as between subdivisions of one and the same journal, and not as between different journals. Repetition could be avoided by proper cross-references. There would never be any very great danger of a lack of sufficient material for such a journal. Its large circulation would also make it a most desirable medium for advertising, and the increased income from this source would still further reduce the cost of publication.

Perhaps the chief objection to such a plan lies in the rapidly increasing amount of material submitted to our various chemical journals. The bulk of this material if not already too great to be handled properly by any one journal, would certainly become so in the course of the next few years.

It may be that a combination of these two plans would appear best, arranging for the issuing of those separate journals which seem most urgently needed at the present time, if there are any such, and meanwhile developing the journal by a segregation of its contents, perhaps with suitable divisional headings, so that when the moment is most opportune these sub-divisions may start an independent career as special journals.

Already an able and energetic committee is at work on the question of the advisability of our publishing a *Journal of Industrial and Engineering Chemistry*, and we hope to have a report from them at this meeting.[1]

III. *Location.*—As far as practicable, opportunities should be provided for our members in all parts of the country to hold periodic meetings. To insure this we have our Local Sections and migratory General Meetings. So far as the latter are concerned, however, the country is so large and our membership so widely scattered, that only a small proportion find it possible to attend. It might be wise, therefore, to hold one general meeting during the Christmas holidays, and during the summer have several separate gatherings in different parts of the country—say, one West of the Rockies and two or more in the East.

To return to my original statement, what the American Chemical Society needs is the enthusiastic and intelligent coöperation of its members. I am sure that the enthusiasm will be forthcoming, and I trust that the data presented may be of some service in helping you to decide intelligently as to the best plans for the development of our Society.

THE BROMATES OF THE RARE EARTHS.

Part I. A New Method for the Separation of the Yttrium Earths.

By C. James.

Received December 6, 1907.

During recent years chemists investigating the rare earths have di-

[1] The report will be found in Proceedings of this number.

rected their efforts more towards the cerium group than towards the yttrium earths, with the result that the elements cerium, lanthanum, praseodymium, neodymium, samarium, europium and gadolinium are fairly well known. On the other hand, the yttrium earths, with the exception of yttrium, ytterbium and scandium are still but poorly defined. Many investigators have been of the opinion that "new" erbium is complex, while almost nothing is known about thulium, holmium, dysprosium and terbium. In addition to the above, victorium, announced by Crookes, is believed by Urbain and some others to be a mixture, although its discoverer still claims that it is a separate and new, individual element.

In the case of the cerium group, several excellent methods of fractional crystallization have been developed. On the other hand, no rapid and simple method has been applied to the yttrium earths with the possible exception of the method of Urbain, using the ethyl sulphates, and some methods employing compounds of a costly nature, such as the acetylacetonates and the metanitrobenzenesulphonates. As one must deal with many kilograms of material, expensive compounds are out of the question unless the separation should prove almost quantitative, which is never the case.

Urbain's ethyl sulphate method[1] gives good results. He says that yttrium, neoerbium and ytterbium accumulate in the most soluble portions, with no trace of the lanthanum group and no earths of the samarium and gadolinium groups. It is very difficult to obtain erbium from fractions rich in holmium by its use and for separating earths of the same group, the method of fusing the nitrates is still the best. Another difficulty is due to the fact that the ethyl sulphates are inclined to hydrolyze unless special precautions are taken.

The fractionation of the simple nitrates from concentrated nitric acid proposed by Demarcay[2] is very tedious and the use of a solvent of such a character causes great inconvenience in the laboratory.

The separation obtained by taking advantage of the difference of solubility of the oxalates in a saturated solution of ammonium oxalate, developed by Carl Auer von Welsbach,[3] gives interesting results. It has drawbacks, however, as it involves the use of two temperatures and requires a large number of operations.

Among the remaining methods only a few need be mentioned: Fusion of the nitrates and separation of the most easily decomposed portions by their insolubility in water, separates ytterbium and scandium at one end, and yttrium and terbium at the other. To obtain ytterbium free

[1] Compt. rend., **126**, 835; **127**, 107; **132**, 136.
[2] *Ibid.*, **122**, 728; **130**, 1020.
[3] Monatsh., **27**, 935.

from erbium and thulium, requires about seventy operations. It is also extremely difficult to get yttrium pure by this method, since terbium clings.

Fractional precipitation of the concentrated neutral nitrate solution by means of magnesium oxide,[1] tending to throw down the less basic elements first, gives similar results.

