Bodenstein,[2] Ramsperger,[3] and Sutton and Mayer.[4] For many purposes the valve described here is more desirable than any of these because it combines ease of construction with ease of operation.

(2) Bodenstein, *Z. physik. Chem.*, **B7**, 387 (1930).

(3) Ramsperger, *Rev. Sci. Inst.*, **2**, 738 (1931).

(4) Sutton and Mayer, *J. Chem. Phys.*, **3**, 20 (1935).

CONTRIBUTION FROM THE
LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
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Periodic Classification of the Rare Earths

BY HERMAN YAGODA

Brauner's[1] distribution of the rare earths in the periodic system, Fig. 1, has the disadvantage of placing several of the members into groups where the other elements are chiefly of an amphoteric or acidic nature. Pearce[2] has criticized the classification on the ground that the periodicities observed by Brauner are not connected with the rest of the system. The tendency of these elements to form stable trivalent compounds seems to mask the underlying fact that the properties, of their other valence states, are a periodic function of the atomic number.

Groups	I	II	III	IV	V	VI	VII
8th series	Cs 55	**Ba** 56	**La** 57	**Ce** 58	**Pr** 59	**Nd** 60	**Il** 61
9th series	**Sm** 62	**Eu** 63	**Gd** 64	**Tb** 65	**Dy** 66	**Ho** 67	**Er** 68
10th series	**Tm** 69	**Yb** 70	**Lu** 71	Hf 72	Ta 73	W 74	Re 75

Fig. 1.

Thus, cerium and terbium are located in the fourth group in agreement with the tetravalence exhibited in their higher oxides CeO_2 and Tb_4O_7. Praseodymium forms two higher oxides, Pr_6O_{11} and PrO_2 in which, according to Prandtl,[3] the metal has a valence of five, in harmony with the position of the element in the fifth group. Again, of all the rare earths only europium[4] and ytterbium[5] form difficultly soluble bivalent sulfates and both elements are allocated to the second group along with the alkaline earths. Evidence for the division of the metals into three series is seen in the variation of the molecular volume of the oxides, Fig. 2, the curve[5a] showing distinct maxima at both samarium and thulium, the initial members of the ninth and tenth series.

If the classification has real significance it should be possible to predict the properties of the rare earth ions in those valency states corresponding with their position in the groups. Thus, Sm^{+} and Tm^{+} should form difficultly soluble chloroplatinates; Ce^{++++} and Tb^{++++} phosphates, that are insoluble in mineral acids,[5b] in the same way that Eu^{++} and Yb^{++} are now known to form insoluble sulfates.

Molecular volume of the rare earth oxides (R_2O_3).

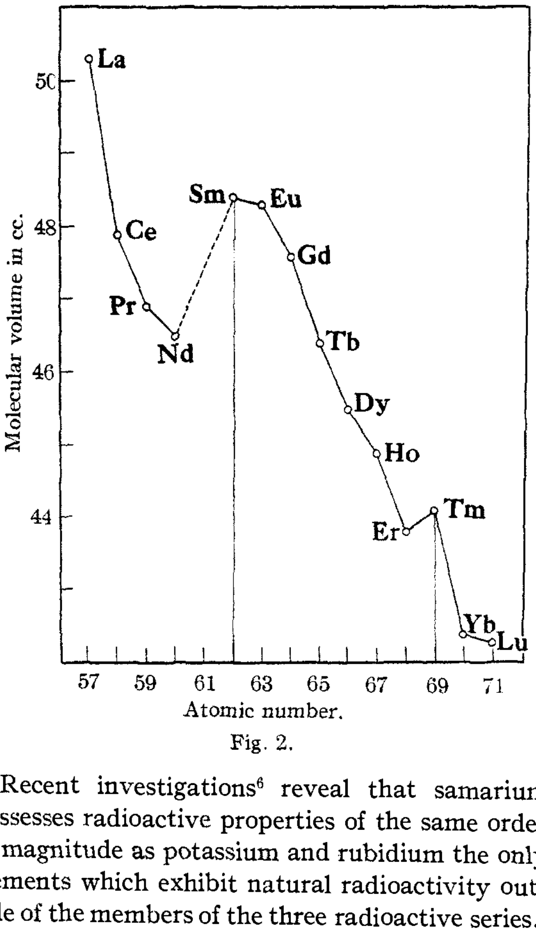

Fig. 2.

Recent investigations[6] reveal that samarium possesses radioactive properties of the same order of magnitude as potassium and rubidium the only elements which exhibit natural radioactivity outside of the members of the three radioactive series.[7] If Brauner's classification of the rare earths is correct, the radioactivity of samarium would seem to indicate that the tendency for nuclear instability in the case of atoms of low atomic weight is centered in the first periodic group. Von Hevesy examined all the members of the rare earths with

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(1) B. Brauner and E. Švagr, *Collection Czechoslov. Chem. Comm.*, **4**, 49, 244 (1932).

