

THE UNIVERSITY OF MANITOBA

STUDIES ON THE SOLUBILITY OF
CUPRIC MONOHYDROGEN ORTHOPHOSPHATE

by

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A dissertation submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
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ABSTRACT

The solubility of cupric hydrogen orthophosphate and copper-hydrogen-orthophosphate complexing have been studied in aqueous solution at 25°C with ionic strength maintained constant using 3M NaClO₄. To determine copper-hydrogen-orthophosphate complexing, a series of potentiometric titrations were used, keeping total acid and total copper in solution constant and varying the total orthophosphate concentration. During these titrations, the free hydrogen ion concentration, h , was measured using a glass electrode and the free cupric ion concentration, c , was measured using a cupric ion selective electrode. From the titration data, the average ligand number for hydrogen ion-orthophosphate complexing, $Z_{H/B}$, and the average ligand number for cupric ion-orthophosphate complexing, $Z_{C/B}$, were calculated. By treating the titration data with the generalized least square program Letagrop, the presence of one copper-hydrogen-phosphate complex, $\text{CuH}_2\text{PO}_4^+$, was established at 25°C over the pH range of 1 to 3.7. The best value of the association constant, $\beta_{1,1,1}$, was

$$\beta_{1,1,1} = \frac{[\text{CuH}_2\text{PO}_4^+]}{c \, h \, [\text{HPO}_4^{2-}]} = (6.9 \pm 0.7) \times 10^7$$

or $\log \beta_{1,1,1} = 7.84 \pm 0.04$

In order to study the solubility of cupric hydrogen orthophosphate (CuHPO_4) in aqueous solution, excess amounts of solid were allowed to equilibrate at 25°C with solutions of known total hydrogen ion concentration or known orthophosphate concentration in 3M ClO₄⁻. After equilibration, it was found that the composition of the solid residues had changed. Using the solubility data, it was possible to calculate values of the solubility products for two cupric orthophosphate compounds,

CuHPO_4 and $\text{Cu}_3(\text{PO}_4)_2$, and the average values are

$$K_{\text{so}} = c [\text{HPO}_4^{2-}] = (2.11 \pm 0.14) \times 10^{-8}$$

$$K'_{\text{so}} = c^3 [\text{PO}_4^{3-}]^2 = (4.95 \pm 2.43) \times 10^{-34}.$$

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1. INTRODUCTION

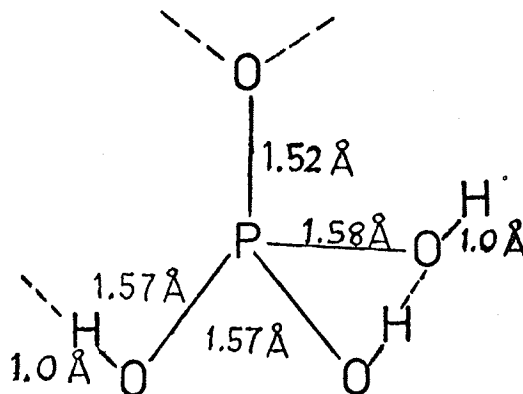
1.1 Some General Properties of the Orthophosphate Ion

The orthophosphates of alkali metals, ammonia, and the lower molecular weight substituted ammonium ions are all quite soluble in water except for trillithium orthophosphate. On the other hand, the orthophosphates of multiply-charged or heavy metals are all relatively insoluble. From the viewpoint of structural chemistry there are two limiting kinds of crystalline orthophosphates. One is the kind of crystal in which the PO_4 groups exhibit three negative charges each (isolated PO_4 groups); and the other is a three-dimensionally bonded crystal in which the oxygen atoms share electrons not only with the phosphorus atoms (four-way branching points) but also with those of another element, also surrounded by four neighbouring oxygen atoms (67).

The orthophosphate ion serves as a good complexing agent for the transition metals and orthophosphoric acid has long been used to decolorize solutions containing small amounts of ferric ion (1, 2).

1.2 Structure of Crystalline Orthophosphoric Acid

X-ray diffraction structure studies have been carried out on both anhydrous crystalline orthophosphoric acid (H_3PO_4) and its hemihydrate ($\text{H}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) (3, 4). In both cases, four formula weights were found per unit cell of the crystals which belong to the monoclinic system. In the anhydrous acid, three of the oxygen atoms of the PO_4 group (shown below) are bonded to hydrogen atoms which form hydrogen bonds to oxygen of other PO_4 groups.



----- hydrogen bonds

In this crystal the PO_4 groups exhibit trigonal symmetry with the axis of symmetry being the bond between the phosphorus and the isolated oxygen atom (67).

1.3 Orthophosphate Complexes in Solution

The complexing of transition metals by orthophosphates has been known for a long time. As early as 1882, the decolorizing action of orthophosphoric acid on ferric ion was used in analytical procedures (1,2). In addition to this decolorizing action, there is considerably more evidence to indicate the existence of orthophosphate-ferric complexes. Thus, the oxidation potential of the ferrous-ferric system is lowered in the presence of orthophosphoric acid, and the conductivity of mixtures of phosphoric acid and ferric salts is found to be higher than the sum of the separate conductivities (5,6). In transference - number experiments, it has been shown (7) that ferric ion in the presence of excess orthophosphoric acid moves toward the anode.

Aluminum acts similarly to iron in that it is strongly complexed by orthophosphoric acid (6, 8, 26, 27, 29, 30, 33). In addition, the probable existence of complexes of the orthophosphoric ion has been reported for a number of metal ions including cobalt (9, 35), copper (10, 35, 49), silver (11, 40), thorium (12), plutonium (13), uranium (14),

and even calcium (15, 16). Solubility constants and equilibrium constants for some metal orthophosphates are given in Table 1.

1.4 Cupric Orthophosphate Compounds

Several cupric orthophosphate compounds and minerals have been prepared, for example $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$, $\text{Cu}_2(\text{PO}_4)(\text{OH})$ (Libethenite), and $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$ (Pseudomalachite). However, the compound of main interest in this report is cupric hydrogen orthophosphate (CuHPO_4).

In 1885, Debray (44) reported the synthesis of cupric hydrogen orthophosphate hydrate ($\text{CuHPO}_4 \cdot \text{H}_2\text{O}$) from cupric carbonate (CuCO_3) and dilute orthophosphoric acid (H_3PO_4).

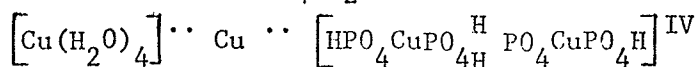
In 1933, Bassett and Bedwell (45) reported the synthesis of cupric hydrogen orthophosphate hydrate ($\text{CuHPO}_4 \cdot \text{H}_2\text{O}$). The compound was synthesized by refluxing a solution of cupric carbonate (CuCO_3) for 3 days. They found that the product was in the form of grayish-blue rosettes of prisms. Analysis gave the following results:

Found: CuO , 44.80; P_2O_5 , 40.20; loss on ignition, 15.41

(Theoretical)

$\text{CuHPO}_4 \cdot \text{H}_2\text{O}$: CuO , 44.82; P_2O_5 , 39.98; loss on ignition, 15.20

Bassett and Bedwell proposed that the "glowing" on ignition of phosphates such as $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ is due to rearrangement and polymerization of structurally unstable molecules. In the case of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ there is only very slight "glowing" on ignition which is consistent with a polymeric structure. Bassett and Bedwell proposed a quadramolecular structure for $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$



This compound "glows" very little on ignition because the rate of

TABLE 1

SOLUBILITY CONSTANTS AND EQUILIBRIUM CONSTANTS OF SOME METAL ORTHOPHOSPHATES			
<u>Ion</u>	<u>Temperature (°C)</u>	<u>Medium</u>	<u>Results</u> <u>References</u>
Cr ³⁺	18-20	varied	$\log K_{so} = -22.62$ (green) (17)
			$\log K_{so} = -17.00$ (violet)
Cr ^{VI}	25	0.25M (NaClO ₄)	$\log \frac{[HCrPO_7^{2-}]}{[HCrO_4^-][H_2PO_4^-]} = 0.48$ (18)
			$\log \frac{[H_2CrPO_4^-]}{[HCrO_4^-][H_3PO_4]} = 0.95$
Mn ²⁺	25	0.2M (Pr ₄ NCl)	$\log \frac{[MnHPO_4]}{[Mn^{2+}][HPO_4^{2-}]} = 2.58$ (19)
Fe ³⁺	30	0.665M (NaNO ₃)	$\log \frac{[FeHPO_4^+]}{[Fe^{3+}][HPO_4^{2-}]} = 9.35$ (20)
	18-20	varied	$\log (K_{so} = [Fe^{3+}][PO_4^{3-}]) = -21.89$ (17)
	---	varied	$\log \frac{[Fe(H_2PO_4)_4^-]}{[Fe^{3+}][H_2PO_4^-]^4} = 9.15$ (21)

TABLE 1 (continued)

Ion	Temperature (°C)	Medium	Results	References
Fe ³⁺	23-25	0 corrected	$\log (K_s = \frac{[\text{Fe}^{3+}][\text{H}_2\text{PO}_4^-]}{[\text{OH}^-]^2})$ = - 33.5 to -35	(22)
	?	0 corrected	$\log \frac{[\text{FeHPO}_4^+]}{[\text{Fe}^{3+}][\text{HPO}_4^{2-}]} = 9.75$	(23)
	25	0	$\log (K_s = \frac{[\text{Fe}^{3+}][\text{H}_2\text{PO}_4^-]}{[\text{OH}^-]^2})$ = -34.56	(24)
Al ³⁺	25	0.4M (NaClO ₄)	$\log \frac{[\text{FeH}_2\text{PO}_4^{2+}]}{[\text{Fe}^{3+}][\text{H}_2\text{PO}_4^-]}$ = 3.49, 3.45	(25)
			$\log \frac{[\text{FeHPO}_4^+]}{[\text{Fe}^{3+}][\text{HPO}_4^{2-}]}$ = 8.23, 8.36	
	18	0.1M	$\log \frac{[\text{Al}(\text{H}_2\text{PO}_4)^{2+}]}{[\text{Al}^{3+}][\text{H}_2\text{PO}_4^-]} = 3$?	(26)
			$\log \frac{[\text{Al}(\text{H}_2\text{PO}_4)^+]}{[\text{Al}(\text{H}_2\text{PO}_4)^{2+}][\text{H}_2\text{PO}_4^-]} = 2.3$	

TABLE 1 (continued)

<u>Ion</u>	<u>Temperature (°C)</u>	<u>Medium</u>	<u>Results</u>	<u>References</u>
Al ³⁺	18	0.1M	$\log \frac{[\text{Al}(\text{H}_2\text{PO}_4)_3]}{[\text{Al}(\text{H}_2\text{PO}_4)_2][\text{H}_2\text{PO}_4^-]} = 2.3$	(26)
			$\log \frac{[\text{H}^+][\text{AlHPO}_4^+]}{[\text{Al}(\text{H}_2\text{PO}_4)_2]^{2+}} = -2.1$	
?	?	0.05M NaCl	$\log (K_s = [\text{Al}^{3+}][\text{H}_2\text{PO}_4^-][\text{OH}^-]^2)$ = -29.55	(28)
			$\log (K_{so} = [\text{Al}^{3+}][\text{PO}_4^{3-}]) = -18.24$	
?	?	0 corrected	$\log (K_s = [\text{Al}^{3+}][\text{H}_2\text{PO}_4^-][\text{OH}^-]^2)$ = -27.7 to -28.4	(31)
			$\log (K_{so} = [\text{Al}^{3+}][\text{PO}_4^{3-}]) = -10.41$	
25	25	0 corrected	$\log \frac{[\text{Al}^{3+}][\text{H}_2\text{PO}_4^-]}{[\text{H}^+]^2} = -2.48$	(34)
			$\log (K_s = [\text{Al}^{3+}][\text{H}_2\text{PO}_4^-][\text{OH}^-]^2)$ = -30.5	

TABLE 1 (continued)

<u>Ion</u>	<u>Temperature (°C)</u>	<u>Medium</u>	<u>Results</u>	<u>References</u>
Co ²⁺	19-20	dilute	$\log (K_S = [\text{Co}^{2+}]^3 [\text{PO}_4^{3-}]^2)$	(35)
			$= -34.7$	
			$\log (K_S = [\text{Co}^{2+}] [\text{HPO}_4^{2-}])$	
			$= -6.7$	
Ni ²⁺	19-20	dilute	$\log (K_{\text{So}} = [\text{Ni}^{2+}]^3 [\text{PO}_4^{3-}]^2)$	(35)
			$= -30.3$	
Ag ⁺	19.5	dilute	$\log (K_{\text{So}} = [\text{Ag}^+]^3 [\text{PO}_4^{3-}])$	(36)
			$= -17.86$	
	18	0.024M	$\log K_{\text{So}} = -19$	(37)
	13-23	varied	$\log K_{\text{So}} = -20.84$	(38)
	18-20	varied	$\log K_{\text{So}} = -19.89$	(17)
	25	0 corrected	$\log K_{\text{So}} = -15.84$	(39)
	25	3M NaClO ₄	$\log K_{\text{So}} = -17.55$	(40)
Pb ²⁺	25	0 corrected	$\log (K_{\text{So}} = [\text{Pb}^{2+}]^3 [\text{PO}_4^{3-}]^2)$	(41)
			$\log (K_S = [\text{Pb}^{2+}] [\text{HPO}_4^{2-}]) = -9.90$	

TABLE 1 (continued)

<u>Ion</u>	<u>Temperature (°C)</u>	<u>Medium</u>	<u>Results</u>	<u>References</u>
Pb ²⁺	37.5	0 corrected	$\log (K_{so} = [Pb^{2+}]^3 [PO_4^{3-}]^2) = -42.00$	(41)
			$\log (K_s = [Pb^{2+}] [HPO_4^{2-}]) = -9.62$	
			$\log (K_{so} = [Pb^{2+}]^3 [PO_4^{3-}]^2)$	(42)
			$= -43.53$	
			$\log (K_s = [Pb^{2+}] [HPO_4^{2-}])$	
Cu ²⁺	18-20	varied	$= -11.36$	
			$\log (K_s = [Pb^{2+}]^5 [PO_4^{3-}]^3 [Cl^-])$	
			$= -79.115$	
	18-20	varied	$\log (K_s = [Pb^{2+}] [HPO_4^{2-}])$	(17)
			$= -9.85$	
	-----	varied	no evidence for complexes	(43)
	25	varied	$\log \frac{[Cu(H_2PO_4)_2]}{[Cu^{2+}] [H_2PO_4^-]^2} = 1.49$	(10)
	19-20	dilute	$\log (K_{so} = [Cu^{2+}]^3 [PO_4^{3-}]^2)$	(35)
			$= -36.9$	

Table 1 (continued)

<u>Ion</u>	<u>Temperature (°C)</u>	<u>Medium</u>	<u>Results</u>	<u>References</u>
Cu ²⁺	37	0.15MKNO ₃	$\log \frac{[\text{CuHPO}_4^0]}{[\text{Cu}^{2+}][\text{HPO}_4^{2-}]}$	(49)
			= 3.3	
			$\log \frac{[\text{CuH}_2\text{PO}_4^+]}{[\text{Cu}^{2+}][\text{H}_2\text{PO}_4^-]}$	
			= 1.2	
			$\log \frac{[\text{CuH}_3(\text{PO}_4)_2^-]}{[\text{CuH}_2\text{PO}_4^+][\text{HPO}_4^{2-}]}$	(49)
			= 3.7	
			$\log \frac{[\text{Cu}_2\text{H}_2(\text{PO}_4)_2^0]}{[\text{CuHPO}_4^0]^2}$	
			= 2.5	

rearrangement on ignition is very slow.

In 1950, Walton (46) reported the formation of cupric hydrogen orthophosphate when CuO is treated with a mixture of 85 percent orthophosphoric acid (H_3PO_4), water, and glycol at 100°C .

In 1963, Royen and Brenneis (47) reported that when $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (prepared as described by Bassett and Bedwell) was heated at 200°C in an attempt to form CuHPO_4 (anhydrous), cupric pyrophosphate ($\text{Cu}_2\text{P}_2\text{O}_7$) was formed.

In 1965, Klement and Haselbeck (48) tried Walton's method and obtained a clear blue solution from which they could not separate a salt. They synthesized $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ according to Debray (44) and obtained the following results:

$\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (177.6) calc. : Cu, 35.80 ; PO_4 , 53.50

expt'l : Cu, 35.68 ; PO_4 , 53.28

Cu : PO_4 = 1 : 1.0

1.5 Solubility of Cupric Orthophosphate Compounds

In 1961, Chukhlantsev and Alyamovskaya (35) determined the solubility of $\text{Cu}_3(\text{PO}_4)_2$ in dilute nitric acid and hydrochloric acid at $19\text{--}20^\circ\text{C}$ by glass electrode and solubility measurements. They calculated the solubility product to be

$$K_{\text{so}} = [\text{Cu}^{2+}]^3 [\text{PO}_4^{3-}]^2 = (1.3 \pm 0.8) \times 10^{-37}.$$

1.6 Cupric-Orthophosphate Complexes in Solution

In 1945, Mercadie (10) determined the equilibrium constant of the reaction $\text{Cu}(\text{H}_2\text{PO}_4)_2 \rightleftharpoons \text{Cu}^{2+} + 2\text{H}_2\text{PO}_4^-$ in solutions containing a large excess of orthophosphate. Using a copper electrode and a saturated KCl calomel reference electrode, Mercadie measured, at 25°C , the potential of solutions which were 0.003865M in Cu^{2+} and varied in $[\text{NaH}_2\text{PO}_4]$

from 0.0727 to 2.09 M. Each solution contained a small amount of phosphoric acid to prevent precipitation. Thus for the reaction $\text{Cu}^{2+} + 2\text{H}_2\text{PO}_4^- \rightleftharpoons \text{Cu}(\text{H}_2\text{PO}_4)_2$ the formation constant at 25°C was calculated to be 31 in solutions containing a large excess of orthophosphate.

In 1970, Childs (49) reported the presence in solution of the species $\text{CuH}_2(\text{PO}_4)_4^+$, CuHPO_4^0 , $\text{CuH}_3(\text{PO}_4)_2^-$, and $\text{Cu}_2\text{H}_2(\text{PO}_4)_2^0$ over the pH range of 3.0 to 4.4. He potentiometrically titrated aqueous solutions of 0.15M potassium nitrate (KNO_3) containing relatively small amounts (about 3×10^{-3} to 9×10^{-3} M) of orthophosphoric acid (H_3PO_4) and cupric nitrate ($\text{Cu}(\text{NO}_3)_2$), with potassium hydroxide (KOH) solution at 37°C. pH measurements were made using the cell
 glass electrode $\left| \text{H}_3\text{PO}_4(\text{C}_1) , \text{Cu}(\text{NO}_3)_2(\text{C}_2) , \text{KOH}(\text{C}) , \text{KNO}_3(0.15 \text{ mol. l.}^{-1}) \right|$
 $\text{KCl}(\text{sat'd.}) \left| \text{calomel electrode} \right|$

Using the computer program SCOGS, Childs used the data to calculate the following equilibrium constants

$$K_{m,1} = \frac{[\text{CuH}_2\text{PO}_4^+]}{[\text{Cu}^{2+}][\text{H}_2\text{PO}_4^-]} \cong 16$$

$$K_{m,2} = \frac{[\text{CuHPO}_4^0]}{[\text{Cu}^{2+}][\text{HPO}_4^{2-}]} \cong 2000$$

$$K_{m1,2} = \frac{[\text{CuH}_3(\text{PO}_4)_2^-]}{[\text{CuH}_2\text{PO}_4^+][\text{HPO}_4^{2-}]} \cong 5000$$

$$K_{m2,m2} = \frac{[\text{Cu}_2\text{H}_2(\text{PO}_4)_2^0]}{[\text{CuHPO}_4^0]^2} \cong 320$$

The results obtained by Childs and Mercadie seem to be inconsistent since different complexes are involved although different media may favor different complexes.

1.7 Techniques for Studying Complex Formation and Solubility

There are several experimental techniques which may be used to study complex formation and solubility. Two of these methods are

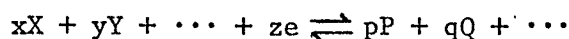
potentiometry and solubility.

POTENTIOMETRY

The potentiometric method is by far the most accurate and widely applicable technique currently available for the study of ionic equilibria. The potentials originate from two main types of phenomena:

(1) oxidation - reduction equilibria, and (2) the formation of ionic concentration gradients across membranes.

If the reversible electron-transfer reaction



can occur, the potential acquired by an electrode in contact with an equilibrium mixture of P, Q, ..., X, Y, ... is given by the Nernst equation

$$E = T_{E_0} + \frac{RT}{zF} \ln \frac{\{X\}^x \{Y\}^y}{\{P\}^p \{Q\}^q}$$

where the standard electrode potential T_{E_0} is the potential acquired when all species are at unit activity. The electrode may be either inert, as in so-called redox systems, or may itself be composed of one of the participating species.

Since the activity of a pure solid or liquid or of a gas at atmospheric pressure is taken to be unity, the Nernst equation may often be considerably simplified. Moreover, if the activity coefficients $\gamma_P, \gamma_Q, \dots, \gamma_X, \gamma_Y, \dots$ are kept constant, e.g., by use of a constant ionic medium, then

$$E = E_0 + \frac{RT}{zF} \ln \frac{[X]^x [Y]^y \dots}{[P]^p [Q]^q \dots}$$

where the formal electrode potential E_0 is given by

$$E_0 = T_{E_0} + \frac{RT}{zF} \ln \frac{\gamma_X^x \gamma_Y^y \dots}{\gamma_P^p \gamma_Q^q \dots}$$

In general, the presence of any other oxidizing or reducing agent which can react with the species P, Q, X, or Y should be avoided.

Membrane electrodes acquire a potential if the solutions on either side of the membrane have different concentrations with respect to one or more ions. Since no electron transfer is involved, membrane electrodes may, in principle, be used in the presence of any oxidizing or reducing agent.

The electrodes usually employed to study ionic equilibria are reversible to metal ions, to protons, or to anions. The potential should reach that predicted by the Nernst equation within a reasonable time, particularly if the titration technique is used and the electrode should not be decomposed by the solution.

SOLUBILITY

Measurement of the solubility of a sparingly soluble solid in the aqueous solution of a complexing agent is one of the oldest methods for studying equilibria in solution. Direct and competitive solubility methods have been used to determine stability constants of metal ion complexes.

Many solubility data are difficult to interpret, since considerable variation has often occurred in the composition of the aqueous phase and hence, in the stoichiometric solubility product

$$S_c = ba^c = {}^T S_c \gamma_B^{-1} \gamma_A^{-c}$$

of the sparingly soluble complex BA_c ; here ${}^T S_c$ is the thermodynamic solubility product. However, a constant ionic medium can be used as well for solubility studies as for work on homogeneous systems and a number of solubility measurements have been made using solutions in which the activity coefficients are adequately controlled.

Equilibration between solid and solution may be effected either by shaking the two together in a closed vessel or by running the aqueous phase through a saturator packed with a column of solid. Equilibration must be carried out in a thermostat. Since equilibrium is often attained slowly, it is advisable to check that the same values of solubility are obtained after different intervals of time.

The solid phase may be separated from the saturated solution by filtration or centrifugation which should be carried out at the equilibrium temperature.

The choice of analytical method depends largely on the magnitude of the solubility to be determined. Moderately high values are usually determined gravimetrically or volumetrically, and low values by polarographic, colorimetric, or radiometric methods.

2.

OBJECT OF THIS RESEARCH

The object of this research was to determine the solubility of cupric monohydrogen orthophosphate in aqueous solution and to investigate the existence of soluble cupric-orthophosphate complexes. Two different types of experimental procedures were used: potentiometric titrations and solubility. The first method involved the potentiometric titrations of acidic copper solutions with acidic orthophosphate solutions keeping the total hydrogen ion concentration and the total cupric ion concentration constant. The free hydrogen ion concentrations, h , and the free cupric ion concentrations, c , were determined using a glass electrode and a cupric ion selective electrode calibrated to measure free hydrogen ion concentration and free cupric ion concentration, respectively. The second method involved the equilibration of cupric hydrogen orthophosphate solid samples in solutions of known total hydrogen ion concentration or known orthophosphate concentration. Determinations of free hydrogen ion concentration, h , and free cupric ion concentration, c , were carried out on each equilibrated solution. In addition, both the equilibrated solutions and their corresponding solid residues were analyzed for total copper and total orthophosphate.

