Polarography of Copper Complexes.   III.   Pyrophosphate Complexes[1,2]

BY H. A. LAITINEN AND E. I. ONSTOTT[3]

In a study of the interaction of pyrosphophate ion with several multivalent cations, Rogers and Reynolds[4] included polarographic measurements on copper(II) in the presence of 0.1 M pyrophosphate. They observed two reduction waves which were attributed to the successive reduction of copper(II) to copper(I) and to the amalgam. The fact that the first wave was smaller than the second was attributed to a suppression of the diffusion current of the first wave by gum ghatti, which was used as a maximum suppressor.

In the present paper, a more detailed study of the copper(II)–pyrophosphate system at various pH values and concentrations is presented to offer evidence that the reduction of copper(II) proceeds directly to the amalgam. The double waves at intermediate pH values probably are caused by the presence of two complexes of copper(II) in sluggish equilibrium.

Experimental

The procedures used in this work were generally the same as those described previously.[1] Equipment used was the same except that polarograms were recorded with a Sargent Model XXI polarograph instead of the Sargent Model XI.

Anhydrous sodium pyrophosphate, made by heating sodium pyrophosphate 10-hydrate at 850° for about thirty hours, was used in making the solutions for analysis. Acetic acid was used to buffer the solutions having a pH less than 6, and a phosphate buffer was used for solutions having a pH of 6 to 8. Potassium nitrate was added as needed to keep the ionic strength of the solutions constant at a predetermined value.

Suitable maximum suppressors were found in brom cresol green and tropeoline 00. Tropeoline 00 gave a reduction wave which fortunately occurred at a potential sufficiently negative so that the diffusion current of the complex ion could be measured directly. When present in excessive amounts, both brom cresol green and tropeoline depressed the diffusion current. Gum ghatti as recommended by Rogers and Reynolds[4] also was found to be effective as a maximum suppressor. In alkaline solutions, however, gum ghatti depressed the diffusion current.

An H-cell with a temporary plug of 3% agar in 0.5 N potassium nitrate was used. The capillary used had an m value of 1.467 mg. sec.$^{-1}$ for a mercury column height of 69.8 cm.

Reversibility of the electrode reactions was

(1) Paper I, Laitinen, Onstott, Bailar and Swann, THIS JOURNAL, 71, 1550 (1949).

(2) Paper II, ibid., 72, 4724 (1950).

(3) Abstracted from the Doctorate Thesis of E. I. Onstott, 1950.

(4) Rogers and Reynolds, THIS JOURNAL, 71, 2081 (1949); Anal. Chem., 21 176 (1949).

tested by determining the slopes of plots of log $(i_d - i)/i$ vs. E. Average current values were obtained by using maximum damping of the recorder at a constant measured potential. However, for the polarographs shown in the accompanying figures, the polarograph recorded instantaneous current as the voltage changed continuously. Half-wave potentials were taken directly from the plots of log $(i_d - i)/i$ vs. E.

For precipitating cupric hydroxide in the study of the equilibrium between the complex ion present in alkaline solution and cupric hydroxide, sodium hydroxide (0.671 N) was added to 50 ml. of the solution for analysis until a permanent precipitate was visible. The pH at which the precipitate first appeared was measured with a Beckman pH meter equipped with a Type E electrode. All measurements were made at $25 \pm 0.1°$.

Discussion

A system containing a complexing ion which is in equilibrium with hydrogen ion as well as cupric ion has been treated previously.[1] The cupric ion–pyrophosphate ion equilibrium is more complicated, however, as pyrophosphate ion can be in equilibrium with up to four hydrogen ions. Here it would seem more simple to calculate the concentration of the complexing ion directly from the acid dissociation constants rather than to derive an equation which shows the variation of the half-wave potential with pH. The necessity of using a buffer in such a hydrogen ion dependent system is again emphasized.

