TABLE I

CHLORIDE ANALYSES

Oxide	% Cl, by wt. Found	% Cl, by wt. Theoretical
Gd	40.2	40.4
50.1 Ho 49.9 Dy	39.3	38.5

below the theoretical values by margins ranging from several tenths to several per cent). One possible explanation for this scatter is based on consideration of precise composition of the rare earth oxides used as starting materials. Although accurate data cannot be obtained readily regarding concentrations of impurities present in the commercial grades of oxides (98–99%) typical analytical figures indicate that Y_2O_3 concentrations present in lots of Dy_2O_3 and Ho_2O_3 used ranged from a trace to 1.5%. If such Y concentrations are considered, then theoretical chloride value for the 50.1 Ho–49.9 Dy mixture could range between 38.5 and 40.0%, which would account for the apparently high chloride concentration found. Likewise, significant concentrations of Th, which are frequently found in the rare earth oxides, could account for apparently low chloride values. Nevertheless, it is felt that very sensitive indication as to the completeness of conversion was obtained by observing clarity of the materials when molten and the extent of reaction between the sample and the Vycor container. Samples produced by the other methods contained residual solids (oxides and oxychlorides) at temperatures above the melting points of the chlorides, and extensively attacked the Vycor containers. In contrast, samples prepared by the chlorination method described in this paper were perfectly clear when molten, and no attack on the containers was observed. No etching of the container walls or other evidence of attack could be detected, even after the chloride samples had been held in the molten state for extended periods of time (*e.g.*, 24 hours).

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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

Separation of the Lanthanons at Amalgam Cathodes. III. Electrochemical Fractionation of the Lanthanons at a Lithium Amalgam Cathode[1]

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Electrolyses of a monazite mixture, an yttrium–earth mixture and a terbium–dysprosium mixture at a lithium–amalgam cathode were studied. The separations obtained show that individual lanthanons are electrolyzed at different rates at a lithium-amalgam cathode. The relative ease of electrolysis is: europium, ytterbium, samarium, lanthanum and other lanthanons in the order of atomic number. Yttrium falls between erbium and thulium. Data were not obtained for lutetium. All of the lighter lanthanons through terbium can be relatively rapidly electrolyzed from aqueous lithium citrate electrolytes, but the rates of electrolysis of the heavier lanthanons except for ytterbium are quite slow from this electrolyte. Rates of electrolysis of the heavier elements are improved considerably by using a methanol electrolyte containing lithium acetate. It appears that europium and ytterbium, and possibly samarium, are rapidly electrolyzed because they are easily reduced to a lower valence state. However, the lanthanons which show only the (III) or higher valence in compounds appear to be reduced by a different mechanism, believed to entail formation of a hydrido species at the cathode surface. The rates of electrolysis of the (III) lanthanons vary widely depending on the electrolysis conditions, but the ratio of rates for any two of these lanthanons appears to be relatively constant. Separations can be predicted from the relative rates of electrolysis.

The electrochemical separation of europium from samarium[2,3] and the separation of samarium from gadolinium[3] proved to be so successful that the work has been extended to the lanthanide series.

Except for the work of McCoy,[4] there has been very little other research reported on the electrochemical separation of the lanthanons by electrolysis into mercury. Several researchers have used electrochemical techniques to prepare amalgams of some of the lanthanons by electrolysis from an ethanolic anhydrous chloride electrolyte.[5] Sodium amalgam was used by Marsh to extract preferentially europium, ytterbium and samarium[6] and by Moeller and Kremers to extract ytterbium from lanthanon mixtures.[7] West and Hopkins used sodium amalgam to prepare several rare earth amalgams by reaction with the anhydrous chlorides in ethanol.[8] Ytterbium separations with amalgam cathodes have been studied.[9]

In this paper the term "lanthanon (III)" is used to describe the lanthanons, including yttrium, which show only (III) or higher valence in compounds. Europium, ytterbium and samarium are thus not included in this designation.

Experimental

Analyses of the lanthanon mixtures were done by classic gravimetric, spectrophotometric and spectrographic procedures. The Cary Model 14X spectrophotometer and a Beckman Model D spectrophotometer were used for lanthanons with suitable absorption coefficients.[10] Europium tracer was used in the same manner as described previously.[2]

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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) E. I. Onstott, *ibid.*, **78**, 2070 (1956).

(4) H. N. McCoy, *ibid.*, **63**, 1622 (1941); **63**, 3432 (1941).

(5) L. F. Audrieth, E. E. Jukkola and B. S. Hopkins, *ibid.*, **53**, 1805 (1931); E. E. Jukkola, L. F. Audrieth and B. S. Hopkins, *ibid.*, **56**, 303 (1934); B. S. Hopkins and L. F. Audrieth, *Trans. Am. Electrochem. Soc.*, **66**, 135 (1934).

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

(7) T. Moeller and H. E. Kremers, *Ind. Eng. Chem.*, **17**, 798 (1945).

(8) D. H. West and B. S. Hopkins, THIS JOURNAL, **57**, 2185 (1935).

(9) H. N. McCoy, *ibid.*, **63**, 1622 (1941); H. N. McCoy and R. P. Hammond, *ibid.*, **64**, 1009 (1942); D. I. Ryabchikov, Yu. S. Sklarenko and N. S. Stroganova, *Zhur. Neorg. Khim.*, **1**, 1954 (1956); *C. A.*, **51**, 5595*e* (1957).

(10) T. Moeller and F. A. J. Moss, THIS JOURNAL, **73**, 3149 (1951); T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950); C. V. Banks and D. W. Klingman, *Anal. Chem. Acta*, **15**, 356 (1956); L. J.

Lanthanons in the amalgams were recovered by first removing the lithium with water, then treating the amalgams with hot concentrated hydrochloric acid. Heating for several days sometimes was required for complete removal. Oxalate precipitations were done for purification prior to analysis of the ignited oxide mixtures.

Cathode potentials in aqueous electrolytes were measured with a Rubicon potentiometer by the technique described previously.[2] No attempt was made to measure cathode potentials with methanol electrolytes.

Monazite Mixture.—The monazite was obtained from the R. M. Kiehn Claim at Petaca, New Mexico, as a primary deposit in a pink microcline. The mineral was worked for the oxide content according to the procedure given in Inorganic Syntheses.[11] Two fractions of the oxide were used for the electrolyses. The first fraction was obtained by dissolving part of the ignited oxide in warm dilute perchloric acid, and the second fraction was the unreacted oxide from the acid treatment.

