fact that very little, if any, exchange occurred over periods of up to three days could be explained either on the basis that a negligible amount of hexacyanocobaltate(II) ion was present, or that while some was formed, the electron exchange process itself was slow. Unfortunately, the choice cannot be made, in the absence of any reliable means of predicting the electron exchange rate.

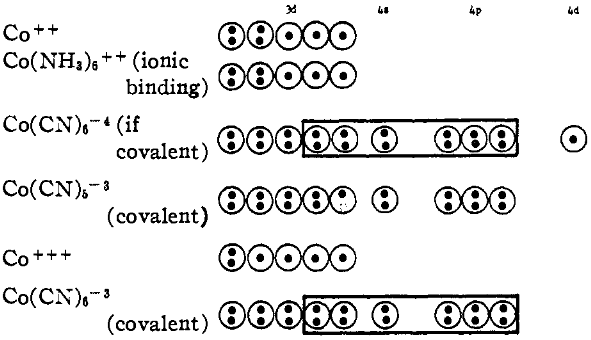
Summary and Conclusions

The foregoing has shown that there is at present no conclusive evidence for the existence of a hexacyanocobaltate(II) complex, either as a solid, or as a reasonably stable species in solution, and that, in excess aqueous cyanide, the most stable cyanide complex contains five cyanides per cobalt, and is covalently bonded. The information presently available does not, unfortunately, definitely distinguish between the two most likely structures for the pentacyanide in solution, namely, hexacoördinated $Co(H_2O)(CN)_5^{-3}$ ion and pentacoordinated $Co(CN)_5^{-3}$ ion. Some preference can be assigned, however, by means of the qualitative arguments outlined below.

The first of the two possibilities might seem to be the more natural and conventional but, actually, if correct, it would constitute the only case of hexacovalently bonded cobalt(II), other cobalt(II) complexes being ionic.[15] Moreover, it has been recognized that hexacovalent cobalt(II) should be unstable because of the required promotion of an electron to an outer orbital.[16] The various electronic configurations are summarized in Table IV. Another point is that if hexacovalency were favored for cobalt(II) over pentacovalency, one would expect that the hexacyanide would be at least as stable as the aquopentacyanide, by analogy with manganese, iron and trivalent cobalt. Hume and Kolthoff[4] note that the polarographic wave for reduction of aquopentacyanocobaltate(III) ion is very irreversible and corresponds to a two electron change, which suggests that a one electron step is ruled out by the non-existence of aquopentacyanocobaltate(II) ion as a stable species. Finally, in view of the apparent stability of the cobalt(II) pentacyanide complex, the immeasurably rapid exchange with radiocyanide is more suggestive of pentacovalency than of hexacovalency; thus exchange has been found to be slow with a number of hexacyanides, but rapid with tetracyanides.[12]

TABLE IV

ELECTRONIC CONFIGURATIONS



The second possible structure, $Co(CN)_5^{-3}$, minimizes the above objections, but needs positive substantiation before a definite conclusion can be reached.

LOS ANGELES, CALIFORNIA RECEIVED APRIL 16, 1951

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[15] See D. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 173ff.

[16] L. Pauling, ref. 10, p. 96.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Critical Temperature and Critical Pressure of Nitrogen[1]

BY DAVID WHITE, ABRAHAM SOLOMON FRIEDMAN AND H. L. JOHNSTON

The critical constants of nitrogen have been determined by observation of the disappearance of the meniscus. The critical temperature is 126.26 ± 0.04°K. and the critical pressure is 33.54 ± 0.02 atm. These results are compared with earlier vapor pressure data and with the critical constants estimated by extrapolation of $P-V-T$ data.

Introduction.—In a recent publication[2] we suggested that extrapolation of $P-V$ isotherms leads to a critical temperature for nitrogen of about 126.15°K. By use of our vapor pressure equation,[3] this temperature gives a critical pressure of 33.181 atm. These values are not in good agreement with those determined at Leiden[4]—namely, $T_c = 125.96$°K. and $P_c = 33.490$ atm. To resolve this slight disagreement, we determined the critical constants of nitrogen in a glass cell by direct observation of the disappearance of the meniscus.

Apparatus.—The apparatus we used was the same as that previously used to determine the critical constants of hydrogen[5] and of deuterium.[6] The pressure was measured by means of an oscillating piston deadweight gage with an uncertainty of less than 1 part in 10,000. The standard copper–constantan thermocouples, which showed an uncertainty of 0.02 deg. in intercomparison with a helium thermometer, were rechecked *in situ* by determining the vapor pressure of nitrogen at a few temperatures.

