253. *The Fractionation of Cerium*(III) *and Neodymium Mixtures on an Ion-exchange Column.*

By B. A. Lister and M. L. Smith.

The possibility of separating simple mixtures of cerium and neodymium salts by preferential ion exchange has been examined. A novel multitube column has been designed and in use has achieved the partial separation of these ions, cerium being taken up preferentially by the exchanger. A decrease in the total concentration of the mixed solution has resulted in increased separation, which may be due to a difference in the relative degree of hydration of the two ion species at different concentrations.

Walton (*J. Franklin Inst.*, 1941, **232**, 305) has reviewed the published data on the equilibria between cations of the same valency in the alkali and the alkaline-earth series on various exchangers, and has shown that for each of these series the higher the atomic weight the more firmly was the ion retained. The experiments of Jenny (*Kolloid-Beih.*, 1927, **23**, 428) appeared especially conclusive in these two series, but in his experimental arrangements the salt concentration was continuously varying.

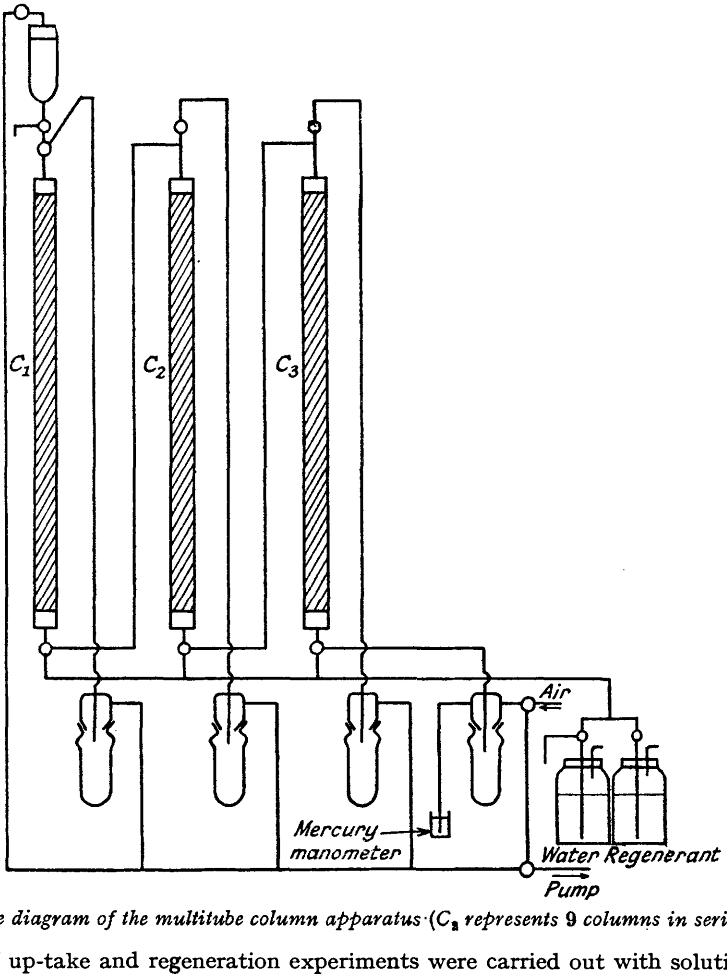
Since with increasing ionic radius there is a decrease in hydration in solution, it also appeared that ion retention increased as the hydration was lower. This latter correspondence was supported by the experiments of Wiegner (*J. Soc. Chem. Ind.*, 1931, **50**, 65T; *Z. Pflanz., Düngung, Bodenk.*, 1929, **14**, *A*, 321) who showed that in a range of alcohol–water mixtures the displacing powers of $Cs^{\cdot}$ and $Na^{\cdot}$ became more nearly alike as the proportion of alcohol was increased, *i.e.*, as the hydration differences fell.

However, Russell and Pearce (*J. Amer. Chem. Soc.*, 1943, **65**, 595), in some preliminary experiments on the separation of a complex mixture of rare-earth group ions on a 50-ft. zeolite column, have reported that the ions of larger radius (*e.g.*, La, 1·22 A., Nd, 1·15 A.) are held less firmly than the smaller ions (Y, 1·06 A.) and consequently appear first in the percolate from the base of the column. This conclusion is confirmed in a general way by the work of Kozak and Walton (*J. Physical Chem.*, 1945, **49**, 471).

We were interested in the separation of members of the rare-earth series by ion exchange, and in order to assess the possibilities, carried out some preliminary experiments with solutions of cerous, praseodymium, and neodymium salts (ionic radii : Ce 1·18 A., Pr 1·16 A., Nd 1·15 A.).