Electrolysis I was done with the perchlorate electrolyte with two lithium citrate moles per mole of lanthanons at a *p*H of 4 to 7. Composition of the 106.3 g. of oxide dissolved in one liter of electrolyte is reported (wt. %): La_2O_3, 16; CeO_2, 37; Pr_6O_{11}, 4.9; Nd_2O_3, 17.5; Sm_2O_3, 5.4; Eu_2O_3. 0.1; Gd_2O_3, 3.1; Tb_4O_7, 0.4; Dy_2O_3, 1.7; Ho_2O_3, 0.2; Er_2O_3, 0.4; Tm_2O_3, 0.03; Yb_2O_3, 0.2; Y_2O_3, 1.2; ThO_2, 6.

Electrolysis II was done with the unreacted oxide mixture after dissolving it in hydrochloric acid, then converting it to acetate by evaporation with acetic acid before dissolving in the citrate electrolyte. Composition of this oxide was: La_2O_3, 14; CeO_2, 30; Pr_6O_{11}, 3.3; Nd_2O_3, 11.4; Sm_2O_3, 3.3; Eu_2O_3, 0.14; Gd_2O_3, 1.4; Tb_4O_7, 0.2; Dy_2O_3, 0.9; Ho_2O_3, 0.08; Er_2O_3, 0.2; Yb_2O_3, 0.2; ThO_2, 26. The total weight of oxide was 92.9 g. and the electrolyte volume was one liter.

The vessel for the monazite electrolysis was a three-liter beaker into which was placed a polyethylene basket cathode with vents to allow electrolyte circulation. The cathode was 200 ml. of mercury with an area of 100 cm.², and the anode was a platinum flag with approximately the same surface area as the cathode. A platinum spiral cooling coil served to cool the cell and also act as the electrical connection to the cathode. The temperature was kept at 25–40°. The power supply was a 110-volt a.c. conventional selenium rectifier without filtering.

During the electrolyses, the *p*H was controlled by adding citric acid. In electrolysis I the lithium from the mercury was returned to the electrolyte after each fraction, but it was not returned in electrolysis II. There seems to be no reason for returning the lithium as long as the cathode remains polarized.

The electrolyte lanthanons were recovered by oxalate precipitation after fuming with nitric–perchloric acid to remove the organic material. *Caution. Perchlorate in organic materials when dry will explode if heated.* Thorium was separated by the iodate procedure.[12]

Yttrium–Earth Mixture.—The oxide was purchased from Lindsay Chemical Company, West Chicago, Illinois, as "Code 1111 Yttrium Oxide." Composition of the oxide was (wt. %): CeO_2, 0.45; Nd_2O_3, 0.45; Gd_2O_3, 6.4; Tb_4O_7, 2.3; Dy_2O_3, 13.2; Ho_2O_3, 2.2; Er_2O_3, 4.2; Tm_2O_3, 0.3; Yb_2O_3, 1.0; Y_2O_3, 70.

Electrolysis III was done with oxide enriched in the middle lanthanons by electrolysis of Code 1111 yttrium oxide from methanol electrolytes (by the method to be described subsequently). Composition of the enriched oxide was (wt. %): Nd_2O_3, 0.2; Gd_2O_3, 22.1; Tb_4O_7, 5.2; Dy_2O_3, 35.6; Ho_2O_3, 4.3; Er_2O_3, 4.7; Y_2O_3, 28. The electrolysis was done with two moles of lithium citrate per mole of lanthanons, and the 14.45 g. of oxide was dissolved as perchlorate in an electrolyte volume of one liter.

The cell was about the same as described for electrolysis I except that it was smaller. The mercury volume was 100 ml. and the cathode area was 43 cm.². The current density was 0.15–0.2 amp./cm.² and the temperature was 40–50°.

Methanol Electrolytes.—Preliminary experiments with methanol electrolytes were concerned with finding a suitable method of preparing the electrolyte salt with as little water present as possible. Results on some thermogravimetric measurements with yttrium (>99% pure) are given in Table I.

Table I

Data on Thermogravimetric Measurements of Li–Y Acetates[a]

Time of heating, hr.	Temp., °C.	Li/Y($C_2H_3O_2$) ratio	Water/Y
44	150	$[Y(C_2H_3O_2)_3]$	0
40	150	$Li[Y(C_2H_3O_2)_4]$	0.8
40	150	$Li_2[Y(C_2H_3O_2)_5]$	2.0
40	150	$Li_3[Y(C_2H_3O_2)_6]$	2.9
40 100	150 180	$Li[Y(C_2H_3O_2)_4]$	0.1
40 100	150 180	$Li_2[Y(C_2H_3O_2)_5]$	1.3
40 100	150 180	$Li_3[Y(C_2H_3O_2)_6]$	2.4

[a] All samples were evaporated to dryness on a hot plate prior to oven heating. Water was figured by difference. There appeared to be a slight hydrolysis of the samples heated at 180°. Heating much above 190° resulted in charring. $LiAc \cdot 2H_2O$ did not lose water even when heated above 190°, the temperature at which some charring occurs.

The methanol used in electrolysis experiments was specified to contain either 0.04–0.06% water or 0.15% water.

Electrolysis IV was done with enriched oxide of composition (wt. %): CeO_2, 0.9; Nd_2O_3, 0.6; Gd_2O_3, 23.3; Tb_4O_7, 6.2; Dy_2O_3, 34.0; Ho_2O_3, 4.8; Er_2O_3, 4.6; Y_2O_3, 25.5. The oxide (16.39 g.) was converted to acetate, mixed with lithium acetate and treated as outlined in Table I to give the approximate composition, $Li[R(C_2H_3O_2)_4] \cdot 0.8H_2O$. This salt was dissolved in methanol and transferred to a water jacketed electrolysis vessel with a total of about 250 ml. of methanol. The anode consisted of nine spectroscopic graphite electrodes placed in the Teflon lid. Each electrode protruded into the electrolyte about 2 cm. The cathode was 60 ml. of mercury with an area of 67 cm.². The electrolyte was not stirred except by the gas evolution at the anode and at the cathode. Temperature of the electrolyte was 40–55°. The current density was kept generally at 0.04–0.05 amp./cm.² during the electrolysis. However, toward the end of the electrolysis the current density dropped as low as 0.01 amp./cm.² because of the increased resistance of the cell. A precipitate formed on the anodes just after the electrolysis was started; but it redissolved after continuing the electrolysis about 100 minutes.

