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THE ELECTROCHEMICAL OXIDATION OF WHITE PHOSPHORUS

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THE ELECTROCHEMICAL OXIDATION OF WHITE PHOSPHORUS

Michael L. Barry
(Ph. D. Thesis)

September 1964

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THE ELECTROCHEMICAL OXIDATION OF WHITE PHOSPHORUS

Michael L. Barry

Inorganic Materials Research Division, Lawrence Radiation Laboratory
Department of Chemical Engineering, College of Chemistry,
University of California, Berkeley, California

ABSTRACT

The electrochemical oxidation of liquid and solid white phosphorus impregnated in porous conducting matrices in alkaline, neutral and acidic electrolytes was investigated. Rates of the spontaneous disproportionation-decomposition reactions of phosphorus and the simple phosphorus oxyacids in these electrolyte solutions were also measured. Coulometric studies of the phosphorus electrode were made by comparing the rates of formation of phosphoric acid, phosphorous acid, hypophosphorous acid, phosphine, and hydrogen at known current densities to the rates of formation at zero current density.

The half-cell potentials measured for the phosphorus electrodes (relative to the standard hydrogen electrode) ranged from 1.08 v in 10 N NaOH to 0.00 v in 10 N H_2SO_4 compared to theoretical values of 1.83 v and 0.48 v for the oxidation of phosphorus to phosphite or phosphorous acid in these solutions. The results indicate that in alkaline media the electrode potentials were actually established by phosphine produced from the disproportionation-decomposition reactions of phosphorus. The reasons for the low electrode potentials in acidic media are not known.

The coulometric studies of the anodic oxidation of phosphorus in a silver-amalgam matrix in neutral and acidic media showed that phosphorus was quantitatively oxidized to phosphorous and phosphoric acids with overall

coulombic efficiencies approaching 100% at current densities up to 10 ma/cm². The coulometric results for the electrode in alkaline media were obscured by the effects of the simultaneous disproportionation-decomposition reactions of phosphorus.

These studies indicate that the electrochemical oxidation of phosphorus could be the basis of processes with direct practical applications.

I. INTRODUCTION

The purpose of this research was to investigate experimentally the electrochemical oxidation of phosphorus and, if feasible, to begin development of processes which would exploit any such electrochemical activity for useful ends.

The first introductory section reviews previous work done in the field of phosphorus electrochemistry, presents some of the possible applications of electrochemical oxidation of phosphorus, and then reviews briefly some elements of phosphorus chemistry to provide background for later sections. Also presented in this section are the available thermodynamic data for phosphorus and some phosphorus compounds. The section ends with the defining of the objectives and scope of the research.

A. Literature Review

Phosphorus and phosphorus compounds have been studied rather extensively, both from a thermodynamic standpoint^{1,2} and from a systematic chemistry standpoint;^{3,4,5} thermodynamic data for large numbers of phosphorus compounds have been determined calorimetrically, mechanisms for many reactions of phosphorus have been postulated and verified, and structures of complex phosphorus compounds have been examined in the light of quantum mechanical bonding theories. However, with a few exceptions, very little work has been done to characterize the electrochemical behavior of phosphorus. These exceptions include some early work on elemental phosphorus, some more recent work with phosphorus oxides and oxy-acids, and some studies

of the electrolysis of metal phosphides and phosphine and the electrochemical production of phosphine.

The early work measuring electrochemical properties of elemental phosphorus was rather empirical: Bonna and Le Royer⁶ reported in 1906 that earlier in 1894 they had succeeded in preparing elemental phosphorus by the electrolysis of a solution of bone ash in fused cryolite, while Schenk⁷ in 1903, using red phosphorus smeared on platinum and immersed in an aqueous electrolyte containing sodium nitrate and piperidine, measured a potential of 0.168 volts relative to a hydrogen electrode in the same solution; however in 1909 Le Blanc and Reichinstein⁸ were not able to measure any potential for phosphorus on platinum immersed in either potassium hydroxide or sulfuric acid electrolytes.

Reports of work on the electrochemistry of oxides and oxy-acids of phosphorus include that of Aleksyeev⁹ in 1907, who reported the anodic oxidation of phosphorus acid to phosphoric acid on lead dioxide electrodes, and some more recent studies by Nylen,¹⁰ who in 1934 measured reproducible potentials for the hypophosphite-phosphite couple on palladium black electrodes. Nylen found the potentials to vary linearly with the logarithms of both hypophosphite concentration and hydrogen ion concentration, but to be independent of phosphite (ortho) ion concentration. In all cases, the electrode potentials were about 20 millivolts higher than the hydrogen electrode potential at the corresponding pH. After noting the earlier work of Bancroft¹¹ and Neumann¹² who measured a potential of -0.264 volts (vs. standard hydrogen electrode) for 0.2 molar sodium hypophosphite with platinized

platinum electrodes, Nylen concluded that palladium black acted as a catalyst for the primary reversible electrochemical oxidation of hypophosphite to an unstable form of phosphite, which then is transformed irreversibly into the stable orthophosphite. In addition to this work, Fichter and Muller¹³ in 1918 reported finding the compounds H_3PO_5 and $H_4P_2O_8$ after electrolysis with platinum electrodes of solutions of potassium phosphate and ammonium phosphate containing also calcium fluoride and potassium chromate. Also, Czuha, Gardiner, and Sawyer,¹⁴ discussing a device used to measure the water content of gases by dehydration over phosphorus pentoxide followed by electrolysis of the hydrated phosphorus pentoxide, suggest that the oxygen liberated comes from a hydroxide group on the polyphosphate chain, implying an electrochemical scission of phosphorus-oxygen bonds.

The electrolysis of copper phosphide in dilute sulfuric acid was reported by Rosenheim and Pinsker¹⁵ in 1910, and a patent was issued to Rosenheim¹⁶ in 1913 for the production of hypophosphoric acid by anodic oxidation of phosphides of various metals. The oxidation was carried out at a cell potential of three to ten volts, and the product consisted primarily of hypophosphoric acid (60%) and orthophosphoric acid (40%). In 1938, Royen¹⁷ reported the electrolysis of phosphine dissolved in liquid ammonia, leaving a deposit believed to be elemental phosphorus at the anode. Grove,¹⁸ in 1863, reported the formation of phosphine during the passage of direct current through moist phosphorus. The electrolytic production of phosphine from phosphorus trioxide was patented by Blumenberg¹⁹ in 1921; it was claimed that the phosphorus trioxide did not enter directly the

electrode reaction, but was reduced to phosphine by hydrogen formed at the cathode. Finally, a recent German patent issued to the Hooker Chemical Company²⁰ and related papers presented by Miller²¹ disclose the production of phosphine by electrolytic reduction of phosphorus at a mercury electrode in acidic electrolytes.

B. Applications

Even considering the papers listed above, it is obvious that there is room for more consistent study of the electrochemistry of phosphorus. Aside from the purely theoretical aspects of obtaining direct thermodynamic data, the electrochemical behavior of phosphorus is of interest from a practical standpoint. Oxidation of elemental phosphorus to phosphoric acid is a major chemical operation;²² the benefits gained by carrying out this reaction in an electrochemical cell consequently are of major interest. The most obvious advantage of the electrochemical process is the recovery of the free energy of the reaction in the form of electrical energy. In addition, regulation of the electrode potential in an electrochemical process allows closer control of competing reaction rates, and thereby selectivity, than is generally possible in the corresponding conventional chemical process, controlled primarily by the reactor temperature and residence time. Furthermore, if phosphorus can be made to undergo electrochemical reactions, it may well be possible to synthesize electrochemically other phosphorus compounds, such as phosphorus-oxy-halogen compounds, which may not now be readily produced.

Another use for the electrochemical oxidation of phosphorus is as a source of energy in remote locations, that is, in a battery or fuel

cell. The major advantage of phosphorus over other fuels for remote energy sources lies in the ease with which phosphorus may be stored. For example, in hydrogen fuel cells now available, storage requirements may exceed fifty pounds of storage facilities per pound of hydrogen.²³ Phosphorus, which may easily be stored in light-weight plastic bags, therefore may more than compensate for its unfavorable equivalent weight relative to hydrogen and result in a favorable energy-to-total-weight ratio.

C. Review of Pertinent Phosphorus Chemistry

This section is designed to provide a brief preview of some of the compounds of phosphorus and concepts of phosphorus chemistry which are important in the study of phosphorus electrochemistry.

1. Elemental Phosphorus

Phosphorus is a non-metallic element appearing in group V of the periodic table, with a ground state electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^3$ and, therefore, with five electrons generally available for bonding. In its compounds, phosphorus exhibits coordination numbers of 1, 3, 4, 5, and 6 and an electronegativity of 2.1. Structures showing these coordination numbers are shown in Table I.³ The triply- and quadruply-connected phosphorus compounds are by far the most common and are the only forms which will be considered further.

The reactivity of phosphorus compounds compared to nitrogen or carbon compounds is explained by the ease by which activated complexes may be formed intermediate to the reacting and product species.

This ease of forming low energy intermediates is due of course to the

Table I. Structures of Phosphorus Compounds

Coordination Number	1	3	4	5	6
Bonding					
-bond hybridization	p	$p^3 + sp^3$	sp^3	sp^3d	sp^3d^2
-bond/ -bond	-	0	ca 0.3	0	0
Geometry	$P-x$
Stability	Unstable	Stable	Most Stable	Very Reactive	Very Reactive
Examples	P_2	P_4PH_3	H_3PO_4	PCl_5	PCl_5^-

electronic structure of phosphorus. In triply-connected phosphorus, the two unshared electrons ($3s^2$) allow additional bonding leading to reactive intermediates at only a slight increase in energy for the system. In quadruply-connected phosphorus, the approximately one σ -bond per phosphorus atom can be converted into a σ -like bond to form activated complexes with little increase in energy. This σ -like bond is formed by the use of d-orbitals of the phosphorus; d-orbitals, of course, are not available to carbon and nitrogen which are first row elements.

Elemental phosphorus exists in several forms: diatomic and tetratomic vapor, tetratomic liquid, and white, red, and black solid phases. Of the solid forms, white (which occurs as P_4) is the most reactive and has the same form as the commonly found tetratomic vapor and liquid forms. White phosphorus is the only form considered in the following studies.

Tetratomic phosphorus occurs as regular tetrahedra with bond lengths equal to 2.2 - 2.3 Å, and bond angles of 60°. The optimum bond angle for tetratomic phosphorus should be about 90°, corresponding to the best spd-hybrid ($\psi = 0.0685s + 0.9958p_z + 0.1530d_z$);²⁴ the small bond angle in tetratomic phosphorus indicates that the bonding orbitals between atoms are bent, or meet at an angle rather than straight on. Actually, a pd^2 hybrid gives the proper bond angle,²⁵ but the two d-orbitals utilized require more energy than does the "bent" bond consisting of predominantly p-orbital with some s- and d-character to provide the "bending." The strain energy which results from the bending is 22.8 kcal/mole of P_4 and is the cause of the higher reactivity of tetratomic phosphorus compounds compared to that of the other forms (that is, red and black solid forms).^{3,26} The remaining two unshared valence electrons per atom of tetratomic phosphorus are predominantly s-like in character.³

White tetratomic solid phosphorus occurs in two varieties; β -phosphorus, the low temperature form, is converted into α -phosphorus at -77°C at atmospheric pressure. White phosphorus in the α -form exists as cubic crystals with unit cells containing 56 molecules of P_4 . The P_4 tetrahedra in this solid phase are apparently free to rotate, the P_4 molecules packing into the lattice like spheres without having to assume any special geometrical configuration. This explains the extremely rapid rate of crystallization of white phosphorus from the molten state. White phosphorus is extremely soluble in carbon disulfide and moderately soluble in benzene and diethyl ether.²⁷ Liquid ammonia^{28,29,30} and liquid sulfur dioxide have also been

reported as good solvents for phosphorus. The solubility of white phosphorus in water is quite low (3.3 mg/liter at room temperature).³¹

Solid white phosphorus melts to liquid phosphorus at 44.1°C at one atmosphere. Liquid phosphorus has a density of 1.740 g/cc and a viscosity of 1.69 cp at 50°C. The surface tension of liquid white phosphorus in contact with its vapor is 43.1 dynes/cm at 78°C.⁴

Water is only slightly soluble in liquid phosphorus (3.6 g/kg at 45°C),³² but saturation with water at 50°C lowers the viscosity of phosphorus by over 40%. Mercury is also slightly soluble in liquid phosphorus (0.29 gHg/kg);³³ this is the only known case of a metal dissolving in a non-metallic liquid by purely physical means.³

Saturation of liquid phosphorus with mercury apparently changes the electrical conductivity from 4×10^{-7} mhos/cm to approximately 10^{-3} mhos/cm;³⁴ this extremely low electrical conductivity, coupled with the low solubility of phosphorus in water, poses special problems in formulating phosphorus electrodes.

Both solid and liquid white phosphorus slowly change to solid amorphous and crystalline red phosphorus, the rate of conversion becoming very significant at temperatures in the range of 250°C. This conversion is catalyzed by iodine and, to a smaller extent, by light. Because of this rapid rate of formation of red phosphorus, liquid white phosphorus has not been observed at temperatures over about 350°C. Red phosphorus melts at about 600°C, depending upon its composition (that is, whether it is amorphous, crystalline, or a mixture of amorphous and/or various crystalline varieties). The conversion of white phosphorus to red phosphorus could seriously

complicate high-temperature electrochemical processes operating with phosphorus vapor.

Liquid white phosphorus vaporizes to the tetratomic vapor at 280.5°C at one atmosphere pressure. The tetratomic vapor has essentially the same molecular form as the tetratomic solid and liquid. Dissociation of the tetratomic phosphorus vapor to the diatomic form, P_2 , is not appreciable below 800°C, except on surfaces of some metals such as tungsten.³⁵

2. Phosphorus Oxyacids

The expected products of electrochemical oxidation of phosphorus in aqueous electrolytes are the phosphorus oxyacids or their anions. These compounds consist of phosphorus, oxygen, and hydrogen and are characterized by sp^3 -hybrid σ -bonds plus about one π -bond per phosphorus atom, leading to configurations of four atoms surrounding the central phosphorus atom. The oxyacids and their anions based on one phosphorus atom are as depicted in Table II.

In this series, the hydrogens connected directly to the phosphorus atom are not ionizable. Also, it must be emphasized that the use of the double bond notation is meaningless; the π -bond character referred to by this convention is actually shared nearly equally by all four σ -bonds.

Hypophosphorus acid, H_3PO_2 , has an apparent oxidation state of +1 for the phosphorus atom, and one ionizable hydrogen. The dissociation constant of the removable hydrogen is 8×10^{-2} ; therefore, hypophosphorus acid is considered a strong monobasic acid. The rates of exchange of the other two hydrogens (attached directly to the

Table II. Phosphorus Oxyacids Based on One Phosphorus Atom

Hypophosphorous Acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{P}-\text{OH} \\ \\ \text{H} \end{array}$	$\longrightarrow$	$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{P}-\text{O} \\ \\ \text{H} \end{array} \right]^{-}$	Hypophosphite
Phosphorous Acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{OH} \\ \\ \text{H} \end{array}$	$\nearrow$ $\searrow$	$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{O} \\ \\ \text{H} \end{array} \right]^{-}$	= Phosphites
			$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{O}-\text{P}-\text{O} \\ \\ \text{H} \end{array} \right]^{-}$	
Phosphoric Acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{OH} \\ \\ \text{O} \\ \\ \text{H} \end{array}$	$\nearrow$ $\longrightarrow$ $\searrow$	$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{OH} \\ \\ \text{O} \end{array} \right]^{-}$	= Phosphates
			$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{O} \\ \\ \text{O} \end{array} \right]^{-}$	
			$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{O}-\text{P}-\text{O} \\ \\ \text{O} \end{array} \right]^{-}$	

phosphorus) with the hydrogen of water has recently been shown to be quite slow, about 1.85 mole/liter/hr in 1 molar H_3PO_2 at 30°C .³⁶

Hypophosphite is usually produced commercially by treating white phosphorus with a boiling lime or barium hydroxide slurry.³⁷ In general, hypophosphite is one of the products of the series of disproportionation-decomposition reactions of phosphorus in alkaline solution. The overall reactions involving hypophosphite appear to be:

Reactions (1) and (2) are the results of what appears to be a complicated sequence of reaction steps; the relative proportions of hydrogen and phosphine, as well as other oxidation products, depend upon the temperature and hydroxyl ion concentration. Reaction (3) has been studied more extensively.^{38,4} The rate equation seems to have the form:

$$\frac{-d(\text{H}_2\text{PO}_2^-)}{dt} = k(\text{H}_2\text{PO}_2^-)(\text{OH}^-)^2,$$

where k is of the order $3 \times 10^{-4} \text{ (l/mole)}^2(\text{min})^{-1}$ at 100°C . The dependence on the hydroxide ion concentration squared, rather than the first power as would be predicted from reaction (3), suggests reactions of the following form:

The same type of decomposition of hypophosphite also occurs in neutral solutions if catalysts such as palladium, platinum black, or finely divided copper are present. A study utilizing isotope exchange methods^{39,3} indicates that the hydrogen evolved in this decomposition comes from both the hypophosphite ion and the water molecule, as indicated in the following reaction:

Hypophosphite is a very strong reducing agent, but its reducing action is often limited by slow kinetics. The oxidation of hypophosphorous acid by many different oxidizing agents has been studied extensively;^{3,4} typical oxidizing agents include the halogens, chromate, arsenate, iodate, and bromate ions, and the salts of metals such as silver, copper, mercury, and iron. In all of these cases, in acidic media, it appears that the rate-determining step is the conversion of one form of hypophosphite, probably the quadruply-connected phosphorus form to a tautomer of the same ions, probably a triply-connected form. This conversion is pictured as:

The concentration of the triply connected form has been shown by nuclear magnetic resonance to be less than 5% of the total hypophosphite; evidence from kinetic rates of oxidation gives an equilibrium constant between the two forms of the order of $10^{-12.3}$. Other evidence indicating that the conversion of quadruply-connected to triply-connected phosphorus is the limiting step in these oxidations is the lack of exchange of phosphorus between hypophosphorous acid and its oxidation product, phosphorous acid. If the rate-limiting step was actually an oxidation step, with an equilibrium between some form of hypophosphorous acid and some form of phosphorous acid, then the rate of phosphorous exchange between these two forms should be of the same order of magnitude as the rate of oxidation. However, since the rate of exchange is zero, then the limiting step must be

between two tautomeric forms of the same compound. Since phosphorous acid also occurs predominantly in the quadruply-connected form,³ it appears that the rate of transformation of one-tautomer of phosphorous acid to the quadruply-connected tautomer could not be the rate-limiting step. This leaves as a suitable mechanism only the transformation of the quadruply-connected form of hypophosphorous acid to an active tautomer form, presumably triply-connected, as the limiting step, followed by a rapid, irreversible oxidation of the active form.

