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# XXXII.—NOTES FROM THE LABORATORY OF THE YORKSHIRE COLLEGE OF SCIENCE, LEEDS.

(Communicated by T. E. THORPE, Ph.D., F.R.S.)

1. On the Action of the Copper-zinc Couple on Potassium Chlorate and Perchlorate.

## By HERBERT ECCLES.

IN 1873 I published an account of the action of the copper-zinc couple of Messrs. Gladstone and Tribe, upon various salts, and I showed that the reducing action exerted by these metals might be made the basis of a quantitative method (see this Journal, 1873, p. 541). Since that time this method has been frequently made use of by myself and my students, more particularly in the cases of nitrates and chlorates, and no difficulty is met with in obtaining complete reduction of a moderate quantity of the salts, provided that the couple is properly made. Chlorates are particularly easy of reduction : on adding a weighed quantity of the salt to the water covering the couple, and boiling a few minutes, zinc hydrate is seen to be formed in quantity, and, on filtering the solution and adding silver nitrate, a precipitate of silver chloride is obtained, which on weighing is found to correspond with the theoretical amount.

In the Journal of the German Chemical Society of Berlin, viii, 1356 (Correspondenz aus Florenz), it is stated, in an account of some experiments made by Sig. G. Pellagri of Bologna, on the reducing action of various metals on oxisalts, that "Kaliumchlorat in wässriger Lösung wird durch Schütteln mit Eisenfeile in der Wärme rasch zu Chlorür reducirt, und Pellagri glaubt, dass dieses Verhalten in der Merkwürdig ist, dass die Eisen-Analyse Anwendung finden könne. kupfer-oder Zinkkupferkette auf Chlorat nur äusserst langsam und unvollständig wirkt." It is possible that the term "Kette" refers simply to plates of copper and zinc joined together by a wire outside the liquid : if, however, it is implied that the conjoint action of the metals is insufficient to effect complete reduction of the chlorate, the statement is at direct variance with experience. The following analytical results, obtained by Mr. Herbert Eccles in the ordinary course of laboratory work, are quoted as substantiating my original statement :---

I. 0.3895 gram KClO<sub>3</sub>, dissolved in water and boiled with a copperzinc couple, made from 10 grams zinc-foil, for 10—15 minutes required, after filtration, 31.80 c.c. of deci-normal silver nitrate solution.

# II. 0.3732 gram KClO<sub>3</sub>, treated in a similar manner, required 30.35 c.c. of the silver-nitrate solution.

	I.	II.	Theory.
Chlorine	 28.98	28.86	28.96

The copper-zinc couple is entirely without action on potassium perchlorate. An aqueous solution of the salt may be boiled for an indefinite length of time with the metals without any reduction occurring. Mr. Eccles has taken advantage of this fact to verify the wellknown statement that the decomposition of potassium chlorate on heating occurs in two phases, with the intermediate production of the perchlorate. The copper-zinc couple, indeed, affords a ready means of determining the rate of the decomposition of the salt by heat. He has also proved by the same method, that when manganese dioxide is added to the chlorate, no perchlorate is formed at any stage of the decomposition

## 2. On Thallium Chlorate.

#### By JOHN MUIR.

THALLIUM chlorate, according to Mr. Crookes, may be obtained by dissolving the metal in chloric acid, or by mixing saturated solutions of thallium nitrate and potassium chlorate. From the description of this salt given in Watts's Dictionary (vol. v, p. 754) it would seem to be an extremely unstable compound : it is stated that its solution when heated becomes yellow and evolves oxides of chlorine, and that the crystals which are deposited on concentrating the liquid are instantly decomposed by water, with formation of the brown thallic oxide. The exceptional behaviour of the thallium compound is remarkable, since the chlorates, as a class, are perfectly stable salts. The chlorates may be broadly divided into the two groups of anhydrous salts, like those of potassium and silver, and of hydrated salts, like those of lead and barium. From the well-known relations of thallium to lead on the one hand, and to the metals of the alkalis on the other, it becomes interesting to determine to which class thallium chlorate belongs. Some years ago I prepared a small quantity of thallium chlorate with a view to determine this point. The salt is easily obtained by mixing equivalent quantities of thallium sulphate and barium chlorate, filtering from the barium sulphate, and concentrating the solution. Thallium chlorate forms white and almost opaque microscopic crystals which are perfectly permanent in the air and readily soluble in hot water, VOL. XXIX. 3 м

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without decomposition. A determination of thallium as chloroplatinate showed that the salt was anhydrous.

> 0.223 gram chlorate gave 0.3138 gram Tl<sub>2</sub>PtCl<sub>6</sub>. Thallium..... = 70.2 per cent. TlClO<sub>3</sub> requires .... 70.9 ,

As the quantity of material at my disposal was too small to enable me to study the properties of the salt more fully, I requested Mr. John Muir, student in this laboratory, to prepare a larger quantity by the same method, in order, if possible, that its crystallographic relations might be determined. He has repeated the analysis with the following results:

> Determination of Thallium. J. 0.6750 gram chlorate gave 0.7744 gram TII. II. 0.7519 ,, ,, ,, 0.8625 ,, ,,

# Determination of Chloric Acid.

The filtrates from the preceding determinations containing the chloric acid, as potassium salt, mixed of course with the excess of potassium iodide, were added together, evaporated to a small bulk, and weighed. The solution was then divided into two portions, in one of which the iodine was determined by precipitation as silver iodide. The remaining portion was heated with three or four copper-zinc couples for a few minutes, filtered, mixed with silver nitrate, and the silver chloride and iodide weighed.

