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XIII.—Contributions to the Chemistry of Rare Earth-Metals.

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WITHIN recent times the chemistry of the rare earth-metals, owing to the discovery of several new elements, has attracted the attention of many chemists. The classical researches of Berzelius, Mosander, Marignac, Bunsen, Rammelsberg, Hermann, and others have certainly furnished us with copious experimental material, and explained many points of the chemistry of the rare earth-metals. These facts, however, could not be arranged systematically, nor could the relations in which this group of elements stand to other groups be determined. So much indeed is this the case, that the rare earth-metals and their compounds have not unfrequently been regarded as holding an exceptional position, finding only a certain analogy in the elements of the magnesium group.

A great step forward was made by Mendelejeff in the years 1870 and 1871, for having established the periodic law in its present state (*Liebig's Annalen*, Suppl. 8, 133), he came to the conclusion that the rare earth-elements can be systematically placed, only by assuming that the hitherto accepted atomic weights are only two-thirds of the truth.

Mendelejeff's view has been confirmed by the determination of the specific heat of cerium by himself (Bull. de l'Acad. de St. Petersbourg, 1870, 445), by the investigations of Cleve (Bull. Soc. Chim. [2], 21, 203), and Nilson (Berl. Ber., 8, 655; 9, 1056, 1142, 1722), and lastly by Hillebrand's (Pogg. Ann., 158, 71) determinations of the specific heats of metallic lanthanum, cerium, and didymium.

The position of the individual members of the cerite metals in the *periodic system* has not yet been satisfactorily established, in spite of the endeavours of several authors. Thus Mendelejeff (*loc. cit.* and *Liebig's Annalen*, **168**, 45) places cerium (Ce = 140) in the fourth group (vertical), but he is doubtful as to the position of lanthanum and didymium.

Lothar Meyer (Moderne Theorien, 3rd Edition, 293), on the other hand, places cerium (Ce = 137) in the third group, lanthanum (La = 139) in the fourth group, and didymium (Di = 147) provisionally in the sixth group; but later on he (*ibid.*, 4th Edit., 138) places all three elements (La = 139, Di = 140, Ce = 141) in the third group.

Several years ago the author of the present communication (*Berl. Ber.*, 11, 873, Note) proposed the hypothesis that the cerite metals might be placed in the 8th *series* (horizontal) of the periodic system as follows:—

G	roup III.	1V.	v.
	La.	Ce.	Di.
Series 8	139	141.6	147

The object of the research, the chief results of which are given in the present paper, is the study of the cerite metals with special reference to their position in the periodic system. It appeared desirable to examine which one of the above-mentioned views is correct, and to collect further facts in its support.

A. Cerium Tetrafluoride.—If cerium stands in the place which was allotted to it by Mendelejeff in the periodic system, a compound of the above composition ought to exist, and though Berzelius (see *Gmelin-Kraut's Handbuch der Chemie*, II, 1, 520) may possibly have prepared a body of this kind, no analysis was made, and it therefore may have been a fluoride, an oxyfluoride, or a double fluoride. The mineral "Fluocerite" is indeed generally regarded as CeF₄, but the only published analysis by Berzelius (see *Dana's System of Mineralogy*, 126) (1818) agrees better with the formula Ce₂F₆ + H₂O, as the percentage of cerium is much too high to agree with CeF₄.

By repeatedly dissolving and precipitating the basic sulphate of cerium (see Bunsen, *Pogg. Ann.*, **155**, 375), and treating the hydroxide several times with chlorine in a solution of potassium hydroxide, the author prepared the pure hydrated dioxide, $Ce_2O_4 + 3H_2O$, the hydrochloric solution of which gave the spark-spectrum of pure cerium without any lines of foreign metals.

By treating the hydroxide with aqueous hydrofluoric acid, the yellow colour of the former disappeared, and after drying at 100°, a brownish powder was obtained, the analysis of which gave numbers agreeing with the formula $CeF_{+} + H_2O$.

				Found.	
С	==	Calculated. 60.00	60.83	60.49	
\mathbf{F}	=	32.34	31.02		
H_2C) =	7.66			7.22
		100.00			

Hydrated tetrafluoride of cerium is an amorphous brownish powder, insoluble in water, which on heating loses its water and a part of its fluorine as hydrofluoric acid; on heating more strongly a gas is given off, which decomposes potassium iodide with liberation of free iodine. The decomposition seems to occur according to both of the following equations :—

(a.)
$$2\text{CeF}_4, \text{H}_2\text{O} = 2\text{CeF}_3 + 2\text{HF} + \text{O} + \text{H}_2\text{O}.$$

(b.) $\text{CeF}_4, \text{H}_2\text{O} = \text{CeF}_3 + \text{H}_2\text{O} + \text{F}$ (?).

