is little evidence that any of them form a thio-acid such as H_3AsS_3, except possibly $TiCl_4$.

The reducing action of hydrogen sulfide accounts for many of the differences encountered in comparing these reactions with similar ones in water, for example, with $TeCl_4$, $SeCl_4$, $TiCl_4$ and $FeCl_3$.

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THE POSITION OF THE ELEMENTS OF THE RARE EARTHS IN THE PERIODIC SYSTEM

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From the time when Mendeléeff enunciated the principles of the periodic system, many attempts have been made to include the elements of the rare earths in the classification. Previous to 1870 the rare earth elements were regarded as divalent, chiefly because of the strongly basic character of their oxides. Mendeléeff, finding difficulty in placing the then known elements of the rare earths in Group II of his system, contended that the metals are tervalent. He, therefore, assigned to yttrium, didymium and erbium positions in Group III and to cerium and lanthanum positions in Group IV. The work done on the rare earths since 1870 has confirmed Mendeléeff's view of the tervalency of these elements and at the same time it has increased their number from five to seventeen. There are included in this remarkable series of elements, scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, illinium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium. The order given above is that of ascending atomic number.

The element illinium (atomic number 61) has recently been recognized by Lapp, Rogers and Hopkins[1] by means of x-ray analysis of rare earth fractions, and thus a complete series of elements of atomic numbers 57 to 71 is made up. In order of atomic number lanthanum (57) follows barium (56) and hafnium (72) follows lutecium (71). Consequently it may be taken that the series of rare earths is complete.

Since the time of Mendeléeff many attempts have been made to arrange these elements either in Mendeléeff's system, in modifications of Mendeléeff's system or in geometrical systems by Brauner, R. J. Meyer, Retgers, Benedicks, Soddy, Stefan Meyer, Steele, Werner, Vogel, Rydberg, Aston, Bohr and others. The arrangements in Mendeléeff's system have failed because of an apparent lack of accommodation and because valencies have been assigned to certain of the elements which could not be sub-

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[1] Lapp, Rogers and Hopkins, *Phys. Rev.*, **25**, 106 (1925).

stantiated. The arrangements in modified forms of the Mendeléeff system have destroyed the symmetry, simplicity and usefulness of the periodic classification, and the arrangement in geometrical systems, whilst often useful, is not necessarily an arrangement in the periodic system.

What follows is an attempt to place these elements in the Mendeléeff system in its original form. Hence, without considering any of the previous attempts in detail, the present attempt may be put forward.

From a consideration of the whole of the elements from the point of view of the ease with which they may be separated from one another it becomes evident that they may be sub-divided into four groups thus: (I) elements which are readily separable from each other, that is, elements like sodium, silver, oxygen, chlorine, etc., (II) elements which are difficult to separate from each other; this group comprises the triads of Group VIII of Mendeléeff's system: iron, cobalt, nickel; ruthenium, rhodium, palladium; osmium, iridium, platinum; (III) elements which are very difficult to separate, this group includes the rare earths; and (IV) elements which, for practical purposes, are inseparable, the isotopes. Each of the elements of the first group occupies alone a place in the Mendeléeff system; the elements of the second group are placed three in a single place of the system and the elements of the fourth group, the isotopes, are placed many in a single space; thus there are at least eleven isotopes of lead, five of bismuth, four of zinc, seven of xenon and six of thorium. The isotopes of a given element have the same atomic number and properties and they are therefore all placed in the same place of the periodic system. Furthermore, this in no way destroys the Mendeléeff system nor impairs its symmetry and usefulness to the chemist.

The tervalency of the elements of the rare earths has been established beyond all doubt from (I) the specific heat of the metals, (II) the molecular weight of the anhydrous chlorides in absolute alcohol solution, (III) the molecular weight of the acetyl acetonates in carbon disulfide solution, (IV) the isomorphism of the octahydrates of the sulfates and (V) the equivalent conductance of aqueous solutions of the chlorides and sulfates. Consequently all of the seventeen elements yield an oxide M_2O_3 and a chloride MCl_3.

In addition, cerium, neodymium, praseodymium and terbium yield a dioxide MO_2, whilst europium and samarium yield a dichloride MCl_2. The two elements of smallest atomic number, scandium and yttrium, find places in the periodic system without difficulty; they fall naturally following the order of atomic numbers into Group III, Series 4 and 6, respectively. This leaves fifteen elements which form a complete series, lanthanum (57)—lutecium (71), to be placed between barium (56) and hafnium (72). Since these elements are basic, show no marked acidic properties and are all tervalent, they must all be accommodated in the six places of the periodic system, in Groups III and IV, Series 8, 9 and 10. Here it is that the difficulty of the problem becomes apparent; any one of these elements with the exception of cerium might from its chemical properties go into Group III, Series 8, and cerium would naturally go into Group IV, Series 8.

It has been shown by Weiss,[2] from measurements of the ionic magnetic moment, made by Cabrera and Stefan Meyer with the octahydrates of the sulfates of these elements, that when the ionic magnetic moments are plotted as abscissas against the number of electrons in the cations, a double curve is obtained (Fig. 1) which divides these elements into two groups, (I) lanthanum, cerium, neodymium, praseodymium and samarium, (II) europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium.

