the results on racemization of trioxalatochromate (III) reported by Bushra and Johnson.[10] Table II gives the values calculated for these reactions.

TABLE II

	$\Delta S^{\ddagger}$, cal./deg.	$\Delta H^{\ddagger}$, kcal.	$\Delta F^{\ddagger}_{298}$, kcal.
trans–cis Isomerization dioxalatodiaquochromate(III)	−15.3	17.5	22.1
Exchange of H_2O for Cl in dichlorotetraaquochromium(III)	−16.3	14.4	19.3
Racemization of trioxalatochromate-(III)	−24.5	14.9	22.3

Long[11] has conclusively demonstrated that the racemization of trioxalatochromate(III) does not involve the separation of oxalate ions from the complex. It is likely that this separation of oxalate ions does not occur in the isomerization of the dioxalatochromate(III). It may be postulated that the reaction could occur upon collision of the *trans* complex ion with a properly oriented water molecule. A reaction intermediate would be formed in which the incoming water molecule would occupy a position in the chromium octahedron. The end of the oxalate thus released could be held loosely by the three water molecules, possibly through hydrogen bonding. If the central water were released the *trans* isomer would be recovered, but if either of the other water molecules were released by rebonding the oxalate, the *cis* isomer would be the product. This reaction may be represented by

$$trans + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{intermediate} \underset{k_4}{\overset{k_3}{\rightleftarrows}} cis + H_2O$$
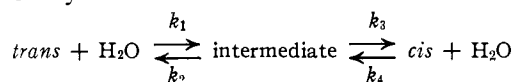
(10) E. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1937 (1939).

(11) F. A. Long, THIS JOURNAL, **61**, 570 (1939).

In order to explain the results obtained, both k_2 and k_3 would have to be very large with respect to k_1, and to explain the final equilibrium being shifted very far in the direction of the *cis* isomer k_1 must be very large with respect to k_4. If the slow steps are those forming the intermediate there will be no appreciable amount of the intermediate present at any time as it will be reacting very rapidly to form the end-products. The negative entropy of activation obtained is in agreement with this postulate, since in addition to requiring a properly oriented water molecule, which will require the water molecule to lose its rotational freedom, there is the formation of the additional bond in the intermediate.

The exchange of a water molecule for a chloride in the dichlorotetraaquochromium(III) has essentially the same entropy of activation and therefore can be assumed to involve the same type process. The greater part of the negative entropy of activation in both cases can be explained by the loss of freedom of rotation of a water molecule. In the case of the racemization of the trioxalatochromate (III) the large negative entropy of activation may involve either the requirement of two properly oriented water molecules or a transmission coefficient which is considerably less than unity.

The lower heat of activation in the case of the racemization of the trioxalatochromate may be explained by the fact that this is a triply negative charged ion instead of a singly negative charged ion as in the case of the dioxalatochromate. This larger negative charge would make it easier to separate the bonds to give the reaction intermediate despite the fact that there are two bonds to be separated.

SALT LAKE CITY 1, UTAH

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE OHIO STATE UNIVERSITY]

Spectrophotometric Investigation of the Complexes Formed between Copper and Pyrophosphate Ions in Aqueous Solution

BY JAMES I. WATTERS AND ARNOLD AARON

A series of complex species, $[Cu(P_2O_7)_2]^{6-}$, $[CuP_2O_7]^{2-}$, $[Cu_2P_2O_7]^0$ and $[Cu_4P_2O_7]^{4+}$ exist in solutions containing the corresponding ratios of copper to pyrophosphate ions. The last two, which have not been reported before, were detected only in very dilute solutions due to the low solubility of precipitates such as $Na_2Cu_3(P_2O_7)_2$·Aq. Dipyrophosphatocuprate(II) ion is the predominant complex of copper(II) in solutions containing a moderate excess of pyrophosphate ion, in the *p*H range of about 10 to 7. If the pyrophosphate ion concentration is decreased or if the solution is made weakly acidic, the equilibrium shifts to form an increasing proportion of monopyrophosphatocuprate(II) complex. With sufficient acid added to yield a *p*H in the range of 5.5 to 2, a precipitate such as $Na_2Cu_3(P_2O_7)_2$·Aq may form. In more acidic solutions no precipitate forms and acidic complexes containing hydrogen ion are obtained. At an ionic strength of unity, the first and second instability constants for the stepwise dissociation of dipyrophosphatocuprate(II) are 2×10^{-4} and 2×10^{-9}.

It has long been evident that copper and pyrophosphate ions form complexes in aqueous solution since the blue color of the mixture is considerably more intense than that due to the hydrated copper ion alone. Bassett, Bedwell and Hutchinson[1] observed that the intensely blue color of the copper complex in solutions persisted in only one crystal, namely, the moderately soluble crystalline $Na_6Cu(P_2O_7)_2$·16H_2O. On the basis of this observation

they concluded that a dipyrophosphatocuprate(II) complex was present in this particular crystalline phase but that the copper ions were hydrated with variable amounts of water in other crystals containing copper and pyrophosphate ions. Rogers and Reynolds,[2] in an investigation of the complexes of copper and other metals with alkali pyrophosphates by potentiometric, conductometric and amperometric titrations, found that the equivalence

(1) H. Bassett, W. L. Bedwell and J. B. Hutchinson, *J. Chem. Soc.*, 1412 (1936).

