TWENTY-FIVE YEARS OF RESEARCH ON THE YTTRIUM EARTHS[1]

G. URBAIN

Professor of Chemistry in the Faculty of Sciences at the University of Paris[2]

The present article is a brief account of the investigations which I have carried on for twenty-five years in the field of the yttrium earths.

These investigations have been published in fragments in various scientific periodicals printed in the French language. I cannot better acknowledge to Yale University the great honor which it has conferred upon me than to write out for it an outline of my work on the yttrium earths.

No other natural group of chemical elements contains so many members as that of the rare earths. It comprises in itself one-sixth of the known elements.

If our knowledge of the rare earths is still limited, it is not because the investigators who have engaged in the study of them have been few. They have in fact been many, and among them are distinguished scientists, such as Berzelius, Mosander, Bunsen, Cleve, de Marignac, Nilson, Auer vonWelsbach, Lecoq de Boisbaudran, and Crookes.

One has only to run over the history of the rare earths to appreciate the considerable volume of work that has been done in that field, by more than two hundred investigators of various nationalities. In spite of this multitude of workers, the problem is not yet completely solved.

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[1] An essay prepared in connection with the dedication of the Sterling Chemistry Laboratory.

[2] Translated from the French by Prof. and Mrs. P. E. Browning; approved by Professor Urbain.

For a long time the scarcity of original material was an obstacle. Twenty-five years ago the minerals which contain the rare earths were very expensive. It was impossible for anyone to obtain large quantities of them. Practically no other deposits were known than those of Norway, and the working of these, which occurred in rocky formations, was always difficult and often uncertain.

But following the industrial development of thorium whose oxide forms 99 per cent of the material used for mantles, in incandescent gas lighting, further search was made, and important deposits of the rare earths were found: monazite sands in America, gold- and diamond-bearing sands in South Africa and Australia, etc. During the past fifteen years it has become easy to obtain rare earths, a condition which should encourage progress in this field of study. As a matter of fact, the lower members of the series, those most abundant and most easily prepared, have been the ones almost exclusively studied. The investigators have for the most part colonized a territory already explored and conquered.

And despite the attraction of the veritable unknown, there are few who have taken up this problem from its most interesting side, namely, the investigation of the elements which compose the yttrium earth group, the higher members in the rare earth series.[3]

To be sure, the pursuit of this work meant going farther than scientists such as Marignac, Cleve, Lecoq de Boisbaudran and Demarçay had gone. Merely to travel afresh the path which they had explored involved a long series of laborious separations. As to discoveries, they were most uncertain.

From the experimental point of view, the study of the yttrium earths consists of two parts, of equal importance: (1) a chemical part, imposed by the necessity of separating the members of the group from one another; (2) a physical-chemical part, imposed by the necessity of characterizing the various elements of the

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[3] Since the death of Demarçay, in 1901, a few investigators only have taken up or carried on the study of the yttrium earths: Auer von Welsbach in Austria; Hoffmann and R. J. Meyer in Germany; Holmberg in Sweden; chiefly James in America; and the author of this article in France.

group by specific, measurable properties. These two parts are complementary, one to the other.

However, that is only method of precedure, or techniqud. With materials such as these, technique is valueless unless it is employed with adequate method and logic. It is here, doubtless, that the principal difficulty of the problem lies.

In order that the method which I used may be understood, I will begin by saying a few words regarding technique.

Analytical procedure: The yttrium earths cannot be separated as one separates the common elements. The latter belong to various families. They differ in a marked degree from one another and it is very easy to separate them by utilizing the different chemical properties which facilitate their identification.

The yttrium earths are members of one and the same family. Consequently their chemical properties are very similar. For more than fifty years the group was regarded as a single element, for the different members are invariably associated in their minerals, and always in practically the same relative proportions.

Not only are their chemical properties almost identical, but their salts are isomorphous. Those who, knowing nothing of this matter, have sought new methods of separation, have achieved only new chemical methods of fractionation. We know that fractionation is a process of separation which depends not upon any essential difference in properties, but upon differences in one property common to the constituents of a mixture. Up to the present time the separation of the yttrium earths from one another has been accomplished only by fractionation.

A fractionation is always a laborious operation, even when two elements only are concerned. But when it is applied to the yttrium group, in which the existence of eleven members has been demonstrated, the fractionation becomes extremely tedious. An illustration of this may be found in a fractionation which I have been carrying on for twelve years, in which the earths have been treated systematically every day, by improved methods, and in which, despite this great amount of effort, certain separations are far from complete.

A false idea of fractionation in general, and of that of the rare earths in particular, is often entertained. Fractionation does not mean subdividing indefinitely the initial material. It means rather moving the collection of elements in a mixture along, until they succeed one another in a state of purity. As soon as this result is attained by a definite number of fractions, this number may remain constant; the whole effort of the investigator should be directed toward reducing more and more the number of intermediate fractions.

I will add that the isomorphous substances may only be separated in this manner, because in practice when two salts are isomorphous the less soluble does not dissolve in a saturated solution of the more soluble, but serves to start a spontaneous crystallization.

Theoretically, the value of a fractionation process depends wholly upon the number of fractions necessary to obtain pure products. In actual practice it depends also upon both apparatus and time required to accomplish each series of operations.

The thankless task of fractionation necessarily absorbs a large part of the time of him who undertakes the study of the rare earths. Time and energy are not the only factors of success. It is essential to choose procedures judiciously, and to conduct simultaneously and methodically a very great number of operations.

Physical-chemical measures. The characteristics which make it possible to recognize the different rare earths, and to follow each in the treatments, are in part qualitative and in part quantitative. Among the former are the spectra. Each element may have different kinds of spectra: spark, arc, absorption, phosphorescence, reversal and X-ray.[4] Among the latter, that is, the quantitative characteristics, are the measures of solubility, of atomic weight, and of the coefficient of magnetism.

It has fallen to me to perfect certain spectroscopic methods, particularly those relating to the phosphorescence spectra; and I have avoided much loss of time by using as a guide in the

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[4] The last two are of recent discovery. See the work of Moseley and of de Broglie on this subject.

treatments the measure of the coefficients of magnetism. This method, as we shall see later, is far superior to the atomic weight method, and especially to the solubility method recommended by Marignac.

Working method recommended in these investigations. As in all experimental science, the progress of the knowledge of the rare earths has followed the progress of its technique. The early investigators were guided at first by observation of coloration. The group is in fact composed of members, some of which form colorless salts, others salts of various colors. The study of absorption spectra has made it possible to express by numbers the sensation due to coloration; and by this scientific procedure different compounds may be distinguished in mixtures, the colors of which differ very little.

Absorption spectra are the easiest to observe, and this method has been recommended by the majority of investigators. Other procedures were not employed until later, but a few students have made use of them.

Additional spectroscopic methods have increased the chance of discoveries. But this situation has given rise to new difficulties, which I will try briefly to indicate.

Let us suppose that three independent investigators fractionate the same unknown earths. Suppose also that each of them takes as guide a different kind of spectrum; the first, for example, the absorption, the second the spark, and the third the phosphorescence spectrum.

Experience shows us that the following fact results. The first will distinguish a certain number, A, of absorption spectra; the second a number, B, of spark spectra; and the third a number, C, of phosphorescence spectra. These investigators have discovered, in all, $A + B + C$ new spectra. Shall we, then, conclude that they have discovered $A + B + C$ new substances? Certainly not, since one element may give at the same time these three varieties of spectra. One element may thus have been discovered three times in succession.

Let us suppose that A is the largest of these numbers. There cannot have been less than A elements discovered. But there may have been more, for not all of the rare earths show necessarily these three kinds of spectra in that part of the spectroscopic field which is easily observed; and moreover the three investigators may not have carried the separations sufficiently far to avoid the danger of confusion or of omission.

Unless these three investigators share with one another the materials which they have treated, no attempt can be made to attribute to a restricted number of elements the different spectra which they have observed.

And finally, even if these investigators should meet to compare results, they would find themselves confronted by so many uncertainties, since they had not isolated pure substances, that the best they could do would be to set up a probable theory of the common origin of certain of their spectra only.[5]

The study of the rare earths was in the state which I have just outlined schematically when I began my investigations. The subject was in certain particulars well advanced, but on the whole it was so confused that most chemists considered it hopeless.

