

The Enrichment of Crude Erbium and Holmium.

By J. K. MARSH.

[Reprint Order No. 5733.]

Use of basic nitrates, for which the formula $\text{Ln}(\text{NO}_3)_3 \cdot \text{Ln}[\text{LnNO}_3(\text{OH})_5] \cdot 6.5$ or $7.5\text{H}_2\text{O}$ is suggested, is considered the best method for enrichment of fractions of erbium and holmium. This and other basic nitrate methods give about the same separation factor, and appear to depend upon the same basic nitrate formation, $\text{Ln}[\text{LnNO}_3(\text{OH})_5]$. Precipitation by ferricyanide gives a larger separation factor, but this advantage is nullified by practical difficulties in its operation.

THE great relative abundance of yttrium results in initial concentrates of erbium of the order of 10%, and of holmium of 2%. Methods of increasing these to over 50% before application of a final method of purification are here considered. Separation factors have been calculated, and although not constant they do not differ widely for the various basic processes in nitrate solution which have been most used. When a binary mixture is submitted to a separational process each of the two fractions is enriched in one component. The ratio richer/poorer is the enrichment factor, and the product of the two enrichment factors is the separation factor, as here calculated.

TABLE 1.* The basic nitrate-nitrite process.

10 g. of nitrate/l. initially (Willard and James)					30 g. of nitrate/l. initially (Wichers, Hopkins, and Balke)							
(a)	27.0	26.6	20.2	14.4	11.9	51.7	47.3	39.2	27.1	20.3	11.3	2.2
(b)	2.50	2.81	3.39	4.00	12.9	1.98	2.02	2.20	2.36	2.98	2.94	2.00
(c)	3.05	3.46	4.00	4.51	14.6	3.03	2.94	2.98	2.86	3.48	3.18	2.02
2 g. of nitrate/l. initially				25 g. of nitrate/l. initially								
(d)	72	66	55		46	30	17					
(e)	1.32	1.49	1.93		1.66	2.30	2.80					
(f)	2.16	2.46	3.04		2.23	2.86	3.17					

- * In all Tables: (a) Er_2O_3 , %, in enriched fraction after conversion into oxide.
- (b) Er_2O_3 enrichment factor.
- (c) Er_2O_3 - Y_2O_3 separation factor.
- (d) Ho_2O_3 , %, in enriched fraction after conversion into oxide.
- (e) Ho_2O_3 enrichment factor.
- (f) Ho_2O_3 - Y_2O_3 separation factor.

The Basic Nitrite-Nitrate Process.—Fogg and James (*J. Amer. Chem. Soc.*, 1922, **44** 307) found that the basic nitrate $4\text{Y}_2\text{O}_3 \cdot 2\text{N}_2\text{O}_5 \cdot 17\text{H}_2\text{O}$ was produced by boiling yttrium nitrate (10 g./l.) with sodium nitrite, but the amount of nitrite in the basic precipitate may be considerable if an excess of sodium nitrite is present in the solution. Data given by Willard and James (*ibid.*, 1916, **38**, 1198) and by Wichers, Hopkins, and Balke (*ibid.* 1918, **40**, 1615) have been used to determine the yttrium-erbium separation factor. Using solutions containing initially about 2 or 25 g./l. of dissolved oxide, the author has determined values for the yttrium-holmium separation factor (Table 1).

Urea Hydrolysis.—An enrichment factor of 1.36 and a separation factor of 2.36 for 73.8% Er_2O_3 are derivable from data by Fogg and Hess (*ibid.*, 1936, **58**, 1751).

The Crystalline ("4/9ths") Basic Nitrate.—This substance has been formulated as $3\text{Y}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 20\text{H}_2\text{O}$ by James and Pratt (*ibid.*, 1910, **32**, 586), or with $18\text{H}_2\text{O}$ (Feit, *Z. anorg. Chem.*, 1934, **243**, 276). James and Pratt prepared it by partial decomposition of the nitrate by heat followed by lixiviation, and Feit by solution of oxide in a hot concentrated nitrate solution. This method is to be preferred. The author's results are shown in Table 2.

TABLE 2. The 4/9ths nitrate process.

(a)	59	51	41	32	22	2.9	1.2	(d)	63	44	36	18
(b)	1.18	1.9	2.4	2.9	4.5	2.1	2.1	(e)	1.5	2.1	2.2	3.4
(c)	2.85	2.83	3.38	3.86	5.45	2.1	2.1	(f)	2.35	2.93	2.94	3.95

The Air-borne Ammonia Process.—Since its introduction by F. Trombe (*Compt. rend.*, 1942, 215, 539) this process has been used by Hilal and Sugden (*J.*, 1949, 135) and by Hilal (*Z. anorg. Chem.*, 1953, 273, 241; 1954, 275, 278) to obtain precipitates from nitrate solutions. These are in general coarsely granular basic nitrates, and not hydroxides as Hilal states, for if dissolved in sulphuric acid they give the brown ring test for nitrates strongly. Some results with holmium material are presented in Table 3.

