ART. XLIII.—*On the Vapor-Densities of Peroxide of Nitrogen, Formic Acid, Acetic Acid, and Perchloride of Phosphorus;* by J. WILLARD GIBBS.

[Continued from page 293.]

*Acetic acid.*—For this substance the densities have been calculated by the formula

$$\log \frac{2{\cdot}073\,(\mathrm{D} - 2{\cdot}073)}{(4{\cdot}146 - \mathrm{D})^2} = \frac{3520}{t_c + 273} + \log p - 11{\cdot}349, \qquad (12)$$

the constants 3520 and 11·349 being derived from the determinations of Cahours and Bineau, which with those of Horstmann and Troost are given in Table IV. The experiments of Cahours and Horstmann were made under atmospheric pressure, those of Horstmann* by the method of Bunsen, those of Cahours presumably by the method of Dumas. The numbers in the first column of the densities observed by Cahours are taken from the twentieth volume (1845) of the Comptes Rendus, except a few cases, distinguished by parentheses, which are taken from the preceding volume (1844). The numbers in the second column are taken from his Leçons de chimie générale élémentaire, 1856. These numbers seem to be based in part

* Lieb. Ann., Suppl. VI, p. 65.

## TABLE IV.—ACETIC ACID.

Experiments of CAHOURS,—HORSTMANN,—BINEAU,—TROOST.

| Temperature. | Pressure. | Density calc. by eq. (12). | Density observed. Cahours. C. R. | Cahours. Legons. | Horstmann. | Excess of observed density. Cahours. C. R. | Cahours. Legons. | Horstmann. |
|---|---|---|---|---|---|---|---|---|
| 338 | (760) | 2·077 | 2·08 | | | ·00 | | |
| 336 | (760) | 2·077 | | 2·082 | | | +·005 | |
| 327 | (760) | 2·078 | 2·08 | 2·085 | | ·00 | +·007 | |
| 321 | (760) | 2·079 | 2·08 | 2·083 | | ·00 | +·004 | |
| 308 | (760) | 2·081 | | 2·085 | | | +·004 | |
| 300 | (760) | 2·082 | 2·08 | | | ·00 | | |
| 295 | (760) | 2·084 | | 2·083 | | | −·001 | |
| 280 | (760) | 2·089 | 2·08 | | | −·01 | | |
| 272 | (760) | 2·093 | | 2·088 | | | −·005 | |
| 254·6 | 747·2 | 2·105 | | | 2·135 | | | +·030 |
| 252 | (760) | 2·108 | | 2·090 | | | −·018 | |
| 250 | (760) | 2·111 | 2·08 | | | −·03 | | |
| 240 | (760) | 2·122 | | 2·090 | | | −·032 | |
| 233·5 | 752·8 | 2·132 | | | 2·195 | | | +·063 |
| 231 | (760) | 2·137 | (2 12) | 2·101 | | (−·02) | −·036 | |
| 230 | (760) | 2·139 | 2·09 | | | −·05 | | |
| 219 | (760) | 2·165 | 2·17 | 2·132 | | +·01 | −·033 | |
| 200 | (760) | 2·239 | 2·22 | 2·248 | | −·02 | +·009 | |
| 190 | (760) | 2·298 | 2·30 | 2·378 | | ·00 | +·080 | |
| 181·7 | 749·7 | 2·359 | | | 2·419 | | | +·060 |
| 180 | (760) | 2·376 | | 2·438 | | | +·062 | |
| 171 | (760) | 2·466 | 2·42 | | | −·05 | | |
| 170 | (760) | 2·477 | | 2·480 | | | +·003 | |
| 165·0 | 754·1 | 2·534 | | | 2·647 | | | +·113 |
| 162 | (760) | 2·575 | | 2·583 | | | +·008 | |
| 160·3 | 751·6 | 2·594 | | | 2·649 | | | +·055 |
| 160 | (760) | 2·601 | 2·48 | | | −·12 | | |
| 152 | (760) | 2·716 | (2·72) | 2·727 | | (·00) | +·011 | |
| 150 | (760) | 2·747 | 2·75 | | | ·00 | | |
| 145 | (760) | 2·826 | (2·75) | | | (−·08) | | |
| 140 | (760) | 2·910 | 2·90 | 2·907 | | −·01 | −·003 | |
| 134·3 | 748·8 | 3·001 | | | 3·108 | | | +·107 |
| 131·3 | 754·1 | 3·055 | | | 3·070 | | | +·015 |
| 130 | (760) | 3·082 | 3·12 | 3·105 | | +·04 | +·023 | |
| 128·6 | 752·9 | 3·103 | | | 3·079 | | | −·024 |
| 125 | (760) | 3·168 | 3·20 | | | +·03 | | |
| 124 | (760) | 3·185 | | 3·194 | | | +·009 | |
| | | | Bineau. | | Troost. | Bineau. | | Troost. |
| 132 | 757 | 3·05 | (2·86) | | | (−·19) | | |
| 130 | 59·7 | 2·31 | | | 2·12 | | | −·19 |
| 130 | 30·6 | 2·21 | | | 2·10 | | | −·11 |
| 129 | 633 | 3·03 | (2·88) | | | (−·15) | | |
| 36·5 | 11·32 | 3·63 | 3·62 | | | −·01 | | |
| 35·0 | 11·19 | 3·65 | 3·64 | | | −·01 | | |
| 30·0 | 6·03 | 3·61 | 3·60 | | | −·01 | | |
| 28·0 | 10·03 | 3·75 | 3·75 | | | ·00 | | |
| 24·0 | 5·75 | 3·71 | 3·70 | | | −·01 | | |
| 22·0 | 8·64 | 3·82 | 3·85 | | | +·03 | | |
| 22 | 2·70 | 3·59 | 3·56 | | | −·03 | | |
| 21·0 | 4·06 | 3·70 | 3·72 | | | +·02 | | |
| 20·5 | 10·03 | 3·86 | 3·95 | | | +·09 | | |
| 20·0 | 8·55 | 3·84 | 3·88 | | | +·04 | | |
| 20·0 | 5·56 | 3·77 | 3·77 | | | ·00 | | |
| 19·0 | 4·00 | 3·73 | 3·75 | | | +·02 | | |
| 19 | 2·60 | 3·65 | 3·66 | | | +·01 | | |
| 12·0 | 5·23 | 3·88 | 3·92 | | | +·04 | | |
| 12 | 2·44 | 3·77 | 3·80 | | | +·03 | | |
| 11·5 | 3·76 | 3·84 | 3·88 | | | +·04 | | |

upon new experiments and in part upon a revision of the observations recorded in the Comptes Rendus, the calculations being carried out to another figure of decimals. They are therefore entitled to a greater weight than the numbers of the preceding column.

