

A STUDY OF EFFECTS OF INHIBITORS
ON CATHODE POTENTIALS OF METALS
IN DILUTE ACIDS

by

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TABLE OF CONTENTS

I.	INTRODUCTION	5
II.	LITERATURE REVIEW	7
III.	EXPERIMENTAL	13
	A. Purpose of Investigation	14
	B. Plan of Experimentation	14
	C. Materials	16
	D. Apparatus	22
	E. Method of Procedure	28
	F. Data and Results	51
	G. Sample Calculations	77
IV.	DISCUSSION	79
	A. Discussion of Results	80
	B. Recommendations	88
	C. Limitations	90
V.	CONCLUSIONS	92
VI.	SUMMARY	95
VII.	BIBLIOGRAPHY	98
VIII.	ACKNOWLEDGMENTS	103
IX.	VITA	105

TABLES

TABLE I	Effect of Nitrogen Flow Rate on Potential.....	53
TABLE II	Current-Potential Relationship of Steel Electrode in 4.9 Per Cent H_2SO_4	55
TABLE III	Relationship of Potential-Time Curves in 4.9 Per Cent H_2SO_4	57
TABLE IV	Potential-Time Relationships of Mild Steel in Inhibited 4.9 Per Cent H_2SO_4	59
TABLE V	Effect of a Commercial Inhibitor Mixture on the Potential-Time Relation- ship of Mild Steel in 4.9 Per Cent H_2SO_4	62
TABLE VI	Effects of Delayed Additions of Inhibitors on Cathode Potentials in 4.9 Per Cent H_2SO_4	64
TABLE VII	Effects of Inhibitors on the Cathode Potential of Copper in 4.9 Per Cent H_2SO_4	67
TABLE VIII	Effect of Inhibitor Concentration on the Cathode Potential of Mild Steel in 4.9 Per Cent H_2SO_4	69
TABLE IX	Cathode Potential-Time Relationships of Mild Steel and Platinum in 5 Per Cent Acetic Acid.....	72
TABLE X	Relationship of Cathode Potentials with Time in 5 Per Cent Phosphoric Acid.....	74

FIGURES

FIGURE 1.	ELECTROCHEMICAL H-CELL.....	30
FIGURE 2.	ELECTRODES.....	31
FIGURE 2(a).	CATHODIC SPECIMEN HOLDER ASSEMBLY.....	34
FIGURE 3(a).	BLOCK DIAGRAM OF APPARATUS.....	37
FIGURE 3(b).	BLOCK DIAGRAM OF NITROGEN TRAIN.....	38
FIGURE 3(c).	ELECTRICAL DIAGRAM OF APPARATUS.....	40
FIGURE 4.	EFFECT OF NITROGEN FLOW RATE ON POTENTIAL.....	54
FIGURE 5.	CURRENT-POTENTIAL RELATIONSHIP OF STEEL ELECTRODE IN 4.9 PER CENT H_2SO_4	56
FIGURE 6.	RELATIONSHIP OF POTENTIAL-TIME CURVES OF ELECTRODES USED.....	58
FIGURE 7.	POTENTIAL-TIME RELATIONSHIPS OF MILD STEEL IN INHIBITED 4.9 PER CENT SULFURIC ACID.....	60
FIGURE 8.	EFFECT OF A COMMERCIAL INHIBITOR ON RELATIONSHIP OF CATHODE POTENTIAL WITH TIME....	63
FIGURE 9.	EFFECTS OF DELAYED ADDITIONS OF INHIBITORS ON CATHODE POTENTIALS IN 4.9 PER CENT H_2SO_4	65
FIGURE 10.	EFFECTS OF INHIBITORS ON THE CATHODE POTENTIAL OF COPPER IN 4.9 PER CENT H_2SO_4	68
FIGURE 11.	EFFECTS OF INHIBITOR CONCENTRATION ON THE CATHODE POTENTIAL OF MILD STEEL IN 4.9 PER CENT H_2SO_4	70
FIGURE 12.	CATHODE POTENTIAL-TIME RELATIONSHIPS OF MILD STEEL AND PLATINUM IN FIVE PER CENT ACETIC ACID.....	73
FIGURE 13.	RELATIONSHIP OF CATHODE POTENTIALS WITH TIME IN 5 PER CENT PHOSPHORIC ACID.....	75

I-INTRODUCTION

II-LITERATURE REVIEW

I-INTRODUCTION

The modern electrochemical theory of corrosion postulates that there are anodic and cathodic areas on the surface of a metal and that the metal enters into solution at the anodes and hydrogen is evolved at the cathodes.

Inhibitors in the electrolyte can affect the anodic areas alone, the cathodic areas alone, or they can affect both of the different types of areas simultaneously.

C. A. Mann (46,47) proposed that any nitrogen-containing organic compound, if at all soluble, should form an ionizable salt with the acid medium and the positive charge would concentrate on the group containing nitrogen. The inhibitor would then be attracted to the cathodic part of the metal through the nitrogen-containing ion. The inhibitor would function by being adsorbed on the metal surface to form a fairly well organized and oriented film which would serve to increase the polarization for hydrogen evolution by introducing a high resistance to electron transfer between the solution and the metal surface.

It was thought that this theory might be tested by measuring the potentials against a standard electrode of steel made cathodic after small amounts of inhibitor or inhibitors had been added to the solution.

It was the purpose of this investigation to determine if there was a relationship between the quantity of inhibitor known to diminish the corrosion rate and the potential of a cathodic surface.

II-LITERATURE REVIEW

Corrosion may be defined as the destruction of a metal by means of an electrochemical reaction with its environment (31). According to the electrochemical theory, corrosion involves the flow of minute electric currents over finite paths from one point to another on the metal surface. There are three requisites for such a mechanism; (1) a potential difference, (2) a conducting path, and (3) the availability of electrode reactions for the transferring of charges across the metal-solution interface (34,37,38). An exposed metal in a corroding medium satisfies these requirements. Surface irregularities set up many points with possible differences in potential. Many solutions (even pure water) provide the conducting path, and there are always possible reactions whereby oxidation-reduction may occur.

Compounds called inhibitors were used to decrease the rate of such corrosion. Hackerman (37) suggested that an inhibitor may function either; (1) by increasing the true ohmic resistance or (2) by interfering with the anodic, the cathodic, or both the electrochemical processes. Inhibition by the formation of an oxide film or by precipitation of a nonconducting reaction product over the metal occurred by increasing the resistance to current flow. Inhibitions caused by an increase in the activation hydrogen overpotential, a decrease of potential differences on the metal surface, or activation polarization of anodic dissolution were given as examples of the second type of inhibition.

Chappell, Roetheli, and McCarthy (28), after studying the effect of quinoline ethiodide on cathodic and anodic polarization of iron and steel in normal sulfuric acid, concluded that inhibition was cathodic and suggested a theory for the action of organic inhibitors. A similar conclusion and theory were suggested by Mann (29,46,47,48). The essential points of his theory were given as follows. Organic inhibitors were capable of forming positively charged ions and accordingly existed in acid solutions as cations. The cations were cathodically adsorbed by virtue of electrostatic attraction and as a result formed a blanket over cathodic areas. The resultant film increased the resistance to passage of current by preventing hydrogen ions from reaching the surface of the cathode. Therefore, depending on the extent of adsorption, the closeness of packing in the adsorbed film, and the cross-sectional area of the molecule, various degrees of inhibition were found for different organic compounds.

Evidence for Mann's theory was obtained from cathodic polarization studies and from changes in inhibitive power brought about by substitution on the inhibitor. In general, the results of measurements of film resistance (3,21,45) are conflicting. Machu (45) found a direct relationship between film resistance and inhibition. Bockris and Conway (3) found a negligible film resistance and concluded that Mann's and Machu's explanation of corrosion inhibition as a resistance effect was not valid.

Mann's theory had numerous supporters primarily because it conformed to the inherent notion that positively charged particles should be adsorbed on negatively charged areas. However, numerous facts could not be explained by this theory. One of the main difficulties was that Mann's theory could not explain the change of the open circuit potential in the cathodic direction generally observed on addition of inhibitors. Hackerman (37) and Hoar (42) explained this shift by assuming that the main effect of the inhibitor was on the anodic reaction.

The second major difficulty with Mann's theory was that both anodic and cathodic effects occurred in polarization studies at small current densities (37). Cavallaro and Bolognesi (27) and Hackerman and Sudbury (39) found by polarization methods that some inhibitors were of a mixed type and some were especially anodic in their actions. Kuznetsov and Iefa (43) reported that in many cases the increase in overpotential caused by inhibitors was observed to be greater on anodic polarization.

A third difficulty with Mann's theory was found in sulfur-containing compounds being better inhibitors than corresponding nitrogen compounds. Mann's theory made no provision for such effects because electrostatic forces are not specific. Hackerman and Cook (40) found that irreversible adsorption of acids, alcohols, and esters took place on the same portion of a steel surface while amines adsorbed irreversibly on a differ-

ent portion of the same surface. This indicated that forces were operating which were not electrostatic.

It was a known fact that the inhibitive power of a compound increased as the number of substituents on the functional group increased. Mann (29,46) attributed this to a more complete coverage of cathodes and increased adsorption. Swearingen and Schram (52) reported that a series of amines possessing approximately equal cross-sectional area exhibited very different inhibitive properties, and concluded that specific adsorption was important in inhibition. Cardwell and Eilers (26) also reported a specific effect upon introduction of a methyl group in the ortho position of various heterocyclic nitrogen compounds used as inhibitors. Hoar (42) pointed out that *o*-tolythiourea probably, and sulfonated castor oil, were neutral molecules in ten per cent sulfuric acid but were still good inhibitors as were methyl sulfide and butyl disulfide. According to Mann's cathodic inhibition theory these compounds would not be inhibitors. Hackerman and Schmidt (8) stated that some compounds giving negatively charged ions in solution functioned as inhibitors.

Bockris and Conway (3) and Elze and Fischer (32) favored a modification in Mann's theory to ascribe inhibition to an increase of hydrogen activation overpotential. This modified theory explained the specific effects by inhibitors, but could not account for the shift in the cathode direction of the open circuit potential on the addition of inhibitors to corrosion

environments.

The difficulties encountered by Mann's theory led to the consideration of corrosion inhibition as the result of general rather than cathodic adsorption. Machu (45) and Fink (35) attributed inhibition to increased ohmic resistance. However, Fink postulated chemical adsorption as opposed to Machu's physical adsorption. Hackerman and Sudbury (39), Hackerman and Schmidt (8) and Hear (42) all favored the theory of general adsorption but could not propose a definite mechanism to account for the observed facts.

Hackerman and Cook (40) studied the adsorption of inhibitors from benzene solution onto steel powder. On the basis of these experiments Hackerman and Makrides (37) postulated the occurrence of chemisorption in the acidic corrosion of steel. They produced experimental evidence that inhibition persists when preheated iron coupons were transferred from protected to unprotected solutions (37).

Anodic polarization was looked upon as the result of chemisorption, and inhibition was considered to be the result of increased resistance to current flow caused by electrostatic adsorption at cathodic areas and of anodic polarization caused by chemisorption (33,37,39). The relative contribution of the two depended on the inhibitor. Three classes of inhibitors were distinguished: (1) Anodic inhibitors (2) Cathodic inhibitors, and (3) Mixed cathodic-anodic inhibitors. Sodium chromate illustrates the first class, quaternary amine

salts, the second, and amines and thiols the third. With the quaternary amine salts cathodic polarization took place and physical adsorption occurred over the entire surface. The inhibitor that Mann called cathodic Hackerman put in the third class, or mixed inhibitors.

Eldredge and Warner (30) tabulated the data of Mann and his coworkers.(46,48). Hackerman and Makrides (37) using the data of Mann and his coworkers explained the actions of polar organic inhibitors by means of the following equilibria involving aliphatic amines:



RNH₂-iron denotes chemisorbed amine. The extent of chemisorption depends on the strength of the amine-metal bond and the solubility of the particular amine." (37).

Potential-time curves under conditions of inhibition and non-inhibition provided little information on the rate of corrosion tendency of a metal in acid solution.

Moore (50) said that a change in the cathodic direction with increased inhibitor concentration was in accordance with previously published results (36,39,51) and indicated that the inhibitor triethanolamine acts principally on the anodic areas of copper increasing its resistance to the flow of ions.

III-EXPERIMENTAL

A. Purpose of Investigation

B. Plan of Experimentation

III-EXPERIMENTAL

A. Purpose of Investigation

It was the purpose of this investigation to determine if there was a relationship between the quantity of inhibitor known to diminish the corrosion rate and the potential of a cathodic surface.

B. Plan of Experimentation

The potential required to keep a constant current flowing to a cathodic corrosion specimen through dilute acid solutions to which one or more pure compounds or commercial cathodic inhibitors had been added was measured. Measurements were made of the potential difference between the cathodic specimen and a saturated calomel reference cell. This potential difference was recorded as the "cathode potential" of the metal under observation. The cathode potential was measured as a function of time and as a function of the concentration of inhibitor.

Platinum, mild steel, copper, monel, inconel, yellow brass, nickel and tin were used as cathodic specimen electrodes. Platinum was also used in each case for the anode of the corrosion cell. Four point nine per cent sulfuric acid, five per cent phosphoric acid, and five per cent acetic acid were used as electrolytes because of the informa-

tion available concerning the properties of the above metals in these acids.

The inhibitors studied in this investigation were: benzaldehyde, diethylamine, 2-nitro-1-butanol, pinacolone, thiourea, tri-n-amylamine, tri-n-hexylamine, and a mixture of three commercial inhibitors; Primene JM-T, Priminox 21 and Priminox 32.

These inhibitors were selected because they were available and information was available as to their effects as inhibitors in 4.9 per cent sulfuric acid (4).

G. Materials

G. Materials

Acetone. Commercial Grade; Lot Number 63716. Obtained from Commercial Solvents Corporation, 196 Blanchard Street, Newark 5, New Jersey. Used in electrode cleaning procedure.

Brass, Yellow. Standard Shim; Thickness 0.005 inch. Distributed by Precision Steel Warehouse Company, Packaged Goods Division, 4409 West Kinzie Street, Chicago 24, Illinois. Used as an electrode.

Copper. "Baker Analyzed" Reagent; Heavy Foil; Thickness 0.005 inch; Catalog Number 1714; Lot Number 20442. Manufactured by J.T. Baker Chemical Company, Phillipsburg, New Jersey. Used as an electrode.

Ethyl Ether. "Baker Analyzed" Reagent, Anhydrous; Catalog Number 9244; Lot Number 27209. Manufactured by J.T. Baker Chemical Company, Phillipsburg, New Jersey. Used in electrode cleaning process.

Glue, Epoxy. Elmer's. Manufactured by The Borden Chemical Company, A Division of The Borden Company, 350 Madison Avenue, New York 17, New York. Obtained from Ridinger Hardware and Gift Company, Blacksburg, Virginia. Used to seal metal electrodes into pyrex glass tubing.

Hydrochloric Acid. "Baker Analyzed" Reagent; Catalog Number 9534; Lot Number 23008. Manufactured by J.T. Baker Chemical Company, Phillipsburg, New Jersey. Used in cleaning electrodes.

Inconel. Thickness 0.003 inch; Lot Number 7348. Contributed by The International Nickel Company, Incorporated, 67 Wall Street, New York 5, New York. Used as an electrode.

Inhibitors.

(a) Benzaldehyde. Catalog Number B-240; Lot Number 705366; Fisher Certified Reagent. Manufactured by Fisher Scientific Company, Fairlawn, New Jersey.

(b) Diethylamine. Catalog Number D-46. Manufactured by Fisher Scientific Company, Fairlawn, New Jersey.

(c) 2-Nitro-1-Butanol. Lot Number 13744L. Manufactured by K&K Laboratories, Incorporated, 29-46 Northern Boulevard, Long Island City 1, New York,

(d) Pinacolone. Made by Mr. James R. Rigney and redistilled at 106°C. by the author.

(e) Prinene JH-T. Principally $\text{I-C}_{18}\text{H}_{37}\text{NH}_2$ to $\text{I-C}_{21}\text{H}_{43}\text{NH}_2$. Reference, July 14, 1958. Manufactured by Rohm and Haas Company, Philadelphia 5, Pennsylvania.

(f) Prininox 21. Various molecular weight polyethoxy amine; Sample Number 3610; Reference, July 14, 1958; General Structural Formula $\text{I-C}_{18-24}\text{H}_{37-49}\text{NH}(\text{CH}_2\text{CH}_2\text{O})_{15}\text{H}$. Manufactured by Rohm and Haas Company, Philadelphia 5, Pennsylvania.

(g) Prinnox 32. General Structural Formula
 $t-C_{18-24}H_{37-49}NH(OH_2CH_2O)_{25}H$; Sample Number 0197;
 Reference, July 14, 1958. Manufactured by Rohm
 and Haas Company, Philadelphia 5, Pennsylvania.

(h) Thiourea. Eastman Kodak Catalog Number 497,
 White Label. Manufactured by Distillation Products
 Industries, Rochester 3, New York.

(i) Tri-n-amyamine. Eastman Kodak Catalog Number
 2355, White Label. Manufactured by Distillation
 Products Industries, Rochester 3, New York.

(j) Tri-n-hexylamine. Eastman Kodak Catalog
 Number 6372, White Label. Manufactured by Distil-
 lation Products Industries, Rochester 3, New York.

