test. The presence of sulphocyanic, formic, acetic or meconic acid, or of any other substance giving with ferric chloride a reddish coloration, would necessitate the performance of confirmatory tests,[1] unless care had been taken at the outset to remove these substances from the sample.

Determination of Hydrazine by Oxidation Methods, and Determination of Oxidizing Agents by Reduction with Hydrazine.—On the assumption that hydrazine is completely oxidized to nitrogen and water several different methods for its determination have been based upon the action of oxidizing agents. In some cases ammonia is formed as one of the products of the reaction, and in others both ammonia and hydronitric acid. This is also true in the case of certain reactions in which weighed amounts of hydrazine have been utilized in the determination of oxidizing agents. It is entirely possible, of course, that conditions might be found under which in any of these cases the oxidation might be made complete. Positive proof of the quantitative conversion of the hydrazine to nitrogen and water should be obtained, however, before reliance is placed upon any method which under ordinary conditions is subject to the error just mentioned.

Analogy between Hydrazine and its Substitution Products.—In addition to the analogies to which reference has already been made in this summary, may be mentioned the following: (1) Formation of aniline and ammonia, respectively, by the action of Fehling's solution upon phenylhydrazine[2] and hydrazine; (2) formation of diazobenzenimide and hydronitric acid, respectively, by the oxidation of phenylhydrazine[3] and hydrazine with hydrogen peroxide; (3) formation of aromatic azoimides and hydronitric acid, respectively, by the oxidation of primary aromatic hydrazines[4] and hydrazine with various oxidizing agents.

CORNELL UNIVERSITY, ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE ELECTROLYTIC PREPARATION OF THE AMALGAMS OF THE ALKALI AND ALKALI-EARTH METALS.

BY G. MCP. SMITH AND H. C. BENNETT.

Received April 29, 1909.

The four methods by which alkali and alkali-earth amalgams have been prepared are: 1. Directly from metals. 2. By the action of an amalgam on a salt solution. 3. By the electrolysis of a complex alkali-mercury salt in aqueous solution, with platinum electrodes. 4. By the electrolysis of a salt solution with a mercury cathode.

---

[1] See THIS JOURNAL, **27**, 551–5 (1905).

[2] E. Fischer, *Ann.*, **190**, 67–183 (1878).

[3] Wurster, *Ber.*, **20**, 2631–3 (1887).

[4] Chattaway, *Loc. cit.*

The first method is satisfactory in the case of sodium and potassium amalgams, and is probably the best for the preparation of amalgams containing a high percentage of alkali metal.[1] It was employed by Kurnakov and Shukovski[2] in the preparation of rubidium and caesium amalgams; it was here necessary, however, to first prepare the free alkali elements. Lithium does not unite readily with mercury, and in the preparation of this amalgam from pure metallic lithium and mercury, at a high temperature, one of us[3] met with a serious accident as the result of a violent explosion which took place upon the union of the two metals. A calcium amalgam of the formula $CaHg_5$ has also been prepared by this method.[4]

The second method was first employed by R. Böttger,[5] in the preparation of barium and strontium amalgams, which, however, he did not analyze, from sodium amalgam. It was also made use of by one of us[6] for the same purpose. By means of it, Kraut and Popp[7] likewise prepared potassium amalgam from sodium amalgam; sodium amalgam may be even more readily prepared from potassium amalgam in the same way.[6]

By means of the third method, the amalgams of ammonium and potassium have been prepared, with solutions of $(NH_4)_2HgI_4$ and K_2HgI_4 as electrolytes.[8]

The fourth method has frequently been employed in the preparation of these amalgams, and it is in many cases preferable to the other methods. The older electrolytic methods, however, require much time and somewhat complicated apparatus.[9] This is especially true in the case of the method employed by Kerp[10] and by Kerp and Böttger[10] for the preparation of potassium, rubidium and lithium amalgams.

The main difficulty encountered in the electrolytic preparation of these amalgams, lies in the fact that the amalgams themselves are more or less readily decomposed by the solution which serves as the electrolyte. In certain cases, this action may take place to such an extent that the current efficiency soon approximates zero. In order to overcome this

---

[1] Cf. Reuter, *Z. Elektrochem.*, **8**, 801 (1902).