Phosphorous acid, H_3PO_3 , or its anion, phosphite, is another oxyacid formed from the disproportionation-decomposition of white phosphorus in alkaline solution. The overall reactions may be written:

Also, phosphite is formed from the oxidation of hypophosphite in alkaline media, as described in the preceding section:

Phosphorous acid is dibasic, having only one hydrogen attached directly to the phosphorus atom; the ionization constants of the acid at 20°C are $\text{pK}_1 = 1.3$ and $\text{pK}_2 = 6.7$.² Phosphorus exhibits an apparent oxidation state of 3 in phosphorous acid and phosphites; the phosphorus atom is generally quadruply-connected, although in many of the organic esters of phosphorous acid, the phosphorus atom is triply-connected. Phosphorus atoms do not exchange between phosphorous acid and either hypophosphorous

or phosphoric acids.⁴⁰

Phosphite is a strong reducing agent, but, like hypophosphite, it reacts only slowly with many oxidizing agents; however, it differs from hypophosphite in that it does not react in alkaline solutions to form hydrogen. The oxidation of phosphite to phosphate in aqueous solution has been studied rather extensively.^{41,42,43} Some investigators⁴¹ postulate that, similar to the case of hypophosphite, the rate-determining step in the oxidation is the transformation of quadruply-connected phosphite to an active tautomer, presumably the triply-connected form. However, other investigators⁴² and reviewers⁴ explain the data on schemes not involving such a tautomeric transformation; at the present time a completely satisfactory mechanism for the oxidation of phosphite has not been described.

Orthophosphoric acid, or orthophosphate, is the most highly oxidized phosphorus oxyacid based on one atom of phosphorus. In this compound, phosphorus shows an apparent oxidation state of +5; the phosphorus atom is connected to four oxygens, and it would appear this quadruply-connected form is the only one possible. The hydrogen atoms of the three OH groups are believed to be shared to some extent by weak hydrogen bonding with the "single" oxygen and to oxygens of other phosphate ions, resulting in a macromolecular network of phosphate ions bridged by hydrogen bonding. In dilute acid solutions, this hydrogen bonding links water molecules to phosphate ions, again forming a macrostructure; this structure is believed to be responsible for the relatively low diffusion coefficients and electrical conductivities of phosphoric acid³ and for the difficulty with which the

third hydrogen of phosphates is ionized.⁴ The macromolecular network formed in phosphoric acid solutions should not be confused with "condensed" phosphoric acids, which are ring and highly-branched chain structures containing more than one phosphorus atom per molecule, the phosphate groups being linked through a strong P-O-P bond.

Orthophosphoric acid is difficult to reduce, and at normal temperatures it is relatively inactive. All three hydrogens are ionizable, the ionization constants being $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, and $K_3 = 10^{-13}$.⁴⁴ Orthophosphate is not formed from the disproportionation-decomposition of white phosphorus in alkaline solution.

In addition to oxyacids based on one atom of phosphorus, there occur other series of oxyacids based on two or more atoms of phosphorus. In these series, the phosphorus atoms may be connected directly together (-P-P-) or through an oxygen atom (-P-O-P).

Of the sixteen possible combinations resulting from surrounding two phosphorus atoms tetrahedrally with hydrogen and oxygen atoms, only five have been isolated and studied. These are shown in Table III.

Diphosphorous acid, $H_4P_2O_5$, was isolated in 1953 by Blaser⁴⁵ from the hydrolysis product of PBr_3 ; the acid is tribasic, and in it, phosphorus shows an apparent oxidation state of +3. Both chemical reactions and nuclear magnetic resonance data indicate that the structure is that given in Table III.^{45,46} Diphosphorous acid is oxidized by iodine in neutral solutions and bromine in acidic solution to hypophosphoric acid. In neutral solution, bromine continues the oxidation all the way to pyrophosphoric acid. Diphosphite does not react with moderately concentrated alkaline solutions at 100°C, but does react with highly concentrated sodium hydroxide at 160°C to form hypophosphate and hydrogen.³

Table III. Known Phosphorus Oxyacids Based on Two Phosphorus Atoms

Diphosphorous Acid

Pyrophosphorous Acid

Hypophosphoric Acid

Isohypophosphoric Acid

Pyrophosphoric Acid

Pyrophosphorous acid, $\text{H}_4\text{P}_2\text{O}_5$, in which phosphorus has an apparent oxidation state of +3, is a dibasic acid which was first prepared by Amat⁴⁷ in 1888. Pyrophosphorous acid is hydrolyzed rapidly in alkaline or acidic acid, forming two molecules of orthophosphorous acid:

The half life for this reaction at 30°C is 1000 hours at pH 5-7, 60 hours at pH 4, 8 hours at pH 3, and 5 minutes at pH 1.5.^{47,48}

Hypophosphoric acid, $\text{H}_4\text{P}_2\text{O}_6$, is a well-known acid with four ionizable hydrogens, and in which phosphorus has an apparent oxidation state of +4. Oxidation of hypophosphite to phosphate is very difficult with most oxidizing agents. Even with oxidants such as dichromate or permanganate in acidic solution, the oxidation is slow, and it is believed the primary reaction is probably hydrolysis of hypophosphoric acid to phosphorous and orthophosphoric acids, as in equation (13), followed by oxidation of the phosphorous acid.³

Hydrolysis is quite slow except at high temperatures and high acid concentrations.⁴⁹ Studies^{40,49} show there is no exchange of phosphorus between hypophosphate, orthophosphate, and pyrophosphate ions and that the hydrolysis reaction as shown in equation (13) does not represent an equilibrium at room temperature, that is, an intermediate step is rate controlling.

An exception to the general difficulty in oxidizing hypophosphoric acid occurs in the case of bromine within the range of pH 5 to pH 11. In this case, hypophosphate is oxidized rapidly and completely to pyrophosphate,

that is, an oxygen is inserted between the two phosphorus atoms. It is believed that in this case utilization of d-orbitals, perhaps in an sp^3d -like hybrid (which has smaller bond angles than sp^3 hybrids), would result in an oxygen linkage forming between the two phosphorus atoms before the phosphorus-phosphorus bond is broken.³ A mechanism of this type would account for the high yield of pyrophosphate rather than a mixture of pyrophosphate and orthophosphate fragments.

Isohypophosphoric acid, $\text{H}_4\text{P}_2\text{O}_6$, is a recently discovered structural isomer of hypophosphoric acid.^{4,5} Isohypophosphoric acid, in which phosphorus has in apparent oxidation state of +4, is a tribasic acid, while hypophosphoric acid is tetrabasic. In addition, isohypophosphoric acid hydrolyzes more readily than its isomer; its half life is 3 minutes in 0.2 N HCl at 25°C and about 7 hours in 1 N NaOH at 20°C. The products of hydrolysis are, as in the hydrolysis of hypophosphoric acid, phosphorous and orthophosphoric acids:

In neutral solutions, isohypophosphoric acid is stable in respect both to hydrolysis and to oxidation by iodine.^{3,4,5}

Pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, has four replaceable hydrogens, with dissociation constants^{51,52} $K_1 = 10^{-1}$, $K_2 = 10^{-2}$, $K_3 = 3 \times 10^{-7}$, $K_4 = 2 \times 10^{-10}$,

and with an apparent oxidation state of +5 for phosphorus. Actually, pyrophosphoric is the second homolog in a long series of chain phosphates which are linked through POP bonds. Pyrophosphoric acid is fairly stable, hydrolyzing to orthophosphoric acid at reasonable rates only in hot, strongly acidic solutions. For example, the time required for 5% hydrolysis of pyrophosphate in pH 10 solution at room temperature is 10^5 hours, while at 100°C it is 6 hours, and in pH 4 solution at 100°C, it is 10^{-1} hours.³

Some oxyacids based on three atoms of phosphorus are known to exist.

Blaser⁴⁵ has isolated two:

The first of these, $\text{H}_6\text{P}_3\text{O}_8$, hydrolyzes slowly in neutral solutions and more rapidly in acidic or alkaline solutions to yield phosphorous and hypophosphoric acids; in strong acids, the hypophosphoric acid undergoes further hydrolysis to phosphorous and phosphoric acids; the half life for hydrolysis is about 100 minutes at 0°C in 0.5 N NaOH.³ In addition this acid can react with orthophosphate to yield both hypophosphate isomers:

This acid, $\text{H}_6\text{P}_3\text{O}_8$, is not oxidized by iodine in neutral solution.

About all that is known about the second acid, $\text{H}_5\text{P}_3\text{O}_9$, is its structure and that it is unaffected by bromine in neutral solution.

Other series of homologous oxyacids may be characterized by three or more quadruply-connected phosphorus atoms, bonded either directly together or through an oxygen atom. The well-known metaphosphates are now believed to be ring structures based on three or more phosphate groups. Very large chains, heavily branched, and containing ring structures, have been shown to exist;³ these are known as condensed phosphoric acids or phosphates, and they evolve into a branch of chemistry as involved, yet as logical, as hydrocarbon chemistry.

3. Phosphine and Other Phosphorus Hydrides

Phosphine, PH_3 , is one of the "reduced" substances produced from the disproportionation-decomposition reactions of white phosphorus in alkaline solutions. Phosphine is a gas at room temperature and atmospheric pressure; it is extremely poisonous, and it reacts with the oxygen in air, spontaneously and explosively if small amounts of an impurity, diphosphine, are present. The solubility of phosphine in water is not too high⁵³ (about 0.006 molar at 40°C under 1 atmosphere partial pressure PH_3), but it slowly decomposes in solution to form phosphorus, hydrogen, and a yellow, phosphorus-hydrogen polymer approaching $(\text{P}_2\text{H})_n$. Solutions of phosphine are neither acidic nor basic; both the acid and base dissociation constants have been shown to be of the order of 10^{-27} .⁵⁴ Thermodynamic data^{2,61} indicate that gaseous phosphine is unstable with respect to dissociation to the elements at all temperatures; however, the rate of dissociation appears immeasurably slow at room temperature.

Biphosphine, P_2H_4 , is also produced in small quantities from the reaction of white phosphorus with alkaline solutions. Biphosphine

boils at 56°C, but above 0°C, decomposition to phosphine and phosphorus-hydrogen polymers occurs quite rapidly.³

4. Disproportionation-Decomposition Reactions of Phosphorus

When white phosphorus is placed in contact with alkaline solutions, a series of complex reactions take place resulting in the disproportionation of phosphorus to oxidized states, hypophosphite and phosphite, and reduced states, phosphine and traces of biphosphine. Also, the decomposition of water occurs so that hydrogen gas is evolved. The overall equations generally believed to describe these reactions are presented below:

It is obvious that these overall reactions must be composed of many complex steps. The number of possible paths from triply-connected phosphorus in the tetrahedral P_4 molecule to quadruply-connected phosphorus in an oxyacid anion appears very large; selecting one of these paths as the most probable reaction route seems almost impossible. As proposed in the bromine oxidation of hypophosphate in neutral solution,³ there is probably a certain amount of oxygen bridging (utilizing d-orbitals) between two phosphorus

atoms before the phosphorus-phosphorus bond is broken. Each phosphorus atom in the P_4 molecule has two s-like electrons easily available for bonding with an electron-acceptor group. In addition, scission may occur in a phosphorus-phosphorus bond, followed by addition of groups to both phosphorus atoms affected; in this case the phosphorus atoms remain triply-connected. After a certain number of additions of oxygen and hydrogen atoms and hydroxyl groups, the original tetrahedral P_4 molecule must undergo some sort of ring-scission and fragmentation to form chain oxyacids which eventually hydrolyze to the mono-phosphorus oxyacids which are the products of the completed reaction. Also, somewhere along the course of the reaction, phosphine and, perhaps, higher polymers of the form P_nH_{n+2} must be formed. Because of the complexity of the reactions involved, most of the work in this area has been directed to more or less empirically increasing the proportions of the various products formed.^{55,56} Hypophosphite, which is used in the pharmaceutical industry^{3,37} and in the "electroless" nickel-plating process,^{57,58} is usually the most desirable product of the reactions.

D. Thermodynamic Data for Phosphorus Compounds

The thermodynamic data which have been determined or estimated for the phosphorus compounds which are of interest in this study are presented in Table IV. The values presented in this table have been derived from calorimetric and solubility data; entropies are known only for elemental phosphorus, phosphine gas, and aqueous phosphoric acid and phosphate ions.¹ The free energies which have been determined for the simple oxidation states of phosphorus can be most easily interpreted by use of the potential diagrams of Latimer¹, as shown in Table V.

Table IV. Thermodynamic Data for Selected Phosphorus Compounds^{1,59,60,61}

Compound	State	ΔH Formation kcal/formula wt.	ΔF Formation kcal/formula wt.	Standard Entropy cal/°K/formula wt.
P_4	c(α -white)	0	0	39.20, ⁵⁹ 42.4 ¹
	l	0.601		42.50(at m.p.)
	g	13.12	5.82	66.90
P^+	g	329.81		
P^{+2}	g	784.51		
PH_3	g	2.21	4.36	50.2
$(P_2H)_n$	c(n=2)	6.9	16.0	(40.)
H_3PO_2	c	-145.5		
H_3PO_2	aq	-145.5	-125.1	(38.)
$H_2PO_2^-$	aq		-122.4	
H_3PO_3	c	-232.2		
H_3PO_3	aq	-232.2	-204.8	(40.)
$H_2PO_3^-$	aq		-202.35	(19.)
HPO_3^{-2}	aq	-233.8	-194.0	
$H_4P_2O_6$	aq	-392		
H_3PO_4	c	-306.2		
H_3PO_4	aq	-308.2	-274.2	42.1
$H_2PO_4^-$		-311.3	-271.3	21.3
HPO_4^{-2}		-310.4	-261.5	-8.6
PO_4^{-3}		-306.9	-245.1	-52.
$H_4P_2O_7$	c	-538.0		
$H_4P_2O_7$	aq	-543.1		
$P_2O_7^{-4}$	aq	-543.1		

Table V. Oxidation Potentials of Some Phosphorus Compounds

Oxidation State									
-3	-2	0	+1	+3	+4	+5			
<u>Acid Media</u>									
PH_3	P_2H_4	P	H_3PO_2	H_3PO_3	$\text{H}_4\text{P}_2\text{O}_6$	H_3PO_4			
(0.0)*	(0.1)	0.51	0.50	-0.38	0.94				
0.065		0.50		0.276					
<u>Basic Media</u>									
PH_3	P_2H_4	P	H_2PO_2^-	HPO_3^{2-}	$\text{H}_2\text{P}_2\text{O}_6^{2-}$	PO_4^{3-}			
(0.8)	(0.9)	2.05	-	1.57					
0.89		1.73		1.12					

* Values in parenthesis are estimated values.

Using these oxidation potentials, it is possible to write the following electrochemical half-cell reactions:

Alkaline Media

Acid Media

These half-cell reactions indicate that phosphorus undergoes disproportionation reactions in alkaline solutions and, to a lesser extent, in acidic solutions. For example, white phosphorus in contact with alkaline solution disproportionates to the +1 and -3 states, hypophosphite and phosphine:

Also, white phosphorus decomposes alkaline solutions to form hydrogen and hypophosphite:

In acidic solutions, the same reactions occur theoretically, but with reduced free energies:

Actually, since the overvoltage for hydrogen evolution is estimated to be about 0.5 volts, reaction (39) proceeds only very slowly, if at all.

Hypophosphorous acid, or hypophosphite ion, is unstable with respect to disproportionation to phosphorous acid and phosphine in both alkaline and acidic media:

Hypophosphite also decomposes alkaline solutions to form hydrogen gas and phosphite ions; the corresponding reaction in acidic media also has a negative free energy, but again, it occurs only very slowly:

The disproportionation reactions of phosphorus to the -3 and +3 states in both acidic and alkaline media are shown in equations (44) and (45), and the decomposition of the aqueous media to form hydrogen and phosphorous acid are shown in equations (46) and (47):

Again, it appears that reactions (45) and (47), although theoretically possible, do not occur to any great extent.

The disproportionation reactions of phosphorous acid and phosphite in acidic and alkaline solutions to form phosphine and phosphoric acid and phosphates are shown in equations (48) and (49). The free energy, as given for the six-electron reaction, is small and negative for alkaline solutions but is positive for acids. Actually, the uncertainty in the free energy of formation of phosphine is great enough so that the free energy of reaction (49) could be either positive or negative. The abilities of phosphorous acid and phosphite ion to decompose acidic and alkaline solutions to form hydrogen and phosphoric acid and phosphates, respectively, are indicated by reactions (50) and (51). Again, these reactions as written for two-electron transitions have small negative free energies.

Reactions (48) through (51) normally do not occur at room temperature; however, at about 250°C, phosphorous acid decomposes to form orthophosphoric acid, red phosphorus, hydrogen, and phosphine.³

For the sake of completeness, the disproportionation-decomposition

reactions of white phosphorus with alkaline and acidic media to form orthophosphates and orthophosphoric acid are given in equations (52) through (55):

Finally, the oxidation of phosphine to phosphorus in either acidic or alkaline solutions and the corresponding reduction of hydrogen ions or water molecules, respectively, is shown in equation (56):

This reaction, as written for a twelve-electron transition, has such a small negative free energy that the reaction occurs only very slowly under normal circumstances.

