

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

III.—*Study of Hydrogen Dioxide and of certain Peroxides*—(continued from page 24).

By T. FAIRLEY, F.R.S.E.

VII. ON SODIUM DIOXIDE.

IN alcoholic solutions this substance may be precipitated by addition of hydrogen dioxide, in a manner closely resembling the precipitation of barium, strontium, and calcium dioxides, by the same reagent, from aqueous solutions of their hydrates. Thus, if to a solution of sodium hydrate containing about 20 per cent. of NaHO we add a solution of hydrogen dioxide containing about 5 per cent. H_2O_2 , and then common alcohol of 80 per cent. in moderate excess, there is rapidly—often immediately, formed a crystalline precipitate of hydrated sodium peroxide. In this preparation it is better to have excess of alkali, rather than of the dioxide. The precipitate should be rapidly separated from the liquid by filtration through a ribbed paper filter, or, still better, a cloth filter, as the crystals gradually decompose when suffered to remain in the liquid.

The crystals of this sodium peroxide have the beautiful pearly lustre characteristic of many hydrated peroxides, and consist of sodium dioxide with eight atoms of water of crystallisation. They do not contain any alcohol. They are identical with the crystalline hydrate described by Vernon Harcourt*, and obtained by the evaporation of the solution of anhydrous sodium dioxide prepared by heating sodium in a current of oxygen. Thus they lose water by exposure over sulphuric acid in a vacuum; and on exposure to the air for a few days they rapidly lose their brilliancy, owing to formation of sodium carbonate from absorption of carbon dioxide and evolution of oxygen.

When considerable quantities are operated on, crystals may sometimes be obtained of considerable magnitude in large mica-like plates. This is observed more especially in cold weather. These plates are transparent, flexible, and can be split with the knife in the same manner as mica. They may be formed from smaller crystals, uniting together in the same way as shown by ice in the process of regelation.

* *Chem. Soc. J.*, xv, 287.

As showing the influence of various proportions of reagents, the following experiments may be quoted :—

(I.) On mixing—

10 c.c. NaHO solution	(20 per cent.)
4 c.c. H ₂ O ₂	„ (5 per cent.)
20 c.c. alcohol	(80 per cent.).

an abundant precipitation of the dioxide was obtained.

(II.)

10 c.c. of the same NaHO solution	
7.5 c.c. „ H ₂ O ₂	„
22 c.c. „ alcohol	

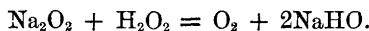
also gave an abundant precipitate of the dioxide, and the precipitation appeared to be facilitated by addition of a little more sodium hydrate.

(III.)

10 c.c. of the same NaHO solution	
20.4 c.c. „ H ₂ O ₂	„
60 c.c. „ alcohol	

gave no precipitate, but only a slight opalescence.* The further addition of alcohol also failed to give a precipitate, which was, however, immediately obtained on addition of sodium hydrate.

These experiments show that while excess of sodium hydrate does not interfere with the precipitation, excess of the hydrogen dioxide interferes with or even prevents it. This may be due to the formation of a double peroxide of sodium and hydrogen soluble in alcohol. It is also to be observed that oxygen is much more freely evolved in presence of excess of the hydrogen dioxide. This may arise either from the decomposition of the unstable double peroxide, if such be formed, or else according to the equation—



By heating this dioxide alone, about seven-eighths of the water are given off and all the peroxide oxygen, and by heating it with silica, or in a current of carbon dioxide, all the water and peroxide oxygen are expelled. The latter, therefore, form convenient processes for the analysis of the dioxide.

In the following analyses the oxygen was generally determined in acid solutions by means of decinormal potassium permanganate :—

- I. 0.1 gram required 9 c.c. of permanganate = 0.0072 oxygen, corresponding to 7.2 per cent.
- II. 0.0705 required 6.35 c.c. permanganate = .00508 oxygen, corresponding to 7.2 per cent.

* On exposing this liquid to cold, it deposits a small quantity of fine crystalline needles. These, though very different in appearance and form from the crystals obtained by Expts. I and II, have the same composition.

- III. 0.1135 evaporated with hydrochloric acid gave 0.0592 gram sodium chloride, and required 10.2 c.c. of decinormal silver nitrate, corresponding to 27.85 per cent. of Na_2O .
- IV. 0.1009 gram decolorised 9.1 c.c. permanganate = 0.00728 oxygen, corresponding to 7.21 per cent.
- V. 0.854 gram decolorised 77 c.c. permanganate = 0.0616 oxygen, corresponding to 7.21 per cent.
- VI. 0.924 gram decolorised 83.2 c.c. permanganate = 0.06656 oxygen, corresponding to 7.21 per cent.
- VII. 0.2 gram boiled with 10 c.c. normal sulphuric acid neutralised 1.8 c.c. = 0.0559 sodium oxide, corresponding to 27.95 per cent.
- VIII. 0.3265 gram heated with silica gave 0.2125 gram water, corresponding to 65.09 per cent.
- IX. 0.4157 gram heated in a current of pure dry carbon dioxide gave water 0.2689 gram, corresponding to 64.68 per cent., and sodium carbonate 0.19875 gram, corresponding to sodium oxide 27.96 per cent.

