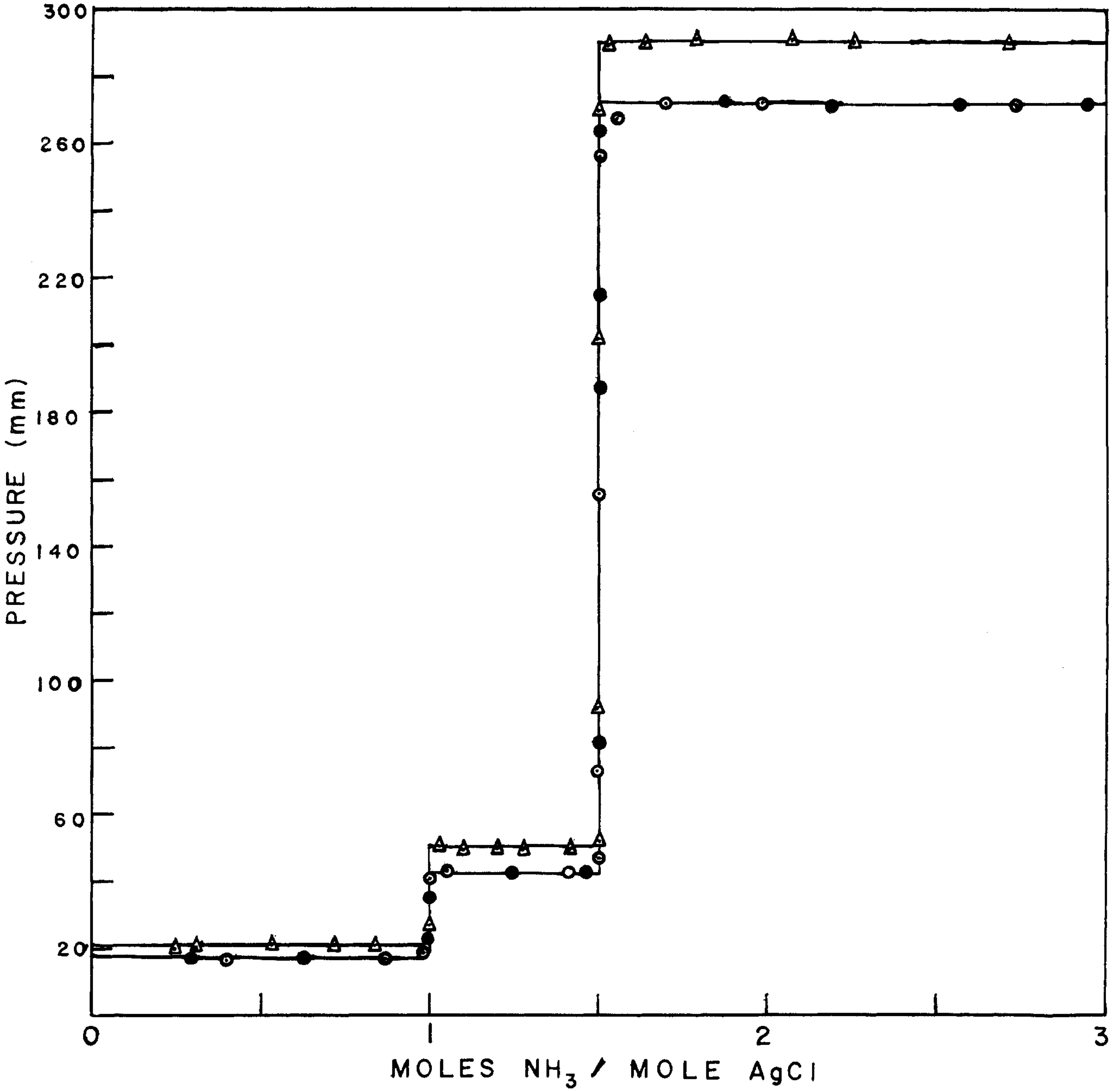

Fig. 1.—Pressure-composition phase diagram for the system AgCl–NH_3 at 0°: ⊙, without sonic cavitation; △, with continuous sonic cavitation; ●, 1 hr. with sonic cavitation followed by 0.5 hr. without sonic cavitation.

hr. Plateau pressures for the AgCl–NH_3 system obtained by this method showed no significant deviations from the values obtained by Biltz and Stollenwerk.

This work indicates that ultrasonic cavitation may be used to reduce the time required to obtain pressure–composition phase diagrams. The stoichiometries of the phases involved are not affected by the ultrasonic cavitation but the equilibrium pressures are. Accurate equilibrium pressures may be obtained, however, by discontinuing ultrasonic cavitation for a short period prior to the pressure measurement.

