XXVIII.—*On a mode of taking the Vapour-density of Volatile Liquids at temperatures below the boiling point.*

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It is commonly said that vapour-densities taken at high temperatures are more correct than those taken at low temperatures.

* This abstract has been revised by the Authors, who have added some additional matter.

A more accurate statement of the case is—vapour-densities taken at a distance from the point of liquefaction are more correct than those taken near that point.

When a vapour approaches the point at which it passes into the liquid state, it loses some of the characteristics of a true gas, it ceases to expand quite uniformly for equal increments of heat, and it manifests a tendency to condense on the sides of the containing vessel. Either of these properties would make the determination of a vapour-density abnormal.

We are, however, inclined to believe that the effects upon the density, which are really due to these causes, have been exaggerated. The examples about to be brought forward show that only a moderate distance (measured either in temperature or in pressure) from the point of liquefaction is enough to render the density of a vapour nearly normal.

We believe that, in the few cases where any great difference is found between a vapour-density taken at a point moderately removed from the point of liquefaction, and one taken at a point far removed from the point of liquefaction, there is a chemical and not a merely physical change. Thus we hold that sulphur-vapour has sometimes one and sometimes another chemical formula, according as it is more or less heated. Peroxide of nitrogen, which we shall show has two radically distinct densities at high and low temperatures, has the composition N_2O_8 , at ordinary temperatures and NO_4 at the temperature of boiling water.

A vapour may be removed from its point of liquefaction, either by raising its temperature, or by diminishing the pressure upon it, or by adding a certain quantity of a permanent gas to dilute it. If it be required to take a vapour-density at a low temperature, the vapour must be removed from its point of liquefaction by one or other of the latter methods. We propose to introduce the employment of the last-named method, to mix vapours with permanent gases instead of lowering the barometric pressure. We shall point out as we proceed, the practical advantages which the method of dilution has over the method of directly diminishing the barometric pressure. Here we bring forward experiments to prove that such dilution is really effective in rendering the density of vapours normal.

For this part of the enquiry, a slight modification of Gay Lussac's method of determining vapour-densities was found to be most convenient. A carefully dried graduated tube is

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filled with warm mercury, and inverted in the mercurial trough. Next, dry hydrogen is introduced. The gas is then

measured, adopting the precautions which are requisite in measurements for a gas analysis. The liquid to be operated upon, of which a weighed portion is contained in a small glass bulb, is subsequently passed up to the hydrogen contained in the graduated tube. The tube, with its contents, is then lifted out of the mercurial trough by means of a small iron cup, and transferred to the bath in which it is to be heated, and which contains some mercury, occupying about an inch of its interior. An adjustment of the graduated tube having been made, water is poured into the bath, and heat applied, until the boiling-point of the liquid under examination has been passed.

After all the liquid contained in the bulb has evaporated, the bath is allowed to cool very slowly, being stirred up constantly, so as to keep its temperature uniform throughout. Before each observation, great care was taken to ensure uniformity of temperature.

The following minute corrections were made:—

1. A correction for meniscus equal 0·3 cubic centimeter.
2. A correction for expansion of the glass tube, which amounts to from ·40 cubic centimeter to 0·1 cubic centimeter.

Both the barometric column and the mercurial column contained in the graduated tube were reduced to zero, according to tables given for that purpose in Bunsen's "Gasometry." The water column occupying the bath was measured in millimeters, corrected for temperature, and reduced to mercurial measure.

Series of Experiments with Slightly Moist Alcohol.