The preparation of pure yttria by Muthman and Bohm's chromate method[2] is comparatively simple, but unfortunately it is of no value for separating the other members.

The fractionation obtained by boiling a solution of the oxalates in ammonium carbonate[3] works well for obtaining erbium free from holmium and dysprosium, on the one side, and thulium, ytterbium and scandium on the other.

Fractional precipitation to be of value must be very rapid. Fractional crystallization is to be preferred, for it is much easier to carry out a large number of operations. As a rule, in fractional precipitation methods, especially where dilute solutions are employed, a good deal, if not most, of the material is washed away. It is highly desirable, therefore, that a method consisting of fractional crystallization of some type of isomorphous compounds, with greatly varying solubilites, should be found. With this object in view, the author has examined the sulphites, xanthates, succinates, double carbonates with sodium glycollates, methyl sulphates, normal propyl sulphates, camphorates, iodates, thiocyanates, monochloracetates, monobromsuccinates, oleates, bromates, etc., besides nearly every compound proposed in literature for the purpose of fractionation. The bromates are the best suited for the purpose of all those examined up to the present time.

The bromates are easily prepared by using barium bromate, which, in turn, is formed by mixing boiling solutions containing the required amounts of barium chloride and potassium bromate. Because barium bromate is not very soluble even in boiling water, it is highly important that the precipitate should be finely divided, otherwise the double decomposition between the rare earth sulphate and barium bromate will take considerable time. The formation of large crystals is prevented by rapidly cooling the mixed boiling solutions. As potassium bromate can be prepared cheaply, the rare earth bromates are not costly to obtain.

The rare earth material, generally in the form of the oxalates, is mixed into a paste with sulphuric acid and the temperature raised until the fumes of sulphuric acid cease to be evolved. The residue is then finely powdered, dissolved in ice-cold water, and the resulting solution poured

[1] Muthman and Rolig, Ber., 31, 1718.

[2] Ber., 33, 49; Chem. News, 81, 169.

[3] This Journal, 29, 495; Chem. News, 95, 181.

over an excess of barium bromate. This operation is best carried out in a large evaporating dish placed on the water-bath, care being taken to keep the mass well stirred.

After a time the precipitate is allowed to settle and some of the clear liquid taken up by means of a pipette and added to a warm solution of barium bromate; if no precipitate is obtained the liquid is filtered off. Sometimes, however, a precipitate is formed which consists of barium bromate and, therefore, it is best to dilute with water and boil. If the precipitate persists, either more stirring or more barium bromate is required.

When the double decomposition is complete a little bromine is often liberated, but there is not sufficient to cause any inconvenience in the laboratory. This is evidently due to the fact that a small amount of bromic acid is formed by the action of a trace of free sulphuric acid accompanying the rare earth sulphates. The latter should, therefore, be well ignited.

The filtered liquid is evaporated until a drop, removed on the end of a glass rod, nearly solidifies when stirred on a watch glass. Under these conditions just about half of the substance in solution crystallizes out on cooling. After a little experience there is absolutely no difficulty in judging the most convenient concentration. If the fractionation is carried out in porcelain dishes a little water should be sprayed on the surface so as to prevent the top from solidifying to a crystalline mass.

Casseroles are by far the best utensils to use for this work, especially if small amounts of substances are being separated, as they can be covered by large watch glasses. This prevents rapid crystallization and the tendency of the material to creep up the sides of the vessel. Also there is no need to spray any water on the surface after evaporating or dissolving. Very often, but usually when working with small quantities, the liquid refuses to crystallize or else the crystals separate out as a fine feathery mass, so that it is quite impossible to pour off the mother liquor. If it does not crystallize, the best procedure is to add a trace of the solid, when the whole immediately solidifies, forming the feathery type of crystals as mentioned above. The mass is then carefully heated so as to dissolve all but a very little, which will start the crystallization as the liquid cools. An even better plan is to commence the operation by the addition of a crystal while the liquid is still quite hot.

When working on the large scale, very fine hexagonal prisms are often obtained, some being more than two inches in length and over a quarter of an inch in thickness.