Electrolyses in methanol could be done only for a limited time, since the cell resistance increased and a hydroxide-like precipitate formed in the bulk of the electrolyte as the electrolyses were continued. Undoubtedly basic salts were formed by the electrosolvolysis reactions at the electrodes. For example, when the methanol electrolyte of an electrolysis done for a considerable length of time was mixed with water, the mixture set up as a hydroxide-like gel. Probably hydroxo-methoxo-carbonato-lanthanon polymers were formed.

Kilogram Scale Electrolyses.—Lindsay Chemical Company "Code 1111" yttrium oxide was used. All 6.5 kg. was electrolyzed for the first three fractions as separate 1.0 or 1.2 kg. batches, but for the last nine fractions a single 1.2 kg. batch was used.

The electrolyte salt was prepared from lithium carbonate, lanthanon oxide and acetic acid. The lithium carbonate was placed on the bottom of a 15-l. battery jar and glacial acetic acid was added periodically along with an equal amount of water until the carbon dioxide evolution ceased. One mole of lithium per mole of lanthanons was used, and the amount of lanthanon oxide per batch was either 1.0 or 1.2 kg. After adding about 4 l. of 50-50 glacial acetic acid and water, the R_2O_3 was added and the mixture was stirred while heating on a steam plate. Complete conversion to the acetate required several hours. The slurry was evaporated with stirring to a

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Heidt and J. Berestecki, This Journal, **77**, 2049 (1955); D. C. Stewart and D. Kato, *Anal. Chem.*, **30**, 164 (1958); E. I. Onstott and C. J. Brown, Jr., *ibid.*, **30**, 172 (1958).

(11) D. W. Pearce, R. A. Hanson and J. C. Butler, "Inorganic Syntheses," Vol. II, W. C. Fernelius, Editor, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 38.

(12) K. Shaver, AEC Report NLM-1031 (Mound Laboratory), Jan. 1955, p. 8.

thick paste, then transferred to enameled trays. After most of the solvent was removed by further evaporation, the mixture was placed in an oven and heated for at least 4 days at 180–190° until ready for use. The final product was a homogeneous, pink, fudge-like mass, easily separable from the enameled trays.

The salt was dissolved in about 25 l. of methanol in a 30-l. glass battery jar. The jar was fitted with an annular plastic lid through which the 4 l. polyethylene beaker containing the mercury could be removed. Slots were cut in the beaker to allow electrolyte circulation, and it was set on a pedestal. A stainless steel vapor condensing coil was placed in the space above the electrolyte, and a polyethylene cooling coil was placed in the electrolyte. The cell was closed with a piece of plastic containing the 8 to 12 spectrographic carbon anodes. Connection to the cathode was made with a platinum wire insulated with polyethylene tubing.

Operating conditions were: mercury, 400 ml.; current, 10 amp. at 40–50 volts, supplied by a 208 volt AC 3-phase selenium rectifier without filtering; C.D. 0.05 amp./cm.^{2}; temperature, ~40°; operating time 5 days total with 3 cathode fractions taken. The electrolyte was stirred with a stream of helium. Proper operation of the cell was checked after a few minutes by monitoring the primary cell voltage. Immediately after turning the current off, the voltage was about 3.5 volts with a 1000 ohm/volt meter, and it decayed within a few seconds to about 3.0 volts.

The optimum operating time before removing the cathode was 24 to 48 hr. During this interval the amount of solid amalgam formed (containing both lithium and lanthanons) was about half of the total cathode volume. Extending the electrolysis time beyond 120 hr. for one electrolyte was not profitable, since the electrolysis rates of the lanthanons diminished greatly and large amounts of basic salts were present in the electrolyte after this time interval. The amount of electricity consumed per 25 l. of electrolyte per 120 hr. was about 4 faradays per mole of mixed lanthanons.

Some of the early experiments were directed to finding a suitable method of revitalizing the electrolyte to get rid of the basic lanthanon salts and organic electro-degradation products. Neutralization with acetic acid prior to reprocessing the electrolyte salt helped, but uniform results were obtained only by removing all organic material by ignition. The spent electrolyte was best revitalized by evaporating to dryness, igniting the residue to oxide at 800°, then converting to the lithium acetato salt as outlined above. Lithium in the mixture caused no difficulty in the ignition except for a gradual degradation of the porcelain dish surfaces. The lithium removed from the amalgam with water was combined with that from the electrolyte before the evaporation step to restore the approximate original Li/R ratio for subsequent electrolyses.

Terbium–Dysprosium Mixture.—The Tb–Dy oxide mixture was purchased from Johnson, Mathy and Co., London, England. Composition of the oxide was: Dy_2O_3, 9.3%; La_2O_3, 2%; Tb_4O_7, remainder.

The electrolysis cell was of design similar to that used previously[2] except that the anode was a platinum tube 0.63 cm. o.d. and about 60 cm. long, wound as a flat spiral and placed parallel to the cathode and 1 to 2 cm. from it. This spiral served as the cooling coil in a number of experiments. It was observed that oxidation of the citrate appeared to be more rapid at lower temperatures of the platinum anode surface. Electrolysis conditions were: cathode area, 67 cm.^{2}; cathode volume, 60 or 100 ml.; electrolyte volume, 150 to 250 ml.; temperature 25 ± 3°. Other complexing agents tried but not listed in Table II were: glycolate, lactate, succinate and nitrilotriacetate. Succinate gave a precipitate and was not usable. The other complexing agents were rapidly oxidized and caused rapid increases in *p*H.

Theory of Electrochemical Separations

An interpretation of equilibrium metal ion separations at a mercury cathode has been given by Rogers[13] and was extended by the author to include lanthanons.[3] Such an interpretation has severe limitations, however, as the conditions of electrochemical equilibrium are difficult to achieve in the laboratory. A more profitable approach appears to be that of *forward reaction rates*, in which the forward rates of the transfer of a pair of different metal ions from the solution to the cathode are considered.

