To the Graduate Council:

I am submitting herewith a thesis written by Guillermo Francisco Torres-Andrade entitled "The Standard Electrode Potentials of a Phosphinic-Acid Ion-Exchange Resin and Its Model Compound." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

George K. Schweitzer
Major Professor

We have read this thesis
and recommend its acceptance:

D. C. Kleinfelter

Jon Alexandt.

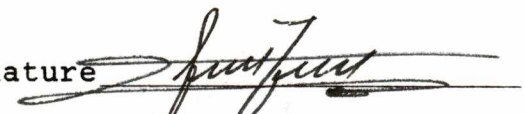
Accepted for the Council:

C. W. Minkel
Vice Provost
and Dean of The Graduate School

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a Master of Science degree at The University of Tennessee, Knoxville, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of the source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Head of Interlibrary Services when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature 

Date 07-27-1988

THE STANDARD ELECTRODE POTENTIALS OF A PHOSPHINIC-ACID ION-EXCHANGE RESIN AND ITS MODEL COMPOUND

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Guillermo Francisco Torres Andrade

August 1988

ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude and deepest appreciation to Dr. George K. Schweitzer for his guidance, advice, and encouragement during the course of this work.

I would like to express my deepest appreciation to my wife for her patience, understanding, and encouragement during the course of this work, and to my daughters, parents, and aunt for their love and support.

ABSTRACT

The oxidation-reduction characteristics of a bifunctional phosphinic acid resin and its model compound, phenylphosphinic acid, were investigated using a series of cationic species. The cations selected were Hg(II), Bi(III), Fe(III), Pb(II), Ni(II), Co(II), and Cu(II). Other species, such as $AuCl_4^-$ and $PtCl_4^{-2}$ were also investigated. Solutions of these species with concentrations ranging between 10^{-1} M and 10^{-4} M were mixed with portions of resin (0.2 g.-0.5 g) and the course of the reaction was followed by visual observation. Similarly, solutions of the model compound at concentrations of 10^{-1} M to 10^{-4} M were allowed to react with the indicated metal ion solutions at equal volumes, the course of these reactions also being followed by visual observation. Both the phosphinic acid resin and the model compound were found to reduce metal ion species having positive standard electrode potentials but were relatively inert for species with negative standard electrode potentials. An exception to this general rule was observed for Bi(III) and Fe(III) ions, which did not oxidize the resin and tended to form insoluble compounds with the phenylphosphinic acid.

The reductions of cationic species occurred at different rates, and no significant differences were observed by variations in the pH of the analyte solutions between 0.50 and 4.02 pH units. Of particular importance in the

experiments were (1) the study of the kinetics of the reaction between the model compound and the Cu(II) solutions and (2) the determination of the thermodynamic equilibrium of the reaction which was quantitatively observed at 60° C, 75° C, and 90° C. Experimental measurements of pH values and the determination of metal concentrations by atomic absorption and potentiometry were used to provide data for calculation of the equilibrium constants for the reactions. By using fundamental thermodynamic relationships among the free energy change,the reaction enthalpy, the equilibrium constant, and the electrode potential, it was possible to estimate the standard electrode potential for the oxidation of the model compound, which is deemed to be approximately equal to that of the redox resin.

TABLE OF CONTENTS

CHAPTER PAGE

I. INTRODUCTION..... 1

A. Ion-exchange resins..... 1
B. Redox resins..... 4
C. The phosphinic acid resin..... 6
D. Proposed problem..... 8
1. Selection of resins..... 8
2. Selection of the model compound and metal-ion species..... 8

II. THEORETICAL BACKGROUND..... 10

A. Redox reactions..... 10
B. Redox potentials for resins (solid state)..... 15
C. The model compound..... 17
D. Kinetic considerations..... 19

III. EXPERIMENTAL APPROACH..... 21

A. Materials..... 21
1. Phosphinic resin..... 21
2. Preparation of solutions..... 21
i. Solutions of model compounds..... 21
ii Metal nitrate solutions..... 22
iii. Gold(III) and Pt(II) solutions..... 22
iv. Primary standards for iodine titrations..... 22
v. Standard solutions for atomic absorption measurements..... 23
vi. Standard solutions for potentiometric measurements..... 23
B. Apparatus..... 24
1. pH meter..... 24
2. Temperature baths..... 24
3. Atomic absorption spectrophotometer..... 25
4. Ion selective electrode..... 26
C. Qualitative Procedures..... 27
1. Resin studies..... 27
2. Model compound studies..... 27
D. Quantitative procedures..... 28
1. Determination of the purity of the phenylphosphinic acid solutions..... 28
2. Equilibrium studies..... 29
E. Measurements..... 30
1. pH measurements..... 30
2. Atomic absorption measurements of Cu concentrations..... 30

CHAPTER PAGE

3. Measurements of Cu^{+2} concentrations with the ion selective electrode..... 32

IV. EXPERIMENTAL RESULTS..... 33

A. Observations on the resin..... 33
B. Observations on the model compound..... 36
C. Calculations..... 42

LIST OF REFERENCES..... 70

VITA..... 73

LIST OF TABLES

TABLE		PAGE
III-1.	Recomended instrument parameters for atomic absorption measurements of copper.....	31
IV-1.	Rate of formation of copper from equal concentrations of PhPH and Cu(II) at 60° C.....	43
IV-2.	Rate of formation of copper from equal concentrations of PhPH and Cu(II) at 75° C.....	44
IV-3.	Rate of formation of copper from equal concentrations of PhPH and Cu(II) at 90° C.....	45
IV-4.	Determination of the equilibrium for the reaction of phenylphosphinic acid with copper(II) solution at 60° C.....	51
IV-5.	Determination of the equilibrium for the reaction of phenylphosphinic acid with copper(II) solution at 75° C.....	52
IV-6.	Determination of the equilibrium for the reaction of phenylphosphinic acid with copper(II) solution at 90° C.....	53
IV-7.	Determination of the equilibrium for the reaction of phenylphosphinic acid with copper(II) solution at 60° C.....	54
IV-8.	Determination of the equilibrium for the reaction of phenylphosphinic acid with copper(II) solution at 75° C.....	55
IV-9.	Determination of the equilibrium for the reaction of phenylphosphinic acid with copper(II) solution at 90° C.....	56
IV-10.	Equilibrium concentrations for the reaction of phenylphosphinic acid and copper(II) solutions obtained from AA measurements and K values at different temperatures.....	57
IV-11.	Equilibrium concentrations for the reaction of phenylphosphinic acid and copper(II) solutions from ISE measurements and K values at different temperatures.....	58

IV-12. Standard potential for the reaction between phenylphosphinic acid and copper(II) solutions and for the couple PhPH/PhPOH..... 62

LIST OF FIGURES

FIGURE		PAGE
IV-1.	Rate of formation of copper from equal concentrations of PhPH and Cu(II) at 60° C.....	46
IV-2.	Rate of formation of copper from equal concentrations of PhPH and Cu(II) at 75° C.....	47
IV-3.	Rate of formation of copper from equal concentrations of PhPH and Cu(II) at 90° C.....	48
IV-4.	Plot of lnK vs. 1/T for the determination of the equilibrium constant at 298K.....	63
IV-5.	Plot of lnK vs. 1/T for the determination of the equilibrium constant at 298K.....	64
IV-6.	Plot of lnK vs. 1/T for the determination of the equilibrium constant at 298K.....	65

CHAPTER I

INTRODUCTION

A. Ion-exchange resins

In most ion-exchange processes, ions held by electrostatic forces to charged functional groups on the surface of a solid material are exchanged for ions present in a solution with which the solid is in contact. This process is often viewed as a sorption process because the ions in the solution experience a phase change when they interchange with the ions attached to the functional groups of the solid phase.

Synthetic ion-exchange resins are presently the most widely used materials in ion-exchange processes. These resins usually consist of an insoluble, three-dimensional, cross linked hydrocarbon network with potentially soluble ionic functional groups attached. The hydrocarbon network, which is the polymer support of the resin, is often prepared by copolymerizing styrene and a smaller amount of divinylbenzene.[1] The divinylbenzene reacts to cross-link polystyrene chains together, increasing the rigidity, the mechanical strength, and the insolubility of the resin.[2] The amount of divinylbenzene added determines the degree of rigidity and mechanical strength of the resin; the

higher the amount of divinylbenzene, the more rigid the resin is. However, when the amount of divinylbenzene is very high, the porosity of the resin is often adversely affected, causing limitations in the rate of mass transfer and reduced diffusion of the exchangeable ions. The usual amount of divinylbenzene ranges between 4 and 30 weight percent. The amount of added divinylbenzene determines the degree of crosslinking, which in turn characterizes the internal pore structure of the resin, which must be sufficiently open to permit the movement of the exchanging ions into and out of the resin.

The functional ionic groups of a resin consist of cations or anions which are exchanged in stoichiometrically equivalent amounts for ions in the solution that have the same sign. Many of the properties and the chemical behavior of the resin depend on the chemical and electrochemical characteristics of the functional ionic groups.

The type of functional groups attached to the resin matrix allows resins to be classified as cation- or anion-exchangers. Cation-exchangers are ion-exchange resins that contain functional groups derived from acids and are capable of exchanging cations with the solution in which they are immersed. They can be further classified as strong, medium, or weak cation exchangers depending on the acidity of the functional group when it has a hydrogen ion

attached. For example, the sulfonic resin, R-SO_3H, is a strongly acidic cation-exchanger, the phosphonic resin, R-PO_3H_2, a medium-strength acidic cation-exchanger, while the carboxylic resin, R-COOH, a weakly acidic cation-exchanger. Anion-exchangers are ion-exchange resins which exchange anions with the medium in which they are immersed and usually contain functional groups derived from primary, secondary, or tertiary amines. The R in the examples given above represents the resin matrix. Functional groups can be attached to this matrix either before the polymerization step to one of the monomers, or by functionalizing the polymeric matrix after its formation.

To characterize an ion-exhange resin, which is generally called an "ion exchanger", the exchange capacity and the ion selectivity must be determined. The ion exchange capacity is defined in terms of the number of equivalents of ionic groups per unit weight of dry resin. The ion selectivity is referred to as the preference of an ion-exchange resin for a certain ion with reference to one or more other ions. In general, exchange resins exhibit greater preferences for ions with high charges. Thus, for a series of cations of different charges the selectivity order is usually:[3]

$$Th^{+4} > La^{+3} > Ca^{+2} > Na^{+}$$

and for a series of anions,[3]

$$PO_4^{-3} > SO_4^{-2} > Cl^{-}.$$

The preferences of a resin for ions of interest are influenced by the nature of the fixed ionic groups, and in general, resins prefer counter ions which tend to form ion pairs or complexes with the fixed ionic groups. The extent of crosslinkage is often an important factor for characterizing the resin selectivity. In general, the greater the crosslinkage, the greater is the selectivity of the resin for one ion over another.[3]

B. Redox resins

Ion-exchange resins containing oxidizable or reducible ions are referred to as redox resins. These materials undergo not only ion exchange, but they also have oxidation-reduction capabilities due to the redox properties of their functional groups. Such resins have been called "electron-transfer polymers", "oxidation-reduction polymers", or "redox polymers". They were first reported by H.G. Cassidy[4] in 1949, and have been subjected to intense study in recent years due to their significant technical applications. The name oxidation-reduction polymer is applied to materials of high molecular weight that have the ability to transfer or exchange electrons via oxidation-reduction reactions with ions in the solution in which they are immersed. The oxidizing and/or reducing capability of such a material will be controlled by the redox potential of the attached redox groups.

Redox resins are usually prepared by adding different redox groups to preformed polymer matrices. The methods of preparation depend on whether the redox groups will be part of an organic network or whether they will be incorporated as substituents.[5] The polystyrene-divinylbenzene support has been widely used due to the large number of functional groups that can be easily attached to it and due to the ease of crosslinking which makes it relatively insoluble, thus facilitating the participation of the functional groups in the chemical reaction with the ions of the liquid medium.

The term "bifunctional resin" has been used to describe a resin which can undergo both ion exchange and a redox reaction.[6] When such a resin is immersed in a solution containing oxidizable or reducible ions, an ion-exchange process and an oxidation-reduction reaction will take place, leaving the exchanged ions in a different oxidation state. For example, if a reducing bifunctional resin is placed in a solution of a reducible metal ion, the metal ion will be exchanged and reduced to a lower-valence state or to its zero valence state. The possibility for the redox process will be dependent upon the standard redox potentials of the resin and of the species involved, as well as other conditions such as the pH of the solution,[7] the hydrophilic character of the resin, and the temperature

of the reaction. All of these conditions can have significant kinetic effects, as will be discussed later.