These results agree with the formula $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$, as the following percentages show:—

	Found.								
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Na ₂ O	—		27·85	—			27·95		27·96
O	7·20	—		7·21			—		—
H ₂ O	—		—	—			65·09		64·68
	Calculated.								Mean found.
Na ₂ O	62	27·97					27·92	
O	16	7·20					7·20	
8H ₂ O	144	64·83					64·88	
	222	100·00						100·00	

VIII. ON NEW OXIDES AND COMPOUNDS OF URANIUM.

Uranium Tetroxide.

On addition of pure dilute hydrogen dioxide to solution of uranic nitrate or acetate, a yellowish-white precipitate is formed somewhat lighter in colour than freshly prepared uranic hydrate. In presence of excess of uranium salt the precipitate is very stable, and may be dried at 100°C . without losing oxygen. If the hydrogen dioxide is in excess, oxygen is evolved during the filtration of the precipitate from the liquid, especially if the latter is not quite cold. In no case

has any lower oxide than that corresponding to the empirical formula UO_4 * been obtained.

The presence of excess of salts of sodium, potassium, barium, calcium, and probably many others, prevents the precipitation of uranium by hydrogen dioxide, and hence the new oxide is either not obtained at all, or slowly and with difficulty, by mixing an acid solution of barium dioxide with the solution of a uranic salt.

A moderate excess of strong hydrochloric, nitric, or sulphuric acids also delays or prevents the precipitation, and sulphuric acid is much more powerful in this respect than any other substance whose action I have observed.

The oxide when dried at 100° is a yellowish-white powder, soluble, especially on heating, in strong hydrochloric acid with evolution of chlorine. A mixture of the oxide with hydrochloric acid readily dissolves gold.

On exposure to heat, this oxide if finely divided, undergoes a very remarkable decomposition. At a comparatively low temperature, much below redness or the softening point of the more readily fusible glass, a red glow passes through the mass, oxygen is freely given off, and the residue contains a considerable proportion of green oxide of uranium.

On treating this oxide with alkaline hydrate, one portion of the uranium is precipitated as ordinary uranic hydrate, and the other enters into solution to form a salt or new oxygen compound with the alkali. These compounds may be viewed as derived from an acid of uranium analogous to perchromic acid, and, if so, would be similarly named as salts of peruranic acid.

The fact of the precipitation of the oxide from acid solutions shows, that unless we attribute to hydrogen peroxide the character of an acid, these compounds cannot be regarded as compounds of hydrogen dioxide. I do not, however, consider this view as untenable on that account, and have borne it in mind throughout the study of this class of compounds. According to this view the salts to be afterwards described are double peroxides.

Neither hypochlorites nor permanganates, nor ozone in acid, neutral or alkaline solutions, nor any other oxidising agents which I have hitherto examined (with the exception of hydrogen dioxide, alkaline peroxides, &c.) give any higher oxidation products with uranic salts. Hypochlorites and permanganates in acid liquids decompose this oxide in common with other peroxides.

Out of a very large number of experiments, the following may be quoted in illustration of the influence of varying proportions of reagents used, the completeness of the precipitation of uranium under

* $\text{U} = 240$.

suitable conditions, and the composition as proved by synthesis of the oxide formed.

On mixing :—

(I.) Uranium acetate solution 100 c.c. containing 4.877 grams UO_3 .

Hydrogen dioxide „ 38 c.c. „ 1.064 „ oxygen

an abundant precipitate was obtained. The filtrate contained no uranium (as proved by evaporation to dryness and also by testing with potassium ferrocyanide), but it contained the excess of H_2O_2 and abundance of free acetic acid.

(II.) Uranium *nitrate* solution 90 c.c. containing 1.72 grams UO_3 .

Hydrogen dioxide solution 10 c.c. containing 0.152 gram oxygen.

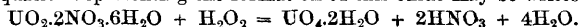
After making up the liquid to 200 c.c. and allowing the precipitate to settle, the clear liquid on testing with ferrocyanide showed uranium in solution. I therefore added to the whole bulk 13 c.c. of normal sodium hydrate solution containing 0.52 gram NaHO , and after thorough mixing and allowing the precipitate to settle, the clear liquid was again tested. It had an acid reaction, and showed no uranium by evaporation or on testing with ferrocyanide. After filtering and washing the precipitate, I observed that 1 c.c. of the normal sodium hydrate solution was sufficient to change the reaction of the filtrate from acid to alkaline, and that it contained hydrogen dioxide, as tested by permanganate, equivalent to 0.056 gram oxygen. The precipitate dried at 100°C . weighed 2.034 grams, and the formula $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ requires that it should weigh 2.0293 grams.* The formula also requires that it should contain 0.0956 gram of peroxide oxygen, and this experiment gives 0.096 gram. This experiment shows that the precipitation of uranium in nearly neutral solutions is complete, and that the oxide precipitated has no acid reaction.

(III.) Uronic nitrate solution 50 c.c. containing 0.93 gram UO_3 .

