

One of the most puzzling questions concerning the rare earth group is its relationship to the periodic table. Many suggestions have been made for the placing of this group in order to show its relationship to the rest of the elements. Figure 1 shows a common method

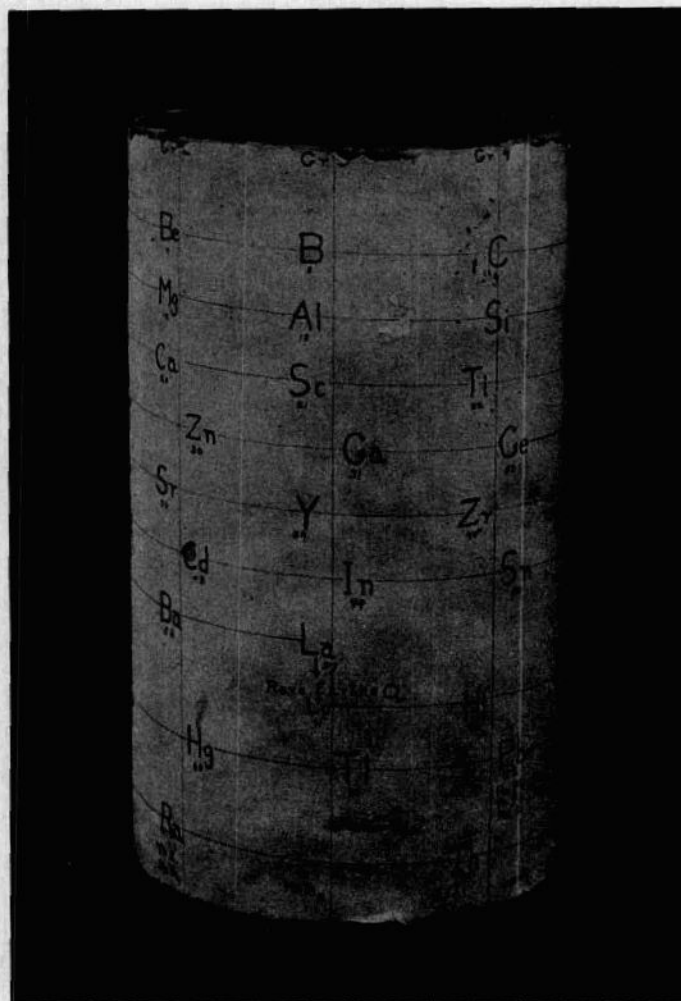


FIG. 2. Periodic table in cylindrical form.

of locating this group on a flat surface arrangement of the table. It emphasizes the fact that the rare earth elements have similar properties with a characteristic valence of three. Each could with perfect propriety be placed in the third group between barium (Group II) and

hafnium (Group IV). Rather than attempt to crowd the 15 elements into this one space, many authors prefer to indicate that the entire group belongs here and then append a supplementary table showing each individual element in its proper sequence.

Figure 2 shows a similar plan applied to a cylindrical arrangement of the table. In Figure 3 there is an interesting helical plan, with all the elements of the rare earth group crowded into the one space by means of an accordion-like extension. This gives an unusually appropriate setting for the group. Figure 4 shows the sequence of the