Preliminary Experiments on Exchangers.—The following exchangers were available (*a*) " Basex ", a synthetic zeolite similar to " Crystallite ". (*b*) " Decalso ", a synthetic siliceous gel. (*c*) " Zeokarb Na ", a sulphonated coal. (*d*) " Zeokarb H.I.M. ", a sulphonated coal. (*e*) " Zeokarb H.I.P. ", a sulphonated coal. The first three were $Na^{\cdot}$-ion, and the last two $H^{\cdot}$-ion exchangers.

FIG. 1.



Line diagram of the multitube column apparatus (C_2* represents 9 columns in series).*

A series of up-take and regeneration experiments were carried out with solutions of cerous nitrate on each of these exchangers, using both the static and the column technique. The results of these tests showed that (*e*) had the most rapid and highest up-take and the most satisfactory regeneration properties. This exchanger was used in all subsequent work.

Static up-take tests to compare the exchange characteristics of $Ce^{\cdot\cdot\cdot}$, $Pr^{\cdot\cdot\cdot}$, and $Nd^{\cdot\cdot\cdot}$ on Zeokarb H.I.P. showed that the exchange characteristics of the three ions are so similar that any differences lie within the limits of sensitivity of the experimental and analytical methods and are therefore not evident.

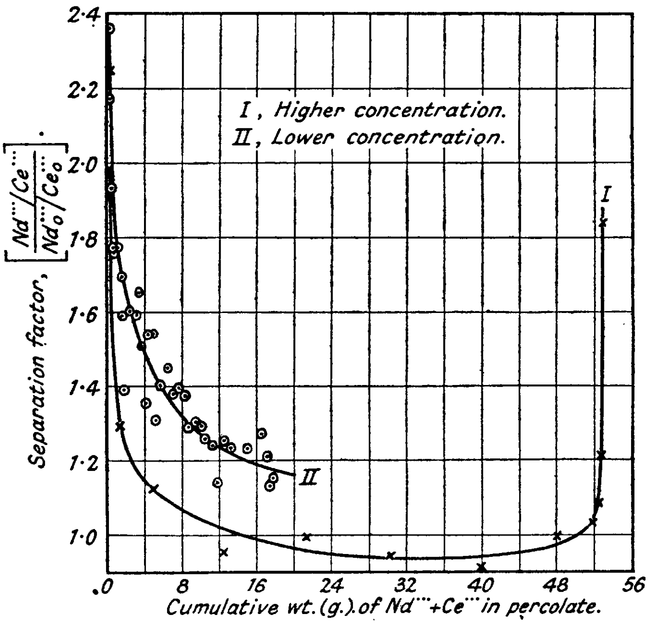
EXPERIMENTAL.

Apparatus.—Preliminary work showed that a long column was essential if any significant separation of cerium-group ions was to be achieved, and clearly a column approximating to the 50-ft. length used by Russell and Pearce was indicated. For convenience, and to avoid the difficulty of support, a multitube model was designed and constructed consisting of eleven columns, each 110 cm. long and 1 cm. in diameter, giving a total length of 12 m. Fig. 1 is a line diagram of the apparatus. In this series construction, to ensure even flow, a departure was made from the normal procedure in that before addition of the mixture the apparatus was completely filled with pure solvent, in this case water. This initial filling was made (from a reservoir attached to the base of each column) by application of suction at the head, together with suitable manipulation of the stop-cocks at each end of the separate limbs.

In the runs with mixtures of cerous and neodymium nitrates the rare-earth solution was allowed to percolate slowly through the apparatus from a reservoir at the head of the initial column. Slight suction was necessary to ensure a reasonable flow rate, a rate of 1·4 ml./min. being maintained with a reduction in pressure of 150 mm. of mercury. Each 10-ml. fraction of the percolate was tested for the presence of rare-earth ions with (*a*) saturated oxalic acid solution and (*b*) alcoholic quinalizarin and sodium hydroxide solutions. When rare-earth ions were detected, the nitrate solution in the reservoir was replaced by water, and 10 ml. fractions of percolate were collected until rare-earth ions were no longer detectable.

For the regeneration of the Zeokarb, two procedures were possible with our apparatus: (*a*) the regenerating liquid could be run straight through all the columns in series and collected as before in the receiver at the base of the terminal column, or (*b*) each column could be regenerated separately. The second of these methods was adopted, 500 ml. of 4N-sulphuric acid being passed in an upward direction through each of the first two and the last two columns at the rate of 10 ml./min.