Weight of solution	39.202	grams.
Weight of liquid taken for iodine estima-		0
tion	16.010	,,
AgI found	0.3002	,,
Calculated for 39.202 grams	0.7355	,,
Weight of liquid taken for chlorine estima-		
tion	23.063	,,
Mixed AgI and AgCl found	0.8398	,,
Calculated for 39.202 grams	1.4280	,,
1.4280 - 0.7355 = 0.6925 AgCl = 0	·1714 Cl.	

Hence the results of the analyses are-

	I.	II.	Mean.	TICIO
Thallium	70.68	70.69	70.69	70.91
Chlorine			12.02	12.36
Oxygen				16.73

100.00

The specific gravity of thallium chlorate at  $9^{\circ}$  (taken in benzol) and compared with water at same temperature, is  $5 \cdot 5047$ .

Like potassium chlorate, it is sparingly soluble in cold water, but readily soluble in hot water. Determinations of its degree of solubility at various temperatures have given the following results. The numbers express the amount of the salt in grams dissolved by 100 grams of water.

°C.	Grams.	°C.	Grams.
10.5	2.83	39.5	8.47
13.8	2.99	47.6	10.56
18.5	3.71	56.0	16.52
24.8	5.04	69.5	25.25
30.9	6.25	81.5	32.79

The curve representing these results may be reproduced with sufficient accuracy by the expression

$$W = 1.99 + .05415t + .00139t^2 + .000036t^3,$$

in which W = the weight of salt dissolved in 100 grams of water at the particular temperature t. The following table calculated by means of this equation shows the amount of the salt dissolved by 100 grams of water at every 10° between 0° and 100°:

°C.	Grams.	°C.	Grams.
0	2.80	60	18.02
10	2.71	70	24.94
20	3.92	80	$33^{-}65$
30	5.84	90	44.37
<b>4</b> 0	8.68	100	57.31
50	12.67		

Up to the present all attempts to procure the salt in a fit state for crystallographic examination have failed. The crystals hitherto obtained are exceedingly small, not exceeding a few tenths of a millimetre in length: when seen through the microscope they are observed to consist of prisms, possessing a number of faces, but, apparently, too dull to admit of accurate measurement.

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3. On the Isometric Relations of Thallium.

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

THALLIUM and potassium chlorates possess the same specific volume— (a.) Potassium Chlorate =  $KClO_3$ . Mol. wt. = 122.6.

Spe	ec. gra	v. =	2.326	Playfair and Jor	le. Spec. vol.	52.7 J Maan
-	,,		2.350	Kremers	,,	$52.2 > \frac{Mean}{52.5}$
	,,		2.325	Buignet	,,	52·7 J
		~ 1			005.1	

Thallium Chlorate =  $TICIO_3$ , Mol. wt. = 287<sup>-1</sup>. Spec. grav. = 5<sup>-5</sup>5047. J. Muir. Spec. vol. 52<sup>-2</sup>.

This remarkable agreement between the two values has induced me to compare other salts of thallium with the corresponding compounds of the alkalis.

Potassium and thallium carbonates appear to have identical specific volumes.

(b.) Potassium Carbonate = K<sub>2</sub>CO<sub>3</sub>. Mol. wt. 138.3. Spec. grav. 2.103 Playfair and Joule. Spec. vol. 65.6.

Thallium Carbonate =  $Tl_2CO_3$ . Mol. wt. 467.3. Spec. grav. 7.164 Lamy and Descloizeaux. Spec. vol. 65.2.

The same agreement is shown between the spec. volumes of the isomorphous thallium and potassium nitrates.

(c.) Potassium Nitrate. KNO<sub>3</sub>. Mol. wt. 101<sup>.</sup>1.

Spec.	grav.	2.103	Playfair and Joule.	Spec. vol.	48.07	
-	,,	2.101	Karsten	,,	48.11	
	,,	2.109	Grassi	••	47.94	Maan
	<b>,</b> ,	2.132	"	• •	47.42	47.9
	,,	2.100	Schiff	,,	48.14	1.0
	,,	2.126	Buignet	,,	47.55	
	,,	2.105	Kopp	"	ر 48·03 (	

Thallium Nitrate. TlNO<sub>3</sub>. Mol. wt. 265.7. Spec. grav. 5.550 Lamy and Descloizeaux. Spec. vol. 47.9.