The overall reactions for a phosphorus-oxygen electrochemical cell for oxidation of phosphorus to hypophosphorous, phosphorous, and phosphoric acids and their corresponding anions are given in equations (57) through (62):

E. Objectives and Scope of Research

The overall objective of this research is to investigate the electrochemical oxidation of phosphorus. Such an investigation would normally include measurement of potentials of phosphorus electrodes, determination of the extent of reversibility of these potentials, and measurement of the polarization (that is, dependence of the potential on the current density) of the electrodes; determination of the primary reactions occurring at the electrode and measurement of the kinetic parameters of these reactions; measurement of coulometric efficiencies of the electrode under various conditions of temperature, rate of discharge, types of electrolyte, etc.; design studies of the optimum geometry of the electrode and the electrochemical cell containing the electrode; and economic studies to determine the situations where development and operation of cells based on this electrode would be feasible. It is obvious that the scope of this specific research program must be severely restricted due to time and manpower limitations.

In addition to time and manpower limitations, the complexity of the problem has placed even more restrictions on the scope of the research. As indicated in previous sections, the high oxidation potentials of phosphorus result in spontaneous disproportionation-decomposition reactions when phosphorus is placed in aqueous media.

This means that phosphorus electrodes are corroding electrodes; there is an effective internal cell current (and resulting displacement from the equilibrium potential) when the external cell current is zero. A method of analyzing corroding electrode systems has been presented by Stearn and Geary⁶² for cases of two and three simultaneous oxidation-reduction reactions where the reversible potentials are known for each reaction. However, for the phosphorus electrode there are at least four simultaneous redox reactions occurring, and, in addition, none of the reversible potentials of these reactions is known. (Actually, the equilibrium potential for the hydrogen evolution reaction is known, but the exchange current for the reaction, which is also required information, is not). For this reason the potentials measured at the corroding phosphorus electrode do not necessarily correspond to the equilibrium potentials of any of the electrode reactions, and therefore these potentials do not necessarily have thermodynamic significance. Another complicating factor is that the products of the spontaneous reactions occurring at the phosphorus electrode are themselves electrochemically active and may contribute to the electrode potential.

Determination of the electrode reactions for the phosphorus electrode is very difficult because of their extreme complexity. As was discussed in the review of phosphorus chemistry, there must be a large number of intermediates in the reactions leading from tetrahedral phosphorus to the mono- and di-phosphorus oxyacids. Some of these steps are electrochemical in nature, i.e., they involve a transfer of electrons from one species to another, while others, consisting only of a rearrangement or tautomeric shift, are not. Therefore, it is

impossible to trace down the reaction paths and state that an electron transfer from reactant to anode occurred at any given step. Also, this large number of intermediate steps and possible reaction paths makes the interpretation of coulometric studies very difficult; for example, it may be possible for a given $P_n O_m H_q$ intermediate to transfer n electrons to the anode in an electrochemical step and then, through a complex series of disproportionation-decomposition reactions, terminate in, say, $1/2 n$ hypophosphite and $1/2 n$ phosphite ions. Analysis for hypophosphite and phosphite ions would indicate that $2n$ electrons ($1/2 n$ for the apparent oxidation level of phosphorus in hypophosphite + $3/2 n$ for the apparent oxidation level in phosphite) had been transferred to the anode. Of course, a complete analysis for all the possible products (including phosphorus itself) of the various disproportionation-decomposition reactions of $P_n O_m H_q$ would show the true number of electrons transferred, but even this information would not show the primary electrode reaction, that is, the electron-transfer step.

Chemical analysis of the products of phosphorus oxidation is another limiting factor in this research program. The mono-phosphorus oxyacids and salts can be determined quantitatively, and some of the known di-phosphorus oxyacids can be detected qualitatively. However, there is some overlap on these analyses; that is, some of the di-phosphorus oxyacids (and probably any tri-phosphorus oxyacids which are stable in aqueous media) are determined as various mono-phosphorus oxyacids, and there is no way of distinguishing them. At the present time, therefore, it is necessary to formulate any electrochemical

reactions of phosphorus in terms of the products which can be quantitatively determined, i.e., the mono-phosphorus compounds.

Taking all these limitations into account, then, the following were the specific objectives of this research program:

1. Development of suitable phosphorus electrodes
2. Measurement of half-cell potentials and polarization characteristics of these electrodes over broad ranges of electrolyte pH and concentration and over a more restricted range of temperature
3. Determination of the gross, overall electrochemical reactions of phosphorus at these electrodes by the following scheme:

- (a) Measure the rates of the spontaneous disproportionation-decomposition reactions of phosphorus with the aqueous electrolyte
- (b) Measure the total overall rates of reaction at the electrode at a known current density
- (c) Determine the rates of the electrochemical reactions from the differences between the rates of (a) and (b).

II. PHOSPHORUS ELECTRODE DEVELOPMENT

In this section a discussion of the criteria for satisfactory phosphorus electrodes is presented first, followed by an outline of the experimental techniques and apparatus used to make and test these electrodes. Presented next is a review of the different systems tested as electrode materials and a summary of the properties of the satisfactory electrode materials.

A. Design Criteria for Phosphorus Electrodes

Since white phosphorus is an electrical insulator (conductivity equals 4×10^{-7} mhos/cm) and is practically insoluble in water ($3.3 \times 10^{-4}\%$ at room temperature³¹), the formulation of phosphorus electrodes presents special problems. The high electrical resistance of phosphorus means that good contact between phosphorus and a conductor must be provided to reduce internal electrode resistances; the non-solubility of phosphorus in aqueous electrolytes means that there must be good three-phase contact between the phosphorus, the electrolyte, and conductor if the electrochemical reaction is to take place.

The mechanisms of electrochemical reactions of three-phase systems, e.g., gas-solid electrode-liquid electrolyte, are not well understood at the present time. Current hypotheses seem to indicate that in gas-solid-liquid systems, such as the oxygen or hydrogen electrodes in aqueous electrolytes, the reacting gas must first go into solution in the electrolyte and then react in solvated form at the liquid-solid interface.^{63,64,65} Another hypothesis⁶⁶ is that the reacting gas adsorbs on the solid electrode at the three-phase interface and then migrates in the adsorbed form along the solid surface until it enters

into the electrode reaction. In neither of these cases is it felt that the electrode reaction can be restricted to the linear three-phase interface between reactant gas, liquid electrolyte, and solid conductor; however, because of the obvious difficulties involved, apparently no analysis has ever been made of just where, physically, such an electrochemical reaction can take place on an electrode. For this reason, the criteria for formulating a satisfactory phosphorus electrode must be only qualitative at this time.

Regardless of whether phosphorus enters an electrochemical reaction at the three-phase interface or migrates either as a dissolved species through the electrolyte or as an adsorbed species along the electrode surface before entering the reaction, it appears that the amount of linear three-phase interface between phosphorus, electrolyte, and conductor is very important for a successful electrode. In the first case, increasing the three-phase interface increases the reaction zone; in the other cases, increasing the three-phase interface decreases the migration path of either the dissolved or the adsorbed reactant. Therefore, the first consideration in preparing a satisfactory phosphorus electrode is the problem of maximizing the interface between phosphorus, the electrolyte, and the conductor.

In general, the maximum amount of three-phase interface at the electrode surface will be provided when phosphorus preferentially wets the solid conductor; that is, the contact angle, θ , is less than 90° , as shown in Figure 1(a). In this case, instead of three-phase contact occurring only at the points of tangency of the non-wetting phosphorus spheres (Fig. 1b) and the conductor particles, the contact between

phosphorus, electrolyte, and conductor follows the contour of the particles exposed at the electrode surface. Interfacial tensions have not been reported for the phosphorus-water system, nor for any system of phosphorus and a solid conductor, so it was necessary to determine experimentally which conductors are wet preferentially by phosphorus under various aqueous electrolyte solutions. The results of this investigation are given in a later part of this section.

Fig. 1. The Three-Phase Interface Between Phosphorus, Aqueous Electrolyte, and Solid Conductor (a). Preferential Wetting of the Solid by Phosphorus; (b). Preferential Wetting of the Solid by Aqueous Electrolyte

Electrical conductivity is another important criteria for evaluating phosphorus electrodes. This is usually not a severe problem if the conductor is a continuous phase; for example, a mercury pool, a metal screen, or a perforated or sintered-metal plate. However, if materials such as metal or graphite powders are used as conductors, it is necessary to ensure that there is some physical contact between the conductor particles; i.e., a conducting path through the electrode must be maintained. This means that if powdered metal or graphite is to be used, the resulting electrode must consist of phosphorus dispersed throughout a metal (or graphite) matrix, not metal particles dispersed in phosphorus. This puts an upper limit upon the phosphorus-to-conductor ratio for a given electrode and may, therefore, have an effect on some practical applications.

Another criteria for good phosphorus electrodes is their internal geometry with respect to possible mass transfer limitations. For example, if a porous sintered-metal disk impregnated with solid phosphorus is used as an electrode, as the phosphorus is consumed, the diffusion path for both the electrolyte reactants and the reaction products becomes longer and longer. In this case, mass transfer can very easily become the limiting process. One solution to this problem is to use a powdered metal as the porous conducting matrix, with phosphorus as the binding agent. Then, as the phosphorus is consumed in the electrode reaction, the uncovered matrix structure collapses and can be swept away from the electrode surface. This results in a nearly planar phosphorus electrode surface and minimizes mass transfer problems. Another method of reducing internal mass transfer limita-

tions in the electrode is to use phosphorus in the liquid state; it can then be circulated through a fixed porous conductor, or it can be mixed with a powdered metal and the resulting slurry stirred to constantly renew the electrode surface. Obviously, this criteria for electrode design is strictly dependent upon the conditions of the specific practical application of the electrode.

B. Techniques of Making and Evaluating Phosphorus Electrodes

The phosphorus used in all the experiments in this research project was N. F. - grade white phosphorus which was re-purified just before using. White phosphorus tends to take on a yellowish cast when it is under water for long periods of time; this discoloration is caused by the formation of phosphorus oxides at the surface, due to the slow disproportionation reactions of phosphorus with water, and by very small amounts of red phosphorus, formed by an ultraviolet-radiation-catalyzed transition from white phosphorus. An effective means of re-purifying white phosphorus consists of immersing it in a hot dilute solution of sulfuric acid and sodium dichromate for several hours, followed by extensive washing with distilled water.

Immediately after being purified, white phosphorus was mixed with the conducting material being tested. (All operations with white phosphorus, including transfer between vessels, mixing, and examination of the final electrode, must be carried out under water, of course, to prevent spontaneous combustion with air.) Visual examination was normally sufficient to determine whether phosphorus wet the surface of the conductor; if the conductor being tested was in powder or granular form, a uniform slurry was formed if the phosphorus preferentially wet

wet the surface, while a non-uniform mixture of small spheres of phosphorus dispersed in the conductor powder resulted if the surface of the conductor was not wetted. In the cases of metal screens and metal and graphite plates, observation of the contact angle at the phosphorus-metal-water interface indicated whether the conductor was preferentially wetted by the phosphorus. In a very few cases, microscopic examination was necessary to ascertain whether the phosphorus wet the conductor.

If phosphorus did not preferentially wet the conducting material under water, mixing was then tried under both acidic and alkaline solutions. However, in no case was it found that the pH of the electrolyte had a noticeable effect on the wetting characteristics of any of the phosphorus-conductor combinations tested.

Some metal amalgams were tried as conducting materials in phosphorus electrodes. These amalgams were made either by direct mixing with mercury or by displacement of mercury ions from mercury sulfate or nitrate solutions in dilute sulfuric or nitric acid, respectively.

Only those electrodes in which phosphorus preferentially wet the conductor surface were tested further. In the cases of powdered or granulated conductors, porosity measurements were made by regular water-saturation tests; in addition, the volume of phosphorus required to saturate the porous electrodes formed from these powders was determined. Electrical conductivities were measured on the dried electrodes under nitrogen blankets at temperatures below the melting point of phosphorus. Conductivities were measured on samples 1-cm

square and 2- to 5-cm long, capped at either end by metallic plates which were connected to a Triplet Model 630 volt-ohm-meter. Conductivities of slurry electrodes, above the melting point of phosphorus, were measured by containing the slurry in small glass cylinders with movable metal pistons on either end attached to the ohmmeter.

C. Summary of Phosphorus Electrodes

In the preliminary studies made in this research program, the phosphorus electrodes consisted simply of liquid or solid phosphorus in which a perforated graphite plate or a silver or platinum screen was immersed or imbedded. Other preliminary experiments were made with liquid phosphorus percolating through a series of tightly-stacked silver screens. In all of these experiments, the potentials measured were unstable (that is, fluctuating in time), and polarization data for the electrodes were not reproducible, either for the same electrode in consecutive runs or for duplicate electrodes in separate experiments. This behavior was found to be caused by the instability of the phosphorus-conductor-electrolyte interface; stabilization of this interface, by using a conductor whose surface was wetted by phosphorus, resulted in stable reproducible phosphorus electrodes.

Attempts were made using the techniques described in the preceding section to make phosphorus electrodes with the following metal powders: Ag, Cu, Fe, Sn, Pb, Zn, and Ni. Phosphorus does not preferentially wet any of these metal powders immersed in acidic, alkaline, or neutral aqueous solutions. One attempt was made to coat a fine silver powder with phosphorus by first dissolving the phosphorus in carbon disulfide, slurring the solution with the silver powder, and then stripping off

the carbon disulfide under a nitrogen blanket. In the resulting electrode, the silver powder appeared visually to be uniformly coated with phosphorus; however, microscopic examination (80x magnification) showed instead that minute, shiny globules of phosphorus were dispersed and imbedded in the silver powder matrix. Other attempts made to wet silver, nickel, and platinum screens with phosphorus were unsuccessful.

Since mercury shows a slight solubility in liquid phosphorus,³³ it was believed that phosphorus might preferentially wet a mercury surface under aqueous electrolytes, and such was found to be the case. When a drop of liquid phosphorus is placed on a mercury-water interface, the phosphorus spreads over the mercury, showing a contact angle of less than 90° . This is probably a purely physical phenomenon stemming from the same forces which make mercury slightly soluble in phosphorus. Although some mercury-phosphorus compounds are known to result from the reactions of mercuric salts with phosphine,⁶⁷ apparently there is no direct reaction between the elements;³ for this reason, the wetting of mercury surfaces by phosphorus is thought to be physical rather than chemical in nature.

Since a drop of liquid phosphorus on a mercury-electrolyte interface actually has only a very small amount of three-phase interface (that is, the circumference of the phosphorus drop), it is necessary to use a solid amalgam as a matrix to provide sufficient contacting between phosphorus, electrolyte, and conductor. One such device tried was a silver screen which had been coated with a thin film of mercury and which was placed flat on the phosphorus-electrolyte interface so that there was three-phase contact around the periphery of each individual

mesh. The advantage of this mesh electrode, in theory, was that the amount of three-phase interface was known quite accurately; the disadvantages were that the interface was still not very large for a mesh of reasonable size and the screen, weakened by the dissolution of much of the silver in the amalgam, was quite fragile. In addition, for the case of liquid phosphorus, it was very difficult to maintain the screen in proper position at the phosphorus-electrolyte interface; the screen tended to be swamped by the phosphorus, especially if there was much stirring or agitation in the electrolyte compartment.

The same limitations of amalgamated screens were found to apply to porous silver plates which had been coated internally with mercury. The amalgamation process itself was very difficult to control; displacement of mercury ions from solution could not provide internal coatings of mercury thick enough to result in wetting by phosphorus, while direct amalgamation with liquid mercury weakened the porous structure to the point of collapse. Furthermore, maintenance of a stable interface within the porous plate was found to be nearly impossible. For these reasons, amalgamated porous metal plates were not used in this work.

Since amalgam screens and porous plates were found generally unsatisfactory as phosphorus electrodes, the next attempts at making a solid amalgam matrix were with metal powders. These metal powders were amalgamated either by direct contact with liquid mercury (Ag and Sn powders) or by displacement of mercurous ion from acidic solutions (Zn, Sn, Cu, Fe, and Ni powders). Of all these powder amalgams, only the silver-mercury compound was wetted by phosphorus under the experimental conditions outlined in the preceding section. In addition

to the silver-amalgam powder, copper wire with a thick coating of mercury was also wetted by phosphorus; however, because of the difficulties noted above in using wire-screen amalgams, no further work was done with the copper-mercury system.

After the initial studies showed that phosphorus did wet silver amalgam powder, further tests were made to determine the minimum Hg : Ag ratio necessary before wetting occurred; these studies showed that at least 0.5 grams of mercury per gram of silver is required to form an electrode with the phosphorus distributed uniformly through the matrix. The properties of the silver-amalgam electrode selected as a standard for use in subsequent experiments are shown in Table VI. A microscopic photograph of the surface of the standard silver-amalgam electrode is shown in Figure 2(a); the light-colored, reflecting areas in this photograph are phosphorus, the gray and black areas, silver amalgam; note the large amount of three-phase interface present in this electrode.

In addition to the work done with metal powders and metal amalgams, some studies were made of phosphorus electrodes with graphite as the conducting matrix. It was found that phosphorus would preferentially wet coarsely ground graphite (mean particle diameter approximately 0.5 mm) after the graphite had been mixed with concentrated nitric acid and then thoroughly washed in distilled water. The properties of the electrode formulation used in the standard phosphorus-in-graphite-matrix electrode are given in Table VII. A microscopic photograph of this electrode is shown in Figure 2(b). In this photograph the light-colored, highly reflective areas are

(a)

100 μ

(b)

100 μ

ZN-4411

Fig. 2.

Table VI. Properties of the Standard Silver-Amalgam Phosphorus Electrodes

Ag/Hg Ratio : 1.00g/g	
Ag Powder Particle-Size Distribution:	
<u>Size, mm</u>	<u>wt%</u>
< 0.175	16
0.175 - 0.246	13
0.246 - 0.420	27
0.420 - 0.589	26
0.589 - 0.833	18

Electrode Porosity: 63% Void Volume
Phosphorus Content at Saturation (60°C): 0.25g P ₄ /g total electrode
Electrode Specific Volume (saturated at 60°C): 0.23 cc/g total electrode
Electrode Resistivity: 0.1 ohm cm

phosphorus; the gray areas are the graphite matrix.