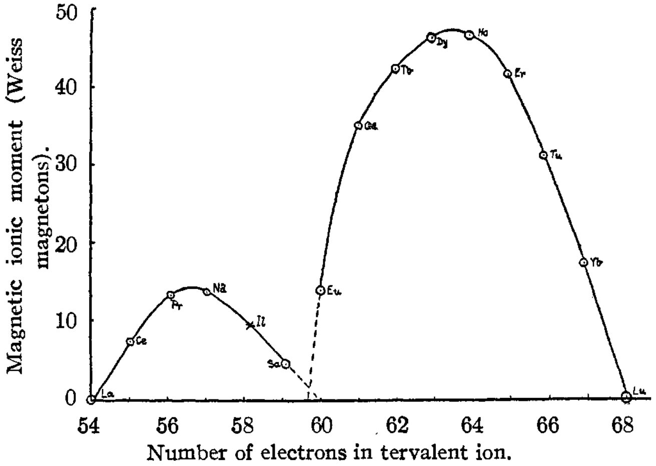

Fig. 1.

The element illinium (61) must be taken to come between neodymium and samarium. These two groups are practically identical with the two groups which may be made from the order of the solubility of the sulfates of the rare earths in saturated solutions of alkali sulfates; (I) practically insoluble, lanthanum, cerium, praseodymium, neodymium and samarium; (II) europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium; the first three members of the second group are sparingly soluble and the remainder are more soluble than in water. The first three elements of the second group, that is, the terbium earths, fall on the ascending branch of the second half of Weiss' curve and the others on the descending branch.

From the above facts and the general chemical characteristics of the

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[2] *Journ. de Phys.*, 1925, Bull., 218, 86 S.

rare earth elements it appears that they may be placed in the periodic system as shown below.

Table I

	II A	II B	III A	III B	IV A	IV B	V A	V B
4	Ca		Sc		Ti		V	
5		Zn		Ga		Ge		As
6	Sr		Yt		Zr		Nb	
7		Cd		In		Sn		Sb
8	Ba		La		Ce, Pr, Nd, Il		...	
9		...		Sa, Eu, Gd		Tb		...
10	...		Dy, Ho, Er, Tu, Yb, Lu		Hf		Ta	

Leaving samarium out of account for the moment, the elements on the first half of Weiss' curve (the cerium earths) fall into Series 8; those on the rising branch of the second half of the curve (the terbium earths) fall into Series 9 and those on the falling branch of the second half of the curve fall into Series 10 (yttrium earths). Samarium sulfate may be equally well regarded as the most soluble of the insoluble cerium earth sulfates in saturated alkali sulfate solutions or as the least soluble of the sparingly soluble sulfates. That is, the solubility series given above may be written (I) insoluble: lanthanum, cerium, neodymium, praseodymium; (II) sparingly soluble: samarium, europium, gadolinium, terbium; (III) soluble: dysprosium, holmium, erbium, thulium, ytterbium, lutecium. The solubility sub-division is now the same as that in the periodic system.

Lanthanum is put in Group III A, Series 8, because its oxide is the strongest base of the rare earths and naturally follows barium; cerium, praseodymium and neodymium are placed in order of atomic number in Group IV A, Series 8, since they all form dioxides and sesquioxides, as also do titanium and zirconium, which precede them in Group IV A. The new element illinium must also be placed there because its ionic magnetic moment will undoubtedly fall between the moments of neodymium and samarium on the Weiss curve; samarium, europium and gadolinium are placed in Group III B, Series 9; of these europium and samarium form dichlorides, a type of compound also formed by the other members of Group III B, gallium, indium and thallium. A dichloride is unknown in the case of gadolinium but in the present state of our knowledge of gadolinium compounds this is no reason for stating that such a compound cannot exist; further, gadolinium is very like europium and samarium in its general behavior, so much so that gadolinium and samarium were separated together from Mosander's didymium by Delafontaine,[3] and for a time regarded as a single element, decipium. The

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[3] Delafontaine, *Compt. rend.*, **87**, 559, 634 (1878).

six elements dysprosium, holmium, erbium, thulium, ytterbium and lutecium come in order of atomic number into Group III A, Series 10. These metals are typically tervalent and each of them could be placed in this position. If the reasons given above be accepted, these six elements must all go into this position. Between lutecium (71) and tantalum (73) in Series 10, there is still a vacant place in group IV A into which hafnium (72) naturally goes. The scheme presented places the whole of the elements of the rare earth group into Mendeléeff's periodic system without destroying its symmetry or impairing its utility in the slightest. It is difficult to submit the scheme to a rigorous test because many essential data are lacking; but a broad line taken through the existing chemical and physical data confirms, in general, the present arrangement.

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SIMPLE BIMETALLIC ELECTRODE SYSTEMS FOR POTENTIOMETRIC TITRATIONS. I. THE APPLICATION OF THE PLATINUM-GOLD AMALGAM SYSTEM TO CERTAIN OXIDATION-REDUCTION TITRATIONS

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Introduction

Hostetter and Roberts[1] suggested the possibility of substituting a palladium wire for the calomel half-cell that is generally used as a reference electrode in potentiometric titrations. Willard and Fenwick[2] have studied a large number of possible systems that consist of two dissimilar metallic electrodes. They did not, however, study amalgamated electrodes.

This investigation grew out of a study of certain platinum electrodes that were unintentionally "poisoned" with mercury. These electrodes behaved temporarily like mercury electrodes. It has not thus far been found possible to prepare amalgamated platinum electrodes that serve over long periods of time as mercury electrodes.

Amalgamated gold electrodes were found to behave like calomel electrodes in solutions that contained chloride and like mercurous sulfate electrodes in solutions that contained sulfate. During the course of most oxidation-reduction titrations the concentration of chloride or sulfate varies. Nevertheless, an amalgamated gold electrode will serve as a satisfactory reference electrode for such titrations. The reducing action of the minute quantity of mercury or gold that is in contact with

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[1] Hostetter and Roberts, THIS JOURNAL, **41**, 1343 (1919).

[2] Willard and Fenwick, *ibid.*, **44**, 2504 (1922).