

BEHAVIOR OF CALCIUM AND SODIUM AMALGAMS AS ELECTRODES IN SOLUTIONS OF NEUTRAL SALTS.

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In 1906 LeBlanc and Novotny¹ published a paper "Über die Kaustizierung von Natriumkarbonat und Kaliumkarbonat mit Kalk" in which they determined the equilibrium constant of the reaction between sodium carbonate and lime when both factors are present both as solutions and in the solid phase. The results obtained by determination of the equilibrium during caustization and those calculated from the solubility of calcium hydroxide and calcium carbonate fail to agree with each other. It seemed of interest therefore to determine the same constant in another way, using the method of Bredig and Knuifer.² To do this it is necessary to determine the electromotive force of the cell



and to calculate the desired constant, K , from the equation:

$$\pi = \frac{RT}{7} \ln \frac{K}{a}$$

The hope of accomplishing this result was based on the very definite and satisfactory potentials measured by Meyer³ using sodium amalgam as an electrode. All attempts to obtain satisfactory determinations for a value of π failed by reason of the rapid action of water upon the calcium amalgam. The attempt led nevertheless to some interesting results in connection with the reaction of solutions of salts upon amalgams.

These results are here detailed:

Experiments with Calcium Amalgam.—Calcium amalgam was prepared by electrolysis of a saturated solution of calcium chloride, using mercury as a cathode. The current used was 1.5–2.0 amperes. After about half an hour the current was interrupted and the amalgam drawn off and washed by spraying through water in an ordinary mercury cleaning apparatus. The washed and dry amalgam was preserved in a dry flask under an atmosphere of dry hydrogen or carbon dioxide. The amalgam so prepared had a value of from 0.01 per cent. to 0.02 per cent. calcium. The amalgam was placed in a separating funnel, which was about 10 cm. long and 2 cm. in diameter. To the funnel was attached a delivery tube which carried a sealed-in platinum wire that served to connect the amalgam as an electrode with the measuring apparatus. The delivery tube was drawn to a fine point in order that the amalgam might flow in a very fine stream. The electrode so prepared was lowered into the various solutions with which it

¹ *Z. anorg. Chem.*, **51**, 181.

² *Z. physik. Chem.*, **26**, 285; also *Z. Electrochem.*, **4**, 544.

³ *Z. physik. Chem.*, **7**, 477.

was used and the fine stream allowed to flow during the process of measurement.

The solutions were placed in a vessel which was provided with an outlet so that but very little amalgam remained in contact with the solution. This vessel was connected by means of a syphon with another vessel containing tenth normal potassium chloride, in which was immersed the arm of the usual normal calomel electrode. The cell so prepared was connected with a bridge, a Siemens-Halske galvanometer and an interrupter key in the ordinary way so that the electromotive force might be measured against two accumulator cells placed in series. The value of the bridge readings was determined at the beginning and end of each series by means of a normal Weston element prepared in the usual way and compared with several standard instruments. The electromotive force was always upward of two volts. The galvanometer used was sensitive to about one-half of one millivolt under the conditions of the experiments.

The electromotive force furnished by our cell should therefore vary approximately by $58/n$ millivolts between each pair of the above solutions taken in order, n being the valence of the metal ion. The results of this as of all the following experiments are given in tabular form below.

It will be seen that with pure calcium chloride values of satisfactory accuracy are obtained between normal and tenth normal and between tenth and hundredth normal dilutions. At greater dilutions the electromotive force remains practically constant. In the more dilute solutions the zero point of the galvanometer was difficult to determine because of the very slight current which passed. In the hope that better results could be obtained if the resistance of the solutions was diminished by means of 'indifferent' electrolytes, solutions of the same concentration of calcium chloride as before were prepared, using potassium nitrate of tenth normal concentration as a solvent. The result as given in the table clearly indicates that the electrode is attacked by the nitrate solution.

Corresponding solutions of calcium chloride were made, using as solvent tenth normal solutions of potassium chloride and of barium chloride. The results as given below indicate reaction between the electrolyte and the electrode the nature of which is given in the conclusion.

Experiments with Sodium Amalgam.—In order to determine a little more closely the nature of this reaction the behavior of sodium amalgam electrodes under similar conditions was studied. The amalgam was prepared by addition of sodium to mercury in an atmosphere of hydrogen. The amalgam used was approximately 0.4 per cent. sodium. It was used exactly as in the case of the calcium amalgam. With the sodium amalgam, also, normal values are obtained for the electromotive force when solutions of pure sodium chloride are used. Beyond a dilution of hun-

dredth normal no definite results are obtainable. Solutions of sodium chloride were then prepared, using as solvents tenth normal potassium chloride, calcium chloride and lithium chloride. The table of results indicates that in each case the added electrolyte reacts with the electrode.

TABLE OF RESULTS.—COMPARISON BETWEEN SOLUTIONS OF CONCENTRATION.

Solvent.	Electrode. <i>n</i> /1— <i>n</i> /10.	Calcium amalgam. <i>n</i> /10— <i>n</i> /100.	Solution calcium chloride.	
			<i>n</i> /100— <i>n</i> /1000.	<i>n</i> /1000— <i>n</i> /10000.
Water.....	26.9	28.2
<i>N</i> /10 KNO.....	81.1	74.6	37.3	7.6
<i>N</i> /10 KCl.....	18.3	6.9	2.0	...
<i>N</i> /10 BaCl ₂	28.0	9.3	4.6	...
<i>N</i> /1 KCl.....	15.3	5.4
<i>N</i> /100 KCl.....	25.2	19.3

Solvent.	Electrode.	Sodium amalgam.	Solution sodium chloride.	
			<i>n</i> /100— <i>n</i> /1000.	<i>n</i> /1000— <i>n</i> /10000.
Water.....	60.1	57.6
<i>N</i> /10 KCl.....	47.2	21.5
<i>N</i> /10 BaCl ₂	57.7	46.2	5.7	2.0
<i>N</i> /10 LiCl.....	58.0	49.9	18.9	9.4

The results as above given represent in each case the mean of many independent measurements.

Conclusions.

The results of our experiments clearly indicate that when amalgams are treated with solutions of salts of alkaline or alkaline earth metals replacement occurs and we have to deal in the above case with the electromotive force of an electrode consisting in part of the amalgam of the metal of the added solution. Such being the case, it is only remarkable that even the approximate results above given are obtainable. That this replacement does occur in the solutions studied was shown by shaking calcium amalgam with barium chloride, washing the amalgam thoroughly and digesting with hydrochloric acid. The presence of barium in the solution was easily demonstrated. Replacement of this character in concentrated amalgams has long been known, and the recent work by Smith¹ contains a list of references to the work done upon the subject. It is to be noted that the method above employed furnishes a sensitive means of detecting the reaction and throws light on the results obtained by Fernekcs² in connection with the action of amalgams upon solutions not containing a common ion.

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¹ *J. Phys. Chem.*, **8**, 208, and **9**, 13.

² *Ibid.*, **7**, 566.