

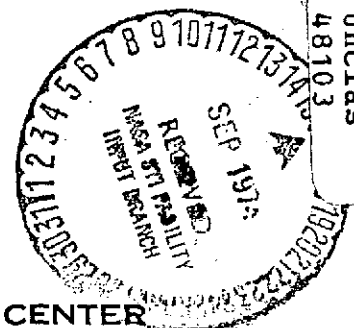
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DISINFECTON STUDIES IN SPACECRAFT WATER  
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ADVANCED ENGINEERING/TECHNOLOGY CENTER  
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CINCINNATI, OHIO 45226

CORROSION CONTROL AND DISINFECTION STUDIES IN  
SPACECRAFT WATER SYSTEMS

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
MANNED SPACECRAFT CENTER  
CONTRACT NO. NAS 9-9431

By

ENGINEERING-SCIENCE, INC.  
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March 1972

A Report Entitled:

**CORROSION CONTROL AND DISINFECTION STUDIES  
IN SPACECRAFT WATER SYSTEMS**

This report is submitted in completion of Contract No. NAS 9-9431, between National Aeronautics and Space Administration and Engineering-Science, Inc. The report is a presentation of the findings of disinfection, corrosion, and membrane studies conducted to evaluate existing or alternative water system design and operation in the spacecraft of the Apollo Applications Program and the Saturn V Orbital Workshop Program.

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March 1972

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CHAPTER I  
INTRODUCTION

BACKGROUND

The objectives of the NASA Manned Spacecraft Program have expanded rapidly in the interval between Project Mercury and the Apollo Program. From the demonstration of manned orbital flight in Project Mercury to limited manner lunar exploration in the Apollo Program, NASA is now planning extended-duration missions such as lunar-surface mapping and survey in the Apollo Application Program and space-science experimentation in the Orbital Workshop Program.

The development of spacecraft and spacecraft life support systems to meet the demands of these missions has been an outstanding technological achievement. A foremost goal of spacecraft design and development is to maximize payload, an objective which has necessitated development of integrated systems capable of maximum multiple use of water, heat, atmospheric gases, and energy for life support. The need for functional flexibility of life support systems has required that a capability exist to transfer a resource (water, gas or electrical energy) from one point to almost any other point in the spacecraft to meet demands and emergencies that arise. The need for weight minimization has required the use of a diversity of metallic and other components in the water system to maximize function (water and heat transfer) and minimize weight. Severe time constraints in the space program have resulted in priorities being placed on propulsion, structural, and communications systems.

There is little doubt that the overall technological approaches developed by the space industry for use in the NASA programs have been successful; the lunar-orbital flight of 1968 and the lunar landings of 1969 have brought worldwide acclaim to the United States. However, compromises have been necessary to accomplish these goals, particularly in the area of water system design. These compromises have led to a series of problems requiring water system disinfection as a standardized procedure, allowing attrition of disinfectant levels caused by interaction with system components, and permitting the transport of dissolved gases into and through the water system to points of use in the spacecraft. The former two situations have resulted in problems of corrosion, interaction of disinfectant with membrane materials, presence of viable organisms, and taste and odors in the water supply. The

latter problem area has resulted in the presence of sufficient quantities of gas in the water supply at the use ports to raise concern as to its direct use for drinking or food preparation.

The above problem areas in no instance have caused an operational failure in the spacecraft water systems used in the Apollo Program. However, there is serious concern that, as the missions conducted by NASA become longer, potential adverse situations in the short term can become real problems in the long term. A commitment has been made by NASA, through the research and development activities conducted or sponsored by the Preventive Medicine Division, to the development of technology to meet future water supply needs in spacecraft. This study is intended to represent a step toward fulfilling the commitment of NASA in bringing environmental engineering support to the conceptualization, design, and testing phases of water system development.

#### OBJECTIVES

The orientation of this study was directed toward evaluation of disinfection and corrosion control technology in the Apollo Command and Lunar Modules and in the Saturn V Orbital Workshop Program (the latter of which was in the early design phase in late 1969). The priorities required in meeting information needs for disinfection and corrosion control in these operational or developing systems related to the development of an understanding of the fundamental mechanisms of the physical, chemical, and/or biological processes governing disinfection and corrosion control as a basis for resolving these problem areas. Within these priorities the specific objectives of the study were as follows:

- (1) Make a general assessment of the basic mechanisms governing the processes of disinfection, corrosion, interaction of disinfectants with membrane materials, permeation of chemicals through membranes, and generation of taste and odor.
- (2) Select experimental conditions to simulate the environment in which the mechanisms postulated in Objective (1) occur and to conduct an experimental program for developing information necessary to define the rate constants and other parameters necessary to document the mechanisms.
- (3) Conduct an engineering evaluation of specific problem situations believed to occur in spacecraft water systems, insofar as avail-

able information permits.

- (4) Evaluate the efficacy of current potable water specifications to generate awareness of, and action to minimize, the perpetration of disinfection, corrosion control, and other problems in existing and future spacecraft water systems.

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The study was performed at the Research and Development Laboratories of Engineering-Science, Inc., Oakland, California. Dr. T. G. Shea served as Project Director, Dr. Ralph Brooks as Technical Coordinator, Messrs. G. Hajek and L. Kolb as Project Engineers, Mr. J. Burns as Chief Chemist, Miss T. Toschi as Biologist, and Mr. B. Kinneburg as Chemist, for Engineering-Science, Inc.. The counsel and assistance of Dr. W. E. Gates of Engineering-Science in all aspects of the study is gratefully acknowledged.

The success of the study is due in a large part to the contributions of the Project Consultants, Dr. K. H. Mancy and Dr. R. C. Cooper. Dr. Mancy, Professor, Department of Environmental Health, University of Michigan, Ann Arbor, provided the technology and instrumentation for measurement of corrosion rates by his polarization resistance techniques. Dr. Cooper, Associate Professor, School of Public Health, University of California, Berkeley, provided counsel and guidance in development of procedures for bacteriological studies and in review of previous studies by NASA and NASA contractors.

## CHAPTER II

### SUMMARY

The original orientation of this study was directed to the evaluation of disinfection and corrosion control technology in the water systems of the Apollo Command and Lunar Modules, and in the additional modules to be used in the Apollo Applications Program. As the study developed, the immediate need by NASA for information in these areas shifted from the operational-phase Apollo systems to the Saturn V Orbital Workshop Program. Within this framework, the problem areas of concern in the study were classified into four general areas: disinfection; corrosion; membrane-associated problems of disinfectant uptake and diffusion; and taste and odor problems arising from membrane-disinfectant interaction.

The results and conclusions of the membrane studies are presented in Chapter IV. Six membrane types (Silastic, Polyisoprene, Butyl Rubber, Nordel, Viton, and Polyurethane) were screened for the development of taste and odor problems in iodinated solutions, and those membranes not associated with the development of taste and odor problems (Silastic, Polyisoprene, and Polyurethane) were subjected to membrane interaction testing. The mechanisms of membrane interaction were defined as: sorption; substitution and/or conversion; and diffusion. Sorption isotherm constants, first-order substitution and reaction conversion constants, and diffusion constants were determined for each of the acceptable membranes as appropriate under laboratory experimental conditions simulating the spacecraft water system environments.

The results and conclusions of the corrosion studies are presented in Chapter V. Potentiometric techniques were used to measure the relative corrosion rates of aluminum (Al 6061 T6) and stainless steel (CREG 316L) in iodinated and chlorinated solutions under conditions of dissolved oxygen saturation and depletion. The test cells used in the experimentation were completely-mixed and temperature-controlled at spacecraft temperature levels. Iodine depletion rates due to interaction of the test aluminum and stainless steel metals with iodinated test solutions, were characterized in terms of first order reaction constants for the conversion of iodine to iodide under completely-mixed conditions.

The results and conclusions of the disinfectant evaluation studies are presented in Chapter VI. Criteria for the selection of the test

organisms (*E. Coli*, *Flavobacter breve*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Bacillus subtilis var. niger*) are presented, and the mechanisms of disinfectant-organism interaction are presented. The disinfection criteria of the United States Food and Drug Administration and the Public Health Department of the State of California (99.999 percent bacterial after 15 seconds of disinfectant solution contact time) were used as a basis for evaluating the relative resistance to inactivation of the five test organisms to defined concentrations of iodine and chlorine at defined pH and temperature levels simulating spacecraft water system environments. With these results, the iodine and chlorine doses required to meet the 99.999 percent inactivation level at a 15-second contact time were determined for each test organism.

An engineering evaluation of the Apollo Command and Lunar Module water systems and the proposed Orbital Workshop system is presented in Chapter VII. The evaluation incorporates information developed in Chapters IV to VI of the present study as well as from other studies to interpret and assess some of the operational problems observed in the Apollo systems and to identify potential areas of concern in the Orbital Workshop system.