In Figure 3(a) and (b) are shown the results of attempts to make a phosphorus-in-graphite electrode with very fine (mean particle diameter approximately 0.1mm) graphite powder. Instead of phosphorus in a graphite matrix, the inverse system, graphite particles dispersed in a phosphorus matrix, was formed. This electrode was macroscopically homogeneous in texture and slate gray in color, having the appearance of soft graphite or molybdenite. However, the electrical resistivity of the material was quite high (20 ohm-cm), and there seemed to be an

$\overline{100\mu}$

(a)

$\overline{100\mu}$

(b)

ZN-4412

Fig. 3.

Table VII. Properties of the Standard Phosphorus-in-Graphite-Matrix Electrode

Graphite Powder Particle Size Distribution:

<u>Size, mm</u>	<u>wt %</u>
< 0.175	11
0.175 - 0.246	10
0.246 - 0.420	16
0.420 - 0.589	15
0.589 - 0.833	26
> 0.833	22

Electrode Porosity: 65% Void Volume

Phosphorus Content at Saturation (60°C): 0.58 g P₄/g Total Electrode

Electrode Specific Volume (saturated at 60°C): 0.52 cc/g Total Electrode

Electrical Resistivity: 3 ohm cm

upper limit to the amount of graphite which could be occluded in the phosphorus matrix. For these reasons, this electrode was not considered to be useful in these studies.

The two electrodes discussed above, phosphorus in a silver-amalgam-powder matrix and phosphorus in a graphite matrix, were chosen for use in further studies because they showed qualitatively large amounts of three-phase interface, had reasonably low resistivities, were reproducible, and were relatively easy to make. At the present time, the reasons why white phosphorus wets or does not wet certain amalgams are not known. In certain cases, such as silver and copper, it appears that if the film of mercury at the solid metal surface is thick enough, wetting will occur.

On the other hand, some amalgams will not be wet by phosphorus regardless of the thickness of the liquid amalgam film. For example, tin forms completely liquid amalgams very easily, and yet these were found not to be wetted by phosphorus under any circumstances. Gallium, the other metal besides mercury which is liquid near room temperature, is not wetted by phosphorus,⁶⁸ so apparently the phenomenon is not specific to liquid metals. Miller²¹ and Price and Gordon²⁰ have reported the phenomenon of "wicking" (that is, creeping up a planar surface) of liquid white phosphorus on certain metals during the cathodic reduction of phosphorus to phosphine. They report this phenomenon may or may not occur at open-circuit conditions in the cell, but always occurs when current is passed. The cause of this may be a shift toward the electrocapillary maximum⁶⁹ of the metal electrode as the electrode is polarized when current is passed; the change in the interfacial tension of the electrode-electrolyte system may be such that phosphorus can displace the electrolyte from the electrode surface. This phenomenon was not observed in the present experiments.

III. PHOSPHORUS ELECTRODE POTENTIALS AND POLARIZATION

The first part of this section describes the experimental apparatus and techniques used to measure half-cell potentials and polarization characteristics for phosphorus electrodes and phosphorus-compound electrodes. Next, the results of measurements of the half-cell potentials of these electrodes are presented, and then, finally, the results of polarization experiments with these electrodes are given.

A. Experimental Apparatus and Techniques

A simplified diagram of the apparatus used in these experiments is presented in Fig. 4. The component parts of this apparatus (the reference electrodes, the electrochemical cell itself, and the voltage- and current-measuring apparatus), together with the techniques for using them in these experiments, are described in the following paragraphs.

1. Reference Electrodes

Two different types of reference electrodes were used in these experiments: a calomel-saturated potassium chloride electrode for acidic solutions and a mercury-mercuric oxide electrode for alkaline solutions. The calomel electrodes used were Beckman Model 39270, with a fiber junction between the external solution and the internal solution of saturated potassium chloride. Beyond this precaution, no attempts were made to compensate for errors (estimated to be less than 0.02V) introduced by liquid-junctions. The calomel electrodes, when measured against each other, proved to be consistent within two millivolts and to be stable within the same limit over periods of several hours.

The mercury-mercuric oxide electrodes used in alkaline solutions are pictured in Fig. 5(a). These electrodes consisted of a 3-mm I.D.

MU-34602

Fig. 4.

MU-34603

Fig. 5.

glass tube sealed into one half of a ground glass joint. The upper end of the glass tube was expanded into a bulb approximately 5-mm I.D. and 5-mm long, containing a small opening approximately 1-mm in diameter. Sealed in the other end and extending about one-half the way up the tube was a 20 gauge platinum wire, used as a lead to the external circuit. The glass tube was filled with mercury to within about 2-mm of the top; the remaining volume at the top was then filled with a slurry of mercuric oxide in the alkaline solution to be used in subsequent experiments. The electrode was then allowed to stand immersed in the appropriate alkaline solution for eight hours or more before using. After this period of stabilization, these electrodes were found to be reproducible within limits of ± 2 millivolts and were within 5 millivolts of the theoretical standard potential, as measured against a calomel electrode connected through a salt bridge to the mercury-mercuric oxide electrode. This error is within the range of uncertainty of the standard potential caused by deviations of the hydroxyl-ion activity coefficient from unity and also is well within the range of accuracy needed for this work. In addition to being reproducible and relatively easy to prepared, these electrodes were found to be insensitive to mechanical vibrations, a quality not shared by many reference electrodes using large pools of mercury.

Either the mercury-mercuric oxide or the calomel electrode was inserted in a reference-electrode cell (Fig. 5(b)) during measurements of electrode potentials. This cell was connected through a stop cock and glass tubing to a capillary probe which was inserted into the main cell and which terminated within 2-mm of the surface of the phosphorus electrode. Vacuum and nitrogen lines were connected through valves to the reference-electrode cell so that it was possible to fill the capillary probe and reference-electrode compartment with electrolyte from the main cell, or, conversely,

to flush them with fresh solution into the main cell. In this way, for alkaline solutions, the reference electrode was immersed in the same electrolyte as the phosphorus electrode, and therefore liquid-junction potentials were avoided.

2. Electrochemical Cell

The electrochemical cell used for phosphorus-electrode potential and polarization measurements, as well as for chemical and electro-chemical reaction rate studies, is shown in Fig. 6. After liquid phosphorus was mixed with the conducting matrix material (for example, silver-amalgam powder) under distilled water in an exterior container, the resulting slurry was cooled to below the ignition point of phosphorus, 38°C, and transferred, still under distilled water, into the assembled electrochemical cell. The cell was then heated until the phosphorus was again liquid, and the electrode slurry was tamped into a compact mass on top of the silver screen at the bottom of the electrode. The silver screen, which acted as a current collector for high-resistance electrodes, was attached by a silver nut to a threaded silver rod, which extended through a sealed glass joint to the exterior of the cell, where it was connected to the external circuit. When the electrode had been packed so as to form a smooth, planar surface, the temperature was again lowered to well below the ignition point. The cell was purged with nitrogen gas, the excess water was removed from above the phosphorus electrode, and the electrolyte solution (previously sparged with nitrogen to remove dissolved oxygen) was added to the cell. If the reaction between the phosphorus and the electrolyte was rapid, the reference-electrode compartment and capillary probe were pre-filled with the electrolyte in order to keep reaction products from contaminating the reference electrode; otherwise the capillary and reference-electrode

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Fig. 6.

compartment were filled with electrolyte from the main cell.

The counter-electrode compartment was separated from the main cell by a side arm 1.5-cm in diameter and 12-cm long. This arm contained a sintered glass filter disk (Pyrex, fine porosity) which reduced convective mass transfer between the compartments and kept both the cathode gas from inadvertently entering the main cell and phosphorus droplets or metal powder from entering the counter-electrode cell. Since some of the concentrated alkaline solutions used in these experiments attacked this filter disk rather severely over the course of an experiment, it was necessary to modify the side arm to simplify replacement of these disks. This was done by using glass flanges whose faces had been ground flat; the filter disk and a concentric outer guard ring were sandwiched between two silicon rubber gaskets and then were clamped between the flanges. This arrangement was found to be quite satisfactory in all experiments.

Because of the odd geometry of this cell, it was feared that the potential might not be constant across the electrode due to large variations in current density in the electrolyte. However, a numerical solution⁷⁰ of the LaPlace Equation for this geometry showed that the variations in the potential across the electrode would be negligible, less than one millivolt.

In any practical application of electrochemical oxidation of phosphorus, the counter electrode would be an oxygen or other oxidizing-gas electrode; however, in this work it was decided that the difficulties in operating a phosphorus electrode would be great enough without adding the complexities and vagaries inherent in oxygen electrodes. For this reason, the counter electrode in these experiments consisted simply of a tightly-rolled cylinder of nickel screen at which hydrogen was evolved when a current was passed between the electrodes. The behavior of the phosphorus

electrode, of course, was not dependent upon the specific reaction taking place at the counter electrode.

Agitation in the electrochemical cell was provided by a vibrating disk attached to an electric vibrator (Vibro-MischerTM) external to the cell. The shaft connecting the disk and the vibrator passed out of the cell through a tightly fitting silicon rubber diaphragm which was tightly clamped to the cell by means of a flange. The vibrator operated at a frequency of 60 cps, and the displacement was so small (1-2 mm) that the rubber diaphragm flexed with the shaft, providing a gas tight seal; the intensity of agitation was increased by increasing the displacement of the vibration. This agitator provided very effective convective mass transfer at the electrode surface, as will be shown later in the section discussing chemical reaction rates of phosphorus. For the present work on the phosphorus electrode, it was found that increasing the rate of stirring at any given current density did not change the amount of electrode polarization, and, therefore, the electrode processes were not limited by mass transfer in the electrolyte.

Other ports in the electrochemical cell were used for withdrawal of liquid samples and for collection of any anode gas produced; an outlet was also provided in the counter-electrode compartment for removal of cathode gas. The temperature of the electrolyte in the electrochemical cell was monitored by a thermocouple inserted in the hollow shaft of the agitator and connected to a recording potentiometer. The entire cell, except the reference-electrode compartment, was immersed in a stirred-water bath; the temperature of the water bath was controlled to within $\pm 0.1^{\circ}\text{C}$ of the desired temperature.

3. Potential- and Current-Measuring Apparatus

The measuring- and polarizing-circuits used in these studies of the phosphorus electrode are shown in Fig. 7. The potential between the phosphorus and reference electrodes was measured by a vacuum tube voltmeter⁷² with an input impedance of 10^{14} ohms; the output from the VTVM was reduced by a voltage divider, and the reduced voltage was fed into a recording potentiometer.⁷³ In the circuit then, the VTVM functioned as a high-impedance unity-gain preamplifier. The voltage divider had a total resistance of 5.00 M Ω and had branches of 2.50 and 6.33 K Ω . The recording potentiometer had two scales; 0-1mv, and 0-10mv. This combination of voltage dividers and potentiometer scales allowed recording cell potentials from 0 to 20 volts in four ranges: 0 - 0.8v, 0 - 2v, 0 - 8v, and 0 - 20v. The potential between the phosphorus electrode and the counter-electrode could be measured by switching the input terminal of the electrometer from the reference electrode to the counter electrode. The VTVM was standardized before and during each experiment by a standard Weston cell. The recording potentiometer could be read to the equivalent of 0.01v on the 0 - 2.00 v scale, and the accuracy of the resistors used in the voltage divider was $\pm 1\%$. Since the VTVM was not read directly, but was used only as a high-impedance preamplifier, the major sources of error in its operation was the zero-point drift, which was claimed to be within 1 mv per hour. Therefore, the relative accuracy of the potential measurements was within $\pm 2\%$, and the absolute precision of the readings was 0.01v.

The polarizing circuit consisted of a D.C. power supply,⁷⁴ a variable resistor, and a current-recording device, all in series between the phosphorus electrode and the counter electrode. The power supply had a

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Fig. 7.

range of 0 - 50 v at 0 - 1.5 amps. The variable resistor consisted of a 1-K Ω wire-wound rheostat in series with a 4-decade, 0 - 10 M Ω resistance box with steps of 1 K Ω . The cell current was increased both by increasing the potential of the power supply to the 50-volt maximum and by decreasing the resistance of the variable resistor. The current-measuring device consisted of a recording potentiometer⁷³ which measured the potential drop across a known resistance in the polarizing circuit. For currents up to 10 ma, carbon-film resistors with $\pm 1\%$ accuracy were used; for higher currents, a precision shunt box⁷⁵ was used. The ranges of currents which could be measured and recorded extended in decades from 0 - 0.1 μ a to 0 - 10 ma, using the precision resistors, and from 0 - 10 ma to 0 - 1 amp, using the precision shunt box. The recording potentiometer could be read to 0.5% of full scale, while the accuracy of the shunt box was within $\pm 0.02\%$; therefore, the accuracy of the measurement was $\pm 1\%$ up to 10 ma and less than $\pm 1\%$ for higher currents, while the absolute precision was 0.5% of the full-scale reading.

B. Summary of Electrode Potentials

The first part of this section presents the half-cell potentials of phosphorus electrodes measured under various experimental conditions, while the second part presents half-cell potentials measured for some phosphorus compounds of interest in this study.

1. Phosphorus Electrode Potentials

The half-cell potentials measured for phosphorus electrodes under various conditions are presented in Table VIII. These half-cell potentials are all reported relative to the standard hydrogen electrode: that is, the reaction, $H_2 = 2H^+ + 2e^-$, with the hydrogen ion at unit activity, the hydrogen gas at one atmosphere fugacity, and the temperature at 25°C.

Table VIII. Phosphorus Electrode Potentials

Electrode Configuration	Temperature, °C	Electrolyte	Concentration, $\frac{\text{moles}}{\text{liter}}$	Half-cell Potential (rel. to Std H_2), V
Standard silver-amalgam powder matrix	60°	NaOH	10.0	1.08
"	60°	NaOH	1.0	0.90
"	40°	NaOH	10.0	1.07
"	40°	NaOH	1.02	0.89
"	40°	NaOH	0.100	0.83
"	40°	NaOH	0.010	0.5
"	40°	Na_2SO_4	0.50	0.28
"	40°	Na_2SO_4	(pH = 5.5)	
"	40°	H_2SO_4	0.5	
"	40°	H_2SO_4	0.0050	0.18
"	40°	H_2SO_4	0.050	0.13
"	40°	H_2SO_4	0.49	0.08
"	40°	H_2SO_4	4.95	0.00
Graphite Matrix	40°	NaOH	1.02	0.89
"	40°	Na_2SO_4	0.50	-0.09
"	40°	Na_2SO_4	0.50	
"	40°	H_2SO_4	0.00525	0.00
"	40°	H_2SO_4	0.049	0.03
"	40°	H_2SO_4	0.485	0.04
"	40°	H_2SO_4	4.90	0.02

Only the potentials of phosphorus in the silver-amalgam-matrix and graphite-matrix electrodes are presented here; the potentials measured for other electrode configurations are presented in Appendix A. In general, the values reported in Table VIII were steady-state potentials obtained over a period of several hours and were reproducible for identical electrodes under the same conditions.

The temperature dependence of the phosphorus electrode appears to be small, a change of less than 0.01v for a temperature change of 20°C. Actually, this variation is within the accuracy of the experimental measuring devices, so this result is not significant. For purposes of comparison, the entropy change for the reaction,

is estimated to be equivalent to 0.52 mv/°C, at 25°C, which would result in a change in the half-cell potential of about 0.01v for a temperature change of 20°C. Therefore, it is evident that the accuracy in this work is not sufficient for estimation of the changes in entropy accompanying the electrode reactions.

The effect of hydroxyl-ion concentration in the electrolyte on the phosphorus electrode potential is shown in Fig. 8. In this figure, the half-cell potential of phosphorus in the standard silver-amalgam powder matrix is plotted as a function of the logarithm of the activity of the hydroxyl ion. The activities were calculated using the stoichiometric mean molal activity coefficients of sodium hydroxide compiled by Parsons.⁷⁶ The dashed line in Fig. 8 is a reference line of slope RT/F (0.0621 volts) drawn through the point corresponding to a 1.0 molar NaOH solution. The deviations from this line are not large for solutions which are fairly

acidic or alkaline, with the exception of 10 N NaOH. The deviation in this case may be partly due to deviations of the stoichiometric mean activity coefficient of sodium hydroxide from true activity coefficient of the hydroxyl ion and partly from departures of the mercury-mercuric oxide reference electrode from ideal behavior in highly caustic solutions. The large deviations of the electrode potentials in neutral and weakly alkaline solutions are unexplained. In the case of neutral solution (Na_2SO_4 , $a_{\text{OH}^-} = 10^{-8}$ molal) the production of hydrogen ions by the reactions,

could shift the hydroxyl ion activity several orders of magnitude to the left. In this specific experiment, after 1485 minutes the H_3PO_2 and H_3PO_3 concentrations were less than 0.0006 and 0.002 molar, respectively. This increase in hydrogen ion concentration would have shifted the hydroxyl-ion activity to about 10^{-11} , which would correspond to an even lower potential than that measured. However, this type of behavior would result in a half-cell potential initially at about 0.40v and then decreasing roughly logarithmically with time (assuming a zero-order, irreversible reaction, $E = 0.43 - 0.061 \log(3.2 + 1.75t)$) to a value of 0.23v at 1485 minutes, while the observed potential actually assumed the steady-state value of 0.28 volts within 2 minutes and stayed at this value ($\pm 0.01\text{v}$) for the remainder of the experiment.

For the case of the weakly alkaline solution, 0.010 molar NaOH, the reaction of phosphorus with the electrolyte would decrease the hydroxyl-ion activity by fifty per cent at the most, while shifts of several orders of

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Fig. 8.

magnitude are required to explain the low potential. In the actual experiment, the electrode potential started at 0.38v and increased to 0.48v within 50 minutes; the potential then stayed at this steady-state value for another 85 minutes until the end of the experiment. No attempt was made to duplicate this experiment, and the results remain unexplained. However, these experiments indicate the uncertainties inherent in measuring half-cell potentials in corroding-electrode systems.

The half-cell potential of the graphite-matrix phosphorus electrode in 1.0 molar NaOH is the same as the corresponding silver-amalgam electrode in the same solution, i.e., 0.89v. However in sulfuric-acid solutions, the potentials of the graphite-matrix electrodes are different from those of the corresponding silver-amalgam electrodes. In addition, the dependence upon the hydroxyl-ion activity is apparently different, reaching a minimum of -0.09v in neutral solution and then remaining fairly constant just above 0.00 v for the acidic solutions.

