

71. *Rare-earth Metal Amalgams. Part I. The Reaction between Sodium Amalgam and Rare-earth Acetate and Chloride Solutions.*

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Samarium, europium, and ytterbium in acid acetate solution pass into the mercury when shaken with dilute sodium amalgam. The reaction gives an efficient means of separating various rare-earth elements. The cerium-group elements all show a lower power of amalgam formation, which decreases in order of atomic number. Higher amalgam yield but lower efficiency has been attained by the use of acid chloride solutions. Europium amalgam and hydrochloric acid give solid europous chloride, but this salt did not exchange metal quantitatively with sodium amalgam. A soluble europous hydroxide results from the action of water on europium amalgam.

RARE-EARTH metal amalgams have hitherto been studied chiefly with a view to the preparation of the metals. Jukkola, Audrieth, and Hopkins (*J. Amer. Chem. Soc.*, 1934, **56**, 303) electrolysed anhydrous chlorides in alcoholic solution and obtained 1–3% of lanthanum, cerium, neodymium, and samarium in mercury, and 0.2% of yttrium. West and Hopkins (*ibid.*, 1935, **57**, 2185) found it simpler to treat the solutions with sodium amalgam, and obtained 2–2.5% yttrium amalgam, but failed to prepare amalgams in presence of water. McCoy (*ibid.*, 1941, **63**, 1622, 3432), however, prepared europium, ytterbium, and samarium amalgams in 95, 22, and 13% yields by electrolysis of aqueous acetate solutions in presence of potassium citrate and carbonate, and found that potassium and sodium amalgams react with acetate-citrate solutions to produce rare-earth metal amalgams.

The author has treated rare-earth solutions, generally the acetate, with dilute sodium amalgam under acid conditions: there is rapid reaction between the sodium and acid with production of nascent hydrogen, and despite such loss of sodium the efficiency is greater than that obtained by more gentle reaction in alkaline solution or by electrolysis. The present work is only preliminary, but indicates that 100% amalgam formation is obtainable by treating europium, samarium, and ytterbium acetate solutions with a weight of sodium equal to that of the rare-earth oxide. This represents an efficiency of 25–30% for the reaction $3\text{Na} + \text{E}^{3+} \longrightarrow \text{E} + 3\text{Na}^+$. In addition to these three earths, which have well-known bivalent states, other earths can be made to afford amalgams by this very vigorous reducing reaction. The yields fell with increasing atomic number and were insignificant on reaching gadolinium, but with lanthanum, cerium, praseodymium, and neodymium considerable amalgam formation occurred.

In the case of the acetates, the exchange of metal is soon brought to a balance as sodium acetate accumulates in the solution. With concentrated lanthanum chloride solution and a large amount of sodium, the solubility of sodium chloride set a limit to the accumulation of sodium in solution and this made possible the extraction of nearly all the lanthanum before the solution became too full of solid sodium chloride for further work.

The applications of amalgam formation to practical problems of separations of the rare earths appear promising. The author has found that traces of europium and samarium may be separated from gadolinium; that a samarium-gadolinium mixture can be resolved immediately into nearly pure components; that a crude yttrium earth can have removed in one operation most of the europium, samarium, and ytterbium, and that lutecium containing a little ytterbium can have this removed in one operation.

The efficiency of the separation of the rare earths from one another by amalgam formation appears to be better than that obtained by reductions to salts in the bivalent state. The separation of the amalgam layer from the aqueous layer at the end of a reaction is more satisfactory than removal of a precipitated salt which retains mother-liquor or is subject to reoxidation, and may itself not be entirely insoluble. The comparative merits of reduction of ytterbium sulphate (Marsh, *J.*, 1937, 1367) and of formation of ytterbium amalgam as a means of preparing pure ytterbium or lutecium salts from their mixture is a case in point. The operations are simple, and no element difficult to remove is introduced. The individuality of the elements appears to be retained more than sometimes occurs in mixed earths, and application of the process to the removal of traces of impurities is very satisfactory.

Another feature of interest is the readiness of samarium to form an amalgam. Although the bivalent samarium salts are less stable than ytterbous salts, the amalgam-forming power of samarium is probably superior to that of ytterbium. Bivalent salts or ions can be produced in solution by the action of sodium amalgam on trivalent salts, as shown by the production of the coloured (Sm and Yb) or colourless (Eu) bivalent solutions. In chemical reactivity samarium, europium, and ytterbium amalgams are much superior to the cerium-group metal amalgams: either there is a difference in combining power with mercury, or the two groups of metals may exist in different valency states in mercury. The stability of the cerium-group metals favours the theory that these exist in a trivalent condition, the other three metals resembling the alkaline-earth metals in reactivity. Klemm and Bommer, and Bommer and Hohmann (*Z. anorg. Chem.*, 1937, **231**, 138; 1939, **241**, 268) conclude from atomic-volume determinations that europium, ytterbium, and to some extent samarium, exist normally in the metallic state in a bivalent condition. This probably holds true also in amalgams.