CHAPTER III  
RATIONALE FOR STUDY

APPROACH

The basic context in which the study developed was that an evaluation of the fundamental physical, chemical, and biological processes relative to the areas of disinfection, corrosion control, and mass transfer, is a pre-requisite to assessment of the origin and extent of operational problems encountered in spacecraft water systems, and for the development of engineering tools needed to evaluate the potential for similar problems to occur in yet-to-be-developed systems. The above areas of inquiry can be considered as specific and well-defined problem areas if a sufficient understanding exists as to the nature and effect of fundamental interactions of the water system at large with factors affecting it, primarily in the areas of: rate and extent to which the systems permit the transfer of gaseous, liquid, and solid components to occur; interaction of system components with reactants and products in the disinfection and corrosion processes; and the aggregate manner in which these circumstances combine to amplify or attenuate an immediate problem.

In order to provide a perspective for the study context and to define its orientation, an approach to the study was developed which necessarily directed the study, in areas where pertinent information was lacking, towards evaluation of fundamental mechanisms, interactions, and rate constants applicable thereto, and *a priori* to evaluation of immediately perceived problems. The approach used is shown in Figure III-1; each of the elements shown in this diagram represents an area of inquiry from which information was developed and made available for a subsequent activity.

The program objectives for the study were defined (Chapter I) not only in deference to developing an immediate solution to disinfection and corrosion control problems, but also, because these areas impinge on both water quality and structural standards relative to spacecraft. The objectives necessarily include a consideration of:

- (1) What overlying priorities relative to propulsion, communication, and system integrity must be considered relative to enhancement of disinfection, corrosion, and other problems;
- (2) How realistic are current water quality standards relative to the performance capabilities of the water systems and to ac-

cepted levels of key parameters applied in water supply and public health engineering fields.

The study utility can be defined only in terms of the level of inquiry which existing information permits to be achieved within the time and budget frame of the study and relative to the desirability of having point utility vs. general utility for the study findings. A point utility study relates to consideration of a single specific aspect of a problem without recognition of broader, more basic factors which could minimize or negate the value of study findings outside of that specific circumstance. A general utility study requires implicitly that fundamental mechanisms be defined before specific questions can be examined. Of necessity, development of the tools to permit engineering evaluation of systems of the complexity of spacecraft water systems requires a general approach. The latter statement assumes greater importance in this study, where the objectives of the program expanded to include not only Apollo Command-Service and Lunar Module water systems, but also the proposed water system of the Saturn V Orbital Workshop as well as materials which may be used in future spacecraft systems.

The problem areas in the study were documented by a definition of the boundary areas of problems as perceived by NASA and NASA contractors. This effort entailed necessarily an evaluation of all the physical, chemical, and biological processes interrelated with the problem area, documentation of the functions and components of all water systems, and documentation of all transfer and conversion phenomena at liquid-gas and liquid-solid interfaces. The basic mechanisms interactive in the problem areas were described by considering process fundamentals apart from particular applications, in order to establish a coherency in theoretical development of the tools for the engineering evaluation.

The above activities were prerequisite to description of the data base required to document the germane unit processes in the approach used in this study. The required data base can be described only after the pertinent variables and their range of variation is defined. A comparison of the required data base (e.g., for describing membrane diffusion processes) with the information available to describe the processes was the basis for establishing data needs for the study and subsequently, data development programs. Data evaluation with the objective of describing mechanisms

of concern was used to identify additional data needs as well as to permit documentation and description of the mechanisms governing process behavior as well as behavior in a specific condition.

A final information link incorporated in the study approach is that between the element in which process behavior was described and the element in which the study objectives were defined. This link is necessary to permit a realistic assessment of the study objectives relative to process capabilities. Without such a feedback process, the validity of developing processes to meet the stated objectives of the study cannot be established.

#### STUDY ELEMENTS

Figure III-2 represents a more detailed statement of the elements of the study. The study system was initiated with a general consideration of the water management systems, directed to:

- (1) Delineation of the configuration of the piping, storage, valuing and recycling systems used in the spacecraft;
- (2) Delineation of the demand and supply rates of water, rates of wastewater generation, pressure and temperature gradients in water and wastewater systems, and chemical dosage programs.
- (3) Collation and evaluation of observations on the physical, chemical, and biological quality profiles in the systems relative to specific sampling or injection points.
- (4) Description conceptually or quantitatively of gas, liquid, and solid phase transfer phenomena in the system.
- (5) Collation and evaluation of information on the problems of disinfection, corrosion, sorption, diffusion, taste and odor, and other areas which have been observed or are believed to exist in the water system.

The physical, chemical, and bacteriological objectives set by NASA have evolved from the overriding concern of the agency for the health and safety of the astronauts. The objectives currently in use by NASA were considered in terms of the premises on which they evolved, or have been accepted, including consideration of one or more of the following premises:

- (1) Established practice
- (2) Technological attainability
- (3) Educated guess

(4) Human toxicology

(5) Mathematical indices

An important aspect of this effort, also carried out at the end of the study, was an evaluation of the relationship of the above standards to the currently perceived and potential problem areas evaluated or uncovered in the study as a basis for reviewing the efficacy of the standards.

The problem areas of concern in the study can be classified in four general areas: disinfection; corrosion; membrane-associated problems; and taste and odor problems. Disinfection can be defined in a general sense by the equation: Final organism count = initial organisms count - (exponential decay rate) (time interval), where the exponential decay rate is specific to single organisms or organism groups emanating from a source known to exist in the system. Two sources can be defined within the spacecraft environment; one related to the gastrointestinal tract and the other to the epidermal areas of the astronauts. The disinfection (deactivation) process occurs fundamentally in only one of two ways: by enzymatic blockage (a process which can lead over time to evolution of disinfectant-resistant species); and by destruction of the integrity of the cell wall of the organism, allowing a lethal interruption of cellular processes.

The concept of a decay rate in the disinfection process has been documented almost ubiquitously as a logarithmic relationship by which organism concentrations approach (but do not attain theoretically) zero population. The total decay rate is a function of the following factors: initial number of organisms, which numbers are generally high for gastrointestinal organisms and low for epidermal organisms; strain of species; and environmental conditions such as temperature; and chemical character of aqueous environment, the foremost factor of which is the disinfectant concentration. Each of the above factors was incorporated into the rationale for selection of the types of organisms and the experimental conditions under which decay rates were established. The choice of organisms was tempered by consideration of available information on the pathogenicity as well as disinfectant resistivity of selected gastrointestinal and epidermal organisms.

Corrosion phenomena can be considered only in terms of the milieu in which corrosion occurs and in deference to factors affecting the transport of rate-limiting reactants to, and products from the zone of corrosion.

Factors affecting the environment in which corrosion occurs include: ionic concentration, affecting the capacity of an electrolyte to transport electrons; metallic incompatibilities; dissolved oxygen concentrations; oxidant concentrations; and magnitude of transfer and surface phenomena associated with delimitation of corrosion, including relative mixing, circulation patterns in the system, concentration peaks, and areal concentrations of reactants relative to reactant surfaces.

Membranes can interact with disinfectants in solution or with gases in one or more of the following ways:

- (1) Sorption, caused by diffusion of the disinfectant into, and solution with, the membrane.
- (2) Upon sorption, any of three types of reactions can occur, viz.,
  - (a) Conversion, in which the component is changed by a reduction-oxidation into another form (e.g.,  $I_2$  to  $I^-$ ), the net effect of which is that the membrane becomes a sink for one form but of equal magnitude for the converted form of disinfectant.
  - (b) Substitution reactions, in which the compound is incorporated into the structure of the membrane.
  - (c) No reaction.
- (3) Diffusion of the disinfectant through the membrane, in which:
  - (a) Gases are diffused through membranes separating gas-liquid interfaces.
  - (b) Gases and ionic species are diffused through membranes separating liquid-liquid interfaces.

A final problem area relates to tastes and odors, which are, in most cases, manifestations of disinfection and corrosion problems; frequently the solution of the above problems will also resolve the problem of tastes and odors.

The unit processes operative in spacecraft water systems can be classified broadly as separation or conversion processes as follows (Figure III-3):

- (1) Conversion processes
  - (a) Biological
    1. Growth propagative
    2. Growth restrictive (enzyme inhibition; cell destruction)
  - (b) Chemical

1. Metal-solute reactions; corrosion of metal and attrition of disinfectant.
  2. Organic polymer-solute reactions: substitution of reactant into polymer or conversion by reduction of reactant into byproduct with polymer oxidation.
- (2) Separation processes
- (a) Adsorption
  - (b) Absorption
  - (c) Diffusion

Each of the above process areas was selected for evaluation because of its identifiable role in the defined problem areas of the study.

The experimental program for evaluating the role of each of the above processes was accomplished by:

- (1) Documentation of the unit processes as to mathematical rational or empirical relationship for describing process behavior.
- (2) Establishment of experimental conditions (range of variables and intermediate points to be evaluated) relative to information needs to define process behavior.
- (3) Development and implementation of data acquisition programs which are defined below for each study area.

The experimental program for disinfection kinetics was directed to a comparative demonstration of the effect of  $\text{Cl}_2$  and  $\text{I}_2$  on the dieaway (or decay) rates of organisms most likely to be indicators of spacecraft microbial contamination. A number of organisms were selected for study in the premises that the organism was detected previously in the spacecraft water supply or that the organism had been given a level of importance in the public health field as an organism indicative of the potential presence of pathogenic organisms. The effects of varying concentration levels of  $\text{Cl}_2$  and  $\text{I}_2$  and of pH on the dieaway rate of the organisms were ascertained, and the relative dieaway rates of the organisms were used to establish acceptable levels of disinfection (but not total sterility).

