

the combined sodium and potassium titrated in the outer compartment. The sodium and potassium could be readily calculated from these data.

| | Grams. | Volts | Amperes | Time, min. |
|--------------------|--------|-------|----------|------------|
| Sodium chloride | 0.1166 | | | .. |
| Potassium chloride | 0.1478 | 3.5-5 | 0.5-0.02 | 45 |
| Chlorine present | 0.1416 | | | .. |
| “ found | 0.1420 | | | .. |
| | 0.1420 | | | .. |
| | 0.1418 | | | .. |
| | 0.1420 | | | .. |
| | 0.1414 | | | .. |

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY].

THE ELECTROLYSIS OF THE HALIDES OF THE ALKALINE EARTH METALS.

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The studies made by Hildebrand and more recently by McCutcheon with the form of cell pictured and described¹ and in which the rotating silver anode and mercury cathode are employed, led us to try out certain lines of thought in the same way. For example, it seemed worth the while to learn just what quantities of barium chloride, let us say, could be electrolyzed in the Hildebrand cell and the analyst be sure of the accuracy of the results both with respect to the barium and the associated halogen. It was very soon found that quantities of barium chloride exceeding 0.2 gram could be electrolyzed with satisfaction in the course of from forty to sixty minutes with a current of 0.3 ampere and from 3.5 to 4 volts. The anode made 300 revolutions per minute.

The appended results appear in the order in which they were obtained.

| Barium present in gram. | Barium found in gram. | Chlorine present in gram. | Chlorine found in gram. |
|----------------------------|--------------------------|------------------------------|----------------------------|
| 0.2277 | 0.2276 | 0.1180 | 0.1177 |
| 0.2277 | 0.2274 | 0.1180 | 0.1178 |
| 0.2277 | 0.2277 | 0.1180 | 0.1181 |
| 0.2277 | 0.2278 | 0.1180 | 0.1180 |
| 0.2277 | 0.2277 | 0.1180 | 0.1180 |
| 0.2277 | 0.2277 | 0.1180 | 0.1181 |

In the electrolysis of strontium bromide, the determination of the bromine was omitted. This halogen adhered firmly to the rotating silver anode to which it attached itself. It was, however, not weighed. The determination of metal alone was made.

| Strontium present in gram. | Strontium found in gram. |
|-------------------------------|-----------------------------|
| 0.0727 | 0.0725 |
| 0.0727 | 0.0727 |
| 0.0727 | 0.0727 |
| 0.0727 | 0.0726 |
| 0.0727 | 0.0726 |

¹ This Journal, 29, 447.

The current was of the same strength as given under barium chloride. The time required was also practically the same.

It was perfectly natural to wish to learn how calcium chloride would conduct itself, although it seemed that it could not fail to behave like its analogues. To our great surprise the amalgam formed in the inner compartment did not diffuse into the outer, larger dish, and there decompose, but contrariwise, it decomposed in the inner vessel forming there a mass of hydroxide. Calcium could not be detected in the outer vessel where the alkalis and barium and strontium appeared as amalgams, decomposed and were determined. Instead of seeking to solve the mystery of this behavior of the calcium amalgam, at that moment, we decided to study the electrolysis of pure magnesium chloride. Upon doing this, large quantities of magnesium hydroxide formed in the inner compartment, while not a trace of magnesium could be detected in the outer vessel. Perhaps then the presence of magnesium chloride in the calcium chloride, which had been electrolyzed with the unexpected result of formation of calcium hydroxide in the inner chamber, was in a measure responsible for this undesired behavior? Accordingly the calcium chloride, employed in the electrolysis, was examined for magnesium. It showed it in abundance. When calcium chloride, free from every trace of magnesium, was subjected to electrolysis, it behaved like the halides of the alkali metals, and like those of barium and strontium, *i. e.*, its amalgam passed into the outer compartment of the cell and was there decomposed and the calcium hydroxide determined.

The next step consisted in bringing together known amounts of pure calcium chloride and pure magnesium chloride, and subjecting the mixtures to electrolysis. The proportions of magnesium varied in amount from one-half to equal that of the calcium. The dilution of the solutions was the same as in all previous experiments. It never exceeded 30 cc. The pressure varied from 3.5 to 4 volts, while the time period did not extend beyond an hour.

In all such trials the results were identical. The inner cup was filled with insoluble hydroxide and in the outer compartment not a trace of calcium or magnesium was detectible. It seemed possible then, to restrain the calcium by merely adding magnesium chloride to its salt solution undergoing electrolysis. Could not calcium be separated in this electrolytic way from magnesium? Evidently not, under the conditions previously outlined. It remained, however, for McCutcheon to show how that separation could be successfully performed. That, however, came later.