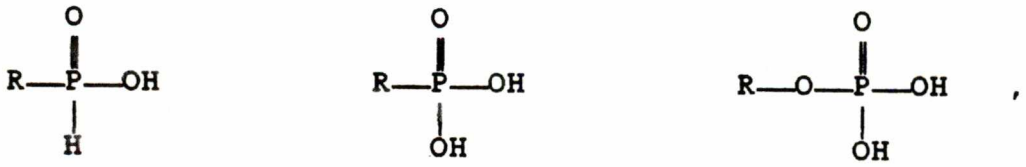
Ion-exchanging redox resins are characterized by their redox capacity as well as by their selectivity, the latter depending on their redox potentials with respect to the redox species in solution. Therefore, it is possible to reduce a specific redox species in the presence of another using a redox resin of a suitable redox potential. The redox capacity is defined as the number of redox equivalents per unit weight of resin and is usually expressed in milliequivalents per gram of dry resin.[8]

The properties of redox resins are also determined by the hydrophobic character of the polymer matrix.[5] In fact, the more hydrophobic the polymer support, the more difficult the diffusion of the reactants into the resin is. Thus, one needs to have a relatively hydrophilic polymer support so that the redox resin will successfully participate in oxidation-reduction reactions in aqueous media.

C. The phosphinic acid resin

Several resins, classified as medium strength acid exchangers, contain phosphorus acids as functional groups. These functional groups are usually derived from phosphinic, phosphonic, and phosphoric acids. The chemical

formulas of these resins can be writen as:



Phosphinic resin Phosphonic resin Phosphoric resin

The phosphinic acid resin is a bifunctional redox polymer of intermediate acidity and relatively high capacity.[7] It consists of a polystyrene-divinylbenzene support containing phosphinic acid ligands which are formed by reaction with PCl_3 followed by mild hydrolysis.

The phosphinic acid resin exhibits a dual-mechanism interaction with reducible ionic species in the solution with which it is in contact: the resin exchanges metal ions with the liquid medium, and then it reduces the metal ions. The following reactions illustrate this process in the particular case of a solution containing silver(I) ions:

$$2RH_2PO_2 + 2Ag^+ = \underset{\text{complex}}{2Ag(RHPO_2)} + 2H^+$$

$$2Ag(RHPO_2) + H_2O = 2Ag + RH_2PO_3 + RH_2PO_2$$

During the process, the metallic ions in solution form a complex with the resin, then the complex is separated into the metal in its zero valent state, the phosphonic form of the resin and the phosphinic form of the resin (unchanged).

Similar reactions occur with other metal ions in solution and all of these are governed by the oxidation-reduction potential of the ionic species, as will be

discussed later. Additionally, these ion-exchange/oxidation-reduction processes are also influenced by the pH of the solution and the temperature of the process, which can have significant effects on the rates of diffusion of the species involved.

D. Proposed problem

1. Selection of resins

Since redox resins containing phosphinic acid groups are not commercially available, information concerning their particular properties is very limited. In recent years, a polymer chemistry group at the University of Tennessee at Knoxville has synthetized several phosphinic acid resins containing different degrees of crosslinking. These resins have shown good reduction capabilities for metal ions in solution. This important property of these redox polymers has been proposed to be dependent on the standard electrode potential of the metallic species as well as on the standard electrode potential of the resins.

2. Selection of the model compound and metal-ion species

In general, the electrochemical properties of redox polymers are not well known due to the practical difficulties of determining them. So, a soluble compound strongly resembling the chemical structure of the functional ionic groups attached to the resin can be

selected for electrochemical studies, and then the properties of the resin may probably be associated with those of the model compound. In the case of phosphinic acid resins, it was proposed to select phenylphosphinic acid as the model compound. It was of interest to determine the properties of the model compound, and through it to establish possible characteristics of the resin such as the dependence of its selectivity for the reduction of cations on the standard potential of the metal species and on the factors that influence its rate of reaction.

The specific metal species to be utilized in the redox reactions with both the resins and the model compound were to be: Ag(I), Hg(II), Au(III), Pt(II), Co(II), Pb(II), Ni(II), Fe(III), Bi(III), and Cu(II). The dependence of the redox reactions on the redox potential of these ions was the fundamental criterion for selecting them.

Kinetic and equilibrium studies were to be conducted on the model compound in order to determine the equilibrium constant for its reaction with copper, and to estimate the standard electrode potential of the model compound which is assumed to be approximately the same as the standard electrode potential of the resin.

CHAPTER II

THEORETICAL BACKGROUND

A. Redox reactions

In studies of oxidation-reduction reactions involving electrochemical species the Nernst equation is the most generally applied relation. For the general equation

$$Ox + ne^- \longrightarrow Red,$$

the Nernst equation can be written as:

$$E = E^\circ + (RT/nF)\ln(a_{ox}/a_{red}) \quad (1)$$

where n is the number of electrons exchanged in the reduction process, the terms a_{ox} and a_{red} represent the activities of the species Ox and Red involved in the reaction, E° is the standard electrode potential for the given reaction and E its electrode potential at the given experimental conditions. Both latter quantities are usually given in volts. The term RT/F associates the universal gas constant R, the temperature at which the reaction occurs T, and the Faraday constant F.

Equation (1) may be written in terms of molar concentrations and activity coefficients of the given species. Thus:

$$E = E^\circ + (RT/nF)\ln(f_{ox}/f_{red}) + (RT/nF)\ln[Ox]/[Red], \quad (2)$$

where [Ox] and [Red] are the concentrations of Ox and Red

in moles/L, and f_{ox} and f_{red} are the corresponding activity coefficients. Since the values of the activity coefficients are often unknown, an alternative expression that is used to deal with this uncertainty involves the "formal potential", $E^{o\prime}$. This quantity is defined as the potential for the reaction when species Ox and Red are present at concentrations so that the ratio [Ox]/[Red] is unity.[9] The formal potential incorporates not only the standard potential but also the logarithmic term involving the activity coefficients, and since they can change with the ionic strength, Eo' will not be constant but will vary in different media. Thus, equation (2) becomes:

$$E = E^{o\prime} + (RT/nF)\ln[Ox]/[Red] \qquad (3)$$

If an oxidation-reduction reaction follows the Nernst equation, the reaction is said to be reversible or Nernstian. The reversibility of a redox reaction involves equilibrium conditions, that is, those conditions in which a system can move in either of two opposite directions from the equilibrium position. In such cases, the fundamental thermodynamic concepts of entropy and Gibbs free energy can be used to describe the redox process thermodynamically. However, since actual processes occur at finite rates[9], they cannot take place under conditions of absolute thermodynamic reversibility. Even so, many occur in such a form that the thermodynamic expressions may still be applied, at least approximately.

For a spontaneous oxidation-reduction reaction, the free energy change involved in it is given by

$$\Delta G = - nFE_{rxn},$$

or, in the case of substances at unit activity:

$$\Delta G^{\circ} = - nFE^{\circ},$$

where E_{rxn} is the potential for the reaction at any conditions different from the standard, and E° is the electrode potential for the reaction at standard conditions (temperature = 25° C, pressure = 1 atm and unit activity of all participating species).

Since the equilibrium constant of a reaction and its free energy change are related through

$$\Delta G^{\circ} = - RT\ln K,$$

it follows that:

$$RT\ln K = nFE^{\circ}. \qquad (4)$$

The equilibrium constant for any reaction varies with temperature and this variation is given by:

$$d\ln K/dT = - 1/R\{d(\Delta G^{\circ}/T)/dT\}. \qquad (5)$$

The temperature dependence of G can be expressed in terms of the enthalpy change, and is given by the Gibbs-Helmholtz equation which has the form[10]

$$d(\Delta G^{\circ}/T)/dT = - H^{\circ}/T^{2}, \qquad (6)$$

with H° being the standard reaction enthalpy at the temperature T. Substitution into equation (5) gives the van't Hoff isochore[10]:

$$d\ln K/dT = \Delta H^{\circ}/RT^{2}.$$

Since $dT/T^2 = - d(1/T)$ one can write:

$$d\ln K/d(1/T) = - \Delta H^\circ /R.$$

In using this equation, equilibrium constants are measured at several temperatures, and then a plot of lnK as a function of 1/T is made. A straight line is expected with a slope equal to - H° /R. The plot may be used to find the value of K at 25° C. This method will usually give a K value as an acceptable approximation, but not as a strictly accurate value, since it does not include the temperature dependence of the reaction enthalpy.

Since the equilibrium constant for a redox reaction and its standard potential are related to each other through expression (4), it is possible to determine the standard potential for a reaction knowing the value of its equilibrium constant.

The equilibrium exchange between ions in solution and ions attached to a resin is in most cases a reversible reaction. Thus, the description of such an equilibrium is independent of the direction from which the equilibrium state is approached. A quantitative description of the equilibria in ion-exchange processes can be approached in a number of ways. In the most general form it can be treated by analogy to a homogeneous chemical reaction. Thus, for a cation exchange process,

$$\underset{\text{solution}}{M^{n+}} + \underset{\text{resin}}{nRH} = \underset{\text{solution}}{nH^+} + \underset{\text{resin}}{(R^-)_n M^{n+}} \qquad (7)$$

where (R^-) represents the resin containing negative functional groups, RH is the resin in its initial hydrogen form, and M^{n+} represents the metal ions in solution.

Applying the law of mass action to describe the distribution of ions between resin phase and the liquid medium, an approximate equilibrium relationship for the reaction described by equation (7) (involving no aqueous complexation) can be written in terms of molar concentrations as follows:

$$K = \frac{[H^+]^n [R_n M]}{[M^{n+}] [RH]^n},$$

where $[R_n M]$ is the concentration of the metal ions in the resin, $[H^+]$ is the concentration of hydrogen ions in the aqueous phase, [RH] denotes the concentration of hydrogen ions in the resin, and $[M^{n+}]$ represents the concentration of metal ions in solution. Since the expression for K does not involve activity coefficients of the species, it does not represent the thermodynamic equilibrium constant for which the activity coefficients must be known. A real limitation in the determination of the thermodynamic equilibrium constants for resin systems is that activity coefficients for ions in them cannot be easily obtained. Therefore an expression for K of the above form is often used for characterization of resin systems, since it can be readily obtained experimentally. This K value is referred to as the apparent equilibrium constant.[3]

The description of the equilibrium for systems involving redox resins follows from a combination of the above considerations. In fact, if the reaction between a redox resin and metal ions in solution is represented by the equation

$$M^{n+} + RPH + H_2O = M + RPOH + nH^+, \quad (8)$$

the apparent equilibrium constant for this reaction will be:

$$K = \frac{[RPOH][H^+]^n}{[RPH][M^{n+}]}, \quad (9)$$

where [RPOH] is the concentration of the oxidized form of the resin, [RPH] is the concentration of the reduced form of the resin, $[H^+]$ is the concentration of hydrogen ions in aqueous phase, and $[M^{n+}]$ is the concentration of metal ions in solution.

B. Redox potentials for resins (solid state)

In the study of oxidation-reduction reactions involving redox resins the determination of their redox properties is of practical importance. However, as has been stated, several factors make the measurement of these properties relatively difficult.[5] One of these factors is that the resin cannot make direct contact with the electrodes and therefore cannot exchange electrons directly with the electrodes used for potentiometric measurements.[8] This is also limited by the fact that most electrometric

parameters include the activity coefficients of the species involved, and this information is relatively difficult to obtain for redox resins.

However, of equal importance in the determination of the electrochemical parameters characterizing this type of material is the slow approach to thermodynamic equilibrium that is often observed. This is usually attributed to the fact that ion-exchange processes as well as redox reactions involving the functional groups of the resin include not only film diffusion but also pore diffusion. These processes establish a kinetic barrier toward commponents of the liquid phase as the components penetrate the pores of the solid phase.

The properties of redox resins depend upon the properties of the polymer support and the properties of the functional groups attached to it. Since the electrochemical properties are strongly influenced by the nature of the functional groups, and because most of the redox polymers cannot make direct contact with electrodes, it is common practice to associate some of the redox resin properties to those of the corresponding functional groups. This is usually the case for the standard electrode potential of a redox resin.[8]

Since most redox reactions involving redox resins occur with the transference of protons, a dependence of the redox potential of the resin on the pH of the solution

would be expected. In fact, applying the Nernst equation to the reaction expressed by equation (8) and using the equilibrium constant for such a reaction given by expresion (9) we have:

$$E = E^{\circ} + (RT/F)\ln([RPOH][H^{+}]^{n}/[M^{n+}][RPH]),$$

or $$E = E^{\circ} + (RT/F)\ln([RPOH]/[M^{n+}][RPH]) + (RT/F)\ln[H^{+}]^{n},$$

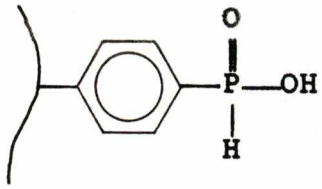
where [RPOH] and [RPH], are the concentrations of the oxidized and reduced forms of the resin, and $[M^{n+}]$ is the concentration of the metallic species in solution. The standard redox potential is the potential when $[H^{+}] = 1$.