Mercurous Chloride. Reagent Grade; Code Number 1981;
 Lot Number G068. Manufactured by General Chemical Division,
 Allied Chemical and Dye Corporation, New York, New York.
 Used as a reagent component of calomel reference cell.

Mercurous Sulfate. Reagent Powder; Baker and Adamson
 Quality; Code Number 1984; Lot Number G089. Manufactured by
 General Chemical Division, Allied Chemical and Dye Corporation,
 New York, New York. Used in making amalgamated zinc.

Mercury. "Baker Analyzed" Reagent; Catalog Number 2564;
 Lot Number 20793. Manufactured by J.T. Baker Chemical Com-
 pany, Phillipsburg, New Jersey. Used in making saturated
 calomel reference cell.

Monel. Sheet; Thickness 0.006 inch; Lot Number M67716BS. Contributed by The International Nickel Company, Incorporated, 67 Wall Street, New York 5, New York. Used as an electrode.

Nickel. Sheet; Thickness 0.003 inch; Lot Number Y7374A. Contributed by The International Nickel Company, Incorporated, 67 Wall Street, New York 5, New York. Used as an electrode.

Nitrogen. Oil-pumped; Commercial Grade. Manufactured by the Air Reduction Company, Dayton, Ohio. Distributed by Industrial Gas and Supply Company, Bluefield, West Virginia. Used to purge acid solutions and cell before and during tests.

Phosphoric Acid. "Baker Analyzed" Reagent; Catalog Number 0264; Lot Number 20075. Manufactured by J.T. Baker Chemical Company, Phillipsburg, New Jersey. Used as a reagent test solution.

Platinum. Sheet; Thickness 0.003 inch; Electrode Grade. Manufactured by Engelhard Industries, Incorporated, American Platinum and Silver Division, 231 New Jersey Railroad Avenue, Newark 5, New Jersey. Used as an electrode.

Potassium Chloride. Fisher Certified Reagent; Catalog Number P-217; Lot Number 773095. Manufactured by Fisher Scientific Company, Fairlawn, New Jersey. Used as a reagent in saturated calomel reference cell.

Potassium Hydroxide. "Baker Analyzed" Reagent Pellets;

Catalog Number 3140; Lot Number 20825. Manufactured by J.T. Baker Chemical Company, Phillipsburg, New Jersey, Used in gas train to remove carbon dioxide from nitrogen tank gas.

Steel. Thickness 28 gauge; double strength stovepipe. Manufactured by Jaques-Evans Manufacturing Company, Saint Louis, Missouri. Analysis; Carbon 0.08 per cent; Manganese 0.35 per cent; Phosphorus 0.092 per cent; Sulfur 0.038 per cent; Silicon, trace; Chromium 0.012 per cent; Copper 0.052 per cent; Analyzed by Lynchburg Foundry Company, Radford, Virginia (23). Used as an electrode.

Sulfuric Acid. "Baker Analyzed" Reagent; Catalog Number 9680; Lot Number 4114. Manufactured by J.T. Baker Chemical Company, Phillipsburg, New Jersey. Used as a reagent solution in H-Cell.

Tin. Purified Foil; Thickness 0.006 inch; Catalog Number 4134; Lot Number 90380. Manufactured by J.T. Baker Chemical Company, Phillipsburg, New Jersey. Used as an electrode.

Vanadyl Sulfate. Purified; Catalog Number V-8; Lot Number 791744. Manufactured and distributed by Fisher Scientific Company, Fairlawn, New Jersey. Used in oxygen absorption tower of gas train.

Zinc. "Baker Analyzed" Reagent; 20 mesh; Granular; Catalog Number 4244; Lot Number 6505. Manufactured by J.T. Baker Chemical Company, Phillipsburg, New Jersey. Used in absorption tower after being amalgamated.

D. Apparatus

D. Apparatus

Battery. Type BB-54-A; Willard Radio 27-2; 2 volts. Manufactured by Willard Storage Battery Company, Cleveland, Ohio. Obtained from War Surplus. Used as a power source for potentiometer and in units of three as a power source for electrochemical cells.

Control. Fisher Unitized Bath Electronic Control, 115 volts, 50-60 cycles. Obtained from Fisher Scientific Company, 7722 Woodbury Drive, Silver Spring, Maryland. Used to regulate the constant temperature bath.

Galvanometer. Type R; Reflecting; Catalog Number 2500; Serial Number 411599; Focal Length one meter; Sensitivity 0.32 microvolts per millimeter; C.D.R.X. 52 ohms; Period six seconds; Resistance 11.1 ohms. Manufactured and distributed by Leeds and Northrup Company, Philadelphia, Pennsylvania. Used with stand described by Kritzer (16).

Heater. Serial Number 15053H114A; 500 watts; 108-115 volts. Manufactured by Outler-Hammer, Incorporated, Milwaukee, Wisconsin. Used to supply heat to constant temperature bath.

Jar, Battery. Cylindrical; pyrex brand glass; diameter 12 inches; height 18 inches; Catalog Number 11-823K. Distributed by Fisher Scientific Company, 7722 Woodbury Drive, Silver Spring, Maryland. Used as a constant temperature bath vessel.

Jar, Purifying. Fleming; height $7\frac{1}{2}$ inches; Catalog Number 7-415. Obtained from Fisher Scientific Company, 7722 Woodbury Drive, Silver Spring, Maryland. Used as a liquid trap between carbon dioxide trap and vanadyl sulfate tower. A second one was used to hold potassium hydroxide solution for carbon dioxide absorption.

Lamp and Scale. Catalog Number 2100; Serial Number 43405A. Manufactured and distributed by Leeds and Northrup Company, Philadelphia, Pennsylvania. Used with a galvanometer and potentiometer as a visual means of checking circuit balance.

Meter, D.C. Milliammeter. Type TDH; Range 0-10 milliamperes; Number N37247. Manufactured by Roller-Smith, Bethlehem, Pennsylvania. Used as a rough indicator for electrode current in H-Cell.

Potentiometer. Type K-2; Catalog Number 7552; Serial Number 532479. Manufactured and distributed by Leeds and Northrup Company, Philadelphia, Pennsylvania. Used for measuring potential differences between electrodes. Also used to measure the IR drop across a Standard One Ohm Resistor to determine current flow through cell.

Regulator, Pressure. Hoke-Phoenix Number 605-B; for oil-pumped nitrogen; Catalog Number 15281. Distributed by Will Corporation of Maryland, P.O. Box 5195, Baltimore 24, Maryland. Used to reduce nitrogen tank pressure to four pounds per square inch.

Rheostat-Potentiometer. Model K; Wire wound; 5000 ohms; 0.14 maximum amperes; Number P-7763300-P10. Manufactured by Ohmite Manufacturing Company, Chicago, Illinois. Obtained as War Surplus. Used to reduce current flow through H-Cell.

Rheostat-Potentiometer. Model H; Series A; Number 0156; 500 ohms; 0.22 maximum amperes. Manufactured by Ohmite Manufacturing Company, Skokie, Illinois. Used to reduce current flow through H-Cell.

Standard Cell. Catalog Number 100; Serial Number 687029; Internal resistance not over 500 ohms; Potential value of 1.01894 International Volts at 24°C.; Cadmium cell of the unsaturated type; Negligible temperature coefficient within the range of ordinary room temperatures. Manufactured by the Eppley Laboratory, Incorporated, Newport, Rhode Island. Distributed by Fisher Scientific Company, 7722 Woodbury Drive, Silver Spring, Maryland. Used as a standard cell for the K-2 potentiometer.

Standard Resistor. One ohm; Serial Number 764102. Manufactured and distributed by Leeds and Northrup Company, Philadelphia, Pennsylvania. Used as a constant resistance for the determination of the amount of current flow through the H-Cell.

Stirrer. Variable speed; Cone-drive; Catalog Number GE383-31. Specifications: Mechanical speed regulation; Continuous duty; Totally enclosed induction motor; Two hollow

spindles; Low speed spindle 18-270 rpm; High speed spindle 150-2250 rpm. Distributed by Arthur S. LaPine and Company, 6001 South Knox Avenue, Chicago 29, Illinois. Used to stir constant temperature bath.

Stoppers. Rubber; Solid; Size 9; Fisher Specifications; Catalog Number 14-130. Obtained from Fisher Scientific Company, 7722 Woodbury Drive, Silver Spring, Maryland. Used as a top and as a holder for the apparatus components that were placed in the H-Cell.

Switch. Pinch type; Double-Pole; Double-Throw; Catalog Number 9-323. Manufactured by Leeds and Northrup Company, Philadelphia, Pennsylvania. Distributed by Fisher Scientific Company, 7722 Woodbury Drive, Silver Spring, Maryland. Used to make and break contacts in electrical circuit of electrochemical corrosion tests.

Switch. Toggle; Double-Pole; Single-Throw. Manufactured by Cutler-Hammer, Incorporated, Milwaukee, Wisconsin. Used as the power switch for the electrodes of the H-Cell.

Thermometer. Catalog Number 15-043; Range -1 to +101°C.; Subdivisions 1/10°; Length 610 millimeters; Mercury filled. Obtained from Fisher Scientific Company, 7722 Woodbury Drive, Silver Spring, Maryland. Used in constant temperature bath.

Thermoregulator. Roto-Stat; Catalog Number 15-180-5; Range 0°F. to 220°F.; Sensitivity \pm 0.02°F. Obtained from Fisher Scientific Company, 7722 Woodbury Drive, Silver Spring,

Maryland. Used to regulate the temperature of the constant temperature bath.

Tube, Gas Dispersion. Straight; pyrex brand glass; Corning Number 39570; Porosity designation of fritted glass disc, medium; Diameter of disc, 30 millimeters; Diameter of tube, 35 millimeters; Catalog Number 15161. Obtained from Will Corporation of Maryland, P.O. Box 5195, Baltimore 24, Maryland. Used in the construction of the H-Cell to separate the anode and cathode compartments.

Vessel, Calomel Electrode. Hildebrand type; pyrex brand glass; Catalog Number 11-506-42. Obtained from Fisher Scientific Company, 7722 Woodbury Drive, Silver Spring, Maryland. Used as a vessel for saturated calomel reference cell.

Voltmeter, Vacuum Tube. Model V-6. Manufactured and distributed by the Heath Company, Benton Harbor, Michigan, Used as an indicator of open bridge and for rough measurements of voltages and resistances.

E. Method of Procedure

E. Method of Procedure

1. Construction of Calomel Cell. A saturated calomel cell for use as a reference electrode was constructed according to directions given by Potter (19). The calomel and a little mercury were ground into a paste in a mortar with saturated potassium chloride solution. This paste was placed over three-fourths of an inch of mercury in the bottom of a Hildebrand calomel cell vessel. The remaining potassium chloride solution used to fill the electrode vessel had previously stood over a little calomel to saturate the solution with the salt.

2. Construction of H-Cell. A reaction vessel in which the electrode compartments could be separated and still be in electrical contact by means of the electrolyte was constructed as shown in Figure 1. The electrode compartments were made in the shape of a test tube from one and three-fourths inch outer diameter pyrex glass tubing. These compartments were separated and connected by a gas diffusion tube 35 millimeters outer diameter and containing in the center a 30 millimeter fritted pyrex glass disc of medium porosity designation. These measurements allowed each side of the H-Cell to hold 250 milliliters of electrolyte with ample space at the top for rubber stoppers, gas bubbling, and gas escape.

