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Separation of Rare-earth Elements† by Electrolysis at a Mercury Cathode

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The review deals with the questions of the mechanism of the reduction of rare-earth elements at a stationary mercury cathode and the conditions of their electrochemical deposition and separation, and of their extraction by alkali metal amalgams, are described and discussed. Examples of the separation of almost all the rare-earth elements at a mercury cathode are quoted. The bibliography incorporates 103 references.

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I. INTRODUCTION

Among the methods for the separation of rare-earth elements available at the present time the most widely used are fractionation based on the gradual variation of the solubility or basicity of rare-earth compounds, ion-exchange and partition chromatography, extraction methods, and electrolysis at a mercury cathode. The last makes it possible, in particular, to separate comparatively readily large amounts of one rare earth from very small amounts of other adjacent elements and can be used in most cases where the separation of large amounts of a rare earth by ion-exchange or fractionation methods involves considerable difficulties.

† Lanthanides is the term used at present in Western literature (Ed.of Translation).

At the present time a large amount of data on the separation of rare earth at a stationary mercury cathode has accumulated. However, unfortunately studies on electrolysis with a mercury cathode for the separation of rare-earth elements has not been reviewed so far. Some information is given in the review of Ryabchikov and Terent'eva[1].

II. APPLICATION OF THE MERCURY CATHODE

The method of the electrolytic reduction of rare-earth elements developed as a result of several studies carried out with different aims. In 1906 Matignon[2] isolated samarium(II) sulphate and in 1911 Urbain and Burion[3] isolated for the first time a europium(II) compound. In

1929 Klemm[4] gave a theoretical explanation of the "anomalous" valencies of the rare earths on the basis of Hund's spectroscopic investigations[5] and theories concerning the structure of rare-earth atoms, and demonstrated the existence of divalent ytterbium. At the present time the "anomalous" properties of rare-earth elements have been fairly adequately elucidated in a series of monographs[6-8].

Studies on the electrolysis of aqueous rare-earth solutions have served as a basis for the development of the method of their electrolytic reduction. Krüss[9] showed that in the electrolysis of aqueous rare-earth chloride solutions with platinum electrodes hydrochloric acid decomposes with the evolution of gaseous chlorine at the anode and of hydrogen and rare-earth hydroxides at the cathode. The decrease of the acidity of the solution observed in this process was subsequently used[10-15] for the separation of rare-earth mixtures by the fractional precipitation of their hydroxides or basic salts.

Yntema[16] replaced the platinum cathode by a mercury cathode and, by virtue of the high hydrogen overvoltage of mercury, achieved the reduction of europium and samarium to the divalent state in a mixture of their chlorides and gadolinium chloride. The divalent state of europium was stabilised by its precipitation as the sparingly solubles sulphate by a small amount of sulphuric acid. Ytterbium was isolated similarly[17]. Prandtl[18] suggested that the electrolysis be carried out directly in rare-earth sulphate solutions but the method used to stabilise the divalent ions in all the studies of this period[19-21] was the same. Electrolytic reduction of rare-earths in the presence of SO_4^{2-} ions gives a relatively low yield of the reduced element and cannot be used to obtain pure preparations of samarium and particularly of other rare-earth elements which do not have a stable divalent state.

A new development in studies in this field was begun by the work of Biltz and Mayer[21], who observed that metallic cerium dissolves in mercury with formation of an amalgam. This suggested the possibility of the preparation of other rare earths by electrolysis with a mercury cathode both in aqueous and in alcoholic solutions[22-25]. However, the electrolytic preparation of rare-earth amalgams is prevented by their precipitation as hydroxides (or basic salts) in the electrolysis of neutral or weakly alkaline solutions. This difficulty was overcome by McCoy[26,27], who suggested that the electrolysis be carried out in weakly alkaline solutions of organic acids (citric and tartaric), from which rare-earth hydroxides in the trivalent state are not precipitated. Under these conditions, rare earths from complexes with the acids, which have been thoroughly investigated and are widely used in analytical practice[28-33].

The method of electrolytic preparation of rare-earth amalgams, in contrast to the electrolytic reduction of rare earths in the presence of sulphate ions, excludes the possibility of the entrainment of the electrolyte solution (occlusion and sorption on the surface) and can yield pure preparations in a single operation. Furthermore, it is possible to select the conditions of electrolysis in such a way that almost all the rare earths can be deposited at a mercury cathode. Using Marsh's experimental data[24], Ryabchikov et al.[35] investigated in detail the effect of different factors on the deposition of ytterbium and increased the degree of its isolation to 93–98%, compared with 23% obtained by McCoy[26]. The electrolysis was carried out at 5°C, pH 6, cathodic current density 25 mA cm^{-2}, ytterbium concentration 0.5–1.0%, and molar ratio $Yb^{3+} : Cit^{3-} = 1 : 2$.

Onstott[36,37] succeeded in separating ytterbium quantitatively (99.98%) from solutions of heavy rare earths by increasing the duration of electrolysis to 8 h and by replacing the potassium amalgam by the lithium amalgam.

Europium was isolated under approximately the same conditions[38-43]. Shvedov and Fu I-pei[41-43] paid particular attention to the effect of the ligand and the alkali metal in the electrolyte as well as the pH of the solution on the degree of isolation of europium. They established that the rate of deposition increases in the sequence Trilon B [sodium salt of EDTA (Ed. of Translation)] > citric acid > > tartaric acid > succinic acid at pH 7.0, 6.8, 9.0, and 9.5 respectively. The yield of europium increases also on raising the current density, the temperature (to 30–40°C), and the pH of the solution (from 4.2 to 9.0 for citrate solutions) and on replacing the alkali metal in the sequence sodium < caesium < potassium < lithium.

