One conclusion derived from these equations is extremely important and accounts for the unique success of the ion-exchange method in separating rare earths. It will be noted that once the ammonia in the eluant is fixed, all variables in the equilibrium eluate and on the column are determined for each individual rare earth present. As the equilibrium constants of the complexes change from rare earth to rare earth, the $Cit^{\equiv}$ concentration in the eluate changes. This means that the rare earths must separate into bands on the resin bed, each band having a specific citrate concentration, hydrogen-ion concentration and ionic strength associated with it. As a result of this, the bands develop autosharpening boundaries, and one band rides immediately on the tail of the preceding band. If an ion of a given rare earth species gets ahead of or behind its own band for any reason, it will be subjected to an adverse citrate concentration and will either be accelerated or retarded in its movement down the column, so that it returns to its own band.

It will be seen, while in theory it is possible to separate tracer quantities of rare earth ions on ion-exchange columns, that in practice, under equilibrium conditions as carried out in *these experiments*, it is impossible to do so. There is always a slight tilting of the band and a small amount of channeling so that when the band front leaves the column one part of the front will have passed the boundary while the other part still remains on the resin bed. For an infinitely thin band, there will always be found a mixture of rare earths, at least binary in composition, in the eluate. The requirement for good separation of rare earths is that the band be long compared with its diameter, so that any tilting of the band is small compared with the length of the band. If tracer quantities are to be separated under these conditions, very small diameter columns should be used and carriers should be present to give the proper type of bands. Of course, carrier-free tracers may be separated if non-equilibrium conditions are used in other citrate ranges, but it is our conclusion that they cannot be separated under the conditions of *these particular experiments*.

Under equilibrium conditions, the equations indicate that flat-topped elution curves should be obtained. However, it is interesting that, if the bands are narrow due to only a small amount of a rare earth species being present, a bell-shaped elution curve may be observed. This results from the fact that the columns are circular in cross-section and that, if a narrow band is tilted, the concentration of a particular rare earth in the eluate is proportional to the area of the band front crossing the boundary at a given moment. This area will vary from zero, at the edge, to a maximum corresponding to the diameter of the column, and then decrease to zero again. The bell-shaped curve observed is really the envelope of a series of equilibrium increments weighted according to the geometry of the sorbed band.

Under non-equilibrium conditions, where the bands are continually spreading out as they progress down the column, true bell-shaped curves are obtained, but the height of these curves continually diminishes as the length of the column is increased, and there is always a certain amount of overlap of one rare earth with the other. Under these conditions, equation 17 is no longer controlling. Instantaneously, at any point in the column, the solution adjusts itself, according to the other ten equations, to the concentrations of the components on the resin at that point, or *vice versa*, but the adjustment is different at each succeeding point, and the concentrations constantly change as the band spreads out.

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# The Use of Copper as the Retaining Ion in the Elution of Rare Earths with Ammonium Ethylenediamine Tetraacetate Solutions

BY F. H. SPEDDING, J. E. POWELL AND E. J. WHEELWRIGHT

RECEIVED DECEMBER 19, 1953

A rapid method for separating mixtures of rare earths into the pure components is described. The method consists of eluting a band of mixed rare earths adsorbed on a cation-exchange resin through a second cation-exchange bed in the $copper^{II}$ state. The eluant consists of an ammonia-buffered solution of ethylenediaminetetraacetic acid. It was found that gram quantities of pure heavy rare earths could be obtained in a few days by this method.

## Introduction

In a preliminary note,[2] the possibility of using ethylenediamine tetraacetic acid as an eluting agent for the separation of adjacent rare earths on cation-exchange resins was discussed. This earlier publication described an experiment in which a mixture of neodymium and praseodymium was eluted through a cation-exchange bed in the $iron^{III}$ state with a solution of ammonium ethylenediamine tetraacetate. The $iron^{III}$ resin bed served as a barrier through which a solution of rare earth–ethylenediamine tetraacetate complex could not pass without decomposition, since the $iron^{III}$ ion forms a more stable complex with EDTA than does any trivalent rare earth ion. In this preliminary experiment, only short sections of resin bed were used and a moderate degree of separation was attained. Subsequent experiments with longer resin beds,

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] F. H. Spedding, J. E. Powell and E. J. Wheelwright, THIS JOURNAL, **76**, 612 (1954).