3. Construction of Electrodes. Figure 2 shows the construction of the three types of electrodes used in this

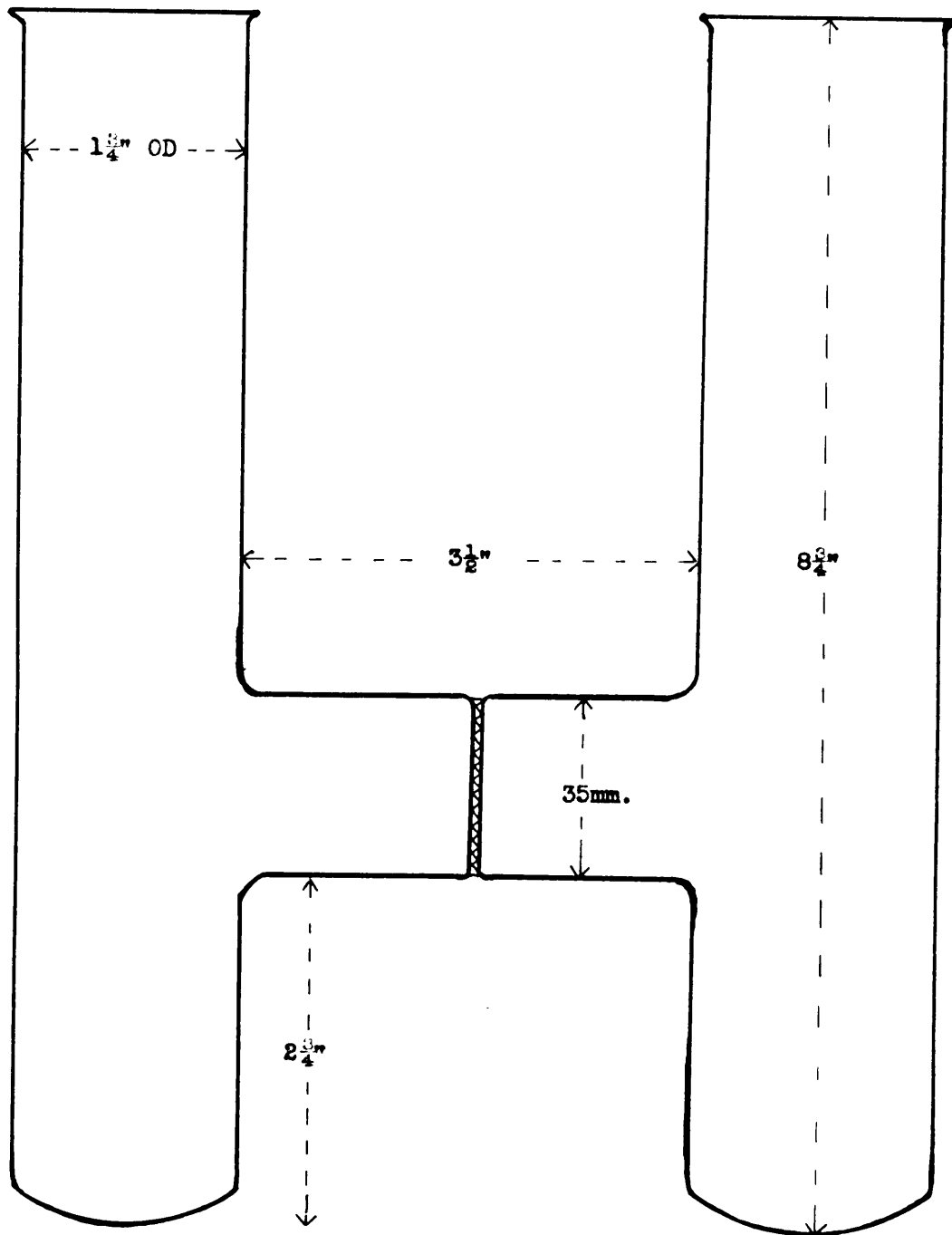


FIGURE I. ELECTROCHEMICAL H - CELL

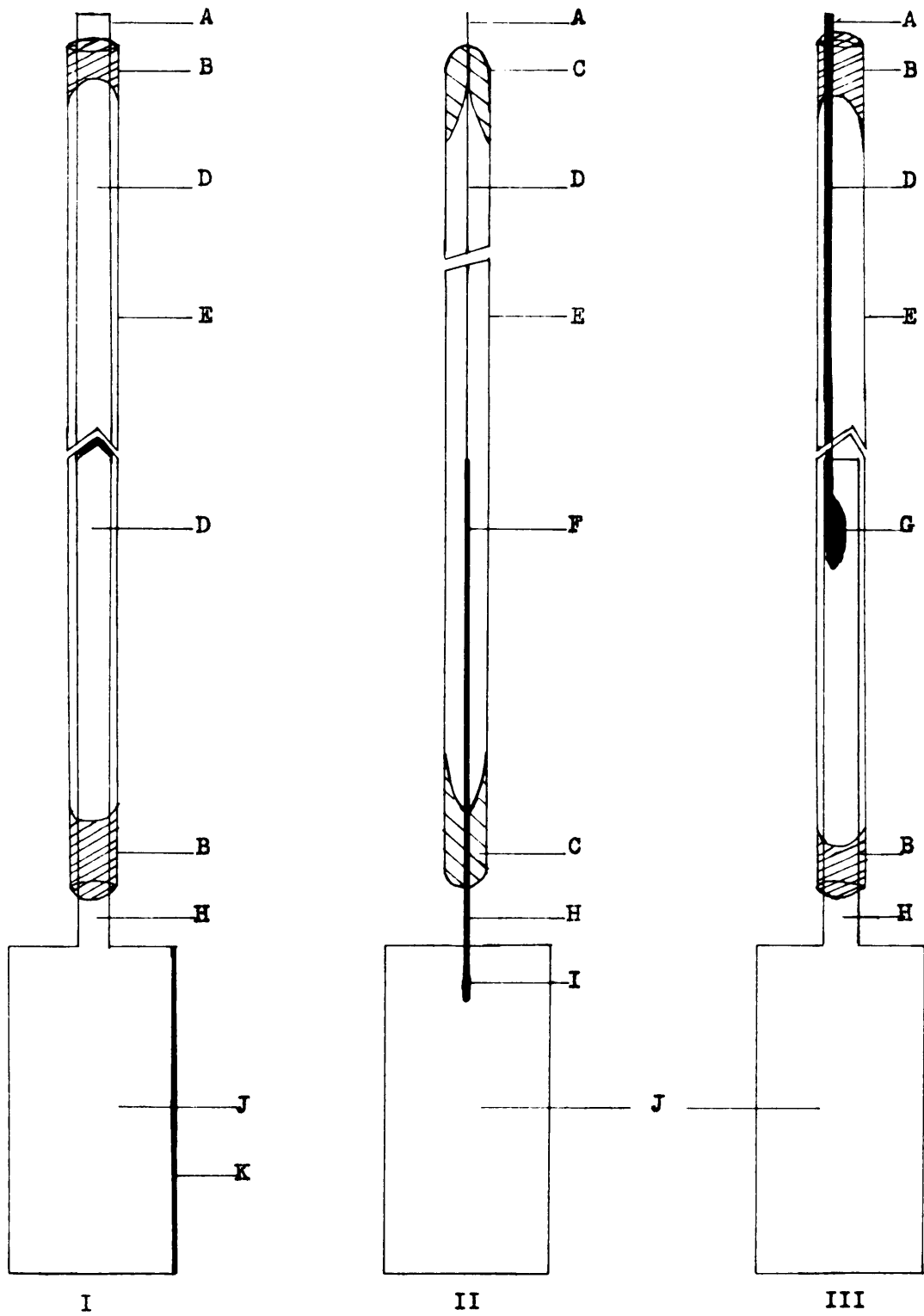


FIGURE 2. ELECTRODES

investigation. Type number II was used for platinum as a cathodic specimen and as the anode in all tests. Types I and III were used for cathodic specimens with the type of electrode used determined by the length of the metal sheet available. The surfaces of all three types had the same area exposed to solutions when immersed. Portions of the electrodes, A, were exposed at all times and to these were attached the lead wires to the electrical circuit of the apparatus. Seals of epoxy glue, B, were found to be the most satisfactory without any danger of changing the surface by heating. Another type of seal, C, was made between the pyrex glass and the platinum lead wires. In some cases, D, a change was made in the lead wire from the original that was connected directly to the electrodes, as in the type II where F was a larger diameter platinum wire than D. E in each case was a six inch length of seven millimeter pyrex glass tubing. In cases where the sheet of metal used was not long enough to make entire leads, a copper wire or a wire of the same metal was silver-soldered onto the electrode lead at G. It was necessary to expose a short length of the lead, H, to the electrolyte in order to prevent either the glass or the glue from getting on the electrode. The electrode proper was one inch wide and two inches long. The platinum electrodes were welded to platinum lead wires at I. The thickness, K, of the electrodes, J, was either 0.006 inch

or 0.003 inch depending on the sheets available.

4. Electrode Cleaning Procedure. All electrodes were cleaned each time they were used immediately before they were immersed in an electrolyte in the cell and after each test. Platinum electrodes were cleaned by rinsing with acetone, rinsing with distilled water, swirling in fresh concentrated hydrochloric acid, and then igniting in a Meker burner flame until red hot. This procedure was followed three times. Electrodes of other metals were cleaned by rinsing with acetone, rinsing with water, swirling in fresh concentrated hydrochloric acid, rinsing with distilled water, polishing by a fine pumice stone powder by means of rubbing under distilled water with the aid of a small cork until a bright surface was exposed, rinsing with distilled water, dried by sponging with a paper towel, rinsed with anhydrous ethyl ether and sponged dry with a second paper towel. This treatment was repeated each time an electrode was used as a cathodic specimen.

5. Cathodic Specimen Holder Assembly. The electrode used as a cathodic specimen was placed in the holder as shown in Figure 2 (a). The electrode could be moved slightly closer to or away from the capillary tip of the portion of the acid bridge that was incorporated in the specimen holder. The holder also held the nitrogen bubble tube which was constructed out of seven millimeter pyrex glass tubing 270 millimeters

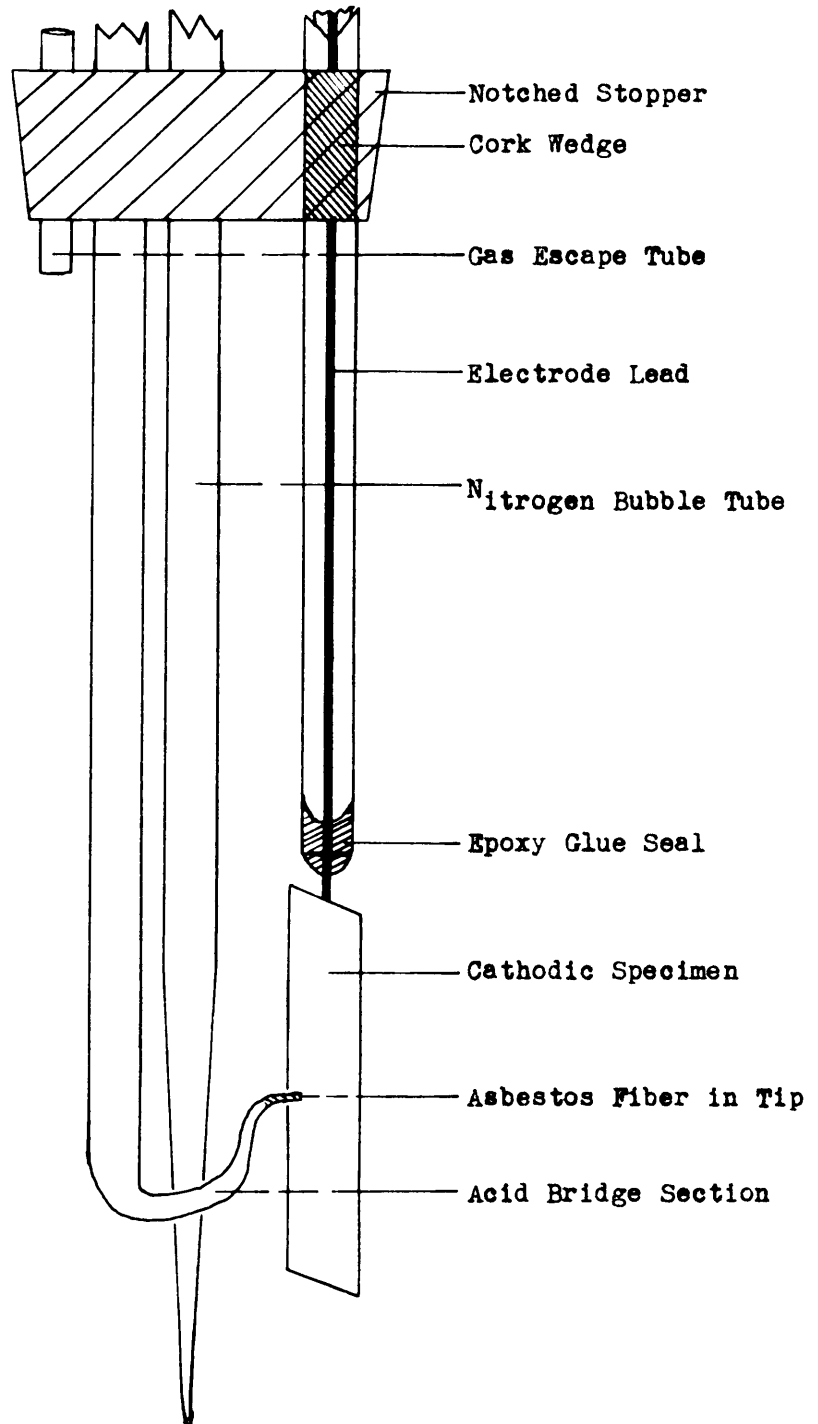


FIGURE 2 (a). CATHODIC SPECIMEN HOLDER ASSEMBLY

from tip to right angle bend then 75 millimeters extension. Approximately 185 millimeters from the right angle bend, the tubing was drawn down 85 millimeters to the one and three-fourths millimeter outer diameter, one millimeter inner diameter tip. The tip of the nitrogen bubbling tube was placed in the holder in such a manner that it was six centimeters from the center of the electrode which was placed in the holder so that its center would be opposite the center of the joining tube of the H-Cell. The portion of the acid bridge held by the holder was 300 millimeters long from bend to top end. Width of the bend was 20 millimeters with the tip rising one centimeter above the bottom of the bend. The tip of the acid bridge was drawn out to one and one-half millimeters outer diameter with three tenths of a millimeter inner diameter sealing in a centimeter length of asbestos fiber. The depth of the bend was such that when an electrode was placed in assembly the tip of the acid bridge was opposite to the center of the electrode.

6. Acid Bridge Construction. The section of the acid bridge which remained with the cathodic specimen holder as part of that assembly has already been described under the previous heading. To the latter was attached a two inch length of tygon tubing forming an elbow. This elbow in turn was attached to a glass "T", the legs of which were three inches long. To the middle leg of the "T" another

two inch length of tygon tubing was used to connect the "T" with a twenty milliliter leveling bulb which could be stoppered with a rubber stopper. To the leg of the "T" on the opposite side from that attached to the cathodic specimen assembly a third two inch length of tygon tubing formed the second elbow in the bridge. From the latter hung a 300 millimeter glass tube ending with a one centimeter right angle bend drawn out to a one millimeter outer diameter, one-half millimeter inner diameter tip. This tip was placed in the electrolyte beaker into which also dipped the tip of the saturated calomel reference cell. The elbows of this acid bridge were provided with hosecock screw clamps.

7. Arrangement of Apparatus. The apparatus was arranged in the following manner, Figure 3 (a): The calomel cell, acid bridge junction beaker and the H-Cell were suspended in a constant temperature bath maintained at a constant temperature of 30°C . $\pm 0.05^{\circ}\text{C}$. Nitrogen gas was fed to the H-Cell from the nitrogen train. A lamp and scale and a galvanometer were provided for the potentiometer. A standard cell and a two volt battery were connected to the potentiometer. By means of the switch box the external electromotive force from the batteries could be connected to the electrodes and they in turn to the potentiometer.

Figure 3 (b) gives the arrangement of the nitrogen train. The oil-pumped commercial nitrogen was reduced in pressure at

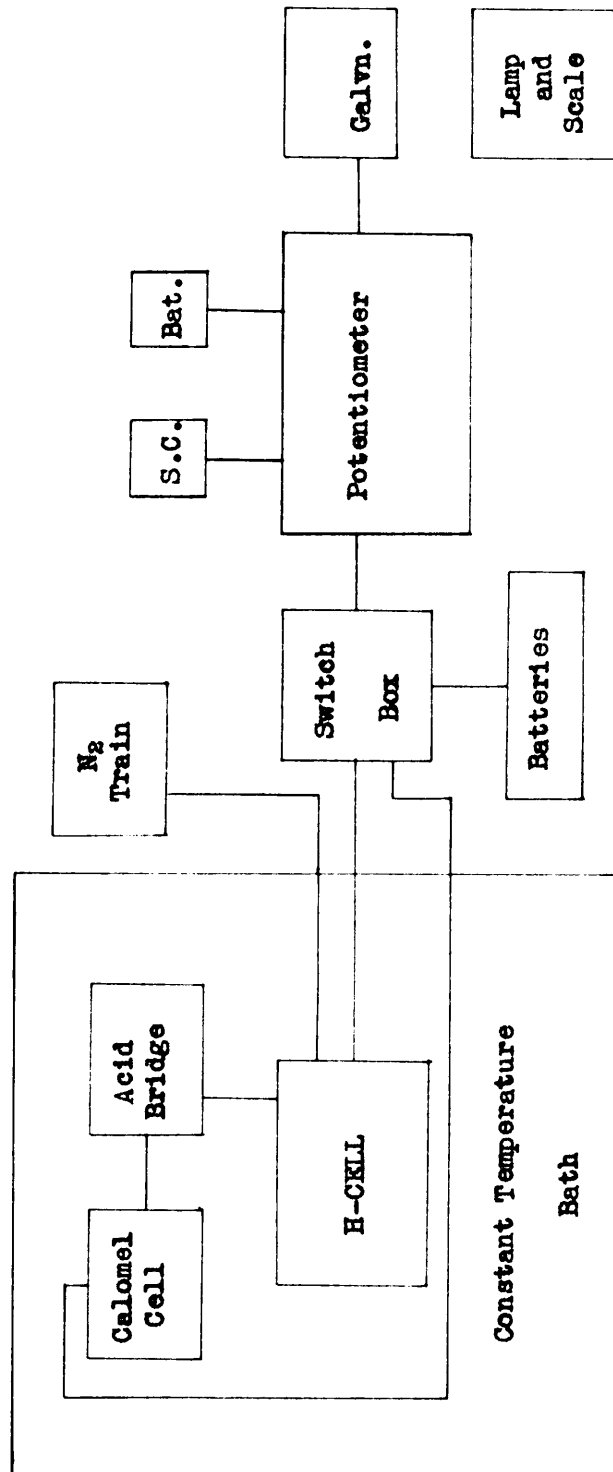


FIGURE 3 (a). BLOCK DIAGRAM OF APPARATUS

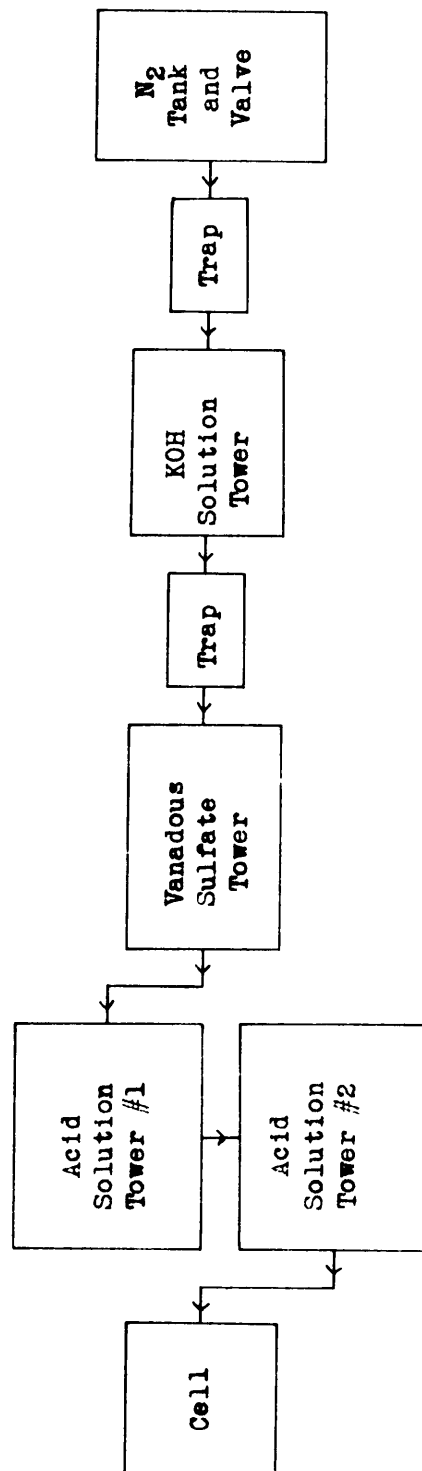


FIGURE 3 (b). BLOCK DIAGRAM OF NITROGEN TRAIN

the tank by the valve. From the valve it flowed through rubber tubing to a trap, thence to the 40 per cent potassium hydroxide solution tower for removal of carbon dioxide, thence to a trap, thence to the vanadous sulfate tower for removal of oxygen, thence to acid solution towers and then to the cell. The traps consisted of 25x200 millimeter test tubes containing small amounts of glass wool. These traps prevented contamination of other components of the train in the event of "suckbacks" or sudden pressure changes as when removing the electrode assembly from the H-Cell. The vanadous sulfate solution tower was furnished by White (25) according to an article by Meites and Meites (18). The acid solution towers were made from various size flasks and were used to prevent contamination of the electrolyte in the H-Cell by any vanadium compounds that might leave the vanadous sulfate tower. The second acid solution tower also kept the nitrogen gas moisturized so there would not be a change in volume of the electrolyte in the H-Cell due to evaporation caused by the flow of the nitrogen gas.