[2] *Z. anorg. Chem.*, **52**, 416 (1907).

[3] G. McP. Smith, *Amer. Chem. J.*, **37**, 506 (1907).

[4] J. Schürger, *Z. anorg. Chem.*, **25**, 425 (1900).

[5] *J. pr. Chem.*, **1**, 302 (1834).

[6] G. McP. Smith, *Loc. cit.*

[7] *Ann. Chem.*, **159**, 188 (1871).

[8] Moissan, *Compt. rend.*, **144**, 790 (1907); G. McP. Smith, *Ber.*, **40**, 2941 (1907).

[9] Nernst, *Z. Elektrochem.*, **3**, 308 (1897); Kerp, *Z. anorg. Chem.*, **17**, 300 (1898); Kerp and Böttger, *Ibid.*, **25**, 1 (1900); E. S. Shepherd, *J. Phys. Chem.*, **7**, 29 (1903); G. McP. Smith and J. R. Withrow, THIS JOURNAL, **29**, 320 (1906).

[10] *Loc. cit.*

difficulty, Kerp and Böttger[1] caused mercury to flow from the capillary end of a funnel, in the form of a thin thread, through a saturated solution of the alkali chloride. The thread of mercury was made the cathode by means of a platinum wire which dipped into the funnel, and carbon rods, immersed in the solution, formed the anode. The vessel containing the electrolyte ended below in a siphon tube, so disposed that in flowing through it the amalgam offered a very small surface to the action of the solution. From the siphon tube, the amalgam flowed into a receiver provided with an outlet tube carrying a glass cock and connected with a dropping funnel. The liquid amalgam was transferred back to the capillary funnel by means of the dropping funnel, and was caused to repeat the circuit of the apparatus until it became too thick to flow in a continuous stream through the capillary, or until the evolution of hydrogen on the thread-like cathode became too rapid. The concentrated, semi-solid amalgam was then removed from the receiver, where it had gradually accumulated during the operation. During the electrolysis, dry hydrogen was kept above the amalgam in the capillary funnel, in the receiver, and in the dropping funnel, in order to prevent oxidation. As an example of the efficiency of this method, Kerp says that at 8–10 volts, 1000 grams of mercury were converted in 4 or 5 hours into about 800 grams of liquid, and 200 grams of solid potassium amalgam, containing 0.45 per cent., and 1.5 per cent. of potassium, respectively, *and that during the electrolysis, the liquid amalgam was made to repeat the circuit of the apparatus about 150 times.* Kerp and Böttger state that rubidium amalgam can readily be prepared in the same way, but that the yield leaves something to be desired. With a saturated solution of lithium chloride and 1000 grams of mercury, which went through the apparatus 100 times at 14–16 volts, they obtained, on filtering the product at 0°, 40–50 grams of solid amalgam, containing 0.71 per cent. of lithium; the mother-liquor contained 0.04 per cent. of lithium.

Starting with the assumption that the rate of decomposition of the amalgam by the solution depends mainly upon the chemical nature of the amalgam itself, we have sought to obtain, in a simpler and less laborious manner, better yields of the pure amalgams. The efficiency of our method can be judged by comparing our yield of lithium amalgam, for example, with that of Kerp and Böttger. By it, we electrolyzed lithium chloride, with 250 grams of mercury as cathode, for 90 minutes, at 7–8.5 volts and 1.5–3.25 amperes, and obtained 105 grams of solid, and 145 grams of liquid amalgam, separated at the ordinary temperature.

The following is a description of the method which we have adopted:

---

[1] Kerp and Böttger's method, which is undoubtedly the best of those cited, is recommended in Abegg's "Handbuch der anorg. Chem." (II. Band, 2 Abteilung, p. 579) for the preparation of these amalgams.