The corrosion studies were oriented to definition of the role of oxygen as activator or as passivator in the corrosion of aluminum by chlorine or the corrosion of aluminum and stainless steel by iodine. Because of the established priority of evaluating the relative rate or corrosion of stainless steel, two 2 x 2 factorial experiments were performed

to measure and distinguish between the effects of iodine levels and oxygen levels on stainless steel as well as on aluminum. These factorial experiments were performed to measure and distinguish between the effects of iodine levels and oxygen levels on stainless steel as well as on aluminum. These factorial experiments were designed to measure the separate effects of  $I_2$  and  $O_2$  on aluminum and stainless steel as well as any effects produced by the interaction between  $I_2$  and  $O_2$ .

The membrane testing was directed to quantification of sorption and diffusion phenomena across the membrane surface. The process of permeation or diffusion of an ionic or diatomic species through a membrane is preceded by several steps, each of which may be rate limiting in the overall transfer process:

- (1) Molecular diffusion of the species across a water mass to the surface of the membrane; diffusion rates are dependent on the concentration gradient of the diffusing substance; in mixed systems the rate of transport of diffusing substance to a membrane surface by eddy dispersion far exceeds the transport rate due to molecular diffusion.
- (2) Solution of the diffusing species into the membrane; the degree of solution is related to the chemical compatibility of the substance with the membrane material; while the species is in solution in the membrane, there exists the possibility that, under appropriate conditions, the substance will react with the membrane in a conversion or substitution reaction.
- (3) Diffusion of the substance out of the membrane into a zone of lower concentration; gases will diffuse through the membrane into a gaseous environment, and both gases and ionic species will diffuse into a liquid environment.

The experimental program for membrane evaluation consisted of preliminary testing of sorption levels of iodine with a number of membranes, in order to determine sorption, attrition of iodine by conversion and/or substitution, and to evaluate taste and odors developed in the liquors of the test vessels. The taste and odor test was used to screen initially the membranes for acceptability or unacceptability. The surviving membranes were subjected to diffusion testing in completely-mixed systems in order to ascertain diffusion constants for iodine in systems where membrane diffusion

rather than aqueous diffusion was limiting.

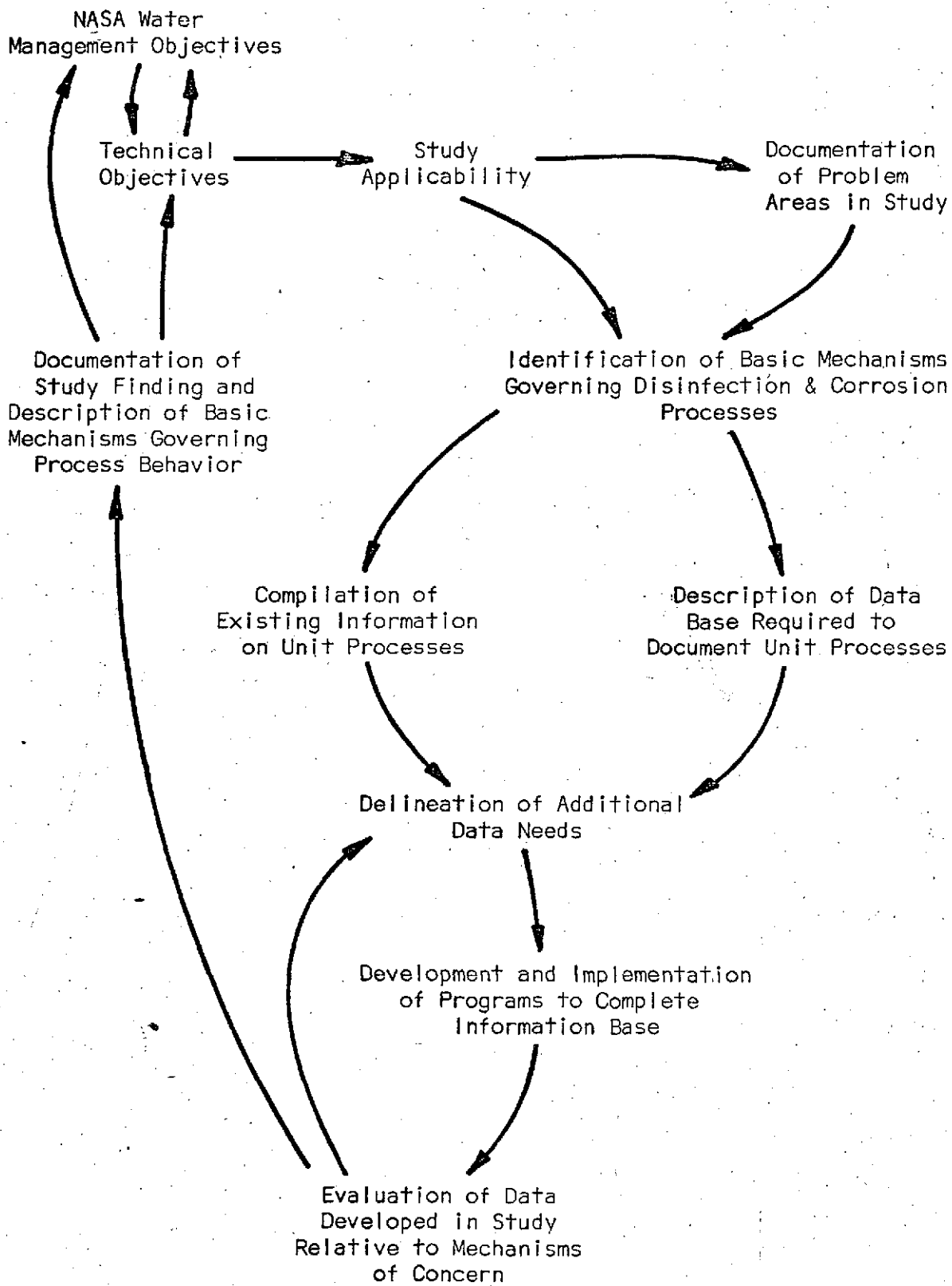
An analysis and evaluation of the data developed in the experimental program provided the rate constants, saturation parameters, and conversion parameters needed to describe unit process performance. This information was used in the engineering evaluation of water system alternatives by the following approach:

- (1) A series of sequential process-level events were predicted as taking place in a spacecraft water system (e.g., continuous flow operation in the Command Module).
- (2) Superimposed on the above were situations which have been accepted as causing problems (e.g., oxygen diffusion into the potable water tank of the Command Module).
- (3) Constants developed in the study were used to evaluate the problem magnitude (e.g., dissolved oxygen concentration in the Command Module).

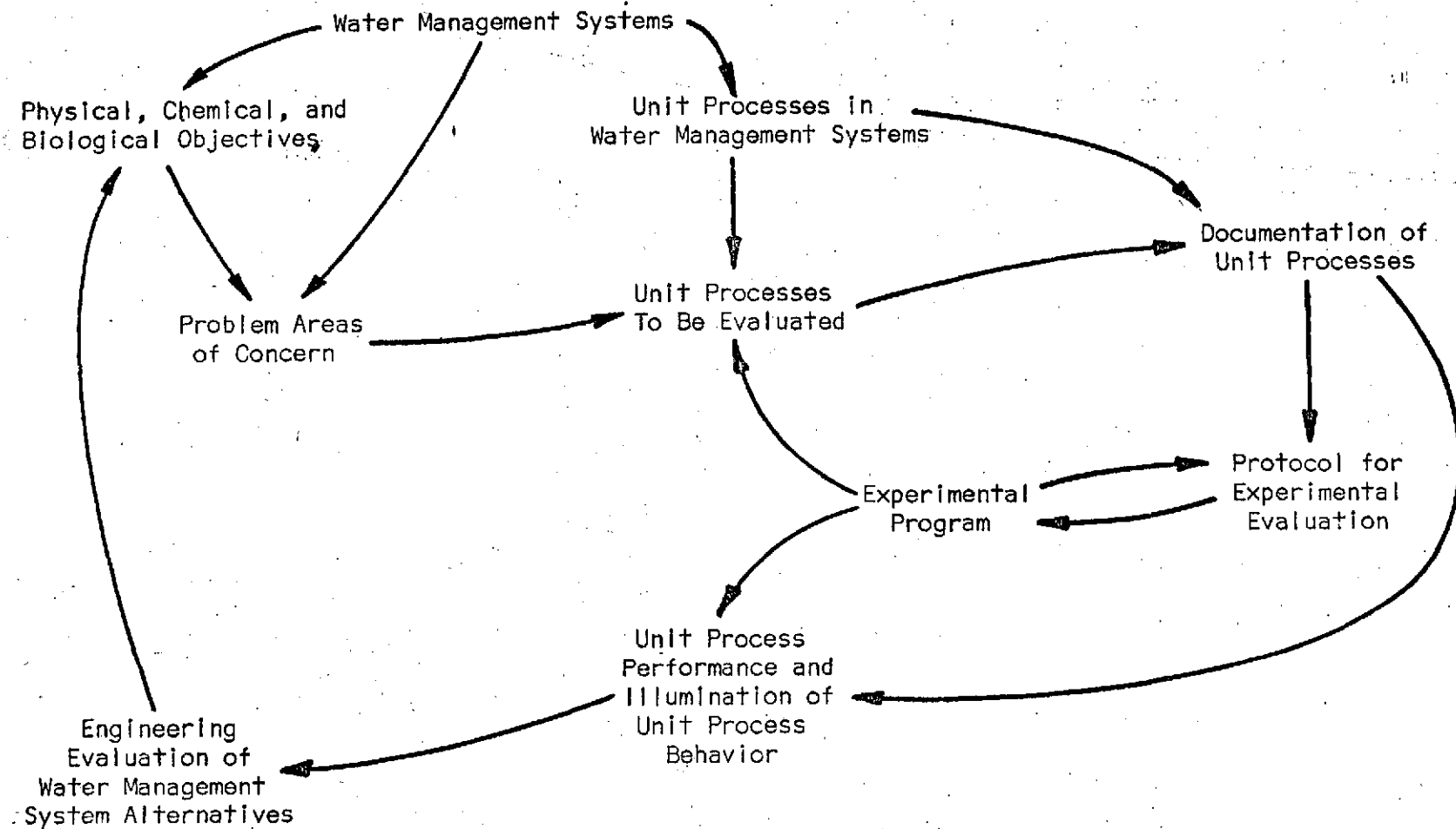
Thus the engineering evaluation approach provided predictive capability in the study for estimating an effect given the causative circumstances.

