in a vacuum, b. p. 156–157° (uncorr.) at 10 mm. (uncorr.). The yields are above 50% but vary considerably with the time of heating. Bis-(β-phenylaminoethyl)-amine is also formed but in smaller amounts.

N-Monophenylpiperazine is insoluble in water and soluble in all common organic solvents, d_4^{20} 1.0621; *neut. eq.* calcd. 162.1; found, 165.0. The hydrochloride of N-monophenylpiperazine was used for analysis for nitrogen. Calcd.: N, 14.11. Found: N, 14.01.

Other mono N-substituted amines have been prepared by this same method and their properties and derivatives will form the basis of a forthcoming publication.

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RECEIVED AUGUST 20, 1934

THE ISOLATION OF 0.1 GRAM OF THE OXIDE OF ELEMENT 91 (PROTACTINIUM)

Sir:

Using a process described previously [A. V. Grosse, *Ber.*, **61,** 233 (1928); THIS JOURNAL, **52,** 1742 (1930)] we have recently been able to work up large quantities of radium residues from Joachimsthal, Czechoslovakia. Thanks to the courtesy of the Lindsay Light Company, a small plant for the treatment of these residues was rigged up at their factory in West Chicago.

The technical process of concentration consists briefly: (1) an extraction of the residues, consisting principally of SiO_2, Fe_2O_3 and PbO with hydrochloric acid; (2) a melt of the silica residue, containing the protactinium, with sodium hydroxide, and (3) separation of the protactinium with zirconium phosphate from the mixture of basic oxides remaining after the melt is leached.

The starting material contains on the average 0.3 g. of protactinium per metric ton or a concentration of 1 part in 3 millions. The plant product contains the element in a concentration of 1 part in 5000, the yield being about 75%.

The plant product is further concentrated in the laboratory by a series of fractional crystallizations of zirconium oxychloride and zirconium phosphate precipitations. At a concentration of about 10% by weight of protactinium, most of the zirconium can be separated by sublimation of the chlorides; protactinium is then best precipitated directly by means of hydrogen peroxide. The purity of the oxide obtained by this method has been proved by x-ray analysis [H. Beuthe and A. V. Grosse, *Z. Physik,* **61,** 170 (1930)].

A detailed description of the technical and laboratory process will be given later.

Up to the present time, the plant product from about 1 ton of residues was worked up and 0.1 g. of protactinium oxide (Pa_2O_5) isolated in the pure state. Larger quantities will be isolated in the near future.

This work required by its very nature large financial expenditures and it has been made possible only by a generous grant of Mr. Hiram J. Halle of New York City, to whom we express our sincere gratitude. We are much indebted to Mr. A. C. Ratchesky, U. S. Minister to Czechoslovakia, and to Mr. Frank Novotny, U. S. Legation in Prague, for their efficient support in obtaining the raw material from the Czechoslovakian Government, and to Prof. Julius Stieglitz for his continuous help and advice.

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RECEIVED SEPTEMBER 10, 1934

METALLIC ELEMENT 91

Sir:

Isolation from radium residues of about 0.1 g. of protactinium oxide has been accomplished recently [A. V. Grosse and M. S. Agruss, THIS JOURNAL, **56,** 2200 (1934)]. The pure oxide (Pa_2O_5) was converted into the metal by two methods: (1) By bombarding the oxide, on a copper target, with a stream of electrons in a high vacuum. The use of 35,000-volt electrons for a few hours at a current strength of 5–10 milliamperes, splits the oxide into oxygen and the metal, the latter remaining as a shiny, partly sintered, metallic mass, stable in air. (2) By transforming it into a halide (Cl, Br, I) and then cracking it in a high vacuum (10^{-6} to 10^{-5} mm.) on an electrically heated tungsten filament, according to the reaction $2PaX_5 \longrightarrow 2Pa + 5X_2\uparrow$, the general method first introduced by Langmuir [I. Langmuir, THIS JOURNAL, **37,** 1139 (1915)]. The protactinium formed a shiny gray white, partly molten, deposit on the filament. The metal does not oxidize in air, in an expected contrast to metallic radium [Marie Curie and A. Debierne, *Compt. rend.*, **151,** 523 (1910)], and retains its luster for quite a while.

The yield of the metal from the pentachloride is poor as compared to the iodide.

