30. *The Place of Yttrium and the Application of Ferricyanide Precipitation in the Rare-earth Group. The Purification of Erbium.*

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Whereas it is believed that ionic and atomic radii sequences of the rare-earth elements (atomic numbers 57—71 inclusive) both follow the atomic number sequence, yttrium interpolates between holmium and dysprosium in ionic radius, and between neodymium and samarium in atomic radius. Examples of yttrium occupying the latter position are collected. Yttrium may be collected first in one and then in a second position in the rare-earth series, and so be readily eliminated and purified. Ferricyanide precipitation is reported upon favourably for the separation of yttrium from holmium and erbium. The reduction of yttrium in erbium from 7 to 0·32 atoms % was accomplished by six precipitations with 50% yield. A sample of 20 atomic % holmium oxide rose to 36% in the first two-fifths to be precipitated, and fell to 6·5% in the tail two-fifths when divided into four fractions.

The ionic radius of yttrium from measurements of the oxide lattice size appears to fall between that of dysprosium and holmium, but other observations, *e.g.*, fractional crystallisations o bromates or dimethylphosphates, or measurement of molecular volume of hydrated sulphates (Hevesy, *Z. anorg. chem.*, 1925, **147**, 217; **150**, 68) place yttrium between holmium and erbium. Now, while the series of elements Nos. 57—71 on passing between ionic and covalent linkage may be expected to have a similarly graded series of properties so as to retain their relative stations, yttrium (No. 39) cannot be expected to maintain its ionic position between Nos. 67 and 68 when in a covalent state. The electron density of yttrium is lower, and it may be that the three additional electrons will produce a proportionately greater increase in radius. Indeed, Klemm and Bommer (*ibid.*, 1937, **231**, 138; 1939, **241**, 264) have measured the atomic volumes and derived atomic radii of the rare-earth metals, and it can be seen that this is so. Abnormally large radii were found for the three elements having distinct bivalent properties, and rather small volumes for cerium, praseodymium, and terbium. The others lay on a smooth curve when plotted against atomic number, and showed a fall from lanthanum (1·871 A.) to lutecium (1·737 A.), with yttrium (1·814 A.) taking a place just below neodymium (1·818 A.). Thus yttrium here rises five or six places in size order as compared with the yttrium ion in the ionic radius sequence. This suggests that separation of yttrium from the yttrium earths should be accomplished by using processes involving covalent linkages in place of ionic. Then we may expect it to accumulate between neodymium and samarium.

The Group VIII complex cyanides are worth studying in this connexion. A number of solubilities of ferro-, ferri-, and cobalti-cyanides have been determined. These are presented on p. 119 recalculated as milligram-atoms of rare earth per litre.

Solubility of rare-earth complex cyanides, in mg.-atoms/l.

	E = Y.	La.	Ce.	Pr.	Nd.	Y.	Sm.	Gd.	Dy.	Er.	Yb.	Y/Er.
(*a*)	—	32·6	—	14·2	9·13	5·33	1·54	0·75	1·60	0·74	—	7·2
(*b*)	—	24·0	24·7	—	9·54	7·23	—	4·10	—	(1·9)	0·81	3·8
(*c*)	—	45·2	19·7	18·8	5·3	4·3	1·6	—	—	—	2·6	—
(*d*)	—	58·0	11·8	8·25	20·6	7·9	4·7	—	—	—	4·4	—
(*e*)	30·9	15·7	—	—	10·6	—	13·9	15·5	19·4	15·8	—	2·0
(*f*)	7·45	4·2	—	—	4·1	—	3·9	3·3	3·35	2·8	—	2·7
(*g*)	58·3	22·4	—	—	9·8	—	14·5	12·6	19·0	19·2	—	3·0

(*a*) Ferricyanides, $EFe(CN)_6,nH_2O$ ($n = 4$, except La and Dy, 4·5; Pr, 3) at 20° (Prandtl and Mohr, *Z. anorg. Chem.*, 1938, **236**, 243; **237**, 160).

