[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY, No. 254.]

THE DENSITIES AND DEGREES OF DISSOCIATION OF THE SATURATED VAPOR OF PHOSPHORUS PENTACHLORIDE.

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The vapor densities of phosphorus pentachloride have been studied by Mitscherlich[1] (one observation) and by Cahours[2] at atmospheric pressure. Wurtz[3] and Troost and Hautefeuille[4] made measurements at reduced pressures, the former mixing the vapor with air for the purpose. Wurtz[5] also studied the effect of excess of phosphorus trichloride on the densities. All these results have been studied in an instructive manner by Willard Gibbs,[6] and the last set also by Wegscheider.[7] Recently Carl Holland,[8] working under Nernst, has published additional measurements which he uses to obtain a general formula and to calculate the heat of reaction. His observations and the results calculated by him from them, however, are not in harmony. Thus, from the first series of four observations, he deduces the following values for α, namely 0.214, 0.740, 0.850, 0.978. Our calculation from the same data shows that the values should be 0.243, 0.752, 0.855, 0.975. If the observed value of d (see below) in the first observation had been 494 instead of 464, the value 0.214 would have been correct. Again, Holland defines log K for acetic acid vapor as $\log \frac{[(\mathrm{CH_3COOH})_2]}{[\mathrm{CH_3COOH}]^2}$. The corresponding formula for the pentachloride is not given, and no particulars as to the units employed in expressing the concentrations for either substance are to be found in the paper. In the dissertation, however, for the loan of which we are indebted to the Librarian of Yale University, Holland states that for acetic acid $\mathrm{K} = \frac{(p-d)^2}{d\ \mathrm{RT}\ 760}$, where p is the observed pressure and d is the difference between the observed pressure and that which would have been exercised if, on cooling from a temperature at which dissociation was complete, only the laws of Boyle and Charles had been in operation and no combination had taken place. Hence d represents the partial pressure of the $\mathrm{PCl_5}$ molecules and $p-d$ the sum of the partial pressures of the two dissociation products. This formula is the inverse of the one

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[1] *Pogg. Ann.*, **29,** 221 (1833).

[2] *Compt. rend.*, **21,** 625 (1845); *Ann. chim. phys.*, [3] **20,** 369 (1847).

[3] *Compt. rend.*, **76,** 601 (1873).

[4] *Ibid.*, **83,** 977 (1876).

[5] *Ibid.*, **76,** 610 (1873).

[6] *Am. J. Sci. and Arts.*, [3] **18,** 381 (1879).

[7] *Monatshefte Chem.*, **20,** 307 (1899).

[8] *Z. Elektrochem.*, **18,** 235 (1912).

indicated in the paper. The values of log K given in Holland's table, however, are entirely different from those which we obtain by substituting his data in the above formula, after adapting it to the case of the pentachloride by substituting $\{(p - d)/2\}^2$ for $(p - d)^2$. Thus, taking the first set of four observations, and assuming $R = 0.0821$, we obtain for log K: $\bar{3}.22239$, $\bar{2}.67977$, $\bar{1}.02926$, $\bar{1}.91442$, while Holland gives the values $\bar{1}.91668$, $\bar{2}.44032$, $\bar{2}.09091$,[1] $\bar{4}.96885$. His values, indeed, diminish progressively while ours increase. Using $p - d$ as the numerator yields, naturally, no better correspondence. Employing the same formula inverted leaves the numbers still wholly discordant. With the formula $K = \frac{dRT}{\{(p - d)/2\}^2}$, which corresponds with the inverted form in the published paper, but omits the correction to atmospheres, we obtain from the same four sets of data the following values for log K: $\bar{1}.89680$, $\bar{2}.43942$, $\bar{2}.08993$, $\bar{3}.20477$. The first three results now agree fairly well with Holland's, but the fourth does not. If in calculating the fourth result we employ the temperature on the centigrade scale, 340° C. instead of 613° abs., we obtain log $K = \bar{4}.94879$, which is much closer to Holland's value. The remaining seven values of log K are all incorrect, but, being too great, cannot be explained in the same way as the fourth. The fifth should be 0.24661 instead of 0.47643. Here, if the value of p in the sixth observation, namely 1779.0 had been used by mistake instead of the value of d (1029.3) in the numerator only, the log K would become 0.48424, which is nearer to his value. Apparently this was the formula employed, although with some inconsistency, the basis of which we have not succeeded in determining. Employment of his incorrect values of α does not remove the inconsistency. Dr. Calvert and Professor C. M. Carson have both been kind enough to make the calculations independently and their results agree with ours.

