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IV.—The Dehydration of Metallic Hydroxides by Heat, with special reference to the Polymerisation of the Oxides, and to the Periodic Law.

By Professor T. CARNELLEY, D.Sc., and Dr. JAMES WALKER, University College, Dundee.

OXYGEN being a much more fusible and volatile element than chlorine it would, à priori, be supposed that the oxides of the elements would also be more fusible and volatile than the corresponding chlorides. Prof. Louis Henry, however, in a most interesting paper (*Phil. Mag.* [5], **20**, 81; Annales de la Soc. Sci. de Brux., 1879) has drawn special attention to the fact that, with but comparatively few exceptions, chiefly those of negative elements, the oxides are by far the less fusible and volatile of the two classes of compounds, and that unlike their chlorides they are distinguished by their comparative fixity and infusibility.

The chlorides and oxides are generally represented by comparable formulæ, but whereas the formulæ usually assigned to the chlorides have been deduced from the determination of their vapour-density, those attributed to the oxides depend, with very few exceptions, solely on analytical determinations, and they are therefore merely empirical, and have no claim to a molecular signification. Henry, for numerous very cogent reasons, concludes that most of the known oxides of the elements, and notably the metallic oxides, are polymerides $n(RO_x)$ of the unknown true oxides RO_x , corresponding to the chlorides RCl_{2x} . Now the fusibility and volatility of a compound are in a very great measure directly dependent on the molecular weight, and he would hence account for the almost general infusibility and fixity of the oxides by their being in most cases polymerides, with molecular weights much higher than those represented by the empirical formulæ usually assigned to them.

The object of the present investigation was: first, to ascertain whether some light could be thrown on the above question of the polymerisation of the metallic oxides from the change in composition of the hydroxides on heating at regularly increasing temperatures; and second, to determine the minimum temperature of complete dehydration of the metallic hydroxides, with a view of ascertaining whether this temperature was a periodic function of the atomic weight of the positive element.

Wurtz, in 1863, showed that when a hydroxide is decomposed by heat, the chemical action is twofold : (1.) Dehydration, which may be partial or complete. (2.) Molecular condensation, resulting from two

or more molecules of the hydroxide entering into combination on the elimination of a part or the whole of the hydrogen of the hydroxide as water. It therefore follows that the compounds thus formed become more and more complex, in proportion to the extent of the dehydration.

By heating certain hydrates at regularly increasing temperatures, and determining the degree of dehydration thus produced, it seemed probable that data could be obtained for the construction of curves, which would indicate whether any compounds were formed intermediate between the normal hydrates and the corresponding oxides, and thus give some information in regard to the general phenomena occurring during the dehydration. The composition of these compounds, if formed, might also afford some clue to the true molecular weights of the oxides. Their existence could be recognised by observing when, for a considerable increase of temperature, little or no decrease in their weight took place.

The hydrates (or precipitated oxides) corresponding to the following were prepared:—

- 1. Ag₂O,
- 2. HgO,
- 3. Al₂O₃, In₂O₃, Tl₂O₃,
- 4. SiO_2 , TiO_2 , ZrO_2 , SnO_2 , CeO_2 , PbO_2 ,
- 5. Sb₂O₃, Bi₂O₃,
- 6. Fe₂O₃, Co₂O₃, Ni₂O₃.

Many hydrates, such as those of calcium, barium, magnesium, zinc, cadmium, &c., absorb large quantities of carbonic anhydride from the air whilst drying, and therefore could not be employed. The moist oxides of silver and bismuth take up small quantities of carbonic anhydride.

To obtain the hydrates as far as possible in the same state of aggregation, they were prepared under the same conditions, as nearly as the differences in the nature of the substances would allow. Solutions of mercuric chloride and silver nitrate were precipitated in the cold, with a slight excess of caustic soda solution. The cold solutions of aluminium sulphate, bismuth nitrate, antimony trichloride, ferric chloride, zirconium sulphate, thallic sulphate, indium chloride, and cerium sulphate were precipitated with ammonia. Anhydrous titanium tetrachloride was added gradually to cold aqueous ammonia. Sodium silicate and sodium stannate were precipitated with cold dilute hydro-Cobalt chloride and nickel sulphate were precipitated chloric acid. with caustic potash, and the precipitate boiled to get rid of any basic salts. Well washed chlorine gas was then passed through the suspended oxides after cooling, until the liquid was thoroughly saturated,

and smelt strongly of chlorine even on long standing and repeated agitation. In the same way, chlorine was passed through a solution of lead acetate precipitated with sodium carbonate solution.

The hydrates (and oxides) obtained as above were washed with cold water, first by decantation, and afterwards on the filter, until the washings were quite neutral, and showed no trace of the acid contained in the salt precipitated or in the precipitant, as the case might be. After being partially air-dried on the filter, the hydrates were spread out on glass plates and allowed to dry in the air for at least 10 days before being used; as the drying proceeded, the substances were powdered as finely as possible. The silver precipitate was kept in the dark during the whole course of the investigation.

For determining the dehydrating action of heat on the hydroxides obtained as above, a small, double-walled copper air-bath with ordinary Bunsen lamp was employed. It was placed inside a draughtcupboard, the flue of which was stopped, so that the temperature inside the bath could be kept constant within less than a degree for several hours at a time, by occasionally regulating the gas pressure by means of the taps. The hydrates were contained in small porcelain crucibles, which were placed on a glass plate resting on a shelf in the middle of the bath. Hydrates of the same group of elements were always heated at the same time. The lowest temperature used was about 50° , and this was afterwards increased by about 10° at each heating. After about two hours' heating at any given temperature, the weight of the hydrates remained sensibly constant, consequently the crucibles were allowed to remain in the bath for fully two hours at each temperature, and were then removed to desiccators, cooled and weighed.

An ordinary mercury thermometer was used up to 300°, and its readings were not corrected, as all that was needed for the purposes of the investigation was that the temperature should increase by comparatively small and tolerably regular intervals. Above 300°, the melting points of different salts were used to measure the temperature ; under these circumstances the crucibles were placed on an iron plate, resting on pieces of asbestos on the floor of a muffle furnace, with the walls of which it was not in contact. The mouth of the muffle was closed by an iron plate, in which was cut a hole for the introduction of a long, shallow, iron trough, containing the salts to be used as indicators. This trough could be slid in and out amongst the crucibles, and, when in the muffle, it rested on the iron plate. When the muffle had attained the correct temperature, the following arrangement was used to keep it constant :--- An india-rubber tube from the gas main was connected with a Υ -tube, and to the branches of the Υ were attached other india-rubber tubes, one going to the muffle, and the other to the



small copper air-bath previously referred to. By means of the pinchcocks b and c, the flow of gas could be so regulated, that when the muffle was at nearly the desired temperature the Bunsen flame under the air-bath was quite sensitive to a small movement of the pinchcock a. which could then be used to get the correct temperature. When this had been attained, the thermometer in the air-bath was read off. and kept by means of a at the same temperature during the whole heating. It was thus assumed that if the flow of gas was so regulated that the temperature of the air-bath remained constant, that of the muffle would remain constant also. The indications of the thermometer in the air-bath were checked several times in the course of each heating by means of the melting points of the salts heated in the muffle. Tests made with the salts showed that there was an almost uniform temperature prevailing at the different parts of the iron plates on which the crucibles rested. The following is a list of the salts employed as temperature indicators, together with their melting points as determined by one of us in a communication made to the Society some years ago. As the temperature of the muffle would

DIAGRAM SHOWING THE DEHYDRATION OF THE METALLIC HYDRATE BY HEAT.

CARNELLY & WALK



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always be a degree or two above that at which the salts melted, the round numbers given in the third column have been used instead of the melting points as determined.

Salt.	Melting point.	Temperature of muffle.
KNO3	339° C.	say 340°
KClO ₃	359	360
PbI_2	383	385
$Ba(ClO_3)_2 \ldots \ldots$	414	415
TlI	439	440
$PbCl_2$	498	500
AgBr	527	530
$\widetilde{Ca(NO_3)_2}$	561	565
KIO ₄	582	585
NaI	628	630
Ag_2SO_4	$\dots 654$	655
NaBr	708	710
NaCl	772	775
$Na_2CO_3 \dots$	814	815

The crucibles and their contents were finally ignited over the blowpipe.

The results obtained are shown in the following series of tables, in which Column I gives the temperature, Column II the weight of the substance after heating for at least two hours at that temperature, Column III the difference from the previous weighing calculated* for an increase of 10° , and Column IV the loss per cent. on the substance dried at about 15° .

The above results are represented graphically in Diagram I, in which the ordinates indicate temperature and the abscissæ the corresponding loss per cent. on the air-dried substance. The numbers affixed at certain points to the right-hand side of the curves give the composition of the hydrate at these positions, and represent the weight of the attached hydrate corresponding to the weight of the anhydrous oxide shown at a higher point in the curve. Thus, in Curve III the expression $[478 = SiO_2, H_2O]$ indicates that at this point the hydrate had the composition SiO_2, H_2O , the number 478 being the weight in mgrms. of this hydrate, which on complete dehydration gave 368 mgrms. of anhydrous SiO_2 . (N.B.—These numbers are taken from column II in the foregoing table.)

^{*} This calculation was necessary, as the actual increase was not always the same, but varied from $10-13^{\circ}$ for temperatures below 300° , and by greater and less regular intervals above that temperature.

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64 CARNELLEY AND WALKER: THE DEHYDRATION Loss per cent. 0.13 $\begin{array}{c} 0. \cdot 44 \\ 0. \cdot 57 \\ 0. \cdot 57 \\ 1. \cdot 13 \\ 1. \cdot 57 \\ 4. \cdot 34 \\ 6. \cdot 29 \\ 6. \cdot 29 \\ 8 \cdot 50 \\ 9 \cdot 82 \\ 9 \cdot 82 \\ 9 \cdot 82 \\ 111 \\ 201 \\ 112 \\ 111 \\ 201 \\ 113 \\ 10 \\ 113 \\ 10 \\ 113 \\ 10 \\ 111 \\ 111 \\ 201 \\ 111 \\ 111 \\ 201 \\ 111 \\ 111 \\ 201 \\ 111 \\$ $\begin{array}{c} 14 \cdot 16 \\ 15 \cdot 27 \\ 16 \cdot 17 \\ 16 \cdot 86 \\ 17 \cdot 62 \\ 17 \cdot 62 \end{array}$ $0.25 \\ 0.31$ ЦЧ. II. Hydrate of HgO (air-dried for five months) previous weighing for an increase of 10°. Difference from -0.3 4000100001470000770000 400017000100701000704 6.0mgrms. III. mgrms. 794 - 57 792 - 5 792 - 5 792 - 5 792 - 5 792 - 5 792 - 5 793 - 5 792 - 5 716 - 5 716 - 5 716 - 5 775 - Weight. H. Temperature. $\begin{smallmatrix} & 15\\ & 56\\ &$ Ŀ. Loss per cent. 0.08 Þ I. Hydrate of Ag₂O (air-dried for six months) previous weighing for an increase of 10°. Difference from $\begin{array}{c} 220.8\\ 7.9\\ 0.8\\ 0.8\end{array}$ $0.4 \\ 0.4$ 0.4mgrms. 4.02℃ 4.05℃ 4.05℃ 1.0-Ξ. 000 Weight. mgrms. 625 ·5 $625 \cdot 0$ $625 \cdot 0$ $625 \cdot 0$ $625 \cdot 0$ $6225 \cdot 0$ $6225 \cdot 0$ $6224 \cdot 5 \cdot 0$ $6217 \cdot 0$ $6617 \cdot 0$ $6617 \cdot 0$ $6621 \cdot 5 \cdot 0$ $5555 \cdot 0$ $55555 \cdot 0$ $55555 \cdot 0$ $5555 \cdot 0$ $55555 \cdot 0$ $55555 \cdot 0$ $55555 \cdot 0$ 554 ·0 553 ·0 551 5 550 5 548 5 542 5 H. Temperature. Ŀ.