Solutions having a pH of 3.6 to 5 gave polarograms typical of a two electron reduction of a cupric complex ion. Thus the equation[5] is valid

$$(E_{1/2})_c - (E_{1/2})_s = 0.0296 \log K_d (f_c/f_s)(D_s/D_c)^{1/2} - p\, 0.0296 \log C_x f_x$$

for interpreting the data in Table I. That two electrons are involved in the electrode reaction is apparent from the values of the slopes of the plots of log $(i_d - i)/i$ vs. E. and the diffusion current constants.

The reciprocal slope of a plot of the logarithm of the total pyrophosphate ion concentration versus the half-wave potential gives the number of coördinated groups attached to each cupric ion, as the concentration of complexing ion varies proportionately with the amount of sodium pyrophosphate put into solution at a constant pH. Such a plot for pH 4.8 is shown in Fig. 1. The reciprocal slope of 0.052 is less than the theoretical value of 0.059 for two pyrophosphate groups, but nevertheless indicative that two groups are coördinated in the predominant species of complex ion.

(5) Lingane, Chem. Rev., 29, 1 (1941).

TABLE I

POLAROGRAPHIC DATA IN ACID SOLUTION

One molar acetic acid added to adjust pH; 0.257 millimolar Cu(NO$_3$)$_2$; 0.0006% tropeoline 00 maximum suppressor; i_d measured at about 0.12 volt more negative than $E_{1/2}$.

Na$_4$P$_2$O$_7$, molar	KNO$_3$, molar	Ionic strength	pH	HP$_2$O$_7^{-3}$ calcd., millimolar	$-E_{1/2}$ vs. S. C. E.	Slope of log plot	i_d μamp.	$i_d/Cm^{2/3}t^{1/6}$
0.138	0	0.70	5.20	4.44	0.138	0.029	1.44[b,c]	1.68
.138	0	.70	4.80	1.81	.109	.030	1.10	2.56
.138	0	.70	4.85	2.02	.111	.030	2.12[b]	2.47
.069	0.25	.60	5.22	2.36	.115	.029	1.57[b,c]	1.83
.069	.25	.60	5.22	2.36	.115	.028	0.91	2.12
.069	.25	.60	5.18	2.08	.119	.029	1.97[b,c]	2.29
.069	.25	.60	4.84	.980	.095	.031	2.27[b]	2.64
.069	.25	.60	4.82	.954	.095	.031	1.16	2.70
.069	.25	.60	4.79	.882	.093	.033	2.22[b,c]	2.58
.069	.10	.60[a]	4.51	.481	.075	.032	1.19	2.77
.069	.25	.60	4.44	.405	.075	.030	1.15	2.68
.069	.25	.60	4.42	.393	.074	.031	1.15	2.68
.069	.25	.60	4.10	.182	.060	.030	2.32[b]	2.70
.035	.375	.55	5.18	1.05	.105	.036	1.69[b,c]	1.97
.035	.375	.55	4.84	.497	.078	.033	1.16	2.70
.035	.375	.55	4.82	.484	.079	.032	1.10	2.56
.035	.375	.55	4.45	.208	.060	.030	1.12	2.60
.035	.375	.55	4.10	.093	.046	.033	1.122	2.84
.035	.375	.55	4.08	.089	.049	.032	1.21	2.82
.035	.375	.55	3.90	.059	.037	.030	1.22	2.84
.017	.44	.52	4.84	.246	.060	.033	1.17	2.72
.017	.44	.52	4.81	.232	.064	.031	1.15	2.68
.100	0	.50[a]	4.52	.716	.085	.030	1.12	2.60
.100	0	.50[a]	4.51	.698	.085	.031	1.11	2.58
.050	.15	.50[a]	4.47	.317	.070	.032	1.15	2.68
.050	.25	.50	4.13	.140	.054	.031	1.18[d]	2.74
.025	.225	.50[a]	4.49	.166	.057	.032	1.15	2.68
.025	.375	.50	3.60	.021	.024	.032	1.22	2.84
.0125	.26	.50[a]	4.47	.079	.046	.032	1.19	2.77
0	.50	.50	..	...	.018	.032	2.75[b]	3.20