Good evidence that the cerium-group elements can give rise to bivalent salts has been obtained by Holleck and Noddack (*Angew. Chem.*, 1937, **50**, 819), who stabilised a proportion of bivalent sulphate by entrainment

with strontium sulphate when strontium amalgam acted on saturated rare-earth sulphate solutions. They concluded that the stability of the bivalent state can be gauged by the proportion of bi- and ter-valent sulphate found. Their results are in line with those of Noddack and Brukl (*ibid.*, p. 362), who measured reduction potentials by polarographic means and gauged the stability of the bivalent state by the difference between the discharge potentials for bivalency and for metal formation. Measured by either method, the elements fall into the same order of bivalent stability (Table I, *a* and *b*). Holleck and Noddack's results,

TABLE I.

| | La. | Ce. | Pr. | Nd. | Sm. | Eu. | Gd. | Yb. |
|--|-------|-------|-------|-------|-------|------|-------|-------|
| (a) % of rare-earth sulphate found in bivalent state (H. and N.). | | 4 | 5.4 | 4.6 | 70 | 90 | 15 | 80 |
| (b) P.D. (volts) between $E^{III} \rightarrow E^{II}$, and $E^{III} \rightarrow$ metal formation (N. and B.) | 0.105 | 0.105 | 0.115 | 0.090 | 0.290 | 1.80 | 0.145 | 0.575 |
| (c) Amounts (mg.) of E_2O_3 ex bivalent sulphate from reduction of 50 ml. of saturated $E_2(SO_4)_3$ with strontium amalgam (H. and N.). | | 16 | 21 | 19 | 75 | 59 | 5 | 1224 |
| (d) Relative amalgam forming power (see Table II). | 284 | 273 | 129 | 104 | 980 | 950 | 2 | 960 |

however, suffer from the defect that different amounts of rare-earth sulphate were used in each experiment. Neither the percentage of bivalent sulphate nor the total bivalent sulphate production is a strictly comparable quantity, but if the latter is taken (Table I, *c*) instead of the former (Table I, *a*) it will be seen that output is roughly parallel to amalgam-forming power.

In the trivalent rare-earth salts, basic strength falls from lanthanum to lutecium, and in a bivalent condition it might be expected that the same would hold true, but that the strength would be much greater and comparable to that of alkaline-earth elements. Similarity of chemical properties and cases of isomorphism between europous and barium and strontium compounds have been proved (McCoy, *J. Amer. Chem. Soc.*, 1937, 59, 1132). It has long been known that alkaline-earth ions in solution and alkali metals in amalgam are reversibly replaceable (Smith, *Amer. Chem. J.*, 1907, 37, 506), but it has not hitherto been regarded as possible to effect an exchange between alkali-metal amalgams and trivalent ions in solution. The attempt results in the reaction of the sodium with hydrogen ions in preference to the trivalent ions, and only hydrogen is produced. If, however, certain trivalent rare-earth metal salts in solutions of suitable p_H are treated with sodium amalgam, the metal now gains the power, usually confined to uni- and bi-valent metals, of exchanging with the sodium in amalgam. The conditions found necessary favour a high concentration of nascent hydrogen at a surface of high overvoltage. The three rare-earth elements with well-known bivalent states are those which can most easily form amalgams. Less acid conditions are required than in the case of the other earths, but it seems reasonable to postulate that a bivalent state precedes amalgam formation in all cases. If the bivalent state is very unstable, high concentrations of nascent hydrogen must be maintained in order to produce a sufficient concentration of bivalent ions to effect an exchange with the sodium in amalgam; but much hydrogen gas will result at the same time. To remove a valency electron becomes progressively more difficult as the lanthanide contraction grows in mounting the rare-earth series, and it is almost impossible when gadolinium is reached.

EXPERIMENTAL.

Preparation of Acetates.—The oxides were dissolved in acetic acid, and the salt crystallised. Ytterbia and lutecia required several hours' digestion with excess of hot 30% acid to effect solution. Samples of acetates were ignited to oxide, which was weighed.

Preparation of Sodium Amalgam.—Sodium slices (25 g.) were added to warm mercury (975 g.). The hot, liquid amalgam was poured into test-tubes, which were corked and at once laid flat. Easily crushed crystalline sticks resulted. When required, a portion was weighed, crushed, and added with 1 drop of water to pure mercury.