ionths).	IV. Loss per cent.	24117 21869 2999 2999 2999 2999 2999 2999 2999 2	
(air-dried for five m	III. Difference from previous weighing for an increase of 10°.	mgrus. - 33:2 - 33:2 - 33:3 - 4:2 - 4:2 - - - - - - - - - -	ten <i>cold</i> .
ydrate of HgO	II. Weight.	mgrms. 646 · 0 646 · 0 646 · 0 646 · 0 646 · 0 656 • 0 601 • 5 601 • 0 144 • 0 0 • 5 0 • 5 1 • 0 1 • 0 1 • 0 1 • 0	cks. nge. he substance wh
П. Н	I. Temperature.	286 2988 340 445 565 565 565 565 565 565 565 565 565	w with white specured bright oran colour refers to t
tths).	IV. Loss per cent.	15 15 15 15 15 15 15 15 15 15 15 15 15 1	n brown to yello and the whole to I other cases the
air-dried for six mor	III. Difference from previous weighing for an increase of 10°.	mgrms. - 3.0 - 3.0 - 4 - 0.2 - 0.4 - 0.4 - 0.4	Colour changed fron Specks disappeared, .B.—In these and al
drate of $\mathrm{Ag}_{2}\mathrm{O}$ (II. Weight.	mgrms. 528 · 0 528 · 0 529 · 0 529 · 0 529 · 0 529 529 529 529 529 529	* + 2
I. H ₃	I. Temperature.	340 340 360 386 386 386 415 440 415 530 585 585 585 585 585 585 585 585 585 58	

OF METALLIC HYDROXIDES BY HEAT.

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в).	IV.	Loss per cent.	1	7.83	11.55	12.72	13.80	14.68	15.17	15.75	16.05	16.34	16.54	16.54	16.73	16.83	16.83	16.83	16.93	17.03	17 -13	17.22	17.32	17.32	17 .62
2 (air-dried for 14 day	III.	Difference from previous weighing for an increase of 10°.	mgrms.	-11.1	15.8	5 0	4.6	3.7	2.3	2 ·3	1:2	1.2	8.0	0	8.0	₽ .0	•	0	₽ ·0	0.4	0.4	0.4	0-4	0	6.0
Hydrate of TiO	II.	Weight.	mgrms. 511 ·0	471.0	452.0	446.0	440.5	436.0	433 •5	430.5	$429 \cdot 0$	427 -5	426.5	426.5	425 ·5	$425 \cdot 0$	$425 \cdot 0$	$425 \cdot 0$	424 •5	424.0	423.5	423.0	422.5	422.5	421.0
IV.	I.	Temperature.		51	63	75	87	66	110	123	135	147	159	171	183	195	207	219	231	243	255	267	279	291	340
ths).	IV.	Loss per cent.		10.95	19.60	20.64	$21 \cdot 12$	22.00	$22 \cdot 29$	$22 \cdot 77$	23.06	23.26	23.46	23.46	23 ·65	24.03	24.13	24.23	24 ·33	$24 \cdot 42$	24.52	24.61	24.71	24.81	24 ·81
air-dried for five mo	III.	Difference from previous weighing for an increase of 10°.	mgrms.	-15.7	37.1	4.6	0.8	0.8	1.4	1.9	1.2	8·0	8.0	0	8.0	1.7	0.4	0.4	0.4	0.4	0.4	0.4	0 ·4	₽·0	0
ydrate of ${ m SiO_2}$ (II.	Weight.	mgrms. 516:0	459.5	415 •0	409.5	406.0	402.5	401.0	398.5	0.7 68	396-0	395 0	$395 \cdot 0$	394.0	392.0	391 · 5	$391 \cdot 0$	390 · 5	390.0	389 -5	0.688	388.5	388 •0	388 0
III. H	I.	Temperature.	150	51	63	75	87	66	110	123	135	147	159	171	183	195	207	219	231	243	255	267	279	291	340

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ув).	IV.	Loss per cent.		17.81	18.3	18.4	18.6	19.18	19.37	19.57	20 · 06	20 ·55	20.55	21.15	$21 \cdot 15$	21.15	21.15
) ₂ (air-dried for 14 da	III.	Difference from previous weighing for an increase of 10°.	mgrms.	-0.5	1.0	0.2	₽ .0	0.5	0.3	0.3	1.2	0.5	0	9.9 0	•	•	0
Hydrate of TiC	II.	Weight.	mgrms.	420 · 0	417.5	417.0	416.0	413.0	412.0	411.0	408.5	406.0	406.0	403.0	403.0	403 .0	403 · 0
IV.	i	Temperature.		360 	385	415	440	500	530	565	585	630	655	710	775	815	Blowpipe
onths).	IV.	Loss per cent.		25.29	25 ·87	26.16	26.36	26.36	26 -46	26.67	27.15	$27 \cdot 15$	27 - 53	28.10	28.69	28.69	28 • 79
(air-dried for five m	III.	Difference from previous weighing for an increase of 10°.	mgrms.	-1 2	1 2	0.5	₽·0	0	0.2	0.3	1.2	0	8.0	9 .0	0.2	0	
Iydrate of SiO ₂	II.	Weight.	mgrms.	385 .5	382 · 5	381 ·0	380.0	380.0	3.676	378.5	376.0	0.976	374.0	371 ·0	368 •0	368.0	367 -5
III. E	I.	perature.	c	360	385	415	440	500	530	565	585	630	655	710	775	815	lowpipe

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nths).	IV.	Loss per cent.		2.00	9.92	21·11	11.93	12.83	13 ·18	13.87	14.49	14.77	15.05	15.33	15.74	16.09	16.30	16.51	16.79	17.06	17.34	17.54	17.75	96.41	
(air-dried for five mo	III.	Difference from previous weighing for an increase of 10°.	mgrms.	-10.0	30.0	7.5	5.0	5.4	2.3	6. S	2 .8	1.7	1.I	1.7	2.5	2.1	1 2	1 ·2	1.7	1.7	1.7	1 2	1.2	8.0	
Iydrate of SnO ₂	II.	Weight.	mgrms. 721 •0	685 •0	649.5	640.5	634 · 5	$628 \cdot 0$	$625 \cdot 5$	620.5	616.0	$614 \cdot 0$	612.0	610.0	0.209	$604 \cdot 5$	603.0	601.5	599 - 5	597.5	595.5	594.0	592 · 5	591 •5	
VI. H	I.	Temperature.	اړ تر	51	63	76	48	66	110	123	135	147	159	171	183	195	207	219	231	243	255	267	279	291	-
ys).	IV.	Loss per cent.		12.89	18.16	20.01	$21 \cdot 79$	24.06	$25 \cdot 19$	26.72	28.00	29.00	29.88	$30 \cdot 49$	31.06	31 ·63	31.82	32 ·01	$32 \cdot 29$	32 58	32 .95	33 •33	33 ·71	3 3 · 90	
(air-dried for 10 da	111.	Difference from previous weighing for an increase of 10°.	mgrma.	- 9.4	2.11	4.2	3.7	5 0	2.7	3.1	5 .0	2.1	2.1	1 ·2	1.2	1.2	0.4	0.4	8.0	0.4	0·8	8.0	8.0	春.0	
Hydrate of ZrO ₂	П.	Weight.	mgrms. 964 • 0	230.0	216.0	211.9	206.5	200.5	197.5	193.5	190.0	187 - 5	185 •0	183 .5	182.0	180.5	180.0	2.621	2.841	178.0	177.0	176.0	175 • 0	174.5	-
V.	ï	Temperature.	°70	51	63	75	87	66	110	123	135	147	159	171	183	195	207	219	231	243	255	267	279	291	

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Υ.	Hydrate of ZrO.	² (air-dried for 10 da	iys).	VI. H	ydrate of SnO ₂	(air-dried for five mo	nths).
I.	II.	III.	IV.	ï	II.	III.	IV.
Temperature.	Weight.	Difference from previous weighing for an increase of 10°.	Loss per cent.	Temperature.	Weight.	Difference from previous weighing for an increase of 10°.	Loss per cent.
	mgrms.	merms.			merms.	mgrms.	
340	172.5	- 0.4	34.66	340	587.5	8.0-	18.52
960	172.0	8.0	34.85	360	586.0	8.0	18.73
385	170.5	9.0	35.42	385+	580.5	2.2	19.50
415*	160 .5	s. S	39.2	415	579.5	0.3	19.63
440	160.0	0.2	39 39	440	575.5	1.6	20.19
£00	159 .5	0.1	85.68	500	574.5	0.2	20.33
530	159.0	0.2	89.77	530	573 .5	0.3	20.47
565	159.0	0	44.68	565	571 ·5	9.0	20.74
585	158.5	0.2	96 · 68	585	2. 292	2.0	$21 \cdot 29$
				630	562 .5	1.1	21.98
				655 1	562 ·0	0.2	22 .05
				710	562 ·0	0	22.05
				775	2. I92	20.0	22.12
				815	561.5	0	22.12
				Blowpipe	559.5	1	$22 \cdot 39$
An accident pre	vented further h	eating.					
		5	•	-			

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Changed from grey to pure white.
Changed from dirty brown to pale yellow.
Took a greenish tinge.

VII.	Hydrate of Cet	O ₂ (air-dried for 12 d	lays).	IIIA	. Hydrate of Pb	02 (air-dried for 10 d	ays).
I.	II.	III.	IΥ.	I.	II.	III.	IV.
Temperature.	Weight.	Difference from previous weighing for an increase of 10°.	Loss per cent.	Temperature.	Weight.	Difference from previous weighing for an increase of 10°.	Loss per cent.
0	mgrms.	mgrms.		0	mgrms.	mgrms.	
15	$644 \cdot 0$	1	1	15	706.5		ł
51	623.5	-5.7	3 ·18	51	696.5	-2.8	$1 \cdot 41$
63	620.0	2 9	3.73	63	695 • 5	8.0	1.55
75	0.719	2.5	4.19	75	695 •5	0	1.55
87	614.0	2.5	4.66	87	$695 \cdot 0$	0.4	1.63
66	0.609	4.2	5.43	66	694.5	0.4	$1 \cdot 70$
110	606.5	2 3	5.82	110	693 . 5	6.0	1.84
Î23	0.009	5 O	6.83	123	693 - 5	0	1.84
135	594.5	4.6	69.2	135	692.5	8.0	1.98
147	584.5	8.2 8	9.24	147	$691 \cdot 5$	8·0	2.12
159	565 -5	15.9	12.19	159	690.5	8.0	2.26
171	554.0	9.6	13.98	171	690.5	•	2.26
183	552.5	1.2	14.21	183	0.069	0.4	2.33
195	550.0	2.1	14.60	195	689	0.4	2.40
207	548.0	1.7	14.91	207	0.689	0.4	2 -47
219	546.5	1.2	15.14	219	688.0	8·0	2.61
231	545 • 0	1.2	15.37	231	0.789	8.0	2.75
243	543 .5	1.2	15.60	243	686.0	8.0	2.90
255	542.5	8.0	15.76	255	$685 \cdot 0$	8.0	3 ·04
267	541.5	8.0	$1.5 \cdot 92$	267	$684 \cdot 5$	0.4	3·11
279	541.0	4.0	16.00	279	$684 \cdot 0$	0.4	3 ·18
291	540.0	8.0	16.17	291	672.5	9.6	4.86
340	536.0	8.0	16.77	340	0.899	6.0	$5 \cdot 45$
360	536.0	0	16.77	360	0.890	0	5.45

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VII.	. Hydrate of Cel	O2 (air-dried for 12 d	lays).	VIII.	Hydrate of Pt	O_2 (air-dried for 10 c	lays.)
ï	II.	III.	IV.	I.	11.	III.	IV.
Temperature.	Weight.	Difference from previous weighing for an increase of 10°.	Loss per cent.	Temperature.	Weight.	Difference from previous weighing for an increase of 10°.	Loss per cent.
	mgrms.	mgrms.			mgrms.	mgrms.	
385*	534 · 0	9. 0 <u>-</u>	17.08	3851	663.0	-2.0	6.16
415	533 .5	2.0	17.16	415	$653 \cdot 0$	9 9 9	7.57
440	533 · 0	0.2	17.24	440	$655 \cdot 0$	+0.8	7.29
500	533 · 0	0	17.24	500	656.0	0.16	7.15
530	532 -5	0.2	17.32	530	0.929	0	7.15
565	531.5	£.0	17.47	5658	643.0	-3 7	66.8
585	531 ·5	0	17.47	585	641.5	L·0	9.20
630+	518.5	2.9	19.49	630 (fused)	641.5	0	9.20
655	513.5	2.0	20.26	655	641.5	0	9.20
710	494.5	3 ·4	23.21	710	639.0	0.4	9.55
775	460.5	5.2	28.49	775	639.0	0	9.55
815	433 ·5 (?)	8.9	32.68 (?)	815	0.689	0	9.55
Blowpipe	437.0	I	32.14				
*	Changed from by	rownish-yellow to br	ight yellow.	t Lig	ht specks began	to appear in the bro	wn.
+-	Turned a pinkisl	h (salmon) colour.		§ Be	came yellow.		