The agreement of the formula with the numbers given in the Leçons de chimie is very good, the greatest divergences being ·080 at 190° and ·062 at 180°. But at 190° the table in the Comptes Rendus agrees precisely with the formula, and at 171° (the next experiment) it shows a divergence in the opposite direction. The next divergences in the order of magnitude are −·033, −·036, −·032 at 219°, 231°, 240°, respectively. Here the table in the Comptes Rendus agrees substantially with that of the Lecons, but the experiments of Horstmann show a divergence to the opposite direction. In fact, the three columns of observed densities nowhere agree in the direction of their divergence from the formula.

The somewhat decided differences between the results of Horstmann and those of Cahours may be due in part to the different methods of observation, especially to the entirely different manner of applying the heat and measuring the temperature. But the higher values obtained by Horstmann cannot be accounted for by too short an exposure to the source of heat, for his experiments were made with decreasing temperatures.

The determination of Bineau are taken from the same sources as those on formic acid, the earlier determinations being distinguished as before by parentheses. One of these (at 132°) was made by the method of Dumas, the other by that of Gay-Lussac. The smallness of the observed densities appears due to the presence of water. (An acidimetric test gave 295 parts of acid in 306.) The other experiments were made with the same apparatus which was used with formic acid and show even greater regularity in their results than the experiments with that substance. Only in one case is the influence of proximity to saturation seen, viz., at 20·5° and 10·03$^{mm}$, the pressure of saturated vapor at this temperature being about 12·7$^{mm}$.* In the remaining fifteen observations of this series, notwithstanding the very low pressures employed (from 2·44 to 11·32), the greatest difference between the observations and the formula is ·04, and the average difference ·02.

The two observations by Troost† were made by the method of Dumas, but at pressures very low for this method. The results obtained differ considerably from the formula, but not so much as in the case of his experiments at low pressure with peroxide of nitrogen.

* This number is obtained from data given by Bineau by the same kind of interpolation which was used for formic acid.

† Comptes Rendus, vol. lxxxvi (1878). p. 1395.

Table V contains the experiments of Naumann* on acetic acid. These consist of ten series (distinguished by the letters

TABLE V.—ACETIC ACID.

Experiments of NAUMANN.

| | | TEMPERATURE. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 78° | 100° | 110° | 120° | 130° | 140° | 150° | 160° | 185° |
| A | Pressure. | | 393·5 | 411 | 432 | 455 | 477 | 498·5 | | 565 |
| | D. calc. | | 3·39 | 3·23 | 3·06 | 2·90 | 2·75 | 2·61 | | 2·28 |
| | D. obs. | | 3·44 | 3·31 | 3·14 | 2·97 | 2·82 | 2·68 | | 2·36 |
| | Exc. of D. obs. | | +·05 | +·08 | +·08 | +·07 | +·07 | +·07 | | +·08 |
| B | Pressure. | | 342·3 | 359·3 | 377·5 | 398·5 | 417·5 | 436·5 | | 495 |
| | D. calc. | | 3·35 | 3·18 | 3·02 | 2·85 | 2·70 | 2·57 | | 2·26 |
| | D. obs. | | 3·37 | 3·22 | 3·06 | 2·89 | 2·75 | 2·63 | | 2·31 |
| | Exc. of D. obs. | | +·02 | +·04 | +·04 | +·04 | +·05 | +·06 | | +·05 |
| C | Pressure. | | 258 | | | | | | | 382 |
| | D. calc. | | 3·26 | | | | | | | 2·22 |
| | D. obs. | | 3·17 | | | | | | | 2·25 |
| | Exc. of D. obs. | | −·09 | | | | | | | + 03 |
| D | Pressure. | | 232 | | 252 | 274 | 287·5 | 300 | | 335 |
| | D. calc. | | 3·23 | | 2·87 | 2·72 | 2·58 | 2·46 | | 2·21 |
| | D. obs. | | 3·12 | | 2·94 | 2·68 | 2·54 | 2·44 | | 2·23 |
| | Exc. of D. obs. | | −·11 | | +·07 | −·04 | −·04 | −·02 | | +·02 |
| E | Pressure. | 164 | 186 | 197 | 209 | 221 | 232 | 243 | 253 | 269 |
| | D. calc. | 3·53 | 3·15 | 2·97 | 2·81 | 2·65 | 2·52 | 2·41 | 2·32 | 2·18 |
| | D. obs. | 3·41 | 3·06 | 2·91 | 2·75 | 2·61 | 2·50 | 2·40 | 2·31 | 2·22 |
| | Exc. of D. obs. | −·12 | −·09 | −·06 | −·06 | −·04 | −·02 | −·01 | −·01 | +·04 |
| F | Pressure. | 149 | 168 | | | 201 | | | | |
| | D. calc. | 3·50 | 3·12 | | | 2·62 | | | | |
| | D. obs. | 3·34 | 3·01 | | | 2·56 | | | | |
| | Exc. of D. obs. | −·16 | −·11 | | | −·06 | | | | |
| G | Pressure. | 137 | 156 | 166·5 | 180 | 188 | 199 | 208·2 | | 230 |
| | D. calc. | 3·48 | 3·09 | 2·92 | 2·75 | 2·60 | 2·47 | 2·37 | | 2·17 |
| | D. obs. | 3·26 | 2·98 | 2·81 | 2·61 | 2·50 | 2·40 | 2·29 | | 2·14 |
| | Exc. of D. obs. | −·22 | −·11 | −·11 | −·14 | −·10 | −·07 | −·08 | | −·03 |
| H | Pressure. | 113 | 130 | 138·5 | 149 | 157·5 | 168·2 | 175 | | 191·5 |
| | D. calc. | 3·42 | 3·03 | 2·85 | 2·69 | 2·55 | 2·43 | 2·33 | | 2·15 |
| | D. obs. | 3·25 | 2·94 | 2·78 | 2·60 | 2·47 | 2·32 | 2·26 | | 2·13 |
| | Exc. of D. obs. | −·17 | −·09 | −·07 | −·09 | −·08 | −·11 | −·07 | | −·02 |
| J | Pressure. | 80 | 92 | 98·5 | 106 | 112·5 | 117·3 | | 129·2 | |
| | D. calc. | 3·32 | 2·91 | 2·73 | 2·58 | 2·45 | 2·35 | | 2·21 | |
| | D. obs. | 3·06 | 2·76 | 2·61 | 2·46 | 2·34 | 2·27 | | 2·11 | |
| | Exc. of D. obs. | −·26 | −·15 | −·12 | −·12 | −·11 | −·08 | | −·10 | |
| K | Pressure. | 66 | 77·7 | 84 | 89·5 | 93 | 98 | 103 | | 110·5 |
| | D. calc. | 3·26 | 2·85 | 2·68 | 2·53 | 2·40 | 2·31 | 2·24 | | 2·12 |
| | D. obs. | 3·04 | 2·66 | 2·49 | 2·37 | 2·32 | 2·24 | 2·16 | | 2·11 |
| | Exc. of D. obs. | −·22 | −·19 | −·19 | −·16 | −·08 | −·07 | −·08 | | −·01 |