I began by making a general review. After a period of preparation,[6] during which I familiarized myself with the processes related to the subject, I undertook long, methodical treatments, taking pains to observe, throughout, all the characteristics of every kind which my predecessors had described; to them I added those that I myself discovered later. So far as the quantity of material at my disposal permitted, I forced myself to pursue the treatments to the point where they were unnecessary, a point which I determined by the invariability of the properties observed.

Not only have I taken pains to prolong the treatments in certain cases beyond the point necessary to obtain pure products, but I have varied the treatments; for certain mixtures, undecom-

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[5] The new method of X-ray spectra leaves no room for such uncertainty, but it is applicable to the rare earths only where the separations have been carried very far, so that the observations can be made with much simplified mixtures; for elements having nearly the same atomic weight have lines which exactly coincide.

[6] Doctorate thesis, 1898, Recherches sur la Sèparation des Terres Rares.

posable by a method based on one principle (differences in solubility, for example), may be decomposed by a method based on another (as differences in the basicity of the oxides).

When the different processes produced no further results, and the properties remained invariable, whatever the principle of the method used, I knew beyond all doubt what group of properties belonged to the isolated element. Furthermore, I always then pursued the study of the mixtures intermediate between pure elements, in order to bring to light, if possible, some property still unknown; and to this end I reduced these intermediate fractions to a minimum by means of long-continued treatment.

In this way I have been able to bring order, which I hope may be definitive, into the first members of the yttrium series. I have reduced to four the number of elements between samarium and holmium, and I have shown that about twenty supposed elements whose separate existence had been considered possible or even probable, are identical with europium, gadolinium, terbium or dysprosium. Previous to this research, none of these elements had been isolated even reasonably pure. They were so ill-defined that only one of them, gadolinium, had a place in the international table of atomic weights, which, to some extent, assures chemical elements an official existence. And nevertheless, the existence of terbium had been announced by Mosander sixty years earlier.

I set myself the task of submitting Marignac's ytterbium to analysis of this sort. It enabled me to discover two new elements, lutecium and celtium. I had given the name of neoytterbium to the principal constituent of the original ytterbium, in order to leave to the illustrious Marignac, in the future, the credit of his fundamental discovery.

SEPARATION OF THE RARE EARTHS

The first problem that presents itself is the treatment of the minerals. Of these there is great variety. Some are phosphates, others are tantalo-niobates or silicates.

In a work surveying the whole field it was necessary to examine very different minerals. It was known about 1895 that the different rare earths are always found associated in nature, but it was not known what are the relative proportions of each of these elements in each mineralogical specimen. It could only be hoped that these proportions differed enough to make it advisable to treat a particular mineral in order to accomplish the special extraction of one of these substances. To this end I treated, in turn, monazite sands, aeschinite, cerite, gadolinite, thorite, and later xenotime. These various minerals are very different from one another, and each requires special treatment.

We know that the group of rare earths is divided into two sub-groups: the cerium earths, which comprise the first members of the series, namely lanthanum, cerium, praseodymium, neodymium and samarium; and the yttrium earths, which comprise the other members.

The earths extracted from the minerals enumerated above are hardly distinguishable except by their content in elements of each of these sub-groups. In general ways, the cerium earths are more abundant than the yttrium earths, but each sub-group has almost always the same composition, so that the relative rarity of each of the rare earths varies only within narrow limits.

That is certainly a notable fact. It probably cannot be explained without resort to hypothesis. While I do not wish to enter upon that path, which I have always avoided as much as possible, I will simply observe that all radio-active minerals contain rare earths, though the converse is not necessarily true. But in some cases in which the rare earths are not accompanied by radio-active substances the presence of helium, which is one of the last products of atomic disintegration may be detected.

Debierne's observation that certain fluorides contain helium led me to look for the rare earths in the fluorides (1). I then proved that the phosphorescence of the fluorides must be attributed in part to the presence of the rare earths, a fact which had never been suspected. These phenomena of phosphorescence had been attributed to mysterious causes or to unknown elements.

Contribution to the study of thorium (2). While I was studying the treatment of the minerals which I have named, I experienced the difficulties which one always encounters not only in separating the rare earths from one another but also in separating them as a whole from the elements associated with them in their mineral sources. Noteworthy among these associates was thorium, a very valuable element at that time (1 kilo of the oxide in the untreated mineral was worth 1000 francs; extracted and purified it was worth, in 1914, 30 francs), and one whose separation from the true rare earths had been worked out only very imperfectly. I found in acetylacetone an excellent reagent for thorium. The acetylacetonate of thorium is soluble in chloroform, which takes it from its aqueous solutions; moreover, this compound may be distilled in vacuo. The corresponding salts of the rare earths do not act in the same way; they are difficultly soluble in chloroform, and they decompose in vacuo under the influence of heat (3).

The analysis of pure thorium sulphate, obtained by this method enabled me moreover to determine the atomic weight of the element with an accuracy of the order of one part in a thousand (4).

Law of seriation of the rare earths. The rare earths, in separating from one another by their differences in solubility always appear in the same order, whatever the character of the salt submitted to fractional crystallization. I have repeatedly emphasized this remarkable fact, and I have found in it a natural law of seriation (5).

It may happen, however, that the series becomes reversed in some measure in the process of fractional crystallization of certain salts, such as the ethylsulphates or the simple nitrates of the type $M(NO_3)_3 5 \cdot H_2O$. I can find nothing better with which to compare this anomaly than the phenomenon of the maximum density of water, or the anomalous dispersion in which the spectrum reverses. Could this law be extended to apply to other groups of elements? The work of Locke upon the alums and the sulphates of the magnesium series makes it seem probable. But in groups which contain only a small number of elements, every anomaly will mask the law; whereas in the case of the rare earths, which are very numerous, the anomalies do not weaken it in any way.

Limits of fractionation. When the attempt is made to separate two closely associated rare earths by any method whatever, it is always found that the progress of the separation is relatively rapid at first, but that the last traces of impurities are very difficult to remove. Sometimes they cannot be completely removed; there is a limit to the separation.

Poor methods are those which admit a limit corresponding to very incomplete separations. If the worker takes as his only guides insufficient characteristics; if he confines himself, for instance, to the determination of atomic weights or of solubilities, the constancy of the numbers which correspond to a limit may deceive him as to the value of the results which he has obtained.

Experimentally, the limit of a fractionation, by crystallization of isomorphous salts, is in general a pure product, but it may by exception be formed of an indecomposable mixture. The mother-liquors have then the same composition as the crystals separating from the solvent. This phenomenon is interpreted as like that of two liquids which distil at a fixed temperature under a given pressure, although the boiling-points of the pure substances are quite different.

A new method of separation of the rare earths: fractionation of the ethylsulphates (6). These studies required a real period of apprenticeship, during which I had to become familiar with the compounds, with the methods of measurement, and also with the processes of separation which had been suggested up to that time, all of which I tried (7).

A good many attempts were made to find some method of separation of the yttrium earths which should be better than the methods of my predecessors, for it was certain that this branch of chemistry could make no real progress until the earths could be separated from one another.

After four years of research I had succeeded in isolating only yttrium practically pure, of all the numerous elements which compose the yttrium series; but I had found, in the crystallization of the ethylsulphates, a process of fractionation of the earths of this group which was to be at least as fruitful as Auer's method of the crystallization of the double ammonium nitrates had been for the earths of the cerium group, in bringing about the separation of lanthanum, praseodymium and neodymium.

This method of the ethylsulphates is very general, and it applies to the group of the yttrium earths as a whole. The first members of the series crystallize first; and the various members of the group come out in the normal order of their seriation. Thus there is obtained by fractional crystallization a first, relatively quick classification, which permits one later to employ, more methodically and easily, other processes better adapted to the particular separations of the members from their closest associates. But this procedure has one inconvenient feature; the ethereal salts saponify in the mother-liquors, upon application of heat or merely in the course of time.

ANALOGIES BETWEEN BISMUTH AND THE RARE EARTHS

Use of bismuth as an agent of separation. If the methods of fractionation permit the obtaining of pure isomorphous compounds, intermediate fractions cannot be avoided. Such separations are not and indeed seem incapable of being quantitative. However, in certain cases Lacombe and I were able to transform the approximate method of fractionation into a quantitative procedure, and so to achieve sharp separations.