The significance of these potentials measured for phosphorus electrodes, together with the results of other measurements, will be discussed in more detail in the part of this report dealing with analysis and interpretation, Section VI.

2. Phosphorus-Compound Electrode Potentials

Because of the disproportionation-decomposition reactions of phosphorus with aqueous solutions, phosphine, hydrogen, and some of the lower oxyacids of phosphorus were present at the electrodes in these experiments. Therefore, tests were made to determine whether these compounds, by themselves or with products of their disproportionation-decomposition reactions, would establish potentials at the electrode. Silver-amalgam powder was used as the electrode in these experiments, immersed in the solution of the

material being tested. The measuring and polarizing circuits, the electrode cell, and the reference electrode were the same as described earlier in this section.

The potentials established at the electrode for acidic and alkaline solutions saturated with phosphine are shown in Table IX.

Table IX. Phosphine Electrode Potentials

Electrolyte Solution	Concentration, $\frac{\text{moles}}{\text{liter}}$		Temperature °C	Half-Cell Potential, V (rel. to Std. H_2)
	Electrolyte	PH_3^*		
NaOH	9.99	-	60°	1.12 ± .04
NaOH	1.00	0.0024	40°	0.94
H_2SO_4	0.49	0.0016	40°	0.11

* Saturation concentration of PH_3 . See Appendix B and Reference 53.

The behavior of the electrode potentials established in alkaline solutions of the lower phosphoric oxyacids is fairly complicated, as shown in Table X. Hypophosphite reacts quite readily with concentrated caustic solutions (say, 5 molar NaOH or more) to form hydrogen and phosphite, so the solution has constantly changing concentrations of hypophosphite and phosphite and, in addition, quickly becomes saturated with hydrogen gas. In the actual experiments, the electrode potential remained at its initial value (that is, the potential for the reaction, $\text{Hg} + 2\text{OH}^- = \text{HgO} + \text{H}_2\text{O} + 2\text{e}^-$) for a period of nearly sixty minutes after the addition of the hypophosphite to the solution. Then, after this initial induction period, the potential rose within another fifty minutes to its steady-state value, where it stayed for the remainder of the experiment. For cases of phosphite in 10 molar NaOH and hypophosphite and phosphite in 1.0 molar NaOH,

the disproportionation-decomposite reactions occurred very slowly, if at all, and the potentials of the electrodes remained at their initial values for the durations of the experiments.

Table X. Hypophosphite and Phosphite Electrode Potentials

Electrolyte Composition, $\frac{\text{moles}}{\text{liter}}$					Temperature °C	Half-Cell Potential, V (rel. to Std. H ₂)
NaOH	H_2PO_2^-		$\text{HPO}_3^{=}$			
	initial	final	initial	final		
10.0	0.050	0.004	0	0.05	60°	0.78
10.0	0	0	0.036	0.036	60°	*
5.84	0.043	0.014	0	0.03	60°	0.70
1.00	0.041	0.041	0	0	60°	*
1.00	0.096	0.096	0.11	0.11	60°	*

* The silver-amalgam powder electrode remained close to the Hg/HgO equilibrium potential

C. Polarization of Phosphorus Electrodes

The results of the anodic polarization of phosphorus electrodes in various media are shown in Figures 9 through 23. The current densities in these figures are based upon the planar geometrical surface area of the electrode-electrolyte interface, not the true surface area of the powder matrix nor the exposed surface area of the phosphorus. It should be emphasized that these polarization curves represent only an empirical relationship between current and potential for these specific electrode materials and electrode configurations. This polarization data is useful for comparison with rates of competing chemical reactions occurring at the identical electrode under the same conditions, and it may also be useful

for evaluating certain practical applications of the phosphorus electrode; however, it should not be used to determine general electrokinetic constants for the phosphorus electrode.

The effect of temperature on the anodic polarization of the silver-amalgam-matrix phosphorus electrode is shown in Figure 9. The electrodes initially used in these polarization studies had an excess of phosphorus over the amount required to fill the void volume of the porous matrix. It was found that this excess phosphorus affected both the rates of chemical reaction at the electrode and, as shown in Figure 10, the anodic polarization of the electrode. The standard silver-amalgam-matrix electrode which was used in subsequent experiments contained no excess phosphorus, but was 100% saturated (that is, the void volume of the porous matrix was completely filled with phosphorus).

In Figure 11, the anodic polarization of the standard silver-amalgam-matrix phosphorus electrode in 1.0 molar NaOH at 40°C is shown. The data are from five separate experiments and show the reproducibility of the standard electrode. Figures 12 through 17 show the anodic polarizations of the standard silver-amalgam-matrix electrode at 40°C in 0.10 molar NaOH, 0.50 molar Na₂SO₄ (pH = 5.5), 0.005 molar H₂SO₄, 0.05 molar H₂SO₄, 0.5 molar H₂SO₄, and 5 molar H₂SO₄, respectively.

The anodic polarizations of the graphite-matrix phosphorus electrode in 1.0 molar NaOH, 0.5 molar Na₂SO₄, 0.005 molar H₂SO₄, 0.05 molar H₂SO₄, 0.5 molar H₂SO₄, and 5 molar H₂SO₄ are shown in Figures 18 through 23. The major characteristics of these electrodes is their strong anodic polarization compared to that of the corresponding silver-amalgam-matrix electrodes, especially in neutral and acidic solutions.

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Fig. 9.

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Fig. 10.

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Fig. 11.

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Fig. 12.

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Fig. 13.

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Fig. 14.

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Fig. 15.

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Fig. 16.

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Fig. 17.

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Fig. 18.

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Fig. 19.

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Fig. 20.

MU-34619

Fig. 21.

MU-34620

Fig. 22.

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Fig. 23.

IV. PHOSPHORUS DISPROPORTIONATION-DECOMPOSITION REACTIONS

This section deals with the measurement of the rates of the various disproportionation-decomposition reactions of phosphorus in aqueous media. These rates were measured in order to determine the extent of participation of phosphorus in the electrode reaction. Ideally, the rate of anodic oxidation of phosphorus should be equal to the difference between the overall rates of the reactions occurring at the phosphorus electrode at a given current density and the rates of the disproportionation-decomposition reactions at the same electrode with zero current density. The influence of the presence of the electrode material on these reactions was determined by measuring the reaction rates of phosphorus both by itself and impregnated in the conducting matrix of the electrode. These studies were based on the following reactions in alkaline media,

and the corresponding reactions in acidic media. However, the rates measured were not those formulated on these specific reactions but, rather, were the rates of formation of the various products (hydrogen,

phosphine, and mono-phosphorus oxyacids) under specific experimental conditions.

The first part of this section describes the experimental apparatus and techniques used to measure these reaction rates, while the second part presents the rates measured for homogeneous reactions taking place in the solution, e.g., reaction (70). The reaction rates of phosphorus by itself in alkaline media are given in the third part, followed by the results for phosphorus impregnated in the electrode matrix in the final part of the section.

A. Experimental Apparatus and Techniques

The general procedure in these experiments was to immerse the phosphorus or phosphorus electrode in the aqueous solution under study and to measure the amounts of the various products formed as a function of time. The same procedure was used for the study of the homogeneous decomposition reaction of hypophosphite (reaction (70)), but no phosphorus was added to the cell. The reaction vessel used was similar to the cell shown in Figure 6 with the arms leading to the reference-electrode and counter-electrode compartments closed off. The procedure for introducing the phosphorus and the electrolyte into the cell was the same as used in the experiments described previously, except that after the addition of the electrolyte, the cell and gas-collecting system were momentarily purged with nitrogen gas to remove any residual oxygen. The product gases from the reactions were collected and measured by water displacement in glass cylinders of an appropriate size. Aliquot portions of these gases were then metered, also by water displacement, into smaller receivers

for chemical analyses. Samples of the solution were withdrawn from the cell by a hypodermic syringe connected to the sample-probe arm; a gas-tight seal at the connection was provided by a rubber serum-bottle cap, through which the hypodermic needle penetrated into the sample-probe. The total liquid sample removed from the cell was placed in a burette, from which aliquot portions were measured for the various chemical analyses.

A detailed discussion of the various chemical analyses used in this work, including procedures and limits of accuracy, is presented in Appendix B. In general, the following techniques were used: (1), phosphine was determined by scrubbing the product gas with saturated mercuric chloride solution and titrating the hydrochloric acid which was formed according to the reaction,

(2), hydrogen was determined as the difference between the total gas produced (corrected for water-vapor content) and the amount of phosphine, as determined above; (3), hypophosphite was determined by oxidation with cerate (Ce^{+4}) ion in sulfuric acid at 60°C ; (4), phosphite was determined by oxidation with iodine in neutral solution at room temperature; and (5), phosphate was determined as the difference between the total phosphorus present in the sample (obtained by oxidizing the entire sample with fuming nitric and perchloric acids and determining the resulting phosphate either by pH-titration of the first and second ionizing hydrogens of H_3PO_4 or by colorimetric analysis as the phosphomolybdate complex) and the amounts of hypophosphite and phosphite as determined above. The main interference in these analyses

was that by dissolved phosphine in the hypophosphite and phosphite determinations. However, this dissolved phosphine could be removed from solution by sparging the samples with nitrogen gas for a few minutes; the difference in the oxidation titers between the sparged and unsparged samples, then, was a measure of the amount of phosphine dissolved in the solution. Duplicate samples were taken for all of these analyses, and the results normally agreed within ten percent for the phosphate, five percent for the phosphine, and three percent for the phosphite and hypophosphite determinations.

The device used for stirring in the reactor cell was the same as that used in the potential-measuring experiments, i.e., a vibrating-disk agitator. Studies of the effectiveness of this agitation in the reactor cell, using limiting-current techniques, showed that mass transfer was not the rate-limiting process in this system. Details of this study are presented in Appendix C.

B. Decomposition Reactions of Hypophosphite and Phosphite Anions

The reaction rate constants for the reaction

under various experimental conditions are shown in Table XI. These rate constants are based on the equation:

$$(73) \quad - \frac{d(\text{H}_2\text{PO}_2^-)}{dt} = \frac{d(\text{HPO}_3^{2-})}{dt} = \frac{d(\text{H}_2)}{dt} = k_1(\text{H}_2\text{PO}_2^-)$$

Table XI. Rate Constants for the Decomposition Reaction of Hypophosphite

Electrolyte	Concentration <u>moles</u> <u>liter</u>	Temperature °C	k_1 min^{-1}	$k_1/(\text{OH}^-)^2$ $\text{molar}^{-2} \text{min}^{-1}$	$k_1/(a_{\text{OH}^-})^2$ * $\text{molal}^{-2} \text{min}^{-1}$
NaOH	10.0	60	6.0×10^{-3}	6.0×10^{-5}	0.74×10^{-5}
"	7.0	"	1.	2.	0.9
"	5.84	"	0.3	1.	0.7
"	1.00	"	0.04	---	---
NaOH	10.1	40	0.81	0.80	0.056
"	1.01	"	0.03	---	---
"	0.10	"	0.07	---	---
H ₂ SO ₄	0.049	40	0.004	---	---

* a = hydroxyl-ion activity from stiochiometric mean molal activity coefficient.

Other studies^{38,4} indicate the rate constant should be of the form,

$$(74) \quad k = \frac{k_1}{(\text{OH}^-)^2},$$

that is,

$$(75) \quad - \frac{d}{dt}(\text{H}_2\text{PO}_2^-) = k(\text{H}_2\text{PO}_2^-) (\text{OH}^-)^2,$$

so for purposes of comparison, k is also presented in Table XI. The presence of the electrode matrix (silver-amalgam powder or graphite) had no significant effect on these reaction rates. The method of calculating these rate constants is shown in Appendix D for a typical run.

The decomposition of phosphite,

was found to be immeasurably slow in 10.0 N and 1.0 N NaOH at 60°C in the presence of the silver-amalgam electrode matrix.

C. Disproportionation-Decomposition Reaction Rates of Phosphorus

The rates of production of hydrogen, phosphine, and hypophosphite from the disproportionation-decomposition reactions of phosphorus in alkaline media were measured at 60°C and 40°C in 0.05 N to 15 N NaOH solutions. The results of these measurements are presented in Table XII, and an example of a typical experiment and calculation is given in Appendix D. The rates given in Table XII are calculated from the expressions:

$$(77) \quad \frac{d}{dt}(\text{H}_2\text{PO}_2^-) = \frac{A r_{\text{H}_2\text{PO}_2}}{V} - k_1 (\text{H}_2\text{PO}_2^-)$$

$$(78) \quad \frac{d}{dt}(\text{H}_2) = \frac{A r_{\text{H}_2}}{V} + k_1 (\text{H}_2\text{PO}_2^-)$$

$$(79) \quad \frac{d}{dt}(\text{HPO}_3^{3-}) = \frac{A r_{\text{HPO}_3}}{V} + k_1 (\text{H}_2\text{PO}_2^-)$$

$$(80) \quad \frac{d}{dt}(\text{PH}_3) = \frac{A r_{\text{PH}_3}}{V}$$

$$(81) \quad \frac{d}{dt}(\text{PO}_4^{3-}) = \frac{A r_{\text{PO}_4}}{V}$$

where A is the surface area of the phosphorus, V is the volume of the solution in the reactor, and the rates, r, are expressed as millimoles/cm².min. In solutions more dilute than 5 N NaOH, the decomposition of hypophosphite is negligible, so in these cases, the last term in Eqn. (77) - (79) may be ignored. In solutions more concentrated than 0.5 N NaOH, the hydroxyl-ion concentration remained essentially constant during the length of these experiments; for more dilute solutions, the rates were found to be dependent upon the hydroxyl-ion concentration to roughly the first order.

The rates of formation of hypophosphite in these experiments were found to be reproducible generally within $\pm 0.1 \times 10^{-4}$ m mole/cm² min; the variations were greater for the other rates, up to about 0.4×10^{-4} for r_{PH_3} and to 0.5×10^{-4} for r_{H_2} in concentrated alkaline solutions.

The reason for the discrepancy in the phosphine rates is the relatively

Table XII. Phosphorus Disproportionation-Decomposition Reaction Rates

Electrolyte	Concentration moles/liter	Temperature °C	Rates of Formation, moles/cm ² min			
			$r_{\text{H}_2\text{PO}_2} \times 10^4$	$r_{\text{HPO}_3} \times 10^4$	$r_{\text{H}_2} \times 10^4$	$r_{\text{PH}_3} \times 10^4$
NaOH	15	60	1.4	-	0	0.28
"	10.1	"	2.2	-	0.9	0.68
"	5.0	"	5.4	-	2.6	1.7
"	2.0	"	11.2	-	6.5	3.2
"	1.0	"	13.0	-	6.4	3.3
"	0.50	"	11.7	-	5.6	2.5
"	0.10	"	4.	-	1.5	0.5
"	0.049	"	2.5	-	0.6	-
"	10.1	40	0.35	-	0.2	0.075
"	1.0	"	4.3	1.	2.3	0.85

high solubility of phosphine in dilute alkaline solutions. For the hydrogen rates the discrepancies arise from the method of calculation, wherein the hydrogen production rate is proportional to the difference between two large, nearly equal numbers. The rate of production of phosphite was determined only in 1.0 N NaOH at 40°C; for the other systems, the phosphite rate can be estimated as the difference between the rates (expressed in terms of milliequivalents rather than millimoles) of the oxidized compound, hypophosphite, and the reduced compounds, phosphine and hydrogen. The rate of formation of phosphate was not determined in these experiments, but as subsequent studies indicated, this rate was negligible.

D. Disproportionation-Decomposition Reaction Rates of Phosphorus Electrodes

The major effect of the electrode matrix on the disproportionation-decomposition reactions of phosphorus was to increase the rates by factors of from 3 to 40. The magnitude of this increase was found to be dependent upon the degree of saturation of the conducting matrix with phosphorus, as shown in Figure 24. That this increase in reaction rates was not a specific catalytic effect of the silver-amalgam matrix is shown in Table XIII, where the rates of disproportionation-decomposition of phosphorus are compared for both the standard silver-amalgam electrode and the standard graphite electrode. Figure 25 shows microscopic photographs of a phosphorus-graphite mixture immersed in 0.5 N NaOH; these photographs indicate that the bubbles of hydrogen and phosphine are formed almost entirely at the phosphorus-graphite-solution interfaces rather than on the phosphorus-solution interface (gray-white

areas). This would be expected, since the sharp corners and edges exposed at the three-phase interface are more conducive to bubble formation than is the nearly planar phosphorus-solution interface.

Table XIII. Comparison of the Rates of Phosphorus Disproportionation-Decomposition Reactions in Silver-Amalgam and Graphite Matrices (1.00 N NaOH, 40°C)

Matrix	Rates of Formation, $\text{mmoles/cm}^2\text{min}$				
	$r_{\text{H}_2\text{PO}_2}$	r_{HPO_3}	r_{PO_4}	r_{H_2}	r_{PH_3}
Silver-Amalgam	20×10^{-4}	5.4×10^{-4}	0	8.8×10^{-4}	4.0×10^{-4}
Graphite	20×10^{-4}	6.0×10^{-4}	-	8.6×10^{-4}	3.6×10^{-4}

The rates of the disproportionation-decomposition reactions of the standard phosphorus electrodes in sodium hydroxide and sulfuric acid solutions of varying concentration are shown in Table XIV. The reproducibility of these experiments varied from within 10% for most cases to about 20% for a few systems. The causes of these discrepancies were probably small variations in the original distributions of the phosphorus in the electrode matrices, although the procedures for making the electrodes were standardized as much as possible. A variation in one specific experiment was particularly disturbing; this was a sudden change in the reaction rates of the phosphorus-silver-amalgam system in 1.0 N NaOH at 40°C. The rates of formation of all the products were constant for the first 600 minutes of the experiment,

MU-34622

Fig. 24.

100 μ

(a)

100 μ

(b)

ZN-4413

Fig. 25.