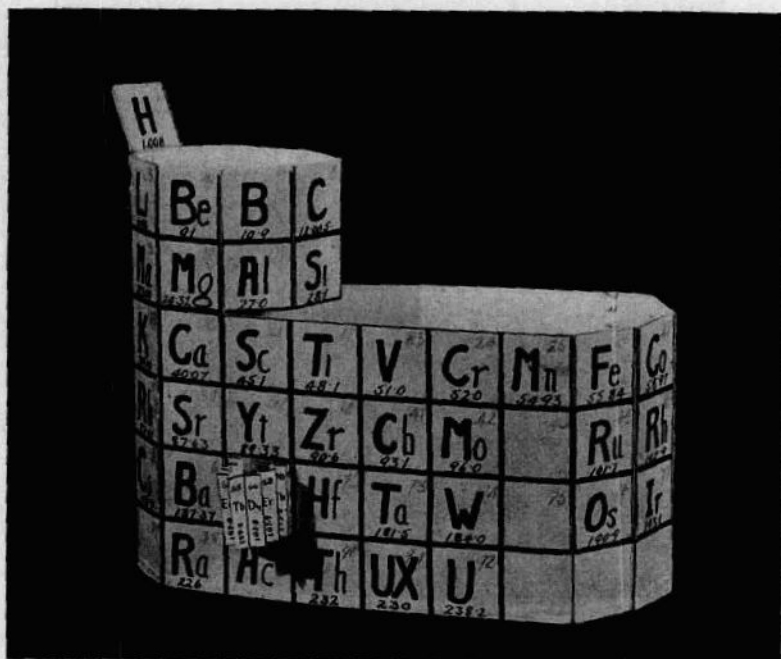


FIG. 3. Periodic table in tower form, after M. Courtines.

elements arranged spirally around a globe. Hydrogen is at the north pole and the short series are conveniently arranged near the pole. As the sequence approaches the equator the longer series fall into position normally. The rare earth group fills the equatorial belt without crowding. While the space adjustments in this arrangement are clever, it brings the individual members of the group into quite unnatural positions with respect to other elements. For example, this arrangement makes it necessary to interpose some members of the rare earth group between such closely related elements as zirconium and hafnium, columbium and tantalum, or molybdenum and tungsten, while other rare earths fall into unnatural positions with respect to the platinum metals

and the alkali group. Similar objections can be raised to most of the arrangements in which an attempt is made to give each member of the rare earth group a separate space in the periodic table.

As the scientific interest in the rare earth group increases there is certain to be a greatly increased importance attached to the amount

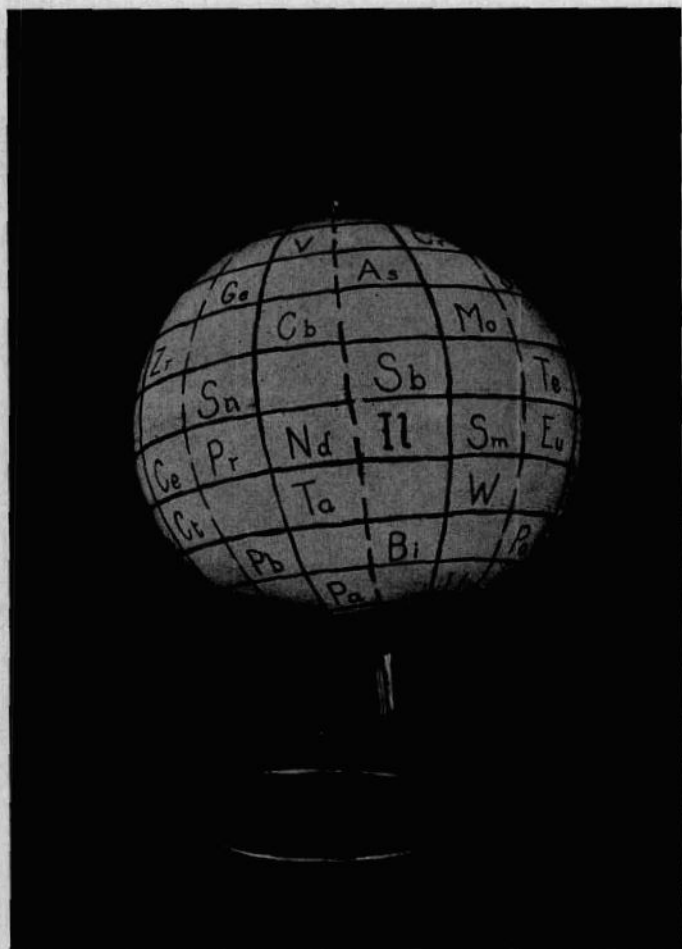


FIG. 4. Periodic table in spherical form.