The principle of the method is as follows:

Let us suppose that to the mixture of salts to be separated by fractionation there is added an isomorphous salt of an element which is of another group and easy to separate from the orginal salts by a quantitative procedure.

If the whole is fractionated, the added salt will take a position, determined by its solubility, among the salts of the original mixture. At a certain point, the progress of the separations may be such that one of the fractions of the systematic treatment will be made up of this foreign salt in a state of purity. Then by the elimination of the fractions above and below the foreign salt, a clear-cut division will have been made between the salts of the natural series. If the initial mixture contains only two constituents, the separation of these two will be complete. The foreign salt has acted as agent of separation.

To make use of this method it was necessary to know of an ordinary element enough like the rare earths to be able to play this part of separator.

We knew of several instances of isomorphism between the rare earths and the alkali earths, but considerations of a purely practical nature prevented our making the experiment with them. Our theory would perhaps have remained fruitless if Göste Bodman, of Upsala, had not pointed out, in 1898, the isomorphism of bismuth nitrate and sulphate with the corresponding salts of the rare earths. After several trials, we succeeded in proving that bismuth could be used as a separating agent when it was intercalated between samarium and europium.

Demarçay had made an approximate separation of these two elements by fractional crystallization of the double magnesium nitrates.

We proved first that bismuth nitrate can be combined with the nitrates of the magnesium series to give, in an acid solution, salts absolutely identical in form and general properties with the corresponding salts of the rare earths. These first results furnished the subject matter of an article published under the title: "On a new series of bismuth compounds" (8).

We described the following salts:

$$3\ Mg(NO_3)_2 + 2\ Bi(NO_3)_3 + 24\ H_2O$$
$$3\ Zn(NO_3)_2 + 2\ Bi(NO_3)_3 + 24\ H_2O$$
$$3\ Co(NO_3)_2 + 2\ Bi(NO_3)_3 + 24\ H_2O$$
$$3\ Ni(NO_3)_2 + 2\ Bi(NO_3)_3 + 24\ H_2O$$
$$3\ Mn(NO_3)_2 + 2\ Bi(NO_3)_3 + 24\ H_2O$$

These various salts bore the closest possible resemblance to the samarium and europium salts of the same type. Their solubility was between that of the samarium and that of the europium salts.

We pursued the study of the remarkable analogy between bismuth and the elements of the rare earth family and showed that it goes very far (9). In a general way bismuth, in acidic solution, belongs by its isomorphism to the family of rare earths, and it should always be placed between samarium and europium.

Thence we were able to work out the theory described above, and to obtain at least one sharp separation in the series of the rare earths.

Experimentation has confirmed our conjectures.

A sharp separation in the rare earth series (10). If a large quantity of the double nitrate of magnesium and bismuth is added to the mixture of double nitrates of magnesium and the rare earths, and the whole is methodically fractionated, the pure double nitrate of magnesium and bismuth is obtained in one of the fractions after several months of daily crystallization. If, next, the bismuth present in the other fractions is eliminated, by means of its special reactions, a clean separation between samarium and europium is established. As may be seen, the problem resolves itself into the obtaining of a pure salt of bismuth by means of fractionation. Samarium acts as its impurity in the preceding fractions, and europium in the succeeding. Bismuth establishes a line of demarcation between the earths of the cerium group (members lower in atomic weight than europium) and those of the yttrium group.

A second sharp separation by the use of bismuth as separating agent. Although bismuth is always inserted between samarium and europium, I discovered later the way to intercalate it between gadolinium and terbium, and thus sharply to separate these two elements. I stated in a previous paragraph (law of seriation of the rare earths) that the series may in certain cases suffer reversals. That is what happens when the simple nitrates crystallizing with 5 molecules of water are fractionated in nitric acid. The series reverses at gadolinium, whose normal place is between europium and terbium.

Of all the simple nitrates crystallizing with 5 molecules of water, that of gadolinium is, indeed, least soluble; so that by this method of fractionation europium and terbium appear again after gadolinium.

If the nitrate of bismuth is added to the mixture, it crystallizes in the same way after that of gadolinium, and it keeps nevertheless its normal position between europium and samarium. But if the mixture has been freed from these two earths by previous treatments, the bismuth intercalates itself between gadolinium and terbium. This separation is long and laborious, and several years were required to bring it about.

On a new method for the isolation of terbia (11). On the other hand, Lacombe and I have shown that in the separation of the rare earths bismuth may be advantageously employed in another way:

On the use of bismuth as agent of separation in the rare earth series (12). The difficulty experienced at times in bringing about crystallization of very soluble salts in syrupy solutions is well known. If a certain amount of much less soluble salts of the same type is added to these syrups, the latter salts readily crystallize; but, because of their isomorphism, in the process of crystallization they carry over in a state of solid solution a certain proportion of the salts which do not crystallize spontaneously in the original syrups.

Now, though the first members of the yttrium group crystallize readily as double magnesium nitrates, the following members crystallize with great difficulty; and beginning with terbium they are absolutely uncrystallizable. The addition of double nitrates of bismuth to these syrups made it possible for us to extract the majority of the earths most closely associated with terbium, and in this way to free them of the greater part of the yttrium, which is very abundant in this series and which constitutes one of the principal difficulties in the isolation of the rarer elements which always accompany it.

SPECIAL METHODS OF SEPARATION

Separation of europium from gadolinium. The solubility of the double nitrate of magnesium and europium differs very little from that of the double nitrate of magnesium and bismuth, but is slightly greater.

In the course of the fractionation, the mass of bismuth rapidly drives the gadolinium into the last fractions; and at the other end a series of fractions is obtained consisting almost exclusively of bismuth, with no gadolinium but with a trace or europium. This element is extremely rare compared with samarium and gadolinium. By elimination of bismuth and magnesium from the fractions, pure europium is obtained at the head of the series (13).

Separation of gadolinium from terbium. The double magnesium nitrates of the earths rich in terbia are much more soluble than magnesium nitrate itself. Consequently the simple nitrate has a marked tendency to form. The relation of the constituents necessary to the formation of the double salts is changed when this takes place, and therefore the fractionations become very difficult to carry on. The situation is changed in the case of the double nitrates in which magnesium is replaced by nickel, salts which, except in color, very much resemble the other. Nickel nitrate, being more soluble in nitric acid than magnesium nitrate, manifests less tendency to form; and if one takes pains to start the crystallization with a few particles of double nitrate of bismuth and nickel, double salts free from simple salts are always produced.

In this new method, gadolinium is concentrated in the first crystals (14).

Separation of terbium from dysprosium. During the whole process of the crystallizations of the double salts, hitherto described, crystallizations were also made of the yttrium ethylsulphates containing the earths of this group, salts of greater stability and more soluble than the ethylsulphates of the erbium earths.

A good separation of terbium from dysprosium may be brought about by means of these crystallizations. They eliminate yttrium in the last fractions, with erbium first and holmium following.

When the results obtained by these treatments seem in danger of being affected by saponification of the ethylsuphates, one may convert these compounds into simple nitrates and add the rare earth nitrates which have resulted from crystallization of the double nickel salts and which have subsequently been completely freed from nickel, care being taken to bring together only products of similar composition.

The methodical fractional crystallization in nitric acid of the simple nitrates having 5 molecules of water of crystallization may then be carried on. This prolonged treatment brings about the separation of terbium from dysprosium (15).

Separation of dysprosium from holmium. This separation is extremely long and arduous.

To accomplish it, it was necessary to continue the crystallizations of the simple nitrates of the two earths over a period of more than two years. At the head of the fractionation series dysprosium is obtained; holmium goes over into the following fractions with yttrium. These methods of separation have been described in detail in a general article entitled: ''Investigations on the separation of the rare earths'' (16).

Separations of the other earths of the series. While carrying on the fractionation of the earths closely associated with yttrium —holmium and erbium—I undertook, about 1905, the study of Marignac's ytterbium, of which I had been able to prepare some 50 grams.

For a long time the earths of this group had engaged my attention, and as far back as 1901, in collaboration with my brother, I had announced a method which effects a comparatively rapid separation of ytterbia and erbia: "On the isolation of yttria, ytterbia and the new erbia" (17).