using concentrated solutions of EDTA, have indicated however that iron$^{III}$ is not the most desirable retaining ion. It was found that the $p$H range of eluant was limited when iron was used, for if the solution was too acidic, the acid $H_4Y$ tended to precipitate in the interstices of the resin bed and, if it was too basic, hydrous ferric oxide clogged the resin pores. When the ammonium EDTA solution encountered the rare earth on the resin bed, hydrogen ions were liberated. As the concentration of EDTA in the eluant was increased, the increased hydrogen ion concentration resulted in the formation of insoluble $H_4Y$ at increasingly higher $p$H values. On the other hand, as the $p$H increased, insoluble hydrous ferric oxide tended to form and this resulted in the trailing of iron into the rare earth bands when concentrated EDTA was used, even in the most favorable cases. Actually, it is desirable to use concentrated EDTA in order to obtain rapid separation of larger amounts of rare earths, but the trailing tendency of the iron$^{III}$ makes necessary a subsequent separation of iron from the rare earths.

It is obvious that some ion having a more soluble hydroxide than iron$^{III}$ would be a more desirable choice for the retaining ion in this type of elution. Consideration of the stability constants for the EDTA complexes of the rare earths and other metal ions[3] showed that copper$^{II}$, nickel$^{II}$ and lead$^{II}$ should serve to retain a number of the rare earth ions. In solutions having an ionic strength of 0.1, the stability constants of these ions lie between the constants for erbium and dysprosium. However, the relative stabilities of the EDTA complexes are not the only factors which determine the order of elution of metal ions from ion-exchange beds. It is also necessary to consider the effect of the relative affinities of the metal ions for the resin. The general rule for the order of affinity of ions for cation-exchange resins is $M^{+4} > M^{+3} > M^{+2} > M^{+}$. This means that, while copper$^{II}$ ion for example is complexed by EDTA more strongly than holmium and the lighter rare earths, the rare earths in general are more firmly attached to the resin. The two effects are complementary and would cause the predicted order of elution of copper$^{II}$ ion with respect to the rare earths to shift toward the heavier rare earth end of the series, possibly causing copper$^{II}$ to elute before lutetium from a cation-exchange bed when EDTA is used as the eluant. For this reason a series of experiments was performed to determine whether copper$^{II}$ would serve as a retaining ion in the elution of rare earths with EDTA.

## Experimental

In each of the following experiments a resin bed completely saturated with a rare earth mixture was connected in series with a second resin bed in the copper$^{II}$ state. An aqueous solution of rare earth chloride was used to saturate the rare earth bed and a solution of cupric sulfate was used to saturate the retaining bed. Both beds were rinsed free of unadsorbed cations with distilled water prior to eluting in series with a solution of an ammonium ethylenediamine tetraacetate. The rare earth which was picked up by the EDTA solution in the first column was displaced by copper$^{II}$ ion in the second column and forced to redeposit on the resin bed. The effluent solution was collected after the rare earth breakthrough occurred and any copper present was eliminated by electrolysis after the solution was made acidic with sulfuric acid. The rare earths present were recovered by the addition of oxalic acid to the copper-free solution.

**1. The Elution of Certain Troublesome Rare Earth Mixtures.**—In the separation of rare earths by the citrate method,[4,5] there are certain groups of elements which separate less readily than other members of the series. These groups (lutetium–ytterbium, dysprosium–yttrium–terbium and gadolinium–europium–samarium) offer a severe test to any separation method which does not make use of different oxidation states.

In the following three experiments the rare earths were adsorbed on −40+50 mesh Nalcite HCR beds, 90 cm. long and 22 mm. in diameter. The loads consisted of

I. 53.0 g. of $R_2O_3$ containing 53.0% $Lu_2O_3$, 33.0% $Yb_2O_3$, 11.9% $Tm_2O_3$, 2.1% $Er_2O_3$, etc.

II. 47.7 g. of $R_2O_3$ containing 45.9% $Gd_2O_3$, 1.7% $Eu_2O_3$, 52.4% $Sm_2O_3$

III. 43.5 g. of $R_2O_3$ containing 0.1% $Dy_2O_3$, 30.7% $Y_2O_3$, 65.5% $Tb_4O_7$, 3.7% $Gd_2O_3$, etc.

dissolved in a minimum of hydrochloric acid. The rare earths were eluted through −100+200 mesh Nalcite HCR beds, 90 cm. long and 22 mm. in diameter, in copper$^{II}$ state, with a solution of approximately 2% EDTA at a $p$H of 8.5 and a linear flow rate of 0.5 cm. per minute. The solution was prepared by diluting 900 g. of diammonium dihydrogen ethylenediamine tetraacetate and 300 ml. of concentrated ammonium hydroxide to 45 liters with distilled water.