"Extraction" by Sodium Amalgam.—It will be convenient to refer to the reaction between sodium amalgam and rare-earth solutions, whereby rare-earth metal amalgams are formed, as a process of extraction. The reaction was carried out by shaking in an extraction funnel. The rare-earth element passed from the aqueous to the mercury layer, and those elements which can form amalgams were thereby extracted from those which cannot.

Effect of Dilution on Amalgam Formation.—(a) *Lanthanum.* 1 G. of lanthana was dissolved in hydrochloric acid, diluted to 5 ml., and brought into reaction with (1) 40 g. of 1.25% sodium amalgam or (2) 200 g. of 0.25% amalgam; (3) before treatment as in (2) the acid solution was diluted to 50 ml. The mixture was shaken in a separating funnel and kept slightly acid by addition of drops of concentrated hydrochloric acid. When the sodium was exhausted, the mercury was run through water in another funnel and then shaken with concentrated hydrochloric acid in a third funnel till calomel began to form. Most of the excess acid was removed by evaporation, the solution diluted, and the lanthanum precipitated with oxalic acid. Yields of oxide: (1) 44, (2) 77, (3) 90 mg.

(b) *Samarium.* 1 G. of samaria, similarly treated, gave yields of oxide: (1) 185, (2) 218, (3) 127 mg.

Extraction of Lanthanum Chloride Solution.—1 G. of lanthana was made into 8 ml. of chloride solution and treated with three portions of sodium amalgam (total 5.7 g. of sodium in 25 ml. of mercury). Concentrated hydrochloric acid was added to keep the solution acid. The reaction went vigorously at the b. p. There remained in the chloride solution only 13% of the lanthanum, as found by precipitation as hydroxide, then as oxalate, and subsequent ignition of the oxalate.

Similar experiments with praseodymium chloride (1.5 g. + 3 g. of sodium in 15 ml. of mercury) and neodymium chloride (1.5 g., 4 g., and 20 ml. respectively) yielded 210 mg. of praseodymium oxide and 70 mg. of neodymium oxide on treating the amalgams with concentrated hydrochloric acid, precipitating the extract with oxalic acid, and igniting the oxalate.

Extraction of Samarium Chloride Solution.—1 G. of samaria was made into chloride solution and shaken with 100-g. portions of 1% sodium amalgam four times. Reaction of the first two lots produced a deep red-brown colour in the chloride solution due to Sm^{++} ions. The yields (mg.) of oxide from the extracts were: (1) 390, (2) 340, (3) 116, (4) 15. The residue recovered from the chloride solution was 22 mg.

Yttrium and terbium chloride solutions treated similarly gave only traces of amalgam formation.

Use of Acetate Solutions.—Better extraction was obtained initially by using acetate solutions and acetic acid, but after 1 g. of sodium had accumulated in 10 ml. of solution little further progress could be made. When chloride solutions were used, the precipitation of sodium chloride set a limit to the sodium concentration, so some rare-earth extraction could still take place. Sodium acetate, on the other hand, sometimes salted out the rare-earth acetate.

Comparative Reducibility of Rare-earth Acetates.—The standard experiment was performed as follows. Rare earth in the form of neutral acetate dissolved in 10 ml. of water was treated with 20 g. of 2.5% sodium amalgam + 15 ml. of mercury. The solution and amalgam were shaken continuously with a rotatory motion in a 100-ml. conical tap funnel, drops of glacial acetic acid being added from a burette to keep the solution acid. A cloud of small hydrogen bubbles made the solution milky, and the rate of reaction was better judged by ear than by eye. Brisk effervescence promoted amalgam formation. A p_{H} of 4–5 was probably the most favourable, but in presence of bivalent salts or nascent hydrogen the B.D.H. universal indicator was bleached, and so could only be used before or after the reaction. The total addition of acetic acid varied from 0.4 ml. in the case of the strongly bivalent earths to 1.4 ml. when little amalgam formation occurred, and nearly all the sodium reacted with the acid. The temperature had but little influence: it was generally above rather than below 50° . The reaction generates considerable heat. The reaction time depended upon the rate of addition of the acetic acid. Yields were optimum at 3–5 mins. At the conclusion of the reaction the amalgam was run off, washed by passing through water in another tap funnel, and then decomposed in a third funnel. The rare-earth metal amalgams react only slowly with water at the concentrations here prepared, so that by running a portion of the mercury into water it could be seen at once approximately how much sodium, if any, was still present. A series of experiments according to this procedure was carried out with a variety of earths. A second extraction was usually made in the same way, but never gave more than 20% of the yield of the first, and when third extractions were attempted they proved fruitless. Unreduced residues of samarium, europium, and yttrium were recovered by precipitation with ammonia. The collected hydroxide was dissolved in nitric acid, and the earth precipitated as oxalate and ignited. In each case the residue proved to be composed at least in large part of less easily reduced earths originally present as impurity. The results are collected in Table II.