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tths).	IV.	Loss per cent.		•••	1.95	2.56	$2 \cdot 77$	2.98	3 ·28	3 ·38	3.64	3.75	3 ·96	$4 \cdot 10$	4.21	4 • 41	4.67	$5 \cdot 02$	$5 \cdot 28$	5.48	$5 \cdot 59$	5.70	5.80	5 .95	6 ·00
(air-dried for five mon	III.	Difference from previous weighing for an increase of 10°.	mgrms.	many	-5.1	5 ·0	1.7	1.7	2.5	8.0	2 3	8.0	1.7	1-4	8.0	1.8	2.1	2 :9	2.1	1.1	8.0	6.0	8.0	1.4	0.4
ydrate of Bi ₂ O ₃	II.	Weight.	mgrms.	975.0	956.0	950.0	948 0	946.0	943.0	942.0	939 - 5	938 5	936 -5	935 •0	934.0	932.0	929 .5	926.0	923.5	921.5	920.5	2.616	918.5	0.719	916 5
Х. Н	I.	Temperature.	•	15	52	64	76	88	100	112	123	135	147	158	170	181	193	205	217	229	241	252	264	275	287
onths).	IV.	Loss per cent.		}	0.05	0.11	0.16	0.16	0.16	0.21	0.27	0.32	0.32	0.32	0.32	0.32	0.32	0.43	0.53	0.59	0.59	0.59	0.64	0.64	04.0
(air-dried for five m	III.	Difference from previous weighing for an increase of 10°.	mgrms.		1.0-	0.4	0 ·4	0	0	7 .0	10.4	0.4	0	0	0	0	0	8.0	8.0	0 ·4	0	0	0.4	0	Ť .0
ydrate of Sb ₂ O ₃	II.	Weight.	mgrms.	932.5	932 ·0	931 •5	$931 \cdot 0$	$931 \cdot 0$	$931 \cdot 0$	930.5	930.0	929 · 5	929 •5	929.5	929.5	929.5	929.5	928 ·5	927.5	0- 729	$927 \cdot 0$	927.0	926.5	926.5	926.0
H. XI	I.	Temperature.	0	15	52	64	26	88	100	112	123	135	147	158	170	181	193	205	217	229	241	252	264	275	287

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-dried for five months).	III. IIV. Difference from revious weighing Loss per cent. of 10°.	$\begin{array}{c} \mbox{mgrms,} \\ -1.4 \\ -1.4 \\ -1.2 \\ 1.2 \\ 1.2 \\ 4.2 \\ 4.2 \\ 4.2 \\ 7.6 \\ 4.2 \\ 1.7 \\ 1.0 \\ 1.7 \\ 1.7 \\ 1.7 \\ 1.7 \\ 1.2 \\ 1.2 \\ 1.2 \\ 1.2 \\ 1.2 \\ 1.2 \\ 1.2 \\ 1.2 \\ 1.2 \\ 1.2 \\ 1.2 \\ 6.3 \\ 0.1 \\ 1.2 \\ 6.3 \\ 0.1 \\ 1.2 \\ 6.3 \\ 0.1 \\ 1.2 \\ 6.3 \\ 1.2 \\ 1.2 \\ 6.3 \\ 1.2 $	
rdrate of Bi ₂ O ₃ (aii	II. Definition	mgrms. 915.0 915.0 900.5 890.0 888.5 888.5 888.5 885.0 855.0 855.0 855.0 852.0 852.0 852.0 852.0 852.0 852.0 ented further heat	hot).
X. H)	I. Temperature.	298 340 340 385 385 385 440 415 440 415 440 555 585 585 585 585 585 585 585 585 58	llow (brown when
onths).	IV. Loss per cent.	gain 0.70 0.811 0.811 0.107 0.811 0.111 0.641 1.127 1.107 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.128 1.148 1.128 1.148 1.128 1.148 1.148 1.148 1.148 1.148 1.148 1.148 1.148 1.148 1.148 1.148 1.148 1.148 1.148 1.148 1.148 1.148 1.14	light to deep yel d light again.
(air-dried for five m	III. Difference from previous weighing for an increase of 10°.	mgrms. 0 - 0 - 2 - 1 - 3 - 4 - 5 - 4 - 1 - 3 - 0 - 1 - 0 - 0 - 1 - 0 - 0 - 0 - 1 - 0 - 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2	* From † Turne
ydrate of Sb ₂ O ₃	II. Weight.	mgrms. 926 0 926 0 925 0 925 0 943 5 943 5 943 5 943 5 957 0 958 5 976 5 976 5 976 5 976 5 976 5 976 5 979 5 979 0 979 0	
IX. H	I. Temperature.	298 340 340 365 360 385 440 500 565 585 585 585 530 630 655 775 775 An accident pre	

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ate of Al ₂ () ₃ (air-dried for six mo	onths).	X	II. Hydrate of	In ₂ O ₃ (air-dried for 10) days).
	III.	IV.	I.	II.	III.	IV.
Diprev	fference from rious weighing an increase of 10°.	Loss per cent.	Temperature.	Weight.	Difference from previous weighing for an increase of 10°.	Loss per cent.
	mgrms.		0	mgrms.	mgrms.	
	ł		15	134.0		I
	-14.3	8 .33	50	127.5	-1.9	4.85
	46.7	17.66	62	125.5	1.7	6.34
	14.2	20.50	74	124.0	1.2	7.46
	9.9	21.92	87	122.5	1.2	8.59
	5 0	22 .92	66	121.5	8.0	9 33
	0.2	23.92	111	120.5	8.0	10.08
	လ လ	24.58	123	0.611	1.2	$11 \cdot 19$
	2 .9	$25 \cdot 16$	135	117.5	1:2	12.31
_	2 ·5	25.66	147	116.5	0.8	13.06
	4.6	26 ·58	159	113.0	2 :9	15.67
	8.8	27.15	171	$111 \cdot 5$	1.2	16.79
	3 ·3	27.91	183	110.0	1.2	17.91
	2.9	28.50	195	109-5	0.4	18.29
	3 i3	29.16	207	108.5	8.0	19.03
	12 5	31.66	219	107.5	8.0	19.77
	21 ·8	35 ·66	230	105.5	1.8	$21 \cdot 27$
	5.8	36 ·83	242	103.5	1.7	$22 \cdot 76$
	2 ·9	37.42	254	101.5	1.7	24.26
	8·0	37 · 58	266	100.0	$1\dot{2}$	25 ·37
	8·0	37.75	279	100.0	0	25.37
	2 :č	38.25	291	100.0	0	25 .37
	4.3	41.75	340	3 . 86	0.3	26.49
,	3.5	42.92	360	98 · 5	0	$26 \cdot 49$

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XI. H	ydrate of Al ₂ O ₃	(air-dried for six mo	onths).	XII.	Hydrate of In,	03 (air-dried for 10 d	ays).
I.	II.	III.	IV.	н	II.	III.	IV.
Temperature.	Weight.	Difference from previous weighing for an increase of 10°.	Loss per cent.	Temperature.	Weight.	Difference from previous weighing for an increase of 10°.	Loss per cent.
0	mgrms.	mgrms.	a contraction of the second se	0	mgrms.	mgrms.	
000	0.142	9 Q 	43.17	3 55	e. 86	, ,	65.97
614	0.888	0. T	43.67	415	0.86	-0.2	56 '86
440	336.0	8·0	44·00	440	67.5	0.2	$27 \cdot 23$
2 00	333 • 5	0.4	44.42	500	97.5	0	27.23
530	333 •5	0	44.42	530	97.5	0	27 ·23
565	332 • 5	0.3	44.59	565	97.5	0	27 ·23
585	331 ·0	2.0	44.83	585	97 · 5	0	27.23
630	329 · 0	0.4	45 · 17	630	97.5	0	$27 \cdot 23$
655	329.0	0	45.17	655	0.76	0.2	$27 \cdot 61$
110	327 ·0	0·4	45.50	710	0.26	0	27.61
Blowpipe	323 •0	I	46.17	775	0.46	0	27.61
				815	0.76	0	27 61
				Blowpipe	0.26	0	27 ·61

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4ys).	IV.	Loss per cent.		ł	98.6	$21 \cdot 45$	25.16	$27 \cdot 71$	$29 \cdot 10$	20.67	31.54	32.29	32.92	33 •51	34.14	34.61	34.78	35 -07	35 36	6 2 · 59	35.82	35 .88	35.94	36.00	36.17
03 (air-dried for 18 d	III.	Difference from previous weighing for an increase of 10°.	mgrms.	1	24 · 3	83 :3	26.7	18.3	10.01	11.2	6.2	5.4	4·6	4·0	4.6		1.2	2.1	2.1	1.7	1.5	0.4	0.4	0.4	1 2
Hydrate of Fe	III.	Weight.	mgrms.	862.5	2.222	2.775	$645 \cdot 5$	623 ·5	611.5	0.862	200 - 2	$584 \cdot 0$	5.875	573-5	568.0	564 ·0	562 ·5	$560 \cdot 0$	557 -5	555 -5	553.5	553 .0	552 .5	552.0	550.5
XIV.	I	Temperature.	•	15	50	62	74	86	86	110	122	134	146	158	170	182	194	206	218	230	244	257	269	281	293
X1111. Hydrate of Tl ₂ O ₃ (air-dried for 14 days).	IV.	Loss per cent.		1	1.42	1.56	1 -70	1.84	1.99	2.13	2.27	$2 \cdot 56$	2.70	2.70	2.70	2.70	2.84	2.98	2.98	3 ·13	3.13	3 ·13	$3 \cdot 13$	3 ·13	3.13
	III.	Difference from previous weighing for an increase of 10°.	mgrms.	1	-1.4	0.4	0.4	0.4	0.4	0 ·4	0.4	8.0	1 .0	0	0	0	0 ·4	0.4	0	0.5	0	0	0	0	0
	II.	Weight.	mgrms.	352.0	347.0	346 - 5	346.0	345 · 5	$345 \cdot 0$	344.5	$344 \cdot 0$	343.0	342 · 5	342 -5	342 ·5	342 - 5	$342 \cdot 0$	341 ·5	341.5	341.0	341 ·0	341.0	$341 \cdot 0$	341 ·0	341 ·0
	ï	Temperature.	•	15	50	62	74	87	66	111	123	135	147	159	171	183	195	207	219	230	242	254	266	279	291