At this period of our experimentation the retention of the calcium by the magnesium suggested very promptly the separation of certain other metals from calcium and magnesium. The subjoined records disclose our line of thought.

Separation of Sodium and Potassium from Calcium and Magnesium.—

A solution containing as chlorides :

0.0222 gram of calcium,
 0.0210 “ “ magnesium, and
 0.0474 “ “ sodium,

was electrolyzed for a period of fifty minutes with a current of 0.25 ampere and 3.5 volts. The calcium and magnesium amalgams decomposed in the inner cup with the formation of their hydroxides, while the sodium amalgam sustained a like decomposition in the outer compartment, where the sodium hydroxide formed was determined by titration with $N/10$ hydrochloric acid :

Sodium found in grams.
 0.0471
 0.0474
 0.0472
 0.0474
 0.0476
 0.0474

On substituting potassium chloride for sodium chloride in the mixture with calcium and magnesium chlorides, and exposing the same to electrolysis under conditions similar to those just given, the amount of potassium separated and determined was :

| Potassium found in gram. | Potassium present in gram |
|-----------------------------|------------------------------|
| 0.0582 | 0.0580 |
| 0.0583 | 0.0580 |
| 0.0580 | 0.0580 |
| 0.0579 | 0.0580 |
| 0.0580 | 0.0580 |
| 0.0580 | 0.0580 |

The alkali metals may, therefore, be readily and accurately separated from calcium and magnesium in the electrolytic way.

Separation of Barium and Strontium from Calcium and Magnesium.—

In attempting the separation of barium from calcium and magnesium the solution contained the following quantities of the three metals as chlorides :

0.0222 gram of calcium
 0.0210 “ “ magnesium
 0.0455 “ “ barium.

A drop of dilute hydrochloric acid was added to the solution in the inner compartment, and the mixture was then electrolyzed with a current of 0.3 ampere and 3.5 to 4 volts. The halogen attached itself firmly to the rotating silver-plated anode, calcium and magnesium amalgams were formed but speedily decomposed in the inner compartment, while the barium amalgam passed to the outer vessel, where it decomposed to hydroxide, which upon titration showed the presence of

| | | |
|--------|--------|----------------|
| 1..... | 0.0456 | gram of barium |
| 2..... | 0.0455 | " " " |
| 2..... | 0.0454 | " " " |
| 4..... | 0.0454 | " " " |
| 5..... | 0.0455 | " " " |
| 6..... | 0.0454 | " " " |
| 7..... | 0.0454 | " " " |

When the quantity of barium was doubled (0.910 gram), the quantities obtained were:

| | | |
|--------|--------|------|
| 1..... | 0.0911 | gram |
| 2..... | 0.0910 | " " |
| 3..... | 0.0912 | " " |
| 4..... | 0.0910 | " " |

Upon substituting strontium bromide for barium chloride in the mixture of chlorides and electrolyzing the solution under the same conditions as previously the results were:

| Strontium present in grams. | Strontium found in grams. |
|--------------------------------|------------------------------|
| 0.0565 | 0.0563 |
| 0.0565 | 0.0565 |
| 0.0565 | 0.0564 |
| 0.0565 | 0.0565 |
| 0.0565 | 0.0566 |
| 0.0565 | 0.0565 |

Separation of Barium and Strontium from Magnesium alone.—These separations were conducted with conditions like those given under the mixtures in which calcium was also present.

| Barium present in grams. | Magnesium present in grams. | Barium found in grams. |
|-------------------------------|--------------------------------|-----------------------------|
| 0.0455..... | 0.0358..... | 0.0455 |
| 0.0455 | 0.0358 | 0.0456 |
| 0.0455 | 0.0358 | 0.0455 |
| 0.0455 | 0.0358 | 0.0455 |
| 0.0455 | 0.0358 | 0.0456 |
| 0.2277..... | 0.0358..... | 0.2277 |
| 0.2277 | 0.0358 | 0.2275 |
| 0.2277 | 0.0358 | 0.2277 |
| Strontium present in grams | Magnesium present in grams | Strontium found in grams |
| 0.0221..... | 0.0358..... | 0.0220 |
| 0.0221 | 0.0358 | 0.0222 |
| 0.0221 | 0.0358 | 0.0221 |
| 0.0221 | 0.0358 | 0.0221 |
| 0.0221 | 0.0358 | 0.0220 |

