or atoms than the other one; however, in a subsequent step some of the radicals (or atoms) might react with the other aldehyde (acetaldehyde) and regenerate the first aldehyde. One process which might be used as an illustration is the reaction of some of the formyl radicals with acetaldehyde:

$$\mathrm{HCO} + \mathrm{CH_3CHO} \longrightarrow \mathrm{H_2CO} + \mathrm{CH_3CO} \qquad (6)$$

This would be of importance only when reaction (6) can compete with the decomposition of the formyl radical; such a process might compensate for the greater loss of formaldehyde in the initial attack. There is evidence that the pre-exponential term in the rate expression for the formyl decomposition may be low.[14]

In view of the lack of precise information concerning some of the radical reactions which might be involved no attempt will be made to interpret the results in detail, but one other aspect of the experiments warrants comment. The rate at which pure acetaldehyde decomposes into methane and carbon monoxide at 476° is much greater than the rate at which formaldehyde decomposes into hydrogen and carbon monoxide (at least five times greater for $P_0 = 125$ mm.). If acetaldehyde and formaldehyde decompose by independent molecular processes, then the decomposition of an equimolar mixture of acetaldehyde and formaldehyde (without sensitizer) should produce a large amount of methane and only a small amount of hydrogen. The fact that the ratio of methane to hydrogen in the experiments without added sensitizer is not more than slightly higher than in those with sensitizer shows that free radical chain processes are probably involved. The results can be explained on the basis that the decomposition of acetaldehyde proceeds by way of an initial split to form radicals which induce the chain decompositions of acetaldehyde and formaldehyde to approximately the same extent. This indication of the free radical character of the acetaldehyde decomposition is in agreement with the results of isotopic tracer experiments involving acetaldehyde.[15]

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[14] F. B. Marcotte and W. A. Noyes, Jr., This Journal, **74**, 783 (1952).

[15] P. D. Zemany and M. Burton, *J. Phys. Colloid Chem.*, **55**, 949 (1951); L. A. Wall and W. J. Moore, *ibid.*, **55**, 965 (1951); F. O. Rice and R. E. Varnerin, This Journal, **76**, 2629 (1954).

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The Preparation of Samarium Metal with Calcium[1]

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Two methods of preparing massive samarium metal in substantial quantity with good yield have been reported.[2,3] The technique of the method presented here is not essentially different from the method of Daane, Dennison and Spedding,[2] except that calcium is used as the reductant instead of lanthanum.

Data compiled by Glassner[4] were used as a basis for choosing calcium as the material for reducing samarium oxide. Thorium metal should work equally well, but it is not as cheap or as readily available as is calcium.

Experimental.—The $\mathrm{Sm_2O_3}$ used was essentially the same as that described previously,[3] except that the $\mathrm{Eu_2O_3}$ content was reduced to <0.002% by electrolysis at a mercury cathode.

High purity Ca metal was supplied by R. D. Baker of this Laboratory.

Equipment used has been described also.[3] The reaction crucible was 1 in. in diameter and 3 in. high and was machined from solid tantalum. The distillation plate section was a Ta sleeve 4 in. high which fit snugly over the reaction crucible. Around the inside wall of this sleeve was placed a sheet of 0.002 in. thick Ta, and 4 to 6 connected Ta discs, which served as plates, were placed in the sleeve.

Freshly ignited $\mathrm{Sm_2O_3}$ in amounts of 10 to 20 g. was mixed with the Ca with a spatula. This charge was heated 30–40 min. at 1000° either in a vacuum or in purified argon. Then the Sm and excess Ca were co-distilled in a vacuum of $<1\ \mu$ at 1050–1100° for 30–40 min. Only the bottom half of the crucible assembly was heated by the induction coil. It was sometimes necessary to cut the top section of the crucible assembly to remove the product.

Conditions for the redistillation of Sm-rich fractions were about the same as those for the initial distillation. The pressure was generally 0.1–0.3 μ.

It was observed that the fractions high in Ca had a distinct yellow luster and adhered tightly to the Ta, while relatively pure Sm fractions had the luster of freshly cut iron and were easily stripped from the Ta. Three to four distillations of the most concentrated Sm fractions (bottom plate) were necessary to obtain Sm metal containing <0.1% Ca.

