XXI.—*On the Peroxides of Potassium and Sodium.*

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In 1810, three years after the discovery of the metals of the alkalies, the products of their oxidation were investigated by MM. Gay-Lussac and Thénard in France, and by Sir Humphry Davy in this country. These metals could then be obtained only in very small quantity. Sir H. Davy seems to have used in his experiments from one to eight grains, and MM. Gay-Lussac and Thénard employed a measured quantity which weighed no more than $\frac{3}{10}$ths of a grain. Another source of error in both sets of experiments was that the oxidation, instead of being allowed to proceed slowly, was suddenly effected at a high temperature by burning the metals in air or oxygen. It is probably to these two causes that we must attribute the fact that these distinguished chemists failed to ascertain the constitution of the alkaline peroxides.

MM. Gay-Lussac and Thénard* give a table of the numbers which they obtained by burning a known weight of potassium in oxygen, and measuring the volume of gas absorbed. These numbers are in truth singularly discordant, and the authors draw from them no other conclusion than that "the potassium had combined with twice and even three times as much oxygen as it requires to pass into the state of potash." In three experiments they weighed the oxide formed, in order to prove that "whatever is the quantity of oxygen which potassium absorbs, the weight of the oxide is always equal to that of the potassium employed and of the oxygen absorbed, and therefore no volatile product is disengaged." In these three experiments, however, the weight of oxide formed, compared with that of the potassium employed, agrees with the supposition that this body is a teroxide. But it is plain from the expressions above quoted that the authors did not regard them as decisive of this point. With reference to the peroxide of sodium, they state similarly, as the result of their experiments, that "sodium can take up half as much oxygen again as it requires to pass into the state of soda, and even more." Sir H. Davy referring to this research says,† "I have been able to confirm in a general way these interesting results, though I have not found any means of ascertaining accurately the quantity of oxygen contained in these new oxides."

These extracts are sufficient to show that the definite statements as to the constitution of these bodies, which have found their way into most works on chemistry, and which are at variance with my conclusions, cannot rightly claim the authority of the great names which they allege.

The experiments of which I am about to give an account originated some time ago in the investigation of the action of carbonic oxide upon potassium made by Professor Brodie, under whose directions the earlier and more critical of them were performed. They have been conducted throughout in the laboratory of the University of Oxford.

The primary experiment consists in submitting a known weight of potassium or sodium to the regulated action of oxygen gas. It is necessary for this purpose that the metal should be pure, and

* Recherches Physico-chimiques, Tome i., p. 132.

† Bakerian Lecture, 1810.

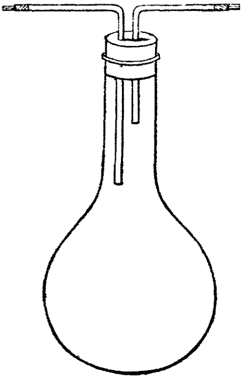
have as clean a surface as possible; both that it may be accurately weighed, and because a crust of hydrate hinders the action of the gas. As its preparation in this condition requires some little care, and is thus essential to the success of the operation, it may not be out of place to describe the means by which it has been effected.

The potassium or sodium was first purified, shortly before being used, by filtration through linen. The arrangement finally adopted for this purpose consists of two tubes, of which the outer is a large and stout test-tube, about eight inches long and rather more than an inch in diameter; the inner is of the same length but one-third narrower, and open at both ends. Over one end of the inner tube, which is bent outwards into a lip, a piece of linen is tightly bound. This smaller tube should reach to within about an inch and a-half from the bottom of the larger, and it is secured in this position by passing through a cork which fits loosely into the outer tube. For a piston, I employ a cylindrical cork, which will pass, by gentle pressure, from end to end of the inner tube, and a stout glass rod for piston-rod. A small hole pierced in the cork permits the air to escape when the piston is being forced down, but does not allow the passage of the melted metal. When the apparatus is thus complete, it is half filled with naphtha, and the globules of potassium (or sodium, as the case may be,) are introduced into the inner tube. Ten or twelve grammes may conveniently be filtered at one operation in tubes of the size described. The temperature is carefully raised until the potassium fuses; the cork is then introduced and pressed gradually down upon the melted metal, which passes in a fine shower through the linen strainer to the bottom of the outer tube, and is perfectly freed from its coating of oxide. When the whole has cooled, the inner tube is removed, and the small metallic particles may be aggregated into globules of a convenient size by being again fused and judiciously stirred and pressed with a glass rod. In order to free from naphtha and introduce into the bulb, in which it is to be subjected to the action of the gas, a sufficient quantity of potassium at one operation, a number of these smaller globules, are cast into a cylinder. I employ for this purpose a glass tube, of about half an inch in diameter, and three inches and a-half in length, which has been closed at one end like a test-tube and then divided by a crack lengthwise, from end to end. The two halves are re-united for the operation by being bound round with thread, and the mould thus formed is placed in a wider but rather shorter test-tube. It is then two-thirds filled with naphtha, which passes also into the outer tube, and the clean globules of potassium are rapidly introduced; by applying heat and stirring with a thin glass rod, the globules are readily united into one. In this way a solid cylinder of potassium is obtained, between one and one and a-half inch in length, and weighing from two to three grammes, which crystallizes on cooling with a brilliant metallic surface.