The rate of transfer of a metal ion across the electrode–electrolyte phase boundary is given by $dN/dt = kC^s$, where N is the number of ions per unit area transferred in unit time t with electrode surface concentration C^s and k is the rate constant.[14] The rate of replenishment of C^s is determined by $D(\partial C/\partial X)$, where D is the bulk diffusion coefficient of the species, C is the concentration and X is the distance from the electrode. In a stirred solution, the bulk concentration C^b will be essentially invariant up to a distance δ (commonly called the diffusion layer thickness) from the electrode. Under steady-state conditions, the flux at distance δ from the electrode will be the same as at the electrode, and furthermore it must be the same throughout the diffusion layer, so that $dN/dt = D(C^b - C^s)/\delta = kC^s$.

The change in C^b with time is

$$-\,dC^b/dt = dN/dt\,(A/V) = \frac{(A/V)Dk\,C^b}{(D + \delta k)} \qquad (1)$$

It is of interest to consider parameters D, δ and k with respect to extreme values of these parameters. When $\delta k >> D$, equation 1 becomes $-dC^b/dt = (A/V)(D/\delta)C^b$, which is the familar application of Fick's first law to electrode processes controlled by diffusion alone.[2,15] At the other extreme, when $\delta k << D$, $-\,dC^b/dt = (A/V)kC^b$. For this latter condition, $C^s \cong C^b$, and the rate is essentially independent of D and δ. Equation 1 can be used to describe separation processes, and is conveniently written

$$-\,dC^b/dt = (A/V)\beta C^b \qquad (2)$$

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

The ratio of electrolyte concentrations of two lanthanons being simultaneously electrodeposited after time t is

$$\frac{C_2{}^b}{C_1{}^b} = \frac{C_2{}^0}{C_1{}^0}\,e^{(A/V)(\beta_1-\beta_2)t} \qquad (3)$$

where $C_1{}^0$ and $C_2{}^0$ are the initial concentrations. This ratio becomes large for large values of t if $\beta_1 > \beta_2$. It becomes large for small values of t when $\beta_1 >> \beta_2$.

Since the concentration of each species in the amalgam is $C_i{}^a = (C_i{}^0 - C_i{}^b)\ V_e/V_a$, where V_e/V_a is the ratio of electrolyte and amalgam volumes, the ratio of lanthanons electrolyzed into the amalgam is

$$\frac{C_1{}^a}{C_2{}^a} = \frac{C_1{}^0}{C_2{}^0}\,\frac{(1 - e^{-(A/V)\beta_1 t})}{(1 - e^{-(A/V)\beta_2 t})} \qquad (4)$$

For small values of t, $C_1{}^a/C_2{}^a \cong (C_1{}^0/C_2{}^0)(\beta_1/\beta_2)$. For large values of t where electrolysis of both lanthanons is almost complete, $C_1{}^a/C_2{}^a \cong C_1{}^0C_2{}^0$.

Discussion of Results

Aqueous Electrolytes.—In previous work[2] it was shown that europium behaves almost ideally at a lithium amalgam cathode, since it is electrolyzed at rates determined primarily by diffusion and

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

(14) P. Delahay, This Journal, **75**, 1430 (1953).

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

TABLE II

DATA FOR Tb–Dy SEPARATION

Starting electrolyte compn.	C.D., amp./cm.^{2}	pH range	Cath. pot. (−v. *vs.* S.C.E.)	Elect. time (min.)	% Elect.	tx[b] (min.)	Tb enrichment in amalgam[c]
0.077 *M* Tb acetate[a] .0080 *M* Dy acetate .2 *M* citrate	0.022–0.06	6.4–6.9	1.69–2.38	285	4.0	15,000	2.7
.031 *M* Tb acetate[a] .0032 *M* Dy acetate .2 *M* citrate	0.03	6.5–7.0	2.24–2.60	2650	21.4	23,000	3.5
.031 *M* Tb perchlorate .032 *M* Dy perchlorate .67 *M* citrate	0.03–0.10	4.5–6.0	2.02–2.64	420	1.3	....	..
.67 *M* citrate	0.12	4.5–6.0	2.68–2.71	200	14.1	3000	2.6
.046 *M* Tb perchlorate .0048 *M* Dy perchlorate 1.0 *M* tartrate	0.075	4.0–5.8	2.49–2.83	60	1.7	7000	3
1.0 *M* tartrate	0.075	4.0–5.8	2.81–2.86	125	13.9	1800	3.0
1.0 *M* tartrate	0.075	4.0–5.8	2.91–2.92	200	22.4	1700	3.0
0.045 *M* Tb perchlorate[a] 0.0046 *M* Dy perchlorate 1.0 *M* malate	0.075–0.10	4.5–6.8	2.45–2.47	135	2.0	14,000	4

[a] Complexing acid added to compensate for rapid anodic oxidation. [b] Time to remove 90% of the Tb calculated assuming a first-order reaction; the reciprocal of this value gives the rate constant. [c] Ratio of Tb/Dy in amalgam multiplied by the reciprocal of the original Tb/Dy ratio in the electrolyte.

almost independent both of current density and cathode potential (at sufficiently high cathode potentials). Europium tracer makes an ideal pilot ion for study of lanthanons, since it establishes the $(A/V)\beta$ value (equation 2) for the limiting case of diffusion control. Previous work showed also that europium complexed by citrate is electrolyzed at rates virtually independent of electrolyte pH,[2,3] whereas samarium shows a dependence of rate on pH.[3] In alkaline electrolyes the rate of electrolysis of samarium is much smaller than the rate in slightly acidic or neutral electrolytes.

An alkaline electrolysis was done with the monazite mixture to enhance the separation of europium and possibly to enhance also the ytterbium separation, since it should behave similarly. Results of the electrolysis are given in Fig. 1. The removal of europium shows the expected first-order dependence and was 99.7% complete after the first fraction. It appears that the electrolysis of ytterbium, like europium, is also relatively independent of pH, but much slower. The suppression in rate of electrolysis of samarium and the (III) lanthanons by the high pH is apparent in Fig. 1.

Data on the behavior of the heavier lanthanons in aqueous electrolytes were obtained with an enriched yttrium earth mixture in electrolysis III. Rates of electrolysis of lanthanons heavier than terbium were so slow as to be impractical. For example, when the fraction of gadolinium electrolyzed was 0.50, the fraction for terbium was 0.36; dysprosium 0.17; holmium, 0.074; erbium, 0.011.

The effects of a number of parameters on the electrolysis behavior of the terbium–dysprosium pair are shown by the data in Table II. The data show a constancy of enrichment of terbium over a wide variety of conditions and with different complexing ligands.