Table XIV. Disproportionation-Decomposition Rates of Phosphorus Electrodes

Matrix	Phosphorus, $\frac{g}{g}$ Matrix	Electrolyte	Concentration moles/liter	Temperature °C	Rates of Formation, $\frac{mmoles}{cm^2 min} \times 10^4$				
					$r_{H_2PO_2}$	r_{HPO_3}	r_{PO_4}	r_{H_2}	r_{PH_3}
Silver-Amalgam									
Powder	0.51	NaOH	10.0	60	10	1	-	3	3.1
"	0.32	"	1.00	60	87	22	-	38	21
"	0.51	"	9.9	40	2.8	1 [†]	-	2	0.8
"	0.33	"	1.02	"	20	5.4	0	8.8	4.0
"	"	"	0.100	"	3.4	1.1	0	0.8	1.7
"	"	Na ₂ SO ₄	0.5	"	0*	0	0	0	0
"	"	Na ₂ SO ₄	0.5	"	0	0	0	0	0
"	"	H ₂ SO ₄	0.0050	"					
"	"	H ₂ SO ₄	0.049	"	0	0	0	0	0
"	"	"	0.49	"	0	0	0	0	0
"	"	"	4.95	"	0	0	0	0	0
Graphite	0.76	NaOH	1.03	"	20	6.0	0	8.6	3.6
"	"	Na ₂ SO ₄	0.5	"	0	0	0	0	0
"	"	Na ₂ SO ₄	0.5	"	0	0	0	0	0
"	"	H ₂ SO ₄	0.0053	"	0	0	0	0	0
"	"	H ₂ SO ₄	0.049	"	0	0	0	0	0
"	"	"	0.485	"	0	0	0	0	0
"	"	"	4.95	"	0	0	0	0	0

* $r = 0.2 \times 10^{-4}$ mmoles/cm²min

† estimated

but then the rates increased rapidly during the next 100 minutes or so, finally becoming relatively constant again at over twice their original magnitude. These higher rates prevailed for a period of 700 minutes, until the end of the experiment. The product concentrations in these anomalous experiments showed neither an exponential nor a quadratic dependence upon time, as would be expected if the reactions were autocatalyzed or catalyzed by an intermediate, respectively. Rather, the data seemed to fit two equations, both linear in time, which intersected at the 600-minute point. Because of the restricted objectives of this study, only the rates determined in the first portion of this experiment (which were reproducible within 10%) are tabulated in Table XIV.

The limits of error in the phosphate analysis in these experiments resulted in an uncertainty of about 0.5×10^{-4} mmoles/cm²min in the measured rate of formation of phosphate; however, since no definite trends were established (that is, the deviations of the rate from zero within each experiment appeared random), it was concluded that the rate of formation of phosphate was negligible in all systems studied.

V. PHOSPHORUS ELECTRODE COULOMETRY

This section describes the coulometric studies made with phosphorus electrodes under various conditions. Coulometry, in this case, means relating the rate of formation of various products of the electrochemical reaction to the equivalent rate of electrons flowing through the electrode, that is, to the current density at the electrode surface. The experimental apparatus and techniques used in these studies are described in the first part of the section, while the results of the coulometric measurements made with phosphorus electrodes in alkaline and acidic media are presented in the last part.

A. Experimental Apparatus and Techniques

In these experiments, the phosphorus electrode was immersed in the electrolyte solution under study, a known current was passed between the phosphorus electrode and the counter electrode, and the amounts of the various products formed were measured as a function of time. The reaction vessel shown in Figure 6 and the current and potential measuring and recording circuits shown in Figure 7 were used. The procedure for preparing the phosphorus electrode and the electrochemical cell, the sampling techniques, and the chemical analyses for the products formed were all as previously described in Section IV-A. The gas liberated at the cathode, hydrogen, was collected and measured as a check on the recorded current density in the cell. Usually, no current was passed for about 100 minutes after the experiment began, to check the initial rates of the disproportionation-decomposition reactions of the phosphorus electrode; the experiments

Table XV. Phosphorus Electrode Coulometry (Standard Silver-Amalgam-Matrix Phosphorus Electrodes)

Electrolyte	Conc. Molar	Temp. °C	Applied Current Density meq/cm ² min x 10 ⁻⁴	Rates of Formation, meq/cm ² min, x 10 ⁴									
				--(With Applied Current Density)--					--(With Zero Current Density)--				
				r _{H₃PO₂}	r _{H₃PO₃}	r _{H₃PO₄}	r _{H₂}	r _{PH₃}	r _{H₃PO₂}	r _{H₃PO₃}	r _{H₃PO₄}	r _{H₂}	r _{PH₃}
NaOH	10.0	60	18.6	6.1	4.5	-	7.6	2.1	10	3	-	6	9.3
"	1.0	"	46.8	125	98	-	102	78	87	66	-	76	63
"	10.3	40	28.4	2.4	12.4	10.8	5.6	1.2	2.8	3 ^b	0	4	2.3
"	1.02	"	19.3	25	21	0	18	8.5	20	16	0	18	12.0
"	1.01	"	62.7	20	22	50	11	6.6	"	"	"	"	"
NaOH	0.010 ^a	"	12.5	0.2	2.1	12	0	0	0	0	0	0	0
Na ₂ SO ₄	0.5	"											
H ₂ SO ₄	0.055	"	31.8	0.9	11.1	19	0	0	0	0	0	0	0
"	0.57	"	11.8	0.3	3.8	7.8	0	0	0	0	0	0	0
"	0.50	"	60.6	1.6	23	33	0	0	0	0	0	0	0

^a Initially 0.010 N(OH⁻), finally 0.069 N(H⁺)^b Estimated

varied from 600 to 2600 minutes in duration.

B. Results of Phosphorus-Electrode Coulometry

The results of coulometric studies of phosphorus electrodes under various conditions of temperature, media, and current density are shown in Table XV. In this table, the rates of formation of the products of the electrode reactions (in units of milliequivalents $\cdot \text{cm}^{-2} \cdot \text{min}^{-1}$) are shown both for the current density given and also for zero current density. These studies were made only with the silver-amalgam-matrix phosphorus electrodes; the current densities possible with the graphite-matrix electrodes resulted in rates of formation which were too low to be measured by chemical analyses of the products.

In the case of alkaline media, the effect of the current density on the rates of the various reactions of the phosphorus electrode appears to be quite complex. In general, it appears that the rate of formation of phosphine decreases, while the rates of formation of hydrogen and hypophosphite are relatively unaffected. At high current densities, small amounts of mercuric oxide were formed (maximum net rate of formation was $0.5 \times 10^{-4} \text{ meq/cm}^2 \text{ min}$) even though, as shown in Figures 10 and 11, the electrode potential was 0.2 to 0.3 volts from the potential required to oxidize the silver-amalgam electrode under the conditions of these experiments. Since mercuric salts oxidize phosphorus oxyacids fairly easily, the formation of mercuric oxide at the electrode by some unknown electrode reaction would be expected to affect the final product distribution in an unpredictable manner.

The effect of the anode current on the rate of production of

phosphite in alkaline media was not consistent; in the cases of 10 N NaOH, the rate of formation of phosphite was determined as the difference between two measured rates, so in these cases, the results were probably not significant. The most significant result of these studies in alkaline media was the formation of phosphate at high current densities. Since the rate of phosphate formation from the disproportionation-decomposition reactions was previously found to be zero, this result was the only direct evidence of any electrochemical effects of the applied current on the phosphorus electrode in alkaline media.

In neutral and acidic media, the evidence of the anodic oxidation of the phosphorus electrode was much clearer. The rates of the disproportionation-decomposition reactions in these media are negligible, so the rates of formation of various products were directly attributable to the applied current. The coulombic efficiencies with respect to each of the products of the anodic oxidation are shown in Table XVI. The overall coulombic efficiencies varied from 96% to 110%, which was quite acceptable considering the limits of accuracy of the phosphate analysis. The results of these experiments in neutral and acidic media at different current densities are shown in Figures 26 through 29. In these figures, the amounts of the various phosphorus oxyacids formed and the amount of current passed are shown as a function of time; for 100% coulombic efficiency, the sum of the various products, expressed as milliequivalents, should be equal to the equivalent current passed at any given time.

Table XVI. Coulombic Efficiency of the Anodic Oxidation of Phosphorus Electrodes

Solution	Conc. normal	Temp. °C	Applied Current Density ma/cm ²	Rates of Formation ma/cm ²			Coulombic Efficiency %		
				$r_{H_3PO_4}$	$r_{H_3PO_3}$	$r_{H_3PO_2}$	H_3PO_4	H_3PO_3	H_3PO_2
NaOH Na ₂ SO ₄	0.010 ^a 1.0	40	2.0	1.9	0.3	0.03	95	15	1.5
H ₂ SO ₄	0.11	"	5.1	3.1	1.8	0.15	61	35	3
"	1.14	"	1.9	1.2	0.6	0.05	64	32	3
"	0.99	"	9.7	5.3	3.7	0.3	55	38	3

^a Initially 0.010 N(OH⁻), finally 0.069 N(H⁺).

Some very brief coulombic studies were made of the anodic oxidation of PH₃ dissolved in alkaline solutions. The potential of a silver-amalgam electrode immersed in 1.00 N NaOH saturated with PH₃ at 40°C was 0.94 v relative to the standard hydrogen potential; the limiting current for the electrode was determined for the given rate of agitation in the cell, and the coulometric studies were run at about 50% of this limiting current. As the solution was depleted in PH₃, the current was reduced so that the electrode potential always remained above 0.4 v relative to the standard hydrogen potential. When essentially all the PH₃ had reacted, the potential fell to zero even for very small current densities; chemical analysis of the solution for PH₃ at various times also indicated the amount of depletion of the solution. The number

MU-34623

Fig. 26.

MU-34624

Fig. 27.

MU-34625

Fig. 28.

MU-34626

Fig. 29.

of coulombs passed when all the PH_3 had been oxidized was equivalent to 5.08 meq, the initial amount of PH_3 present was 1.7 mmoles (0.0024 molar); therefore, the equivalents per mole of PH_3 relative to the electrode reaction was $5.08/1.7 = 3.0$. This implies the electrode reaction of PH_3 in these experiments was:

The limiting currents for this phosphine electrode at different stirring intensities are shown in Figure 30.

MU-34627

Fig. 30.

VI. INTERPRETATION AND DISCUSSION

Two important results emerged from the experimental study of the phosphorus electrode as outlined in the preceding sections: the first of these was that the half-cell potential of the phosphorus electrode was significantly lower than the electrode potentials predicted for the oxidation of phosphorus to the various oxyacids; the second result was that, in neutral and acidic media, the anodic oxidation of phosphorus in a silver-amalgam matrix occurred with a coulombic efficiency approaching 100%, based on rates of formation of various phosphorus oxyacids. The significance of these and other related results is discussed in the following section.

A. Phosphorus Electrode Potentials

The half-cell potentials of the phosphorus electrode measured in various solutions were all considerably lower than the theoretical oxidation potentials of phosphorus; this discrepancy is of the order of one volt for alkaline media and a few tenths of a volt in acidic media. Also, the electrode potential, once established, remained constant for the duration of the experiment rather than decreasing as the concentration of the reaction products increased, as predicted by the Nernst Equation. Three hypotheses are advanced to explain these results:

- (1) Phosphorus did enter into the electrode reaction to form the various oxyacids, but since the reactions took place spontaneously in aqueous media, that is, the electrode was corroding, the potential was displaced from the equilibrium value.

(2) Phosphorus took part in the electrode reaction, but the equilibrium was between phosphorus and some intermediate phosphorus-oxy compound; this intermediate compound then reacted irreversibly to form the mono-phosphorus oxyacids.

(3) Phosphorus did not enter directly into the electrode reaction; the electrode potential was established by a product of the disproportionation-decomposition reactions, probably phosphine.

The first hypothesis can be refuted by a calculation of the total current density at the electrode, that is, the sum of the external applied current density and the internal corrosion current density.

The corrosion current density was the rate of formation of the phosphorus oxyacids from the disproportionation-decomposition reaction. These rates, together with the associated decrease in potential from the theoretical value, are shown in Table XVII for the phosphorus silver-amalgam-matrix electrodes in alkaline media. The oxidation of phosphorus to hypophosphite was chosen arbitrarily as the assumed electrode reaction; therefore, the theoretical value of the equilibrium potential at unit activity hydroxide was taken as 2.05 v.

The results presented in Table XVII indicate that a six-fold increase in the corrosion current density had little effect on the degree of electrode polarization. However, this analysis assumes the electrode reaction was the same for both concentrated and dilute alkaline solutions, while the maximum which occurred in the rates of corrosion reactions at 1 N NaOH implies that the mechanisms, or at least the rate controlling steps of these reactions, may be different in these solutions.

Table XVII. Corrosion Currents of Silver-Amalgam-Matrix Phosphorus Electrodes in Alkaline Media. (40°C)

Electrolyte	Concentration moles/liter	Corrosion Current ma/cm ²	Electrode Potential, E (Rel. to Std. H ₂)	(E° - E) *
NaOH	9.9	1	1.07	1.17
"	1.02	6	0.89	1.14
"	0.100	1	0.83	1.09

* $E^\circ = 2.05, \frac{1}{4}P_4 + 2OH^- \rightarrow H_2PO_2^- + e^-$

More significant evidence that the electrode potential was not displaced from a higher, equilibrium value because of the corrosion current is presented in Figure 31, where the electrode potential is shown as a function of the total current density. The dotted line in this graph was drawn arbitrarily to represent the polarization caused by the corrosion current alone. At the point where small external currents were applied, the potential appears in this figure to be almost discontinuous; this type of behavior cannot be reconciled with the behavior of a corroding system, and it must be concluded that the potential-determining reaction (which should respond to small external applied currents by small shifts from the equilibrium potential) was different from the overall corrosion reactions. Other evidence for this conclusion was the higher sensitivity of the graphite-matrix electrode to polarizing currents compared to the

silver-amalgam-matrix electrode. Since the corrosion reactions occurred at both electrodes with nearly equal rates, this also implied that the potential-determining electrode reaction was different from the corrosion reactions.

The second hypothesis, that the electrode potential was associated with an equilibrium between phosphorus and a partially oxidized intermediated, can neither be proved nor refuted with the evidence at hand. Calculations of the energies involved in partial electrochemical oxidation of the P_4 molecule, based on approximate bond energies, indicated that the first oxidation step is perhaps less energetic than subsequent steps. For example, if the potential determining reaction is of the type:

then the difference in enthalpy between P_4O and P_4 can be estimated from bond energies (enthalpies of formation from monatomic gases in their spectrographic ground states)^{3,77} as about 132 kcal; that is, the sum of the approximate energies of the P-P σ -bonds, the P-O σ -bonds, one π -type bond, and the ionic contribution to the P-O bond is assumed equal to the total bond energy of the molecule. The value of 132 kcal compares favorably with the differences in bond energies between $POCl_3$ and PCl_3 (128 kcal) and between $POBr_3$ and PBr_3 (124 kcal), which may be considered as roughly analogous to POP_3 and PP_3 , respectively. Then, assuming further that entropy differences between P_4 and P_4O are small, the free energy of reaction (83) is in the order of 10 kcal, so the electrode potential

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Fig. 31.

for the two-electron transition would be very approximately 0.2 volts. This low potential for the initial step in the oxidation of phosphorus is contrary to the trend observed for the oxidation potentials of phosphorus to the regular oxyacids: $P_4 \rightarrow H_2PO_2^-$, 2.05 v; $P_4 \rightarrow HPO_3^{2-}$, 1.73 v; and $P_4 \rightarrow PO_4^{3-}$, 1.49 v. However, the low potential calculated for partial oxidation of phosphorus to some intermediate compound such as P_4O agrees qualitatively with the phosphorus electrode potentials actually measured. In addition, the dependence of the measured phosphorus potentials on the hydroxyl-ion activity was the same as predicted for partial oxidations such as reaction (83). For these reasons, it appears that the potential-establishing reaction may have been the oxidation of phosphorus to some intermediate oxidation state.

The third hypothesis, that the electrode potential was established by phosphine produced by the disproportionation-decomposition reactions of phosphorus, also appears reasonable, at least for alkaline media. The equilibrium potential of the electrode remained constant as the reactions proceeded because the phosphine concentration in the electrolyte remained constant after reaching the saturation level. In addition, the measured half-cell potentials of the phosphorus electrode were quite close to the theoretical potential for the oxidation of phosphine to phosphorus in alkaline media, and these potentials showed the same dependence upon hydroxyl-ion activity as expected of the phosphine electrode. The inconsistencies of this interpretation are that in neutral and acidic media the production of phosphine appeared to be negligibly small and the electrolytes

were never saturated with phosphine, while the electrode potential soon reached and maintained a constant value. Also, the measured potentials of phosphine solutions at silver-amalgam electrodes were a few hundredths of a volt higher than the potentials of the phosphorus electrodes in the corresponding solutions, corrected for the differences in the concentrations of phosphine. Another inconsistency is that although the potentials of the graphite-matrix and silver-amalgam-matrix phosphorus electrodes were the same in alkaline solutions, they varied significantly in acidic media.

The conclusion drawn from these studies is that the open-circuit potential measured for the phosphorus electrode in alkaline media was actually established by phosphine formed in situ by the disproportionation-decomposition reactions of phosphorus. There is some evidence which indicates that the electrode potential in acidic media is established by some species other than phosphine, but this evidence is inconclusive.

B. Phosphorus Electrode Coulometry

The results of coulometric studies of the phosphorus electrode in alkaline solution indicated the reactions taking place at the electrode were quite complex. The agreement between the known current density applied to the electrode and the changes in the rates of formation of the various products was not too good; this inconsistency may have resulted from changes in the physical electrode, leading to increased overall reaction rates, or it may have been the result of increases of the rates of individual reactions which affect indirectly the other simultaneous reactions. However, some general conclusions can be drawn from these results.

The oxidation of phosphine, presumably to phosphorus, appeared to be only one of the reactions taking place at the phosphorus electrode at relatively high current densities. The polarization studies of the phosphine electrode in alkaline media showed that the electrode reaction was limited by mass-transfer alone up to rates of 5 ma/cm^2 ; at the phosphorus electrode, therefore, where phosphine was produced in-situ right at the electrode surface, rates of oxidation of phosphine of at least this magnitude were possible. In 1.0 N NaOH at 40°C , however, the decrease in the rate of phosphine production at current densities of both 3 and 10 ma/cm^2 was less than 1 ma/cm^2 . At high current densities, the increased production of phosphate and phosphite were significant, while the rates of hypophosphite and hydrogen remained relatively constant.