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ays).	IV.	Loss per cent.		36.23	36.40	37.32	37 ·32	37 ·79	38 ·03	38.03	38 ·03	38.03	38.03	38.03	38.03	60 .88		
O ₃ (air-dried for 18 d	III.	Difference from previous weighing for an increase of 10°.	mgrms.	0·1	8.0	3.2	0	1.6	0.3	0	0	0	0	0	0]		
Hydrate of Fe_2	II.	Weight.	mgrms.	550 · 0	548.5	540.5	540.5	536.5	534.5	534.5	534.5	$534 \cdot 5$	534.5	534.5	534.5	534 0		
XIV.	i	Temperature.		340	360	385	415	440	500	530	565	585	630	655	710	Blowpipe		
lays).	IV.	Loss per cent.		3 '13	3.13	3.42	3 ·98	4 - 27	4.27	4.27	4 · 27	4.69	14.35	17 - 61	23 .72	30 ·68	31.96	31 ·96
O ₃ (air-dried for 14 c	III.	Difference from previous weighing for an increase of 10°.	mgrms.	0	0	₽.0-	4.0	0.4	0	0	0	8-0	2·6	4.6	6.8	8.8	1.1	0
Hydrate of Tl ₂ (H.	Weight.	mgrms.	341.0	$341 \cdot 0$	340.0	338 ·0	337 •0	337 ·0	337 · O	337 · O	335 . 5	301.5	290 ·0	268.5	244 •0	239.5	239 • 5
XIII.	I.	Temperature.	c	340	360	385	415	440	500	530	565	585*	630 fused+	655	710	775	815	Blowpipe

* Lost its gloss and became dull-black.
† To a dirty green liquid.

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lays).	IV.	Loss per cent.	14.59	14.71	15 34	15.34	15.34	15 · 34	15.34	15.34	15.34	15 -47	15.47	15 - 47	15.47	15 ·47								
) ₃ (air-dried for 15 da	.111	Difference from previous weighing for an increase of 10°.	mgrms. 0 · 1	0.2	1.0	0	0	0	0	•	0	0.2	0	0	0	0								
Hydrate of Co ₂ (II.	Weight.	mgrms. 339 ·5	339.0	336.5	336 • 5	336 5	336 5	336 -5	336.5	336 5	336.0	336.0	336.0	336.0	336.0								
XV.	H	Temperature.	340 340	360	385	415	500	530	565	585	630	655	710	775	815	Blowpipe	1							
XV. Hydrate of Co ₂ O ₃ (air-dried for 15 days).	IV.	Loss per cent.		0	0	0	0.25	0.50	1.01	1.63	2.01	2 ·38	2.64	2.89	3.14	3.40	3.90	4.91	6.92	9.43	12.95	14.22	14.47	14 • 47
	III.	Difference from previous weighing for an increase of 10°.	mgrms.	0	0	0	8·0	8·0	1.7	2.1	1.2	1.2	0 ·8	8·0	8.0	8.0	1.7	00 00 00	L·9	1·1	10.7	4 ·2	8·0	0
	II.	Weight.	mgrms. 397 •5	397.5	397 -5	397.5	396.5	395 -5	393 - 5	$391 \cdot 0$	389 - 5	388 •0	387 · 0	386.0	385 0	384 ·0	382.0	378.0	370.0	360.0	$346 \cdot 0$	341.0	340.0	340.0
	ï	Temperature.	15°	50	62	74	80	98	110	122	134	146	158	170	182	194	206	218	230	244	257	269	281	293

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CARNELLEY AND WALKER: THE DEHYDRATION

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I.	п.	III.	IV.
Temperature.	Weight.	Difference from previous weighing for an increase of 10°.	Loss per cent.
	mgrms.	mgrms.	
15	864.5	-	
50	792.0	20.7	8.38
62	715.0	64.2	17 • 29
74	700.5	12 .1	18.97
86	689.0	9.6	20.30
98	680.5	7.1	21.28
110	669.5	9.2	22.55
122	659.0	8.7	23.77
134	648.5	8.7	24.99
146	637.5	9.2	26.26
158	623.5		27.88
170	601.0	18.7	30.32
182	587 5	11.2	32.04
194	579.0		33.02
206	573.0	0.0	33.72
218	570.0	2.5	34.07
230	007 U	2.9	34.41
Z44 Stannad	by an assidant	at this point	34.71

XVI. Hydrate of Ni₂O₃ (air-dried for 10 days).

As regards the several curves the following remarks will explain the results indicated :----

I. Hydrate of Ag_2O .—The precipitate obtained on adding caustic soda to a solution of silver nitrate absorbed a very small quantity of carbonic anhydride on drying. The product after drying in the air for six months appeared to be the normal hydroxide AgOH. On heating, this was comparatively stable up to about 100°, but on further heating it lost water and a small quantity of oxygen, and was converted gradually into Ag₂O (admixed with a small quantity of metallic silver). At a higher temperature, the whole of the oxygen was given off, leaving a residue of pure silver.

The various phenomena, therefore, were :---

(1.) AgOH comparatively stable up to about*	100°
(2.) Rapid loss of water and small quantity of	
oxygen*	$100 - 180^{\circ}$

* Watts' Dictionary, 5, 302, states that precipitated silver oxide becomes anhydrous on drying at $60-70^{\circ}$; and that it gives off a certain quantity of oxygen at 100°, but whether Ag₄O or Ag is thus formed is not known (comp. Bailey, Trans., 1887, 416; and v. der Pfordten, Ber., 20, 1468).

(3.)	Ag_2O (containing a small quantity of Ag)	
	comparatively stable	$180-270^{\circ}$
(4.)	Rapid decomposition of Ag ₂ O with reduction	
• •	to metallic silver*	270—3 00°
(5.)	Reduction complete at about	$300 - 340^{\circ}$

II. Hydrate of HgO.-The precipitate obtained on adding caustic soda to a solution of mercuric chloride, after drying in the air for five months, had the composition $Hg(OH)_2$. On heating this remained tolerably stable up to about 100°, at which temperature (after heating in all about 10 hours) it had lost only about one-half per cent. of its weight, whereas complete dehydration to HgO would require a loss of nearly 8 per cent. Above 100°, it lost water more and more rapidly, and became completely dehydrated to HgO at about 175°. Above this temperature, incipient decomposition into mercury and oxygen commenced and continually increased up to about 360°, when it became much more rapid, and developed into full decomposition at from 415° to 440°. The changes in colour which the substance exhibits when cold after heating above 360° are noteworthy. After heating from 360° to 385°, the colour had changed from brown to yellow specked with white. These specks disappeared on heating from 415° to 440°, and the whole became bright orange. This last change probably indicated the conversion of the yellow oxide into the more stable allotropic ordinary red oxide of mercury.

We have therefore :---

(1.) H	Ig(OH) ₂ almost stable up to about †	100°
(2.) I	Rapid dehydration	11 0— 1 75°
(3.) (Complete dehydration to HgO about	175°
(4.) I	ncipient decomposition into Hg and O ⁺	$175 - 360^{\circ}$
(5.) H	full decomposition sets in, whilst the still	
	undecomposed HgO changes from the yel-	
	low to the red modification, ‡ about	415 - 440

III. Hydrate of SiO₂.—The precipitated silica obtained on adding hydrochloric acid to a solution of sodium silicate, after air-drying for

* Pure Ag₂O begins to give off oxygen at 250° (Watts' Dictionary, 1, 792).

+ According to *Watts' Dictionary*, **3**, 908, yellow mercuric oxide is anhydrous, whereas Schaffner (*Annalen*, **51**, 181) states that the yellow precipitate formed by the addition of caustic potash to mercuric salts is the hydrate HgO_3H_2O .

 \ddagger These results, obtained by heating in a covered but not air-tight crucible, are in accord with those of Meyers (Ber., 6, 11), who determined the course of the decomposition by the tension of the gas evolved. Debray (Compt. rend., 77, 123), however, has shown that if the mercury and oxygen be heated in a sealed tube maintained throughout at a uniform temperature, the oxygen is almost completely absorbed by the mercury even at 440°. five months, retained a quantity of water corresponding very nearly to the formula $3SiO_{2,4}H_2O$. On heating, this lost water at an almost uniform rate up to 63° , passing through the compositions indicated by $SiO_{2,}H_{2}O$ and $2SiO_{2,}H_{2}O$, without showing any indication of the formation of definite hydrates of this or other composition. At about 63° , the curve turns upward rather sharply, and thence assumes almost a straight line until it reaches the position for anhydrous silica at a temperature somewhat above 815° (say 850°).*

These results show that precipitated silica when heated at successively increasing temperatures forms no hydrates which are stable through a range of temperature of at most 13°. The phenomena are in fact such as to indicate that probably numerous successive hydrates are formed as the temperature increases, but that all these are so very unstable that a small further rise in temperature causes an additional loss of water. The rapid rise of the curve above 63° would seem to show either that the hydrates formed below were much less stable than those formed above that temperature, or more probably that the latter were much more complicated in composition.

It was at one time supposed that hydrates of a definite and constant composition could be obtained by drying gelatinous silica under various conditions, and the following have been stated to exist by different observers :---

Dialysed	silicic acid	$\mathrm{SiO}_2, 2\mathrm{H}_2\mathrm{O}.$
Dried at	ordinary temperature	${ m SiO}_2, { m H}_2{ m O}.$
,,	$20-25^{\circ}\dots\dots\dots$	$2\mathrm{SiO}_2,\mathrm{H}_2\mathrm{O}.$
,,	60°	$3\mathrm{SiO}_2,\mathrm{H}_2\mathrm{O}.$
,,	80—100°	$4\mathrm{SiO}_2,\mathrm{H}_2\mathrm{O}.$
,,	$250-270^{\circ}\dots\dots\dots\dots$	$8 \mathrm{SiO}_2, \mathrm{H}_2\mathrm{O}.$

More recent investigations, however, have shown that the quantity of water contained in the artificial, as well as in the natural amorphous silica, varies within very considerable limits, whilst the water can be driven off at such low temperatures that it has been suggested that this water is, to some extent at least, mechanically admixed, and that at any rate these hydrates must be considered to be very loose compounds of silica and water (Roscoe and Schorlemmer's *Treatise* on *Chemistry*, **1**, 572). This is entirely confirmed by our results.

IV. Hydrate of TiO₂.—This curve is very similar to that for silica, and similar remarks, therefore, apply in this case. The chief differ-

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^{*} By the term "stable hydrate" as used in this paper, is meant a hydrate which undergoes no loss of weight on further heating through an appreciable range of temperature above that at which it had been formed by the dehydration of a higher hydrate, whereas a hydrate which is unstable is one which loses more water on a slight rise of temperature above that at which it had been formed.

ence is that the steep upward turn of the curve is not nearly so abrupt as for the hydrates of silica. Titanic acid becomes completely dehydrated at about 710°. A very large number of hydrates of TiO₂ are said to have been obtained, for a list of which see Watts' Dictionary, 6, 1098. As in the case of the silicic hydrates, it is very doubtful whether these are of definite or constant composition (compare Rose, Annalen, 53, 267; Gmelin's Handbook, 3, 475; Roscoe and Schorlemmer's Treatise, 2, ii, 259). The regular and unbroken form of the curve obtained by us is certainly against the existence of definite hydrates of any evident degree of stability.

