

II.—*Note on the Iodates and Periodates of the Alkali Metals and the Ammonium Radicle.*

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THE present communication deals with the chemical part of an investigation of certain iodates and periodates which were chiefly prepared for a crystallographic examination; the results of the latter will appear shortly in the *Zeitschrift für Krystallographie*.

Of the analyses, the halogen estimations were effected by the Carius method, which the author had previously found to answer well for the perchlorates; the heating was carried out in two operations, each lasting four hours, the first to 150° and the second to 250°. The metal was estimated by the usual sulphate method.

The specific gravity determinations were made in capped specific gravity bottles with carbon tetrachloride as displacing liquid; the solubility determinations were carried out with 20 c.c. of the saturated solutions.

Rubidium Iodate, RbIO_3 .—This salt, as well as the corresponding caesium compound, was first prepared by Wheeler (*Amer. J. Sci.*, 1902, [iii], 44, 123) by adding iodic anhydride to solutions of the carbonates. A good yield is obtained by passing chlorine into a hot concentrated

solution of a mixture of rubidium iodide and hydroxide, whereby the sparingly soluble iodate is precipitated :

Specific gravity at $14^{\circ}/4^{\circ} = 4.559$. Mol. vol. = 57.14.

Solubility : 100 parts of water dissolve 2.1 parts at 23° (Wheeler

Caesium Iodate, CsIO_3 .—This salt was prepared in the same way as the rubidium compound :

Specific gravity at $16^{\circ}/4^{\circ} = 4.831$. Mol. vol. = 63.68.

Solubility : 100 parts of water dissolve 2.6 parts at 24° (Wheeler).

The iodates of potassium, rubidium, and caesium form an isomorphous group, crystallising in what appear to be cubes, but which are really made up of four monoclinic sub-individuals, interpenetratingly twinned.

Potassium periodate, KIO_4 , is readily prepared by oxidising the iodate ; a suitable method is to pass chlorine into a hot, strongly alkaline solution of the iodate (Rammelsberg, *Ann. Phys. Chem.*, 1868, [ii], 134, 368) ; the very sparingly soluble periodate separates in tetragonal bipyramids * :

0.3080 gave 0.3106 AgI . $\text{I} = 54.5$.

KIO_4 requires $\text{I} = 55.1$ per cent.

Specific gravity at $15^{\circ}/4^{\circ} = 3.618$. Mol. vol. = 63.60.

Solubility : 100 parts of water dissolve 0.66 part at 13° , and the specific gravity of the saturated solution at $13^{\circ}/4^{\circ}$ is 1.0051.

Rubidium periodate, RbIO_4 , has not previously been obtained. It was prepared by the method mentioned above for the potassium compound. The precipitated crystals were washed and recrystallised twice :

0.3090 gave 0.2664 AgI . $\text{I} = 46.6$.

0.4045 „ 0.1930 Rb_2SO_4 . $\text{Rb} = 30.54$.

RbIO_4 requires $\text{I} = 45.9$; $\text{Rb} = 30.91$ per cent.

The high value for iodine and the low value for rubidium point to the presence of a small amount of potassium. The salt forms beautiful, colourless, tetragonal crystals, strictly isomorphous with the potassium compound :

Specific gravity at $16^{\circ}/4^{\circ} = 3.918$. Mol. vol. = 70.56.

Solubility : 100 parts of water dissolve 0.65 part at 13° , and the specific gravity of the saturated solution at $16^{\circ}/4^{\circ}$ is 1.0052.

* Potassium periodate was stated by Rammelsberg to be orthorhombic and isomorphous with the perchlorate, but, in spite of all efforts, the author did not succeed in obtaining an orthorhombic modification, so he communicated with Prof. Groth, of Munich, who fortunately had in his possession the preparation originally measured by Rammelsberg. Prof. Groth kindly had the crystals analysed, and they were found to contain no trace of iodine, being, in fact, practically pure potassium perchlorate.

Cæsium periodate, CsIO_4 , was first prepared by Wells (*Amer. Chem. J.*, 1901, **26**, 278) by neutralising periodic acid with cæsium carbonate. The salt may also be prepared by the chlorine method, but the yield is by no means good, much iodate precipitating with the crystals of the periodate; the bulk of the author's salt was therefore obtained by Wells's method:

0.4601 gave 0.3321 AgI . $I = 39.02$.

CsIO_4 requires $I = 39.20$ per cent.

Cæsium periodate is fairly soluble in water, and crystallises in well-defined plates belonging to the orthorhombic system, and is therefore not isomorphous with the potassium and rubidium compounds:

Specific gravity at $15^\circ/4^\circ = 4.259$. Mol. vol. = 76.04.

Solubility: 100 parts of water dissolve 2.15 parts at 15° , and the specific gravity of the saturated solution at $15^\circ/4^\circ$ is 1.0166.

Ammonium periodate, NH_4IO_4 , was obtained by neutralising a solution of periodic acid prepared by Wells's method (*loc. cit.*) with aqueous ammonia; the salt is isomorphous with the potassium and rubidium compounds:

Specific gravity at $18^\circ/4^\circ = 3.056$. Mol. vol. = 68.39.

Solubility: 100 parts of water dissolve 2.70 parts at 16° , and the specific gravity of the saturated solution at $16^\circ/4^\circ$ is 1.0178.

Sodium periodate, NaIO_4 , crystallises in two forms: one anhydrous, isomorphous with the ammonium salt; the other with 3 molecules of water, in the rhombohedral system:

Specific gravities: NaIO_4 at $16^\circ/4^\circ = 3.865$. Mol. vol. = 55.37.

„ $\text{NaIO}_4 \cdot 3\text{aq.}$ at $18^\circ/4^\circ = 3.219$. Mol. vol. = 83.28.

The periodates of potassium, rubidium, ammonium, sodium, as well as of silver and lithium (according to Rammelsberg) form therefore an isomorphous group, crystallising in the tetragonal system. The group is interesting, not only because the majority of the elements in the first group of the periodic classification are represented, but also because the crystalline form is extraordinarily similar to that of the minerals of the scheelite group. The cause of this is, no doubt, to be found in the similarity of the type of composition, $\text{KIO}_4, \text{CaWO}_4$, just as it is in certain other pairs of compounds, for example, calcium carbonate and sodium nitrate, and potassium perchlorate and barium sulphate.

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