On heating for some time over the blowpipe, in contact with moist air, pure cerium dioxide is left behind :

$$CeF_4, H_2O + H_2O = CeO_2 + 4HF.$$

Double Salt of Cerium Tetrafluoride.—The hydrated dioxide was treated with a solution of potassium-hydrogen fluoride, and a salt was obtained, the composition of which corresponded with the formula $3KF_{2}CeF_{4} + 2H_{2}O$:

					Found.		
K	=	Calculated.	19.61	19.33			
Ce	=	43.79	42.39	42.31	43.39	43.25	
F	=	32.45			32.32	32.33	
H_2O	=	5.59					5.31
		100.00					

It is a slightly yellowish-white crystalline powder, consisting of very small microscopical octohedrons and cubes (?). It is insoluble in water, and is converted by sulphuric acid into a mixture of potassium sulphate with the orange-yellow sulphate of cerium dioxide, hydrofluoric acid being given off at the same time. On heating, it behaves similarly to the hydrated tetrafluoride.

B. Peroxide of Didymium.—Mosander, Marignac (Ann. Chim. Phys. [4], **38**, 148), Hermann (J. pr. Chem., **82**, 385), and Zschiesche (J. pr. Chem., **104**, 74) observed, that didymium forms, besides the grey oxide (now Di_2O_3), a higher oxide of a brown colour; but they were unable to determine its true composition, finding that the substance contained only 0.32 to 0.88, or 0.446 or 0.35 per cent. of oxygen more than the ordinary oxide. Afterwards this body was obtained in a purer state by Frerichs and Smith (Lieb. Ann., **191**, 331), who succeeded in converting 100 parts of Di_2O_3 into 107.13 parts of the higher oxide, this corresponding to the formula Di_4O_9 , which formula Lothar Meyer (Moderne Theorien, 3rd Edit., 322) considers as doubtful.

Some years ago the author suggested that the composition of this higher oxide, in the pure state, would be found to correspond with the formula Di_2O_5 , and that didymium would find its proper position among the elements in the fifth group. Cleve (*Bihang till K. Svenska Akad. Handl.*, Bd. 2, 88) and Nilson (*Berl. Ber.*, 8, 655) regard this oxide as DiO_2 ; Mendelejeff (*Principles of Chemistry*, 3rd Edit., 936) considers it to be either Di_2O_5 or DiO_2 .

Cleve (*Berl. Ber.*, **11**, 910) repeated the preparation according to Frerichs and Smith's method, but was unable to obtain an oxide of the formula Di_4O_9 , his brown oxide showing only a very small loss of 0.98 per cent. on reduction in hydrogen, so that almost all handbooks contain the statement that this oxide does not exist.

In spite of these negative experiments, the existence of such a peroxide appeared so probable, that the author deemed it necessary to attack the question again, starting from pure material.

Didymium sulphate was first purified by a long series of crystallisations, and the hot aqueous solution partially precipitated by oxalic acid. On igniting, transforming into the anhydrous sulphate, dissolving in water, reprecipitating, and repeating this process very many times, an oxide was finally obtained, the hydrochloric solution of which gave the spark-spectrum of pure didymium and an atomic weight as follows :---

Experi-	Weight of	Weighed	Percentage pha	in the sul- te of	Atomic weight of	
ment.	D1 ₂ O ₃ .	sulphate.	Di ₂ O ₃ .	SO3.	didymium.	
I	0 .82867	1 .41228	58 ·676	41 .324	146 .55	
II	0.82183	1 • 40050	58 ·681	41.319	146.58	
III	1 .18879	2 .02473	58.685	41 .315	146.60	
Mean			58.681	43 . 319	146.58	

The atomic weight of didymium is 146.58, if O = 16, S = 32.074, or Di = 146.18, if H = 1 and O = 15.96.

It was only after a long series of negative results that the author succeeded in preparing peroxide of didymium in the pure state. He first confirms Cleve's experiment, showing that an oxide, Di_4O_9 , cannot be prepared by Frerichs and Smith's method, 100 parts of Di_2O_3 having taken up only 1.22, 2.18, 2.77, 3.55 parts of oxygen, instead of 7.13 parts.

