29. *The Magnetic Susceptibilities of the Rare-earth Elements. Part I. Yttrium.*

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Yttrium has been purified by fractional precipitation by ammonia carried in a current of air, and the process followed by magnetic susceptibility measurements. The limiting value found for $10^6\chi_{\mathrm{Y}^{\cdots}}$ is $0{\cdot}21 \pm 0{\cdot}02$.

This series of papers records the results obtained in experiments with the rare-earth elements which have been carried out since 1936. The raw material for the separation of yttrium was derived from a Norwegian gadolinite. This had been fractionally crystallised from water as bromate until it showed only weak bands of holmium at the head and erbium at the tail. The bromate method gives a very slow separation of other rare earths from yttria, so it was decided to try a method based on the greater basicity of yttria, namely, the fractional precipitation of the hydroxide by ammonia carried in a current of air (cf. Trombe, *Compt. rend.*, 1942, **215**, **539**). This gave a fairly rapid separation which was followed by determining the magnetic susceptibility of the $\mathrm{Y}^{\cdots}$ in a chloride solution. The last two series of fractionating gave the following results:

Fraction	1	2	3	4	5	6	7	8	9	10
Penultimate series:										
$10^6\chi_{\mathrm{Y}^{\cdots}}$	+0·49	+0·37	+0·33	+0·25	+0·24	+0·22	+0·24	+0·21	—	—
Ultimate series:										
$10^6\chi_{\mathrm{Y}^{\cdots}}$	+0·67	+0·57	+0·53	+0·38	+0·27	+0·26	+0·23*	+0·20*	+0·19*	+0·20*

The susceptibility of the original material (305 g.) was $5{\cdot}78 \times 10^{-6}$ and its equivalent 38·05. The experimental error in the determination of χ was estimated to be $\pm 0{\cdot}02 \times 10^{-6}$. The fractions marked with an asterisk were regarded as pure yttria. They amounted to about 18 g. and had $10^6\chi = 0{\cdot}21 \pm 0{\cdot}02$ and equivalent 37·64.

The purest oxide was tested by its emission spectrum on a copper–graphite arc using a small quartz spectrograph. No lines other than those of yttrium were found; in particular, the persistent lines of holmium and erbium were looked for but were absent.

EXPERIMENTAL.

The apparatus used for the precipitation consisted of two Winchester bottles and a flow-meter containing mercury connected in series to the water-pump. The ammonia solution was placed in the first bottle and the rare-earth solution in the second; the flow-meter was calibrated roughly, and an air speed of *ca.* 2 l./min. usually employed. Preliminary experiments showed that the separation improved as the concentration of ammonia was decreased but a practical limit was reached at about 10 g./l. With this concentration the ammonia was exhausted in some precipitations and was replaced by fresh solution.

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† After a violent explosion this method of drying was abandoned.

The rare-earth solution in the second bottle was adjusted to a concentration of about 40 g./l. It was found that with chloride as anion, especially when the yttrium content was low, the precipitate did not filter readily; when nitrate was used as anion this difficulty was not encountered. The general procedure was as follows. The rare-earth oxide was dissolved in nitric or hydrochloric acid and evaporated to small bulk to remove most of the excess acid; it was then diluted to 40 g./l. and partly precipitated by the current of ammonia and air, and allowed to stand for a few hours. The precipitate was then filtered off, and the solution returned to its bottle for further precipitation. In the second series the head fraction, dissolved in acid and adjusted to *ca.* 40 g./l., was treated similarly; when about half of this had been precipitated a solution of the second fraction was added. This process was continued until all the material had been again precipitated. The fractionation was followed by determinations of the equivalent of the oxide and the magnetic susceptibility of the ion.

Determination of Equivalent.—Satisfactory results could not be obtained by determining the ratio oxalate/oxide since the degree of hydration of the oxalate varies with small changes in the conditions of precipitation. The method found best was as follows. A suitable weighed amount of freshly ignited oxide was dissolved in a known volume of N/2-sulphuric acid. Excess of approximately N/2-potassium oxalate was then added, and the precipitated oxalate filtered off. The filtrate and washings were then titrated with N/2-sodium hydroxide, a mixture of bromocresol-green and methyl-red being used as indicator. This mixture gave a very sharp end-point and was not affected by carbonates. In this way the equivalent could be determined to 0·1 unit.

Magnetic Susceptibility.—This was determined at room temperature by the Gouy method described earlier (this vol., p. 132). In following the fractionation of yttria a solution of about 10% oxide was made by weighing freshly ignited oxide, dissolving it in excess of hydrochloric acid, and evaporating to a small bulk to remove excess acid. The solution was diluted to about 10%, weighed, and its susceptibility determined.

Let w be the weight of oxide used and q be its equivalent. Assuming complete dissociation or negligible effect of incomplete dissociation, the weight of rare earth ion $M^{\cdots}$ is $w_1 = w(q - 8)/q$. The chloride ion which is equivalent to $w_2 = 35{\cdot}5\, w/q$. Let w_3 be the weight of excess hydrochloric acid, and w_4 the weight of water in the solution. Obviously $w_4 = W - (w_1 + w_2 + w_3)$, where W is the total weight of solution. The susceptibilities of chloride ion, hydrochloric acid, and water were taken as

$$10^6\chi_{\mathrm{Cl}'} = -0{\cdot}673 \text{ (Stoner, `` Magnetism and Matter '', p. 270)}$$

$$\left.\begin{aligned} 10^6\chi_{\mathrm{HCl}} &= -0{\cdot}661 \\ 10^6\chi_{\mathrm{H_2O}} &= -0{\cdot}720 \end{aligned}\right\}\text{International Critical Tables}$$

Assuming that the susceptibilities of the components of the solution are additive, it is readily shown that

$$10^6\chi_{\mathrm{M}^{\cdots}} = \frac{W}{w}\frac{q}{q-8}(10^6\chi_{\mathrm{soln.}} + 0{\cdot}720) - 0{\cdot}720 - \frac{1{\cdot}67}{q-8} - 0{\cdot}059\,\frac{w_3}{w}\frac{q}{q-8}$$

where $\chi_{\mathrm{M}^{\cdots}}$ is the susceptibility per g. of the ion $M^{\cdots}$. It is assumed that the salt is completely dissociated; if this is not true the effect on $\chi_{\mathrm{M}^{\cdots}}$ will probably be very small.

The excess hydrochloric acid was in some cases estimated by titration. It was usually less than 5% so that the term in w_3 could be neglected. The value of $10^6\chi_{\mathrm{soln.}}$ could be determined to within 0·002; W/w was approximately 10, and q approximately 38; the consequent error in $10^6\chi_{\mathrm{M}^{\cdots}}$ was approximately ±0·02.

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