a compound more rapidly auto-reduced by hydrogen peroxide than the first intermediate. Several new cases of promotion have been discovered by means of this hypothesis.

5. Promotion may be provisionally defined as a change in the path of reaction with a concomitant displacement of the steady state.

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THE SOLUBILITIES IN WATER OF RUBIDIUM AND CESIUM CHLOROPLATINATES

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Potassium, rubidium and cesium form a group of elements very closely related and with very interesting characteristics. Any relationship among the properties of their compounds is of corresponding interest, and not the least interesting of the properties that must be considered in this connection is the solubility of their salts in water. One of the first of the salts of rubidium and cesium to be tested as to its solubility in water was the chloroplatinate. Bunsen[1] published certain results dealing with the solubilities of these two compounds as early as 1861. But as the methods of separating potassium from rubidium and cesium material now available are better than those known at the time Bunsen made his determinations, and as a knowledge of the correct values for the solubilities of the three chloroplatinates seemed desirable, it was thought worth while to make some further measurements in the case of the rubidium and cesium compounds.

Preparation of Materials

Cesium Chloroplatinate.—A good sample of pollucite (an aluminum silicate of cesium) was used as a source of cesium. The mineral had been finely ground, and 167 g. of it was digested for 40 hours in hot, concd. hydrochloric acid. The residue was filtered off, the filtrate was mixed with water and the iron and aluminum were precipitated as hydroxides by the addition of ammonium hydroxide. After the precipitates had been removed and the liquid evaporated to expel any excess of ammonia, hydrochloric acid was added and the solution was evaporated almost to dryness. This left cesium chloride mixed with some ammonium, sodium, potassium and perhaps rubidium chlorides.

For the purpose of purifying the cesium chloride, the residue last obtained was dissolved in water, the solution diluted to 200 cc. and 30 g. of iodine added. The mixture was then heated nearly to boiling and a stream

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[1] Bunsen, *Pogg. Ann.*, **113**, 337 (1861); *Chem. News*, **4**, 44 (1861).

of pure chlorine passed into it until the iodine had just disappeared. On cooling this solution, pale orange crystals of cesium dichloro-iodide settled. These crystals were filtered off and washed with cold water. The mother liquor was evaporated to 150 cc. and another crop of crystals of the dichloro-iodide obtained. These crystals were also filtered off and washed with cold water. The two crops of crystals were then combined, placed in a porcelain dish, dried and heated to a high enough temperature to decompose the salt and drive off the iodine. This left cesium chloride, which was again dissolved and reprecipitated as the dichloro-iodide in the same manner as before.

As spectroscopic examination showed that, if rubidium were present at all in the crude chloride, it must be in very small amounts, and as the dichloro-iodide of rubidium is a great deal more soluble than the corresponding compound of cesium, it was considered that two crystallizations from so dilute a solution would give a cesium salt completely free from rubidium.[2] Further, as the dichloro-iodides of ammonium, sodium and potassium either do not form or are very unstable and soluble, we felt safe in assuming that salts of these elements could not be present in appreciable amounts in the final cesium product. As shown below, the purity of the cesium chloride was tested through the analysis of the chloroplatinate.

Rubidium Chloride.—The rubidium for these experiments was supplied as rubidium sulfate by E. de Haen of Hanover. Thirty g. of the sulfate was dissolved in water and to the solution was added the calculated amount of barium chloride, also in solution. After filtering and washing, there will remain in the filtrate any sodium, potassium or cesium in the original salt as well as the rubidium. To eliminate the sodium and potassium, the rubidium was converted into the dichloro-iodide as described for cesium chloride, except that in this case the solution has a much smaller bulk, as the rubidium salt is much more soluble than the cesium, and the crystals were washed with hydrochloric acid solution, being much less soluble in this liquid than in water. After two such precipitations the rubidium material was assumed to be free from potassium and sodium salts.