V. Hydrate of ZrO₂.-With one or two marked exceptions, this curve indicates that phenomena occur on heating similar to those in the case of silicic and titanic hydrates. The upward turn of the curve takes place even more gradually than with titanic acid. The two special characteristics of this curve, however, are :-(1) For temperatures below 385° it shows that though the percentage loss is greater at any given temperature, yet a much greater quantity of water is retained per molecule of ZrO_2 than in the case of either SiO₂ or TiO₂. Thus, whereas silica is dehydrated to 2SiO₂,H₂O at about 60°, and titania to 2TiO₂, H₂O at about 70°, zirconia is dehydrated to 2ZiO₂, H₂O only at 385°. (2) The most noteworthy difference, however, is the sudden break in the continuity of the curve between 385° and 415°, the sudden increase in the loss per degree of rise in temperature being much greater than it had been for the previous 280°. Unfortunately no observation was made between 385° and 415°, but somewhere between these temperatures a very sudden increase in the elimination of water took place; for, whereas the hydrate at 385° had the composition 2ZrO₂,H₂O, it had at 415° the composition 24ZrO₂,H₂O, and soon after became completely anhydrous.

Curiously enough, this phenomenon was accompanied by a change in colour from grey to pure white, whilst other observers state that this change in colour occurs at the same time as a vivid incandescence, and a considerable modification in the chemical properties of the zirconia. Owing to the conditions of the experiment, we could not tell whether this incandescence took place or not. The peculiar incandescence referred to was first noticed by Sir Humphry Davy, whilst Chevreul observed that it was preceded by blackening; the latter was ascribed by Hermann to the presence of impurities (compare Gmelin's Handbook, 3, 342). Gmelin states (loc. cit.) that zirconia becomes anhydrous considerably below red heat, and that the above incandescence only occurs after all the water has been This must be an error, as we found that at or very near driven off. the temperature at which incandescence takes place the composition was represented by 2ZrO₂, H₂O, and that even after the incandescence

a loss of at least 0.76 per cent. occurred on further heating to 585°. The actual loss on complete dehydration may possibly have been even slightly greater, for an accident unfortunately prevented heating to a higher temperature. These results seem to show that the incandescence which occurs at about 400° is not due as hitherto supposed to the conversion of one form of anhydrous zirconia into a denser and more stable modification, but to the sudden elimination of water, accompanied probably by a considerable condensation of the zirconia from the comparatively small molecule $n(2\text{ZrO}_2,\text{H}_2\text{O})$ to the large molecule $n(24\text{ZrO}_2,\text{H}_2\text{O})$.

The form of the curve appears to indicate that no definite stable hydrate is formed by heating precipitated zirconia, and this is confirmed by the discordant results obtained by other observers, thus :-According to Berzelius, the dry hydrate has the composition, ZrO_2 , H_2O = 12.9 per cent. H_2O , whereas Davy stated that it contained 20 per cent., and Klaproth gave as much as 33 per cent. Hermann found that the hydrate dried at 17° was represented by $ZrO_2, 2H_2O$ = 23 per cent.

VI. Hydrate of SnO_2 .—This curve is very similar to those for silica and titania and, like them, shows that no definite stable hydrates were formed. The oxide became anhydrous at 630—655°. A little above 360°, it had the composition indicated by $3SnO_2$, H₂O, and was of a dirty brown colour. On a further small rise in temperature, it suddenly changed from brown to pale yellow, and simultaneously lost weight at a rate nearly three times as great as during the previous 100°, after which the rate of loss during the next 30° or 40° was reduced to less than one-seventh of that which occurred during the change of colour. After changing colour, it had the composition 7SnO₂,2H₂O.

The following stannic hydrates are said to have been obtained by different observers :---

(a.)	Of ordinary	Stannic Act	0.9	$_{2},\mathrm{H}_{2}\mathrm{O}.$	(By action	of Acids
		on Solu	64	nnates.)	

Dried in stream of dry air (Fremy)	$3SnO_{2},7H_{2}O.$
Dried at ordinary temperature in air (Weber)	$\mathrm{SnO}_2, 2\mathrm{H}_2\mathrm{O}.$
Dried in a vacuum (Fremy)	$\mathrm{SnO}_2,\mathrm{H}_2\mathrm{O}.$
Dried at 140° (Fremy)	$3 SnO_2, 2H_2O.$

(b.) Of Metastannic Acid, Sn_5O_{10} , $5H_2O$. (By oxidation of Tin with Nitric Acid.)

Dried at ordin	nary tempera	ature (Fremy)	$5 SnO_2, 10 H_2O$,
,,	,,	(?) (Berzelius)	$\mathrm{SnO}_2,\mathrm{H}_2\mathrm{O}.$
,,	,,	(Thomson)	${ m SnO}_2, { m H}_2{ m O}.$
Dried over su	lphuric acid	(Weber)	${ m SnO}_2, { m H}_2{ m O}.$
Dried in a vac	cuum or at .	100° (Fremy)	$5{ m SnO}_{2}, 5{ m H}_{2}{ m O}.$
Dried at 130°	(Fremy)		$5 SnO_{2}, 4H_{2}O.$
Dried at 160°	,,		$5 \mathrm{SnO}_2, 3 \mathrm{H}_2\mathrm{O}.$
Dried at 55°	(Thomson)	••••	$2\mathrm{SnO}_2,\mathrm{H}_2\mathrm{O}.$

(c.) Intermediate Acids (Musculus), Sn₂O₄,2H₂O and Sn₃O₆,3H₂O.

VII. Hydrate of CeO_{2} .—This curve is a characteristic one, and is distinguished from those of the other metals of the silicon-group, which it otherwise resembles to temperatures of about 600°, by the fact that after rising almost perpendicularly from 200° to 600°, it begins at the latter temperature to curve towards the horizontal, and this continues even up to 815°. The composition at 600°, just before this change occurs, is represented by $CeO_2, 2H_2O$. This would seem to be a definite hydrate, for the composition had previously remained nearly constant, the loss of water for 12 hours between 385° and 600° not having amounted to more than 0.39 per cent., or for eight hours' heating between 440° and 600° to 0.23 per cent. Further, the rate of loss which commences at 600° is 20 times as great as the average rate during the previous 220°, and, moreover, at 600° the colour suddenly changes from a light yellow (presumably the colour of the hydrate $CeO_2, 2H_2O$) to salmon colour, the latter prevailing until complete dehydration. Finally, at the temperature at which the composition became practically constant (385°), and therefore presumably that at which the hydrate Ce₂O,2H₂O was formed, there was a change of colour from brownish-yellow to bright-yellow. We may therefore conclude that ceric oxide forms a definite hydrate, $CeO_2, 2H_2O$, or normal ortho-ceric hydrate, H_4CeO_4 or $Ce(OH)_4$, which is very nearly stable even up to 600°, at which temperature rapid dehydration We have, as regards colour, the following :--begins.

Hydrates, CeO_2 , $(2 + a)H_2O$	brownish-yellow.
Hydrate, $CeO_2, 2H_2O$	bright-yellow.
Hydrates, CeO_2 , $(2 - b)H_2O$	salmon colour.
Anhydrous oxide, CeO ₂	ditto.

Pure cerium dioxide is said to be a white or pale straw-coloured powder, but that after an hour's ignition it acquires a reddish tinge (Mosander). Watts states that it is fawn- or salmon-coloured. The hydrate precipitated from ceric salts by alkalis is pale or sulphuryellow according to Berzelius and Mosander, but they do not state what its composition is. A sulphur-yellow hydrate, of the formula $2CeO_2,3H_2O$, is formed on heating the acid sulphate with caustic potash, or by the action of chlorine on the hydroxide of the sesquioxide suspended in water (Roscoe and Schorlemmer, *Treatise*, **2**, i, 428).

VIII. Hydrate of PbO₂.—This curve has a form quite different from those for SiO₂, SnO₂, &c., owing to the decomposition which the oxide itself undergoes on heating, being ultimately converted into PbO and O. Precipitated lead dioxide, after drying in the air for 10 days, had very nearly the composition $3PbO_2,H_2O$. On heating, it gradually lost water and became dehydrated to PbO₂ at about 230°, on further heating, its weight remained nearly constant up to 280°, at which temperature it suddenly lost oxygen and was converted into Pb₂O₃. This was stable up to about 365°, when a further loss of oxygen occurred, with the formation of Pb₃O₄; the latter was stable up to 530—565°, when it lost more oxygen, became yellow, and formed PbO; this last change being complete at 585°. The PbO thus formed subsequently fused between 585° and 630°.

We have therefore-

Hydrate dried in air = $3PbO_2, H_2O$.

2 ×7 ×	
Complete dehydration to PbO ₂ at about.	230°
PbO ₂ stable up to about	280
Loss of oxygen with formation of Pb ₂ O ₃ .	$280 - 290^{\circ}$
Pb_2O_3 stable between about	290 - 360
Loss of oxygen with formation of Pb ₃ O ₄ .	360-415
Pb ₃ O ₄ stable between about	415 - 530
Loss of oxygen with formation of PbO	530 - 580
PbO stable from	580 to above 815°
PbO fused somewhere between	$585-630^{\circ}$

Becquerel (Ann. Chim. Phys. [3], 8, 405) states that the hydrate, PbO₂,H₂O, is deposited at the positive pole during the electrolysis of lead salts. This is the only previous notice of a hydrate of PbO₂. The difficulties which occur in the manufacture of red lead from massicot (PbO) are doubtless due to not employing the most suitable temperature. Mercier (Annalen, 160, 252) says that the principal point to be attended to, next to the access of sufficient air, is constancy of the right temperature; for the temperature at which massicot takes up oxygen and that at which red lead loses it lie very near to each other. He states that the most favourable temperature approaches that of a dull-red heat, without, however, reaching it. The results

we have given above may possibly be of service in this important manufacture.

IX. Precipitated Sb_2O_3 .—Precipitated antimony trioxide, after drying in the air for five months, was found to be anhydrous. On heating, it underwent but a slight loss in weight, and appeared to be very nearly stable up to 360°, at which temperature it took up oxygen, forming an oxide approximating to $Sb_{20}O_{32}$; this remained comparatively constant between 415° and 440°, gaining only 0.11 per cent. in weight. Above 440°, it again took up oxygen with the formation apparently of Sb_4O_7 . This remained comparatively constant up to about 565°; above 565° it again took up oxygen with the formation of Sb_2O_4 , which then remained stable up to 775°, which was the highest temperature reached.

We have therefore-

$Sb_{20}O_{30} = 5Sb_4O_6 = 10Sb_2O_3$ stable up to	360°
Rapid absorption of oxygen	$360-400^{\circ}$
Sb ₂₀ O ₃₂ comparatively stable	415 - 440
Rapid absorption of oxygen somewhere be-	
tween	440 - 500
$Sb_{20}O_{35} = 5Sb_4O_7$ comparatively stable	500 - 565
Rapid absorption of oxygen	565 - 585
$\mathrm{Sb}_{20}\mathrm{O}_{40} = 5\mathrm{Sb}_4\mathrm{O}_8 = 10\mathrm{Sb}_2\mathrm{O}_4$ stable	590 to above 775°

Antimony trioxide is usually said to be anhydrous; Regnault, however (*Cours de Chimie*, **3**, 239), describes the hydrate Sb_2O_3 , H_2O , and Schaffner (*Annalen*, **51**, 168) the hydrate Sb_2O_3 , $2H_2O$; but neither of these was prepared by direct methods.