	Observed volume in Cub. Centi- meters.	Tempe- rature C.	Pressure in Milli- meters.	Vol. in Cub. Cent. corrected at 0° C. and 760 m.m. Pressure.
Dry Hydrogen	68·18	7° C.	600	52·482
Dry Hydrogen and Alcohol } Vapour—Observation 1, }	130·94	101°	732·9	92·189
Dry Hydrogen and Alcohol } Vapour—Obs. 2, .. }	126·04	84°	724·6	91·916
Dry Hydrogen and Alcohol } Vapour—Obs. 3, .. }	124·28	77·5°	720·9	91·840
Dry Hydrogen and Alcohol } Vapour—Obs. 4, .. }	122·68	70·5	717·9	92·117
Dry Hydrogen and Alcohol } Vapour—Obs. 5, .. }	120·02	61°	712	91·922

The numbers contained in the last column are obtained from those in the other columns, by applying Marriotte's law, and using the coefficient ·00366 for the expansion of 1° C. Inspection will show that the pressures are nearly alike in the five observations made of hydrogen mixed with alcohol-vapour, whilst the temperatures vary 40° C.

Since the numbers in the last column are almost identical, it follows that the coefficient of expansion adopted in their calculation is correct.

The alcohol in this instance was supposed to have been dry, but subsequent examination showed that a small quantity of water had escaped the action of the dehydrating agents. The vapour-density of this moist alcohol may be found by the following calculation. We will take Observation 1 :—

$$\begin{array}{rcl}
 & & \text{Cubic cent.} \\
 \text{Vol. of hydrogen + alcohol vapour} & = & 92\cdot189 \\
 \text{Vol. of hydrogen} & = & 52\cdot482 \\
 \hline
 & & 39\cdot707
 \end{array}$$

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The weight of the alcohol which was introduced was $\cdot 0775$ grm.

Therefore, $39\cdot 707$ cub. cent. of alcohol vapour weigh $\cdot 0775$ grm.

$39\cdot 707$ cubic cent. of air weigh $\cdot 05137$ grm.

$\cdot 0775$

———— = $1\cdot 508$, the vapour-density of the moist alcohol.

$\cdot 05137$

If the other observations be calculated, the numbers will be found to differ very little from that obtained from the first; indeed Observation 3rd, which departs furthest from Observation 1st, gives for the vapour-density the quantity $1\cdot 522$.

The same sample of moist alcohol was made the subject of an experiment, in which its vapour-density was determined in the usual way, without the employment of a permanent gas :—

The results were :—

Temperature.	Vapour-density.
95°	$1\cdot 551$
83°	$1\cdot 565$

In the first described experiment, where hydrogen was present, we found the vapour-density of the alcohol to lie between $1\cdot 508$ and $1\cdot 522$. It would appear, therefore, that the presence of hydrogen lowers the density of alcohol vapour; the lowering cannot be due to difference of pressure; for in the experiment where the higher vapour-density was obtained, the pressure was about 630 millimeters, whilst in the other experiment it was about 730.

Experiments on perfectly Anhydrous Alcohol.

Weight of the Alcohol taken = $\cdot 0889$. grm.

	Observed volume in Cub Centi- meters.	Tempe- rature C.	Pressure in Milli- meters.	Vol. in Cubic Cent. corrected at 0° C. and 760 Millimeters.
Vol. of Dry Hydrogen ..	43 $\cdot$ 16	7°	572 $\cdot$ 07	31 $\cdot$ 676
Hydrogen and Alcohol Va- pour—Observation 1, .. }	110 $\cdot$ 84	99°	710 $\cdot$ 6	76 $\cdot$ 073
Hydrogen and Alcohol Va- pour—Obs. 2, ... }	107 $\cdot$ 16	$83\cdot 5^{\circ}$	699 $\cdot$ 7	75 $\cdot$ 565
Hydrogen and Alcohol Va- pour—Obs. 3, ... }	102 $\cdot$ 74	63°	695 $\cdot$ 1	75 $\cdot$ 238

A correction of 0·4 cub. cent. for air contained in the alcohol bulb has to be made. This quantity must be subtracted from the volume of alcohol vapour.

The vapour-densities, as deduced from the three observations, are as follows:—

			Vapour Density.
Observation 1 at	99°	.	1·562
„ 2 at	83·5°	.	1·580
„ 3 at	68°	.	1·592

The same sample of anhydrous alcohol gave without hydrogen:—

Temperature.	Vapour-density.
At 100·5°	1·599
At 86·5°	1·602

Here, again, we notice the same peculiarity as in the former experiments with the specimens of moist alcohol, viz., the vapour-densities taken with hydrogen are rather lower than those taken without it.

