.

The pressure in the isoteniscope, at each temperature, was found to rise at a very rapidly decreasing rate for a few minutes. Then the increase in pressure became slower and almost uniform. Thus, in a preliminary experiment, at 276.0°, the change in pressure with the time, after the boiling out process was stopped, was as follows:

Time (min.).......	0	5	10	15	20	25	50
Pressure (mm.)....	224.9	308.7	326.6	338.5	344.1	349.8	375.7
Δ P..............	...	83.8	17.9	11.9	5.6	5.7	5 × 5.2

The consideration of the time-pressure curve shows clearly that the rapid rise in the pressure for the first 15 minutes and the slower increase during the next 35 minutes cannot be due to the same cause. It seems certain also that the rapidity of the first change must be due to the dissociation into trimethylamine and methyl iodide.

$$N(CH_3)_4I \rightleftarrows N(CH_3)_3 + CH_3I$$

Then the methyl iodide, in turn, undergoes decomposition, a change observed by Lawson and Collie,[1] and confirmed by the darkening of the tetramethylammonium iodide and the walls of the isoteniscope

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[1] *Loc. cit.*

[2] *Z. Kryst. Min.*, 43, 180 (1907).

during measurement. That the confining liquid played no part in this decomposition was shown by substituting bismuth and various alloys for the nitrates. In each case the same results were obtained. Also, the darkening of the material and isoteniscope occurred in parts of the apparatus never reached by the confining liquid. Since we desired only the pressure of the undissociated molecules and of the primary dissociation products of the salt, we have corrected all pressures, read at the end of the period of rapid increase, back to the time when the "boiling out" was stopped. The method used is described in the section on ammonium bromide.

The Results.—The temperatures and corrected pressures were plotted, on a large scale, and a smoothed curve (see Fig. 4) was drawn to fit the observations. From three points on this curve (264°, 188 mm.; 290°, 455 mm.; 302°, 678 mm.) the following equation was derived:

$$\log p = 1493.085/T + 24.96449 \log T - 68.65910$$

The results are tabulated in the form already described.

TABLE VIII.—DISSOCIATION PRESSURES OF $N(CH_3)_4I$—OBSERVATIONS.

Press. Mm.	Temperature.		Δ.
	Obsd.	Calc.	
781	306.2	306.1	+0.1
698	303.0	302.8	+0.2
547	295.8	295.5	+0.3
421	287.4	287.7	—0.3
298	276.6	277.5	—0.9
166	260.6	260.6	0.0
88	242.6	242.3	+0.3

The following data show the pressures, calculated from the equation, for rounded temperatures:

Temp.	240°	260°	280°	290°	300°	305.5°	307°
Pressure (mm.)	81	164	325	455	635	760	799

Phosphonium Iodide.

Previous Observations.—Phosphonium iodide, when warmed gently, volatilizes rapidly and dissociates according to the equation:

$$PH_4I \text{ (solid)} \rightleftarrows PH_4I \text{ (gas)} \rightleftarrows PH_3 + HI.$$

F. M. G. Johnson[1] has measured the dissociation pressure at various temperatures, a fact which came to our attention only after our measurements were completed. A *stirred* water bath was used for heating the bulb containing the phosphonium iodide and the attached spiral manometer. Since the temperatures were all below 62°, the errors due to the mercury thermometer and to the shifting of the zero-point of the glass spiral were at a minimum. The chief sources of uncertainty which characterized

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[1] THIS JOURNAL, 34, 877 (1912).

Johnson's earlier vapor-pressure measurements (with the exception of the adsorbed gases), were thus eliminated. Our results are published, partly, to show the concordance in the values obtained by the isoteniscope and the spiral manometer when the necessary precautions are used in both cases. Confirmation of Johnson's work seems desirable, also, since his results lower the boiling point of phosphonium iodide from 80°, the commonly accepted value,[1] to 62°.

The Present Measurements.—The static isoteniscope was used, fractionated benzyl benzoate serving as the confining liquid. The fraction chosen had a vapor pressure of 718 mm. at 310°, 329 mm. at 280°, and 53 mm. at 220°. The curve connecting these points shows that, at 66°, benzyl benzoate would have a vapor pressure lower than that of mercury, which is negligible at this temperature.