A foremost advantage of the applied mechanistic approach is that it permits a substantive evaluation of materials, system geometry, interfaces, etc. to be done on a laboratory basis rather than requiring the development of a prototype. A second key advantage of the approach used above is that the efficacy of objectives in deference to which the systems should have been developed can be evaluated on a broad perspective relative to system performance rather than on a narrow or point utility basis.

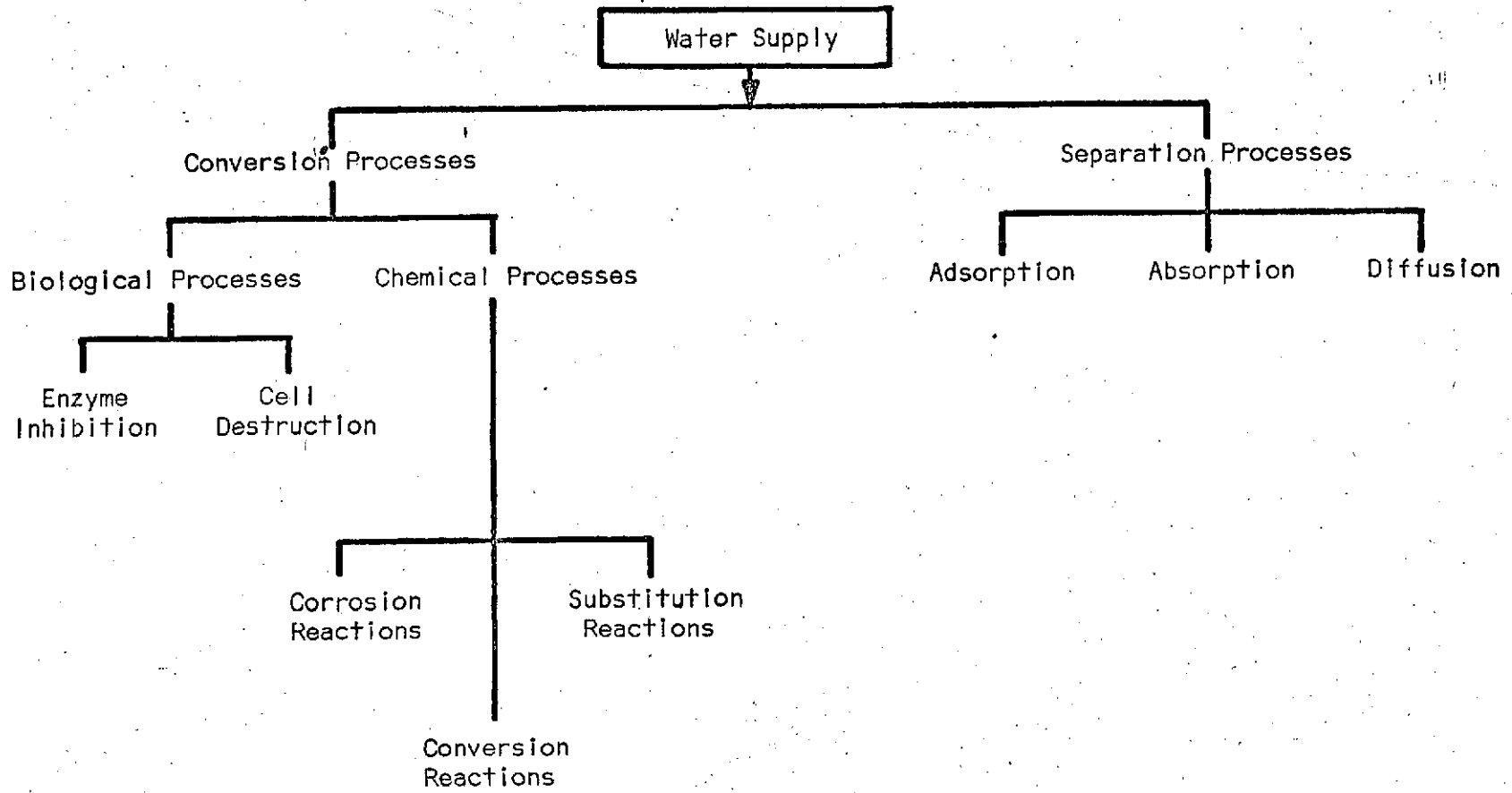




APPROACH TO TECHNICAL STUDIES



STRUCTURE AND ELEMENTS OF STUDY SYSTEM



PROTOCOL FOR EXPERIMENTAL PROGRAM

## CHAPTER IV

### MEMBRANE STUDIES

#### INTRODUCTION

The criteria used in the selection of disinfecting agents for potable water supplies include palatability at concentrations adequate to accomplish the requisite reduction in viable organism levels, and the maintenance of required residual disinfectant concentrations during the time interval between addition of the agent and use of the water, the latter criteria of which is interrelated with the degree and manner of interaction between the selected membrane materials in the water system and the disinfectant. In view of the shift in study priorities (Chapter I) from the operational phase Apollo program to the Saturn V Orbital Workshop program (in which iodine was selected as the disinfectant for the water system), the primary emphasis in the program of membrane studies described herein was placed on description of the interactions between iodine in aqueous solution and different types of candidate membranes for the Orbital Workshop. Within this perspective, the objective of the membrane studies was to evaluate the interactions between iodine solutions and selected elastomers currently being used or of potential interest for use as membrane materials for bladders in spacecraft potable water systems.

#### THEORETICAL CONSIDERATIONS

The experimental program for the membrane studies was based on the hypothesis that the following kinds of interaction are possible between iodine solutions and membrane materials:

1. Sorption of iodine on the membrane surface or within the membrane layer.
2. Diffusion of iodine through and out of the membrane.
3. Conversion of iodine to an oxidized form (iodide) ineffective for dis<sup>in</sup>fection either at the surface of the membrane or within the membrane.
4. Substitution of iodine into the membrane molecular structure either at the surface or within the membrane.

In all of the above interactions, diffusion of iodine from the bulk aqueous phase to the membrane surface is a prerequisite step to initiation of the interaction. Conversion and substitution reactions can occur either on the surface or within the layer of the membrane. Sorption of the iodine in the membrane structure at the surface or within the membrane occurs as a function of the affinity of iodine for the molecular structure of the membrane. Conversion and substitution reactions between iodine and the membrane material may or may not require sorption as a prerequisite interaction.

### Conversion Reactions

The conversion reactions of interest in the study were those which resulted in a conversion of iodine to iodide. Iodine conversion is expected to occur in oxidation reactions with reactive sites in the membrane molecular structure. In the absence of other interactions, the iodine concentration is expected to decrease during conversion reactions while the TI (total iodine) concentration (sum of concentrations of iodine and iodide species) is expected to remain constant.

An initial premise of the study was that conversion is a first-order reaction in which the mass reacting per unit time may be expressed as follows for completely-mixed systems:

1. Unit area basis:

$$\frac{VdX}{d\theta} = AK_{C-A}X \quad (IV-1)$$

2. Unit volume basis:

$$\frac{VdX}{d\theta} = AtK_{C-V}X \quad (IV-2)$$

where: V = Volume of solution containing the reactant (L<sup>3</sup>)

X = Reactant concentration (M/L<sup>3</sup>)

A = Membrane surface area (L<sup>2</sup>)

t = Membrane thickness (L)

θ = Time

K<sub>C-A</sub> = Reaction constant, conversion, per unit area of membrane surface (L<sup>3</sup>/L<sup>2</sup>-T, or L/T)

K<sub>C-V</sub> = Reaction constant, conversion, per unit volume of membrane (L<sup>3</sup>/L<sup>2</sup>-L-T, or 1/T)

The reaction constants  $K_{C-A}$  and  $K_{C-V}$  can be used to estimate the conversion rate on the basis of membrane surface area and membrane volume exposed to the aqueous phase respectively. Equations IV-1 and 2 can be integrated to yield the expression:

$$K_{C-A} = \frac{V}{A} (\theta_2 - \theta_1) \ln \frac{X_1}{X_2} \quad (IV-3)$$

and

$$K_{C-V} = \frac{V}{At} (\theta_2 - \theta_1) \ln \frac{X_1}{X_2} \quad (IV-4)$$

where:  $X_1$  and  $X_2$  are reactant concentrations at times  $\theta_1$  and  $\theta_2$  respectively.