We had shown that the old method of heating the nitrates gives excellent results when the earths submitted to the treatment have been previously freed from earths of the terbium group by the ethylsulphate method.

The crystallization of the nitrates, although less efficacious, was recognized as less laborious (18), and it is to this method that I had recourse when I set about the breaking up of ytterbium into its constituents, an undertaking which led me to discover first lutecium, then celtium.

The work of fractionation was most arduous. At certain periods my assistants and I completed as many as 800 crystallizations in one day.

CHARACTERISTICS OF THE YTTRIUM EARTHS

At this point it is advisable to become more definite respecting the general and necessarily somewhat vague statements made at the beginning of this article.

In 1898 the subject of the rare earths was in great confusion. There was an abundance of documents of very unequal value. In these, truth and error were closely associated, and there was no way to distinguish with certainty one from the other. It was even quite difficult to separate facts from the hypotheses and interpretations which, more often than not, needlessly encumbered them.

Moissan's treatise on inorganic chemistry, which appeared in 1904, contains a historical sketch of the subject, under my signature; this outline covers a century's work on the part of the chemists, and shows how the problem, stated simply at first, became by degrees so complicated that even the specialists themselves sometimes lost their way.

A thorough knowledge of the history of the subject would be necessary to follow my investigations in all their details; but I will confine myself to giving a brief sketch of the work of the more important of my predecessors. This process of selection brings before us the results obtained by Lecoq de Boisbaudran, Crookes, Demarçay, and Exner (of Vienna).

In the very brief outline which follows, I will show that their work was not all on the same plane.

Sir William Crookes studied chiefly phosphorescence spectra. His skill was rewarded by the discovery of one of the most beautiful phenomena that it is possible to observe in the vacuum tubes that bear his name.

But he assumed, a priori, that the phosphorescence spectra behave like the spark or absorption spectra. This assumption led him to consider as new substances the yttrium earths, which emit distinct phosphorescence. But since all these earths gave him the same spark spectrum, that of yttrium, and since they could not at the same time be yttrium and elements distinct from one another, he formed the conception of the meta-elements, a paradox which consists in looking upon an element characterized by a constant spark spectrum as being composed of scarcely distinct atoms which the fractionation process differentiates, because of the difference of their phosphorescence spectra, but which are generally reduced to a single band.

This idea, incorrect as applying to the chemical elements of the rare earth group, has been recognized as correct in the realm of the isotopes, to which the rare earths, as they are considered in this article, are not comparable.

Moreover, Crookes proposed, one after another, various interpretations of the beautiful phenomena that he had discovered; but if his theories are not always tenable, the facts that he observed are of unquestioned value, and deserve to command attention.

We shall have to describe precisely the nature of the elements or meta-elements that he designated by G_α, G_β,. . . G_θ, G_δ,. . . etc., the bands of which may be observed in the visible spectrum, and of the phosphorescent elements that he designated as victorium, ionium and incognitum, the bands of which may be observed in the ultra-violet region.

Were they new? Had they not already been described, thanks to some other characteristic? Were they even really distinct from one another?

Lecoq de Boisbaudran thought that Crookes' visible bands in the phosphorescence spectrum of yttria belonged to earths that he had previously designated by the characters Z_α and Z_β; he had observed the phosphorescence of these earths in connection with the interesting phenomenon that he had discovered, in the case of certain solutions, by reversing the direction of the non-condensed induction spark.

But what were the elements Z_α and Z_β themselves? Lecoq de Boisbaudran, indeed, told us that Z_β is concentrated in the dark-colored terbias, and Z_α in the light-colored terbias, which are less basic than the dark. But this subject of the terbias was most complicated, for the same author had distinguished among the dark terbias an element Z_δ, characterized by an absorption band, and in the light terbias an element Z_γ, characterized by a spark spectrum, and another which he named dysprosium, characterized by one part only of the spectrum of the original holmium (X of Marignac and Soret). What were the relations among these elements, or rather among these spectroscopic characteristics?

Demarçay, who had developed a new spectroscopic technique, added new properties to the existing abundance of characteristics, and new designations to the large number of tentative names. Among the thousands of lines in the ultra-violet field, he distinguished a dozen which he attributed to an element Γ, and as many more to an element Δ. The first is to be found in the dark terbias, the second in the lighter earths, those that appear later in the series.

Exner described an arc spectrum of terbium. But what exactly was this terbium? The descriptions of the successive authors who had discussed the question since it was first propounded, sixty years earlier, were hardly in accord. To Mosander, who discovered it, it was an element to which was due the yellowish color of the yttrium earths between white yttrium oxide and pink erbium oxide.[7] To Marignac it was orange-colored earth, whose place was between gadolinium and earth X (original holmium). To Lecoq de Boisbaudran there was no terbium, but there were terbias, and he thus designated all the yttrium earths of this group having colored oxides, the color varying from yellow (light terbias) to dark brown (dark terbias). In these terbias he observed many spectroscopic characteristics belonging to elements which might be distinct.

The spectroscopist Exner also described an arc spectrum of holmium. But this holmium, prepared by Cleve, who so named the X of Marignac and Soret, contained as impurities most of the yttrium earths and considerable quantities of yttrium and terbium. It corresponded to the purer, light-colored earths in which Lecoq de Boisbaudran observed not only true holmium, but also dysprosium, Z^{γ}, and Z_{α}. Exner distinguished X_1, X_2, X_3 in Cleve's holmium. Such, in résumé, is the history of the earths forming the heart of the yttrium series.

On the other hand, the history of the first members of the yttrium series, europium and gadolinium, was not yet free from obscurity; and the individuality of these two elements still presented many uncertainties.

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[7] Mosander had distinguished only these three earths in yttria. But he had given the name of erbium to that which, in consequence of confusion, was later called terbium.

Crookes was the first to observe one of the characteristics of europium: it was a band of orange-colored phosphorescence which he at first thought an anomalous band resulting from the combined phosphorescence (?) of yttrium and samarium, and which he later attributed to a meta-element, S , of samarium.

Some years later Lecoq de Boisbaudran observed, by this method of reversing the spark with solutions, an analogous band of fluorescence which he attributed to an element Z_ζ. He stated that this element was probably not without relation to the anomalous band of Crookes.

Demarçay's europium showed all these characteristics, and Demarçay doubted the simplicity of this element, not only because of the previous experiments of Lecoq de Boisbaudran, but also because europium exhibited an absorption spectrum rich in lines, but in general extremely faint; and because its spark spectrum showed, besides numerous strong lines, a background of extremely numerous but very faint lines. He considered these facts as so many spectroscopic anomalies in conflict with all that he had so carefully observed in the pure earths of the cerium group.

There, assuredly, was an array of presumptions, but no direct proof of the complex character of europium.

The homogeneity of gadolinium was not debated, but my own research was to bring up, in connection with this element, an unexpected problem, which I myself stated in the following way: is the element victorium, whose discovery Crookes has recently announced, a constant impurity of gadolinium, or has it been confounded with that element?

In order briefly to indicate the degree of our knowledge of Crookes's victorium, I cannot do better than to transcribe here what I wrote on the subject in my article. "The Rare Earths," for Moissan's treatise on inorganic chemistry.

> In 1898, Crookes announced the existence of a new element intermediate between yttrium and terbium. This element is characterized by a particular phosphorescence spectrum, and its atomic weight is about 118. At first Crookes called this substance monium, but later, in 1899, victorium. Further research is needed to establish the exact

relation of victorium to the terbias of Lecoq de Boisbaudran and to the earth Δ of Demarçay.

In consideration of the facts that I have since established, namely, the identity of victorium and gadolinium (19) and the identity of dysprosium and the element Δ (20); and further of the fact that terbium separates gadolinium and dysprosium in the series; it becomes manifest that the information given out by Crookes was very inaccurate. But what he did was important; the discovery of victorium was the confirmation of the investigations which this scholar had been carrying on for fifteen years on the phosphorescence of the rare earths. Victorium was the first element which this method of spectroscopic observation led him to discover.[8]

The problems to be solved recalled those confronting the chemists who, in the dawn of chemical science, devised proximate analysis: mixtures manifested properties corresponding to different sensations—taste acid, color green, for example. Those chemists had at first considered these characteristics separately, as one may legitimately do for light, heat and electricity, which are produced by material means, and they sought to separate the acidity principle from the color principle.