of material available for the study of each member of the group. Accordingly there is increasing interest not only in the deposits of rare earth minerals themselves but also in the relative abundance of each individual element. Table 1 gives a tabulation which is based on various estimates. The figures in the third vertical column show the average per cent of each individual element in the rare earth content of

all available rare earth ores¹. It is interesting to note that cerium, the most abundant member, makes up nearly one-third of the entire group, while illinium, the rarest member, is not more abundant than 0.02 of one per cent. When these values are plotted against atomic numbers as in Figure 5 we see graphically that the even numbered members of the group are always more abundant than the neighboring odd numbered members. This interesting fact suggests that there must be some reason connected with the structure of these atoms which

TABLE 1.—Abundance of the rare earths

Atomic number	Symbol	Per cent of the rare earth group	Per cent in the earth's crust
57.....	La	7	0.00007
58.....	Ce	31	0.00031
59.....	Pr	5	0.00005
60.....	Nd	18	0.00018
61.....	II	0.02	0.000002
62.....	Sm	7	0.00007
63.....	Fu	0.2	0.00002
64.....	Gd	7	0.00007
65.....	Tb	1	0.00001
66.....	Dy	7	0.00007
67.....	Ho	1.2	0.000012
68.....	Er	6	0.00006
69.....	Tm	1	0.00001
70.....	Yb	7	0.00007
71.....	Lu	1.5	0.000015
		99.92	

gives greater stability to the groupings with an even number of electrons. At present our information does not furnish a satisfactory explanation.

The last vertical column in Table 1 shows the fraction of the earth's crust that is composed of the rare earth group. These figures are based on Dr. H. S. Washington's statement that the entire group comprises about 0.001 per cent of the earth's crust. While the percentage of the most abundant members of the group is extremely small it is to be noted that cerium is more common than cadmium, tin, mercury, antimony, molybdenum, silver, tungsten, bismuth, gold or platinum. Likewise the least abundant member of the group, illinium,

¹ These figures are furnished by Goldschmidt and Thomassen, *Videnskapsel-skalets skrifter I Matemat-Naturv. Klasse, Kristiana 1924, No. 5, p. 49*. The estimate for illinium is based on the statement of Dr. G. R. Sherwood that illinium in monazite is approximately one-tenth as abundant as europium.

which makes up only about two ten-millionths of one per cent of the earth's crust, is still presumably a thousand times more abundant than radium, whose commercial importance is considerable. Therefore it seems safe to conclude that if any single member of the rare earth group is shown to possess striking individual properties of value, the scarcity of the element will not be an insurmountable obstacle in the pathway of its commercial development.

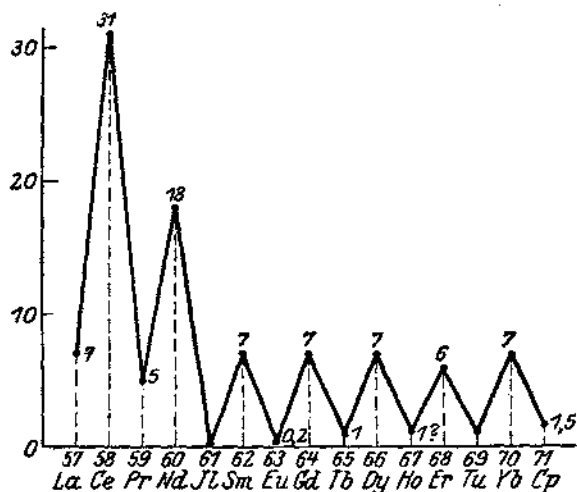


Fig. 5. Abundance of the rare earths against atomic numbers.

A study of the atomic structure of the members of the rare earth group (Table 2), shows the slight differences between succeeding members. For comparison there are also shown the structures of cesium and barium immediately preceding the rare earths as well as hafnium and tantalum, the first elements following the group. It is to be noted that the valence of the rare earths remains essentially constant and that the only structural differences come from the addition of successive electrons in the 4_f shell. With such strikingly similar structures, it is natural to expect that these atoms will have similar properties and that their separations from one another will be extremely difficult.

Formerly the valence of the rare earth group was by definitions limited to three, and any member like cerium which showed a valence of four was eliminated as though it were an intruder. While the rare earths are still to be regarded as characteristically trivalent in nature, recent studies have shown that both higher and lower valences exist.