Even after six series of crystallizations a considerable change is easily apparent, although this is shown more by the spectroscope than by the color. The most soluble fraction is very pink and it gives an intense

erbium spectrum. The thulium red is also very strong and the band in the blue has made its appearance while the bands of holmium and dysprosium have nearly disappeared. The least soluble fraction is still pinkish and gives intense dysprosium and holmium bands and a weak erbium spectrum. The color of the oxide of this fraction is orange, showing that terbium accumulates at this end. After the process has been continued until some twenty fractions have been obtained, the least soluble portion forms brilliant colorless crystals, which dissolve in water with a tinge of greenish yellow color, seen only in concentrated solution. The absorption spectrum of this fraction shows very faint samarium and holmium bands, while those of dysprosium are much stronger. Practically the whole of this fraction consists of an earth giving a colorless salt, yttrium. And as the oxide is of a brown ochre color it shows that terbium collects in the least soluble portion. As one goes down the series, the fractions become yellower and the oxides paler. In the fractions that show the strongest yellow, the dysprosium and holmium bands are very intense, and the oxide becomes yellowish. Farther along the series, the lines of erbium make their appearance and even while the erbium absorption is still weak the liquid assumes a pink color. This increases until it reaches a rosy pink, at which stage the spectroscope shows only erbium bands, and the oxide is of a pure rose tint. Further on still the thulium band in the red shows itself, while the solutions become paler and give a very stong thulium spectrum, the erbium bands becoming decidedly weaker. The most soluble fraction is reached when the solution is nearly colorless, the erbium spectrum is faint, while that of thulium, although fainter, is still intense. The oxide of this last fraction is white and dense and consists largely of ytterbium.

The above series show that the rare earth bromates arrange themselves in the following order of solubility:

Samarium (Europium?, Gadolinium?), Terbium, Yttrium, Dysprosium, Holmium, Erbium, Thulium and Ytterbium—which is similar to the solubilities of the oxalates in ammonium oxalate, but different from the ethyl sulphates; since according to Urbain, yttrium, erbium and ytterbium ethyl sulphates are found in the most soluble portion.

A fair conclusion can be drawn that the use of the ethyl sulphate method would prove valuable in conjunction with the bromate, especially for the separation of yttrium from dysprosium and holmium and perhaps for the separation of thulium from ytterbium.

Finally, the author would like to point out some of the rapid separations obtained by this method, the most remarkable being the separation of thulium from erbium. And since ytterbium is still more soluble than thulium, its removal is even easier. For example, erbium material, supposed to be quite free from thulium, was converted into

the bromate and crystallized four times, when the most soluble portion gave the thulium spectrum.

Dysprosium and holmium also separate from erbium with comparative ease, and as yttrium places itself between terbium and dysprosium, the latter element can be obtained terbium-free. The division between dysprosium and holmium is not so marked.

The absorption spectra and the colors of the various fractions show curious changes which are not altogether understood and may be simply due to the comparatively small amount of material under examination.

More material (15 kilos) is at present being fractionated and in the near future the less basic portion of earths derived from about 100 kilos of euxenite and 100 kilos of yttrotitanite, etc., will also be included. The bromate method will be further investigated and also applied to the cerium group and the results published at an early date.

NEW HAMPSHIRE COLLEGE,
Durham, N. H., November 18, 1907.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF LEAD.

Preliminary Paper—The Analysis of Lead Chloride.

GREGORY PAUL BAXTER AND JOHN HUNT WILSON.

Received December 2, 1907.

Although lead is one of the most common elements, its atomic weight has received comparatively little attention, the value at present accepted being based almost wholly upon the work of Stas.[1] Of the earlier determinations of this constant those of Döbereiner[2] and Longchamps[3] can hardly be considered as possessing other than historic interest. The first results which can lay claim to accuracy are those of Berzelius,[4] who obtained values ranging from 206.7 to 207.3 by reduction of litharge in a current of hydrogen. Berzelius also synthesized the sulphate from metallic lead with the result 207.0.[5] Shortly after, Turner[6] criticized

[1] Earlier work on the atomic weight of lead has been carefully summarized by Clarke. Smithsonian Miscellaneous Collections, Constants of Nature, "A Recalculation of the Atomic Weights," 1897.

In recalculating the data of earlier determinations the following atomic weights have been used in this paper:

O=16.000; Ag=107.88; Cl=35.46; N=14.01; S=32.07

Richards and Wells, Pub. Car. Inst., No. 28 (1905); Richards and Forbes, *Ibid.*, No. 69, p. 47 (1907); Richards and Jones, *Ibid.*, No. 69, p. 69; Report of International Committe on Atomic Weights, This Journal, 29, 110 (1907).

[2] Schweig. J., 17, 241 (1816).

[3] Ann. chim. phys., 34, 105 (1827).

[4] Pogg. Ann., 19, 314 (1830).

[5] Lehrbuch, 5th ed., 3, 1187 (1845).

[6] Phil. Trans., 527 (1833).