In a 250 cc. beaker, with an internal diameter of 5.5 cm., a suitable quantity of mercury was made the cathode by contact with a platinum wire, fused through the end of a glass tube; the latter contained a little mercury, into which dipped the negative wire of the electric circuit. The mercury cathode was covered with a solution of a pure alkali or alkali-earth salt, into which dipped the platinum anode. This was a piece of heavy foil, 7.5 cm. in length and 2.1 cm. wide, bent at a right angle, so that the surface immersed (2.5 cm. × 2.1 cm.) was parallel with that of the mercury. The platinum anode was connected with a heavy copper wire by means of a brass connector, coated with paraffin to protect it from the action of the gas evolved. During the electrolysis, the current strength was read from a Weston standard ammeter; a standard voltmeter indicated the e. m. f. between the electrodes.

According to our experience, it is essential to employ very pure salts, since traces of certain impurities, such as iron and aluminium, greatly accelerate the interaction between the amalgam and the solution. The salts used in the following experiments were obtained from Kahlbaum. Shortly after starting the electrolysis, crystals of the specifically lighter solid amalgam begin to cover the surface of the cathode; these soon prevent the access of the metal deposited to the uncombined mercury underneath, so that hydrogen is rapidly evolved, to the detriment of the current efficiency. This can at first be remedied by gently agitating the beater; as soon as the amalgam becomes pasty, however, it is necessary to push the crystals underneath by means of a flattened glass rod, bent at a right angle. In some cases, the electrolysis can be continued until the amalgam becomes a solid mass of crystals, which can be lifted from the beaker without the separation of mother-liquor.[1]

Caesium Amalgam.—With 200 grams of mercury as the cathode, a solution of 17 grams of caesium chloride in 50 cc. of water was electrolyzed for 80 minutes at 6.5 volts and 2.6 amperes; the temperature rose during the process to 57°.

The resulting amalgam, after it had been washed with cold water and dried with filter paper, was a liquid; but, on setting down the dish containing the clean, dry amalgam, crystals suddenly appeared on its surface, and, upon gently stirring, the whole mass became semi-solid, owing to the separation of crystals. After having stood for several days in a small, glass stoppered bottle, the amalgam was filtered through chamois skin at 17°, in a Gooch crucible, on the filter pump;[2] it gave 72 per cent. of solid, and 28 per cent. of liquid amalgam. The solid amalgam in the lower part of the crucible held back a little mother liquor with great tenacity. Analysis:[3]

---

[1] The crystalline amalgams possess the property of absorbing considerable quantities of liquid amalgam without themselves becoming liquid. The liquid can be removed for the most part by filtration through chamois skin with suction (cf. Kerp and Kerp and Böttger, *l. c.*).

[2] In all cases the clean, dry amalgams were filtered as rapidly as possible, in order to avoid oxidation. The filtrates were caught in test tubes, and placed in the suction flask, into which the Gooch funnel projected.

[3] In the analysis of the solid amalgams, samples were taken from below the slightly

I. Crystals near the top, 4.72 per cent. Cs; II. crystals near the bottom, 4.46 per cent. Cs. The filtrate gave on analysis: I. 2.74 per cent. Cs; II. 2.76 per cent. Cs. The average composition of the mass was therefore 4.08 per cent., indicating a current efficiency of about 50 per cent.

A second, less concentrated preparation, which was liquid, did not crystallize perceptibly, even on the addition of a few crystals of the previously prepared solid amalgam. After 24 hours, however, it had separated into approximately 1/3 solid, and 2/3 liquid amalgam.[1]

Rubidium Amalgam.—With 100 grams of mercury as the cathode, a solution of 10 grams of RbCl in 50 cc. of water was electrolyzed for 40 minutes at 8 volts and 2.25 amperes. The temperature gradually rose to 54°.

On washing the pasty mass obtained at 54° with cold water, it became a solid cake and could be picked up without the separation of any liquid. It was allowed to stand 24 hours in a small, glass-stoppered bottle, after which it was filtered through chamois on the suction pump, at 19.5°, and gave 68 per cent. of solid, and 32 per cent. of liquid amalgam.