The concentration parameters ( $X_1$  and  $X_2$ ) used in solving Equations IV-3 and 4 for the reaction constants are the iodine ( $I_2$ ) concentrations at time  $\theta_1$  and  $\theta_2$  respectively.

#### Substitution Reactions

The substitution reactions of interest to this study were those chemical reactions between the membrane materials and iodine in which a form of iodine is removed from solution and incorporated into the membrane material. Iodine substitution is a common occurrence in unsaturated organic compounds and is manifested by a decrease in the  $I_2$  concentration of the source iodine solution. It has been assumed in this study that substitution is a first-order reaction as discussed previously for the conversion reactions. The equations for determining the reaction constants for substitution, on a membrane surface area and membrane volume basis respectively, are:-

$$K_{S-A} = \frac{V}{A} (\theta_2 - \theta_1) \ln \frac{X_1}{X_2} \quad (IV-5)$$

$$K_{S-V} = \frac{V}{At} (\theta_2 - \theta_1) \ln \frac{X_1}{X_2} \quad (IV-6)$$

where:  $K_{S-A}$  = Reaction constant, substitution, per unit area of membrane surface (L/T)

$K_{S-V}$  = Reaction constant, substitution, per unit volume of membrane (l/T)

The  $I_2$  concentration is used as the concentration parameter in estimating  $K_{S-A}$  and  $K_{S-V}$  with Equations IV-5 and 6.

## Diffusion

### Background

Diffusional operations involve the contact of a fluid, either a gas or a liquid, with another phase, accompanied by a transfer of material between the contacted phases. Bulk fluid movement plays an important part in the diffusion process in that if movement (mixing) exists, there will occur a replenishment at the phase interface of molecules of the diffusing component which can replace molecules previously diffused across the interface and concentration gradient into the other phase.

Two types of diffusion exist, molecular diffusion and eddy diffusion. Molecular diffusion is the transport of matter on a molecular scale through a fluid which is stagnant or, if in laminar flow, in a direction perpendicular to the flowing streamlines. Eddy diffusion is the connotation used to describe diffusion in turbulent flow.

Diffusion can take place in solids or semisolids as well as in fluids. In such operations the diffusion involves the solid phase and may proceed according to several mechanisms. Diffusion may occur by solution of the diffusing component in the solid, resulting in formation of a solid solution. A porous solid, however, may permit the flow of a liquid or gas through the interstices and capillaries. Because of the structural characteristics of membrane materials, diffusion through membranes is associated with the former rather than the latter type of operation.

With reference to the diffusion of iodine in spacecraft water systems, two mechanisms are of concern:

- (1) Diffusion of iodine in bulk solution from points of introduction into the confines of the water system.
- (2) Diffusion of iodine across membrane interfaces by a process of solution in the membrane at the liquid-membrane interface, and dissolution from the membrane into the gas phase at the gas-membrane interface, i.e., diffusion into, through, and from the membrane.

Major emphasis in this study was placed on the latter mechanism rather than the former because of the identification at the onset of the study of the importance of membrane diffusion in the depletion of iodine residuals in the LM.

### Study Considerations

Diffusion in the context of iodine depletion is expected to manifest itself in terms of equal depletion of both  $I_2$  (iodine) and TI concentrations. In closed systems these depletions would continue only until the concentration gradient driving the diffusional operation was reduced to zero. It is probable, but unverified, that iodine diffusion in the LM occurs in an open system under transient conditions in which a change is effected continually in the concentration gradient driving the operation as it proceeds. The rate of mass transfer in a diffusion process can be described by Fick's Law (Reference IV-2), which may be expressed as:

$$V \frac{dX}{d\theta} = \frac{ADX}{t} \quad (IV-7)$$

where:  $D$  = Diffusion constant for species diffusing through membrane ( $L^2/T$ )  
 $A$  = Membrane surface area ( $L^2$ )  
 $t$  = Membrane thickness ( $L$ )  
 $V$  = Volume of solution containing the diffusing species.  
 $X$  = Concentration ( $M/L^3$ )

Because it is assumed in the derivation of Equation IV-7 that the concentration  $X$  is uniform throughout the solution of volume  $V$ , Equation IV-7 is applicable to mixed systems. Integration of this expression yields:

$$\ln \left( \frac{X_1}{X_2} \right) = \frac{ADX}{Vt} (\theta_1 - \theta_2) \quad (IV-8)$$

Several important factors must be considered in the design of experiments to measure diffusion constants:

- (1) Diffusivity is dependent on the temperature and viscosity of the bulk medium.
- (2) Diffusivity is a function of the ionic or nonionic, and atomic or diatomic character of the diffusing substance.
- (3) Diffusivity varies with concentration of diffusing component in the liquid phase over large concentration ranges, as well as with the partial pressure of the components of the gas mixture on the gas-phase side of the membrane in spacecraft water systems.



## Sorption

Sorption, as used in this report, is a general term for the adsorptive and absorptive processes taking place in the membrane. Sorption of iodine may occur reversibly (in the absence of substitution or conversion reactions) or irreversibly. The sorption of iodine is manifested by an initial depletion of total iodine from the solution to the extent that an equilibrium is established between the resulting solution and the concentration of the sorbed iodine on the membrane.

Sorption can be described by isotherms such as the empirical Langmuir or Freundlich Isotherms. The Langmuir Isotherm is formulated as follows (Reference IV-3):

$$X_S = \frac{X_S^M X_L}{S + X_L}$$

where:  $X_S$  = mass of reactant sorbed per unit area of membrane ( $M/L^2$ )

$X_L$  = liquid equilibrium reactant concentration ( $M/L^3$ )

$X_S^M$  = saturation mass of reactant sorbed per unit area of membrane ( $M/L^2$ ), a constant.

$S$  = saturation constant ( $M/L^3$ )

The linear form of Equation IV-9 is as follows:

$$\frac{1}{X_S} = \frac{1}{X_S^M} + \left(\frac{S}{X_S^M}\right) \left(\frac{1}{X_L}\right) \quad (IV-10)$$

The constants  $X_S^M$  and  $S$  can be determined by evaluation of the slope ( $S/X_S^M$ ) and y-intercept ( $1/X_S^M$ ) in a plot of ( $1/X_S$ ) vs ( $1/X_L$ ), as presented in Appendix C. The mass of reactant sorbed,  $X_S$ , is equal to  $V(X_1 - X_L)/A$ , where  $V$  is the volume of test solution and  $X_1$  is the initial reactant concentration.

The Freundlich Isotherm is formulated as follows:

$$X_S = k_F X_L^{\frac{1}{n_F}} \quad (IV-11)$$

where:  $X_S$  and  $X_L$  are as defined for the Langmuir Isotherm

$K_F$  = Freundlich constant

$n_F$  = Freundlich constant

The implication of Equation IV-11; is that if  $\log X_S$  is plotted against  $\log X_L$ , a straight line will be obtained with slope  $1/n_F$ .

#### MEMBRANE SELECTION

Six membrane materials were selected for evaluation on the basis of: current usage in the Apollo potable water systems; and (in the case of candidate membranes for the Orbital Workshop) a consideration of the general resistance of the membranes to chemical attack, of their mechanical properties (flexibility and elasticity), and of their availability. The materials selected were:

- (1) Silastic, a silicone-based elastomer noted for stability, which is used currently in the LM.
- (2) Polyisoprene - A synthetic rubber currently used in the CM.
- (3) Butyl rubber - a common synthetic rubber.
- (4) Viton - a fluoroelastomer with excellent chemical stability and resistance to heat.
- (5) Nordel - an ethylene-propylene terpolymer resistant to oxidation, water, and most chemicals.
- (6) Polyurethane - a polymer containing a large fraction of polarized oxygen groups which were considered as a factor which could lead to reduction of diffusion of diatomic iodine.

The thickness, areal density, and specific gravity of the materials tested are summarized in Table IV-1.

#### METHODOLOGY

##### Experimental Apparatus

The basic diffusion cell used in all membrane studies was a Kerr-Mason jar (Figure IV-1). This container, used in both pint and quart sizes, proved ideal for the purposes of the study in that the cover arrangement permitted the insertion of membrane discs between the contents of the test vessel and the atmosphere.

