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Separation of the Lanthanons at Amalgam Cathodes. II. The Separation of Samarium from Gadolinium and Purification of Europium at a Lithium Amalgam Cathode[1]

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Samarium is efficiently separated from gadolinium by electrolysis of the citrate complexes at a lithium amalgam cathode. Separation factors varying between 340 and 6220 were calculated. The separation can also be done in acid solution at a *p*H of about 5 with citrate absent. Data were obtained which show how the electrolysis is dependent on the cathode potential and the *p*H of the electrolyte. Lithium amalgam is shown to be superior to sodium amalgam for the separation. It is shown that europium is electrolyzed into a lithium amalgam cathode at a rate approximately equal to that predicted when the parameters of electrolyte volume, cathode area, and temperature are changed. Europium of better than 99.9% purity was isolated from europium–samarium mixtures by proper control of the cathode potential.

The amalgam cathode separation of the lanthanons appears to offer unusual promise for rapid enrichment of specific lanthanons. The separation by this method depends on the relative distribution of the lanthanons between the mercury phase and the electrolyte phase. Consequently, any parameter which influences the property of a lanthanon in either phase will affect its relative distribution between the phases. Complexing of the lanthanons in the aqueous phase will make electrolysis more difficult, but the lightest lanthanon will be relatively more easy to electrolyze because of the increasing stability of the complex ions with increasing atomic number in the lanthanon series. Introduction of a soluble foreign metal into the mercury should change its solvent properties for each lanthanon and some effect on the separation would be anticipated.

It was on the basis of the latter argument—and the previous finding[2] that lithium amalgam dissolves relatively large amounts of samarium—that this work on the lithium amalgam cathode separation of samarium from gadolinium was done.

The previous work on the separation of europium from samarium[2] was extended to include a study of some of the parameters controlling the rate of electrolysis. A study of the separation of europium from the europium-rich fractions also was done.

Experimental

Experimental methods were about the same as described previously.[2]

Gadolinium oxide (90%), loaned by Charles E. Holley of this Laboratory, was purchased from Research Chemicals, Inc. Analysis with the Cary spectrophotometer with both 1 cm. and 10 cm. cells[3] showed it to contain 5.6% Sm_2O_3, 0.1% Nd_2O_3 and 2.5% Dy_2O_3. The Dy peak used was at 352 mμ, molar extinction coefficient 2.68, obtained experimentally with 400 mg. of 98.5% pure Dy_2O_3 (source not known). The amount of Gd_2O_3 present was found to be about the same spectrophotometrically[4] as by difference (91.8%). Hence, it was assumed that no other rare earth impurities were present.

For determining the small amount of samarium oxide left in the europium oxide, a differential spectrophotometric technique was used.[5] High purity europium oxide, purchased from Johnson, Mathy and Co., was converted to the chloride and placed in a 10-cm. cell in the reference beam of the Cary spectrophotometer. The unknown, containing approximately the same concentration of europium as the reference, was placed in the sample beam. By this technique the europium spectrum was compensated and the samarium peak (when present) could be measured directly. In a test of the method, a sample known to contain 4.1% Sm_2O_3 by tracer measurements, was found to contain 3.9% Sm_2O_3 by differential spectrophotometric measurements.

In previous work an electrolysis vessel was used which allowed a mercury surface area of 55 cm.^{2}. A larger vessel with an area of 106 cm.^{2} also was used in this work.

Samarium tracer, Sm^{153} (47 hr. half-life), was obtained by irradiation of 150 mg. of 99.98$^+$% pure oxide in the Los Alamos Water Boiler. The tracer was followed by counting liquid samples in a scintillation counter.[2] In the europium–samarium separation, europium tracer was used as before.

Discussion

The equilibrium distribution of a simple ion between mercury and the electrolyte as a result of electrolysis has been discussed by Rogers.[6] The specific case for trivalent lanthanons is described here.

For a trivalent lanthanon the equilibrium distribution between the mercury phase and the electrolyte phase at 25° is given approximately by the simplified Nernst equation in which activity coefficients are neglected

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

E is the cathode potential, E^a is the standard amalgam potential, C^a is the amalgam concentration of lanthanon, C^e is the electrolyte concentration of lanthanon.

When two lanthanons are being electrolyzed simultaneously, each may be assumed to act independently. Equation 1 describes the behavior of each. Since the cathode potential has a common value for both electrode processes, the distribution of lanthanons 1 and 2 at cathode potential E is described by

$$E_1^a - E_2^a = 0.02 \log C_1^a C_2^e / C_1^a C_2^e \qquad (2)$$

It is seen that the combination of concentration terms in equation 2 is the same as the separation factor which is commonly used to describe solvent extraction and ion-exchange separations.

Equation 2 shows that the separation factor is a constant which depends on the difference in amalgam potentials between the two lanthanons, and not on the value of the cathode potential. Thus for a difference of only 20 mv. in amalgam potentials, a separation factor of 10 is predicted.

