conventional methods and distilled at 12 mm. As seen from the refractive indices (n^{25}_D 1.4149 reported for caproic acid, and n^{25}_D 1.4387 and n^{25}_D 1.4454 for the two nonenoic acids which could form[4]), the second and third fractions were largely nonenoic acids.

TABLE IV

Wt., g.	B.p., °C.	$n^{21.5}_D$
1.47	70–110	1.4229
3.49	110–132	1.4354
1.34	133–137	1.4421

Reaction of 2-Methoxyoctane with Isopropyllithium.—2-Methoxyoctane (36.0 g., 0.25 mole) was added to a filtered pentane solution (300 ml.) which contained 0.33 mole of isopropyllithium. After two hours of refluxing the reaction mixture became turbid. Heating was continued for a total of 66 hours, then water was added and the organic layer separated, dried and distilled. The fractions are given in Table V.

Fraction 2 showed 100% unsaturation in a bromine titration,[30] and gave an infrared spectrum virtually identical with that for a sample of 1-octene (Beckman IR-2T spectrophotometer).

TABLE V

Fraction	Wt., g.	B.p., °C.	n^{25}_D
1	1.06	117.5–119.8	1.4061
2	2.57	120.0–121.0	1.4063
3	0.43	121.2–126.8	
Residue	25.62	155–177	

Reaction of Isopropyllithium with 2-Octene.—2-Octene (27.85 g., n^{25}_D 1.4117) was added to a solution of isopropyllithium, prepared from 9.7 g. of lithium and 39.2 g. of isopropyl chloride and refluxed in a nitrogen atmosphere for 72 hours. The solution was then decomposed on ice and worked up as before. Distillation yielded 22.6 g. of octene, b.p. 122.8–124.2° (more than 90% boiled at 124.0–124.2°), n^{25}_D 1.4116. The infrared analysis showed that this material was 2-octene; isomerization, if any, amounted to less than a few per cent. Therefore, the 1-octene from the reaction of isopropyllithium and 2-methoxyoctane must have resulted from the elimination reaction, and not from a subsequent isomerization of 2-octene to 1-octene *via* a metalation reaction.

EVANSTON, ILLINOIS RECEIVED JUNE 22, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Exchange Studies with Complex Ions. III. The Nature of the Complex Formed between Cobalt(II) and Potassium Cyanide, and its Exchange with Radiocyanide Ion in Aqueous Solution[1]

BY ARTHUR W. ADAMSON

The only solid complex that is known to form from cobalt(II) and potassium cyanide has been shown to have the empirical formula $K_3Co(CN)_5$, rather than $K_4Co(CN)_6$, as previously supposed. The solid is diamagnetic with specific susceptibility -0.196×10^{-6}, but is paramagnetic in excess aqueous cyanide, with susceptibility corresponding to one unpaired electron per cobalt. Evidence is presented which indicates that the cobalt(II) cyanide complex in excess aqueous cyanide exists primarily as a pentacyanide rather than as a hexacyanide. The complex is found to undergo complete exchange with radiocyanide ion in two minutes, but the exchange with hexacyanocobaltate(III) ion is negligible in several days. The above data, and other information available on cobalt(II) complexes, indicate that the existence of hexacovalent cobalt(II) is improbable, and this the cobalt(II) pentacyanide may exist in aqueous solution as $Co(CN)_5^{-3}$ rather than as the hexacoordinated ion $Co(H_2O)(CN)_5^{-3}$.