(*b*) Cobalticyanides, $ECo(CN)_6,4{\cdot}5H_2O$ at 20° (James and Willand, *J. Amer. Chem. Soc.*, 1916, **38**, 1497).

(*c*) Cobalticyanides, found to be anhydrous (Karantaissis, Vassiliadis, and Perakis, *Compt. rend.*, 1939, **298**, 1720).

(*d*) As (*c*), but in 0·1N-hydrochloric acid.

(*e*) Ferrocyanide, $NaEFe(CN)_6,nH_2O$ ($n = 5$, 6, 7, 8, or 10) in 0·1N-HCl (Prandtl and Mohr, *loc. cit.*).

(*f*) Ferrocyanide, $KEFe(CN)_6,nH_2O$ ($n = 4$, 5, or 8) in 0·1N-HCl (*idem, ibid.*).

(*g*) Basic ferrocyanide, $E(OH)[EFe(CN)_6]_2,nH_2O$ ($n = 14$, 15, or 18) (*idem, ibid.*).

The above data serve to show that the solubility of yttrium is much greater in all instances than its neighbours in an ionic radius sequence. Among the ferri- and cobalti-cyanides it appears to take again a position as in the atomic volume sequence of the metals.

The behaviour of yttrium as a base may also be considered. It is well known to act as a stronger base than its neighbours in an ionic radius sequence. The situation has been fully reviewed recently by Moeller and Kremers (*Chem. Rev.*, 1945, **37**, 97; *J. Physical Chem.*, 1944, **48**, 395) who conclude that " the anomalously high basicity of yttrium as obtained by measurements upon natural mixtures is undoubtedly a concentration effect ". They bring evidence to show that yttrium can take its rightful place in the ionic sequence in an evaluation of basicity if disturbing factors are eliminated. This is shown by the pH of 0·1M-solutions after 40% precipitation as hydroxide. Here the pH value for yttrium falls between the values for erbium and gadolinium. On the other hand, at incidence of hydroxide precipitation the value found for yttrium placed it between samarium and neodymium. Trombe (*Compt. rend.*, 1943, **216**, 888) finds that pure yttrium shows a remarkably large dilution factor in its basic strength as measured by pH at initiation of hydroxide precipitation by gaseous ammonia in nitrate solutions. In dilute (0·005M) solution it appears to be almost as strong a base as lanthanum, but in concentrated (0·5M) solution it is weaker than dysprosium at the same concentration. Thus we may deduce that the high concentration of yttrium in natural mixtures should mask the potentially high basic strength of yttrium in dilute solution, and separation of pure yttrium by basic methods should fail whereas separation of a little yttrium from erbium should be easy. This is exactly the reverse of well-established practical experience. Some other factor of over-riding importance must be operative. Moeller and Kremers cite twelve orders of basicity of the rare earths arrived at by different experimental methods. In four cases (ammonia precipitation, and sulphate, nitrite, and azide hydrolysis) yttrium takes a place between neodymium and samarium, in three cases it lies somewhere between samarium and dysprosium, and in two (carbonate hydrolysis and electro-reduction) it lies next to holmium. Gaps in data leave the yttrium position in some doubt in the other three cases. The basic salts of yttrium are probably in general more stable than those of its neighbours in the ionic radius sequence. Moeller and Kremers find equilibrium pH to be established less quickly after each addition of alkali to yttrium solutions than with other rare-earth solutions. They ascribe this to the stability of a basic nitrate, and account similarly for the strong apparent basicity of yttrium which they regard as in reality spurious, but which is indicated by the high pH value for the incidence of precipitation of hydroxide from nitrate and sulphate solutions, as well as by much practical experience. The higher values for the pH at incidence of hydroxide precipitation from acetate solutions for all the rare earths as compared with nitrate and sulphate they ascribe to co-ordination, but obviously the same reasoning would apply to the high values for yttrium in nitrate and sulphate solutions. A co-ordinating tendency may masquerade as a strengthening of basic character.