In the dissertation (p. 25) Holland states that the eleven sets of data given were chosen from a large number, and were selected on account of the fact that they were very consistent. The confusion in his figures raises the question whether, after all, he did make the best selection, as well as the question whether it is ever advisable to publish only those results which appear to be favorable. It is worth noticing also that the temperatures, which reach as high as 358°, were determined with a mercury thermometer. There are also numerous misprints (Gay-Cassac for Gay-Lussac, 462° abs. for 465° abs., etc.). Then, too, the same symbol is used for different things and different symbols for the same thing. Thus, on p. 24, in line 1, he employs p for the total observed pressure while in line 5 it is equivalent to the partial pressure of the associated molecules. Again, on p. 23, line 2 from below, he defines P as the pressure calculated for no

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[1] In the published paper, this value is given as $\bar{1}.09091$.

reaction—that is, no association on cooling. But on the same page, he gives the formula $K = \frac{4P(\delta - \Delta)^2}{(2\Delta - \delta)\delta}$, which is correct only if P is the total observed pressure (one of the senses in which p was employed). He also gives $K^1 = \frac{Px^2}{1 - x^2}$, where x is a misprint for α used in the table, and the formula is correct only provided P is the total observed pressure.

All the published observations mentioned above refer to the unsaturated vapor. The present measurements concern the saturated vapor, in equilibrium with the solid phase.

The Apparatus.—The bath and thermometer were the same as in the study of the ammonium halides,[1] except that paraffin was used as the bath-liquid. The bulb was modified. The phosphorus pentachloride was placed in bulb A (Fig. 1). The bottom of this bulb was blown very thin to facilitate subsequent breaking. After being filled, the neck was drawn out to a capillary, about half of the substance was distilled out, and the capillary was sealed at B. This distillation removed impurities, such as the trichloride and oxychloride of phosphorus, chlorine, and phosphorus, which might have been present. The charged bulb was then cleaned and enclosed in the bulb C, and the latter was attached at N to the vapor density bulb D. The drying tube E contained soda-lime and phosphorus pentoxide. The apparatus, with the exception of the part containing the drying agents, was then warmed with a Bunsen flame to drive off moisture adhering to the inner surface of the glass. When cold,

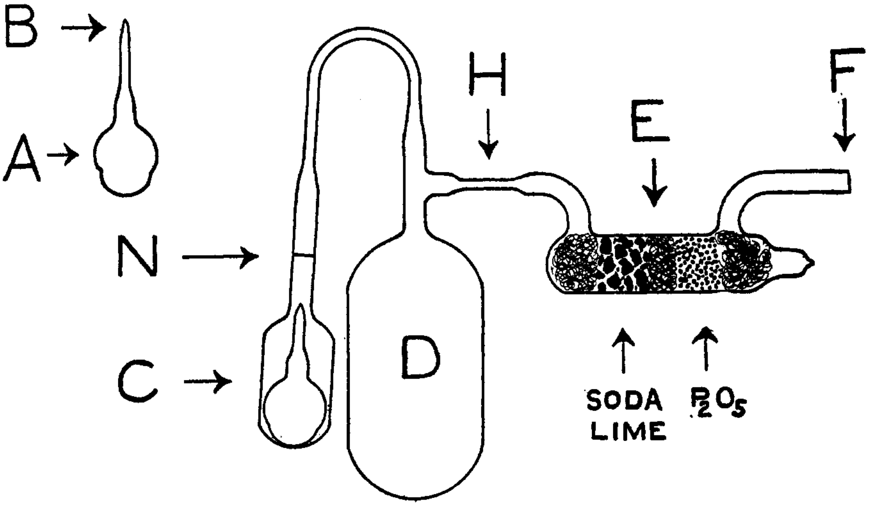

Fig. 1.—Vapor Density Bulb.

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[1] Smith and Lombard, This Journal, 37, 38 (1915).

it was sealed at F. After lying in this condition twenty-four hours, the bulb containing the pentachloride was broken by shaking the apparatus. The tube was then opened at F, sealed at that point on to the pump, evacuated to 0.1 mm., and finally sealed off from the pump at H. The heating and pentoxide ensured the absence of moisture when the pentachloride bulb was broken, and the pentoxide prevented access of moisture while the bulb was being sealed to the pump. The soda-lime was used to prevent chlorine or hydrogen chloride from entering the pump.

TABLE I.—DENSITIES OF PCl_5 VAPOR (SATURATED)—DATA.