(2) L. B. Rogers and C. A. Reynolds, THIS JOURNAL, **71**, 2081 (1949).

point varied between one and two pyrophosphate ions for each copper ion depending on the dilution. Similar experiments and conclusions were reported without data by Haldar.[3]

The complexes have been investigated polarographically by Eriksson[4] and by Laitinen and Onstott.[5] Both papers reported reversible waves for the complex only if the pH was below 5. Laitinen and Onstott concluded that the complex, Cu-$(HP_2O_7)_2^{4-}$, was present in solutions having a pH smaller than 5.

Characteristic extinction curves were obtained in the present investigation for the various copper pyrophosphate complexes. Consequently spectrophotometric measurements in conjunction with polarographic and pH measurements have permitted an extensive interpretation of the equilibria.

Throughout this paper, Beer's law is in the form $\log_{10} I_0/I = \epsilon cl$, where $\log_{10} I_0/I$ is called the extinction, c is the molar concentration, l is the length of cell in cm. and ϵ is the molar extinction coefficient.

Experimental

Apparatus.—The spectrophotometric measurements were made in the Beckman D. U. spectrophotometer with 1-cm. glass cells unless 10-cm. cells are specified. The pH measurements were made with the Beckman model G pH meter standardized with the Clark and Lubs borate buffer having a pH of 10. The solutions were placed in a thermostatically controlled bath kept at 25 ± 0.1°. The polarographic measurements were made with a manual polarograph. The design of the instrument and experimental technique are described by Watters.[6] The capillary had a drop time of 4.76 seconds and delivered 1.38 mg. of mercury per second at the potential of the saturated calomel electrode.

Reagents.—0.2 M sodium pyrophosphate was prepared by weighing $Na_4P_2O_7 \cdot 10H_2O$ and diluting to exact volume. The molarity was verified by an electrometric pH titration with standardized hydrochloric acid; 0.1 M copper sulfate was prepared in a similar manner using $CuSO_4 \cdot 5H_2O$ and was standardized gravimetrically by electroplating copper. Approximately 1 M perchloric acid was prepared by diluting the 60% solution. It was standardized against sodium carbonate.

Solid $Na_2CuFe(CN)_6$ was prepared as follows: 25 g. of $CuSO_4 \cdot 5H_2O$ and 85 g. of $Na_4P_2O_7 \cdot 10H_2O$ were dissolved in 700 ml. of water and heated to about 50°. Then 25 g. of $K_4Fe(CN)_6$, dissolved in 200 ml. of water, was added to this solution with vigorous stirring. The precipitate, which consisted of very small reddish-brown colored crystals,

was washed nine times with 200-ml. portions of 0.3 M $NaNO_3$ by vigorously mixing the slurry, centrifuging, and finally decanting off the wash solution. The precipitate was found to contain copper and ferrocyanide ions in the mole ratio of exactly 1:1 by spectrophotometric measurements of its air free solution in concentrated sodium pyrophosphate at 370 and 740 mμ. At 370 mμ the molar extinction coefficient of ferrocyanide ion was found to be 53.4 M^{-1} cm.$^{-1}$ while those for the copper complexes investigated were practically zero. The dipyrophosphatocuprate(II) was determined at 740 mμ where the extinction of the copper complex reached a maximum and that due to the ferrocyanide ion was negligible. Sodium was determined spectrographically.

Copper-to-Pyrophosphate Ratio Experiments.—The general procedure consisted of transferring various volumes of 0.2 M sodium pyrophosphate by pipet to 100-ml. volumetric flasks. Then, after adding most of the water, 20 ml. of 0.1 M $CuSO_4$ was added slowly with stirring. The solution was diluted to the mark, mixed well, and a portion was transferred to a 1-cm. cell for the extinction measurements shown in Fig. 1. The extinction curves for solutions containing more pyrophosphate than the 1:2 ratio are not shown since they practically coincide with that for the 1:2 ratio. No extinction curves are shown for less than the 1:1 ratio since a precipitate formed immediately. Consequently, a second series of extinction curves was obtained using more dilute solutions which were one millimolar in copper ion with greatly varied concentrations of pyrophosphate ion. These solutions were prepared by mixing, from burets, various proportions of solutions, all of which contained one millimolar copper ion but different pyrophosphate concentrations. Precipitates also formed in some of these solutions on standing several hours. Several of the extinction curves obtained using 10-cm. cells are shown in Fig. 2.
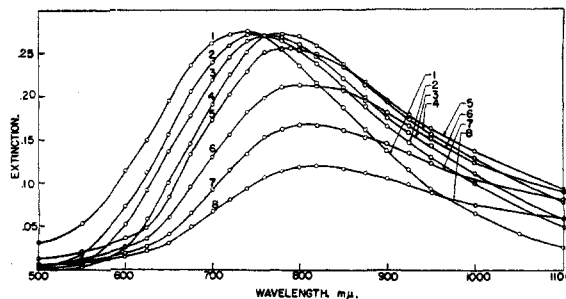
Fig. 2.—Effect of increasing the pyrophosphate concentration in very dilute solutions. All solutions were 0.001 M in $CuSO_4$ with the following concentrations of $Na_4P_2O_7$, (10 cm. cells were used): 1, 0.1 M; 2, 0.002 M; 3, 0.0016 M; 4, 0.001 M; 5, 0.0008 M; 6, 0.0004 M; 7, 0.0002 M; 8, none.

