

RECENT ADVANCES IN RARE EARTH CHEMISTRY

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Increasing interest in the rare earths is indicated by the large number of papers which have appeared during the past few years. The present article is a review of the more important recent advances in rare-earth chemistry with particular reference to those of a fundamental character including those carried out in the Chemical Laboratory of the University of Illinois.

The principal source of rare earths for commercial and scientific work is monazite sand, vast deposits of which are found in India and in Brazil. The use of cerium misch-metal in tracer bullets and star shells has long been known, but an even more important use from a military standpoint has recently been suggested in the extraction of helium from monazite sands. As such, monazite constitutes the only practical source of helium outside the boundaries of the United States.

Probably the most active division of rare-earth research during the past few years has had to do with spectroscopy. Numerous tables of wave-lengths have been published of which the work of Meggers¹ may be singled out for special mention. He has determined the wave-lengths and Zeeman effects for about one thousand lines in the arc and spark spectra of yttrium from 2,100 to 9,500 Angstrom units. Important work by King² on the temperature classification of the stronger lines of cerium and praseodymium has shown that while the longer wave-lengths in the emission spectra of these elements are produced by the neutral atom, in the blue and violet the more intense lines are produced by the ionized atom.

Phillips³ has investigated the visible radiation characteristics of incandescent oxides. The oxides of the rare earths are unique in that when heated to incandescence they emit bands of light corresponding roughly to their characteristic absorption bands, rather than a general radiation. Some of the more recent publications on rare-earth spectra are of more interest to the physicist than to the rare-earth chemist. Of such may be mentioned the work of Jevons⁴ on the band spectrum of lanthanum monoxide. Cathodic phosphorescence spectra continue to be a source of interest, and a method has been devised for estimating the

¹ Bureau of Standards Journal of Research 1, 319 (1928).

² Astrophysical Journal 68, 194 (1928).

³ Phys. Rev. 32, 832 (1928).

⁴ Proc. Phys. Soc. (London) 41, 520 (1929).

compositions of mixed phosphors by the positions of the phosphorescent bands⁵.

Freed and Spedding⁶ in California have studied the absorption spectra of rare earth crystals at low temperatures. Among their many interesting observations, one of the most striking is the evidence they have obtained indicating that samarium as commonly known is a mixture of two electronic isomers. Both magnetic susceptibility and spectral measurements indicate that the equilibrium between the two forms is displaced by change in temperature.

Rare-earth absorption spectra is becoming a fertile field for the study of molecular structure and intra-molecular forces. Brunetti⁷, in an examination of the spectra of praseodymium salts, reports that the absorption bands tend with increasing concentration to take up positions similar to those they have in the crystalline state. This observation parallels that of one of the authors on neodymium nitrate, which will be described later. Ephraim⁸ and co-workers have studied a large number of rare-earth compounds by means of their reflection spectra, with particular reference to the interionic forces between cation and anion in various solvents.

The unique property of the colored rare earth compounds in possessing sharply defined absorption bands in the visible region of the spectrum has led during the past few months to an investigation of the displacement of electron shells when a rare-earth ion is approached by a neighboring ion. It is apparent that the electrical forces acting upon the electrons of an ion in dilute solution may be very different from those to be found in concentrated solution. We may therefore expect those properties of the ion which are dependent on the arrangement of the outermost layers of electrons to be modified by change in concentration or other external influence. This is precisely what takes place in the case of solutions of, say, neodymium nitrate. It has been found that the absorption bands of neodymium salts are displaced toward the red end of the spectrum when the concentration of the solution is increased. If now the spectrum of neodymium nitrate crystals is examined, it will be found that the bands have shifted still farther to the red. We may therefore conclude that whatever forces were producing the comparatively small shifts seen in the spectrum of the solution are acting to a more intense degree in the crystal.

Now from the classical theory of dielectrics it has been shown that a shift of spectral bands to the red, that is to say, a decrease of spectral

⁵ *Ann. Physik.* 84, 840 (1928).

⁶ *Nature* 123, 525 (1929), *Phys. Rev.* 34, 945 (1929).

⁷ *Nuovo cimento (N.S.)* 5, 391 (1928).

⁸ *Ber.* 62B, 1509, 1520, 1639 (1929).

frequency, will be attended with an increase of refractive index. It has recently been shown by one of the authors that such is the case for neodymium perchlorate, and at the present time measurements are being made on other rare earth salts. Efforts are also being made to relate the changes in absorption spectra to other properties such as magnetic susceptibility, magnetic optical rotation, and dielectric polarization.