The theoretical vapour-density of alcohol calculated from the specific gravity of hydrogen is $\frac{4}{9} \times 0\cdot691 = 1\cdot5893$, a number which agrees with our experiment.

In several elementary works on Organic Chemistry, in Regnault's "Manual" for example, the following vapour-densities for alcohol at different temperatures are given:—

Temperature.	Vapour-density.
88° C.	1·725
98°	1·649
110°	1·610
125°	1·603
150°	1·604
175°	1·607
200°	1·602

Our observation does not confirm the decrease of ·08 in density between 88° C. and 98° C. Between 86·5° and 100·5, we have an decrease of ·003 only.

Experiments made in like manner with Ether which had been purified and dried with great care, gave:—

With hydrogen:—

	Temperature.	Vapour-density.
At	69·5° C.	2·499
At	20·8°	2·539

Without hydrogen :—

		Temperature.		Vapour-density.
At	.	94° C.	.	2·541
At	.	52° C.	.	2·580

The theoretical vapour-density of ether is $\frac{7}{2} \times \cdot 0691 = 2\cdot 5567$.

These experiments show that admixture of hydrogen with the vapour of alcohol or ether renders it capable of being cooled down much below the boiling point, without losing its normal density.

Some experiments by Regnault, undertaken for meteorological purposes, have shown that the aqueous vapour suspended in the atmosphere has the normal-density 0·622. We may, therefore, regard the first question as satisfactorily answered.

But whether it is *more* effective to add a permanent gas than to diminish barometric pressure, will require a set of very careful experiments. The practical advantage of using the gas, rather than lowering the pressure, will be evident from the following considerations :

Let it be required to expand 10 cub. centimeters of a vapour to double the volume. To do so, half the barometric pressure must be taken off by means of a column of mercury between the lower level of the gas and the level of the mercury in the trough.

We thus get volume = 20 C.C.; mercurial column in the bath = $\frac{1}{2}$ barometric height.

But let the expansion be made by adding an equal volume of permanent gas, and we have volume of gas and vapour = 20 C. C.; mercurial column in the bath = 0.

Thus it appears that by using a gas the long mercurial column is saved. Several other advantages attend the use of the gas; but the circumstance that the gas requires an apparatus only of the ordinary size, while to work at low pressures would require at least double the ordinary capacity of tube, bath, and everything else, is alone sufficient to make the former method much more practicable than the latter.

We next describe the way of proceeding when it is desirable to avoid heating the substance which is operated upon, when a degree of heat approaching that at which the substance boils would produce decomposition.

By the plan about to be described, the vapour is never heated higher than the temperature at which its density is to be taken.

The principle is that of Dumas' method—viz., the weighing of a given volume of vapour: the mode of carrying it out is, however, so different, that a minute description of the apparatus will be necessary.

Those who have occupied themselves with Dumas' mode of taking vapour-densities, will be well aware, that one of the difficulties of using it for temperatures near the boiling point of a liquid, is due to the circumstance that it is impossible to know when all the liquid has assumed the state of vapour.

Our modification of the method consists in placing the liquid to be vaporized outside of that part of the apparatus which, when hermetically sealed, will contain the vapour mixed with gas. The apparatus consists of a pair of large bulbs, connected together by means of a neck, and terminating on either side in narrow glass tubes, which are bent and blown into small bulbs, as represented in the drawing. The bulbs C and C are large, and together capable of holding from 200 to 400 cubic centimetres. The bulbs *b* are very small, being mere dilations of the narrow tube. They are to contain the liquid to be examined. The bends *a* and *a'* should be

on the same level, and thin, so as to admit of fusion by the lamp. Altogether the apparatus should not weigh more than 65 grm. The following mode is employed in making an experiment with the apparatus.