The pH data are plotted in Fig. 4. Curve 2 is a tenfold enlargement of the first part of curve 1. Data from these experiments were used to obtain the continuous variation results[7] shown in curves 2 to 6, Fig. 5. Curve 1, Fig. 5, was obtained by continuously varying a solution which was 25 millimolar in copper and pyrophosphate ions with a second solution which was 25 millimolar in pyrophosphate ion.

Acidity Variation Experiments.—Copper sulfate, sodium pyrophosphate in a known small excess of that needed for complex formation, and varying amounts of 0.87 N perchloric acid were mixed as in the ratio experiments. The pH data reported in the first two columns of Table I and the extinction curves shown in Fig. 3 were obtained immediately. A very pale blue precipitate formed in the pH range of about 5.5 to 2 and a soluble complex, curve 8, Fig. 3, remained in solution below a pH of 1.70. A preliminary analysis summarized below indicates that, in the absence of potassium ion, the formula of this precipitate is $Na_2Cu_3(P_2O_7)_2 \cdot Aq$. Spectrographic analysis of the pale blue precipitate obtained in the presence of potassium ion revealed considerable potassium as well as sodium. This compound has been reported by Fleitmann and Hennberg[8]
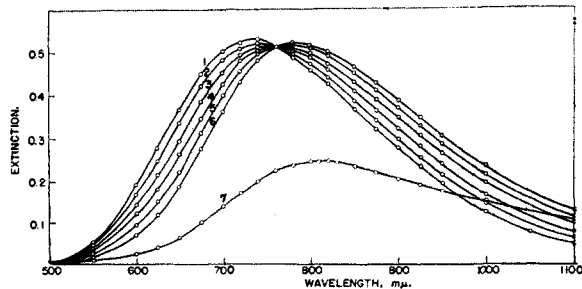
Fig. 1.—Effect of varying the ratio of copper-to-pyrophosphate ions. All solutions contained 0.020 M $CuSO_4$ with the following concentrations of $Na_4P_2O_7$: 1, 0.04 M; 2, 0.036 M; 3, 0.032 M; 4, 0.028 M; 5, 0.024 M; 6, 0.02 M; 7, none.

(3) B. C. Haldar, *Science and Culture*, **14**, 341 (1949).

(4) Erik Eriksson, *Kungl. Lantbruks Hogskolans ann.*, **16**, 72 (1949).

(5) H. A. Laitinen and F. I. Onstott, THIS JOURNAL, **72**, 4729 (1950).

(6) J. I. Watters, *Rev. Sci. Instruments*, **22**, 851 (1951).

(7) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

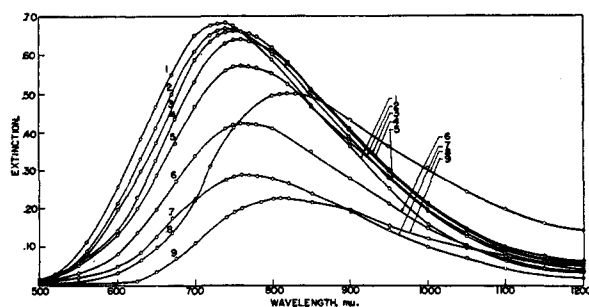(8) T. Fleitmann and W. Hennberg, *Ann.*, **65**, 387 (1848).

Fig. 3.—Effect of increasing acidity. All solutions were 0.025 M in $CuSO_4$, 0.075 M in $Na_4P_2O_7$, and the ionic strength was adjusted to unity with KNO_3. The total concentrations of hydrogen ion added were: 1, none; 2, 0.04 M; 3, 0.05 M; 4, 0.07 M; 5, 0.08 M; 6, 0.09 M; 7, 0.10 M; 8, 0.18 M; 9, 0.16 M. Solutions were filtered for curves 4, 5, 6, 7 and 9 since precipitates formed in these solutions.

to have crystals that are somewhat efflorescent at room temperature but that 3.5 H_2O are retained at 100°. The sample was dried and water of crystallization was removed by heating to 260° for three hours. Copper was determined electrolytically and sodium was determined gravimetrically as sodium zinc uranyl acetate.[9] Pyrophosphate was determined gravimetrically as magnesium pyrophosphate after hydrolyzing to phosphate by boiling the acidified solution.