The instances here mentioned [atomic volume, solubility of ferricyanide, pH at incidence of precipitation of hydroxide from nitrate or sulphate solution by ammonia, or from chloride solution by sodium hydroxide (Britton, *J.*, 1925, **127**, 2142), four fractionation methods by basic processes] in which yttrium takes a position in the series of rare earths between neodymium and samarium are too numerous to be fortuitous. In yet other instances, yttrium may occupy a position between samarium and its place (close to holmium) where it is found in the pure ionic state. The former position appears to be connected with co-ordination or a covalent reaction and demonstrates that yttrium is not in all respects a typical yttrium group element. It may show a resemblance to scandium not seen in the earths of high atomic weight and comparable basicity. There is a qualitative difference between the yttrium ion and the holmium ion not taken into account by quantitative measurements of their respective basicities, but due to the differing inner constitutions of nucleus and electons.

Some reactions which can be formulated as ionic, for instance that between potassium ferricyanide and yttrium chloride, do not appear to be in fact ionic. It is possible to bring these substances together at high concentrations without any precipitate forming, and reaction only takes place slowly on gentle warming. Although yttrium in the product shows a normal ionic radius, the reaction separates yttrium from the yttrium earths in a manner to be expected in a non-ionic reaction.

The Purification of Erbium and Holmium.—The complex potassium ferrocyanide of yttrium and erbium was used by Prandtl (*Z. anorg. Chem.*, 1931, **198**, 157) for the purification of erbium, but his preparation was found later to be much less pure than he had supposed (Hönigschmid and Wittner, *ibid.*, 1937, **232**, 112). Moeller and Kremers (*J. Amer. Chem. Soc.*, 1944, **66**, 307) have further studied the purification of erbium by means of ferrocyanide. According to the data tabulated above, potassium yttrium ferrocyanide is 2·7 times as soluble as potassium erbium ferrocyanide. Ferricyanides on the other hand will be seen to show a 7-fold greater solubility for yttrium than for erbium. Prandtl and Mohr (*loc. cit.*) have recommended the use of ferricyanides for the preliminary elimination of yttrium from the yttrium earths before proceeding with their separation, but give few details of the method. The author has found it useful not only for the preliminary separation of yttrium but also for the ultimate purification of erbium and for the concentration of holmium following a bromate fractionation. He has previously recommended the use of dimethylphosphates (*J.*, 1939, 554) for separation of holmium and yttrium, and this salt probably remains the most useful for the final stage, but after a bromate fractionation has separated erbium and holmium the use of ferricyanide precipitation will again be useful to eliminate the bulk of the yttrium to yield a 80—90% holmium preparation for dimethylphosphate treatment. Since dimethylphosphates tend to hydrolyse, especially the less soluble ones, and since the sparingly soluble hydrolysis products tend to collect at the head, the dimethylphosphate fractionation of erbium will not be expected to eliminate yttrium satisfactorily. Any slight loss of holmium through hydrolysis will collect with yttrium at the head and leave pure holmium lower down the series, but the purification of erbium must be completed by the ferricyanide process. The six best holmium oxide fractions from the author's previously reported holmium fractionation have now been quantitatively analysed for yttrium by the cathode layer method and found to average about 0·03% of yttrium oxide by weight.

A loss of 1—2% was common in each ferricyanide precipitation and hydrolysis. Considering the comparatively few operations required, these losses are not intolerable. The technique of the process is simpler than for the ferrocyanides and the separation more rapid. Six precipitations of 93% erbium gave a 50% yield of 99·7 atomic % material, or by weight 96% oxide became 99·80 ± 0·05%.

EXPERIMENTAL.