Hydrogen dioxide solution 6 c.c. containing 0.0912 gram oxygen.

On making up the solution to 100 c.c. and filtering, 25 c.c. of the filtrate required 12.2 c.c. permanganate, showing that the excess of hydrogen dioxide in the filtrate contained oxygen amounting to 0.03904 gram. This gives peroxide oxygen contained in the precipitate 0.05216 gram, while the formula requires 0.052 nearly. In this experiment, nearly the whole of the uranium was precipitated, only a minute portion being kept in solution by the acid set free from the

* The equation representing the formation of this oxide may be written :—



nitrate. To determine this amount, another portion of 25 c.c. (one-fourth of the filtrate), evaporated to dryness and ignited, gave .009 of residue, consisting chiefly of UO_3 , and to determine the acid set free, I found that 25 c.c. of the filtrate required 20 c.c. of decinormal sodium hydrate, proving that the total filtrate contained 0.504 gram HNO_3 . The formula $\text{UO}_3 \cdot \text{N}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$, would give 0.407 gram, and the examination of the crystalline salt from which the above solution was prepared, showed that free nitric acid was present, the crystals no doubt having been formed in a strongly acid liquid. The free acid contained in the hydrogen peroxide used was very minute, corresponding to 1.8 c.c. of decinormal sodium hydrate solution.

(IV.) To show that there is, practically, no decomposition of hydrogen dioxide in such liquids as the above during the time of an experiment, I took 2 c.c. of the hydrogen dioxide used in Experiment 3, and 10 c.c. of the uranic nitrate solution, and after allowing the mixture to stand over four hours titrated with permanganate. There was decolorised 38 c.c. = .0304 oxygen, corresponding to 3.23 per cent. of real dioxide—exactly the percentage found in the dioxide titrated directly. This proves that, at ordinary temperatures, uranic oxide does not induce decomposition in the same manner as chromic and permanganic acids acting on hydrogen dioxide.

The following analyses have been made of this oxide after drying at 100°C . :—

- I. 0.279 gram ignited till its weight remained constant, gave 0.228 gram U_2O_5 , corresponding to 70.07 per cent. of uranium, or 84.08 per cent. of UO_3 .
- II. 0.329 gram treated with dilute sulphuric acid and titrated with permanganate, decolorised 19. c.c. = .01552 gram oxygen, corresponding to 4.71 per cent. of oxygen.
- III. 0.336 gram decolorised 19.7 c.c. permanganate solution = .01576 gram oxygen, corresponding to 4.69 per cent.
- IV. 0.336 gram decolorised 20 c.c. permanganate = 0.016 gram oxygen, corresponding to 4.76 per cent.
- V. 0.34 gram decolorised 20 c.c. permanganate = 0.016 gram oxygen, corresponding to 4.705 per cent.
- VI. 0.34 gram of this oxide decomposed by ignition and then dissolved in dilute nitric acid and titrated after addition of ammonia and acetic acid with standard solution of pure sodium phosphate (1 c.c. = 0.01858 gram UO_3 = 0.01548 U), required 15.5 c.c. = .2879 UO_3 , corresponding to 70.56 per cent. uranium, or 84.67 per cent. UO_3 .
- VII. 0.7 gram decolorised 41.3 c.c. permanganate solution = 0.3304 gram oxygen, corresponding to 4.72 per cent. of oxygen.

- VIII. 0·81 gram decolorised 48 c.c. permanganate = ·0384 gram oxygen, corresponding to 4·74 per cent.
- IX. 0·82 gram, after decomposition in acid solution by permanganate, was treated in the flask with granulated zinc and dilute sulphuric acid to reduce the uranium to uranous salt. (The liquid should scarcely cover the zinc, and the reduction is finished within 30 minutes more or less according to the proportions used. The liquid is then diluted, decanted clear or filtered, the zinc washed, and the washings added to the liquid, and the titration proceeded with after addition of dilute sulphuric acid.) There was decolorised in this case 48 c.c. of decinormal permanganate solution (1 c.c. = ·0008 gram oxygen = ·012 gram uranium) = 0·576 gram uranium, corresponding to 70·24 per cent. of uranium, or 84·28 of UO_3 .
- X. 0·81 gram titrated with permanganate required 48 c.c. permanganate = ·0384 gram oxygen, corresponding to 4·74 per cent. After reduction, it required 47·5 c.c. permanganate = 0·57 gram uranium, corresponding to 70·37 per cent., or 84·44 UO_3 . These numbers give water by difference as 10·82 per cent.
- XI. 0·81 gram gave 0·089 gram water, corresponding to 10·98 per cent.
- XII. 0·38 gram gave 0·04 gram water, corresponding to 10·52 per cent.

The following analyses have been made of the *air-dried* oxide prepared by pressure between folds of filter-paper :—

- XIII. 0·958 decolorised 51 c.c. permanganate = 0·0408 oxygen, corresponding to 4·25 per cent.
- XIV. 0·2572 heated in a current of dry carbon dioxide gave off 0·05 gram water = 19·44 per cent., and ·016 gram oxygen. The residue contained a certain proportion of green uranous oxide, so that when dissolved in sulphuric acid it reduced 6·25 c.c. of permanganate solution = ·005 gram oxygen. Deducting this oxygen from the total given off, we have ·011 gram due to the change of UO_4 into UO_3 , corresponding to 4·23 per cent. The residue weighed 0·191 gram, and adding the above oxygen = 0·196 gram UO_3 , corresponding to 76·20 per cent.