It was only the constant association of characteristics so different that led to the idea of a definite substance, an idea thanks to which modern proximate analysis differs from the decomposition of the mixtures of the alchemists.

In the study of the yttrium earths it was necessary to transfer the problem from the field of proximate to that of elementary analysis; in the terbium group there had been announced a principle of color (Mosander's terbium), principles of phosphorescence (G_β, G_δ. . . Z_α, Z_β. . .), of absorption (Z_δ, dysprosium), of emission (Γ, Δ, Z_γ. . . .X_2. . .) as varied as possible. In order to arrive at a definite chemical element, the constant association of certain of these principles, to the exclusion of the others, must be established.

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[8] In the observation of his anomalous band, Crookes had really discovered europium, but he had interpreted his observations in a very different way.

The exclusion was the only part of the problem corresponding to positive experiments: methodical fractionations made success possible there. But to prove the constant association of simultaneous characteristics, a method of experimentation must be adopted which should not be limited to negative experiments. The rare earths must be obtained pure before it would be possible to state precisely the laws obeyed by their spectroscopic properties, which had been shown to be so different and so differently preceptible.

I venture to emphasize this point. The problem was not so much to obtain "pure" products, as products in which the different characteristics should coincide absolutely, without variation, during definite and sufficiently prolonged stages reached in the course of fractionation; stages of constant atomic weights, of constant and constantly associated spectra of different kinds.

If a product at a given stage has withstood a variety of tests; if at similiar stages, products obtained from earths which have been extracted from different minerals coming from different sources, are identical with one another and with the original product, there is justification for considering the material at this stage as formed of a single element (except for the common elements with which it is combined in a salt), conforming to the definition of an element; of which one may only presume that it will not sometime be resolved into a still simpler body.[9]

I wondered for a long time whether this experimental reasoning did not in some degree beg the question. I established, for example, certain laws of cathodic phosphorescence, by the use of specimens taken at the definite stages of fractionation, and I seemed thenceforward to be depending on these laws to prove homogeneity of these same stages. If that were really so, I should perhaps have made a vicious circle. In reality, I by no means absolutely proved that europium, gadolinium, terbium and dysprosium are homogeneous. The complexity of a body may be proved, but the opposite is incapable of proof. The

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[9] These considerations have become of historic interest only, now that the chemical elements have been defined by their atomic number (Moseley), which may be obtained by means of the X-ray spectra.

simplicity of the elements will always be a hypothesis. What my method permitted me to demonstrate positively is that the variations formerly observed among certain characteristics are apparent variations only. After putting together, somewhat reluctantly, substances which it had cost so much labor to separate, I showed that variations in the proportions of the mixtures brought about the combination of all those appearances which were wrongly supposed to be due to the beginnings of separation, obtained by fractionation.

It is evident that if certain peculiarities presented by iron, for instance, should be explained by the supposition that it is complex, that hypothesis might remain a dead letter up to the time when two dissimiliar irons were really obtained.

CATHODIC PHOSPHORESCENCE OF THE YTTRIUM EARTHS

On either side of a stage of constant properties, that is, in the intermediate fractions comprised between pure products, no variations have ever been observed in the absorption, the spark, or the arc spectra which could not be attributed to differences in perceptibility in these different groups of spectra, but such was not the case with the phosphorescence spectra.

Crookes had considered the phenomena of phosphorescence as characteristics of elements which the other spectra were unable to reveal. Lecoq de Boisbaudran held the view that phosphorescence was apparent only in case of mixtures, and that it was due to the presence of elements which other spectroscopic characteristics could indicate equally well. These two noted scientists had engaged in a long dispute which served only to emphasize their disagreement. We shall see that the view of Lecoq de Boisbaudran was correct. Nevertheless the several scientists who had taken up this problem agreed with Crookes, possibly because they had worked with mixtures that were too impure.

I was obliged to take up this particularly delicate question. In the effort to solve certain problems relating to the history of the rare earths I engaged in the study of a more general subject, that of the phosphorescence of solid solutions. I succeeded in completing the task begun by Lecoq de Boisbaudran. I will summarize briefly the notes that bear upon this matter:

On the law of optimum of phosphorescence in binary phosphorescent systems (21). The phosphorescence of solid solutions is a property of dilute material:

1. As Lecoq de Boisbaudran has stated, differing from Crookes, pure substances have no perceptible phosphorescence; strong phosphorescence is always the result of a mixture of at least two substances (binary phosphorescent system); one acts as "phosphorogen" and the other as "diluent."
2. In a binary phosphorescent system, the optimum of phosphorescence always corresponds to small quantities of the phosphorogen. In mixtures of pure rare earths and lime, this optimum, never sharply defined, corresponds to the content of pure rare earths, of the order of one part in a hundred.
3. The law of the optimum is general. It applies equally to the common elements and the rare earths.
4. The coloration of the phosphorescence, as well as its spectrum, varies with the dilution of the phosphorogen.
5. We may reproduce, with preparations made from pure substances, the marked spectroscopic variations observed in the intermediate mixtures which fractionations of rare earths give.

Such variations do not prove, then, that by fractionation an element, the final term arrived at by analysis (Lavoisier), has been broken up into several constituents.

6. The law of the optimum becomes much more precise, if instead of being applied to the phosphorescence as a whole, it is applied singly to each of the bands whose sum total makes up the spectrum.

The correct statement of the law is the following:

In every binary phosphorescent system in which the relative content of phosphorogen and diluent is made to vary, it is proved:

1. That each phosphorescent band passes through an optimum.
2. That the optima of the different bands do not necessarily coincide, although they always correspond to relatively weak proportions of the phosphorogen.

The cathodic phosphorescence of the rare earths (22). The first part of this article sums up our present knowledge of the phosphorescence of solid solutions. The cathodic phosphorescence of the rare earths is here more especially studied.

Experiments showed that the reversal spectra of Lecoq de Boisbaudran should be considered as cathodic phosphorescence spectra of liquid solutions, and that this phenomenon should be attributed to the ions of the phosphorogen. Generalizing from this result, we may assume that the same should be true in the case of solid solutions.

There follows a summary of my general observations upon the phosphorescence of the fractionated earths.

Of the first four members of the yttrium series which I considered to be pure, none showed perceptible phosphorescence. On the other hand, the intermediate mixtures were in general phosphorescent.

Only the earths comprised between terbium and dysprosium do not glow under the influence of the cathode rays. This result is due to the fact that the colorless earths alone may act as diluents. To be more exact, the earths which give a phosphorescent spectrum cannot play the part of diluent to those earths whose phosphorescent spectrum is in the same spectroscopic region.

For the first members of the yttrium series, gadolinium alone may act as diluent; europium-bearing gadolinium emits a beautiful red light and terbium-bearing gadolinium a beautiful green light.

For the higher members of the series, yttria (oxide of yttrium) acts as diluent. The yttrium earths at the beginning of the series, those carrying dysprosium, give a yellow phosphorescence; those at the end of the series, carrying erbium, a green phosphorescence.

Each of these phosphorescences was described in detail. Their variations, as a function of their concentration, were the object of special study. The question was, really, to find a correct interpretation of a phenomenon which a superficial analysis might attribute to a possible complexity of earths capable of phosphorescence. It was certainly such variations that suggested to Crookes his theory of meta-elements.

Confining himself to the analytical side of the research, this scientist thought that these variations in spectra were due to the beginning of a separation of distinct elements. The synthetic study of mixtures prepared from the beginning from pure substances showed that this is not the case; the relative intensity of the bands varies only with the concentration. In the consecutive parts of a fractionation the concentration necessarily varies, and consequently the relative intensity of the bands of the phosphorogen. This variation is not due to a separation of the supposed constituents of the phosphorogen; it simply appears to be.

If, as an unverifiable theory, the spectroscopic variations of binary systems may be considered as resulting from elementary complexity, they may with equal reason be attributed to complexity of structure or to movement of atoms, molecules, or even of the ions which we suppose to constitute all matter; but there is not sufficient justification for the assertion that variations in cathodic phosphorescence, observed in course of the fractionation of the rare earths, result from a separation of the constituents which the first hypothesis supposes, unless the fact of a separation has been confirmed by the study of other spectra.