3. GENERAL PROCEDURE , APPARATUS AND REAGENTS

3.1 General

Although the copper phosphate solids were not moisture sensitive, they were kept either in tightly capped bottles (e.g. the original $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ samples) or in a desiccator over Drierite to prevent the solids from picking up further moisture. The concentrated aqueous solutions of sodium perchlorate (NaClO_4) were kept in tightly capped glass bottles previously used to store concentrated perchloric acid (HClO_4).

3.2 Instrumental

Infrared spectra were recorded by a Perkin-Elmer, Model 337, grating spectrophotometer, linear in wave number and covering the range of 4000-400 wave numbers. All the samples were ground with dried KBr and run as KBr discs. In addition some of the samples were run as nujol mulls which resulted in a less resolved spectrum for some samples and a spectrum similar to the KBr disc spectrum for some other samples. Most of the discs were made using a Beckman (Cat. No. 5020) vacuum die. Later the discs were made using a Wilks "Mini-Press" KBr Pellet Press and Holder which was found to produce much more transparent discs than the other die. Later, the Wilks Press became unavailable and the last few discs were made using an International Crystal Laboratories KBr Quick Press. All peak positions were determined to $\pm 1.0 \text{ cm.}^{-1}$ using polystyrene for calibration.

X-ray diffractograms were recorded on a Philips X-ray Diffractometer Type No. 12045/3 over the range of $4^\circ 2\theta$ to about $65^\circ 2\theta$ using $\text{CuK}\alpha$ radiation and a Ni filter.

Potentiometric measurements were made reading either a Dynamco Digital Voltmeter (Type (DM2022S)) or a Metrohm Compensator (E388).

Atomic absorption measurements were carried out on a Perkin Elmer 306 Atomic Absorption Spectrophotometer with a Varian Techtron Cu lamp (No. DT764).

Colorimetric measurements were made on a Carl Zeiss PMQ II Spectrophotometer using matched quartz cells. The reference solutions were 3 N ammonium hydroxide (NH_4OH) solution for the copper determinations and a 1:1 tert-butanol:benzene mixture for the orthophosphate determinations.

A Coleman Metrion III pH meter, calibrated against standard buffer solution (pH4 and pH7), was used when adjusting solutions to a particular pH before preparing some of the copper orthophosphate solids.

3.3 Chemicals

All chemicals used were at least of reagent grade purity. Sodium perchlorate (NaClO_4) was synthesized from reagent grade perchloric acid (HClO_4) and reagent grade sodium carbonate (Na_2CO_3) and purified as described by Biedermann (50).

The water used was purified from in-house distilled water by distillation from alkaline potassium permanganate solution and acidic potassium dichromate solution as described by Hickling (51).

3.4 Potentiometric Titration Apparatus

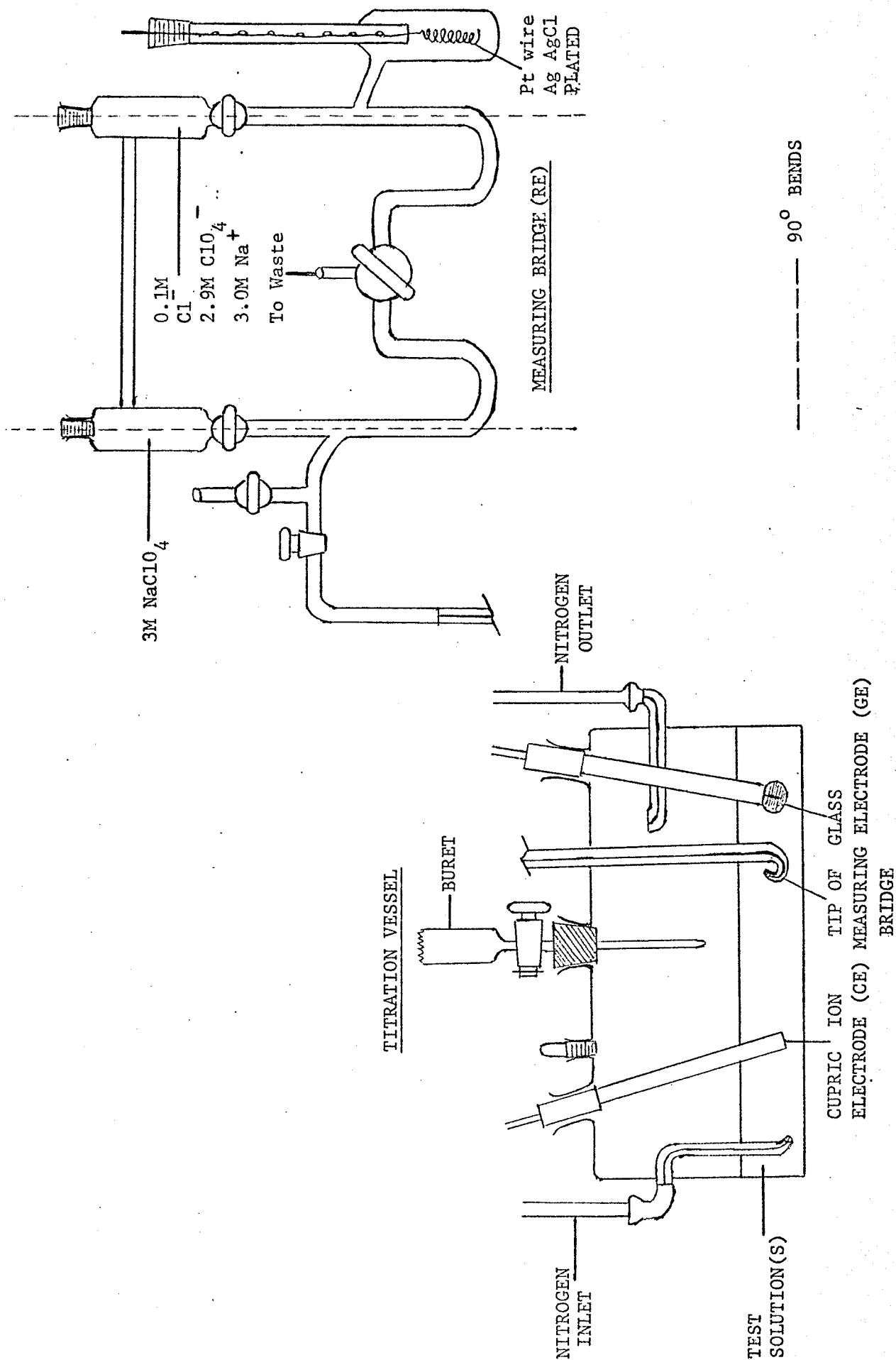
Figure 1 shows the all glass apparatus used in the potentiometric titrations. It consists of a titration vessel and one "Wilhelm bridge" (52). The bridge serves to isolate the reference electrode from the titration vessel, electrical contact being maintained via a 3-way stopcock to a 3M NaClO_4 salt bridge, dipping into the test solution. The apparatus was kept in a paraffin oil thermostat at $25.0 \pm 0.1^\circ\text{C}$ in a room at $23 \pm 2^\circ\text{C}$. The oil level was such that the vessel and electrode compartment were completely submerged, but all stopcocks were readily accessible.

FIGURE 1

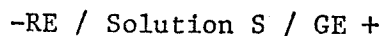
Potentiometric Titration Apparatus (not to scale)

The parts of the measuring bridge outside the dashed lines are actually bent 90° out of the plane of the paper away from the viewer.

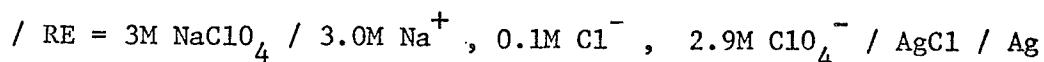
FIG. 1



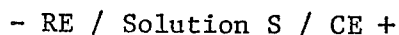
The e.m.f. measurements were made using a Sargent-Welch glass electrode (Type S-30050-15) and an Orion cupric ion selective electrode (Model 94-29A). The reference electrode was an Ag/AgCl coil prepared according to Brown (64). The free hydrogen ion concentration, h , was measured by means of the cell



where GE denotes a glass electrode, S the test solution, and RE a reference half cell of the composition



The following cell was used to measure free cupric ion concentration, c



where CE denotes the cupric ion selective electrode and RE is the same reference half-cell as described previously.

The equilibrium solution was stirred by a stream of nitrogen gas which had been washed to remove acidic and basic impurities and saturated with the ionic medium by passing through four bottles containing 10% H_2SO_4 , 10% NaOH, 3M $NaClO_4$, 3M $NaClO_4$, respectively.

A block diagram of the apparatus is given in Figure 2.

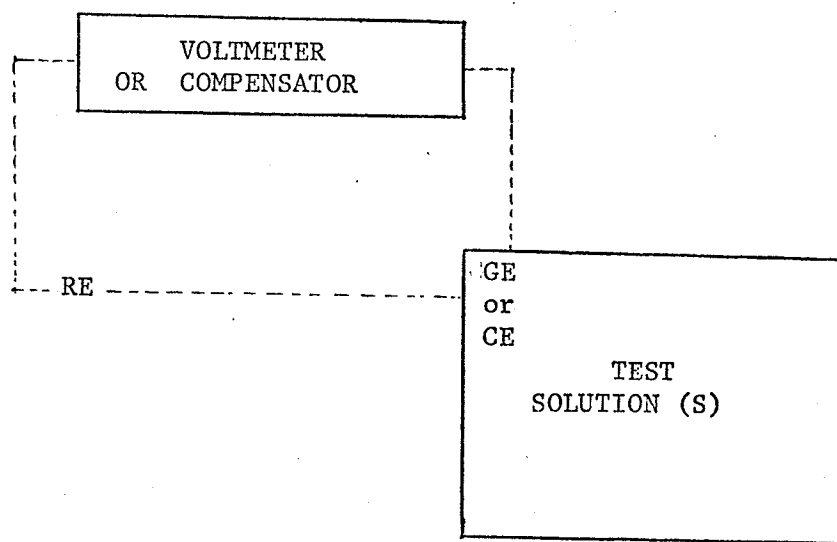


Figure 2

Block Diagram of the Apparatus used for Potentiometric
Measurements

4.

EXPERIMENTAL

4.1 The Original $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ Samples

Two different methods were used to synthesize $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ from cupric carbonate (CuCO_3) and phosphoric acid (H_3PO_4) to see if more than one form of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ could be synthesized. Analyses for total copper content and total orthophosphate content for both samples confirmed that the empirical formula for both samples was $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$. The experimental details are described below.

Preparation I

Following Debray (44), cupric monohydrogen orthophosphate monohydrate ($\text{CuHPO}_4 \cdot \text{H}_2\text{O}$) was prepared by adding, in portions, 50 g. of cupric carbonate (CuCO_3) to a mixture of 100 ml. of orthophosphoric acid (H_3PO_4) and 100 ml. of water. The undissolved solid was filtered off and the resulting blue solution concentrated on a steam bath for several hours. A pure blue coloured product separated out of the solution and the product was filtered onto a sintered glass crucible by suction. The product was washed with small amounts of water, was dried at 95°C for 1 hour, and then stored in a desiccator overnight. The product consisted of fairly large blue crystals.

(Theoretical) $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$: Cu, 35.79 ; PO_4 , 53.49

Found : Cu, 34.77 ; PO_4 , 52.86

molar Cu / PO_4 ratio = 0.983

Preparation II

Following Bassett and Bedwell (45), cupric monohydrogen orthophosphate monohydrate ($\text{CuHPO}_4 \cdot \text{H}_2\text{O}$) was prepared by adding, in portions, 62 g. of cupric carbonate (CuCO_3) to a mixture of 77 ml. of phosphoric acid (H_3PO_4) and 200 ml. of water. The resulting solution was well stirred

until evolution of carbon dioxide ceased and refluxed for 3 days during which a solid formed in the reaction flask. The product was filtered off by suction, washed, dried, and stored as described in Preparation I. The product consisted of small blue needlelike crystals.

(Theoretical) $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$: Cu, 35.79 ; PO_4 , 53.49

Found : Cu, 35.66 ; PO_4 , 52.26

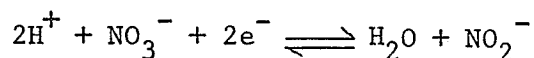
molar Cu / PO_4 ratio = 1.020

Analyses

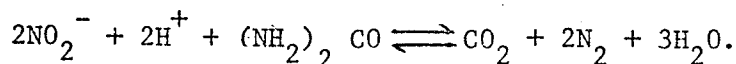
The two $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ samples were analyzed for total copper content and total orthophosphate content.

(i) The two samples were analyzed in duplicate for total copper content by electrodeposition (53) of copper on a platinum cathode.

The electrodepositions were performed by electrolyzing at about 100 milliamperes a stirred aqueous solution, acidified with a few milliliters of sulfuric acid (H_2SO_4), of an accurately known amount of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ sample. Nitric acid (HNO_3) improves the nature of the copper deposit by preventing the evolution of hydrogen at the cathode. The reaction involved produces nitrite (NO_2^-) via



After the blue color of the solution had disappeared, the NO_2^- was removed by the addition of urea which reacts



The removal of NO_2^- is necessary to enable the complete deposition of copper.

(ii.) Triplicate analyses of the two $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ samples for total copper content were performed by iodometric titration (54).

Results of both methods of analysis agreed within \pm 0.10 percent.

(iii.) The total orthophosphate content of the two samples was determined in duplicate by a gravimetric method (55) involving the precipitation of orthophosphate as magnesium ammonium phosphate and ignition at about 1000°C to magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$).

Infrared Spectra

The infrared spectra of both $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ samples, ground with dried KBr and also as nujol mulls, over the range of 1333 to 400 cm^{-1} are shown in Figure 3. Absolute peak intensities of the infrared spectra cannot be compared since all spectra were run under different conditions. It is obvious that the spectra taken as nujol mulls are less resolved than the spectra taken as KBr discs and therefore the latter will be used for comparison with themselves and other spectra. Both samples give a very similar spectrum; for example, Preparation I shows peaks at 1272 and 1238 cm^{-1} in the $\text{P}=\text{O}$ stretching region, peaks at 1083 , 1065 , 1012 , 990 , 925 , and 904 cm^{-1} in the $\text{P}-\text{O}$ stretching region, and peaks at 572 and 525 cm^{-1} in the $\text{O}-\text{P}-\text{O}$ bending region. Preparation II shows peaks at 1278 and 1245 cm^{-1} in the $\text{P}-\text{O}$ stretching region, and peaks at 1086 , 1072 , 1017 , 991 , 927 , and 906 cm^{-1} in the $\text{P}-\text{O}$ stretching region, and peaks at 571 and 523 cm^{-1} in the $\text{O}-\text{P}-\text{O}$ bending region. Since the peaks are not particularly sharp, small discrepancies in the peak positions are to be expected. Overall, the spectra suggest that both samples have the same structure in the solid state.

Referring to Figure 3, to Table 2 (Nakamoto (57)), and to Stranks and Lincoln (56), the spectra show evidence of C_{2v} symmetry in the molecule. Stranks and Lincoln (56) found the following frequencies for the phosphate ligand of bidentate $\text{Co}(\text{NH}_3)_4\text{PO}_4$ ν_1 : 900 m and ν_3 : 920 s , 1045 s , and 1110 s cm^{-1} . In the spectrum of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation I),

Figure 3

Infrared Spectra of the Two $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ Preparations

- (i.) $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation I)
 - (a.) KBr disc (solid line)
 - (b.) Nujol mull (dashed line)

- (ii.) $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II)
 - (a.) KBr disc (solid line)
 - (b.) Nujol mull (dashed line)

The calibration peaks indicate 1028.0 cm^{-1}

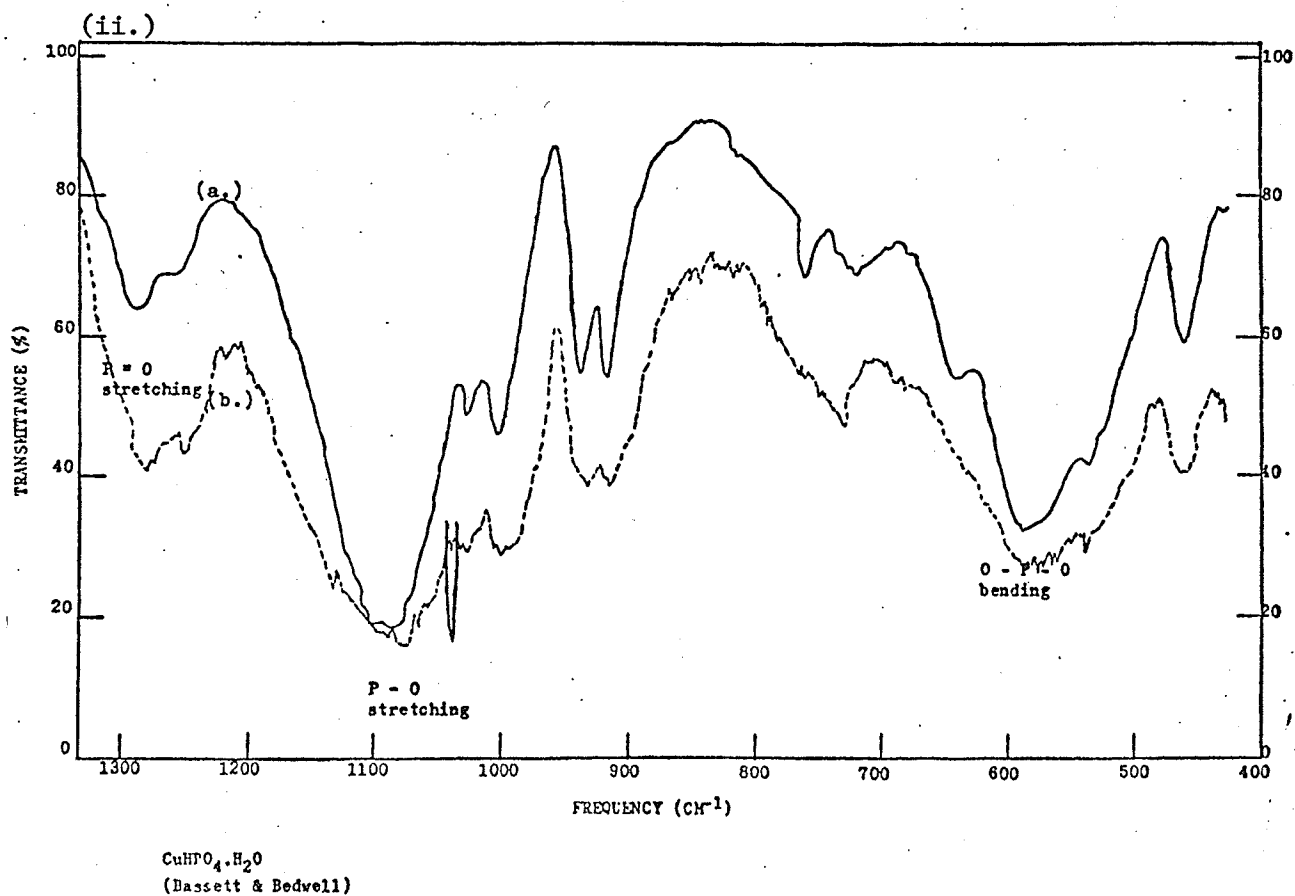
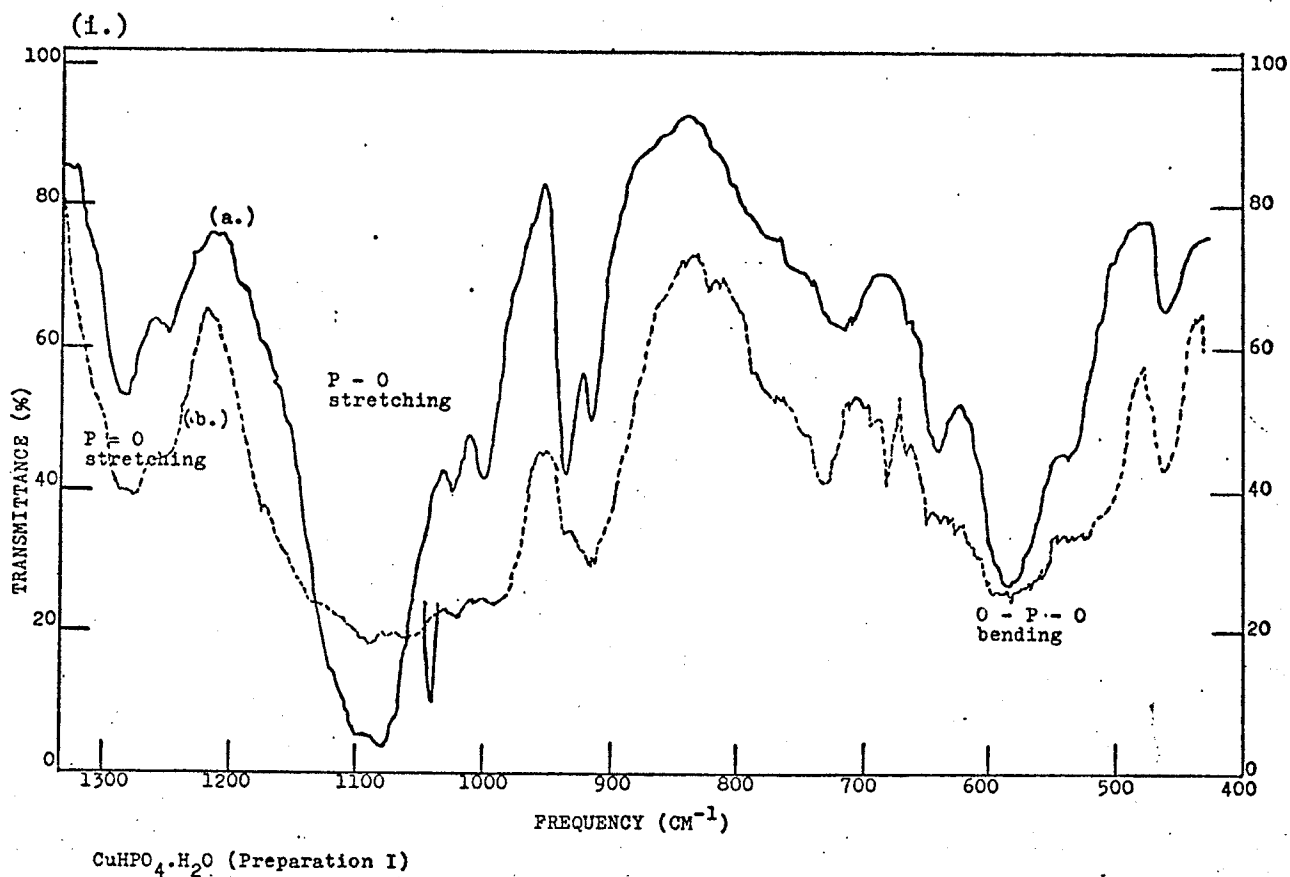


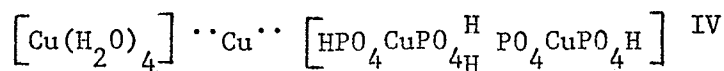
TABLE 2

CORRELATION TABLE FOR T_d , C_{3v} , AND C_{2v}

Point Group	1	2	3	4
T_d	$A_1(R)$	$E(R)$	$F_2(I,R)$	$F_2(I,R)$
C_{3v}	$A_1(I,R)$	$E(I,R)$	$A_1(I,R) + E(I,R)$	$A_1(I,R) + E(I,R)$
C_{2v}	$A_1(I,R)$	$A_1(I,R) + A_2(R)$	$A_1(I,R) + B_1(I,R)$	$A_1(I,R) + B_1(I,R)$
			$+ B_2(I,R)$	$+ B_2(I,R)$
I	Infrared Active		R	Raman Active

the ν_1 peak seems to appear at 805 cm^{-1} , however, it seems that the ν_3 peaks are each split into doublets (perhaps due to complexed water) and appear at 1083 and 1065 cm^{-1} , 1012 and 990 cm^{-1} , and 925 and 904 cm^{-1} . According to Table 2, C_{2v} symmetry should result in three ν_4 bending peaks but $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ seems to show only two peaks at 572 and 525 cm^{-1} . However, it is probable that the third bending peak is buried under other peaks. The peaks at 1276 and 1243 cm^{-1} seem to correspond to P=O stretching, but the other peaks in the range of 800 to 400 cm^{-1} are difficult to assign and may be due to complexed water. The small peak at 751 cm^{-1} appears in all the infrared spectra; its source is unknown but it may be instrumental. Interpretation of the spectrum of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II) is the same as for Preparation I. For both samples the spectrum in the range 4000 to 1500 cm^{-1} is rather ill-defined and is probably due to lattice water. In addition, KBr picks up water from the atmosphere during grinding and this will absorb in this region.