The crystals gave on analysis, 3.59 and 3.52 per cent. Rb; the filtrate gave 1.22 and 1.20 per cent Rb.

From these figures, the calculated rubidium content of the original amalgam was 2.81 per cent., indicating a current efficiency of about 60 per cent.

Potassium Amalgam.—With 250 grams of mercury as the cathode, 50 cc. of saturated potassium chloride solution were electrolyzed for 50 minutes at 6 volts and 3 amperes. On washing the warm, semi-solid amalgam with cold water, it changed to a solid cake of fine needle-like crystals. This was dried between filter paper and at once analyzed, giving 1.20 and 1.18 per cent. K. The remainder of the amalgam was later filtered through chamois skin by suction; it gave 58.8 per cent. of solid, and 41.2 per cent. of liquid amalgam. The separation was carried out at 20°. Analysis:[2]

Crystals, 1.70; filtrate, 0.46%K.

On calculation, these results give 1.20 per cent. as the potassium content of the whole, showing that the first samples taken were representative. The current efficiency was, therefore, 83 per cent.

In order to see if a better yield could be obtained with potassium hydroxide as the electrolyte, a solution of 25 grams of Kahlbaum's pure potassium hydroxide in 50 cc. of water was electrolyzed for 16 minutes at 4.5 volts and 3.8–4 amperes, until the evolution of hydrogen became stormy. The cathode was 125 grams of mercury. The product, separated as before, gave 58.6 per cent. of solid, and 41.4 per cent. of liquid amalgam. Although the concentration of the amalgam could be made no greater, the current efficiency approximated 100 per cent. A great deal of inconve-

---

oxidized surface at the top of the crucible. The amalgams were analyzed by decomposition with 0.1 *N* HCl in excess with methyl orange as indicator, an excess of 0.1 *N* NaOH was then added, and this was titrated back with 0.1 *N* acid. Immediately preceding the end-point in the decomposition of an amalgam, a cloud of minute hydrogen bubbles was suddenly expelled from its surface, and the amalgam visibly shrank together. After this, on shaking the beaker, the mercury was broken up into small globules on striking the glass rod; the globules slowly coalesced on standing. This division did not take place as long as an appreciable quantity of alkali metal was present in the mercury (cf. G. McP. Smith, *J. Am. Chem. Soc.*, **31**, 31 (1909)).

[1] Kerp and Böttger observed an analogous phenomenon in the case of strontium amalgam; they did not work with caesium amalgam.

[2] Kerp and Böttger obtained 1.55 per cent. of potassium in the solid phase at 20°; in the liquid they, too, obtained 0.47 per cent., at 20°.

nience was, however, experienced in stirring, owing to the mechanical transmission of alkali by the gases evolved.

Sodium Amalgam.—With 250 grams of mercury as the cathode, 50 cc. of saturated sodium chloride solution were electrolyzed for 105 minutes at 6 volts and 3 amperes. The product formed a solid, brittle mass of crystals. It was washed, dried with filter paper, and analyzed, giving 1.53 and 1.52 per cent. Na. These figures indicate a current efficiency of 84 per cent.

The remainder of the amalgam was later filtered through chamois, by suction, at the ordinary temperature, and gave 72 per cent. of solid and 28 per cent. of liquid amalgam. The two phases were not analyzed, but, according to Kerp and Böttger, they contain, at 25°, 1.76 per cent. and 0.65 per cent. of sodium, respectively. On calculation, these figures give 1.45 per cent. as the sodium content of the whole, a value closely approximating that obtained by us.

Lithium Amalgam.—With 250 grams of mercury as the cathode, 50 cc. of a saturated solution of lithium chloride were electrolyzed for 30 minutes at 7 volts and 1.5 amperes, and then for 60 minutes at 8.5 volts and 3.25 amperes. It was found essential for the success of this preparation to keep the surface of the amalgam covered throughout the electrolysis with crystalline lithium chloride, and to keep the crystalline amalgam, which began to form in about 20 minutes, constantly pressed under the surface of the liquid amalgam. In all, 50 grams of lithium chloride were added to the original saturated solution during the electrolysis; this was necessary, owing to the fact that the temperature rose to 70°.