These numbers agree with the empirical formulæ :—

For the oxide dried at 100°C UO_4 . $2\text{H}_2\text{O}$
 And the air-dried oxide UO_4 . $4\text{H}_2\text{O}$

as the following comparisons show :—

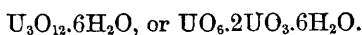
The oxide dried at 100° C.

	Calculated.	Found.									
		I. II.	III.	IV.	V. VI.	VII.	VIII. IX.	X.	XI.	XII.	Mean.
U ..	240	84.08	—	—	84.67	—	84.28	84.44	—	—	84.37
O ₃ ..	48	—	—	—	—	—	—	—	—	—	—
O ..	16	4.71	4.69	4.76	4.705	4.72	4.74	4.74	—	—	4.72
2H ₂ O	36	—	—	—	—	—	—	10.82	10.98	10.52	10.77
		—	—	—	—	—	—	—	—	—	—
	340	100.00									99.86

The air-dried oxide.

		Calculated.			Found.		
		XIII.	XIV.	Mean.			
U	240	63.83	76.60	76.20	—	—	—
O ₃	48	12.77	—	—	—	—	—
O	16	4.26	4.25	4.23	4.25	4.23	4.24
4H ₂ O ..	72	19.14	—	19.44	—	—	19.44
	—	—	—	—	—	—	—
	376	100.00					99.88

The decomposition of this oxide by alkaline hydrates and the study of the alkaline-compounds corresponding to it, lead to the adoption of a formula of thrice the molecular weight of the above, viz. :—



According to this view, it is the uranium-salt of peruranic acid.

Anhydrous Uranium Tetroxide.

When uranic nitrate solution is added to a mixture of hydrogen dioxide and large excess of sulphuric acid, no precipitate is obtained. On standing, however, a sufficient length of time, sometimes after a week, sometimes several weeks, a precipitate is slowly formed, which, as yet, I have only obtained in very small quantity. It is almost white in colour, generally heavy and crystalline, and is much more inert than the hydrated oxide previously described. Thus it is difficult to decompose it with permanganate, even in presence of large excess of sulphuric acid. On applying heat, the permanganate is slowly decolorised. The titration with permanganate is much facilitated by mixing the oxide in a mortar with a little strong alkaline hydrate solution, and then adding excess of sulphuric acid.

When carefully dried, this oxide gives off no moisture on heating alone. On heating it with hydrochloric acid, chlorine is evolved.

The analyses of this and the following compound must be regarded as provisional, pending attempts to obtain them in larger quantity.

- I. 0.0602 decolorised 3.95 c.c. permanganate
 = .00316 oxygen, or 5.24 per cent.
 „ gave .057 UO_3 , or 94.68 per cent., corresponding to 78.94
 per cent. of uranium.
- II. 0.154 decolorised 10 c.c. permanganate = .008 oxygen or 5.19 per
 cent., and gave .146 UO_3 or 94.8 per cent., corresponding
 to 79 per cent. of uranium.

These numbers agree with the formula UO_4 .

		Calculated.		Found.		Mean.
				I.	II.	
U 240	78.95	} 94.74	94.78	94.8	94.79
O_3 48	15.79				
O 16	5.26		5.24	5.19	5.21
	<hr/> 304	<hr/> 100.00				<hr/> 100.00

Higher Uranium Oxides.

I have not obtained the oxide U_2O_5 in a pure state or free from moisture. I have, however, determined the ratio of the uranium to

the oxygen in precipitates obtained by the slow decomposition of liquids prepared with a view to the isolation of peruranic acid (double peroxide of uranium and hydrogen, $\text{UO}_6 \cdot x\text{H}_2\text{O}$?).

5.04 grams ($= \frac{1}{160}$ atom in gram units) of pure crystallised uranic nitrate, were dissolved in the smallest possible quantity of water, and added gradually to a mixture of 20 c.c. of strong nitric acid of 60 per cent., and 45 c.c. hydrogen dioxide of 2.4 per cent. The liquid was made up to 75 c.c., and allowed to stand overnight. There was a very slow evolution of oxygen and deposition of a quantity of crystalline precipitate, which was collected and dried on clean bricks.

It was found to be completely soluble on triturating with sodium hydrate solution (20 per cent.), forming a liquid resembling in colour and characters the solution of the red-sodium salt to be afterwards described (p. 139).

Different portions of the precipitate gave the ratio—

$$\left. \begin{array}{l} \text{UO}_3 : \text{O} :: .489 : .04 \\ .489 : .0408 \\ .489 : .039 \end{array} \right\} = 12 : 1$$

This corresponds to the ratio of uranium to peroxide oxygen = 10 : 1 as required by the formula $\text{U}_2\text{O}_9 \cdot x\text{H}_2\text{O}$.