A, B, C, etc.) of observations by Hoffmann's method.† The temperatures of the observations in the different series are for

* Lieb. Ann., vol. clv, S. 325.

† This is a modification of the method of Gay-Lussac, in which the heat is supplied by a vapor bath.

the most part the same, so that for each temperature we have observations through a wide range of pressures. Within each compartment of the table are given in order the pressure of an experiment, the density calculated by equation (12), the observed density, and the excess of observed density, the temperature of the experiment being given at the head of the column. These experiments, taken by themselves, seem to show an effect of pressure upon the density about one third greater than is indicated by the formula. But the divergences (of which the greatest is ·26 and the average ·085), are not large in view of the fact that the experiments were undertaken rather with the desire of obtaining a great number of observations with moderate labor, than with the intention of attaining the greatest possible accuracy.

The quantity of acid diminishes somewhat regularly from ·2084 grams in series A to ·0185 in series K. The volume, which was 154$^{cc}$ in the experiment at 185° in series A, diminishes in the successive series, and in the same series with diminishing temperature, to 69·6$^{cc}$ in the experiment at 78° in series K. It is worthy of notice that the greatest deviations from the formula occur where the liability to error is most serious with respect to pressure (which was measured without a cathetometer), to volume, and to the quantity of acid.

Far more serious than the absolute amount of these divergences, is the regularity which they exhibit. But it must be remembered that the observations are by no means entirely independent, and many sources of possible error, such as the calibration of the tube and the determination of the quantity of acid, might affect the results with considerable regularity.

Only to a slight degree can the divergences from the formula be accounted for by an insufficient exposure to the temperature of the experiment. The observations, except those at 78°, were made with increasing temperatures, and the greatest divergences from the formula are not in the positive direction. Yet the positive divergences occur where we should most expect to find them, if they were due to this cause, viz., in the series in which the greatest quantities of acid were used, and in cases in which the temperature seems to have been raised at once an unusual number of degrees. (See especially the observation at 120° in series D, and in general the observations at 185°, which exhibit if not a positive at least a diminution of negative excess.) In the observations at 78°, which were the last of each series, and therefore followed a fall of temperature from 185°, we find in some cases, especially in series G, H, and J, a negative divergence much greater than in the other determinations of the same series, and which appears to be referable to this circumstance.

In Table VI are exhibited the results of experiments by Playfair and Wanklyn,* in which the vapor of the acid was diluted with hydrogen or, in a single case (the experiment at 95·5°), by air. Columns I and II of the observed densities relate each to a series of observations by the method of Gay-Lussac, column III contains four independent determinations by the method of Dumas. The numbers in the column of pressures are, as in other similar cases, the partial pressures obtained by subtracting from the total pressure (which was never very much less than that of the atmosphere) that which would be exerted by the hydrogen or air alone.

TABLE VI.—ACETIC ACID.

Experiments of PLAYFAIR and WANKLYN.

| Temperature. | Pressure. | Density calc. by eq. (12). | Density observed. | | | Excess of observed density. | | |
|---|---|---|---|---|---|---|---|---|
| | | | I. | II. | III. | I. | II. | III. |
| 212·5 | 322·8 | 2·124 | | 2·060 | | | −·064 | |
| 194 | 326·0 | 2·168 | | 2·055 | | | −·113 | |
| 186 | 254·4 | 2·173 | 1·936 | | | −·237 | | |
| 182 | 319·4 | 2·213 | | 2·108 | | | −·105 | |
| 166·5 | 289·5 | 2·293 | | 2·350 | | | +·057 | |
| 163 | 245·8 | 2·290 | 2·017 | | | −·273 | | |
| 132 | 227·5 | 2·628 | 2·292 | | | −·336 | | |
| 130·5 | 285·7 | 2·729 | | 2·426 | | | −·303 | |
| 119 | 269·0 | 2·914 | | 2·623 | | | −·291 | |
| 116·5 | 211·3 | 2·876 | 2·371 | | | −·505 | | |
| 95·5 | (123·8) | 3·105 | | | 2·594 | | | −·511 |
| 86·5 | (200·4) | 3·432 | | | 3·172 | | | −·260 |
| 79·9 | (83·3) | 3·297 | | | 3·340 | | | +·043 |
| 62·5 | (46·2) | 3·473 | | | 3·950 | | | +·477 |

The first observation of the first series gives the density 1·936, which is doubtless too small, since it is much less than the theoretical limit 2·073. Since the greater part of the measurements from which this number was calculated, were also used in reducing the other observations of the series, the error probably affects the other observations, and in a somewhat increased degree. This will account only for a part of the difference between the observations and the formula. The remaining part of the differences in this series, and the somewhat smaller differences in the next, may be due to the fact that the experiments of both series were conducted with descending temperatures. Yet the experiments of the third column, which were made by Dumas' method, do not exhibit any preponderance of positive values for the excess of observed density, but rather the opposite.