C. The model compound

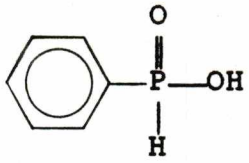
The electrochemical properties of redox resins may be related to those of their model compounds. The properties of the phosphinic acid resin, such as the redox capacity and the redox potential may be said to closely resemble those of its model compound, phenylphosphinic acid. Both the model compound and the resin show strong reducing properties toward those metals whose reduction potentials are higher than that of hydrogen ($E^{\circ} = 0.00$ volts). The rates of the reactions in which the resin is involved, would be expected to be similar or slower to those involving the model compound.

By looking at the chemical structure of the phosphinic acid resin and that of the phenylphosphinic acid, one finds that the functional groups attached to the

polymeric chain have the same chemical structure as those attached to the phenyl group of the phenylphosphinic acid. The following formulas illustrate this statement:



Phosphinic acid resin



Phenylphosphinic acid

An example of the similarity in the properties of the redox resin and the model compound is the reaction with copper(II) solutions. Although this reaction has a very slow rate, it is possible for the model compound to reduce copper(II) ions to their zero valence state. The rate of reaction can be increased by increasing the temperature. The reaction that takes place can be represented by the following equation:

$$PhPH + Cu^{+2} + H_2O = PhPOH + Cu + 2H^{+}, \quad (10)$$

for which the equilibrium constant is:

$$K = \frac{[PhPOH][H^{+}]^2}{[PhPH][Cu^{+2}]}, \quad (11)$$

where [PhPOH] is the concentration of phenylphosphonic acid formed by the oxidation of phenylphosphinic acid, [PhPH] is the final phenylphosphinic acid concentration, $[H^{+}]$ is the final concentration of hydrogen ions in solution, and $[Cu^{+2}]$ the final concentration of the metallic species in solution.

Equation (10) may be separated into two equations

corresponding to two half-reactions, the reduction of copper(II) ions to the zero valence state, and the oxidation of phenylphosphinic acid to phenylphosphonic acid:

$$Cu^{+2} + 2e^- = Cu \quad (12)$$

$$PhPH + H_2O = PhPOH + 2H^+ + 2e^-. \quad (13)$$

The determination of the equilibrium constant for the overall reaction will allow one to find its redox potential, and since the reduction potential for the couple Cu^{+2}/Cu is well known, it is therefore possible to determine the oxidation potential for the couple PhPH/PhPOH.

The experimental studies carried out on the phosphinic resin and its model compound will be described latter.

D. Kinetic considerations

Reactions occurring in ion-exchange processes as well as those involving redox polymers are likely to have different rates. Therefore, it is important to be able to determine how fast a reaction approaches equilibrium.

It is common practice to associate the slowness of the equilibrium approach in resin/solution systems with transport phenomena, associated with diffusion of particles from the solution phase to a hypothetical film at the surface of the resin, as well as to diffusion of them

through the pores of the resin. These phenomena create an additional requirement for the liquid phase to penetrate into the pores of the solid phase.

In redox resin/solution systems a chemical reaction takes place, and the reaction of the functional groups may be even slower than the diffusion phenomena.[6] For such systems, these considerations indicate that the rate determining step may be either the intraparticle diffusion or the chemical reaction itself. If a chemical reaction is the rate determining step, not all chemical reactions which are possible according to the standard electrode potential may be fast enough.[6]

If diffusion is the rate-determining step, the velocity of the process can be increased by increasing the surface of the resin particles as well as by increasing the temperature. On the other hand, if the rate is controlled by a chemical reaction, increasing the temperature will increase the velocity of the reaction.

In reactions involving the model compound, the rate at which the equilibrium is attained should also be increased by temperature increases. The limitation in this case would be the possibility of compound decomposition or thermal degradation of species during temperature increases. The catalytic effect of certain species formed during the course of the reaction could also influence the reaction rate.

CHAPTER III

EXPERIMENTAL APPROACH

A. Materials

1. Phosphinic resin[7]

The redox resin used in our experiments was obtained by synthesis of polystyrene in the form of beads via suspension polymerization. The polystyrene network was cross-linked with divinylbenzene which was added in definite amounts, usually 2%-16%. Divinylbenzene gives the polystyrene support rigidity and insolubility in the aqueous medium. The polymer support obtained was reacted with phosphorous trichloride in the presence of aluminum chloride for 4 hours at 73° C. After cooling to room temperature, the resin beads were hydrolysed with 1 M NaOH solution and then washed with a 4% HCl solution and water.

2. Preparation of solutions

i) Solutions of model compounds

Phenylphosphinic acid, $C_6H_5P(O)(OH)(H)$, F.W. 142.09 a.m.u., and phenylphosphonic acid, $C_6H_5P(O)(OH)_2$, F.W. 158.09 a.m.u., of the highest purity available, were weighed in definite amounts and diluted in deionized water to obtain 0.10 M solutions of each compound. To ensure

complete dilution of the reagent, slight heating was sometimes necessary.

ii) Metal nitrate solutions

Reagent grade nitrate salts of the cations being tested were used to prepare the corresponding 0.10 M solutions. When necessary, dilutions of the original solutions with deionized water were made to obtain the required concentrations.

iii) Gold(III) and Pt(II) solutions[11]

A small amount of gold was weighed and dissolved in aqua regia (1 volume of concentrated HNO_3 and 3 volumes of concentrated HCl) under heating to ensure dissolution and evaporation of any excess of HNO_3. Deionized water was added to obtain a 0.10 M solution of $AuCl_4^-$.

The $PtCl_4^{-2}$ solution was obtained following essentially the same procedure.

iv) Primary standards for iodine titrations

Solutions of iodine, sodium thiosulfate, and potassium biiodate with concentrations all 0.10 N were prepared following standard procedures[12] and using reagents of the highest purity. The starch indicator[13] was obtained by mixing 0.500 g of soluble starch and 25 mg of HgI_2. To this mixture 10 mL of water was added and thoroughly mixed

to form a paste which was diluted in 250 mL of boiling water and heated until the color disappeared. The solution was then cooled.

v) Standard solutions for atomic absorption (AA) measurements

A primary 1000 ppm standard solution of Cu^{+2} was used for the preparation of a series of standards of lower concentrations within the range recommended by the manufacturers of the instrument.[14] Standards were stored in plastic bottles.

vi) Standard solutions for potentiometric measurements

1. The same solutions used for AA analyses served as standards for measurements with the ion selective electrode (ISE). In addition, $1.00*10^{-2}$ M, $1.00*10^{-3}$ M, and $1.00*10^{-4}$ M solutions of Cu^{+2} were prepared by serial dilution of the standard 0.10 M solution of cupric nitrate.

2. To adjust the ionic strength of samples and standards, a 5.00 M $NaNO_3$ solution was prepared following the procedure recommended by the manufacturers.[15]

B. Apparatus

1. pH meter

A Fisher Model 805 MP pH meter was used for the determination of the pH of each solution. The pH meter was set for the temperature at which the measurements were to be performed and calibrated using buffer solutions of pH 4.01 and 10.00. A combination pH glass electrode was introduced into a glass beaker containing the analyte and the pH value was recorded.

2. Temperature baths

a) Oil bath

A parafin oil was placed in a 0.5-L glass container and heated with a hot plate. The temperature was measured with a thermometer and regulated using a small knob located in one of the sides of the hot plate.

b) Air flow oven

A single door temperature controlled oven, operating by mechanical convection, was used for prolonged heating. the operating temperature of the device was 40° C-120° C. the temperature control was performed with a simple thermostat in the front side of the instrument. The temperature uniformity was $\pm$2.0° C.

3. Atomic Absorption Spectrophotometer

The equipment used for specific metal concentration measurements was a Varian AA-1475 atomic absorption spectrophotometer that operates in both single-beam and double-beam modes and allows atomic absorption and atomic emission experiments to be carried out.

Before performing any experiment, the instrument was set up for the best conditions of flame type and lamp current. The flame generally used was an air/acetylene flame which provided a temperature high enough for the atomization to be efficient under the conditions of absorption measurements of cationic species in the sample solutions. The oxidant (air) was maintained at a flowrate of approximately 8 L/min and the fuel (acetylene) at a flowrate of 5-6 L/min. These values were set up in the instrument manually using the scales of the corresponding flow meters. The burner height was adjusted in order to optimize the flame. The lamp was aligned by moving two small knobs until the maximum signal was obtained on the peak-current meter. The lamp current was set up at the recommended value for the determination of the element of interest.[16]

The wavelength required for the range of concentrations in which the experiment was conducted was selected with the appropriate switches in the central panel of the instrument. The equipment was calibrated and all

parameters checked using the copper hollow-cathode lamp. Copper was not only the analyte but also the standard used to test the instrument. Copper is one of the few elements that exhibits no interferences in the specified flame and the determination is virtually independent of the stoichiometry of the flame and the lamp current.[16]

4. Ion selective electrode

For determinations of metal ion concentrations in solutions and specifically for Cu^{+2} determinations a potentiometric cell containing a copper ion selective electrode, a reference electrode, and a pH meter was used.

The copper ion selective electrode was an Orion 94-29 electrode which has a solid-state membrane composed of a mixture of silver sulphide and cupric sulphide[17] and is capable of determining concentrations in the range of 0.10 M to $1.00*10^{-8}$ M. The reference electrode was a standard calomel electrode. These electrodes were connected to the potentiometer and introduced into a glass beaker containing the analyte solution under continuous stirring. The response of the cell was checked by a linear calibration procedure in which several standard solutions with tenfold increases in concentration between them were tested. The direct measurement of the cell potential for each standard was recorded and with the obtained results it was possible to draw a calibration line that in most cases was a

straight line with a slope of approximately 28 millivolts/decade (the theoretical Nernstian slope).[15]

C. Qualitative procedures

1. Resin studies

Small samples of phosphinic acid resin (approximately 0.2 g) were placed into 5 mL samples of 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4} M nitrate solutions of Ag^{+1}, Hg^{+2}, Cu^{+2}, Bi^{+3}, Pb^{+2}, Ni^{+2}, Co^{+2}, Au^{+3}, and Pt^{+2} in 20-mL screw capped glass bottles. The pH values of these solutions were adjusted to desired values using dilute HNO_3. The resin/solution systems were allowed to stand at room temperature for various periods of time and the course of the reaction was qualitatively monitored by visual observations of the color change in the resin (normally from light orange-tan to brown, dark brown, or black). Similar systems were prepared and observed as they were held at several elevated temperatures.

2. Model compound studies

Several solutions of phenylphosphinic acid with concentrations of $1.00*10^{-1}$, $1.00*10^{-2}$, $1.00*10^{-3}$, and $1.00*10^{-4}$ M were prepared and mixed with nitrate solutions of the species indicated in Section C.1. at different pH values. Equal volumes of reactants were used (usually 3 mL of each). The systems were allowed to stand for different

periods of time and the course of reaction was visually observed.

Similarly, nitrate solutions of different species were allowed to react with phenylphosphonic acid solutions in the same range of concentrations as those of the phenylphosphinic acid under the same conditions.

D. Quantitative procedures

1. Determination of the purity of the phenylphosphinic acid solutions

Iodine titrations were performed on solutions of the model compound. For these experiments standard solutions of iodine, sodium thiosulfate, and potassium biiodate were prepared.[12]

The standardization of the sodium thiosulfate solution was carried out by titration of 50.00-mL samples with the standard potassium biiodate solution in presence of starch indicator.[18] The standardized solution of thiosulfate was used as the titrant for the standardization of 50.00-mL samples of the iodine solution. The end point of this titration was determined by the starch indicator.

To 12 glass bottles, containing 10.00-mL portions of the phenylphosphinic acid (0.0500 N solution), a standard 0.0500 N iodine solution was added in volumes from 1.00 mL to 12.00 mL, respectively. The mixtures were heated at 75° C for 15.00 hours since the oxidation-reduction reaction

of phenylphosphinic acid with iodine goes at a slow rate and it can be conveniently measured only under conditions of high temperature. After establishing the end point of the titration by the disappearance of the iodine color, in order to get a more accurate volume of titrant consumed in the previous titration, the amount of titrant added to 10.00-mL portions of the acid was varied by 0.10-mL increments and then heated at the same temperature for 15.00 hours. The exact end point of the titration was determined using the same procedure but now changing the amount of titrant in 0.01-mL increments within the interval at which the solution changed color.