TABLE IV-1  
PROPERTIES OF MEMBRANE MATERIALS

Material	Manufacturer	Thickness		Specific Gravity	Areal Density gm/cm <sup>2</sup>
		Mils	Millimeters		
Silastic	Dow Corning*	31.5	0.80	1.75	0.140
Polyisoprene	Unknown*	69.9	1.78	1.48	0.263
Butyl rubber	Unknown	61.5	1.56	1.83	0.285
Viton	Du Pont	33.5	0.85	2.84	2.41
Nordel	Du Pont	33.5	0.85	1.69	0.144
Polyurethane	American Polytherm	33.9	0.86	1.65	0.141

NOTE: \*Samples tested were supplied by NASA, and were identical to those employed in Apollo potable water systems.

Two modes of operation of the diffusion cell were used: an initial mode in which sorption, substitution, and conversion phenomena were studied; and a second mode in which diffusion of iodine from the cells was studied. In the initial mode of operation the cells were sealed by inserting a teflon lid outside of the membrane being studied to prevent the loss of iodine to the atmosphere. In the second mode, the teflon lid seal was removed, allowing the diffusion process to proceed to equilibrium. As is documented subsequently, the teflon lid (0.165cm thick) was found to be highly non-reactive and impermeable to iodine.

The sensitivity of diffusion processes to temperature variations has been discussed previously. For this reason, the ambient temperature of the room in which the experiments were conducted was controlled during membrane testing in the range of 24 to 26°C, to simulate the spacecraft temperature of 24.4°C (76°F).

Stirring of the diffusion cells was accomplished by means of teflon-coated magnetic stirrer bars activated by electric or water-driven magnetic stirrers. In those cases where water-driven stirrers were used, styrofoam sheets of approximately 1/4 inch thickness were inserted between the stirrer unit and the container being stirred to minimize the cooling effects of the flowing water on the liquids being stirred.

#### Analytical Techniques

Analyses for iodine and taste and odor were conducted during the membrane studies. Iodine determinations were conducted by withdrawing measured amounts of solution from diffusion cells and running analyses using the colorimetric method developed by Black and Whittle (Reference IV-4). This method proved satisfactory for both  $I_2$  and  $TI$  determinations.

All iodine solutions were prepared by dissolving elemental iodine in distilled and deionized water. The test solutions were prepared from the stock solutions, and allowed to equilibrate for approximately four hours before analysis.

The taste and odor of the water in the diffusion cells were evaluated at the termination of all tests by removing the diffusion cell cover, tasting small quantities of the iodine solutions, and recording subjective impressions. A minimum of two observers was used for each determination. The subjective evaluation method was used in deference to methods in

"Standard Methods" (Reference IV-5) for two reasons; first, the presence of substantial quantities of iodine in the solutions tested complicated the quantification of membrane-induced tastes and odors; and second, it was found during the course of studies that membranes readily fell into two categories; those imparting taste levels which could be judged readily as unacceptable, and those producing faint or imperceptible tastes. For these reasons it was found feasible to summarize the results of the taste and odor testing as either acceptable or unacceptable.

### Experimental Program

#### Initial Screening

The initial screening phase served two purposes:

- (1) To eliminate from further consideration those materials having excessively high uptake rates or those imparting serious taste and odor problems to the iodine solutions in which they were immersed.
- (2) To determine the approximate rate of iodine uptake as a guide in selecting initial concentrations and sampling intervals for subsequent studies.

The initial screening of the selected membranes consisted of immersing a 3-in x 3-in sample of each membrane into an iodine solution of approximately 30 mg/l initial  $I_2$  concentration in a closed container, and monitoring concentration changes with time. The test vessel capacity was nominally one pint (470 ml). After approximately 24 hours, the contents of the test vessel were evaluated for taste and odor, and the test was terminated.

#### Uptake Studies

The uptake studies consisted of bringing membrane samples into contact with iodine solutions on one side only in the closed (teflon-lidded) diffusion cell system (Figure IV-1), followed by a monitoring of iodine concentration changes with time. The duration of the uptake tests was generally dependent upon the iodine depletion rates observed. The exception to this procedure occurred in the studies conducted on silastic, in which membrane samples were brought into contact with iodine solutions for preset periods.

The initial iodine concentration chosen for the uptake tests was approximately 30 mg/l, the level used by NASA in a one-hour pre-soak of

the LM water system. Tests at initial concentrations above and below this concentration level were run depending upon the results of the initial test.

At the conclusion of the iodine concentration monitoring, test vessels were opened and the contents evaluated for taste and odor.

The results of the uptake studies were used to define the magnitude of the interactions which occur between membrane samples and iodine solutions in closed systems, and to identify, where possible, the mechanisms responsible for iodine uptake.

#### Diffusion Studies

Diffusion studies were conducted using the same procedures and apparatus as used in the uptake studies but with the teflon lid removed from the apparatus. All reasonable efforts were made to approximate spacecraft environmental conditions. The diffusion cells were mixed in all of the experiments so that diffusion of iodine through the membrane rather than iodine diffusion in the bulk fluid was the rate-limiting step. Because the degree of mixing effected in the water storage tanks of the LM under normal operating cycles is unknown, it is unknown how closely the laboratory mixing simulated that occurring under prototype operating conditions.

#### RESULTS

This section contains a summary and analysis of the experimental results. The data for all the experiments are presented in Appendix B.

##### Control Experiments on Iodine Uptake in the Diffusion-Cell Apparatus

A series of control on blank experiments were conducted in advance of the initial screening and uptake studies to determine diffusion-cell iodine losses and taste and odors generated in the diffusion cells capped only with teflon lids. The tests were conducted using initial  $I_1$  and  $I_2$  concentrations of about 8, 15, and 35 mg/l over a time period of 13 days.

The results of the control experiments are presented in Figure IV-2 and the data presented therein indicate that both the  $I_2$  and  $I_1$  concentrations decreased at gradual and nearly equal rates over the duration of the experiments, i.e., the observed depletion appears to have been the result of a first-order substitution reaction between iodine and the components of the test vessel. For this reason, a linear best-fit curve

is shown for each set of test results in Figure IV-2. Inasmuch as the concentrations of  $I_2$  and  $TI$  did not decrease significantly in the initial hours of the experiment, initial uptake due to sorption was deemed to be negligible. Additionally, because of the approximately parallel linear relationships defined for both  $I_2$  and  $TI$  at each concentration level, it did not appear that significant conversion of  $I_2$  to the iodide form occurred over the duration of the experiment.

The rate constants for the first order substitution reactions observed for each of the three control experiments were calculated using Equations IV-5 and 6 and are reported in Table IV-2. The mean value of  $K_{S-A}$  is  $1.32 \times 10^{-8}$  cm/hr (areal basis) and the mean value of  $K_{S-C}$  is  $1.65 \times 10^{-7}$  hr<sup>-1</sup>.

In view of the stability observed for the stock iodine solutions when stored in glass vessels, it is believed that the depletion observed in the control experiments described above was due predominantly to interactions between iodine ( $I_2$ ) and the teflon lids. Additionally the depletions observed in the control experiments were insignificant in comparison with the magnitudes of depletions observed in the experiments with the membrane materials. Inasmuch as the rates shown in Table IV-2 imply that almost three days are required for blank losses to exceed the three percent coefficient of variation for the analytical method for iodine blank uptake, due to the teflon lid in the apparatus, it was deemed insignificant and not considered in subsequent evaluation of experimental results.

#### Silastic

Silastic is the material currently utilized in the LM potable water storage tanks. The results of initial screening test indicated that silastic imparted only very faint tastes to iodinated water supplies.

The uptake and mass transfer studies were conducted in sequence after the initial screening test. A total of three sets of diffusion experiments were conducted at zero exposure time and after four and 12 days exposure time to permit assessment of the effect of the exposure time history of the silastic in iodine solutions on the diffusion constants. The uptake tests were run in duplicate at initial concentrations of approximately 34, 15, and 8 mg/l  $I_2$ , according to the experimental program shown in Table IV-3.