An idea of the separability of trivalent juxta-lanthanons can be ascertained by looking at the value of the standard electrode potentials. Amalgam potentials are not known with sufficient accuracy to be used. However, the amalgam potentials should

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(1) Work done under the auspices of the Atomic Energy Commission.

(2) E. I. Onstott, THIS JOURNAL, **77**, 2129 (1955).

(3) T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950).

(4) T. Moeller and F. A. J. Moss, THIS JOURNAL, **73**, 3149 (1951).

(5) M. Beroza, *Anal. Chem.*, **25**, 112 (1953).

(6) L. B. Rogers, *J. Electrochem. Soc.*, **99**, 267 (1952).

vary in somewhat the same manner as the standard electrode potentials. The difference in potentials between juxta-lanthanons is the order of 20 mv.[7]; consequently, with relatively few electrolyses, it should be possible to separate pairs of lanthanons if sufficient quantities can be electrolyzed as to be practical.

For a practical separation of two lanthanons, the purity and yield of each must be considered. Equation 1 may be used to determine the proper cathode potential for obtaining the desired result. The cathode potential should be set close to the value of E^a_1 or E^a_2, depending on the relative amount of each lanthanon. For example, if the cathode potential were set at say 1 volt more negative than the most negative amalgam potential, then at equilibrium practically all of each lanthanon would be electrolyzed. The enrichment would take place in the electrolyte, but the quantity of enriched lanthanon would be so small as to be inconsequential. On the other hand, if the cathode potential were set at a value close to zero, then the enrichment would take place in the mercury, but the amount of enriched lanthanon would not be measurable. Equal simultaneous enrichment of both phases is attained at a cathode potential half-way between E^a_1 and E^a_2.

The separation of a divalent lanthanon from a trivalent lanthanon should be considered also. For the reduction of a divalent lanthanon, equation 1 becomes

$$E_{II} = E^a_{II} - 0.03 \log C^a_{II}/C^e_{II} \qquad (3)$$

Combination of equation 1 and equation 3 gives

$$3E - 2E = 3(E^a - 0.02 \log C^a/C^e) - 2(E^a_{II} - 0.03 \log C^a_{II}/C^e_{II})$$

which simplifies to

$$E = 3E^a - 2E^a_{II} - 0.06 \log \alpha \qquad (4)$$

Here the separation factor α depends on the cathode potential, and a semilog plot of α *vs.* E should give a straight line if an equilibrium distribution is achieved simultaneously for both electrode processes. The values of E^a and E^a_{II} determine where the cathode potential should be set to achieve an optimum separation.

The effect of a ligand other than water on the separation of two trivalent lanthanons can be depicted as follows (the reader will correct for ionic charges)

$$R^{+++} + mL \rightleftharpoons RL_m^{+++}$$

$$C^e = \frac{K_d[RL_m]}{[L]^m}$$

where K_d is the dissociation constant, and brackets indicate concentrations.

$$C^e_1/C^e_2 = \frac{K_{d_1}[R_1L_m]}{K_{d_2}[R_2L_m]}$$

Substitution of the above expression in (2) and assuming that the concentration of uncomplexed lanthanons is negligible gives

$$E^a_1 - E^a_2 = 0.02 \log \alpha + 0.02 \log K_{d_2}/K_{d_1} \qquad (5)$$

The substitution of different ligands for water may change the value of K_{d_2}/K_{d_1}, but gross changes would not be expected because of the definite basicity trend in the trivalent lanthanons. If the ligand is a very strong complexing agent (for example, ethylenediaminetetraacetate ion) the separation may become impractical or impossible because of the high potential required for electrolysis.

Complexing can have an adverse effect on separations, especially if the heavier lanthanon is more easily electrolyzed. Complexing increases the potential required for electrolysis, but a greater increase for the heavier lanthanon would be expected so that the inherent difference due to the amalgam potentials would be partially compensated.

The standard amalgam potential is related to the standard electrode potential (reduction potential) and the free energy of amalgamation of the lanthanon[8]

$$E^a = E^m + E^s + RT/3F \ln A^s \qquad (6)$$

where E^m is the standard potential, E^s is proportional to the free energy change associated with solid compound or solid solution formation of the lanthanon with mercury, and A^s is the activity of the lanthanon in the solid phase. All of the parameters in equation 6 are fixed at a given temperature. Therefore, there is an inherent separation factor between two lanthanons which are soluble in mercury.

The amount of a lanthanon which is electrolyzed at a given potential may be increased by changing the value of the free energy of amalgamation by introduction of a third component into the amalgam. Lithium has been found to be superior to potassium as an amalgam cathode for the separation of europium from samarium.[2]

Rate phenomena at mercury cathodes are sufficiently well understood to be used to advantage in separations. It was shown previously[2] that a lanthanon present in the electrolyte in small concentrations is electrolyzed at a rate controlled primarily by diffusion. However, if the concentration is large, the rate is decreased by the high concentration of electrolyzed lanthanon at the mercury surface. Thus, if two lanthanons are present in amounts which are quite different, then the minor constituent, if more easily electrolyzed, is relatively more rapidly electrolyzed and a greater enrichment of both phases is achieved.