2. Equilibrium studies

The equilibrium point for the reaction of phenylphosphinic acid with copper(II) nitrate solution was determined by heating mixtures of solutions of the two at different temperatures during different time intervals. 5.00-mL samples of the Cu^{+2} solution, the phenylphosphinic acid, and the phenylphosphonic acid solutions were heated separately at 60°C for 30 min. Then the three solutions were mixed to give a final volume of 15.00-mL and heated at the indicated temperature. After selected times the solutions were taken from the constant temperature bath and allowed to stand for 2.00 hours at room temperature. The pH of each of these solutions was measured. The aqueous

phase was taken from each sample and filtered to ensure that no particles of solid precipitate were left in the remaining solution.

Portions of 5.00 or 10.00-mL of each filtrate were diluted to 50.00-mL with deionized water. The concentrations of Cu^{+2} ions in the obtained solutions were measured by atomic absorption spectroscopy and by potentiometry using the copper ion selective electrode.

E. Measurements

1. pH measurements

After the calibration of the pH meter following the procedure described above, sample solutions were placed in a glass beaker and the combination electrode introduced in them. The pH value shown in the display of the instrument was recorded.

2. Atomic absorption measurements of Cu concentrations

The general procedure used in the determination of the concentration of copper left in solution after the reaction with phenylphosphinic acid was the "analytical calibration curve method."[19] For the construction of the working curve, three standard solutions were prepared within the range recommended for the selected wavelength as it is indicated in Table III-1. 10.00 mL of the solutions obtained after filtration were taken and diluted to 50.00

mL so that the concentrations of the analyte were within the working range. The absorbance values of the standards were measured as well as that of a blank used for zero absorbance. The sample solutions were aspirated and their absorbances measured. From the calibration curve, which is the plot of the absorbance versus the concentration of the analyte in the standards, the concentrations of the samples were read.

TABLE III-1

RECOMMENDED INSTRUMENT PARAMETERS FOR ATOMIC ABSORPTION MEASUREMENTS OF COPPER[14]

WAVELENGTH (nm)	SPECTRAL BAND PASS (nm)	OPTIMUM WORKING RANGE (ppm)
324.70	0.50	2 - 8
327.40	0.20	6 - 24
217.90	0.20	15 - 60
218.20	0.20	20 - 80
222.60	0.20	70 - 280
249.20	0.50	200 - 800
244.20	1.00	500 - 2000

3. Measurements of Cu^{+2} concentrations with the ion selective electrode

Standard solutions of Cu^{+2} with concentrations $1.00*10^{-4}$ M, $1.00*10^{-3}$ M, $1.00*10^{-2}$ M, and $1.00*10^{-1}$ M were prepared. 25.00 mL volumes of standard solution were pipetted into a 50 mL glass beaker containing a plastic-coated stirrer bar. Then, 0.50 mL of ionic strength adjustor were added. The electrodes were rinsed with distilled water, dried with a paper tissue, and immersed in the solution. The solution was stirred. When a steady reading was obtained, the potential indicated in the display was noted. The same procedure was applied to all standards and analyte solutions. From the calibration plot prepared with the data obtained for the standards, the concentration of the analyte was read for the given potential value.[15]

Since the potential values tended to shift upward after 1 to 2 hours of continuous work, the calibration procedure was repeated often.

The direct measurement of the potential of solutions remaining after a given period of heating was not possible and shifts to high potential values were observed.

However when the solutions were diluted 5 to 10 times, and after dilution allowed to stand for several hours, it was possible to obtain stable potential values.

CHAPTER IV

EXPERIMENTAL RESULTS

A. Observations on the resin

The results of the experimental observations on the resin can be summarized as follows:

1) Reduction of silver(I) by a 2%DVB phosphinic acid resin

When the yellow phosphinic acid resin was immersed in a 0.10 M silver nitrate solution, the resin turned brown in less than 1 min., and black in approximately 3 min. The resin was separated from the remaining solution and treated with 1% wt. KCN solution. Since silver dissolves in KCN solutions forming $[Ag(CN)_2]^-$ ions, after reaction with KCN the resin changed its color from dark to yellow. This suggested that silver ions had been originally reduced to their zero-valent state. Identical results were observed for concentrations of silver ions lower than 0.1 M. The pH of the experimental solutions was modified using nitric acid and no differences were observed for this reaction within a pH range of 0.50-4.03.

Since the reduction potential of Ag^+/Ag is +0.80 v, it was proposed to investigate several metal ions with higher and lower reduction potentials.

2) Reaction of mercury(II) solutions with phosphinic acid resin

Mercury has a slightly higher standard reduction potential than silver (E^{o} = +0.85 v). Therefore it was expected to be reduced by the resin, and in fact, the resin in contact with a 0.10 M solution of the analyte turned black in approximately 2 min. The pH of the 0.10 M solution was varied within the range 0.50-3.80 with no significant changes in the rate of reduction of mercury by the resin. However, at lower concentrations of mercury(II) ions the process slowed slightly.

3) Reaction of gold(III) solutions with the resin

The couple $AuCl_4^-/Au$ has a reduction potential of +1.00 v. When the phosphinic acid resin was placed in a solution of these ions, the reduction of gold ions to their zero-valent state was immediate even for concentrations lower than 10^{-3} M. The pH range over which observations were carried out was 0.50-3.00. When necessary, the pH of the analyte solution was modified using a 5.00 M NaOH solution and this addition had no effect in the reduction of gold over the indicated pH range.

4) Reaction of bismuth(III) solutions with the resin

Bismuth nitrate solutions with concentrations varying from 10^{-1}-10^{-3} M were allowed to react with the resin. No changes in the system were observed over approximately 10 days.

5) Reaction of Ni^{+2}, Co^{+2}, and Pb^{+2} solutions with the resin

These species have negative values of the standard reduction potential, for Ni(II) E^{o} = -0.23 v, for Co(II) E^{o} = -0.28 v, and for Pb(II) E^{o} = -0.13 v. When the resin was immersed in the corresponding solutions, no oxidation-reduction was observed over approximately 10 days.

6) Reaction of Fe(III) solutions with the resin

The phosphinic acid resin did not react with the Fe(III) solutions although the reduction potential for the couple Fe^{+3}/Fe^{+2} is +0.77 v.

7) Reaction of Pt(II) solutions with the resin

No changes in the system $PtCl_4^{-2}$ solution/resin were observed under the same experimental conditions at which the reactions betweeen $AuCl_4^-$ solutions and the resin were carried out.

8) Reduction of Cu(II) species by the resin

The Cu^{+2}/Cu couple has a reduction potential of +0.34 v. The reaction of the Cu^{+2} ions with the resin was observed to have a very slow rate. Only after 8 days was it possible to distinguish a slight change in the color of the resin which turned brown. However, it was speculated that the rate of reaction would significantly increase by heating the system at an elevated temperature. The reduction of copper(II) by the resin occurred in approximately 15 min after heating the system to 60° C, and

the reaction also occurred at a slightly higher rate (10-15 min) when heating at 75° C.

B. Observations on the model compound

As was indicated earlier, the properties of a redox polymer can be expected to resemble those of a sufficiently similar model compound. In accordance with this expectation, reactions of solutions of phenylphosphinic acid with solutions of the above metallic species were carried out following the procedure described in CHAPTER II Section C.2.

1) Reaction with silver(I) solutions

When equal volumes of reactants having the same concentrations (0.10 M) were mixed, a black precipitate was formed immediately, gradually turned bright. A silver mirror was formed on the walls of the container, and a very fine powder of black silver precipitated at the bottom. The pH of the system was then varied within the range of 0.80-4.01 using dilute nitric acid. The variation of pH had no significant influence on the reaction rate. Additionally, the remaining solution was filtered after 4 hours and treated with a small portion of NaCl. No formation of AgCl indicated that the reduction of silver by the phenylphosphinic acid had occurred to 100% completion.

Reactions of the phenylphosphinic acid with silver nitrate solutions of lower concentrations ($1.00*10^{-2}$ M -

$1.00*10^{-4}$ M) also occurred but the rates of such reactions were slightly slower at these concentrations of silver(I). The pH range was the same as for the previous reactions.

2) Reaction with mercury(II) solutions

The reaction of the model compound with these solutions readily occurred with the instantaneous formation of a black precipitate after reactants were placed in the container. The variation of pH had no measurable effect on the reaction rate.

3) Reduction of gold(III) species

Since the above described reactions occurred relatively fast, it was expected that species having reduction potentials higher than those of the silver(I) and mercury(II) ions would rapidly undergo reduction by the model compound. In fact, the reaction of a 0.10 M solution of $AuCl_4^-$ with the phenylphosphinic acid solution at equal volumes and concentrations occurred extremely fast forming gold which precipitated as solid at the bottom of the container. Similar effects were observed at lower concentrations of $AuCl_4^-$ and within a pH range of 1.00 to 3.00. The addition of 5-M NaOH solution, used to adjust the pH, had no effect on the rate of reaction.

4) Reaction with bismuth(III) solutions

Phenylphosphinic acid reacted with Bi(III) solutions to form a white precipitate that probably corresponds to a bismuth compound which was not identified.

5) Reaction with Nickel(II), Co(II), and Pb(II) solutions

No reaction was observed with these species even under the influence of continuous heating over 30 min.

6) Reaction with $PtCl_4^{-2}$ solutions

A white precipitate was formed when solutions of $PtCl_4^{-2}$ species of different concentrations were mixed with the model compound solutions. However this observation was not sufficient to verify a redox reaction between these species because the white precipitate was not identified.

7) Reaction of copper(II) solutions

As with the resin, these reactions were found to occur at very slow rates at room temperature. Solutions of Cu^{+2} ions having concentrations $1.00*10^{-1}$ M $-1.00*10^{-4}$ M, were mixed with equal volumes of the 0.10 M solution of the model compound. After 2 days only a slight change in the color of the solutions was observed. Approximately 10 days after the reagents were mixed a brown precipitate had formed at the bottom of the container. To further characterize the kinetic behavior, mixtures of the test solutions were heated at different temperatures within the interval of 50°C to 90°C. The reduction of copper to its metallic form occurred at different rates depending on the temperature of heating. The higher the temperature, the faster was the reduction of copper(II) ions, and the greater was the amount of the precipitate formed.

Once the reduction of copper by the acid had been observed, the reactants were heated further for different intervals of time. The resulting solutions were separated from the solid precipitate and then mixed with small volumes of silver(I) solution. In all cases the reduction of silver(I) to its zero valence state readily occurred. This was taken as direct evidence that the oxidation of phenylphosphinic acid had not gone to completion, and indirectly that copper ions had not been completely reduced in the previous reaction. This was also indicated by the blue color of the separated solution.

When the model compound/copper(II) solutions were heated more than 27 hours at 60° C, 22 hours at 75° C, and 8 hours at 90° C, a secondary reaction appeared to occur. The copper formerly precipitated began to return to solution in its ionic form, perhaps by forming a complex with the oxidized form of the model compound. If the heating was continuously maintained for approximately 72 hours all the the copper metal disappeared and an insoluble compound was formed. This compound was not identified. The remaining solution was then separated and treated with a small portion of a 0.10 M Ag(I) solution. The reduction of Ag(I) ions was observed to occur to a very small extent, demonstrating the presence of only small amounts of phenylphosphinic acid after the prolonged heating. It was suspected that the phenylphosphonic acid, resulting from

the oxidation of phenylphosphinic acid, had reacted with metallic copper and since the reverse reaction had a much slower rate than the forward reaction, for the time during which observations were made, only a very small amount of phenylphosphinic acid was regenerated.

In order to verify the validity of these statements, several test reactions were carried out. The precipitated copper powder, obtained after heating the model compound/copper(II) solution, was separated, placed in a bottle containing a 0.10-M solution of phenylphosphonic acid, and heated for approximately 30 hours at 75° C. All the copper that had originally precipitated disappeared, and the solution which at the beginning was yellow, turned slightly blue after 15 hours. After that time an insoluble blue compound was formed at the bottom of the container. The remaining solution was mixed with a 0.10 M $AgNO_3$ solution at equal volumes. The reduction of silver(I) ions occurred to a very small extent. This fact demonstrated what was previously suspected: Phenylphosphonic acid oxidizes metallic copper at a slow rate to produce only a very small amount of phenylphosphinic acid and an insoluble unidentified compound.

8) Iodine titrations of the model compound

The observations carried out on the metallic species above indicated revealed the relatively strong reducing power of phenylphosphinic acid. Since iodine is a

relatively weak oxidizing agent, it is used for determination of strong reductants. Iodine titrations were performed on the model compound in order to determine its purity, following the procedure indicated in CHAPTER III, Section D-1. The standard electrode potential for the reaction $I_3^- + 2e^- = 3I^-$ is 0.54 v. Therefore it was expected that oxidation of the phenylphosphinic acid solution would occur. The endpoint of the titration was determined under conditions of continuous heating at 75° C for 15 hours since this redox reaction occurred at a very slow rate at room temperature. The starch indicator, added to colorless solutions after the heating period, produced no change in color.