The rare earths displaced the copper$^{II}$ ions from the resin beds very nicely and except for channeling effects the copper–rare earth boundary was sharp. In each experiment

TABLE I

THE ELUTION OF A MIXTURE OF LUTETIUM, YTTERBIUM, THULIUM AND ERBIUM WITH EDTA THROUGH A BED OF NALCITE HCR IN THE COPPER$^{II}$ STATE

| Fraction no. | Total vol., l. | Wt. $R_2O_3$, g. | $Lu_2O_3$, % | $Yb_2O_3$, % | $Tm_2O_3$, % | $Er_2O_3$, % |
|---|---|---|---|---|---|---|
| 1 | 4.6 | 0.4036 | 99.8 | 0.2 | .. | .. |
| 2 | 4.8 | 1.2157 | 99.5 | 0.5 | .. | .. |
| 3 | 5.0 | 2.2398 | 99.0 | 1.0 | .. | .. |
| 4 | 5.2 | 2.2642 | 99.0 | 1.0 | .. | .. |
| 5 | 5.4 | 2.2613 | 97.5 | 2.5 | .. | .. |
| 6 | 5.6 | 2.2755 | 97.5 | 2.5 | .. | .. |
| 7 | 5.8 | 2.3111 | 95.5 | 4.5 | .. | .. |
| 8 | 6.0 | 2.3027 | 92.1 | 7.9 | .. | .. |
| 9 | 6.2 | 2.2936 | 88.1 | 11.9 | .. | .. |
| 10 | 6.4 | 2.2746 | 82.7 | 17.3 | .. | .. |
| 11 | 6.6 | 2.2530 | 77.5 | 22.5 | .. | .. |
| 12 | 6.8 | 2.1256 | 75.6 | 24.4 | .. | .. |
| 13 | 7.0 | 2.1822 | 73.7 | 26.3 | .. | .. |
| 14 | 7.2 | 2.1243 | 69.6 | 30.4 | .. | .. |
| 15 | 7.4 | 2.2149 | 57.1 | 42.9 | .. | .. |
| 16 | 7.6 | 2.1959 | 28.9 | 71.1 | .. | .. |
| 17 | 7.8 | 2.1914 | 7.2 | 92.8 | .. | .. |
| 18 | 8.0 | 2.1102 | 3.5 | 96.5 | .. | .. |
| 19 | 8.2 | 2.2627 | 0.5 | 99.5 | .. | .. |
| 20 | 8.4 | 2.3058 | 0.2 | 99.5 | 0.3 | .. |
| 21 | 8.6 | 2.3037 | 0.1 | 76.2 | 23.0 | .. |
| 22 | 8.8 | 2.2040 | .. | 14.0 | 86.0 | .. |
| 23 | 9.0 | 2.1737 | .. | 1.0 | 96.5 | 2.4 |
| 24 | 9.2 | 1.8525 | .. | .. | 78.0 | 16.3 |
| 25 | 9.4 | 0.3150 | .. | .. | 22.1 | 41.8 |

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(3) (a) G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 576, 1503 (1951); (b) E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, THIS JOURNAL, **75**, 4196 (1953).

(4) F. H. Spedding, E. I. Fulmer, J. E. Powell, T. A. Butler and I. S. Yaffe, *ibid.*, **73**, 4840 (1951).

(5) B. H. Ketelle and G. E. Boyd, *ibid.*, **69**, 2800 (1947)