The chemical yield of Sm was determined by recovery of $\mathrm{Sm_2O_3}$ which did not react and distill from the reaction crucible.

Spectrographic analyses of the purified Sm were performed by O. R. Simi. Impurities found were: Ca, 0.01–0.1%; Y, 0.001–0.1%; Mg, Si, Mn, Co, Ag, Pb, each 0.001–0.01%; Na, Sb, each <0.001%. The Ta content was estimated to be <0.1% by weighing the residue left after dissolving a sample in dilute HCl.

Discussion.—In Table I are data which show the effect of three parameters on the chemical yield and concentration of samarium in the vapor distilled from the reaction mixture.

Table I

Excess Ca,[a] %	Ca, size-mesh	Reaction atmos.	Chem. yield Sm, %	Sm in distillate, %
17	60–100	Argon	26	42
83	20	Argon	48	47
128	20	Argon	58	46
203	20	Argon	54	35
108	40–60	Argon	50	44
136	40–60	Argon	59	45
193	40–60	Argon	70	46
201	40–60	Argon	66	41
104	40–60	Vacuum	40	38
208	40–60	Vacuum	54	35

[a] Excess over that needed for 100% Sm yield.

Only about 40% of the chemical yield of samarium was recovered as the high purity metal. Redistillation losses were relatively great, since some

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[1] Work done under the auspices of the Atomic Energy Commission.

[2] A. H. Daane, D. H. Dennison and F. H. Spedding, This Journal, **75**, 2272 (1953).

[3] E. I. Onstott, *ibid.*, **75**, 5728 (1953); Los Alamos Scientific Laboratory Document LA-1622 (Dec. 1953).

[4] A. Glassner, "A Survey of the Free Energy of Formation of the Fluorides, Chlorides, and Oxides of the Elements to 2500°K.," Argonne National Laboratory Document ANL-5107 (Aug. 1953).

metal was lost to the walls of the distillation tube, and some remained in the samarium lean fractions which were not redistilled.

About 30 g. of high purity samarium metal has been prepared by the method outlined here.

Undoubtedly calcium could be used for partial separation of the rare earths by fractional distillation of the metals from a calcium–rare earth oxide mixture. Spedding and Daane[5] have shown that lanthanum is quite effective for this type of separation.

[5] F. H. Spedding and A. H. Daane, "Methods of Producing Rare Earth Metals as Developed at Iowa State College," Paper presented at the Annual Meeting of the AIME (Feb. 1954).

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Anion-exchange Studies. XIV. The Alkali Metals in Ethylenediaminetetraacetic Acid Solutions[1,2]

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The alkali metals, lithium and sodium, have been shown to form reasonably stable complexes with the chelating agent, ethylenediaminetetraacetic acid, at high *p*H[3] according to the equilibrium

$$M^+ + A^{-4} \rightleftharpoons MA^{-3} \qquad (1)$$

where M^+ is the alkali ion and A^{-4} is ethylenediaminetetraacetate (EDTA). The concentration quotients $k^m{}_{01} = m_{MX^{-3}}/m_{M^+}m_{A^{-4}}$ were estimated to be $k^m{}_{01} = 620$ for Li^+ and $k^m{}_{01} = 46$ for Na^+ at 20° in 0.1 *M* KCl. Under the same conditions negligible complexing of potassium ions was assumed. One might also expect negligible complexing of cesium and rubidium ions by EDTA. The apparent formation of negatively charged complexes of lithium and sodium in alkaline EDTA solutions suggested that their separation from each other and from other alkali metals might be accomplished by anion exchange in a manner similar to the separation of the alkaline earths in citrate solutions which was described earlier.[2] In this connection it might be mentioned that the effect of another chelating agent, uramil-diacetic acid[4] in the cation-exchange separation of alkali metals was recently investigated.[5] Although uramil-diacetate forms better complexes with lithium and sodium than EDTA (compare references 3 and 4), the latter was chosen for the anion exchange experiments because of its easier availability.