Much work has been done on the electrolytic isolation of samarium[26,44-50]. The electrolysis was usually carried out[48] in a vessel similar to a separating funnel (Fig. 1) and fitted with a cooling jacket, a two-way tap, and a balancing flask designed to facilitate the renewal of mercury; the volume of solution was 10 ml, the pH was 6, the potential 8–12 V, and the initial current density 50–100 mA cm^{-2}. The electrolyte and mercury were mixed.

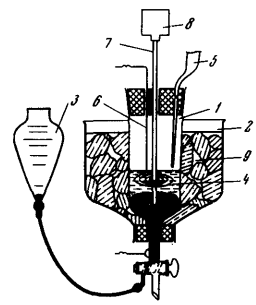


Figure 1. Apparatus for electrolysis with a mercury cathode[48]: *1*) electrolytic cell; *2*) cooling jacket; *3*) balancing flask with mercury serving as the cathode; *4*) initial solution; *5*) tube for the introduction of solution; *6*) platinum anode; *7*) stirrer; *8*) motor; *9*) mixture of dry ice and water.

For example, it was established that the degree of deposition of samarium increases with increasing current density, area of the cathode, the amount of mercury (and its renewal), and duration of electrolysis, and also when potassium ions are replaced by lithium ions; it decreases on raising the concentration of samarium (up to a certain limit) and its content in the amalgam[47-49].

It is interesting to note that the degree of transfer of samarium to mercury at a constant concentration of complex-forming ligand ($Sm^{3+} : CH_3COO^- : Cit^{3-} = 1 : 1 : 2$) is almost constant in the Sm^{3+} concentration range 6×10^{-3}–6×10^{-2} M, amounting to about 95%. At low concentrations (10^{-4}–10^{-6} M) the degree of its isolation is also high and constant even when the ratio $Sm^{3+} : Cit^{3-}$ is increased by a factor of 5000.

The conditions for the isolation of samarium, europium, and ytterbium in the form of amalgams by the electrolysis of their solutions containing complex-forming ligands (Table 1) were used also for the investigation of the behaviour of other rare earths at the mercury cathodes.

The isolation of promethium was first mentioned by Nauman and Heyne[45] and the conditions for the isolation of this element and other rare earths were investigated in detail in subsequent studies[42,47-53]. The optimum conditions for the isolation of certain rare earths are given in Table 2.

Table 1. Optimum conditions for the electrolytic reduction of ytterbium, samarium, and europium at a mercury cathode.

Rare earth	Cathodic current density, mA cm^{-2}	pH of medium	Type of amalgam	Temp., °C	Molar ratio Ln_2O : Cit^{3-}	Concn. of Ln_2O_3, %	Duration of electrolysis, min	Yield, %	Refs.
Yb	50	6,0	K	+5	1:2	1.5—2	60	93.2	35
Sm	100	5.8—6.0	K, Li	0—2	1:2.3	1.8	60	97.2	49
								99.7	47
Eu + Sm	12.6	8.4	Li	+20; +25	1:1.5	2.3	240	99.8	39
Eu	4.2	7.0	Li	+18	1:14	0.12	25	98.1	41
Eu	50	6.6	K	0—2	1:2	3.7—4.2	60	97.1	44

Table 2. Isolation of rare-earth elements (without a stable divalent state) by electrolysis at a mercury cathode (volume of electrolyte 10–25 ml; $c_{Ln^{3+}}$ between 10^{-7} and 10^{-8} M).

Rare earth	Optimum conditions for isolation						Refs.
	cathodic current density, mA cm^{-2}	pH of soln.	in the presence of alkali metal	temp., °C	duration of electrolysis, min	yield, %	
La	3.98	7	Li	30	60	99.5	43
Ce	3.98	7	Li	30	60	93.0	43
Nd	3.98	7	Li	30	60	79.2	43
Pm	3.98	7	Li	30	60	84.3	43
Pm	3.98	7	K	30	60	12.7	43
Pm[a]	100	6	K	0—2	90	83.5	47
Pm[b]	100	6	Li	0—2	60	96.7	47
Er	3.98	7	Li	30	60	18.5	43
Lu	3.98	7	Li	30	60	8.8	43

[a] Trace amounts. [b] In the presence of samarium (8.8 mg ml^{-1}).

Table 3. Effect of alkali metal amalgams on the isolation of certain rare-earth elements[42].

Amalgam	Yield, %								
	^{140}La	^{144}Ce	^{147}Nd	^{147}Pm	$^{152, 154}$Eu	^{91}Y	^{169}Er	^{175}Yb	^{177}Lu
Lithium	99.5	93.0	89.2	84.3	99.0	90.5	18.5	86.7	8.8
Potassium	—	18.0	37.0	12.7	98.7	19.8	11.0	76.1	7.5
Caesium	70.0	14.6	35.0	8.0	96.0	7.8	8.5	53.6	6.2

The type of alkali metal amalgam has the main effect on the yield of the rare earth (Table 3). Tables 2 and 3 show that lithium amalgam favours the most complete separation of the rare earth; cerium group elements are more readily isolated than the elements of the yttrium group (see also Fig. 2). The smallest yield is obtained with erbium and lutetium. The effect of the excess of complex-forming ligand and of the concentration of rare earths which do not have a stable divalent state on the degree of their separation is smaller than in the isolation of europium, ytterbium, and samarium. Differences of this kind are used for the enrichment and separation of rare earths,

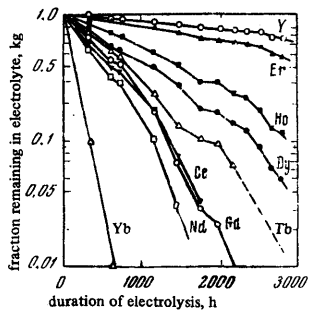


Figure 2. Dependence of the degree of liberation of certain rare-earth elements at a mercury cathode on the duration of electrolysis[46,88].

which can be divided into three groups as regards the relative ease of their electrolytic deposition at a stationary mercury cathode: (1) elements of the cerium group; (2) elements with a stable divalent state under the electrolysis conditions (europium, ytterbium, and samarium); and (3) elements of the yttrium group.