Anal. Found: Na, 8.37; Cu, 32.8; P_2O_7, 57.9. Calcd. for $Na_2Cu_3(P_2O_7)_2$: Na, 7.88; Cu, 32.6; P_2O_7, 59.6.

After standing several weeks these crystals had been replaced by larger sky-blue crystals which were considerably less soluble. The properties of the latter correspond to $Na_2CuP_2O_7\cdot2/3H_2O$.[8]

TABLE I

EFFECT OF ADDING ACID TO SOLUTIONS CONTAINING A
KNOWN EXCESS OF PHOSPHATE

2.5 millimoles $CuSO_4$, 7.5 millimoles $Na_4P_2O_7$, 100 millimoles KNO_3 in 100 ml. of solution

H+ added, millimoles	pH	X^a	X'^b	$K_{11}^c \times 10^4$
2.99	6.39	0.10	0.10	1.5
3.98	5.85	.26	.26	1.5
5.07	5.53	.42	.42	1.3
6.06	5.35	.59	.58	1.5
6.52	5.23	.62	.63	1.2
8.06	5.09	precipitate formed		
17.11	1.78	in this range		
18.10	1.70	soluble acidic complex formed		
21.09	1.42	in this pH range		

^{a} Mole fraction $[CuP_2O_7]^{-2}$ based on equation (1). ^{b} Mole fraction $[CuP_2O_7]^{-2}$ based on equation (6). ^{c} See equations (2) and (3).

$Na_2CuFe(CN)_6$ **Equilibration Experiments.**—Portions of the precipitate, in excess, were shaken for 2 hours with oxygen-free solutions containing various concentrations of

TABLE II

EQUILIBRATION OF SODIUM COPPER FERROCYANIDE WITH
VARIOUS CONCENTRATIONS OF COMPLEXING AGENT

Complex electrolyte molar concn. (initial)	[Fe(CN)$_6$]$^{4-}$ molar concn. (at equil.)	Cu complex molar concn. (at equil.)	pK_t (calcd.)
0.02 M $Na_4P_2O_7$ + 0.8 M $NaNO_3$	0.00214	0.00215	12.48
.05 M $Na_4P_2O_7$ + 0.8 M $NaNO_3$	.00691	.00695	12.59
.10 M $Na_4P_2O_7$	.0212	.0220	12.78
.10 M $Na_4P_2O_7$	.0235	.0223	12.75
.25 M $Na_2C_2O_4$	.00110	.001082	...
		Av.	12.65 ± 0.17

(9) H. H. Barber and I. M. Kolthoff, THIS JOURNAL, **50**, 1625 (1928).
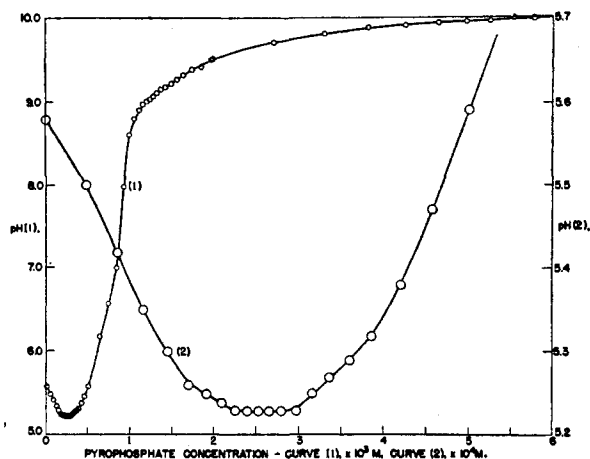

Fig. 4.—pH titration of 0.001 M $CuSO_4$ with $Na_4P_2O_7$ without dilution. Curve (2) is a tenfold enlargement of the first portion of curve 1. pH values for curve (2) are indicated on right margin and numerical values of the pyrophosphate concentration are tenths millimolar per millimolar concentration of copper ion.
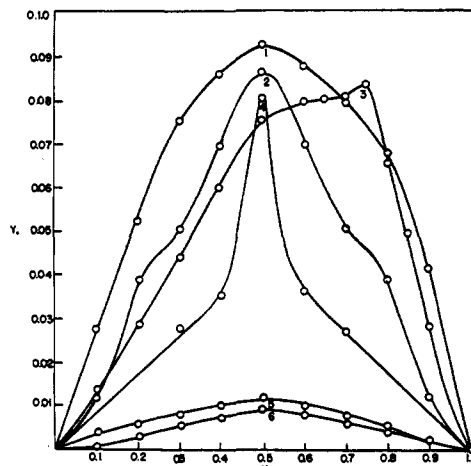