From the very faint "glowing" of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ on ignition, Bassett and Bedwell (45) proposed a quadramolecular structure for $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$



The above structure appears to have C_{2v} symmetry which is the symmetry indicated by the experimental infrared spectra of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$.

X-ray Diffractograms

An X-ray diffractogram was taken for both $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ samples to aid in the identification of samples in subsequent experiments. The results obtained are presented in Table 3. Comparing the X-ray diffractograms of the two $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ samples, it is easily seen that the positions (although not the intensities) of most of the peaks are quite comparable. Therefore, it appears that the crystal structures of the

TABLE 3

RESULTS OF X-RAY DIFFRACTOGRAMS OF $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$

Preparation I			Preparation II		
2θ	$d(\text{\AA})$	I/I_1	2θ	$d(\text{\AA})$	I/I_1
17.5	5.07	100	17.4	5.10	100
19.3	4.60	24	19.3	4.60	10
			20.8	4.27	11
21.6	4.11	8			
27.7	3.22	17	27.7	3.22	12
29.2	3.06	24	29.1	3.07	32
30.1	2.97	8	30.1	2.97	10
31.2	2.87	23	31.1	2.88	10
32.5	2.75	52	32.5	2.75	26
34.5	2.60	16	34.4	2.61	63
35.3	2.54	45	35.2	2.55	98
37.3	2.41	11	37.1	2.42	14
37.9	2.37	11	37.7	2.39	7
			38.2	2.36	7
39.0	2.31	17	38.9	2.32	7
42.4	2.13	10	42.2	2.14	8
			42.6	2.12	8
43.6	2.08	12	43.5	2.08	6
			44.2	2.05	5
45.3	2.00	14	44.6	2.03	8
			45.3	2.00	7
52.5	1.74	10	51.5	1.77	7
54.0	1.70	17	52.5	1.74	5
			53.8	1.70	24
57.1	1.61	13	55.4	1.66	12
60.2	1.54	14	57.0	1.62	9
			60.1	1.54	8
			62.1	1.49	7

two $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ samples are quite similar.

In X-ray diffractometry several factors can cause variations in intensities, line breadths, and shifts in the positions of lines. If the goniometer is not properly aligned so that the specimen surface remains tangent to the focusing circle, then the intensities are decreased, line breadths increased, and line positions are shifted. Besides instrumental errors, sample preparation also has an effect. Ideally, the sample should consist of very small highly absorbing crystals in random orientation. Small crystals in random orientation give a true representation of relative intensities and high absorption prevents diffraction at various depths. Unfortunately, these criteria cannot be completely met in practice.

Some of the uncertainties involved in the interpretation of the diffractograms must also be taken into consideration. Firstly, the lower the 2θ value of the peak position, the greater the uncertainty in the corresponding d values. For example, if the 2θ value is 5.0 ± 0.1 degrees, then the corresponding d value is $(17.67 \pm 0.35) \text{ \AA}$; if 2θ is 10.0 ± 0.1 degrees then the d value is $(8.84 \pm 0.09) \text{ \AA}$; and if 2θ is 15.0 ± 0.1 degrees then the d value is $(5.91 \pm 0.04) \text{ \AA}$. Therefore, whenever possible, diffractogram results will be compared using 2θ values rather than d values. Secondly, it is sometimes difficult to tell the difference between peaks and noise, especially in the high 2θ range. Therefore, some of the minor peaks may have been overlooked, although the major peaks should not be affected.

In conclusion, the reproducibility of the X-ray diffractograms should be fairly good as far as peak positions are concerned although the relative intensities would be somewhat variable depending on sample

preparation. To get accurate intensities, it may be necessary to take many diffractograms of each sample and average them.

4.2 Temperature Study of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II)

In order to determine the effect of heat on the composition of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ and also to try to produce CuHPO_4 (anhydrous) and cupric pyrophosphate ($\text{Cu}_2\text{P}_2\text{O}_7$), it was decided to do a temperature study on $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$. In the previous section, it has been shown that the two $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ samples are quite similar in crystal structure and essentially identical in molecular structure and chemical composition. A temperature study on one of the two $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ samples should be sufficient to investigate changes which occur after heating.

Preparations and Analyses

(i.) An accurately weighed sample of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II) was heated in an oven at 110°C for 2 hours which resulted in no noticeable color change. After cooling in a desiccator, the sample was weighed again and the percent weight loss calculated. The results obtained are presented in Table 4. If the solid remains unchanged after heating, then the percent weight loss is expected to be

Theoretical % wt. loss calc'd. for $\text{CuHPO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CuHPO}_4 \cdot \text{H}_2\text{O} = 0\%$

(ii.) An accurately weighed sample of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II) was heated at $120\text{--}130^\circ\text{C}$ for 1 hour which resulted in no noticeable color change. After cooling in a desiccator, the sample was weighed again and the percent weight loss calculated. The results obtained are presented in Table 4. If the solid remains unchanged after heating, then the percent weight loss is expected to be

Theoretical % wt. loss calc'd. for $\text{CuHPO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CuHPO}_4 \cdot \text{H}_2\text{O} = 0\%$.

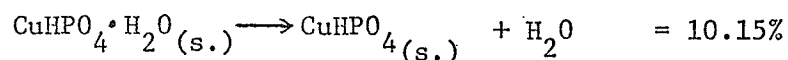
TABLE 4
SUMMARY OF SAMPLE WEIGHTS AND WEIGHT LOSSES

Temp. (°C)	(g.) Sample wt.	(g.) Weight loss	(Experimental) % Wt. loss	(Theoretical) % Wt. loss	(Experimental) % Cu	(Theoretical) % Cu
110	1.7019	0.0003	0.02	0	-	35.79
120-130	1.6342	0.0009	0.06	0	-	35.79
180	1.7297	0.1915	11.07	10.15	39.69	39.83
700	0.7433	0.1149	15.46	15.22	41.94	42.22

All samples are from Preparation II

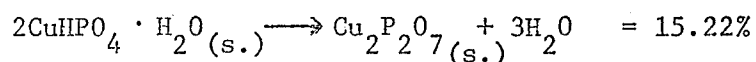
(iii.) An accurately weighed sample of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II) was heated at 180°C for 2 hours which resulted in a color change going from blue to light green. The percent weight loss was calculated and the sample was analyzed for percent Cu content by electrodeposition. The results obtained are presented in Table 4. If the solid only loses water of hydration after heating, then the percent weight loss is expected to be

Theoretical % wt. loss calc'd. for



(iv.) An accurately weighed sample of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II) was heated at 700°C overnight in a muffle furnace which resulted in a color change going from blue to very pale green. The percent weight loss was calculated and the sample was analyzed for percent Cu content by electrodeposition. The results obtained are presented in Table 4. If the solid is converted to cupric pyrophosphate after heating, then the percent weight loss is expected to be

Theoretical % wt. loss calc'd. for



Infrared Spectra

The infrared spectra of all the heated samples and the original $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II) sample, ground with dried KBr, over the range 1333 to 400 cm^{-1} are shown in Figure 4. The absolute peak intensities of the spectra cannot be compared since all spectra were run under different conditions.

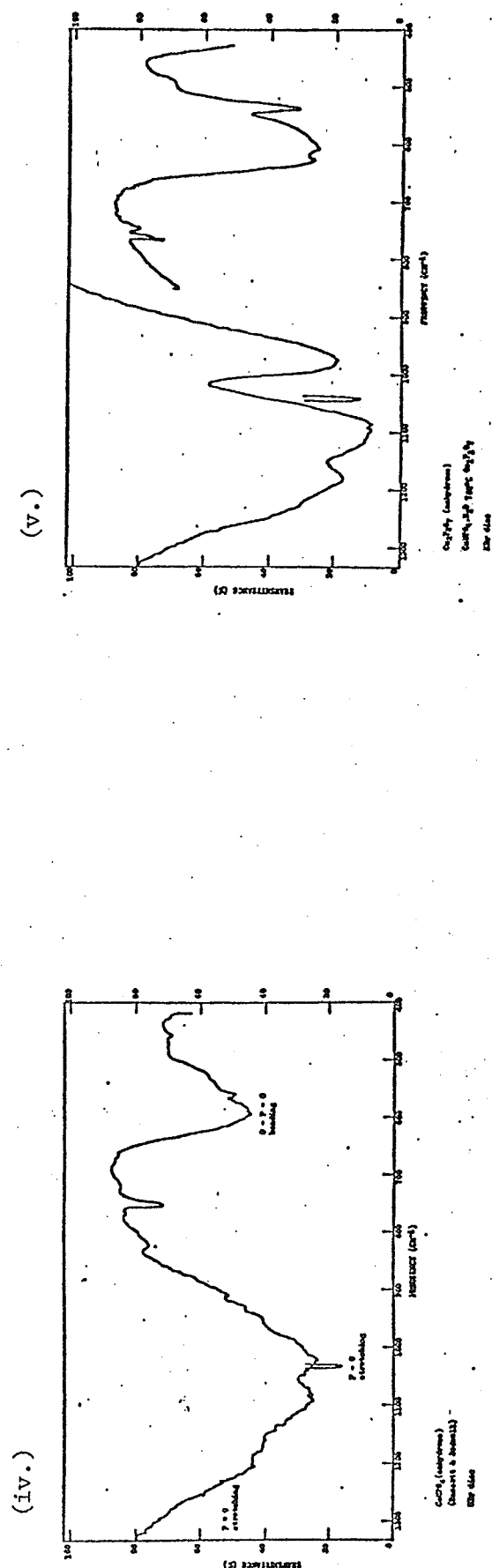
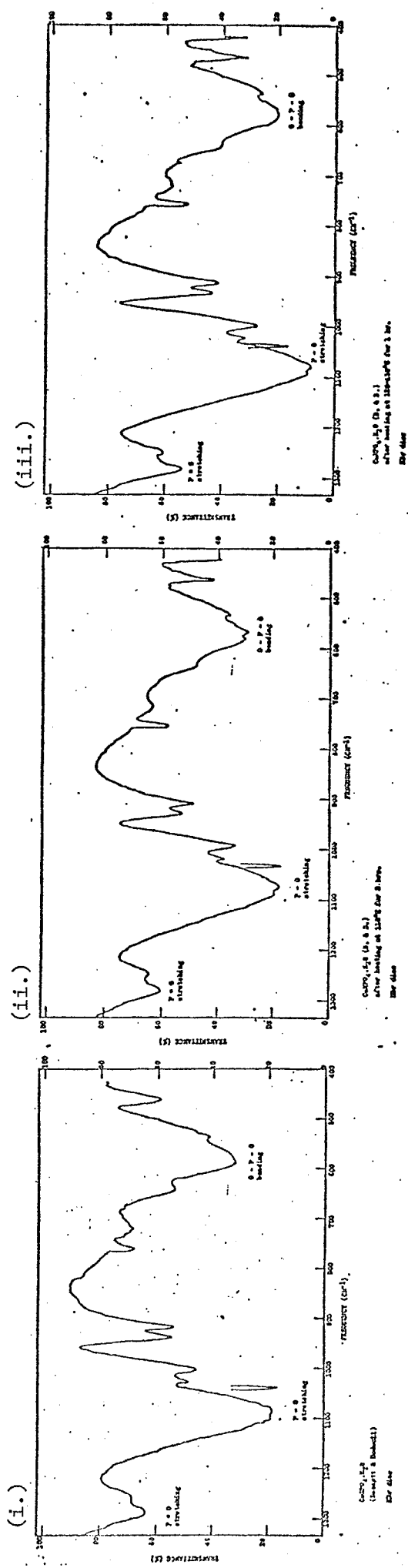
Both the 110° sample and the 120 - 130° sample appear to give the same spectrum as the original $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ sample indicating that they

Figure 4

Infrared Spectra of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II)
and all the heated samples

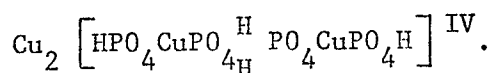
- (i.) $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Ppn.II) (ii.) 110° Sample (iii.) $120-130^\circ$ Sample
(iv.) 180° Sample (v.) 700° Sample

The calibration peaks indicate 1028.0 cm^{-1}

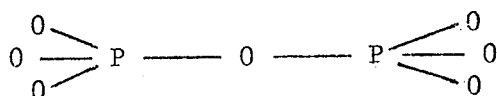


all have the same molecular structure.

However, the 180° sample gives a much less resolved spectrum than $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ due to the loss of water of hydration. For example, the peaks at 1278 and 1245 cm^{-1} seem to have disappeared and the four peaks at 1086, 1072, 1017, and 917 cm^{-1} in the $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ spectrum have been replaced by two broad peaks at 1090 and 1019 cm^{-1} . The peaks at 927, 906, and 629 cm^{-1} also seem to have disappeared and the peak at 450 cm^{-1} is reduced to a small bump. However, the spectrum still seems to be consistent with C_{2v} symmetry perhaps



The spectrum of the 700° sample is obviously different from the original $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ sample and is apparently different from the spectrum of the 180° sample in both the P-O stretching and O-P-O bending regions. The spectrum of the 700° sample is consistent with the following structure



In the O-P-O bending region, the spectrum is similar in appearance to orthophosphate probably indicating the presence of $\text{--- O --- P} \begin{array}{c} \text{O} \\ \diagdown \\ \text{O} \end{array}$ in the molecule.

X-ray Diffractograms

The results of the X-ray diffractograms of the heated samples, the original $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II), and the CuHPO_4 diffraction results reported by Royen and Brenneis (47) are shown in Table 5. The diffractograms of the original $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ sample, the 110° sample, and the 120-130° sample are all very similar suggesting that they are all $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$.

TABLE 5

X-RAY DIFFRACTOGRAMS OF HEATED SAMPLES

(Preparation II) $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$		110° Sample		120-130° Sample		180° Sample		700° Sample		CuHPO_4 (47)	
$d(\text{\AA})$	I/I_1	$d(\text{\AA})$	I/I_1	$d(\text{\AA})$	I/I_1	$d(\text{\AA})$	I/I_1	$d(\text{\AA})$	I/I_1	$d(\text{\AA})$	I/I_1
5.10	100	5.07	100	5.07	100	6.11	22	5.04	7	7.93	10
4.60	10	4.58	6	4.62	10	5.01	29				
4.27	11	4.25	7	4.27	12	4.29	22	4.29	15	4.10	40
						3.45	29	3.80	8		
3.22	12	3.20	6	3.22	13			3.14	100		
3.07	32	3.05	15	3.07	28					3.07	70
2.97	10	2.95	4	2.97	10	2.99	80	2.95	97	3.01	30
2.88	10	2.86	8	2.88	11	2.90	100			2.864	20
										2.812	50
2.75	26	2.75	7	2.76	25						
2.61	63	2.59	31	2.61	36						
2.55	98	2.54	68	2.55	81	2.54	29	2.53	23		
						2.47	28	2.49	22		
2.42	14	2.41	5	2.42	11					2.434	90
2.39	7	2.37	3	2.39	5					2.399	100
2.36	7	2.34	3	2.35	4						

TABLE 5 (Continued)

(Preparation II) CuHPO ₄ · H ₂ O		110° Sample		120-130° Sample		180° Sample		700° Sample		CuHPO ₄ (47)	
d(Å)	I/I _i	d(Å)	I/I _i	d(Å)	I/I _i	d(Å)	I/I _i	d(Å)	I/I _i	d(Å)	I/I _i
2.32	7	2.30	5	2.32	9			2.16	15	2.300	80
2.14	8	2.13	6	2.14	8						
2.12	8	2.12	6	2.13	7						
2.08	6	2.07	5	2.08	5			2.09	8		
2.05	5	2.05	4	2.05	4			2.05	21		
2.03	8	2.02	5	2.03	6						
2.00	7	2.00	9	2.00	9	2.01	20			1.993	60
1.77	7	1.77	4	1.77	6			1.96	8		
1.74	5	1.74	4	1.74	6			1.90	19		
1.70	24	1.70	21	1.70	23			1.74	9		
1.66	12	1.65	14	1.66	19			1.69	9		
1.62	9	1.61	6	1.62	9						
1.54	8	1.53	7	1.54	10	1.52	22	1.57	16		
1.49	7			1.49	7			1.54	19		

The 180° sample and the 700° sample give diffractograms which are noticeably different from each other and from the original $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ suggesting that changes in crystal structure have taken place. In Table 5, it can be seen that there is poor agreement between the diffractogram of the 180° sample (proposed to be CuHPO_4) and the CuHPO_4 results reported by Royen and Brenneis (47).

Conclusions of Temperature Study

It has been shown that anhydrous cupric hydrogen orthophosphate (CuHPO_4) may be prepared by careful heating of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ at a temperature somewhat below 200°C and that overnight heating of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ at high temperature results in the formation of cupric pyrophosphate ($\text{Cu}_2\text{P}_2\text{O}_7$).

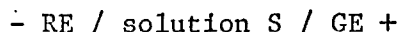
4.3 Potentiometric Titration of Acidic Copper Solutions with Acidic Orthophosphate Solutions

In this research, two different methods were used to investigate the solubility of cupric hydrogen orthophosphate and cupric-hydrogen-phosphate complexing. The first method was to titrate acidic copper solutions potentiometrically with acidic orthophosphate solutions. The second method involves allowing $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ or CuHPO_4 samples to equilibrate in 3M ClO_4^- solutions of known H^+ concentrations or known orthophosphate concentrations. The first method seems to be the more useful one for studying cupric-hydrogen-phosphate complexing and the second method seems to be the more useful one for studying solubility. The first method is described below.

The E.M.F. Measurements

The investigation was made as a series of potentiometric titrations at 25° C. The extent of complexation was followed by measuring the free hydrogen ion concentration, h , and the free cupric ion concentration, c . The free hydrogen ion concentration, h , was measured at

equilibrium by means of the cell

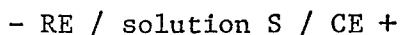


where GE denotes a glass electrode, RE a reference electrode as described in Section 3.4, and S the test solution. The e.m.f. of the cell can be written as

$$E_g = E_g^0 + 59.156 \log h + E_j \quad \text{----- (1)}$$

where E_g^0 is a constant for the glass electrode and E_j is the liquid junction potential between the test solution S and 3M NaClO₄. Following Biedermann and Sillen (58), E_j can be expressed as a function of h , $E_j = jh$, where j is a constant ≈ -17 mV / M. Titration of 1M HClO₄, against 3M NaClO₄ performed by Fincham (59) confirmed that the cell used gave a comparable value of j .

The free cupric ion concentration, c , was measured at equilibrium by means of the cell



where CE denotes a cupric ion selective electrode, RE the reference electrode described in Section 3.4, and S the test solution. The e.m.f. of the cell can be written as

$$E_{\text{Cu}} = E_{\text{Cu}}^0 + 29.578 \log c + E_j \quad \text{----- (2)}$$

where E_{Cu}^0 is a constant for the cupric ion selective electrode and E_j is the liquid junction potential described earlier ($E_j = jh$ where $j \approx -17$ mV / M).

Before each titration, E_g and E_{Cu} were measured for a solution of known total hydrogen ion concentration and known total cupric ion concentration which contained no orthophosphate. Then using equations (1) and (2), the values of E_g^0 and E_{Cu}^0 , respectively, were calculated. For these calculations it was assumed that the total hydrogen ion concentra-

tion = h and the total copper ion concentration = c because there was no orthophosphate present for complexing.

The Z Values

To determine the degree of complexation of orthophosphate by H^+ ions and Cu^{2+} ions, it was decided to calculate values of average ligand number for H^+ -orthophosphate complexing, and Cu^{2+} -orthophosphate complexing.

After each addition of titrant, the average ligand number, Z, was calculated using equations (3) and (4).

$$Z_{H/B} = (H_{TOT} - h) / B \quad \text{-----}(3)$$

where $Z_{H/B}$ is the average ligand number for H^+ -orthophosphate complexing, B is the total analytical concentration of orthophosphate, H_{TOT} is the total analytical concentration of hydrogen ions, and h is the free hydrogen ion concentration calculated using equation (1). Similarly,

$$Z_{C/B} = (Cu_{TOT} - c) / B \quad \text{-----}(4)$$

where $Z_{C/B}$ is the average ligand number for Cu^{2+} -orthophosphate complexing, Cu_{TOT} is the total analytical concentration of copper, c is the free cupric ion concentration calculated using equation (2), and B is the same as in equation (3). The values of $Z_{H/B}$ and $Z_{C/B}$ are given in Tables 6,7,8, and 9.

In addition, theoretical $Z_{H/B}$ values were calculated, for a series of pH values, from the dissociation constants for orthophosphoric acid determined by Baldwin and Sillén (60) by the following procedure:

$$Z_{H/B} = \frac{H_{TOT} - h}{B} \quad \text{-----}(3)$$

assuming that HPO_4^{2-} is originally present in solution and neglecting PO_4^{3-}

$$H_{TOT} = h + [H_2PO_4^-] + 2 [H_3PO_4]$$

$$B = [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]$$

$$Z_{H/B} = \frac{[H_2PO_4^-] + 2 [H_3PO_4]}{[HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]}$$

$$Z_{H/B} = \frac{\frac{[H_2PO_4^-] + 2 [H_3PO_4]}{[HPO_4^{2-}]}}{\frac{[HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]}{[HPO_4^{2-}]}}$$

$$\text{Substituting } \beta_1 = \frac{[H_2PO_4^-]}{h [HPO_4^{2-}]} \text{ and } \beta_2 = \frac{[H_3PO_4]}{h^2 [HPO_4^{2-}]}$$

$$Z_{H/B} = \frac{\beta_1 h + 2 \beta_2 h^2}{1 + \beta_1 h + \beta_2 h^2} \quad \text{-----}(5)$$

where $\beta_1 = 1.86 \times 10^6$ and $\beta_2 = 1.44 \times 10^8$. The above formula neglects Cu^{2+} - orthophosphate complexing and assumes that PO_4^{3-} is negligible in the solutions measured.

The Potentiometric Titrations

Four different types of titrations were performed at 25°C covering a pH range of about 1 to about 3.7. Higher pH values resulted in precipitation. 50 ml Class A burets were used for all titrations except for Type IV where two 10 ml burets were used. In Tables 6,7,8, and 9 the following subscripts are used:

o means initial solution before titration

t means titrant

t_{Cu} means copper titrant

t_p means orthophosphate titrant

(i.) The Type I-titration was a one buret titration and was performed as follows: 50 ml. of 0.1016 M H^+ , $0.01002 \text{ M Cu}^{2+}$, 3 M ClO_4^- solution was pipetted into the titration vessel. Using a glass electrode and a cupric ion selective electrode, E_g and E_{Cu} were determined at 25°C . Using E_g , E_{Cu} , and assuming $[\text{H}^+]_{\text{TOT}} = h$ and $[\text{Cu}^{2+}]_{\text{TOT}} = c$, the standard potentials, E_g^0 and E_{Cu}^0 , were calculated. The solution was then titrated with 0.1016 M H^+ , $0.01002 \text{ M Cu}^{2+}$, $0.02367 \text{ M orthophosphate}$, 3 M ClO_4^- solution. After each addition of orthophosphate solution, E_g and E_{Cu} were determined using a glass electrode and a cupric ion selective electrode, respectively. Using E_g and E_{Cu} and the values E_g^0 and E_{Cu}^0 calculated previously, the values of free hydrogen ion concentration, h , and free cupric ion concentration, c , were calculated. The Dynamco Voltmeter was used to measure all potentials. See Table 6 and Figures 5 and 6 for experimental data.

(ii.) The Type II titration was a one buret titration and was performed in duplicate as follows: 50 ml. of 0.1016 M H^+ , $0.01002 \text{ M Cu}^{2+}$, 3 M ClO_4^- solution was used to determine E_g^0 and E_{Cu}^0 as before. This solution was then titrated with 0.1016 M H^+ , $0.01002 \text{ M Cu}^{2+}$, $0.05019 \text{ M orthophosphate}$, 3 M ClO_4^- solution. For each addition of titrant, the values of h and c were calculated as for titration Type I. The Dynamco Voltmeter was used to measure all potentials. See Table 7 and Figures 5 and 6 for experimental data.