[a] Sodium acetate concentration constant at 0.2 molar. [b] 0.514 millimolar Cu(NO$_3$)$_2$. [c] 0.003% brom cresol green maximum supprsssor, i_d measured at −0.5 volt. [d] Gum ghatti maximum suppressor as recommended by Rogers and Reynolds.[4]

The complexing ion in the pH range of 3.6 to 5 was found to be monohydrogenpyrophosphate ion. In Fig. 2 is a plot of the logarithm of the monohydrogen pyrophosphate ion concentration, calculated from the acid dissociation constants[6,7] ($K_1 = 0.11$, $K_2 = 0.014$, $K_3 = 2.1 \times 10^{-7}$, $K_4 = 4.06 \times 10^{-10}$), versus the half-wave potential. The reciprocal slope of 0.058 shows that two monohydrogenpyrophosphate ions are coördinated when more than one excess monohydrogen pyro-
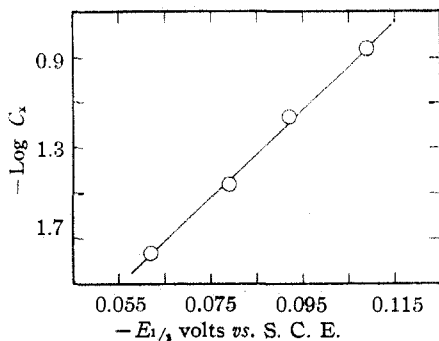

Fig. 1.—Variation of half-wave potential with total pyrophosphate concentration at pH 4.8.
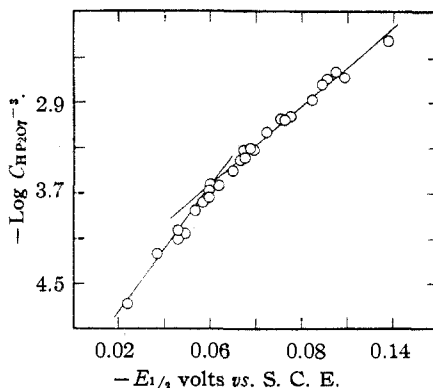

Fig. 2.—Variation of half-wave potential with monohydrogen pyrophosphate ion concentration, pH 3.6 to 5.

(6) Abbot and Bray, THIS JOURNAL, **31**, 729 (1909).
(7) Kolthoff and Bosch, Rec. trav. chim., **47**, 826 (1928).

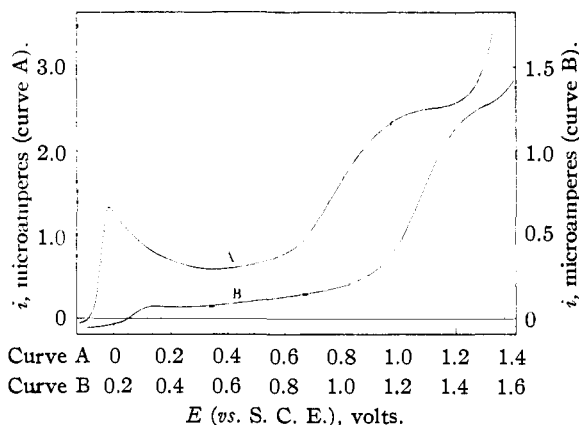Curve A　0　0.2　0.4　0.6　0.8　1.0　1.2　1.4
Curve B　0.2　0.4　0.6　0.8　1.0　1.2　1.4　1.6
E (vs. S. C. E.), volts.

Fig. 3.—Curve A, 5.14 × 10⁻⁴ M copper(II) in 0.05 M Na₄P₂O₇ and gum ghatti, pH adjusted to 5.75 with acetic acid; curve B, 2.57 × 10⁻⁴ M copper(II) in 0.10 M Na₄P₂O₇ and gum ghatti, pH 10.4.

phosphate ion per cupric ion is present, while the value of 0.035 shows that but one monohydrogen pyrophosphate ion is coördinated at lower concentrations of the complexing ion.