Electrically, the apparatus was connected as shown in Figure 3 (c). The negative end terminal of three two volt lead storage cells in series was connected directly to the electrode in the cathodic compartment of the H-Cell. The end positive terminal of the batteries was connected to a 5000 ohm rheostat, R_1 . In series with this rheostat was a

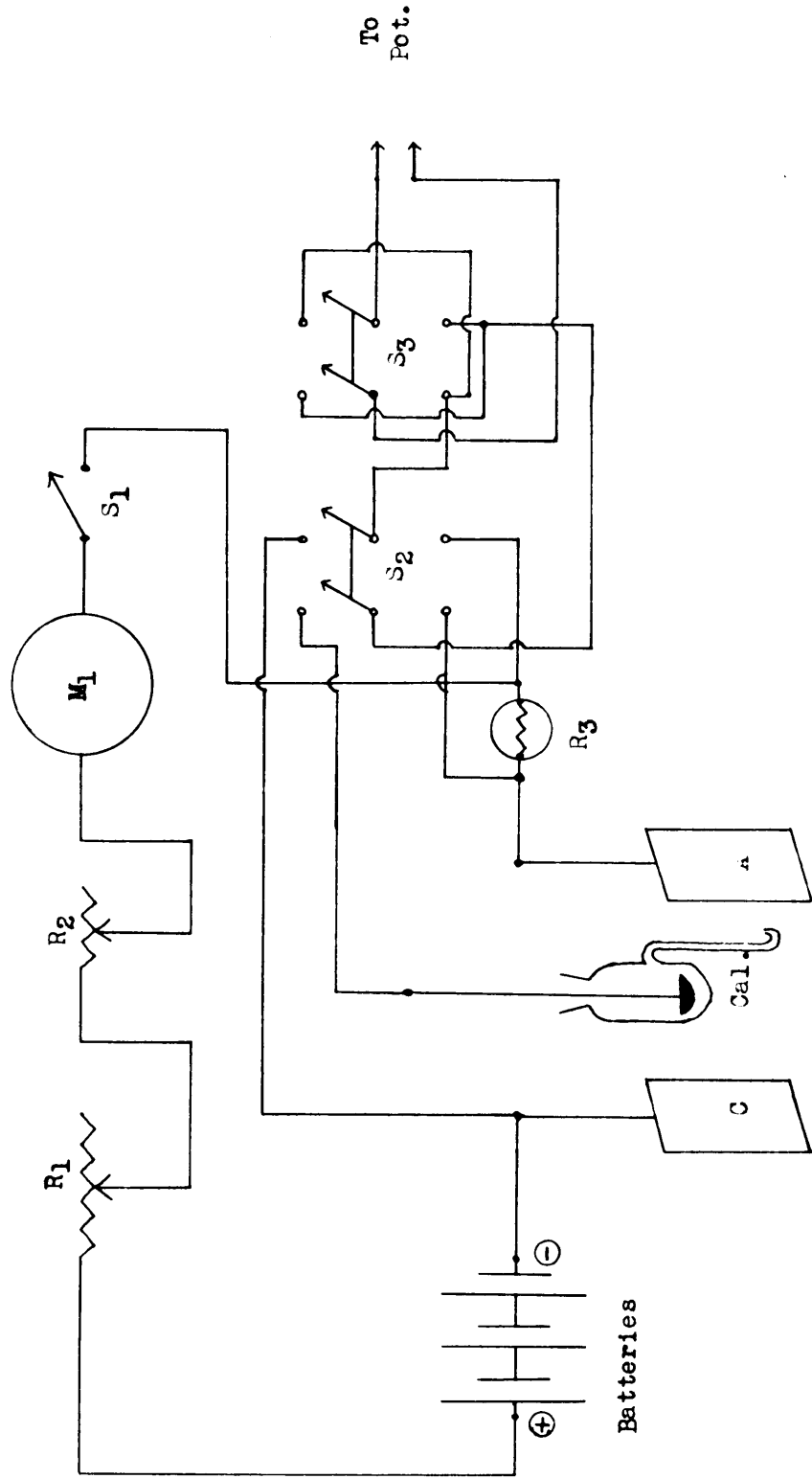


FIGURE 3 (c). ELECTRICAL DIAGRAM OF APPARATUS

500 ohm rheostat, R_2 , to which was connected a 0-10 milliammeter, M_1 , used as an indicator, and thence to a switch, S_1 . The opposite terminal of switch S_1 was connected to one side of a one ohm standard resistor, R_3 . The anode was connected to the other terminal of the standard resistor. Switch S_2 was also connected to the standard resistor so that the potential drop across the resistor could be measured by the potentiometer. This potential drop was a direct measure of the amount of current flowing in the electrochemical cell. Switch S_2 was used so that one could either measure the current flowing in the circuit or the potential difference between the cathodic specimen and the saturated calomel cell. Switch S_3 was used to reverse the polarity of the leads to the potentiometer without having to disconnect the leads from the potentiometer. Switch S_1 was a toggle switch used as a power switch. The calomel cell could be used with either the cathode, C , or with the anode, A , by making one different connection.

8. Removal of Oxygen. Each electrolyte was boiled for three minutes and then cooled to 30°C. by bubbling nitrogen through it. Likewise, the H-Cell, connecting tubes, and electrolyte were purged with nitrogen prior to dipping electrodes into the solution. Nitrogen from the nitrogen train was bubbled through the solution in both compartments of the H-Cell throughout each test.

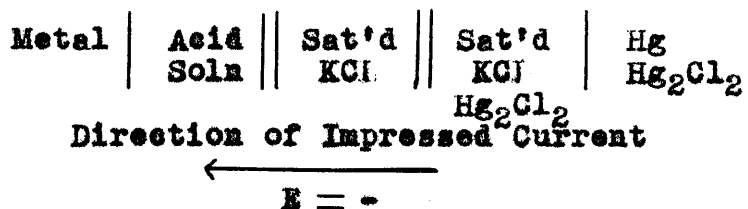
9. Preparation of Electrolytes. Electrolytes used in the investigation were 4.9 per cent (1 normal) sulfuric acid, five per cent phosphoric acid, and five per cent acetic acid. Reagent grade, concentrated acids were diluted in each case to the required concentration. The amount of acid present was determined by titration of samples with previously standardized sodium hydroxide solution. Electrolytes of required concentrations were stored in large glass carboys. Removal for use was accomplished by means of siphons.

10. Preparation of Inhibitor Solutions. Solutions of inhibitors were prepared by dissolving small amounts (6.25%) of the inhibitors in the acid solutions used as electrolytes. These inhibitor solutions were stored in bottles and used according to the acid solution under investigation. For example, if the cathode potential of iron in sulfuric acid was under observation, an inhibitor solution for use in this electrolyte was tri-n-amyamine dissolved in deoxygenated sulfuric acid. Additions to the cathode compartment were made with calibrated pipets.

11. Current Measurements. The total current flowing between cathode and anode was maintained constant at one milliamperere by adjustment of the rheostats in the anode circuit. The potential drop across the one ohm standard resistor was measured with the potentiometer and considered a numerical measurement of the total current flowing in the

circuit. Adjustment was made until the galvanometer gave zero deflection for a value of 0.00100 ampere.

12. Cathode Potential. All potential differences between the saturated calomel cell and the electrode in the cathode compartment of the H-Cell were considered as cathode potentials. The saturated calomel cell potential was designated as zeropotential. This was equivalent to the following cell:



13. General Procedure. At the beginning of each test the H-Cell was scrubbed with a test tube brush and detergent solution, then rinsed with tap water until the water would drain completely and then rinsed three times with distilled water and once with electrolyte solution to be used in the test. Electrodes were then cleaned according to prescribed procedure.

The H-Cell was purged with nitrogen and filled with pretreated acid solution to a previously marked line (250 milliliters) on each side of the cell. Glass tubes of the electrode assemblies were rinsed with nitrogen and then the assemblies were placed in the H-Cell. Assemblies were adjusted so that the electrode surfaces were perpendicular by sight to each other and the acid bridge tip was approximately one-eighth inch from the electrode. The H-Cell was then placed in the constant temperature bath.

Nitrogen lines from the nitrogen train were connected to the bubbling tubes in each side of the cell and the flow rate was adjusted to approximately 60 bubbles per minute in the cathode compartment and approximately 50 bubbles per minute in the anode compartment. Hosecock screw clamps on the rubber tubing from the nitrogen train aided in the latter adjustments along with the nitrogen tank needle valve. The nitrogen tank needle valve was used to adjust the bubble flow in the potassium hydroxide tower to 50 bubbles per minute.

After filling the liquid junction beaker two-thirds full of electrolyte the screw clamp on the acid bridge elbow away from the cathode compartment was closed. The reservoir of the acid bridge was then filled and connected to the tube in the cathode compartment electrode assembly. Nitrogen in this tube was allowed to flow through the acid bridge tip until the tube and tip were completely filled with acid solution. Then the screw clamp on that side was closed. Procedure was repeated for the other side and then the reservoir and junction beaker were filled with acid solution and a rubber stopper inserted in the top of the reservoir.

The screw clamp on the acid bridge elbow above the liquid junction beaker was opened approximately half way. After connecting the electrodes to the switch box a vacuum tube voltmeter was used to measure the resistance between the

cathodic specimen and the calomel cell and the resistance was adjusted to a minimum value by opening the stopcock of the calomel cell and slightly opening the screw clamp on the acid bridge elbow on the cathode compartment side of the bridge. Adjustment of the potentiometer to the standard cell was made and a measurement of the potential difference between the calomel cell and the cathodic corrosion specimen was taken and recorded.

The external e.m.f. was then applied and the current flow was adjusted to 0.00100 ampere as shown by the potentiometer. With the constant current flowing a measurement was made of the cathode potential. Switches S_2 and S_3 were opened until time for the next measurement.

Shortly before the next measurement the resistance between the calomel cell and the cathode was checked with the vacuum tube voltmeter to see if the bridge was continuous. The standard cell and potentiometer were balanced, and the cathode potential value and time of measurement were recorded. Values of cathode potentials were plotted against times of measurements to determine the time required for the potential to reach a steady state (less than one mv. change per hour).

When tests were made in which inhibitor solutions were required, pipets were made out of seven millimeter glass tubing drawn out to very small tips. Drops of inhibitor solutions were added to the cathode compartment of the H-Cell by placing

the calibrated pipet through the gas escape tube of the cathode electrode assembly stopping when the tip of the pipet was one-fourth inch from the surface of the electrolyte in the H-Cell compartment.

Measurements of the cathode potentials, time and quantity of inhibitors or inhibitor added were made and recorded as outlined above in tests where applicable.

Distilled water was added to the constant temperature bath at intervals to maintain a constant level in the bath.

14. H-Cell Immersion Depth. It was found that the most satisfactory depth of immersion of the H-Cell in the constant temperature bath was given when the H-Cell was supported by a three-pronged clamp around the cathode compartment with the top prong being placed one-half inch from the top of the compartment. This allowed the H-Cell and contents to be immersed to a depth of two inches above the horizontal member of the H-Cell when the clamp arm was supported one-eighth inch above glass bath vessel, the water in the bath being one-half inch below the clamp arm.

Thus, the temperature of the H-Cell and its contents were kept at 30°C. The liquid junction beaker and the calomel cell were immersed to a depth which maintained a constant temperature of 30°C.

15. Specific Procedure.

(a) Determination of the Effect of Nitrogen Flow Rate on Potential. The nitrogen flow rate to the cathode and

anode compartments was adjusted by means of two screw clamps, one at the cell and one at the end of the nitrogen train. Adjustment of the screw clamps allowed different quantities of nitrogen to flow through glass "Y" tubes and rubber tubing to the electrode assemblies. The cell was set up and the cathode potential was measured and recorded for several values of nitrogen flow rate. Flow rate is defined as the number of nitrogen gas bubbles leaving the nitrogen tube of the electrode assembly per minute.

(b) The Current-Potential Relationship of a Steel Electrode in 4.9 Per Cent Sulfuric Acid. The potential and the total amount of current in milliamperes flowing through the cell were measured at several different values. The cathode potential corresponding to each cell potential was also measured and recorded. The direction in which the switch, S₃, was placed for each measurement was also recorded.

(c) Relationship of Potential-Time Curves of Electrodes Used. Using a total current of one milliampere the cathode potentials of several metals were measured as a function of time in 4.9 per cent sulfuric acid. Mild steel, platinum, copper, tin, nickel, inconel, monel and yellow brass were used for specimen electrodes. Their cathode potentials were measured over a period of several hours and recorded with the corresponding time of measurement.

(d) Potential-Time Relationships of Mild Steel in Inhibited Sulfuric Acid. The cathode potential of mild steel was measured and recorded as a function of time in 4.9 per cent sulfuric acid in which an excess of an inhibitor had been added and mixed. The excess was determined by using larger quantities than those given by Eldredge and Warner (4) for 90 per cent inhibition. Tri-n-amylamine, benzaldehyde, tri-n-hexylamine, thiourea and pinacolone were used as inhibitors. Separate tests were made with each inhibitor. The cathode potential as a function of time was also measured for uninhibited 4.9 per cent sulfuric acid.

(e) Effect of a Commercial Inhibitor Mixture on the Potential-Time Relationship of Mild Steel in 4.9 Per Cent H₂SO₄. A mixture was made of three commercial inhibitors in the ratio of one part Primene JM-T to three parts Priminox 21 to two parts Priminox 32 (20). The cathode potential of mild steel was measured and recorded as a function of time in a 4.9 per cent sulfuric acid solution to which one-tenth of one per cent of the above mixture had been added.

(f) Effects of Delayed Additions of Inhibitors on Cathode Potentials in 4.9 Per Cent H₂SO₄. The previously determined potential-time curves of mild steel, monel, platinum, and copper were used to locate a point of steady potential in the potential-time relationship of these metals. Separate tests were made in which the cathode potential was allowed to

vary with time until the previously mentioned point of time had been reached. At this point an excess of tri-n-amylamine (0.10 per cent) was added directly to the cathodic compartment of the H-Cell. The potential of the cathode in the inhibited solution was then measured and recorded as a function of time.

(g) Effects of Inhibitors on the Cathode Potential of Copper in 4.9 Per Cent H_2SO_4 . The cathode potential of copper was measured and recorded as a function of time in uninhibited 4.9 per cent sulfuric acid and also in sulfuric acid to which an inhibitor had been added in excess. The inhibitors used were thiourea, pinacolone and 2-nitro-1-butanol. Excess quantities were the same as in (d).

(h) Effects of Inhibitor Concentration on the Cathode Potential of Mild Steel in 4.9 Per Cent H_2SO_4 . The cathode potential of mild steel in sulfuric acid was measured as a function of concentration of inhibitor. Inhibitor solutions were made up by dissolving a known amount of the pure organic compound in a known weight of deoxygenated 4.9 per cent sulfuric acid. Quantities of the inhibitor solution were added to the cathode compartment of the H-Cell by using calibrated pipets inserted through the gas escape tube of the electrode assembly. Thiourea, tri-n-amylamine and the commercial inhibitor mixture were used as inhibitors.

(i) Cathode Potential-Time Relationships of Mild Steel and Platinum in 5 Per Cent Acetic Acid. The cathode

potential of mild steel as a function of time and the cathode potential of platinum as a function of time were measured in five per cent acetic acid solution. Potential measurements and times of measurements were recorded.

(j) Relationship of Cathode Potentials with Time in 5 Per Cent Phosphoric Acid. Observations of the cathode potentials of several metals were made and recorded as a function of time in five per cent phosphoric acid. The cathode potentials of mild steel and copper were made and recorded as a function of time in phosphoric acid to which an inhibitor had been added. The inhibitors used were tri-n-nylamine, 2-nitro-1-butanol and the commercial inhibitor mixture. The quantity added was an excess as in (d).

16. Sign of Cell Potentials. The signs of the cell potentials were determined by noting the direction of current flowing through a galvanometer, which had been checked for direction of deflection in a circuit whose direction of current flow was known.

F. Data and Results

F. Data and Results

(a) Effect of Nitrogen Flow Rate on Potential.

The data in Table I were plotted in Figure 4 to show the effect of the rate of flow of nitrogen gas on the cathode potential. The figure shows that there was a very small change in the cathode potential over a wide range of bubbles of nitrogen gas per minute.

(b) Current-Potential Relationship of Steel Electrode in 4.9 Per Cent H₂SO₄.

The data given in Table II were plotted in Figure 5 to show by experiment that the electrodes placed in the so-called cathodic compartment of the H-Cell were acting as cathodes. A positive current of one milliampere was in the cathodic area.

(c) Relationship of Potential-Time Curves of Electrodes Used.

The potential and time measurements tabulated in Table III for the various metals used as cathodic specimens in this investigation were plotted in Figure 6 to show the relationship of the potential versus time curves of the metals used under the conditions of the investigation.

(d) Potential-Time Relationships of Mild Steel In Inhibited Sulfuric Acid.