After being cleaned and filled with the dry air of the balance-case, the bulb-apparatus is weighed, and then transferred to the bath, being grasped by a retort-holder, which takes hold of the neck connecting the large bulbs C and C. The end A is then jointed to a hydrogen-apparatus by means of a small caoutchouc tube; the other extremity D, which projects out of the bath through an orifice in the side of that vessel, is likewise connected, by means of a caoutchouc tube, with a long narrow glass tube pointing downwards, and designed to prevent diffusion. Dry

hydrogen gas is then passed through the apparatus to repletion. Whilst this is going on, warm water is poured into the bath—the hole in its side through which the extremity D passes being stopped up with putty, which makes a very convenient water-tight stopping. The addition of water is continued, until the bends *a a* are totally submerged. When the apparatus is full of hydrogen, the connection at A is interrupted, and the liquid, of which a vapour-density determination is made, introduced at A.

On re-establishing the communication with the hydrogen-apparatus, a stream of dry hydrogen passes through the dilatation *b*, and becoming more or less saturated with vapour, enters the great bulbs C and C.

No more liquid is placed in *b* than is sufficient to fill that bulb half-full, the three supplementary dilatations near *b* acting as safety-bulbs, to avoid the effects of splashing.

The temperature of the bath is raised very slowly, the water being constantly stirred, so as to ensure uniformity of temperature. When the temperature is three or four degrees below the point at which a vapour-density determination is required, the current of hydrogen is nearly stopped.

The object of this is to avoid complete saturation of the gas with vapour. By this device, the greater part of the gas which is present in C and C, at the end of the operation, has entered at a lower temperature than that at which the apparatus is sealed, and, consequently, is only partially saturated at the moment of sealing the apparatus.

The desired temperature having been attained, sufficient water to expose the bends *a a*, but not the large bulbs C C, is suddenly let out of the bath, by opening a large tap situated close to the bottom of the bath. The current of hydrogen having been entirely stopped, the flame is applied to *a* and *a*, until the apparatus is sealed up in both places. The temperature of the bath having been again noted, and also the height of the barometer, the bulbs C and C which contain the vapour and hydrogen, are removed from the bath, carefully cleaned, and subsequently, along with the other two fragments (viz., the portion A to *a* and the portion *a* to D, also carefully cleaned), transferred to the balance-case and weighed.

The difference between this latter weighing and that at the beginning of the operation gives, when the weight of the displaced air is added to it, the weight of C C filled with a mixture of

hydrogen and vapour at the barometric pressure and temperature of the bath at the time of sealing.

The remainder of the operation having for its object to find how much hydrogen is enclosed in C C, and also the capacity of C C, is conducted thus :—The hermetically sealed C C, is placed in cold water, and one of its sealed extremities nipped off whilst still under water, which enters and occupies the space not filled with hydrogen. After remaining in water for a number of hours, until the vapour has been completely absorbed, the apparatus is lifted vertically out of the water, care being taken not to heat the hydrogen contained in the bulbs, for which purpose a holder is employed. The temperature of the water is observed ; also the height of the barometer.

The apparatus, together with the water which has thus entered, is then weighed. It is afterwards completely filled with water, and again weighed.

The difference between the weight of the bulbs empty, and filled with water, gives the total capacity of the apparatus.

The difference between the weight after the first portion of water has entered, and the weight of the apparatus quite full of water, gives the volume of the hydrogen at the temperature of the water and at the barometric pressure, minus the column of water contained in the bulbs when they are held over the water out of which they had been lifted. This column is measured after the first weighing of bulbs and water has been made.

Such is the process which we employ to take vapour-densities of bodies incapable of being heated to their boiling points without decomposition.

Exception may perhaps be taken to the mode of measuring the hydrogen included on sealing the bulbs. We will answer some objections which might naturally be raised.

It might be feared that the vapour would not be perfectly absorbed by water ; but when it is considered how much water there is, and how little vapour has to be acted upon by it, it will be evident that only in those instances where the vapour is nearly insoluble in water, will there be any chance of appreciably incomplete absorption. Only in those instances where the substance is at once insoluble in water and possesses a high tension at ordinary temperatures, could error arising from this source become serious.

