The differences in basicity between these three elements are very slight and careful work was necessary to establish any differences at all. The separation of these three elements by any method which depends upon their basicities seems to be impracticable.

If scandium, yttrium and cerium are omitted, the order of decreasing basicity is the same as the order of increasing atomic number throughout the entire rare earth group. Because of the scarcity of illinium its relative basicity is made the subject of a separate paper which follows this one.

Summary

1. The sodium nitrite method of precipitating the rare earths has been modified in such a manner as to emphasize the differences in basicity which are found in the rare earth group. The efficiency of this method for fractionation has been greatly increased.
2. The order of decreasing basicity of the members of the rare earth group is identical with the order of increasing atomic number; the elements scandium, yttrium, cerium and illinium are not included in the present study.
3. While we have shown that samarium is more basic than europium and that europium is more basic than gadolinium, these differences are extremely slight, which accounts for the contradictory statements regarding these elements.

URBANA, ILLINOIS

RECEIVED MARCH 17, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. XXXIIIa. The Basicity of Illinium and Yttrium

BY GORDON HUGHES AND B. S. HOPKINS

The preceding paper[1] reports the basicity of the more common rare earths whose presence may be established by the usual methods. The object of this work was to determine the basicity of illinium and yttrium and thus complete the list of basicities of all the members of the rare earth group.

Material and Methods

The material was derived from two sources. The first quantity was prepared from the monazite residues of the gas mantle industry. It originally consisted of practically all the rare earth content of monazite sand after the removal of thorium. These residues were dissolved in acid and the cerium removed as completely as possible by precipitation with sodium phosphate.[2] After filtering the ceric phosphate, there was obtained a solution composed mostly of the salts of lanthanum, praseodymium, neodymium, illinium,

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[1] Sherwood and Hopkins, THIS JOURNAL, **55**, 3117 (1933).

[2] Neckers and Kremers, *ibid.*, **50**, 955 (1928).

samarium, europium, gadolinium and a small proportion of the other elements of higher atomic number. No attempt was made to remove these latter elements because of their small amount and the fact that they are rapidly concentrated at the soluble end in the process of fractional crystallization. Accordingly this mixture was converted to the magnesium rare earth double nitrate and subjected to fractional crystallization until the various fractions consisted of relatively simple mixtures. The fractions selected for this investigation were composed of about equal parts neodymium and samarium with traces of illinium, gadolinium and europium.

The second quantity of material was derived from gadolinite. It was found to contain a considerable proportion of the elements of higher atomic numbers. Salts of these elements are more soluble and when present in too great abundance they interfere with the crystallization of the magnesium–rare earth double nitrates. Accordingly it was necessary to precipitate the elements of lower atomic numbers by the addition of solid sodium sulfate. The precipitated earths were converted to the nitrate and cerium removed in the manner described in the preceding paragraph. The resulting mixture was subjected to fractional crystallization as the double magnesium nitrate, with the addition of bismuth–magnesium nitrate. The fractions selected for the present study were those which were more soluble than the bismuth–magnesium nitrate. They consisted mainly of yttrium, samarium and gadolinium, with traces of illinium, europium, terbium, holmium and erbium. To this mixture was added some crude neodymium–samarium oxide.

Materials from both these sources were dissolved in hydrochloric acid and to the slightly acid solutions hydrogen sulfide was added to remove any of the heavy metals which might be present. It was found necessary to remove the last traces of bismuth because the presence of small amounts of this element produced a gelatinous precipitate when sodium nitrite was added. In the absence of bismuth the precipitate is granular and easily filtered.

The fractional precipitation scheme described in the previous paper was followed in this work.

The quantitative determination of illinium in the various samples was made by the magneto-optic method of analysis. The technique involved in the use of this method for quantitative analysis has been described.[3] The relative concentration of yttrium in the various samples was determined spectroscopically from the arc spectra.

Results

As a result of the intensive method of fractional precipitation with sodium nitrite, illinium was found to have a basicity slightly less than neodymium but a little greater than yttrium. The latter element is slightly more basic than samarium. By combining these statements with the order of decreasing basicity as reported in the preceding article and assuming the universally accepted basicity of cerous salts, it is possible to make a complete summary of the order of decreasing basicity of the entire rare earth group. This order[4] is La, Ce^{+++}, Pr, Nd, Il, Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. It is to be noted that this order is exactly that of increasing atomic number except in the case of yttrium. The anomalous position of yttrium in a basicity series is not surprising because a similar situation is found in regard to the solubility of most yttrium salts. It is

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(3) Bishop and Dollins, THIS JOURNAL, **54**, 4585 (1932).

(4) Compare Table 1, preceding article, page 3118.

evident that the characteristics of yttrium show that this element does not conform to the general behavior of the members of the rare earth group. It is possible that these peculiarities on the part of yttrium are due to the combined effect of the difference in atomic weight and similarity in atomic structure.

Summary

1. The basicity of illinium when measured by the intensive sodium nitrite precipitation has been found to be slightly greater than that of yttrium, these two elements being less basic than neodymium but more basic than samarium.

2. The order of decreasing basicity for the entire group has been shown to agree with the increasing order of atomic numbers, with the single exception of yttrium.

3. The quantitative determination of illinium was made by the magneto-optic method, while yttrium was determined spectroscopically.

URBANA, ILLINOIS

RECEIVED MARCH 17, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Volumetric Determination of Arsenic. Potentiometric Titrations of Reduced Arsenic Solutions with Potassium Iodate in Sulfuric and Hydrochloric Acid Solutions

BY IRL C. SCHOONOVER AND N. HOWELL FURMAN

The more commonly used volumetric methods for the determination of arsenic are those in which the arsenic in the trivalent form is oxidized with iodine or iodate. The first of these methods has been studied carefully from a theoretical standpoint by E. W. Washburn[1] and experimentally by Thiel and Myer[2] and later by I. M. Kolthoff.[3]

The second method, that of the oxidation with iodate, was developed by G. S. Jamieson,[4] who extended L. W. Andrews'[5] work on iodate oxidations in strong hydrochloric acid to the determination of arsenic. This method depends upon the oxidation of the iodine first formed to iodine monochloride and the disappearance of the iodine color from an inert solvent such as carbon tetrachloride.

In this investigation, the oxidation of arsenious oxide with iodate in hydrochloric and sulfuric acid solutions has been studied; the potentiometric method was employed. Oxidations of arsenious oxide in hydrochloric acid to which mercuric salt was added were also studied.

(1) Washburn, THIS JOURNAL, **30**, 31 (1908); **35**, 681 (1913).

(2) Thiel and Myer, *Z. anal. Chem.*, **55**, 177 (1916).

(3) Kolthoff, *ibid.*, **60**, 393 (1921).

(4) Jamieson, *J. Ind. Eng. Chem.*, **10**, 290 (1918).

(5) Andrews, THIS JOURNAL, **25**, 756 (1903).