In the second place, Marignac and Hermann's method was tried, but without success. This consisted in heating the nitrate in the air and then treating the mixture of oxides thus obtained, either with dilute nitric acid or with a boiling solution of ammonium chloride. It is well known that no higher oxide is formed by melting the lower oxide with a mixture of potassium hydroxide and chlorate, or on treating it with hypochlorous acid. The methods finally adopted are as follows:—

I. Hydrated peroxide of didymium is obtained as an amorphous greenish precipitate by the addition of dilute potash-solution to a mixture of the solutions of didymium nitrate and hydrogen dioxide, until a slightly alkaline reaction occurs. After drying this precipitate in a vacuum, a light red powder was obtained, corresponding with the formula $Di_2O_5 + 3H_2O$.

	Calculated.	Found.
$Di_2O_3 \dots$	79.87	78.48
O ₂	7·4 9	8·51 (by diff.)
H_2O	12.64	13.01
	100.00	100.00

This hydrate is analogous to the hydrates of lanthanum and cerium, the amount of oxygen increasing with increasing atomic weight. CHEMISTRY OF RARE EARTH-METALS.

 $La_2O_3 + 3H_2O$ $Ce_2O_4 + 3H_2O$ $Di_2O_5 + 3H_2O$.

II. Anhydrous Didymium Pentoxide.—On carefully heating basic nitrate of didymium to dull redness, in a current of oxygen in a porcelain boat, the oxide Di_2O_5 was obtained as an amorphous chocolate-brown mass, according to the equation

$$Di_2O_3 \cdot 2N_2O_5 + xO = Di_2O_5 + 4NO_2 + xO_2$$

It was found, as an average of many determinations, that 109.44 parts of the pentoxide gave 100 parts of Di_2O_3 , or in percentage :----

	Calculated.	Found.
$Di_2O_3 \dots$	91.42	91·37
O ₂	8.58	8.63
	100.00	100.00

The specific gravity varies according to the mode of preparation. The following numbers were obtained for the specific gravity in benzene at 15° C.:—

5.171
5.261
5.262
5.358
5.651
5.969

On heating to a high temperature, oxygen is given off, as can be easily shown by applying a red-hot splint of wood to the gas contained in the crucible. The oxide may be heated in hydrogen above the boiling point of sulphur, without being reduced; the reduction begins to take place only at dull red heat, when water is deposited in the colder part of the tube.

Pentoxide of didymium dissolves in dilute nitric acid or sulphuric acid without evolution of gas, but on dissolving it in stronger acids, oxygen, containing some ozone, is given off. On treating the pentoxide with concentrated hydrochloric acid, only a small quantity of chlorine is given off, whilst hydrofluoric acid does not act upon it. It is only slightly soluble in a cold concentrated solution of ammonium nitrate. A solution of the same strength dissolves the oxides named below, in the following proportions :—

Di ₂ O ₅ .	$\mathrm{Di}_{2}\mathrm{O}_{3}$.	La_2O_3 .
1 part	10 parts	29 parts

This different solubility of the oxides of lanthanum and pentoxide of didymium in ammonium nitrate could not, however, be used for a quantitative separation of the above-named oxides, though it furnishes a simpler mode of preparing pure lanthanum and didymium oxides than the methods hitherto proposed. For this purpose a mixture of lanthanum and didymium nitrates, free from yttrium and cerium, is heated in a current of oxygen, to convert the didymium into the peroxide, and then treated with a cold neutral solution of ammonium nitrate, sufficient to bring half of the oxides into solution. The dissolved, as well as the undissolved, portion is treated in the same way two or three times with smaller quantities of ammonium nitrate, and in this manner very nearly pure preparations may be obtained.

III. The following experiments were made, with the view of ascertaining whether salts of didymium pentoxide can be prepared. A solution of the pentoxide in acids leaves on evaporation in a vacuum only the salts of the lower oxide. On mixing a solution of the pentoxide in sulphuric acid with one of potassium sulphate, the salt $Di_2O_3.3SO_3 + 3K_2O.SO_3$ is thrown down :---

		Calculated.	Fou	nd.
$\mathrm{Di}_2\mathrm{O}_3$	• • • • • • • • • • • •	= 30.86	30.68	
K_2O		= 25.68	$25 \cdot 80$	
SO_2		= 43.46	_	43.99

100.00

From a mixture of didymium sulphate solution with hydrogen dioxide, potassium sulphate throws down the precipitate $Di_2O_3.3SO_3 + 4K_2O.SO_3$.

	Calarlated -		Found.			
$Di_2O_3\ldots$	= 26.68	27.75	28.16	_	_)
K₂O	= 29.49	29.98	29.94			—
$SO_3 \ldots$	= 43.83			43.51	43.86	44.02
	100.00					

Both of these salts form pink crystalline powders.