The apparatus used in the actual oxidation of the metal consists of a gas-holder of air and a gas-holder of oxygen; a washing bottle, containing solution of caustic potash, with which, by means of two separate tubes dipping into the fluid, both gas-holders communicate; a Liebig's bulb-apparatus, filled with the same solution; two U-tubes, containing respectively fragments of caustic potash, and pumice impregnated with strong sulphuric acid; a bulb of hard glass, in which the metal is exposed to the action of the gas; an air-bath for maintaining the bulb and its contents at a uniform temperature; and, lastly, a bulb-tube containing sulphuric acid, through which the gas passes as it issues from the apparatus. This bulb-tube (fig. 1) serves to close the apparatus against diffusion, to mark the rate of passage and pressure of the gas, and to dry any bubbles of air which a too rapid absorption may draw back into the bulb. The capacity of the bulb itself (fig. 2) is about 150 c. c. It is provided with an india-rubber cork, through which two small tubes, bent at a right

Fig. 1.

Fig. 2.



angle, pass into its interior. These, when gas is to be transmitted, are connected by pieces of caoutchouc tubing, one with the drying apparatus, and the other with the bulb-tube. They are closed when the bulb is removed from the apparatus with plugs of india-rubber.

The first operation is to dry the bulb absolutely by connecting it with the apparatus, and heating it while a current of air is passed through. When cool it is again disconnected, closed by replacing the plugs in the delivery-tubes, and weighed. It is next filled with dry nitrogen, and again weighed. Meanwhile the split-tube in which the metal has been cast is transferred to a dish containing naphtha of a low boiling point, and the thread, with which it is bound together, is removed; the solid cylinder is readily detached on opening the mould, and may be washed for a moment in the fresh naphtha. It is then rapidly transferred, still covered with naphtha, to a tube through which a current of dry nitrogen is being passed; and the tube is immediately closed by a cork holding a piece of small tubing drawn out to a fine point. By the application of a gentle heat, the naphtha may be completely distilled off in the current of nitrogen. When this is effected, and the bulb is in readiness, the two corks are removed simultaneously, and the mouth of the bulb applied to the end of the tube; by depressing this end the cylinder of potassium is caused to glide, protected by the nitrogen, from one into the other. The cork with its glass tubes is replaced and the bulb and potassium weighed. I have never succeeded in bringing the metal into the bulb with its lustre unimpaired, owing, probably, to the presence of a trace of oxygen in the nitrogen used; but the undiminished sharpness of the lines of crystallization on the surface, and the dull metallic appearance which it still retains, seem to show that the superficial oxidation is quite insignificant. When the surface of the metal is dried with blotting-paper, an opaque white crust is formed, and a little naphtha always remains behind, however rapidly and carefully the operation is performed. The bulb is now placed in an air-bath, and re-connected with the drying apparatus before described; heat is applied, and when the metal is in a state of fusion, air is very slowly passed through. The point at which the action commences has varied in different experiments. With potassium it is generally rather above 100° C., and with sodium, about 200° C. In both cases, when the action is once set up, it will continue at a much lower temperature, down apparently to the point of solidification of the metal.

The phenomena of the oxidation of potassium are remarkable.* Soon after the dry air has begun to mix with the nitrogen in the bulb, the grey film which covers the molten metal changes to a deep blue; the surface gradually becomes roughened by little wrinkles and projections, and a moment arrives when a single, spluttering spark appears at one point and a dust of white oxide rises in the bulb. At this instant the absorption begins. If very little oxygen is present in the bulb, the action is perfectly manageable, and the quantity of white oxide floating about is insignificant. But if the nitrogen has been replaced by air too quickly, a rapid absorption takes place, until the degree of dilution requisite for a gradual action has been attained, and a cloud of oxide covers the inner surface of the bulb, and passes, with each bubble of gas, through the sulphuric acid out of the apparatus. If, to obviate this, a plug of asbestos is placed in the exit tube, it becomes choked, and the transmission of gas is no longer possible. At the point at which the spark makes its appearance, the blue crust becomes white, and this change passes in a moment over its whole extent. Immediately afterwards it disappears entirely beneath the liquid metal, whose smooth surface is soon broken by innumerable projections which ascend and ramify with a steady, visible growth, having the white lustre of frosted silver. At the same time the metal climbs rapidly up the surface of the glass, extending in broad foliations, which grow together from side to side and cover sometimes the whole of the interior of the bulb. In more than one instance, the experiment has been abruptly terminated by this exuberant growth having reached to the delivery-tubes and stopped the passage of the gas. This phenomenon is probably due to the rising of the liquid metal by capillary attraction through the bulky powder which is being constantly formed upon its surface. At each point to which it thus ascends, it is converted into fresh oxide, which is flooded in its turn by fresh metal. After two or three hours, according to the rate at which air has been introduced, the whole becomes solid and the growth ceases. Gradually, as the oxidation proceeds, the metallic coating of the

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* The changes which take place may conveniently be observed by using a beaker for air-bath during the first stages of the action.

inner surface of the bulb changes to a dead white, and the brilliant undergrowth crumbles down into a shapeless powder.

No one who has watched these changes can doubt that the action consists of at least two stages. By carefully regulating the heat and the supply of air, nearly the whole of the potassium may be converted into a white oxide. I have endeavoured, by discontinuing the action and weighing the bulb and its contents, to determine exactly the amount of oxygen which had been absorbed when this point was reached. But, in every case, before the dark metallic foliations had quite disappeared, some portions of the oxide had assumed the yellow colour characteristic of the final product. Two weighings made at this point render it probable that the white oxide is a binoxide; but I have never yet terminated the action at this stage and made an analysis of the product, because of the evident want of homogeneity above mentioned. Finally the temperature is raised, and oxygen transmitted in the place of air. Even at this point, the operation may be ruined by a too speedy admission of the pure gas; for great heat is produced by the rapid absorption thus set up, sufficient even to melt the oxide which has been formed; the glass is attacked, and the fused mass, having become impervious to the gas, is incapable of complete oxidation. The safest course is to employ air until nearly the whole is converted into yellow oxide.