It is well known that cobalt(II) ion forms some type of complex cyanide. For example, on adding dilute potassium cyanide solution to one of a cobalt(II) salt, a brownish-green precipitate forms, which dissolves in excess cyanide to give a yellowish-green solution; from this solution, by the addition of alcohol, or by cooling, a violet crystalline material can be precipitated, whose formula has been reported to be $K_4Co(CN)_6$.[2]

The present investigations were initiated with the object of studying the exchange behavior of the hexacyanocobaltate(II) ion which has been supposed to be present in an aqueous solution of the violet crystals. It became apparent, however, that the evidence for the existence of this ion was questionable, and that a study of the nature of the cobalt(II) cyanide complex would be a necessary precursor to the interpretation of any exchange results, as well as a subject of interest in itself. Thus while many investigators have referred to the cobalt(II) complex as a hexacyanide,[3] this supposition appears to have been based primarily upon the reported formula for the violet solid and the reasonable assumption that the same structure would persist in solution. This argument is vitiated by the findings, reported below, that the solid actually has the empirical formula $K_3Co(CN)_5$. Moreover, Hume and Kolthoff[4] have pointed out that there is reason to believe that in moderately concentrated solutions the dominant form is a pentacyanide, which they take to be an aquopentacyanide. Thus the initial precipitate formed on addition of cyanide to a solution of a cobalt(II) salt dissolves at the point of five cyanides per cobalt. Hume and Kolthoff, in addition, found that after oxidation of the cobalt(II) complex, the observed polarographic wave corresponded to pentacyanoaquocobaltate(III) ion rather than to hexacyanocobaltate(III) ion.

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[1] These investigations were carried out under contract N6 onr 23809 between the University of Southern California and the Office of Naval Research.

[2] (a) W. Biltz, W. Eschweiler and A. Bodensiek, *Z. anorg. allgem. Chem.*, **170**, 161 (1928); (b) A. Descamps, *Ann. chim. phys.*, [5] **24**, 178 (1881); (c) A. Rosenheim and I. Koppel, *Z. anorg. Chem.*, **17**, 67 (1898).

[3] (a) H. Brintzinger and H. Osswald, *ibid.*, **225**, 217 (1935); **220**, 172 (1934); (b) S. S. Bhatnagar, M. L. Khauna and M. B. Neugi, *Phil. Mag.*, **25**, 234 (1938); (c) J. Cremoux and P. Mondain-Monval, *Bull. soc. chim.*, 700 (1949); (d) H. G. Grube, *Z. Elektrochem.*, **32**, 561 (1926); (e) L. Szego and P. Ostinelli, *Gazz. chim. ital.*, **60**, 946 (1930). See also reference 4.

[4] D. N. Hume and I. M. Kolthoff, THIS JOURNAL, **71**, 876 (1949).

Results and Discussion

I. The Solid Cobalt(II) Cyanide Complex

Experimental

Preparation and Analysis of the Complex.—Cool, concentrated potassium cyanide solution was added to cooled 0.2 *f* cobalt(II) nitrate, in nitrogen atmosphere, in amount corresponding to *ca.* 6.2 cyanides per cobalt, then an equal volume of 80% alcohol was added, and the mixture slowly chilled until a mass of thin violet platelets appeared. These were filtered rapidly, washed briefly with cold 80% alcohol, pressed dry by attaching a rubber over the filter funnel, then dried in a vacuum desiccator. This variation of Descamps' method[2b] was the most satisfactory, although Rosenheim's procedure,[2c] namely, the cooling of a very concentrated mixture of the reagents, gives a similar product. The crystals were biaxial under a petrographic microscope.

The equivalent weight was determined by adding a solution of the complex in dilute potassium cyanide to excess ferricyanide and titrating the excess by the method of Muller and Diefenthaler.[5] All steps but the last were carried out in nitrogen atmosphere, by an adaptation of the apparatus of Fig. 1. For the cobalt and potassium analyses, reagent grade sulfuric acid was added to samples of the solid, and the cyanide removed by fuming to dryness; the residue was then taken up in water, and the resulting solution analyzed either for cobalt, by precipitation as potassium nitrocobaltate(III) and titration of the nitrite with permanganate,[6] or for potassium, as potassium chloroplatinate. Nitrogen was determined by a micro Dumas method, with added V_2O_5 to enhance the completeness of the oxidation; even so, the result is probably low. Attempts to determine carbon by combustion, or cyanide, by Colman's method,[7] gave obviously low results.