The data of Table IV were plotted in Figure 7 to show the effects of various quantities of different inhibitors on

TABLE I

Effect of Nitrogen Flow Rate on Potential

Flow in Bubbles per Minute	Cathode Potential Volts
8	-0.50235
24	-0.50225
40	-0.50233
62	-0.50225
65	-0.50230
110	-0.50235
196	-0.50230
272	-0.50230

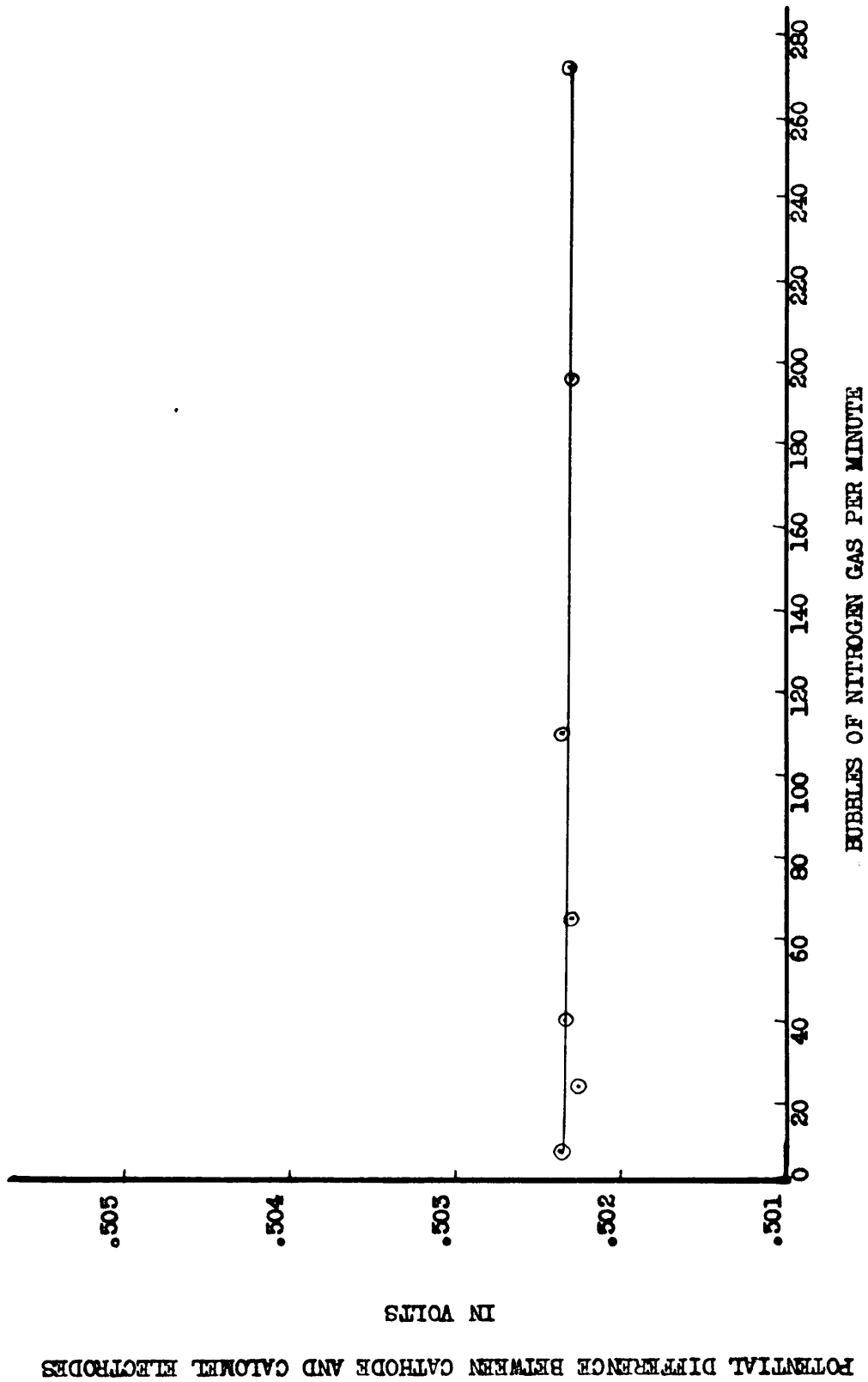


FIGURE 4. EFFECT OF NITROGEN FLOW RATE ON POTENTIAL

TABLE II

Current-Potential Relationship of Steel Electrode
in 4.9 Per Cent H₂SO₄

Direction of S ₃ Switch	Current I Milliamperes	Cathode Potential Volts	Cell Potential E Volts
Left	-0.00	-0.42	-1.15
Right	0.00	-0.42	-1.20
Left	-8.75	-0.42	-0.26
Left	-19.9	-0.42	-0.035
Right	3.9	-0.43	-1.80
Right	26.1	-0.48	-2.18
Right	56.2	-0.52	-2.45
Right	104.2	-0.54	-2.85
Right	213.2	-0.56	-3.77

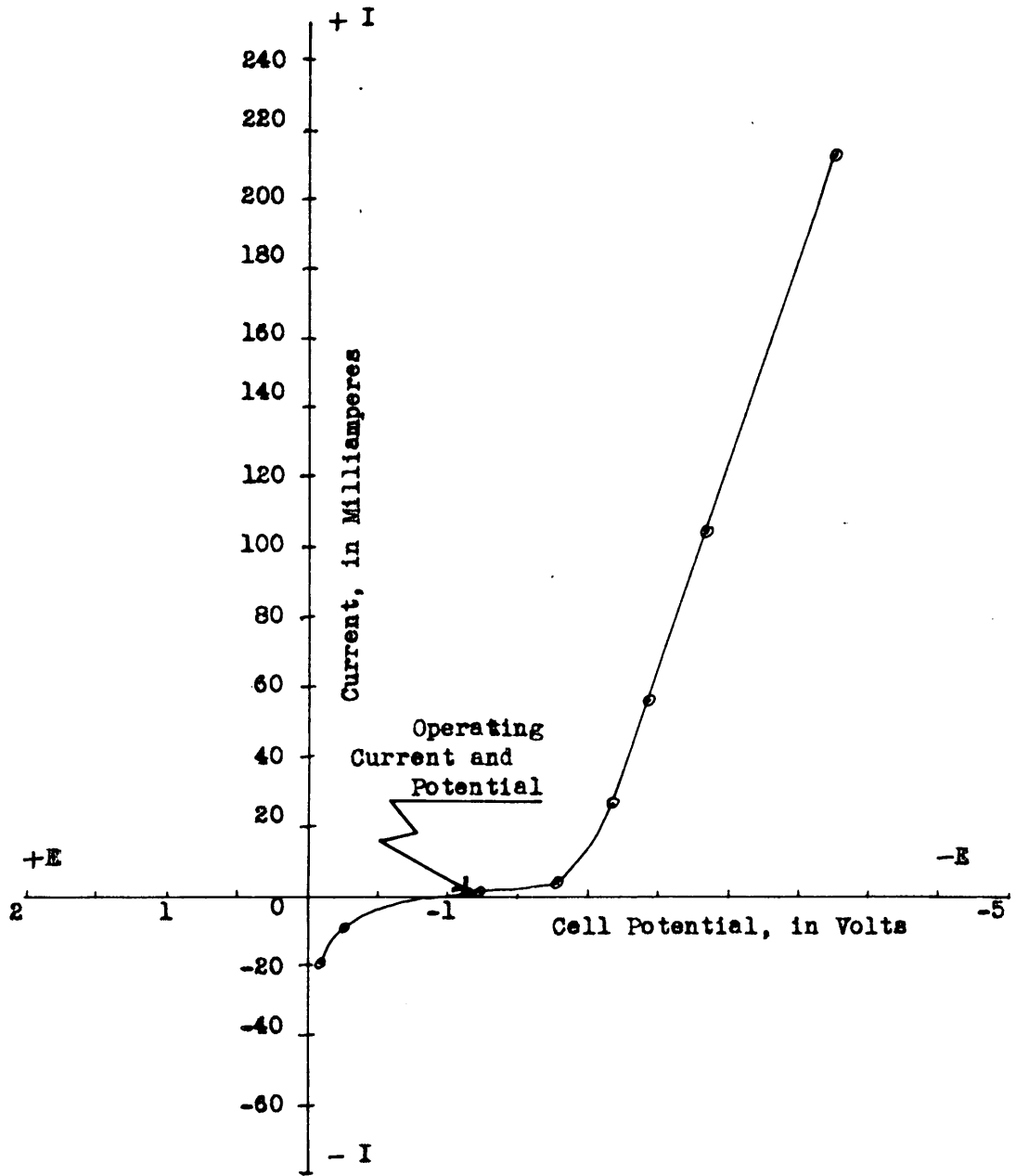


FIGURE 5. CURRENT-POTENTIAL RELATIONSHIP OF STEEL

ELECTRODE IN 4.9 PER CENT H_2SO_4

TABLE III

Relationship of Potential-Time Curves
in 4.9 Per Cent H₂SO₄*

Metal	Cathode Potential Volts	Time Hours	Metal	Cathode Potential Volts	Time Hours
Steel	-0.4851	0.00	Nickel	-0.3525	0.00
Steel	-0.5005	1.50	Nickel	-0.4165	1.00
Steel	-0.5072	2.75	Nickel	-0.4435	3.67
Steel	-0.5080	3.34	Nickel	-0.4470	4.67
Steel	-0.5083	6.00	Nickel	-0.4500	5.50
Steel	-0.5081	8.00	Nickel	-0.4559	19.3
Steel	-0.5092	19.0	Inconel	-0.2640	0.00
Platinum	-0.2467	0.00	Inconel	-0.3656	2.00
Platinum	-0.2609	1.34	Inconel	-0.4500	8.25
Platinum	-0.2818	3.00	Inconel	-0.4590	11.6
Platinum	-0.3644	12.0	Inconel	-0.4710	15.0
Platinum	-0.3749	14.5	Monel	-0.3546	0.00
Platinum	-0.4000	19.0	Monel	-0.4250	1.00
Copper	-0.5910	0.00	Monel	-0.4705	2.00
Copper	-0.6015	0.34	Monel	-0.5010	6.00
Copper	-0.6295	1.34	Monel	-0.5065	15.0
Copper	-0.6345	12.3	Brass	-0.5774	0.00
Copper	-0.6363	13.3	Brass	-0.6325	2.00
Copper	-0.6363	14.0	Brass	-0.6640	4.50
Tin	-0.7029	0.00	Brass	-0.6811	7.00
Tin	-0.7343	2.25	Brass	-0.6980	10.0
Tin	-0.7394	3.25	Brass	-0.7268	20.0
Tin	-0.7575	9.00			
Tin	-0.8075	18.0			

*Total Current 0.00100 Ampere

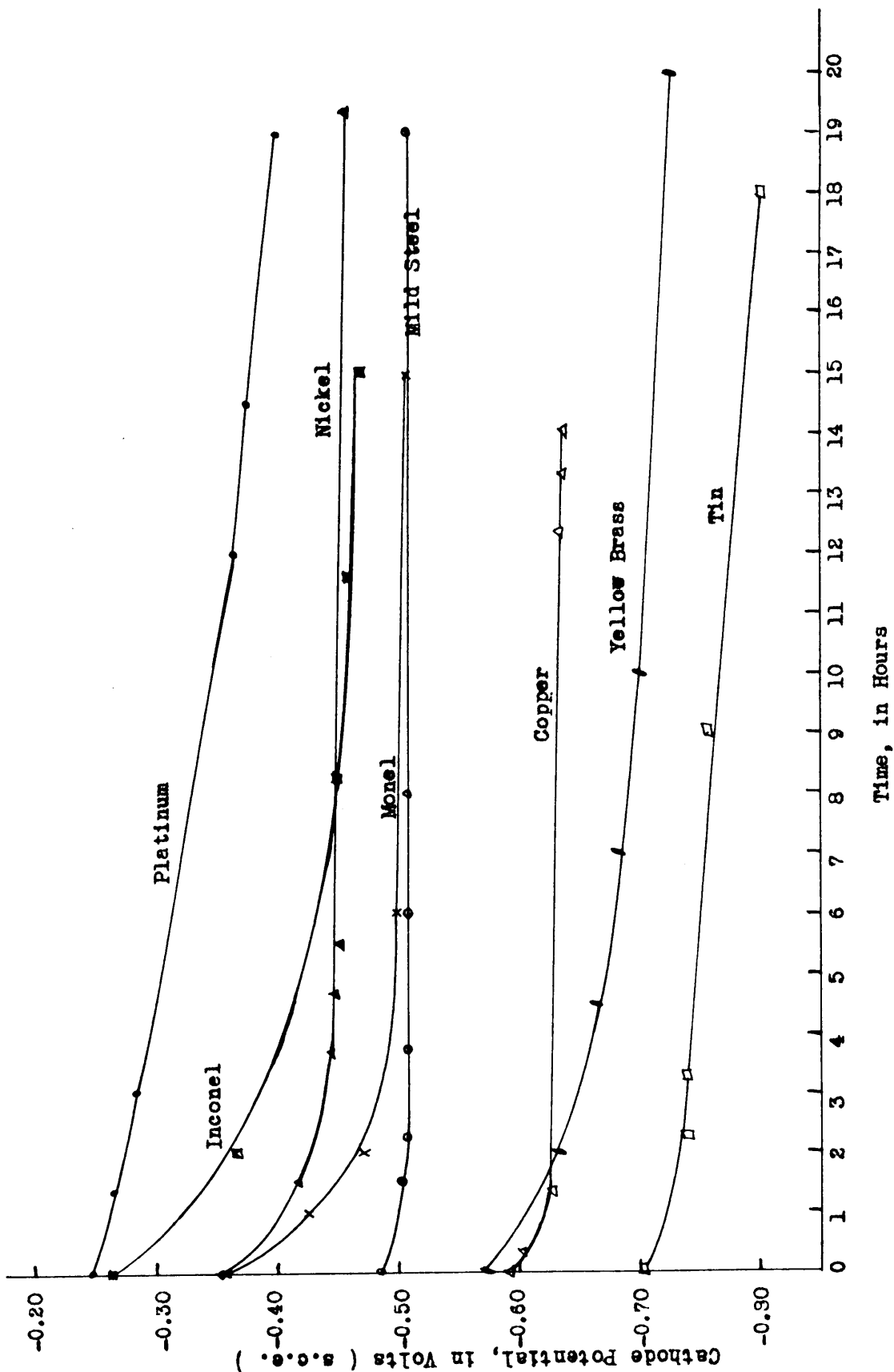


FIGURE 6. RELATIONSHIP OF POTENTIAL-TIME CURVES OF ELECTRODES USED

TABLE IV

Potential-Time Relationships of Mild Steel
in Inhibited 4.9 Per Cent H₂SO₄

Cathode Potential Volts	Inhibitor in Excess	Time Hours	Cathode Potential Volts	Inhibitor in Excess	Time Hours
-0.4963	Zero	0.00	-0.4978	Tri-n-hexylamine ^c	0.00
-0.5006	Zero	0.50	-0.4959	Tri-n-hexylamine	0.50
-0.5075	Zero	0.75	-0.4858	Tri-n-hexylamine	1.25
-0.5105	Zero	1.00	-0.4850	Tri-n-hexylamine	2.75
-0.5121	Zero	1.80	-0.4823	Tri-n-hexylamine	4.25
-0.5123	Zero	6.80	-0.4807	Tri-n-hexylamine	8.50
-0.5125	Zero	15.0	-0.4783	Tri-n-hexylamine	15.3
-0.4872	Tri-n-amylamine ^a	0.00	-0.5375	Thiourea ^d	0.00
-0.4863	Tri-n-amylamine	1.00	-0.5333	Thiourea	0.30
-0.4854	Tri-n-amylamine	2.00	-0.5233	Thiourea	2.75
-0.4832	Tri-n-amylamine	3.00	-0.5204	Thiourea	4.80
-0.4817	Tri-n-amylamine	4.34	-0.5167	Thiourea	10.0
-0.4793	Tri-n-amylamine	11.3	-0.5153	Thiourea	18.0
-0.4990	Benzaldehyde ^b	0.00	-0.4898	Pinacolone ^e	0.00
-0.5062	Benzaldehyde	2.25	-0.4894	Pinacolone	1.00
-0.5060	Benzaldehyde	4.00	-0.5002	Pinacolone	2.00
-0.5061	Benzaldehyde	13.0	-0.5037	Pinacolone	3.80
-0.5022	Benzaldehyde	14.0	-0.5038	Pinacolone	6.00
-0.4880	Benzaldehyde	17.0	-0.5032	Pinacolone	10.0
			-0.5003	Pinacolone	13.0
a-0.10%	Tri-n-amylamine				
b-0.41%	Benzaldehyde				
c-0.10%	Tri-n-hexylamine				
d-0.04%	Thiourea				
e-2.0%	Pinacolone				

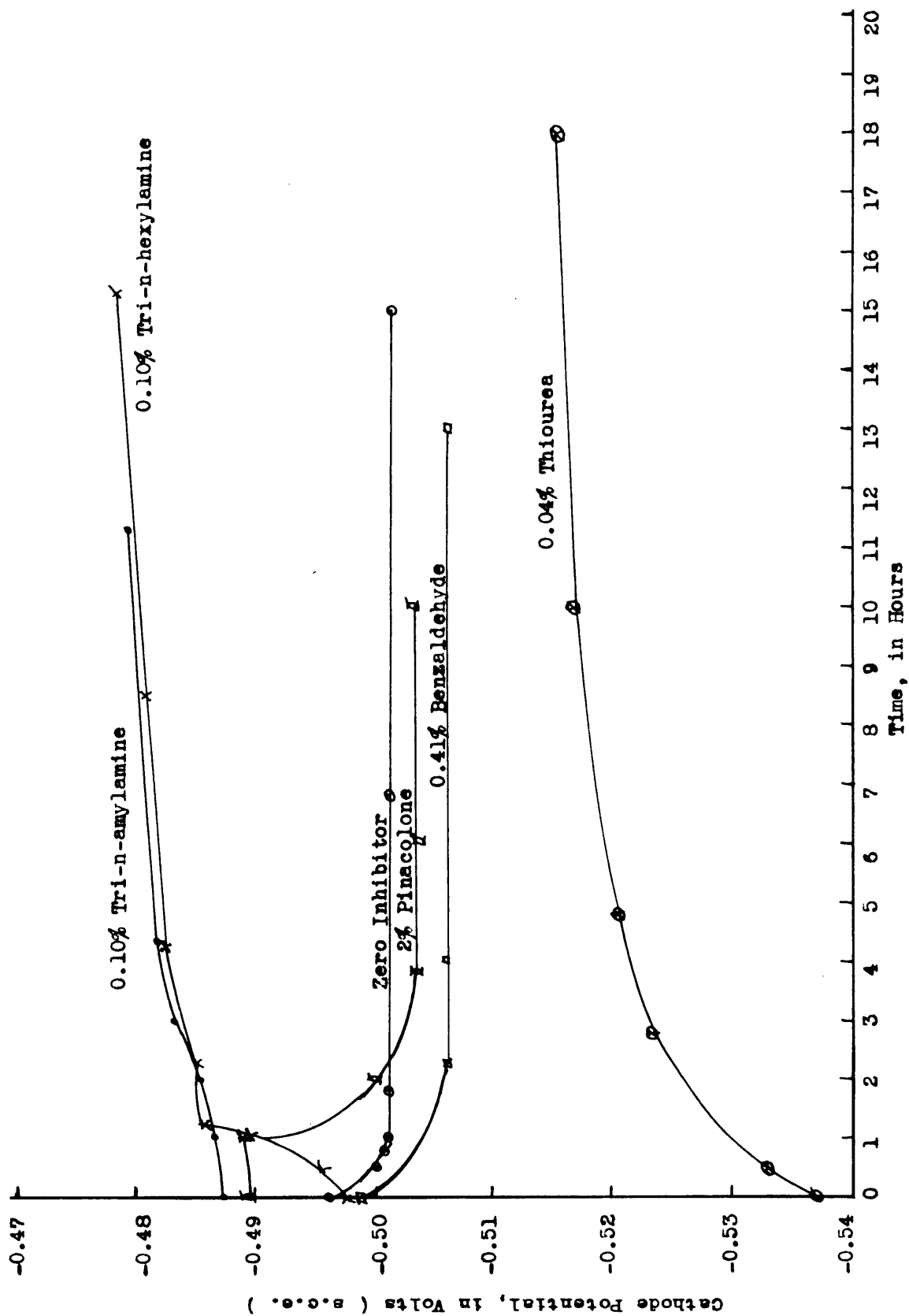


FIGURE 7. POTENTIAL-TIME RELATIONSHIPS OF MILD STEEL IN INHIBITED, 4.9 PER CENT SULFURIC ACID

the cathode potential of mild steel in 4.9 per cent sulfuric acid. The curves of tests in which tri-n-amylamine, tri-n-hexylamine and thiourea were used as inhibitors sloped in the electropositive direction while those curves of tests in which benzaldehyde and pinacolone were used as inhibitors sloped in the electronegative direction.