The action is brought to a close only with difficulty, or at least after a long time. I give one example:—The weight of potassium in the experiment was 1·608 gms. The first weighing was made when the conversion into yellow oxide appeared to be effected.

Weight of bulb and oxide			29·2624
Do. after the passage of oxygen for	8 hrs. at	210° C.	29·2924
„ „	4 „	280°	29·3497
„ „	8 „	230°	29·3645
„ „	4 „	230°	29·3658
„ „	8 „	230°—280°	29 3725
„ „	4 „	270°—280°	29·373

The final product is a powder of the colour of chrome yellow. It cakes together when subjected for some hours to a temperature of 280° C., but may in great part be broken up within the bulb, and separated from the sides by gentle tapping and shaking. When exposed to the air, it rapidly absorbs moisture and gives off oxygen. It effervesces strongly on being thrown into water. It contains four atoms of oxygen, and is represented by the formula K_2O_4.* The action of water upon it consists in the formation of two atoms of oxygen gas and one atom of binoxide of potassium, thus:—

$$K_2O_4 = K_2O_2 + O_2$$

I have ascertained the constitution of this body by determining, (1) the potassium which it contains, (2) the oxygen evolved from it by the contact of water and platinum black, (3) the oxygen evolved by the contact of water alone, and (4) the oxygen remaining in form of binoxide in the aqueous solution.

1.—*a.* 2·7665 grms. of potassium yielded 4·925 grms. of peroxide.

b. 1·6079 grms. potassium yielded 2·8779 grms. peroxide.

c. ·2946 grm. peroxide gave ·3648 grm. sulphate of potassium.

d. ·2276 grm. peroxide gave ·2765 grm. sulphate of potassium.

e. ·4495 grm. peroxide gave ·4481 grm. sulphate of potassium.

f. ·1414 grm. peroxide required for neutralization 7·07 c. c. of a standard solution of sulphuric acid, of which 1 c. c., according to a determination with chloride of barium, corresponded to ·01115 grm. potassium.

g. ·5093 grm. peroxide required 49·26 c. c. of a sulphuric acid solution, of which 1 c. c. corresponds to ·005682 grm. potassium.

2.—*a.* ·5844 grm. peroxide was introduced into a small apparatus contrived by Professor Brodie, consisting of a flask, in which the weighed amount of oxide is placed, together with, in these experiments, a small quantity of platinum-black,—a stoppered bulb, containing the fluid which is to be brought into contact with the oxide, and a potash-tube to dry the escaping gas. By loosening the stopper of the bulb, the water is suffered to descend upon the peroxide; a violent effervescence ensues. Five or ten minutes are generally sufficient to complete the action. The loss of oxygen in this experiment amounted to ·1894 grm.

b. ·584 grm. peroxide, treated in the same way, lost ·1825 grm. oxygen.

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* O = 16; S = 32; C = 12.

3.—These experiments were made in exactly the same way as the last two, except that no platinum-black was placed in the flask.

a. ·4495 grm. peroxide lost ·0906 grm. oxygen.
b. ·2927 grm. peroxide lost ·0624 grm. oxygen.
c. ·5184 grm. peroxide lost ·124 grm. oxygen.
d. ·5291 grm. peroxide lost ·1098 grm. oxygen.

In *a*, the flask was immersed in a freezing mixture during the decomposition. In *b*, the water used was acidulated with sulphuric acid. Both methods were successful in preventing the decomposition of the solution of binoxide which is formed. In *c*, neither precaution was taken, and bubbles continued to rise through the fluid after the termination of the first action. The number representing the loss of oxygen is for this reason too high, and the binoxide remaining in the liquid, determined immediately afterwards with permanganate solution, was proportionately too low.

4.—*a.* ·2954 grm. peroxide, dissolved in water acidified with sulphuric acid, decolorized 54·39 c. c. of a solution of permanganate of potassium,* of which 1 c. c. corresponded to ·000595 grm. oxygen.

b. ·2049 grm. peroxide thrown into water containing ice, effervesced equally on the first contact, and decolorized 37·53 c. c. of the same standard solution of permanganate.

c. ·0899 grm. peroxide similarly treated, required 16·27 c. c. of permanganate.

d. ·0595 grm. peroxide required 10·8 c. c.

e. ·0614 grm. peroxide required 11·1 c. c. of a permanganate solution, of which 1 c. c. corresponded to ·000616 grm. oxygen.

These numbers, calculated on a hundred parts of the peroxide used, are compared below with those deduced from the atomic weight assigned to it.

		At. W.	p. c.	*a.*	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
1.	K_2	78	54·93	56·17	55·87	55·51	54·45	55·86	55 ·8	54·96
	O_4	64	45·07							
	K_2O_4	142	100·00							

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* This reaction has been ascertained by Professor Brodie to be perfectly definite, the two solutions losing exactly equal quantities of oxygen.