On the whole, these experiments furnish no decisive indication of any influence of the hydrogen or air upon the vapor.

* Trans. Roy. Soc. Edinb., vol. xxii, p. 455.

They may be thought to corroborate slightly the tendency observed in the experiments of Naumann and Troost toward lower densities than the formula gives at very low pressures. Yet where the experiments of Naumann show the greatest deficiency in observed density (at 78° and 80$^{mm}$), an experiment of Playfair and Wanklyn, at almost precisely the same temperature and pressure, gives a trifling excess of observed density, and at a little lower temperature and pressure, where we should expect from the experiments of Naumann that the deficiency would be still greater, an experiment of Playfair and Wanklyn shows a great excess of density.

By combining the experiments of Cahours, Naumann and Troost, we may obtain observations of density at 130° for a very wide range of pressures. For one atmosphere, we may regard the formula as coinciding with the average of the numbers given by Cahours. For pressures between three-quarters and one-half of an atmosphere the experiments of Naumann show an excess of density; at pressures below half an atmosphere the experiments both of Naumann and of Troost show a deficiency of density as compared with the formula. For an indefinite diminution of pressure, there can be little doubt that the real density, like the value given by the formula, approaches the theoretical value 2·073. The greatest excess in the numbers obtained by experiment is ·07; the greatest deficiency is ·19, which occurs at 59·7$^{mm}$; the next in order of magnitude is ·11, which occurs more than once. These discrepancies are certainly such as may be accounted for by errors of observation. They do not appear to be greater than we might expect on the hypothesis of the entire correctness of the formula. On the other hand, the agreement is greater than we should expect, if we reject the theory on which the formula was obtained. It is about such as we might expect in a suitable formula of interpolation with three constants, which have been determined by the values of the density for one atmosphere, for half an atmosphere, and for infinitesimal pressures. But we must regard the actual formula, in its application to this single temperature, as having only two constants, of which one is determined so as to make the formula give the theoretical value for infinitesimal pressures, and the other so as to make it agree with the experiments of Cahours at the pressure of one atmosphere.

An entirely different method has been employed by Horstmann* to determine the vapor-density of this substance. A current of dried air is forced through the liquid acid, which is heated to promote evaporation, and the mixture of air and vapor is

* Berichte der deutschen chemischen Gesellschaft, Jahrg. iii (1870), S. 78; and Jahrg. xi (1878), S. 1287.

cooled to any desired temperature, with deposition of the excess of acid, by passing upward through a spiral tube in a suitable bath. The acid is then separated from the air, and the quantity of each determined. It is assumed that the air is exactly saturated with vapor on leaving the coil, and that it has the temperature of the bath. If we know the pressure of saturated vapor for that temperature, and assume the validity of Dalton's law, it is easy to calculate the density of the vapor. For the pressure of the air is found by subtracting the pressure of the vapor from the total pressure, (the experiments were so conducted that this was the same as the actual pressure of the atmosphere,) and the ratio of the weights of the acid and the air obtained by analysis, divided by the ratio of their pressures, will give the ratio of their densities. The pressures of saturated vapor employed by Horstmann are those given by Landolt,* and differ greatly from the determinations of Regnault, in some cases being nearly twice as great,—a difference noticed but not explained by Landolt, who however gives determinations (previously unpublished) of Wüllner, which somewhat exceed his own. (On the other hand, the observations of Bineau substantially agree with those of Regnault.)

If we compare the observations of Horstmann with the values given by equation (12), on the basis of Landolt's pressures, we find a very marked disagreement, as may be seen by the following numbers, which relate to the highest temperatures of Horstmann's experiments, where the disagreement is least.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Temperature | 63·1 | 62·9 | 59·9 | 51·1 | 49·0 | 48·7 | 44·6 | 41·4 |
| Pressure (Land.) | 110·0 | 109·2 | 97·0 | 69·0 | 63·4 | 63·0 | 53·1 | 46·6 |
| Density calc. eq. (12) | 3·67 | 3·67 | 3·69 | 3·75 | 3·77 | 3·77 | 3·79 | 3·81 |
| Density obs. | 3·19 | 3·11 | 3·12 | 3·16 | 2·89 | 2·98 | 2·75 | 2·62 |

It will be observed that while the values obtained from equation (12) increase with diminishing temperatures, the values obtained from Horstmann's experiments diminish. This diminution continues as far as the experiments go, until finally at 12° or 15° the densities are only one half as great as those obtained by Bineau, by direct experiment at the same temperatures and at somewhat less pressures, in a series of observations which bear every mark of a very exceptional precision. (Compare Tables VII and IV.) The explanation of this disagreement is doubtless to be found in the values of the pressures employed in the calculations, and it will be interesting to see how the results may be modified by the adoption of different pressures.

In determinations of the pressure of saturated vapors, too great values are so much more easily accounted for than errors in the opposite direction, especially when the pressures are small, that especial interest attaches to the lowest figures which

* Lieb. Ann., Suppl. vi (1868), p. 157.

are supported by a competent authority. The experiments of Regnault* were made with three different preparations of acetic acid, of which the second was once, and the third twice, purified by distillation over anhydrous phosphoric acid. Each distillation considerably diminished the pressure of the saturated vapor, the effect of the second distillation being about half that of the first. The numbers obtained with the third preparation are given in the following table with their logarithms, and the differences of the logarithms for one degree of temperature.

| Temperature. | Pressure. | log. pressure. | diff. per 1°. |
|---|---|---|---|
| 9·71 | 6·42 | ·8075 | |
| | | | ·0239 |
| 12·12 | 7·33 | .8651 | |
| | | | ·0272 |
| 14·33 | 8·42 | ·9253 | |
| | | | ·0161 |
| 14·87 | 8·59 | ·9340 | |
| | | | ·0252 |
| 17·23 | 9·85 | ·9934 | |
| | | | ·0251 |
| 19·84 | 11·455 | 1·0590 | |
| | | | ·0237 |
| 22·37 | 13·15 | 1·1189 | |
| | | | ·0232 |
| 25·28 | 15·36 | 1·1864 | |

The uniformity of the numbers in the last column shows the remarkable precision of the determinations. At the same time it is evident that the differences in these numbers are due principally to the errors of observation, so that numbers obtained by interpolation between the logarithms of the observed pressures will be somewhat better (on account of averaging of the errors) than the original determinations.