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Contribution from the
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Oxides of Neptunium(V) and Neptunium(VI) from Molten Salts[1]

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Although the neptunium–oxygen system has similarities to the uranium–oxygen system, the highest

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

oxide which has been prepared for neptunium was Np_3O_8.[2] Evidence is presented in this paper to show the existence of $NpO_3 \cdot 2H_2O$. In a previous communication[3] it was reported that a brown precipitate was formed when bubbling ozone through a solution of Np(V) in a $LiNO_3$–KNO_3 eutectic at 150°. This brown precipitate was separated from the salt by washing the salt mixture with water and then drying the product. This product has been identified as $NpO_3 \cdot 2H_2O$.

The brown precipitate is separated from the molten nitrate by cooling the melt and washing the water-insoluble solid many times with distilled water to remove all traces of the soluble salt matrix. The compound then is dried in an air oven at 90 to 100° overnight. This compound is very soluble in dilute mineral acids to give a solution of essentially pure NpO_2^{+2} (at least 98%) as shown by spectrophotometry. Thus this compound contains neptunium in the (VI) state. Emission spectroscopy shows that no other metallic cation is present; neither lithium nor potassium exist in any significant amounts in this compound. Thus the brown compound is not a neptunate such as K_2NpO_4.

The X-ray powder pattern of the compound is similar to $UO_3 \cdot 2H_2O$. Table I is a comparison of the $\sin^2 \theta$ values for the strongest lines of $NpO_3 \cdot 2H_2O$ with those of $UO_3 \cdot 2H_2O$.[4]

TABLE I

COMPARISON OF $\sin^2 \theta$ FOR $NpO_3 \cdot 2H_2O$ AND FOR $UO_3 \cdot 2H_2O$

$NpO_3 \cdot 2H_2O$	$UO_3 \cdot 2H_2O^4$
0.0103	0.0110 s
.0415	.0440 mw
.0465	.0462 s
.0484	.0485 ms
.0569	.0571 s
.0587	.0591 ms
.1538	.1545 m+

Specific activity measurements show the compound to contain 72 ± 2% neptunium; $NpO_3 \cdot 2H_2O$ contains 73.8% neptunium. Thus it is concluded that $NpO_3 \cdot 2H_2O$ has been made.

Similar preparations were attempted using molten $LiClO_4$ at 260° as the solvent. Again, with ozone bubbling through a solution containing Np(V), a brown precipitate is formed. However, the identity of the recovered compound is unknown. This time the compound is soluble in dilute acids with difficulty. The resulting solution contains neptunium only in the (V) state. Again emission spectroscopy shows no other metallic ions to be present. The X-ray pattern of this compound is similar to Np_3O_8.[5] Table II compares the $\sin^2 \theta$ values for this compound with those of Np_3O_8[6]; only the strong lines are given. However, this compound cannot be Np_3O_8 because Np_3O_8 dissolves in dilute acid to yield both NpO_2^+ and NpO_2^{+2} ions. This must be a neptunium(V) oxide.

TABLE II

COMPARISON OF $\sin^2 \theta$ FOR NEPTUNIUM(V) OXIDE AND Np_3O_8

Neptunium(V) oxide	$Np_3O_8^6$
0.0489	0.0492
.0543	.0547
.0828	.0831
.0882	.0886
.1414	.1422
.1579	.1587
.2178	.2190
.3318	.3326

Unfortunately the mechanism of oxide formation is more complicated than so far indicated. The preparations from the molten nitrate eutectic did not always result in $NpO_3 \cdot 2H_2O$. Sometimes the unknown Np(V) compound, the same as from the molten perchlorate, was produced. The similarity was verified by the X-ray patterns. In only a single instance was $NpO_3 \cdot 2H_2O$ prepared from the lithium perchlorate melt. It is likely that the temperature is the important variable. The furnace used in these experiments had considerable temperature gradients. It already has been shown[3] that Np(VI) in molten salts is reduced to Np(V) with increasing temperature which in turn is unstable to still higher temperatures.

Further work is in progress with both these compounds. Oxygen analysis must be performed. Precipitation reactions from molten salts should prove to be a valuable technique in the preparation of many new and interesting compounds.

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JOINT CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY
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Some Observations Relative to Digallane

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The literature contains references to digallane, Ga_2H_6,[1,2] to a polymeric $[GaH_3]_n$,[3b] to a gaseous GaH,[4] to a gallium–hydrogen solid of unknown formula,[5] and to a diethyl etherate, $(C_2H_5)_2OGaH_3$.[3] The compounds Ga_2H_6 and GaH have been questioned on the basis of periodic relationships.[6] The doubts on Ga_2H_6 and $[GaH_3]_n$ are now reinforced by experiment. Recent studies on gallium hydrides, initiated independently in

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