TABLE I

Expt.	Material irradiated	Method of sepn.	Retention from gamma irradiation, %	Retention from neutron bombardment,[1] %
1	1 g. solid complex	Complex washed with H_2O; 10 mg. copper as $Cu(Ac)_2 \cdot H_2O$ added to filtrate; pptd. as CuS	95 ± 1	97
2	1 g. solid complex	Complex dissolved in 50 ml. pyridine; soln. made 0.0032 M in $Cu(Ac)_2 \cdot 1Py$; complex pptd. by 10-fold addn. of 15% HAc; carrier pptd. as CuS	45 ± 2	48
3	50 ml. pyridine soln. 0.053 M in complex	Soln. made 0.0032 M in $Cu(Ac)_2 \cdot 1Py$ then as in expt. 2	18 ± 2	18[a]
4	50 ml. pyridine soln. 0.052 M in complex and 0.0032 M in $Cu(Ac)_2 \cdot 1Py$	As in expt. 3 but no more carrier added	15 ± 2	
5	50 ml. pyridine soln. 0.053 M in complex and 0.027 M in $Cu(Ac)_2 \cdot 1Py$	As in expt. 4	9 ± 2	3[b]

[a] Bombarded solution was 0.0152 M in complex. [b] Bombarded solution was 0.0152 M in complex and 0.0152 M in $Cu(Ac)_2 \cdot 1Py$.

minute half-life Cu^{62}. The uncertainties reported include an estimate of the uncertainty in the self-absorption correction, as well as the statistical counting error.

For comparison, the retentions resulting from neutron bombardment of this complex were calculated from the activities in the organic and carrier fractions as reported by Duffield and Calvin,[1] and are included in the table. Presumably the activities reported by them have not been corrected for self-absorption. It should be pointed out that, in order to obtain sufficient activity by irradiation in the betatron beam, it was necessary, in the work reported here, to use solutions of the complex approximately three and one-half times as concentrated as those used by Duffield and Calvin.

For those experiments in which the complex was irradiated in the solid state, there appears to be little difference between the retentions resulting from the (γ,n) and the (n,γ) reactions on Cu^{63}, although the recoil energies imparted to the resulting radioactive copper nuclei differ by several orders of magnitude.

Comparisons of the retentions resulting from nuclear reactions in the solutions are not so direct, since the concentrations of the chelate complex are not the same for the γ-ray and neutron activation experiments. It was found that the bombardment with nuetrons of a 0.015 molar solution of the complex in pyridine gives the same retention as does the irradiation with γ-rays of a 0.53 molar solution.

If carrier copper in the form of copper acetate is present during the irradiation with γ-rays, the retention is dependent upon the concentration of carrier copper. For solutions 0.053 molar in the chelate complex, retentions of 18, 15 and 9% were observed for solutions which were also 0, 0.0032 and 0.027 molar, respectively, in copper acetate. Due to the limited solubility of copper acetate in pyridine, it was not possible to prepare solutions in which the molarities of the chelate complex and carrier copper acetate were both equal to 0.053, but it appears probable from these results that in such a solution the retention would be less than 9%. In the neutron bombardment experiments, Duffield and Calvin's results indicate a retention of about 3% in a solution where the molarities of chelate complex and copper acetate were both equal to about 0.015.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SASKETCHEWAN
SASKATOON, SASK., CANADA

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Composition of W-6 Raney Nickel Catalyst[1]

BY V. N. IPATIEFF AND HERMAN PINES

In performing hydrogenation experiments, it was found necessary to make a precise determination of the composition of W-6 Raney nickel. The Raney nickel, which was prepared by the method of Adkins and Billica[2] was found to contain about 77% nickel, 21% alumina, 1.4% metallic aluminum and the remainder sodium aluminate. This is in contradiction with the data obtained by Adkins and Billica who reported the catalyst to be composed of about 11% of aluminum, the remainder being nickel.

The presence of alumina in W-6 Raney nickel can be easily confirmed by the following simple experiment: a small amount of the catalyst placed in a 9% aqueous solution of nitric acid all dissolves except for a white precipitate, which consists of powdered alumina. This alumina is not the oxide of any aluminum present originally in the catalyst and oxidized by the nitric acid, as may be seen from the fact that neither the aluminum–nickel alloy nor an aluminum powder will give any aluminum oxide precipitate on reacting with dilute nitric acid.

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(1) This work was made possible through the financial assistance of the Universal Oil Products Company. The authors wish to thank the Analytical Laboratory of the Universal Oil Products Company for the analysis of the catalyst.

(2) H. Adkins and H. R. Billica, THIS JOURNAL, **70**, 695 (1948).

It is very possible that the high activity of Raney nickel is not only due to the large surface area of the catalyst but also to the presence of aluminum oxide; Ipatieff[3] has already demonstrated the pronounced effect of alumina upon a nickel catalyst.

Experimental Part

Samples of freshly prepared W-6 Raney nickel were introduced into weighed ampoules. Special precautions were taken not to expose the catalyst to the air and to have it covered with absolute ethanol during the transfer of the sample into the ampoules. The ampoules were then attached to an interchangeable joint which was sealed to the high vacuum line. The alcohol was removed under high vacuum; this evacuation was done gradually in order to avoid any bumping of the alcohol and splashing of the catalyst into the upper part of the ampoules. Best results were achieved by cooling the ampoules to about −78° and then raising the temperature slowly to about 40–50°. After all the alcohol was removed the ampoule was sealed off under vacuum at the upper restriction and weighed. The weight was determined to the nearest milligram. Each ampoule contained about one gram of the catalyst.