		At. W.	p. c.	*a.*	*b.*
2.	K_2O	94	66·2		
	O_3	48	33·8	32·41	31·25
	K_2O_4	142	100·0		

				a.	*b.*	*c.*	*d.*
3.	K_2O_2	110	77·46				
	O_2	32	22·54	20·19	21·3	23·9	20·75
	K_2O_4	142	100·00				

				a.	*b.*	*c.*	*d.*	*e.*
4.	K_2O_3	126	88·73					
	O	16	11·27	10·95	10·9	10·77	10·98	11·14
	K_2O_4	142	100·00					

I am sensible that numbers might be obtained, agreeing more closely than some of these do with the calculated results; but—regarding especially the ratio of the weights of oxygen in the three sets of determinations,—these seem to me already sufficient to leave no doubt as to the constitution of this peroxide.

The phenomena of the oxidation of sodium resemble, in some degree, those already described as occurring in the case of potassium. But they are far less striking. The growth upon the surface of the fused metal, in the first stage of oxidation, is lower and less tree-like; its lustre is soon dulled by a covering of white oxide. The metal does not spread itself on the glass, and in consequence a larger quantity may be operated upon at once in a bulb of the same size. I have several times employed Florence flasks for the oxidation of sodium; but they are always attacked to some extent by the oxide, which has more action upon glass than the peroxide of potassium at the same temperature. A shorter time and a rather lower temperature is required for the complete peroxidation of sodium than of potassium. The peroxide of sodium is of a pure white colour; like the oxides of zinc and tin, it becomes yellow when heated, and on cooling again loses this tint. Exposed to the air, it slowly deliquesces, and after a while resolidifies as carbonate. Great heat is produced on mixing it with water, and a small quantity of gas is evolved;* the quantity is least when the peroxide is in the state of fine powder, and is projected little

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* This evolution of gas probably results from the local heating of the moistened peroxide: for the concentrated alkaline solution is rapidly decomposed at the boiling point.

by little into a large excess of acidulated water. If a small heap of it is moistened, it becomes yellow with heat, and the disengagement of gas is considerable. It contains two atoms of oxygen, and is represented by the formula Na_2O_2. The normal action of water upon it consists in the simple solution of the binoxide.

I have determined, in order to ascertain its constitution, (1) the sodium which it contains, and (2) the weight of oxygen which it loses by the contact of water and platinum-black, or when reduced by a standard solution of permanganate of potassium.

1.—*a.* 2·5225 grms. sodium yielded 4·2443 grms. peroxide.
b. 3·6418 grms. sodium yielded 6·1233 grms. peroxide.
c. 11·8085 grms. sodium yielded 19·79 grms. peroxide.
d. ·2861 grm. peroxide gave ·522 grm. sulphate of sodium.
e. ·4461 grm. peroxide gave ·8075 grm. sulphate of sodium.
f. ·3118 grm. peroxide required for neutralisation 28·1 c. c. of a standard solution of sulphuric acid, of which 1 c. c. corresponds to ·00658 grm. sodium.
g. ·352 grm. peroxide required 61·7 c. c. of sulphuric acid, of which 1 c. c. corresponds to ·003358 grm. sodium.
h. ·4132 grm. peroxide required 72·6 c. c. of the same acid.

2.—*a.* ·0979 grm. peroxide required, to impart colour to its solution, 31·6 c. c. of a solution of permanganate of potassium, of which 1 c. c. corresponded to ·00063 grm. oxygen.
b. ·1124 grm. peroxide required 42·75 c. c. of a solution of which 1 c. c. corresponded to ·000516 grm. oxygen.
c. ·0327 grm. peroxide required 8·4 c. c. of a solution of which 1 c. c. corresponded to ·000774 grm. oxygen.
d. ·1302 grm. peroxide required 33·46 c. c. of the same solution.
e. ·0715 grm. peroxide required 18·33 c. c. of the same.

The results per cent., derived from these numbers, are exhibited below :—

				a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
1.	Na_2	46	58·97	59·43	59·47	59·6	59·1	58·64	59·28	58·86	59
	O_2	32	41·03								
	Na_2O_2	78	100·00								

				a.	*b.*	*c.*	*d.*	*e.*
2.	Na_2O	62	79·49					
	O	16	20·51	20·33	19·64	19·88	19·89	19·84
	Na_2O_2	78	100·00					

Several experiments were made in the flask-and-bulb apparatus, before described, of the action upon the binoxide of water and platinum-black. The numbers arrived at agreed perfectly with those obtained in the determinations with permanganate of potassium.

When a solution of this binoxide of sodium is evaporated on a water-bath, oxygen is given off, slowly at first, but rapidly when the solid residue is beginning to separate. But if the evaporation is allowed to proceed slowly, at ordinary temperatures, by placing the solution under a bell-jar over sulphuric acid, large tabular crystals, of a hexagonal form, make their appearance.

These crystals are a hydrate of the binoxide of sodium. Their constitution was determined in the following manner:

When nearly the whole of the water had evaporated, the crystals were spread rapidly between two thick folds of blotting paper, round which a sheet of india-rubber was wrapped to prevent the access of carbonic acid. The whole was then strongly pressed for eight or ten hours.

In two preparations, the crystals thus dried were at once divided into two portions and analysed. One portion was dissolved in dilute acid, and the oxygen contained in it determined by a standard solution of permanganate of potassium. The other was placed in a silver boat and heated in a current of dry carbonic acid, by which the binoxide is readily converted into simple carbonate; the water which separates was collected at the same time in a weighed drying-tube. The increase in weight of this tube and the weight of the carbonate which has been formed, indicate at once the amount of water and of sodium which the hydrate contains. The following are numbers obtained in these analyses; they show that the crystallized hydrate consists of a combination of one atom of the anhydrous binoxide with eight atoms of water.