I attempted to prepare double fluorides containing didymium as DiF_5 or $DiOF_3$. For this purpose a solution of acid potassium fluoride was evaporated to dryness with anhydrous didymium pentoxide, and the salt fused. The oxide lost its brown colour, and was converted into the salt $3KF.2DiF_3 + H_2O$.

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	Coloulated			Found.		
Di	= 48.91	49.00	4 9·23	48.79	47.98	49.17
К	= 19.57	19.40	18.93		—	
F	= 28.52		_	23.67	25.87	26.82
H_2O	= 3.00			—		2.94
	100.00					

The salt forms a pink powder, insoluble in water, yielding on evaporation with sulphuric acid hydrofluoric acid and a mixture of the sulphates of didymium and potassium.

Another salt, prepared in the same way, was the following:--- $3KF.3DiF_3 + H_2O.$

	Calcula	ited.	For	und.
Di_3	 = 54.7	75	54.43	_
Κ	 = 14.6	31	14.67	
\mathbf{F}	 = 28.4	40		
H_2O	 = 2.2	24	_	2.73
	100.0	00		

On treating the hydrated pentoxide with a cold solution of acid potassium fluoride, it was converted into a pink salt having the composition 3KF, $4DiF_3 + 3H_2O$.

	Calculated	Found.			
Di	= 56.14	56.77	57.14	_`	
к	= 11.25	11.41	10.69		
F	= 27.33				
${ m H}_2{ m O}\ldots\ldots$	= 5.18			4.85	
	100.00				

The three last-mentioned salts are the first double fluorides of a rare earth R_2O_3 that have been prepared.

The transformation of Di_2O_3 into Di_2O_5 , involving an increase of weight of 8.58 per cent., may be regarded as the only chemical reaction by which the purity of didymium preparations can be tested.

C. On the Atomic Weight of Lanthanum.—Pure lanthanum salts were prepared by heating a solution of anhydrous sulphate in six parts of water to 35°, and recrystallising six times in this way. The oxide finally obtained was treated with ammonium nitrate, and the same process was repeated several times with the part dissolved. After examining the spark and absorption spectrum of the last product, it was found to be perfectly pure lanthanum.

The atomic weight determinations gave the following numbers :--

Weight of oxide.	Sulphate.	P. c. of La ₂ O ₃ .	Atomic weight	
1·75933	3·05707	57 [.] 566	139:94	
0·92417	1·60589	57 [.] 549	139:83	
		Mean.	139.88	

The mean atomic weight of lanthanum is 139.88 (O = 16), which is the same that has been found by Marignac and Cleve. The round number 139 may therefore be considered to be the atomic weight of lanthanum.

Conclusion.

Whilst the above experiments were in progress, Nilson and Pettersson (*Berl. Ber.*, **13**, 1459) published a series of objections to the periodic system, one of which consisted in the statement, that insurmountable difficulties present themselves to the classification in the system of the numerous rare earth-elements.

The results obtained in the present communication prove that with the metals cerium, lanthanum, and didymium, this is not the case; but that, on the contrary, each of these metals is now found to occupy its own characteristic position in the system. This is seen from the following facts :--

Cerium, with the atomic weight Ce = 141.6 (Bührig) and the higher oxide CeO_2 , finds its place in the fourth group, 8th series (see the table below). It forms salts analogous to the salts of other elements belonging to the same group, *e.g.*, the sulphates:—

 $TiO_2.2SO_2$ anhydrous and $+ 3H_2O$. $ZrO_2.2SO_3$ anhydrous and $+ 4H_2O$. SnO_22SO_3 anhydrous and hydrated. $CeO_2.2SO_3 + 4H_2O$ and $7H_2O$. $ThO_2.2SO_3$ anhydrous and + 3, 4, $4\frac{1}{2}$, 9, and $9H_2O$.

The position of cerium in the fourth group is further confirmed by the existence of the compounds :---

 $CeF_4 + H_2O$ and $3KF_2CeF_4 + 2H_2O$.