TABLE IV-2

## SUMMARY OF RESULTS OF MEMBRANE STUDIES WITH IODINE

Material	Approximate Iodine (I <sub>2</sub> ) Concentration or Range (mg/l)	Sorption Uptake		Reaction Constant-Conversion		Reaction Constant-Substitute		Diffusion Constant D(sq cm/hr)	Taste and Odor Observations	Notes
		X <sub>S-A</sub> (mg/sq cm)	X <sub>S-V</sub> (mg/cu cm)	K <sub>C-A</sub> (cm/hr)	K <sub>C-V</sub> (hr <sup>-1</sup> )	K <sub>S-A</sub> (cm/hr)	K <sub>S-V</sub> (hr <sup>-1</sup> )			
Teflon	8	-	-	-	-	1.27 × 10 <sup>-5</sup>	1.59 × 10 <sup>-7</sup>	-	Very Slight	Control Experiment
	15	-	-	-	-	1.44 × 10 <sup>-8</sup>	1.80 × 10 <sup>-7</sup>	-	"	
	35	-	-	-	-	1.25 × 10 <sup>-8</sup>	1.56 × 10 <sup>-7</sup>	-	"	
	Mean	-	-	-	-	1.32 × 10 <sup>-8</sup>	1.65 × 10 <sup>-7</sup>	-	"	
Silastic	7-35	$X_S = \frac{0.130 X_L}{7.6 + X_L}$	$X_S = \frac{1.63 X_L}{7.6 + X_L}$	-	-	-	-	10.5 × 10 <sup>-2</sup>	-	
	6	-	-	3.67 × 10 <sup>-8</sup>	4.58 × 10 <sup>-7</sup>	-	-	-	Very Slight	
	11	-	-	3.04 × 10 <sup>-8</sup>	3.80 × 10 <sup>-7</sup>	-	-	-	"	
	28	-	-	2.52 × 10 <sup>-8</sup>	3.15 × 10 <sup>-7</sup>	-	-	-	"	
	Mean	-	-	3.08 × 10 <sup>-8</sup>	3.85 × 10 <sup>-7</sup>	-	-	-	"	
Polyisopreno	7-90	$X_S = 0.0089 X_L$	$X_S = \frac{2.35 X_L}{20 + X_L}$	2.02 × 10 <sup>-6</sup>	1.14 × 10 <sup>-5</sup>	-	-	-	-	Strong Discoloration of Membrane
	14.5	-	-	2.02 × 10 <sup>-6</sup>	1.14 × 10 <sup>-5</sup>	-	-	-	Very Slight	
	30	-	-	2.02 × 10 <sup>-6</sup>	1.14 × 10 <sup>-5</sup>	-	-	4.5 × 10 <sup>-2</sup>	"	
	67	-	-	1.93 × 10 <sup>-6</sup>	1.09 × 10 <sup>-5</sup>	-	-	-	"	
	90	-	-	2.11 × 10 <sup>-6</sup>	1.19 × 10 <sup>-5</sup>	-	-	-	"	
Butyl Rubber	30	N/A	N/A	N/A	N/A	N/A	N/A	N/A	Intense - Unacceptable	
Nordel	32	N/A	N/A	N/A	N/A	N/A	N/A	N/A	"	
Viton	30	Nil	Nil	Nil	Nil	N/A	N/A	Nil	Rubbery Taste	
Polyurethane	18	0.563	6.56	2.66 × 10 <sup>-7</sup>	3.09 × 10 <sup>-6</sup>	1.05 × 10 <sup>-7</sup>	1.22 × 10 <sup>-6</sup>	Nil	Very Slight	

- Notes: 1. All studies conducted in completely-mixed systems at 76° F.  
 2. In all tests, V = 0.92 l or 920 cu cc; A = 29.4 sq cm  
 3. Membrane thicknesses are reported in Table IV-1



TABLE IV-3

SILASTIC TEST PROGRAM

Initial I <sub>2</sub> Conc. in each of Dupli- cate Test Vessels (mg/l)	Test Program Schedule
8.2	Uptake testing for 4 days followed by diffusion testing
8.2	Uptake testing for 12 days followed by diffusion testing
14.8	Uptake testing for 4 days followed by diffusion testing
14.8	Uptake testing for 12 days followed by diffusion testing
34.0	Diffusion testing with no prior uptake testing

### Results of Uptake Experiments

The results of the iodine uptake experiments (obtained with the teflon lid in position over the silastic membrane) are shown in Figure IV-3. Best-fit curves have been drawn through each data set, and the following trends are indicated by the shapes of these curves:

- (1) Total iodine: The TI concentration decreased at a decreasing rate during the first two to five days of experimental duration (initial phases) after which little or no change in TI concentration occurred with increasing time (second phase).
- (2)  $I_2$ : The  $I_2$  concentration also decreased at a decreasing rate during the initial phase, after which (in a second phase) the  $I_2$  concentration decreased in a first-order reaction (linearly on a semilogarithmic scale).
- (3) The magnitude of the changes in the TI and  $I_2$  concentrations at the end of each initial phase are similar at each initial concentration of  $I_2$  or TI (8, 15, and 35 mg/l), but vary with initial concentration, i.e.:
  - (a)  $\sim 3.5$  mg/l uptake at  $X_1^I = 35$  mg/l
  - (b)  $\sim 25$  mg/l uptake at  $X_1^I = 15$  mg/l
  - (c)  $\sim 2$  mg/l uptake at  $X_1^I = 8$  mg/l

The similarity in the magnitude and manner of TI and  $I_2$  concentration changes during the initial phases of the experiments are indicative that a sorption process is taking place. For this reason the data for the TI concentrations were fitted to a Langmuir Isotherm by taking as sorption losses the difference between the initial and equilibrium liquid concentrations. The basic data are presented in Figure C-1 and the associated calculations are presented in Table C-1 of Appendix C. The data fit the Langmuir model well, as shown in Figure C-1, and the expressions obtained for silastic are as follows (as summarized in Table IV-2):

- (1) Unit area of membrane basis:

$$X_S = \frac{0.130 X_L}{7.6 + X_L} \quad (IV-12)$$

where:  $X_S$  = total iodine sorption, mg/sq cm of membrane area

$S_L$  = liquid equilibrium total iodine concentrations, mg/l

(2) Unit volume of membrane basis (silastic thickness of 0.08 cm, per Table IV-1):

$$X_A = \frac{1.63X_L}{7.6 + X_L} \quad (IV-13)$$

where:  $X_A$  = total iodine sorption, mg/cu cm of membrane volume.

Based on the preceding analysis, it was concluded that the changes in the concentrations of the iodine forms during the initial phase of the experiment were associated with sorption and that, because the concentration changes for both  $TI$  and  $I_2$  were similar for any given experiment, that the iodine form undergoing sorption was  $I_2$ .

The trend lines for the second phase of concentration change relative to time (Figure IV-3) indicate that the  $TI$  concentrations remain essentially constant, while the  $I_2$  concentrations are depleted according to a first-order type of reaction. This implies that, in the second phase, iodine uptake was due primarily to conversion of  $I_2$  to iodide, unaccompanied by any substitution reactions with the membrane material. Equations IV-3 and 4 were used to determine values of  $K_{C-A}^S$  and  $K_{C-V}^S$  respectively for  $I_2$  conversion for each of the three data sets shown in Figure IV-3, and the results are tabulated in Table IV-2. On a unit area basis, the value of  $K_{C-A}^S$  decreased from  $3.67 \times 10^{-8}$  cm/hr at an  $I_2$  concentration of 6 mg/l to a value of  $2.52 \times 10^{-8}$  cm/hr at an  $I_2$  concentration of 28 mg/l. The value of  $K_{C-V}^S$  (volume basis) decreased from  $4.58 \times 10^{-7}$  hr<sup>-1</sup> to  $3.15 \times 10^{-7}$  hr<sup>-1</sup> as the  $I_2$  concentration increased from 6 to 28 mg/l. This variation in the conversion reactant constant for silastic with concentration is indicative that the actual reaction taking place may not be completely irreversible, i.e., the products of the conversion reaction themselves may interfere, at higher reactant ( $I_2$ ) concentration, with the rate of the reaction of concern, i.e., the rate of iodine conversion.

#### Results of Diffusion Experiments

The diffusion tests were started at the termination of uptake testing by removing the teflon lids from the diffusion cells. The data from these experiments are presented on semi-log plots in Figures IV-4 to IV-6 for membrane conditioning times of zero, four, and 12 days respectively.

The data presented in Figures IV-4 to IV-6 indicate that the rate of change of the  $TI$  concentration in the diffusion cells approximated closely

the rate of change of the  $I_2$  concentration, indicating that the  $I_2$  losses from the test cells were due primarily to diffusion. Whatever losses attributable to the conversion of  $I_2$  to iodide on the test cell were insignificant in comparison with the diffusion losses. For this reason the data were analyzed directly using Equation IV-7. Diffusion constants were computed by taking a time weighted mean of constants calculated for adjacent data points using Equation IV-4, correcting in all cases for changes in the volume of the iodine solution to account for the sample aliquots taken during the experiment. The results of these calculations are presented in Table IV-4.

The mean diffusion constants reported in Table IV-4 for silastic varied from a minimum of  $9.41 \times 10^{-2}$  sq cm/hr for four days conditioning time to approximately  $11.4 \times 10^{-2}$  sq cm/hr at zero conditioning time and 12-days conditioning time. Based on the foregoing, the mean diffusion constant for silastic is  $10.5 \times 10^{-2}$  sq cm/hr. Because of the limit variation of  $D^S$  with respect to concentration there exists no apparent trend in the magnitude of the diffusion constant with respect to conditioning time.

#### Polyisoprene

In the initial screening assessment of polyisoprene, interaction between the iodine and the polyisoprene resulted in a high rate of uptake of both species of iodine which was accompanied by severe discoloration of the normally flesh-colored material to shades of brown and green. However, in contrast to other materials which showed high uptake rates, little taste or odor was imparted to the iodine solutions by the polyisoprene-iodine interactions.

Uptake studies were run with polyisoprene at five initial concentrations varying from 7.4 to 90 mg/1  $I_2$ . The higher iodine concentrations were used in the polyisoprene experiments in an attempt to develop a conditioned membrane which would not continue to sorb high levels of  $I_2$ .

