Silver fluoride was found to be more useful for the reaction; the application of titanium tetrafluoride resulted in a considerable drop in the reaction time and eliminated the necessity for using solvents. After standing for a few minutes, a mixture of titanium tetrafluoride and B-trichloroborazine spontaneously warmed to about 40°. The mixture then was gradually heated to 130° under reduced pressure (*ca.* 50–80 mm.) and titanium chloride and B-trifluoroborazine were distilled off. The solid borazine was filtered from the distillate in an inert atmosphere and was washed with *n*-hexane. Final purification of the product was achieved through sublimation under vacuum.

B-Trifluoroborazine is a white crystalline material melting at 122° (subl.). It is soluble in such anhydrous solvents as ether and benzene, and was found to be sufficiently stable in the presence of moisture to be handled in the atmosphere.

Anal.[9] Calcd. for $B_3N_3F_3H_3$: B, 24.2; N, 31.2; F, 42.4; H, 2.2; mol. wt., 134.5. Found: B, 23.9; N, 31.1; F, 42.9; H, 2.2; mol. wt., 132.

Antimony fluorides and their mixtures with antimony chlorides also reacted spontaneously with B-trichloroborazine to yield B-fluorinated derivatives. On the basis of existing evidence it appears that, through variation of the experimental conditions, this procedure can be made to yield partially fluorinated borazines.

Furthermore, the metathetical reaction described in eq. 1 is not restricted to the fluorination of B-trichloroborazine itself, but certain substituted borazines can be reacted in an analogous manner. Thus B-trifluoro-N-trimethylborazine, m.p. 90.5° (lit.[4,5]: 85 and 88–89°, respectively), was obtained by a procedure analogous to that described above.

Since no special high vacuum equipment is necessary for the transhalogenation procedure, this method seems to be of general interest for preparing B-fluorinated borazines.

Experiments now are being done to improve the yields, which at present range between 25 and 40%, and to investigate the partially fluorinated products in more detail. Preliminary results indicate that, in the latter, chlorine is more reactive than fluorine and therefore is more easily replaced by other groups. This behavior could lead to the preparation of unsymmetrically substituted borazines of great variety.

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[9] Analysis by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. The molecular weight was determined cryoscopically in benzene; melting points were taken on a Mel-Temp Block in sealed tubes.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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Phase Relation in the System Uranium Trioxide–Nitric Acid–Water at Various Temperatures[1]

BY J. R. LACHER, KEITH ENSLEY, AND J. D. PARK

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In 1926 Coloni[2] studied the UO_3–H_2O–HNO_3 system at 25.0°. He reported the existence of the following hydrates of uranyl nitrate: $UO_2(NO_3)_2 \cdot 6H_2O$, $UO_2(NO_3)_2 \cdot 3H_2O$, and $UO_2(NO_3)_2 \cdot 2H_2O$. In 1941 Kraus and co-workers at Brown University made a further study of the system extending the curve into the UO_3 region.[3] They postulated a hydrate $UO_3 \cdot nH_2O$ as the solid phase as shown in Fig. 1.

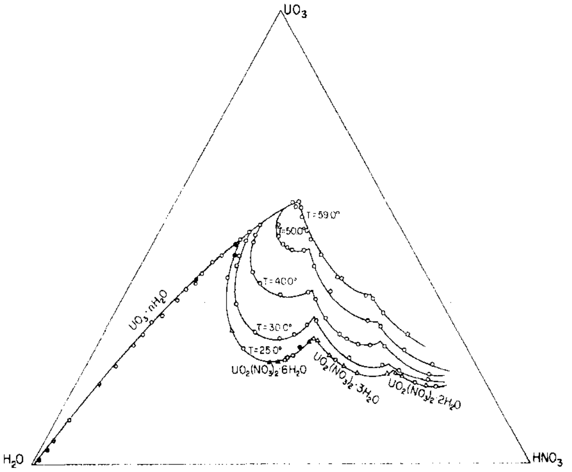

Fig. 1.—Phase diagram for the system UO_3–H_2O–HNO_3: Δ, Coloni; ●, Brown University; ○, this research.

This paper concerns the extension of the curve into the HNO_3-rich region and an investigation at higher temperatures. Standard procedures[4] were used to produce and equilibrate mixtures of

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[1] This research is supported in part by the Atomic Energy Commission through the Uranium Division of the Mallinckrodt Chemical Works, St. Charles, Missouri.

[2] A. Coloni, *Bull. soc. chim.*, (4) **39**, 1243 (1926).