Discussion of Results

Part I. The Separation of Samarium from Gadolinium. Electrolyses at a Lithium Amalgam Cathode with Citrate Present.—When the electrolysis is started with an electrolyte with a *p*H of about 5.5 (plots A and B), the cathode potential is less negative than at higher *p*H values because the hydrogen discharge consumes a relatively large part of the current through the cell. As the electrolysis progresses, the amount of hydrogen ion in the electrolyte diminishes, and the *p*H goes up. Simultaneously the cathode potential becomes more negative because of less hydrogen discharge. When the *p*H of the electrolyte is purposely kept low and reasonably constant as shown by plot B in Fig. 1, the cathode potential also becomes constant and stays at a less negative value than at

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[7] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, p. 291.

[8] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1952, p. 199.

higher *p*H values. Above a *p*H of about 7 the cathode potential is practically independent of *p*H and depends primarily on the current put through the cell.

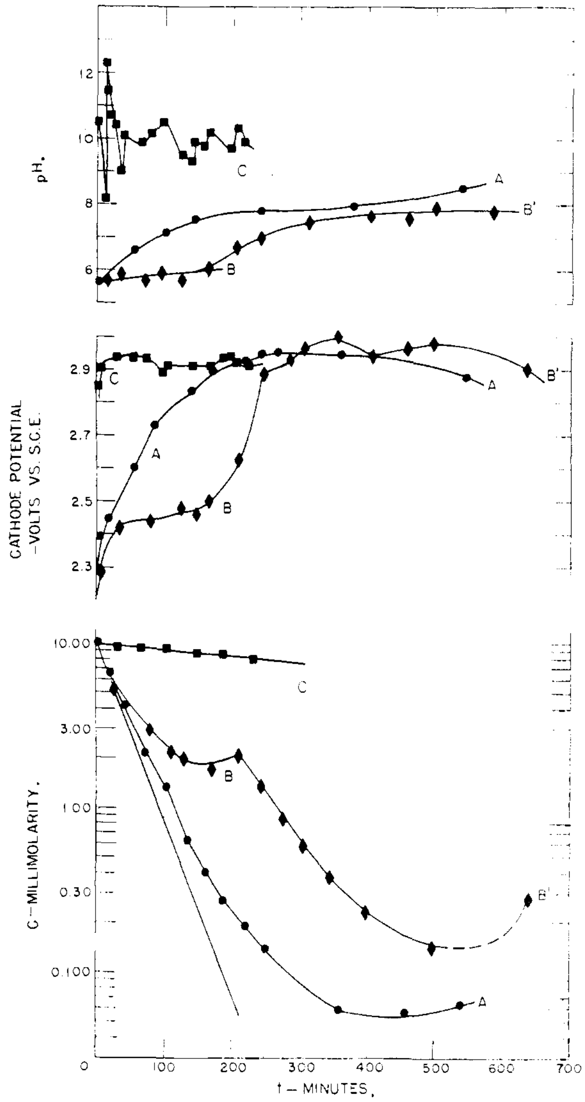

Fig. 1.—Electrolysis of samarium at a lithium amalgam cathode with citrate present in the electrolyte. Effect of *p*H and cathode potential on the electrolysis. See Table I for experimental details. The *p*H of B was controlled by adding glacial acetic acid. The *p*H of C was kept high by adding lithium hydroxide.

The cathode potential required to electrolyze samarium is dependent upon the amalgam potential of samarium ion and the free energy of complex formation with citrate ion. Since the citrate ion concentration varies with *p*H, then the potential required to electrolyze samarium also varies. However, the citrate ion concentration varies only by a factor of about two in going from a *p*H of 5.5 to the *p*H of 100% ionization. Hence the effect of change of the citrate ion parameter can be neglected.

For an electrode potential sufficiently negative, the rate of electrolysis of samarium ion complexed by citrate should not be much different than that for europium ion under the same conditions. However, it is more difficult to get ideal behavior for samarium because of the more negative potential required for electrolysis. It was shown previously[2] that the electrolysis of europium is controlled primarily by diffusion, and a plot of the log of the electrolyte concentration *versus* time should give a straight line. Plots A and B show that during the first part of electrolysis the deviation from a straight line is not great. However, as the electrolysis progresses and the working potential of the cathode approaches the equilibrium potential required for electrolysis, the deviation is considerably greater.

The tenth-time taken from the line in plot A is 90 minutes (time to remove 90% of the samarium), which compares favorably with the value of 55 minutes obtained for europium under similar experimental conditions.[2] Thus it is reasonable to assume that the rate controlling parameters for electrolysis of samarium and europium are the same.

Plot C in Fig. 1 shows the effect of keeping the *p*H high with lithium hydroxide. The slope of this plot is similar to that obtained when europium was electrolyzed at a potassium amalgam cathode.[2] Since the citrate concentration is constant above a *p*H of about 7.5, then citrate should not be the parameter controlling the low rate of electrolysis. However, hydroxide ion is present in relatively high concentration. A hydroxo-citrate complex ion of samarium is probable,[9] and this species could account for the lower rate by requiring a higher cathode potential for electrolysis.