Preparation 1.—*a.* ·2546 gm. of crystallized hydrate required 29·72 c. c. of permanganate solution, of which 1 c. c. yielded ·0006116 grm. oxygen.

b. ·3968 grm. of hydrate gave ·1912 grm. carbonate of sodium, and ·2527 grm. water.

Preparation 2.—*a.* ·2350 grm. of hydrate required 26·82 c. c. of the same permanganate solution.

b. ·3614 grm. of hydrate gave ·176 grm. carbonate of sodium, and ·2305 grm. of water.

To place it beyond a doubt that the residue in these experiments consisted purely and simply of carbonate of sodium, it was washed into a flask, coloured with litmus, and determined by means of a standard acid solution. The results obtained were conclusive,—*e. g.*, ·176 grm.,—the weight of carbonate obtained in the last experiment,—required 22·72 c. c. of an acid solution, of which 1 c. c. corresponded to ·003358 grm. of sodium. This weight of pure carbonate of sodium ought theoretically to have required 22·74 c. c. of such a solution.

The percentage composition of this hydrate calculated from the foregoing data is compared below with that deduced from the formula assigned to it; the oxygen actually found being half that which the binoxide contains, its number is doubled:—

			Prep. 1.	Prep. 2.
Na_2	46	20·72	20·91	21·10
O_2	32	14·42	14·28	13·96
$8H_2O$	144	64·86	63·68	63·78
$Na_2O_2,8H_2O$	222	100·00	98·87	98·84

In a third preparation of the hydrate, the quantity of water which it loses when left to effloresce over sulphuric acid, was determined. The crystals, after having been dried as before, and weighed between watch-glasses, were exposed under a bell-jar over sulphuric acid, and re-weighed at intervals of two or three days. After nine days the weighings became constant, and the residue was determined as in the preceding experiments.

a. ·647 grm. of crystallized hydrate yielded ·3287 grm. of effloresced hydrate, and lost consequently ·3183 grm. of water.

b. ·2226 grm. of effloresced hydrate, heated in a current of dry carbonic acid, yielded ·2071 grm. of carbonate of sodium. The water given off weighed ·071 grm.

c. ·0268 grm. of effloresced hydrate, dissolved in acidified water, decolorized 5·98 c. c. of a solution of permanganate of potassium, of which 1 c. c. corresponded to ·0006116 grm. of oxygen.

The weight of water lost by the crystallized hydrate in Exp. *a*, corresponds to six out of the eight atoms which it contains. The residue must therefore have the constitution Na_2O_2, $2H_2O$. Determinations *b* and *c* confirm this conclusion.

		Theory.		Found.
a.	$Na_2O_3,2H_2O$	114	51·35	
	$6H_2O$	108	48·65	49·2
	$Na_2O_2,8H_2O$	222	100·00	
b.	Na_2	46	40·35	40·37
	O_2	32	28·06	
	$2H_2O$	36	31·59	31·89
	$Na_2O_2, 2H_2O$	114	100·00	
c.	Na_2O	62	54·38	
	O	16	14·03	13·65
	$2H_2O$	36	31·59	
	$Na_2O_2, 2H_2O$	114	100.00	

It is worthy of remark that this hydrate stands in the same relation to a sesquihydrate and a protohydrate in which the binoxide stands to a sesquioxide and a protoxide. For if we subtract the formula of a protoxide from that of a sesquioxide, we obtain the formula of a binoxide; and similarly, by subtracting the formula of a protohydrate from that of a sesquihydrate, we obtain the formula of the hydrate of this binoxide :—

$$\begin{array}{lll} M_4O_3 & M_2H_3O_3 & = \tfrac{1}{2}\,(M_4O_3 + 3H_2O) \\ M_2O & M\ H\ O & = \tfrac{1}{2}\,(M_2O + H_2O) \\ \hline M_2O_2 & M\ H_2O_2 & = \tfrac{1}{2}\,(M_2O_2 + 2H_2O) \end{array}$$

Or again, as we compare a sesquioxide and the hydrate corresponding with a protoxide and its hydrate by the assumption of a distinct atomic weight, writing *e. g.* fe_2O, and feHO where $fe = \tfrac{2}{3}$ Fe, so the binoxide with its hydrate may, for the sake of a similar comparison, be represented by the formulæ na_2O and naHO, where $na = \tfrac{1}{2}$ Na.

The formation of these hydrates, together with the fact of the increased stability of a solution of peroxide when acidified, suggested the expectation that corresponding salts might be obtained. Accordingly, three portions of a solution of binoxide of sodium were exactly neutralized with sulphuric, nitric, and hydrochloric acids respectively, and evaporated to dryness by exposure over sulphuric acid. The crystals which were formed consisted simply of sulphate, nitrate, and chloride of sodium. This experiment was repeated with the same result.

It has been stated that when the tetroxide of potassium is projected into water, a solution of binoxide is formed. It seemed probable that, by the slow evaporation of this solution, a hydrate might be obtained corresponding to the hydrate of the binoxide of sodium. Such, however, is not the case. Upon reaching a certain degree of concentration, the solution is entirely decomposed, with evolution of oxygen. The ultimate residue is opaque and slightly crystalline. It contains no binoxide.

The behaviour of these peroxides with various chemical reagents offers an interesting subject for investigation. I have already made a few experiments of this kind, a brief account of which I may be allowed here to append.