The values obtained by such an interpolation have been used for the comparison of Horstmann's experiments with the formula (12) which is given in table VII. Unfortunately this comparison cannot be extended above 25°, which is the limit of Regnault's experiments. The first three columns of the table give the temperatures of Horstmann's experiments, the pressures corresponding to these temperatures according to the determinations of Landolt, and the density deduced from Horstmann's experiments by the use of these pressures. To these columns, which are taken from Horstmann's paper, are added the pressure derived from Regnault's observations by the logarithmic interpolation described above, the density calculated by equation (12) from these pressures and the temperatures of the first column, and the densities obtained by combining Horstmann's experiments with Regnault's pressures. This column is derived from the second, third and fourth, as follows. If $w$ and W denote respectively the weights of vapor and of air which pass through the apparatus in the same time, P the height of the barometer, and $p_L$ the pressure of saturated vapor as determined by Landolt, the densities obtained on the basis of Landolt's pressures, and given in the third column, are

* Mém. Acad. Sciences, vol. xxvi, p. 758. The experiments date from 1844.

evidently represented by $\frac{w(P-p_L)}{Wp_L}$. The numbers of the fifth column, which are represented in the same way by $\frac{w(P-p_R)}{Wp_R}$, where $p_R$ denotes the pressure as determined by Regnault's experiments, have been calculated by the present writer by multiplying the numbers of the third column by $\frac{p_L(P-p_R)}{p_R(P-p_L)}$.

TABLE VII.—ACETIC ACID.

Determinations of Vapor-density by Distillation.

| Temperature. | Pressure acc. to Landolt. | Density observed, Horstmann and Landolt. | Pressure acc. to Regnault. | Density calc. from Regnault's pressures by eq. (12). | Density observed, Horstmann & Regnault. | Excess of observed density. I. | Excess of observed density. II. |
|---|---|---|---|---|---|---|---|
| 25·0 | 23·5 | 2·42 | 15·13 | 3·86 | 3·80 | —·06 | |
| 23·8 | 22·4 | 2·23 | 14·19 | 3·86 | 3·56 | | —·30 |
| 22·6 | 21·6 | 2·29 | 13·31 | 3·87 | 3·76 | —·11 | |
| 21·5 | 20·4 | 2·24 | 12·54 | 3·87 | 3·68 | —·19 | |
| 20·4 | 19·2 | 2·05 | 11·81 | 3·88 | 3·37 | | —·51 |
| 20·2 | 19·0 | 2·28 | 11·68 | 3·88 | 3·75 | —·13 | |
| 20·0 | 18·9 | 2·13 | 11·56 | 3·88 | 3·52 | | —·36 |
| 17·4 | 16·8 | 2·09 | 9·95 | 3·89 | 3·56 | —·33 | |
| 15·6 | 15·6 | 1·98 | 8·96 | 3·90 | 3·48 | —·42 | |
| 15·3 | 15·3 | 1·95 | 8·81 | 3·90 | 3·42 | | —·48 |
| 15·3 | 15·3 | 1·85 | 8·81 | 3·90 | 3·24 | | —·66 |
| 14·7 | 15·1 | 1·78 | 8·54 | 3·91 | 3·18 | —·73 | |
| 12·7 | 13·7 | 1·96 | 7·60 | 3·91 | 3·56 | —·35 | |
| 12·4 | 13·5 | 1·89 | 7·46 | 3·92 | 3·45 | —·47 | |

As the height of the barometer in Horstmann's experiments is not given, it has been necessary to assume P=760. The inaccuracy due to this circumstance is evidently trifling. The last two columns of the table, which relate to different series of experiments by Horstmann (a distinction not observed in other parts of the table), give the excess of the densities thus obtained from Horstmann's and Regnault's experiments above the values calculated from equation (12) with the use of Regnault's determinations of pressure.

The densities obtained by experiment are without exception less than those obtained from equation (12). At the highest temperatures, where the liability to error is the least, both in respect to the measurement of the pressure of saturated vapor and in respect to the analysis of the product of distillation, the results of experiment are most uniform, and most nearly approach the numbers required by the formula. At the lowest temperatures, the greatest observed density is about one-eleventh less than that required by the formula, the difference being about the same as between the highest and lowest observed values for the same temperature.

Since each successive purification of the substance employed by Regnault diminished the pressure of its vapor, it is not improbable that the pressures might have been still farther diminished by farther purification of the substance. The pressures which we have used are therefore liable to the suspicion of being too high, and it is quite possible that more accurate values of the pressure would still farther reduce the deficiency of observed density.

*Perchloride of phosphorus.*—For this substance, we have at atmospheric pressure a single determination of vapor-density by Mitscherlich,* and a series of determinations by Cahours;† at lower pressures we have determinations by Wurtz‡ and by Troost and Hautefeuille.§ In the experiments of Wurtz the

TABLE VIII.—PERCHLORIDE OF PHOSPHORUS.

Experiments of MITSCHERLICH, CAHOURS, WURTZ, and TROOST and HAUTEFEUILLE.