Attempts made to isolate the highest of these oxides corresponding to the salts have hitherto been unsuccessful. I shall, however, continue my efforts by application of very low temperatures for the isolation of the solid or liquid body, $\text{UO}_6 \cdot x\text{H}_2\text{O}$.

The decomposition of acid liquids containing uranic oxide and hydrogen dioxide in the proportions required by the formula UO_6 , varies considerably according to the temperature, the acid used, and other circumstances. It appears most apt to proceed to the limit of uranium tetroxide in the case of hydrochloric acid,* and least so in the case of sulphuric acid.

Ammonium Peruranate.

(Double Peroxide of Uranium and Ammonium.)

This salt is precipitated on addition of alcohol to uranic solutions to which hydrogen dioxide and ammonia in excess has been added.

On mixing a solution of 2.52 grams of crystallised pure uranic nitrate containing 1.2 gram uranium, 10 c.c. of hydrogen dioxide of 3.23 per cent., and then ammonia solution in excess, the precipitate at first formed was dissolved. Oxygen was also evolved, though to a less extent than in the preparation of the potassium salt. On addi-

* A bottle exploded in my hands in which this mixture had stood overnight.

tion of strong alcohol, the greater portion of the uranium was gradually precipitated. After standing one hour, the precipitate was collected on the filter.

Another experiment made by mixing 50 c.c. of uranic nitrate solution containing 0.774 gram of uranium with 10 c.c. of the same hydrogen dioxide and excess of ammonia gave, on addition of alcohol, and standing for one and a half hours a much less successful result. Excess of hydrogen dioxide therefore interferes with the precipitation of this compound.

The salt thus prepared is an orange-yellow precipitate readily soluble in water. In the dry solid state it is less affected by exposure to the air than the corresponding potassium or sodium compounds. It is the only ammonium salt that I have as yet obtained. Its solutions are precipitated by sodium and potassium hydrates, ordinary uranic hydrate being separated and sodium or potassium peruranates remaining in solution. Its solution gives precipitates with the solutions of most of the metals.

On heating the dry salt it glows like tinder and leaves a residue containing uranic and lower oxides of uranium.

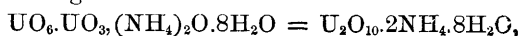
The following analyses have been made:—

- I. .372 gram salt titrated with permanganate required 27.3 c.c. = .0218 gram oxygen, corresponding to 5.86 per cent.
- II. .25 gram salt ignited gave residue U_2O_5 .173 gram = .176 UO_3 , corresponding to 70.4 per cent. UO_3 , or 58.67 per cent. uranium.
- III. .24 gram ignited, the residue dissolved in nitric acid, required, after addition of ammonia and acetic acid, 9.2 c.c. standard sodium phosphate solution to precipitate the uranium = .01548 \times 9.2 gram uranium = .1425 gram, corresponding to 59.35 per cent.
- IV. .41 gram dissolved in water required 10.2 c.c. decinormal sulphuric acid = 0.01734 gram NH_3 , corresponding to 4.22 per cent.

N.B.—The change of colour of the solution may be used as an index of the end-reaction and corresponds to the tests shown by litmus paper.

- V. .82 gram distilled with sodium hydrate and the ammonia estimated in the distillate required 20 c.c. standard acid = .034 NH_3 , corresponding to 4.15 per cent. ammonia.
- VI. .205 gram decolorised 15 c.c. permanganate = .012 gram oxygen, corresponding to 5.85 per cent.
- VII. .205 gram decolorised 15 c.c. permanganate = .012 gram oxygen, corresponding to 5.85 per cent.

These results agree with the formula—



as the following comparisons show :—

			Found.							
			Calculated.	I. II. IV. III. V. VI. VII.						
U ₂	480	58.54				58.67			59.35	
* O ₁₀	160	19.51				19.55			19.69	
† (NH ₄) ₂	36	4.39				4.47			4.39	
8H ₂ O	144	17.56	Difference			17.31			16.57	
	<hr/> 820	<hr/> 100.00				<hr/> 100.00			<hr/> 100.00	
Peroxide oxygen.										
* O ₃	48	5.85				5.86			5.85	
† (NH ₃) ₂	34	4.15				4.22			4.15	

The experimental numbers give the ratios—

Weight of uranium present : oxygen estimated by permanganate,
10 : 1 = 480 : 48.

Weight of uranium present : to ammonium,
40 : 3 = 480 : 36,

results which agree with the above formula.

Regarded as a double peroxide of uranium and ammonium, the formula of this compound becomes 2UO₄ . (NH₄)₂O₂ . 8H₂O. In this point of view this body may indicate the possible existence of ammonium peroxide. Attempts made to isolate this compound have hitherto failed, though I have observed that the smell of a mixture of concentrated hydrogen peroxide and ammonia is peculiar, and I have also obtained a crystalline double peroxide of silver and ammonium. I am therefore not without hopes of success in the isolation of ammonium peroxide.

Sodium Peruranate, UO₆ . 2Na₂O . 8H₂O.