During the course of this work a valuable application was found in the use of the europium absorption spectrum as a reference standard in spectrum photography. Ordinarily the positions of absorption or other spectral lines are determined by interpolation from known lines, generally of iron, which are independently placed in juxtaposition to the unknown. For spectrum plates from which it is desired to make microphotometric curves, however, it is desirable to have some reference lines directly superimposed on the unknown spectrum and, if possible, put there at the same time. The comparatively few and exceedingly sharply defined absorption bands of europium salts are suitable for this purpose, and fortunately two or three grams of the rare and very costly europium were available, having been prepared by the authors during the past three years. In photographing the spectrum of, say, neodymium nitrate, a small quartz vessel containing a solution of europium nitrate was placed in the path of the incident light, so that the reference lines were automatically recorded on the photographic plate.

The ionization potentials of the rare earth in relation to their position in the periodic system have been studied by Rolla and Piccardi⁹, who used a method involving the electrical conductance of a flame in which rare earths were volatilized. The ionization potentials show a slight increase with increasing atomic number, but they show no indication of the periodicity found in certain rare-earth properties, such as magnetic susceptibility and the recurrence of variable valence. Europium, which shows the readiest reducibility, was unfortunately not available for the measurements.

The magnetic susceptibility of erbium sulfate octohydrate at low temperatures has been determined by de Haas, Wiersma, and Capel¹⁰, who give full experimental details of the elaborate procedure required for these measurements.

In the field of atomic weights, Boss and Hopkins¹¹, and Hönigschmidt and Holch¹², have revised the atomic weights of erbium and of cerium respectively. The former is placed at 167.64 and the latter at 140.125, both of which values have been accepted by the International Committee on Atomic Weights.

⁹ Phil. Mag. (7), 7, 286 (1929).

¹⁰ Proc. Acad. Sci. Amsterdam 32, 739 (1929).

¹¹ Jour. Amer. Chem. Soc. 50, 298 (1928).

¹² Z. Anorg. allgem. Chem. 177, 91 (1929).

The electromotive potentials of rare earth metals and their amalgams have been measured by Müller¹³, the method, which involves the equilibrium between the metal and its ions in the form of the anhydrous bromide dissolved in pyridine, at once suggests the possibility of an analogous method in the preparation of the rare earth metals. Preliminary steps have already been taken by one of the authors for the preparation of metallic neodymium with every evidence of success. The pyridine solution of anhydrous neodymium chloride used is, however, such a poor conductor of electricity that only a minute quantity of the supposed metal has been obtained.

Biltz and Meyer¹⁴ have isolated a compound CeHg_4 from cerium amalgam. Such amalgams are pyrophoric if they contain more than 15% of cerium. Andrieux¹⁵ has prepared the borides of cerium, lanthanum, neodymium, gadolinium, yttrium, erbium, and ytterbium by electrolysis of the oxides in fused boric acid or borates.

Of great interest during the past year have been the various investigations dealing with the divalent and quadrivalent compounds of the rare earths. Pagel and Brinton¹⁶ have prepared praseodymium dioxide of 99.2% purity by heating the sesquioxide in oxygen at high pressures. No higher oxides were, however, formed by the elements lanthanum, neodymium, samarium, gadolinium, erbium, or ytterbium. Klemm and co-workers¹⁷ in Germany have suggested an ingenious systematic classification of the rare earths from the standpoints of their physical and chemical properties. The halides of the rare earths have been studied by Klemm¹⁸ and by Jantsch and co-workers¹⁹ with some remarkable results. Almost pure samarium dihalides have been prepared by hydrogen reduction. The magnetic susceptibility of samarium dibromide shows a four or five-fold increase over that of the tribromide. Europium dichloride has been shown to be quite stable in aqueous solution, and europous sulfate is formed as an amorphous white precipitate on the addition of a soluble sulfate. During the past few weeks this observation has been subject to brilliant confirmation in our own laboratory by Dr. L. F. Yntema, who by electrolytic reduction in dilute sulfuric acid has achieved in one step an almost quantitative separation of europium and samarium. From considerations of atomic structure Klemm predicted that ytterbium would also form stable divalent compounds, and this has been found to be the case. It is probable that this element also will prove to be separable from its neighbors by reduction

¹³ Monatsh. 53-54, 215, 224 (1929).

¹⁴ Z. Anorg. allgem. Chem. 176, 23 (1928).

¹⁵ Andrieux Thesis (1929). Chem. Abstracts 23, 4893 (1929).

¹⁶ Jour. Amer. Chem. Soc. 51, 42 (1929).

¹⁷ Z. anorg. allgem. Chem. 184, 345, 352 (1929); 187, 29 (1930).

¹⁸ Z. anorg. allgem. Chem. 176, 181 (1928).

¹⁹ Z. anorg. allgem. Chem. 185, 49 (1929); Monatsh. 53-54, 305 (1929).

and precipitation. If so, it will without doubt be the most important contribution made to rare-earth chemistry since the discovery of illinium.