The pentachloride can be prepared readily at 550°, by reaction of the oxide with phosgene, according to the equation $Pa_2O_5 + 5COCl_2 \longrightarrow 2PaCl_5 + 5CO_2\uparrow$. Under these conditions the oxide is volatilized quantitatively; the pentachloride sublimes in beautiful transparent nearly colorless long needles, reaching a length of 1 cm. and more, if sublimed slowly. The chloride melts at 301° at atmospheric pressure to a pale yellow liquid, but sublimes appreciably below its melting point. The substance is ideally suited for an atomic weight determination of protactinium, which is under way.

The present experiments are of a preliminary nature; M. Agruss and the writer are planning to prepare larger amounts of the metal and study its properties quantitatively.

We take this opportunity to express our sincere gratitude to Mr. Hiram J. Halle of New York City, who made this work possible by a generous financial grant. We are very much indebted to Dr. Gustav Egloff for placing at our disposal for this work the facilities of the Research Laboratories of the Universal Oil Products Company. It is also a pleasure to acknowledge the assistance of M. Agruss and L. Borst.

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RECEIVED SEPTEMBER 10, 1934

THE EFFECT OF FRACTIONAL CRYSTALLIZATION ON THE ISOTOPIC COMPOSITION OF WATER

Sir:

In a recent communication Professor G. Bruni [THIS JOURNAL, **56,** 2013 (1934)] has discussed the possibility of separating the isotopic species present in ordinary water by fractional crystallization. His conclusion, based on experiment, is that "*if* a fractionation takes place it amounts to less than $^1/_{10,000}$ ..... when the original mass is reduced to $^1/_{14,300}$." The figure probably refers to change in specific gravity.

I have recrystallized distilled water by freezing half the amount taken and advancing the fractions as was done by Richards and Hall [*ibid.*, **39,** 531 (1917)]. The water was thoroughly stirred during the two hours required for freezing. Samples were further purified and specific gravities were taken in the way already described [E. S. Gilfillan, Jr., THIS JOURNAL, **56,** 406 (1934)]. Blank runs were made between each two determinations; the average deviation of these from the mean was 0.1 p. p. m. The results are given in Table I.

TABLE I

Crystns.	10	10	8	12	8	12
Sp.-gr., 1, p. p. m.	1.2	1.0	0.9	1.1	0.7	1.3

The average effect per crystallization is 0.10 p. p. m. The effect was also determined for 6% sodium chloride solutions and found to be 0.5 ± 0.3 p. p. m.

The experiments of La Mer, Eichelberger and Urey [THIS JOURNAL, **56,** 248 (1934)] permit an approximate thermodynamic calculation of the effect to be expected due to concentration of deuterium. The following assumptions are made: (1) In mixtures of protium and deuterium oxides the molecular species H^1H^2O, H^1H^2O, and H^2H^2O, are present in mobile equilibrium. (2) The equilibrium constant $K_c = [H^1H^2O]^2/[H^1H^1O][H^2H^2O] = 4$. (3) These species form "perfect solutions" in the sense of Lewis [G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 221] in both liquid and solid phases. (4) The heats of fusion of the three kinds of water are the same. (5) The freezing point of deuterium oxide is 3.82°. (6) The specific gravity of ordinary water is 22.2 p. p. m. higher than that of H^1H^1O. The first two assumptions have been made by Lewis and Cornish [THIS JOURNAL, **55,** 2616 (1933)]. The result is that one crystallization should change the specific gravity of ordinary water by 0.22 ± 0.01 p. p. m. This indicates that fractional crystallization concentrates O^{16} with respect to O^{18} and that the freezing point of $H^1H^1O^{18}$ is $-0.1 \pm 0.05°$.

From each of the measurements of La Mer, Eichelburger and Urey the freezing point of H^1H^2O can be calculated. The values found are 2.20, 2.21 and 2.28, average 2.23°. From this value one can calculate the freezing point of the water studied by Washburn, Smith and Frandsen [*Bur. Standards J. Research,* **11,** 453 (1933)] to be 0.053° in agreement with the value found.

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PUBLICATION NO. 338 FROM THE
RESEARCH LABORATORY OF PHYSICAL CHEMISTRY
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RECEIVED SEPTEMBER 12, 1934