The resulting amalgam was washed, dried, and analyzed. It gave 0.398 and 0.397 per cent. Li. These figures indicate a current efficiency of 88 per cent.

The remainder of the amalgam was filtered through chamois skin by suction; it gave 42 per cent. of solid, and 58 per cent. of liquid amalgam. The separate phases were not analyzed. Taking Kerp and Böttger's values, 0.70 per cent. and 0.07 per cent.[1] for the composition of the solid and liquid phases, respectively, the calculated lithium content of the whole is 0.33 per cent., a figure which our result exceeds by about 20 per cent. We therefore repeated the experiment as follows:

With 250 grams of mercury as the cathode, the electrolysis was carried out as before for 55 minutes at 8.75–7 volts and 2.9–4 amperes (average about 3.5 amperes). The end temperature was 78°. The amalgam was then washed, dried, and allowed to stand for two days in a small glass-stoppered bottle, which it completely filled. On filtration it gave 27.9 per cent. of solid amalgam. The separation was carried out at 22°.

The crystals, which were bright and unoxidized, gave, on analysis, 0.89 and 0.86 per cent. Li.

The liquid amalgam gave, on analysis, 0.047 and 0.047 per cent. Li.

These figures indicate a lithium content of 0.278 per cent. in the amalgam as a whole; the current efficiency was therefore about 85 per cent.

If now we calculate the lithium content of the first preparation, taking our values of 0.875 per cent. and 0.047 per cent. as the lithium content of the solid and liquid amalgams, respectively, we arrive at the value 0.394 per cent., a figure in excellent agreement with our analytical results.

Barium Amalgam.—With 250 grams of mercury as the cathode, 50 cc. of saturated barium chloride solution were electrolyzed for 2 hours and 20 minutes at 7–6 volts and 1.75–2.1 amperes. The amalgam was very readily formed and less attention was required than in the other cases. The amalgam, which could be lifted from the beaker

---

[1] The value 0.07 per cent. was calculated by Kerp and Bottger for 25°; they made no experimental determinations between 0° and 64.5°.

without the separation of any liquid, was washed, dried with filter paper, and analyzed. It gave 3.49 and 3.48 per cent. Ba. These figures indicate a current efficiency of about 78 per cent.

The remainder was filtered by suction, and gave 65 per cent. of solid, and 35 per cent. of liquid amalgam. Taking 4.95 per cent. and 0.34 per cent. as the barium content of the solid and liquid, respectively (Kerp and Böttger's figures at 25°), the calculated barium content of the amalgam as a whole is 3.44 per cent. This is in good agreement with our analyses.

A second equally concentrated preparation was made in 35 minutes, by carrying out the electrolysis at 9 volts and $4^1/_2$ amperes, with 185 grams of mercury as the cathode.

Strontium Amalgam.—With 260.0 grams of mercury as the cathode, a saturated solution of strontium chloride in 50 cc. of water was electrolyzed for 90 minutes at 7.5–7 volts and 2.5–2.75 amperes. The end temperature was 43°. During the electrolysis, the surface of the cathode was kept constantly covered with a layer of strontium chloride crystals. This is essential to the success of the preparation.[1]

The resulting amalgam, which was of a pasty consistency, was washed, and then dried with filter paper. It weighed 265.5 grams, the increase in weight indicating the presence of 2.07 per cent. of strontium. The amalgam was kept for 3 days in a small glass-stoppered bottle; it was then washed, dried, and filtered, giving 52 per cent. of solid,[2] and 48 per cent. of liquid amalgam.

The solid gave, on analysis, 2.80 and 2.82 per cent. Sr; the filtrate gave 1.12 and 1.12 per cent. Sr. The calculated strontium content of the amalgam as a whole is, therefore, 2.00 per cent. The current efficiency was 73 per cent.