The specific volumes of a number of thallium salts are, however, more strictly comparable with those of the corresponding ammonium compounds. Schröder has already pointed out this fact in the case of the sulphates and di-hydrogen phosphates (*Deut. Chem. Ges. Ber.*, 1874, p. 676). I give below all the observations which I have been able to find :—

(d.) Ammon	ium Cl	hloride. NH	L₄Cl. Mol. v	vt. 53·5.		
Spec. grav.	1.533	Playfair a	nd Joule.	Spec. vol.	34·97	
,,	1.500	Kopp		,,	35.6	
,,	1.528	Mohs		,,	35.0	Mean
,,	1.578	Playfair a	nd Joule	,,	$33 \cdot 9$	34.8
"	1.544	Hassenfra	tz	,,	34.7	1

(e.) Ammonium Dihydrogen Phosphate.  $NH_4H_2PO_4$ . Mol. wt. 115. Spec. grav. 1.758 Schiff. Spec. vol. 65.4 ,, 1.779 Schröder. ,, 64.6 Mean 65.0.

Thallium Dihydrogen Phosphate. TlH<sub>2</sub>PO<sub>4</sub>. Mol. wt. 300<sup>.</sup>6. Spec. grav. 4.723 Lamy and Descloizeaux. Spec. vol. 63<sup>.</sup>7.

(f.) Ammonium Sulphate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Mol. wt. 132. Spec. grav. 1.750 Playfair and Joule. Spec. vol. 75

c. grav.	1.720	Playfair and Joule.	Spec. vol.	75.44	
,,	1.770	Kopp	- ,,	74.57	
,,	1.768	Hassenfratz	,,	74.66	Mean
,,	1.761	Playfair and Joule	"	75.00	<b>74</b> .9
,,	1.771	Schröder	,,	74.50	
,,	1.750	Buignet	,,	75.44	
				-	

 Thallium Sulphate.
 Tl<sub>2</sub>SO<sub>4</sub>.
 Mol. wt. 503.2.

 Spec.
 grav.
 6.77
 Lamy
 Spec. vol.
 74.33

 ,,
 6.603
 Lamy and Descloizeaux
 ,
 76.05

 ,,
 6.598
 Thorpe\*
 ,
 76.28

 (g.) Ammonium Hydrogen Oxalate. NH<sub>4</sub>.HC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O. Mol. wt. 12L.
 Spec. grav. 1.563 Playfair and Joule. Spec. vol. 79.98 \ Mean ,, 1.556 Schiff ,, 80.34 \$\int 80.1

Thallium Hydrogen Oxalate. TlH.C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O. Mol. wt. 310<sup>.</sup>6. Spec. grav. 3<sup>.</sup>971 Lamy and Descloizeaux. Spec. vol. 78<sup>.</sup>0.

(h.) Ammonium Tartrate.  $NH_4.HC_4H_4O_6$ . Mol. wt. 167. Spec. grav. 1 680 Schiff. Spec. vol. 994.

Thallium Tartrate. TlH.C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>. Mol. wt. 352<sup>.</sup>6. Spec. grav. 3<sup>.</sup>496 Lamy and Descloizeaux. Spec. vol. 100<sup>.</sup>7.

These salts are isomorphous as well as isometric.

The spec. vol. of thallium is about 17.3, as is evident from the following observations :---

Tl. Mol. wt. = 203.6.

Spec. grav.	11.862	Lamy.	Spec. vol.	17.2	
,,	11.853	De la Rive	,,	17.2	
"	11.808	,,	"	17.3	Mean
,,	11.777	Werther	,,	17.3	17.3
,,	11.81	Crookes	,,	17.3	

\* At 9°, compared with water at same temperature.

Schröder has pointed out that in certain compounds, as for example in the isomorphous calc-spar and sodium nitrate, and in arragonite and potassium and ammonium nitrates, which are also isomorphous, the groups  $NO_3$  and  $CO_3$  possess the same spec. volume; and the same fact would seem to be shown by Kopp's determinations of the spec. vols. of ethyl carbonate and ethyl nitrate:—

Ethyl carbonate 
$$(C_2H_5)_2CO_3$$
—observed spec. vol. = 139.4  
less spec. vol.  $2(C_2H_5^*) = 99.0$   
Spec. vol. of  $CO_3 = 40.4$   
Ethyl nitrate,  $C_2H_5NO_3$ —observed spec. vol = 90.0  
less spec. vol.  $C_2H_5 = 49.5$   
Spec. vol. of  $NO_3 = 40.5$ 

Further evidence of the same fact is afforded by the case of thallium nitrate and carbonate, if we assume that thallium occupies the same volume in both combinations which it possesses in the free state.

Observed sp. vol. of $Tl_2CO_3$	65.2
Deduct observed sp. vol. of $Tl_2 = 17.3 \times 2$	34.6
Spec. vol. $CO_3 =$	30.6
Observed sp. vol. of TlNO <sub>3</sub>	47.9
Deduct observed sp. vol. of Tl	17.3
Spec. vol. $NO_3 =$	30.6

It will be observed that the difference between the values for the carbonate and nitrate is  $17\cdot3$ , *i.e.*, exactly equal to the number directly obtained for Tl in the free state. It is also worthy of note that this value  $17\cdot3$  is almost identical with that calculated by Kopp for ammonium, NH<sub>4</sub>, in its salts, viz.  $17\cdot4$ .

\* Calculated from Kopp's values, C = 11, H = 5.5.