The distribution of samarium between the two phases follows rather closely the cathode potential. An equilibrium distribution is established when the cathode potential remains constant for a long enough period of time. It is also apparent that the tailing up in plots A and B resulted from the respective change in the cathode potential.

Electrolyses with Citrate Absent.—Several experiments were done in order to show the value of citrate in keeping the lanthanons from precipitating in basic solution and in allowing a higher cathode potential for the separations.

Close *p*H control was necessary for successful electrolyses. When the *p*H was less than 5, hydrogen discharge was excessive and the cathode potential was unnecessarily low. If the *p*H was allowed to rise above about 5.75, the solution began to froth, the resistance increased, and the cathode potential became less negative. This phenomenon is attributed to a change in the ionic species by coordination with oxo or hydroxo ligands.

Plot D shows that the samarium distribution between the mercury and electrolyte follows closely the lithium amalgam cathode potential. Removal and replacement of the mercury, as represented by the discontinuity, results in a repeat of the electrolysis. A practical consideration of the mechanics of separating the phases is demonstrated here. After removal of the mercury, there was a gain in activity (samarium) in the electrolyte. There must have been a separation of part of the electrolyzed

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[9] E. I. Onstott, This Journal, **74**, 3773 (1952).

samarium from the mercury prior to its removal. Undoubtedly what happened was that droplets of electrolyte were trapped underneath the mercury as a result of the stirring, and the samarium went back into solution in these droplets. Removal of the mercury then allowed mixing with the main electrolyte. In a practical separation, if the electrolyte is the purified phase, then the electrolyte, rather than the mercury, should be removed prior to turning off the current.

The cathode potential attainable without citrate present is about half a volt lower than the citrate present, since the electrolysis can be run only in acid solution. Plot E shows the effect of lowering the current and at the same time lowering the cathode potential. Less samarium is electrolyzed.

In complexing the lanthanons, citrate ion increases the potential required for electrolysis, but evidently the increase required is less than the gain in potential attained by the use of alkaline solutions. Thus the detrimental effect of complexing is more than offset by the gain in the amount of samarium electrolyzed when citrate is used in conjunction with the lithium amalgam cathode.

Work by Marsh[10] showed that sodium amalgam is quite effective for separating some of the lanthanons. A sodium amalgam cathode was tried here under similar experimental conditions. Plot F shows the results of an electrolysis run at two different current densities. The magnitude of the cathode potential is practically the same as with lithium at the same current density. Less samarium is electrolyzed at the sodium amalgam cathode; hence, lithium amalgam has some advantage over sodium amalgam.

Separation Factors.—The data in Table I show that the separation of samarium from gadolinium is quite good, though not as good as the separation of europium from samarium. For the latter separation, a separation factor as large as 2.6 × 10^4 was calculated for the removal of a small amount of europium from a large amount of samarium, although the separation factor for removal of a large amount of europium from a small amount of samarium was much smaller (see Part II).

TABLE I

ELECTROLYSIS OF SAMARIUM

Composition of solutions: Gd^{+++}, 0.158 *M;* Sm^{+++}, 0.010 *M;* Dy^{+++}, 0.0042 *M;* Li^+, 0.75 *M;* acetate, 0.55 *M;* citrate, 0.25 *M*. Amount of solution, 200 ml.; amount of Hg, 100 ml.; cathode area, 106 $cm.^2$; temperature, 24 ± 2.5°.

Plot	Electrolyte *p*H	C.D. amp./$cm.^2$	% Sm electrolyzed[a]	% Gd electrolyzed[b]	α
A	See plot	0.014	99.4	10.4	1570
B	See plot	.014	98.5	9.8	604
	9.7–7.5	.014	97	8.4	340
C	See plot	.014	20	Not analyzed	..
	5.4–7.8	.010	99.5	3.1	6220
	5.4–7.8	.014[c]	95	1.0	1880
D	5.3 ± 0.5	.014[d]	76	0.2	1580
D'	5.3 ± .5	.014[d]	70	<0.1	>2300
E	5.3 ± .5	.007[d]	20	Not analyzed	..
E'	5.3 ± .5	.010[d]	57	Not analyzed	..
F	5.3 ± .5	.010[e]	2	Not analyzed	..
F'	5.3 ± .5	.014[e]	50	Not analyzed	..

[a] Determined from rate plot. [b] Determined colorimetrically with Cary spectrophotometer. [c] Temperature 35 ± 2°. [d] No citrate present; Li^+, 0.8 *M;* acetate, 1.35 *M*. [e] No citrate present; Li^+ replaced with 0.8 *M* Na^+; acetate, 1.35 *M*.