(Double Peroxide of Uranium and Sodium, UO₄ . Na₄O₄ . 8H₂O.)

This compound is readily obtained by dissolving ordinary uranic hydrate or hydrated uranic tetroxide in sodium hydrate solution by addition of excess of hydrogen dioxide. It is well to use excess of alkaline hydrate, so as to avoid the formation of a second salt containing more uranium than the above.

If strong solutions be used, the salt crystallises out in a few hours in the form of yellow needles, sometimes grouped in star-like clusters. If more dilute solutions be used, the salt may be readily separated in crystalline needles or plates by addition of a little alcohol, in which it is much less soluble than sodium peroxide.

When freshly prepared this compound has a beautiful golden lustre.

On exposure to the air, it slowly effloresces with absorption of carbon dioxide and loss of oxygen. It is, however, much less affected by exposure to the air than pure sodium peroxide: an exposure of days in the one case producing little more effect than that of as many hours in the other.

It gives off a proportion of oxygen amounting to three atoms in the above formula in contact with solutions of acidified permanganate, alkaline hypochlorites, and other unstable oxygen compounds.

It gives precipitates with solutions of most of the metals. These precipitates are dissolved or modified by addition of acetic acid.

When heated alone it gives off oxygen gas equal to three atoms in the above formula and about three-fourths of its water, amounting to 17 per cent.

When heated in a current of carbon dioxide it gives off the same proportion of oxygen and all its water, amounting to 24 per cent.

The hydrochloric acid solution of the ignited salt does not dissolve gold, whereas that of the unchanged salt readily does so.

The solution of this salt is not completely decomposed by boiling, either alone or with addition of ammonia.

A solution containing 0.9565 gram boiled with excess of ammonia, and the liquid further left overnight to evaporate on the water-bath, gave a dry residue which was still entirely soluble in water, and on addition of dilute sulphuric acid decolorised 28 c.c. permanganate, showing that about one-third of the peroxide oxygen still remained in solution. During the boiling a precipitate of crystalline scales was observed.

The following experiments may be quoted relating to the preparation of the salt:—

Uranic nitrate solution containing 0.929 gram uranic oxide, dissolved in 50 c.c. of water, was mixed with 10 c.c. of hydrogen dioxide of 3.2 per cent. and excess of sodium hydrate solution. A portion of uranic oxide remained undissolved.

A solution containing half the above quantity of uranic oxide, 0.4645 gram, was mixed with 10 c.c. of hydrogen dioxide of 3.2 per cent. and 2 c.c. of 10 per cent. sodium hydrate solution added. Perfect solution of the uranium took place, and on addition of alcohol there was precipitated first a red crystalline salt and afterwards the yellow salt.

The salt was prepared for analysis by pressure between folds of filter paper. If the filter on which the crystalline precipitate, separated by alcohol, has been collected be spread out on a dry brick, it is easy to dry the salt rapidly. If the wet precipitate be left on the filter in the ordinary way to drain a considerable proportion of the salt may be lost by re-solution, especially in warm weather.

The following analyses have been made :—

- | | |
|------------------|--|
| 1st preparation. | I. 0.207 gram salt titrated with permanganate, required 20.6 c.c. = 0.01648 gram. oxygen, corresponding to 7.96 per cent. |
| | II. 0.207 gram salt required 20.5 c.c. permanganate = 0.0164 gram oxygen, corresponding to 7.92 per cent. |
| | III. 0.302 gram salt required 29.9 c.c. permanganate = 0.02392 gram oxygen, corresponding to 7.92 per cent. |
| 2nd preparation. | IV. 0.302 gram salt, ignited and dissolved in acetic acid, required for precipitation of the uranium 7.8 c.c. of sodium phosphate solution = 7.8×0.01858 gram UO_3 = 0.145 gram UO_3 , corresponding to 47.99 per cent., or 39.99 per cent. of uranium. |
| | V. 0.2 gram salt after two days' exposure to the air, decolorised 19.7 c.c. permanganate = 0.01576 oxygen, corresponding to 7.88 per cent. |
| | VI. 0.2 gram salt, ignited in a covered porcelain crucible, lost 0.0498 gram, amounting to 24.9 per cent. |
| 3rd preparation. | VII. 0.35 gram salt ignited lost 0.087 gram, corresponding to 24.86 per cent. |
| | Experiments VI and VII were made from the same portion of slightly decomposed salt as Experiment V, and the residue after ignition in each case effervesced on addition of acetic acid. |
| | VIII. 0.2 gram ignited dissolved in dilute hydrochloric acid; the uranium precipitated by ammonium hydrate: the filtrate evaporated, and the residue ignited, weighed 0.0785 gram consisting of sodium chloride, equivalent to 0.0416 gram sodium oxide, or 20.8 per cent. |
| 4th preparation. | The purity of this residue was ascertained by titration with decinormal silver nitrate solution, of which it required 13.2 c.c. This is equivalent to 13.2×0.0031 gram Na_2O = 0.0409 gram Na_2O or 20.45 per cent. |
| | IX. The residue from Experiment VII dissolved in nitric acid, and the uranium precipitated by ammonia, gave after ignition 0.163 gram U_3O_8 , corresponding to 47.45 per cent. UO_3 or 39.54 per cent. uranium. |
| | X. 0.9565 decomposed, dissolved in hydrochloric acid and precipitated by ammonia, gave 0.45 gram U_3O_8 , corresponding to 47.93 per cent. UO_3 or 39.94 per cent. of uranium. |

XI. 0.2039 gram heated in a current of carbon dioxide gave 0.049 gram water and 11.1 c.c. of oxygen gas reduced to standard temperature and pressure. This corresponds to water 24.03 per cent. and oxygen 7.8 per cent.