TABLE II

THE ELUTION OF A MIXTURE OF GADOLINIUM, EUROPIUM AND SAMARIUM WITH EDTA USING COPPER$^{II}$ AS A RETAINING ION

| Fraction no. | Total vol., l. | Wt. $R_2O_3$, g. | $Gd_2O_3$, % | $Eu_2O_3$, % | $Sm_2O_3$, % |
|---|---|---|---|---|---|
| 1 | 5.0 | 0.1094 | 99.9 | W | ... |
| 2 | 5.2 | 1.4659 | 99.9 | M | ... |
| 3 | 5.4 | 2.0482 | 99.9 | MS | ... |
| 4 | 5.6 | 2.2322 | 99,7 | S | ... |
| 5 | 5.8 | 2.2824 | 99.5 | S | ... |
| 6 | 6.0 | 2.3200 | 99.0 | S | ... |
| 7 | 6.2 | 2.3364 | 98.5 | 1.5 | 0.05 |
| 8 | 6.4 | 2.3152 | 97.8 | 1.7 | 0.5 |
| 9 | 6.6 | 2.2512 | 90.8 | 3.9 | 5.3 |
| 10 | 6.8 | 2.1581 | 74.5 | 5.3 | 20.2 |
| 11 | 7.0 | 2.1884 | 56.1 | 5.5 | 38.4 |
| 12 | 7.2 | 2.2094 | 40.6 | 5.1 | 54.3 |
| 13 | 7.4 | 2.1108 | 22.1 | 4.6 | 73.3 |
| 14 | 7.6 | 2.1223 | 12.6 | 3.4 | 84.0 |
| 15 | 7.8 | 2.1164 | 6.4 | 2.1 | 91.5 |
| 16 | 8.0 | 2.2282 | 3.9 | 1.5 | 94.6 |
| 17 | 8.2 | 2.1684 | 2.2 | 0.3 | 97.5 |
| 18 | 8.4 | 2.2222 | 1.0 | 0.2 | 98.8 |
| 19 | 8.6 | 2.1642 | 0.5 | 0.15 | 99.3 |
| 20 | 8.8 | 2.0995 | .5 | .09 | 99.4 |
| 21 | 9.0 | 2.1298 | .2 | .09 | 99.7 |
| 22 | 9.2 | 2.1020 | .1 | .03 | 99.9 |
| 23 | 9.4 | 1.7836 | .05 | .02 | 99.9 |
| 24 | 9.6 | 0.5484 | .05 | .02 | 99.9 |

less than 400 ml. of eluate contained both copper and rare earth. The results are given in Tables I, II and III.

**2. The Elution of a Neodymium–Praseodymium Mixture.**—A $-40+50$ mesh Nalcite HCR resin bed, 25 cm. long and 22 mm. in diameter, was saturated with a load of 11.6194 g. of a mixture containing 50% $Nd_2O_3$ and 50% $Pr_6O_{11}$ dissolved in hydrochloric acid. A second bed of $-40+50$ mesh resin, 67 cm. long and 22 mm. in diameter, was saturated with copper$^{II}$ ions. The two columns were connected in series and were eluted with a solution containing 10 g. of the diammonium dihydrogen salt of EDTA per liter and adjusted to a *p*H of 7.97 by addition of concentrated ammonium hydroxide. The linear flow rate was kept at a constant value of approximately 0.3 cm. per minute and the eluate was collected in 250-ml. fractions. Under the above conditions the rare earth–copper boundary was very sharp. Only the intermixing due to the tilting of the band front could be detected. The eluate fractions were analyzed both spectrophotometrically and spectrographically. The results are given in Table IV. Similar separations were carried out using eluant *p*H values of 7.46 and 8.47. In both cases the degree of separation was about the same as that for the experiment described above.

## Discussion of Results

The above experiments show that it is possible to make rapid separation of complex mixtures of rare earths either into individually pure fractions or at worst into binary mixtures of adjacent elements by eluting the mixtures down resin beds in the copper$^{II}$ state by means of an ammonium hydroxide-buffered EDTA solution. It will be noted that the concentrations of the rare earth ions in the EDTA solution are from 10 to 20 times as great as was found expedient in citrate elutions.[4] This results in greatly increasing the elution rate and considerably less eluant has to be used in the operation. It will further be noted that in all the above experiments, except the last one, those groups of adjacent rare earths which were the most difficult to separate in case of elution by citrate[4] were deliberately chosen. With EDTA the separation factors were very much better considering the high solution concentrations and speed of elution. The method suffers from the fact that, since the solutions are much more concentrated, the overlap portions due to inadvertent tilting of the band fronts, channeling, etc., are larger.