	G. PCl_5 in large bulb.	Vol. cc. large bulb.	Vapor dens. G. per cc.	Deviation from mean.	Vapor dens. Moles per L.
90°	0.0117	59.29	0.000197	00	0.000945
	0.0145	73.74	0.000196	− 1	0.000942
	0.0126	61.76	0.000204	+ 7	0.000980
	0.0135	70.66	0.000190	− 7	0.000914
Average vapor density.........			0.000197	± 2, or ± 1.0%	0.000945
100°	0.0279	84.08	0.000332	00	0.00159
	0.0293	87.06	0.000337	+ 5	0.00162
	0.0245	74.08	0.000331	− 1	0.00159
	0.0236	73.72	0.000320	− 12	0.00154
	0.0283	83.87	0.000338	+ 6	0.00162
Average vapor density.........			0.000332	±2, or 0.6%	0.00159
110°	0.0320	55.86	0.000573	+ 4	0.00275
	0.0490	87.06	0.000563	− 6	0.00270
	0.0485	85.19	0.000569	00	0.00273
	0.0420	73.72	0.000570	+ 1	0.00274
Average vapor density.........			0.000569	± 1, or 0.2%	0.00273
120°	0.0575	61.67	0.000933	+ 4	0.00448
	0.0603	65.07	0.000927	− 2	0.00445
	0.0781	84.29	0.000927	− 2	0.00445
	0.0589	63.50	0.000928	00	0.00446
Average vapor density.........			0.00929	±0.5, or ±0.1%	0.00446
140°	0.1737	74.39	0.002335	+ 59	0.01121
	0.1484	63.59	0.002333	+ 47	0.01120
	0.1658	77.91	0.002129	−157	0.01022
	0.1617	68.88	0.002348	+ 62	0.01127
Average vapor density.........			0.002286	±41, or ± 1.8%	0.01098
150°	0.2874	84.55	0.003399	− 49	0.01632
	0.3021	87.02	0.003471	+ 23	0.01666
	0.2473	70.93	0.003487	+ 39	0.01674
	0.2547	73.83	0.003450	+ 2	0.01656
	0.2550	74.27	0.003433	− 15	0.01648
Average vapor density.........			0.003448	± 12, or ±0.35%	0.01655
160°	0.3110	65.24	0.004767	−166	0.02288
	0.4029	81.00	0.004974	+ 41	0.02388
	0.4264	84.28	0.005059	+126	0.02429
Average vapor density.........			0.004933	±64, or ± 1.3%	0.02368

The Data.—As the vapor pressure of phosphorus pentachloride reaches 760 mm. at 162.8°, the measurements extended from 160° down to 90°. Since immersion in the bath for 45 and 25 minutes at 100° gave identical results, the period of immersion was 25 minutes at all the other temperatures. The weight of phosphorus pentachloride in the large bulb (Col. 2) was determined by precipitating the chlorine as silver chloride. The method of calculating the results was the same as that used by us in the case of the ammonium halides.[1]

In Table II the results are summarized. The dissociation pressures (Col. 7) are those determined by Smith and Calvert,[2] and the values at