Experimental Technique and Results.—Liquid nitrogen just below the critical temperature was introduced into the cell until the meniscus was midway up the pipet. The temperature was then slowly increased and the meniscus was maintained at this level by the addition of more gas, until the temperature was within a few hundredths of a degree below the critical. The critical constants were de-

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] A. S. Friedman and D. White, THIS JOURNAL, **72**, 3931 (1950).

[3] $\log P_{atm} = 3.720822 - 293.94358/T + 10.31993 \times 10^{-4}T$ (see reference 2).

[4] H. Kamerlingh Onnes, C. Dorsman and G. Holst, *Commun. Phys. Lab. Univ. Leiden*, No. 145B (1915).

[5] D. White, A. S. Friedman and H. L. Johnston, THIS JOURNAL, **72**, 3565 (1950).

[6] A. S. Friedman, D. White and H. L. Johnston, *ibid.*, **73**, 1310 (1951).

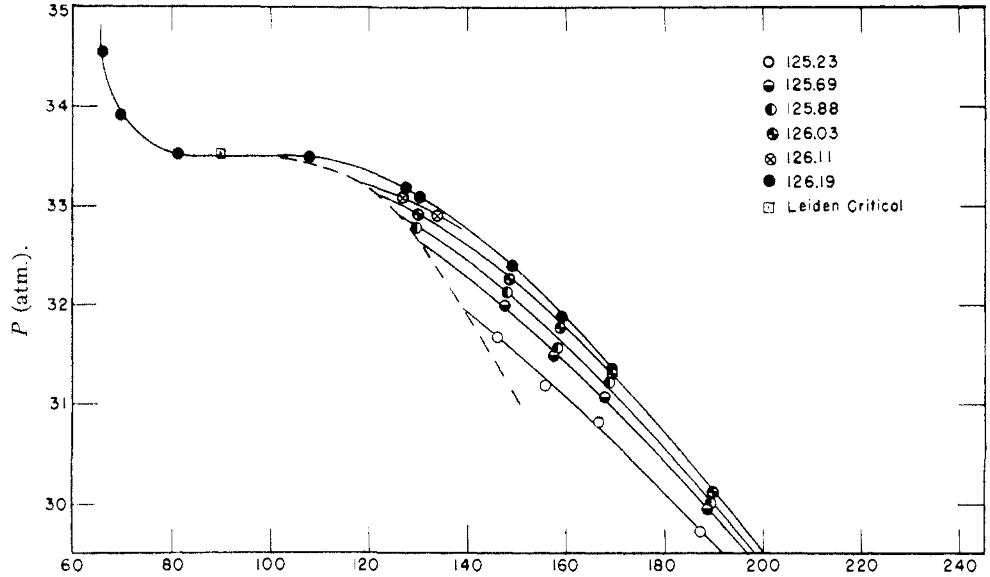

Fig. 1.—P-V isotherms of nitrogen near the critical point.

termined by observing the disappearance of the meniscus. At first the meniscus is very flat; as the critical temperature is approached it becomes fainter and fainter and slight shaking of the apparatus distorts it markedly. We found that it disappeared completely at 126.26 ± 0.04°K. The pressure at this temperature was 33.54 ± 0.02 atm.

It is interesting to note that no critical opalescence was observed as the nitrogen was heated very slowly through the critical region. However, when the supercritical gas was a few thousandths of a degree above the critical point a sudden change of pressure of only a few hundredths of an atmosphere produced a heavy, short-lived opalescence (the pressure change was brought about by pushing the deadweight gage piston down and then up). This experiment indicates that the opalescent system is an unstable one, produced by sudden small density fluctuations owing to adiabatic compressions and expansions.

Discussion.—The critical constants thus directly determined may be compared to those estimated from the P-V isotherms in the neighborhood of the critical point that were determined in this Laboratory (see Fig. 1). The isotherm at 126.19°K. is practically flat at a pressure of 33.50 atm. The critical pressure and critical volume determined at Leiden,[4,7] also shown in Fig. 1, fall in about the center of this flat portion of the isotherm. Thus they are in excellent agreement with our experimentally determined results, since the critical isotherm would occur just slightly above this curve. Our original estimate of 126.15°K. for the critical temperature was too low, since an error of 0.070 deg. had been made in computing the temperature of the 126.19°K. isotherm. The critical pressure was calculated, by means of our vapor pressure equation,[2] from this erroneous temperature.