To remove any cesium salts from the rubidium chloride, the chloride was dissolved in water, sulfuric acid added and the solution evaporated until all of the hydrogen chloride had been expelled. Water was then added to the rubidium sulfate, followed by a little less than the calculated amount of barium hydroxide. The sulfate was filtered off, and to the filtrate twice as much tartaric acid was added as was necessary to neutralize the rubidium hydroxide. The rubidium hydrogen tartrate that crystallized as the liquid stood is less soluble than the corresponding cesium salt. The latter would therefore remain in solution. A second crystallization of the rubidium salt gave a product that we regarded as

[2] Wells, *Am. J. Sci.*, **3**, 43 (1901).

sufficiently pure for our purpose. That this was a pure material is shown by the results of the analysis of the chloroplatinate of rubidium given below.

The acid tartrate was then ignited to yield the carbonate. This was treated with hydrochloric acid, and the solution filtered and evaporated to dryness. Two more evaporations with hydrochloric acid gave the rubidium chloride with which the chloroplatinate was prepared.

Chloroplatinic Acid.—Platinum foil was dissolved in aqua regia and the solution evaporated to dryness twice with concd. hydrochloric acid, to remove all but a trace of nitric acid. A slight residue of iridium appeared after the solution of the platinum was filtered. To the solution of the residue of platinum salt obtained after final evaporation, some hydrochloric acid was added and the platinum then precipitated as chloroplatinate with a solution of ammonium chloride. The precipitate was filtered, washed with cold water, dried at 90° in an electric oven and then reduced in a stream of pure hydrogen. The platinum black so obtained was thoroughly washed with hot water and then dissolved in hydrochloric acid by making it the anode for an electric current in a solution of concd. hydrochloric acid.[3] The solution of chloroplatinic acid that resulted from this electrolysis was used for the preparation of the chloroplatinates.

The Rubidium and Cesium Chloroplatinates.—The chloroplatinates were prepared by adding the cesium or rubidium chloride solution to a portion of the chloroplatinic acid solution. The precipitates thus formed were collected on a Gooch filter, well washed with a dilute solution of hydrochloric acid and dried at 90° in an electric oven.

It was thought best to test the purity of the rubidium and cesium chlorides by analyzing the chloroplatinates for platinum and fixed chlorine. Accordingly, two portions of each salt were carefully weighed out, placed in porcelain boats and reduced in a current of pure hydrogen. The chloride remaining with the platinum black was in each case thoroughly leached out with hot water, the solution filtered through a small filter and diluted to approximately 400 cc. The chloride was then precipitated and weighed as silver chloride and the equivalent alkali chloride calculated. The plati-

TABLE I

RESULTS OF ANALYSES OF CHLOROPLATINATES

	Chloroplatinate taken G.	Chloride found G.	Chloride calc. G.	Pt found G.	Pt calcd. G.
			CESIUM		
1	0.33645	0.16833	0.16804	0.09756	0.09746
2	.35666	.17888	.17814	.10316	.10331
			RUBIDIUM		
1	.40304	.19883	.19916	.13598	.13591
2	.34809	.17177	.17201	.11730	.11738

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[3] Weber, THIS JOURNAL, **30**, 29 (1908).

num left in each case was collected and weighed. The results of the analyses together with the corresponding calculated values are given in Table I.

These results indicate that there may still be a trace of potassium or rubidium in the cesium salt, but certainly not enough to affect the solubility measurements. Altogether, the results appear quite satisfactory.

Apparatus.—As it was necessary to agitate the solutions and salt thoroughly, at a constant temperature and over a considerable period of time, a 15-liter enameled kettle supplied on the outside with thick saddler's felt to prevent heat radiation was nearly filled with water and provided with the necessary thermostat for keeping the water at a constant temperature. For temperatures up to 40° a carbon filament lamp used inside the bath and connected with the necessary telegraph relay was used as heating element. Between 40° and 60° the lamp was supplemented with a small gas burner. For temperatures above 60° the lamp was removed and a larger gas flame used, controlled of course through a thermostat.

It was found that the temperature could be kept constant within 0.05° for the lower temperatures and 0.1° for the higher points.

A thermometer standardized by the United States Bureau of Standards and graduated to 0.1° was available for this work.

The rubber stoppers used were thoroughly washed and soaked in dil. alkali. The flasks in which the solutions were agitated were of Pyrex glass.

