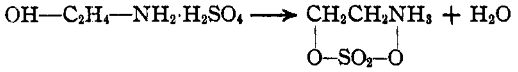
products, with a somewhat higher formation of tarry products.

UNIVERSITY, VIRGINIA RECEIVED AUGUST 9, 1935

The Preparation of Ethylene Imine from Monoethanolamine

BY HENRY WENKER

In view of the readiness with which compounds containing a β-aminoethyl group can be obtained from ethylene imine, a method may be of interest by which 80 g. of this base can be prepared conveniently in the laboratory in one day from inexpensive commercial material. The process consists, firstly, in preparing β-aminoethyl sulfuric acid[1,2] by thermic dehydration of monoethanolamine acid sulfate according to the equation



$$OH—C_2H_4—NH_2 \cdot H_2SO_4 \longrightarrow \underset{O—SO_2—O}{CH_2CH_2NH_3} + H_2O$$

secondly, in distilling this compound with alkali.

An equimolar mixture of monoethanolamine and sulfuric acid is heated rapidly over a free flame until, at a temperature of about 250°, charring begins, necessitating the end of the operation. Only 75% of the mole of water indicated by the formula can be expelled since, irrespective of the rate of heating, the product begins to turn brown rapidly when this degree of dehydration has been reached. As much as 10 moles—610 g., of monoethanolamine and 1020 g. of 96% sulfuric acid—may be used for one operation. On cooling, the thin, clear brown liquid solidifies to a hard, white crystalline cake. It is ground in a mortar with one-half its weight of 60% ethanol, filtered by suction and washed with ethanol; yield, 100 g. per mole of starting material or 71%. It is convenient to dilute both components with their own weight of water previous to mixing, and then to boil off the excess of water.

282 grams of β-aminoethyl sulfuric acid is distilled with 880 g. of 40% caustic soda solution from a 3000-cc. flask. Shortly before the boiling point is reached, a reaction occurs which keeps the mixture boiling for several minutes; during this time, heating must be discontinued. When the reaction ceases, heating is resumed and a total of 240 cc. is distilled over. One distillation requires about forty-five minutes. On addition of potassium hydroxide to the distillate, 65 cc. of base separates; this is dried repeatedly with potassium hydroxide, then with sodium, and finally fractionated. The use of an efficient distilling column is recommended since the crude base contains higher boiling by-products; yield, 23 g. of ethylene imine boiling at 55–56.5° or 26.5%.

ELIZABETH, N. J. RECEIVED JULY 29, 1935

(1) Gabriel, *Ber.*, **21**, 1056, 2667 (1888).

(2) Fraenkel and Cornelius, *ibid.*, **51**, 1660 (1918).

An All-Glass Valve

BY JOHN WILLARD

An all-glass valve for use in systems where stopcocks are objectionable is illustrated in Fig. 1. It is easily constructed and may be opened and closed by merely heating a quartz tube which surrounds a fine Pyrex capillary. It is particularly useful for admitting a corrosive but thermally stable gas from a reservoir to a reaction.

The tube D is of quartz, about 6 mm. in diameter. Part C is a quartz-to-Pyrex graded seal and the portion of the device above C is of Pyrex. E is a fine Pyrex capillary. The outlet A is connected to a gas reservoir and the outlet B to an evacuated system to be filled from the reservoir.

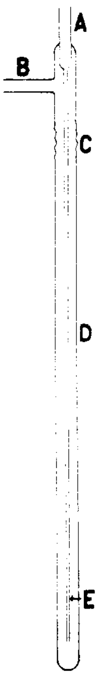


Fig. 1.

A small flame from a hand torch applied to the quartz near the tip of the capillary, when there is only a few mm. greater pressure on the A side than on the B side, will cause the capillary to blow out without affecting the quartz. When pressure has been equalized the capillary may be sealed again by similar application of heat. Repeated openings and closings of the valve may be carried out without difficulty if the capillary is long and fairly small even though it may stick to the side of the quartz tube. During an investigation in this Laboratory this device has been in constant use for several months. As many as twenty fillings have been made with it before it was necessary to seal in a new Pyrex capillary.

Alyea[1] has developed a valve which is similar in purpose to the one here described but which is made completely of Pyrex glass. It is opened by the use of a magnetic pellet and closed by sealing off the outer tube and the capillary together. Other types of greaseless valves are described by

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[1] Alyea, THIS JOURNAL, **52**, 1937 (1930).

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
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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).

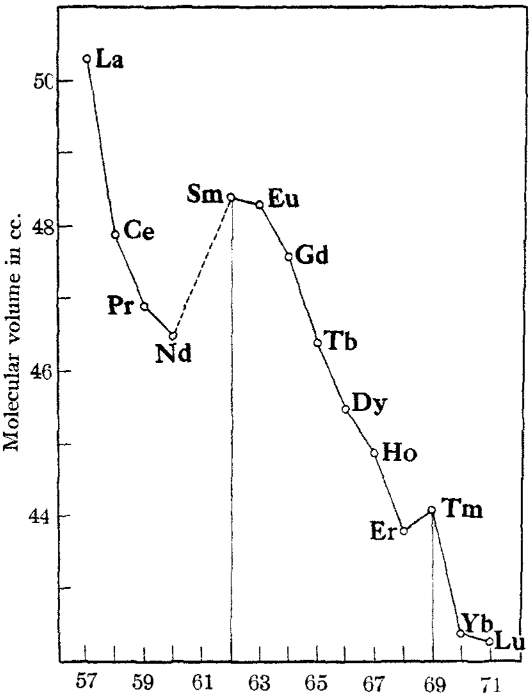

Fig. 2.

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.