TABLE 3. *The ammonia gas process.*

(d)	63	59	15
(e)	1.4	1.8	2.9
(f)	2.23	2.98	3.27

The Ferricyanide Precipitation Process.—This has been described previously (*J.*, 1947, 118). The separation factor for erbia is now calculated and values for holmia determined, and the results are presented in Table 4.

TABLE 4. *The ferricyanide precipitation process.*

(a)	80	75	67	60	45	(d)	57	49	39	27	25	10.6	6.5
(b)	1.73	1.86	1.97	2.16	2.64	(e)	1.97	2.39	2.47	2.87	4.22	4.10	2.80
(c)	4.65	4.46	3.94	3.88	4.00	(f)	3.25	3.23	3.46	3.83	4.45	5.45	2.92

The analyses in Tables 1 (a), 2 (a), and 4 (a) were based on apparent atomic-weight determinations; the others are spectrophotometric.

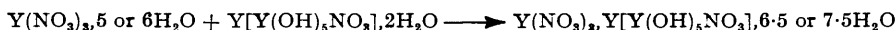
EXPERIMENTAL

The "4/9ths" Basic Nitrate.—This salt is only metastable. It may withstand one recrystallisation but it soon breaks down, and attempts at recrystallisation are unrewarding. The stability and solubility in hot solutions are greater for yttrium than for holmium or erbium, but solubilities in the cold are almost zero.

In carrying out a fractionation by means of this salt, a nitrate solution is prepared of density 1.3—1.35. To this, when just below its boiling point, is added a slurry of oxide, and the whole well stirred till the oxide dissolves. The crystal crop is collected next day. A second crop is obtained by taking a portion of the solution, about 1/8th if rich in erbium, but as much as 1/5th for fairly pure yttrium. This is converted into oxide *via* the oxalate and used as above. The basic salt crops are likely to be contaminated with sulphate at first if the material has previously undergone a separation by double alkali sulphate. The basic nitrate has only a low solubility in hot, very concentrated normal nitrate. The solubility rises with dilution of the nitrate till hydrolysis suddenly sets in, as found by James and Pratt (*J. Amer. Chem. Soc.*, 1910, 32, 873) to occur also at 25°. The success of the process therefore depends upon control of the concentration to near the density stated, and of the basicity of the solution by limiting the quantity of oxide added. The presence of carbonate or sulphate appears to assist in the breakdown of the crystalline basic salt and so should be avoided. Before addition of oxide, nitrate solutions are rendered distinctly acid and well boiled.

DISCUSSION

As expected, the separation factors for holmium are in all cases below the values for erbium. The ferricyanide precipitation values are larger than for the basic nitrate processes, but no distinct differences can be seen between any of the latter for mixtures of comparable composition. This, it is suggested, is because all are due to the formation of the same basic nitrate which we may term the 1/6th nitrate, and for which the formulation $Y[Y(OH)_5NO_3]_2 \cdot 2H_2O$ is suggested in the case of the yttrium salt. [Fogg and James's formulation (*loc. cit.*) indicates that four molecules combine with loss of H_2O .] The crystalline, or 4/9ths, basic nitrate, prepared only from concentrated nitrate solutions and unstable in water, is seen to be a double salt of normal nitrate and the 1/6th nitrate:



The low stability of this salt will be understood from the very small loss of water of crystallisation from its constituent simple salts which its formation occasions. It breaks down in insufficiently concentrated nitrate solution, and even in concentrated solution if kept too long especially if hot.

In the cerium group only 1/3rd nitrates are known for lanthanum, cerium, praseodymium, and neodymium (Dutt, *J. Indian Chem. Soc.*, 1945, 22, 97). The 4/9ths nitrate does not occur earlier in the lanthanon series than samarium, and for this element it is difficult to prepare. Samarium is the point in the series where the pH at incidence of precipitation by alkali is least affected by the lanthanon nitrate concentration (M. Trombe, *Compt. rend.*, 1943, 216, 888. We may conclude that this Trombe effect is the consequence of the formation in nitrate solution of a somewhat stable and soluble basic nitrate; thus high solubility of the basic nitrate and the large Trombe effect in the case of yttrium are seen to be linked, and likewise the small Trombe effect and the low stability of any basic nitrate of samarium.

Although the separation factor for the ferricyanide precipitation process exceeds those for basic nitrate processes, the labour involved in decomposing the ferricyanide and eliminating iron makes it less advantageous than the 4/9ths basic nitrate process. The latter process makes possible the handling of large amounts of material in small bulk and appears unrivalled for eliminating yttrium from holmium and erbium concentrates.

THE DYSON PERRINS LABORATORY, OXFORD.

[Received, September 16th, 1954.]