These conclusions were reached only after long consideration, and it was in order to clear up a number of doubtful points that I undertook a careful study of the optima of phosphorescence.

To avoid all uncertainty, I abandoned temporarily the rare earths and turned my attention to the common elements, whose simple character could hardly be doubted. With the assistance of Bruninghaus I studied with great care the phosphorescence of the manganese-lime system. The chief difficulty of the problem consisted in obtaining pure lime, free from phosphorescence. But all commercially pure lime contains some manganese, which, under the action of the cathode rays gives it a beautiful orange phosphorescence. In order to obtain lime free from phosphorescence we were obliged to carry on daily for three months sixteen fractions of the pure commercial nitrate of calcium. It is only then that we obtained, in the head fraction, lime free from manganese. Next, we mixed this lime by chemical methods with known proportions of the oxide of manganese and we determined that the luminous optimum corresponded to the proportion of one per cent of manganese oxide. Above and below that amount the phosphorescence was more and more feeble. The coloration of the phosphorescence of the mixtures varied slightly, but we were not able to determine whether or not that variation was due to some impurity, since despite all our efforts our reagents were not spectroscopically pure, and moreover the spectroscopic analysis of the phosphorescence showed only a single band, very broad and with ill-defined outlines.

In case of the rare earths, on the contrary, the phosphorescence spectra are always made up of narrow bands, in general sharply defined and numerous.

In order to analyze the phenomenon, we had recourse to an earth of the cerium group, samarium, which Lacombe and I (23) had successfully isolated nearly quantitatively, and which, after purification, had been pronounced spectroscopically pure by Professor Eberhard of the Potsdam Observatory, after a very complete study of it by means of a grating of wide dispersion.

It was shown by previous researches of Demarçay that samarium was an element defined in the same way as any common element. The use, then, of such material gave all the desirable guarantees, and could serve as the starting-point for very delicate experiments. Now, the study of the samarium-lime system showed spectroscopic variations which could leave no doubt as to their origin.

It was necessary to reject definitely Crookes' hypothesis of the meta-elements.

The phosphorescence of the different members of the fractionations was then studied with lime as the diluent. This method had the initial advantage of avoiding the necessity of mixing the rare earths, after all the trouble of separating them. Moreover, by the use, in each mixture, of the rare earth in the proportion of 1 per cent only, which corresponds to the optimum in the case of pure earths, the spectra of phosphorescence presented no difficulty of interpretation; all the consecutive members of the fractionation of each pure earth showed the same phosphorescence spectrum, just as they showed the same absorption, spark, and arc spectra. These spectra agreed exactly, and there was no doubt whatever that they characterized the element, in the same way that the other kinds of spectra characterized it.

This new method of analysis of the rare earths removed all difficulties relative to the phosphorescent elements. I was able to identify the different meta-elements of Crookes as elements which I had isolated, and to give a very detailed description of the phosphorescence spectra of the different yttrium earths:

On victorium and the ultra-violet phosphorescence of gadolinium (24).

On the cathodic phosphorescence of europium (25).

Cathodic phosphorescence of europium diluted in lime (26).

Spectra of cathodic phosphorescence of terbium and of dysprosium diluted in lime (27).

On the nature of certain phosphorescent elements and meta-elements of Sir W. Crookes (28).

In connection with this subject, the phosphorescence of the rare earths diluted in calcium sulphate and in calcium fluoride was described; and we showed by the examination of a large number of fluorites of many colors and origins that the fluorites practically always contain rare earths.

THE MAGNETISM OF THE RARE EARTHS

The properties which serve to define the elements should be atomic in character. In other words, they should be independent, to a certain extent, of the nature of the combinations in which the elements exists.

The spectra and the atomic weights are of this nature; also, these properties are necessary and sufficient to define an element and to establish, in some sort, its status.

All the elements give spectra and have atomic weights. There are other properties which may be considered as atomic, for example, radioactivity. But this property is possessed, at least in a perceptible degree, by certain elements only. In particular, the rare earths are not radioactive.

Between exclusively atomic properties and molecular properties we may imagine transitions; some properties are found, although in different degrees, in the majority of the compounds of an element. Such is the case with magnetic properties.

Indeed, according to a law of Wiedemann's, which is, however, only approximate, all the compounds of a paramagnetic element have the same molecular magnetism.

As a matter of fact, all the combinations of a paramagnetic element do not follow this rule, but the law is essentially true for all the salts of a given element, with the reservation that it does not form complex salts, in which the chemical and physical reactions would be masked.

Now, the rare earths do not form complex salts, and the greater number of them have been found to be paramagnetic. This then is a property which in the case of the rare earths has the characteristics of an atomic property. Now, because of the work of P. Curie, the coefficients of magnetism are easily measurable. These measurements are capable of rendering a service, in the study of the yttrium earths, comparable to the determinations of atomic weight. According to the determinations of certain physicists, notably those of Stephan Meyer, of Vienna, different rare earths possess widely differing magnetic properties, while the atomic weights remain grouped within quite narrow limits. While these determinations were based upon products which were, in general, rather impure, they conveyed a useful suggestion, and I set myself the task, with the aid of Jantsch, of determining the coefficient of magnetism of the different rare earths which I had already been able to isolate in the pure state:

On the magnetism of the rare earths (29). The results obtained are of especial interest; certain rare earths are diamagnetic (negative coefficients of magnetism); but most of them are paramagnetic (positive coefficients of magnetism). The different values ranged from -1×10^{-6} to 300×10^{-6}. The difference for two closely associated earths was considerable; the ratio of their magnetic coefficients was frequently as high as 1 to 6, while their atomic weights did not differ more than two or three units for values of the order of 160.

Although the determination of the atomic weights required great precision, the determination of the magnetic coefficients could be made by the remarkably simple method devised by P. Curie and Cheneveau. While the determination of an atomic weight requires ten days, that of the coefficient of magnetism requires only a quarter of an hour. The new quantitative technique was thus an ideal guide for treatments which require numerous and frequent checks.

Such are the practical considerations, which have so great a bearing on the final results of investigations consisting of the definition and isolation of the successive members of this perplexing yttrium group.

From a theoretical standpoint the results of these researches are not less worthy of attention:

The earths of the cerium group—lanthamum, cerium, praseodymium, neodymium and samarium were sharply distinguished from those of the yttrium group—europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and the original ytterbium. Yttrium, which is diamagnetic, occupied a place by itself.

In each of these series, the magnetism, at first very faint or even negative, gradually increased, attained a maximum and then decreased. From this point of view, the yttrium series, more complex than that of cerium, was notable also on account of the unexpectedly high degree of magnetism of its members.

Not only did the entire rare earth series show two magnetic maxima, but bismuth, which Lacombe and I showed as taking its place between the cerium and the yttrium groups by virtue of the chemical properties of its salts, took the same place by virtue of its magnetic properties.

Before making, with the assistance of Jantsch, a systematic study of the earths of the series as a whole, I had made several measurements of dysprosium, and I had been struck with the high paramagnetism of that element, whose compounds are fifteen times as paramagnetic as those of iron:

On the ultraviolet spectrum of dysprosium and the remarkable magnetic properties of that element (30). Since that time I have always followed the progress of my fractionations, from a quantitative point of view, by measuring the coefficients of magnetism.

This method, which gives the service generally required of gravimetric analysis, can moreover be combined with it to advantage for the solution of certain problems of exact elementary analysis. I gave an instance of this and described the new method of analysis in a more recent note:

On the magneto-chemical analysis of the rare earths (31). In mixtures, the magnetism of the rare earths is, like the mass, an additive property.

Since, moreover, the coefficients of magnetism of the rare earths are not proportional to their atomic weights, we may demonstrate, by the aid of appropriate diagrams, the existence of an intermediate earth between two end fractions containing pure substances.

The principle of this method of research upon the elements recalled, in a certain measure, the principle of the method used in investigations upon radioactive substances. I applied this, by way of illustration, to the earths existing between dysprosium and pure yttrium, and I demonstrated by a study of the magnetic properties of the successive members of the fractionations that the holmium contained in the mixtures could not have disappeared. Along with these investigations of magnetism I succeeded in establishing the fact that Marignac's ytterbrium is not an element, and I uniformly followed the progress of my fractionations by means of measurements of magnetism.