TABLE II.

Comparative reducibility of rare-earth acetates by sodium amalgam. Yields (in mg.) of oxide recovered on treating the equivalent of 1 g. of oxide with 0.5 g. of sodium in 15 ml. of mercury.

| Element. | Extract. | | Residue. | Element. | Extract. | | Element. | Extract. | |
|----------|----------|-----|----------|----------|----------|-----|----------|----------|-----|
| | 1. | 2. | | | 1. | 2. | | 1. | 2. |
| Sm | 900 | — | 75 | La | 285 | 20 | Nd | 113 | 0.4 |
| | 895 | — | 95 | | 255 | — | | 96 | — |
| | 888 | 88 | 2.5 | | 255 | 8 | Gd | 2 | — |
| Eu | 894 | 25 | 5 | Ce | 248 | 49 | | 2 | — |
| | 933 | 15 | 4.5 | | 244 | 4 | Dy | 0.5 | — |
| | 931 | 34 | 4.4 | Pr | 108 | 0.5 | | 0.4 | — |
| Yb..... | 704 | 265 | 18 | | 150 | — | Yt | 0.4 | — |
| | 810 | 142 | 23 | | | | | | |

Ytterbium amalgam is the least stable; samarium and europium amalgams are a little more stable, but care was necessary with these three elements not to over-run the end-point: it was best to run off the mercury while it still contained a little sodium. Amalgams of lanthanum, cerium, praseodymium, and neodymium are more stable, and in these cases it was best to keep the solution rather more acid and to allow the sodium to react completely.

Very dilute europium, samarium, and yttrium amalgams, but most readily the last, react peculiarly with water. At first, on shaking, if any sodium amalgam is present this is decomposed; then suddenly on continued shaking the mercury breaks into droplets and forms a sludge, rare-earth hydroxide beginning to appear in suspension. When all of any one of these three metals has reacted, the mercury suddenly coalesces again, but if any cerium-earth metal was present in the amalgam it will still be found there at this juncture. If the amalgams are not dilute the separation from sodium is not quite sharp, the same droplet formation does not occur, but the hydroxide is stained black by admixture with very finely divided mercury. In this case it is better to treat the amalgam with 2N-hydrochloric acid; most of the sodium will still react first and may be fairly sharply separated—any rare earth accompanying it may be precipitated with alkali. For removing the cerium-group metals even more concentrated acid is preferable; shaking is continued until calomel begins to appear, and if the solution is too acid it is then partly evaporated, diluted, and the rare earth precipitated as oxalate.

Ytterbium.—Bivalent ytterbium in solution gives rise to a green colour which deepens to yellow or orange as the concentration rises. When ytterbium amalgam is treated with concentrated hydrochloric acid only a faint transient green is seen, but a strong green colour develops on treatment with 2N-acid. The green colour in acetate solutions treated with sodium amalgam decreases as the solution becomes alkaline and vanishes before precipitation of hydroxide starts. It is restored on addition of acetic acid if there is sufficient ytterbium still in solution. Extraction of ytterbium can take place without the development of any colour. Strong orange tints were produced on treating acetate + citric acid with potassium amalgam, and extraction occurred. Good extraction took place from ytterbium acetate and acetic acid by strontium but not barium amalgam. The reduction of ytterbium requires rather more alkaline conditions than that of the other earth metals. At the end of the run which left the least residue (18 mg.), a p_{H} of 6.5 was found and much sodium was still present in the mercury. The residues from the ytterbium always showed in the oxide form a reflection band in the green region due to erbium.

Europium.—The material used was known to contain a small amount of neodymium and other earths. The reduced solution was faintly green, possibly due to ytterbium. After the first extraction no absorption bands were visible. Only half the quantity of sodium amalgam was used for the second extraction. The 5 mg. of residue gave strong absorption bands of neodymium, and the oxide was yellow. Low total recoveries of europium were experienced and are ascribed to a loss as $\text{Eu}(\text{OH})_2$.

Evidence of a Soluble Europous Hydroxide.—Europium amalgam (30 ml.; about 0.45%) was kept in an open 400-ml. beaker with 60 ml. of water for 40 hours. Much yellow-green hydroxide was formed, and was filtered off. The filtrate was alkaline but quickly bleached methyl-orange. It was boiled and treated with nitric and oxalic acids.

