

RECENT ADVANCES IN THE CHEMISTRY OF
THE RARE EARTHS

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The outstanding achievements in rare earth chemistry in recent years have come from investigations concerned with the fundamental chemical properties of these elements. This paper is an abstract of the more important articles of this nature, and of the work done at the University of Illinois during the past two years.

Fractional crystallization of the cerium group double magnesium nitrates and of the yttrium group bromates still continue to be the most important methods for the separation of the individual rare earths. Rolla and Fernandez¹ have suggested the use of the mixed double magnesium and double manganese nitrates for the separation of the cerium group earths. From their studies, the solubilities, in water, of the pure double manganese nitrates and the double magnesium nitrates increase with increasing atomic number, while the solubilities, in the solid state, of the double manganese salts in the corresponding double magnesium nitrates decrease with increasing atomic number.

The separation of certain rare earth sulfates by a partial thermal decomposition of the sulfates and a subsequent leaching with water has been undertaken by Willard and Fowler². They determined the products formed in such decompositions and the dissociation pressures of the pure anhydrous sulfates at definite temperatures. Separations were attempted by maintaining the partial pressure of the sulfur trioxide above the heated mixed sulfates at a value intermediate between those of the pure constituents, so that the sulfate of one rare earth would be decomposed to its insoluble oxide, while the other remained as the soluble sulfate. The results were negative, since a solid solution of the oxides results when a mixture of the isomorphous sulfates is decomposed. Since cerium sulfate decomposes to the non-isomorphous cerium dioxide, separations of this element are successful. The procedure was applied to various types of mixtures.

Wells³ has reported the varying solubility in ether of mixtures of rare earth nitrates which have been very carefully heated. He has suggested that the startling differences in the solubilities of the individual

¹ Atti. Acad. Lincei. 6, 7, 370. (1928)., Gazz. Chim. Ital. 57, 704. (1927).

² Jour. Am. Chem. Soc. 54, 496 (1932).

³ Trans. Wash. Acad. Sci. 20, 146 (1930).

rare earths may be due to variations in the degree of dehydration of these salts. Studies at the University of Illinois have shown that, under uniform conditions, the minimum temperature to convert the rare earth monohydrate to the anhydrous salt varies considerably from one rare earth to the next.

Jantsch and Skalla⁴ have prepared anhydrous samarium tri-iodide by gradually heating the hydrated salt with ammonium iodide to 350° C. and finally to 650°. The tri-iodide, when heated in a steam of dry hydrogen to about 760° C., decomposes to the deep green samarium di-iodide. Some of the properties of the di-iodide are given. Jantsch, Skalla and Jawurek⁵ have studied the thermal decomposition of the trihalides into the dihalogen compounds.

Yntema⁶ has prepared europous sulfate by the electrolytic reduction of an europic salt in the presence of the sulfate-ion, thus separating europium from gadolinium and samarium. Ball and Yntema⁷ used the same method to obtain ytterbium containing only traces of the other earths from crude material containing only about ½ per cent of ytterbium.

New compounds of the rare earth elements have been described by Kolthof and Elmquist⁸, Pagel and Brinton⁹, Klemm¹⁰ and his coworkers, Zhukov¹¹, Sieverts and Gotta¹², Picon and Cogné¹³. Physical constants of most of these compounds are also given.

Schwarz and Geise¹⁴ and Lejeune¹⁵ consider the compound formed when cerium salts are oxidized by air or by hydrogen peroxide in alkaline solution as a derivative of cerium dioxide in contradistinction to the views of previous investigators who held that the compound was a derivative of CeO₃, in which cerium had a valence of six.

Concentrated amalgams of lanthanum and neodymium have been prepared by Audrieth¹⁶ and coworkers and that of cerium by Biltz and Meyer¹⁷ and by Muller and Schmidt¹⁸.

Baxter and Behrens¹⁹ have redetermined the atomic weight of lanthanum as 138.926, a value 0.026 higher than the present international value. Prandtl²⁰ has prepared very pure samples of erbium for atomic weight determinations by a combination of several basic precipitation methods.

Spedding²¹ has diagrammed some of the energy levels of GdIV for the temperatures of liquid air and liquid hydrogen as a result of his study on the ultra violet absorption spectra of GdCl₃·6H₂O and GdBr₃·6H₂O in a magnetic field. Uzumasa and Okino²² suggest a relationship between the dielectric constant of the solvent and the shifts in the absorption bands as a result of their studies on the absorption spectra of praseodymium and neodymium hydrated nitrates in glycerol, acetone, methyl alcohol and pyridine.

⁴ Z. anorg. allgem. Chem. 193, 391 (1930).

⁵ Z. anorg. allgem. Chem. 201, 207 (1931).

⁶ Jour. Am. Chem. Soc. 52, 2782 (1930).

⁷ Jour. Am. Chem. Soc. 52, 4264 (1930).

⁸ Jour. Am. Chem. Soc. 53, 1225 (1931).

⁹ Jour. Am. Chem. Soc. 51, 42 (1929).

¹⁰ Z. anorg. allgem. Chem. 190, 123 (1930).

¹¹ Ann. inst. phys. Chem. 3, 461 (1926); 3, 600 (1927).

¹² Z. anorg. allgem. Chem. 172, 1 (1928).

¹³ Compt. Rend. 193, 595 (1931).

¹⁴ Z. anorg. allgem. Chem. 176, 209 (1928).

¹⁵ Compt. Rend. 191, 665 (1930).

¹⁶ Jour. Am. Chem. Soc. 53, 1805 (1931).

¹⁷ Z. anorg. allgem. Chem. 176, 23 (1929).

¹⁸ Monatsh. 53-54, 224 (1929).

¹⁹ Jour. Am. Chem. Soc. 54, 591 (1932).

²⁰ Z. anorg. allgem. Chem. 198, 157 (1931).

²¹ Phys. Rev. 38, No. 4, 670 (1931).

²² Bull. Chem. Soc. Japan. 6, No. 6, p. 147.

The work of Willard ²³ and Furman²⁴ and their coworkers has shown the usefulness of ceric sulfate solutions as oxidizing agents for volumetric analysis.

Takvorian ²⁵ using an Indian monazite as starting material, obtained about five hundred grams of neodymium-samarium concentrates which he examined for the K and L series lines of illinium. His failure to find any trace of the element is undoubtedly due to the small quantity of original material he used. The arc spectra of these samples were also recorded and photometered and were found to correspond well with artificial mixtures of supposedly pure neodymium and samarium. Analyses made by one of us of samarskite by the magneto optic method have shown illinium to be present in this ore to the extent of about one part in ten million, showing that it is absolutely necessary to start with very large amounts of original material to get any detectable concentration of this rarest of the rare earths.