Calcium Amalgam.—A saturated solution of calcium chloride was electrolyzed with a mercury cathode, but the amalgam obtained was very dilute, and a great deal of a black mixture of calcium hydroxide with finely divided mercury was formed, especially around the platinum wire in the cathode. This broke the circuit after a short time. Several other solutions were tried, and the best results were obtained with a solution of recrystallized calcium acetate, prepared from pure calcium carbonate and acetic acid.

With 250 grams of mercury as the cathode, 35 cc. of saturated calcium acetate solution were electrolyzed for 40 minutes at 10 volts and 1.25 amperes. Hydrogen was rapidly evolved, although solid calcium acetate was added from time to time, and the solution darkened, and foamed, so that constant stirring was necessary. After 20 minutes, white calcium hydroxide could be seen between the amalgam and the walls of the beaker, together with some dark spots, and the temperature had risen to 75°. The beaker was then immersed in cold water and the temperature kept at 35°; this, however, did not appear to diminish the action of the amalgam on the solution. After 40 minutes, the e. m. f. was increased to 12.75 volts, which gave a current of 2.25 amperes. At the end of 10 minutes more, the end of the glass tube and the platinum wire projecting from it, which dipped into the cathode, were completely covered with

---

[1] Kerp and Böttger prepared strontium amalgam in a similar manner by the electrolysis of a saturated solution of strontium chloride. They state that the chlorate formed during the process greatly reduces the current efficiency, and to avoid this, they renewed the solution several times during the electrolysis. This, however, is much less efficient in the production of a good yield of solid amalgam than the addition of crystalline strontium chloride.

[2] Owing to a low water pressure at the time this amalgam was filtered, the separation of the mother liquor was far from complete. Kerp and Böttger obtained a solid amalgam which contained 3.33 per cent. of strontium.

solid, white calcium hydroxide; this broke the circuit and the electrolysis was discontinued.

The amalgam was at once washed, dried, and analyzed; it gave 0.091 and 0.092 per cent. Ca. The current efficiency was, therefore, 29 per cent.

The remainder of the amalgam was filtered through chamois skin by suction, but no solid was obtained.

Upon comparing our yields of these amalgams with those of Kerp and Böttger, it will be seen that, by means of a simpler and much less laborious process, we have succeeded in obtaining far better results. The chlorine evolved during the electrolysis had no appreciable action on the platinum foil, so it was not considered necessary to use a carbon anode.

In the analysis of the solid amalgams left behind on filtration, our results are in several instances higher than those obtained by Kerp and Böttger. This is especially true in the case of solid lithium amalgam, in which we obtained 0.875 per cent. of lithium, while Kerp and Böttger found only 0.70 per cent. It is possible that, owing to the greater quantity of the solid amalgam at our disposal, the separation was more complete; we also increased the efficiency of the filtration, however, by alternately pressing the palm of the hand over the top of the Gooch crucible until the pressure became very low in the suction flask, and then lifting it off and allowing the air to rush through and sweep the mother liquor along with it. This was repeated 4 or 5 times. The significance of our analytical difference can be seen from the fact that the formula $LiHg_5$ theoretically requires 0.70 per cent. of lithium, while the formula $LiHg_4$ corresponds to 0.87 per cent. We have reason to believe that Kerp and Böttger did not succeed by filtration in entirely removing the mother liquor from the crystalline amalgams, and we are repeating their work, with the addition that we separate the last traces of the mother liquor left behind on filtration, by means of a high-speed electric centrifugal machine. The results will be published in the near future.

URBANA, ILL.

[PHOENIX PHYSICAL LABORATORY CONTRIBUTIONS, NO. 19.]

THE CHANGE IN REFRACTIVE INDEX WITH TEMPERATURE. II.

BY K. GEORGE FALK.

Received May 10, 1909.

In the first paper[1] the results obtained in determining the refractive indices for the three hydrogen and the sodium lines for diisoamyl, dimethylaniline, *n*-heptyl alcohol, benzyl alcohol, *n*-butyric acid, and acetylacetone at a number (thirty to fifty) of temperatures between 15° and 75° were given. The equations showing the relation between the refractive indices and the temperatures as well as the densities (which

---

[1] THIS JOURNAL, 31, 86 (1909.)