The Reaction between Rare-earth Chloride and Potassium Ferricyanide.—The precipitation of rare-earth ferricyanide is possible from chloride solution at any temperature between 15° and 100° by addition of concentrated potassium ferricyanide solution, but at low temperatures high concentrations of rare earth, of the order of 200 g./l. of oxide, must be used. Initiation of the reaction is not always smooth, but slow precipitation gives the best fractional separations. Thus it was sometimes advantageous to warm a small portion of the chloride–ferricyanide solution separately till a heavy precipitate was formed and to add this to the main bulk. The main warming was done not more rapidly than 1°/5 mins. at temperatures where precipitation was expected to begin. It was also advantageous to lower the temperature with cold water or ice by 10—15° once the precipitation was well established. Mechanical stirring was applied while the ferricyanide solution was added dropwise. Precipitates formed in boiling solution are bright blood-red, crystalline, and settle immediately; those from cold solutions clay-like and more brick-red. Precipitation temperatures of 40—60° appeared most favourable, with precipitation starting by the time one-third of the potassium ferricyanide to be used had been added. The addition took 1—2 hours but the precipitate became more crystalline when the reaction mixture was kept warm and stirred for a further 3 hours. Precipitation was tried from a boiling chloride solution containing 10 g./l. of oxide but the separation was less effective than from warm solutions of 50—100 g./l. of oxide. Small amounts of free hydrochloric acid, or the accumulation of potassium chloride in the mother-liquors, caused no difficulty. The presence of a small amount of iron was also immaterial.

The ferricyanide precipitates were treated with an equivalent of cold 5N-alkali, whereby ready hydrolysis took place and potassium ferricyanide could be recovered. The filter cake of hydroxides required treating two or three times again with more dilute cold alkali till the filtrate showed little colour. There was an equilibrium between hydroxide and ferricyanide which made quantitative removal of iron impracticable. The almost iron-free filter cake was dissolved in hydrochloric acid to yield a blue solution. The Prussian-blue, if desired, was destroyed by boiling with a little potassium chlorate. The solution was neutralised, and provided the rare-earth oxide did not amount to more than 100 g./l., ferric hydroxide was precipitated satisfactorily and was removed before proceeding to the next ferricyanide precipitation.

Ferricyanide Precipitation of a Crude Yttrium Earth.—The following table shows the apparent atomic weights and proportions of a crude yttrium earth from gadolinite, following a double sulphate treatment, when submitted to fractional precipitation as ferricyanide. The final fraction (6) was the unprecipitated portion remaining in the mother-liquor and recovered as hydroxide.

	(*a*) 250 G./l.; boiling.		(*b*) 100 G./l.; boiling.		(*c*) 40 G./l.; boiling.		(*d*) 75 G./l.; 40–60°	
	At. wt.	%.	At. wt.	%.	At. wt.	%.	At. wt.	%.
1	115	11	116	9	118	12	120	13
2	111	16	118 *	18	112	22	112	16
3	108	15	109	20	107	19	107	16
4	102	22	99	24	101	22	101	13
5	96	22	94	20	91	21	98	12
6	90	14	90	9	90	4	92	30

* Reaction interrupted.

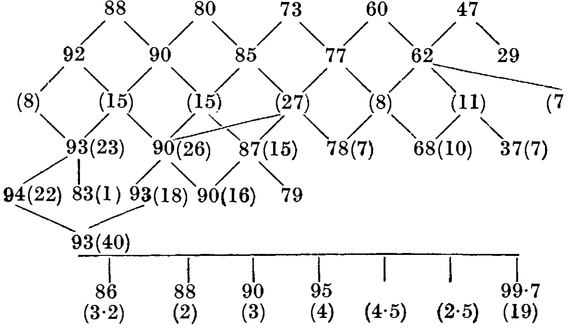
The reactions at 100° were each completed in about 20 mins. in solutions stirred by a steam jet with the ferricyanide solution (1 g. in 3 ml.) added dropwise in 15 mins. Each precipitate in (*d*) was produced by adding potassium ferricyanide amounting to one-third of the original weight of rare earth. After the second precipitation the solution was concentrated to its original concentration. Precipitates 1—4 were obtained at 40—50°, but 5 required heating to 60° as the solution again became dilute. This series, rather more successful than those at 100°, took longer to perform but not more attention.