With regard to the absorption of hydrogen by water, it may be

remarked that since between 8° and 11° C, the absorption-coefficients of hydrogen and common air, as determined by Bunsen, are nearly identical, the measurement of hydrogen over water is so far unobjectionable.

As an example of the method, we subjoin the particulars of a vapour-density determination of absolute alcohol, made 30° C. below its boiling point:—

Temperature of the balance-case, 7.5° C.

Temperature at the time of sealing 48° C.

Weight of apparatus + water (at 5.2° C.) = 191.76 grm.

water column, 122 m.m.

Weight of apparatus filled with water = 545.36 grm.

Volumes corrected
at 0° C, and 760 m. m. pressure,
Cubic centimetres.

	Cubic centimetres.		gm.
Hydrogen + vapour,	406·43	weighing	0·1695
Hydrogen,	341·27	„	0·0306
	65·16		0·1389

Therefore, 65.16 cub. c. of alcohol vapour weigh .1389 grm.

But 65.16 cub. c. of air weigh .0843 grm.

$$\text{Vapour-density of alcohol} = \frac{.1389}{.0843} = 1.648.$$

Two experiments made upon very small quantities of water showed results almost as near the theoretical quantity as the balance will admit. In neither case did the weight of aqueous vapour each 10 milligrammes:—

Exp. 1. Vapour-density of water = 0.671.

Exp. 2. Vapour-density of water = 0·654.

Theoretical density of water, $\frac{18}{2} \times 0.691 = 0.6219$.

When Dumas' method of vapour-density determination is employed, the practical advantages of diluting with a gas rather than working at diminished pressures are very obvious. We may call attention to two points.

When the gas is used, in the manner described above, the sealing up of the apparatus is managed whilst there is no difference between the pressure inside and outside. Let the apparatus be connected with an air-pump, and let the attempt be made to work in vacuo, and great difficulty will be experienced in quickly sealing up at the bends of the apparatus.

Further a very thin and light glass vessel may be used when gas is employed; for when the sealed bulbs become cold, they have to withstand only a fraction of the barometric pressure; and, precisely in those cases where the lightest and largest bulbs are desirable, where the proportion of vapour to gas is the smallest, just there does it happen that the fraction of barometric pressure to be afterwards withstood is the very smallest.

Experiments upon Acetic Acid vapour.

Cahours has obtained by the usual processes;

	Temperature.	Density.
Density of acetic acid vapour at 125° C .		3·180
„ „ 150 .		2·727
„ „ 200 .		2·248
„ „ 270 .		2·088

	Vapour-density.
The theory requires $C_4H_4O_4$.	2·073
$C_8H_8O_8$.	4·146

Stated in general terms, our results are :—by adding hydrogen, a vapour-density of 2·073 can be got at least as low as 150° C.; whereas at 60° C., even in spite of 16 vols. of hydrogen to one of vapour, the vapour-density of acetic acid approaches to 4·0

Instances of the employment of the foregoing methods.

Nitrate of Ethyl.—Among the nitrates, the nitrate of methyl alone has been made the subject of a vapour-density determination. Bodies of this kind become explosive on being raised only a few degrees above their boiling points, and hence are difficult to treat by the usual methods.

We have deemed it interesting to estimate the vapour-density of nitrate of ethyl.

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The vapour-density determination was made by the modification of Gay-Lussac's method. The gas employed as the diluent was dry nitrogen.

The results were—

Temperature.		Vapour Densities.
at 85.5°C	.. ..	3.112
„ 90°	.. ..	3.094
„ 70.3°	.. ..	3.065
„ 64.9°	.. ..	3.079

$\left. \begin{matrix} \text{C}_4\text{H}_5 \\ \text{NO}_4 \end{matrix} \right\} \text{O}_2$ requires $\frac{91}{2} \times .0691 = 3.144$, which is sufficiently near the experimental density.