| Temperature. | Pressure. | Density calc. by eq. (13). | Density observed. Mitsch. | Density observed. Cahours. | Excess of observed density. Mitsch. | Excess of observed density. Cahours. |
|---|---|---|---|---|---|---|
| 336 | (760) | 3·610 | | 3·656 | | +·046 |
| 327 | 754 | 3·614 | | 3·656 | | +·042 |
| 300 | 765 | 3·637 | | 3·654 | | +·017 |
| 289 | (760) | 3·656 | | 3·69 | | +·034 |
| 288 | 763 | 3·659 | | 3·67 | | +·011 |
| 274 | 755 | 3·701 | | 3·84 | | +·139 |
| 250 | 751 | 3·862 | | 3·991 | | +·129 |
| 230 | 746 | 4·159 | | 4·302 | | +·142 |
| 222 | 753 | 4·344 | 4·85 | | +·506 | |
| 208 | (760) | 4·752 | | 4·73 | | —·021 |
| 200 | 758 | 5·018 | | 4·851 | | —·167 |
| 190 | 758 | 5·368 | | 4·987 | | —·381 |
| 182 | 757 | 5·646 | | 5·078 | | —·568 |
| | | | Wurtz. | T. & H. | Wurtz. | T. & H. |
| 178·5 | 227·2 | 5·053 | | 5·150 | | +·097 |
| 175·8 | 253·7 | 5·223 | | 5·235 | | +·012 |
| 167·6 | 221·8 | 5·456 | | 5·415 | | —·041 |
| 154·7 | 221 | 5·926 | | 5·619 | | —·307 |
| 150·1 | 225 | 6·086 | | 5·886 | | —·200 |
| 148·6 | 244 | 6·169 | | 5·964 | | —·205 |
| 145 | 391 | 6·45 | 6·55 | | +·10 | |
| 145 | 311 | 6·37 | 6·70 | | +·33 | |
| 145 | 307 | 6·36 | 6·33 | | —·03 | |
| 144·7 | 247 | 6·287 | | 6·14 | | —·147 |
| 137 | 281 | 6·53 | 6·48 | | —·05 | |
| 137 | 269 | 6·51 | 6·54 | | +·03 | |
| 137 | 243 | 6·48 | 6.46 | | —·02 | |
| 137 | 234 | 6·47 | 6·42 | | —·05 | |
| 137 | 148 | 6·31 | 6·47 | | +·16 | |
| 129 | 191 | 6·59 | 6·18 | | —·41 | |
| 129 | 170 | 6·56 | 6·63 | | +·07 | |
| 129 | 165 | 6·55 | 6·31 | | —·24 | |

* Pogg. Ann., vol. xxix (1833), p. 221.

† Comptes Rendus, vol. xxi (1845), p. 625; and Annales de Chimie et de Physique, Ser. 3, vol. xx (1847), p. 369.

‡ Comptes Rendus, vol. lxxvi (1873), p. 601. § Ibid., vol. lxxxiii (1876), p. 977.

pressure was reduced by mixing the vapor with air. In Table VIII all these determinations are compared with the formula

$$\log \frac{3{\cdot}6\,(\mathrm{D}-3{\cdot}6)}{(7{\cdot}2-\mathrm{D})^2} = \frac{5441}{t_C+273} + \log p - 14{\cdot}353. \qquad (13)$$

The differences between the calculated and observed values are often large, in six cases exceeding ·30; but they exhibit in general that irregularity which is characteristic of errors of observation. We should expect large errors in the observed densities, on account of the difficulty of obtaining the substance in a state of purity, and because the large value of the density renders it very sensitive to the effect of impurities which diminish the density,—also because the specific heat of the vapor is great, as shown by the numerator of the fraction in the second member of (13),* and because the density varies very rapidly with the temperature as seen by the numbers in the third column of Table VIII.

But at the two lowest temperatures of Cahours' experiments, the differences of the observed and calculated densities (·381 and ·568) are not only great, but exhibit, in connection with the adjacent numbers, a regularity which suggests a very different law from that of the formula. In fact, the densities obtained by Cahours at atmospheric pressure and those obtained by Troost and Hautefeuille at pressures a little less than one-third of an atmosphere seem to form a continuous series, notwithstanding the abrupt change of pressure. Yet it is difficult to admit that the density is independent of the pressure. So radical a difference between the behavior of this substance and that of the others which we have been considering requires unequivocal evidence. Now it is worthy of notice that the experiment at 182°, in which the greatest discrepancy is seen, is not given in the first record of the experiments, which was in the Comptes Rendus in 1845. It is given in the Annales de Chimie et de Physique in 1847, where it is called the first experiment. (The experiment at 336° is also omitted in the Comptes Rendus and that at 208° in the Annales,—otherwise the lists are the same.) If it was the first experiment in point of time, which is apparently the meaning, it was made before the publication in the Comptes Rendus, and we can only account for its omission by supposing that it was a preliminary experiment, in which its distinguished author did not feel sufficient confidence to include it at first with his other determinations, although he afterwards concluded to insert it. If we reject this observation as doubtful, the disagreement between the formula and observation, appears to be within the limits of possible

* Compare Trans. Conn. Acad., vol. iii, p. 243, and pp. 286, 287 of this volume.

error, but additional experiments will be necessary to confirm the formula.*

Experiments have also been made by M. Wurtz in which the vapor of the perchloride of phosphorus was diluted with that of the protochloride.† These experiments may be used to test equation (8), which, when the values of its constants are determined by equation (13), reduces to the form

$$\log \frac{p_5}{p_2 p_3} = \frac{5441}{t_C + 273} - 13{\cdot}751, \tag{14}$$

where $p_5$, $p_2$, and $p_3$ denote the partial pressures due respectively to the $PCl_5$, the $Cl_2$, and the $PCl_3$, existing as such in the gas-mixture. Since these quantities cannot be the subjects of immediate observation, a farther transformation of the equation will be convenient. Let $M_3$, $M_2$ denote the quantities of the protochloride and of chlorine of which the mixture may be formed, and $P_3$, $P_2$ the pressure which would belong to each of these if existing by itself with the same volume and temperature. These quantities will be connected by the equations

$$P_2 = \frac{kt\,M_2}{2{\cdot}22\,v}, \qquad P_3 = \frac{kt\,M_3}{4{\cdot}98\,v}, \tag{15}$$

where $k$ denotes the same constant as on page 286. From the evident relations

$$P_2 = p_2 + p_5, \qquad P_3 = p_3 + p_5, \qquad p = p_2 + p_3 + p_5,$$

we obtain

$$p_5 = P_2 + P_3 - p, \qquad p_2 = p - P_3, \qquad p_3 = p - P_2;$$

and by substitution of these values in equation (14),

$$\log \frac{P_2 + P_3 - p}{(p - P_2)(p - P_3)} = \frac{5441}{t_3 + 273} - 13{\cdot}751. \tag{16}$$

In view of the relations (15), this may be regarded as an equation between the pressure, the temperature, the volume, and the quantities of protochloride of phosphorus and chlorine into which the gas-mixture is resolvable.