Fig. 5.—Continuous variations: curve 1, soln. A, 0.025 M $CuSO_4$, 0.025 M $Na_4P_2O_7$; soln. B, 0.025 M $Na_4P_2O_7$, 740 mμ. In curve 1 multiply ordinate values by 3.33. X is fraction of solution B in all curves. Curve 2, soln. A, 0.001 M $CuSO_4$, 0.002 M $Na_4P_2O_7$; soln. B, 0.001 M $CuSO_4$, 780 mμ. Curve 3, same as curve 2 at 820 mμ. Curve 4, soln. A, 0.001 M $CuSO_4$, 0.001 M $Na_4P_2O_7$; soln. B, 0.001 M $CuSO_4$, 820 mμ. Curve 5, soln. A, 0.001 M $CuSO_4$; soln. B, 0.001 M $CuSO_4$, 0.0005 M $Na_4P_2O_7$, 1000 mμ. Curve 6, same as curve 5 at 1100 mμ.

sodium pyrophosphate and sufficient sodium nitrate to make the ionic strength approximately unity. In preliminary experiments equilibrium was approached from both directions by diluting some of the solutions to their final concentrations and repeating the procedure after first following this procedure at higher pyrophosphate concentrations. The equilibrium concentration of ferrocyanide and dipyrophosphatocuprate(II) in solution, Table II, were determined spectrophotometrically as described before.

Discussion

The existence of an isosbestic point at 760 mμ in Figs. 1 and 2 for dilute and more concentrated solutions, respectively, indicates the presence of two copper complexes other than the aquo ion in solutions containing copper-to-pyrophosphate ion con-

centration ratios greater than 1:1 in pyrophosphate. The tendency for precipitates to form in solutions having ratios less than 1:1 indicates that one of these is monopyrophosphatocuprate(II) and the similarity of the extinction coefficients for the dilute solutions, curve 4, Fig. 2 and more concentrated solutions, curve 6, Fig. 1, indicates that this ion is very stable. The similarity of the extinction curves for the 1:2 ratio in the more concentrated solutions, curve 1, Fig. 1, with those containing more pyrophosphate, which practically coincide with curve 1, indicates that the second complex is dipyrophosphatocuprate(II). The continuous variation results shown in curves 1 and 2, Fig. 5, confirm the existence of these two complex ions since the maxima at $X = 0.5$ correspond to the formulas $[Cu(P_2O_7)_2]^{6-}$ and $[CuP_2O_7]^{2-}$, respectively.

Since the extinction curve for the dilute 1:2 solution, curve 2, Fig. 2, is not completely shifted to the position for the solution containing an excess of pyrophosphate, curve 1, Fig. 2, it follows that the dipyrophosphatocuprate(II) is partially dissociated to the monopyrophosphatocuprate(II). The degree of dissociation at various dilutions, Table III, will be used to evaluate the first instability constant of the dipyrophosphato complex.

TABLE III

EFFECT OF DILUTION ON THE DEGREE OF DISSOCIATION OF DIPYROPHOSPHATOCUPRATE(II)

(KNO₃ added to produce ionic strength of unity)

Complex concn., m	α	$K_{i_1} \times 10^4$	Complex concn., m	α	$K_{i_1} \times 10^4$
0.0005	0.43	1.7	0.008	0.13	1.6
.0008	.36	1.6	.02	.09	1.8
.001	.34	1.7	.025	.08	1.7
.005	.17	1.7			

It is reasonable that, in both of these complexes, the copper is bonded with the pyrophosphate by six-membered chelate rings of the type proposed by Kolthoff and Watters[10,11] for the trivalent manganese complex. Any remaining coördination bonds of copper in any of the complexes with pyrophosphate are probably satisfied by water. In the dipyrophosphato complex, copper's usual coördination number of four is satisfied by the two pyrophosphate ions.

That the pyrophosphate ions in both the mono- and dipyrophosphato complexes hydrolyze to a negligible extent is evident from the pH values of 7.6 and 8.6, respectively, measured in solutions 25 millimolar in these ions. This is reasonable since a pyrophosphate ion complexed with a positive ion, copper in this case, must have less tendency to associate with hydrogen ions than does a free pyrophosphate ion.

Additional complex species were discovered in solutions containing an excess of copper ion. These complex ions were detected only in very dilute solutions due to the insolubility of precipitates such as $Na_2Cu_3(P_2O_7)_2·Aq$. The continuous variation data of curves 3 and 4, Fig. 5, prove the existence, in very dilute solutions, of a neutral complex, mono-

(10) I. M. Kolthoff and J. I. Watters, Ind. Eng. Chem., Anal. Ed., 16, 8 (1943).

(11) J. I. Watters and I. M. Kolthoff, THIS JOURNAL, 70, 2455 (1948).

pyrophosphatodicopper(II), having the formula $[Cu_2P_2O_7]^0$. The maximum in curve 3 at $X = 0.75$ and in curve 4, Fig. 5, at $X = 0.50$ prove the existence of $[Cu_2P_2O_7]^0$. The bulge in curve 3 at $X = 0.50$ is caused by the formation of $[CuP_2O_7]^{2-}$ which was confirmed by curve 2. A model having two copper ions in six-membered chelated rings with a single pyrophosphate ion can be readily constructed. It is probable that in this complex each copper ion is coördinated with two water molecules. The pH of 5.59, in a one millimolar solution of the complex, Fig. 4, indicates that the complex hydrolyzes to the same extent as does the aquo complex, which has a pH of 5.58.