The general form of these experiments has been the same. The peroxide was placed in a boat of glass, silver, or platinum, and weighed in a small test-tube. The boat, with its contents, was then transferred to a piece of combustion-tubing connected at one end with an apparatus for drying the gas to be transmitted, and at the other with a bulb-tube (fig. 1) containing sulphuric acid. Heat was applied, as seemed requisite, by means of a lamp placed beneath the tube. When the action appeared to be complete, the boat and its contents were withdrawn, replaced in the test-tube, and again weighed. The operation was repeated a second time, or several times if necessary, until two successive weighings gave nearly the same result.

The first of these experiments consisted in heating the peroxides in an atmosphere of nitrogen, in order simply to ascertain their behaviour at a high temperature. 0·2288 grm. of binoxide of sodium were exposed in a silver boat to the strongest heat of a large Argand gas-burner. The powder passed from white to a full yellow, and caked together, but neither fused nor decomposed. The flame from a wire-gauze gas-burner, playing round the glass tube which contained the boat, produced partial fusion; at the same time, the silver was strongly acted upon, but no oxygen was evolved. The temperature was then allowed to fall. The colour of the fused mass was black while hot, brown on cooling. It weighed ·2244 grm. On treating it with water, a quantity of oxide of silver separated, which was at the same moment reduced, with effervescence, by the excess of unaltered binoxide of sodium. Hence the only reaction which can be thus observed is that of the binoxide upon the silver: $Na_2O_2 + Ag_2 = Na_2O + Ag_2O$.

The tetroxide of potassium, similarly heated, became first of a deep orange colour, and then melted to a black fluid, which, when the temperature was allowed to fall, crystallized with shining tabular surfaces; the whole, on further cooling, gradually became yellow again. Its weight after it had been thus fused was unaltered. On applying the full heat of a large gas flame the black fluid was gradually decomposed with evolution of oxygen; the residue became grey and infusible. The loss of weight corresponded to a loss of two atoms of oxygen.

·504 grm. of tetroxide of potassium left a residue weighing ·3933 grm., or 78·4 per cent. If 2 atoms of oxygen are evolved, the proportion of the residue should be 77·47 per cent.

The weight of silver acted upon was ·597 grm., or rather more than 1½ atom for 1 atom of peroxide. The action, whose completion the infusibility of the residue may have hindered, is doubtless the following:

$$K_2O_4 + Ag_2 = K_2O + Ag_2O + O_2.$$

From the fact that 2 atoms of oxygen were evolved while less than 2 atoms of silver were acted upon, it would seem to follow that the former action occurs independently of the latter.

Several attempts have been made, by bringing together sulphur and the tetroxide of potassium, to obtain the reaction,

$$K_2O_4 + S = K_2SO_4.$$

When these two bodies are heated together, a violent deflagration takes place; but by distilling the vapour of sulphur over the peroxide in an atmosphere of nitrogen, the action may be made to proceed gradually. In all the experiments, some sulphate was formed, and in one a large proportion; but, unless the temperature and the supply of sulphur vapour are most carefully regulated, the principal products are a polysulphide, of liver-colour, and sulphurous acid. Binoxide of sodium also readily combines with sulphur vapour, forming a brown fusible mass which contains a polysulphide and a little sulphate. Sulphurous acid is disengaged.

When binoxide of sodium is similarly heated in the vapour of iodine, the two gradually combine. The product is a white fusible body, apparently quite homogeneous.

·203 grm. of binoxide of sodium yielded ·8181 grm. of this substance; whence the amount of product corresponding to 100 parts of the binoxide is 403 parts.

According to the equation,

$$Na_2O_2 + I_2 = Na_2OI_2 + O;$$

100 parts should yield 405 parts. This equation represents in the simplest form the change of weight that has taken place, the substitution for an atom of oxygen of the equivalent quantity of iodine; but the residue may also consist of a mixture of iodide of sodium with iodite of sodium or iodate, *e. g.*:

$$3Na_2O_2 + 3I_2 = 5NaI + NaIO_3 + 3O.$$

On dissolving the product and adding an acid, a copious precipitate of iodine was formed. This iodine was determined, and the quantity found agreed with the conclusion above stated.

Action of Carbonic Oxide upon Binoxide of Sodium.

The dry gas, in this and the succeeding experiments, was slowly led through the tube in which the boat with its contents was placed, and the current from time to time discontinued; any absorption or evolution of gas could thus be readily noted by watching the movements of the fluid in the sulphuric acid bulb-tube (Fig. 1). At a temperature of 100°—150° C., a slight absorption took place. On raising the heat, it proceeded rapidly, a dark shade passing over the surface of the binoxide, which was at the same time partially fused. After a while, it again proceeded slowly, and the contents of the boat became once more white.

The weight of binoxide of sodium taken was ·352 grm.: the weight of the product ·4753 grm.; being in the ratio of 100 : 135.

According to the equation,

$$Na_2\,O_2 + CO = Na_2\,CO_3,$$

100 parts of binoxide of sodium should yield 135·9 parts of carbonate. The product was also identified qualitatively.

Action of Carbonic Acid upon Binoxide of Sodium.

At a temperature below 100° C. the first sign of action appeared. A shade of brown, as in the preceding experiment, passed over the binoxide, and at the same moment a slight absorption took place. On raising the temperature, after an hour's slow passage of the gas, a similar further action ensued. Finally the residue was perfectly white.

The weight of binoxide of sodium taken was ·4132 grm. that of the product ·5565 grm., being in the ratio of 100 : 134·7.

The product is, therefore, as before, carbonate of sodium; and the reaction which takes place is the following:

$$Na_2\,O_2 + CO_2 = Na_2\,CO_3 + O.$$

Action of Carbonic Oxide upon Tetroxide of Potassium.