An oxalate precipitate was formed from which 60 mg. of europium oxide were recovered, indicating that europous hydroxide with a solubility of at least 1 g./l. must have been present in solution.

Samarium.—No colour developed in acetate solutions on treatment with amalgams, but by the action of sodium or strontium amalgam on samarium chloride and hydrochloric acid the deep red-brown colour of samarous compounds was developed. The extractions obtained, however, were poor. The colour never persisted for more than 1 minute after withdrawal of the amalgam. The experiment affords a simple demonstration of the bivalency of this element.

Lanthanum.—The low solubility of lanthanum acetate necessitated solution in 25 ml. of water in place of the usual 10 ml.; 25–30% extractions were obtained. A trial in which the solution was kept more faintly acid gave only 18% extraction. The solutions tended to froth and to yield a basic acetate.

Cerium.—15 ml. of solution were used, and basic salt formation was apt to occur.

Gadolinium.—The 2 mg. yield was examined by arc spectroscopy and found to be mainly gadolinium, but europium and samarium were also present in considerable quantity although the oxide used was supposed to be quite free from these.

Lutecium.—Some oxide from the tail of a bromate fractionation of earths freed as far as possible from ytterbium by precipitation of ytterbous sulphate (Marsh, J., 1937, 1367) gave an extract amounting to 2.8%, and the resulting lutecium oxide showed only two or three of the very strongest ytterbium arc lines.

Samarium-Gadolinium Mixture.—The oxides (5 g.) in acetate solution (50 ml.) were treated three times with 0.5 g. of sodium in 16 ml. of mercury, the successive yields being 300, 118, and 125 mg. of oxide from amalgams. The absorption spectrum of the residue was examined in chloride solution and compared with a standard samarium chloride solution. The samarium content was thus estimated to be 0.3%. The first two extracts appeared to be fairly pure samarium but the absorption spectrum of the third was weak.

Extraction from Crude Yttrium Earths.—A quantity of gadolinite from Iveland, Norway, was opened up, and the resulting rare-earth chlorides treated with potassium sulphate till the absorption spectrum of neodymium could no longer be seen in solution. The resulting yttrium earths were given a single fractional precipitation as ferricyanide. The first precipitate had the highest average atomic weight (115), as found by titration of a sample of oxalate with standard permanganate, and by igniting another sample of oxalate to oxide. 5 G. of the head fraction were made into acetate solution (30 ml.) and treated twice with 0.5 g. of sodium in 16 ml. of mercury, the yields being 33 and 83 mg. (total, 116 mg.). A slight green colour developed for a time. The absorption spectrum of the yield showed considerable samarium, estimated by comparison with standards to be 20 mg. There was just a trace of erbium absorption. The arc spectrum showed much samarium and ytterbium, but only a little europium. Numerous yttrium lines were also seen. A little ytterbium was left with the other earths, but the arc lines were faint compared with those of its scarce neighbour lutecium, which gives a similar type of arc spectrum. The colour of the extracted oxides was the same as that of the original. A pair of strong terbium lines were identified in the extract.

Action of Hydrochloric Acid on Europium Amalgam.—The amalgam from a triple-scale standard experiment was left in contact with 10 ml. of concentrated hydrochloric acid for $\frac{1}{2}$ hour in an atmosphere of carbon dioxide in a tap funnel with occasional shaking. The mercury was then found to be free from europium, which was now in the form of a white salt with a carmine-red fluorescence. The salt was readily soluble in water and had no visible absorption spectrum. The fluorescence was not as strong when the salt was dry, in a carbon dioxide atmosphere or in a vacuum, as when damp and oxidising in air. The salt was dried by warming and attaching the tap funnel to a water-pump. No similar salt was obtained by treating ytterbium or samarium amalgam with concentrated hydrochloric acid.

Attempted Exchange between Sodium Amalgam and Europous Chloride.—The europous chloride (4 g.) just described was dissolved in 10 ml. of water and shaken with 0.25 g. of sodium in 8 ml. of mercury for 10 minutes. Much europium hydroxide was formed, and 0.28 g. of europium oxide was recovered from the amalgam ($\text{EuCl}_2 + 2\text{Na} \rightarrow 2\text{NaCl} + \text{Eu}$ requires 0.945 g.). A similar experiment in which the separation of hydroxide was prevented by addition of acetic acid gave with 3 minutes' shaking 0.451 g. of oxide from the amalgam. The sodium appeared to be exhausted. Neither experiment, therefore, proves satisfactorily that direct exchange of europium for sodium in amalgam can take place without hydrogen formation.