III. MECHANISM OF THE REDUCTION OF RARE-EARTH ELEMENTS

The mechanism of the reduction of rare earths at a mercury cathode was investigated mainly in two ways—in connection with the extraction of rare-earth elements by alkali metal amalgams and polarographically. In the first studies on the conditions of isolation of ytterbium at a mercury cathode[34,35] it was already shown that ytterbium is initially reduced to the divalent state and then to the metal, forming an amalgam with mercury. Somewhat later a similar mechanism was proposed also for the reduction of europium and samarium[38,41,47]. The two-stage reduction of europium, samarium, and ytterbium and also of certain other rare-earth elements is demonstrated by numerous facts, mainly by the presence of two waves in polarograms obtained at a dropping mercury cathode[54-62], corresponding to the consecutive reduction of triply-charged ions to doubly-charged species and then to the metal with formation of an amalgam.

More complex relations indicating a different cathodic process were obtained in other investigations[63-74].

It has been shown[41,47,50] that the transfer of samarium, cerium, and promethium to the mercury cathode is due to electrolytic reduction. However, in the electrolysis of acetate–citrate solutions more complex chemical reactions take place than was believed earlier[35]. The anions Ac^-, H_2Cit^-, $HCit^{2-}$, and Cit^{3-} form ionic complexes of different compositions with rare-earth cations. Their relative concentrations depend on the pH of the solution, the instability constant, and the ratio of the concentrations of the rare earths and the complex-forming ligands. The optimum conditions for electrolysis are thus directly related to the correct choice of ligand[32,33,43]. Apart from the rare earths, the alkali metal and hydrogen cations are reduced at the mercury cathode; the order of their reduction depends on the relative potentials and the pH of the solution. In the presence of complex-forming ligands the reduction potentials of the rare earths, which can be

estimated from the half-wave potentials (Table 4), are displaced towards more negative values and approach under the experimental conditions the reduction potential of alkali metal (Table 5). Consequently the efficiency of the deposition of rare-earth elements is related to the difference between the potentials of the alkali metal and the element being deposited. Thus in the presence of lithium, which has a more negative reduction potential than potassium, caesium, and sodium, the rate and degree of isolation of rare-earth elements are higher.

Table 4. Half-wave potentials of rare-earth elements[54].

Reaction	$E_{1/2}$, V	Composition of electrolyte
$La^{+3} \rightarrow La^0$	−1.92	in the presence of 0.01 M LiCl
$Ce^{3+} \rightarrow Ce^0$	−1.97	ditto
$Pr^{3+} \rightarrow Pr^0$	−1.75	in the presence of 0.1 M LiCl, 0.01% gelatine, and 2.5×10^{-3} M Pr^{3+}
$Pr^{3+} \rightarrow Pr^0$	−1.82	in the presence of 0.1 M LiCl, 0.01% gelatine, and 8.9×10^{-3} M Pr^{3+}
$Nd^{3+} \rightarrow Nd^0$	−1.81	in the presence of 0.1 M LiCl, 0.01% gelatine, and 4.1×10^{-3} M Nd^{3+}
$Nd^{3+} \rightarrow Nd^0$	−1.77	in the presence of 0.1 M LiCl, 0.01% gelatine, and 1.6×10^{-3} M Nd^{3+}
$Sm^{3+} \rightarrow Sm^{3+}$	−1.77	in the presence of 0.01 M LiCl, 0.01% gelatine, and 5.0×10^{-3} M Sm^{3+}
$Sm^{3+} \rightarrow Sm^0$	−1.96	ditto
$Eu^{3+} \rightarrow Eu^{2+}$	−0.78	in the presence of 0.01 M LiCl.
$Eu^{2+} \rightarrow Eu^0$	−2.14	ditto
$Gd^{3+} \rightarrow Gd^0$	−1.74	in the presence of 0.1 M LiCl and 8×10^{-4}M Gd^{3+}
$Tb^{3+} \rightarrow Tb^0$	−1.85	in the presence of 0.1 M LiCl and 0.005% gelatine
$Dy^{3+} \rightarrow Dy^0$	−1.85	–
$Ho^{3+} \rightarrow Ho^0$	−1.85	–
$Er^{3+} \rightarrow Er^0$	−1.85	–
$Tu^{3+} \rightarrow Tu^0$	−1.85	–
$Yb^{3+} \rightarrow Yb^{2+}$	−1.17	in the presence of 0.1 M LiCl, 0.005% gelatine,
$Yb^{3+} \rightarrow Yb^0$	−2.05	and 5×10^{-4}M Yb^{3+}
$Lu^{3+} \rightarrow Lu^0$	−1.8	–

Table 5. Standard potentials and half-wave potentials of alkali metals at the mercury electrode (relative to the saturated calomel electrode[75].

Metal	E^0, V	$E_{1/2}$, V	$E_{1/2}-E^0$, V
Li	−3.25	−2.26	+0.99
K	−3.16	−2.12	+1.04
Na	−2.99	−2.04	+0.95

Shvedov and Fu I-pei[42,43] give preference to amalgam cathodes. However, it is noteworthy that the deposition of rare-earth elements at a mercury cathode cannot be explained by simple replacement of alkali metal ions in the amalgam; this is confirmed by the data of Shvedov and Fu I-pei[41] concerning the constancy of the concentration of caesium in the solution during the electrolysis of europium. It is most likely that the efficiency of the isolation of rare-earth elements at an amalgam cathode is related, as mentioned above, to the difference between the potentials of the alkali metal and the element being isolated and that the alkali metal in the amalgam behaves as an additional reducing agent.