It was not anticipated that the monohydrogen pyrophosphate ion would be the complexing ion in the pH range of 3.6 to 5 where more than 90% of the pyrophosphate is present as dihydrogen pyrophosphate ion. But in acting as electron pair acceptors, both cupric ion and hydrogen ion are in competition for the pyrophosphate ion. Thus, cupric ion on coördination should replace hydrogen ion(s). A similar case has been observed by Watters and Kolthoff,[8] who found that both manganese(II) and manganese(III) coördinate three dihydrogen pyrophosphate ions at zero pH where the main pyrophosphate species is the undissociated acid.

Van Wazer and Campanella[9] have discussed the release of hydrogen ions from polyphosphates upon coördination with metal ions.

Dissociation constants for bis-(monohydrogen pyrophosphate) cuprate(II) ion and (monohydrogen pyrophosphate) cuprate(II) ion were calculated, assuming the ratio of the activity coefficients of the ions and of the diffusion coefficients to be unity. For the former complex ion a dissociation constant of 1×10^{-10}, and for the latter a value of 4×10^{-7} was calculated.

Solutions having a pH of 5 to 12.5 gave unusual polarograms in that a double wave was observed, the height of each wave varying with pH (see Figs. 3, 4). The current of the first wave, which had the same value as the total current at a pH less than 5, decreased rapidly as the pH was increased from 5 to 7. At this latter pH it had a very small value which did not decrease much further as the pH was increased to about 10. However, when the pH was increased above 10, the

(8) Watters and Kolthoff, THIS JOURNAL, 70, 2455 (1948); Ind. Eng. Chem., Anal. Ed., 15, 8 (1943).
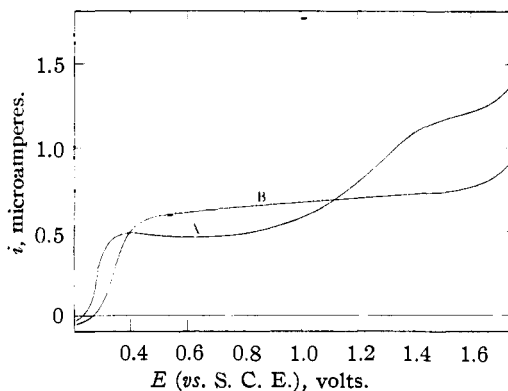(9) Van Wazer and Campanella, ibid., 72, 655 (1950).

0.4　0.6　0.8　1.0　1.2　1.4　1.6
E (vs. S. C. E.), volts.

Fig. 4.—Curve A, 2.57 × 10⁻⁴ M copper(II) in 0.05 M Na₄P₂O₇ and gum ghatti, pH adjusted to 12.0 with NaOH; curve B; same as A, except pH 12.35.

current of the first wave increased until it became equal to the total current at a pH of about 12.5. Thus, the wave occurring at the more negative potential was not observed at a pH less than 5 or at a pH greater than 12.5.

TABLE II

EFFECT OF pH ON FIRST WAVE HEIGHT; EFFECT OF GUM GHATTI

Solutions contained 0.257 millimolar Cu(NO₃)₂; gum ghatti maximum suppressor (4); current of first wave measured at −0.75 volt, total current measured at −1.5 volt.