The production of small amounts of mercuric oxide at high current densities in alkaline media indicated that the silver-amalgam matrix might have entered in some manner into the electrode reaction. The oxidation potentials of mercury and silver were considerably below the potential of the phosphorus electrode in these experiments, and analysis of the electrode geometry indicated that the potential was essentially equal at all parts of the electrode⁷⁰. Therefore, some type of complex formation must occur between mercury and phosphorus or a phosphorus compound. The higher sensitivity to polarization of the graphite-matrix phosphorus electrode compared to the silver-amalgam-matrix electrode also indicated that the silver-amalgam might have affected the electrode reaction. The maximum current density of the graphite-matrix phosphorus electrode in 1.0 N NaOH at 40°C was about

1 ma/cm², which corresponded to the current density equivalent to the decrease in the rate of formation of phosphine at the silver-amalgam-matrix phosphorus electrode under the same conditions. This implies that the initial electrode reaction in alkaline media might have been the oxidation of phosphine, probably to phosphorus, and then, as the current density was increased, the oxidation of phosphorus to phosphate and phosphite occurred, perhaps through some oxidation-reduction couple involving mercury and mercuric oxide.

The results of the coulometric studies of the silver-amalgam-matrix phosphorus electrode in acidic and neutral media were very promising. These results show that phosphorus can be quantitatively oxidized at an anode, with a coulometric efficiency approaching 100%. This coulometric efficiency is on the basis of transfers of 1, 3, and 5 electrons for the oxidation of phosphorus to hypophosphorous, phosphorous, and phosphoric acids, respectively. It could not be determined from these results whether phosphorus took part in the electrode reaction directly, or whether a redox couple with the silver-amalgam matrix was involved. The differences in the sensitivity to polarization between the silver-amalgam-matrix and the graphite-matrix phosphorus electrodes and the fairly abrupt changes in slope of the polarization curves of the silver-amalgam-matrix electrodes at potentials of about -0.3 v indicate that some such redox couple may have been involved. However, the facts that no mercuric or silver ions were detected in these experiments and the increased current density did not result in loss of coulombic efficiency, indicated that reactions associated with a phosphorus-mercuric oxide or phosphorus-silver oxide

couple would have to be relatively fast. Attempts to determine the rates of oxidation of phosphorus by mercuric sulfate solutions (under conditions comparable to the phosphorus electrode experiments) were unsuccessful because of interferences in the chemical analysis of the products.

If a redox couple between phosphorus and a metal ion were involved in the anodic oxidation of phosphorus, then the electrode potentials should be different for different electrode matrices. Experiments designed to measure shifts in the polarization characteristics of electrodes of phosphorus in matrices of various metals were unsuccessful because of lack of stability of the electrodes, as described in Section II-C.

The interpretations of the results of the coulometric experiments in this study were based on the assumption that the total amount of phosphate determined after complete conversion of all phosphorus compounds to orthophosphoric acid was the sum of the oxyacids based on one phosphorus atom only. Therefore, any di- and tri-phosphorus oxyacids produced by anodic oxidation of phosphorus were actually counted as orthophosphoric acid. There was some fragmentary evidence that some phosphoric acids beside the ortho form were formed by anodic oxidation of the silver-amalgam-matrix phosphorus electrode. If oxidation to phosphate of all the phosphorus compounds in the sample was done by boiling with alkaline hydrogen peroxide rather than by fuming with nitric and perchloric acids, the final product had a number of pH-titration endpoints instead of just two, indicating that other phosphorus oxyacids in addition to orthophosphoric acid were

present. Utilization of the alkaline-hydrogen-peroxide procedure with standard samples of hypophosphorous and phosphorous acids resulted in quantitative oxidation to orthophosphoric acid, while the oxidation and hydrolysis reactions of all the stable di-phosphorus oxyacids to orthophosphoric acid are known to occur only in strong acids.

Qualitative tests for the detection of hypophosphoric acid made in a few experiments were negative; the separation and analysis of many of the other multi-phosphorus oxyacids can be made by chromatographic methods,³ but this was outside the scope of the present work. Since the final results of the phosphate analysis in these experiments agreed quite well with the total amount of current passed, either pyrophosphoric acid (apparent oxidation number of phosphorus is 5) was the only multi-phosphorus oxyacid formed, or else the total amount of di- and tri-phosphorus oxyacids formed was small. A separation and analysis of the multi-phosphorus oxyacids by chromatographic techniques would probably yield interesting information about the steps involved in the anodic oxidation of phosphorus.

VII. CONCLUSIONS

When an electrode consisting of phosphorus impregnated in a conducting matrix is immersed in aqueous solutions of various electrolytes, a potential (relative to some reference electrode) is established at the phosphorus electrode. These potentials, which depend primarily upon the pH of the solution, are considerably lower than the corresponding potentials calculated for the oxidation of phosphorus to the various phosphorus oxyacids. In alkaline solutions, where the phosphorus electrodes undergo spontaneous disproportionation-decomposition reactions, the potential established at the electrode is believed to correspond to the oxidation of phosphine (a product of the disproportionation-decomposition reactions) to phosphorus. In neutral and acidic solutions, where the rates of the disproportionation-decomposition reactions are negligible, the reasons for the low potentials of the phosphorus electrodes are not clear.

Coulometric studies of the anodic oxidation of phosphorus in a silver-amalgam-matrix in neutral and acidic media show that phosphorus is quantitatively oxidized to phosphorous and phosphoric acids with coulombic efficiencies approaching 100% at current densities of up to 10 ma/cm^2 . Results of coulometric studies of the phosphorus silver-amalgam-matrix electrode in alkaline media are obscured by the simultaneous disproportionation-decomposition reactions; however, it appears that one electrode reaction is the oxidation of phosphine, probably to phosphorus, and then, as the current density is increased, other electrode reactions occur, leading eventually to the formation of phosphate. There is some indication that the silver-amalgam matrix

takes part in these reactions in some manner.

The results of anodic oxidation of phosphorus in a silver-amalgam matrix in neutral and acidic media appear quite promising; it is possible that processes based on this method of oxidizing phosphorus may have direct practical applications.

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APPENDIX A

Miscellaneous Phosphorus-Electrode Potentials

<u>Electrode Configuration</u>		<u>Temperature °C</u>	<u>Electrolyte</u>	<u>Concentration moles/liter</u>	<u>Half-Cell Potential (rel. to Std. H₂), v</u>
Ag Screen,	Hg Pool	60	NaOH	5.0	0.81
"	"	60	NaH ₂ PO ₂	0.5	0.12
"	"	60	NaH ₂ PO ₂	5.0	0.25
Ag-Hg Screen		60	NaH ₂ PO ₂	5.0	0.24
Ag Screen		80	KH ₂ PO ₂	1.0	0.14
"		90	H ₃ PO ₄	7.6	-0.1
Ag Screen,	Hg Pool	60	H ₃ PO ₂	0.50	0.01
"	"	60	H ₃ PO ₂	5.44	-0.02

APPENDIX B
Chemical Analyses

1. Hypophosphorous Acid

Hypophosphorous acid was determined by its quantitative oxidation to phosphorous acid by excess sulfatoceric acid, followed by back titration of the unreacted sulfatoceric acid with standard ferrous ammonium sulfate.

The procedure developed by Bernhart⁷⁸ was used, with a few minor modifications. A 5-ml sample was measured from a burette into a 200-ml flask containing 50 ml of 4 M H_2SO_4 and a measured volume of 0.1 N $(NH_4)_2Ce(NO_3)_6$ solution in 1 M H_2SO_4 ; the cerate was at least 100% in excess of the required amount. The flask and contents were heated in a water bath at 60°C for 30 to 45 minutes, then cooled, and the excess cerate was titrated with standard 0.1 N $(NH_4)_2Fe(SO_4)_2$ solution, using two drops of 0.01 M 5-nitro-1, 10-phenanthrolineferrous sulfate as indicator. The cerate solution was found to be stable over periods of several months, but it was necessary to restandardize the ferrous sulfate solution every day.

The results of this method of analysis for standard $H_2PO_2^-$ solutions are shown in Table B-1. In these experiments, weighed quantities of purified $NaH_2PO_2 \cdot H_2O$ and reagent-grade H_3PO_3 were dissolved to make up one-liter solutions; aliquot portions of these solutions were then analyzed for $H_2PO_2^-$ by the standard procedure described above. These results indicated there was very little interference of phosphorous acid in the hypophosphite analysis.

Dissolved phosphine did interfere in the hypophosphite analysis;

Table B-I. Accuracy of Hypophosphite and Phosphite Analyses

Weight $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, g	1.3581				1.3251			
$(\text{H}_2\text{PO}_2^-)$, moles/liter	0.0128				0.0125			
Weight H_3PO_3 , g	1.0185				1.0607			
(H_3PO_3) , moles/liter	0.0124				0.0129			
Sample Volume, ml	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Vol. 0.1035 N Ce^{+4} , ml	5.00	5.00	5.00	5.00	6.00	6.00	6.00	6.00
Ce^{+4} , meq.	0.517	0.517	0.517	0.517	0.621	0.621	0.621	0.621
Vol. Fe^{+2} sol'n, ml	3.81	3.82	3.78	3.79	4.99	5.00	5.00	5.02
(Fe^{+2}) , N	0.1021				0.0993			
Fe^{+2} , meq.	0.389	0.390	0.386	0.387	0.496	0.497	0.497	0.498
H_2PO_2^- , meq.	0.128	0.127	0.131	0.130	0.125	0.124	0.124	0.123
$(\text{H}_2\text{PO}_2^-)$ by analysis, molar	0.0128	0.0127	0.0131	0.0130	0.0125	0.0124	0.0124	0.0123
Vol. I_2 , ml	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
(I_2) , N	0.1008				0.1038			
I_2 , meq.	1.008	1.008	1.008	1.008	1.038	1.038	1.038	1.038
Vol. 0.1000 N As^{+3} , ml	8.84	8.85	8.81	8.85	9.08	9.08	9.10	9.09
As^{+3} , meq.	0.884	0.885	0.881	0.885	0.908	0.908	0.910	0.909
H_3PO_3 , meq.	0.124	0.123	0.127	0.123	0.130	0.130	0.128	0.129
(H_3PO_3) by analysis, molar	0.0124	0.0124	0.0127	0.0123	0.0130	0.0130	0.0128	0.0129

to eliminate this interference, the phosphine was removed by bubbling nitrogen gas through the sample solutions. The procedure was to take duplicate sets of samples for hypophosphite analysis: one set of samples were each added to 50 ml of 4 M H_2SO_4 , and these solutions were sparged with nitrogen for 5 to 10 minutes at room temperature. After the sparging was completed, cerate was added to the solutions, and the rest of the procedure was performed in the usual manner. As will be shown in the section dealing with phosphine analyses, nitrogen sparging removed essentially all dissolved phosphine from solution, but had no noticeable effect on $(\text{H}_2\text{PO}_2^-)$ analysis.

2. Phosphorous Acid

Phosphorous acid, or phosphite, was analyzed by oxidation to phosphoric acid with excess iodine in neutral media, followed by back titration of the unreacted iodine with standard arsenite solution. A 5-ml sample of the solution to be analyzed was measured from a burette into a 250-ml, glass-stoppered flask containing 25 ml distilled water. The resulting solution was neutralized with either NaOH or H_2SO_4 of an appropriate concentration, with one drop of 0.03 M phenolphthalein as indicator. Two grams of Na HCO_3 were added to the neutralized solution, followed by 10 ml of standard 0.1 N iodine solution measured from a burette; the reaction time was 45-60 minutes, during which the flask and contents were at room temperature and were protected from light. The excess iodine was titrated with standard 0.1 N As_2O_3 alkaline solution with a starch indicator.

The results of analysis of a standard H_3PO_3 solution (containing NaH_2PO_2 also) are shown in Table E-I; there was apparently no interference from hypophosphite using this method of analysis. Phosphine

interfered with the phosphorous acid analysis to the same extent as with the hypophosphite analysis. In each sample, then, the same correction for phosphine which was determined in the hypophosphite analysis was applied to the phosphite analysis.

Determination of phosphorous acid by oxidation to phosphoric acid with sulfatoceric acid at 100°C, according to the method of Bernhart,⁷⁸ was found to be too inaccurate for this work. The inaccuracies in this analysis appeared to stem from the insolubility of the sodium salt of the reduced form of sulfatoceric acid. Relatively large quantities of this compound were formed because of the oxidation of both hypophosphorous and phosphorous acids to phosphoric acid, and the heavy yellow-white precipitate which was formed apparently either adsorbed or occluded relatively large amounts of unreacted cerate. In any case, this method usually gave high and inconsistent results.

3. Phosphoric Acid

Phosphoric acid, or phosphate, was determined by two methods, both involving complete oxidation of all phosphorus compounds in the sample, measuring the total amount of the resulting phosphoric acid, and subtracting the amounts formed from the known concentrations of hypophosphite and phosphite. The methods varied in the determination of the total phosphate: one method measured total phosphate by the pH titration of the first and second ionizable hydrogens of phosphoric acid, the other by colorimetric analysis of the phosphomolybdate complex.

The general procedure was to measure 5 ml of sample from a burette into a 150-ml beaker containing 15 ml each of 70% perchloric acid and 70% nitric acid; the mixture was then gently heated and fumed nearly to dryness. In the first method (i.e., by pH titration), the sample

was diluted to about 50 ml and neutralized to about pH 2.5 with CO_2 -free concentrated NaOH. The pH titration was with standardized CO_2 -free 0.05 N NaOH, using a Beckman Model 76 pH-meter. The initial point of the titration (i.e., the neutralization of the first hydrogen ion of H_3PO_4) occurred in the range pH 3-5.5, and the end point occurred at pH 7-10. For standard, known samples, this method of analysis was fairly accurate; however, for samples from experimental runs, the results were not as satisfactory. This was probably because these samples had low phosphate contents but fairly high hypophosphite and phosphite concentrations, so that the net phosphate concentration was determined as a small difference between relatively large numbers. The pH titration was very tedious and time consuming for the large numbers of samples to be analyzed, and it was difficult to prepare and maintain concentrated alkaline solutions completely free of CO_2 .

The second method of measuring the total phosphate was by colorimetric analysis.⁷⁹ After being fumed nearly to dryness with HNO_3 and HClO_4 , the samples were neutralized and diluted so that the final solution contained 1-15 ppm phosphate. Aliquot portions of the diluted solutions were then acidified with HClO_4 and mixed with Na_2MoO_4 solution so that the final solution was 0.04 M in molybdate and 0.25 M in acid. The absorbance of light at 380 mμ wavelength was measured by a Beckman D U Spectrophotometer; the concentrations were determined from a calibration curve, which followed Beer's Law. The results of phosphate analysis by this procedure agreed within 10% for duplicate samples and were within ±6% for known standard samples. Although the reproducibility of this method was no better than that of pH-titration method, the absolute accuracy was improved because the systematic errors (such as caused by CO_2

adsorption in the pH-titration method) was reduced. This analysis, although fairly time consuming (about 20-25 minutes per sample) was not too tedious and was reasonably satisfactory.

4. Phosphine

The analysis of phosphine in the gas phase was based on the reaction of phosphine with mercuric chloride to form an insoluble phosphide complex and hydrochloric acid.⁶⁷

A 25-ml sample of the gas to be analyzed displaced its equivalent volume from a stoppered 125-ml flask completely filled with saturated $HgCl_2$ solution. The flask was then shaken vigorously, the volume of the reacted PH_3 being replaced with fresh $HgCl_2$ solution. After the reaction was complete, the contents of the flask were filtered and then washed with CO_2 -free distilled water. The filtrate and washings were combined, and the resulting solution was titrated with standard 0.05 N NaOH with methyl-orange indicator, three moles of NaOH being equivalent to one mole of PH_3 .

This method of determining the phosphine content was quite accurate. The mass spectrum of a typical gas product of these experiments showed that the reaction with $HgCl_2$ removed all PH_3 ; the scrubbed gas contained only hydrogen with small traces of oxygen, nitrogen, water, and carbon dioxide. Analyses of duplicate samples generally gave results within 3% of each other; and the absolute accuracy of the method was estimated at $\pm 2\%$. The absolute accuracy could not be checked directly because of unavailability of reference samples with known PH_3 concentration. Pure PH_3 was generated by reacting re-crystallized PH_4I (synthesized by the

method of Work⁸⁰) with dilute NaOH; unfortunately, the requirement that the entire generating and collecting system be purged with inert gas resulted in the PH_3 being contaminated with an unknown amount of nitrogen. However, measured samples of this mixture were mixed with known volumes of nitrogen, the resulting mixtures were analyzed for PH_3 , and the composition of the original mixture was calculated; these results agreed within 3%, as shown in Table B-II.

Table B-II. Accuracy of Phosphine Gas Analyses

$\text{PH}_3\text{-N}_2$ mixture, ml	54.0				39.0			
N_2 added, ml	39.0				60.0			
Sample vol, ml	23.5	24.2	19.2	26.2	25.4	24.6	24.8	24.8
Vol. 0.100 N NaOH ml	12.47	12.55	10.00	13.85	9.46	8.99	9.07	8.93
(PH_3) Sample moles/liter	0.0177	0.0173	0.0174	0.0176	0.0124	0.0122	0.0122	0.0120
(PH_3) Original moles/liter	0.0301 ± 0.0004				0.0310 ± 0.0005			

Phosphine dissolved in the electrolyte solutions was analyzed essentially by oxidation with excess sulfatoceric acid as described in the section dealing with hypophosphite analysis. Duplicate sets of 5-ml samples were measured into 200-ml flasks containing 50 ml of 4 M H_2SO_4 , and one set of samples was sparged with nitrogen for 10 minutes at room temperature; then standard 0.1 N Ce^{+4} solution was added to all samples, the resulting solutions were heated at 60°C for 30 minutes, and the excess Ce^{+4} was titrated with standard 0.1 N Fe^{+2} . The difference to the

in Ce^{+4} utilized for the different sets of samples was proportional to the PH_3 content of the unsparged samples.