Curve 2, Fig. 4, has a minimum pH of 5.38 in the region where the copper-to-pyrophosphate concentration ratio is 4:1. Since the partial conversion of $[Cu(H_2O_4)]^{2+}$ having a pH of 5.58 to $[Cu_2P_2O_7]$ having a pH of 5.59 cannot account for the increase in acidity, the existence of a complex cation containing four copper ions for each pyrophosphate ion is indicated. The small maxima at $X = 0.5$ in the continuous variation curves 5 and 6, Fig. 5, confirm the existence of the complex cation, $[Cu_4P_2O_7]^{4+}$. The effects are too small to verify the complex containing three copper ions which probably also exists.

It is possible that this complex cation, $[Cu_4P_2O_7]^{4+}$, contains two of the copper ions in six-membered rings and retains the additional copper ions in four-membered rings containing one phosphorus atom and two oxygen atoms, one of which may be shared with a copper ion in a six-membered ring. The tendency of the coördinated water molecules to lose hydrogen ions which is manifested by the low pH of 5.38 may be due to the relatively large positive charge resulting from the proximity of two copper ions sharing an oxygen atom.

The anomalous drop in pH observed by Rogers and Reynolds[2] at the beginning of titrations of metal ions such as copper, zinc and cadmium by pyrophosphate ion was undoubtedly caused by the formation of complex cations similar to $[Cu_4P_2O_7]^{4+}$. Furthermore, the abnormally large capacity of pyrophosphate for complexing iron and other metal ions in hard water, which is well known, can be explained by the formation of complex cations of this type.

In the acidity variation experiments, the added hydrogen ion, in addition to combining with free pyrophosphate ions, might compete with copper ion for pyrophosphate ions or it might associate with pyrophosphate ions in the complex. The similarity of curves 1 to 3, Fig. 3, to curves 1 to 6, Fig. 1, and the existence of the isosbestic point at 760 mμ indicate that the dipyrophosphato complex is converted to the monopyrophosphato complex in the pH range of about 7 to 5. This conclusion will be confirmed by equilibrium calculations. A precipitate, such as $Na_2Cu_3(P_2O_7)_2·Aq$, may form somewhere in the pH range of 5.5 to 2, depending on the composition of the solution. Below a pH of 2 or 3, the solution contains soluble complexes which Laitinen and Onstott have identified as $[Cu(HP_2O_7)]^-$ and $[Cu(HP_2O_7)_2]^{4-}$. Their conclusion that complexes containing hydrogen ions do exist is sup-

ported by the fact that extinction curve 8, Fig. 3, is distinctly different from that for the mono- or dipyrophosphato complex.

In the following section the successive instability constants of dipyrophosphatocuprate(II) will be calculated by independent equilibrium calculations based on pH and extinction data. The formation of complexes containing other ions and molecules in addition to copper and pyrophosphate ions, will be considered in a second paper.

Equilibria and Equilibrium Constants.—As the amount of pyrophosphate in the complex changes from one to two, one property undergoing a particularly large change is the ratio of the extinction at 650 mμ to that at 950 mμ. The following expression for x, the mole fraction of the copper present as the monopyrophosphatocuprate(II), is readily derived.

$$x = \frac{b_1 - rb_2}{(b_1 - a_1) + r(a_2 - b_2)} \quad (1)$$

In this equation, a_1 and a_2 are the molar extinction coefficients of the monocomplex at 650 and 950 mμ, b_1 and b_2 are the corresponding coefficients of the dipyrophosphato complex, and r is the extinction of the mixture at 650 mμ divided by the extinction at 950 mμ. The values of a_1, a_2, b_1 and b_2 are 9.6, 15.5, 18.3 and 9.6 m.$^{-1}$ cm.$^{-1}$, respectively.

For calculating total concentrations of mixtures of the mono- and dipyrophosphato complex, the molar extinction coefficient of 25.5 molar^{-1} cm.$^{-1}$ at the isosbestic point, 760 mμ, is useful. The maximum molar extinction coefficients, of the mono- and dicomplexes, respectively, are 26.1 molar^{-1} cm.$^{-1}$ at 780 mμ and 26.5 molar^{-1} cm.$^{-1}$ at 740 mμ.

Considering the equilibrium

$$[Cu(P_2O_7)_2]^{6-} \rightleftharpoons [CuP_2O_7]^{2-} + P_2O_7^{4-} \quad (2)$$
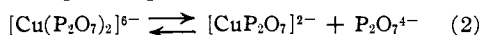
one obtains the following expression for the first instability constant of dipyrophosphatocuprate(II), K_{i1}

$$K_{i1} = \frac{[CuP_2O_7^{2-}][P_2O_7^{4-}]}{[Cu(P_2O_7)_2^{6-}]} = \frac{\alpha^2}{1-\alpha} C_{Cu} \quad (3)$$

where C_{Cu} is sum of the concentrations of the two complex ions and α is the degree of dissociation of the di- to the monocomplex in solutions containing copper ion to pyrophosphate ion concentration ratios of 1:2. α was calculated from spectrophotometric data by equation 1. These values of α and the corresponding values of K_{i1} are shown in Table III. The mean value of K_{i1} at an ionic strength of unity is 1.7×10^{-4}. The magnitude of K_{i1} and the consequent variation in the degree of dissociation with dilution accounts, quantitatively, for the Rogers and Reynolds[2] observation that the equivalence point in conductometric titrations varied between one and two pyrophosphate ions per copper ion depending on the dilution.