Nitric Acid.—It can hardly be said that the state of condensation of the acids has been determined by direct experiment. Most of the acids are too little volatile, or suffer decomposition at temperatures too low to admit of such experiments. And those acids whose vapour-densities have been actually observed are seldom in perfect accordance with theory. The vapour-density of sulphuric acid, for example, is abnormal: and although we are far from demurring to the explanation that that acid suffers decomposition into anhydride and water, it must be allowed that direct experiment has not yet established the molecular weight indicated by the formula $\left. \begin{matrix} \text{S}_2\text{O}_4 \\ \text{H}_2 \end{matrix} \right\} \text{O}_4$

Again, the series of fatty acids, although normal at high temperatures, are abnormal at low temperatures: indeed, it is difficult to find an example of an acid which does not offer some anomaly of the kind.

We have selected nitric acid for experiment. As will be apparent by-and-by, this acid is regular, having for its molecular weight the number answering to the formula $\left. \begin{matrix} \text{NO}_4 \\ \text{H} \end{matrix} \right\} \text{O}_2$

The acid employed was distilled from sulphuric acid, then from dried sulphate of copper, and lastly, warmed in a stream of dry carbonic acid, so long as its colour became less yellow. The final product was found to be quite free from sulphates and chlorides. Its strength, as indicated by alkalimetry, was satisfactory. Its colour was a very pale yellow, which the transmission of carbonic acid was incapable of rendering fainter.

From our observation, we are inclined to believe that the last yellow tinge cannot be removed from monohydrated nitric acid by

warming for any length of time in a current of perfectly dry gas; but the presence of a minute trace of moisture in the transmitted gas at once decolorises the acid. The success of the employment of urea as a means of depriving nitric acid of colour, depends partly on the production of water. We need hardly remark that we avoided the use of urea. We believe, moreover, that the quantity of peroxide of nitrogen requisite to give the yellow tinge is imponderable.

As nitric acid attacks mercury, Gay-Lussac's process is quite inapplicable to it; and since nitric acid undergoes some decomposition on boiling, Dumas' process would not answer without some modification.

The following determinations have been made by the method previously described. The gas used to dilute the nitric acid vapour was dried air.

I.

Determination of Vapour-density of Nitric Acid at 68.5° C.

	Cubic Centimeters at 0° C. and 760 m. m.		Grm.
Vol. of Air + Vapour	= 384.60	weighing	.7255
„ Air	= 962.48	„	.3395
	132.12		.3860

Hence 132.12 cub. cent. of nitric acid vapour weigh .3860 grm. Vapour density = 2.258. In the above experiment the bulbs, when sealed up, were perfectly colourless.

II.

Determination of Vapour-density of Nitric Acid at 40.5° C.

	Cubic Centimeters at 0° C. and 760 m. m.		Grm.
Vol. of Air + Vapour	317.62	weighing	.4664
„ Air	286.28	„	.0705
	31.24		.0959

Hence 31.24 C. C. of nitric acid vapour weigh .0959 grm. Vapour density = 2.373. In this instance the bulbs were very faintly tinged with peroxide of nitrogen. Possibly this may be the real reason why in this case the number is a little higher than in the former experiment.

The results are :—

Temperature.		Vapour-densities
at 68·5°	. . .	2·258
„ 40·5	. . .	2·373

The formula $\text{NO}_4\left\{\begin{smallmatrix} \text{N} \\ \text{H} \end{smallmatrix}\right\} \text{O}_2$ requires $\frac{63}{2} \times \cdot 0691 = 2\cdot 1766$.

It thus appears that nitric acid vapour is nearly normal, even at many degrees below the boiling point, under ordinary atmospheric pressures.

Here the remark may be made, that one of the sources of uncertainty belonging to Dumas' method is avoided. Several grammes of substances are generally taken for Dumas' vapour-density determination. Fractional distillation takes place in course of the operation, so that unless the substance be of extreme purity, the specific gravity obtained is liable to depart widely from the mean specific gravity of the sample.