A small amount of phenylphosphinic acid (1.24 g.) was weighed and dissolved in deionized water to obtain 100.00 mL of solution. The solution was titrated with a standard NaOH solution, and was found to have a concentration of 0.08517 N. A 10.00-mL sample of this solution required 18.25 mL of 0.0901 N solution of iodine at the endpoint of the titration, therefore, the concentration of the model compound solution obtained from iodine titration was 0.08222 N. This difference in concentration can probably be referred to a slightly incomplete reaction of the model compound with iodine, kinetic factors being responsible. The reaction appears to be about 97% complete as compared to the NaOH titration.

C. Calculations

1. Rate studies

Since the reaction of the model compound with copper(II) solutions exhibited a very slow rate at room temperature, it was deemed of interest to determine the rate of formation of copper at elevated experimental temperatures. Following the procedures described in CHAPTER III, the concentrations of copper in the remaining solutions after defined periods of heating were determined. The percentage of copper formed after each period of heating was calculated using the following expression:

$$\% \text{ Cu formed} = \frac{[Cu^{+2}]_i - [Cu^{+2}]_f}{[Cu^{+2}]_i} * 100,$$

where the subscripts i and f denote the initial and final concentrations of copper species determined by atomic absorption experiments, since they include the total amount of these species in solution. With the data obtained it was possible to construct the corresponding curves describing the reaction rates at different experimental conditions. Tables IV-1, IV-2, and IV-3 show the values of concentration and percent of copper formation at three different temperatures, and from equal concentrations of Cu(II) and phenylphosphinic acid. Plotting the percentages against the time of heating, the indicated curves were obtained (see Figures IV-1, IV-2, and IV-3). The plateaus of these curves, which generally are at the maxima,

TABLE IV-1

RATE OF FORMATION OF COPPER FROM EQUAL CONCENTRATIONS OF PHENYLPHOSPHINIC ACID AND COPPER(II) SOLUTIONS AT 60° C

TIME(h)	pH	Copper conc.(M)		% of Cu
		AA	ISE	
0.00	1.43	0.04982	0.04982	0.00
1.00	1.41	0.04598	0.03987	7.70
3.00	1.36	0.03921	0.03165	21.30
5.00	1.31	0.03789	0.02984	23.95
8.00	1.31	0.03694	0.02876	25.85
12.00	1.29	0.03632	0.02876	27.10
17.00	1.29	0.03606	0.02291	27.62
18.00	1.27	0.03233	0.02188	35.11
19.00	1.31	0.03309	0.02188	33.58
20.00	1.27	0.03228	0.02188	35.21
21.00	1.27	0.03229	0.02188	35.19
22.00	1.34	0.03669	0.02188	26.36
24.00	1.34	0.03590	0.02188	27.94
27.00	1.43	0.04078	0.02876	18.15

Initial concentrations: PhPH = 0.1002 M

PhPOH = 0 M

Cu^{+2} = 0.1000 M

Total volume = 10 mL

TABLE IV-2

RATE OF FORMATION OF COPPER FROM EQUAL CONCENTRATIONS OF PHENYLPHOSPHINIC ACID AND COPPER(II) SOLUTION AT 75° C

TIME	pH	Copper conc.(M)		% of Cu
		AA	ISE	
0.00	1.28	0.04982	0.04982	0.00
1.00	1.26	0.03984	0.03546	20.00
3.00	1.24	0.02346	0.01987	52.91
5.00	1.22	0.02283	0.01854	54.17
6.00	1.22	0.02331	0.01854	53.21
8.00	1.22	0.02337	0.01854	53.09
10.00	1.22	0.02448	0.01854	50.86
12.00	1.22	0.02462	0.01854	50.57
14.00	1.24	0.02709	0.02546	45.62
16.00	1.25	0.02992	0.02546	39.94
19.00	1.26	0.03921	0.02367	21.30
20.00	1.27	0.04150	0.02546	16.70
21.00	1.26	0.03921	0.02156	21.30
22.00	1.26	0.03937	0.02156	20.98
23.00	1.28	0.04797	0.02738	3.71
24.00	1.27	0.04693	0.02546	5.80

Initial concentrations: PhPH = 0.1002 M, PhPOH = 0 M,

Cu^{+2} = 0.1000 M

Total volume = 10 mL

TABLE IV-3

RATE OF FORMATION OF COPPER FROM EQUAL CONCENTRATIONS OF PHENYLPHOSPHINIC ACID AND COPPER(II) SOLUTIONS AT 90° C

TIME(h)	pH	Copper conc.(M)		% of Cu
		AA	ISE	
0.00	1.43	0.04981	0.04981	0.00
1.00	1.18	0.02394	0.01585	51.94
2.00	1.17	0.02220	0.01585	55.43
3.00	1.16	0.02031	0.01585	57.74
4.00	1.15	0.02043	0.01585	59.23
5.00	1.15	0.02012	0.01585	58.75
6.00	1.16	0.02264	0.01585	54.55
8.00	1.22	0.03055	0.02786	38.67
9.00	1.27	0.02693	0.02291	45.94
11.00	1.26	0.03228	0.02080	35.20
12.00	1.36	0.03120	0.02291	37.36
14.00	1.31	0.03071	0.01945	38.35

Initial concentrations: PhPH = 0.1002 M

PhPOH = 0 M

Cu^{+2} = 0.1000 M

Total volume = 10.00 mL

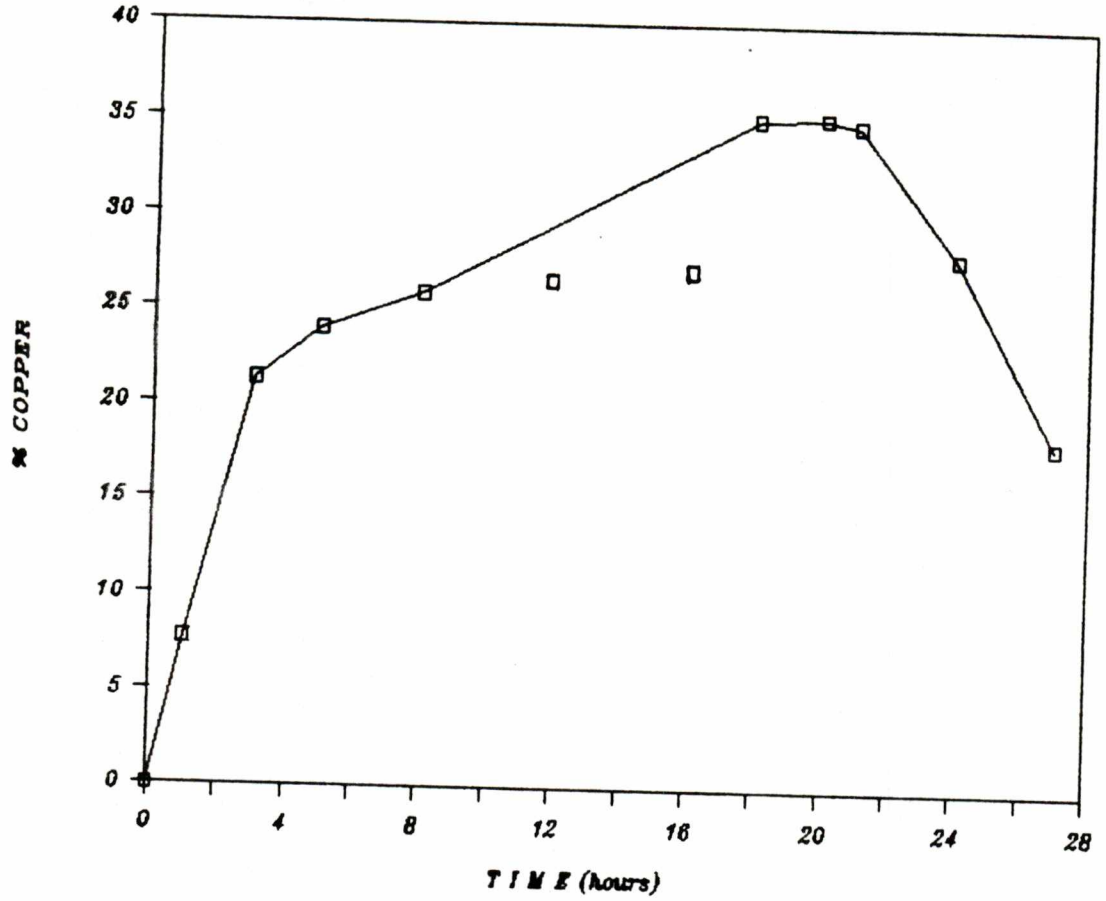


Figure IV-1. Rate of formation of copper from equal concentrations of PhPH and Cu(II) at 60° C

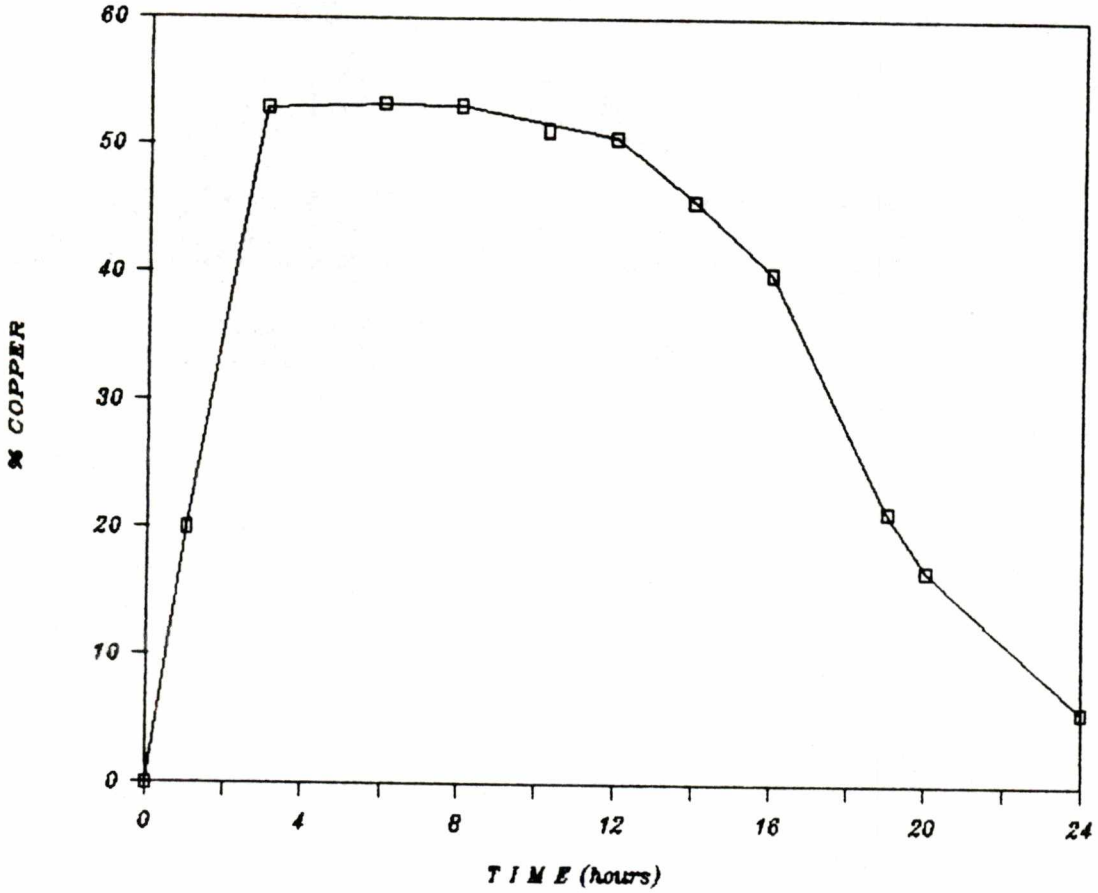


Figure IV-2. Rate of formation of copper from equal concentrations of PhPH and Cu(II) at 75° C