(e) Effect of a Commercial Inhibitor Mixture on the Potential-Time Relationship of Mild Steel in 4.9 Per Cent H₂SO₄.

The data in Table V were plotted in Figure 8 to show the effect of a mixture of known commercial inhibitors on the cathode potential of mild steel in 4.9 per cent sulfuric acid. The curve of the test in which the commercial inhibitor was added is shown to be displaced in a more electropositive direction. After several hours the slope of this curve is slightly toward the electropositive direction while that of the test in which no inhibitor was added slopes slightly in the electronegative direction. The inhibitor used was a mixture of Primene JM-T, Priminox 21 and Priminox 32 in a ratio of 1:3:2 parts, respectively (20).

(f) Effects of Delayed Additions of Inhibitors on Cathode Potentials in 4.9 Per Cent H₂SO₄.

The data from Table VI were plotted in Figure 9 to show the effects of making additions of inhibitors to the corrosion cell after the cathode potential-time curves had reached a steady state. One-tenth of one per cent tri-n-amylamine

TABLE V

Effect of a Commercial Inhibitor Mixture on the
Potential-Time Relationship of Mild Steel
in 4.9 Per Cent H_2SO_4

Cathode Potential Volts	Inhibitor	Time Hours
-0.4963	Zero	0.00
-0.5006	Zero	0.50
-0.5075	Zero	0.75
-0.5105	Zero	1.00
-0.5121	Zero	1.80
-0.5123	Zero	6.80
-0.5125	Zero	15.0
-0.4555	JMT:Pr121:Pr132	0.00
-0.4569	JMT:Pr121:Pr132	0.25
-0.4568	JMT:Pr121:Pr132	0.50
-0.4569	JMT:Pr121:Pr132	1.00
-0.4568	JMT:Pr121:Pr132	1.50
-0.4558	JMT:Pr121:Pr132	15.0

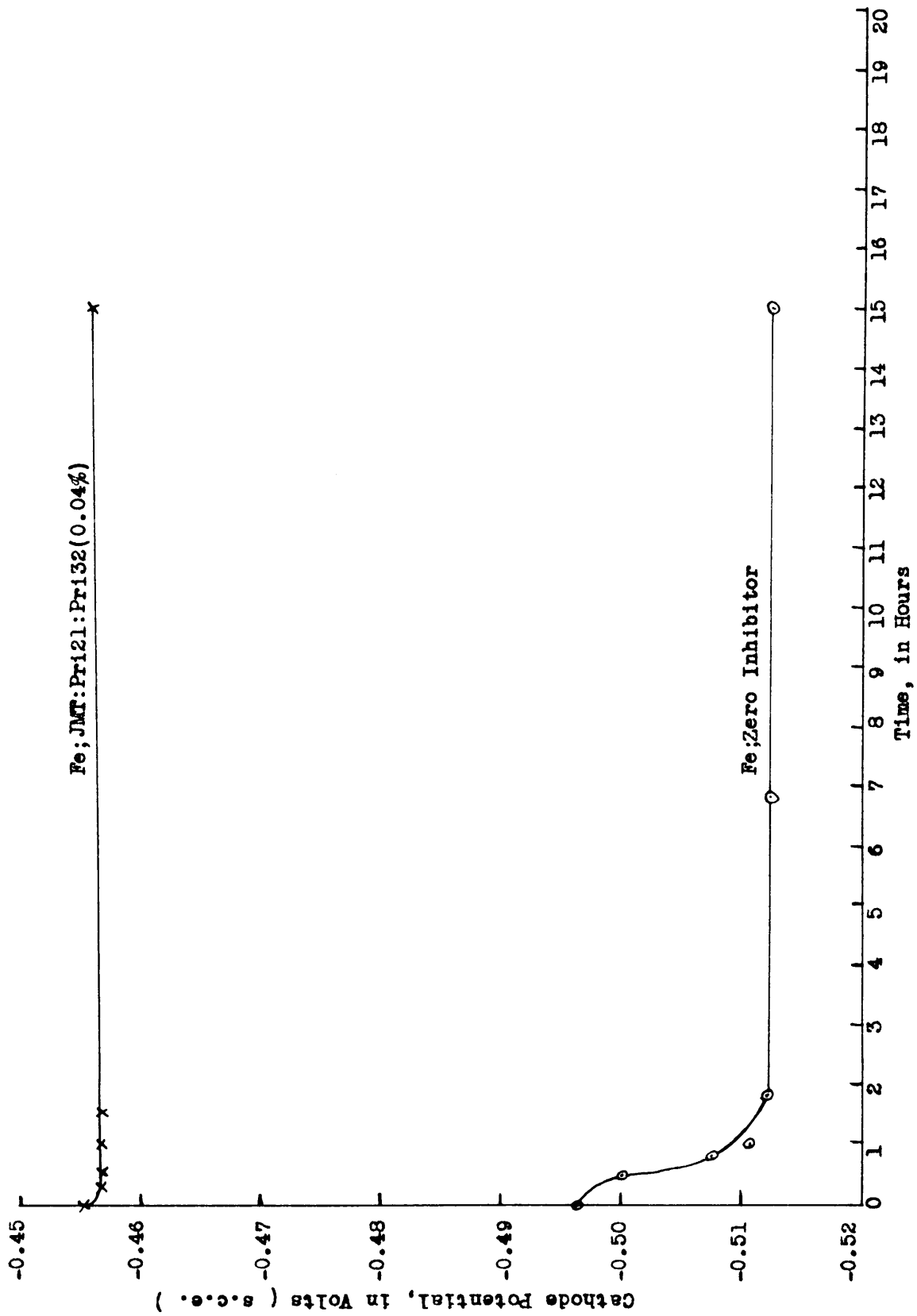


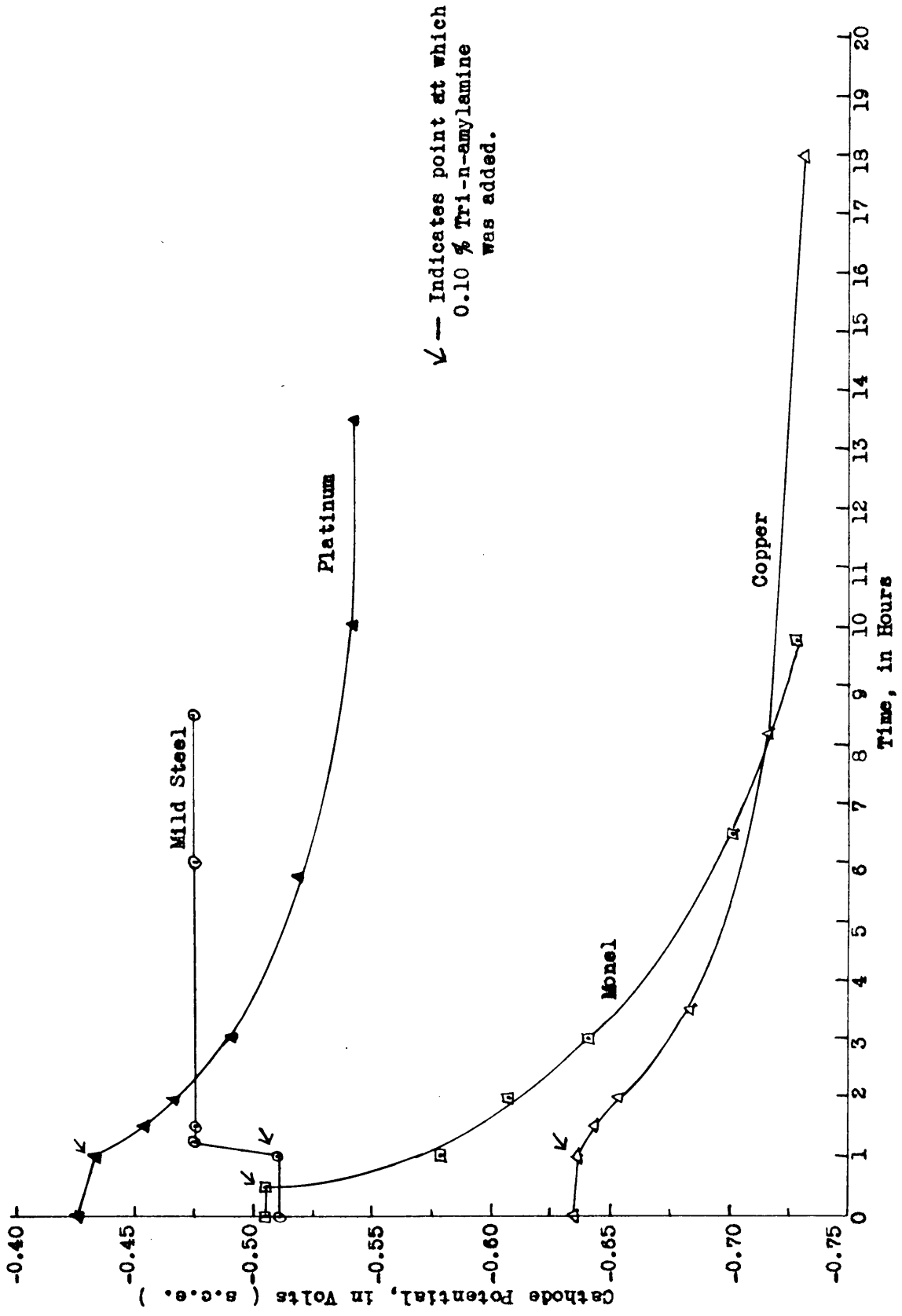
FIGURE 8. EFFECT OF A COMMERCIAL INHIBITOR ON THE RELATIONSHIP OF CATHODE POTENTIAL WITH TIME

IN 4.9 PER CENT H_2SO_4

TABLE VI

Effects of Delayed Additions of Inhibitors on
Cathode Potentials in 4.9 Per Cent H₂SO₄

Metal Used	Cathode Potential Volts	Time Hours	Inhibitor Added Tri-n-amyamine
Steel	-0.5105	0.00	0
Steel	-0.5107	1.00	0
Steel	-0.4760	1.25	Excess
Steel	-0.4770	1.50	Excess
Steel	-0.4752	6.00	Excess
Steel	-0.4740	8.50	Excess
Monel	-0.5059	0.00	0
Monel	-0.5065	.50	0
Monel	-0.5792	1.00	Excess
Monel	-0.6075	2.00	Excess
Monel	-0.6411	3.00	Excess
Monel	-0.7024	6.50	Excess
Monel	-0.7295	9.75	Excess
Platinum	-0.4251	0.00	0
Platinum	-0.4327	1.00	0
Platinum	-0.4537	1.50	Excess
Platinum	-0.4673	2.00	Excess
Platinum	-0.4906	3.00	Excess
Platinum	-0.5188	5.75	Excess
Platinum	-0.5411	10.0	Excess
Platinum	-0.5420	13.5	Excess
Copper	-0.6358	0.00	0
Copper	-0.6363	1.00	0
Copper	-0.6429	1.50	Excess
Copper	-0.6548	2.00	Excess
Copper	-0.6845	3.50	Excess
Copper	-0.7164	8.20	Excess
Copper	-0.7313	18.0	Excess



↓ -- Indicates point at which
 0.10 % Tri-n-amyamine
 was added.

FIGURE 9. EFFECTS OF DELAYED ADDITIONS OF INHIBITORS ON CATHODE POTENTIALS IN 4.9 PER CENT H₂SO₄

was the inhibitor added. The delayed additions of tri-n-amyamine displaced the curves of platinum, monel and copper in a more electronegative direction while that of mild steel was displaced in an electropositive direction.

(g) Effects of Inhibitors on the Cathode Potential of Copper in 4.9 Per Cent H_2SO_4 .

The data in Table VII were plotted in Figure 10 to show the effects of various inhibitors on the cathode potential of copper in 4.9 per cent sulfuric acid. The curve of the test in which thiourea was used as an inhibitor was displaced slightly in the electronegative direction with a slope, after several hours, slightly more electropositive than that of the uninhibited test. Pinacolone caused a more noticeable displacement in the electronegative direction. However, after several hours the curve became more electropositive and its slope was greater than that of thiourea in the electronegative direction. In 4.9 per cent sulfuric acid 2-nitro-1-butanol displaces the cathode potential of copper to a large extent in the electropositive direction but the slope of the curve is in the electronegative direction. The quantities of inhibitors used were the same as indicated in Table IV.

(h) Effects of Inhibitor Concentration on the Cathode Potential of Mild Steel in 4.9 Per Cent H_2SO_4 .

The data from Table VIII were plotted in Figure 11 to show the effects of concentration changes of thiourea, tri-

TABLE VII

Effects of Inhibitors on the Cathode Potential
of Copper in 4.9 Per Cent H₂SO₄

Inhibitor in Excess	Cathode Potential Volts	Time Hours
Zero	-0.5910	0.00
Zero	-0.6015	0.34
Zero	-0.6295	1.34
Zero	-0.6345	12.3
Zero	-0.6363	13.3
Zero	-0.6363	14.0
Thiourea	-0.6145	0.00
Thiourea	-0.6315	0.50
Thiourea	-0.6383	1.00
Thiourea	-0.6450	2.00
Thiourea	-0.6475	2.75
Thiourea	-0.6605	11.0
Pinacolone	-0.4950	0.00
Pinacolone	-0.5865	1.18
Pinacolone	-0.6663	5.00
Pinacolone	-0.6777	7.00
Pinacolone	-0.7144	17.5
Pinacolone	-0.7209	19.5
2-Nitro-1-Butanol	-0.2217	0.00
2-Nitro-1-Butanol	-0.2765	1.50
2-Nitro-1-Butanol	-0.3200	3.50
2-Nitro-1-Butanol	-0.3620	7.50
2-Nitro-1-Butanol	-0.3975	16.0
2-Nitro-1-Butanol	-0.4062	20.0