The holmium absorption band λ 5360 was compared in fractions (*d*, 1) and (*d*, 6) by bringing it to the same small intensity in each as matched by eye with a direct vision spectroscope. It was concluded that it was 8 times stronger in (*d*, 1). The erbium bands in the green region could not be compared, for a trace of neodymium interfered. About 0·1% of neodymium was found in (*d*, 1) and 0·6% in (*d*, 6) by comparison of light absorption in the orange region. The colour of the oxides decreased from head to tail, showing that terbium was collecting at the head. The head fraction is estimated to have contained about 40% of non-yttrium oxides, and the tail 4—5%. The first 45% contained 75% and the last 30% about 6·4% of the original non-yttrium oxides.

Separation of Yttrium and Erbium.—The starting material had been fractionated as bromate and by nitrate fusions. It was converted into neutral chloride, and the solution fractionally precipitated with potassium ferricyanide (1 g. in 3 ml.) from solutions originally containing the equivalent of about 100 g./l. of oxide. The fractionation was controlled by determinations of the apparent atomic weight from oxide–oxalate ratios in separate portions of oxalate, about 50 mg. of oxalate and 0·02N-potassium permanganate being used for each oxalate titration. The following is a typical result :

	Input.	Output.					
Fraction.		1.	2.	3.	4.	5.	6.
Atomic weight	120	141	134	128	123	113	97
% of total erbium atoms	—	29	21	17	12	14	7
Erbium atoms, % of metal	40	67	59	51	44	31	10
% of output	102	17	14	13	11	18	26
Erbium oxide, % by wt. (approx.)	52	80	75	67	60	45	17
Erbium oxide, % by wt. } M. and K.	57	89	86	80	62	38	Low
% of output	104	12	5	14	17	16	36

Comparison is shown with a ferrocyanide fractionation reported by Moeller and Kremers (*loc. cit.*) after 28 fractional precipitations (five series on five or six fractions). The results of 27 precipitations on some rich earths are shown diagramatically. The figures in parentheses show the weights (in g.), and the others show the % of erbium atoms.



For the final purification of erbium the rich material (93%) was precipitated with excess of ferricyanide from solutions containing initially 25—40 g./l. of oxide, at 40—50° with stirring for 5—6 hours. The mother-liquors then contained about 2 g./l. of unprecipitated oxides. Six such precipitations decreased the earth by 50% but reduced the yttrium to 0·32 ± 0·07 atomic %.

Fractionation of Holmium.—A sample of yttrium–holmium oxide, about 20 molecular % Ho_2O_3, was made into chloride solution equivalent to 20 g./l. of oxide and precipitated at 55° with potassium ferricyanide (1 g. in 3 ml.) equal to half the weight of oxide. The solution was then concentrated to 30 g./l., and two more precipitations made at 40—50° with further portions of ferricyanide. The yields were : (1) 18% of input with 39% Ho; (2) 20% with 33% Ho; (3) 18% with 17·5% Ho; (4) 40% with 6·5% Ho (not precipitated). There are thus over five times as many holmium atoms in the first 40% to be precipitated as in the last 40%.

The estimates of yttrium in the purified holmium and erbium oxides were made by diluting the oxides with 4 and 9 times their weights of alumina respectively and arcing and spectrographing the cathode layer. The resulting spectrograms were compared with standards prepared from pure yttria in alumina. The possible effect of the holmia and erbia on the intensities of the yttrium arc lines could not be estimated but was not considered likely to exceed 20% in the case of erbium.

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