[3] Private communication.

[4] E. K. Ensley, "A Study of Some Chemical Properties of Uranium Compounds," Ph.D. Thesis, University of Colorado 1960.

uranium trioxide, nitric acid, and water. The schematic diagram of the phase relations at the various temperatures is shown in Fig. 1 as per cent by weight.

It is seen from this triangular diagram that the hexahydrate has the greatest solubility while the dihydrate shows the least solubility. It also is noted that an increase of temperature influences the solubility of the hexahydrate to a greater extent than the lower hydrates. The solubility curves were determined for 30, 40, 50, and 59°; the highest temperature of 59° is one degree below the melting point of the hexahydrate. At this temperature, near extinction of the hexahydrate is noted due to the infinite solubility at 60°.

In the nitric acid-rich region, the acid decomposes and it becomes impossible to study the system in three components. In this region the compound $UO_2(NO_3)_2 \cdot N_2O_4 \cdot H_2O$ was identified. It had been prepared previously by Gibson and Katz[5] by treating uranium trioxide monohydrate with liquid nitrogen tetroxide.

The solubility curve in the region where $UO_3 \cdot n H_2O$ is the saturating phase shows that uranyl nitrate will dissolve uranium trioxide. In dilute solution one equivalent of acid will dissolve as much as 1.75 equivalents of uranium trioxide.[6] Sutton observed that the uranyl ion was capable of dissolving uranium trioxide and postulated the mechanism

$$UO_3 + UO_2^{++} \rightleftarrows U_2O_5^{++}$$

Heidt[7] and later Harris and Kolthoff[8] suggested that the following reaction represents the hydrolysis of the uranyl ion

$$UO_2^{++} + H_2O \rightleftarrows UO_2OH^+ + H^+$$

The equation representing the solution of uranium trioxide would be

$$UO_3 + UO_2^{++} + H_2O \rightleftarrows 2UO_2OH^+$$

Since the UO_2OH^+ ion probably can polymerize, the two equations are essentially the same and both illustrate the acidic characteristics of the uranyl ion.

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(5) G. Gibson and J. J. Katz, *J. Am. Chem. Soc.*, **73**, 5436 (1951).

(6) J. Sutton, *J. Chem. Soc.*, S275 (1949).

(7) L. T. Heidt, *J. Phys. Chem.*, **46**, 624 (1942).

(8) W. E. Harris and I. M. Kolthoff, *J. Am. Chem. Soc.*, **69**, 446 (1947).

CONTRIBUTION FROM THE
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Structure and Magnetism of K_2ReH_8 and K_2TcH_8

BY K. KNOX AND A. P. GINSBERG

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The recently reported compounds K_2ReH_8[1] and K_2TcH_8[2] are unique in being ternary transition metal hydrides having only hydrogen as the complexing ligand. As such their structure and physical properties are of considerable interest. In the present note we present a preliminary report on an X-ray structure determination for K_2ReH_8 and K_2TcH_8 and on the magnetic susceptibility of K_2ReH_8.

X-Ray Diffraction

Several single crystals of K_2ReH_8, grown by slow evaporation of an aqueous KOH solution and shown to be water-free by their infrared spectra, were mounted in sealed glass capillaries. Precession and Weissenberg photographs (MoKα) showed the Laue symmetry to be $D_{6h}-6/mmm$ with no systematic absences. The lattice constants are $a = 9.61$ and $c = 5.51$ Å. The measured density of 3.07 ± 0.10 g./cc., obtained pycnometrically in isopropanol, indicates definitely three formula weights per unit cell, the calculated density being 3.09 g./cc. The gross features of the diffraction intensities can only be fitted by placing three Re atoms in positions 1(a), 000, and 2(d), $\pm\ {}^1/_3\ {}^2/_3\ {}^1/_2$, of space group D_{6h}^1-P6/mmm, positions also most logical on stereochemical grounds. Unfortunately the crystals were so large, 0.1–1.0 mm., that the absorption corrections are quite appreciable. Without accurate intensities the potassium atoms could not be located unambiguously, either in P6/mmm or any of its hexagonal or trigonal subgroups. We are in the process of mounting a well shaped, small crystal on which accurate intensities can be collected and absorption corrections made. When the potassium atoms have been located by X-rays, the hydrogens will be placed by neutron diffraction.

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(1) A. P. Ginsberg, J. M. Miller, and E. Koubek, *J. Am. Chem. Soc.*, **83**, 4909 (1961).

(2) A. P. Ginsberg, to be published.