(iii.) The Type III titration was a two buret titration and was performed in triplicate as follows: 25 ml of 0.1016 M H^+ , $0.01002 \text{ M Cu}^{2+}$, 3 M ClO_4^- solution and 25 ml of 3 M NaClO_4 solution were pipetted into the titration vessel. By measuring E_g and E_{Cu} of this solution, values of E_g^0 and E_{Cu}^0 were calculated as in titration Type I. A known volume of 0.1016 M H^+ , $0.01002 \text{ M Cu}^{2+}$, 3 M ClO_4^- solution was added with a buret

and E_g^0 and E_{Cu}^0 were calculated again. The averages of the two E_g^0 and E_{Cu}^0 values were used in subsequent calculations. An equal volume of 0.1001M orthophosphate, $3M ClO_4^-$ solution was added with another buret and h and c were calculated. The titration was continued by adding equal volumes of Cu^{2+} solution and orthophosphate solution and the values of h and c were calculated for each addition of titrants. The electrode potentials were measured on the Dynamco Digital Voltmeter as before except for Trial 1 in which the Metrohm Compensator was used. See Table 8 and Figures 5 and 6 for experimental data.

(iv.) The Type IV titration was a two buret titration which, unlike the others, proceeded to precipitation. This titration was performed once as follows: 25 ml of 0.00997 M H^+ , 0.01002M Cu^{2+} , $3M ClO_4^-$ solution and 25 ml. of $3M NaClO_4$ solution were pipetted into the titration vessel. Measurements of E_g and E_{Cu} made on this solution were used to calculate E_g^0 and E_{Cu}^0 for the electrodes. 0.00997 M H^+ , 0.01002 M Cu^{2+} , $3M ClO_4^-$ solution and 0.1001 M orthophosphate, $3M ClO_4^-$ solution were then added in 0.5 ml portions with burets. For each addition of titrants, the values of h and c were calculated as before. The Dynamco Voltmeter was used to measure all potentials. After about 4 ml of each titrant was added, a fluffy light blue cupric orthophosphate precipitate of unknown composition began to form in the titration vessel. After precipitation had occurred, the value of E_{Cu} remained fairly constant with time but E_g began to rise slowly perhaps indicating a reaction releasing hydrogen ions. Refer to Table 9 and Figures 5 and 6 for experimental data.

TABLE 6

TYPE I TITRATION OF ACIDIC COPPER SOLUTION WITH ACIDIC ORTHOPHOSPHATE SOLUTION

$H^+_O = 0.1016 \text{ M}$, $Cu^{2+}_O = 0.01002 \text{ M}$, $P_O = 0 \text{ M}$
 $H^+_t = 0.1016 \text{ M}$, $Cu^{2+}_t = 0.01002 \text{ M}$, $P_t = 0.02367 \text{ M}$

$E^O_g = 366.18 \text{ mV}$, $E^O_{Gu} = 231.97 \text{ mV}$, $V_O = 50 \text{ ml}$.

Vol. added (ml.)	$E_g(\text{mV})$	$E_{Gu}(\text{mV})$	$\log h$	Z_H/B	$\log c$	Z_C/B
0.00	305.70	171.11	-0.9931	-	-1.9991	-
2.03	305.29	170.99	-1.0006	1.8	-2.0042	0.13
4.05	304.96	170.95	-1.0067	1.7	-2.0066	0.096
6.03	304.61	170.89	-1.0129	1.8	-2.0093	0.090
8.04	304.16	170.79	-1.0210	1.9	-2.0137	0.10
10.05	303.82	170.71	-1.0271	1.9	-2.0171	0.10
15.07	303.03	170.71	-1.0413	1.95	-2.0208	0.089
20.05	302.28	170.57	-1.0532	1.93	-2.0252	0.086
25.03	302.00	170.55	-1.0599	1.84	-2.0265	0.077
35.16	301.05	170.50	-1.0770	1.82	-2.0303	0.071
45.05	300.17	170.39	-1.0927	1.85	-2.0356	0.072

TABLE 7

TYPE II TITRATION OF ACIDIC COPPER SOLUTION WITH ACIDIC ORTHOPHOSPHATE SOLUTION

$H_o^+ = 0.1016 \text{ M},$ $Cu_o^{2+} = 0.01002 \text{ M},$ $P_o = 0 \text{ M}$
 $H_t^+ = 0.1016 \text{ M},$ $Cu_t^{2+} = 0.01002 \text{ M},$ $P_t = 0.05019 \text{ M}$

$V_o = 50 \text{ ml.}$

Run #1	E_g^o	E_g (mV)	E_{Cu} (mV)	log h	Z_H/B	log c	Z_C/B
(ml.)							
Vol. added							
0.00	306.14	169.71	-0.9931	-	-	-1.9991	-
2.00	305.17	169.70	-1.0107	2.1	0.031	-2.0018	0.031
4.06	304.50	169.69	-1.0229	1.8	0.029	-2.0039	0.029
6.03	303.58	169.50	-1.0395	1.91	0.056	-2.0123	0.056
8.07	302.85	169.45	-1.0525	1.86	0.053	-2.0154	0.053
10.00	302.17	169.39	-1.0648	1.85	0.054	-2.0191	0.054
15.05	300.47	169.38	-1.0951	1.83	0.045	-2.0225	0.045
20.04	298.98	169.30	-1.1218	1.82	0.045	-2.0282	0.045
25.07	297.53	169.29	-1.1475	1.81	0.042	-2.0309	0.042
35.03	295.11	169.26	-1.1902	1.79	0.039	-2.0356	0.039
45.06	293.01	169.18	-1.2272	1.78	0.039	-2.0414	0.039

$Run \#1$ $E_g^o = 366.62 \text{ mV},$ $E_{Cu}^o = 230.57 \text{ mV}$

TABLE 7 (continued)

Run #2 (ml.)	$E_g^0 = 366.24 \text{ mV}$	$E_{Cu}^0 = 229.28 \text{ mV}$				
Vol. added	$E_g \text{ (mV)}$	$E_{Cu} \text{ (mV)}$	$\log h$	Z_H/B	$\log c$	Z_c/B
0.00	305.76	168.42	-0.9931	-	-1.9991	-
2.03	305.90	168.42	-1.0087	1.8	-2.0012	0.03
4.02	304.01	168.44	-1.0248	1.9	-2.0025	0.03
5.99	303.26	168.43	-1.0383	1.86	-2.0045	0.022
7.97	302.60	168.46	-1.0503	1.81	-2.0052	0.020
10.01	301.77	168.51	-1.0651	1.85	-2.0052	0.017
15.00	300.09	168.40	-1.0951	1.84	-2.0120	0.025
20.00	298.59	168.38	-1.1219	1.82	-2.0157	0.026
25.00	297.20	168.39	-1.1467	1.81	-2.0177	0.025
34.98	294.81	168.43	-1.1889	1.79	-2.0201	0.022
44.98	292.81	168.47	-1.2242	1.76	-2.0218	0.021

TABLE 8

TYPE III TITRATION OF ACIDIC COPPER SOLUTION WITH
ACIDIC COPPER SOLUTION AND ACIDIC ORTHOPHOSPHALF SOLUTION

H_o^+	$= 0.05076$	$Cu_o^{2+} = 0.005010 M$	$P_o = 0 M$
H_{tCu}^+	$= 0.1016 M$	$Cu_{tCu}^{2+} = 0.01002 M$	$P_{tCu} = 0 M$
H_{tp}^+	$= -0.00008 M$	$Cu_{tp}^{2+} = 0 M$	$P_{tp} = 0.1001 M$

$V_o = 49.98 ml.$

Run #1 $E_g^o = 366.8 mV$, $E_{Cu}^o = 230.2 mV$

(ml.)

Vol. Cu soln.	Vol. PO_4 soln.	E_g (mV)	E_{Cu} (mV)	log h	$Z_{H/B}$	log c	$Z_{C/B}$
0.00	0.00	289.3	161.5	-1.2945	-	-2.3002	-
1.98	0.00	290.3	161.6	-1.2780	-	-2.2957	-
1.98	2.00	286.1	160.8	-1.3507	1.66	-2.3261	0.0776
4.04	4.04	282.8	161.0	-1.4082	1.678	-2.3227	0.0365
6.00	6.03	279.9	160.3	-1.4589	1.641	-2.3497	0.0553
7.96	8.09	276.5	160.0	-1.5180	1.657	-2.3632	0.0544
9.95	10.02	273.3	159.9	-1.5654	1.639	-2.3666	0.0492
12.96	13.02	269.9	159.7	-1.6313	1.593	-2.3768	0.0470
16.03	16.07	266.2	159.6	-1.6955	1.559	-2.3835	0.0445
19.96	20.11	261.5	159.5	-1.7749	1.515	-2.3869	0.0402
24.98	25.06	256.6	159.3	-1.8595	1.470	-2.3971	0.0398

TABLE 8 (continued).

Run #2	$E_g^0 = 366.67 \text{ mV}$	$E_{Cu}^0 = 228.10 \text{ mV}$					
(ml.)	(ml.)						
Vol. Cu soln.	Vol. PO_4 soln.	E_g (mV)	E_{Cu} (mV)	log h	Z_H/B	log c	Z_C/B
0.00	0.00	289.31	159.23	-1.2945	-	-2.3002	-
3.08	0.00	290.56	159.86	-1.2725	-	-2.2770	-
3.08	3.07	284.18	159.37	-1.3839	1.73	-2.3007	0.0013
6.02	6.05	279.54	159.42	-1.4645	1.677	-2.3031	0.0019
8.95	9.06	275.22	159.43	-1.5390	1.630	-2.3057	0.0041
11.99	12.12	270.82	159.45	-1.6148	1.612	-2.3078	0.0048
15.01	15.07	267.20	159.45	-1.6767	1.574	-2.3095	0.00547
20.00	20.06	261.50	159.37	-1.7744	1.520	-2.3146	0.00717
30.02	30.07	252.10	159.14	-1.9348	1.429	-2.3254	0.0102
40.06	40.00	244.88	158.96	-2.0576	1.364	-2.3332	0.0120
49.80	49.76	239.07	158.83	-2.1563	1.314	-2.3386	0.0128
Run #3	$E_g^0 = 366.69 \text{ mV}$	$E_{Cu}^0 = 228.00 \text{ mV}$					
0.00	0.00	288.10	159.13	-1.2945	-	-2.3002	-
3.12	0.00	290.67	159.77	-1.2494	-	-2.2750	-
3.12	3.03	284.35	159.42	-1.3800	1.70	-2.2946	-0.010
6.08	6.03	279.68	159.31	-1.4609	1.666	-2.3024	0.0031
8.97	9.05	275.18	159.27	-1.5387	1.634	-2.3072	0.0056
12.20	12.02	271.41	159.33	-1.6036	1.602	-2.3075	0.0059
15.03	14.97	267.73	159.35	-1.6666	1.561	-2.3085	0.00528
20.02	20.10	261.77	159.20	-1.7688	1.509	-2.3162	0.00793
30.02	30.05	252.58	159.11	-1.9255	1.422	-2.3224	0.00907
40.05	39.97	245.38	158.95	-2.0482	1.360	-2.3295	0.0107
49.92	49.85	239.49	158.83	-2.1483	1.311	-2.3345	0.0115

TABLE 9
TYPE IV TITRATION OF ACIDIC COPPER SOLUTION WITH
ACIDIC COPPER SOLUTION AND ACIDIC ORTHOPHOSPHATE SOLUTION

H_o^+	= 0.00495 M,	Cu_o^{2+}	= 0.005025 M,	P_o	= 0 M
H_{tCu}^+	= 0.00997 M,	Cu_{tCu}^{2+}	= 0.01005 M,	P_{tCu}	= 0 M
H_{tp}^+	= -0.00008 M,	Cu_{tp}^{2+}	= 0 M,	P_{tp}	= 0.1001 M

$V_o = 49.98$ ml.

$E_g^o = 365.87$ mV, $E_{Cu}^o = 228.228.13$ mV

(ml.) Vol. Cu soln.	(ml.) Vol. PO_4 soln.	E_g (mV)	E_{Cu} (mV)	log h	$Z_{H/B}$	log c	$Z_{C/B}$
0.000	0.000	229.44	160.05	-2.305	-	-2.2989	-
0.505	0.503	222.00	160.15	-2.431	1.26	-2.2963	-0.029
1.003	1.008	213.36	160.12	-2.577	1.18	-2.2977	-0.0072
1.508	1.505	202.65	160.07	-2.759	1.13	-2.3001	-0.0049
2.008	2.005	186.53	160.00	-3.032	1.08	-2.3028	0.012
2.510	2.510	151.51	159.90	-3.623	1.03	-2.3068	0.020

Figure 5

Average $Z_{H/B}$ as a function of average pH plotted
for all titrations

- Titration Type I
- Titration Type II
- △ Titration Type III
- ▽ Titration Type IV

———— Theoretical $Z_{H/B}$
(assuming no Cu-Orthophosphate
Complexing)

FIGURE 5

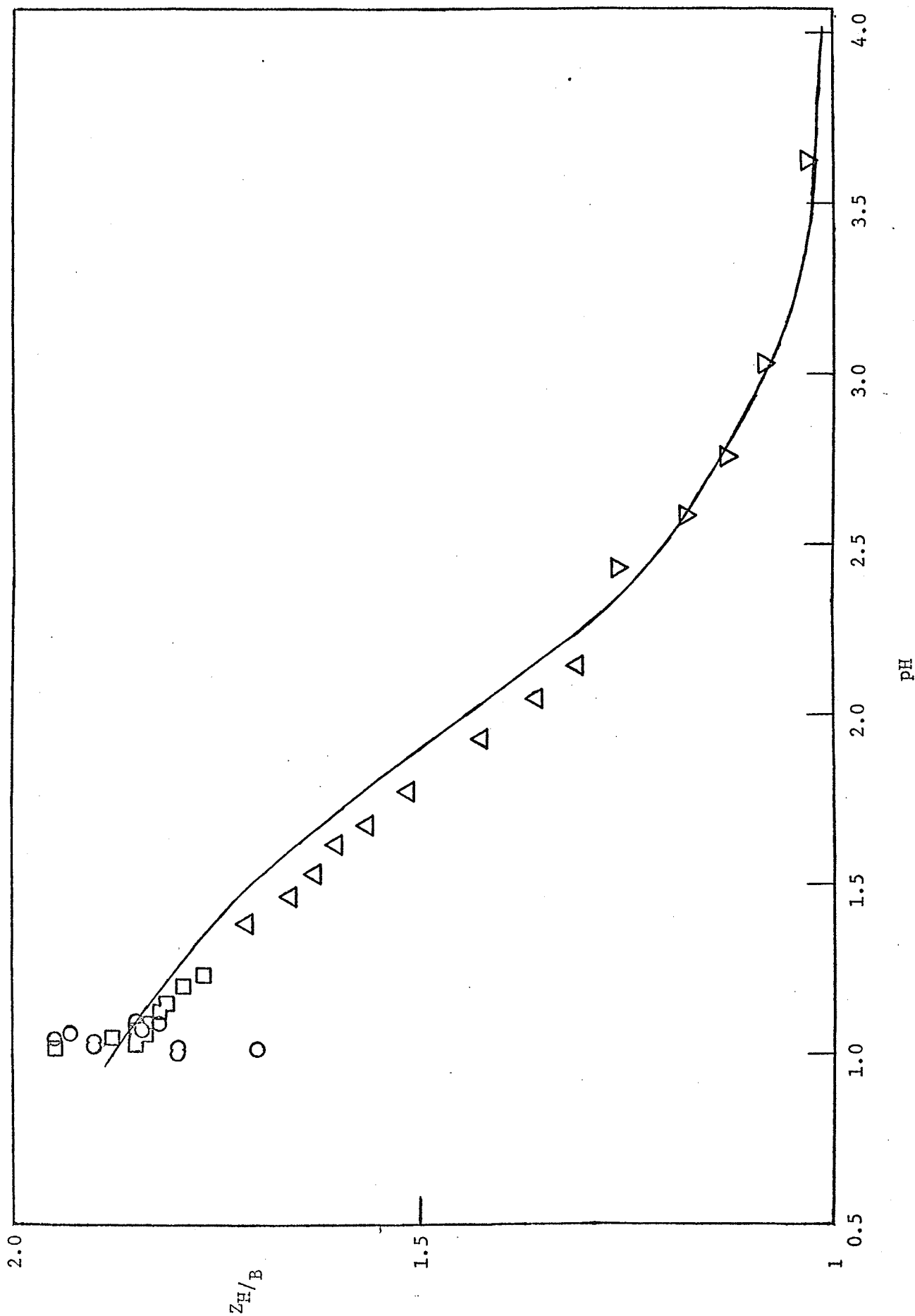
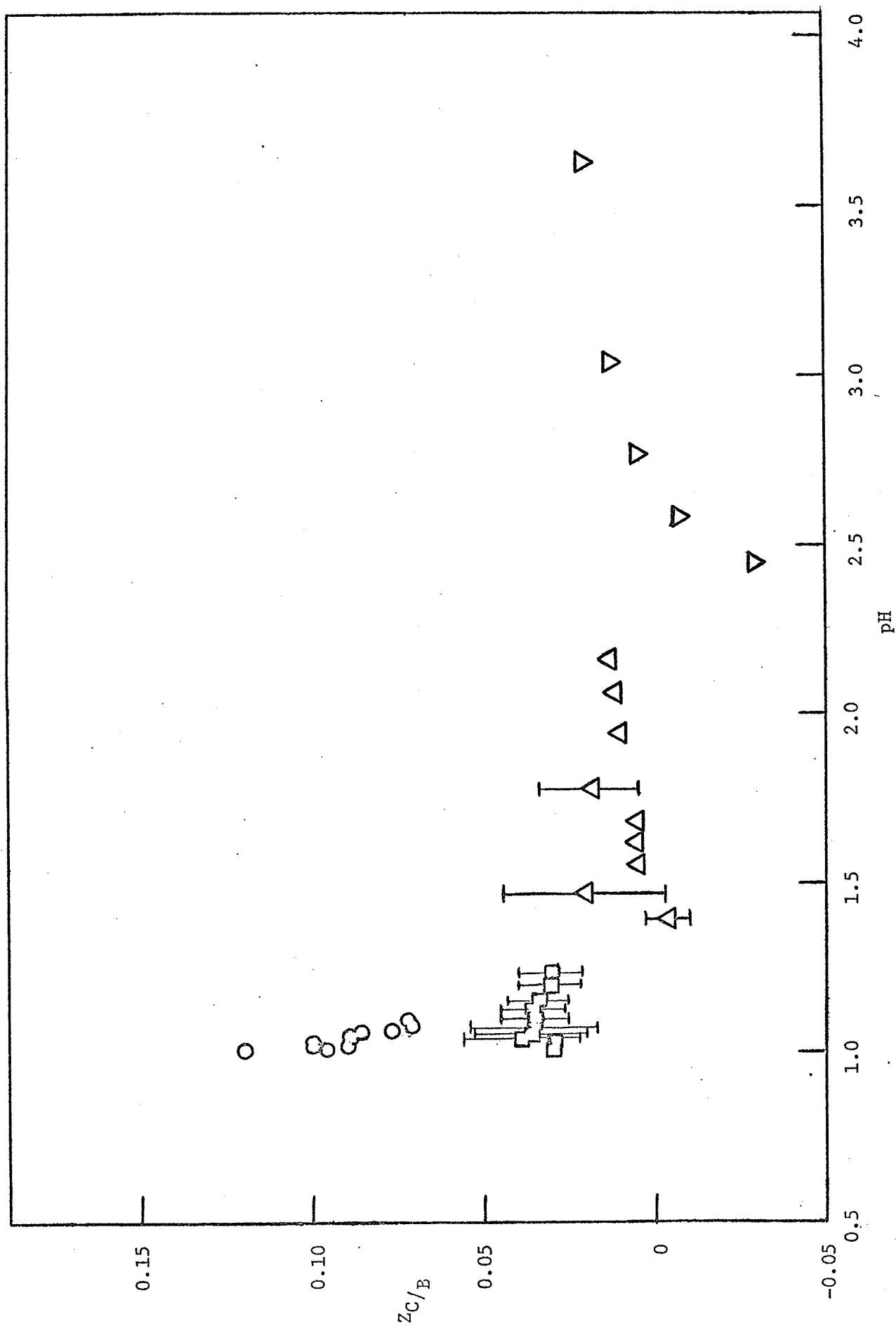


Figure 6

Average $Z_{C/B}$ as a function of average pH plotted for all titrations

- Titration Type I
- Titration Type II
- △ Titration Type III
- ▽ Titration Type IV

FIGURE 6



Results of Titrations

Referring to Figures 5 and 6 which are plots of average Z versus pH (i.e. for titration Types II and III the results of two or three trials were averaged) for all titrations, it can be seen that the experimental $Z_{H/B}$ values are generally somewhat lower than the theoretical curve for titration Types I, II, and III (pH 1 to 2.3) and for titration Type IV (pH 2.3 to 3.7) the experimental $Z_{H/B}$ values are similar to or somewhat higher than the theoretical $Z_{H/B}$ values. It can be seen that the experimental $Z_{C/B}$ values do not conform to any smooth curve and are very small compared to $Z_{H/B}$. In Figure 6 the error bars represent the deviations in average $Z_{C/B}$.

Apparent Equilibrium Constants for Copper-Hydrogen-Phosphate Association

The experimental data were treated using the generalized least squares program Letagrop (66) in order to determine if the complexes reported by Childs (49) were present and to calculate their association constants. Since the reproducibility of the data is not as high as that obtained by other workers, Letagrop is particularly useful since it allows for adjustments to compensate for experimental errors.

In calculating the equilibrium constants for copper-hydrogen-phosphate association, the components of the system were taken to be Cu^{2+} , H^+ , and HPO_4^{2-} whose concentrations will be denoted c , h , and b , respectively.

The potentiometric titration data were treated using the generalized least squares program Letagrop (66) which minimizes the error square sum, U . $U = \sum (H - H_{\text{calc}})^2$ where H_{calc} is the computed total hydrogen ion concentration. The program allowed for adjustments to the characteristics of the electrodes used (j and E^0), the equilibrium

constants (β 's), and the analytical concentration H_{TOT} to compensate for possible analytical errors.

Two series of calculations were done: Series A which assumed only the glass electrode potential, E_g , was known and Series B which assumed that both E_g and the cupric ion selective electrode potential, E_{Cu} , were known.

A total of eight calculation sequences were done as follows: (i.) calculation A I assumed that H_{TOT} , Cu_{TOT} , P_{TOT} , and E_g^0 were correct. (ii.) calculation A II assumed that E_g^0 was in error and was corrected in calculation. (iii.) calculation A III varied j along with the β values and E_g^0 . (iv.) calculation A IV varied the β values, E_g^0 , and assumed a constant error δH in H_{TOT} . (v.) calculation B I assumed that H_{TOT} , Cu_{TOT} , P_{TOT} , E_g^0 , and E_{Cu}^0 were correct. (vi.) calculation B II assumed that E_g^0 and E_{Cu}^0 were in error and were corrected in calculation. (vii.) calculation B IV varied the β values, E_g^0 , E_{Cu}^0 , and assumed a constant error δH in H_{TOT} . (viii.) calculation A V assumed that only one complex, $CuH_2PO_4^+$, was present, varied the β values, E_g^0 , and assumed a constant error δH in H_{TOT} . The results are summarized in Table 10.