The equivalence between PH_3 and Ce^{+4} (that is, the level to which PH_3 was oxidized by Ce^{+4} in acidic solution at 60°C) was determined by comparing the Ce^{+4} utilization of PH_3 -saturated distilled water with the known solubility of PH_3 in water under identical conditions.⁵³ The results of this study, which are presented in Table B-III. indicate that phosphine is oxidized to phosphorus by sulfatoceric acid or, at least, that one mole of PH_3 is equivalent to 3 moles of Ce^{+4} .

Table B-III. Analysis of Dissolved Phosphine

Solvent	Distilled Water			
Temperature, °C	27.8		24.8	
(PH ₃) gas phase moles/liter	0.0364		0.0315	
(PH ₃) liquid phase ⁵³ moles/liter	0.0067		0.0063	
Sample Vol., ml	5.00	5.00	5.00	5.00
N ₂ sparge, min.	0	11	0	10
Vol. 0.0969 N Ce ⁺⁴ , ml	10.00	10.00	10.00	10.00
Ce ⁺⁴ , meq.	0.969	0.969	0.969	0.969
Vol. 0.0910 N Fe ⁺² , ml	9.58	10.64	9.61	10.63
Fe ⁺² , meq.	0.872	0.968	0.875	0.967
ΔCe ⁺⁴ , /meq.	0.097	0.001	0.094	0.002
(ΔCe ⁺⁴), $\frac{\text{equiv}}{\text{liter}}$	0.0194	-	0.0188	-
$\frac{\text{Ce}^{+4}}{\text{PH}_3}$ $\frac{\text{equiv}}{\text{mole}}$	2.9	-	3.0	-

APPENDIX C

Mass Transfer Studies

Mass transfer studies were made in the electrochemical cell for two purposes: (1), to verify that mass transfer was not the limiting rate in the studies of the disproportionation-decomposition reactions of phosphorus, and (2), to determine the rate of the reaction,

occurring in the mass-transfer boundary layer at the phosphorus electrode compared to the rate occurring in the bulk of the solution. The first item was of obvious importance in all the studies of the chemical reaction rates; while the second item was of importance in studies of concentrated alkaline solutions (e.g., 10 N NaOH). In this case, the rate of reaction (C-1) was comparable to the rate of formation of hypophosphite and the concentration of hypophosphite reached a steady-state value in the bulk of the solution. Since this steady-state concentration of hypophosphite was used to determine the rate of oxidation of phosphorus to hypophosphite, it was important to ascertain that significant amounts of hypophosphite did not react before diffusing through the mass-transfer boundary layer to the bulk of the solution.

Limiting-current techniques were used to measure the effectiveness of mixing in the electrochemical cell. Since the phosphorus electrode was not suitable for limiting-current measurements because of the type of electrode reactions involved, it was necessary to use an analogous system which duplicated the actual system in all aspects important for mass transfer. The system chosen utilized the reduction of cupric ions at a planar copper electrode; the electrolyte was 0.010 M CuSO_4 in 1.5 M H_2SO_4 , with glycerine added to increase the viscosity to the desired value.

The limiting-current measurements were made in the same cell and under the same mixing conditions as used for the studies of the phosphorus electrodes; the results are shown in Table C-I. The two viscosities, 1.3 and 3.3 centipoise, were comparable to the viscosities of 5 N and 10 N NaOH at 60°C. The mixing intensity was an arbitrary reference (actually, the setting of the rheostat used to regulate the power to the mixer-vibrator) with a maximum of 120; an intensity of 75 was the maximum which could be used with liquid phosphorus without emulsifying the phosphorus in the electrolyte, while 90 was the maximum which could be used for solid phosphorus without seriously eroding the powder matrix. The mass transfer coefficients, k_L , in this table were calculated from the relation:

$$(C-2) \quad k_L = \frac{i_L}{nFC}$$

where F was Faraday's constant, n was the number of electrons transferred in the electrode reaction, and C was the bulk concentration of Cu^{++} .

Table C-I. Mass Transfer Characteristics of the Phosphorus-Electrode Cell (25° C, 0.01 M CuSO_4 , 1.5 M H_2SO_4)

Viscosity cp	Mixing Intensity	Limiting Current i_L , ma/cm ²	Mass-Transfer Coefficient, k_L , $\frac{\text{cm}}{\text{sec}}$
1.3	75	3.5	1.8×10^{-3}
1.3	90	7.8	4.0×10^{-3}
3.3	75	1.8	0.9×10^{-3}
3.3	90	3.6	1.9×10^{-3}

The mass-transfer rates calculated from the results shown in Table C-I were much higher than the reaction rates measured for the phosphorus

electrodes. For example, the rate of the reactions of the phosphorus electrode in 1 N NaOH at 60°C can be expressed as 2.2×10^{-4} mmoles/cm²sec of OH⁻ utilized; the limiting mass-transfer rate of OH⁻ to the electrode (calculated from k_L in Table C-I for mixing intensity = 75, viscosity = 1.3 cp, and corrected for the larger diffusion coefficient of OH⁻ compared to that of Cu⁺⁺ (71) was approximately 1.3×10^{-2} mmoles/cm²sec, or about 50 times greater than the rate of the chemical reactions.

The problem of determining the amount of hypophosphite which reacted in the boundary layer of the electrode in concentrated alkaline solutions was solved by using the following simple, one-dimensional model. A diffusion boundary layer of thickness, δ , was assumed to cover the surface of the electrode. Hypophosphite was formed at a constant rate at the electrode surface by the reaction of phosphorus and OH⁻ (which was present in great excess), diffused through the boundary layer to the position $x = \delta$, and then was carried into the bulk of the electrolyte by convection. The hypophosphite could react with the large excess of OH⁻ either within the boundary layer or in the bulk of the electrolyte. The concentration of hypophosphite increased until the rate of disappearance of hypophosphite by reaction (C-1) was equal to the rate of formation of hypophosphite at the electrode; after this point, there was no longer any variation of hypophosphite concentration with time. At steady state, then, the diffusion equation was:

$$(C-3) \quad D \frac{d^2 C}{dx^2} = k_1 C, \quad ,$$

with the boundary conditions:

$$(C-4) \quad \text{at } x = \delta, \quad C = C_b$$

$$(C-5) \quad \text{at } x = \delta, \quad -D \frac{dC}{dx} = \frac{V}{A} k_1 C_b ;$$

that is, flux of hypophosphite through the plane $x = \delta$ was equal to the disappearance of hypophosphite in the bulk solution. In these equations, D was the diffusion coefficient of hypophosphite; V , the reactor volume; A , the planar surface area of the electrode; k_1 , the rate constant for reaction (C-1); and C , the molar concentration of hypophosphite. The solution to (C-3) with these boundary conditions was:

$$(C-6) \quad C(x) = \frac{C_b}{2} \left[(1 + \lambda K) e^{-K(x-\delta)} + (1 - \lambda K) e^{K(x-\delta)} \right]$$

$$\text{where } \lambda = \frac{V}{A} \text{ and } K = \sqrt{\frac{k}{D}}.$$

Now, the total rate of reaction in the boundary layer was:

$$\begin{aligned} (C-7) \quad R_{bl} &= \int_0^\delta k_1 C(x) dx = \\ &= \frac{k_1 C_b}{2} \left[(1 + \lambda K) e^{K\delta} \int_0^\delta e^{-Kx} dx + (1 - \lambda K) e^{-K\delta} \int_0^\delta e^{Kx} dx \right] \\ &= \frac{k_1 C_b}{2K} \left[(e^{K\delta} - e^{-K\delta}) + \lambda K (e^{K\delta} - e^{-K\delta}) - 2\lambda K \right] \end{aligned}$$

Then, the ratio of the total rate of reaction occurring in the boundary layer to that occurring in the bulk was :

$$\begin{aligned} (C-8) \quad \frac{R_{bl}}{R_{bulk}} &= \frac{\frac{k_1 C_b}{2K} \left[(e^{K\delta} - e^{-K\delta}) + \lambda K (e^{K\delta} - e^{-K\delta}) - 2\lambda K \right]}{\lambda k_1 C_b} \\ &= \frac{\sinh(K\delta)}{K\lambda} + \cosh(K\delta) - 1. \end{aligned}$$

For the case of 10 N NaOH at 60°C, $K_1 = 6.0 \times 10^{-3} \text{ min}^{-1} = 1.0 \times 10^{-4} \text{ sec}^{-1}$,

$$\lambda = V/A = 745 \text{ cm}^3 / 26 \text{ cm}^2 = 28.9 \text{ cm, and } D_{\text{H}_2\text{PO}_2^-} \approx 1 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}.$$

$$\begin{aligned} \text{From the limiting-current data, } \delta \approx D_{\text{Cu}^{++}}/k_L &= \frac{0.72 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}}{0.9 \times 10^{-3} \text{ cm sec}^{-1}} \\ &= 0.8 \times 10^{-2} \text{ cm.} \end{aligned}$$

Then, $R_{\text{bl}}/R_{\text{bulk}} \approx 0.0006$; that is, essentially no hypophosphite

reacted in the boundary layer, and the rate of formation of hypophosphite at the electrode surface could be calculated accurately from the steady-state hypophosphite concentration in the bulk electrolyte.

APPENDIX D

Sample Calculations

1. Decomposition of Hypophosphite

The results of a typical experiment designed to measure the decomposition of hypophosphite in concentrated NaOH are shown in Fig. 32. The logarithm of the hypophosphite concentration and the logarithm of the difference between the initial hypophosphite concentration, C_0 , and the equivalent hydrogen concentration were found to be a linear function of the time. The reaction rate constant, k , based on the equations:

$$(D-1) \quad -\frac{d}{dt} (H_2PO_2^-) = k_1 (H_2PO_2^-)$$

$$(D-2) \quad \frac{d}{dt} (H_2) = k_1 (H_2PO_2^-) = k_1 (C_0 - (H_2)),$$

where the hydrogen concentration, (H_2) , was the number of moles of hydrogen produced divided by the volume of the reacting solution, was calculated as:

$$(D-3) \quad k_1 = \ln\left(\frac{0.0560}{0.0200}\right) / 165 \text{ min} = 6.2 \times 10^{-3} \text{ min}^{-1}$$

based on hypophosphite disappearance, and

$$(D-4) \quad k_1 = \ln\left(\frac{0.0560}{0.0215}\right) / 165 \text{ min} = 5.8 \times 10^{-3} \text{ min}^{-1}$$

based on hydrogen production.

2. Disproportionation-Decomposition of Phosphorus Electrodes

The production of hypophosphite, hydrogen and phosphine from the reaction of phosphorus in a silver-amalgam matrix, with 10 N NaOH at 60°C is shown in Fig. 33. The hypophosphite concentration became constant

MU-34629

Fig. 32.

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Fig. 33.

at a value of 0.0127 molar; at this point, the rate of production of hypophosphite equaled the rate of decomposition:

$$(D-5) \quad r_{H_2PO_2} = V_{k_1} (H_2PO_2^-)_{ss} / A = 720 \times 6.0 \times 10^{-3} \times 0.0127 / 26.0 = 21 \times 10^{-4} \frac{\text{mmoles}}{\text{cm}^2 \text{ min}}$$

where $(H_2PO_2^-)_{ss}$ is the steady-state concentration of hypophosphite. The rate of hydrogen production from decomposition of water by phosphorus was equal to the difference between the total final rate of production of hydrogen and the rate of decomposition of hypophosphite:

$$(D-6) \quad r_{H_2} = r_{H_2}(\text{final}) - V_{k_1} (H_2PO_2^-)_{ss} / A \\ = (35 \times 10^{-4} - 21 \times 10^{-4}) = 14 \times 10^{-4} \frac{\text{mmoles}}{\text{cm}^2 \text{ min}}$$

The rate of production of phosphite was calculated directly from the slope of the PH_3 -curve in Fig. 33:

$$(D-7) \quad r_{PH_3} = \frac{11.8 \text{ mmoles}}{565 \text{ min} \times 26.0 \text{ cm}^2} = 8.0 \times 10^{-4} \frac{\text{mmoles}}{\text{cm}^2 \text{ min}}$$

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FIGURE CAPTIONS

Fig. 1. The three-phase interface between phosphorus, aqueous electrolyte, and solid conductor. (a). Preferential wetting of the solid by phosphorus. (b). Preferential wetting of the solid by aqueous electrolyte.

Fig. 2. Microscopic phototgraphs of standard phosphorus electrodes. (a). Standard silver-amalgam-matrix phosphorus electrode. (b). Standard graphite-matrix phosphorus electrode.

Fig. 3. Microscopic photographs of graphite-in-phosphorus-matrix electrodes. (a). Graphite particles approximately 100 μ diameter in the phosphorus matrix. (b). Graphite particles imbedded in cubic crystal matrix of white phosphorus.

Fig. 4. Apparatus for measuring phosphorus-electrode potentials and polarization.

Fig. 5. Mercury-mercuric oxide reference electrode.

Fig. 6. Electrochemical cell for phosphorus-electrode studies.

Fig. 7. Measuring and polarizing circuits for the phosphorus electrode.

Fig. 8. Variation of phosphorus-electrode potentials with hydroxyl-ion activity. (White phosphorus in silver-amalgam matrix, 40°C, potentials relative to the standard hydrogen electrode.)

Fig. 9. The effect of temperature on the polarization of silver-amalgam-matrix phosphorus electrodes. (10 M NaOH, phosphorus volume is 155% of matrix saturation volume, potentials relative to standard hydrogen electrode.)

Fig. 10. The effect of excess phosphorus on the polarization of silver-amalgam-matrix phosphorus electrodes. (10 M NaOH, 40°C, potentials relative to standard hydrogen electrode.)

Fig. 11. Anodic polarization of the standard silver-amalgam-matrix phosphorus electrode in 1.0 M NaOH. (40°C, potentials relative to standard hydrogen electrode.)

Fig. 12. Anodic polarization of the standard silver-amalgam-matrix phosphorus electrode in 0.10 M NaOH. (40°C, potentials relative to standard hydrogen electrode.)

Fig. 13. Anodic polarization of the standard silver-amalgam-matrix phosphorus electrode in 0.50 M Na_2SO_4 . (pH = 5.5, 40°C, potentials relative to standard hydrogen electrode.)

Fig. 14. Anodic polarization of the standard silver-amalgam-matrix phosphorus electrode in 0.0050 M H_2SO_4 . (0.50 M Na_2SO_4 , 40°C, potentials relative to standard hydrogen electrode.)

Fig. 15. Anodic polarization of the standard silver-amalgam-matrix phosphorus electrode in 0.049 M H_2SO_4 . (40°C, potentials relative to standard hydrogen electrode.)

Fig. 16. Anodic polarization of the standard silver-amalgam-matrix phosphorus electrode in 0.49 M H_2SO_4 . (40°C, potentials relative to standard hydrogen electrode.)

Fig. 17. Anodic polarization of the standard silver-amalgam-matrix phosphorus electrode in 4.95 M H_2SO_4 . (40°C, potentials relative to standard hydrogen electrode.)

Fig. 18. Anodic polarization of the graphite-matrix phosphorus electrode in 1.0 M NaOH. (40°C, potentials relative to standard hydrogen electrode.)

Fig. 19. Anodic polarization of the graphite-matrix phosphorus electrode in 0.50 M Na_2SO_4 . (40°C, potentials relative to standard hydrogen electrode.)

Fig. 20. Anodic polarization of the graphite-matrix phosphorus electrode in 0.0053 M H_2SO_4 . (40°C, 0.50 M Na_2SO_4 , potentials relative to standard hydrogen electrode.)

Fig. 21. Anodic polarization of the graphite-matrix phosphorus electrode in 0.049 M H_2SO_4 . (40°C, potentials relative to standard hydrogen electrode.)

Fig. 22. Anodic polarization of the graphite-matrix phosphorus electrode in 0.49 M H_2SO_4 . (40°C, potentials relative to standard hydrogen electrode.)

Fig. 23. Anodic polarization of the graphite-matrix phosphorus electrode in 4.9 M H_2SO_4 . (40°C, potentials relative to standard hydrogen electrode.)

Fig. 24. The effect of the phosphorus-to-matrix weight ratio on the disproportionation-decomposition reaction rates of phosphorus electrodes. (Silver-amalgam matrix, 10.0 M NaOH, 60°C).

Fig. 25. Formation of hydrogen and phosphine on the graphite-matrix phosphorus electrode. (0.5 M NaOH, 25°C)

Fig. 26. Anodic oxidation of the silver-amalgam-matrix phosphorus electrode in neutral media. (40°C, 0.010 M OH^- initially, 0.069 M H^+ finally, current density = 2.0 mA/cm², area = 26.4 cm²)

Fig. 27. Anodic oxidation of silver-amalgam-matrix phosphorus electrode in 0.055 M H_2SO_4 . (40°C, current density = 5.1 mA/cm², area = 26.0 cm²)

Fig. 28. Anodic oxidation of silver-amalgam-matrix phosphorus electrode in 0.57 M H_2SO_4 . (40°C, current density = 1.9 mA/cm², area = 26.0 cm²)

Fig. 29. Anodic oxidation of silver-amalgam-matrix phosphorus electrode in 0.50 M H_2SO_4 . (40°C, current density = 9.7 mA/cm², area = 26.0 cm²)

Fig. 30. Anodic polarization of phosphine in 1.0 M NaOH. (40°C, silver-amalgam electrode, PH_3 concentration = 0.0024 M, scale of stirring intensity is arbitrary, potentials relative to standard hydrogen electrode.)

Fig. 31. Polarization of corroding phosphorus electrode. (Total current density equals sum of external current density and corrosion current density, 40°C, silver-amalgam matrix, potentials relative to standard hydrogen electrode.)

Fig. 32. Decomposition of hypophosphite in alkaline solution. (10.0 M NaOH, 60°C)

Fig. 33. Disproportionation-decomposition reactions of phosphorus electrode in concentrated alkaline solution. (60°C, 10.0 M NaOH, phosphorus-to-matrix ratio = 0.37, electrode area = 26.0 cm², reactor volume = 720 ml)

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