Na₄P₂O₇, molar	pH	i of first wave, μamp.	i_d total, μamp.	$i_d/Cm^{2/3}t^{1/6}$
0.050	4.45[a]	1.15[d]	1.15[e]	2.68
.069	4.8[a]	1.16[d]	1.16[e]	2.70
.069	5.2[a]	.91[d]	...	..
.050	5.75[a]	.46	2.19[e,f]	2.63
.050	6.9[b]	.08	0.99[e]	2.38
.050	7.45[b]	.05	1.00[e]	2.40
.050	10.2	.01	0.90	2.18
.100	10.4	.05	.91	2.21
.050	11.55[c]	.09	.92	2.23
.050	12.0[c]	.40	.92	2.23
.050	12.35[c]	.61	.68	1.65
.200	12.5[c]	.66	...	1.53
.100	12.55[c]	.60	.58	1.41
.050	12.6[c]	.57	.52	1.33

[a] pH adjusted with acetic acid. [b] 0.05 M KH₂PO₄ added to solutions. [c] pH adjusted with sodium hydroxide. [d] Tropeoline 00 maximum suppressor; current measured at −0.2 volt. [e] Current measured at −1.4 volt. [f] Solution contained 0.514 millimolar cupric ion.

TABLE III

EFFECT OF pH ON TOTAL DIFFUSION CURRENT

No maximum suppressor present; refer to Table II for other experimental conditions.

Cu(NO₃)₂, millimolar	Na₄P₂O₇, molar	pH	i_d total, μamp.	$i_d/Cm^{2/3}t^{1/6}$
0.257	0.050	7.5	0.99	2.38
.514	.069	7.8	2.00	2.40
.257	.050	10.3	1.00	2.42
.257	.050	12.0	1.01	2.45
.257	.100	12.5	1.14	2.65
.257	.050	12.6	1.16	2.70

Results of experiments to find the effect of pH on the current of the two waves are given in Tables II and III. In Table II are listed data which show the change in current with pH of the first wave and the total diffusion current of both waves in the presence of gum ghatti. Data in Table III are included to show the effect of pH on the total diffusion current in the absence of gum ghatti, which depressed the current in alkaline solutions.

That the current of the first wave is diffusion controlled is questionable, as the current–time relationship is not normal for a diffusion controlled process (Fig. 3). However, it was found that the current varied approximately with the square root of the mercury column height, as would be expected if the current were controlled by diffusion above.

Reversibility of the electrode reaction of the first reduction process was not tested for solutions having a pH between 5.3 and 12.5, as the maximum was not completely suppressed. A plot of log $(i_d - i)/i$ vs. E was made for a solution having a pH of 12.5, however, and a value of 0.061 was formed for the slope. Such a value is usually indicative that one electron is added reversibly but, as will become apparent later, this value can be more logically interpreted as being evidence for an irreversible two electron reduction. Qualitatively it was observed that the approximate half-wave potential of the first reduction process shifted from -0.1 volt to -0.3 volt (vs. S.C.E.) when the pH was increased from 5 to 12.5, the total pyrophosphate concentration remaining constant at 0.05 molar.
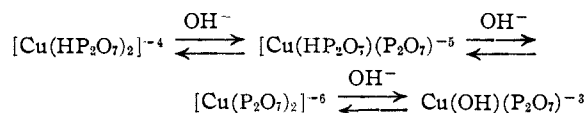
The reversibility of the electrode reaction of the reduction process occurring at the more negative potential was not tested, as it was apparent from the polarograms that the drawn-out waves would not give slopes for plots of log $(i_d - i)/i$ vs. E comparable to even a one-electron reduction. The half-wave potential of this reduction process also shifted to more negative values as the pH was increased. At a pH of 5.75, the approximate half-wave potential was -1.0 volt (vs. S.C.E.), and at a pH of 12 it was -1.3 volt, the total pyrophosphate concentration being 0.05 molar in both cases.

Rogers and Reynolds[4] have previously studied the polarography of pyrophosphate complexes of copper, but their studies were confined to a much narrower pH range. Thus they did not observe the behavior in the low and high pH ranges. They interpreted the double wave as being two independent one electron reductions of dipyrophosphatecuprate(II) ion, but for this to be true, the waves should be of equal height, and the ratio of their heights should not vary with pH. The polarographic behavior of cupric ion in the presence of pyrophosphate above a pH of 5 but lower than a pH of 12.5 seems to be typical of that described by Lingane[10] for ferric ion in the presence

of tartrate at a pH of 6 to 8. He ascribes the appearance of the two waves of unequal height to the reduction of two different complex ions which are not rapidly and reversibly interconverted on reduction, one being more easily reduced than the other. A similar interpretation here seems logical.