As the result of some recent investigations, Holt and Meyers[2] have concluded that, in carefully dried phosphonium iodide vapor, there occurs a secondary reaction in which the hydrogen iodide and phosphine give some free hydrogen and phosphorus iodide. Such a change was indicated in our experiments by a slow, uniform increase in the pressure with the time. Correction has been made for this effect. Holt and Meyers state that phosphorus iodide is not formed if a trace of moisture is present. For this reason, perhaps, Johnson obtained no evidence of its formation. His method did not provide with certainty for the removal of the last trace of moisture (and foreign gases) from the spiral manometer and from the material in the vaporization chamber.

The Results.—The results obtained by us are tabulated below (Table IX).

TABLE IX.—DISSOCIATION PRESSURES OF PH_4I—OBSERVATIONS.

Series I.		Series II.	
Press. (Mm.).	Temp.	Press. (Mm.).	Temp.
914.0	65.92	922.1	66.22
795.0	63.47	798.3	63.52
662.8	60.13	667.7	60.08
532.6	56.06	533.2	56.19
401.2	51.29	408.7	51.46
301.0	46.69	301.9	46.58
195.3	39.82	196.0	39.78
109.0	30.63	118.1	31.01
39.3	16.08	40.9	16.98

The agreement between the values found by Johnson (J.) and those by us (S. & C.) is shown for rounded pressures in Table X (see also Fig. 5).

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[1] Abegg, "Handb. anorg. Chemie," Vol. III, Pt. 3, p. 398; Moissan, *Chim. Min.*, I, 758.

[2] *Z. anorg. Chem.*, **82**, 281 (1913).

TABLE X.—DISSOCIATION PRESSURES OF PH_4I—ROUNDED VALUES.

Dissoc. Press.	Temperature.		
	J.	S. & C.	Δ.
50	19.26	19.21	+0.05
100	29.33	28.92	+0.41
200	39.89	40.09	—0.20
300	46.40	46.55	—0.15
400	51.08	51.16	—0.08
500	54.94	55.02	—0.08
600	58.16	58.20	—0.04
700	60.73	61.10	—0.37
760	62.00	62.61	—0.61
800	...	63.56	...
900	...	65.68	...

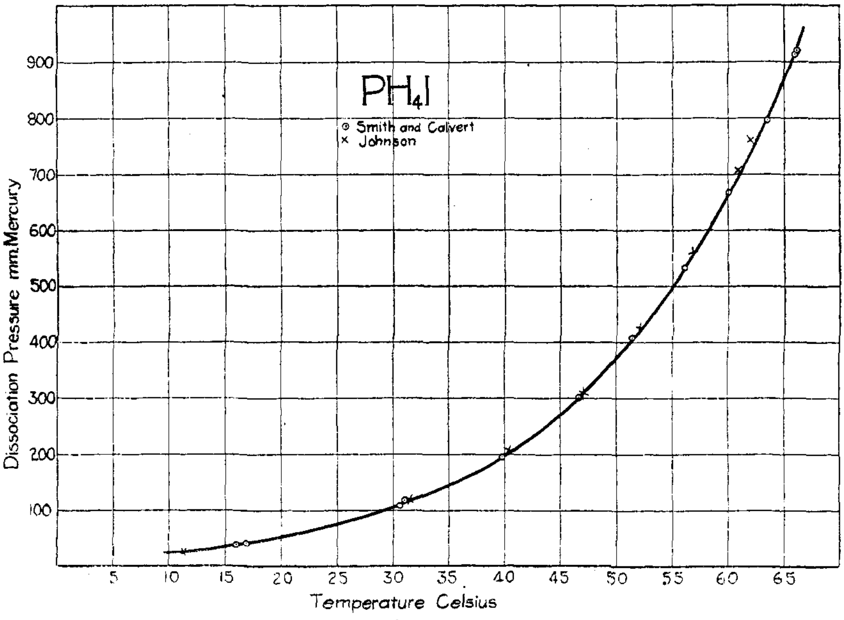

Fig. 5.

The dissociation pressures read for rounded temperatures, from our curve are:

Temp.	15°	30°	40°	50°	60°	62.6°	66°
Pressure (mm.)	36.0	107.8	199.0	368.1	660.0	**760.0**	917.5

Phosphorus Pentachloride.