These results agree with the formula $\text{UO}_6 \cdot 2\text{Na}_2\text{O} \cdot 8\text{H}_2\text{O}$ or $\text{UO}_6\text{Na}_4 \cdot 8\text{H}_2\text{O}$, as the following comparisons show :—

		Found.					
		Calculated.	I. IV. VIII.	II. VII. IX.	III. X.	XI.	Mean.
U	240	39.74	47.99	47.45	47.93	—	47.79
O_3	48	7.94					
O_3	48	7.95	7.96	7.92	7.92	7.8	7.90
$2\text{Na}_2\text{O}$..	124	20.53	20.45	—	—	—	20.45
$8\text{H}_2\text{O}$	144	23.84 (Difference	23.60)	—	—	24.03	23.81
		<hr/> 604	<hr/> 100.00				<hr/> 99.95

Red Sodium Peruranate, $\text{U}_2\text{O}_5 \cdot \text{Na}_2\text{O} \cdot 6\text{H}_2\text{O} = \text{UO}_6 \cdot \text{UO}_3 \cdot \text{Na}_2\text{O} \cdot 6\text{H}_2\text{O}$
(on the peroxide view $2\text{UO}_4 \cdot \text{Na}_2\text{O}_2 \cdot 6\text{H}_2\text{O}$).

This salt is precipitated before the preceding when a minimum quantity of sodium hydrate solution is used. On addition of alcohol it often separates out as a deep red oil, slowly becoming crystalline.

The following analyses have been made :—

- I. 0.85 gram salt gave 0.619 UO_3 , corresponding to 72.82 per cent. UO_3 or 60.68 per cent. uranium.
- II. 0.85 gram salt decolorised 65 c.c. permanganate = 0.052 gram oxygen, corresponding to 6.11 per cent.
- III. 0.85 gram salt gave 0.125 NaCl , equivalent to 0.0662 Na_2O , or 7.78 per cent.
- IV. 0.918 gram salt decomposed by heat and titrated with sodium phosphate solution, after dissolving the residue in acetic acid, required 36 c.c. = $36 \times 0.01858 \text{ UO}_3 = 0.6689 \text{ UO}_3$, corresponding to 72.86 per cent. UO_3 , or 60.72 per cent. uranium.

These results agree with the above formula, thus :—

			Found.			
			I. II. III.			IV.
U ₂	480	60.45	}	72.82	72.86	
O ₆	96	12.09				
O ₃	48	6.05			6.11	
Na ₂ O	62	7.81			7.78	
6H ₂ O ...	108	13.60	(Difference.. 13.29)			
	<hr/>	<hr/>				
	794	100.00				

The ratio of the weights in this salt of the peroxide oxygen and of the uranium is 1 : 10 as in the case of the ammonium salt.

Potassium Peruranate, $\text{UO}_6.2\text{K}_2\text{O}.10\text{H}_2\text{O}$.

(*Double peroxide of uranium and potassium*, $\text{UO}_4.\text{K}_4\text{O}_4.10\text{H}_2\text{O}$.)

This salt is obtained by adding alcohol to its solution prepared by treating uranic nitrate with potassium hydrate and hydrogen dioxide in excess. It separates as a yellow or orange precipitate, which is much more unstable than the corresponding sodium and ammonium compounds, rapidly absorbing carbon dioxide when exposed to the air, and losing oxygen. It is also readily decomposed by heat, giving off water and oxygen.

Both the analyses and the formation of the salt show that it contains three atoms of peroxide oxygen to one of uranium.

The following experiments may be quoted :—

25 c.c. of uranic nitrate solution containing 0.387 gram of uranium treated with 10 c.c. of hydrogen dioxide (3.23 per cent.) and potassium hydrate (10 per cent.) gave, on addition of 25 c.c. of alcohol (80 per cent.), a crystalline precipitate which slowly separated out of the liquid. The salt must be separated as rapidly as possible from the liquid to prevent decomposition and loss of oxygen.

The following experiment, made before the analysis of the salt, is instructive as showing the proportion of peroxide oxygen required for its formation.

78 c.c. of uranic nitrate solution containing 1.2 gram of uranium were mixed with excess of pure potassium hydrate solution, — 10 c.c. of a 20 per cent. solution. Hydrogen dioxide was then slowly run in from a burette into the liquid, which was thoroughly shaken after each addition of the dioxide. It was found that to effect complete solution of the uranic hydrate in the alkaline liquid 12 c.c. were required containing 0.24 gram of peroxide oxygen. One atom or 240 parts of uranium would, therefore, require three atoms or 48 parts of

oxygen from the hydrogen dioxide* to produce the new soluble compound.