The action was set up at a temperature of rather more than 100° C.; a single scintillation and a deepening of the colour of the peroxide marked its commencement. A weighed Liebig's potash-bulb apparatus and potash-tube had been attached to the apparatus, in order to determine the carbonic acid which it seemed probable might be formed. The even passage of the gas through the bulbs, while its action upon the peroxide was proceeding rapidly, showed that its volume suffered neither diminution nor increase. The residue in the boat, when the action was completed, was white. ·2314 grm. of tetroxide of potassium yielded ·2245 grm. of this product, numbers in the ratio of 100: 97. 100 parts of the tetroxide should yield, theoretically, 97·2 parts of carbonate of potassium. The product was also identified qualitatively.

The potash-bulbs and tube gained only ·005 grm. In another experiment, where the gas issuing from the apparatus was passed through lime-water, no turbidity whatever was produced.

The reaction is, therefore, that expressed by the following equation:

$$K_2O_4 + CO = K_2CO_3 + O_2.$$

The perfect constancy in the volume of the gas throughout the experiment goes to prove, not only that the volume of oxygen evolved is equal to that of the carbonic oxide absorbed, but that the two actions proceed proportionally. The carbonic oxide is substituted for an equivalent quantity of oxygen,

$$K_2O_2,O_2 + CO = K_2O_2,CO + O_2.$$

Action of Carbonic Acid upon Tetroxide of Potassium.

In the cold apparently no action took place, but it was set up below 100° C. The contents of the boat changed colour gradually from yellow to white. A quantity of oxygen was evolved. ·4498 grm. of the tetroxide yielded a product which weighed ·4379 grm. These numbers are in the ratio of 100 : 97·35. The product consisted of carbonate of potassium. The reaction is represented by the equation,

$$K_2O_4 + CO_2 = K_2CO_3 + O_3.$$

Action of Protoxide of Nitrogen upon Binoxide of Sodium.

The gas employed was prepared in the usual manner from nitrate of ammonium, washed with solutions of sulphate of iron and of caustic potash, and carefully dried. It had no action upon the binoxide until a temperature had been reached at which the latter showed signs of fusion, and of attacking the silver boat. At this point, a few particles became suddenly of a deep red, and this change passed by degrees upon the whole mass, which, though the heat was lowered, fused gradually with effervescence. A slight absorption took place, and the issuing gas lost for a while its power of brightening a glowing splinter of wood. The product was examined qualitatively. It had an alkaline reaction and gave off nitrous fumes in great abundance upon the addition of sulphuric acid.

A little of the substance had been thrown, by the effervescence which followed its fusion, out of the silver boat upon the sides of the glass tube in which it was placed. These spirtings were washed out, after the close of the experiment, and converted into chloride. The chloride thus formed weighed ·0791 grm. The weight of binoxide of sodium originally taken was ·9068 grm.; which, after subtracting the weight of the amount lost, as deduced from the above determination, becomes ·8542 grm. The product, which was shown by the qualitative examination to consist principally of nitrite of sodium, weighed 1·4049 grm. These numbers are in the ratio of 100 : 164.

According to the reaction,

$$Na_2O_2 + 2N_2O = 2NO_2Na + N_2,$$

100 parts of binoxide of sodium should yield 176·9 parts of nitrite.

The alkaline reaction of the solution revealed one cause of the above deficiency, viz., the presence in the product of binoxide of sodium which had not been acted upon. The reaction might be due also to the presence of caustic alkali; but its formation under the above circumstances is exceedingly improbable, except through the action of the silver, and this action is insignificant in amount.

The phenomena of a second experiment exactly resembled those of the first; the absorption and the formation of nitrogen were well marked. There was again some loss by spirting, some action on the silver boat, and some alkali, presumably binoxide, remaining in the product. The error from these sources seemed more capable of being determined and thus eliminated, than of being avoided in any repetition of the experiment.

Accordingly, the spirtings were converted into sulphate and weighed; the amount of unchanged binoxide was determined by a standard acid solution; the silver boat was cleaned from oxide and its loss of weight ascertained; and, finally, the total amount of nitrite was determined by means of permanganate of potassium.

a. The sulphate formed from the spirtings weighed ·083 grm.

b. The solution of the total product required for its neutralization 10·4 c. c. of an acid solution, of which 1 c. c. corresponded to ·003376 grm. of sodium.

c. The same solution, largely diluted, and acidified, decolorized 305·6 c. c. of a solution of permanganate of potassium, of which 1 c. c. corresponded to ·0006116 grm. of oxygen.

d. The silver boat had lost by oxidation ·022 grm.

Hence we have,—

Weight of binoxide originally taken . . .		·6047 grm.
Deduct—*a*. For loss by spirting .	·0456 grm.	
b. For unchanged binoxide	·0595 grm.	
Total . .		·1051 grm.
Weight of binoxide which has taken part in the reaction		·4996 grm.
Weight of the total product		·9491 grm.
Deduct—*b*. For unchanged binoxide	·0595 grm.	
d. For oxidation of the silver boat . . .	·0016 grm.	
Total . .		·0611 grm.
Actual product of the reaction . .		·888 grm.

·4996 : ·888 :: 100 : 177·7

A ratio closely coinciding with that calculated from the equation already given.

If we suppose the small quantity of binoxide of sodium reduced to protoxide by the silver of the boat to have remained in that condition and not to have been reoxidized by the protoxide of nitrogen, the ratio becomes 100 : 178.