The equilibrium between mono- and dipyrophosphatocuprate(II) in the pH range of about 8 to 5 resulting from the addition of hydrogen ions is shown in equation (4).

$$[Cu(P_2O_7)_2]^{6-} + 2H^+ \rightleftharpoons [CuP_2O_7]^{2-} + H_2P_2O_7^{2-} \quad (4)$$
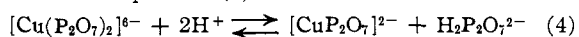
A quantitative treatment of this equilibrium permits the evaluation of K_{i1} by the spectrophotometric procedure already discussed and also on the

basis of pH measurements by a procedure similar to that used by Bjerrum[12] and others.

In the latter method, combinations of equations for the conservation of copper, pyrophosphate and hydrogen ions with the third and fourth dissociation constants of pyrophosphoric acid yield the following equations which are valid in the pH range of 10.2 to 7.2 and 7.2 to 4, respectively.

$$x' = 2 - C_p/C_{Cu} + \left(\frac{K_4}{a_{H^+}} + 1\right) C_H/C_{Cu} \quad (5)$$

$$x' = 2 - C_p/C_{Cu} + \left(\frac{K_3 + a_{H^+}}{K_3 + 2a_{H^+}}\right) C_H/C_{Cu} \quad (6)$$

where x' is the fraction of the copper present as the mono complex and C_{Cu}, C_p and C_H are the total concentrations of copper, pyrophosphate and hydrogen ions, respectively, in all forms. In these equations K_3 and K_4 are the third and fourth dissociation constants of pyrophosphoric acid. These and other equilibrium constants are expressed in terms of concentrations except that the activity of hydrogen ion determined from pH measurements was retained since the activity coefficient of hydrogen ion cancels out if the ionic strength is kept constant. The values of K_3 and K_4 obtained at 25° were 3.1×10^{-6} and 2.1×10^{-8}, respectively, at an ionic strength of unity and 9.6×10^{-7} and 4.4×10^{-9}, respectively, in solutions containing only $0.05M$ sodium pyrophosphate, in good agreement with the data of Kolthoff and Bosch.[13] The values obtained by equations (5) or (6), shown in Table I, are in complete agreement with the corresponding values of x which were obtained spectrophotometrically using equation (1).

The equilibrium constant, K_a, for the equilibrium in equation (1) can be used to evaluate K_{i1}, thus

$$K_a = \frac{[Cu(P_2O_7)^{2-}][H_2P_2O_7^{2-}]}{[Cu(P_2O_7)_2^{6-}]a_{H^+}^2} = \frac{K_{i1}}{K_3K_4} \quad (7)$$

The values of K_{i1} obtained on the basis of the pH data using equation (7) are also summarized in Table I. The agreement of the mean value $(1.4 \pm 0.2) \times 10^{-4}$ is in satisfactory agreement with the value 1.7×10^{-4}, Table III, for solutions containing no acid, particularly when one considers that two addition ionization constants for pyrophosphoric acid are involved.

As the instability constant for monopyrophosphatocuprate(II), K_{i2}, was too small for a direct determination by spectrophotometric measurements, it was obtained indirectly by first determining K_t, the total instability constant of dipyrophosphatocuprate(II), where

$$K_t = \frac{[Cu^{2+}][P_2O_7^{4-}]^2}{[Cu(P_2O_7)_2^{6-}]} = K_{i1}K_{i2} \quad (8)$$

K_t was evaluated from the data obtained in the copper ferrocyanide equilibration experiments.

For the chemical equilibrium

$$Na_2Cu[Fe(CN)_6](crystal) + 2P_2O_7^{4-} \rightleftharpoons$$
$$[Cu(P_2O_7)_2]^{6-} + [Fe(CN)_6]^{4-} + 2Na^+ \quad (9)$$
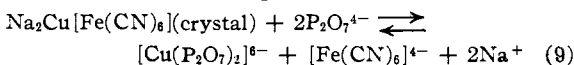
one obtains the following expression for K_{sp}, the solubility product of sodium copper ferrocyanide

(12) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941.

(13) I. M. Kolthoff and W. Bosch, Rec. Trav. Chim., 47, 826 (1928).

