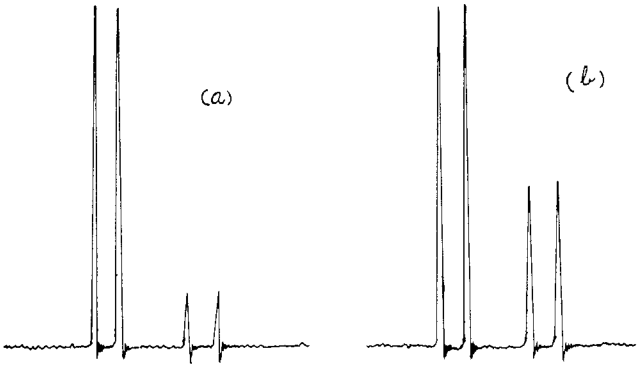

Figure 1.—The proton nmr spectra of (a) $[\{(CH_3)_2N\}_3PCH_3]Cl$ and (b) $[\{(CH_3)_2N\}_2P(CH_3)_2]Cl$. The ratios of the areas under the doublets are 6:1 in (a) and 2:1 in (b).

ammonia plus chloramine and with ammonia-free chloramine yields the expected aminophosphonium chloride. However, the reaction of tris(dimethylamino)phosphine with dimethylchloramine is unusual in the sense that the expected tetrakis(dimethylamino)phosphonium salt is not obtained. Analytical and infrared data for this reaction product are identical with those for tris(dimethylamino) chlorophosphonium chloride, reported earlier by Nöth and Vetter (see Table II). These authors established the phosphonium-salt-like nature of this substance by measuring its equivalent conductivity and by preparing various derivatives. The proton nmr spectrum of this compound is comparable to that of the corresponding bromophosphonium bromide and so is the chemical shift of phosphorus comparable to that of other phosphonium salts as shown in Table II. It is interesting to note that the analogous reaction of the tris(dimethylamino)arsine with dimethylchloramine yields the tetrakis(dimethylamino)arsonium salt.[11] The tetrakis(dimethylamino)phosphonium salt is not obtained, perhaps because of the steric hindrance resulting from the interaction of four dimethylamino groups. The reaction probably occurs in accordance with the equation

$$[(CH_3)_2N]_3P + 2(CH_3)_2NCl \longrightarrow [\{(CH_3)_2N\}_3PCl]Cl + (CH_3)_2NN(CH_3)_2$$

Evidence of the presence of tetramethylhydrazine in the reaction mixture is provided by the strong reducing properties of the supernatant liquid.

Infrared data for the new phosphonium salts are presented in Table I. Some of the characteristic bands can be readily identified, *e.g.*, C–H stretch at 2940–2800 $cm^{-1}$, C–H deformation at 1450 $cm^{-1}$, $P-CH_3$ or $P-N(CH_3)_2$ vibration at 1315–1300 $cm^{-1}$, and $P-N(CH_3)_2$ at 1000–990 $cm^{-1}$. These spectra are similar to those of other phosphonium salts reported earlier[2,4] and can be assigned accordingly.

**Acknowledgment.**—The authors are pleased to acknowledge the partial support of this research by the National Science Foundation through project No. GP4505, and by the National Institutes of Health through grant No. CA08263-02, both with the University of Florida.

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[11] H. G. Vetter and H. Nöth, *Z. Anorg. Allgem. Chem.*, **330**, 233 (1964).

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# The Melting-Point Diagram for the System Uranium Hexafluoride–Plutonium Hexafluoride

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In order to obtain information on condensed-phase equilibria in the system $UF_6$–$PuF_6$, a thermal analysis study was carried out, yielding a temperature–composition phase diagram. The only other literature reference[1] to condensed-phase equilibria in a binary mixture of actinide hexafluorides indicates that solid solutions are formed in the system $UF_6$–$NpF_6$.