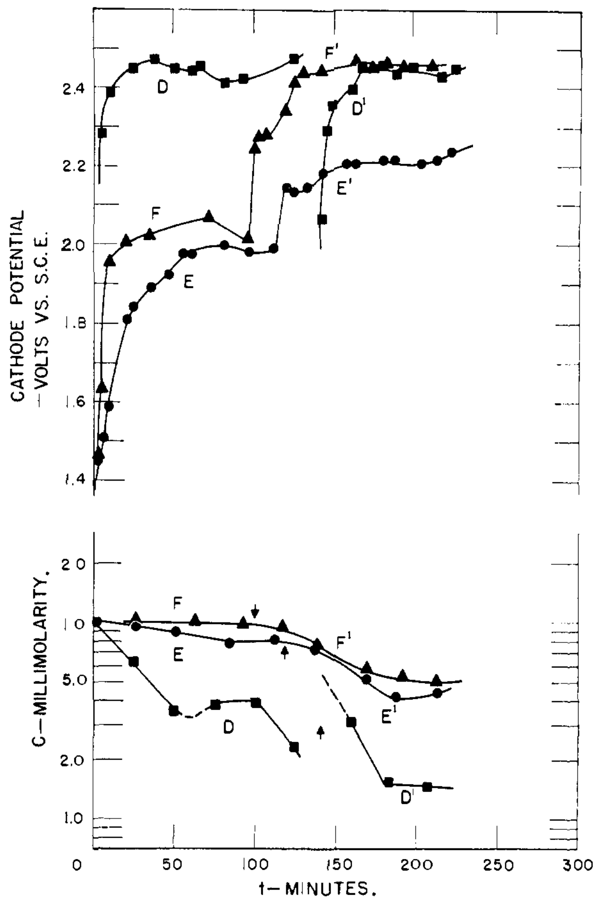

Fig. 2.—Electrolysis of samarium at lithium amalgam and sodium amalgam cathodes with acetate present in the electrolyte and citrate absent. Arrow on E and F represent an increase in current density. Arrow on D represents removal and replacement of mercury. See Table I for experimental details.

Samarium(II) ion is sufficiently stable in aqueous solution to be produced in measurable quantities at a dropping mercury electrode.[11] However, the potential shift due to the enhanced complexing of samarium(III) over samarium(II) with citrate should be sufficient to make the samarium(II) complex ion unstable, and the reduction should go by direct reduction of the trivalent ion to the amalgam. A potential shift of less than 0.2 volt would be required for the latter process to predominate.[11] The potential shift of the europium(III)–europium(II) reduction due to complexing with ethylenediamine tetraacetate is about 0.6 volt.[9] As large a shift would not be expected for the samarium citrate couple, but certainly it should be greater than 0.2 volt.

With both samarium and gadolinium behaving as trivalent lanthanons, then the separation factor should be a constant if both reach an equilibrium

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(10) J. K. Marsh, *J. Chem. Soc.*, 398 (1942); 523, 531 (1943).

(11) A. Timnick and G. Glockler, THIS JOURNAL, 70, 1347 (1948).

distribution at the time of the separation. The variation in the separation factor as shown by the data in Table I suggests that gadolinium had not reached an equilibrium distribution between the phases when the separations were made. The separation factors obtained are larger than would be expected for equilibrium separations, since the samarium is electrolyzed at a more rapid rate than is gadolinium.

Complexing should enhance the separation of samarium from gadolinium by making the gadolinium relatively more difficult to electrolyze. Equation 5 shows that a dissociation constant for gadolinium which is smaller by a factor of ten than that for samarium would make the separation factor larger by a factor of 10. Although separation factors were obtained for both citrate present and citrate absent, they show no trend, since equilibrium data were not obtained. The separation with citrate absent is also quite good, but is not practical because of the necessity of continually adding acid when acetate is present.

The lanthanons which were electrolyzed into the amalgam cathodes in the experiments represented by the first six entries in Table I were analyzed with the Cary spectrophotometer after combining all of the cathode fractions. Only samarium and gadolinium were detected with a 10-cm. cell. The amount of neodymium present in this 40–60 mixture of samarium–gadolinium was <0.04%, and the amount of dysprosium was <0.3%. Thus neodymium and dysprosium are preferentially left in the electrolyte and a separation of gadolinium from dysprosium and from neodymium is also effected.

Oxidation of Acetate.—The fact that it was necessary to add acetic acid to electrolytes containing no citrate in order to maintain the *p*H at a constant value is direct evidence that acetate ion is oxidized at the platinum anode. Just from a consideration of the expected electrode reactions, *i.e.*, the oxidation of water at the anode, reduction of hydrogen ions at the cathode and the electrolysis of lithium or sodium ions at the cathode, the net electrode reactions should give a decrease in *p*H, which is exactly the opposite of that found experimentally. However, if acetate ion were oxidized at the anode in a Kolbe reaction,[12] then hydrogen ions would be consumed at the cathode in excess of those produced at the anode

$$\text{Anode: } 2CH_3COO^- \longrightarrow C_2H_6 + 2CO_2 + 2e^-$$
$$\text{Cathode: } 2H^+ + 2e^- \longrightarrow H_2$$
$$\text{Net: } 2CH_3COO^- + 2H^+ \longrightarrow C_2H_6 + 2CO_2 + H_2$$

Part II. The Purification of Europium. Separation Factors for Dilute Europium Solutions.—A larger electrolysis vessel was used than that used in previous experiments[2] in order to study the effect of a change in the cathode area and a change in the volume of electrolyte (discussed in the following section). A secondary effect of this change was the more negative cathode potential attainable with the same applied potential of about 8 volts. Evidently this change resulted from a lower cell resistance. Table II shows that cathode potentials as negative as −2.9 volts *vs.* S.C.E. were measured.