In calculation A I, the association constants (β) of four possible copper-hydrogen-phosphate complexes ($CuH_2PO_4^+$, $CuH_3(PO_4)_2^-$, $CuHPO_4$, $Cu_2H_2(PO_4)_2$) were calculated but negative β values were obtained for two of these complexes ($CuHPO_4$ and $Cu_2H_2(PO_4)_2$), therefore, these complexes were rejected. It is seen for calculations A II, A III, and A IV that as more parameters are corrected, the better the observed fit (i.e. the U value is lowered). However, since the β values are dependent on j , it is not considered justified to vary j

Table 10

APPARENT EQUILIBRIUM CONSTANTS FOR COPPER-HYDROGEN-PHOSPHATE
ASSOCIATION CALCULATED BY LETAGROP FOR BEST FIT

25°C, 3M NaClO₄, 7 titrations, 69 points, $U = \sum (H_{\text{calc.}} - H)^2$

	A I	A II	A III	A IV	B I	B II	B IV	A V
j	-17	-17	3.2±4.0	-17	-17	-17	-17	-17
$\log \beta_{-1,0,0}(\text{OH}^-)$	-14.24	-14.24	-14.24	-14.24	-14.24	-14.24	-14.24	-14.24
$\log \beta_{1,0,1}(\text{H}_2\text{PO}_4^-)$	6.27	6.27	6.27	6.27	6.27	6.27	6.27	6.27
$\log \beta_{2,0,1}(\text{H}_3\text{PO}_4)$	8.16	8.16	8.16	8.16	8.16	8.16	8.16	8.16
$\log \beta_{-1,0,1}(\text{PO}_4^{3-})$	-10.85	-10.85	-10.85	-10.85	-10.85	-10.85	-10.85	-10.85
$\log \beta_{1,1,1}(\text{CuH}_2\text{PO}_4^+)$	7.88±0.17	7.99±0.20	8.54±0.24	8.04±0.11	7.89±0.10	7.91±0.07	7.84±0.04	7.95±0.10
$\log \beta_{1,1,2}(\text{CuH}_3(\text{PO}_4)_2^-)$	13.07	13.02	13.53	13.07	-	-	-	-
U	10.81	9.18	7.68	7.58	10.03	6.46	5.53	5.93

Complexes rejected in calculation A I, ($\beta \pm 3\sigma$) given

CuHPO_4^0 with $\beta = (-6.59 \pm 6.30) \times 10^4$

$\text{Cu}_2\text{H}_2(\text{PO}_4)_2^0$ with $\beta = (-6.21 \pm 2.24) \times 10^{12}$

Complexes rejected in calculation B I

CuHPO_4^0 with $\log \beta < 4.48$ ($\beta > 0$, but $\beta/\sigma < 1$)

$\text{Cu}_2\text{H}_2(\text{PO}_4)_2^0$ with $\log \beta < 11.54$ ($\beta < 0$, $\log(\beta + 3\sigma)$ given)

$\text{CuH}_3(\text{PO}_4)_2^-$ with $\log \beta < 13.01$ ($\beta > 0$, but $\beta/\sigma < 1$)

(calculation A III). In calculation B I, the association constants (β) of four possible complexes ($\text{CuH}_2\text{PO}_4^+$, $\text{CuH}_3(\text{PO}_4)_2^-$, CuHPO_4 , and $\text{Cu}_2\text{H}_2(\text{PO}_4)_2$) were calculated but three of these complexes ($\text{CuH}_3(\text{PO}_4)_2^-$, CuHPO_4 , and $\text{Cu}_2\text{H}_2(\text{PO}_4)_2$) were rejected either because the β value was negative or because the β values were less than the standard deviation (σ). Since the reproducibility of the data was not as high as that obtained by other workers, it was felt that quite a stringent test could be applied to determine if a particular complex was actually present; hence the requirement that $\beta/\sigma > 1$. It is seen from calculations B II and B IV that as more parameters are corrected, the fit is improved. If only one complex ($\text{CuH}_2\text{PO}_4^+$) was assumed (calculation A V), it resulted in a better fit than any of the other Series A calculations but of all the eight calculations performed, the best fit is obtained in Calculation B IV. Therefore the best association constant value is

$$\beta_{1,1,1} = \frac{[\text{CuH}_2\text{PO}_4^+]}{c \, h \, b} = (6.9 \pm 0.7) \times 10^7$$

$$\text{or } \log \beta_{1,1,1} = 7.84 \pm 0.04 .$$

In 1970, Childs (49), using a different medium and a temperature of 37°C, reported the following association constant

$$\log K_{m,1} = \log \frac{[\text{CuH}_2\text{PO}_4^+]}{[\text{Cu}^{2+}][\text{H}_2\text{PO}_4^-]} = 1.2$$

Using the experimental value of $\log \beta_{1,1,1}$ and the value of $\log \beta_{1,0,1}$ determined by Baldwin and Sillén (60), $\log K_{m,1}$ at 25°C was calculated

$$\begin{aligned} \log K_{m,1} &= \log \frac{[\text{CuH}_2\text{PO}_4^+]}{c \, h \, b} + \log \frac{h \, b}{[\text{H}_2\text{PO}_4^-]} = \log \beta_{1,1,1} - \log \beta_{1,0,1} \\ &= 7.84 - 6.27 = 1.57 \end{aligned}$$

The agreement seems reasonable considering the differences in temperature and media.

Estimate of the Effect of Copper-Hydrogen-Phosphate Complexing on $Z_{H/B}$

If $\text{CuH}_2\text{PO}_4^+$ is present in solution, the $Z_{H/B}$ values could be calculated as follows:

$$Z_{H/B} = \frac{H_{\text{TOT}} - h}{B} \quad \text{-----}(3)$$

assuming that HPO_4^{2-} is originally present in solution and neglecting PO_4^{3-}

$$\begin{aligned} H_{\text{TOT}} &= h + [\text{H}_2\text{PO}_4^-] + 2[\text{H}_3\text{PO}_4] + [\text{CuH}_2\text{PO}_4^+] \\ B &= [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{H}_3\text{PO}_4] + [\text{CuH}_2\text{PO}_4^+] \\ Z_{H/B} &= \frac{[\text{H}_2\text{PO}_4^-] + 2[\text{H}_3\text{PO}_4] + [\text{CuH}_2\text{PO}_4^+]}{[\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{H}_3\text{PO}_4] + [\text{CuH}_2\text{PO}_4^+]} \\ &= \frac{[\text{H}_2\text{PO}_4^-] + 2[\text{H}_3\text{PO}_4] + [\text{CuH}_2\text{PO}_4^+]}{[\text{HPO}_4^{2-}]} \\ &= \frac{[\text{H}_2\text{PO}_4^-] + 2[\text{H}_3\text{PO}_4] + [\text{CuH}_2\text{PO}_4^+]}{[\text{HPO}_4^{2-}]} \end{aligned}$$

$$\text{Substituting } \beta_1 = \frac{[\text{H}_2\text{PO}_4^-]}{h [\text{HPO}_4^{2-}]}, \quad \beta_2 = \frac{[\text{H}_3\text{PO}_4]}{h^2 [\text{HPO}_4^{2-}]}$$

$$\text{and } \beta_{1,1,1} = \frac{[\text{CuH}_2\text{PO}_4^+]}{c h [\text{HPO}_4^{2-}]}$$

$$Z_{H/B} = \frac{\beta_1 h + 2\beta_2 h^2 + \beta_{1,1,1} c h}{1 + \beta_1 h + \beta_2 h^2 + \beta_{1,1,1} c h} \quad \text{-----}(6)$$

$$\text{where } \beta_1 = 1.86 \times 10^6$$

$$\beta_2 = 1.44 \times 10^8$$

$$\beta_{1,1,1} = 6.9 \times 10^7$$

Using a number of experimental points covering the pH range of 1 to about 3.7, it was found that $Z_{H/B}$ values calculated using equation (6) were somewhat lower than the theoretical $Z_{H/B}$ values calculated from equation (5) which did not use experimental points. These results are generally consistent with the experimental $Z_{H/B}$ values for titration Types I, II, and III (Figure 5). However, the experimental $Z_{H/B}$ values for the Type IV titration were somewhat higher than those predicted by equation (6) perhaps due to analytical errors.

Experimental Errors

The corrected values of E_g^0 , E_{Cu}^0 , and δH calculated using Letagrop are presented in Table 11. It can be seen that in most cases the E_g^0 values do not change much (except for Calculation A III where j is varied) from the experimental results and the uncertainties in E_g^0 are generally fairly small. However, the corrected E_{Cu}^0 values are often considerably different from the experimental results and there are large uncertainties in E_{Cu}^0 . It can be seen that the δH values, which represent the error in H_o , are not very significant for the first three titrations but become much more significant as H_o is reduced. The large uncertainties in δH are to be expected due to the small values of δH .

The Dynamco Digital Voltmeter is capable of measuring potentials within ± 0.05 mV and the Metrohm Compensator (used for titration 4) within ± 0.2 mV.

Taking into consideration the results for E_g^0 and E_{Cu}^0 calculated

TABLE 11

 E_g^0 , E_{Cu}^0 , AND δH CALCULATED BY LETAGROP FOR

"BEST FIT" FOR THE DIFFERENT CALCULATIONS

Titn. No.	Cu_o (mM)	H_o (mM)	$E_g^0 \pm 3\sigma$ (mV)	$E_{Cu}^0 \pm 3\sigma$ (mV)	$\delta H \pm 3\sigma$ (mM)
Calculations A II					
1	10.02	101.6	366.11 ± 0.09	-	0
2	10.02	101.6	366.54 ± 0.06	-	0
3	10.02	101.6	366.19 ± 0.04	-	0
4	5.010	50.76	366.80 ± 0.14	-	0
5	5.010	50.76	366.69 ± 0.09	-	0
6	5.010	50.76	366.57 ± 0.63	-	0
7	5.025	4.95	365.23 ± 2.64	-	0
Calculations A III					
1	10.02	101.6	364.11 ± 0.11	-	0
2	10.02	101.6	364.56 ± 0.07	-	0
3	10.02	101.6	364.21 ± 0.08	-	0
4	5.010	50.76	365.64 ± 0.19	-	0
5	5.010	50.76	365.51 ± 0.17	-	0
6	5.010	50.76	365.43 ± 0.56	-	0
7	5.025	4.95	364.75 ± 3.45	-	0
Calculations A IV					
1	10.02	101.6	365.69 ± 0.08	-	2.028 ± 0.402
2	10.02	101.6	365.68 ± 0.05	-	3.776 ± 0.227
3	10.02	101.6	365.76 ± 0.04	-	1.808 ± 0.187
4	5.010	50.76	367.42 ± 0.13	-	-1.176 ± 0.238
5	5.010	50.76	367.51 ± 0.08	-	-1.551 ± 0.147
6	5.010	50.76	366.00 ± 0.57	-	1.025 ± 1.056
7	5.025	4.95	369.01 ± 0.31	-	0.506 ± 0.142
Calculations A V					
1	10.02	101.6	365.77 ± 0.08	-	1.687 ± 0.399
2	10.02	101.6	365.98 ± 0.05	-	2.548 ± 0.208
3	10.02	101.6	366.32 ± 0.04	-	-0.516 ± 0.168
4	5.010	50.76	366.72 ± 0.13	-	0.230 ± 0.244
5	5.010	50.76	366.24 ± 0.14	-	0.979 ± 0.263
6	5.010	50.76	360.97 ± 0.39	-	11.423 ± 0.864
7	5.025	4.95	366.36 ± 0.25	-	-0.121 ± 0.030

TABLE 11 (continued)

Titn. No.	Cu _o (mM)	H _o (mM)	E _g ^o ± 3σ(mV)	E _{Cu} ^o ± 3σ(mV)	δH ± 3σ(mM)
Calculations B II (analogous to A II)					
1	10.02	101.6	366.17±0.11	260.62±144.90	0
2	10.02	101.6	366.58±0.07	232.93±5.70	0
3	10.02	101.6	366.21±0.05	229.62±3.81	0
4	5.010	50.76	366.84±0.18	230.42±5.70	0
5	5.010	50.76	366.74±0.08	229.88±1.75	0
6	5.010	50.76	366.31±0.72	221.43±9.36	0
7	5.025	4.95	365.70±0.49	277.74±3.87	0
Calculations B IV (analogous to A IV)					
1	10.02	101.6	366.25±0.09	370.76±26.31	-0.383±0.393
2	10.02	101.6	366.73±0.07	231.36±6.03	-0.622±0.200
3	10.02	101.6	366.48±0.05	228.46±3.98	-1.158±0.153
4	5.010	50.76	366.92±0.19	227.95±5.76	-0.156±0.239
5	5.010	50.76	367.11±0.08	226.92±1.55	-0.704±0.101
6	5.010	50.76	361.17±0.50	229.02±14.34	10.997±0.864
7	5.025	4.95	366.26±0.16	265.19±117.6	-0.079±0.016
Experimental Results (for reference)					
1	10.02	101.6	366.18	231.97	-
2	10.02	101.6	366.62	230.57	-
3	10.02	101.6	366.24	229.28	-
4	5.010	50.76	366.8	230.2	-
5	5.010	50.76	366.67	228.10	-
6	5.010	50.76	366.69	228.00	-
7	5.025	4.95	365.87	228.13	-

using Letagrop, it appears that the measurements of free hydrogen ion concentration, h , are probably fairly reliable but the validity of the measurements of free cupric ion concentration, c , is questionable.

Conclusions

By this method, the presence in aqueous solution, at 25°C , of one copper-hydrogen-phosphate complex, $\text{CuH}_2\text{PO}_4^+$, was established over the pH range of 1 to 3.7 and an association constant of $(6.9 \pm 0.7) \times 10^7$ was calculated for the complex.

The experimental $Z_{\text{H/B}}$ values calculated were quite reasonable in most cases due to the relatively large values of $Z_{\text{H/B}}$ and the reliability of the h determinations. However, the experimental $Z_{\text{C/B}}$ values calculated did not seem reasonable due to the relatively small values of $Z_{\text{C/B}}$ and more significantly to the unreliability of the c determinations.

4.4 Solubility Studies of Cupric Hydrogen Orthophosphate in Aqueous Solution

To determine the solubility product of cupric hydrogen orthophosphate (CuHPO_4), it was decided to allow samples of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ or CuHPO_4 to equilibrate in 3M ClO_4^- solutions of known total hydrogen ion concentration or known orthophosphate concentration. After equilibrium had been achieved, the solutions and the solid residues were analyzed as described later. Infrared spectra and X-ray diffractograms were also taken of the solid residues to determine if they had changed. The experimental details are described below.

Preparation of Standard Solutions

(A) A series of 50 ml. solutions of varying total hydrogen ion concentrations in 3M ClO_4^- were prepared and transferred into 125 ml.

plastic bottles. An excess quantity of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation I) was added to each solution and the solutions were equilibrated in a water bath at 25°C . The six solutions of this group will be referred to as 0A, 1A, 2A, 3A, 4A, and 5A. The hydrogen ion concentrations of the original standard solutions are presented in Table 12.

(B) A series of 100 ml solutions of varying hydrogen ion concentrations in 3M ClO_4^- were prepared and transferred into 125 ml plastic bottles. An excess quantity of CuHPO_4 (Preparation II dried at 180°C for 2 hours) was added to each solution and the solutions were equilibrated at 25°C in a water bath. The four solutions in this group will be referred to as 1B, 2B, 3B, and 4B. The hydrogen ion concentrations of the original standard solutions are presented in Table 12.

(C) A series of 100 ml solutions of varying orthophosphate concentrations in 3M ClO_4^- were prepared, transferred into 125 ml plastic bottles, and an excess quantity of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II) was added to each solution. The solutions were then equilibrated at 25°C in a water bath. The five solutions will be referred to as 1C, 2C, 3C, 4C, and 5C. The orthophosphate concentrations of the original standard solutions are presented in Table 12.

Analyses of Solutions after Equilibration

After being stored in the water bath at 25°C for at least one month, the solutions were analyzed, at weekly intervals, for free hydrogen ion concentration, h , and free cupric ion concentration, c . After a few months, when the standard deviation of three consecutive determinations of h and c was less than 2%, the solutions were considered to be at equilibrium. For each solution Table 12 shows the average of three determinations of h and c along with the average

TABLE 12
EQUILIBRATED STANDARD SOLUTIONS

Soln.	$[H^+]_{TOT}$ (M) orig	$[P]_{TOT}$ (M) orig	h (M)	c (M)	$[Cu]_{TOT}$ (M) A.A	$[Cu]_{TOT}$ (M) color	$[P]_{TOT}$ (M)
0A	-8.374×10^{-5}	-	$(1.119 \pm 0.008) \times 10^{-3}$	$(5.925 \pm 0.015) \times 10^{-3}$	$(6.39 \pm 0.10) \times 10^{-3}$	$(7.02 \pm 0.09) \times 10^{-3}$	$(1.04 \pm 0.03) \times 10^{-2}$
1A	2.039×10^{-3}	-	$(1.539 \pm 0.002) \times 10^{-3}$	$(7.894 \pm 0.034) \times 10^{-3}$	$(7.82 \pm 0.11) \times 10^{-3}$	$(9.29 \pm 0.33) \times 10^{-3}$	$(1.26 \pm 0.02) \times 10^{-2}$
2A	4.165×10^{-3}	-	$(1.648 \pm 0.010) \times 10^{-3}$	$(8.751 \pm 0.014) \times 10^{-3}$	$(8.25 \pm 0.10) \times 10^{-3}$	$(9.39 \pm 0.17) \times 10^{-3}$	$(1.22 \pm 0.02) \times 10^{-2}$
3A	1.065×10^{-2}	-	$(2.317 \pm 0.020) \times 10^{-3}$	$(1.192 \pm 0.015) \times 10^{-2}$	$(1.26 \pm 0.02) \times 10^{-2}$	$(1.36 \pm 0.05) \times 10^{-2}$	$(1.52 \pm 0.03) \times 10^{-2}$
4A	2.144×10^{-2}	-	$(4.280 \pm 0.026) \times 10^{-3}$	$(2.017 \pm 0.037) \times 10^{-2}$	$(2.19 \pm 0.15) \times 10^{-2}$	$(2.20 \pm 0.06) \times 10^{-2}$	$(2.39 \pm 0.00) \times 10^{-2}$
5A	5.368×10^{-2}	-	$(6.588 \pm 0.101) \times 10^{-3}$	$(4.451 \pm 0.042) \times 10^{-2}$	$(4.14 \pm 0.06) \times 10^{-2}$	$(4.49 \pm 0.12) \times 10^{-2}$	$(4.41 \pm 0.21) \times 10^{-2}$
1B	2.044×10^{-3}	-	$(2.407 \pm 0.023) \times 10^{-3}$	$(3.175 \pm 0.042) \times 10^{-3}$	3.26×10^{-3}	$(3.59 \pm 0.01) \times 10^{-3}$	$(3.21 \pm 0.06) \times 10^{-3}$
2B	5.195×10^{-3}	-	$(4.726 \pm 0.012) \times 10^{-4}$	$(5.066 \pm 0.026) \times 10^{-3}$	4.89×10^{-3}	$(5.35 \pm 0.02) \times 10^{-3}$	$(4.74 \pm 0.14) \times 10^{-3}$
3B	1.072×10^{-2}	-	$(4.621 \pm 0.014) \times 10^{-3}$	$(5.283 \pm 0.040) \times 10^{-3}$	5.37×10^{-3}	$(5.83 \pm 0.01) \times 10^{-3}$	$(5.03 \pm 0.10) \times 10^{-3}$
4B	2.151×10^{-2}	-	$(1.026 \pm 0.006) \times 10^{-2}$	$(8.786 \pm 0.124) \times 10^{-3}$	8.72×10^{-3}	$(9.62 \pm 0.10) \times 10^{-3}$	$(8.38 \pm 0.19) \times 10^{-3}$

TABLE 12 (continued)

Soln.	$[H^+]_{TOT}$ (M) orig	$[P]_{TOT}$ (M) orig	h (M)	c (M)	$[Cu]_{TOT}$ (M) A.A.	$[Cu]_{TOT}$ (M) color	$[P]_{TOT}$ (M)
#1C	~ 0	1.949×10^{-3}	$(5.754 \pm 0.053) \times 10^{-4}$	$(3.303 \pm 0.009) \times 10^{-3}$	3.38×10^{-3}	$(3.60 \pm 0.09) \times 10^{-3}$	$(8.59 \pm 0.03) \times 10^{-3}$
#2C	~ 0	4.906×10^{-3}	$(4.027 \pm 0.013) \times 10^{-4}$	$(1.594 \pm 0.009) \times 10^{-3}$	1.49×10^{-3}	$(1.65 \pm 0.00) \times 10^{-3}$	$(1.00 \pm 0.00) \times 10^{-2}$
#3C	~ 0	9.827×10^{-3}	$(7.771 \pm 0.047) \times 10^{-6}$	4.857×10^{-6}	-	unmeasurable	$(1.06 \pm 0.01) \times 10^{-2}$
#4C	~ 0	1.965×10^{-2}	$(2.669 \pm 0.038) \times 10^{-7}$	7.250×10^{-8}	-	unmeasurable	$(2.12 \pm 0.02) \times 10^{-2}$
#5C	~ 0	4.927×10^{-2}	$(5.130 \pm 0.031) \times 10^{-7}$	4.651×10^{-8}	-	unmeasurable	$(5.36 \pm 0.03) \times 10^{-2}$

deviations. Glass and cupric ion selective electrodes were used, reading the Dynamco Voltmeter, to determine the electrode potentials, E_g and E_{Cu} , with reference to a Ag / AgCl reference electrode. Before and after measurements on the solutions, the standard electrode potentials, E_g^0 and E_{Cu}^0 , were determined for the glass electrode and the cupric ion selective electrode, respectively, by potentiometrically titrating a solution of 25 ml of 3M NaClO₄ solution and 25 ml of 0.01 M H⁺, 0.01 M Cu²⁺, 3M ClO₄⁻ solution with 0.01M H⁺, 0.01M Cu²⁺, 3M ClO₄⁻ solution. The deviation between E_g^0 values and E_{Cu}^0 values obtained before and after the measurements ranged from ± 0.02 mV to ± 0.16 mV for the glass electrode and ranged from ± 0.02 mV to ± 0.09 mV for the cupric ion selective electrode. After the standard electrode potentials had been calculated, the free hydrogen ion concentrations, h, and the free cupric ion concentrations, c, were calculated using the following equations:

$$E_g = E_g^0 + 59.156 \log h + E_j \quad \text{-----(1)}$$

$$E_{Cu} = E_{Cu}^0 + 29.578 \log c + E_j \quad \text{-----(2)}$$

where $E_j = jh$ ($j \approx -17$ mV/M). Since $\log h$ and h were present in the same equation, the best values of h were calculated by successive approximations. The values of h and c for the equilibrated solutions are given in Table 12.

Each equilibrated solution was analyzed for total copper concentration by atomic absorption spectrophotometry on a Perkin-Elmer 306 Atomic Absorption Spectrophotometer and also by colorimetry involving the formation of the copper-ammonia complex as described by Snell and Snell (61). The instrument used for the colorimetry was the Carl Zeiss Spectrophotometer. Since it has been established that there is copper-

hydrogen-phosphate complexing in aqueous solution (Section 4.3), the total copper concentration, $[\text{Cu}]_{\text{TOT}}$, should be significantly greater than c . The $[\text{Cu}]_{\text{TOT}}$ values obtained by colorimetry appear to be much more reliable than the atomic absorption results which are lower than c in some cases. The $[\text{Cu}]_{\text{TOT}}$ values obtained by both methods are presented in Table 12.

An analysis for total phosphorus concentration was carried out for each solution by the spectrophotometric measurement of extracted phosphomolybdic acid using the Carl Zeiss Spectrophotometer. The procedure used is that suggested by Mozersky, Pettinati, and Kolman (62) except that 1:1 tert-butanol:benzene mixture was used as the extractant. The results are given in Table 12.

Analyses of Equilibrated Solids

After all of the equilibrated solutions had been analyzed, the solid residues were filtered off by suction and sucked dry. The solid residues were then analyzed for total copper content by colorimetry involving the copper-ammonia complex and for total phosphorus content by the same method as was used for the solutions. Infrared spectra and X-ray diffractograms were also taken of all the solid residues. The solid residues will be referred to using the same labels as for the corresponding solutions. The results of the analyses and the Cu:P ratios are given in Table 13.

Uncertainties in Analyses of Equilibrated Solutions and Solids

From Table 12, it can be deduced that for the equilibrated solutions, the maximum standard deviation (σ) is ± 1.5 percent for h , ± 1.4 percent for c , ± 3.7 percent for $[\text{Cu}]_{\text{TOT}}$, and ± 3 percent for $[\text{P}]_{\text{TOT}}$. Assuming that the uncertainty (u) is 3σ , then the uncertainty

TABLE 13
SUMMARY OF %Cu, %P, AND Cu:P RATIOS OF SOLIDS

Solids	Av. % Cu	Av. % P	Av. % PO_4	% Cu + % PO_4	100% - (% Cu + % PO_4)	Cu:P ratio
0A	38.7	15	46	85	15	1.26:1
1A	32.9	12	37	70	30	1.34:1
2A	35.2	12	37	72	28	1.43:1
3A	33.1	11	34	67	33	1.47:1
4A	35.4	13	40	75	25	1.33:1
5A	33.1	12	37	70	30	1.35:1
*0B	17.3	6.2	19	36	64	1.36:1
1B	22.9	5.4	17	40	60	2.07:1
2B	24.1	2.2	6.7	31	69	5.34:1
3B	23.7	3.2	9.2	33	67	3.62:1
4B	21.7	3.8	12	34	66	2.78:1
1C	29.1	10	31	60	40	1.42:1
2C	23.5	10	31	55	45	1.15:1
3C	20.8	10	31	52	48	1.01:1
4C	24.2	13	40	64	36	0.907:1
5C	22.5	11	34	56	44	0.997:1

* This solid was CuHPO_4 (anhyd.) equilibrated in 3M NaClO_4 soln. in a flask at 25°C in order to determine whether CuHPO_4 would revert back to $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ in 3 M NaClO_4 solution.

is about ± 4.5 percent for h , about ± 4.2 percent for c , about ± 11 percent for $[Cu]_{TOT}$, and about ± 9 percent for $[P]_{TOT}$. Experimental errors in the calculated Cu:P ratios of the solids (Table 13) result from errors in the determinations of percent Cu and percent P and also possibly from variations in the amount of solid residue present after equilibration. If the solid residue is totally unaltered or totally altered after equilibration, then variations in the amount of solid residue are not important, but if only a fraction of the residue is altered then the composition of the residue is dependent on the amount of residue present. Since the amount of solid residue present after equilibration is generally quite small, any change in composition should be readily apparent from the Cu:P ratios. All of the group A solids give similar infrared spectra and X-ray diffractograms (Figure 10 and Table 15), therefore the uncertainty in Cu:P ratios may perhaps be estimated by averaging the Cu:P ratios of the group A solids and calculating the uncertainty (3σ) which is about ± 15 percent. For the group B solids, #0 and #1 give similar infrared and X-ray data as do #2, #3, and #4 (Figure 11 and Table 16). The estimated uncertainties in Cu:P ratios are about ± 63 percent for solids #0B and #1B and about ± 72 percent for solids #2B, #3B, and #4B. For the group C solids, #1 and #2 give similar infrared and X-ray data as do #3, #4, and #5 (Figure 12 and Table 17). The estimated uncertainties in Cu:P ratios are about ± 33 percent for solids #1C and #2C and about ± 12 percent for solids #3C, #4C, and #5C. The estimated uncertainties in Cu:P ratios represent a combination of the uncertainties in percent Cu, the uncertainties in percent P, and possible uncertainties due to variations in the amount of solid residue present.