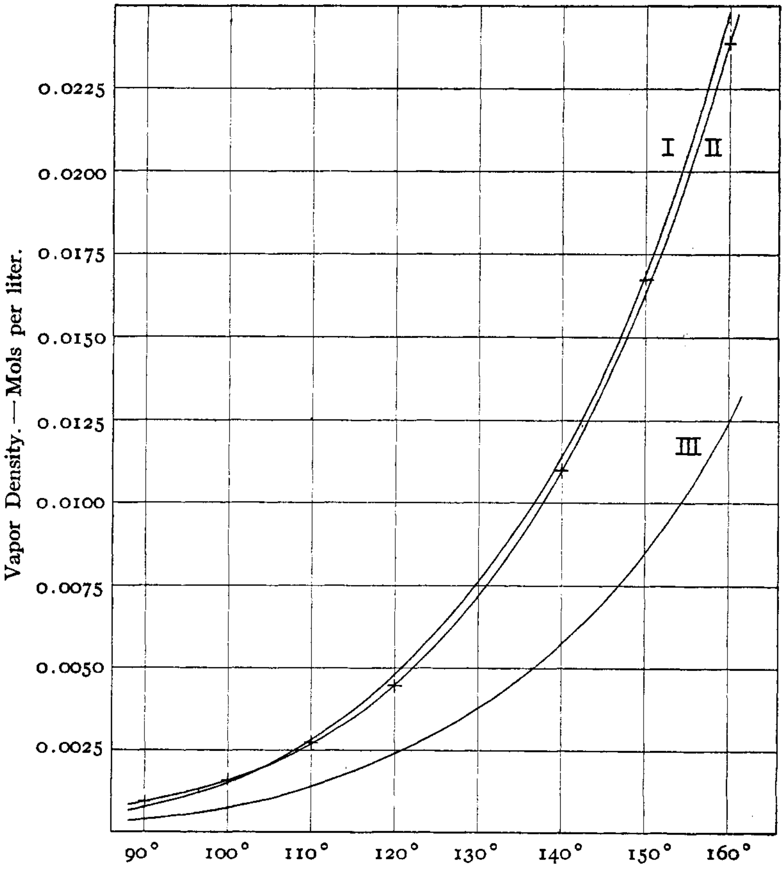

Fig. 2.—Density of Saturated Phosphorus Pentachloride Vapor. Curve I: Undissociated (calculated). Curve II: Observed. Curve III: Completely Dissociated (calculated).

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[1] *Loc. cit.*

[2] THIS JOURNAL, 36, 1363 (1914).

90° and 100° are correct ±3 mm. and at the higher temperatures ± 5 mm. For the purpose of comparison, the densities which the vapor would possess if it were undissociated (Col. 5) and completely dissociated (Col. 6), and yet exercised the measured dissociation pressures, are given. To show the relationship between the observed vapor densities and those calculated for no dissociation and for complete dissociation the values are plotted in Fig. 2. It will be seen that the curve of observed values lies close to that calculated for the densities of the undissociated substance. Above 100° the curves are practically parallel, showing that the effect of higher temperatures in increasing the degree of dissociation is almost exactly counterbalanced by the effect of the higher dissociation pressures in inhibiting dissociation.

TABLE II.—DENSITIES OF PCl_5 VAPOR (SATURATED)—SUMMARY.

Temp.		Vapor density.				Dissoc. press.
		Observed (Δ).		Calculated.		
C.	Abs.	G. per cc.	Mols per L.	Undissoc. Mols per L.	Compl. dissoc. Mols per L.	Mm.
90	363	0.000197	0.000945	0.000795	0.000398	18
100	373	0.000332	0.00159	0.001505	0.000753	35
110	383	0.000569	0.00273	0.00281	0.00140	67
120	393	0.000929	0.00446	0.00477	0.00239	117
130	403	....	....	0.00760	0.00380	191
140	413	0.002286	0.01098	0.01142	0.00571	294
150	423	0.003448	0.01655	0.01688	0.00844	445
160	433	0.004933	0.02368	0.02481	0.01241	670

The percentage dissociation of the saturated vapors, calculated from the data in Table II, is given in Table III.

TABLE III.—PCl_5, PERCENTAGE DISSOCIATED—α.

Temp.	90°.	100°.	110°.	120°.	130°.	140°.	150°.	160°.
Percentage...	apparently assoc.	apparently assoc.	2.8	7.1	...	4.0	2.0	4.8

Even if we assume an error of —3 mm. in the dissociation pressure at 90°, and use the maximum value, 21 mm., the vapor density of the undissociated substance would be 0.000927 moles per liter, or slightly less than the value found. There appears therefore to be a slight degree of association at 90° and possibly at 100°.

On account of the form of the relation between the density and the value of α, a very slight error in the former produces a large divergence in the latter. The results, therefore, although irregular, are not inconsistent with the estimated accuracy of the measurements, involving a limit of error of from 0.1 to 1.8%.

General Formula for the Dissociation Pressures.—A Kirchoff-Rankin-Dupré equation for the dissociation pressures, based on three points (160°, 670 mm; 140°, 294 mm; 108.2°, 60 mm.) was computed: $\log P = -6724.22/T - 19.1978 \log T + 68.9701$, This formula represents the pressures up to 160° with a divergence of not more than 5 mm. (see Table IV).

TABLE IV.—OBSERVED AND CALCULATED PRESSURES—PCl_5.

Temp.	Pressure. S. & C.	Pressure. Calc.	Pressure. Diff.	Temp.	Pressure. S. & C.	Pressure. Calc.	Pressure. Diff.
90.0	18	20	+2	140.0	294	294	....
98.1	31	33	+2	150.0	445	450	+ 5
108.2	60	60	...	157.7	608	612	+ 4
120.0	117	113	—4	160.0	670	670	..
133.0	219	214	—5	162.8	760	745	—15

Latent Heat of Vaporization.—With the assistance of the above equation, the molar latent heat of vaporization was calculated by the method used in the case of the ammonium halides. The Clausius-Clapeyron equation, with the values inserted, is as follows:

$$L = T\frac{P}{760}\left[\frac{6724}{0.4343\,T^2} - \frac{19.20}{T}\right]\frac{0.02419}{\Delta m}\text{ Kg. cal.}$$

The molar heats of vaporization are given in Table V.