TABLE III

THE ELUTION OF A MIXTURE OF DYSPROSIUM, YTTRIUM, TERBIUM AND GADOLINIUM WITH EDTA USING COPPER$^{II}$ AS A RETAINING ION

| Fraction no. | Total vol., l. | Wt. $R_2O_3$, g. | $Dy_2O_3$, % | $Y_2O_3$, % | $Tb_4O_7$, % | Other $R_2O_3$, % |
|---|---|---|---|---|---|---|
| 1 | 4.9 | .... | 1.0 | 99.0 | .. | .. |
| 2 | 5.1 | 1.1734 | 0.5 | 99.5 | .. | .. |
| 3 | 5.3 | 1.2472 | 0.1 | 99.9 | .. | .. |
| 4 | 5.5 | 1.2360 | 0.05 | 99.95 | .. | .. |
| 5 | 5.7 | 1.2185 | 0.02 | 99,8 | 0.2 | .. |
| 6 | 5.9 | 1.1942 | .. | 97 | 3 | .. |
| 7 | 6.1 | 1.3377 | .. | 80 | 20 | .. |
| 8 | 6.3 | 1.3904 | .. | 55 | 45 | .. |
| 9 | 6.5 | 1.6286 | .. | 49 | 51 | .. |
| 10 | 6.7 | 1.6642 | .. | 46 | 54 | .. |
| 11 | 6.9 | 1.6517 | .. | 45 | 55 | .. |
| 12 | 7.1 | 1.6860 | .. | 41 | 59 | .. |
| 13 | 7.3 | 1.7255 | .. | 36 | 64 | .. |
| 14 | 7.5 | 1.8480 | .. | 32 | 68 | .. |
| 15 | 7.7 | 1.9772 | .. | 13 | 87 | .. |
| 16 | 7.9 | 2.1522 | .. | 3.0 | 97 | .. |
| 17 | 8.1 | 2.2284 | .. | M | 99 | .. |
| 18 | 8.3 | 2.2686 | .. | W | 99 | .. |
| 19 | 8.5 | 2.3215 | .. | W | 99 | .. |
| 20 | 8.7 | 2.3250 | .. | W | 99 | .. |
| 21 | 8.9 | 2.2380 | .. | VW | 99 | .. |
| 22 | 9.1 | 2.3187 | .. | VW | 99 | .. |
| 23 | 9.3 | 2.2093 | .. | T | 97.5 | 2.5 |
| 24 | 9.5 | 2.1604 | .. | FT | 72.5 | 27.5 |
| 25 | 9.7 | 1.2476 | .. | ... | 25.5 | 74.5 |
| 26 | 9.9 | 0.0757 | .. | ... | 10.0 | 90.0 |

TABLE IV

THE ELUTION OF A MIXTURE OF NEODYMIUM AND PRASEODYMIUM WITH EDTA USING COPPER$^{II}$ AS A RETAINING ION

| Sample no. | $R_2O_3$ recovered in eluate, g. | $Pr_6O_{11}$, % | $Nd_2O_3$, % |
|---|---|---|---|
| 1 | 0.4126 | <0.08 | >99.9 |
| 2 | .9584 | <0.08 | >99.9 |
| 3 | .9519 | <0.08 | >99.9 |
| 4 | .9867 | <0.08 | >99.9 |
| 5 | .9575 | <0.08 | >99.9 |
| 6 | .9453 | 11 | 88 |
| 7 | .9400 | 64 | 34 |
| 8 | .9283 | 96 | 4 |
| 9 | .9213 | >99.9 | 0.1 |
| 10 | .9156 | >99.9 | <0.06 |
| 11 | .9122 | >99.9 | <0.06 |
| 12 | .9167 | >99.9 | <0.06 |
| 13 | .6265 | >99.9 | <0.06 |

However, this can be minimized if the quantities of the rare earths adsorbed are sufficiently great that the length of the individual rare earth bands which develop are long compared to the diameter of the column. If the individual rare earth bands are short, a number of the binary mixtures obtained can be saved until a sufficient quantity has been accumulated to load another column.[6] One subsequent elution with EDTA will then separate a major portion of the two rare earths in a highly pure state.

These experiments do not establish optimum conditions for separation; however, they do demonstrate that rare earths can be separated rapidly by means of EDTA and that considerable quantities of pure rare earths can be obtained by this method in a period of four to five days with very little attention to the column operation being required during the interim period. We are continuing the study of these systems.

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[6] If one of the components of the binary mixture has a divalent state (Yb, Eu, Sm) a rapid chemical separation might be preferred at this point; see J. K. Marsh, H. N. McCoy.[7,8]

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

[8] H. N. McCoy, THIS JOURNAL, **58**, 2279 (1936); **63**, 1622 (1941).