A large number of rare-earth amalgams obtained in electrolysis with a mercury cathode and by the extraction method have been investigated polarographically and electrochemically. For example, Barrett carried out the extraction of rare-earth elements with about 0.1% alkali metal amalgams from acetate media at pH 4 until the onset of precipitation of the hydroxide[63,64]. Lanthanum, cerium, praseodymium, and neodymium and also samarium, europium, and ytterbium were extracted. The results are presented in Table 6, which shows that the degree of extraction of the elements of the lanthanum–neodymium group decreases in the sequence lithium > sodium > > potassium, while the sequence for europium, samarium, and ytterbium is different: sodium > potassium > lithium, the degree of extraction also decreasing with decrease of the concentration of the alkali metal (Fig. 3). The measured potentials of most of the rare-earth amalgams prove to be lower than those of the corresponding alkali metal amalgams. This evidently accounts for Barrett's[63,64] observation of only single reduction waves at potentials in the range 1.84–2.04 V.

Table 6. Percentage extraction of rare-earth elements by potassium, sodium, and lithium amalgams[63] (c_{Ln} = 0.5 M).

Rare earth	Amalgam*		
	Li	Na	K
La	38	21	17
Ce	—	13	8
Pr	31	13	14
Nd	23	7	5
Sm	45	66	50
Eu	41	50	50
Yb	25	47	37

* 0.04 M amalgam was used.

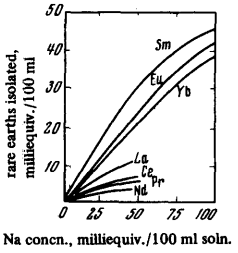


Figure 3. Variation of the degree of extraction of rare-earth elements with the concentration of sodium amalgam[56].

Samarium, europium, and ytterbium are extracted to a higher extent than elements of the lanthanum–neodymium group; the degree of extraction falls with increasing atomic number of the element and does not correspond to the stability of divalent ions in solution. This may be because rare-earth elements form with acetate ions complexes of indefinite composition and low stability, which is independent of the atomic number of the element[76], and also may be associated with hydrolytic phenomena. The size of hydrated rare-earth cations is known to increase with their atomic number[77], which accounts for the increasing tendency of rare earths towards hydrolysis on going from lanthanum to lutetium[78–80]. Biedermann and Giavatta[81] showed that in solution at pH ≥ 6.5 lanthanum is hydrolysed, forming ions of the type $La(OH)^{2+}$ and $La_2(OH)^{5+}$. In this connection, it is logical to expect the formation of

hydrolysed rare-earth species at a lower pH when the atomic number is higher. Thus hydrolysis, which includes also the formation of non-reducible polynuclear ions, can explain the observed tendency of the extraction coefficient to decrease with increasing atomic number. This can also account for the behaviour of non-extractable rare-earth elements:

$$Ln^{3+} + nH_2O + Na \rightleftarrows Ln(OH)^{2+} + Na^+ + H .$$

However, there is no direct proof of the formation of intermediate rare-earth ions in the extraction of elements of the lanthanum–neodymium group[82,83].

The data of Barrett et al.[64] supplement the classification of these elements given above. In extraction by alkali metal amalgams elements of the first group (lanthanum–neodymium) are reduced in one stage[64]. Since the extraction process is the sum of the electrochemical and hydrolytic processes and the tendency towards hydrolysis increases with the atomic number, three-electron reduction becomes impossible for samarium, europium, and ytterbium (second group), which are reduced in two stages. The third group (gadolinium–lutetium) does not have a divalent state and three-electron reduction can be achieved only under very severe conditions in view of the increasing tendency of these elements towards hydrolysis, and for this reason they are hardly reduced by alkali metal amalgams.

The reduction of samarium, europium, and ytterbium takes place in stages, the divalent rare-earth cations formed initially showing some similarity to the alkaline earth elements. In this case the degree of hydrolysis is low, since, for example, europium(II) hydroxide is appreciably soluble in an alkaline solution. Furthermore, divalent rare-earth cations are hydrolysed at higher pH, in contrast to the trivalent cations, which is important in their subsequent reduction to the metal under conditions of a higher hydroxide ion concentration near the cathode than in the bulk phase. This in fact explains why unhydrolysed rare-earth cations are capable of stepwise reduction by alkali metal amalgams in the opposite sequence, i.e. sodium > potassium > lithium.

Treindl[84] made a polarographic and oscillographic study of certain rare earths. On the basis of data showing the high reducing power of the reduction products obtained, the presence of hydroxide ions at the overvoltage potential[85], the dependence of the depth of the minima on the capacity of the anions for deformation and on their concentration, the dependence of the limiting current on the concentration of deformable anions, etc., he suggested that the reduction products are the hydrides and halide hydrides of the corresponding rare earths:

$$xH^+ + 2xe^- = xH^- ,$$
$$Ln^{3+} + xH^- + (3-x)X = LnH_xX_{3-x} ,$$
$$LnH_xX_{3-x} + x\,H_2O = Ln^{3+} + (3-x)X + xH_2 + xOH^- ,$$
$$H^+ + 2e^- + H_2O = H_2 + OH^- ,$$

where x = 1, 2, 3 and X is a halide ion. The quantitative proportions of the hydrides depend on the electrode potential.