Because of the irreversible character of the electrode processes at pH values above 5, it is not possible to deduce with certainty the nature of the complex ions present. As will be shown below, the complex at very high pH is the hydroxopyrophosphate cuprate(II) ion which exists in equilibrium with cupric hydroxide when the latter begins to precipitate.

Accordingly, as the pH is increased beyond 5, the following series of equilibria may be postulated as the simplest which would be consistent with the experimental data

$$[Cu(HP_2O_7)_2]^{-4} \underset{\longleftarrow}{\overset{OH^-}{\rightleftharpoons}} [Cu(HP_2O_7)(P_2O_7)]^{-5} \overset{OH^-}{\rightleftharpoons}$$

$$[Cu(P_2O_7)_2]^{-6} \underset{\longleftarrow}{\overset{OH^-}{\rightleftharpoons}} Cu(OH)(P_2O_7)^{-3}$$

The decreasing height of the first wave in the pH range of 5 to 10 may be attributed to the decreasing concentration of the bis-(monohydrogen pyrophosphate) cuprate(II) ion. The wave at the more negative potential probably results from the reduction of increasing amounts of pyrophosphate (monohydrogen pyrophosphate) cuprate-(II) ion or dipyrophosphatecuprate(II) ion. The fact that the diffusion current constant at a pH of 7 to 10 is about 10% lower than at a pH of 5 is evidence for the formation of an ion of higher charge and/or a lower equivalent ionic conductance. The diffusion coefficient of an ion varies directly with its equivalent ionic conductance and inversely with its charge.[11] Increasing the charge of an ion would cause a proportional increase in equivalent ionic conductance, if it were not partially compensated by an increase in the degree of hydration. The diffusion coefficient varies with the degree of hydration, and hence indirectly is a measure of the charge, as long as two pyrophosphate groups are attached to each cupric ion.

At pH values between 10 and 12.5, the early reduction wave increased in height with increasing pH, until a wave height about equal to that for bis-(monohydrogen pyrophosphate) cuprate(II) ion was reached. It is particularly striking that in the narrow pH interval of 12.0 to 12.6 (Fig. 4) the polarographic curve changed from two waves of nearly equal height to a single wave, and that in this same pH interval the total diffusion current increased by nearly 10% (Table III). The large diffusion current constant at high pH is evidence for the formation of an ion of decreasing charge in highly alkaline solution. That this ion is the hydroxopyrophosphate cuprate(II) ion was shown by determining the pH at which cupric hydroxide was precipitated from solutions containing

(10) Lingane, This Journal, 68, 2448 (1946).

(11) Lingane and Kolthoff, ibid., 61, 825 (1939).

copper in the presence of an excess of pyrophosphate ion.

It was possible to evaluate the equilibrium constant for the reaction

$$[Cu(OH)(P_2O_7)]^{-3} + OH^- \rightleftharpoons Cu(OH)_2 + P_2O_7^{-4}$$
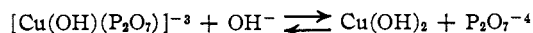
where $K_{eq.} = C_{P_2O_7^{-4}}/C_{complex\ ion}\ C_{OH^-}$. Data obtained in this part of the investigation are listed in Table IV.

TABLE IV

EQUILIBRIUM CONSTANT FOR PRECIPITATION OF $Cu(OH)_2$

$Na_4P_2O_7$,[a] molar	Complex ion, millimolar	Ionic strength	pH of pptn.	$K_{eq.} \times 10^{-3}$
0.0456	0.973	0.5	12.28	2.5
.0461	0.973	.5	12.25	2.7
.0459	2.50	.5	11.67	3.9
.0437	5.06	.5	11.45	3.1
.0437	5.06	.5	11.33	4.1
.0935	5.05	1.0	11.60	4.7

[a] Corrected for coördinated $P_2O_7^{-4}$.