Methanol Electrolytes.—Methanol was tried as the solvent for the purpose of improving electrolysis rates. The effect of electrolyte composition on rates is demonstrated in Table III. Without lithium present the cell resistance is so high that no appreciable electrolysis results. Water has an exceedingly deleterious effect, but if the amount of water is kept small, there is a considerable improvement in electrolysis rates.

TABLE III

EFFECT OF ELECTROLYTE COMPOSITION ON ELECTROLYSIS RATES OF YTTRIUM–HEAVY LANTHANON MIXTURE

Electrolysis conditions were about as described for electrolysis IV in Experimental section. Composition of mixture was: Tb_4O_7, 0.3%; Dy_2O_3, 4.3%; Ho_2O_3, 1.8%; Er_2O_3, 5.8%; Tm_2O_3, 0.4%; Y_2O_3, 87%. Weight of starting oxide was 8 to 9 grams.

Electrolyte salt	H_2O/R[a]	R from amalgam as oxide, g.
$[R(C_2H_3O_2)_3]$	0	0
$Li[R(C_2H_3O_2)_4]$	0.2	1.607
$Li[R(C_2H_3O_2)_4]$	0.8	0.841
$Li[R(C_2H_3O_2)_4]$	2.0	.005
$Li_2[R(C_2H_3O_2)_5]$	2.0	.010
$Li_3[R(C_2H_3O_2)_6]$	2.4	.270

[a] Amount of water in salt prior to dissolving in methanol.

An extended kilogram scale electrolysis in methanol was done to demonstrate that the separations are real and of fundamental and practical significance. Pertinent data are given in Table IV and plotted in Fig. 2.

Ytterbium shows the expected fastest rate of removal. Cerium is in the anomalous position higher than neodymium; this behavior can be attributed to the formation of insoluble ceric oxide at the anode. Yttrium clearly falls between erbium and thulium.

Oxidation Experiments.—To try to understand more fully the processes responsible for the separa-

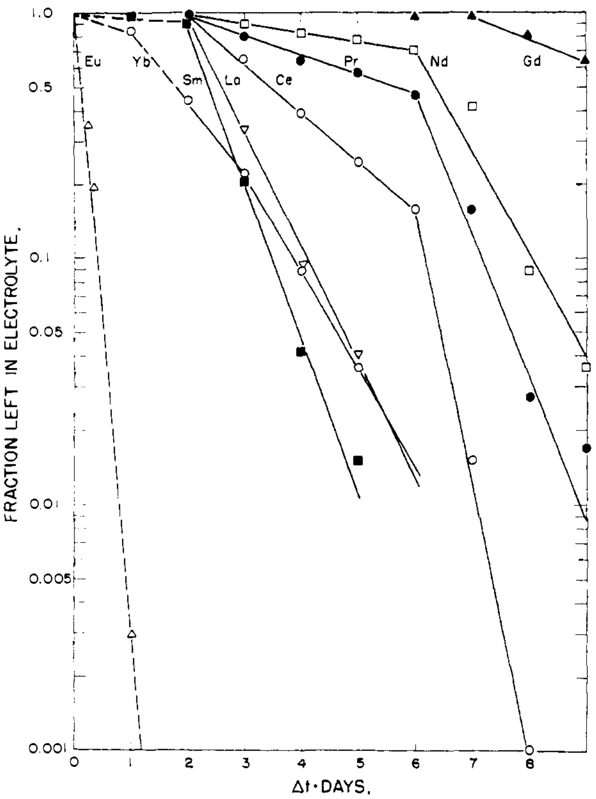

Fig. 1.—Electrolysis II with the first two fractions done at *p*H 8 to 10 (dashed lines) and subsequent fractions at *p*H 4.5 to 8. Cathode potential, −2.4 to −2.8 volts *vs.* S.C.E.; current density, 0.02–0.10 amp./cm.^{2}; data for Eu are instantaneous values with tracer; others are from analyses of amalgam fractions.

tions, some experiments on the reverse reaction were done. Lanthanon (III) amalgams, prepared in electrolysis experiments, were subjected to oxidation under controlled conditions. Oxidants used were cupric ion and cadmium ion since these elements show polarographic reversibility[16] and give a high driving potential (free energy change) to the reaction. There was no indication that appreciable separations were effected by the oxidation reactions for (III) lanthanons. However, in other experiments, fairly large enrichments were observed for europium, ytterbium and samarium with water as the oxidant. Columns three and four of Table IV show these enrichment data.

Interpretation of Rate Behavior.—Equation 2 can be integrated and used to describe separations if β is constant. Such constancy can be expected at complete concentration polarization for one extreme, or for a kinetically slow electrode reaction at the other extreme, if the model in the theoretical section is correct. Europium is the only lanthanon which shows complete concentration polarization behavior with a lithium amalgam cathode. The light lanthanons show a kinetic electrolysis rate dependence, but the electrode reactions can be sufficiently rapid as to give partial concentration polarization. Hence, an interpretation of separations behavior for lanthanons lighter than gadolinium based on equation 2 is not correct unless β is invariant and is not correct if the rate of electrolysis is limited by the current passed through the cell.

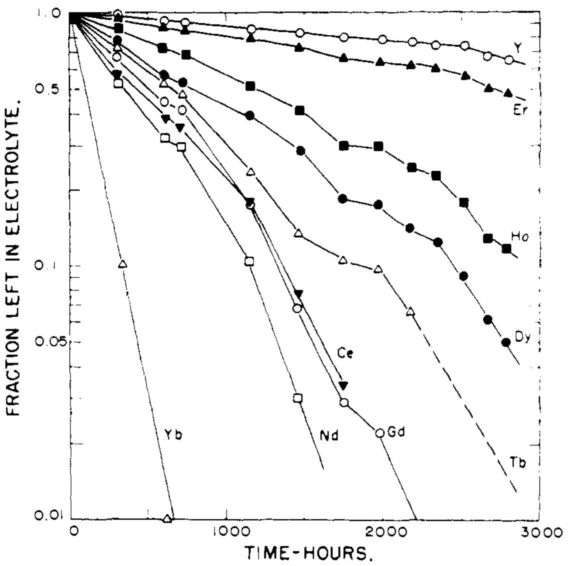

Fig. 2.—Data for kilogram scale electrolysis.

