SEPARATION OF POTASSIUM FROM CESIUM.

KCl present in gram.	CsCl present in gram.	K present in gram.	K found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time. minutes.
0.0830	0.0850	0.0435	0.0437	0.0395	0.0399	2.33	0.019	1 hr. 50 m.
0.0852	0.0900	0.0447	0.0445	0.0405	0.0406	2.33	0.021	1 hr. 45 m.

SEPARATION OF POTASSIUM FROM LITHIUM.

KCl present in gram.	LiCl present in gram.	K present in gram.	K found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time, minutes.
0.0715	0.1021	0.0375	0.0371	0.0340	0.0332	2.30	0.019	85
0.0622	0.1021	0.0326	0.0325	0.0296	0.0299	2.27	0.017	90
0.0636	0.1021	0.0333	0.0331	0.0302	0.0302	2.30	0.020	85

SEPARATION OF CESIUM FROM RUBIDIUM.

RbCl present in gram.	CsCl present in gram.	Rb present in gram.	Rb found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time.
0.0509	0.0690	0.0360	0.0367	0.0149	0.0160	1.20	0.008	2 hr. 10 m.
0.0493	0.0690	0.0347	0.0350	0.0146	0.0143	1.23	0.010	2 hr. 10 m.
0.0473	0.0690	0.0334	0.0326	0.0139	0.0131	1.20	0.008	2 hr. 30 m.
0.0508	0.0690	0.0359	0.0358	0.0149	0.0150	1.23	0.010	2 hr. 30 m.
0.1009	0.1235	0.0713	0.0711	0.0296	0.0306	1.20	0.010	5 hr.

SEPARATION OF LITHIUM FROM RUBIDIUM.

LiCl present in gram.	RbCl present in gram.	Li present in gram.	Li found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time, minutes.
0.0237	0.0560	0.0039	0.0037	0.0198	0.0190	2.47	0.012	70
0.0237	0.0560	0.0039	0.0039	0.0198	0.0199	2.45	0.015	75

SEPARATION OF LITHIUM FROM CESIUM.

LiCl present in gram.	CsCl present in gram.	Li present in gram.	Li found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time. minutes.
0.0451	0.0520	0.0074	0.0033	0.0377	0.0361	2.30	0.012	60
0.0328	0.0520	0.0054	0.0052	0.0274	0.0270	2.30	0.013	120
0.0328	0.0520	0.0054	0.0054	0.0274	0.0273	2.30	0.015	125

The decomposition values of potassium and ammonium salts lie so close together that no success was had in the attempts to separate them.

It may be of interest to add in conclusion that Wolcott Gibbs[1] in 1880 predicted that possibly sodium and potassium might be separated in the electrolytic way with the use of a mercury cathode.

UNIVERSITY OF PENNSYLVANIA.

ON THE PREPARATION AND THE COMPOSITION OF THE ACID CARBONATES OF CALCIUM AND BARIUM.

BY EDWARD H. KEISER AND SHERMAN LEAVITT.

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The acid carbonates of calcium, strontium and barium have never been isolated or separated from solution as far as we have been able to find by searching the chemical literature at our command. We first

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[1] *Chem. News*, **42**, 291.

attempted to isolate these acid carbonates by adding an excess of alcohol and ether to the aqueous solution of the acid carbonate, made by conducting an excess of carbon dioxide through the hydroxide. A white flocculent precipitate was formed but it rapidly decomposed, giving off carbon dioxide. Several experiments made in this way convinced us that at the ordinary temperature of about 15°, the acid carbonate of calcium decomposes rapidly into the normal carbonate and carbon dioxide and water and that in order to isolate this compound the temperature must not be allowed to rise much above zero.

We now attempted to prepare the acid carbonate of calcium by precipitating a solution of calcium chloride with a solution of bicarbonate of potassium, keeping the temperature in the neighborhood of zero. 5.5 grams of pure calcium chloride were dissolved in 50 cubic centimeters of water in one beaker and 20 grams of bicarbonate of potassium were dissolved in 50 cc. of water in another beaker, both solutions were cooled to 0° C. by placing each beaker into a freezing mixture of ice and salt. Thereupon the bicarbonate of potassium solution was poured into the calcium chloride solution. Instantly a heavy white flocculent precipitate was formed. This was rapidly filtered by suction upon a hardened filter and the precipitate washed with alcohol and ether and dried between folds of filtering paper. A little of the precipitate was added to water containing a drop of phenolphthalein. The indicator remained colorless. Upon warming, however, bubbles of gas were given off and in a few moments the solution became pink. Some of a similar solution was allowed to stand and acquire the temperature of the air; in the course of an hour and a half it also became pink. The bubbles of gas could be seen coming off from the precipitate quite rapidly until finally the crystalline normal carbonate was left.

The experiment was repeated. This time the filtering funnel had a copper jacket around it with a space of about an inch between the funnel and the jacket. This space was kept packed with ice and salt. The precipitate was washed with absolute alcohol and ether; the latter had stood over calcium chloride for twelve hours and had then been distilled over metallic sodium to make it anhydrous.