Previous Observations.—Although there has been much work and discussion on the dissociation of the superheated vapor of phosphorus pentachloride, neither the pressure nor the density of the vapor in equilibrium with the solid phase has ever been determined. The sublimation point for phosphorus pentachloride, based on qualitative work of Casselmann,[1] is usually given as 140–148°. Recently, Prideaux,[2] by introducing a thermometer into vapor of phosphorus pentachloride, found the vapor to condense at a temperature of 160°. This he accepts as the lower limit for the sublimation point. The upper limit is the melting point, found by him to be 162°. Our work gives somewhat higher values for both the boiling and the melting point. This was to have been expected, since, in our experiments, the repeated fractionation expels the last traces of all volatile impurities.

The Present Measurements.—Since the chlorinating power of phosphorus pentachloride is extremely high, it was very difficult to find a suitable confining liquid. A fused mixture of saturated chlorides might be expected to have no action on the vapors. We were unable, however, to devise such a mixture, of melting point sufficiently low, that was not hygroscopic or that had no considerable vapor pressure of its own. Other liquids tried were the eutectic of silver and thallium nitrates (m. p. 67°), the eutectic of silver and potassium nitrates (m. p. 131°), purified mercury, sulfur, and paraffin. Paraffin, the least active, was chosen for the final experiments. The sample of paraffin used was freed from its more volatile constituents by heating at 200°, under a pressure of 20 mm. for an hour. It was then placed in the *dynamic* isoteniscope in which slow interaction between the vapor and confining liquid can be neglected.[3]

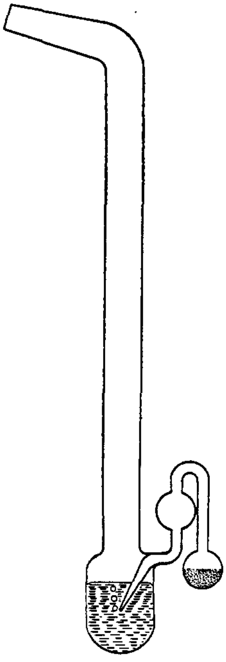
Fig. 6.—Dynamic isoteniscope.

The phosphorus pentachloride is contained in the small bulb to the right (Fig. 6). To obtain a reading, the pressure in the isoteniscope is lowered until the pentachloride sublimes rapidly, giving a rapid stream of bubbles through the paraffin. Then the pressure is raised until the point is reached at which the vigorous bubbling ceases. The pressure required to stop the sublimation is the vapor pressure for that particular temperature. The readings are not so accurate as are those taken with the static isoteniscope since bubbles of gas continue to be produced *slowly*, as a result of the interaction of the paraffin and phosphorus pentachloride. However, the bubbling due to boiling is so much more vigorous than that due to secondary chemical action that it is not difficult to determine, with fair accuracy (±5 mm.),

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[1] *Lieb. Ann.*, 83, 257 (1852).

[2] *J. Chem. Soc.*, 91, 1714 (1907).

[3] Smith and Menzies, THIS JOURNAL, 32, 1457 (1910).

when the former ceases. A small correction must be applied for the depth to which the tip is submerged below the surface of the paraffin and for capillarity in the tip.[1]

The sample of phosphorus pentachloride used was the product of a standard manufacturer. The impurities suspected were the trichloride (b. p. 76°) and oxychloride (b. p. 107–110°). These impurities were removed from the phosphorus pentachloride, after it had been placed in the bulb of the isoteniscope, by lowering the pressure to 30 mm. and keeping the temperature of the surrounding bath at 120° until over half of the sample had been volatilized. It may safely be assumed that, in this way, all the easily volatile impurities were driven out past the paraffin seal. This conclusion was confirmed by the fact that subsequent boiling out did not alter the pressure found at a given temperature. Nonvolatile impurities would have no effect on the vapor pressure, so long as any pure phosphorus pentachloride remained as solid phase.

The Results.—The results are tabulated in the usual form.

TABLE XI.— DISSOCIATION PRESSURES OF PCl_5—OBSERVATIONS.