The ampoules were opened in the absence of air and treated with 100 ml. of 9% of nitric acid. On boiling, the nickel dissolved leaving a dense white residue. After cooling, 10 ml. of concd. sulfuric acid was added and the solution was boiled till all the residue dissolved. The clear solution was then transferred to 500-ml. volumetric flask and made to volume.

Nickel was determined on $^1/_{20}$th aliquots by precipitation as nickel dimethylglyoxime[4a] and weighed as such: The amount of aluminum present was established on $^1/_{10}$ aliquots by precipitation as basic succinate[5] followed by filtration and ignition to oxide at 1200°. Sodium was determined on $^1/_{10}$ aliquots by precipitation as sodium magnesium uranyl acetate.[4b]

In all determinations aliquots of two separate samples were used. The results obtained are summarized in Table I.

TABLE I

ANALYSIS OF W-6 RANEY NICKEL

	Sample 1	Sample 2	Average
Nickel	77.00	76.95	76.97
Aluminum	12.75	12.69	12.72
Sodium	0.15	0.15	0.15
Total	89.90	89.79	89.84

On the basis of the above data, the calculation reveals the following percentage composition of the W-6 Raney nickel: metallic nickel, 76.97; aluminum oxide, 21.13; sodium aluminate, 0.54; metallic aluminum, 1.36.

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(3) V. N. Ipatieff, *Ber.*, **45**, 3205 (1912).

(4) "Scott's Standard Methods of Chemical Analysis," N. H. Furman, Editor, 5th edition, Vol. I, D. Van Nostrand Company, Inc., New York, N. Y., 1939 (a) p. 619, (b) p. 879.

(5) H. H. Willard and N. K. Tang, *Ind. Eng. Chem., Anal. Ed.*, **9**, 357 (1937).

THE IPATIEFF HIGH PRESSURE AND
CATALYTIC LABORATORY
DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

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Note on the Ion Exchange Separation of Europium, Gadolinium and Terbium

BY G. H. HIGGINS AND K. STREET, JR.

In connection with the general problem of comparing the behavior of the actinide elements with their rare earth homologs, it was desirable to know the relative rates of elution of the rare earth triad europium, gadolinium and terbium on eluting with citrate solutions from Dowex-50 cation resin. Ketelle and Boyd[1] in Fig. 6c show an elution (run at 100°) of the heavy rare earth elements from Dowex-50 cation resin using 5% ammonium citrate solution of *p*H 3.25. In their experiment the activity peak that eluted in about 0.7 the time required to elute their europium peak is labeled Gd thus implying a large separation between europium and gadolinium. B. B. Cunningham and H. G. Hicks[2] ran europium and gadolinium under somewhat different conditions (room temperature and *p*H 3.05 citrate) and found practically no separation of europium and gadolinium. In addition, J. O. Rasmussen[3] ran europium, gadolinium and terbium under still different conditions (75° and *p*H 3.2 citrate) and again found essentially no separation of europium and gadolinium. In addition, he found that terbium was eluted well ahead of europium and gadolinium. It thus appeared that there was a real discrepancy between this later work and that of Ketelle and Boyd.

In order to check this point a run was made under conditions very close to those used by Ketelle and Boyd. Figure 1 shows the results of an elution of yttrium, terbium, gadolinium and europium made at 97° using 5% ammonium citrate solution of *p*H 3.25. Tracer Y^{91}, $Gd^{<154}$ and $Eu^{152-154}$ were used and in addition approximately

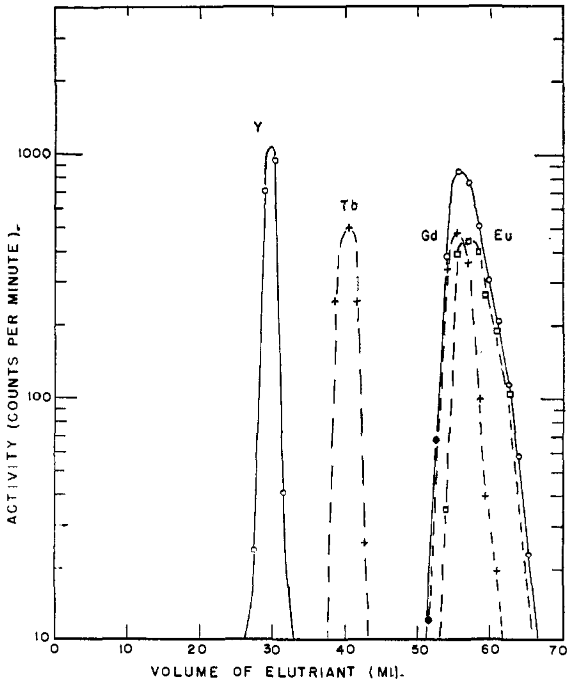

Fig. 1.—Elution of Y, Tb, Gd and Eu with *p*H 3.25 ammonium citrate at 97°.

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(1) B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947).

(2) B. B. Cunningham and H. G. Hicks, unpublished work.

(3) J. O. Rasmussen, unpublished work.