(2) D. W. Pearce, *Chem. Rev.*, **16**, 135 (1935).

(3) W. Prandtl and K. Huttner, *Z. anorg. Chem.*, **149**, 235 (1925).

(4) L. F. Yntema, THIS JOURNAL, **52**, 2782 (1930); P. W. Selwood, *ibid.*, **57**, 1145 (1935).

(5) R. W. Ball and L. F. Yntema, *ibid.*, **52**, 4264 (1930); J. K. Marsh, *J. Chem. Soc.*, 1972 (1934); W. Prandtl, *Z. anorg. Chem.*, **209**, 13 (1932).

(5a) The molecular volumes were derived from density measurements recorded by von Hevesy in his "Seltenen Erden von Standpunkte des Atombaues," Berlin, 1927, *p.* **53**. The molecular weights were computed from the International **Atomic Weights of** 1935.

(5b) Cerium can be separated electrolytically from nitric acid solutions as ceric phosphate [J. W. Neckers, THIS JOURNAL, **50**, 955 (1928)].

(6) G. von Hevesy and M. Pahl, *Nature*, **130**, 846 (1932); M. Curie and F. Joliot, *Compt. rend.*, **198**, 360 (1934).

(7) "Radiation from Radioactive Substances," Rutherford, Chadwick and Ellis, Cambridge, 1930, p. 541.

the exception of illinium and thulium and concluded that samarium was the only one of the group whose radioactivity persisted after purification.[8] As thulium is classified in the first group, it also may possess radioactive properties of a magnitude comparable with that of samarium. Hence, a study of the radioactivity of thulium preparations is well worth investigating.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY,
NEW YORK CITY

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[8] G. von Hevesy and M. Pahl, *Nature*, **131**, 434 (1933); *ibid.*, *Z. physik. Chem.*, **A169**, 147 (1934).

COMMUNICATIONS TO THE EDITOR

ATTEMPTED PREPARATION OF VANILLOYLFORMIC ACID

Sir:

In an attempt to repeat the oxidation of apocyanin to vanilloylformic acid with nitrobenzene in alkaline solution as described by H. O. Mottern [THIS JOURNAL, **56**, 2107 (1934)] no action whatever was observable under the conditions described by the author. Nitrobenzene was recovered quantitatively from the reaction mixture and neither aniline nor azobenzene was detectable by qualitative means.

Difficulty was also experienced in repeating the author's description of the preparation of apocyanin by means of the Fries reaction. The aluminum chloride double compound with guaiacol acetate is quite solid at the temperatures described (0–5°). Before a third of the required amount of aluminum chloride has been added, the mass is so hard as to be impenetrable to a stirring rod, making it impossible to incorporate the balance. The apocyanin used was prepared by the method for low temperature Fries isomerizations described by Baltzly and Bass [*ibid.*, **55**, 4293 (1933)] which differs from the authors in the use of nitrobenzene as a solvent.

FARMINGDALE, L. I. W. E. BARCH

RECEIVED MARCH 12, 1935

NOTE BY THE EDITOR

After the receipt of this Communication a repetition of the oxidation of apocyanin to vanilloylformic acid with nitrobenzene in alkaline solution as described by H. O. Mottern was attempted by a member of the Editorial Board and independently by the Director of Research of a firm manufacturing vanillin on a large scale. Both were unsuccessful; their concordant conclusion is expressed by the latter's statement: "The synthesis of vanillin cannot be carried out following the disclosures of the paper published in THIS JOURNAL, 1934, page 2107."

OCTOBER 10, 1935 ARTHUR B. LAMB, *Editor*

THERMAL DECOMPOSITION OF $CrO_4 \cdot 3NH_3$

Sir:

Some unusual observations recently made in this Laboratory, and which we hope to study in greater detail, should prove of considerable general interest. While attempting the preparation of the tetroxide of chromium, CrO_4, by deammonating $CrO_4 \cdot 3NH_3$ (I) [made according to Riesenfeld, *Ber.*, **38**, 4070 (1905)], the following was noted. (1) Compound (I) loses practically no ammonia upon standing for four months over concentrated sulfuric acid *in vacuo* and at room temperature. (2) If the pressure in a tube containing some (I) is reduced to less than 1 mm. and the tube, still attached to the vacuum line, is immersed in a bath whose temperature may be controlled, a vigorous reaction ensues at $120 \pm 10°$. Particles of (I) become incandescent and dart about in spectacular fashion. The action is reminiscent of the thermal decomposition of ammonium dichromate and also of certain models that have been constructed to portray molecular motion in gases. (3) The solid residue of the above mentioned decomposition of (I) is composed of microscopic, elongated square prisms of black $CrO_3 \cdot NH_3$ (II). Analysis of (II) for ammonia was made by distilling into standard acid and for chromium by forming lead chromate. The re-