$K_{sp} = [Na^+]^2[Cu^{2+}][Fe(CN)_6^{4-}] =$

$K_t[Cu(P_2O_7)_2^{6-}][Fe(CN)_6^{4-}][Na^+]^2/[P_2O_7^{4-}]^2$ (10)

The solubility product of sodium copper ferrocyanide[14] was found to be 4.9×10^{-15} at an ionic strength of about unity by an analogous equilibration procedure using 0.25 M sodium oxalate to dissolve sodium copper ferrocyanide through the formation of dioxalatocuprate(II). The instability constant of this complex has been determined by Meites[15] on the basis of the shift of the polarographic half-wave potential of copper ion due to complex formation.[16]

Substituting the value 2.7×10^{-13} for K_t from Table II into equation (8) yields a mean value, 1.6×10^{-9}, for K_{i2}.

The difference in the magnitude of the first and second dissociation constants can be explained on the basis of ionic charge. The first pyrophosphate ion is attracted by the oppositely charged copper ion while the second pyrophosphate ion must combine with a similarly charged monopyrophosphatocuprate(II) ion.

The above value for K_t is supported by the fol-

(14) J. I. Watters, unpublished.

(15) L. Meites, THIS JOURNAL, **72**, 180 (1950).

(16) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 164.

lowing polarographic evidence. Laitinen and Onstott,[2] as well as Eriksson,[5] showed that the polarographic reduction of the pyrophosphate complex present in the pH range of 2 to 5 is reversible. The beginnings of the waves which were obtained at larger pH's are similar. However, at more negative potentials, the normal current growth discontinues abruptly and an appreciable current decrease may even be observed. The authors, after performing polarographic experiments with solutions containing 10^{-4} to 10^{-2} M copper ion and 10^{-4} to 1 M pyrophosphate ion with similar results, concurred with Eriksson in his opinion that film formation rather than thermodynamic irreversibility was responsible for the strange wave shape. Using Eriksson's technique of extrapolating along the normal beginning of the wave, the authors have obtained the half-wave potential of -0.2451 volt (S.C.E.) for a solution 1 millimolar in $[Cu(P_2O_7)_2]^{6-}$, 8 millimolar in $P_2O_7^{4-}$, 1 M in KNO_3, and 0.003% in gelatin. Combining this data with the experimentally determined value, $+0.002$ v. (S.C.E.), for the half-wave potential of tetraaquocuprate(II),[14] yields a value, 3×10^{-13}, for K_t in excellent agreement with the value 2.7×10^{-13} obtained by equation (10).

COLUMBUS, OHIO

The Heat Capacity of cis- and trans-Decahydronaphthalene and the Possible Existence of a λ-Region for the cis Form at 50.1-50.5°

BY WILLIAM F. SEYER

In attempting to measure the heat capacity of cis- and trans-decahydronaphthalene between 20° and 140° by the Williams and Daniels adiabatic method irregularities in the behavior of the cis modification were noted in the temperature interval 50–60°. Heating and cooling caves indicated a discontinuity between 50.1° and 50.4°. By slightly-altering the set-up of the calorimeter and adding definite increments of heat, a curve was obtained suggesting a λ-region over this temperature interval. Other physical measurements made on the cis isomer appear to support this view.

In making a series of measurements on the physical properties of cis- and trans-decahydronaphthalene in the liquid state none was found more difficult than that of the heat capacity. This was particularly true for the cis-form. Several experiments had shown an irregularity in the case of this compound in respect to change in properties with temperature so that it was deemed desirable to investigate the specific heats of these two compounds in the hope of getting more information on the peculiar temperature behavior of the cis isomer. A study of the various calorimetric methods in use resulted in the selection of the Williams and Daniels adiabatic calorimeter type as the most suitable for the purpose in mind.[1] Preliminary measurements to test the operation of this type of calorimeter showed a regular increase in the heat capacities of benzene, toluene and trans decahydronaphthalene but not with the cis isomer.[2] Here the results were extremely irregular, espe-

(1) J. W. Williams and F. Daniels, THIS JOURNAL, **46**, 904 (1914).

(2) G. P. Davies, M.Sc. Thesis, University of British Columbia, 1939.

cially in the neighborhood of 50°. It soon became apparent that in order to be able to reproduce the shape of the curves the utmost care would have to be taken in the experimental procedures. Hence a new calorimeter was constructed after the model mentioned above with special efforts devoted to the minimizing of those errors so thoroughly discussed by W. P. White in his treatise, "The Monern Calorimeter."[3]

Calorimeter Characteristics.—The specific factors which have a bearing on the results obtained are stated briefly below. The stirring in the inner cup gave a temperature rise of not over 0.0001° per minute and was therefore considered to be a negligible quantity. The samples of hydrocarbons used weighed between 150 and 160 g. Prior to each run, the purity of each cis or trans isomer to be used was tested by measuring the freezing point. The thermel was made from 36 B & S gage copper wire and 30 B & S gage special copel wire. Five couples were used to each thermopile. They were constructed with extreme care so as to ensure the least possible inherent potential. When tested at 23° and at 100° a potential of 0.8 microvolt was developed which amounted to 200 microvolts per degree

(3) W. P. White, "The Modern Calorimeter," The Chemical Catalog Co., New York, N. Y., 1928.