The amount of nitrite calculated from determination *c*, after making a correction for the admixture of binoxide,[*] is ·859 grm. The deficiency was due to insufficient dilution causing the escape of a little nitrous gas.

Nitrous oxide does not act upon tetroxide of potassium at any temperature to which the latter can be heated without decomposition in a silver vessel.

Action of Nitric Oxide upon Binoxide of Sodium.

The gas was prepared by the action of nitric acid upon copper, washed in a large volume of water, and dried by passage through sulphuric acid. The apparatus was filled with nitrogen before the

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[*] Nitrous acid is immediately oxidized by an acid solution of binoxide of sodium. Besides the source of error mentioned above, the determination of nitrous acid with permanganate of potassium is liable to the objection that the reaction towards the close of the experiment proceeds very slowly.

introduction, and again before the withdrawal, of the boat containing the binoxide, to prevent the formation of hyponitric acid. The first signs of action appeared at a temperature of about 150° C. Portions of the substance became of a deeper colour and began to fuse. The whole was by degrees converted into a clear colourless liquid, an absorption of the gas taking place throughout. ·6456 grm. of binoxide of sodium were taken: the product weighed 1·1396 grm. These numbers are in the ratio of 100 : 176·5. According to the equation

$$Na_2O_2 + N_2O_2 = 2NO_2Na.$$

100 parts of binoxide of sodium should yield 176·9 parts of nitrite of sodium.

Action of Nitric Oxide upon Tetroxide of Potassium.

From the analogy of the preceding reaction, it seemed probable that in this case a combination equally simple would lead to the formation of nitrate of potassium:

$$K_2O_4 + N_2O_2 = 2NO_3K.$$

This, however, is certainly not the principal reaction, and probably does not take place at all. In three experiments, the product consisted of a mixture of nitrate and nitrite of potassium. In the first, the two were formed in atomic proportions: the relation was probably accidental, since, in the succeeding experiments, the proportion of nitrite was larger. The action was set up either in the cold or upon the application of a gentle heat. The yellow colour of the peroxide changed to white in parts gradually, in parts after first assuming a deeper tint and undergoing semi-fusion. Copious red fumes were formed, which passed on into the bulb-tube (nitric oxide being all the while slowly transmitted,) and formed crystals with the sulphuric acid which it contained. At the same time, an absorption of gas was apparent. When no further change could be observed, the nitric oxide was expelled from the apparatus, as before, by a current of nitrogen, and the boat and its contents removed and weighed. A second exposure to the action of the gas at a higher temperature produced no change in the weight.

1.—·3735 grm. of tetroxide of potassium yielded a product weighing ·488 grm.

2.—·2633 grm. of tetroxide yielded a product weighing ·3394 grm.
3.—·3752 grm. of tetroxide yielded a product weighing ·4737 grm.

These numbers, referred to 100 parts of the tetroxide, become,

1.	2.	3.
130·6	128·9	126·2.

If the product consist of nitrite, 100 parts of tetroxide of potassium should yield 119·7 parts; if of nitrate, 142·3 parts.

The product of Exp. 1 was dissolved in water, and the solution was divided into three equal parts.

a. Part 1 was determined with a standard solution of permanganate, to ascertain the amount of nitrite in the product. It required 24·77 c. c. 1 c. c. of the solution corresponded to ·000561 grm. of oxygen.

b. Part 2 was mixed with sulphuric acid, evaporated, ignited, and weighed. The weight of the sulphate of potassium thus obtained was ·1533 grm.

c. Part 3 was introduced into a flask containing solution of caustic potash and fragments of zinc and iron. The ammonia evolved on boiling was collected and determined by means of a standard acid solution.* It required 11·5 c.c. of a solution, of which 1 c. c. corresponded to ·00204 grm. of nitrogen.

From *a*, the total product must contain ·2215 grm. of nitrite of potassium, and therefore, supposing it to consist entirely of a mixture of the two, ·2665 grm. of nitrate. The supposition may be tested by comparing the proportion of potassium and nitrogen which such a mixture should contain, with the results of the determinations *b* and *c*. ·2215 grm. of nitrite of potassium contain by calculation ·1016 grm. of potassium and ·0365 grm. of nitrogen; ·2665 grm. of nitrate of potassium contain ·1029 grm. of potassium and ·0369 grm. of nitrogen.

		b.	*c.*
Total potassium in mixture	·2045	·2062	—
Total nitrogen	·0734	—	·0707.

The products of Exps. 2 and 3 were similarly determined with the same result.

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* The details of this method, which is both expeditious and exact, I hope to make the subject of a future communication.

Therefore, by the reaction of nitric oxide upon tetroxide of potassium, are formed hyponitric acid, and nitrate and nitrite of potassium in variable proportions. The only two palpable sources of variation are differences of temperature, depending upon the greater or less violence of the action, and differences in the time during which the hyponitric acid formed is in contact with the solid product, depending mainly upon the rate of transmission of the nitric oxide. The latter, I believe, to be the true cause of the variation in the product. If so, it is probable that three separate reactions play a part in producing the final result.

$$\begin{aligned}
&(1.)\ K_2O_4 + N_2\,O_2 = K_2O_2 + N_2O_4\,;\\
&(2.)\ K_2O_2 + N_2O_2 = 2KNO_2\,;\\
&(3.)\ K_2O_2 + N_2O_4 = 2KNO_3.
\end{aligned}$$

Long digestion, with a small quantity of nitric oxide, ought in this case to produce little but nitrate, and the action of a rapid current of the gas little but nitrite. Future experiments, especially upon the action of hyponitric acid on these peroxides, may decide this point.