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

# Formation, Stability and Crystal Structure of the Solid Aluminum Suboxides: $Al_2O$ and AlO[1]

BY MICHAEL HOCH AND HERRICK L. JOHNSTON

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The study of the reactions (1) $4Al(l) + Al_2O_3(s) \rightarrow 3Al_2O(s)$ and (2) $Al(l) + Al_2O_3(s) \rightarrow 3AlO(s)$ between 1000 and 2000°, by means of a high temperature X-ray technique, indicated the formation of solid $Al_2O$ and AlO above certain temperatures. At 1000° no reaction occurs. Between 1100 and 1500° $Al_2O(s)$ is formed according to reaction 1. Between 1500 and 1600°, both reactions 1 and 2 occur simultaneously, whereas above 1600° the latter reaction occurs. On cooling or rapid quenching both compounds disproportionate into Al and $Al_2O_3$. From the X-ray diffraction patterns the crystal structure and lattice constants of $Al_2O$ and AlO were determined. Both are cubic, the lattice constants being 4.98 Å. for $Al_2O$ at 1110°, and 5.67 Å. for AlO at 1700°.

## Introduction

The existence of gaseous AlO has been known from spectroscopic investigations.[2] From their investigation on the gaseous species of the $Al-Al_2O_3$ system, Brewer and Searcy[3] concluded that two suboxides of aluminum must exist in the gas phase; these they identified as $Al_2O$ and AlO. A phase diagram study of $Al-Al_2O_3$, made by Baur and Brunner,[4] revealed the presence of a compound, $Al_8O_9$, melting at 2323°, with a eutectic between $Al_8O_9$ and $Al_2O_3$. Beletskii and Rapoport[5] reported the formation of hexagonal $Al_2O$ by heating Al and $Al_2O_3$ *in vacuo* in the presence of $SiO_2$ and C and condensing the volatile products.

In the present investigation the formation, in the solid state, of the lower oxides of aluminum, which are not stable at room temperature, was studied by photographing X-ray diffraction patterns at high temperatures. The presence of a new compound is shown by the appearance of a new set of diffraction lines. By varying the temperature, the stability of the compound with respect to disproportionation into Al and $Al_2O_3$ can be determined. From the position of the lines in the diffraction patterns, lattice constants and crystal structure can be determined, and from the relative intensity of the pattern the approximate composition of the compound can be estimated.

## Materials and Experimental Procedure

The X-ray diffraction patterns were taken in our high temperature camera which has been described elsewhere.[6] Besides the changes already made,[7] a new collimator was designed, which lowered the exposure time to 1 hour. This was necessary, due to the high evaporation rate of aluminum, even in the presence of 1 atm. of helium. The temperature was measured with a Leeds and Northrup disappearing-filament optical pyrometer which had been calibrated against a standard lamp obtained from the National Bureau of Standards. The temperature calibration of the camera was carried out by placing a "black body," made from a piece of tantalum tube, in place of the X-ray specimen. By taking account of the various calibration and correction factors, the uncertainty in the reading of the pyrometer, and the slight temperature variations during the runs, the temperature may be considered accurate to within 20°. Ni-filtered Cu K$\alpha$ radiation, obtained from a Machlett Tube operated at 50 kv. and 20 ma., was used.

The Al and $Al_2O_3$ were obtained from the J. T. Baker Chemical Co., and were of "Purified" and "Analyzed" grades, respectively. Rods of $^1/_{32}$ in. diameter and $^1/_4$ in. length were pressed from $Al_2O_3$ and $Al_2O_3$ + Al and placed into the camera. After filling with helium, the camera was heated and the X-ray diffraction patterns were photographed. For every X-ray determination a new sample was employed.

## Experimental Results

The $\alpha$-$Al_2O_3$ was found to have the same crystal structure at 2000° as at room temperature. Since aluminum is a liquid above 660°, it does not contribute any lines to the X-ray diffraction patterns.

Two sets, or series, of experiments were carried

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[1] This work was supported in part by the Office of Naval Research under contract with the Ohio State University Research Foundation.

[2] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

[3] L. Brewer and A. W. Searcy, THIS JOURNAL, **73**, 5308 (1951).

[4] E. Baur and R. Brunner, *Z. Elektrochem.*, **40**, 155 (1934).

[5] M. S. Beletskii and M. B. Rapoport, *Doklady Akad. Nauk SSSR*, **80**, 751 (1951).

[6] J. W. Edwards, R. Speiser and H. L. Johnston, *Rev. Sci. Inst.*, **20**, 343 (1949).

[7] M. Hoch and H. L. Johnston, THIS JOURNAL, **75**, 5224 (1953)