Figure 6 shows these anomalous valences. Quadrivalent compounds of cerium are well known and important. Praseodymium is also quadrivalent, possibly occasionally pentavalent. Quadrivalent compounds of terbium have recently been shown to exist. Since cerium, praseodymium and terbium may be oxidized, it might be logical to expect that dysprosium would also show a higher valence, although no such compounds have yet been reported.

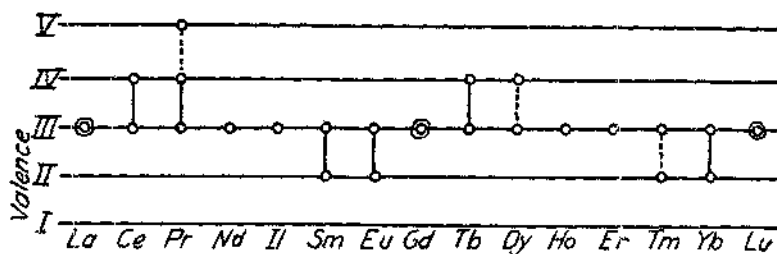


FIG. 6. Valence of the rare earths.

TABLE 2.—Atomic structures of the elements

Atomic number	K			L			M			N				O					P	
	1 ₁	2 ₁	2 ₂	3 ₁	3 ₂	3 ₃	4 ₁	4 ₂	4 ₃	4 ₄	5 ₁	5 ₂	5 ₃	5 ₄	5 ₅	6 ₁	6 ₂			
Cs 55.....	2	2	6	2	6	10	2	6	10	0	2	6	0	0	0	1	...			
Ba 56.....	2	2	6	2	6	10	2	6	10	0	2	6	0	0	0	2	...			
La 57.....	2	2	6	2	6	10	2	6	10	0	2	6	1	0	0	2	...			
Ce 58.....	2	2	6	2	6	10	2	6	10	1	2	6	1	0	0	2	...			
Pr 59.....	2	2	6	2	6	10	2	6	10	2	2	6	1	0	0	2	...			
Nd 60.....	2	2	6	2	6	10	2	6	10	3	2	6	1	0	0	2	...			
Il 61.....	2	2	6	2	6	10	2	6	10	4	2	6	1	0	0	2	...			
Sa 62.....	2	2	6	2	6	10	2	6	10	5	2	6	1	0	0	2	...			
Eu 63.....	2	2	6	2	6	10	2	6	10	6	2	6	1	0	0	2	...			
Gd 64.....	2	2	6	2	6	10	2	6	10	7	2	6	1	0	0	2	...			
Tb 65.....	2	2	6	2	6	10	2	6	10	8	2	6	1	0	0	2	...			
Ds 66.....	2	2	6	2	6	10	2	6	10	9	2	6	1	0	0	2	...			
Ho 67.....	2	2	6	2	6	10	2	6	10	10	2	6	1	0	0	2	...			
Er 68.....	2	2	6	2	6	10	2	6	10	11	2	6	1	0	0	2	...			
Tu 69.....	2	2	6	2	6	10	2	6	10	12	2	6	1	0	0	2	...			
Yb 70.....	2	2	6	2	6	10	2	6	10	13	2	6	1	0	0	2	...			
Lu 71.....	2	2	6	2	6	10	2	6	10	14	2	6	1	0	0	2	...			
Hf 72.....	2	2	6	2	6	10	2	6	10	14	2	6	2	0	0	2	...			
Ta 73.....	2	2	6	2	6	10	2	6	10	14	2	6	3	0	0	2	...			

In similar manner samarium, europium and ytterbium may be induced to show a valence of two by electrolytic reduction. Since terbium

is the seventh element from cerium and ytterbium is the seventh element after europium, it might be assumed that these anomalous valences occur at uniform distances. If this reasoning is correct, then thullium, the seventh element after samarium should form bivalent compounds. While none have yet been prepared, efforts are being made to find the conditions under which thullium salts will be reduced. Here again is a peculiar situation whose explanation requires an extended study of atomic structures.