Although estimates have been made of the uncertainties in various measurements, the actual errors in these measurements are unknown.

4.5 Preparation of other Cupric Orthophosphate Compounds

After the equilibrated solids were analyzed and infrared spectra and X-ray diffractograms taken, it became obvious that the solid residues had changed during equilibration. In order to determine what changes had taken place it was decided that it would be useful to try to prepare other cupric orthophosphate compounds and compare them with the equilibrated solids. Attempts were made to prepare four compounds:

$\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cu}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$, $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (by a different method than Debray or Bassett and Bedwell) and $\text{Cu}_2(\text{PO}_4)(\text{OH})$. These preparations will be referred to as Preparation III, Preparation IV, Preparation V, and Preparation VI, respectively. The experimental details are given below.

Preparation III

This preparation was carried out according to the "Steinschneider principle" as described by Klement and Haselbeck (48) by adding at room temperature, dropwise, with stirring, a solution of 5 g of diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) in 100 ml of water (adjusted to pH 6 with acetic acid using the Coleman Metrion III pH meter) to a solution of 50 g cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 200 ml of water. Although a precipitate was formed immediately upon addition of the orthophosphate solution, the resulting mixture was stirred for a few hours before the solid was filtered off by suction, washed with water and acetone, and left under vacuum overnight. The product was dried in an oven at 95°C for 1 hour and stored in a desiccator overnight. The final product was a light blue powder.

(Theoretical) $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$: Cu, 43.86 ; PO_4 , 43.71

Found : Cu, 43.32 ; PO_4 , 41.89

molar Cu / PO_4 ratio = 1.55 : 1 .

Preparation IV

This sample was prepared as described by Klement and Haselbeck (48) by adding at room temperature, dropwise, with stirring, a solution of 4.42 g of sodium phosphate monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) in 100 ml. of water (adjusted to pH 7 with NaOH solution) to a solution of 20 g of cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 100 ml. of water. The resulting mixture was stirred for a few hours before the solid residue was isolated and treated using the same procedure as for Preparation III. The final product was a light blue powder.

(Theoretical) $\text{Cu}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$: Cu, 41.17 ; PO_4 , 49.23

(Theoretical) $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$: Cu, 43.86 ; PO_4 , 43.71

Found : Cu, 41.69 ; PO_4 , 45.33

molar Cu / PO_4 ratio = 1.38:1

Preparation V

This sample was prepared by the same procedure as for Preparation IV except that the proportion of copper to orthophosphate was different (Klement and Haselbeck (48)). A solution of 8.85 g of sodium phosphate monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) in 100 ml of water (adjusted to pH 7 with NaOH solution) was added at room temperature, dropwise, with stirring, to a solution of 10 g of cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 100 ml of water. After the resulting mixture had been stirred for a few hours, the residue was isolated and treated as before. The final product was a light blue powder.

(Theoretical) $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$: Cu, 35.79 ; PO_4 , 53.49

(Theoretical) $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$: Cu, 43.86 ; PO_4 , 43.71

Found : Cu, 40.42 ; PO_4 , 46.48

molar Cu / PO_4 ratio = 1.30:1

Preparation VI

About 1 g of Preparation III was placed in a thick-walled glass tube and 10 ml of triply-distilled water was added. After mixing, the tube was sealed and then heated in an oven at about 185°C for 18 hours. After cooling to room temperature, the tube was broken open and the solid residue was filtered off by suction, washed with water and acetone, and sucked dry. The final product was a finely crystallized light green solid.

(Theoretical) $\text{Cu}_2(\text{PO}_4)(\text{OH})$: Cu, 53.16 ; PO_4 , 39.73

Found : Cu, 52.98 ; PO_4 , 33.91

molar Cu / PO_4 ratio = 2.33:1

Analyses

The four preparations were analyzed for total copper content and total orthophosphate content.

(i.) All four preparations were analyzed for total copper content by iodometric titration (54). The first three preparations (III, IV, and V) were analyzed in triplicate but due to the small amount of sample, Preparation VI was analyzed only once.

(ii.) The total orthophosphate content of each of the four preparations was determined by a gravimetric method (55) involving the precipitation of orthophosphate as magnesium ammonium phosphate and ignition at about 1000°C to magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$). The first three preparations (III, IV, and V) were analyzed in duplicate but again due

to the small amount of sample, Preparation VI was analyzed only once.

Infrared Spectra

The infrared spectra of all four samples, ground with dried KBr and also as nujol mulls, over the range of 1333 to 400 cm^{-1} are shown in Figure 7. It can be seen that there are few significant differences between the spectra taken as nujol mulls and those taken as KBr discs, therefore, only the latter will be discussed. The first three preparations give fairly similar spectra except that the spectrum seems to become more resolved going from Preparation III \rightarrow Preparation IV \rightarrow Preparation V. For example, Preparation III shows peaks at 1147 , 1092 , 1062 , and 993 cm^{-1} in the P - O stretching region and peaks at 628 and 558 cm^{-1} in the O-P-O bending region. Preparation IV shows a slight bump at 1206 cm^{-1} in the P=O stretching region, peaks at 1151 , 1093 , 1060 , 991 , 953 , and 863 cm^{-1} in the P - O stretching region, and peaks at 622 , 556 , and 506 cm^{-1} in the O-P-O bending region. Preparation V gives a spectrum essentially similar to Preparation IV except that it seems to be slightly better resolved. The infrared spectrum of Preparation VI is obviously different from those of the first three preparations (III, IV, and V) and is rather unresolved due perhaps to the lack of water of hydration.

X-ray Diffractograms

The X-ray diffractogram results obtained for the four preparations and the results for $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Cu}_2(\text{PO}_4)(\text{OH})$ reported by Hanawalt et al (65) are shown in Table 14. For the first three preparations (III, IV, and V), it is seen that the results obtained for Preparation III are somewhat different from the results obtained for Preparation IV and V which indicates some crystal structure differences between Preparation

Figure 7

Infrared Spectra of Preparations III, IV, V, and VI

(i.) Preparation III

(a.) KBr disc (solid line)
(b.) Nujol mull (dashed line)

(ii.) Preparation IV

(a.) KBr disc (solid line)
(b.) Nujol mull (dashed line)

(iii.) Preparation V

(a.) KBr disc (solid line)
(b.) Nujol mull (dashed line)

(iv.) Preparation VI

(a.) KBr disc (solid line)
(b.) Nujol mull (dashed line)

The calibration peaks indicate 1028.0 cm^{-1}

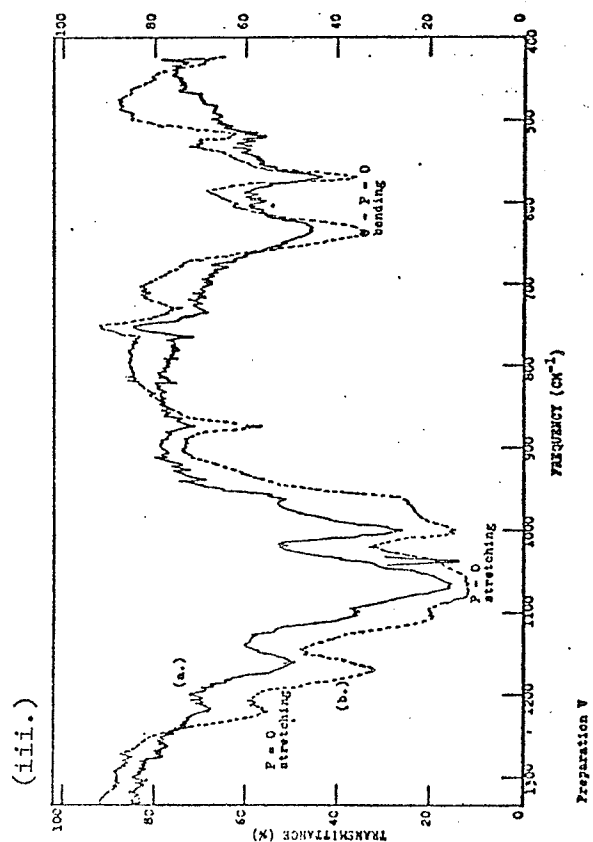
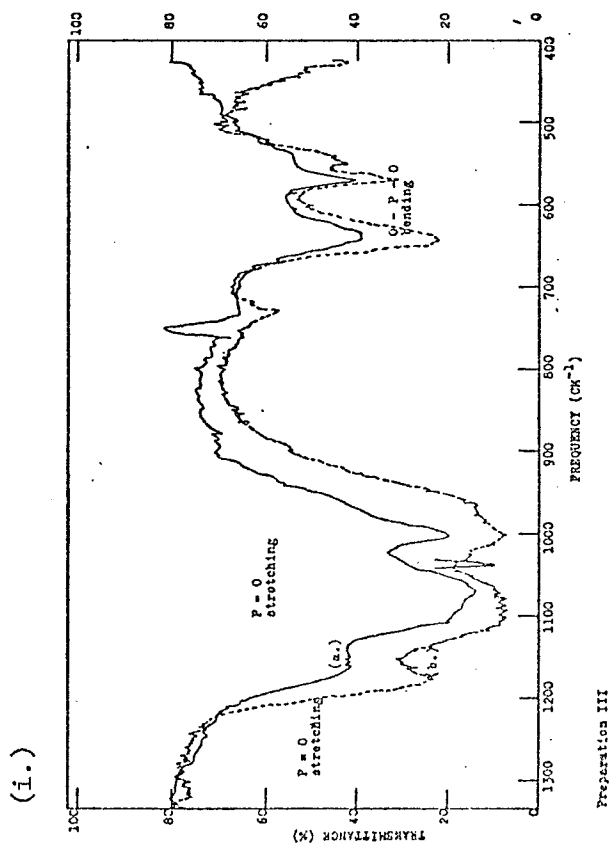
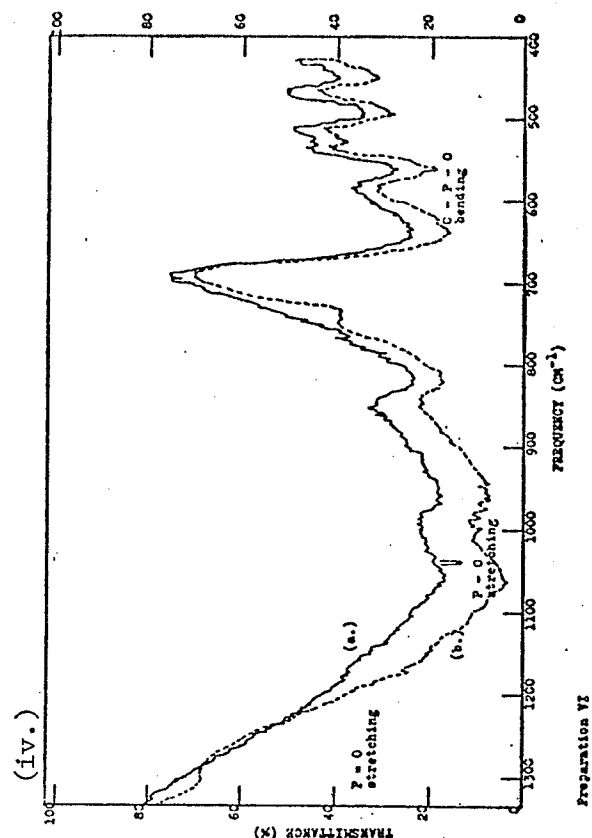
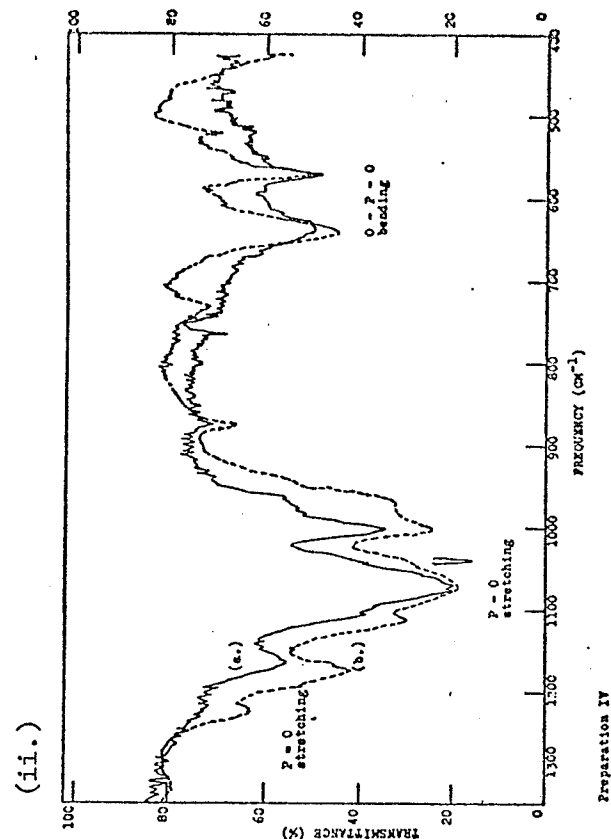


TABLE 14

X-RAY DIFFRACTOGRAMS OF PREPARATIONS III, IV, V, AND VI

Preparation III		Preparation IV		Preparation V		(65) Cu ₃ (PO ₄) ₂ ·3H ₂ O		Preparation VI		(65) Cu ₂ (PO ₄)(OH)	
d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁
10.65	100										
		9.83	53	9.72	51	9.9	100				
6.81	46	6.76	38	6.76	42	6.9	25				
						4.80	8	5.79	76	5.8	40
								4.77	29	4.81	100
4.35	37					4.32	15	4.72	31		
4.25	33	4.21	32								
								4.10	7		
						3.90	5				
								3.71	71	3.71	28
								3.60	30		
3.18	54					3.34	10				
		3.03	100	3.02	100	3.02	87				
2.92	90										
2.65	30	2.65	40	2.64	42	2.65	20	2.89	100	2.91	50
								2.64	67	2.63	100
								2.60	28		
2.51	29					2.54	5	2.56	78	2.55	12
						2.49	5	2.51	31		
								2.44	16		
2.42	27	2.41	34	2.40	24	2.41	5	2.40	60	2.41	16
								2.37	22		
						2.34	5	2.34	19		
		2.16	21	2.15	19			2.30	27	2.30	16
						2.15	8	2.25	7		

III and Preparation IV and V. From Table 14, it can also be seen that the X-ray diffractogram results for $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ reported by Hanawalt et al (65) agree quite well with the results obtained for Preparations IV and V. There is quite good agreement between the experimental results obtained for Preparation VI and the $\text{Cu}_2(\text{PO}_4)(\text{OH})$ results reported by Hanawalt et al (65) except that the experimental diffractogram has several extra peaks. Finally, it should be noted that Preparation VI gave a diffractogram with very sharp peaks due to its definite fine crystalline structure. However, the diffractograms obtained for Preparations III, IV, and V had very broad peaks due to the ill-defined crystal structure of the solids.

Conclusions

Taking into consideration the analytical results, infrared spectra, and X-ray diffractograms, it appears that Preparations III, IV, and V are essentially $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ and Preparation VI is essentially $\text{Cu}_2(\text{PO}_4)(\text{OH})$.

5. RESULTS AND CONCLUSIONS OF SOLUBILITY STUDIES

5.1 Comments on the Equilibration of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ or CuHPO_4 in Aqueous Solutions of Known $[\text{H}^+]$ or Known [Orthophosphate]

To determine if any changes had taken place in the cupric orthophosphate solids during equilibration, the Cu:P ratios of the equilibrated solids were calculated and will be compared with the relative $[\text{Cu}]_{\text{TOT}}$ and $[\text{P}]_{\text{TOT}}$ values for the corresponding solutions. In addition, any unexpected changes in pH of the solutions after equilibration will be noted and finally, the infrared spectra and the X-ray diffractograms of the equilibrated solids will be compared with each other, with those of the original solids, and the prepared $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ samples.

Comments on the Analyses of Solutions and Solids after Equilibration

(A) In Table 12 it can be seen that for solution #0A, the free hydrogen ion concentration, h , is surprisingly high considering that the 3M NaClO_4 solution was slightly basic. This would indicate that more than the simple dissolution of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ may be involved.

For the equilibrated solutions of group A (Table 12), the value of $[\text{P}]_{\text{TOT}}$ is considerably greater than $[\text{Cu}]_{\text{TOT}}$ in the case of solution #0A, but the difference in concentrations gradually narrows until for solution #5A $[\text{Cu}]_{\text{TOT}} \sim [\text{P}]_{\text{TOT}}$. However, for the corresponding solids there is not much change in the Cu:P ratios (Table 13).

Plots of $[\text{Cu}]_{\text{TOT}}$ vs. pH (Figure 8) and $[\text{P}]_{\text{TOT}}$ vs. pH (Figure 9) for the six solutions of group A show a correlation between solubility and pH.

(B) In Table 12, it can be seen that going from solution #2B to solution #3B, the h value increases by about a factor of ten but the c value increases only about four percent.

Figure 8

$[\text{Cu}]_{\text{TOT}}$ as a function of pH for the equilibrated solutions of groups A, B, and C

- Group A
- △ Group B
- Group C
- ⬡ Data from Reference (35) (HNO_3 medium)
- ☆ Data from Reference (35) (HCl medium)

FIGURE 8

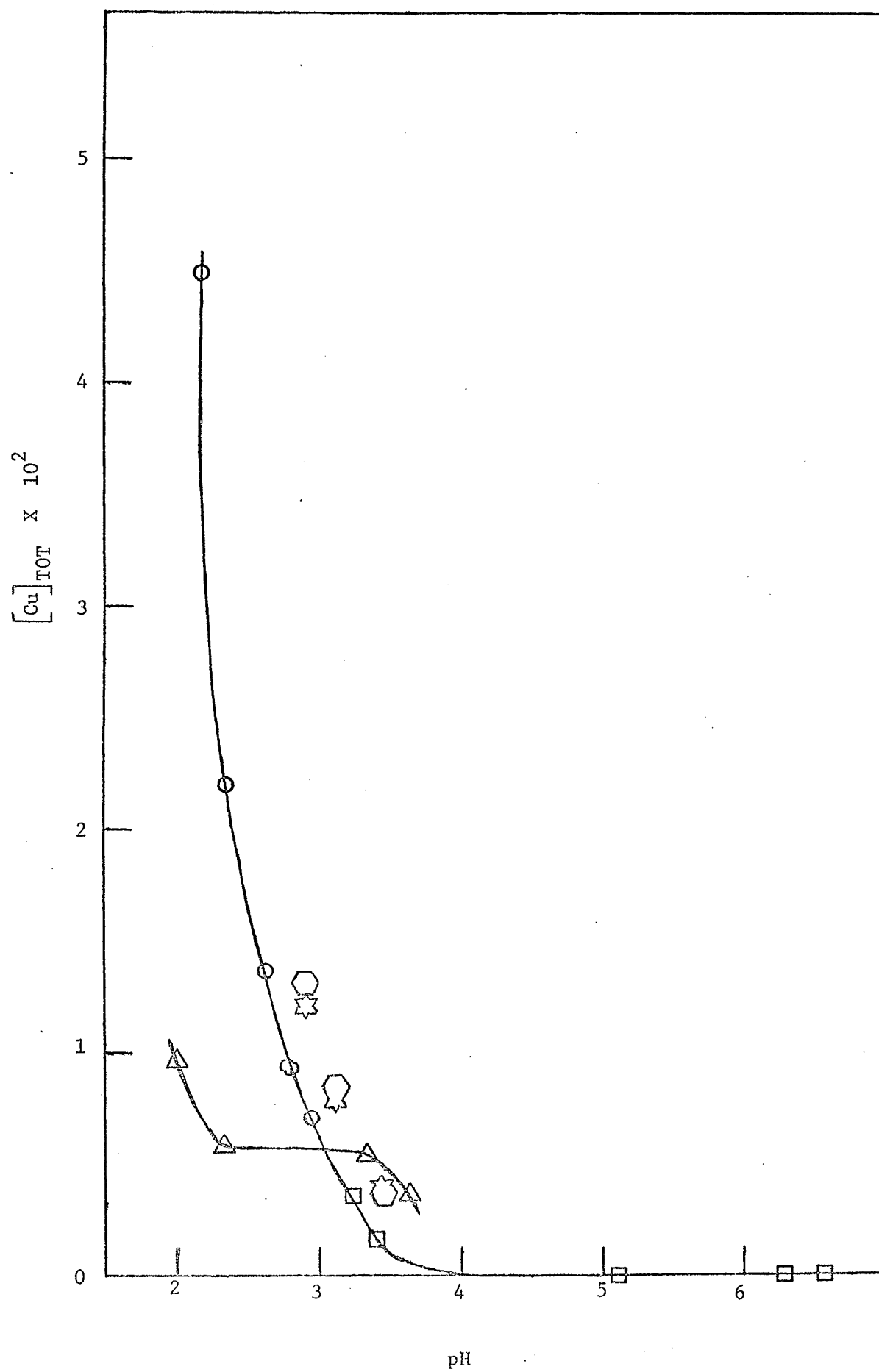
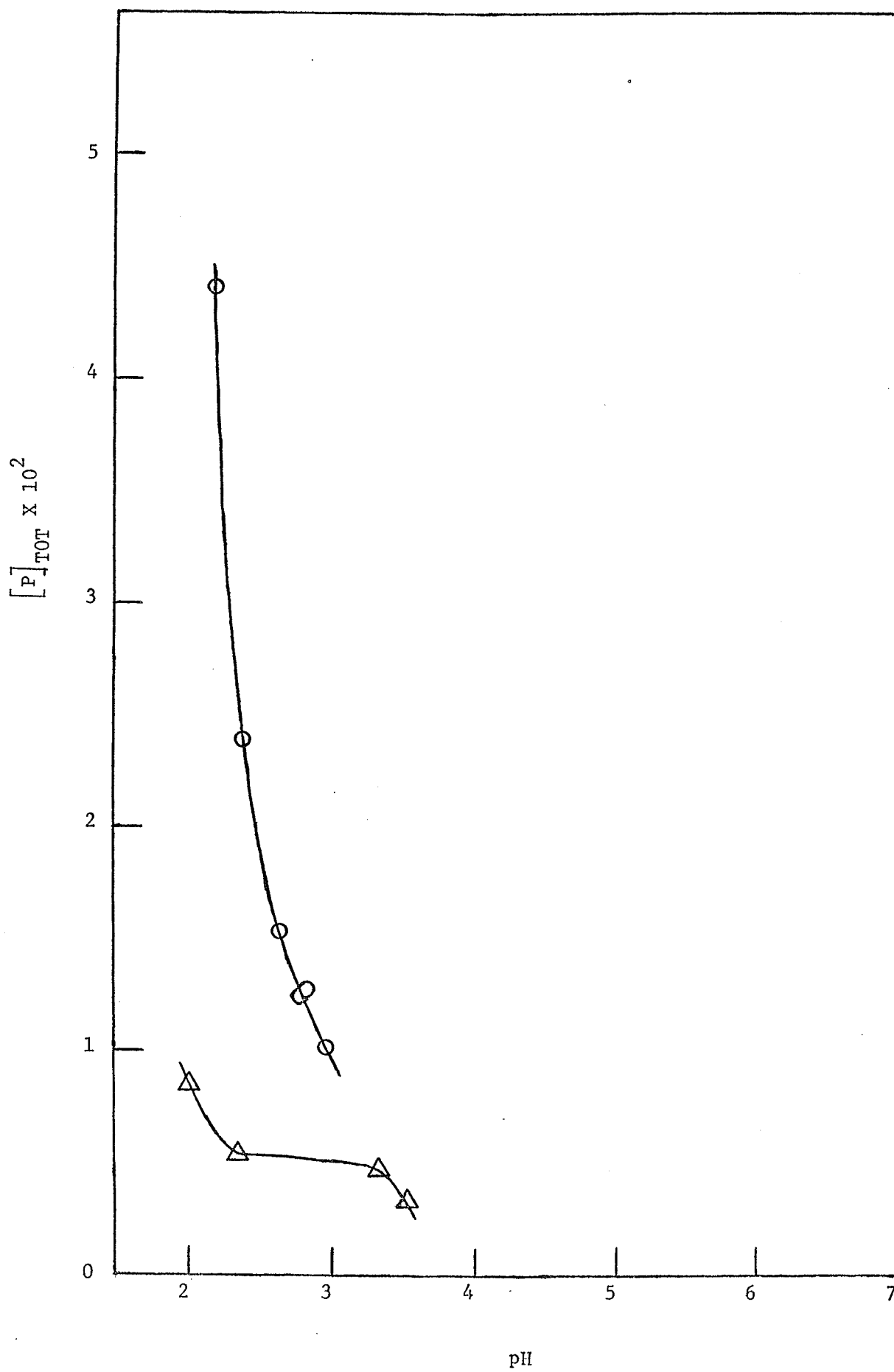


Figure 9

$[P]_{TOT}$ as a function of pH for the equilibrated
solutions of groups A and B

○ Group A

△ Group B



It should be noted that for all four equilibrated solutions of group B (Table 12), the $[\text{Cu}]_{\text{TOT}}$ values are somewhat higher than the $[\text{P}]_{\text{TOT}}$ values. However, for the corresponding solids and also solid #0B (Table 13), the molar Cu:P ratios are also greater than 1. It seems inexplicable that there can be an excess of copper in both the solutions and solids. There are also wide variations in the Cu:P ratios of the solids perhaps due to the relatively small values of % P which would tend to increase experimental errors.