	Temperature.		
Press. (Mm.).	Obsd.	From curve.	Δ.
31	98.08	98.13	—0.05
60	108.31	108.22	+0.09
158	126.10	125.96	+0.14
219	132.71	133.00	—0.29
347	143.68	144.02	—0.34
492	152.42	152.46	—0.04
608	157.63	157.69	—0.06
748	162.58	162.30	+0.28
915	166.89	(liquid)	...

The phosphorus pentachloride melted at a point just below the last temperature observed. As was to have been expected, the pressure (marked +, Fig. 7) of the liquid (915 mm. at 166.89°) fell considerably below the corresponding point on the smoothed curve for the vapor pressure of the solid (= 1.0°, equivalent to about 40 mm.).

The dissociation pressures for rounded temperatures are:

Temp..........	90°	120°	140°	150°	160°	162.8°	167°
Pressure (Mm.).	18	117	294	445	670	**760**	919(liq.)

The heats of vaporization for the various substances will be calculated after the degrees of dissociation have been determined.

Summary.

1. The dissociation pressures of seven substances have been determined for the following ranges of temperature and pressure: NH_4Br

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[1] For the simple method of finding the sum of these corrections, see Smith and Menzies, THIS JOURNAL, **32**, 1449 (1910).

(300°-403°; 35-935 mm.), NH_4I (310°-410°; 48-857 mm.), NH_4Cl (250°-350°; 50-1063 mm.), $N(CH_3)_4Cl$ (190°-233.3°; 120-760 mm.), $N(CH_3)_4I$ (240°-307°; 81-799 mm.), PH_4I (19.2-65.7°; 50-900 mm.), PCl_5(90-167°; 18-919 mm.).

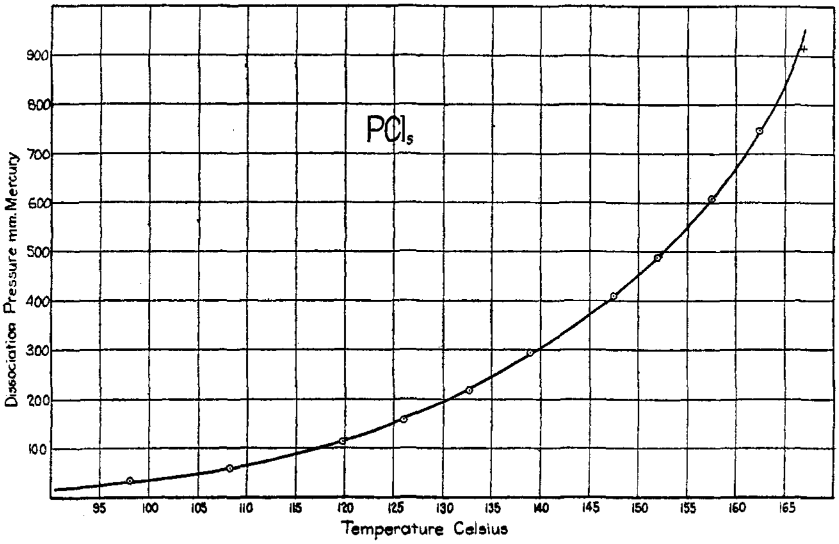

Fig. 7.

2. The measurements on PCl_5 were made with the dynamic isoteniscope; all the others with the static isoteniscope, by means of which the pressure may be determined to ±0.1 mm. A platinum resistance thermometer sensitive to ±0.1° was used.

3. The temperatures at which the various compounds were found to have a dissociation pressure of 760 mm. are: NH_4Br (394.6°), NH_4I (404.9°), NH_4Cl (337.8°), $N(CH_3)_4I$ (305.5°) PH_4I (62.6°), and PCl_5 (162.8°).

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK CITY.

POSITIVE IONS FROM NON-METALLIC ELEMENTS. I. A STUDY OF THE PRECIPITATION OF METALS FROM SOLUTIONS OF THEIR SALTS BY YELLOW PHOSPHORUS.

BY R. M. BIRD AND S. H. DIGGS.

Received April 23, 1914.

Introduction.

It has long been known that yellow phosphorus will precipitate certain metals (Pt, Au, Ag, Hg, Cu) from a solution of the salts of these metals. Berzelius made use of the fact that silver is completely precipitated from