Method of Determination.—We first attempted to determine the amount of salt in a filtered portion of the saturated solution. However, the likelihood of hydrolytic action and of further decomposition taking place during evaporation led us to think that it would be advisable from the point of view of accuracy to weigh carefully the amount of salt added to the flask and later to weigh the undissolved excess. Therefore, in making a determination, from 0.35 to 0.5 g. of the salt was carefully weighed out, transferred to a 125cc. flask and exactly 100 g. of water added. The flask was then placed in the constant-temperature bath for a few minutes to allow the water in the flask to attain very nearly the temperature of the bath. The stopper was then wired in and the flask rotated for a definite length of time. During this rotation the flasks were protected from sunlight to lessen any danger of hydrolytic action taking place. A Gooch filter had meanwhile been prepared, with a well-washed asbestos mat, dried and weighed and when the solution had become saturated the flask was removed from the bath and the solution filtered as quickly as possible, the salt being entirely washed onto the filter with cold, dil. hydrochloric acid. The crucible and salt were then dried and weighed. At least two and usually three such measurements were made for each temperature. The results agreed within 0.5 mg. for any one temperature.

Below 50° the flasks were rotated from 24 to 48 hours. For 50° and above, five hours' rotation was found sufficient. We assured ourselves by careful measurement that these periods of rotation were sufficiently long to allow the solutions to become saturated.

The results obtained for both compounds are set forth in Table II.

They show the number of grams of substance dissolved by 100 g. of water. The values for 100° were obtained by interpolation. In Cols. 3 and 5 are shown a few values given by Bunsen.[1]

TABLE II

SOLUBILITY VALUES FOR RUBIDIUM AND CESIUM CHLOROPLATINATES

Grams of chloroplatinate per 100 g. of water

Temp., °C.	0	10	20	30	40	50	60	70	80	90	100
Rb salt	0.0137	0.0200	0.0283	0.0397	0.0565	0.0737	0.0997	0.1324	0.1824	0.2472	0.3340
Bunsen			.141			.203					.634
Cs salt	.0047	.0064	.0086	.0119	.0158	.0212	.0290	.0389	.0525	.0675	.0915
Bunsen			.079			.177					.377

The above results show that the rubidium salt is slightly more than thrice as soluble as the cesium salt. The much greater values obtained by Bunsen may be due either to hydrolysis or possibly to the presence of potassium compounds in the salt.

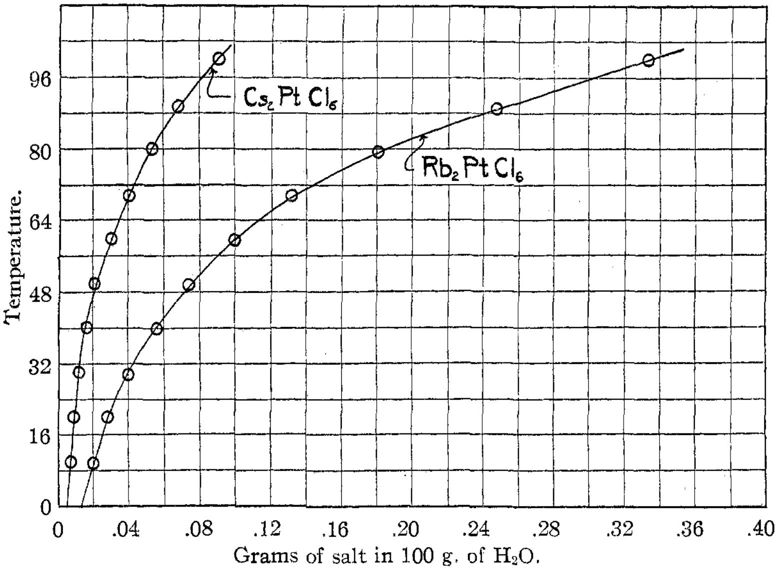

Fig. 1.

In Fig. 1, we have plotted the solubility values for each salt against the temperatures and obtained a smooth curve in each case.

Summary

1. Pure rubidium and cesium chlorides have been prepared and the chloroplatinates of each metal have been prepared from these.
2. The solubility of each chloroplatinate in water has been measured at temperatures between 0° and 100° at 10° intervals.

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