corresponding light hydrogen reaction. Owing to uncertainties in the purity of the deuterium and as to the complete role of exchange reactions, full publication is being deferred.

The catalytic experiments using copper indicated at 0° a ratio of rates $H_2/D_2$ of 1.59. Since Farkas, Farkas and Rideal [*Proc. Roy. Soc.* (London), **A146,** 630 (1934)] found no exchange at low temperatures over nickel, it is likely that no exchange occurred in this reaction over the comparatively less reactive copper catalyst. However, this point is being investigated. At higher temperatures (184 to 306°) the observed ratio fell from 1.34 to 1.04. How much of this decrease is due to exchange will be determined.

In the homogeneous reaction at 524 and 560° the ratios were 2.10 and 2.0, respectively. This seems to point to a real difference in the activation energies of the homogeneous reactions, but again further investigation (which will be shortly undertaken) is required.

These preliminary results point to the likelihood that comparative rates of hydrogenation can be obtained at 0° on the copper catalyst and at 500–550° in the homogeneous reaction, without serious interference from exchange reactions. Such measurements are now being made with deuterium of known purity.

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RECEIVED APRIL 15, 1935

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## THE SEPARATION OF CERTAIN RARE EARTHS

*Sir:*

It has been shown by Yntema [THIS JOURNAL, **52,** 2782 (1930)] and by Ball and Yntema [*ibid.*, **52,** 4264 (1930)] that europium and ytterbium may be separated from other rare earths by precipitation as sulfate after electrolytic or other reduction to the divalent state. However, because of the small amounts of these elements found in rare earth mixtures, it has still been necessary to resort to fractional crystallization over a period of a year or more before the reduction method becomes applicable.

Using several samples of pure rare earths put at his disposal through the kindness of Professor B. Smith Hopkins of the University of Illinois, the writer has attempted to facilitate the separation of europium through the use of a co-precipitant. In a mixture of terbium group earths too dilute in europium to give any direct precipitate of europous sulfate, it has been found possible to obtain a substantially complete co-precipitation with barium sulfate of all the europium present. The europium is then readily removed from the filtered barium sulfate by repeated washing with a little hot concentrated nitric acid. There seems, therefore, no reason why europium, and probably ytterbium also, cannot be removed practically quantitatively from a crude rare earth mixture in as many days as it formerly took years.

The writer has also examined a possible separation of neodymium and samarium. The mixture of anhydrous chlorides is treated with hydrogen at 700°. This results in reduction of the samarium to $SmCl_2$. Treatment of the resultant mixture with water brings about a reaction probably represented by $6SmCl_2 + 3H_2O \longrightarrow 4SmCl_3 + Sm_2O_3 + 3H_2$, the neodymium trichloride simply dissolving. Part of the samarium is precipitated but seems always to be contaminated with some neodymium. Although the separation obtained is good, as rare earth separations go, it is nevertheless only fractional, and because of its difficulty probably cannot compete with the usual double nitrate fractional crystallization.

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RECEIVED APRIL 24, 1935

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## THE THERMAL REACTION BETWEEN CHLORINE AND FORMALDEHYDE

*Sir:*

Krauskopf and Rollefson [THIS JOURNAL, **56,** 2542 (1934)] have isolated formyl chloride from the photochemical interaction of chlorine and formaldehyde, and have suggested [*ibid.*, **57,** 590 (1935)] that this substance occurs as an intermediate in the corresponding thermal reaction [Spence and Wild, *Nature,* **132,** 170 (1933); *J. Chem. Soc.*, 1588 (1934)]. Furthermore, they suggest that the excess of carbon monoxide produced in our experiments over that calculated from the pressure change is due not to an induced polymerization of the formaldehyde, but to the presence of formyl chloride, which is produced without change of pressure. If the formyl chloride decomposed in the process of analysis giving HCl and CO, it is claimed that this explanation would account for our results equally well. Consideration of a number of