The experiments were carried out with a strong base quaternary amine polystyrene divinylbenzene resin (Dowex-1) of relatively low cross-linking (4%) and mesh size 50–100. EDTA solutions were prepared by dissolving ethylenediaminetetraacetic acid (H_4A) in KOH solutions. The resin, initially in the chloride form, was treated with *ca.* 0.25 *M* EDTA solution of *p*H *ca.* 11. At this *p*H, H_4A may be considered to be largely dissociated to A^{-4}[6] and thus the resin treated with 0.25 *M* EDTA of *p*H 11 might be expected to be principally in an $A^{-4} - HA^{-3}$ form with A^{-4} possibly predominating. After the resin had been treated with several volumes of alkaline EDTA solution, it was washed with water to remove excess EDTA. A portion of the resin was then analyzed for chloride. It was found that the resin retained significant amounts of chloride which could be removed only slowly by further washing with EDTA solution.

In a typical experiment designed to demonstrate separation of alkali metals, an 0.41 cm.² × 23 cm. column of this resin was pretreated with *ca.* 2 column volumes of 2.5×10^{-3} *M* EDTA solution at *p*H 10.9. A 1.0-ml. aliquot of a solution containing 0.12 *M* LiOH, 0.015 *M* NaOH (Na^{22}), Cs^{137} and 0.13 *M* EDTA at *p*H 10 was then added to the column and elution was carried out with the same dilute EDTA solution which was used to pretreat the column. The effluent was analyzed radiometrically for Cs^{137} and Na^{22} and spectrographically or flame spectrophotometrically for Li.[7]

As shown in Fig. 1, cesium appeared in the effluent first, essentially unadsorbed, and was satisfactorily separated from sodium which was slightly retained by the column. It is predicted that rubidium and potassium ions in this medium would also have shown negligible adsorption. The cesium and sodium fractions were analyzed spectrographically and found to be free of lithium within the limits of the spectrographic method. Satisfactory elution of lithium was achieved with 0.25 *M* EDTA solution at *p*H 4.2. Effluent solutions were analyzed by flame spectrophotometry.[7] Appearance of lithium in the effluent was paralleled by a decrease in *p*H as shown by the dashed line in Fig. 1. This decrease in *p*H was delayed as shown in Fig. 1, suggesting that acid ions of EDTA (*e.g.*, $H_2A^=$) are adsorbed by the resin as expected on the basis of earlier work on acid adsorption by "strong base" resins containing polyvalent anions.[8]

Adsorption of base can also be demonstrated with this "strong base" resin in the EDTA form. Thus when the resin was pretreated with a 0.25 *M* EDTA solution near *p*H 11, reasonably good (total) adsorption of LiOH occurred, *e.g.*, *ca.* 3–4 column volumes of a 0.08 *M* LiOH solution could be passed into the columns before breakthrough of lithium occurred. When the resin was pretreated with *ca.* 0.25 *M* EDTA solution near *p*H 4.2 adsorption of lithium hydroxide also occurred, although some lithium appeared in the effluent almost immediately. These experiments suggest that adsorption of base may occur according to reactions of the type

$$(A^{-4})_r + Li^+ + OH^- \longrightarrow (Li\,A^{-3})_r + (OH^-)_r \qquad (2)$$

or

$$(HA^{-3})_r + Li^+ + OH^- \longrightarrow (Li\,A^{-3})_r + H_2O \qquad (3)$$

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous paper: F. Nelson and K. A. Kraus, THIS JOURNAL, **76**, 801 (1954).

[3] G. Schwartzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

[4] G. Schwartzenbach, E. Kampitsch and R. Steiner, *ibid.*, **29**, 364 (1946).

[5] W. Buser, *ibid.*, **34**, 1635 (1951).

[6] *pK* values for the ionization constants of H_4A in 0.1 *N* KCl (20°) are reported as $pK_1 = 1.996$, $pK_2 = 2.672$, $pK_3 = 6.161$ and $pK_4 = 10.262$ (ref. 3). See also F. F. Carini and A. E. Martell, THIS JOURNAL, **74**, 5745 (1952).

[7] We are indebted to Mr. M. Murray of the ORNL Analytical Division for the spectrographic analyses and to Mr. W. R. Laing of the same Division for the flame spectrophotometric analyses.

[8] (a) K. A. Kraus, F. Nelson and J. F. Baxter, THIS JOURNAL, **75**, 2768 (1953); (b) F. Nelson and K. A. Kraus, *ibid.*, **76**, 329 (1954).