to be impure $Cr(OP(C_6H_5)_2O)_3$. *Anal.* Calcd.: Cr, 7.4; C, 61.5; H, 4.3; P, 13.2. Found: Cr, 7.2; C, 60.4; H, 4.2; P, 12.4.

Infrared Spectra.—Infrared spectra were measured with a Perkin Elmer Model 21 or 221 spectrophotometer employing a sodium chloride prism in the 6–15 μ region. Spectra were obtained for solids in Nujol and hexachlorobutadiene mulls.

The infrared spectrum of the dimer corresponds to what is expected. Absorption bands clearly due to the diphenylphosphinate group are observed at the following frequencies (cm.$^{-1}$): 1440 (m), 1180 (vs), 1126 (vs), 1065 (sh), 997 (m), and 727 (s). Additional peaks overlapped with picolinate absorptions occur at approximately 1022 (m), 758 (s), and 690 (s). With the exception of the OPO stretching mode, these frequencies closely parallel those reported for $Co[OP(C_6H_5)_2O]_2$[4] in this region of the spectrum. Two sharp peaks attributed to the OPO antisymmetric stretching vibration are noted at 1180 and 1126 cm.$^{-1}$, and these correspond closely to the absorption pattern observed in the spectrum of $(AcCHAc)_2Cr[OP(C_6H_5)_2O]_2Cr(AcCHAc)_2$.[2]

Absorption maxima for the picolinate group are as follows (cm.$^{-1}$): 1665 (vs), 1610 (s), 1568 (m), 1477 (m), 1438 (s), 1340 (sh), 1330 (s), 1286 (s), 1257 (w), 1238 (w), 1155 (vs), 1093 (w), 1050 (s), 1022 (m), 860 (s), 758 (s), 714 (s), 680 (s), and 655 (s). Frequency values of these absorptions are practically similar to those observed in $Cr(C_5H_4NCOO)_3 \cdot H_2O$, thus showing that the picolinate ring structure is preserved in the dimer. In particular the bands at 1286, 1155, 1050, and 1022 cm.$^{-1}$ are characteristic of the *ortho*-substituted pyridine group and corresponding vibrations[5] for compounds of similar structure are very close to the values observed for the dimer.

Discussion

The experimental results clearly show that the substitution of the picolinate ligand for the acetylacetonate ligand makes polymer formation difficult. Compositions lying between that of an infinite linear double-bridged polymer and that of a dimer give ebullioscopic molecular weights in benzene and $CHCl_3$ in the monomer-to-dimer range in value. It thus is apparent that either a polymer was not formed at all in the reaction or else that any polymer formed is quite unstable compared to $[Cr(AcCHAc)(OP(C_6H_5)_2O)_2]_x$.[2] An attempt to build a model of the double-bridged polymer containing picolinate instead of acetylacetonate ligands leads to the observation that there is considerable steric interaction between the chelating picolinate group and the phenyl groups of the catenating diphenylphosphinate anion. In fact models indicate that any chelating group larger than the acetylacetonate ion will interact sterically with the double-bridging diphenylphosphinate ions, severely limiting the possibilities for preparing analogs to $[Cr(AcCHAc)(OP(C_6H_5)_2O)_2]_x$. The picolinate group appears to be large enough to prevent the isolation and characterization of any units larger than the dimer. It is to be noted that theoretically the dimer can exist in six isomeric geometrical forms because the chelating group is not symmetrical. We have not investigated this possibility in any detail.

Acknowledgment.—We are indebted to the Office of Naval Research for partial support of this work, to our Analytical Department for chemical and instrumental analysis, in particular, Miss Ruth Kossatz for the infrared spectra and Mr. Howard Francis for the ebulliometric molecular weight determinations, and to Mr. Gene Mincarelli for assistance with the experiments.

---

[4] G. E. Coates and D. S. Golightly, *J. Chem. Soc.*, 2523 (1962).

[5] H. Shindo, *Pharm. Bull.* (Tokyo), **5**, 472 (1957).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO

Use of Ultrasonic Cavitation for Rapid Determination of Pressure–Composition Data

BY SAMUEL A. HARRELL AND DARL H. MCDANIEL

Received January 31, 1963

The time required for determination of the pressure–composition phase diagrams of systems with relatively long equilibration times (several hours to several days) has been greatly reduced by applying ultrasonic cavitation to the samples.

The system $AgCl–NH_3$, studied by Biltz and Stollenwerk,[1] was examined by standard vacuum line techniques with the sample tube immersed in an ice bath through which ultrasonic waves of 38 kc./sec. were transmitted.[2] An essential feature of the ice bath, which is contained in the sonic generator tank, is that the liquid column surrounding the sample tube be relatively free of solid. This condition may readily be achieved by freezing part of the bath liquid on a suitably shaped cooling coil through which refrigerant is passed intermittently. The cooling coil, which encircles the sample tube, and the bath liquid frozen on the coil should be kept at least 5 cm. from the sample tube and free from the bottom of the tank. Automatic control of such a bath has been described elsewhere.[3] The use of crushed ice, instead of the single ice helix formed on the cooling coil, was found to greatly impede cavitation of the bath liquid, thus increasing the time required for equilibration to occur.