FIG. 2.



The separation of Ce$^{\cdots}$ *and* Nd$^{\cdots}$ *on the multitube column at two different concentrations.*

Analytical Procedure.—Owing to the possibility of the presence of traces of iron in the percolate fractions, an oxalate separation was carried out as the first stage in the analysis. The procedure then adopted was as follows: (*a*) Cerium and neodymium were precipitated as oxalates, ignited to oxides in a porcelain crucible and weighed (Ce all assumed to be CeO_2). (*b*) The weighed oxides were brought into solution with sulphuric acid and hydrogen peroxide, the hydrogen peroxide boiled off, the cerium oxidised to the quadrivalent state with ammonium persulphate and silver nitrate in sulphuric acid solution, and ceric ion titrated with ferrous ammonium sulphate and potassium permanganate. (*c*) The neodymium content of the fractions was calculated by difference.

Results.—Two full-scale runs were made with total concentrations approximately M and M/4, the ratio of Ce$^{\cdots}$/Nd$^{\cdots}$ in each case being 8·5 : 1. The run at the higher concentration took 22½ hours, and that at the lower concentration 47½ hours.

In the run with M-solution the leading fractions showed a considerable increase in the proportion of neodymium, the ratio of neodymium to cerium having been more than doubled. As was to be expected, this ratio became less until, towards the end of the run, a sharp increase was noticed. This increase was unexpected, but an estimation of the concentration gradient in the solution leads to a likely explanation. As the apparatus was initially filled with water, there will have been a decrease in the concentration of rare-earth ions at the head of the advancing solution. The final washing with water will have caused a similar decrease in concentration at the tail of the solution, and it may well be this dilution effect which produced a more favourable neodymium/cerium ratio. This conclusion was confirmed by the results of the run at the lower concentration in which a significant increase in the degree of separation was achieved (Fig. 2).

Regeneration of the first and the last two columns showed, in both runs, that the ratio of Nd$^{\cdots}$ ions to $\mathrm{Ce}^{\cdots}$ ions held on the exchanger increased towards the terminal column. Each column, however, contained a greater proportion of $\mathrm{Ce}^{\cdots}$ ions than did the original solution.

DISCUSSION.

A partial separation of rare-earth ions has been achieved by preferential ionic exchange on a column. Runs with Ce(III) and Nd mixtures have shown definitely that the former ion, of larger Goldschmidt radius, is relatively more strongly held. This is in agreement with the general experience of Jenny (*loc. cit.*) but contrary to that of Russell and Pearce (*loc. cit.*). No data are available on the relative hydrations of these ions.

The concentration of the solution has a marked influence on the degree of separation achieved, but this effect works in the direction which makes large-scale application difficult because of the large volumes involved. Russell and Pearce (*loc. cit.*) and Bray (*J. Amer. Chem. Soc.*, 1942, **64**, 954) have shown that changes in the ratio of the ions in the liquid phase affect the relative accumulation of ions on the zeolite, but there is no evidence that, with mixtures of ions of the same valency, a change in the absolute concentration without any alteration in the relative ratios of ions in solution would have any such effect. In fact, Ivanov and Gapon (*J. Physical Chem. U.S.S.R.*, 1941, **45**, 659) have concluded that dilution of the solution does not affect the relative uptake in such mixtures, and Renold (*Kolloid-Beih.*, 1935, **43**, 1) has found that, below 0·1N, dilution does not affect the relative uptakes of $\mathrm{Ca}^{\cdot\cdot}$ and $\mathrm{K}^{\cdot}$ ions. The conclusion in the present work that a reduction in the total concentrations has actually decreased the relative uptake of cerous ion requires explanation, and it is suggested that this lies in the relative dependence of ion hydration on dilution.

It might be suspected that the greater oxidisability of Ce(III) and tendency to formation of ceric ion would bias the results, since it is usually accepted (Walton, *loc. cit.*) that the ion of higher valency is relatively more greatly adsorbed with increased dilution. However, there was no evidence of the presence of ceric ion.

Conclusions.—(1) In a column test with a mixture of cerium and neodymium salts at approximately M-concentration, cerium was more strongly held on Zeokarb H.I.P.; *i.e.*, there was greater retention of the larger ion.

(2) This direction of separation is contrary to the experience of Russell and Pearce (*loc. cit.*) who, using a complex mixture of rare-earth ions, found that ions of smaller Goldschmidt radius were more strongly held.

(3) The degree of separation of these two ions was greater in a test with M/4-solution.

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