In some experiments the amount of europium electrolyzed into the amalgam was larger than previously observed. This increase is attributed to the more negative cathode potential.

Separation factors vary considerably, and there appears to be no definite trend. Actually the experiments depicted in Table II were designed for a maximum removal of europium rather than for a maximum separation factor, since the samarium is recovered from the electrolyte as the pure component. The separation factors calculated have little meaning on the basis of equilibrium experiments, since in each electrolysis the mercury was once removed and replaced to enhance the europium removal. However, the separation factors are useful for comparison to other lanthanon separations.

TABLE II

ELECTROLYSIS OF DILUTE SOLUTION OF EUROPIUM

Composition of electrolyte: Sm^{+++}, 0.44 *M;* Eu^{+++}, 0.0066 *M;* citrate, 0.90 *M;* Li^+, ~ 3.3 *M;* acetate, ~ 1.5 *M;* initial *p*H, 8.2–9.7. Cathode area, 106 cm.²; amount of Hg, 150 ml.; Hg removed and replaced after >95% removal of Eu; C.D., 0.014 amp./cm.².

Temp., °C.	Electrolyte, vol., ml.	Cath. pot., v. *vs.* S.C.E.	Amp., hr.	% removal of Eu[a]	% removal of Sm	$\alpha \times 10^{-3}$
33 ± 3	600	2.82–2.92	35	99.95	26.2	5.6
34 ± 1.5	900	2.82–2.92	34	99.73	18.7	1.6
35 ± 4	200	2.75–2.95	7.5	99.84	14.6	3.7
38.5 ± 0.5	200	....	8.3	99.96	15.9	13.2
35 ± 3	200	2.33–2.40[b]	9.0	99.83	17.6	2.7
40 ± 1.5	200	2.73–2.83[b,d]	10.5	99.94	15.2	9.3
20–33[c]	800	....	36	99.95	13.5	12.8
20–31[c]	885	....	34	99.95	7.2	25.8

[a] Accurate to within 0.02%. [b] Cathode area, 55 cm.². [c] No control of temperature. [d] Current density, 0.027 amp./cm.².

A higher temperature does not appear to change the separation very much. For practical separations, there is no need for close temperature control.

Enrichment and Purification of Europium.—During the course of electrolyzing samarium solutions to remove the europium, about 1.5% Eu_2O_3 in 1.2 kg. of Sm_2O_3–Eu_2O_3 was enriched to about 17% Eu_2O_3 in 102 g. of Sm_2O_3–Eu_2O_3. Thus with one electrolysis the europium was enriched about eleven-fold in the mercury phase. The samarium recovered from the electrolyte (91% of the initial amount of impure oxide) contained <0.005% Eu_2O_3.

Re-electrolysis of the enriched europium at a lithium amalgam cathode further enriched it to 87–99% purity. A third electrolysis gave a good yield of high purity europium as shown by the data in Table III.

The data in Table III indicate that possibly equilibrium conditions for the separation are approached. The europium–samarium pair offer the opportunity of studying the separation of a divalent lanthanon from a trivalent lanthanon. However, the data obtained are not of such a nature as to be interpreted on this premise. The concentration of europium is undoubtedly too high to study the separation ideally, since the free energy of amalgamation of samarium probably is changed by the pres-

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(12) S. Swann, Jr., "Electrolytic Reactions," "Technique of Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1948, p. 195.

ence of the large amount of europium in the amalgam.

TABLE III

PURIFICATION OF EUROPIUM

Cathode potential,[a] v. *vs.* S.C.E.	Purity of starting Eu_2O_3	Purity of separated Eu_2O_3	% Eu Electrolyzed	α
2.04	87.0[b]	>99.9	79.4	>723
2.05	98.3[b]	>99.9	82.0	> 91
2.05	99.1[b]	>99.9	79.3	> 39
2.06	33.9[c]	98.0	68.2	286
2.90	25.0[c]	94.4	>95	>990

[a] Potential at conclusion of electrolysis. [b] Enriched by two previous electrolyses. [c] Mixed fractions—some electrolyzed once, some electrolyzed twice previously.