The method which we have described completely avoids this. Only a small quantity of substance is necessary, and even that need not be completely evaporated, since the portion of the apparatus containing the substance is afterwards separated from the portion filled with gas and the vapour.

Peroxide of Nitrogen NO_4 .—Peroxide of nitrogen offers one of the examples of physical and chemical properties in opposition. Whereas NO_4 represents Cl. (one equivalent of NO_4 , replacing just as much as one equivalent of Cl), NO_4 is physically equivalent to Cl_2 . The wonderful deepening in colour which peroxide of nitrogen undergoes on being heated, led us to suspect that molecular change might also occur. This expectation has been fully realised. We deduce from our experiments that peroxide of nitrogen exists in two states; that there are two bodies having the same percentage composition as peroxide of nitrogen, but which are polymeric.

The body existing at high temperatures requires the formula NO_4 , that existing at low temperatures requires the formula N_2O_8 .

The peroxide of nitrogen used in this research was prepared partly by distilling nitrate of lead, and partly by distilling a mixture of nitrate of lead with chloro-chromate of potash. The products from several operations were purified together, and placed in a single hermetically sealed tube. Analysis showed that it was pure.

Before proceeding to take the specific gravity of peroxide of nitrogen at different temperatures by the methods under consideration, it was requisite to settle certain points relating to the reactions of the body.

In a preliminary determination of specific gravity, made by Dumas' method, some months before the chief investigation, it was found that peroxide of nitrogen was completely absorbed by water, without any evolution of NO_2 , at any rate at ordinary temperatures. In that experiment, the Dumas flask filled completely with water when opened under water at the end of the determination; and after several days even, no appreciable amount of gas had made its appearance in the flask.

At first we employed air as the diluent gas in these vapour-density determinations, but were subsequently compelled to have recourse to nitrogen: for direct experiment showed that, when a measured volume of air is sealed up with water and peroxide of nitrogen, absorption of oxygen takes place, the ultimate volume measuring much less than the initial volume of air. Notwithstanding this source of error, which would tend to make the peroxide of nitrogen seem lighter than it really was, the specific gravity of that body at 8.5°C. was obtained as high as 2.46.

The following determinations of the vapour-density of peroxide of nitrogen were made, using as the diluent nitrogen gas, prepared by burning phosphorus in air collected in a gas-holder, finally passing through a strong solution of pyrogallate of potash, and dried with sulphuric acid:—

I.

Vapour-density determination at 97.5°C.

	Cubic Cent. at 0°C. and 760 m. m.		Grm.
Vol. of $\text{N} + \text{NO}_4$	263.97	weighing	.4473
„ N	159.47	„	.2063
	104.50		.2410

Therefore 104.50 c. c. of NO_4 weigh .2410 gm. Vapour-density = 1.783. Dilute solution of potash (sp. gr. 1.0043) was used to absorb the peroxide of nitrogen. The residual nitrogen was then calculated as being quite saturated with moisture: for potash of so low a specific gravity would not sensibly differ from pure water in point of tension.

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In this and the following experiments, it was carefully ascertained that the residual nitrogen was quite colourless: also, on making repeated experiments, no coloration could ever be seen on admitting air to the residual gas.

II.

Vapour-density determination at 24.5° C.

	Cubic Cent. at 0° C. and 760 m. m.		Grm.
Vol. of N + NO ₄	425.29	weighing	.8963
„ N	244.39	„	.3070
	180.90		.5893

Therefore 180.90 C. C. of NO₄ weigh .5893 grm. Vapour-density = 2.52.

The absorption of NO₄ was made by means of water.

III.

Vapour-density determination at 11.3° C.

	Cubic Cent. at 0° C. and 760 m. m.		Grm.
Vol. of N + NO ₄	442.05	weighing	.7556
„ N	349.4	„	.4390
	92.65		.3166

Therefore 92.65 cub. cent. of NO₄ weigh .3166 grm. Vapour-density = 2.645. In this determination, strong caustic soda (sp. gr. 1.348) was used to absorb the NO₄. In making the calculation, the gas in contact with such a solution was considered half dry. By this means, absolute precision is sacrificed to certainty. It cannot be doubted that the strong alkali would completely absorb all NO₄ without evolving NO₂.