Plots of $[\text{Cu}]_{\text{TOT}}$ vs. pH (Figure 8) and $[\text{P}]_{\text{TOT}}$ vs. pH (Figure 9) both illustrate the large jump in pH between solutions #2B and #3B.

(C) For the group C solutions (Table 12) the increase in $[\text{P}]_{\text{TOT}}$ is significantly greater than $[\text{Cu}]_{\text{TOT}}$ and even for solutions #3C, #4C, and #5C, where $[\text{Cu}]_{\text{TOT}}$ is immeasurably small, the $[\text{P}]_{\text{TOT}}$ values are about 8 percent higher than the $[\text{P}]_{\text{TOT}}$ values of the original phosphate values of the original phosphate solutions. For the corresponding solid residues (Table 13), the Cu:P ratios seem to decrease as orthophosphate concentration is increased until the ratio reaches about 1:1 for solids #3C, #4C and #5C.

A plot of $[\text{Cu}]_{\text{TOT}}$ vs. pH (Figure 8) for the group C solutions seems to correlate smoothly with the curve for the group A solutions.

In groups A, B, or C there does not appear to be any apparent absorption of copper by the plastic vessels although no blank samples were run. However, if some absorption of copper did occur, the copper/phosphate ratios of the equilibrated solutions would be reduced but the solubility products of the solid residues would be unaffected because the equilibrium would shift in order to keep the solubility product constant.

Infrared Spectra

Figure 10 shows the infrared spectra of the group A solids along with

Figure 10

Infrared Spectra of the Group A solids $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$
(Preparation I), and $\text{Cu}_3\text{PO}_4 \cdot x\text{H}_2\text{O}$ (Preparation V)

- | | |
|---|---|
| (i.) $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Ppn. I) | (ii.) Solid #0A |
| (iii.) Solid #1A | (iv.) Solid #2A |
| (v.) Solid #3A | (vi.) Solid #4A |
| (vii.) Solid #5A | (viii.) $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ (Ppn. V) |

The calibration peaks indicate 1028.0 cm^{-1}

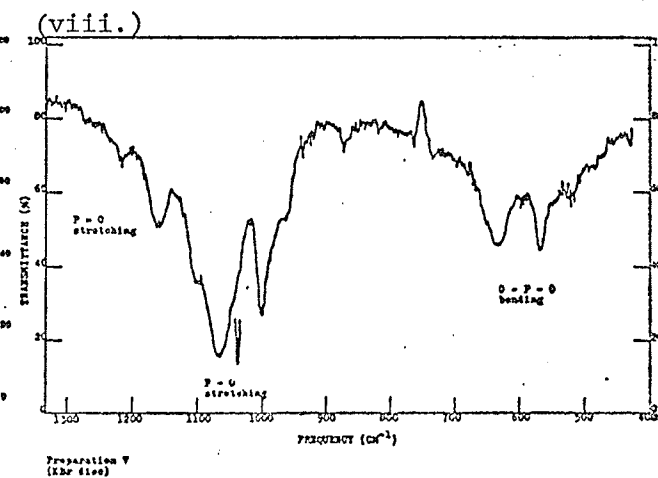
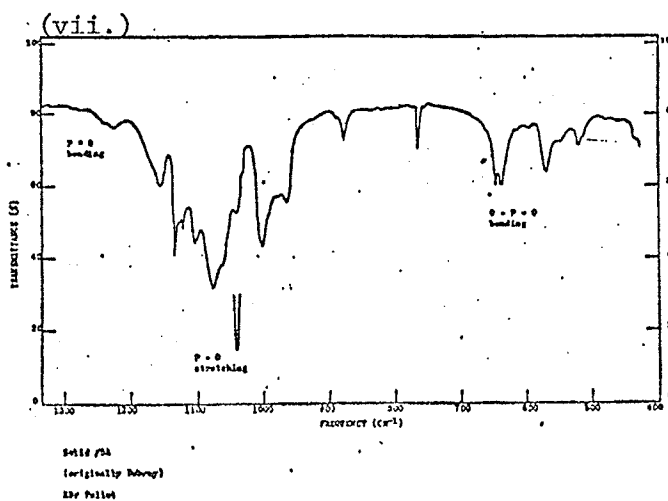
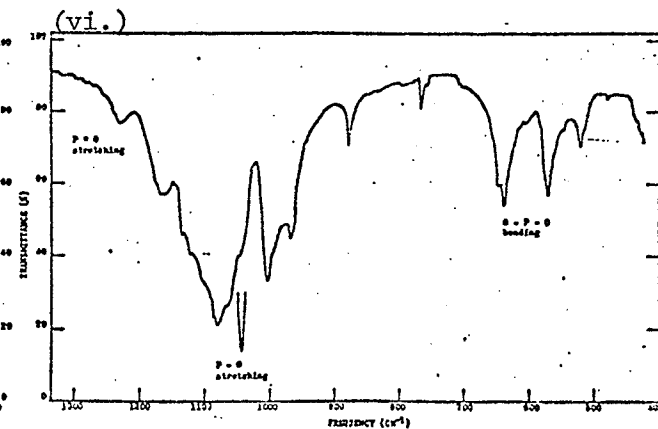
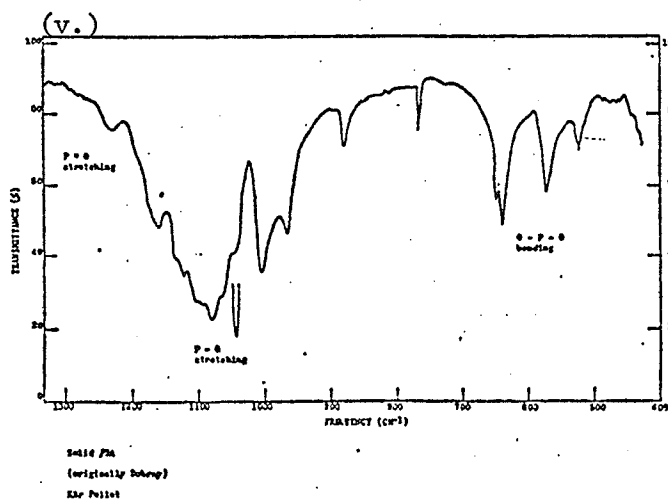
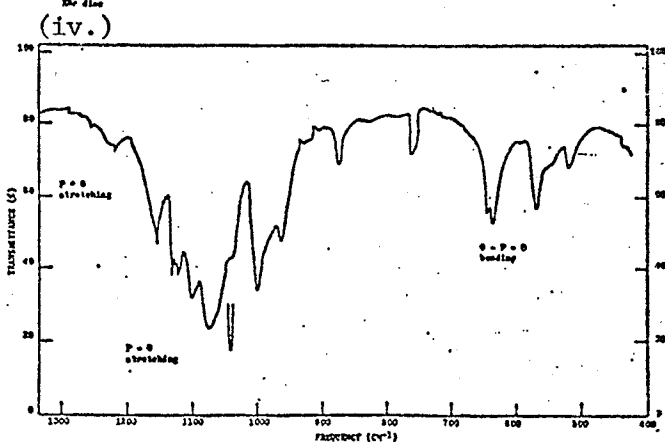
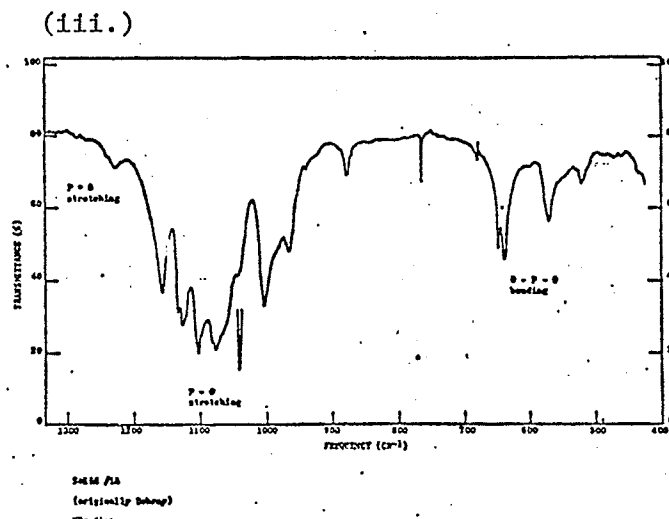
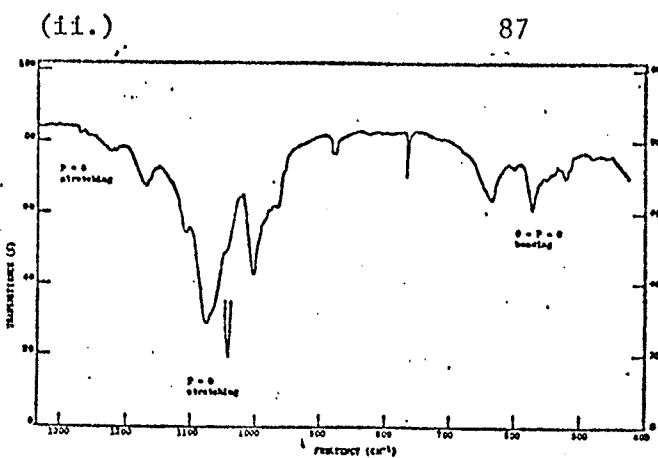
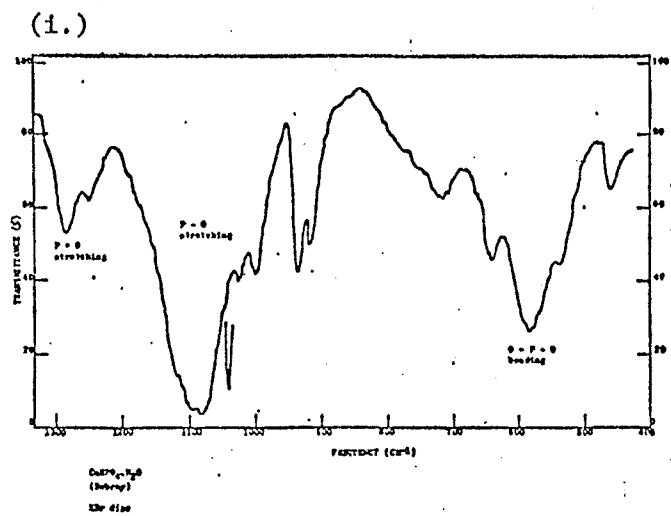


Figure 11

Infrared Spectra of the Group B solids , CuHPO_4 ($\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ heated at 180°C for 2 hours), and $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II)

- (i.) $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Ppn. II) (ii.) CuHPO_4 ($\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ heated at 180°C)
 (iii.) Solid #0B (iv.) Solid #1B
 (v.) Solid #2B (vi.) Solid #3B
 (vii. Solid #4B

The calibration peaks indicate 1028.0 cm^{-1}

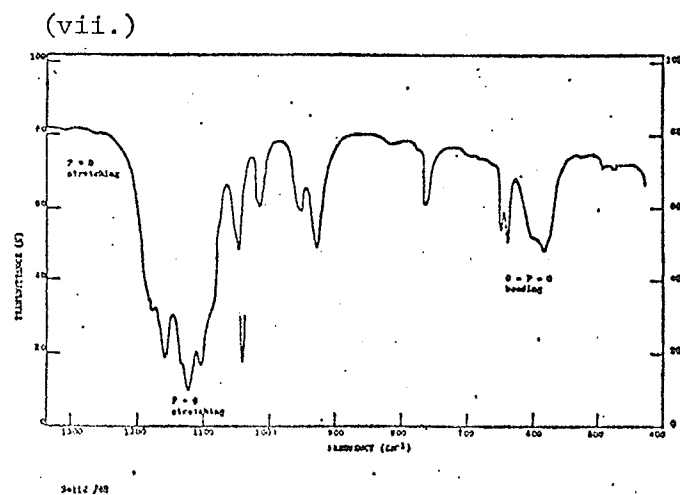
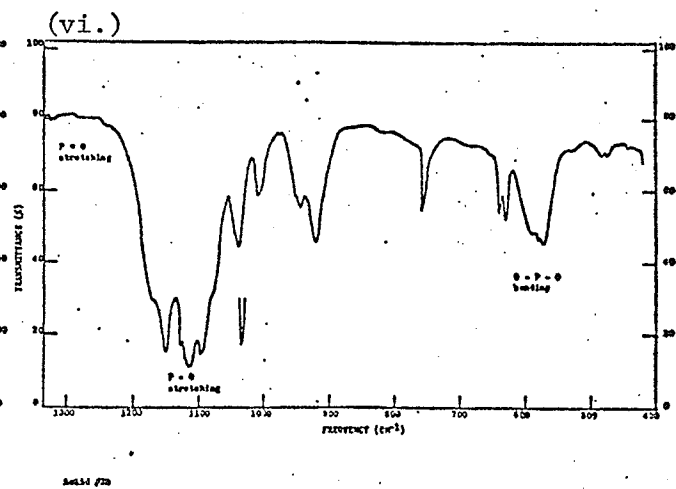
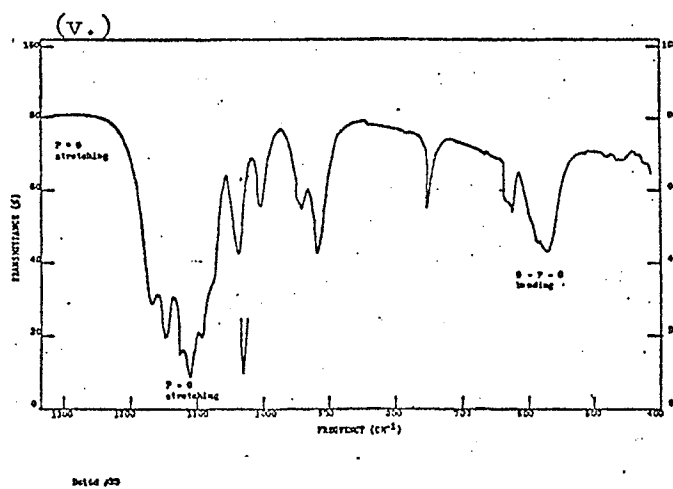
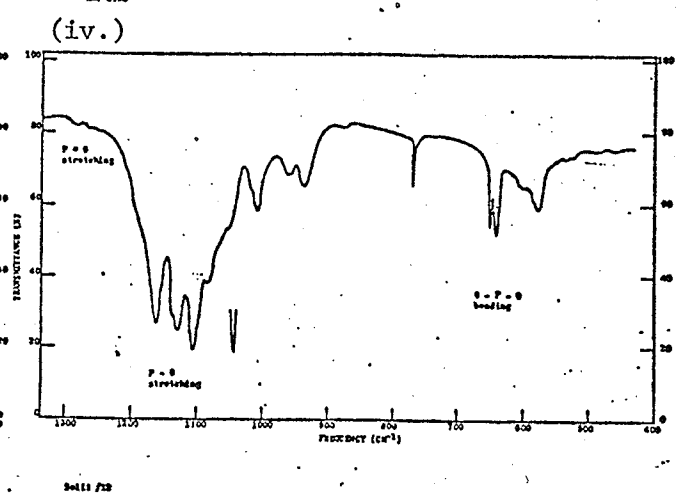
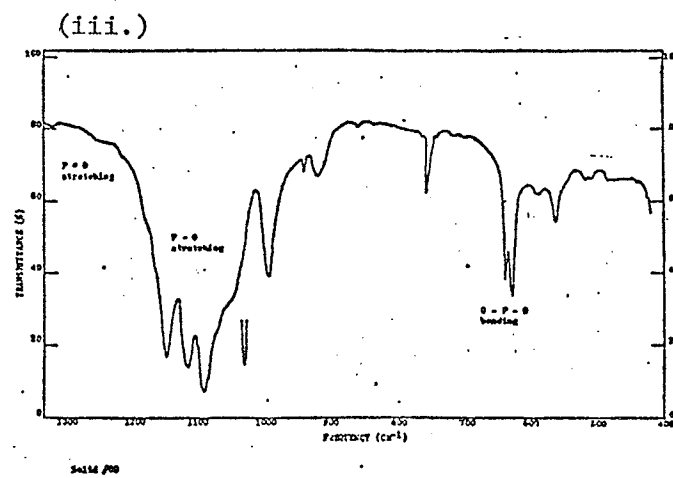
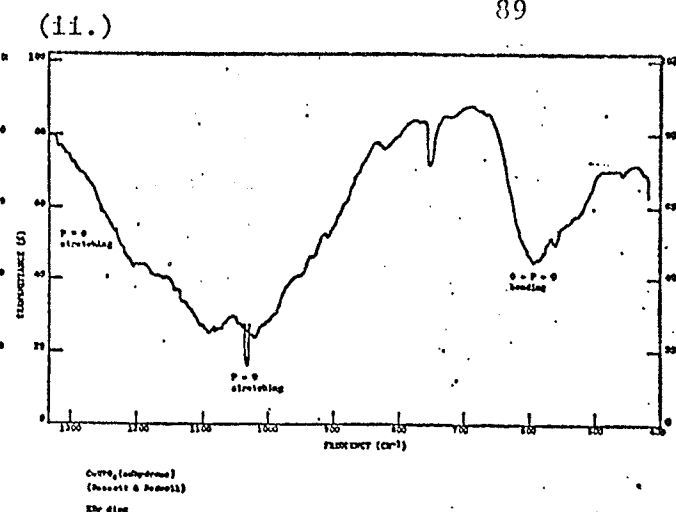
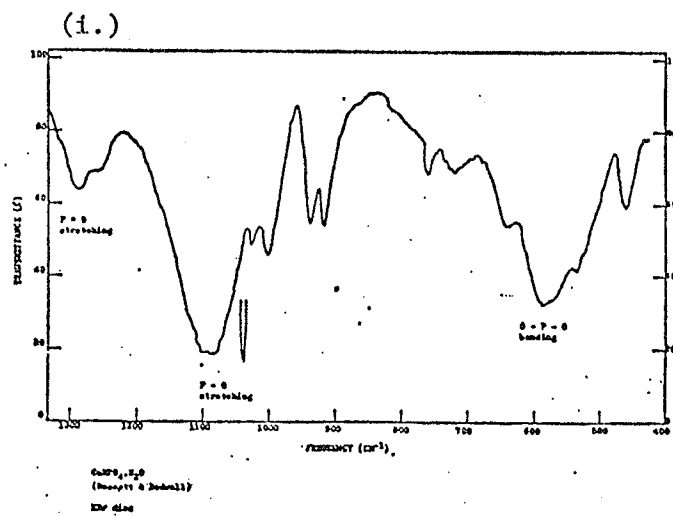


Figure 12

Infrared Spectra of the Group C solids, $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$
 (Preparation II), and $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ (Preparation V)