THE ATOMIC WEIGHTS OF THE RARE EARTHS

The chemical elements are not officially recognized until they appear in the table of the International Atomic Weight Committee. This decision, which was made at the International Chemical Congress of Paris, in 1900, is justified by the important part which the atomic mass plays in the mutual relations of the elements.

Determinations of atomic weights are of the greatest interest. From the beginning of these studies I have been obliged to pay much attention to this delicate matter. In the course of my work I have made several hundred determinations:

Revision of the atomic weights of the rare earths (32). The rare earths comprise the following sixteen elements, arranged in the order of their increasing atomic weights:

Scandium
Yttrium
Lanthanum
Cerium
Praseodymium
Neodymium
Samarium
Europium
Gadolinium
Terbium
Dysprosium
Holmium
Erbium
Thulium
Neoytterbium
Lutecium

Among these elements, holmium, thulium, erbium, neoytterbium, and lutecium are still little known. The isolation of europium, terbium, and dysprosium, in a state of purity, is of very recent date. There is as yet only a small amount of information concerning their atomic weights. These values therefore should be considered as first approximations, although they probably are not far from correct, especially those which agreed for several consecutive fractions of the series by means of which these earths were isolated.

In fact the constancy of the atomic weights in successive steps of a methodical and lengthy fractionation of a pure earth of this group permits the establishment of a value to a high degree of probability. A value determined solely from a specimen selected from among the members of a fractionation is, in general, a point chosen arbitrarily on a continuous curve, unless it is established that this curve becomes a straight line representing constant atomic weights. It is therefore absolutely necessary in the case of elements which cannot be sharply separated from one another by any method, and which can be purified only by progressive treatments, to prove the constancy of the atomic weight by prolonging the fractionation beyond the point which seems necessary to obtain pure products.

If this consideration, essential in the determination of the atomic weight of a rare earth, is neglected, and if measurement is limited to the fraction which appears to be the purest, the value obtained has but a limited claim to probability. Many similar measurements made by different investigators would have to agree before they would lose this character. A comparison of the determinations given below is enough to show that this generally holds true.

The history of the atomic weight of terbium offers indeed a good illustration of the foregoing statement. These are the values successively announced:

Delafontaine	(1864)	113.0
Smith	(1878)	153.7
Delafontaine	(1878)	147.0
Marignac	(1878	148.5
Lecoq de Boisbaudran	(1886)	161.4-163.1
Lecoq de Boisbaudran	(1890)	159.0-159.95
Kruss and Hofmann	(1893)	148.9-162.2
Marc	(1902)	151.9-161.2
Feit	(1905)	158.6
Melle Potraz	(1905)	154.0
G. Urbain	(1906)	159.2

A table like this needs no comment.

In the case of the common elements, which may be obtained fairly easily in a degree of purity superior to that which the accuracy of the measurements permits, the whole effort of the experimenter is necessarily directed toward everything that may increase that accuracy. In the case of a rare earth, of which it has been practically impossible until recently to determine the degree of purity, the effort to secure great accuracy was evidently somewhat illusory. Great accuracy has no meaning unless there is the assurance that the inaccuracy due to the presence of impurities does not much outweigh that which is inherent in the methods of measurement themselves. Success is possible only if the successive members of a fractionation give identical results with an identical method of measurement.

In every other case, the influence which impurities may produce is a matter of judgment, or of rough spectroscopic comparisons, and there is thus introduced into the determinations a class of errors which defy the resources of the calculus of probability.

It follows from the foregoing considerations that in the present state of the case the only determinations which deserve acceptance are those which have been made upon products sufficiently purified; for the analysis and synthesis of sulphates, applied in this kind of measurements, give rise to errors of the second order in comparison with those which come from the impurity of the products.

ISOLATION AND DEFINITION OF THE EARTHS OF THE YTTRIUM GROUP

Samarium

On samarium; its isolation and atomic weight (33). Samarium is the last member of the cerium series.

We published a method, already alluded to for its exact and quantitative separation from europium, the first member of the yttrium series.

After making a suitable purification, we obtained samarium spectroscopically pure, a result up to that time unknown in research of this kind. Samarium behaved like an element throughout our treatments; its characteristics remained invariable.

Subsequently I studied the subject of the phosphorescence spectra of samarium, and demonstrated that the constituents of samarium discovered by Crookes had no real existence.

Europium

On europium; its isolation and atomic weight (34). We determined a constant atomic weight for europium extracted from monazite sands. This element was subjected to a long fractionation after its separation from samarium, which precedes it in the rare earth series, and from gadolinium which follows it.

Later I carried on a similar study of the other properties of europium, and especially of its absorption spectrum, which, in the spectroscopic field earlier studied by Demarçay, was extremely faint. I observed far over in the ultraviolet field some very pronounced absorption bands belonging to that element. The chief consideration that had led Demarçay to doubt the homogeneity of europium existed no longer. The absorption, spark, and arc spectra of europium remained constant throughout the duration of our fractionations.

Europium extracted from monazite, from gadolinite, from xenotime and from the very radioactive rare earths of pitchblende manifests identical characteristics (35).

Nevertheless these results were not entirely satisfactory. Crookes, to whom I had given a sample of europium, had claimed that this earth was not the same as his Sδ.

I knew very well that Crookes had observed up to that time only fairly complex mixtures; but the profound spectroscopic differences which he described between the phosphorescence of Sδ and that of europium left room for doubt.

I made up my mind that the anomalies pointed out by Crookes depended upon laws of cathodic phosphorescence not yet understood. Experiments justified that point of view, and I was at length able to assert that *Sδ* (Crookes), and also *Zζ* (Lecoq de Boisbaudran) are really identical with europium (*Zε* of Lecoq de Boisbaudran) (36).

Gadolinium

The results of those studies that had to do with the isolation and definition of gadolinium have been outlined in the following notes:

On gadolinium; purification and atomic weight (37).

On a new spectrum observed in gadolinium (38).

On victorium and the ultraviolet phosphorescence of gadolinium (39).

Gadolinium was defined very incompletely on account of its colorless salts and the absence of absorption spectrum. Demarçay, who had obtained it in a reasonably pure condition, had described only a spark spectrum. The number 156 had been accepted as its atomic weight, after the very interesting investigations of Benedicks, although his gadolinium always carried a little terbium and europium.

After having fractionated gadolinium well beyond the point necessary to obtain it pure, I performed a very extended series of constant atomic weights. The measurements raised by 1.3 the value 156 then recognized by the International Atomic Weight Committee. This correction seems small. In reality it is considerable, in view of the atomic weights 152 and 159.2, those of europium and terbium, which are the common impurities of gadolinium.

In exploring the spectroscopic regions well over in the ultraviolet, I found that this earth gave a new absorption spectrum. This characteristic belongs exclusively to gadolinium.

The spectrum of phosphorescence assigned by Crookes to victorium belongs also to gadolinium alone. But Crookes was not ready to admit the identity of his victorium with gadolinium. I then attempted in vain by new methods of fractionation to obtain either gadolinium free from victorium, or victorium free from gadolinium. As the result of these experiments and of a critical study of the work of Crookes, I arrived at the conclusion that victorium with its atomic weight of 118 must be a mixture of gadolinium and yttrium (40). Finally, by mixing suitable proportions of yttrium and gadolinium, I obtained an earth which possessed all the properties assigned by Crookes to victorium.

Terbium

In 1846, Mosander had observed that the yttrium earths contained in his fractions between the pink oxide of erbium and the white oxide of yttrium had a yellow coloration. He attributed this coloration to the existence of a new element, which was named terbium. Some years later, Delafontaine obtained the same results and confirmed the conclusions of Mosander.

Nevertheless there was a question as to the existence of terbium, for there was nothing to prove that the yellow coloration was not due to the presence of some element already known. Thus, in 1866, Bunsen concluded from his researches upon the yttrium earths that their yellow color chould be attributed to a trace of cerium. In 1878, Cleve and Hoglund confirmed the conclusions of Bunsen.