Rate of Electrolysis of Dilute Europium Solutions.—It was shown previously[2] that the equation[13]

$$-\ln C/C^\circ = \frac{DA}{V\delta}t$$

adequately describes the rate of electrolysis of the europium. The parameters *D* (diffusion coefficient), *A* (electrode area), *V* (electrolyte volume), and δ (diffusion layer thickness) all influence the change of the electrolyte concentration of europium, *C*, with respect to time, *t*.

The rate equation is conveniently used as a tenth time function.

By setting C/C^0 equal to one-tenth, and solving for *t*, then the time required to remove 90% of the europium from solution is ascertained—base ten logarithms being used. Multiplication of the tenth-time by two gives the time to remove 99%, and multiplication by three gives the time for 99.9% removal. The tenth-time is conveniently taken directly from a semi-log plot of *C vs. t*.

In Table IV are given data which show the changes in the value of the tenth-time, t_x, as several parameters are changed. Fair agreement is obtained when these values are compared to the values expected according to the rate equation.

TABLE IV

EFFECT OF ELECTROLYTE VOLUME, CATHODE AREA AND TEMPERATURE ON THE RATE OF ELECTROLYSIS OF EUROPIUM

See Table II for experimental conditions. Rate data obtained only during the first half of the electrolysis prior to removal and replacement of the Hg.

Temp., °C.	Electrolyte vol., ml.	Cathode area, cm.²	Increase in *D*, %[a]	t_x, min. measured	t_x, min. calcd.
22.5 ± 1	200	55	..	122[b]	..
35 ± 3	200	55	25	93	98
40 ± 1.5	200	55	35	62[c]	90[c]
35 ± 4	200	106	25	46	51
38.5 ± 0.5	200	106	32	40	48
33 ± 3	600	106	21	198	157
35 ± 1.5	900	106	23	265	232

[a] Taken to be 2% per degree. [b] Value obtained in previous work[2] and used for finding the reference value of *DA*/*V*δ. Current density 0.0126 amp./cm.². [c] Current density, 0.027 amp./cm.². No allowance made for the effect of increased gas evolution and stirring causing a decrease in the value of δ.

Rigorous adherence of the data to the rate equation would not be expected because the value of δ was assumed to be constant. An exact treatment of the diffusion problem as done by Delahay[14] is not justified here because of the stirring of the electrolyte, both mechanically and by the gas evolution.

Rate of Electrolysis of Concentrated Europium Solutions.—It was pointed out previously[2] that the simple rate equation above may not be valid when the concentration of europium in solution is high. For this condition, the concentration of europium at the electrode surface is not zero. The europium is reduced in such quantity that the mercury surface concentration of reduced europium is high. Hence, the back reaction must be considered, and the potential of the cathode is primarily determined by the europium.

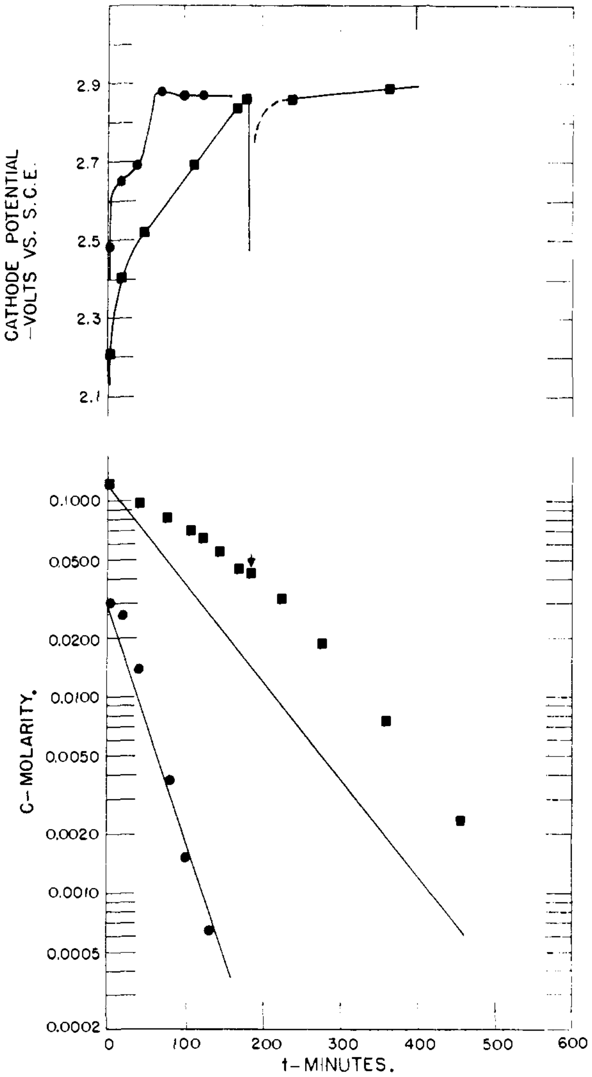

Fig. 3.—Electrolysis of concentrated europium solutions. Variation of cathode potential with time: lower plot, electrolysis of 285 ml. of 0.039 *M* Eu^{+++}-0.32 *M* Sm^{+++}; upper plot, electrolysis of 498 ml. of 0.12 *M* Eu^{+++}-0.37 *M* Sm^{+++}. Arrow represents removal and replacement of mercury. Other experimental conditions were about the same as described in Table II. Lines represent expected rates for dilute Eu^{+++} solutions.