Although the equilibrium constant shows nearly a two-fold variation over the range of experimental conditions used, the constancy may be deemed satisfactory in view of the uncertainty of the activity coefficients of multivalent ions, even at a constant ionic strength, and the uncertainty of liquid junction potentials at high pH values.

Trial calculations of an equilibrium constant based on the assumed presence of dipyrophosphate cuprate(II) ion in equilibrium with cupric hydroxide gave values varying by twenty-fold.

The dissociation constant for hydroxopyrophosphate cuprate(II), $K_d = C_{Cu^{++}}C_{P_2O_7^{-4}}C_{OH^-}/C_{Complex\ ion} = K_{eq}K_{sp}$, was calculated to be 2×10^{-16}, using the value of 3.3×10^3 for K_{eq} and the value of 5.6×10^{-20} for K_{sp}.[12]

Summary

1. From polarographic data it was shown that cupric ion coördinates two monohydrogen pyrophosphate ions in solutions having more than onefold excess of the complexing ion present. One monohydrogen pyrophosphate ion is coördinated when less than onefold excess of the complexing ion is present. These complex ions were identified in the pH range of 3.6 to 5.3. Evidence was given for the existence of pyrophosphate (monohydrogen pyrophosphate) cuprate(II) ion and/or dipyrophosphate cuprate(II) ion in the pH range of 7 to 10.

It was shown from data obtained with a glass electrode that hydroxopyrophosphate cuprate(II) ion exists in strongly alkaline solution.

2. Dissociation constants for bis-(monohydrogen pyrophosphate)-cuprate(II) ion and (monohydrogen pyrophosphate)-cuprate(II) ion were calculated from polarographic data. The dissociation constant of hydroxopyrophosphate-cuprate(II) ion was calculated from pH measurements.

(12) Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, p. 174.

URBANA, ILL.   RECEIVED MARCH 11, 1950

Low Temperature Heat Capacities of Inorganic Solids.[1] I. The Heat Capacity of Boric Acid from 16 to 296°K. Description of The Ohio State University Solid Calorimeters

BY HERRICK L. JOHNSTON AND EUGENE C. KERR

Introduction

This Laboratory is engaged on a program of measuring the low temperature heat capacities and the derived thermal functions of the simple compounds of the lighter elements, including compounds of boron. The present paper deals with boric acid, a compound of thermodynamic interest because of its widespread technological uses. It is also of interest because of the unique type of disorder phenomena that it displays. No previous measurements of the heat capacity of boric acid have been reported in the literature.

Apparatus

Calorimeter.—Measurements were made with a Nernst vacuum calorimeter of the general design developed by Giauque and his co-workers[2] at the University of California, but incorporating some improvements in the cryostat,[3] block, wire, seals and vacuum fittings. In most of its details, the calorimeter assembly is similar to the Ohio State condensed gas calorimeter described in detail in our paper on hydrogen.[4] Seven of these solid calorimeters, constructed and assembled in this Laboratory, are being used in determining the low temperature heat capacities of various inorganic solids, of which this paper describes only boric acid.

Figure 1 is a view of the calorimeter and block assembly with the lower block and vacuum-tight container removed. This instrument is similar to our condensed gas calorimeter[5] with elimination of the monel capillary that served as a filling tube.

The solid calorimeter is suspended from the upper block by three loops of silk thread and is made from 40-mm.

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

(2) (a) W. F. Giauque and R. Wiebe, THIS JOURNAL, 50, 101 (1928); (b) W. F. Giauque and H. L. Johnston, ibid., 51, 2300 (1929).

(3) H. L. Johnston, Rev. of Sci. Instr., to be published.

(4) H. L. Johnston, J. T. Clarke, E. B. Rifkin and E. C. Kerr, THIS JOURNAL, 72, 3933 (1950).

(5) Cf. Fig. 1 of ref. 4.