Table IV

Enrichment Data for Kilogram Scale Electrolysis Composition, Wt. Per Cent.

Fraction weights (as oxide) were as follows: starting, 1200 g.; I, 99.4 g.; II, 84.2 g.; III, 21.0 g.; IV, 99.4 g.; V, 57.5 g.; VI, 47.9 g.; VII, 4.3 g.; VIII, 30.9 g.; IX, 9.8 g.; X, 32.0 g.; XI, 34.0 g.; XII, 9.7 g.

	Starting oxide	Oxide from Li strip Amalgam I	Amalgam fraction			Residual electrolyte oxide
			I	III	XII	
CeO_2	0.45	4.2	2.2	0.8	..	<0.005
Nd_2O_3	0.45	3.5	2.4	0.5	..	<0.005
Sm_2O_3	<0.5	5.2	<0.5	..	..	...
Eu_2O_3	<0.5	3.2	<0.5	..	..	...
Gd_2O_3	6.4	21.4	24.4	11.5	0.8	<0.06
Tb_4O_7	2.3	5.2	7.0	4.3	<0.4	<0.3
Dy_2O_3	13.2	15.2	32.7	27.4	14.8	1.5
Ho_2O_3	2.2	1.1	3.1	3.9	2.8	0.6
Er_2O_3	4.2	0.9	2.3	4.6	6.5	4.9
Tm_2O_3	0.3	..	..	..	0.1	0.4
Yb_2O_3	1.0	33	7.4	..	..	<0.001
Y_2O_3	70	9	18	47	75	92.6

The data for the kilogram scale electrolysis in methanol (Fig. 2) show that the middle and heavy lanthanons are electrolyzed at rates which are approximately first order. The elements heavier than gadolinium serve to illustrate electrode reactions that undoubtedly are almost completely kinetic in nature with little bulk concentration polarization dependence. Values of β_1/β_2 for juxtalanthanon pairs calculated from the data in Fig. 2 are given in Table V. Values of β_1/β_2 also were calculated for enriched lanthanons (electrolysis IV), assuming a first-order dependence. Comparison of the two sets of data show that β_1/β_2 is relatively constant and independent of the concentration ratio of lanthanons. It is also independent of electrolytic geometry and electrode geometry as expected.

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(16) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 435.

TABLE V

VALUES OF β_1/β_2 FOR METHANOL ELECTROLYTES

Pair	β_1/β_2, kg. scale	β_1/β_2 enriched mixture (electrolysis IV)
Nd–Gd	1.4	1.9
Gd–Tb	1.3	1.3
Tb–Dy	1.3	1.5
Dy–Ho	1.5	2.0
Ho–Er	2.5	2.0
Er–Y	1.6	1.2

Another way to test the validity of equation 2 is to measure the enrichment factor $C_1^aC_2^0/C_2^aC_1^0$, for electrolysis of a pair of lanthanons and see if it is reasonably constant as predicted by equation 4 for partial electrolyses with a small amount of lanthanon 1 removed. Data on the terbium–dysprosium aqueous separation in Table II show that the enrichment is reasonably constant over a wide range of conditions, and thus support the ideas developed in the section on theory. The electrode reactions for terbium and dysprosium in aqueous solutions probably are first order and undoubtedly both are kinetically controlled.

Separation Mechanism.—The rate behavior of the (III) lanthanons could be due to the slowness of a transfer reaction as depicted in the section on theory. However, it could also be due to a potential barrier for reduction of an activated complex to a hydrido species in the electrolyte phase, this hydrido species being an intermediate product in the reduction mechanism. Evidence is presented below that the latter interpretation is more logical. For either case the electrolysis rate would be proportional to the bulk concentration of lanthanons. Hence the mathematical interpretation is applicable to either limiting reaction.

Below are considered some of the conditions which influence the electrolyses, with remarks as to their significance. (1) *Need for an amalgam cathode.* Electrolysis of most of the lanthanons apparently will not take place appreciably unless a *cation which supplies a free electron in the bulk of the mercury* is present (such as the alkali metals). (2) *Need for a complexing agent.* Electrolysis rates are improved tremendously by the presence of carboxylic acid anion ligands. The simple inorganic salts of the heavy (III) lanthanons cannot be electrolyzed appreciably from aqueous solution even with lithium in the cathode. (3) *Dependence of electrolysis rates on pH.* With aqueous electrolytes the rates of electrolysis appear to be greatest at a *p*H of 4 to 6 for (III) lanthanons. In contradistinction, the electrolysis of europium and possibly ytterbium is little affected by the electrolyte *p*H. Samarium shows a *p*H dependence also, but it is more rapidly electrolyzed than any of the (III) lanthanons. (4) *Dependence of rates on oxidation number.* The lanthanon ions which show an oxidation number less than (III), europium, ytterbium and samarium, are most rapidly electrolyzed in the order as written. The (III) lanthanons are electrolyzed at slower rates which decrease as the atomic number is increased. The property of the lanthanons which corresponds to the change in rate with atomic number is the ionic radius change due to the lanthanide contraction. The smaller the ion, the slower is the rate. This effect must be primarily an electrostatic one, with the charge-to-ionic-radius-ratio being important. It is clear that there is a large activation energy associated with one of the electrode processes, and the activation barrier increases as the ion size is decreased. This behavior is not predictable on the basis of standard reversible electrode potentials, since these show a gradual decrease in value from lanthanum to lutetium.[17] (5) *Effect of solvent.* Use of methanol instead of water increases the rate of electrolysis of the (III) lanthanons at the same current density. Consequently the current efficiency is improved since a larger fraction of the diffusing lanthanon species is transferred to the cathode phase. These results indicate that a type of electrosolvolysis reaction at the electrode surface may be a major electrode reaction and important to the separation mechanism. (6) *Dependence of separations on electrolysis direction.* Appreciable separations take place for the (III) lanthanons only by the procedure of electrolysing in the forward direction. Undoubtedly the discriminatory reactions responsible for the large separations take place in the electrolyte phase at the electrode surface. (7) *Hydride formation.* Hydride is electrolyzed into the bulk mercury phase with the lanthanons at some stage of the electrode reaction with a lithium amalgam cathode,[18] and some amalgamated hydride remains with the lanthanons even after the lithium is removed. It appears that a solvated hydrido species is formed in the electrode reaction. (8) *Unusual position of yttrium.* In ion-exchange separations where basicity and complexing are of prime importance, yttrium falls at about terbium.[19] On the basis of the standard reversible electrode potential, yttrium should fall between terbium and dysprosium[17] in the electrochemical separation scheme. Its much higher position between erbium and thulium is indicative that an unusual mechanism comes into prominence in the electrochemical separation.