TABLE V.—LATENT HEATS OF VAPORIZATION (Kg. cal. per mol).

Temp.	90°.	100°.	110°.	120°.	140°.	150°.	160°.
Lat. heat..........................	14.2	15.6	16.6	16.9	15.6	14.9	14.9

Average value 15.5 ±0.28, or ±1.8%.

The observed values of the degrees of dissociation were too small and too irregular to permit of the calculation of the heat of dissociation. It is evident, however, that the value is negative, *i. e.*, heat is absorbed by the dissociation of the saturated vapor.

Note on the Previous Results with Ammonium Iodide.—It will be recalled that below 345° the vapor of this substance was found to be in part associated and above 345° but little dissociated. That no secondary reaction was responsible for this result was shown by the fact that when the bulbs were opened under water, no permanent gas, such as nitrogen or hydrogen, was found.[1] A colleague has suggested that a soluble gas, such as hydrogen iodide or ammonia might have been present. Although it is not clear to us how this could have occurred, without the simultaneous presence of an insoluble gas, nevertheless it seemed worth while to settle the question by a decisive experiment. Two vapor density-bulbs (60–75 cc. capacity, with attached small bulb), similar to those used in the published experiments, were used. Ammonium iodide was placed in the small bulb. After evacuation and sealing, they were kept for 30 minutes, one at 330°, and the other at 340°. To avoid the risk of cracking, they were removed from the bath without being sealed apart. When opened under mercury, they filled up at once and only a small bubble of gas (estimated by comparison with a buret to be not over 0.3 cc.) remained.

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[1] *Loc. cit.*, p. 107.

This was undoubtedly the air not originally removed by the pump and absorbed air liberated from the surface of the salt and of the glass by the heating. The original conclusion, that ammonium iodide in the state of saturated vapor is in part associated, is therefore undoubtedly correct.

Summary.

1. The vapor densities of the saturated vapor of phosphorus pentachloride were determined from 90° to 160°.
2. The degrees of dissociation calculated from the vapor densities show that the saturated vapor is somewhat associated at 90°, and dissociated to an approximately constant extent of about 4% from 110° to 160°.
3. The latent heat of vaporization was calculated to be 15.5 Kg. cal. per mol.
4. A note on the case of ammonium iodide, previously investigated, is appended.

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NOTES.

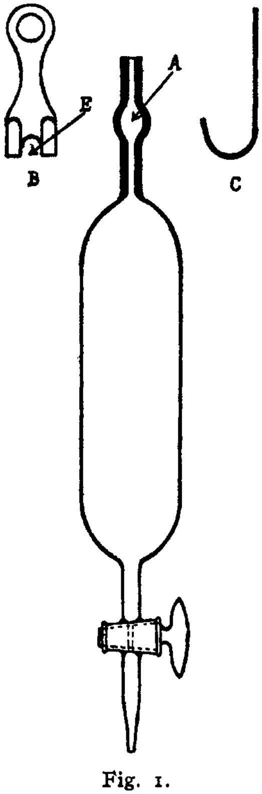

Fig. 1.

A Convenient Weighing Pipet.—Recent work of the author has made necessary the extensive use of a weighing pipet. One of the type suggested by Mertes[1] was first adopted, but was found to have the following disadvantages:

1. It is inconvenient to fill and difficult to clean.
2. The necessary size of the tubing for the neck, to permit of its being hung on the balance, makes the larger sizes too fragile.

To remove these defects the form shown in Fig. 1 was devised. It consists essentially of an ordinary pipet body fitted with a stopcock at the bottom, and a short neck of thick-walled narrow glass tubing with a bulb, A, blown in it. The purpose of this latter is two-fold: first, to serve as an overflow bulb when filling, and second, to serve as a means of support by preventing the neck from slipping through the supporting hook B, which hangs from the balance arm. The supporting hook is made out of some sheet metal, such as brass, about one millimeter thick. Two elevations of the latter, front B, and side C, are shown. The slot E is cut slightly wider than the diameter of the

[1] *J. Ind. Eng. Chem.*, 7, 236 (1915).