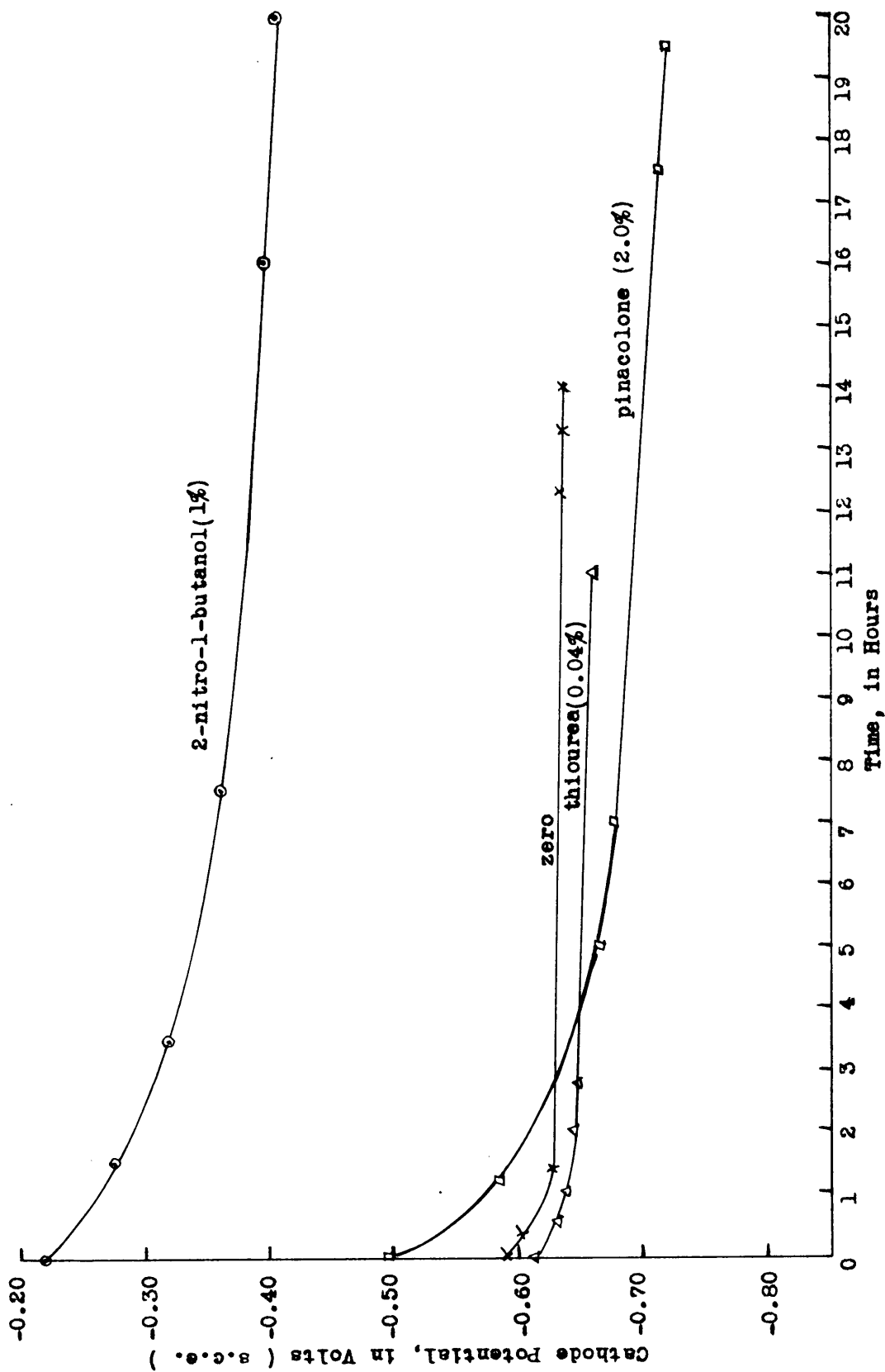


FIGURE 10. EFFECTS OF INHIBITORS ON THE CATHODE POTENTIAL OF COPPER IN 4.9 PER CENT H_2SO_4

TABLE VIII

Effect of Inhibitor Concentration on the Cathode
Potential of Mild Steel in 4.9 Per Cent H_2SO_4

Inhibitor	Concentration of Inhibitor in Per Cent by Weight	Cathode Potential Volts
JNT: Pri 21: Pri 32	0.00	-0.5078
JNT: Pri 21: Pri 32	0.0008	-0.4810
JNT: Pri 21: Pri 32	0.0024	-0.4777
JNT: Pri 21: Pri 32	0.0080	-0.4716
JNT: Pri 21: Pri 32	0.0119	-0.4644
JNT: Pri 21: Pri 32	0.0156	-0.4653
JNT: Pri 21: Pri 32	0.0452	-0.4644
Thiourea	0.00	-0.5166
Thiourea	0.0039	-0.5118
Thiourea	0.0077	-0.5128
Thiourea	0.0106	-0.5120
Thiourea	0.0116	-0.5115
Thiourea	0.0191	-0.5140
Thiourea	0.0395	-0.5179
Tri-n-amylamine	0.00	-0.5125
Tri-n-amylamine	0.0122	-0.4995
Tri-n-amylamine	0.0243	-0.4938
Tri-n-amylamine	0.0364	-0.4902
Tri-n-amylamine	0.0485	-0.4878
Tri-n-amylamine	0.1081	-0.4789
Tri-n-amylamine	0.4677	-0.2000
Tri-n-amylamine	1.028	-0.4560

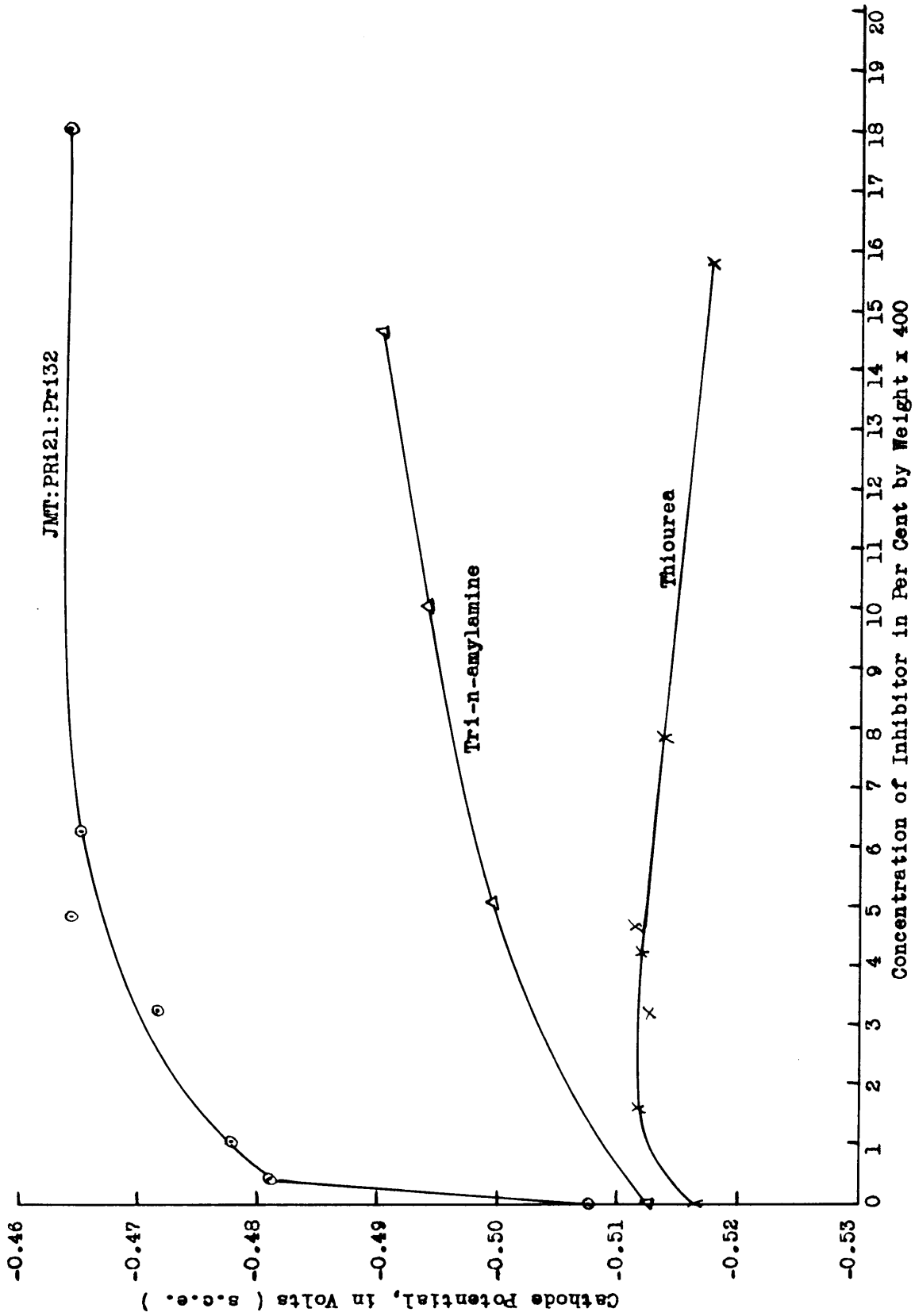


FIGURE 11. EFFECTS OF INHIBITOR CONCENTRATION ON THE CATHODE POTENTIAL OF MILD STEEL IN 4.9 PER CENT H₂SO₄

n-amylamine, and a mixture of commercial inhibitors on the cathode potential of mild steel in 4.9 per cent sulfuric acid. The largest displacement of the cathode potential in the electropositive direction was caused by the commercial inhibitor mixture. Tri-n-amylamine caused a gradual change of the cathode potential in the electropositive direction. Thiourea caused the cathode potential to change in the electropositive direction and then to gradually change in an electro-negative direction.

(i) Cathode Potential-Time Relationships of Mild Steel and Platinum in 5 Per Cent Acetic Acid.

A plot of the data of Table IX as in Figure 12 shows the relationship between time and the cathode potential of mild steel and platinum in five per cent acetic acid. The cathode potential of platinum in five per cent acetic acid increases sharply in the electronegative direction before it comes to a gradual slope in the same direction. After several hours the cathode potential of mild steel slopes very gradually in the electronegative direction.

(j) Relationship of Cathode Potentials with Time in 5 Per Cent Phosphoric Acid.

Data in Table X were plotted in Figure 13 to show the relationship of time with the cathode potentials of several metals in five per cent phosphoric acid. Figure 13 also shows the effect of the so-called inhibitor solutions on the cathode

TABLE IX

Cathode Potential-Time Relationships of Mild Steel
and Platinum in 5 Per Cent Acetic Acid

Metal	Cathode Potential Volts	Time Hours
Mild Steel	-0.5843	0.00
Mild Steel	-0.5943	1.00
Mild Steel	-0.6008	1.80
Mild Steel	-0.6012	3.80
Mild Steel	-0.6012	5.00
Mild Steel	-0.6025	12.0
Platinum	-0.3017	0.00
Platinum	-0.5500	3.00
Platinum	-0.5835	4.50
Platinum	-0.5930	7.25
Platinum	-0.6320	20.0

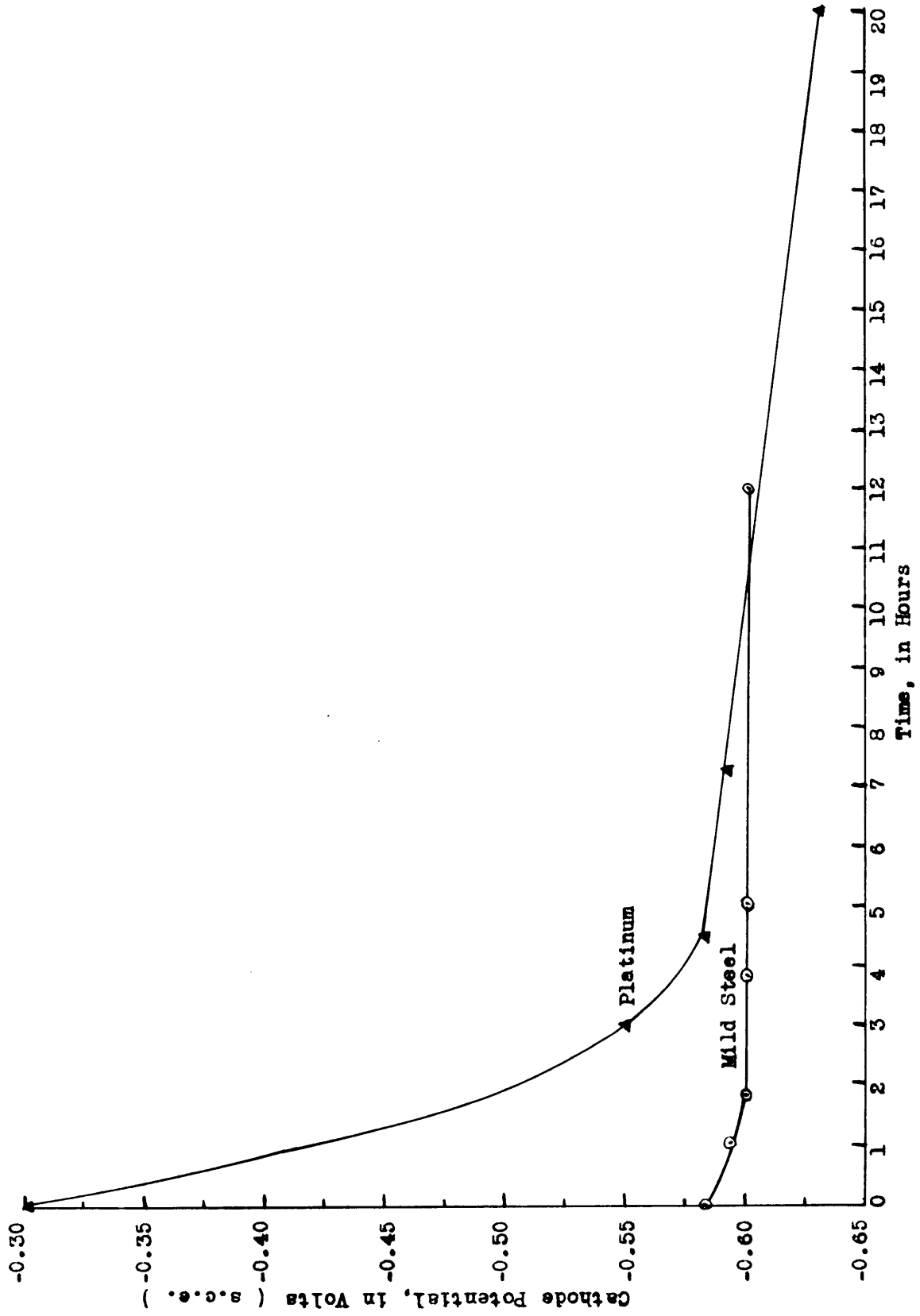


FIGURE 12. CATHODE POTENTIAL-TIME RELATIONSHIPS OF MILD STEEL AND PLATINUM IN 5 PER CENT ACETIC ACID

TABLE X

Relationship of Cathode Potentials with Time in
5 Per Cent Phosphoric Acid

Metal	Inhibitor	Cathode Potential Volts	Time Hours
Platinum	Zero	-0.2815	0.00
Platinum	Zero	-0.3862	2.56
Platinum	Zero	-0.4215	5.06
Platinum	Zero	-0.4390	15.5
Mild Steel	Zero	-0.5371	0.00
Mild Steel	Zero	-0.5395	0.50
Mild Steel	Zero	-0.5482	7.62
Mild Steel	Zero	-0.5485	9.75
Mild Steel	Tri-n-nylamine	-0.5284	0.00
Mild Steel	Tri-n-nylamine	-0.5296	0.50
Mild Steel	Tri-n-nylamine	-0.5310	1.56
Mild Steel	Tri-n-nylamine	-0.5285	14.2
Mild Steel	JMT;Pri21;Pri32	-0.4680	0.00
Mild Steel	JMT;Pri21;Pri32	-0.4683	7.42
Mild Steel	JMT;Pri21;Pri32	-0.4685	10.8
Copper	Zero	-0.1464	0.00
Copper	Zero	-0.5340	0.50
Copper	Zero	-0.5765	1.00
Copper	Zero	-0.6122	2.40
Copper	Zero	-0.6383	12.5
Copper	Zero	-0.6432	13.8
Copper	2-Nitro-1-Butanol	-0.3315	0.00
Copper	2-Nitro-1-Butanol	-0.3915	0.60
Copper	2-Nitro-1-Butanol	-0.4040	9.70
Copper	2-Nitro-1-Butanol	-0.4000	12.7
Copper	2-Nitro-1-Butanol	-0.3990	14.7
Copper	Tri-n-nylamine	-0.6570	0.00
Copper	Tri-n-nylamine	-0.7114	1.50
Copper	Tri-n-nylamine	-0.7220	2.25
Copper	Tri-n-nylamine	-0.7660	5.25
Copper	Tri-n-nylamine	-0.8000	9.25

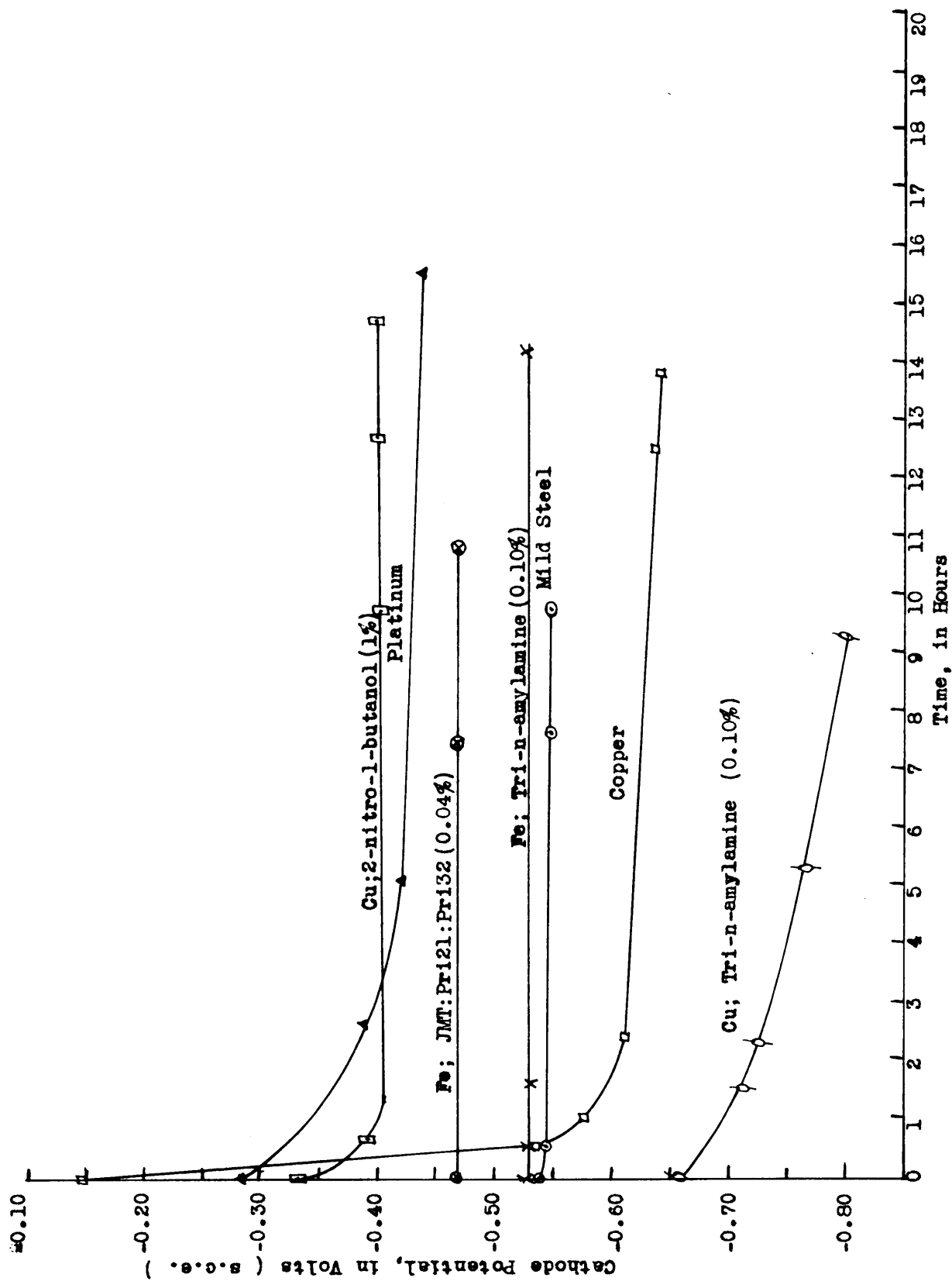


FIGURE 13. RELATIONSHIP OF CATHODE POTENTIALS WITH TIME IN FIVE PER CENT PHOSPHORIC ACID

potentials of copper and mild steel in five per cent phosphoric acid. After several hours, the copper cathode potential curve of the test in which 2-nitro-1-butanol was used slopes gradually in the electropositive direction. All other curves slope in the electronegative direction.