X. Hydrate of Bi_2O_3 .—The precipitated hydrate, after drying in the air for five months, had nearly the composition Bi_2O_3 , $3H_2O$;* this hydrate was not stable, but on heating lost water gradually up to 340° , and then much more rapidly up to 415° , at which temperature it contained less water than corresponds to the formula Bi_2O_3 , H_2O . It became completely dehydrated at about 600°, and afterwards fused somewhere between 655° and 710°. There did not appear to be any decisive indication of a definite hydrate of any evident degree of stability. Muir states (*Chem. Soc. Jour.*, 1877, i, 648—649) that the following hydrates of bismuth trioxide are known:— Bi_2O_3 , $3H_2O$; Bi_2O_3 , $2H_2O$; Bi_2O_3 , H_2O .

An inspection of Curve No. X, however, shows that none of these are stable, or only through a very small range of temperature, and

* It also contained some carbonic acid, so that the results obtained in this case cannot be considered as conclusive.

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that on heating, the highest hydrate passes gradually into the lowest, and finally into the anhydrous oxide.

XI. Hydrate of Al₂O₃.—The precipitated hydrate of alumina, after drying in the air for six months, had the composition Al₂O₃,5H₂O. It attained the composition Al₂O₃,3H₂O on heating at 65°, after which the rate of loss diminished considerably up to about 150°, when it again increased up to 160°, and again diminished up to about 200°. Between 160° and 200°, the composition approximated to Al₂O₃,2H₂O. From 200° to 250°, the rate of loss was again very rapid, but became very much less between 250° and 290°, when the composition was approximately Al₂O₃, H₂O. Above 290°, the rate of loss rapidly increased again up to 360°, beyond which it slackened, and water was gradually but slowly expelled until complete dehydration was reached at a temperature of about 850°. At no point did the composition remain constant, an increase of 10° always caused a further loss of water, except at temperatures above 500°, when the alumina was very nearly dehydrated. A certain comparative-but only comparativestability, however, was attained at or about the three following temperatures, viz .:---

$Al_2O_3, 3H_2O$	comparatively	stab	le	65—150°
$Al_2O_3, 2H_2O$,,	"		160 - 200
$\mathrm{Al_2O_3,H_2O}$,,	,,	• • • • • • • • • •	250 - 290

The following hydrates have been previously noticed :-

Precipitated at a boiling heat and dried at	
ordinary temperature (Ramsay)	$Al_{2}O_{3}, 5H_{2}O.$
Hydrargillite and gibbsite; also the arti-	
ficial hydrate obtained by precipitation	
and dried (in air?) (Torrey, Berzelius,	
Bonnsdorff)	$Al_2O_3, 3H_2O.$
By heating aluminium acetate at 100° for	, -
some days and drying the resulting pre-	
cipitate at 100° (Crum)	$Al_{2}O_{3}, 2H_{2}O.$
By prolonged ebullition of Al ₂ O ₃ ,3H ₂ O sus-	
pended in water (St. Gilles)	$\mathrm{Al}_{2}\mathrm{O}_{3}, 2\mathrm{H}_{2}\mathrm{O}.$
Native hydrate from Beaux (Berthier)	Al ₂ O ₃ ,2H ₂ O (?).
Diaspore	$Al_2O_3, H_2O.$
Precipitated hydrate dried at 300° (Ram-	
say)	Al_2O_3, H_2O_2
Al ₂ O ₃ ,H ₂ O does not part with its water	
below 360° (Dufrénov).	

Our results agree very closely with the above and with those of

Ramsay on the dehydration of alumina (*Chem. Soc. Jour.*, 1877, ii, 395). Ramsay's and our own results show either that there are no definite stable hydrates of alumina, or what is more probable, that a very large number of hydrates exist, but so unstable that the smallest rise in temperature is sufficient to convert a higher into a lower hydrate.

XII. Hydrate of In_2O_3 .—The air-dried hydrate had very nearly the composition $In_2O_3, 6H_2O$. On heating, it lost water gradually, and at a nearly uniform rate up to 150° , when it had the composition $In_2O_3, 3H_2O$. The rate of loss then rapidly increased up to 160° , beyond which it proceeded almost uniformly at the previous rate, and the substance passed successively through the compositions $In_2O_3, 2H_2O$, $2InO_3, 3H_2O$, and In_2O_3, H_2O , without giving any evidence of the formation of a stable hydrate. Soon after passing through In_2O_3, H_2O , and at about 280°, the rate of loss suddenly diminished, the curve taking a sharp curve upward, and becoming nearly perpendicular. Complete dehydration, however, was finally attained only at 655° , the last traces of water being lost very slowly.

The two following hydrates are said to have been obtained (*Watts'* Dict., 6, 732):--

Hydrate precipitated at boiling heat and airdried 2In₂O₃,7H₂O. Dried at 100°..... In₂O₃,3H₂O.

But generally speaking the same remarks apply here as in the case of alumina, in so far as there is no indication of the formation of any definite stable hydrates.

XIII. Hydrate of Tl₂O₃.--Precipitated and air-dried thallic hydrate had almost exactly the composition Tl₂O₃, H₂O. This, however, was not stable, but on heating gradually lost water until complete dehydration was attained at about 230°. The weight then remained perfectly constant up to 360°, between which and 440° a further very slight diminution occurred, due apparently to loss of oxygen. Above 440°, and up to between 565° and 585°, the weight again remained perfectly constant, and corresponded exactly to 3Tl₂O₃, Tl₂O. Somewhere between 565° and 585° the substance lost its gloss, and became It then rapidly lost weight, owing partly to loss of dull black. oxygen, and partly to volatilisation of the Tl₂O formed. It fused at 630° to a dirty-green liquid. It continued rapidly to lose weight up to 815°, but above this temperature the weight again remained constant, and no further loss occurred on heating over the blowpipe; the total loss then amounted to 31.96 per cent. The final product probably consisted of undecomposed Tl_2O_3 . It could not be Tl_2O , as the latter is readily volatile at the temperature employed. The most probable explanation seems to be that at 585° Tl₂O₃ loses oxygen with partial conversion into Tl₂O, but above 815° any Tl₂O so formed again takes up oxygen, re-forming non-volatile Tl₂O₃. We have therefore—

Air-dried at $15^{\circ} = \text{Tl}_2\text{O}_3, \text{H}_2\text{O}$, but unstable on he	eating.
Complete dehydration with formation of Tl ₂ O ₃	
about	230°
$\mathrm{Tl}_2\mathrm{O}_3$ perfectly stable	$230 - 360^{\circ}$
Reduction to $3\text{Tl}_2\text{O}_3, \text{Tl}_2\text{O}$	360 - 440
3Tl ₂ O ₃ ,Tl ₂ O perfectly stable	440 - 565
Rapid loss of oxygen and volatilisation of Tl ₂ O	
formed, the rate of loss gradually diminish-	
ing after fusion at 630°	585 - 815
Remaining Tl ₂ O ₃ constant from	815° upwards.

The following observations have been noted by others :---

Precipitated thallic hydrate dried at 100°	
(Werther)	$\mathrm{Tl}_{2}\mathrm{O}_{3},\mathrm{H}_{2}\mathrm{O}.$
Ditto dried over sulphuric acid (Birnbaum)	$\mathrm{Tl}_{2}\mathrm{O}_{3},\mathrm{H}_{2}\mathrm{O}.$
Ditto dried at 100° (Birnbaum)	$\mathrm{Tl}_{2}\mathrm{O}_{3}.$
Ditto dried at 260° (Crookes)	Tl_2O_3 .

Pure anhydrous Tl_2O_3 melts at 759° (Carnelley); Tl_2O_3 gives off oxygen at a red heat with reduction to Tl_2O (*Watts' Dict.*, 5, 753); Tl_2O melts at about 300°, and at higher temperatures volatilises and partially oxidises at the same time to Tl_2O_3 (*ibid.*, 752).

XIV. Hydrate of Fe_2O_3 .—Precipitated ferric hydrate, after drying at about 15° for 18 days, contained more water than corresponded to $Fe_2O_3,5H_2O$. On heating, it attained the composition $Fe_2O_33H_2O$ at about 55°, but with a further rise in temperature water was gradually given off until the oxide was completely dehydrated at 500° ; beyond this there was no more alteration in weight. The curve shows that at no point was there any indication of the formation of a definite hydrate, stable through a further rise in temperature, except that at about 385° a hydrate was formed represented exactly by $10Fe_2O_3, H_2O$; this remained perfectly constant in weight on heating for two hours from 385° to 415°, and was possibly stable through a much larger range of temperature.

Ramsay (*Chem. Soc. J.*, 1877, ii, 395) has also investigated the dehydration of ferric hydrate, and he also concludes that no definite stable hydrates are formed, except perhaps Fe_2O_3 , H_2O ; our results, however, give no indication of the formation of the latter.

The following minerals are well-known natural crystallised hydrates :----

00	CARNELLEY AND WALKER: THE DEHYD	DRATION
	Limonite	$Fe_2O_3, 3H_2O.$
		$F_{2}O_{3}, 2\Pi_{2}O_{2}$
	Gounte	Fe_2O_3, H_2O_2
		$2 \operatorname{Fe}_2 \operatorname{O}_3, 3 \operatorname{H}_2 \operatorname{O}_2$
	Turgite	$2 \operatorname{Fe}_2 \operatorname{O}_3, \operatorname{H}_2 \operatorname{O}_2$
	,,	$3\mathrm{Fe}_{2}\mathrm{O}_{3},5\mathrm{H}_{2}\mathrm{O}.$
Т	he following have been prepared artificially :	
	Precipitated when cold (Wittstein)	Fe ₂ O ₃ ,3H ₂ O.
	,, ,, (Gmelin and Lefort).	$Fe_2O_3, 2H_2O.$
	,, hot (Lefort, Schaffner)	Fe ₂ O ₃ ,2H ₂ O.
	, when cold and dried at 100°	
	(Muck)	$Fe_{2}O_{3}, 2H_{2}O_{2}$
	and dried in a vacuum	2Fe ₃ O ₃ .3H ₃ O.
	By freezing ferric hydrate suspended in water	2Fe ₃ O ₃ ,3H ₃ O.
	Precipitated when cold (Pean St. Gilles)	2Fe.0.3H.0
	Precipitated and dried at 100 (Muck)	$Fe_{0}O_{0}H_{0}O_{0}$
	Prolonged ebullition of hydrate in water (Peau	10203,1120
	St. Gilles)	FeoO. H.O
	Formia hydrato duiod at 100°	$2 \mathbf{F}_0 \mathbf{O} \mathbf{H} \mathbf{O}$
	Terric liyurate urieu at 100	$21e_{2}O_{3}, 11_{2}O.$
	Totally denydrated by prolonged ebuiltion in	E O
	water to	Fe_2O_3 .
	Precipitated and dried at temperatures between	
	15° and 100° gives hydrates intermediate	
	between Fe_2O_3 , $2H_2O$ and Fe_2O_3 , H_2O (Muck).	

XV. Hydrate of Co_2O_3 .—Air-dried precipitated cobaltic oxide had almost exactly the composition 5Co₂O₃,8H₂O. At this it remained perfectly constant on heating for six hours at temperatures ranging up to 74°. When heated beyond this, it gradually lost water, and at 100° had exactly the composition 2Co₂O₃,3H₂O; the latter, however, was not stable, for on further heating it lost more water at a rate which gradually increased up to 260°, when the rate of loss rapidly diminished, the curve turning sharply upwards, and becoming very The product had now exactly the composition nearly perpendicular. $10Co_2O_3$, H_2O (or Co_2O_3 , see below), and at this it remained almost constant (losing but 1 mgrm.) between 280° and 360°. At the latter temperature, it underwent a further slight loss, and became completely dehydrated at 385°, or possibly lost a small quantity of oxygen, giving a product consisting of Co₂O₃ admixed with a little Co_3O_4 (see below).

We have therefore-

OF METALLIC HYDROXIDES BY HEAT.