## Experimental Section

**Materials.**—The materials, $UF_6$ and $PuF_6$, were manipulated by vacuum distillation in apparatus constructed of nickel tubing and fittings and Monel diaphragm valves. The manifold was located in a glove box to contain the $\alpha$ hazard.

Emission-spectrographic analysis of the $UF_6$ indicated that the predominant impurities were P, at a concentration of <400 ppm, and As, B, Cs, Pd, Re, Sb, Sn, and Th, each present at concentrations of <100 ppm. Two determinations of the triple point of a sample of the $UF_6$ yielded values of 64.1 and 64.2°. The best literature value[2] for the triple point of $UF_6$ is 64.05°.

The $PuF_6$ was prepared by reaction of fluorine with $PuF_4$ at 550°; it was purified by a trap-to-trap distillation similar to that described by Weinstock and Malm.[3] The purity of the $PuF_6$ product was indicated by the triple point and also by an emission-spectrographic analysis of the $PuF_4$ used in its preparation. The $PuF_4$ contained Ca (<25 ppm), Fe (<20 ppm), and Sb (<20 ppm) as predominant impurities. Two determinations of the triple point of a sample of purified $PuF_6$ yielded values of 51.5 and 51.3°. The best literature value[2] for the triple point of pure $PuF_6$ is 51.59° obtained by extrapolation of vapor pressure data.

**Thermal Analysis.**—For thermal analysis, mixtures were contained in a nickel sample tube which could be closed by a bellows valve assembly with a Teflon seat. The temperature of a mixture was measured by a thermocouple positioned within a well in the bottom of the tube.

For either thermal analysis or differential thermal analysis, sample tubes were positioned in cavities within a cylindrical nickel block, the temperatures of which could be varied as a linear function of time by the aid of a program controller. Most of the analyses were performed at a heating rate of 0.3°/min; some were performed at 0.6°/min. The signal of the thermocouple in the sample tube was measured by a recording potentiometer, which was periodically calibrated against a Leeds and Northrup Type K-3 potentiometer.

The composition of each mixture was determined by weighing the sample tube after each component had been added to it by vacuum distillation. Small samples (1–4 g) were used to promote homogeneity in the absence of stirring.

## Results and Discussion

The shapes of the melting curves were characteristic of those exhibited by solid solutions, and the solidus and liquidus points were determined by intersections

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[1] C. A. Hutchison, Jr., T. Tsang, and B. Weinstock, *J. Chem. Phys.*, **37**, 555 (1962).

[2] B. Weinstock, E. E. Weaver, and J. G. Malm, *J. Inorg. Nucl. Chem.*, **11**, 104 (1959).

[3] B. Weinstock and J. G. Malm, *ibid.*, **2**, 380 (1956).

of linear portions of the curves as suggested by Findlay.[4] Liquidus points could not be determined accurately from cooling curves because of supercooling effects and the heat-transfer characteristics of the sample block assembly. All data accepted as measures of the solidus and liquidus points were obtained from the records of melting determinations.

All mixtures melted at temperatures between the melting points of the pure compounds. There was no evidence for the formation of constant-melting mixtures.

Figure 1, a plot of the solidus and liquidus temperatures against composition, shows the lens-shaped diagram characteristic of a continuous series of solid solutions. Each of the points in Figure 1 representing solidus and liquidus temperatures is an average of two to five determinations, and the uncertainty values are standard deviations of the averages. Two minor correction terms were applied to the values of mole fraction of $UF_6$ calculated from the initial weights of the components: A correction for change in composition owing to partial vaporization of the hexafluorides was made by assuming that the liquid and solid solutions both follow Raoult's law. An exact correction could not be made for the change in composition resulting from destruction of the hexafluoride molecules by the $\alpha$ radiation of the plutonium, but an upper limit for this correction term was calculated by assuming that the destruction of $PuF_6$ in the condensed phase occurs at a rate of 2%/day.[5]

A review of the physical properties of $UF_6$ and $PuF_6$, in the light of Hildebrand and Scott's discussion[6] of the influence of physical properties on solid miscibility, suggests that solid miscibility in the system $UF_6$–$PuF_6$ is to be expected. Since the crystals of $UF_6$ and $PuF_6$ are isomorphous,[7,8] and the difference between the calculated unit cell volumes is small,[7] both the heat of mixing[9] and the distortion energy will be small,[6] and compatibility of mixtures of $UF_6$ and $PuF_6$ crystals is indicated.