It was established[86,87] that in the presence of 0.1 M lithium chloride at pH 4 all rare-earth elements give rise to a double reduction wave and are reduced irreversibly at a dropping mercury cathode; the diffusion-limited waves observed in some studies[65–74] can be caused by the reduction of hydrogen in the aquo-complexes of these elements:

$$Ln(H_2O)_6^{3+} \rightarrow Ln(H_2O)_{6-x}(OH)_x^{3-x} + xH ,$$
$$xH^+ + xe^- \rightarrow x/2\,H_2 ,$$
$$Ln(H_2O)_6^{3+} + xe^- = Ln(H_2O)_{6-x}(OH)_3 + x/2\,H_2 .$$

On the basis of data derived from the electrochemical separation of rare-earth elements at a mercury cathode in the presence of lithium ions and various complex-forming ligands (acetate, perchlorate, tartrate, and citrate ions), Onstott[88] explained the reduction of rare-earth elements (without a stable divalent state) by the formation of hydrides according to the following mechanism:

$$[Ln(H_2O)A_m]^{3+} + e^- \xrightarrow{\text{fast}} [Ln(H)(OH)A_m]^{2+}$$
$$\downarrow e^- \ (\text{slow})$$
$$[Ln(H)(OH)A_m]^+$$
$$[Ln(H)(OH)A_m]^+ + 2e^- \rightleftarrows LnH(Hg) + OH^- + mA.$$

It is noteworthy that the electrolytic reduction of rare-earth elements at a mercury cathode is still insufficiently elucidated. The data of the investigations quoted above make it possible to distinguish the following main types of cathodic processes.

Consecutive reduction to the metal with formation of an amalgam:

$$Ln^{3+} + e^- \rightarrow Ln^{2+} ,$$
$$Ln^{2+} + 2e^- \rightarrow Ln^0(Hg) .$$

Direct reduction of triply charged rare-earth ions to the amalgam:

$$Ln^{3+} + 3e^- \rightarrow Ln^0(Hg) .$$

Reduction with formation of hydrides and halides hydrides:

$$Ln^{3+} + xH^+ + 2xe^- + (3-x)X^- = Ln\,HxX_{(3-x)} .$$

Reduction of hydrogen in the aquo-complexes or in the hydrate shells of the rare-earth ions:

$$Ln(H_2O)x^{3+} + 3e^- \rightarrow Ln(OH)_3 + (x-3)H_2O + {}^3/_2\,H_2 .$$

For rare-earth elements without a stable divalent state, the last two types, in which the cathodic process is regarded as catalytic reduction of hydrogen ions, are the most likely; the mechanism of the catalysis consists in the formation and decomposition of hydrides[87].

IV. SEPARATION OF RARE-EARTH ELEMENTS

1. Conditions of Electrochemical Separation

The separation of rare-earth elements by electrolysis with a mercury cathode depends on the relative distribution of the rare-earths between mercury and the electrolyte. In other words, any parameter which influences the properties of the rare-earth elements in each phase will influence their relative distribution between the two phases[70]. For example, the formation of rare-earth complexes in the aqueous phase complicates the electrolysis. The degree of complication is greater the more stable are the complexes.

The equilibrium distribution of any trivalent element between the mercury phase and the electrolyte at 25°C can be formulated[46]‡ as follows in accordance with the Nernst equation:

$$E = E^a - 0.02\log(c^a/c^e) , \qquad (1)$$

where E is the cathode potential, E^a the standard potential of the amalgam, c^a the concentration of the rare earth in the amalgam, and c^e its concentration in the electrolyte.

‡ In the calculations account was not taken of the irreversibility of the cathodic-anodic behaviour of rare-earth elements. Nevertheless, they can be used for practical purposes.

The cathode potential E is the same for the electrode processes of any two rare earths (1 and 2) and therefore the distribution is described by the equation:

$$\Delta E = E_1^a - E_2^a = 0.02 \log (c_1^a \, c_2^e / c_1^e \, c_2^a) . \quad (2)$$

Eqn. (2) shows that the partition coefficient is a constant quantity, which depends only on the difference between the amalgam potentials (ΔE) of any two rare-earth elements. For example, a difference as low as $\Delta E = 20$ mV corresponds to a partition coefficient of 10.

To describe the separation of a mixture of trivalent rare-earth elements, data on standard electrode potentials can also be invoked, particularly if the amalgam potentials have been determined imprecisely. The amalgam potentials of rare-earth elements differ approximately to the same extent as their standard electrode potentials and therefore differences between the potentials of adjacent rare-earths of approximately 20 mV permit satisfactory separation, as stated.

For practical separation of two adjacent rare-earth elements, account must be taken of the purity and the yield of each element. For this purpose, it is necessary to determine the cathode potential from the known values of E_1^a or E_2^a, which can be done with the aid of Eqn. (2). It is also possible to predict whether or not the separation of divalent from trivalent rare-earths is possible. For the description of the reduction of divalent rare-earth elements, Eqn. (1) becomes

$$E_{II} = E_{II}^a - 0.03 \log (c_{II}^a / c_{II}^e) . \quad (3)$$

From Eqns. (1) and (3), we obtain

$$3E - 2E = 3[E^a - 0.02 \log (c^a/c^e)] - 2[E_{II}^a - 0.03 \log (c_{II}^a/c_{II}^e)]$$

and therefore

$$E = 3E^a - 2E_{II}^a - 0.06 \log \alpha , \quad (4)$$

where α is the separation factor, which depends on the cathode potential.

If equilibrium distribution is attained simultaneously for both electrode processes, the variation of E should be represented by a straight line. The time of attainment of a stable cathode potential after optimum equilibrium is reached is determined by the values of E^a and E_{II}^a. In the presence of a complex-forming ligand, Eqn. (2) becomes, from the law of mass action,

$$E_1^a - E_2^a = 0.02 \log \alpha + 0.02 \log \frac{K_{d_2}}{K_{d_1}} , \quad (5)$$

where K_d is the instability constant. If the ligand is a very powerful complex-forming agent, for example EDTA, separation may be difficult because of the high potential necessary to break down the complex.