It appears that europium and ytterbium are reduced to the (II) state prior to transfer to the mercury phase. However, samarium probably shows a dual nature in being partially electrolyzed by prior reduction to a lower valence state but also in being partially transferred to the mercury phase by the same mechanism as that for the (III) lanthanons.

The mechanism for reduction of (III) lanthanons is postulated as an electrosolvolysis reaction followed by electron reduction

$$[\mathrm{R(H_2O)L}_n]^{+++} + \mathrm{e}^- \xrightarrow{\text{fast}} [\mathrm{R(H)(OH)L}_n]^{++}$$

(activated complex containing H)

$$\mathrm{e}^- \Big\downarrow \text{slow}$$

$[\mathrm{R(H)(OH)L}_n]^{+}$(complex containing hydrido ligand)

The hydrido complex can now be reduced rapidly

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[17] W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952, p. 284, 291.

[18] E. I. Onstott and A. N. Syverud, paper presented at San Francisco meeting of the American Chemical Society, April 17, 1958.

[19] F. H. Spedding, J. E. Powell and E. J. Wheelwright, THIS JOURNAL, **76**, 2557 (1954).

and transferred to the cathode phase which contains free electrons in the bulk (from the lithium) to stabilize the hydrido species

$$[R(H)(OH)L_n]^+ + 2e^- \underset{\text{(reversible?)}}{\overset{\text{fast}}{\rightleftarrows}} RH_{(Hg)} + OH^- + nL$$

The above reactions satisfactorily account for the electrolysis rate dependence of (III) lanthanons on *p*H, complexing ligand, solvent and also the effect of free electrons in the bulk cathode phase.

It should be pointed out also that the exchange of hydroxide ligand for hydride ligand at the electrode surface may be a more fundamental process than the reduction of an activated complex.

Practicality of the Method.—Figure 1 shows that europium, samarium and ytterbium are rapidly enriched and easily removed from the bulk of the mixture. Europium is very easy to separate in almost quantitative yield.

In Fig. 3 are enrichment data on the (III) lanthanons. This plot shows the large enrichment of individual lanthanons in the sequence of the increasing atomic numbers. The light lanthanons through europium can be quantitatively removed from the bulk of the lanthanons heavier than europium. Enrichment of the mixed (III) lanthanons heavier than europium (plus yttrium) is about 20-fold after removal of the thorium. Thorium appears to be more difficult to electrolyze than any of the lanthanons.

The data in Table IV for the kilogram scale electrolyses show the large enrichment of the middle lanthanons and the ease of separation from yttrium. The terbium-yttrium separation is of particular interest because of the difficult ion-exchange separation of these elements. Ion-exchange data are available for comparison of the two methods. Spedding, Powell and Wheelwright[19] ran 43.5 g. of oxide (0.1% Dy_2O_3; 30.7% Y_2O_3, 65.5% Tb_4O_7, 3.7% Gd_2O_3) by band elution with about 400 liters of dilute ethylenediaminetetraacetic acid with copper present. The yield of 99.9% pure yttrium oxide was about 3.7 g. (12%).

By the electrochemical method, all of the oxide could have been contained as acetate in an electrolyte volume of one liter. Extrapolation of the data in Fig. 2 shows that the yield of 99.9% Y_2O_3 would be 44%, starting with the same oxide mixture used by Spedding, Powell and Wheelwright. The electrolyte would have to be revitalized about 23 times, and the total electrolysis time with the same geometry used in this work would be about 5300 hours. However, rates could be improved by at least a factor of 20 by making the cathode area large compared to the electrolyte volume. Not only is the yield better by electrochemical fractionation, but these figures also show the advantage of the electrochemical method in being able to handle large amounts of lanthanons with small equipment. Initial solvent volume requirements are smaller by a factor of 400 to 1 for the electrochemical method, but the methanol must be recovered or replaced 23 times. The electrolyses can be run continuously without attention.

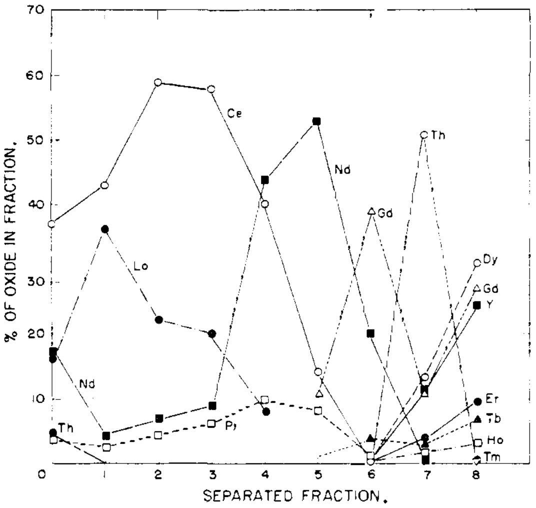

Fig. 3.—Enrichment data for electrolysis I. Fraction 7 represents the electrolyte after taking 6 amalgam fractions, and fraction 8 represents the electrolyte fraction after Th removal. For each fraction the total mixed oxide adds to 100%.

The electrochemical method and ion-exchange method are complementary for purifying yttrium. By using both methods it should be possible to obtain pure yttrium in high yield with rapidity.

Interpretation of Separations with Separation Factors.—The separation factor for lanthanons 1 and 2 being simultaneously electrodeposited in mercury is defined as

$$\alpha = \frac{C_1{}^a}{C_2{}^a} \times \frac{C_2{}^b}{C_1{}^b} \tag{5}$$

where $C_1{}^a$ and $C_2{}^a$ are the concentrations in the amalgam phase. Substitution of equations 3 and 4 into 5 yields

$$\alpha = \frac{[1 - e^{-(A/V)\beta_1 t}]}{[1 - e^{-(A/V)\beta_2 t}]} \times e^{(A/V)(\beta_1 - \beta_2)t} \tag{6}$$

Equation 6 shows that when $\beta_1 = \beta_2$, $\alpha = 1$, and there is no separation. When t is small, $\alpha \cong \beta_1/\beta_2$.