In Fig. 1 a plot of pressure *vs.* composition with and without ultrasonic cavitation reveals that the stoichiometries of the new phases formed ($AgCl \cdot NH_3$, $2AgCl \cdot 3NH_3$, $AgCl \cdot 3NH_3$) may be determined accurately using ultrasonic cavitation of the sample. The time required for the sample to reach equilibrium without ultrasonic cavitation was from 30 min. to 20 hr., in agreement with earlier work.[1] With cavitation the time was shortened to a minimum of 10 min. and a maximum of 2.5 hr.

When ultrasonic cavitation was applied, a definite increase in equilibrium pressure was observed at a given composition, but when the cavitation was discontinued, the pressure returned to its original value.

A procedure yielding accurate equilibrium pressures was developed in which ultrasonic cavitation was applied to the sample for 1 hr., after which the sample was allowed to equilibrate without cavitation for 0.5

---

[1] W. Biltz and W. Stollenwerk, *Z. anorg. allgem. Chem.*, **114**, 174 (1920).

[2] Sonogen Ultrasonic Generator, Model AP-10-B, Branson Ultrasonic Corp., Stamford, Conn. This model has a one-half gallon tank and a power rating of 50 watts.

[3] R. E. Valleé and S. A. Harrell, *Rev. Sci. Instr.*, **33**, 567 (1962).

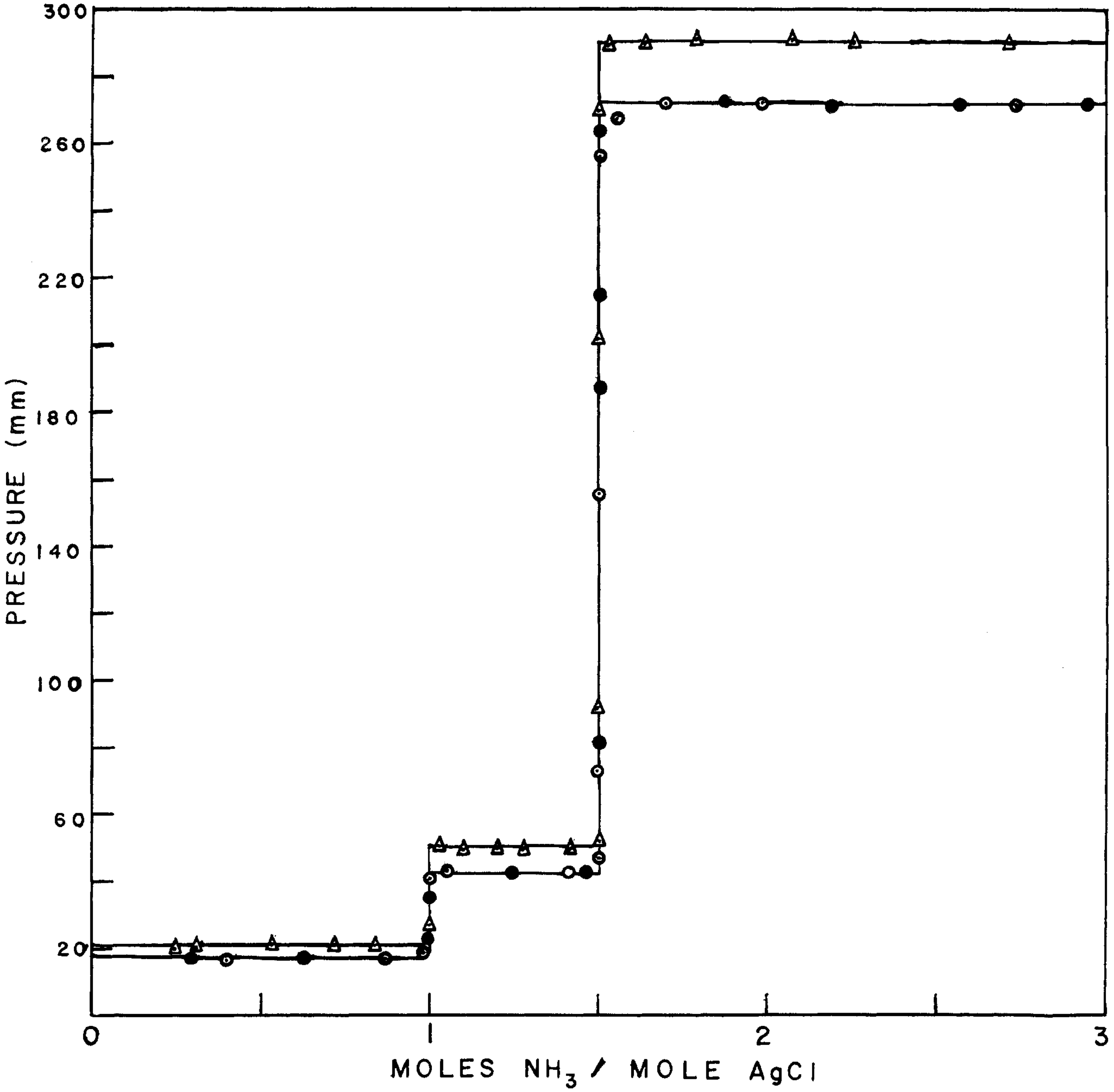

Fig. 1.—Pressure–composition phase diagram for the system AgCl–NH_3 at 0°: ⊙, without sonic cavitation; △, with continuous sonic cavitation; ●, 1 hr. with sonic cavitation followed by 0.5 hr. without sonic cavitation.

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.

Acknowledgment.—Financial support by the National Science Foundation is gratefully acknowledged.

Contribution from the
Argonne National Laboratory, Argonne, Illinois

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

By Donald Cohen

Received December 10, 1962

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

---

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