These irregular valences are becoming useful in the difficult task of separation. Cerium has long been separated effectively from its neighbors in a single step consisting of boiling the oxidized solution. Ceric salts are easily hydrolyzed and precipitated as a basic salt. Similar methods are being sought for the separation of praseodymium, terbium and possibly dysprosium.

When the rare earth elements become bivalent the solubilities of their salts are like those of barium. Accordingly when europium and ytterbium salts are subjected to cathodic reduction in the presence of the sulfate ion, difficultly soluble EuSO_4 and YbSO_4 are precipitated. These separations from simple mixtures are nearly quantitative and they mark a distinct advance in rare earth chemistry, because both of these elements have up to the present been almost impossible to isolate. If by modifying the conditions we could devise a method for the isolation of samarium and thullium the work of the rare earth chemist would be vastly simplified.

All metals of the rare earth group are fairly active, but their hydroxides do not furnish a high concentration of hydroxyl ion because of their insolubility. There are considerable differences in the basicity of the various members of the group. Table 3 shows an attempt to reduce these values to a ratio by using the basicity of $\text{Y}(\text{OH})_3$ as unity. It is to be noted that lanthanum is much the most basic member of the group and it is safe to say that $\text{La}(\text{OH})_3$ is the strongest trivalent base that we know. It is also important to notice that the ratios between these values are relatively large, at least in some cases. For example lanthanum is 11 times as basic as praseodymium while neodymium is nearly 6 times as basic as samarium.

TABLE 3

Atomic number	57	59	60	62	64	39	66
Element	La	Pr	Nd	Sm	Gd	Y	Dy
Basicity ratio.....	1300	80	47	8	3.4	1	0.5

Some of our most useful methods of separation are based upon these differences in basicity. As a consequence the order of decreasing basicity becomes a matter of great importance. In Table 4 we have a tabulation of the order as it is reported by various workers, using

various methods and conditions. It is evident that there is little question concerning the order of decreasing basicity in Zones 1 and 3, but in the center the order of basicity is in much doubt. This situation undoubtedly results from the fact that in the center of the group there are less differences in basicity than at either end. Because of the importance of accurate information upon the order of basicity we have undertaken to measure these values for the entire group, using a common method throughout. The hydrolysis of the rare earth nitrite was selected as a suitable method because conditions can be accurately controlled and the method is easily applied to all parts of the group. As

TABLE 4

	A	B	C	D	E	F	G
Zone 1	La	La		La	La	Dy La	La
	+++	+++		+++			
	Ce	Ce		Ce			
	Pr	Pr		Pr	Pr	Pr	Pr
	Nd	Nd		Nd	Nd	Nd	Nd
	Y			Y	Y	Y	
Zone 2		Eu					
		Gd	Gd		Gd		
	Sm	Sm	Sm	Sm	Sm	Sm	Sm
	Eu			Eu			
	Gd		Gd			Gd	
Zone 3	Tb	Tb	Tb	Tb	Tb	Tb	Tb
	Dy	Dy		Dy	Dy		Dy
	Ho	Ho		Y			
	Er	Er		Er	Er		
	Tm	Tm		Tm			
	Yb	Yb		Yb			
	Lu	Lu					
	Sc	Sc					
	+++						
	Ce						

usually applied this method consists in adding NaNO_2 to a neutral solution of the rare earth nitrates and boiling until those elements which are the least basic are precipitated while the elements of greater basicity remain in solution. By filtering off the precipitate there is accomplished a partial separation of the mixture of salts in accordance with the relative basicity of the elements present. We found that the differences in basicity between illinium, samarium, europium and gadolinium, the elements in zone 2, were so slight that the usual methods of procedure were not adequate. Consequently there was devised a method of fractionation by which these slight differences were magnified. Figure 7 shows diagrammatically the method used. The solid arrows indi-

cate the way in which the precipitates were combined and the broken arrows the path of the mother liquor. In this way slight differences in basicity were intensified and actual separations accomplished. As a result of this work it has been established that the order of decreasing basicity throughout the rare earth group is exactly the order of increasing atomic number. If yttrium (No. 39) is included in the rare earth group it would form an exception to this statement since its basicity falls between illinium (No. 61) and samarium (No. 62).