Complex formation can alter the conditions of the deposition of rare-earth elements and can have a favourable effect on their separation when the complex-forming agent is chosen correctly [33,43].

As already stated, direct deposition of rare-earth elements at a mercury cathode depends on the distribution of their ions between mercury and the electrolyte [46,89] and on the rate of transfer of rare-earth ions through the electrode–electrolyte interface, which is defined by the following equation:

$$-\frac{dc}{dt} = \frac{DA}{V\delta}(c - c^e), \quad (6)$$

where c is the concentration of the diffusing ion in the electrolyte, c^e the concentration of the ion on the surface of the electrode, t the duration of electrolysis, D the diffusion coefficient, A the area of the electrode, V the volume of the electrolyte, and δ the thickness of the diffusion layer.

Integration of Eqns. (6) with $c^e = 0$ yields

$$\ln \frac{c}{c^0} = -\frac{DA}{V\delta} t , \quad (7)$$

where c^0 is the initial concentration of the ions in solution. The plot of ln c against t is a straight line with slope $DA/V\delta$, which can be regarded as a rate constant (k).

Rare-earth elements present in the electrolyte at low concentrations are hydrolysed at a rate which is mainly determined by diffusion in the region near the electrode [90–92]. The rate of diffusion depends in turn on the concentration at the mercury surface of the ions undergoing electrolysis. When $k = DA/V\delta$, Eqn. (7) is of the form

$$dN/dt = k \, c^s , \quad (8)$$

where N is the number of ions per unit area transferred during time t from the surface of the electrode on which the concentration of ions is c^s. [93] The rate of removal of c^s is determined by the quantity $D(dc/dl)$, where D is the bulk-phase diffusion coefficient of the ions and l the distance from the electrode. In a stirred solution the bulk-phase concentration c^b does not vary significantly with δ, so that

$$dN/dt = D(c^b - c^s)/\delta = k \, c^s . \quad (9)$$

Since c^b depends on time, we obtain

$$-\frac{dc^b}{dt} = \frac{dN}{dt} \times \frac{A}{V} = \frac{\frac{A}{V} \times D k \, c^b}{D + \delta k} . \quad (10)$$

At the extreme values of the parameters δ, D, and k, for example when $\delta k \gg D$, Eqn. (10) acquires the form of Eqn. (6), which reflects Fick's first law applied to electrode reactions [57]. When $\delta k \ll D$, we obtain $-dc^b/dt = (A/V)kc^b$. In this case $c^s \simeq c^b$ and the rate is almost independent of D and δ.

Eqn. (10)can be used to describe the rare-earth separation processes, and one can write

$$-\frac{dc^b}{dt} = \frac{A}{V} \beta \, c^b \quad (11)$$

where $\beta = Dk/(D + \delta k)$.

The ratio of the concentrations of the two rare earths in the electrolyte after a time t can be represented by the relation

$$\frac{c_2^b}{c_1^b} = \frac{c_2^0}{c_1^0} e^{\frac{A}{V}(\beta_1 - \beta_2)t} , \quad (12)$$

where c_1^0 and c_2^0 are the initial concentrations of the rare earths. This ratio is high for high values of t when $\beta_1 \gg \beta_2$.

Since the concentration of any of the two rare earths in the amalgam is defined as $c_i^a = (c_i^0 - c_i^b)V_e/V_a$, where V_e/V_a is the ratio of the volumes of the electrolyte and the amalgam, the ratio of the rare earths transferred to the amalgam is given by the equation

$$\frac{c_1^a}{c_2^a} = \frac{c_1^0\left(1 - e^{-\frac{A}{V}\beta_1 t}\right)}{c_2^0\left(1 - e^{-\frac{A}{V}\beta_2 t}\right)} . \quad (13)$$

For low values of t, the ratio $c_1^a/c_2^a \simeq (c_1^0/c_2^0)(\beta_1/\beta_2)$; for high values of t, when the electrolysis of both rare earths is almost complete, $c_1^a/c_2^a \simeq c_1^0/c_2^0$.

Knowing the rate of deposition of any two rare-earth elements at the mercury cathode and their partition coefficients between the two phases, it is possible to predict the efficiency of the separation of the rare earths. The partition coefficient of two rare-earths (1 and 2) deposited simultaneously at a mercury cathode depends on the ratio of their concentrations in the electrolyte (c^e) and in the amalgam (c^a), i.e.[88]

$$\alpha = \frac{c_1^a c_2^e}{c_2^a c_1^e} \quad . \qquad (14)$$

When c_1^a, c_2^a, c_1^e, and c_2^e from Eqns. (12) and (13) are substituted in Eqn. (14), we obtain

$$\alpha = \frac{[1 - e^{-\frac{A}{V}\beta_1 t}]}{[1 - e^{-\frac{A}{V}\beta_2 t}]} \times e^{\frac{A}{V}(\beta_1 - \beta_2)t} \quad . \qquad (15)$$

It follows from Eqn. (15) that, when $\beta_1 = \beta_2$, we have $\alpha = 1$ and there is no separation. For low values of t, $\alpha \simeq \beta_1/\beta_2$; when $t \to \infty$, we have

$$\log \alpha = \frac{At}{V \times 2.303}(\beta_1 - \beta_2) \quad . \qquad (16)$$

Eqn. (16) shows that, when the transfer of both rare earths to mercury is almost quantitative, the ratio of the concentrations of the rare earths remaining in the electrolyte becomes very high. In this case α may be very large compared with the value obtained under conditions of equilibrium separation where α is constant. Fig. 4 shows a plot of α (calculated with the values of β_1/β_2 adopted) for the transfer of rare earth 1 (Ln).