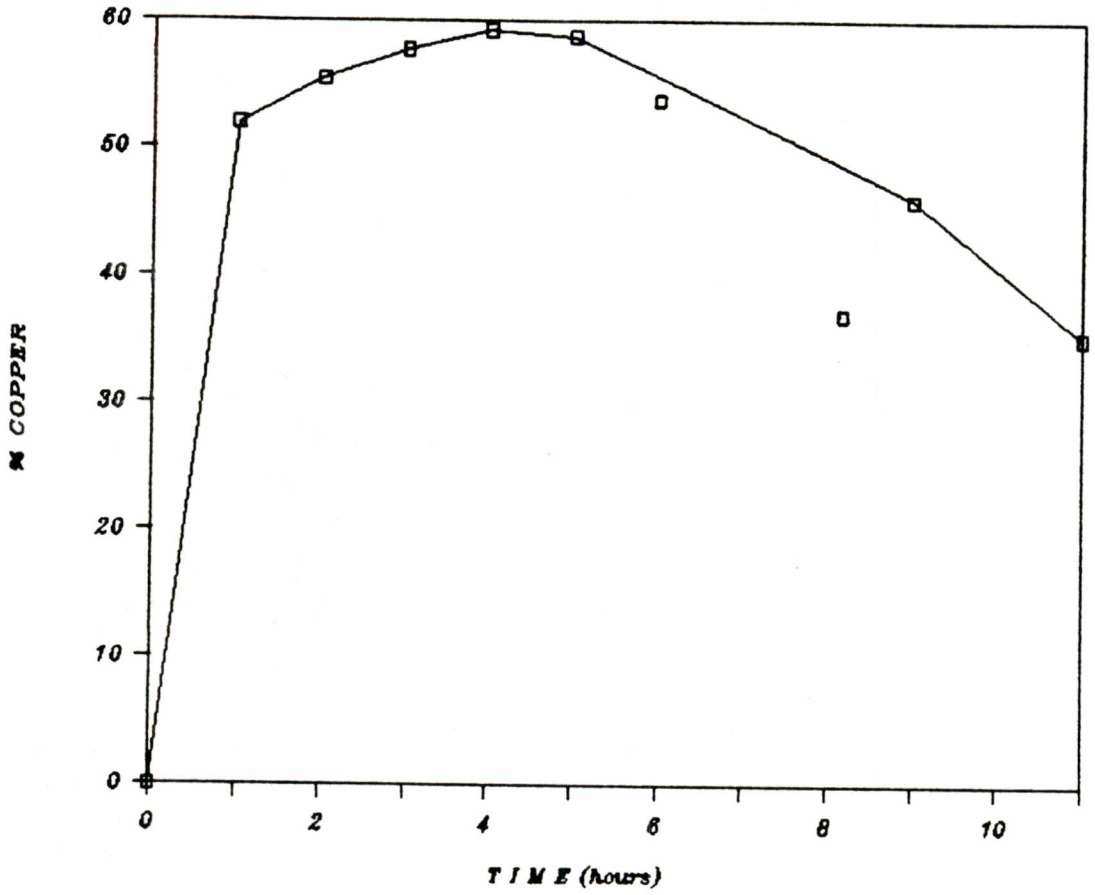


Figure IV-3. Rate of formation of copper from equal concentrations of PhPH and Cu(II) at 90° C

indicate the position of the reaction at which the equilibrium was obtained.

2. Determination of the equilibrium constant

Similar experiments were carried out in order to determine the fundamental quantities that characterize the equilibrium position of the reaction between the Cu^{+2} solutions and the model compound. These quantities are the pH of the final solutions after defined periods of heating and their concentrations.

The equilibrium position for the reaction is defined as that position at which the reduction of copper(II) ions no longer takes place, such that one would expect to have a constant concentration of Cu^{+2} ions in the final solutions. These concentrations, as it was explained before, were measured by AA as well as by using the ISE. The former shows the total copper concentration in the solution while the latter shows the concentration of Cu^{+2} ions in solution. Since there is probably some degree of complexation of the Cu^{+2} species, these two quantities should be different, the latter being less than the former.

In calculations of the equilibrium constant for the reaction of interest from expression (11), the concentrations of the H^{+} ions, Cu^{+2} ions, and those for the phenylphosphinic acid and phenylphosphonic acid must be determined. Since, $pH = -\log[H^{+}]$, $[H^{+}]$ can be obtained from the pH value experimentally obtained.

The difference between the initial and the final concentration of copper will give the amount of copper that has been reduced, and it should be equal to the amount of phenylphosphinic acid reacted, provided the reaction remains simple. Then, the concentration of phenylphosphinic acid unreacted will be:

$$[PhPH]_{remaining} = [PhPH]_{initial} - [Cu^{+2}]_{reacted},$$

and the $[PhPH]_{reacted}$ will be converted during the course of the reaction to [PhPOH] as in equation (10), page 18.

The experimental results as well as the results of these calculations for every set of experimental conditions are indicated in Tables IV-4 to IV-11.

With all quantities already defined, the apparent equilibrium constant at each established temperature is calculated using expression (11). These values are also indicated in Tables IV-10, and IV-11.

3. Determination of the equilibrium constant at 25°C

As was indicated in CHAPTER II, Section 2, a plot of lnK as a function of 1/T would give a straight line with a slope of $-\Delta H^{\circ}/R$. Extrapolation of this line to the point at which it intersects the perpendicular to the horizontal axis drawn at the point 1/T = 1/298 = 0.00276, will give $\ln K^{298}$, which is read at the vertical axis. Once the value of K^{298} has been calculated, from expresion (4), page 12, the E° value for the reaction of phenylphosphinic acid with copper(II) ions can be obtained.

TABLE IV-4

DETERMINATION OF THE EQUILIBRIUM FOR THE REACTION OF PHENYLPHOSPHINIC ACID WITH COPPER(II) SOLUTION AT 60° C

TIME(h)	pH	Copper conc.(M)		% diff.
		AA	ISE	
0.00	1.60	0.03341	0.03341	0.00
2.00	1.55	0.03297	0.02896	12.16
3.00	1.47	0.03107	0.02812	9.49
3.50	1.46	0.02899	0.02723	6.07
4.00	1.46	0.02973	0.02876	3.26
4.50	1.44	0.02893	0.02790	3.56
5.00	1.44	0.02694	0.02534	5.94
6.00	1.35	0.02635	0.02468	6.34
8.00	1.35	0.02576	0.02345	8.97
20.50	1.33	0.02528	0.02015	20.29
22.00	1.35	0.02550	0.02432	4.63
24.00	1.42	0.02470	0.01834	25.75
25.00	1.42	0.02520	0.01834	27.22
26.00	1.42	0.02520	0.01834	27.22

Initial concentrations: PhPH = 0.1027 M

PhPOH = 0.04108 M

Cu^{+2} = 0.1000 M

Total volume = 15 mL

TABLE IV-5

DETERMINATION OF THE EQUILIBRIUM FOR THE REACTION OF PHENYLPHOSPHINIC ACID WITH COPPER(II) SOLUTION AT 75° C

TIME(h)	pH	Copper conc.(M)		% diff.
		AA	ISE	
0.00	1.63	0.03341	0.03341	0.00
2.00	1.41	0.02731	0.02153	21.16
3.00	1.35	0.02459	0.02153	12.44
3.50	1.28	0.02137	0.02084	2.48
4.50	1.28	0.02098	0.01834	12.58
5.00	1.28	0.02001	0.01900	5.05
5.50	1.28	0.02137	0.01900	11.09
6.00	1.28	0.01945	0.01900	2.31
19.00	1.24	0.02005	0.01834	8.53
21.00	1.32	0.02293	0.02009	12.39
24.00	1.38	0.02350	0.02289	2.60
25.00	1.46	0.02390	0.02289	2.55
26.00	1.53	0.02710	0.02432	10.26

Initial concentrations: PhPH = 0.1027 M

PhPOH = 0.04108 M

Cu^{+2} = 0.1000 M

Total volume = 15.00 mL

TABLE IV-6

DETERMINATION OF THE EQUILIBRIUM FOR THE REACTION OF PHENYLPHOSPHINIC ACID WITH COPPER(II) SOLUTION AT 90° C

TIME(h)	pH	Copper con.(M)		% diff.
		AA	ISE	
0.00	1.63	0.03341	0.03341	0.00
1.00	1.37	0.01622	0.01413	12.89
2.00	1.31	0.01323	0.01258	4.84
3.00	1.31	0.01244	0.01122	9.81
4.00	1.30	0.01181	0.00910	22.95
5.00	1.30	0.00913	0.00910	0.33
6.00	1.31	0.01008	0.00910	9.72
7.00	1.40	0.01999	0.01679	16.01
9.00	1.43	0.01779	0.01679	5.62

Initial concentrations: PhPH = 0.1027 M

PhPOH = 0.04108 M

Cu^{+2} = 0.1000 M

Total volume = 15 mL

TABLE IV-7

DETERMINATION OF THE EQUILIBRIUM FOR THE REACTION OF PHENYLPHOSPHINIC ACID WITH COPPER(II) SOLUTION AT 60° C

TIME(h)	pH	Copper conc.(M)		% diff.
		AA	ISE	
0.00	1.63	0.03341	0.03341	0.00
1.00	1.61	0.03275	0.02371	27.60
3.00	1.60	0.03023	0.02238	25.97
5.00	1.53	0.02661	0.01995	25.03
7.00	1.51	0.02567	0.01995	22.28
9.00	1.55	0.02318	0.01995	13.93
11.00	1.51	0.02134	0.01778	16.68
13.00	1.42	0.02031	0.01585	21.96
14.00	1.43	0.02038	0.01585	22.22
16.00	1.45	0.02025	0.01585	21.73
18.00	1.46	0.02195	0.01585	27.79
20.00	1.46	0.02047	0.01585	22.57
22.00	1.51	0.02146	0.01995	7.04
23.00	1.51	0.02142	0.01778	16.93
24.00	1.53	0.02346	0.01585	32.44

Initial concentrations: PhPH = 0.1052 M

PhPOH = 0 M

Cu^{+2} = 0.1000 M

Total volume = 15.00 mL (5.00 mL of each reactant was mixed with 5.00 mL of water)

TABLE IV-8

DETERMINATION OF THE EQUILIBRIUM FOR THE REACTION OF PHENYLPHOSPHINIC ACID AND COPPER(II) SOLUTION AT 75° C

TIME(h)	pH	Copper conc.(M)		% diff.
		AA	ISE	
0.00	1.63	0.03341	0.03341	0.00
1.00	1.42	0.02583	0.02114	18.16
3.00	1.31	0.01842	0.01479	19.71
5.00	1.31	0.01575	0.01349	14.35
7.00	1.31	0.01567	0.01479	5.62
9.00	1.33	0.01602	0.01585	1.06
11.00	1.31	0.01580	0.01479	6.39
13.00	1.31	0.01572	0.01349	14.18
15.00	1.31	0.01569	0.01479	5.74
18.00	1.36	0.02079	0.01479	28.86
19.00	1.53	0.02504	0.01798	28.20
20.00	1.47	0.02646	0.01906	27.97
21.00	1.47	0.02504	0.02114	15.58
22.00	1.47	0.02441	0.02114	13.40
23.00	1.46	0.02315	0.02239	3.28

Initial concentrations: PhPH = 0.1052 M, PhPOH = 0 M, Cu^{+2} = 0.1000 M

Total volume = 15.00 mL (5.00 mL of each reagent was mixed with 5.00 mL of water).

TABLE IV-9

DETERMINATION OF THE EQUILIBRIUM FOR THE REACTION OF PHENYLPHOSPHINIC ACID AND COPPER(II) SOLUTION AT 90° C

TIME(h)	pH	Copper conc.(M)		% diff.
		AA	ISE	
0.00	1.61	0.03341	0.03341	0.00
1.00	1.40	0.01921	0.01768	7.96
2.00	1.25	0.01134	0.00976	13.93
3.00	1.24	0.01024	0.00976	4.69
4.00	1.25	0.01165	0.00976	16.22
5.00	1.27	0.01101	0.00976	11.35
6.00	1.25	0.01134	0.00976	13.93
7.00	1.27	0.01157	0.00976	15.64
8.00	1.35	0.01668	0.00976	41.49

Initial conditions: PhPH = 0.1052 M

PhPOH = 0 M

Cu^{+2} = 0.1000 M

Total volume = 15.00 mL (5.00 mL of each reactant was mixed with 5.00 mL of water).

TABLE IV-10

EQUILIBRIUM CONCENTRATIONS FOR THE REACTION OF PHENYLPHOSPHINIC ACID AND COPPER(II) SOLUTIONS OBTAINED FROM AA MEASUREMENTS AND K VALUES AT DIFFERENT TEMPERATURES

TEMP.(°C)	Cu^{+2} (M)	PhPH(M)	PhPOH(M)	H^{+} (M)	K
60*	0.02031	0.02197	0.01310	0.03802	0.04244
75*	0.01578	0.01744	0.01763	0.04860	0.15133
90*	0.01119	0.01285	0.02222	0.05559	0.47753
60**	0.03228	0.03256	0.01754	0.05370	0.04813
75**	0.02350	0.02378	0.02632	0.06026	0.17023
90**	0.02029	0.02057	0.02953	0.07025	0.34920
60***	0.02518	0.02600	0.02276	0.04093	0.05824
75***	0.02054	0.02136	0.02657	0.05329	0.17198
90***	0.01087	0.01252	0.02255	0.04955	0.40677

* Data obtained from experimental results shown in Tables IV-7, IV-8, and IV-9.