Another series of corresponding compounds is the following :---

 TiO_2 ZrO_2 Type $RX_4 \begin{cases} CO_2 \\ CCl_4 \end{cases}$ SiO_2 SnO. CeO₂ PbO₂ ThO₂ SiCl₄ TiCl₄ ZrCl₄ SnCl₄ CeF₄ (PbCl₄) ThCl₄ Type RX₃ $\begin{cases} (C_2O_3) & -\\ C_2Cl_6 & Si_2Cl_6 \end{cases}$ Ti₂O₃ Ce₂O₃ Pb₂O₃ Ti_2Cl_6 Ce₂Cl₆

Didymium, with its atomic weight Di = 146.6, the peroxide, Di_2O_5 and its hydrate, $Di_2O_5 + 3H_2O$, finds its place in the fifth group, 8th series. Moreover, the elements vanadium and bismuth, belonging to

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the same group, form oxides, which give the peroxide reaction. The specific volume of didymium pentoxide is = 34.8, and from this number didymium finds a position in the fifth group, 8th series, if we arrange the specific volumes of the *higher* oxides according to the periodic system (Brauner and Watts, *Phil. Mag.* [5], **11**, 60).

The other corresponding compounds are the following, most of them being *lower* compounds :---

Type RX5	$\{ N_2O_5$	P_2O_5	V_2O_5	As_2O_5	$\rm Nb_2O_5$	$\mathrm{Sb}_2\mathrm{O}_5$	$\mathrm{Di}_{2}\mathrm{O}_{5}$	${\operatorname{Bi}}_{2}{\operatorname{O}}_{\mathfrak{z}}$
Type RX3	$\begin{cases} \mathbf{N_2O_3}\\ \mathbf{NCl_3}\\ \mathbf{NOCl} \end{cases}$	(P ₂ O ₃) PCl ₃	V2O3 VCl3 VOCl	As ₂ O ₃ AsCl ₃ AsOCl	$rac{\mathrm{Nb}_2\mathrm{O}_3}{\mathrm{NbCl}_3}$	Sb ₂ O ₃ SbCl ₃ SbOCl	Di ₂ O ₃ DiCl ₃ DiOCl	Bi ₂ O ₃ BiCl ₃ BiOCl

Lanthanum, La = 139, can be placed only in Group III, series 8, between barium, Ba = 137, and cerium, Ce = 141.6, as it forms only the oxide La₂O₃. Its compounds are in like manner analogous to the compounds of the other elements belonging to the same group.

	VIII.	$\substack{ (\mathrm{R_2H}) \\ (\mathrm{R_2O_8}), }$		Fe 56, Co 59, Ni 59, Cu 63.	Ru 104, Rh 104, Pd 106, Ag 108.	P. 152, P. 153, P. 154, P. 156.	Os 193, Ir 193, Pt 195, Au 107.	
	VII.	$^{ m RH}_{ m R_2O_7.}$	F 19	35 5 Cl Mn 55	9 80 Br 9 100	9 127 I	p 169 P P 190	219 P P 244
f Elements.	VI.	${ m RH}_2^{ m R}{ m G}_6^{ m a}.$	0	32 S Cr 52	Mo 96	126 ? Te Tb ? 148·8	167 ? W 184	214 ? U 240
The Periodic System of	Υ.	${ m RH_3} { m RO_5}.$	N 14	$\begin{smallmatrix}&31\\V&51\end{smallmatrix}$	75 As Nb 94	120 Sb Di 146·6	166 Er ? Ta 182	210 Bi ? 237
	IV.	${ m RH_4} { m R2} { m 0_4}.$	C 12	28 Si Ti 48	72 ? Zr 90	118 Sn Ce 141 6	9 162 P	207 Pb Th 234
	III.	R_2O_3 .	B 11	27 Al Sc 44	69 Ga Y 89	114 In La 139	159 ? Yb 173	204 TI ? 230
	11.	$-R_2O_2$	Be 9	24 Mg Ca 40	65 Zn Sr 87	112 Cd Ba 137	158 P P 172	200 Hg 225
	ľ	R20.	Li 7	23 Na K 39	(63 Cu) Rb 85	(108 Ag) Cs 133	ا 156 ب ^ا ا 170 با	(197 Au) ? 221
	Groups :	Series :	- 03	c0 4₁	ee	8-1	10	11 12

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With regard to the *better studied* of the other rare earths, it appears from the experiments of Cleve, Nilson, and Pettersson, that the same conclusion, as regards the positions in the system, may confidently be drawn. Thus, e.g., ytterbium, studied by Nilson, finds its position in the third group after lanthanum, the compounds of the two exhibiting a close analogy. The same follows from the experiments of Cleve or Nilson, as regards scandium, yttrium, thorium, and beryllium, the oxide of which, BeO, is a dyad rare earth (see Brauner, *Phil. Mag.* [5], **11**, 65).

Is it not natural to expect that the other rare earth-metals, which have as yet been but slightly investigated, will in like manner find in time their own positions, especially if attention be directed to the higher oxides and their corresponding compounds?