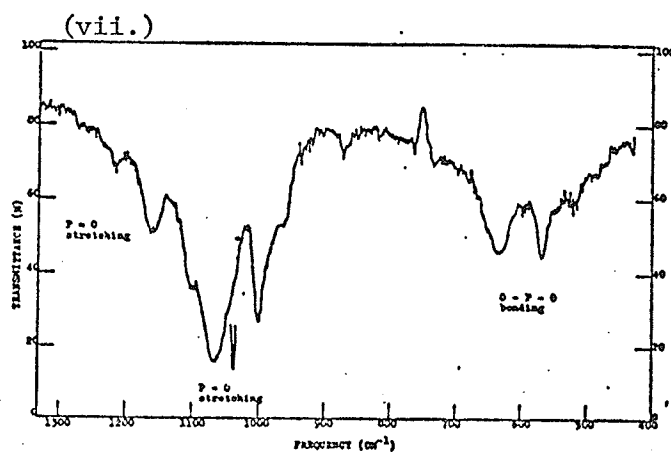
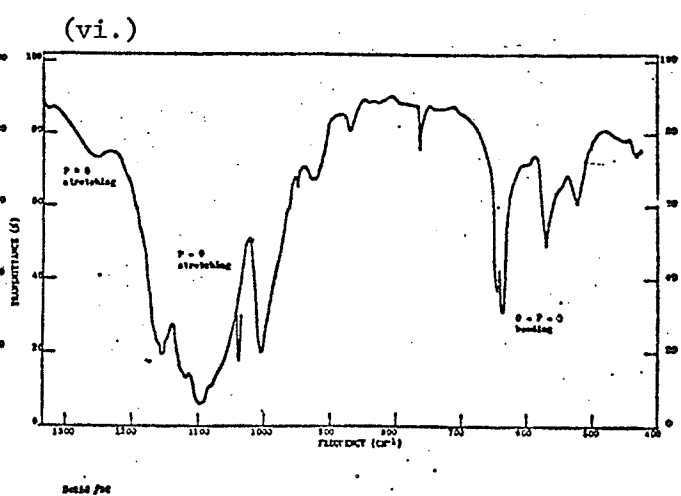
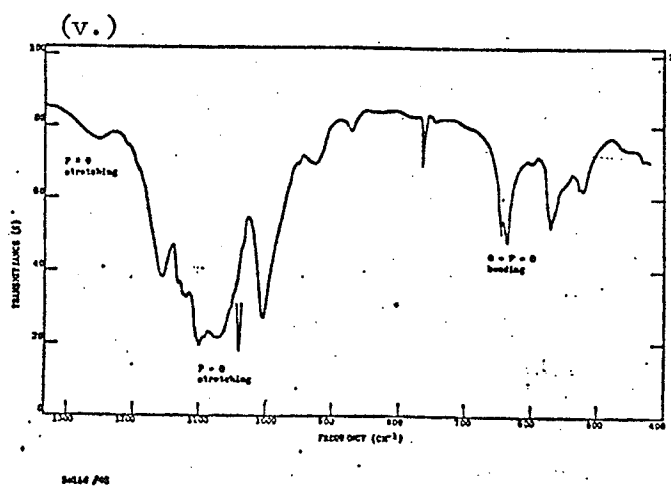
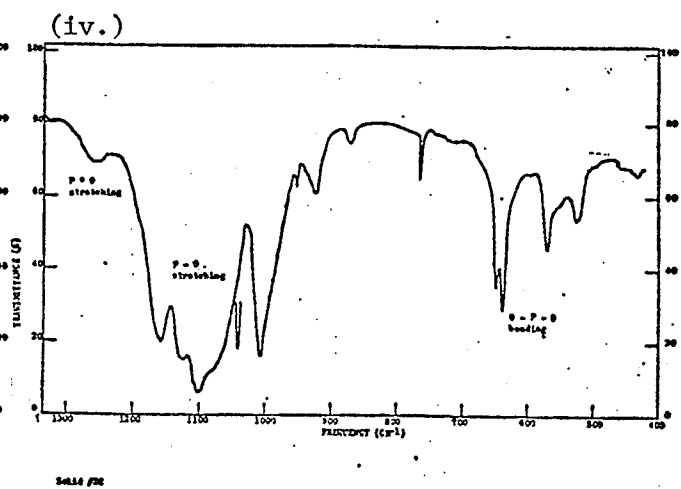
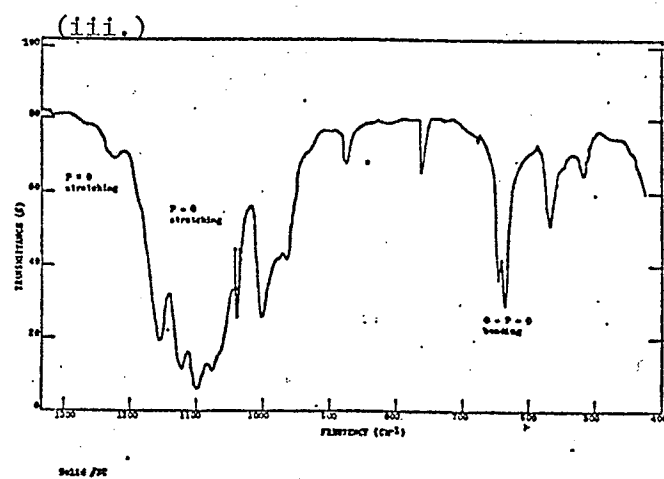
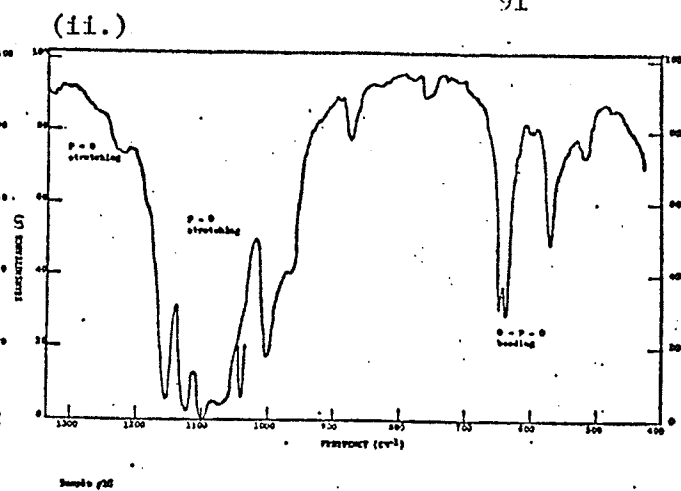
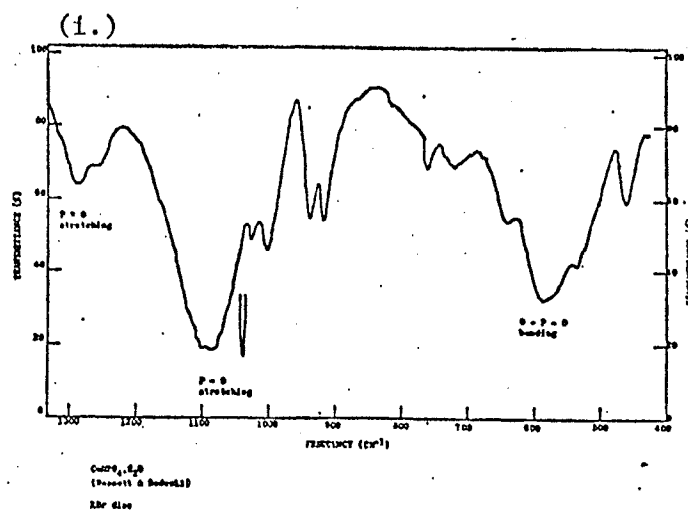
(i.) $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Ppn. II) (ii.) Solid #1C

(iii.) Solid #2C (iv.) Solid #3C

(v.) Solid #4C (vi.) Solid #5C

(vii.) $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ (Preparation V)

The calibration peaks indicate 1028.0 cm^{-1}



the spectra of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation I) and $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ (Preparation V); Figure 11 shows the infrared spectra of the group B solids along with the spectra of CuHPO_4 ($\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ heated at 180°C for 2 hours), and $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II); and Figure 12 shows the infrared spectra of the group C solids along with the spectra of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II) and $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ (Preparation V).

From Figures 10, 11, and 12 it is obvious that the solid residues had changed during equilibration. The infrared spectra of the group A solids (Figure 10) are similar to the spectrum of $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ (Preparation V). The spectra of solids #1C and #2C (Figure 12) are similar to the spectra of group A solids except that the peak at about 1090 cm^{-1} is much more prominent which indicates that perhaps some $\text{CuHPO}_4 \cdot x\text{H}_2\text{O}$ is present as well as $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$. The differences between the spectrum of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II) and the spectra of solids #3C, #4C, and 5C (Figure 12) may be due to an increase in water of hydration during equilibration (i.e. $\text{CuHPO}_4 \cdot x\text{H}_2\text{O}$ where x is much greater than 1). In Figure 11, it may be seen that there is a definite difference in spectrum going from solid #0B to solid #1B to solid #2B. The original CuHPO_4 ($\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ heated at 180°C for 2 hours) may actually have contained some $\text{Cu}_2\text{P}_2\text{O}_7$ and after equilibration this mixture may have been converted to a mixture of $\text{CuHPO}_4 \cdot x\text{H}_2\text{O}$ and $\text{Cu}_2\text{P}_2\text{O}_7 \cdot x\text{H}_2\text{O}$. The composition of this mixture would vary with pH which could explain the variation in infrared spectrum between solid #0B and solid #2B.

X-ray Diffractograms

Table 15 shows the results of the X-ray diffractograms of the group A solids along with the results for $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation I) and $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ (Preparation V); Table 16 shows the results of the dif-

TABLE 15

X-RAY DIFFRACTOGRAMS OF THE GROUP A SOLIDS

(Preparation I) CuHPO ₄ ·H ₂ O		#0A	#1A	#2A	#3A	#4A	#5A	(Preparation V) Cu ₃ (PO ₄) ₂ ·xH ₂ O	
d(Å)	I/I _i	d(Å)	I/I _i	d(Å)	I/I _i	d(Å)	I/I _i	d(Å)	I/I _i
5.07	100	9.61	100	9.72	100	9.72	100	9.72	51
		6.81	24	6.81	10	6.81	6	6.81	6
4.60	24	4.82	7		4		4		
		4.31	11	4.27	12	4.25	8	4.27	7
4.11	8								
3.22	17								
3.06	24	3.01	44	3.03	27	3.03	18	3.02	16
2.97	8								100
2.87	23								
2.75	52								
2.60	16	2.65	15		12			2.66	3
2.54	45								2.64
2.41	11	2.41	10				5	2.39	3
2.37	11								24
2.31	17								
2.13	10	2.14	7						19
2.08	12								
2.00	14	1.90	12						
									25
1.74	10								
1.70	17	1.71	14						
1.61	13	1.61	7						32
1.54	14								
		1.50	9						
				1.36	6	1.36	3	1.36	3

fractograms of the group B solids along with the results for CuHPO_4 ($\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ heated at 180°C for 2 hours) and $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II); and Table 17 shows the results of the diffractograms of the group C solids along with the results for $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ (Preparation II) and $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ (Preparation V).

It is apparent from Tables 15, 16, and 17 that the solids had changed during equilibration. The X-ray diffractogram results of the group A solids (Table 15) are similar to the diffractogram results for $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ (Preparation V). The diffractogram results of solids #1C and #2C (Table 17) show characteristics of both $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ and $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ which indicates that they may be mixtures of $\text{CuHPO}_4 \cdot x\text{H}_2\text{O}$ and $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$. The diffractogram results for solids #3C, #4C, and #5C (Table 17) do not agree with either $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ or $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ but it is speculated that equilibration resulted only in a large increase in water of hydration. It is speculated that CuHPO_4 ($\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ dried at 180°C for 2 hours) actually contained some $\text{Cu}_2\text{P}_2\text{O}_7$. After equilibration, both components would probably become hydrated and the diffractogram results for the group B solids (Table 16) do show some peaks in common with $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ and with the supposed mixture of CuHPO_4 and $\text{Cu}_2\text{P}_2\text{O}_7$. Due to different solubilities of $\text{CuHPO}_4 \cdot x\text{H}_2\text{O}$ and $\text{Cu}_2\text{P}_2\text{O}_7 \cdot x\text{H}_2\text{O}$, the composition of the mixture would vary with pH which could explain the variation in diffractogram results going from solid #0B to solid #2B.

Summary

- (A) From the Cu:P ratios (Table 13), infrared spectra (Figure 10), and X-ray diffractograms (Table 15), it seems reasonable to conclude that the equilibrated solid of group A consist essentially of $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$.
- (B) It is speculated that the original CuHPO_4 solid equilibrated in

group B actually contained some $\text{Cu}_2\text{P}_2\text{O}_7$ which resulted in a mixture of $\text{CuHPO}_4 \cdot x\text{H}_2\text{O}$ and $\text{Cu}_2\text{P}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ after equilibration. This could explain the relatively low values of percent P and the very high apparent Cu:P ratios (Table 13) calculated for some of the group B solids since the analytical technique used for phosphate would only detect orthophosphate.

(C) From the Cu:P ratios (Table 13), infrared spectra (Figure 12), and X-ray diffractograms (Table 17), it is speculated that the equilibrated solids #1C and #2C are mixtures of $\text{CuHPO}_4 \cdot x\text{H}_2\text{O}$ and $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ and equilibrated solids #3C, #4C, and #5C are highly hydrated forms of $\text{CuHPO}_4 \cdot x\text{H}_2\text{O}$. From the analytical data given in Table 13, estimated values of x were calculated and are ~ 8 for solid #3C, ~ 5 for solid #4C, and ~ 7 for solid #5C.

5.2 Calculation of the Solubility Products of CuHPO_4 and $\text{Cu}_3(\text{PO}_4)_2$

The results of the solubility studies may be used to calculate solubility products (K_{so}) for CuHPO_4 and $\text{Cu}_3(\text{PO}_4)_2$ depending on whether the compound is present in the equilibrated solid. In Section 5.1, it was speculated that $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ was present after equilibration in all the group A solids and solids #1C and #2C and therefore solubility product values for $\text{Cu}_3(\text{PO}_4)_2$ may be calculated using the analytical results from the corresponding solutions. Similarly, it was speculated that $\text{CuHPO}_4 \cdot x\text{H}_2\text{O}$ was present after equilibration in all the group B solids and all the group C solids and therefore solubility product values for CuHPO_4 may be calculated using the analytical results from the corresponding solutions except for solutions #3C, #4C, and #5C in which the solubility was apparently negligible. Values of the solubility product for $\text{Cu}_3(\text{PO}_4)_2$ may be calculated from

$$K_{so} = c [\text{HPO}_4^{2-}] \quad \text{-----}(7)$$

and similarly, values of the solubility product for $\text{Cu}_3(\text{PO}_4)_2$ may be calculated from

$$K'_{so} = c^3 [\text{PO}_4^{3-}]^2 \quad \text{-----}(8)$$

The values of $[\text{HPO}_4^{2-}]$ and $[\text{PO}_4^{3-}]$ for each equilibrated solution may be calculated from h , c , $[\text{P}]_{\text{TOT}}$, the equilibrium constants for orthophosphoric acid, and the association constant for the $\text{CuH}_2\text{PO}_4^+$ complex as follows:

$$[\text{HPO}_4^{2-}] = \frac{h [\text{P}]_{\text{TOT}}}{\beta_{-1} + h + \beta_1 h^2 + \beta_2 h^3 + \beta_{1,1,1} h^2} \quad \text{-----}(9)$$

$$\text{and } [\text{PO}_4^{3-}] = \frac{\beta_{-1} [\text{P}]_{\text{TOT}}}{\beta_{-1} + h + \beta_1 h^2 + \beta_2 h^3 + \beta_{1,1,1} h^2} \quad \text{-----}(10)$$

where

$$\beta_1 = \frac{[\text{H}_2\text{PO}_4^-]}{h [\text{HPO}_4^{2-}]} = 1.86 \times 10^6$$

$$\beta_2 = \frac{[\text{H}_3\text{PO}_4]}{h^2 [\text{HPO}_4^{2-}]} = 1.44 \times 10^8$$

$$\beta_{-1} = \frac{h [\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 1.4 \times 10^{-11}$$

$$\text{and } \beta_{1,1,1} = \frac{[\text{CuH}_2\text{PO}_4^+]}{c h [\text{HPO}_4^{2-}]} = 6.9 \times 10^7$$

The calculated and average values of K_{so} and K'_{so} are given in Table 18.

The calculated K_{so} values for solutions #3B and #4B appear to be in error and were ignored in the calculation of average K_{so} . Therefore, the average calculated solubility product for CuHPO_4 is

TABLE 18
CALCULATED SOLUBILITY PRODUCTS

SOLUTION	K_{so}	K'_{so}
#0 A	-	4.76×10^{-34}
#1 A	-	3.94×10^{-34}
#2 A	-	3.64×10^{-34}
#3 A	-	2.84×10^{-34}
#4 A	-	1.83×10^{-34}
#5 A	-	5.17×10^{-34}
#1 B	1.99×10^{-8}	-
#2 B	2.23×10^{-8}	-
#3 B	$1.99 \times 10^{-9*}$	-
#4 B	$1.82 \times 10^{-9*}$	-
#1 C	2.27×10^{-8}	1.01×10^{-33}
#2 C	1.94×10^{-8}	7.29×10^{-34}

Average: $(2.11 \pm 0.14)^{\dagger} \times 10^{-8}$ $(4.95 \pm 2.48)^{\dagger} \times 10^{-34}$

* neglected in average

\dagger standard deviations are given

$$K_{so} = (2.11 \pm 0.14) \times 10^{-8}$$

and the average calculated solubility product for $\text{Cu}_3(\text{PO}_4)_2$ is

$$K'_{so} = (4.95 \pm 2.48) \times 10^{-34}$$

In 1961, Chukhlantsev and Alyamovskoya (35) determined the solubility of $\text{Cu}_3(\text{PO}_4)_2$ in dilute nitric acid and hydrochloric acid at 19 - 20°C by glass electrode and solubility measurements. They calculated the solubility product to be

$$K_{so} = [\text{Cu}^{2+}]^3 [\text{PO}_4^{3-}]^2 = (1.3 \pm 0.18) \times 10^{-37}$$

The large discrepancy between this result and the value obtained above may be due to several factors: different temperature, different medium, the questionable reliability of the c measurements (Section 4.3), and the questionable accuracy of the very small calculated $[\text{PO}_4^{3-}]$ values. Any errors in c and $[\text{PO}_4^{3-}]$ would be greatly magnified in the calculation of K'_{so} .

The solubility data for $\text{Cu}_3(\text{PO}_4)_2$ ($[\text{Cu}^{2+}]$ vs. pH in both HNO_3 and HCl media) reported by Chukhlantsev and Alyamovskoya (35) are shown plotted in Table 8 along with the experimental solubility data obtained for this thesis. It is easily seen that the points from Reference (35) are essentially parallel to the solubility curve for the group A solutions which lends credence to the conclusion that the group A solids are essentially $\text{Cu}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$.

6.

SUGGESTIONS FOR FURTHER RESEARCH

Since it was demonstrated in Section 4.3 that the cupric ion selective electrode used for this research was of questionable reliability, it would be useful to repeat the potentiometric titration of acidic copper solutions with acidic orthophosphate solutions using different cupric ion selective electrodes and hopefully obtain more reliable measurements of free cupric ion concentrations. It would also be useful to isolate and analyze the cupric orthophosphate precipitate formed at a pH greater than 3.7.

It would be useful to repeat the equilibration of $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ in 3M ClO_4^- solutions starting with accurately known amounts of solid, using a more reliable cupric ion selective electrode, and using more refined techniques for some of the analyses. For the analyses of total copper concentration, the method using ammonia is probably satisfactory for most solutions but for solutions in which $[\text{Cu}]_{\text{TOT}}$ is very small (e.g. solutions #3C, #4C, and #5C in this thesis) a more sensitive analytical method could be tried such as extraction with dithizone. For the analyses of total orthophosphate, it would be useful to try an alternative method in addition to the method used in this thesis, for example, the direct determination of phosphorus by atomic absorption flame spectrophotometry suggested by Kirkbright and Marshall (63).

In spite of some of the complications involved, fairly good results were still obtained for this thesis.

7.

REFERENCES

- (1) Weller, A., Berliner Ber., 15, 25, 92 (1882)
- (2) Rhinehart, C., Stahl u. Eisen, 4, 709 (1884); Chem. Ztg., 13, 323 (1889)
- (3) Furberg, S., Acta. Chem. Scand., 9, 1557 (1955)
- (4) Smith, J.P., Brown, W.E., and Lehr, J.R., J. Am. Chem. Soc., 77, 2728 (1955)
- (5) Carter, S. R. and Clews, H. D., J. Chem. Soc., 125, 1880 (1924)
- (6) Dede, L., Z. anorg. u. allgem. Chem., 125, 28 (1923)
- (7) Attebury, R.W., quoted by Van Wazer, J. R., Phosphorus and its Compounds, Vol. I, P. 557, Interscience (1958)
- (8) Jensen, K. A., Z. anorg. u. allgem. Chem., 221, 1 (1934)
- (9) Duval, C., Compt. rend., 224, 1362 (1947)
- (10) Mercadie, J., Compt. rend., 221, 581 (1945)
- (11) Saraswat, H. C., Proc. Indian Acad. Sci., 30A, 329 (1949)
- (12) Zabroski, E. L., Alter, H. W., and Heumann, F. K., J. Am. Chem. Soc., 73, 5646 (1951)
- (13) King, E.L., AECD-2521 (CN-3360) Oct. 1945, Declass. Mar.1949, Nuclear Sci. Absts., 2, 330 (1949)
- (14) Dounce, A.L., Flagg, J.F., Fanta, P.E., Tishkoff, G.H., Lan, T.H., and Kaley, M., NaH. Nuclear Energy Ser., Manhattan Project Tech. Sect. Div. VI, I, Pt. I, 55 (1949)
- (15) Gosselin, R.E. and Coghlan, E.R., Arch. Biochem. Biophys., 25, 301 (1953); J. Pharmacol. Exptl. Therap., 104, 180 (1952)
- (16) Greenwald, I., Redish, J., and Kilbrick, A.C., J. Biol. Chem., 135, 65 (1940)
- (17) Zharovskii, F. G., Trudy Komissii Analit Khim Akad Nauk SSSR, 3, 101, (1951)
- (18) Holloway, F., J. Amer. Chem. Soc., 74, 224 (1952)
- (19) Smith, R.M., and Alberty, R.A., J. Am. Chem. Soc., 78, 2376 (1956)

- (20) Sanford, O.E. and Kiehl, S.J., J. Am. Chem. Soc., 64, 291 (1942)
- (21) Ram, A., Bose, A.K. and Kumar, S., J. Sci. Ind. Res. (India), 13, B, 217 (1954)
- (22) Chang, S.C. and Jackson, M.L., Proc. Soil Sci. Soc. Amer., 21, 265 (1957)
- (23) D'Amore, G., Atti. Soc. peloritana sci. fis mat. e nal., 3, 95 (1956-1957)
- (24) Egan, E.P., Jr., Wakefield, Z.T., and Luff, B.B., J. Phys. Chem., 65, 1265 (1961)
- (25) Galal-Gorchev, H. and Stumm, W., J. Inorg Nuclear Chem., 25, 567 (1963)
- (26) Bjerrum, N. and Dahm, Z. Phys. Chem., Bodenstein-Festband, 627 (1931)
- (27) Jensen, K.A., Z. anorg. Chem., 221, 1 (1934)
- (28) Cole, C.V. and Jackson, M.L., Proc. Soil Sci. Soc. Amer., 15, 84 (1950-51)
- (29) Jameson, R.F. and Salmon, J.E., J. Chem. Soc., 269 (1954)
- (30) Holroyd, A. and Salmon, J.E., J. Chem. Soc., 269 (1956)
- (31) Kiltrick, J.A. and Jackson, M.L., Proc. Soil Sci. Soc. Amer., 19, 455 (1955)
- (32) Taranaev, I.V. and Vinogradova, A.D., Zhur. neorg. Khim., 2, 2455 (1957)
- (33) Salmon, J.E. and Wall, J.G.L., J. Chem. Soc., 1128 (1958)
- (34) Lindsay, W.L., Peech, M., and Clark, J.S., Proc. Soil Sci. Soc. Amer., 23, 357 (1959)
- (35) Chukhlantsev, V.G. and Alyamovskaya, K.V., Izvest. V. U. Z., Khim., 4, 706 (1961)
- (36) Böttger, W., Z. phys. Chem., 46, 521 (1903)
- (37) Harbo, J., Farm. Tidende No. 30, (1942)
- (38) Tananaev, N.A. and Lovi, R.A., Zhur. priklad. Khim., 15, 214 (1942)
- (39) Talipov, Sh. T. and Obel'chenko, P.F., Trudy sredneasiat gosud Univ., 55, 3(1954)

- (40) Baldwin, W.G., Arkiv for Kemi, 31, 407 (1969)
- (41) Millet, H. and Jowett, M., J. Am. Chem. Soc., 51, 997 (1929)
- (42) Jowett, M. and Price, H.I., Trans. Faraday Soc., 28, 531 (1932)
- (43) Genge, J.A.R., Holroyd, A., Salmon, J.E. and Wall, J.G.L. Chem. and Ind., 357 (1955)
- (44) Debray, M., Liebigs Ann. Chem., 133, 234 (1865)
- (45) Bassett, H. and Bedwell, W.L., J. Chem. Soc., 854 (1933)
- (46) Walton, H.F., J. electrochem. Soc., 97, 219 (1950)
- (47) Royen, P. and Brenneis, H., Naturwissenschaften, 50 (16) 547 (1963)
- (48) Klement, R. and Hazelbeck, H., Z. anorg. allgem. Chem., 334 (1-2), 27 (1964)
- (49) Childs, C.W., Inorg. Chem., 9, 2465 (1970)
- (50) Biedermann, G., Arkiv. Kemi., 9, 277 (1956)
- (51) Hickling, G.G., Master of Science Thesis, University of Manitoba, 1968
- (52) Forsling, W., Hietanen, S., Sillén, L.G., Acta Chem. Scand., 6, 901 (1952)
- (53) Day, R.A., Underwood, A.L., Quantitative Analysis (2nd ed.) p. 163, Prentice-Hall (1967)
- (54) Day, R.A., Underwood, A.L., Quantitative Analysis (2nd ed.) p. 111, Prentice-Hall (1967)
- (55) Kolthoff, I.M. and Sandell, E.B., Textbook of Quantitative Analysis (3rd ed.) p. 381, MacMillan (1952)
- (56) Lincoln, S.F., Stranks, D.R., Aust. J. Chem., 21, 37-56 (1968)
- (57) Nakamoto, K., Infrared Spectra of Inorganic and Coordination Compounds (2nd ed.) p. 113, Wiley-Interscience (1970)
- (58) Biedermann, G., Sillén, L.G., Arkiv. Kemi., 5, 425 (1952)
- (59) Fincham, C.G., Master of Science Thesis, University of Manitoba, 1972

- (60) Baldwin, W.G. and Sillén, L.G., Arkiv for Kemi, 31, 391-399 (1969)
- (61) Snell, F.D. and Snell, C.T., Colorimetric Methods of Analysis (3rd ed.), Vol. II, pp. 119-120, van Nostrand (1949)
- (62) Mozersky, S.M., Pettinati, J.D. and Kolman, S.D., Analytical Chemistry, 38, Vol. 9, pp. 1182-1187 (1966)
- (63) Kirkbright, G.F. and Marshall, M., Analytical Chemistry, 45, No. 9, 1610 (1973)
- (64) Brown, A.S., J.A.C.S., 56, 646 (1934)
- (65) Hanawalt et.al., Anal. Chem. 10, 475-512 (1938)
- (66) Sillén, L.G. et. al., Arkiv. Kemi 31, 315, 341, 353, 365 (1969)
- (67) Van Wazer, J. R., Phosphorus and its Compounds, (Volume I: Chemistry), pp. 479-558, Interscience (1966)