Separation of the Alkali and Alkaline Earth Metals from Iron and Aluminium.—In the separation of barium from iron the chlorides, as in all other instances, were employed. The conditions prevailing here were identical with those observed in the preceding experiments. The iron amalgam, if produced, decomposed almost immediately with the forma-

tion of ferric hydroxide in the inner compartment, while the barium passed to the outer chamber and there underwent decomposition. The current equaled 0.3 ampere and 3 to 5 volts. The time period did not exceed fifty minutes.

| | | |
|-------------------|-------------------|-----------------|
| Barium present | Iron present | Barium found |
| 0.0455..... | 0.0276..... | 0.0452 |
| 0.0455 | 0.0276 | 0.0454 |
| 0.0455 | 0.0276 | 0.0455 |
| 0.0455 | 0.8276 | 0.0456 |
| 0.0455 | 0.0276 | 0.0455 |
| 0.0455 | 0.0276 | 0.0455 |
| Strontium present | | Strontium found |
| 0.0565..... | 0.0276..... | 0.0564 |
| " | " | 0.0565 |
| " | " | 0.0562 |
| " | " | 0.0565 |
| Potassium present | | Potassium found |
| 0.0580..... | 0.0276..... | 0.0579 |
| " | " | 0.0581 |
| " | " | 0.0580 |
| " | " | 0.0581 |
| " | " | 0.0582 |
| Sodium present | | Sodium found |
| 0.0474..... | 0.0276..... | 0.0471 |
| " | " | 0.0475 |
| " | " | 0.0474 |
| " | " | 0.0473 |
| " | " | 0.0474 |
| " | " | 0.0474 |
| Barium present | Aluminium present | Barium found |
| 0.0455..... | 0.0199..... | 0.0454 |
| " | " | 0.0453 |
| " | " | 0.0455 |
| " | " | 0.0455 |
| " | " | 0.0453 |
| " | " | 0.0455 |
| Strontium present | | Strontium found |
| 0.0221..... | 0.0199..... | 0.0220 |
| " | " | 0.0220 |
| " | " | 0.0221 |
| " | " | 0.0220 |
| " | " | 0.0221 |
| " | " | 0.0221 |
| Potassium present | | Potassium found |
| 0.0580..... | 0.0199..... | 0.0582 |
| " | " | 0.0581 |
| " | " | 0.0580 |
| " | " | 0.0579 |
| " | " | 0.0580 |
| " | " | 0.0580 |
| Sodium present | | Sodium found |
| 0.0474..... | 0.0199..... | 0.0474 |
| " | " | 0.0474 |
| " | " | 0.0475 |
| " | " | 0.0474 |
| " | " | 0.0474 |
| " | " | 0.0473 |

In none of these separations has there been an effort made to ascertain

the exact decomposition pressure of any particular chloride. This was not done in the study carried out by Hildebrand (*loc cit.*). This point is receiving attention at present in this laboratory, more especially in the determination and separation of anions by use of a silver or some other suitable anode.

A very interesting feature of the particular studies here described as well as a portion of those communicated by McCutcheon (p. 1449) is that by the current, applied as it has been in this laboratory, many interesting separations are now possible in the groups of the alkali and alkaline earth metals. Even inexperienced persons can carry out such separations. Further, many of these surpass the ordinary gravimetric procedures both in accuracy and in the short time necessary for their execution.

The analyst is not restricted any longer, in the application of the current in analysis, to the determination of such metals as copper, nickel, zinc, lead, etc. The field is now vastly broader. Anions may be most accurately determined and probably be separated in many instances more successfully than in any other way. While not desiring to anticipate another investigation now in progress, it may be mentioned that in plating anodes like those used in the present study and by McCutcheon, and by Hildebrand in their particular researches, with a suitable, adherent coating, such as calcium hydroxide, soluble fluorides may be electrolytically analyzed in the cell used in this laboratory, with the outcome that both the anion, fluorine, and the cation, sodium, can be most accurately determined. What further progress in this field may bring, one can scarcely say, yet in the language of the immortal Faraday we may rest assured "that advancement in it, whether in degree great or small, instead of exhausting the subject of research, will open doors to future and more abundant knowledge, overflowing with beauty and utility to those who will be at the * * * * * pains of undertaking its experimental investigation."

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THE ELECTROLYSIS OF METALLIC CHLORIDE SOLUTIONS WITH THE USE OF ROTATING SILVER ANODE AND MERCURY CATHODE.

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In previous communications it has been shown how readily certain bodies, *e. g.*, barium chloride, may be electrolyzed in the cell of Hildebrand.¹ It occurred to us that a study of metallic halides, in general, might reveal something of interest. To this end solutions of chlorides, as neutral as they could be obtained, were made up so that in a dilution of 50 cubic

¹ This Journal, 29, 447.