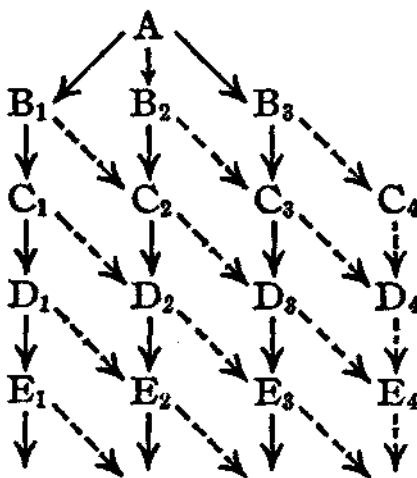


FIG. 7. Plan showing steps in the concentration of the rare earths by intensive basicity method.

The concentration of illinium by methods of fractional crystallization is well nigh impossible because this extremely rare element is always associated with other elements which are vastly more abundant and whose salts differ but slightly in solubility. By applying this new method of intensifying the differences in basicity we have greatly speeded up the concentration of illinium. In Figure 8 the per cent of illinium is plotted against the number of fractionations by the two methods. It is seen that 25 basicity fractionations effect about twice as great a concentration as is accomplished by 2000 fractionations of the double magnesium nitrates.

The metals of the rare earth group are interesting from their magnetic behaviors. When carefully measured it is found that their magnetic susceptibilities show greater variation than can be detected with regard to any other property. The magnetic susceptibility of mixtures is strictly additive. As a consequence in simple mixtures this property furnishes the most accurate means of analysis that we have.

An accuracy of 0.1 per cent has been claimed for mixtures of the compounds of two elements. Figure 9 shows the coefficient of magnetization plotted against the atomic numbers.

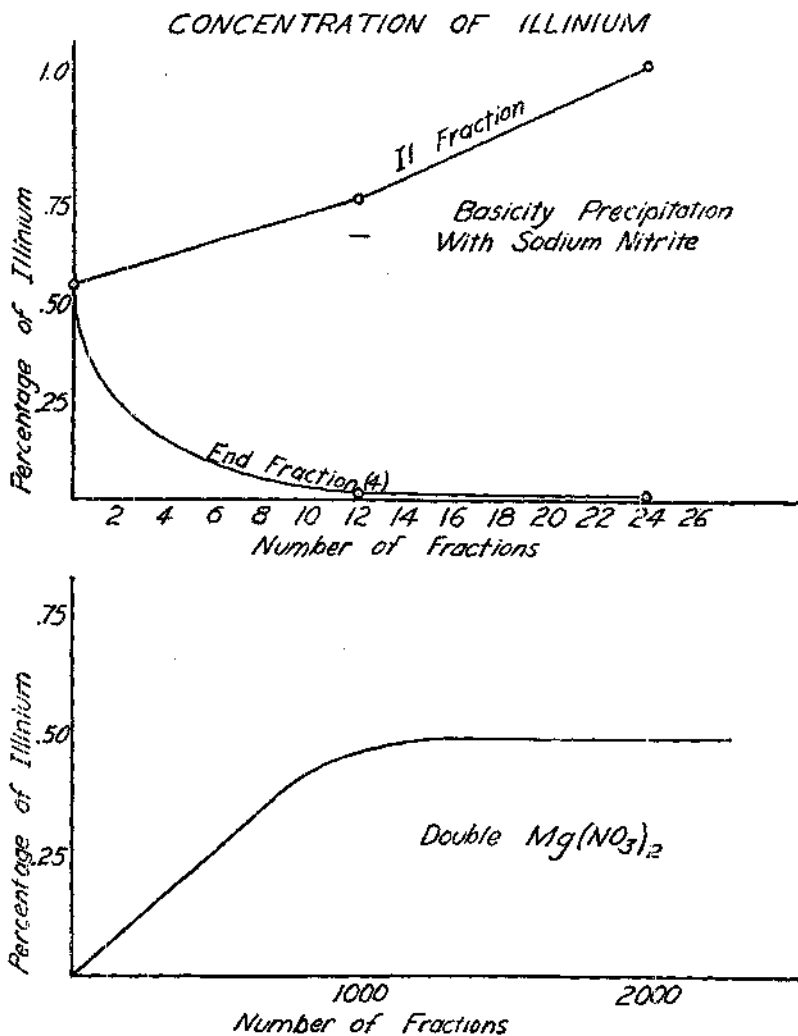


FIG. 8. Fractional crystallization increases the illinium content rapidly at first, but it soon becomes ineffective (lower curve). The upper curve shows that 24 fractionations by intensive basicity precipitation double the illinium content.