A number of attempts were made to prepare a cobalt(II) compound containing six cyanides per cobalt, by varying the concentration of reagents in aqueous solution, by using dry reagents, and by mixing methyl alcohol solutions of cobalt(II) chloride and potassium cyanide; in all cases either the same violet material resulted, or the product consisted of mixtures of cobalt(II) and (III) cyanides or oxides.

The solid reported to be $K_4Co(CN)_6$ was prepared by Descamps' method,[2b] and the results of the analyses are given in Table I.

TABLE I

ANALYSIS OF THE POTASSIUM COBALT(II) CYANIDE COMPLEX

	Equiv. wt.	Weight, % Co	Weight, % K	Weight, % N
Found	318	18.7	39.0	22.1
	317	18.7	40.3	
Av.	317.5	18.7	39.7	
Calcd.				
$K_4Co(CN)_6$	371	15.9	42.2	22.6
$K_3Co(H_2O)(CN)_5$	324	18.1	36.1	21.6
$K_3Co(CN)_5$	306	19.2	38.4	22.9
$K_3Co(CN)_5 \cdot 0.17$ KCN	317	18.6	39.1	22.9

It is seen that the results correspond to the formula $K_3Co(CN)_5$, provided that about 0.17 mole or 3.5% potassium cyanide are assumed present. Some of such a contaminant is to be expected since the crystals were formed from a mother liquor containing excess cyanide; they could not be recrystallized without excessive decomposition.

This solid, here considered to be $K_3Co(CN)_5$, has been reported to be diamagnetic,[3e,8] an interesting result in view of the odd number of electrons in cobalt(II). To confirm this observation, the specific susceptibility was determined by Dr. S. S. Dharmatti, by means of a Gouy balance, and found to be -0.196×10^{-6}.[9] Taken in conjunction with the apparent coördination number of five, this diamagnetism suggests that pairing of the odd electron in cobalt(II) occurs by dimer or polymer formation. Superficially, at least, iron enneacarbonyl might represent an analogous case; the spins of the two iron atoms are paired to give a diamagnetic complex.[10] There are three ketone type carbonyl bridges in iron enneacarbonyl, and the analogous structure for $K_3Co(CN)_5$ would contain two cyano bridges.[10a] Such bridges seem unlikely, however, and it appears desirable to delay further speculation on possible structures until more evidence, such as X-ray diffraction data, is available.

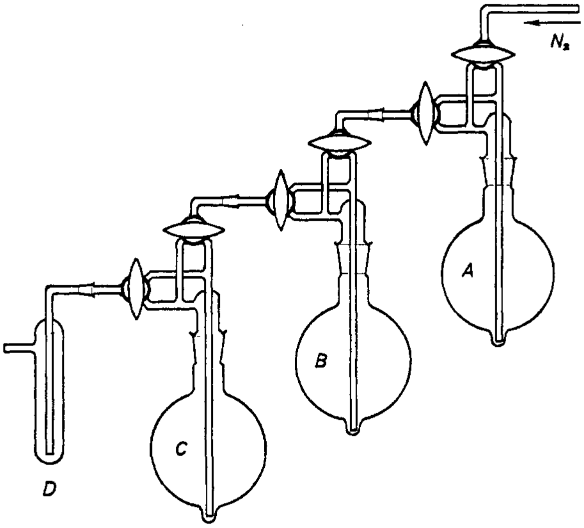

Fig. 1.—Apparatus for exchange experiments.

II. The Cobalt(II) Cyanide Complex in Aqueous Solution

Experimental

Determination of the Magnetic Susceptibility of the Cobalt(II) Cyanide Complex in Solution.—The measurements were made by means of the same Gouy balance as before,[11] using a Gouy tube containing a small cup centered in the upper portion. The tube was filled with 0.1 *f* deaerated potassium cyanide, and the cup, with sufficient solid to give a 0.1 *f* solution of the complex when dissolved; air was then removed by aspirator suction, and the tube sealed. The weight of the tube in the field was determined before and after dissolution of the solid. The calculated specific susceptibility was corrected for the diamagnetism of the constituents, using the value found for the solid. Any small amount of oxidation would not have affected the results drastically, since the resulting cobalt(III) complexes are diamagnetic.

