The old idea of Arrhenius might apply here. This was to the effect that in solution the ester existed in two forms, "active" and "inactive," the first being probably a single molecule, while the inactive form was a complex. Addition of a salt disturbs the equilibrium between these forms in favor of the active form. Later[1] on Arrhenius gives a little greater clearness to his idea by attributing the accelerating effect to an increase in osmotic pressure of the ester. He says: "Since foreign substances in general increase the osmotic pressure of a compound, they should, in general, accelerate the velocities or reaction, which is actually the case."

These appear to be the most logical of the many attempted explanations of the phenomenon. It should be noted, however, that not one of them really *explains* the facts, but simply seeks to express them in terms of other facts a trifle more familiar. The question as to which is the most reasonable of these various hypotheses, is difficult, or impossible, to answer. Each has its merits, and each at some point fails to explain all of the circumstances connected with the case. Fortunately, it is not at present necessary to accept as final any of the theories thus far proposed. It is hoped that the work already planned for the immediate future may throw some light on the subject.

In conclusion, I wish to thank Dr. W. E. Henderson, of the Chemical Department, and Dr. A. D. Cole, of the Physics Department, for kindly interest and advice during the course of the work, and for placing at my disposal every facility for its prosecution.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

AN ATTEMPT TO SEPARATE THE ALKALINE EARTH METALS IN THE ELECTROLYTIC WAY.

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The electrolytic separation of the alkali metals[2] by strict attention to differences in decomposition potentials suggested the thought that the metals of the alkaline earths might be separated by an application of the same method. The halides of the latter metals had been analyzed by McCutcheon,[3] Lukens and Smith,[4] and separations of the alkalies from the alkaline earths, and of barium, strontium and calcium from magnesium were effected by the same chemists, but the separation of

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[1] *Z. physik. Chem.*, **28**, 317–335.

[2] THIS JOURNAL, **30**, 1705.

[3] *Ibid.*, **29**, 1445.

[4] *Ibid.*, **29**, 1455.

barium, strontium and calcium from each other still remained to be done. (See also Coehn and Kettembeil, *Z. anorg. Chem.*, **38,** 198.)

The purpose of the present communication is to submit results obtained in attempting these separations. The principle of the rotating silver anode and mercury cathode was employed, and the decomposition cell and apparatus were arranged identically in the way described under the separation of the alkali[1] metals. The chlorides of barium, strontium and calcium were obtained pure and free from magnesium.

On experimentation it was found that the decomposition potential of strontium chloride was 0.16 volt higher than that of barium chloride, while the decomposition value of magnesium-free calcium chloride was 0.13 volt higher than that of the corresponding strontium salt. With these facts at hand, a neutral aqueous solution of a mixture of barium and strontium chlorides was introduced into the inner decomposition cell of the double cup. The circuit was closed and the voltage was adjusted to and carefully maintained at 0.07 volt above the decomposition potential of the mixture of chlorides. In this way only the barium chloride was decomposed, the barium passing into the mercury and the chlorine attaching itself to the silver anode. It was found impossible to prevent traces of decomposition of the barium amalgam in the inner cup. This consequently resulted in the formation of a minute quantity of barium hydroxide, which in turn was changed to carbonate by the carbon dioxide of the air. Despite the fact that carbon dioxide free air, was passed into the inner cup during electrolysis and that freshly boiled water was used, some air gained entrance and barium carbonate formed, which naturally increased the weight of the anode. To obviate this difficulty, the anode, after the decomposition was complete, was dipped into some of the standard hydrochloric acid solution used to titrate the barium hydroxide formed in the outer cup. (The excess of acid was retitrated with standard alkali.) The carbonate was thus dissolved and the anode was then thoroughly washed with distilled water and dried in an electric oven at 330°. The anode now held only chloride of silver, which was weighed. The increase in weight represented the halogen content of the salt.

Results:

SEPARATION OF BARIUM FROM CALCIUM.

$BaCl_2.2H_2O$ present. Gram.	Calcium chloride present. Gram.	Ba present.	Ba found.	Cl_2 present.	Cl_2 found.	Volts.	Amperes N D_{20}.	Time. Hrs.	Time. Min.
0.0613	0.0500	0.0345	0.0361	0.0178	0.0186	2.30	0.021	1	35
0.0600	0.0500	0.0338	0.0351	0.0174	0.0180	2.30	0.022	1	30
0.0621	0.0500	0.0349	0.0355	0.0180	0.0185	2.30	0.019	1	40
0.0618	0.0500	0.0347	0.0350	0.0179	0.0184	2.30	0.021	1	25
0.0454	0.0500	0.0255	0.0260	0.0132	0.0135	2.30	0.019	1	25

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[1] THIS JOURNAL, **30,** 1705.

SEPARATION OF STRONTIUM FROM CALCIUM.

$SrCl_2.6H_2O$ present. Gram.	Calcium chloride present. Gram.	Sr present.	Sr found.	Cl_2 present.	Cl_2 found.	Volts.	Ampere. $N D_{20}$.	Time. Hrs.	Time. Min.
0.0635	0.0500	0.0209	0.0219	0.0169	0.0180	2.30	0.022	1	40
0.0630	0.0500	0.0207	0.0215	0.0168	0.0172	2.30	0.022	1	30
0.0703	0.0500	0.0231	....	0.0187	0.0190	2.30	0.020	1	45
0.0622	0.0500	0.0204	....	0.0165	0.0170	2.30	0.021	1	30

The analysis of a mixture of barium, strontium and calcium chlorides was then attempted, with the idea of separating first the barium from the strontium and calcium, inserting a fresh anode, and afterward separating the strontium from the calcium in the mixture that remained. On closing the circuit it was found that the "break point" was much lower than was expected from the separate behavior of each salt. Moreover, on maintaining the voltage at 0.03 volt above the decomposition potential as determined and allowing the current to pass until it was estimated that all the barium chloride had been decomposed, there was no evidence of a change in the decomposition potential corresponding to the change from the barium, strontium, calcium to a strontium calcium mixture, similar to that observed, for instance, in the separation of sodium from potassium. Because of this it was impossible to determine precisely just when all the barium chloride was decomposed and when it was necessary to interrupt the current and introduce a new anode to take up the chlorine ion of the strontium chloride.

Some separations were, however, attempted and approximate results obtained. Only the halogen content of each salt was determined. This was because all the barium amalgam had not passed into the outer cup at the point when a new anode had to be inserted for the decomposition of the strontium chloride; that is, a complete determination of the barium by titrating the barium hydroxide formed in the outer cup was impossible, since some of the barium amalgam was still retained in the inner cup. The determination of the halogen content was, however, sufficient to indicate the amount of barium combined with it.

It is only fair to state that in analyzing a mixture of barium, strontium and calcium chlorides the approximate results were obtained because of a previous knowledge of the proportions of each salt originally present, thus enabling us to interrupt the current at about the right time.

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A STUDY IN TELLURIDES.

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Introduction.

Sir Humphry Davy,[1] in the course of his investigations upon the alkali

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[1] *Phil. Trans. Roy. Soc.*, **27**, 16 (1810).