It is in this form that we shall apply the equation to the experiments of M. Wurtz, the results of which are exhibited in Table IX. The first column gives the number distinguishing each experiment in the original memoir; the second, the temperature; the third the observed pressure ($p$) of the mixture

* Additional experiments on the density of this vapor have been made by M. Cahours, concerning which he says in 1866: "Les déterminations qui je viens d'effectuer à 170 et 172 degrés (ce corps bout vers 160 à 165 degrés) m'ont donné des nombres qui, bien que notablement plus forts que ceux que j'ai obtenus antérieurement à 182 et 185 degrés, sont encore bien éloignés de celui que correspond à 4 volumes." Comptes Rendus, t. 63, p. 16. So far as the present writer has been able to ascertain, these determinations have not been published. The formula gives 6·025 for 170° and 5·973 for 172°, at atmospheric pressure. The number corresponding to four volumes is 7·20.

† Comptes Rendus, vol. lxxvi (1873), p. 601.

of $PCl_5$, $PCl_3$, and $Cl_2$, which is the barometric pressure corrected for the small quantity of air remaining in the flask; the fourth, the pressure $\pi$ due to the *possible perchloride*, found by subtracting the pressure due to the excess of protochloride (this pressure is calculated from the theoretical density of the protochloride) from the total pressure; the fifth, the density $\delta$ of the possible perchloride calculated from its pressure $\pi$ with the temperature and volume. The numbers of these five

TABLE IX.—PERCHLORIDE AND PROTOCHLORIDE OF PHOSPHORUS.

Experiments on the mixed vapors by WURTZ.

| No. of exp. | $t_C$ | $p$ (obs.) | $\pi$ | $\delta$ | $P_2$ | $P_3$ | $p$ calc. by eq. (16). | Excess of obs. value of $p$. |
|---|---|---|---|---|---|---|---|---|
| XII | 173·29 | 756·1 | 423 | 6·68 | 392·4 | 725·5 | 760·7 | −4·6 |
| X | 165·4 | 748·4 | 413 | 6·80 | 390·1 | 725·5 | 747·9 | + ·5 |
| VII | 176·24 | 751·0 | 411 | 6·88 | 392·7 | 732·7 | 773·1 | −22·1 |
| VIII | 169·35 | 724·1 | 394 | 7·16 | 391·8 | 721·9 | 750·5 | −26·4 |
| V | 175·26 | 743·3 | 343 | 7·03 | 334·9 | 735·2 | 764·4 | −21·1 |
| II | 164·9 | 758·5 | 338 | 7·38 | 346·4 | 766·9 | 782·9 | −24·4 |
| XI | 175·75 | 760·0 | 318 | 7·00 | 309·2 | 751·2 | 776·8 | −16·8 |
| IV | 175·26 | 756·3 | 271 | 7·06 | 265·7 | 751·0 | 770·9 | −14·6 |
| IX | 160·47 | 753·5 | 214 | 7·44 | 221·1 | 760·6 | 766·8 | −13·3 |
| I | 165·4 | 760·0 | 194 | 7·25 | 195·3 | 761·3 | 768·5 | − 8·5 |
| VI | 170·34 | 751·2 | 174 | 8·30 | 200·6 | 777·8 | 787·6 | −36·4 |
| III | 174·28 | 742·7 | 168 | 7·74 | 180·6 | 755·3 | 766·5 | −23·8 |

columns are taken from the memoir cited, except that the correction of the barometric pressures has been applied by the present writer in accordance with the data furnished in that memoir. The two next columns contain the values of $P_2$ and $P_3$. These would naturally be calculated from $M_2$ and $M_3$ by equations (15). But since the values of $M_2$ and $M_3$ have not been given explicitly, those of $P_2$ and $P_3$ have been calculated from the recorded values of $\pi$ and $\delta$. Since the weight of the *possible perchloride* is $\frac{7\cdot2}{2\cdot22} M_2$, we have

$$\delta = \frac{7\cdot2\, M_2\, k\, t}{2\cdot22\, v\, \pi} = \frac{7\cdot2}{\pi} P_3.$$

Moreover,

$$p - \pi = P_3 - P_2,$$

since both members of the equation express the pressure due to the excess of the protochloride. The values of $P_2$ and $P_3$ were obtained by these equations.

The eighth column of the table gives the values of $p$ calculated from the preceding values of $t_C$, $P_2$, and $P_3$, by equation (16); and the last column, the difference of the observed and calculated values of $p$. The average difference is $18^{mm}$, or a little more than two per cent, the observed pressure being

almost uniformly less than the calculated value. This deficiency of pressure is doubtless to be accounted for by a fact which MM. Troost and Hautefeuille have noticed in this connection. The protochloride of phosphorus deviates quite appreciably from the laws of Mariotte, Gay-Lussac, and Avogadro, the product of the volume and pressure of a given quantity of vapor at 180° and the pressure of one atmosphere being 1·548 per cent less than at the same temperature and the pressure of one-half an atmosphere.* Now we may assume as a general rule that when the product of volume and pressure of a gas is slightly less than the theoretical number (calculated by the laws of Mariotte, Gay-Lussac, and Avogadro) the difference for any same temperature is nearly proportional to the pressure.† It is therefore probable that between 160° and 180°, at pressures of about one atmosphere, the product of volume and pressure for protochloride of phosphorus is somewhat more than three per cent less than the theoretical number. The experiments of Wurtz, as exhibited in Table IX, show that the pressure, and therefore the product of volume and pressure, (we may evidently give the volume any constant value as unity,) in a mixture consisting principally of the protochloride is on the average a little more than two per cent less than is demanded by theory, the differences being greater when the proportion of the protochloride is greater. The deviation from the calculated values is therefore in the same direction and about such in quantity as we should expect.‡

M. Wurtz has remarked that the average value of $\delta$ (the density of the *possible perchloride*) is nearly identical with the theoretical density of the perchloride, and appears inclined to attribute the variations from this value to the errors of experiment. Yet it appears very distinctly in Table IX, in which the experiments are arranged according to the value of $\pi$ (the pressure due to the *possible perchloride*), that $\delta$ increases as $\pi$ diminishes. The experiments of MM. Troost and Hautefeuille show that the coincidence remarked by M. Wurtz is due to the fact that on the average in these experiments the deficiency of the density of the possible perchloride (compared with the

* Troost and Hautefeuille, Comptes Rendus, vol. lxxxiii (1876), p. 334.

† Andrews, "On the Gaseous State of Matter." Phil. Trans., vol. clxvi (1876), p. 447.