Air-dried cobaltic hydrate, 5Co₂O₃,8H₂O, stable

up to	75°
Gradual loss of water without formation of	
stable hydrate	$75 - 270^{\circ}$
$10Co_2O_3, H_2O$ (or else pure Co_2O_3) stable	280 - 360
Complete dehydration or slight loss of oxygen	
with formation of a small quantity of Co ₃ O ₄ .	385°

Winkelblech states that precipitated hydrate of cobalt after drying over sulphuric acid has the composition $Co_2O_3,3H_2O$, whereas Hess found that under the same conditions it had the composition $Co_2O_3,2H_2O$. When cautiously heated to 600° or 700°, it yields the anhydrous oxide (*Watts' Dict.*, 1, 1049). Exposed to a low red heat, it loses oxygen with formation of Co_3O_4 (Hess, Braun; comp. also Russell, *Chem. Soc. J.*, 1863, 16, 51).

XVI. Hydrate of Ni_2O_3 .—The completion of the dehydration in this case was prevented by an accident, so that no definite conclusions are possible, except that so far as the curve runs there was no indication of the formation of any definite stable hydrate.

A general consideration of all the curves shows-

(1.) That in no instance [except in the case of Ag(OH), Hg(OH)₂, CeO₂,2H₂O, and perhaps 5Co₂O₃,8H₂O] is there any certain indication of the formation of definite hydrates which are stable* through any but possibly a very small range of temperature. From this we must conclude either that there are no definite hydrates formed on heating the precipitated hydrates at gradually increasing temperatures; or that a very large number of such hydrates are formed under these conditions, but that they are so unstable that a very small further rise in temperature is sufficient to convert a higher into a lower hydrate.

If the first alternative be correct, then the so-called hydrates would be mechanical mixtures of the oxide with water, but this is a supposition which is very improbable, for it would be difficult to suppose that mechanically admixed water could be retained at the high temperatures frequently required to produce complete dehydration, in some cases a full red heat.

The second supposition that there are a large number of definite but unstable hydrates formed is far more probable. That definite hydrates of Fe_2O_3 , Al_2O_3 , &c., exist is proved by their natural occurrence in the form of several well-crystallised minerals, and by the artificial production of many crystallised hydrates. The forms of the dehydration curves would also, one would think, be far more regular did the dehydration consist in the expulsion of merely mechanically

* For definition of "stable hydrate" see p. 81.

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admixed water, whereas their greater or less irregularity in most cases seems to indicate the formation of hydrates at certain temperatures which are relatively more stable than hydrates formed at other temperatures. The unstable character of the hydrates is further shown by the frequently discordant results obtained by different observers, and by the apparently slight circumstances which seem in many cases to influence the quantity of water retained by an oxide. The summary of previous work on this subject given above at the end of the discussion of each curve will serve to illustrate this.

In view then of the following facts---

1. That certain well-defined hydrates are known, which are stable through a considerable range of temperature, though the number of these is smaller than is usually supposed;

2. That many well-defined and well-crystallised hydrates are found as minerals, and may also be obtained artificially;

3. That the artificial hydrates produced by heat and of the same composition as these minerals, on further heating lose water more or less gradually at or only very slightly above the temperature at which they were formed;

4. That the temperatures required for complete dehydration are often high;

5. That the dehydration curves frequently seem to indicate the formation of hydrates, which though unstable themselves, except through a very small increase of temperature, are relatively much more stable than other hydrates of the same oxide :--

We conclude that when a precipitated oxide is heated, it gradually loses water with the successive formation of a large number of definite hydrates, each of which is further decomposed on a small rise in temperature with the formation of a hydrate containing a smaller proportion of water. As the elimination of water proceeds, the molecule becomes larger and more and more complex, until ultimately, when the last molecule of water is given off, a highly complex molecule of the anhydrous oxide is left, its formula being some multiple $n(RO_x)$ of the generally received simple formula RO_x .

The polymeric character of the oxides we have examined seems to accord fully with our results, and this taken in connection with the facts and arguments advanced by Henry (*loc. cit.*) seems to prove, or at least to give a very high degree of probability to, the truth of his theory that the known metallic oxides are polymerides $n(\text{RO}_x)$ of the unknown simple oxides RO_x . If this be so, then our results also show that in most cases, especially those of SiO₂, TiO₂, Al₂O₃, &c., the coefficient *n* of polymerisation must be very large: thus, for the oxides of silicon, titanium, and tin it would be at least 10, and probably much higher, so that the molecules of these oxides would be at least $R_{10}O_{20}$; whilst oxide of zirconium would be at least $Zr_{24}O_{48}$, ferric oxide at least $Fe_{20}O_{30}$. In the case of antimonious oxide the results seem to indicate $Sb_{20}O_{30}$ as the smallest value of its molecule.

The most infusible oxides, such as silica, titania, stannic oxide, alumina, &c., are those which the curves would indicate as having the highest coefficient of polymerisation, and this is what one would expect if the theory of polymerisation be true.

DEHYDRATION AND THE PERIODIC LAW.

Having now considered the question of the polymerisation of the oxides, we next turn to the second problem which we had in view in commencing this research, viz.:—The relation of the phenomena of the dehydration of the oxides to the Periodic Law.

In dealing with this question, the difference between affinity in *intension* and in *extension* must be well borne in mind. The affinity of sodium for chlorine in sodium chloride is greater in *intension* than that of tin for chlorine in stannic chloride, in so far as the force of combination between one atom of sodium and one atom of chlorine is greater than between the atom of tin and any one of the atoms of chlorine. On the other hand, the affinity of tin for chlorine is greater in *extension* than that of sodium for chlorine, in so far as one atom of tin is capable of combining with four atoms of chlorine, whereas one atom of sodium can combine with one atom of chlorine only.

In like manner, the affinity of two oxides for water may differ from one another. An oxide may combine with but a small quantity of water, but it may retain that with great force, whereas another oxide may combine with a greater quantity of water, but give up the whole of it with comparative ease.

The Affinity in Intension of the Oxides for Water.

The affinity of the oxides for water in *intension* will be indicated by the temperature required to produce complete dehydration. A careful comparison of these temperatures in the case of the different normal oxides shows that they vary periodically with the atomic weight of the positive element, as seen in the table on p. 95.

In this table, it is found necessary to distinguish between odd and even series. In order to render this distinction more evident, the even series are printed in ordinary type, and the odd series in thick type. Group VIII is omitted, as there are not data to draw any conclusions in regard to it. This table shows—

A. As regards oxides belonging to the same group-

(1.) That in the case of odd members of the same group, the temperature of complete dehydration, and (therefore the affinity of the normal oxides for water), diminishes as the atomic weight of the positive element increases. (There is not a single exception to this rule.)

(2.) That in the case of even members of the same group, the temperature of complete dehydration increases as the atomic weight of the positive element increases.

There is no well-marked exception to this rule, for in the case of ZrO_2 the determination, owing to an accident, was not completed, so that the temperature of complete dehydration might have been higher than that given.

Similar relationships, in so far as the meagre data will allow, are also brought out on comparing the heats of combination of the normal oxides with water in the formation of the hydrates, for example :--Though the temperatures of complete dehydration of calcium, strontium, and barium have not been determined, the heat of combination of the oxides with water shows that they would follow the above rule, thus :-- (Compare also Bloxam, Chem. Soc. Journ., **13**, 15; and Smith, Phil. Mag. [3], **9**, 87.)

 $\begin{array}{c|c} Even \begin{cases} CaO + H_2O = 15500 \\ SrO + H_2O = 17700 \\ BaO + H_2O = 22300 \\ \end{array} \begin{array}{c} \text{in thermal units} \\ \text{in the second of the second of$

So far as oxides of the first and second groups are concerned, it seems as though the temperature of complete dehydration, and therefore the *intensive* affinity of the oxide for water, increases as we pass from the oxide of the element with highest atomic weight in an odd series to the one with the lowest atomic weight, and thence again increases as we pass from the element with lowest atomic weight in an even series to the one with the highest atomic weight; for instance, in the second group we have—

C: 10 +107 /01 /C7 II	Heat.	Group VII. R207.
he Metallic Hydroxides by 1	Group VI. $R_2O_6 = 2RO_3$.	
DOWINDAUCU DY DINYCIALLY	Dehydration of the M	Group V. R ₂ O ₅ .
01 January 1000.	es of Complete	Group IV. $R_2O_4 = 2RO_2$.
	um Temperatun	Group III. $\mathbf{R}_{2}\mathbf{O}_{2}$.
	ing the Minimu	Group II. $R_2O_2 = 2RO.$
	Table show	Group I. R ₂ O.

3. R2O7.		ses on $\operatorname{Cl}_2 \mathbf{O}_7 = \mathbf{P}$	ration. $Mn_2O_7 = ?$	65°, at $Br_2O_7 = P$ rature		$160^{\circ}, \ \mathbf{I}_{2}\mathbf{O}_{7} = 160^{\circ}(\mathbf{P})$ a red		0°, but		
Group VI. $R_2O_6 = 2R($		$SO_3 = decompc$	$CrO_3 = on evapo$	$SeO_3 = not at 2$ which tempe	it decomposes MoO ₃ = above 17	$TeO_3 = not at$ but nearly at		$WO_3 = not at 10$		$UO_3 = 300.$
$\begin{array}{l} {\rm Group} \ {\rm V}, \\ {\rm R}_2 {\rm O}_5. \end{array}$	$N_2O_5 = affinity for H_2O_1$ less than that of $P_2O_4^{-1}$, d. at 260° into N_2O_4 .	$0, \text{ and } H_2 0.$ $P_2 0_5 = \text{ not } d. \text{ by heat.}$	$V_2O_5 = on evaporation.$	$As_2O_5 = a. 206^\circ$; dull red heat.	$Nb_2O_5 = not at 100^\circ$;	$Bb_{2}O_{5} = above 200^{\circ}$, but below redness.	$\mathrm{Di}_2\mathrm{O}_5 = ?$	$Ta_2O_5 = low redness.$	$\mathbf{Bi}_20_5=150^\circ.$	1
Group IV. $R_2O_4 = 2RO_2$.	$CO_2 = b. 100^\circ.$	Si0 ₂ =a. 850°.	$TiO_2 = 700^{\circ}$.	$GeO_2 = P$	$ZrO_2 = about$	$SnO_2 = about$ 655°.	$CeO_2 = about$ 850°.		PbO ₃ = about	$ThO_2 = red$ heat (?)
Group III. R2O2.	$B_2O_3 = b. 577^\circ.$	$\mathbf{Al}_{0}\mathbf{O}_{3} = \mathbf{g}.$	$S_2O_3 = ?$	$\mathbf{G}\mathbf{a}_{2}\mathbf{O}_{3}=\mathbf{P}$	${ m Yt_2O_3}={ m red}_{ m heat}$	$In_2O_3 = 655^\circ.$	$La_2O_3 = P$		$TI_2O_3 = 230^{\circ}.$	1
Group II. $R_2O_2 = 2RO.$	BeO = high temperature.	$Mg0 = 630^{\circ}.*$	CaO=red heat.	Zn0 = 585°.*	SrO = dull red	CdO = 385°.*	BaO = full red heat.+	.]	HgO = about	.
Group I. \mathbf{R}_2 O.	H 2 0. Li20 = ?	$Na_2O = not at$	$K_2O = not at$	$Cu_2 O = 360^{\circ}.$	$Rb_2O = $?	$Ag_2O = about$ 150°.	$Cs_2 0 = P$	1	$Au_{5}O = below$	2 2
eries.	મંજાં	°.	4	<u>م</u>	6.	r;	æ	9. 10.	11.	12.