The following information was obtained on the stoichiometry of the complex in solution. First,

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(5) E. Muller and O. Diefenthaler, *Z. anorg. Chem.*, **67**, 418 (1910).

(6) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, p. 605.

(7) H. G. Colman, *Analyst*, **33**, 267 (1908); **35**, 295 (1910).

(8) D. M. Bose, *Z. Physik*, **65**, 677 (1930).

(9) If the values -18.5×10^{-6} and -10.3×10^{-6} are taken for the molar susceptibilities of potassium and cyanide ions, respectively, the value for cobalt is 50.6×10^{-6}. This small positive value is comparable to that found by Welo (L. A. Welo, *Phil. Mag.*, [7] **6**, 481 (1928)) for cobalt(III) in diamagnetic cobaltic complexes.

(10) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 254.

(10a) See K. A. Jensen and R. W. Asmussen, *Z. anorg. Chem.*, **252**, 234 (1944).

(11) The measurements were made by Mr. O. Holecek.

it was confirmed that the first permanent precipitate on titration of potassium cyanide with cobalt(II) chloride occurred at five cyanides per cobalt. Secondly, if excess potassium cyanide is added to dilute cobalt(II) chloride, and the complex oxidized with ferricyanide, the free cyanide, on back titration by the Liebig method, corresponded to 5.1 bound cyanides per cobalt. The same result was obtained with a waiting period of 2.5 hours (in nitrogen atmosphere) before oxidation and back titration. The potentiometrically determined ferricyanide titer corresponded to 1 and 17% oxidation of the cobalt in the two experiments, respectively. These results show that even in excess cyanide, the oxidation product is a pentacyanide and suggest that if hexacyanocobaltate(II) ion does exist in such a solution, it is in rapid equilibrium with a stable species containing five cyanides per cobalt.

The nature of the complex was further studied through its magnetism. It was found that, when dissolved in dilute potassium cyanide, the diamagnetic $K_3Co(CN)_5$ became paramagnetic, with a molar susceptibility of 1240×10^{-6}, giving a $\mu_{eff.}$ of 1.72 for the cobalt, which corresponds to one (1.28) unpaired electron, assuming no orbital contributions. This finding rules out any associated form such as for the solid, and indicates that the complex is covalent rather than ionic, but does not permit a choice between pentacoördinated cobalt (as $Co(CN)_5^{-3}$) and hexacoördinated cobalt (as $Co(H_2O)(CN)_5^{-3}$) since both should have one unpaired electron.

III. Exchange Experiments

Experimental

Apparatus.—The cobalt(II) cyanide complex is a strong reducing agent, and it was essential that the exchange experiments be carried out in the absence of oxygen. A train of three 250-ml. flasks was set up, as shown in Fig. 1, by means of which solutions could be deaerated, and also transferred from one flask to another by means of nitrogen pressure. The tank nitrogen used was purified by passage through aqueous chromous chloride (with suspended amalgamated zinc), and scrubbed by passage through silver nitrate solution and then water. Before proceeding with a run, the absence of oxygen in the effluent nitrogen was tested by bubbling it through oxygen-free alkaline pyrogallol solution and noting if any darkening occurred in ten or fifteen minutes. The bubbler labeled D was a test-tube containing cadmium nitrate solution into which solution from flask C could be delivered when taking an exchange point.

Separation Procedure and Radioactivity Analysis.—The separation method was analogous to that described previously for hexacyanocobaltate(III) ion,[12] namely, precipitation of the cobalt complex by means of cadmium nitrate, then precipitation of the remaining radiocyanide as silver cyanide, and conversion of the latter to zinc cyanide for specific activity determination. The samples were counted by means of a flow counter employing an atmospheric pressure mixture of 1.3% butane in helium, and were corrected for coincidence and self absorption.

