CCCXI.—*The Order of Fractionation of Rare-earth Bromates, and a Search for Illinium.*

By JOSEPH KENNETH MARSH.

THE theory of the method of concentrating illinium for detection by its absorption spectrum employed by Harris and Hopkins (*J. Amer. Chem. Soc.*, 1926, **48**, 1585) is based upon the assumption that the solubilities of the rare-earth bromates increase in the order (Eu), Sm, Gd, Il, Tb, Nd, according to which illinium will concentrate between two colourless earths. James and Bissell (*ibid.*, 1914, **36**, 2060), however, found that terbium bromate is more soluble than the neodymium salt, and this conclusion was supported by Jordan and Hopkins (*ibid.*, 1917, **39**, 2614). More recently, Zernike and James (*ibid.*, 1926, **48**, 2871) published a note giving the order of separation as Eu, Sm, Gd, Tb, Nd, Dy, Pr, Ho, Yt, La, Er, at a minimum temperature of 20—25°, and suggested that at lower temperatures the order might be different. James, Fogg, McIntire, Evans, and Donovan (*ibid.*, 1927, **49**, 132) determined the solubilities of the pure bromates of each of the elements from lanthanum to terbium (except Il and Eu) at intervals of 5° from 0° to 45°. The data show that, as the temperature is raised, a more rapid increase in solubility takes place in the salt of the elements of lower than in those of higher atomic weight. The solubilities of samarium and gadolinium are almost the same, as also are those of neodymium and terbium, the last except at 0° being very slightly the more soluble.

The author has recently fractionated 300 g. of cerium- and lanthanum-free earths from Joachimstal pitchblende residues by the bromate method (*Phil. Mag.*, 1929, **7**, 1005). Yttrium and the

elements erbium to lutecium were quickly eliminated at the tail. Further tail fractions were removed as soon as they appeared fairly poor in neodymium. Fractionation was carried out on about 20 fractions, usually twice daily, through 130 series; the greater part of the praseodymium had then been eliminated, but the tail contained a little terbium. Samarium, europium, and neodymium, and presumably gadolinium, still ran through all these fractions: no separation whatever of the first two could be detected. The fractionation was conducted during the winter months, and the fractions cooled each time to 15° and often to 10° or below. The order of fractionation was Sm and Eu, Gd, Nd, Tb.

The fractions containing Tb, Pr, Dy, Ho, etc., which had been eliminated in the above fractionation, were united and then again spread to about 20 fractions and put through a series of 40 crystallisations during the months of October and November, their night temperature frequently falling nearly to 0°. Absorption spectrograms through equal thicknesses of mother-liquors from alternate fractions then gave the following results:

Erbium was strongest in fraction	21 (tail)
Holmium	17
Dysprosium	13
Praseodymium	10
Neodymium	1 (head)

Terbium was later proved to be strongest at about fraction 7, and was virtually absent from the head fractions, for these gave blue-grey oxides on strong ignition.

It must therefore be concluded that the order of separation at low temperatures is Sm and Eu, Gd, Nd, Tb, Pr, Dy, Ho, Yt, which shows certain inversions when compared with the above results of Zernike and James for temperatures above 20°. When mixed with yttrium earths, the lanthanum earths behave as if they had smaller solubilities, especially at low temperatures, than the determinations on the pure bromates would lead one to expect.

Illinium.—The results recorded above were the outcome of a search for illinium (No. 61). It was hoped that the rare earths in Joachimstal pitchblende might prove to be unusually rich in this element, in view of the facts (1) that europium (No. 63) is at least 1000 more abundant in the crude earth mixture than in a similar mixture of earths from monazite sands, and many times more abundant than in any other known source; (2) samarium (No. 62) and praseodymium (No. 59) are both present in unusually high proportions; and (3) the elements of odd atomic number in general seem rather more abundant than usual.

Although the amount of material was small (300 g.), had illinium

showed any approach to the abnormal abundance of europium, its detection should have been possible.

The bromate method of fractionation was used initially, but after 130 series of fractionations on 20—24 fractions it was apparent that the separation of neodymium and samarium was proceeding exceedingly slowly, and insufficient terbium and gadolinium were available to act as separating elements. In consequence, the fractions were reduced to 12, then individually converted into double magnesium nitrates, and again fractionated in presence of bismuth magnesium nitrate until the separation of neodymium and samarium was practically quantitative, only very small intermediate fractions remaining. Bismuth and magnesium were removed and the chloride absorption spectrum examined, but no indications of the bands ascribed to illinium could be found.

In conclusion, I desire to thank Professor Soddy, F.R.S., for the supply of rare earths, and for his interest in the work; also Mr. T. C. C. Adam, M.Sc., for assistance in part of the fractionation.

THE SIR DONALD CURRIE LABORATORIES,
QUEEN'S UNIVERSITY, BELFAST. [*Received, August 17th,* 1929.]