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	Tem d	p. of complete ehydration.	Heat of combination of RO·H ₂ O.
	(HgO	175°	٩ ٦
- 3 3		385	80
ouu .	\mathbf{ZnO}	585	2700
	{ MgO	630	3100
Group II	(BeO	high temperature	?
-	CaO	above 630°	15500
Leven.	$\left\{ SrO \dots \right\}$	$ \left\{ \begin{array}{c} \text{above the temp.} \\ \text{for CaO, dull} \\ \text{red heat} \end{array} \right\} $	17700
	(BaO	full red heat	22300

B. As regards oxides belonging to the same period or to the same series.*

That there is a regular periodic variation of the temperature of complete dehydration with the atomic weights of the elements is quite evident from the table, but the data are not quite decisive as to whether this variation is according to periods or according to series. The data on the whole are more favourable to variation by periods. If this be the case the rule would run thus:—

(3.) For oxides of elements belonging to the same period, the temperature of complete dehydration seems to diminish from the beginning to about the middle of the period, and then to increase again to the end of the period, thus following the same rule as the specific volumes of the elements as represented in Lothar Meyer's curve of the elements, and therefore rising and falling with that curve. The only apparent exceptions are MgO, Bi_2O_5 , and possibly I_2O_7 , the existence of the last oxide, however, is doubtful.

The very few cases in which the heats of combination of the oxides with water have been determined are in favour of the above form of the rule, thus:—Na₂O + H₂O = 35600; MgO + H₂O = 3100; Al₂O₃ + H₂O = ?; SiO₂ + H₂O = ?; P₂O₅ + H₂O = 10700; SO₃ + H₂O = 21300. If the variation be according to series, instead of according to periods, though this seems less likely, the rule would be :—For oxides of elements belonging to the same series the temperature of complete dehydration increases as we pass from the

^{*} Elements in the same horizontal line belong to the same series, so that there are seven in each series. *Periods* are of two kinds: a *short period* contains but seven members, thus from Li to F, and from Na to Cl, are two short periods; a *long period*, on the other hand, embraces 17 members (including Group VIII), thus from K to Br, and from Rb to I, form two long periods, for we have to pass over 16 elements before we come to one, namely, Rb, in which the properties of K are more or less repeated, whereas starting from Li we have to pass over but six elements before we come to Na, or a point at which the properties of Li are in some measure repeated.



DIAGRAM II SHOWING THE NUMBER OF MOLECULES OF WATER RETAINED BY ONE MOLECULE OF AN OXIDE AT DIFFERENT TEMPERATURES.





NUMBER OF MOLECULES OF WATER RETAINED BY ONE MOLECULE OF OXIDE.

beginning (positive end or Group I) to the middle (Group IV) of each series, and then diminishes to the end (negative end or Group VII) of the series.

The exceptions to this form of the rule are more numerous and more serious than those to the form of the rule previously given; they are, P_2O_5 , the whole of the oxides of the second series, most probably all the alkaline oxides, and ZrO_2 . The temperature given for the last is, however, doubtful for the reasons already stated.

The Affinity in Extension of the Oxides for Water.

Of two oxides belonging to the same group, it does not follow that the one which requires the highest temperature for complete dehydration, and which has therefore the greatest intensive affinity, will also at any other lower temperature combine with the greater quantity of water per molecule of oxide, that is, will have a greater affinity in extension. The very opposite in fact is the case sometimes, though usually the two phenomena run parallel with one another, as will be shown in the following table (p. 98).

From this table, it is seen that in the case of the TiO₂, P_2O_5 , and SO₃ groups the order of affinity for water in *extension* is the same as in *intension*, whereas in the SiO₂ and Al₂O₃ groups, so far as the first two members are concerned, the reverse holds good. The last member of each of these groups, however, viz., PbO₂ and Tl₂O₃, follows the same order both in intension and in extension. It is note-worthy that the two corresponding triplets, SiO₂, SnO₂, PbO₂ and Al₂O₃, Tl₂O₃, of two different groups, are exactly analogous in this respect.

Change of Colour occurring in Dehydration.

Some of the substances in the course of being heated changed their colour (when cold) during a single heating, and when this occurred the loss was always greater than the average before the change. Such a permanent change in colour probably indicated the formation of a definite hydrate or oxide. This change in colour must be carefully distinguished from the temporary alteration in colour which many substances undergo when heated, in which case the change is always towards the red end of the spectrum, as first pointed out by Ackroyd (see *Phil. Mag.* [5], **2**, 423, and *Chem. News*, **34**, 76). Here the original colour is regained on cooling, whereas the changes in colour we refer to are permanent in the cold. The following are the colour changes we have noted :—

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Table showing the Temperatures at which one Molecule of the several Oxides of the same Sub-group retains the same number of Molecules of Water.

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- CdO. 300-340°.-Light-brown to dark-brown. Loss 12 per cent.; previous average loss* 4.5 per cent. Indicates change from Cd(OH)₂ to CdO.
- HgO. 415-440°.-Dirty-yellow to bright-orange. Loss 45 per cent. Indicates change of yellow into red modification of HgO, accompanied by rapid decomposition into Hg and O.
- ZrO_2 . 385-415°. Grey to white. Loss 4 per cent., previous average loss 0.6 per cent. Due to conversion of $2ZrO_2$, H₂O into $24ZrO_2$, H₂O (comp. *Gmelin*, 3, 342).
- SnO_2 . 360—385°.—Brownish to pale-yellow. Loss 0.8 per cent., previous average loss 0.26 per cent. Due to conversion of $3SnO_2$, H_2O to $7SnO_2$, $2H_2O$.
- CeO₂. 585-630°.-Light-yellow to salmon colour. Loss 2 per cent., previous average loss 0.1 per cent. Due to conversion of $CeO_{2,2}H_{2}O$ into $CeO_{2,2}(2 - b)H_{2}O$ and finally to CeO_{2} .
- PbO_2 . 530-565°.-Brown to yellow. Loss 1.8 per cent., previous average gain 0.01 per cent. Due to conversion of Pb₃O₄ to PbO.
- Tl_2O_3 . 585-630°.-Brownish-black to green (fused). Loss 10 per cent., previous average loss 0.4 per cent. Due to partial conversion of Tl_2O_3 to Tl_2O .
- Bi_2O_3 . 385—415°.—Light-yellow to deep-yellow. Loss 2 per cent., previous average loss 1.3 per cent. Due to conversion of Bi_2O_3 , H_2O to Bi_2O_3 .

It did not of course follow that for a great loss of weight there was any change in colour.

GENERAL CONCLUSIONS.

(1.) Precipitated antimony trioxide is anhydrous. On heating, it underwent the following changes:— Sb_2O_3 or $Sb_{20}O_{30}$, stable up to 360° , then rapid absorption of oxygen with formation of $Sb_{20}O_{32}(?)$, the latter comparatively stable at $415-440^\circ$; then further absorption of oxygen with formation of $Sb_{20}O_{35}(?)$, the latter comparatively stable, $500-565^\circ$; third absorption of oxygen with formation of Sb_2O_4 or $Sb_{20}O_{40}$, the latter stable from 590° to above 775°.

(2.) The following definite stable hydrates appear to exist :---

(a.) Ag(OH) stable up to about 100° , then rapid loss of water with

* That is, during the like interval of temperature immediately preceding the lower limit of the interval in which the colour change was observed.

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formation of Ag₂O, (containing a little metallic silver); the latter stable, 180-270°; then reduction to metallic silver, this reduction being complete at $300-340^{\circ}$.

(b.) $Hg(OH)_2$ stable up to about 100°; complete dehydration to HgO at about 175°, when incipient decomposition into Hg and O commences, followed by full decomposition at about 415° to 440°.

(c.) $CeO_2, 2H_2O$ or $Ce(OH)_4$ = orthoceric hydrate; this hydrate was formed on heating precipitated hydrate of cerium dioxide to about 385°. It remained stable from about 385° to 600°. It was of a light yellow colour. On heating to over 600°, it underwent dehydration to CeO₂ and became salmon-coloured. This is the only definite stable hydrate of the oxides RO_2 of the silicon-titanium-group we obtained. In other respects cerium hydrate on dehydration behaved like the hydrates referred to in § 5.

(d.) $5Co_2O_38H_2O$. This was the composition of air-dried cobaltic hydrate, and was perfectly stable up to 75° .

(3.) The following data with regard to the action of heat on the hydrate of PbO, will possibly be of interest in the manufacture of red lead :—Hydrate dried in air = $3PbO_2$, H₂O, complete dehydration at about 230°; PbO₂, stable up to about 280°, loss of oxygen with formation of Pb₂O₃, 280-290°; Pb₂O₃, stable, 290-360°, loss of oxygen with formation of Pb₃O₄, 360-415°; Pb₃O₄, stable, 415-530°, loss of oxygen with formation of PbO at 530-580°; PbO, stable from 580° to above 815°; PbO fused somewhere between 585° and 630°.

(4.) Air-dried thallic hydrate = Tl_2O_3, H_2O , but unstable on heating, complete dehydration to Tl₂O₃ at about 230°; Tl₂O₃, perfectly stable between 230° and 360°, reduction to 3Tl₂O₃, Tl₂O at 360-440°; 3Tl₂O₃,Tl₂O, perfectly stable between 440° and 565°; rapid loss of oxygen and volatilisation of Tl₂O formed at 585-815°; the rate of loss gradually diminishing after fusion at 630°; remaining Tl₂O₃ constant from 815° upwards.

(5.) An examination of all the results shows that, with the exceptions referred to in § 2, there is no certain indication of the formation of definite hydrates which are stable through any but possibly a very small range of temperature (less than about 13°). From this we must conclude either that there are no definite hydrates formed on heating at gradually increasing temperatures, or that a very large number of such hydrates are produced under these conditions, but are so unstable that a further small rise in temperature is sufficient to convert a higher into a lower hydrate. Of these the second alternative is, for reasons given, by far the more probable.

Our results accord entirely with Henry's theory that the known metallic oxides are polymerides $n(RO_x)$ of the unknown simple oxides RO_x . The results also show that in most cases, especially those of SiO_2 , TiO_2 , SnO_2 , Al_2O_3 , &c., the coefficient *n* of polymerisation must be very large, as might be expected from the infusible character of these oxides. Minimum values for this coefficient are indicated in some cases.

(6.) The retention of water by many oxides at comparatively high temperatures, at and above a red heat, is noteworthy. This is especially interesting in the case of the hydrate of cerium dioxide, $Ce(OH)_4$, which is stable to as high a temperature as 600°. The retention of water at such high temperatures illustrates the great importance in quantitative analysis of the thorough ignition of the hydrates in order to drive out the last traces of water before weighing.

(7.) The minimum temperature of complete dehydration is a periodic function of the atomic weight, as follows :---

(a.) For normal oxides of odd members of the same group, the minimum temperature of complete dehydration diminishes as the atomic weight of the positive element increases. (No exception.)

(b.) For even members of the same group it increases as the atomic weight of the positive element increases. (No well-marked exceptions.)

(c.) For normal oxides of elements belonging to the same period, the minimum temperature of complete dehydration diminishes from the beginning to the middle, and then increases to the end of the period. The only apparent exceptions are MgO, Bi_2O_5 , and I_2O_7 (?).

These results also accord with the heats of combination of the normal oxides with water in the formation of hydrates.

(8.) Of two oxides belonging to the same group, the one which requires the highest temperature for complete dehydration will usually combine at any other lower temperature with a greater quantity of water per molecule of oxide; this, however, is not always the case, the pairs SiO₂, SnO₂ and Al₂O₃, In₂O₃ being marked exceptions. From this we may conclude that the order of affinity of the oxides for water is usually the same both in intension and in extension, though not always.

(9.) Changes of colour on dehydration, which are *permanent* on *cooling*, usually indicate the formation of a definite hydrate, or that the dehydration is complete, or that some other definite chemical change has occurred.