** The same from Tables IV-1, IV-2, and IV-3.

*** The same from Tables IV-4, IV-5, and IV-6.

TABLE IV-11

EQUILIBRIUM CONCENTRATIONS FOR THE REACTION OF PHENYLPHOSPHINIC ACID AND COPPER(II) SOLUTIONS FROM ISE MEASUREMENTS AND K VALUES AT DIFFERENT TEMPERATURES

TEMP.(°C)	Cu^{+2} (M)	PhPH(M)	PhPOH(M)	H^{+} (M)	K
60*	0.01585	0.02197	0.01310	0.03802	0.05438
75*	0.01349	0.01744	0.01763	0.04860	0.17700
90*	0.00976	0.01285	0.02222	0.05559	0.54750
60**	0.02188	0.03256	0.01754	0.05370	0.07100
75**	0.01854	0.02352	0.02658	0.06026	0.22134
90**	0.01585	0.02057	0.02953	0.07025	0.44698
60***	0.01990	0.02599	0.02276	0.04093	0.07372
75***	0.01909	0.02136	0.02657	0.05329	0.18504
90***	0.00889	0.01252	0.02255	0.04955	0.49743

* Data obtained from experimental results shown in Tables IV-7, IV-8, and IV-9.

** The same from Tables IV-1, IV-2, and IV-3.

*** The same from Tables IV-4, IV-5, and IV-6.

Substituting the values of the universal gas constant R, the Faraday constant F, and the number n of electrons gained or lost in the redox reaction, an expression equivalent to expression (4) is obtained,

$$E^{\circ} = - \log K/33.8 \ , \qquad (12)$$

with n = 2 for a two-electron process.

4. Example of calculations

From Tables IV-1, IV-2, and IV-3, the position of the equilibrium appears to be attained after heating the solutions for 20.00-24.00 hours at 60° C, 3.50-19.00 hours at 75° C, and 3.00-6.00 hours at 90° C. The average equilibrium concentrations of copper at the corresponding temperatures were:

60° C : $[Cu^{+2}] = 0.03228$ M,

75° C : $[Cu^{+2}] = 0.02350$ M,

90° C : $[Cu^{+2}] = 0.02029$ M.

The difference between each of these values and the initial copper concentration corresponds to the concentration of copper that has reacted, and as was stated before, would be equal to the concentration of PhPOH formed as a result of the oxidation of PhPH during the reaction. At the given temperatures these PhPOH concentrations were:

60° C : [PhPOH] = 0.01754 M,

75° C : [PhPOH] = 0.02632 M,

90° C : [PhPOH] = 0.02953 M,

and the differences between each of the latter values and

the initial PhPH concentration are the concentrations of PhPH that remained unreacted in the final solutions:

60° C : [PhPH] = 0.05260 - 0.01754 = 0.03256 M,

75° C : [PhPH] = 0.05260 - 0.02632 = 0.02378 M,

90° C : [PhPH] = 0.05260 - 0.02953 = 0.02057 M.

The final concentrations of H^+ ions at each of the experimental temperatures were:

60° C : $[H^+]$ = 0.05370 M,

75° C : $[H^+]$ = 0.06026 M,

90° C : $[H^+]$ = 0.07025 M.

Substituting the obtained values in expression (9), the equilibrium constant at each given temperature was obtained. A plot of lnK vs. 1/T was constructed, and from it, by extrapolation, the value of K at 298K was estimated. In this example, this value was 0.003061. The logarithm of K^{298} was substituted in expression (12), and the standard potential for the reaction of phenylphosphinic acid with copper was calculated:

$$E^\circ = \frac{\log 0.003061}{2 * 16.9} = -0.0744 \text{ v.}$$

Since the E° value for the half-reaction $Cu^{+2} + 2e^- = Cu$ is +0.339 v, the standard electrode potential for the half-reaction

$$PhPH + H_2O = PhPOH + 2H^+ + 2e^-$$

is:

$$E^\circ = -0.0744 - 0.339 = -0.413 \text{ v.}$$

The calculated K values for each set of experiments are given in Table IV-12. Figures IV-4, IV-5, and IV-6 show the corresponding lnK vs. 1/T plots (based on atomic absorption measurements of final copper concentrations) that have been used for the determination of K values at 298K. The values for E° resulting from atomic absorption and ion selective electrode measurements are given in Table IV-12. The difference between these values can probably be attributed to complexation of chemical species. The average value for the overall redox reaction is: -0.0771v, and the average electrode potential for the couple PhPH/PhPOH is -0.416 v, using data resulting from AA experiments. The average values obtained from ISE measurements are -0.0730 v for the overall reaction, and -0.412 v for the PhPH/PhPOH couple.

The reaction between phenylphosphinic acid and copper(II) ions is pH dependent. For the half reaction PhPH/PhPOH, the Nernst equation can be written as:

$$E = E^{\circ} - RT/nF\{\ln([PhPOH][H^{+}]^{2}/[PhPH])\}$$

and for equal final concentrations of PhPH and PhPOH, this expression will have the form:

$$E = E^{\circ} - 0.059\log[H^{+}].$$

Letting $[H^{+}] = 1.00*10^{-1}$, and $E^{\circ} = -0.412$ v, E = -0.353 v, and for the overall reaction involving Cu(II) species, E = 0.339 - 0.353 = -0.014 v. This indicates

TABLE IV-12

STANDARD POTENTIAL FOR THE REACTION BETWEEN PHENYLPHOSPHINIC ACID AND COPPER(II) SOLUTIONS AND FOR THE COUPLE PhPH/PhPOH (FOR Cu^{+2}/Cu E° = +0.339 v)

METHOD	K	log K	E° (reaction)	E° (PhPH/PhPOH)
AA*	$1.36*10^{-3}$	-2.867	-0.085	-0.423
ISE	$2.02*10^{-3}$	-2.695	-0.080	-0.419
AA**	$3.06*10^{-3}$	-2.514	-0.0744	-0.413
ISE	$5.44*10^{-3}$	-2.264	-0.0707	-0.410
AA***	$3.74*10^{-3}$	-2.428	-0.0718	-0.411
ISE	$4.77*10^{-3}$	-2.322	-0.0687	-0.408

* Data obtained from Table IV-11, and Figure IV-4.

** Data obtained from Table IV-11, and Figure IV-5.

*** Data obtained from Table IV-11, and Figure IV-6.

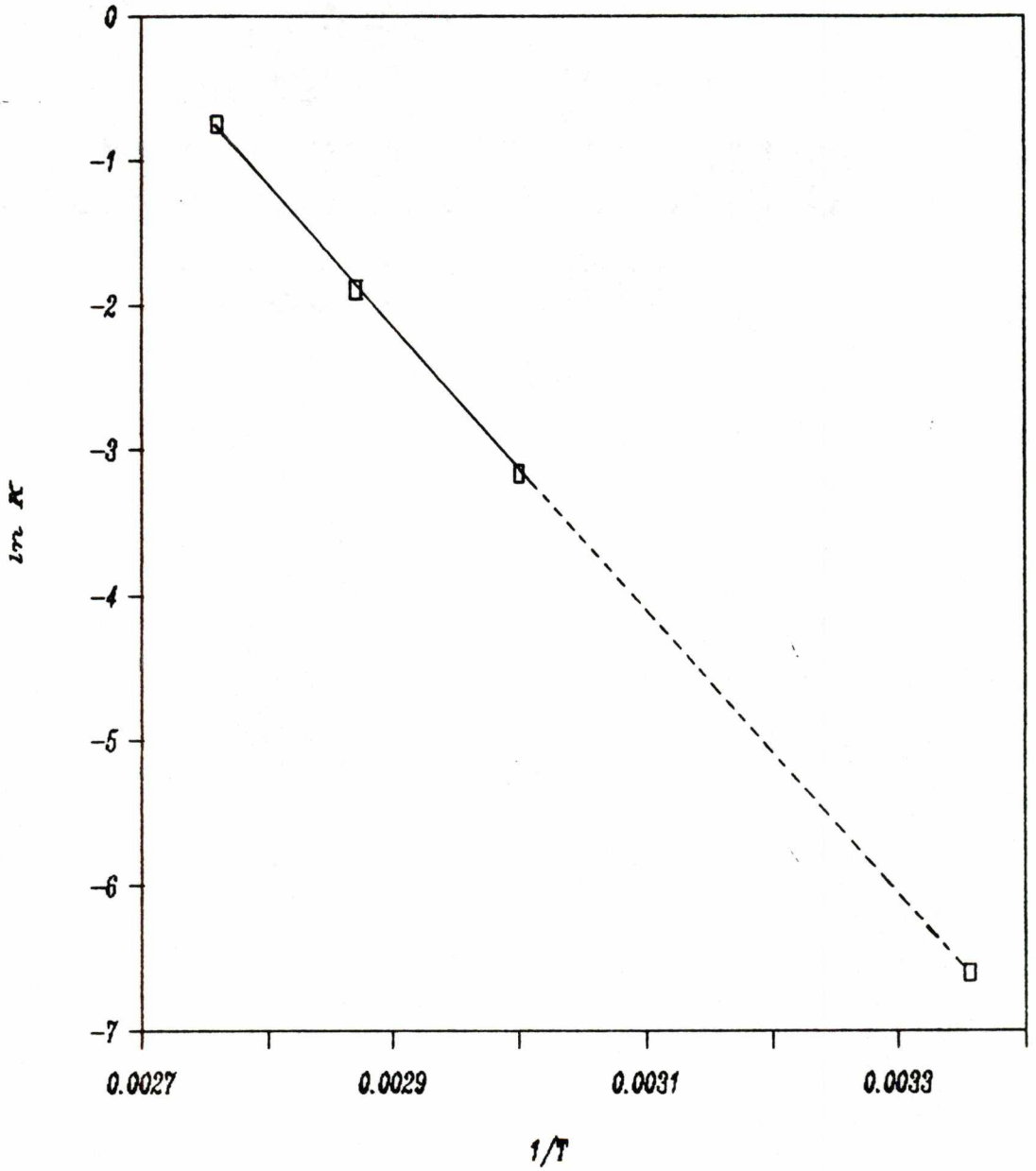


Figure IV-4. Plot of lnK vs. 1/T for the determination of the equilibrium constant at 298K (K values were obtained from experimental results indicated in Tables IV-7, IV-8, and IV-9).

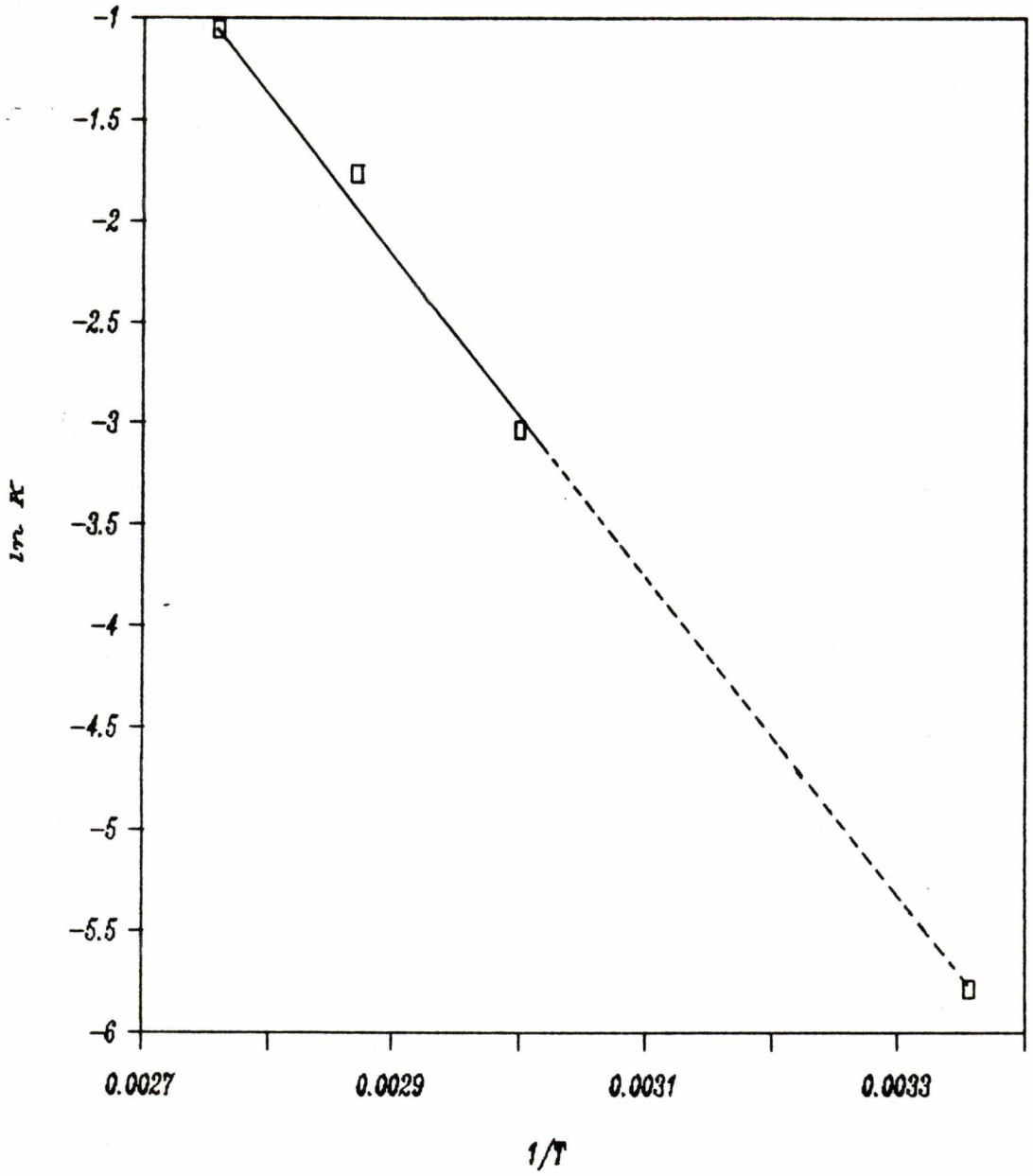


Figure IV-5. Plot of lnK vs. 1/T for the determination of the equilibrium constant at 298K (K values were obtained from experimental results indicated in Tables IV-1, IV-2, and IV-3).