The influence of the possible tension of aqueous vapour from strong solution of caustic soda does not seriously affect the calculation. If we reckon the gas absolutely dry, we get vapour-density of NO₄ = 2.69.

If absolutely wet, we have vapour-density of NO₄ = 2.60.

IV.

Vapour-density at 4·2° C.

	Cubic Cent. at 0° C. and 760 m. m.		Grm.
Vol. of N + NO ₄	354·38	weighing	·5711
„ N .	294·15	„	·3695
	60·23		·2016

Therefore 60·23 C. C. of NO₄ weigh ·2016 grm. Vapour-density = 2·588.

Here weak solution of caustic potash (sp. gr. = 1·0045) was employed, and considered to have the same tension as pure water.

The results obtained were as follows:—

Temperature.	Vapour-densities.
At 97·5° C	1·783
„ 24·5°	2·520
„ 11·3°	2·645
„ 4·2°	2·588

The vapour-density of NO₄, given in Regnault's "Cours Élémentaire de Chimie;" is 1·72,—a number which is a little less than the first number in the preceding list:—

The formula NO₄ requires $\frac{46}{2} \times \cdot 0691 = 1\cdot5893$.

The formula N₂O₈ requires $\frac{92}{2} \times \cdot 0691 = 3\cdot1786$.

It will be observed that, even at 97·5° C., the vapour-density of peroxide of nitrogen is rather too high for the first formula, whilst at 24·5° and downwards, the vapour density is much nearer that required by the second formula than that required by the first.

If it be allowed that there exist two peroxides of nitrogen, NO₄ and N₂O₈, and that these bodies pass readily into one another, the above results find a simple and natural explanation. At 100° C., the gas consists chiefly of NO₄; at ordinary temperatures, chiefly of N₂O₈; whilst at intermediate temperatures, intermediate quantities of NO₄ and N₂O₈ are present.

If change of composition be denied, the peroxide of nitrogen must have an expansion-coefficient widely differing from that of other gases. To admit such an exception to one of the best physical generalisations, seems unphilosophical.

In general, gases when exposed to pressures not exceeding the usual barometric pressure, and when no incipient liquefaction is

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taking place, have an expansion-coefficient not differing widely from .00366. No exception has yet been established; for, in those cases of which sulphur is the representative, it is at least probable that truly polymeric bodies exist.

Another illustration of the vapour-density methods above described consists in an inquiry into the existence of hydrated oxide of ammonium.

Can hydrated oxide of ammonium exist at 100° C., and in the gaseous state? To solve the problem, a quantity of dry ammonia was measured over mercury, then a small portion of water, which had been accurately weighed in a thin glass bulb, was introduced into the ammonia. The whole was then heated up to 100° C., and the volume of mixed gas and aqueous vapour noted. It will be obvious that the formation of hydrated oxide of ammonium would be indicated by contraction. If, on the other hand, the NH_3 and aqueous vapour, when mixed, had the same volume as when separate, no hydrated oxide of ammonium had been produced.

The following are the details of the experiment:—

	Observed volume in Cub. Centi- meters.	Tempe- rature Centi- grade.	Pressure in Milli- meters.	Corrected Vol. in Cubic Cent. at 0° C. and 760 m. m.
Vol. of dry NH_3 , ...	34.19	12.5°	558.08	24.008
Vol. of NH_3 + water, ..	107.32	102° C.	709.66	72.973

.0402 grm. of water taken.

But .0402 grm. of water, when converted into vapour, measures 49.95 cub. centimeters at 0° C. and 760 mm. The difference between the readings before and after the addition of that amount of water is 48.965 cub. cent. Therefore, at 100° C., ammonia and aqueous vapour can exist side by side without suffering any considerable contraction.