Owing to partial decomposition, I have been compelled to reject a large number of analyses made of this salt. The following were made the same day that the salt was prepared:—

I. 0.71 gram decolorised 60 c.c. permanganate = 0.048 gram oxygen, corresponding to 6.76 per cent.

The same, after being reduced by treatment with zinc and sulphuric acid, required 20.5 c.c. permanganate equivalent to 0.295 gram UO_3 , or 41.55 per cent. UO_3 , or 34.61 per cent. uranium.

II. 0.126 gram decolorised 10.8 c.c. permanganate = 0.00864 gram oxygen, corresponding to 6.87 per cent.

The same after reduction required 3.6 c.c. permanganate, equivalent to 0.05184 gram UO_3 , or 41.14 per cent., or 34.18 per cent. of uranium.

III. 0.13 gram decolorised 11 c.c. permanganate = 0.0088 gram oxygen, corresponding to 6.77 per cent.

These results agree with the above formula, thus:—

			Found.				
			I.	II.	III.	Mean.	
U	240	$\left. \begin{array}{l} 34.07 \\ 6.81 \end{array} \right\} \text{UO}_3$ 40.88	41.55	41.14	—	41.29
O ₃	48					
O ₃	48					
2K ₂ O	188.4	6.76	6.87	6.77		6.80
10H ₂ O	..	180					
		<hr/>					
		704.4	100.00				

The water in this formula is given only as that agreeing with the percentage composition of the salt dried by pressure between folds of filter paper.

IX. ON HIGHER OXIDES OF TUNGSTEN AND MOLYBDENUM. (Preliminary Notice.)

Tungstic dihydrate dissolves readily in solution of hydrogen dioxide, even in presence of much free acid, forming a liquid comparatively stable in dilute solutions, but which, in the case of strong acid solutions, gradually deposits insoluble tungstic oxide.

* 1 c.c. of this dioxide titrated at the same time required 25 c.c. permanganate solution, and contained therefore .02 gram oxygen. An experiment, with similar result, was made with sodium hydrate.

The solution evaporated to dryness over sulphuric acid *in vacuo*, gives transparent scales of a greenish-yellow colour, perfectly soluble in water. The solution so formed can be analysed by titration with permanganate in acid solutions, and as the titration proceeds, the insoluble tungstic hydrate re-appears.

The new tungstic oxide appears to form crystalline compounds with alkaline peroxides, which, however, are very unstable, and necessitate working at low temperatures.

Molybdic trioxide also reacts with hydrogen dioxide to form a compound which dissolves in acid solutions to form a yellow or deep orange liquid, and which gradually deposits an insoluble molybdic oxide of a yellow colour.

The solutions of molybdic trioxide in excess of alkaline hydrate and hydrogen dioxide are exceedingly unstable at ordinary temperatures, but appear to give crystalline compounds capable of existing at ice-cold temperatures.

I have, therefore, postponed the further study of these compounds until the prevalence of very cold weather renders this branch of the subject more accessible.

CONTENTS OF THE PAPER.

		PAGE
Part I.	<i>Hydrogen Dioxide and Metals</i>	1-6
	History and theories published.....	1
	Recurrent chemical action	2
	Action of metals under various conditions and new solvents for gold, silver, and platinum.....	3
	(Composition of hydrogen dioxide used. Note to page 3.)	
	Explanation of catalytic action of the metals.....	5
Part II.	<i>Hydrogen dioxide and metallic oxides</i>	6-8
	Theories of the reactions and discussion of the transmutations of energy involved in them.....	7
	Formation of unstable higher oxides	7
Part III.	<i>Thermo-chemistry of the oxygen molecule</i>	8-22
	The energy due to the formation of hydrochloric acid.....	8
	Energy due to the formation of water.....	9
	Method of approximating to the energy of the oxygen molecule..	9
	General observations on the energy due to chemical attraction ..	9
	The energy due to the formation of H_2O_2 and O_3 , &c.....	10-11
	The nascent state of elements	11
	Description of methods and apparatus used	11-15
	Results obtained by others	15
	Experiments with permanganic acid and hydrogen dioxide.....	15-17
	„ argentic oxide „	17-20
	„ hypochlorites „	21-22

WRIGHT ON THE ALKALOIDS OF THE ACONITES.

143

	PAGE
Part IV. <i>Hydrogen dioxide and chlorine, bromine, and iodine</i>	23
" V. " " sulphides	24
" VI. " " alcohol	24
Part VII. On <i>sodium dioxide</i> —new method of preparation, properties, and analyses	125-127
Part VIII. On <i>New Oxides and Compounds of Uranium</i>	127-141
Uranium tetroxide preparation, properties and analyses.....	127-141
Higher uranium oxides	133
Ammonium peruranate	134
Sodium peruranate	136
Red sodium peruranate	139
Potassium peruranate	140
Part IX. On <i>higher oxides of Tungsten and Molybdenum</i> (preliminary notice)	141