G. Sample Calculations

G. Sample Calculations

Calibration of Pipet for Inhibitor Additions. Pipets made from seven millimeter pyrex glass tubing drawn down to a fine tip about four inches long were calibrated for the addition of inhibitors as shown by the following example.

Inhibitor solution Tri-n-amyamine in purged H_2SO_4

Weight of weighing bottle plus solution	29.4532 grams
Weight of empty weighing bottle	<u>19.4530 grams</u>
Net weight of 720 drops	10.0002 grams

$\frac{720 \text{ drops}}{10 \text{ grams}} = 72 \text{ drops per gram of solution}$

Concentration of Inhibitor.

Total weight of H_2SO_4 used	300.0 grams
Weight of Tri-n-amyamine added	<u>20.00 grams</u>
Total weight of Inhibitor Solution	320.0 grams

$\frac{20.00}{320.0} = 0.0625 \text{ g. Tri-n-amyamine in 1 gram of inhibitor solution}$

10 drops inhibitor solution added to corrosion cell

Total weight of solution is 256 grams.

$1 \times \frac{10}{72} \times \frac{0.0625}{1} \times 100 = 0.0034 \text{ Per Cent Inhibitor by Weight}$

$1 \times \frac{\text{drops added} \times \text{grams inhibitor}}{\text{drops/g. soln gram of inh. soln}} \times 100 = \text{Concentration of Inhibitor}$

Total weight in grams

IV-DISCUSSION

A. Discussion of Results

IV - DISCUSSION

A. Discussion of Results

It was found that the nitrogen flow rate could be varied over a wide range without any appreciable changes in the cathode potential measurements, as shown in Figure 4.

In Figure 5 the result was shown of a test to determine if the value of the total current flow being used in all tests was in the correct quadrant so that all measurements of the potential difference between the electrode specimens placed in the cathodic compartment of the H-Cell and the saturated calomel cell were in the true cathodic direction. It was established in the case of mild steel that the electrode was always acting as a cathode. The values for the cathode potentials, as shown in Table II, never changed their sign of potential.

It was evident that the procedure outlined resulted in very precise potential measurements for the type of experiments conducted (15). For example, the precision of measurements of the cathode potential of a mild steel electrode made several days, and in some cases several weeks apart, varied from three-tenths to seven-tenths of one per cent, based on the deviation divided by the largest potential recorded. There was one exception that varied one and seven-tenths per cent.

Potential-Time Behavior. A comparison between the variations of the potentials of several metals with time was shown in Figure 6. Even though these potentials were not the standard equilibrium potentials, the potential-time curves were in fairly good agreement with the order listed for the galvanic series (14).

An excess quantity of inhibitor was arbitrarily set as more than the quantity of inhibitor necessary for ninety per cent inhibition as presented for mild steel in 4.9 per cent sulfuric acid by Eldredge and Warner (4). In each case the quantity was considered to be an excess for mild steel under the experimental conditions. One per cent 2-nitro-1-butanol and one per cent diethylamine were considered to be in excess. The potentials of mild steel in sulfuric acid solutions of inhibitors were shown in Figure 7. Also in Figure 7 the fact was illustrated that the same mild steel cathode would have a different potential-time relationship when immersed in a different lot of 4.9 per cent sulfuric acid solution, each solution containing a so-called excess of a different inhibitor.

Relatively good agreement existed between the electro-positive position of the potential-time curves for the various inhibitors with the effectiveness of the same inhibitors as determined by gravimetric methods and listed by Eldredge and Warner (5). The close potential relationship of tri-n-amyamine.

and tri-n-hexylamine was emphasized in Figure 7. Eldredge and Warner listed a concentration of 0.023 per cent for tri-n-amyamine and 0.027 per cent for tri-n-hexylamine to give 90 per cent inhibition in 4.9 per cent sulfuric acid. They also listed 0.011 per cent for thiourea to give 90 per cent inhibition.

The effect of time on the potential curves of benzaldehyde and pinacolone in the electronegative direction contrasted with the trend in the electropositive direction for the curves of tri-n-amyamine, tri-n-hexylamine and thiourea. All specimens were under cathodic conditions at all times.

The wide variations in the initial potentials of mild steel in the acid solutions of inhibitors were reproducible when an excess of the various inhibitors were premixed in the cathodic compartment of the H-Cell for each test before the immersion of the electrode. This was demonstrated by the comparison of the cathode potential versus time curves of mild steel in sulfuric acid without any inhibitor, and with the mixture of commercial inhibitors as was shown in Figure 8. Although the two curves seemed to run parallel, the curve due to the commercial inhibitor mixture sloped in an electropositive direction while the curve of the uninhibited became more electronegative, indicating increasing cathodic tendency and anodic tendency, respectively (12,22).

The total current flow of one milliampere held electrolysis to an insignificant amount. Inhibitors were added in solutions of deoxygenated acids that were in use at the time.

Delayed additions of inhibitors were used to determine the effect on the potential-time relationships of the various electrodes. The effect of delayed additions of tri-n-amylamine on the cathode potentials of mild steel, platinum, copper and monel was illustrated in Figure 9. The starting potentials were actually not the values for the cathode potentials at zero time without inhibitors. However, they were the potentials taken from steady state positions (less than one millivolt change per hour) on the potential-time curves of the electrode or electrodes in acid to which no inhibitor had been added. That is, the inhibitor was added after the cathode potential-time curves had reached a fairly steady value in each case. The curve for mild steel shifted in an electropositive direction, and the other curves progressed in an electronegative direction, as expected (13).

The effect of additions of the various inhibitors on the potential-time relationship of the cathode potential of copper in 4.9 per cent sulfuric acid was shown in Figure 10. The effect was to make the potential more electronegative.

Cathode potential-time relationships of mild steel and platinum in five per cent acetic acid were shown in Figure 12. After two hours, the mild steel curve sloped very gradually in the electronegative direction while the slope of the pla-

tinum curve was markedly in the electronegative direction.

Relationships between the cathode potential-time curves of mild steel and copper in five per cent phosphoric acid to which an inhibitor had been added and five per cent phosphoric acid to which no inhibitor had been added were shown in Figure 13. Again the commercial mixture and the tri-n-amylamine curves were more electropositive than the zero inhibitor curve of mild steel. A comparison of Figures 10 and 13 showed the potential of copper to be more electropositive in five per cent phosphoric acid and more electronegative in 4.9 per cent sulfuric acid by 2-nitro-1-butanol. It is interesting to note that Whaley (24) established the fact that the corrosion of copper is inhibited by 2-nitro-1-butanol in aerated five per cent phosphoric acid.

It was noted that there was a shift in the cathode potential-time curves for all electrodes used and a gradual change in the electropositive direction for most of the inhibitor concentration curves.

Potential-Concentration of Inhibitor Behavior. The shift of the cathode potentials in the electropositive direction may have indicated that the inhibitors were affecting the anodic as well as the cathodic surfaces and possibly the anodic potentials were affected to a greater extent than the cathodic potentials. Examples of the shifts in potentials are shown in Figures 7, 8, 9, 11, and 13. Thiourea, which was chosen for study because it is noncationic, caused little change in the

cathode potential of steel with increasing concentration of inhibitor. Comparison of the thiourea curve of Figure 11 with that of the other two inhibitors shows that a non-cationic inhibitor had much smaller effects on the cathode potential of steel than cationic inhibitors. Also, pinacolone and benzaldehyde, both non-cationic, do not cause an appreciable shift of the cathode potential of steel, as shown in Figure 7.

Ancillary Observations. Several determinations of the pH of the solutions during tests were made, but indications were that time and presence of inhibitor had very little effect on the pH of the solutions.

The presence of the asbestos fiber sealed in the capillary tip of the acid bridge had no appreciable effect on the cathode potential measurements. This probably was because of the small diameter of the tip.

Epoxy glue seals provided a convenient and efficient method of sealing the electrode leads in the glass tubing so the leads would not be in contact with the corroding medium.

Although the electrodes were under a cathodic potential at all times the mild steel electrodes showed some pitting type corrosion. Obviously the pitting must have been due to some factor other than electrolytic solution.

The batteries used as a power supply were charged and allowed to stand disconnected for ten days before use.

The variation in the initial slope of the mild steel cathode potential-time curves was assumed to be an effect of oxide film formation before the electrode was immersed in the acid solutions. After cleaning the electrode, it was exposed to the atmosphere for different periods of time. Potential-time measurements were made on such cathodes, and it was observed that the initial slopes of the curves were different. However, since these experiments were of a qualitative nature, and were not deemed relevant to the problem at hand, no data is shown in this report.

A constant temperature of 30°C. had a slight effect on the volume of solutions in the H-Cell. The volumes were adjusted by the addition of deoxygenated distilled water when necessary. This adjustment had no appreciable effect on the cathode potentials.

Resistance to Electron Transfer. It was noted that the known inhibitors of the corrosion of mild steel in 4.9 per cent sulfuric acid caused a decrease in the resistance to electron transfer at the cathodic surface. In the case of copper in phosphoric acid the known inhibitor for the copper corrosion also caused a decrease in the resistance to electron transfer at the cathodic surface.

This decrease in the resistance to electron transfer at the cathodic surface was in direct contradiction to G. A. Mann's theory of cathodic inhibition.

B. Recommendations

B. Recommendations

On the basis of the information obtained from this investigation the following recommendations are made:

1. An investigation should be made using different inhibitors under similar conditions.
2. An investigation should be made to determine the effects of inhibitors on the potentials of the same metals made anodic under similar conditions.
3. An investigation should be made to determine if possible what factors may have caused the pitting of the mild steel cathodes.

C. Limitations

C. Limitations

This investigation was carried out under the following limitations:

1. A constant current of one milliamperere was maintained throughout the investigation.

2. Oxygen was assumed to be reduced to a concentration which did not affect the cathode potential measurements.

3. Changes in the cathode potential measurements due to concentration changes in the acid solutions as a result of electrolysis and evaporation were assumed negligible.

4. The concentrations of the acid solutions were limited to 4.9 per cent sulfuric acid, five per cent phosphoric acid, and five per cent acetic acid.

5. The temperature in all measurements was limited to 30°C. plus or minus 0.05°C.

6. The saturated calomel cell was used as a reference electrode.

7. Inhibitors used were thiourea, tri-n-amylamine, tri-n-hexylamine, pinacolone, benzaldehyde, 2-nitro-1-butanol, diethylamine, and a mixture of three commercial inhibitors; Primene JM-T, Priminox 21 and Priminox 32 in a ratio of one to three to two parts, respectively.

8. The metals used for cathodic specimens were limited to mild steel, copper, platinum, brass, Inconel, Monel, tin and nickel.

V-CONCLUSIONS

V-CONCLUSIONS

From this investigation into the effects of various compounds, which were known to be inhibitors of the acid corrosion of steel in 4.9 per cent sulfuric acid, on the cathode potential of various metals made cathodic at a total current flow of one milliampere at 30°C, the following conclusions were made:

1. Tri-n-amylamine, tri-n-hexylamine, and the mixture of commercial inhibitors shifted the cathode potential of steel in the electropositive direction.

2. Thiourea, pinacolone and benzaldehyde have practically no effect on the potential of a steel cathode.

3. The results of this investigation indicated that it may take as long as ten hours before the effect of an inhibitor on the cathode potential reaches equilibrium.

4. Known inhibitors for acid corrosion of steel may make the cathode potential more electropositive, more electronegative, or have no appreciable effect.

5. The addition of tri-n-amylamine, tri-n-hexylamine, or the commercial inhibitor mixture decreases the resistance to electron transfer at the cathodic surface as indicated by the shift in the cathode potential; this is a direct contradiction of Mann's theory of cathodic inhibition.

6. A known inhibitor for copper in phosphoric acid,

2-nitro-1-butanol, shifted the cathode potential of copper in an electropositive direction.

7. Tri-n-amylamine, a known accelerator for the corrosion of copper in phosphoric acid, makes the potential of a copper cathode more electronegative or anodic.

VI-SUMMARY

VI-SUMMARY

The purpose of this investigation was to determine if there was a relationship between the quantity of inhibitor known to diminish the corrosion rate and the potential of a cathodic surface.

The potential required to keep a constant current of one milliamperes flowing from cathodic corrosion specimens through dilute acid solutions to which one or more known or commercial inhibitors had been added was measured against a saturated calomel reference electrode.

Platinum, mild steel, copper, monel, inconel, yellow brass, nickel and tin were used as cathodic specimen electrodes. Platinum was also used as the anode. Four point nine per cent sulfuric acid, five per cent acetic acid and five per cent phosphoric acid were used as electrolytes.

The inhibitors used in this investigation were benzaldehyde, diethylamine, 2-nitro-1-butanol, pinacolone, thiourea, tri-n-amylamine, tri-n-hexylamine, and a mixture of Primene JM-T, Priminox 21 and Priminox 32.

Temperature was maintained at a constant value of 30°C. by immersion of the reaction vessels in a constant temperature bath.

Deoxygenated nitrogen gas was used to agitate the solutions and purge the apparatus.

The outlined procedure furnished a practical method for obtaining precise relative electrode potential measurements in dilute acid solutions.

The results of this investigation indicated that it may take as long as ten hours before the effect of the inhibitor on the cathode potential reaches equilibrium.

Known inhibitors for the acid corrosion of steel may make the cathode potential more electropositive, more electronegative, or have no appreciable effect.

The results of this investigation do not substantiate C. A. Mann's theory of cathodic inhibition.

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VII-ACKNOWLEDGMENTS

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IX-VITA

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ABSTRACT

An investigation was planned to determine if there was a relationship between the quantity of inhibitor known to diminish the corrosion rate and the potential of a cathodic surface.

The potential required to keep a constant current of one milliamperes flowing from cathodic corrosion specimens through dilute acid solutions to which one or more known or commercial inhibitors had been added was measured against a saturated calomel reference electrode.

A large H-Cell was constructed as a test vessel and especially designed electrodes and electrode holder assemblies were provided for each compartment of the H-Cell.

Platinum, mild steel, copper, monel, inconel, yellow brass, nickel and tin were used as cathodic specimen electrodes. Platinum was also used as the anode. Four point nine per cent sulfuric acid, five per cent acetic acid and five per cent phosphoric acid were used as electrolytes.

The inhibitors used in the investigation were benzaldehyde, diethylamine, 2-nitro-1-butanol, pinacolone, thiourea, tri-n-amylamine, tri-n-hexylamine, and a mixture of Primene JM-T, Priminox 21 and Priminox 32.

Temperature was maintained at a constant value of 30°C by immersion of the test vessels in a constant temperature bath.

Deoxygenated nitrogen gas was used to agitate the solutions and purge the apparatus.

The results of this investigation did not substantiate C. A. Mann's theory of cathodic inhibition.

Known inhibitors for the acid corrosion of steel may make the cathode potential more electropositive, more electronegative, or have no appreciable effect on the cathode potential.