The filter paper on which the precipitate was finally dried was kept in a deep glass trough which had been placed in a large clay sink. The space between the trough and the sink was kept packed with ice and salt. The alcohol and ether that were used in washing the precipitate were also kept in ice and salt until used.

The dried acid calcium carbonate in the form of a fine powder was poured into a weighing tube, tightly stoppered and weighed. In the course of two or three minutes, as the temperature of the weighing tube rose, the dry compound became pasty and considerable gas was given off, sufficient to eject the stopper out of the tube with force. The open tube was then heated in an air bath to 120° to constant weight and the loss in weight determined.

Weight of acid carbonate taken.	Loss on drying at 120°.	Per cent.
0.4900	0.2663	53.7
0.5716	0.2906	50.8

The dry residue that was left was examined in each case and was found to contain some potassium chloride, so that evidently the precipitate had not been washed sufficiently.

In the next series of experiments, ammonium bicarbonate was used as the precipitating agent instead of potassium bicarbonate, as it was thought that the ammonium chloride could be more readily washed out of the precipitate. 5.3 grams of calcium chloride were dissolved in 50 cc. of water and 15 grams of ammonium bicarbonate in 100 cc. of water and both solutions kept at zero by means of ice. The bicarbonate was then poured into the calcium chloride solution. The precipitate was filtered upon paper in an ice-jacketed funnel and was washed first with ice-cold water saturated with carbon dioxide, then with ice-cold alcohol and finally with ice-cold ether. The precipitate was then dried as before by pressing between filter paper in the trough surrounded by the freezing mixture. The whole operation was carried on in the storage room of an ice plant where the air temperature was near zero. Weighed quantities of the acid calcium carbonate were dried in an air bath at 120° and the loss determined. The results were, 37.1, 51.19 and 51.68 per cent.

The residue obtained in each of these three separate preparations was examined quantitatively and gave 56.3 per cent. CaO in the first and 56.03 and 56.0 in the second and third residues, thus showing that pure calcium carbonate was left in each case. The first sample of acid calcium carbonate had evidently undergone partial decomposition.

From these results it is evident that the acid carbonate of calcium can be formed by double decomposition and that it can be separated from the solution and analyzed provided the temperature is not allowed to go more than one or two degrees above zero. Even at this temperature there is slow decomposition as shown by the variation in the analytical results. Our results also indicate that the composition of the acid calcium carbonate is different from that ordinarily assumed for it. This compound by analogy with the acid carbonates of the alkali metals is written $H_2Ca(CO_3)_2$; our results agree more closely with the formula $Ca(CO_3).1.75(H_2CO_3)$.

The acid carbonate of barium was prepared by dissolving 12 grams of crystallized barium chloride in 50 cc. of water and precipitating the ice-cold solution with 15 grams of crystallized ammonium bicarbonate dissolved in 100 cc. of water and cooled to zero. The washing and filtering of the precipitate were carried out as described above. In each preparation the precipitate was washed with ice water saturated with carbon dioxide, then with alcohol and ether and finally it was dried on the cold filter paper in the ice trough. Five preparations were made and analyzed, showing the following percentage loss of weight on drying at 120°: (1), 16.4, 16.3; (2) 25.48, 23.01; (3) 47.18, 39.87; (4) 38.52, 37.43; (5) 40.86, 39.75.

Evidently the first and second preparations had undergone partial decomposition and the high results in the first determination of the third preparation must have been due to the presence of a small quantity of ether which had not evaporated. The remaining analyses indicate that the acid carbonate of barium like that of calcium has a higher proportion of carbonic acid than is ordinarily assigned to it. Our results show that the acid carbonate of barium, like that of calcium, can be prepared by double decomposition of an alkali bicarbonate and barium chloride, provided the temperature be kept near zero. The barium acid carbonate can be separated from the solution, washed and dried, but owing to slow decomposition it is difficult to determine its quantitative composition.

In preparing it, it is also necessary to have the solutions not too dilute. If the solutions are diluted with ice water to three or four times the volumes mentioned, and then mixed, they remain perfectly clear because of the solubility of acid barium carbonate. Now, on heating the clear solution, as the temperature goes up, the normal carbonate is precipitated in granular form.

The experiments described in this paper were made during the winter of 1903–04.

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ON THE COMPOSITION OF THE ACID CARBONATES OF CALCIUM AND BARIUM.

BY EDWARD H. KEISER AND LEROY MCMASTER.

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The work of Keiser and Leavitt, in the preceding paper, has shown that it is possible to prepare the acid carbonates of calcium and barium by double decomposition and to separate them from the solution in which they have been formed. It is difficult, however, to get them in dry condition for analysis without having them undergo partial decomposition. Thinking that there may perhaps have been a trace of moisture or of ether in the compounds that were analyzed, we determined to modify the method of analysis and without attempting to dry and weigh them to