

influence the relation between the degrees of dissociation of the zinc and the nickel salts respectively. Accordingly, two solutions were prepared, both fairly dilute, and differing not too extensively in the relative concentrations of the nickel and the zinc salts. The data for these solutions are:—

(a) Solution same as for Series 4, except that the total volume of the solution is fifteen liters (i.e. three times as much as before). With current densities above two amperes the alloys obtained were practically of constant composition. The alloy obtained with C.D. = 3 amp. contained 4.6 per cent. nickel. Hence the ratio of zinc to nickel (by equivalents) in the alloy equals 5.4 times their ratio in the electrolyte.

(b) Nickel sulphate .....	131.5 grams
Zinc sulphate .....	182 "
Ammonia alum .....	100 "
Volume of solution .....	5000 cc.
Ratio of nickel to zinc equivalents.....	0.74:1

With current-densities above two amperes, the alloys obtained were practically of constant composition. The alloy obtained with C.D. = 3 amp. contained 11.2 per cent. nickel. Hence, ratio of zinc to nickel (by equivalents) in the alloy equals 5.3 times their ratio in the electrolyte. This indicates that the cause produces a *constant* factor.

We are not ready to say anything as to the nature of the cause itself. We thought it might be due to a possible difference in the rates of migration of the nickel and zinc ions, but we have since learned that the equivalent conductivities of the sulphates and of the chlorides of these metals at corresponding concentrations are practically the same, and hence have given up this explanation.

Further work on this problem is in progress.

CHEMICAL LABORATORY,  
THE UNIVERSITY OF TEXAS.

## THE ELECTROLYTIC PREPARATION OF AMALGAMS.

BY GEORGE MCP. SMITH AND JAMES R. WITHROW.

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The older methods of preparing amalgams with the help of the electric current<sup>1</sup> require much time and somewhat complicated apparatus. Considerable labor is also frequently involved. E. S. Shepherd,<sup>2</sup> however, has proposed, as a lecture experiment, the electrolytic preparation of sodium amalgam. He points out that the amalgam formed is not so heavy as the mercury itself, and therefore serves to retard action by rising to the surface and thus separating the mercury from the electrolyte to

<sup>1</sup> Nernst, *Z. Electrochem.*, 3, 308 (1897); Kerp, *Z. anorg. Chem.* 17, 300 (1898); Reuter, *Z. Electrochem.* 8, 801 (1902).

<sup>2</sup> *J. Phys. Chem.* 7, 29, (1903).

avoid the effects of this behavior the mercury was placed in a porous cup which dipped slightly into the electrolyte, thus bringing the latter in contact with the bottom of the mercury. The objections to the older methods as indicated above seem thus to be in a large measure obviated. The results obtained, too, seem to have been very satisfactory.

As solid amalgams were needed by one of us, we decided to try the method of Shepherd for sodium amalgam and then apply it to the preparation of other amalgams.

The porous cups used were  $4 \times 8$  cm. in size. They were soaked a day or two in water or a solution of the salt to be electrolyzed or sometimes they were boiled in this solution just before using. The latter and preferable course was not always necessary, owing to the great irregularity in the porosity of the cups themselves. From 100–500 grams of mercury were used in each preparation. This mercury was made the cathode by contact with a platinum wire. This wire was covered almost to its end by a glass tube into which it was fused. A little mercury in this tube served to connect the platinum wire with the copper wire of the storage battery circuit. The porous cup now containing the mercury cathode was lowered one centimeter into the electrolyte and at the same time it was two centimeters distant from the bottom of the hemispherical platinum dish (9 cm. in diameter) which served as the anode. Saturated solutions of the salts electrolyzed were generally used.

No trouble with sparking against the sides of the cup, as mentioned by Shepherd, was encountered, even with the very high currents sometimes used. Much decomposition of the amalgams however, took place, due to the water which soaked through the pores of the cups. This sometimes rose to the very top of the cup but was finally obviated by using solid caustic soda or some suitable salt, depending upon the electrolyte, on top of the mercury. This kept a saturated solution of a salt of the amalgamated metal on top of the accumulating amalgam and assisted in preventing decomposition. The platinum dish was as a rule heated externally during each run and the temperature inside the cup usually stood  $10\text{--}15^\circ$  higher than that of the electrolyte in the dish. The temperatures mentioned throughout this paper are those of the electrolyte outside the cup. The current conditions are those read directly from Weston Standard Portable instruments.