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(13) J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1953, p. 193.

(14) P. Delahay, THIS JOURNAL, **75**, 1430 (1953).

In Fig. 3 are plots showing the rate of electrolysis with two different initial concentrations of europium. With the smaller initial concentration of europium, the deviation from ideality was great only at the beginning of the electrolysis. Thus the deviation must have been caused by a high concentration of europium ion at the amalgam surface. With the higher initial concentration, the rate did not become normal until after the amalgam was removed and replaced. Here the average concentration of europium in the bulk amalgam as well as the concentration of the europium in the amalgam surface was high prior to the time amalgam was removed.

The upper plots in Fig. 3 show the change in cathode potential with time at constant current density. The potential during the first part of the electrolysis was low because of the buffering action of the europium in the amalgam, but eventually reached the value for dilute solutions of europium.

Separation of Samarium from Neodymium.—The purchased samarium oxide was analyzed with 10 cm. cells in the Cary Spectrophotometer and found to contain 0.07% neodymium oxide. The samarium which was electrolyzed into the mercury simultaneously with the europium was kept separate from that remaining in the electrolyte. After re-electrolysis to remove the last traces of europium, analysis with the Cary showed that no neodymium was present. Thus the electrolysis of samarium into mercury separates it from neodymium, which remains in the electrolyte. Purity of the samarium oxide fraction which was recovered from the mercury phase is believed to be >99.98% with respect to other rare earths.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Dependence of Dissociation Pressure Measurements by the Knudsen Effusion Method on Effusion Hole Area. The Dissociation Pressure of Mo_3Ge[1,2]

BY ROBERT J. PEAVLER AND ALAN W. SEARCY[3]

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The pressure of germanium measured by the Knudsen effusion method for the reaction $Mo_3Ge(s) = 3Mo(s) + Ge(g)$ depends on the effusion hole area in the Knudsen cell. This dependence appears to arise from depletion of Mo_3Ge at the sample surface. An equation is derived by means of which the equilibrium dissociation pressure is calculated from the apparent pressures obtained with effusion holes of different areas. The calculated pressures are in good agreement with pressures measured by use of a sample of high effective surface area. The dissociation pressure is given by the equation $\log P = -2.14 \times 10^4/T + 6.68$. The heat of formation of Mo_3Ge from solid molybdenum and liquid germanium at 1800°K. is -14.5 ± 5.0 kcal. per mole.

The Knudsen effusion method,[4] which was developed for determination of vapor pressures, can be applied to measurement of dissociation pressures for reactions of the type

$$-\mathrm{MX}_m(\mathrm{s}) = -\mathrm{M}(\mathrm{s}) + \mathrm{X}(\mathrm{g})$$

The pressure P inside a chamber whose lid is pierced by a small hole is given by $P = Z(2\pi MRT)^{1/2}$ where Z is the weight loss per unit time per unit area through the hole, M is the molecular weight of the escaping vapor, R is the gas constant, and T is the absolute temperature.

The dissociation pressures of rhenium silicides were measured by the Knudsen method in this Laboratory with no difficulties that are not encountered in measuring vapor pressures in the same high temperature range.[5] Difficulty has arisen, however, in application of the method to measurement of the germanium dissociation pressure established by the reaction $Mo_3Ge(s) = 3Mo(s) + Ge(g)$. Equilibrium pressures could not be obtained inside the effusion cell, apparently because of depletion of Mo_3Ge at the surface of the samples with consequent reduction in the effective areas of vaporization. The effect of surface depletion apparently has not been noted previously in dissociation pressure measurements by the Knudsen method.

In this paper an equation is derived by means of which the equilibrium dissociation pressure can be calculated from the results of pressure determinations with effusion cells of different hole areas. The calculated pressures are compared with pressures obtained by use of a sample of high effective area.

Experimental

Molybdenum powder of stated 99.5% purity was obtained from Fansteel Metallurgical Corporation. Bar germanium was obtained from Eagle-Picher Company and crushed to powder for our experiments. Spectroscopic examination of these materials showed iron, probably to the extent of less than 0.1%, to be the major impurity in the molybdenum, while the germanium showed only trace amounts of other elements. Mixtures of the metal powders were heated *in vacuo* to cause reaction, and the phases produced were identified by X-ray diffraction investigation of the products. Mixtures of molybdenum and Mo_3Ge,[6] an easily identified cubic phase, were used for the dissociation pressure measurements. Before dissociation pressure determinations were made, the samples were heated *in vacuo* to drive out any volatile impurities.

For experiments with high effective vaporization area, molybdenum sheet cut into pieces $^1/_4$ in. × $^1/_8$ in. × 0.001

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[2] Supported by the Office of Naval Research.

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[4] M. Knudsen, *Ann. Physik*, [4] **28**, 999 (1909).

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