The radiocyanide tracer was prepared from $BaC^{14}O_3$ by the sodium azide method.[13,14]

Procedure for the Exchange Runs.—Solutions of cobalt(II) nitrate (standardized by the cobaltinitrite method[6]), potassium cyanide and potassium radiocyanide were placed in flasks A, B and C, respectively. After deaeration, the contents of flask A were transferred to flask B, forming the characteristic yellowish-green solution of the complex. After a pre-equilibration time, the contents of flask B were transferred to flask C, and, after the desired exchange time, a portion of the contents of C were delivered into D. Tube D was then removed from the train and the rest of the separation procedure carried out in the open.

The procedure for the determination of the exchange with hexacyanocobaltate(III) was quite similar, except that flask B contained potassium radiocyanide solution, and C, the cobalt(III) complex.

Exchange of Radiocyanide with the Cobalt(II) Cyanide Complex.—The results of the experiments on the rate of exchange of radiocyanide with the cobalt(II) pentacyanide complex are given in Table II. The concentrations given are those for the final mixture, while the letters A, B and C denote the flask into which the initially separate solutions were placed (see Fig. 1 and Experimental). In one instance, a pre-equilibration time of four hours was used, to determine whether there was any slow formation of a complex stable to exchange. It is seen, however, that the exchange was essentially complete in all cases; moreover, it seems improbable that this result could be due to catalysis during separation since the same method has been employed for other transition metal complex cyanides without difficulty.[12]

TABLE II

EXCHANGE OF RADIOCYANIDE WITH THE COBALT(II) PENTACYANIDE COMPLEX

Concentrations, *f*					
Co^{++} A	CN^- B	$C^{14}N^-$ C	Pre-equil. time, min.	Exch. time, min.	Exch.,[a] %
0.0166	0.108	0.0086	2	2	94
			2	2	117
.025	.285	.0129	240	11	91[b]

[a] Defined as ay/bx where a and b denote the moles of free cyanide and of cyanide assumed to be complexed, respectively, and x and y the corresponding activities. [b] In the dark.

Exchange between the Cobalt(II) Cyanide Complex and Hexacyanocobaltate(III) Ion.—Hexacyanocobaltate(III) ion does not exchange with free cyanide,[12] and if any such exchange did occur in the presence of cobalt(II) ion, it would presumably have to take place through an electron transfer process involving hexacyanocobaltate(II) ion, and, therefore, be a direct indication of the existence of at least small amounts of this species. This possibility was tested, with the results shown in Table III, where, again, the concentrations are those of the final mixture and the letters A, B and C have the same significance as before. The

TABLE III

EXCHANGE OF RADIOCYANIDE WITH $Co(CN)_6^{-3}$ IN THE PRESENCE OF COBALT(II) ION

Concentrations, *f*					
Co^{++} A	$C^{14}N^-$ B	$Co(CN)_6^{-3}$ C	Pre-equil. time, hr.	Exch. time	Exch., %
0.0100	0.120	0.0207	5	8 min.	2.8
				20	−1
				157	7.0
				18 hr.	8.0
.0100	.118	.0207	4	15 min.	12
				20 hr.	0
				97	7

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(12) A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

(13) A. W. Adamson, *ibid.*, **69**, 2564 (1947).

(14) The $BaC^{14}O_3$ was obtained from the Isotopes Division of the Atomic Energy Commission.

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.

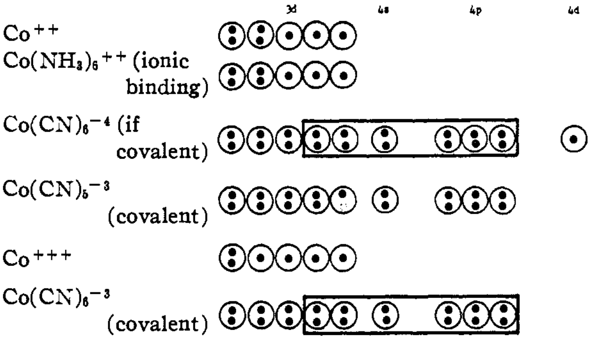
Summary and Conclusions

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).