The critical pressure of 33.54 atm. directly determined in this research is almost 0.2 atm. higher than the computed vapor pressure of nitrogen at 126.26°K. However, its agreement with the original vapor pressure data[2] in the neighborhood of the critical point is good, as is evident in Fig. 2. An attempt to get a better analytical equation for the experimental data was made by calculating a new vapor pressure equation, with an additional term from the original data and the newly determined values of the critical constants. The result was

$$\log P_{\text{atm}} = 3.730697 - 294.51750/T + 9.9433 \times 10^{-4}T - 1.284 \times 10^{-8}T^2$$

At 126.26°K., the new equation gives a vapor pressure of 33.38 atm. This equation also deviates in

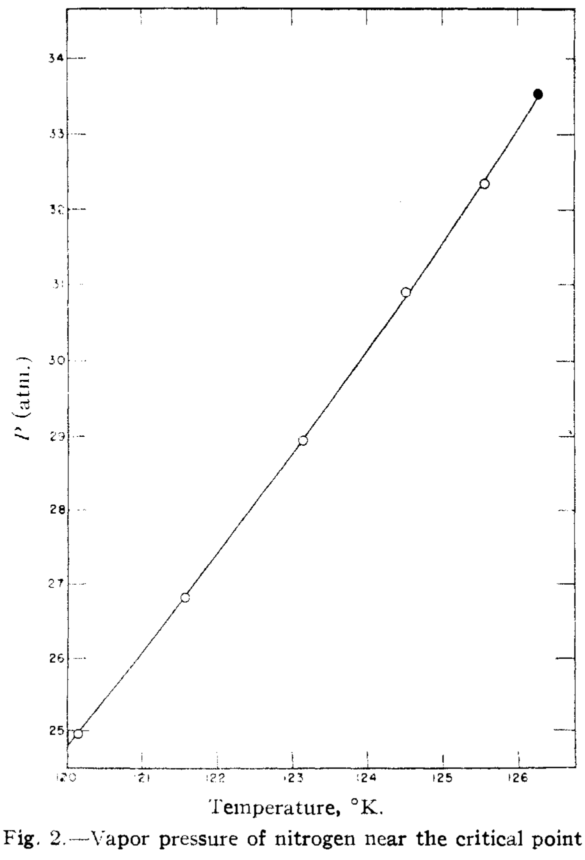

Fig. 2.—Vapor pressure of nitrogen near the critical point.

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(7) E. Mathias, H. Kamerlingh Onnes and C. A. Crommelin, *Commun. Phys. Lab. Univ. Leiden*, No. 145C (1915).

the neighborhood of the critical region, but accurately represents the remaining vapor pressure data above the boiling point. It is evident that an equation obtained by a least squares solution in which all the vapor pressure points are weighted equally does not lead to a satisfactory solution in the neighborhood of the critical temperature. Heavy weighting of the vapor pressure data in the neighborhood of the critical point, however, would tend to give poorer agreement near the boiling point.

Acknowledgment.—We wish to acknowledge the aid of Mr. James A. Seiler in the experimental work.

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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

Hexavalent Americium[1]

BY L. B. ASPREY, S. E. STEPHANOU AND R. A. PENNEMAN

Americium in the formal oxidation state of plus six has been prepared by the oxidation of Am(III) and Am(V) in acid solution. Various methods of obtaining Am(VI) are described, including the disproportionation of Am(V). Sodium americyl acetate, $NaAmO_2(OOCCH_3)_3$, was prepared and identified by optical crystallography and X-ray analysis. From its crystal and chemical similarity to uranyl, neptunyl and plutonyl ions, americyl ion is assigned the formula, AmO_2^{++}. The absorption spectrum of Am(VI) in perchloric acid solution shows a narrow absorption peak at 992 mμ, a minor peak at 666 mμ and ultraviolet absorption. The potential of the Am(III)-Am(VI) couple is estimated to be −1.8 ± 0.15 volts.

Introduction

In the 5f- series of elements, the hexavalent oxidation state is well known for uranium, neptunium and plutonium, but was discovered only recently for americium.[2] Previous work on oxidation states of americium higher than (III) had demonstrated the existence of Am(IV) (only as the oxide, AmO_2), and of Am(V).[3,4,5] Evidence has been obtained at this laboratory characterizing Am(VI). Methods of preparation, identification, absorption spectrum and other properties of this new oxidation state are discussed.