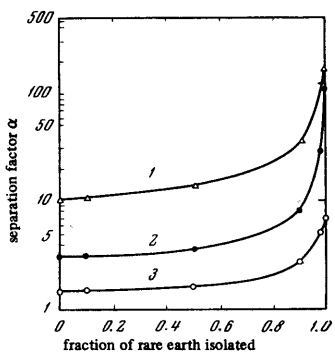


Figure 4. Variation of the separation factor α with the ratio β_1/β_2:[88] *1*) $\beta_1/\beta_2 = 10$; *2*) $\beta_1/\beta_2 = 3$; *3*) $\beta_1/\beta_2 = 1.5$.

In the separation of samarium and europium[8] the results obtained do not meet the requirements of equilibrium separation, but they can be used to obtain a general idea about the rate of the forward reaction. Thus it has been established that 90% of europium is extracted during 55 min of electrolysis of 20.4% of samarium after 230 min; then the ratio $\beta_1/\beta_2 = 42$. It follows from Eqn. (15) that, for 99 and 99.9% of extraction of europium, $\alpha = 856$ and 5570 respectively. These values agree fairly well with the measured α, which is respectively 974 for 99.2% extraction and 2810 for 99.9% extraction of europium[88].

More complete data were obtained in experiments on the separation of europium and samarium where the cathode potential was high and the extraction of europium was almost quantitative[46]; these are presented in Table 7, which shows that α increases rapidly when the degree of extraction of europium is high.

Table 7. Electrolysis of the citrate complexes of europium and samarium at a lithium amalgam cathode in alkaline solutions (cathode potential 2.3–3.0 V, t = 30–39°C)[88].

Extraction, %		α
Eu	Sm	
99.73	18.7	1600
99.83	17.6	2700
99.84	14.6	3700
99.95	26.2	5600
99.96	15.9	13 200

The rate equation for the reaction can be used also to determine the time required for the isolation of the rare earth (europium) at the required concentration[46]. It is noteworthy that better agreement between experimental and calculated data is observed for dilute solutions (Fig. 5, curve *2*).

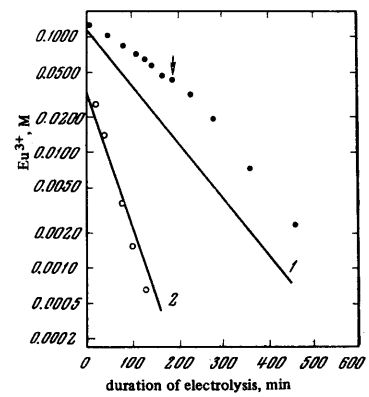


Figure 5. Electrolysis of europium solutions[46]: *1*) volume of electrolyte 498 ml, $c_{Eu^{3+}} = 0.12$ M, $c_{Sm^{3+}} = 0.37$ M; *2*) volume of electrolyte 285 ml, $c_{Eu^{3+}} = 0.039$ M, $c_{Sm^{3+}} = 0.32$ M (current density ~ 14 mA cm^{-2}; amount of mercury 150 ml). Circles—experimental data; straight lines—calculated data; the arrow indicates the renewal of mercury.

It is also possible to calculate α and β for rare earths without a stable divalent state. On the basis of experimental data for the electrolysis of trivalent rare-earth elements presented in Fig. 2, Onstott[88] obtained a series of values of the ratio β_1/β_2 (Table 8). Comparison with the observed and calculated values for a mixture of rare earths at a different concentration shows that β_1/β_2 is

almost the same and independent of the rare-earth concentration ratios in the mixture. The observed variation of β_1/β_2 with the separation factor α is shown in Fig. 4.

2. Examples of the Separation of Certain Rare-Earth Elements

On the basis of the conditions which they developed for the isolation of europium, ytterbium, and samarium, Ryabchikov and coworkers[35,40,44] described the possible ways of separating these elements. Europium can be separated from ytterbium by the electrolysis of their acetate–citrate solutions at high pH and it can be separated from samarium at an $Ln^{3+}:Cit^{3-}$ ratio $> 1:2$. Conditions have also been found for the isolation of ytterbium from a mixture of the elements of the yttrium group[94,95].

Table 8. The ratios β_1/β_2 for a methanol electrolyte containing rare-earth elements.

Rare earth	β_1/β_2 1 (initial mixture)	β_1/β_2 2 (enriched mixture)	Rare earth	β_1/β_2 1 (initial mixture)	β_1/β_2 2 (enriched mixture)
Nd—Gd	1.4	1.9	Dy—Ho	1.5	2.0
Gd—Tb	1.3	1.3	Ho—Er	2.5	2.0
Tb—Dy	1.3	1.5	Er—Y	1.6	1.2

Onstott[37] showed that lithium amalgam is best for the isolation of europium; when potassium citrate is replaced by lithium citrate, the yield of samarium changes only slightly[39]. Onstott notes that samarium, europium, and ytterbium can be separated from other rare earths (whose deposition at a mercury cathode requires more severe conditions) and also from one another if they are present at different concentrations. For example, for an initial ratio of europium and samarium of 1:62 (0.447 M samarium and 7.2×10^{-3} M europium), the concentration of the europium impurity in samarium can be reduced by a thousand-fold by electrolysis.

Shvedov and Antonov[52] investigated the conditions of the separation of samarium from neodymium and praseodymium at different concentrations of the elements (ranging from 0.1 to 1.34 M) in the presence of lithium tartrate at a current density of 15.5 mA cm^{-2}. The proportions of samarium, neodymium, and praseodymium were equimolar, i.e. 1:1:1. It was established that an increase of the concentration of lithium tartrate does not influence the liberation of samarium, and neodymium and praseodymium at tartrate concentrations of 0.4 and 0.7 M respectively do not form amalgams and are not liberated at the mercury cathode. Neodymium and praseodymium can be separated[52] at a current density of 7.7 mA cm^{-2} and a tartrate concentration of 0.34 M. Thus during 60 min electrolysis 47% of praseodymium and 1.5% of neodymium were liberated from 20 ml of solution at a 200 g mercury cathode; the separation factor was 58.