The curves in Figure 1 representing the locus of ideal solidus and liquidus temperatures were calculated from the equations developed by Seltz.[10] For the system $UF_6$–$PuF_6$, the observed liquidus points all lie in the vicinity of the ideal liquidus curve, whereas the observed solidus points all lie below the ideal solidus curve. Possible causes of the apparent bias of observed solidus points with respect to the ideal solidus curve are soluble impurities, fractional crystallization, and thermodynamic deviation from ideality.

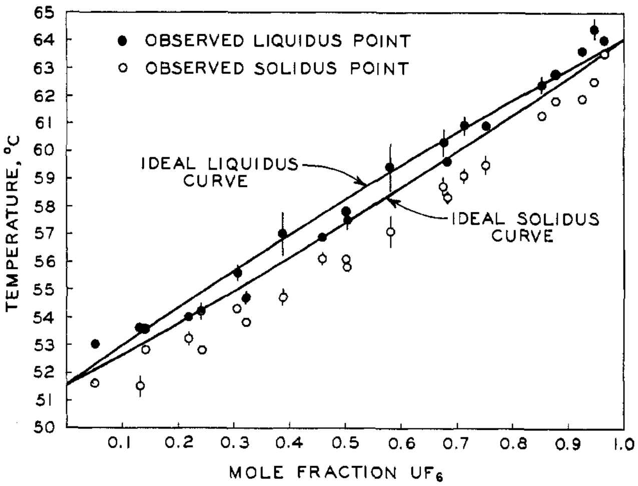

Figure 1.—Melting-point diagram for the system $UF_6$–$PuF_6$.

Soluble impurities can lower the solidus points of mixtures with little effect on the liquidus points. In the present work, however, a soluble impurity is an unsatisfactory explanation of the deviation because an impurity also would produce a lowering of the end points of the observed solidus curve, and this behavior was not observed. If equilibrium is not established between solid and liquid phases as a mixture cools, fractional crystallization occurs, resulting in an observed solidus curve which is lower than the true value. In order to avoid the effects of fractional crystallization, it is recommended that a mixture be annealed at a temperature just below the solidus point.[11] Annealing was not considered for the system $UF_6$–$PuF_6$ because of the undesirable effects of extensive radiation decomposition of $PuF_6$, which would have occurred during the time sufficient for solid-state annealing. Since the mixtures were not annealed, a treatment of the deviation of the observed solidus points from ideality in terms of thermodynamic activity coefficients would not be justified.

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[4] A. Findlay, "The Phase Rule and Its Applications," Longmans, Green and Company, Inc., New York, N. Y., 1938, pp 474–476; republished by Dover Publications, New York, N. Y.

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[6] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1950, pp 300–319.

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[8] A. E. Florin, I. R. Tannenbaum, and J. F. Lemons, *J. Inorg. Nucl. Chem.*, **2**, 368 (1956).

[9] Reference 6, p 129, eq 36.

[10] H. Seltz, *J. Am. Chem. Soc.*, **56**, 307 (1934).

[11] W. Hume-Rothery, J. W. Christian, and W. B. Pearson, "Metallurgical Equilibrium Diagrams," The Institute of Physics, London, 1952, p 153.

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## Reactions of Triphenyltin Azide

BY W. L. LEHN

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Over the past 5 years there has been a marked increase in the number of publications appearing dealing