However, Delafonatine maintained that the conclusions of Mosander alone were correct, and requested Marignac to verify the foundation of his claims. Marignac furnished incontestible proofs of the existence of terbium, but he did not succeed in isolating pure terbia.

In 1885 Lecoq de Boisbaudran took up the matter. He considered what was then called terbia to be really a group of elements. By the study of reversal spectra, he distinguished two substances, which he provisionally designated as Z_α and Z_β. Furthermore, he observed in the light-colored terbium earths a spark spectrum which he attributed to an element Z_γ, and in the dark-colored terbium earths an absorption spectrum which he attributed to an element Z . Finally, Demarçay attributed to an element Γ a spectrum of ultraviolet lines observed with the earths of the group. In fact the whole question since the time of Mosander was singularly complicated, and it had not been possible to isolate any substance having constant properties.

I succeeded in separating this very dark-colored earth with constant characteristics and an atomic weight of 159.2. This is the earth which, owing to the strong coloring power of its oxide, gives to the yttrium earths the yellow color which led Mosander seventy-seven years ago to suspect its existence.

This subject was discussed in the following notes:

On an yttrium earth closely associated with gadolinium (41).

On the isolation of terbium (42).

Atomic weight and spark spectrum of terbium (43).

Cathodic phosphorescence spectra of terbium and dysprosium diluted in lime (44).

On the nature of certain phosphorescent elements and meta-elements of Sir W. Crookes (45).

On some compounds of terbium and dysprosium (46).

The isolation of terbium did much to clear up the confusion that existed with regard to the earths of this group, for it enabled me to identify as terbium a certain number of substances which writers had designated by provisional symbols and occasionally even by new names:

NAMES OR SYMBOLS	CHARACTERISTICS	AUTHORITIES
Terbium	Yellow color of oxides	Mosander
Z β	Reversal spectrum	Lecoq de Boisbaudran
G β	Visible phosphorescence spectrum	Crookes
Z δ	Absorption spectrum	Lecoq de Boisbaudran
Ionium	Ultraviolet spectra of phosphorescence	Crookes
Incognitum		
Γ	Spark spectrum	Demarçay

Dysprosium

Pure dysprosium, which in the yttrium series immediately follows terbium and precedes holmium, was likewise isolated for the first time somewhat later.

Lecoq de Boisbaudran had so named an earth characterized by an absorption spectrum which came from the splitting up of an absorption spectrum observed by Soret in some of Marignac's fractionation products. Soret's spectrum had been attributed to the elements *X*, which Cleve named holmium.

Lecoq de Boisbaudran observed the presence of dysprosium in mixtures only, and he could not observe the color of its salts.

I isolated a few grams of dysprosium characterized by constant properties and by salts of a pale yellowish-green color.

This subject has been outlined in the following notes:

On the isolation and the various atomic properties of dysprosium (47).

Cathodic phosphorescence spectra of terbium and dysprosium diluted in lime (44).

Atomic weights of dysprosium (48).

On the nature of certain phosphorescent elements and meta-elements of Sir W. Crookes (45).

On some compounds of terbium and dysprosium (46).

On the ultraviolet spectrum of dysprosium and the remarkable magnetic properties of that element (30).

These investigations also showed that a certain number of substances whose individual existence had been considered as possible or probable are identical.

NAMES OR SYMBOLS	CHARACTERISTICS.	AUTHORITIES
Dysprosium	Absorption spectrum	Lecoq de Boisbaudran
Δ	Ultraviolet spark spectrum	Demarçay
Z α	Reversal spectrum	Lecoq de Boisbaudran
Z γ	Visible spark spectrum	Lecoq de Boisbaudran
G δ	Phosphorescence spectrum	Crookes
X_2	Ultraviolet arc spectrum	Exner and Hascheck

Holmium, erbium and thulium

I have not succeeded up to the present time in obtaining in a pure state the elements of the group; nevertheless I have been able to determine some of their characteristics (49).

THE CONSTITUENTS OF MARIGNAC'S YTTERBIUM

Discovery of celtium, Neoytterbium and lutecium

This is perhaps the most important of my investigations upon the rare earths. It resulted in the discovery of two elements: lutecium and celtium. But it is not yet completed.[10]

In 1878 Marignac had succeeded in separating from erbia, whose salts are pink, a colorless substance of the atomic weight of 173, to which he gave the name ytterbium.

In 1904 I began the fractionation of an ytterbium corresponding approximately to the description of that element given by Marignac. My object was to assure myself of the constancy of its atomic weight, and to determine its value in case I should find it constant.

In 1907 I published my observations:

Starting from that part of the fractionation where I observed only faintly the absorption spectrum of thulium, never very bright, the atomic weights, instead of being constant, varied in a very regular fashion from 170 to 174. Ytterbium was not an element.

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[10] I obtained with the collaboration of Blumenfeld a neoytterbium series of fractions containing twelve members of identical properties; but there is here a limit of fractionation, for this neoytterbium carries still a small amount of lutecium, which doubtless raises its atomic weight of 173.5.

The discovery of lutecium is certainly due to the method of work the principles of which I explained in the early part of this paper.

In the early members of the fractionation the presence of thulium lowered the atomic weight. The higher atomic weight of the final members of the series might be caused by the presence of thorium (atomic weight 233). I removed completely the very small trace of it. But this trace was not influencing the atomic weight determinations, as I ascertained. Then I compared the arc spectra of the fractions at opposite ends of the series, taking care to photograph the spectra upon the same plate, one above the other. The fraction having the higher atomic weight showed strong lines, which were either absent or very faint in the fraction having the lower atomic weight.

I then supposed that this difference was simply a physical phenomenon due to the arc, and I compared in the same way the spark spectra, which showed exactly the same peculiarities.

Next I made use of a device of Lecoq de Boisbaudran, which made it possible to obtain with ytterbium solutions a spark spectrum not of lines but of bands. It was by means of this spectrum that Marignac's earth had been characterized by Lecoq de Boisbaudran, to whom Marignac had given his preparation.

A comparison of the extreme ends of the ytterbium series showed that a band of 3°, called γ by Lecoq de Boisbaudran, was the most pronounced in the ytterbium of higher atomic weight, and was entirely wanting in the earth of lower atomic weight.

There was noting to do but to yield to the evidence. I gave the element having the band γ and the new spark and arc spectra the name lutecium.

A new element: lutecium, resulting from the splitting up of Marignac's ytterbium (50). One month later, Auer von Welsbach announced to the Vienna Academy of Sciences the same results as mine.

He tried to bring up the question of priority; I firmly contested that claim (51).

An additional note, *On lutecium and neoytterbium* (52), contained all the atomic weight determinations of the successive members of my fractionation, as well as the measurements which related to the coefficients of magnetism.

As stated above, I had been stopped in my fractionations by lack of material. It became necessary to prepare a fresh supply, and therefore to begin new treatments. With this in view, I turned to earths extracted from gadolinite (my previous work had been conducted upon earths extracted from xenotime).

Bourion and Maillard were good enough to give part of their time to this undertaking, in which we made use of new methods:

Extraction of lutecium from the earths of gadolinite (53). Subsequently I added these earths to those previously prepared, so doing it as not to lose the benefit of the fractionations of both. The progress of the separations was followed by magnetic measurements.

Celtium

The oxides contained in the final mother-liquors, which refused to crystallize, showed properties which I could interpret only as due to the presence of a new element; this I called celtium.

My investigations continue to be halted by lack of material, and it was impossible for me to submit the case of celtium to the rigorous method which made possible the identification, without uncertainty or possible mistake, of the different yttrium earths which are the subject of this paper.

Meanwhile, Moseley, having discovered his celebrated law, advanced the hypothesis that celtium was perhaps identical with the unknown element of atomic number 72. Investigations which Moseley and I made on this subject in June, 1914, yielded no results. But de Broglie having perfected the original method of X-ray spectra, the product containing celtium was turned over to him; and Dauvillier, his pupil and collaborator, found in it, in 1922, lines characteristic of element 72. These lines gave to celtium, up to that time ill defined, a correct definition.

Coster and Hevesy, who in 1923 found the same spectrum in zirconia, gave the same element the name Hafnium. Dauvillier and I should have established our rights of priority, and claimed for element 72 the name celtium, which we agreed to give it.

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