Clusius and Ramirez[96] used the slight differences in the mobilities of neodymium and praseodymium ions for the separation of the elements. Onstott[97] studied the possibility of the separation of the elements by the electrolysis of their chlorides in the presence of lithium citrate. The maximum separation factor in this process was 3.

Lavrukhina and coworkers made a detailed study of the conditions governing the liberation of samarium at a mercury cathode[47–50] and, using the differences in the behaviour of promethium, cerium, and other rare-earth elements, they proposed a method for their separation. In particular, on periodic addition of potassium citrate during electrolysis (the ratio $Ln^{3+}:Cit^{3-}$ decreases) or on renewal of mercury (the electrode potential remains constant and insufficient for the liberation of promethium and cerium), rare-earth elements without a stable divalent state remain in solution. This method was used for the separation of the products of nuclear reactions, the radioisotopes of lanthanum, cerium, praseodymium, neodymium, and promethium, from the main bulk of samarium and europium irradiated by protons having energies between 220 and 660 MeV.[48,49,98,99,100] Radioactive isotopes of the yttrium group elements were separated by the electrolysis of their acetate–citrate solutions from ytterbium irradiated with high-energy protons[101].

Shvedov and Antonov suggested a scheme for the separation of yttrium, ytterbium, and erbium, and lutetium, and also europium and lanthanum[42,43]. They investigated[53] the conditions for the formation of gadolinium, terbium, dysprosium, and holmium amalgams in the electrolysis with a mercury cathode of the acetate–citrate solutions in the presence of lithium ions. It was established that the concentration of lithium ions, the molar ratio $Ln^{3+}:Cit^{3-}$, and the concentration of the rare earths have a considerable influence on the yields of the elements. The optimum molar ratios $Ln^{3+}:Cit^{3-}$ are different for gadolinium, terbium, holmium, and dysprosium, amounting respectively to 12–15, 13, 26, and 17. The following separation factors have been found for binary mixtures of rare-earth elements[53]: 6–8 for gadolinium–terbium, 10–40 for gadolinium–holmium, 5–10 for terbium–dysprosium, 10–30 for terbium–holmium, 20–40 for terbium–erbium, and 30–60 for terbium–thulium. The yield of the rare-earth elements as a rule decreases with their concentration. For example, at a concentration in excess of 0.01 M holmium is not liberated at a mercury cathode; the transfer of dysprosium and terbium to the amalgam becomes negligible when their concentrations in the electrolytes are greater than 2.5×10^{-2} M and 4.0×10^{-2} M. This is associated with the smaller degree of dissociation of the complexes of these rare-earth elements as their concentration is raised.

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In the development of a number of new manufacturing processes and the current extensive application of semiconductor materials the problem of the preparation of ultrapure substances and the determination of many elements as impurities at very low concentrations (down to 10^{-10}%) has become particularly urgent[102,103]. In this respect electrolysis with a mercury cathode is one of the promising methods for the concentration of elements with their subsequent determination by different procedures.

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Some Electrochemical Properties of Mercury

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The first information about the application of mercury as an electrode material dates back to the end of the 19th century[1]. At the same time it was noted that mercury is not an indifferent metal and is capable of reacting with a number of ions in solution. Further extensive application of mercury as an electrode material stimulated systematic investigation of its electrochemical properties: electrocapillary phenomena at the mercury-solution interface, equilibrium and steady-state potentials, kinetics and mechanism of the discharge-ionisation process at the equilibrium and steady-state potentials, and reducing and other properties of mercury. These questions are discussed in the present review. The bibliography comprises 65 references.

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I. ELECTROCAPILLARY PHENOMENA AT THE MERCURY–SOLUTION INTERFACE

The electrical double layer arising under equilibrium conditions at the mercury–solution interface is known to consist of anions in the liquid component, the surface of the mercury being positively charged relative to the liquid. The displacement of the potential towards negative values leads to a decrease of the concentration of anions in the double layer. On further displacement of the potential, the charge of the double layer is reversed. The change in potential and the associated charge reversal of the double layer alters the surface tension of mercury.

The first measurement of the surface tension of mercury as a function of the applied potential was made by Lippman[2] with the aid of the capillary electrometer of his design. Paschen[3] and then Gouy[4,5] made systematic studies on the surface tension of mercury as a function of the potential in solutions of different electrolytes (hydrochloric acid, sulphuric acid, nitric acid, potassium hydroxide, etc.) and determined the form of the capillary curve. In all cases the dependence of the surface tension of mercury on the applied potential was represented by a curve passing through a maximum. The maximum surface tension corresponds to the zero charge of the mercury surface. The surface tension and correspondingly the surface energy of the electrode are a maximum at this point.

Adsorption of anions displaces the electrocapillary maximum towards more negative potentials, while adsorption of cations has the opposite effect. Anions can be arranged in the same depolarising effect sequence as that of their effect on the surface tension of mercury. Thus, in the series of anions $NO_3^- < SO_4^{2-} < Cl^- < Br^- < < CN^- < S^{2-}$ their depolarising effect increases from NO_3^- to S^{2-} and the shift of the electrocapillary maximum of mercury towards negative potentials increases in the same direction.

The nature of the anion influences not only the equilibrium or steady-state potential of mercury but also the essential features of the potential-determining process. Members of the Soviet electrochemical school have played