‡ The deviation of the protochloride of phosphorus from the laws of ideal gases shows the imposibility of any *very close* agreement between such equations as have been deduced in this paper and the results of experiment in the case of gas-mixtures in which this substance is one of the components. With respect to the question whether future experiments on the vapor of the perchloride (alone, or with an excess of chlorine or of the protochloride). will reduce the disagreement between the calculated and observed values to such magnitudes as occur in the case of the protochloride alone, it would be rash to attempt to anticipate the result of experiment.

theoretical value) is counterbalanced by the excess of density of the protochloride. When $\pi > 400$, the effect of the deficiency in the density of the possible perchloride distinctly preponderates; when $\pi < 250$, the effect of the excess of density in the protochloride distinctly preponderates. But the magnitude of the differences concerned is not such as to invalidate the general conclusion established by the experiments of M. Wurtz, that the dissociation of the perchloride may be prevented (at least approximately) by mixing it with a large quantity of the protochloride.

*Table for facilitating calculation.*—The numerical solution of equations (10), (11), (12) and (13) for given values of $t$ and $p$ may be facilitated by the use of a table. If we set

$$\Delta = \frac{D}{D_1}, \tag{17}$$

$$L = \log \frac{1000\, D_1 (D - D_1)}{(2D_1 - D)^2} = \log \frac{1000\, (\Delta - 1)}{(2 - \Delta)^2}, \tag{18}$$

we have for peroxide of nitrogen,

$$L = \frac{3118{\cdot}6}{t_C + 273} + \log p - 9{\cdot}451; \tag{19}$$

for formic acid,

$$L = \frac{3800}{t_C + 273} + \log p - 9{\cdot}641; \tag{20}$$

for acetic acid,

$$L = \frac{3520}{t_C + 273} + \log p - 8{\cdot}349; \tag{21}$$

and for perchloride of phosphorus,

$$L = \frac{5441}{t_C + 273} + \log p - 11{\cdot}353. \tag{22}$$

By these equations the values of L are easily calculated. The values of $\Delta$ may then be obtained by inspection (with interpolation when necessary) of the following table. From $\Delta$ the value of D may be obtained by multiplying by $D_1$, viz., by 1·589 for peroxide of nitrogen or formic acid, by 2·073 for acetic acid, and by 3·6 for perchloride of phosphorus.*

The constants of these equations are of course subject to correction by future experiments, which must also decide the more general question—in what cases, and within what limits,

* The value of $\Delta$ diminished by unity expresses the ratio of the number of the molecules of the more complex type to the whole number of molecules. Thus, if $\Delta = 1{\cdot}20$, in the case of peroxide of nitrogen there are 20 molecules of the type $N_2O_4$ to 80 of the type $NO_2$, or in the case of perchloride of phosphorus there are 20 molecules of the type $PCl_5$ to 40 of the type $PCl_3$ and 40 of the type $C_2$. A consideration of the varying values of $\Delta$ is therefore more instructive than that of the values of D, and it would in some respects be better to make the comparison of theory and experiment with respect to the values of $\Delta$.

TABLE X.

For the solution of the equation: $\log \frac{1000\,(\Delta - 1)}{(2 - \Delta)^2} = \mathrm{L}$.

| L | Δ | Diff. | L | Δ | Diff. | L | Δ | Diff. |
|---|---|---|---|---|---|---|---|---|
| ·7 | 1·005 | | 3·0 | 1·382 | | 5·3 | 1·932 | |
| ·8 | 1·006 | 1 | 3·1 | 1·421 | 39 | 5·4 | 1·939 | 7 |
| ·9 | 1·008 | 2 | 3·2 | 1·461 | 40 | 5·5 | 1·945 | 6 |
| 1·0 | 1·010 | 2 | 3·3 | 1·500 | 39 | 5·6 | 1·951 | 6 |
| 1·1 | 1·012 | 2 | 3·4 | 1·537 | 37 | 5·7 | 1·956 | 5 |
| 1·2 | 1·015 | 3 | 3·5 | 1·574 | 37 | 5·8 | 1·961 | 5 |
| 1·3 | 1·019 | 4 | 3·6 | 1·609 | 35 | 5·9 | 1·965 | 4 |
| 1·4 | 1·024 | 5 | 3·7 | 1·642 | 33 | 6·0 | 1·969 | 4 |
| 1·5 | 1·030 | 6 | 3·8 | 1·673 | 31 | 6·1 | 1·972 | 3 |
| 1·6 | 1·037 | 7 | 3·9 | 1·703 | 30 | 6·2 | 1·975 | 3 |
| 1·7 | 1·046 | 9 | 4·0 | 1·730 | 27 | 6·3 | 1·978 | 3 |
| 1·8 | 1·056 | 10 | 4·1 | 1·755 | 25 | 6·4 | 1·980 | 2 |
| 1·9 | 1·069 | 13 | 4·2 | 1·778 | 23 | 6·5 | 1·982 | 2 |
| 2·0 | 1·084 | 15 | 4·3 | 1·800 | 22 | 6·6 | 1·984 | 2 |
| 2·1 | 1·102 | 18 | 4·4 | 1·819 | 19 | 6·7 | 1·986 | 2 |
| 2·2 | 1·122 | 20 | 4·5 | 1·837 | 18 | 6·8 | 1·987 | 1 |
| 2·3 | 1·146 | 24 | 4·6 | 1·854 | 17 | 6·9 | 1·989 | 2 |
| 2·4 | 1·172 | 26 | 4·7 | 1·868 | 14 | 7·0 | 1·990 | 1 |
| 2·5 | 1·202 | 30 | 4·8 | 1·882 | 14 | 7·2 | 1·992 | |
| 2·6 | 1·234 | 32 | 4·9 | 1·894 | 12 | 7·4 | 1·994 | |
| 2·7 | 1·268 | 34 | 5·0 | 1·905 | 11 | 7·6 | 1·995 | |
| 2·8 | 1·305 | 37 | 5·1 | 1·915 | 10 | 7·8 | 1·996 | |
| 2·9 | 1·343 | 38 | 5·2 | 1·924 | 9 | 8·0 | 1·997 | |
| 3·0 | 1·382 | 39 | 5·3 | 1·932 | 8 | 9·0 | 1·999 | |

and with what degree of approximation, the actual relations can be expressed by equations of such form. In the case of perchloride of phosphorus especially, the formula proposed requires confirmation.