A subject of increasing interest in the rare earth field has to do with their utilization. Extensive uses are now made of mixtures of

this group and great interest has lately developed in regard to the commercial applications of some of the more abundant members of the group. It is obvious that uses for the pure forms of the less abundant members of the group will be much more difficult to produce. One of the most interesting developments of recent months has been the utilization of the octohydrate of gadolinium sulfate for the production of extremely low temperatures. This work is noteworthy because of the near approach to the absolute zero, because it uses an entirely new principle in achieving this end, and because it uses a single member of the rare earth group which is relatively rare in a high state of purity for a specific purpose.

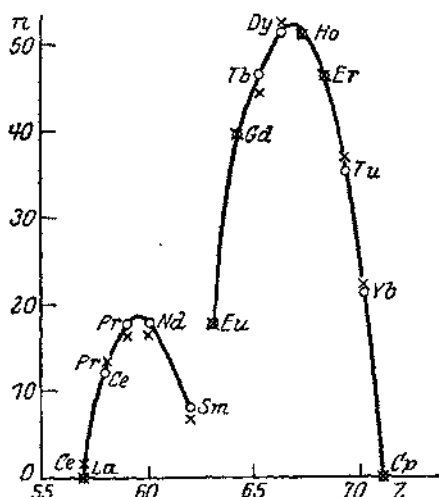


FIG. 9. Magnetic susceptibility plotted against atomic numbers.

When $Gd_2(SO_4)_3 \cdot 8H_2O$ is placed in a magnetic field it transforms some of the magnetic energy into heat and becomes warm. Under ordinary conditions the temperature change is not great. If however the octohydrate is first cooled to the temperature of boiling helium and a magnetic field of 20,000 gauss is used, the thermal transition is relatively large. Figure 10 shows an apparatus for this work. The gadolinium material is placed in a tube suspended from a balance. This tube is placed in a container which is filled with gaseous helium at low pressure, and surrounded by liquid helium. The system is isolated from external heat by two concentrically placed Dewar tubes. When a powerful field is applied to the rare earth material it becomes warm and imparts part of its heat to the helium gas. If this is now pumped

off and the magnetic field removed, the resulting temperature must be lower than the initial temperature. This method has yielded temperatures within 0.18° C. of the absolute zero, the nearest approach to that mythical point yet obtained. It is interesting to speculate as to what results might be obtained if alternate magnetizations and demagnetizations were applied in cycle fashion.

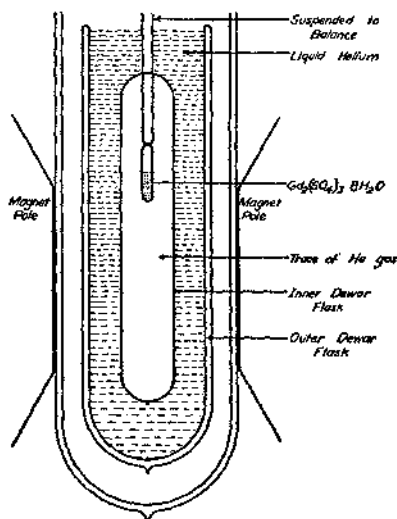


FIG. 10. Diagram of the apparatus used in the production of extremely low temperatures by the use of rare earth salts.

Similar Results have been obtained with the use of $Ce_2(SO_4)_3 \cdot 8H_2O$. It is quite probable that other members of the group may show similar properties. We should like to know what peculiarities of atomic and molecular structures make this behavior possible. We would also like to learn whether the pure salts are needed for the display of this phenomenon or whether a mixture of rare earth salts would be equally effective.