The catalytic behavior of rare-earth oxides has been the subject of several recent investigations, one of the most important of which has demonstrated that a ceria-thoria catalyst containing 0.96% ceria is most efficient for the oxidation of carbon monoxide.²⁰ This composition is precisely that used to obtain maximum light from the Welsbach gas mantle. Cremer²¹ has studied the catalytic decomposition of ethyl alcohol with various elements of group three, while other investigators²² have shown that the efficiency of nickel oxide as a catalyst for organic hydrogenation may be increased by the presence of ceria.

The use of ceric sulfate as a volumetric oxidizing agent in analytical chemistry has received much attention from Furman²³ and from Willard²⁴ and their co-workers at Princeton and Michigan, respectively. So numerous are the applications and advantages of this reagent that the reader must be referred to the original papers for particulars.

A Japanese worker²⁵ has discovered that certain rare earth compounds have a remarkable activating influence on galena used as a detector in wireless telegraphy. In the field of medicine it has been found²⁶ that metals of the cerium group produce an enormous increase in the white corpuscles of the blood without any attendant bodily disorder.

After some thousands of series fractionations over a period of several years, the authors have been rewarded with about three grams of europium oxide. Europium is, next to illinium, probably the rarest of all the rare earths. It is of exceptional interest to the rare-earth chemist, not only because of its scarcity, but also because of its unusually sharp absorption spectrum, an application of which has already been described, and because of its ready reducibility to the divalent state. The europium material was concentrated and isolated from about 300 kilos of crude cerium-free rare-earth oxide, representing about three times that weight of monazite sand. The concentration was accomplished by fractionation of the magnesium double nitrate with the liberal use of bismuth magnesium nitrate, which permitted a practically quantitative separation of europium and samarium. The europium has been found spectroscopically to contain less than 0.1% of samarium and gadolinium and none of any other rare earth. At present the atomic weight is being determined by the chloride to silver ratio, and the absorption spectrum

²⁰ J. Chem. Soc. (1928) 2667.

²¹ Z. physik. Chem. A, 144, 231 (1929).

²² Ber. 61B, 1792 (1928).

²³ Jour. Amer. Chem. Soc. 51, 1128 (1929).

²⁴ Jour. Amer. Chem. Soc. 51, 139, 149 (1929).

²⁵ Jour. Soc. Chem. Ind. (Japan) 31, 476 (1928).

²⁶ Chem. Abstracts 23, 4743 (1929).

is being mapped by a method which has already indicated the presence of several hitherto undiscovered bands.

The purification of europium was attended with the preparation of several hundred grams of pure samarium and about one hundred grams of pure gadolinium oxides. A new absorption band of the former has been found at 5,960 Angstrom units, but all efforts to detect in solution the bands in the visible reported by Freed for gadolinium chloride crystals have been unsuccessful.

The preparation of very pure samples of rare earths has necessitated the development of sensitive methods for the detection and estimation of such impurities as might be expected to be present. One of the authors has therefore studied the applicability of the spectrographic method to the detection and estimation of traces of the elements manganese, magnesium, calcium, barium, silicon, bismuth, aluminium, beryllium, samarium, gadolinium, and lanthanum in various rare earth mixtures.²⁷ Such a method is particularly useful when the elements in question is present in the proportions of from 10 to 0.001%. In some instances it is possible to detect less than one part in a million of the impurity.

Progress in the concentration and isolation of illinium continues to be exceedingly slow. Since the untimely death of Professor James of New Hampshire, only one paper bearing directly on element 61 has appeared, and it gave only negative results. J. Marsh²⁸ investigated the small amount of rare earths obtained from pitchblende, but without finding any illinium. It appears from his work, and from that in our own laboratory, that the serial order of fractionation of rare-earth bromates is more dependent on the temperature at which crystallization takes place than was heretofore known.

From work at present being carried on, it seems that illinium is much less abundant than any of the other rare earths. It is so scarce that by our present means of identification, which are sensitive to about 0.1%, about three years of daily fractional crystallization, involving some tens of thousands of operations, must be done before the illinium may be detected. So closely does illinium resemble its fairly abundant neighbors, neodymium and samarium, that it may be ten years before it will be isolated. At the present time large scale operations are being conducted for the concentration of illinium from a ton of monazite residues in which it was originally discovered, from 250 pounds of gadolinite, and from smaller samples of various other possible mineral sources, including twenty pounds of the rare silicate "thalenite." At the same time no efforts are being spared for the development of new methods and improved technique for the separation of all members of the rare-earth group.

²⁷ *Industrial and Engineering Chemistry, Analytical Edition* 2, 93, (1930).

²⁸ *J. Chem. Soc.* (1929) page 1387.