When t becomes large, the value of the fraction in brackets in equation 6 approaches unity so that

$$\log \alpha = \frac{(A/V)t}{2.303}(\beta_1 - \beta_2)$$

The latter expression shows that when removal of both lanthanons is almost quantitative, the ratio of the amounts remaining in the electrolyte becomes very large and approaches infinity in an exponential manner depending on the relative rates. Here α can become very large in comparison to equilibrium separations, where α is a constant.[3]

In Fig. 4 are plotted values of α calculated for assumed values of β_1/β_2 and removal of lanthanon 1 (R_1).

It is interesting that in the forward reaction rate concept it is predicted that the mercury phase does not influence the rates at constant potential; hence it should be possible to change the mercury a large number of times without changing α, if α is figured on the combined electrolyzed fractions. This interpretation cannot be given to equilibrium separations, since both forward and backward reactions determine α.

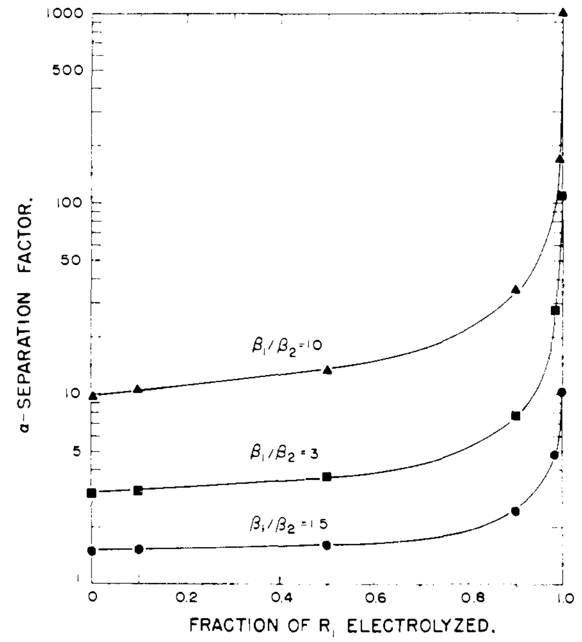

Fig. 4.—Plot of equation 6 for assumed values of β_1/β_2 in terms of completeness of removal of the most easily electrolyzed component.

The data which were obtained for the europium–samarium separation[2] were not compatible with an equilibrium interpretation, but they can be used here to test the forward reaction rate concept. For europium, 90% was removed after 55 minutes[2]; and for samarium, in an independent experiment, 20.4% was removed after 230 minutes.[3] Extrapolation of the latter value gives $\beta_1/\beta_2 \cong 42$. From equation 6, predicted values of α for 99 and 99.9% removal of europium are 856 and 5570, respectively. These values compare favorably with the measured values of 974 for 99.2% removal, and 2810 for 99.9% removal.[2,3]

More accurate data are available for the separation of europium and samarium, from experiments in which the cathode potential was high and the removal of europium was more nearly complete.[3] These data are listed in Table VI and show definitely the large increase in α as the europium removal is more nearly complete. Pure samarium in high yield was recovered from the electrolyte in these experiments.

Table VI

Europium–Samarium Separations[3]

Electrolyses of citrate complexes at a lithium amalgam cathode in alkaline solution. Cathode potential − 2.3 to − 3.0 volts *vs.* S.C.E. Temperature 30 to 39°.

% removal of Eu[a]	% removal of Sm	α
99.73	18.7	1600
99.83	17.6	2700
99.84	14.6	3700
99.95	26.2	5600
99.96	15.9	13200

[a] Accurate to within 0.02%.

Acknowledgments.—The spectrographic analyses were done by O. R. Simi. Some of the experiments on the terbium–dysprosium separation were done by C. J. D'Agostino, Jr. Approaches to the problem and interpretation of the results were helped considerably by discussions with R. D. Fowler, R. D. Baker, R. J. Bard, Henry Taube, H. A. Laitinen, J. C. Bailar, Jr., H. L. Friedman, R. N. R. Mulford, F. H. Ellinger, T. W. Newton, R. A. Penneman. The solution to the combined diffusion-rate equation was demonstrated by W. P. Ellis. The mineral was supplied by R. M. Kiehn. John F. Suttle and students at the University of New Mexico helped with cracking the monazite.

Los Alamos, New Mexico

[Contribution from the William Albert Noyes Laboratory of Chemistry, University of Illinois]

Concerning the Existence of Diphosphorus Trisulfide

By A. R. Pitochelli[1,2] and L. F. Audrieth

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Phosphorus trichloride undergoes quantitative thiosolvolysis in liquid hydrogen sulfide to give a product with the empirical composition P_2S_3. Extraction with CS_2 leads to isolation of P_4S_7; recrystallization from CS_2 at 170° yields both P_4S_5 and P_4S_7; chromatography using the same solvent suggests that this product is a mixture. The presence of P_4S_7, and possibly P_4S_5, in the alleged P_2S_3 is indicated by comparison of its X-ray diffraction pattern with those of the known sulfides. The infrared spectrum differs slightly from those of the well-characterized sulfides but demonstrates presence of a P=S linkage. Although diphosphorus trisulfide may be formed initially, it is undoubtedly quite unstable at ambient temperature and most certainly undergoes disproportionation in carbon disulfide.

Introduction

Only four sulfides of phosphorus with the formulas P_4S_3, P_4S_5, P_4S_7 and P_4S_{10} thus far have definitely been shown to exist. Reports have nevertheless continued to persist in the literature,[3] and in modern text books and reference sources, to the effect that the reaction between the phosphorus trihalides and liquid hydrogen sulfide leads to the formation of diphosphorus trisulfide. Earlier claims that such a compound is formed when the stoichiometric amounts of red phosphorus and sulfur are heated together were shown to be incorrect by Helff[4] who demonstrated that a mixture of the tri- and hepta-sulfides actually is obtained. The nature of the product obtained by the thio-

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[1] Abstracted from the thesis submitted to the Graduate College of the University of Illinois in partial fulfillment of requirements for the doctorate degree, 1958.

[2] Universal Match Foundation Research Fellow in Chemistry 1955–1957. Fellowship Grants by the Universal Match Foundation of St. Louis, Missouri, are acknowledged with gratitude.

[3] A. W. Ralston and J. A. Wilkinson, This Journal, **50**, 258 (1928).

[4] A. Helff, *Z. physik. Chem.*, **12**, 196 (1893).