32. *The Magnetic Susceptibilities of the Rare-earth Elements. Part IV. Thulium.*

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Thulium has been isolated by prolonged fractional crystallisation of the bromate followed by treatment with sodium amalgam to remove ytterbium. The value found for $10^6\chi^{20°}_{Tm}$... is 136·5.

The material used in this investigation originated from a Swedish gadolinite. The fractions showing the thulium absorption bands were collected from a bromate fractionation, and the recrystallisation as bromate continued until pink erbium ceased to separate at the head (about 7200 crystallisations). Attempts were made to separate any traces of ytterbium by means of sodium amalgam (Marsh, *J.*, 1943, 8). This materially increased the magnetic susceptibility of some of the later fractions. Fractional precipitation with ammonia carried in a current of air (this vol., p. 135) was also tried but gave no further change. Nine fractions of constant susceptibility were united and precipitated twice as oxalate to remove any non-rare-earth impurities, and determinations of equivalent and magnetic susceptibility were made by the methods already described (Found: equiv., 64·13, 64·06, 64·27. Calc.: equiv., 64·47): $10^6\chi^{20°}_{Tm}\cdots = 136·5 \pm 0·1$, $\mu_{eff.} = 7·39$. The values found by other investigators are:

Date.	Investigator.	Source of material.	$\mu_{eff.}$
1925	Stefan Meyer, *Physikal. Z.*, **26**, 51, 478	Von Welsbach	7·5
1925	Cabrera, *Compt. rend.*, **180**, 668	,,	7·2
1929	Cabrera & Duperier, *ibid.*, **188**, 1640	,,	7·0

The experimental value is appreciably lower than the value 7·6 predicted by Van Vleck (" Electric and Magnetic Susceptibilities ", Oxford Univ. Press, 1932, 243).

Experimental.

The bromates containing thulium were crystallised in test-tubes from water as solvent. The erbium proceeded to the head and lutecium and some ytterbium to the tail. (We are indebted to Dr. J. K. Marsh for removing most of the ytterbium as bivalent sulphate.) Head and tail fractions were rejected when thulium absorption bands could no longer be detected in them. After 7200 crystallisations each fraction was converted into oxide by boiling with hydrochloric acid until no more bromine was evolved, then precipitated as oxalate and ignited. The magnetic susceptibility of the thulium ion was then measured with the results shown below:

Magnetic susceptibility of thulium ion.

Fraction.	Colour of oxide.	$10^6\chi^{20°}_{Tm}$... (bromates).	$10^6\chi^{20°}_{Tm}$... (after amalgam treatment).
77 (head)	Pink	181·6	—
78	Pink	153·4	144·9
79	Faint pink	146·9	151·0
80	Very faint pink	142·3	139·4
81	White	136·9	138·0
82	Very faint green	139·2	137·8
83	,, ,,	137·2	136·7
84	,, ,,	133·5	137·0
85	,, ,,	135·8	137·2
86	,, ,,	134·6	137·1
87	,, ,,	133·5	135·2
88	,, ,,	132·6	135·2
89	,, ,,	131·2	136·2
90	,, ,,	126·4	137·2
91	,, ,,	120·6	135·4

+ 4 tail fractions of lower susceptibility.

The separation of ytterbium was then carried out by the method described by Marsh (*loc. cit.*) in which about 25 mg. of Sm_2O_3 were added to each fraction, and the acetates treated with sodium amalgam. After 5 extractions with sodium amalgam had been made the excess of sodium salt was removed as recommended by Marsh. A further 5 treatments with sodium amalgam were then given, the traces of heavy metals precipitated with hydrogen sulphide, rare-earth oxides were recovered and their magnetic susceptibilities measured with the results given in the last column of the above table. It will be seen that the values for the later fractions were raised considerably by this treatment. Fractions 81—91 have a nearly constant magnetic susceptibility; they were united and fractionally precipitated by ammonia in a current of air (cf. this vol., p. 135). This method had previously been found to be capable of removing traces of ytterbium from erbium which were not removed by the amalgam treatment. After systematic

separation involving 25 precipitations, nine fractions were obtained and their magnetic susceptibilities determined, with the following results:

Fraction	1.	2.	3.	4.	5.	6.	7.	8.	9.
$10^6\ \chi^{20°}_{Tm}$...	135·4	135·3	134·9	133·9	134·8	135·2	134·4	135·0	134·6

No. 1 is the least basic and No. 9 the most basic. The figures quoted above are not absolute values, since the calibration of the tube was suspect. They should give correct relative values and it will be seen that there is no indication of the separation of a less basic fraction of lower susceptibility.

To determine the absolute susceptibility, the nine fractions were united and twice precipitated as oxalate and ignited to oxide. The equivalents and magnetic susceptibilities were then determined with the results quoted on p. 139.

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