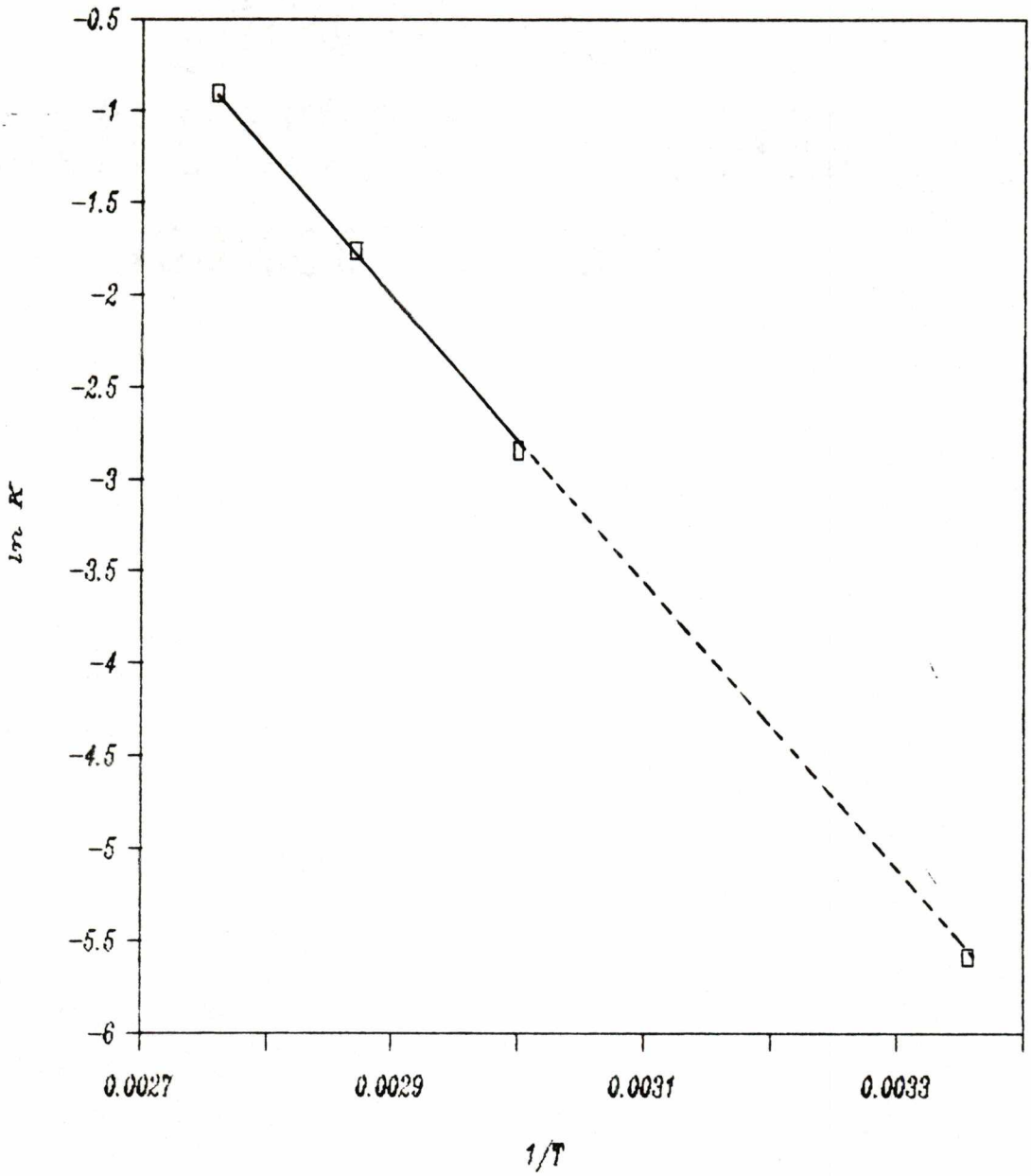


Figure IV-6. Plot lnK vs. 1/T for the determination of the equilibrium constant at 298K (K values obtained from experimental results indicated in Tables IV-4, IV-5, and IV-6).

that from a thermodynamic point of view, the reaction will not occur appreciably at pH = 1.00. For pH = 2.00, E = -0.294 v, and for the total reaction E = 0.045 v, indicating the reaction is spontaneous. For pH = 1.24, E = -0.03388 v, the potential for the overall reaction is 0.3390 - 0.3388 = 0.0002 v.

The last calculations demonstrate that the reaction between phenylphosphinic acid and copper(II) ions is strongly influenced by the pH of the solutions as well as by the concentrations of the PhPH and PhPOH species. When these latter concentrations are equal, $[H^+]$ should be $10^{-1.24}$ M or less for the reaction to occur. The expression for the apparent equilibrium constant of this reaction, when the ratio [PhPH]/[PhPOH] is unity, can be modified to read:

$$K = [H^+]^2/[Cu^{+2}].$$

Thus, for pH = 1.24 and $K = 3.74*10^{-3}$, the final concentration of Cu(II) ions expected to remain in solution will be:

$$[Cu^{+2}] = 10^{-1.24}/3.74*10^{-3} = 0.1539 \text{ M}.$$

5. Error analysis of experiments

Since a plot of lnK vs. 1/T should be a straight line, in order to perform a more accurate extrapolation for finding the value of $\ln K^{298}$, the best straight line was calculated using the program "Statgraphics", with all errors assumed to be in the y-direction.

The errors in K values at different temperatures are associated with the experimental method used for determination of the final concentrations of copper(II) ions in the solutions, and the temperature variations. The probable sources of errors in the experiments were the weighing of the reactants during the preparation of solutions, the dilution procedure, the pH measurements, the measurement of potentials with the ion selective electrode, and to a lesser extent the atomic absorption measurements of copper concentrations. The error in weighing can be estimated to be ±0.001 g, the volume errors ±0.10 mL, the error in pH values is usually estimated to be ±0.02 pH units.[19] The error in the potential values using the ion selective electrode can be estimated to be ±0.001 v, and the error in concentration associated with it can be calculated using the expression:[20]

$$\% \text{ error} = 4/z/\ E$$

where z is the charge of the ion to be determined (z = 2, for Cu^{+2}), and E is the error in millivolts of the potential measurement. Therefore, the estimated error is approximately 2%, and in terms of the concentrations herein used, it can be estimated to be about 0.0006 M. Although the atomic absorption measurements are accurate, it is possible that errors in the preparation of standards and analyte solutions can lead to errors in the concentrations

to be determined. In the present case it is estimated to be no more than 1%.

With all of these considerations it would be conservative to round the estimated potential values from Table IV-12 to the nearest one-hundredth. Therefore, the average standard electrode potential for the couple PhPH/PhPOH is estimated to be -0.41 v.

6. Conclusions

As was stated previously, information concerning the selectivity of redox resins containing phosphinic acid functional groups is not available. The studies performed on the model compound, phenylphosphinic acid, as well as on the resins, show that for the ions investigated, these redox resins are capable of reducing Au(III), Hg(II), Ag(I), and to a lesser extent Cu(II) ions. Bi(III), Fe(III), Pb(II), Co(II), and Ni(II) were not reduced either by the resins, or by the model compound, Bi(III) and Fe(III) formed non-identified compounds upon reaction with phenylphosphinic acid.

The reaction of the resins and the model compound with Cu(II) ions occurred very slowly at room temperature and was pH dependent. At temperatures greater than 40° C the reduction of Cu(II) ions to their zero valence state occurred at an increased rate. The higher the temperature, the greater the amount of Cu(II) ions reduced.

Equilibrium studies on the model compound and Cu(II) ions allowed the calculation of the standard reduction potential of the PhPH/PhPOH couple which is estimated to be -0.41 volts. This value is assumed to be equal to the standard reduction potential of the phosphinic acid resins. Considering the pH of the system model compound/metallic ions, and their concentrations, it is possible to predict that any chemical species with a standard reduction potential of +0.33 volts or higher would be reduced by phenylphosphinic acid solutions when the pH is 1.24 or higher. This statement can also be applied to the resins containing phosphinic acid ligands as functional groups.

LIST OF REFERENCES

LIST OF REFERENCES

1. M. Marhol, "Ion Exchange in Analytical Chemistry", G.Svehla, Ed., Elsevier, Amsterdam, 1982, Comprehensive Analytical Chemistry, Vol.14, Chapter 1.
2. L. Johnson, and R. Stevenson, "Basic Liquid Chromatography", Varian Associates, Inc., Palo Alto, CA., 1978, Chapter 5, pp 121-125.
3. W. J. Weber, "Physicochemical Processes for Water Quality Control", J. Wiley & Sons, Inc., 1972.
4. H. G. Cassidy, J.Am.Chem.Soc., 71, 402 (1949).
5. Encyclopedia of Polymer Science and Technology, Vol. 5, J. Wiley & Sons, Inc., 1966.
6. S. D. Alexandratos, D. L. Wilson, M. A. Strand, D. R. Quillen, and A. J. Walder, Macromolecules, 18, 835 (1985).
7. S. D. Alexandratos and D. L. Wilson, Macromolecules, 19, 280 (1986).
8. F. Helfferich, "Ion Exchange," McGraw-Hill Company, Inc., New York, N. Y. 1962.
9. A. J. Bard, and L. R. Faulkner, "Electrochemical Methods", J. Wiley & Sons, New York, N. Y., 1980, Chapter 1, pp 51-52.
10. P. W. Atkins, "Physical Chemistry", 3th. Ed., W. H. Freeman and Company, New York, 1986.
11. N. V. Sidgwick, "The Chemical Elements and their Compounds," vol. I, Claredon Press, London, 1950.

12. W. F. Hillebrand, and G. E. F. Lundell, "Applied Inorganic Analysis," 2nd. Ed., Wiley & Sons, Inc., New York, London, 1962.

13. D. A. Skoog, and D. M. West, "Analytical Chemistry", 3th. Ed., Saunders College Publs., Philadelphia, PA, 1980, p 603.

14. Instruction Manual for the Atomic Absorption Spectophotometer Varian AA-1475. Varian Associates Inc. Palo Alto, CA, 1978.

15. Instruction Manual for Cupric Ion Selective Electrode, Orion Research Incorporated, Cambridge, MA, 1979.

16. B. Welz, "Atomic Absorption Spectrometry," 2nd. Ed., V. C. Publs., Deerfield Beach, Fla., 1985.

17. P. L. Bailey, "Analysis with Ion Selective Electrodes", Heyden & Son Ltd., London, 1976, Chapter 5, pp 78-79.

18. Standard Methods for the Examination of Water and Wastewater, 16th edition, AWWA, Washington D. C., 1985, p 419.

19. D. C. Harris, "Quantitative Chemical Analysis," W. H. Freeman & Company, New York, 1982.

20. H. H. Willard, L. L. Merrit, J. A. Dean, F. A. Settle, "Instrumental Methods of Analysis", Wadsworth Publishing Company, Belmont, CA, 1981, pp 650-652.

VITA

Francisco Torres Andrade was born in Ambato, Ecuador on October 4, 1954. He is a son of Ernesto e Ines Torres of Ambato, Ecuador. He attended the Azherbaidzhan Institute of Petroleum and Chemistry in Baku, Soviet Union, and graduated in June 1979 with a Master of Science degree in Chemical Engineering. In October 1979 he began to work at the Polytechnic School of Litoral in Guayaquil, Ecuador, where he is principal professor at the present. In the fall of 1986, he entered the Graduate School of The University of Tennessee, Knoxville. He received the Master of Science degree in Chemistry in August 1988.

The author is married and has two daughters.