Materials.—The chemicals used were all of reagent grade. The isotope of americium employed was Am^{241}, an alpha emitter of 475 years half-life.[6] In all experiments, carrier-free americium exceeding 95% purity was used. The americium had been purified originally in coöperation with S. G. Thompson of the Berkeley Radiation Laboratory using methods previously reported.[3,5,7,8] The total americium concentration was determined by radiometric methods, while the concentration of Am(III), Am(V) and Am(VI) were measured spectrophotometrically. Due to the quantity of alpha emission from this element, it was necessary to carry out all the work in gloved boxes through which a current of air was drawn.[5]

Preparation of Am(VI).—In the following oxidation experiments, the concentrations of americium varied from 0.002 to 0.035 *M*.

Oxidation to Am(VI) was achieved by the addition of solid ammonium peroxydisulfate (in excess of the stoichiometric amount) to Am(III) in 0.2 *M* nitric, perchloric or sulfuric acids, and heating in a water-bath at about 85°. In approximately ten minutes the characteristic pink color of Am(III) was replaced by a straw-yellow color which changed to a reddish-brown. In stronger acid, *e.g.*, 2 *M*, the oxidation did not occur.

Addition of solid argentic oxide to a solution of Am(III) in 0.3 *M* perchloric acid gave complete oxidation to Am(VI). Argentic oxide added to Am(V) in perchloric acid solution also yielded Am(VI). An experiment with cerium (at a IV/III ratio of 12/1) gave only 5% oxidation of Am(III) to Am(VI) in hot 6 *M* perchloric acid. Cerium(IV) added to Am(V) caused oxidation to Am(VI) in 1 *M* perchloric acid. Periodic acid and hypochlorous acid both failed to oxidize Am(III) in dilute acid solution.

The anodic oxidation of Am(III) in various concentrations of perchloric acid was studied. A single compartment cell was used with platinum electrodes having an anode to cathode surface ratio of about 200:1 and a current density of *ca.* 0.025 amp./sq. cm. at the anode. The maximum yield (*ca.* 80%) of Am(VI) was obtained in 6 *M* perchloric acid after an hour of electrolysis. At lower acidities, no measurable oxidation occurred.

The acidification of a dilute acid solution of Am(V) to 3 *M* hydrogen ion concentration or greater was found to cause rapid disappearance of Am(V) with corresponding growth of Am(VI) and Am(III). Preliminary experiments show that the disproportionation reaction is second order with respect to Am(V) and has a fourth order hydrogen ion dependence.

Identification of Am(VI). (1) Sodium Americyl Acetate.—A 0.02 *M* solution of Am(VI) in 0.3 *M* perchloric acid was made 2 *M* in sodium acetate. A lemon-yellow precipitate formed which was centrifuged and dried with acetone. Under the microscope, the precipitate was found to consist of isotropic crystals with tetrahedral habit, similar, except for color, to the sodium uranyl and sodium plutonyl acetates. The index of refraction of the crystals was in the range expected for sodium americyl acetate. No Am(III) or Am(V) absorption lines were observed in the compound. (The refractive index of sodium neptunyl acetate also was measured in this study.) Comparison of refractive index values for the $NaMO_2(OOCCH_3)_3$ compounds are given in Table I.

TABLE I

REFRACTIVE INDICES OF $NaMO_2(OOCCH_3)_3$ n_D

Compound	Refractive index
$NaUO_2(OOCCH_3)_3$[9]	1.5015 ± 0.0005
$NaNpO_2(OOCCH_3)_3$	1.5105 ± .0005
$NaPuO_2(OOCCH_3)_3$[9]	1.518 ± .001
$NaAmO_2(OOCCH_3)_3$	1.528 ± .002

X-Ray diffraction patterns revealed a cubic structure with a lattice constant a_0 = 10.6 Å., the same as that of the uranyl, neptunyl and plutonyl analogs.

Further proof of the existence of Am(VI) in this com-

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[1] Presented in part before the Division of Physical and Inorganic Chemistry at the Chicago Meeting of the American Chemical Society in September, 1950. This work sponsored by the A.E.C.

[2] L. B. Asprey, S. E. Stephanou and R. A. Penneman, THIS JOURNAL, **72**, 1425 (1950).

[3] B. B. Cunningham, "The Transuranium Elements," National Nuclear Energy Series, IV, Vol. 14B, Part II, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 1363.

[4] S. G. Thompson, L. O. Morgan, R. A. James and I. Perlman, *ibid.*, p. 1339.

[5] L. B. Werner and I. Perlman, *ibid.*, p. 1586.

[6] B. B. Cunningham, private communication.

[7] S. G. Thompson, B. B. Cunningham and G. T. Seaborg, THIS JOURNAL, **72**, 2798 (1950).

[8] K. Street, Jr., and G. T. Seaborg, *ibid.*, **72**, 2790 (1950).

[9] E. Staritzky, unpublished work.