The melted amalgams were thoroughly washed three or four times with hot distilled water. After this treatment a portion of each preparation, of the alkaline amalgams except that of lithium, was covered with distilled water and an excess of  $N/10$  HCl added. After warming a short time on the water-bath, the excess of acid was titrated, using methyl orange as indicator. In the case of the alkaline earth amalgams ordinary pure hydrochloric acid was used, and after warming sufficiently on

the water-bath to decompose the amalgam, the dilute chloride solution was carefully separated from the mercury and excess of acid expelled by evaporating twice to dryness on the water-bath. The resulting alkaline earth chloride was taken up in water and the chlorine was determined by means of  $N/100 \text{ AgNO}_3$ . From the data obtained in these two methods the amounts of the respective amalgamated metals were computed. The residual mercury in every case was washed with alcohol and ether, dried and weighed. The sum of the weights of the two constituents of the amalgam was called the amount of amalgam originally taken for analysis, and from this the percentage composition was calculated.

Sodium amalgam, too thick to flow, was obtained from a sodium sulphate electrolyte, with a current of 3.5-4 amperes at 12-13 volts. The temperature was 50-60°. The amount of mercury used was 300 grams and the time was five hours.

From sodium acetate a perfectly solid amalgam (like cast metal) was obtained, with a sodium content of 1.3 per cent. The current used was 3.5-4 amperes and 12-17 volts. The temperature was 80°. The amount of mercury used was 170 grams and the time one hour.

These two results were considered as a sufficient confirmation of the results given by Shepherd, without attempting to make use of the chloride as he had done. Chlorides were not used in the present work so as to avoid possible contamination of amalgams by platinum from the dish. After the successful preparation of solid sodium amalgam from a salt other than the chloride, attention was given to applying the method to potassium salts.

Potassium sulphate gave a thick pasty amalgam with a current of 3-4 amperes and 18-22 volts. The temperature was 70-90°. The amount of mercury used was 507 grams and the time necessary three hours.

A solid amalgam was obtained from potassium hydroxide with a current of 3.5-4.25 amperes and 5-7.5 volts. The temperature averaged 75°. The amount of mercury used was 165 grams and the time was forty-five minutes. This amalgam was a hard matt of splendid metallic needles among which were a number of equally brilliant crystals of a tetrahedral aspect. In another preparation from the same electrolyte the temperature was kept between 60° and 70°. The current conditions were, 3-4 amperes and 9-12 volts. The amount of mercury used was 300 grams and the time consumed two hours and twenty minutes. In this case the amalgam was extremely hard, and when the hot amalgam was poured into water at room temperature, it solidified instantly to a cake which resembled freshly cast lead. This amalgam contained 1.50 per cent. of potassium.

A still harder amalgam was obtained from potassium nitrate as the electrolyte. The current used was 3.2-5 and 5.5-8.8 volts. The temper-

ature was 60°. One hundred and seven grams of mercury were used and the time was fifty minutes. The resulting amalgam contained 1.66 per cent. potassium. As no loss in weight on the part of the platinum dish could be detected with this electrolyte it was concluded that nitrates were suitable electrolytes for the work in hand.

A very thick mass of needle-like crystals of barium amalgam containing 1.43 per cent. of barium was obtained from barium nitrate. The current used was 3.5 amperes and 11-13 volts. The temperature was 90°. Five hundred grams of mercury were used and the time was four hours. While sodium amalgam was readily obtained and potassium amalgam was obtained with still greater ease, barium offered not a little difficulty. It seemed to decompose persistently and the resulting salt clogged the pores of the cup and lowered the current density. In attempting to overcome this difficulty the hot amalgam from a clogged cell was poured into a freshly treated cell and the electrolysis continued with but a minute's time lost. In this way 206 grams of mercury were run for six hours and the resulting amalgam contained 1.73 per cent. barium. At no time however was a barium amalgam obtained as hard as the potassium amalgam.

In using strontium nitrate, difficulties akin to those under barium, were very much augmented. Great crusts of strontium hydroxide accumulated around the glass tube and platinum wire and also the sides and bottom of the cells so as to gradually shut down the current. The best amalgam analyzed contained only 0.70 per cent. strontium. In this case 0.02 per cent. of potassium was also present, apparently coming from the cell material itself. Calcium acetate gave still more unsatisfactory results than the strontium salt. Both lithium acetate and sulphate gave only weak amalgams as in the case of calcium. Fifty-three grams of this lithium amalgam gave  $\text{Li}_2\text{SO}_4 + \text{K}_2\text{SO}_4$ , 0.1345 g and  $\text{K}_2\text{PtCl}_6$ , 0.1910 g and so contained 0.0084 g Li and 0.0306 g K.

It should perhaps be emphasized here that with the possible exception of potassium amalgam none of the amalgams obtained were pure. They all contained more or less potassium probably derived from the porous cup which frequently gave evidence of disintegration within a few days after use. For the reason that the amalgams did contain traces of potassium they could not be used for the purpose intended by one of us, and resort was had to the weaker amalgams made without the use of the porous cup. While only a few trials have as yet been made with lithium and calcium, still it seems as though the difficulty in making solid amalgams of the alkali and alkaline earth metals by electrolysis increases inversely as their atomic weights.