#### Results of Uptake Experiments

The results of the iodine uptake experiments, obtained with the teflon lid in position over the silastic membrane, are shown in Figures IV-7 to 11. Best-fit curves have been drawn through each of the five data sets, and the following trends are indicated in every case:

TABLE IV-4

SUMMARY OF DIFFUSION CONSTANTS-IODINE  
DIFFUSION THROUGH SILASTIC

Conditioning Time (Days)	$D^S$ , sq cm/hr $\times 10^2$			Mean $D^S$
	Initial $I_2$ @ 30mg/l	Initial $I_2$ @ 12mg/l	Initial $I_2$ @ 6mg/l	
0	11.34	-	-	11.34
4	10.41	8.25	9.58	9.41
12	11.50	12.15	10.75	11.47

- (1) The concentration of TI decreased at a decreasing rate to an equilibrium level, indicative of a sorption reaction.
- (2) The first-order rates of decrease of  $I_2$  concentration after equilibration of the total iodine concentration are indicative that, during and after the initial sorption took place, conversion rather than substitution reactions were taking place.

In order to characterize mathematically the initial sorption, the data in Figures IV-7 to IV-11 were fitted to the empirical isotherm models by taking as sorption losses the difference between initial concentrations of TI and those found after stable TI levels were reached (about 60 hours). The basic data used in the evaluation are presented in Table C-2 and Figures C-2 and C-3. As shown in Figure C-2, the trend line through the data using the linearized form of the Langmuir isotherm resulted in a negative y-intercept (negative value of  $1/X_S$ ), invalidating the applicability of this isotherm. The data were fitted reasonably to the Freundlich isotherm as shown in Figure C-3, and for this reason the latter model has been selected to describe polyisoprene sorption of total iodine. The equation describing the sorption for polyisoprene is as follows:

$$X_S = 0.0089 X_L^{1.75} \quad (IV-14)$$

The relative significance of iodine sorption by polyisoprene is evident from inspection of the sorption isotherm for silastic and polyisoprene presented in Figure IV-12. For example, at a liquid equilibrium iodine concentration ( $X_L$ ) of 15 mg/l, the sorbed iodine concentration with polyisoprene is  $\sim 1.1$  mg/sq cm, or nearly 13-fold greater than that for silastic ( $\sim 0.085$  mg/sq cm). It is also apparent that the sorbed concentration ( $X_S$ ) is predicted to approach a maximal value (0.130 mg/sq cm) with increasing values of  $X_L$  for silastic, but  $X_S$  increases exponentially with increasing  $X_L$  over the range of observations made in the present study ( $X_L = 0$  to 19 mg/l, per Table C-2). The foregoing observations are overwhelming evidence that sorption is a major factor of concern with respect to the use of polyisoprene membranes in spacecraft water systems.

The trends of the best-fit lines of Figures IV-7 to 11 indicate that, during and subsequent to the initial-phase sorption of iodine on polyisoprene, the  $I_2$  form is undergoing a first-order conversion to the

iodide form. Reaction constants were calculated using Equations IV-3 and 4 for this conversion at each concentration and are summarized in Table IV-2. The mean reaction constants are as follows:

(1) Unit area of membrane basis:

$$K_{C-A}^P = 2.02 \times 10^{-6} \text{ cm/hr}$$

(2) Unit volume of membrane basis:

$$K_{C-V}^P = 1.14 \times 10^{-5} \text{ hr}^{-1}$$

These conversion reaction constants for polyisoprene are over 100-fold greater than those determined for silastic, as reported in Table IV-2. Additionally, the reaction constants for conversion show little variation over a wide range of iodine concentrations.

#### Results of Diffusion Experiments

An evaluation of the rate of diffusion of iodine through polyisoprene was conducted at an initial  $I_2$  concentration of 30.0 mg/l. As shown in Figure IV-9, the depletion curves for  $I_2$  in the diffusion experiment were virtually identical to those developed for the uptake studies, and it is apparent that the primary modes of  $I_2$  depletion in mass transfer testing were the sorption and the first order reaction of iodine with polyisoprene described above.

Data for total iodine indicated that some mass transfer occurred, but the data do not permit reliable determination of a diffusion constant. An estimate was made of the diffusion constant by assuming that sorption was complete after 38.5 hours (per Figure IV-9) and that the losses which followed were attributable solely to diffusion. For this case the diffusion constant was estimated to be  $4.5 \times 10^{-2}$  sq cm/hr, or about half the magnitude of the diffusion constant determined for silastic.

#### Butyl Rubber and Nordel

Butyl rubber and Nordel were subjected to initial screening tests (as described previously) in which both materials exhibited extremely high uptake rates, and imparted highly unpleasant tastes to the solutions. For these reasons, butyl rubber and Nordel were judged unacceptable for use in potable water systems containing iodine, and no further testing was carried out.

#### Viton

The initial screening assessment showed that the exposure of Viton

to an iodine solution resulted in no detectable uptake but did result in the generation of a rubbery taste in the iodine test solutions.

Uptake and mass transfer tests were conducted for Viton, using an initial  $I_2$  concentration of 32 mg/l. The results of these tests are shown in graphical form in Figures IV-13 and IV-14 for uptake and mass transfer respectively. As evidenced by the horizontal trends of data shown in Figures IV-13 and 14 over the 14-day test period, no significant iodine depletion was observed relative to blanks for  $I_2$  or TI in either the uptake or diffusion testing. No significant tastes were imparted to the test solutions. Of the six materials tested (including polyurethane, to be discussed subsequently), Viton showed the least tendency to interact with iodine solutions in any way.

#### Polyurethane

The initial screening test with polyurethane for taste and odors indicated that a very slight taste was imparted to the iodinated test solution in contact with the membrane.

On the basis of this initial feasibility, uptake and diffusion studies were conducted with the polyurethane membrane using iodinated solutions with initial  $I_2$  concentrations of 28 mg/l.

#### Results of Uptake Experiments

The results of the iodine uptake experiments are shown in Figure IV-15. The best-fit curves through the data sets indicate the following trends:

- (1) An initial phase in which the TI and  $I_2$  concentrations decreased at a decreasing rate with respect to time to a time of about 30 hours exposure.
- (2) A second phase in which both the TI and  $I_2$  concentrations decreased according to first order rates, the rate of decrease for  $I_2$  exceeding that for TI.

The implications of the above trends are as follows:

- (1) The occurrence of a sorption of iodine by the polyurethane membrane in the initial phase.
- (2) The conversion of  $I_2$  to the iodide form, as evidenced by the greater first-order rate of decrease of  $I_2$  relative to that for TI.
- (3) The substitution of iodine, as evidenced by the first-order



rate of decrease of TI after termination of the initial phase.

Inasmuch as the uptake tests for polyurethane were conducted at one initial  $I_2$  concentration (28 mg/l), it was not possible to define the type of, or isotherm constants appropriate for, this sorption. On the assumption that the TI concentration at the end of 30 hours of exposure (18 mg/l) represented a pseudoequilibrium liquid concentration, the concentration of sorbed iodine in the membrane can be computed as equal to 0.563 mg/sq cm, and the iodine uptake ( $X_1 - X_L$ ) is equal to 28-18, or 10 mg/l.

The relationship of this sole data point for polyurethane sorption to the predicted isotherm relationships for polyisoprene and silastic is evident from the information shown in Figure IV-12. At a liquid equilibrium iodine concentration of 18 mg/l, the sorbed concentration ( $X_S$ ) for polyurethane (0.56 mg/sq cm) is equal to about 40 percent of the predicted concentration for polyisoprene and is six-fold greater than predicted concentration for polyurethane. Based on the preceding observations, as well as visual observation of the trend lines in Figure IV-15, it is apparent that sorption is a significant factor in the consideration of polyurethane as a candidate membrane for spacecraft water systems.

The first-order reaction constants for substitution of iodine in the polyurethane test cells were calculated using Equations IV-5 and 6 and are reported in Table IV-2 and as follows:

- (1) Unit area of membrane basis:

$$K_{S-A}^U = 1.05 \times 10^{-7} \text{ cm/hr}$$

- (2) Unit volume of membrane basis:

$$K_{S-V}^U = 1.22 \times 10^{-6} \text{ hr}^{-1}$$

The above reaction constants for substitution are about eight-fold greater than those reported in Table IV-2 for the teflon (control experiments).

The first-order reaction constants for conversion of iodine by polyurethane were determined using Equations IV-3 and 4 and are reported in Table IV-2 and below.

- (1) Unit area of membrane basis:

$$K_{C-A}^U = 2.66 \times 10^{-7} \text{ cm/hr}$$

(2) Unit volume of membrane basis:

$$K_{C-V}^U = 3.09 \times 10^{-6} \text{ hr}^{-1}$$

The reaction constants for iodine conversion on polyurethane are about seven-times greater than those observed for silastic and eight-times less than those observed for polyisoprene.

#### SUMMARY AND CONCLUSIONS

Six membrane types (silastic, polyisoprene, butyl rubber, Nordel, Viton, and polyurethane) were examined in the test program to assess the reactivity of the membranes with iodinated solutions in terms of taste and odor observations as an initial screening test, and in terms of sorption, conversion and substitution-type depletions of  $I_2$  resulting from iodine-membrane interaction. Teflon was used as a control membrane in the experiments. The results of the experiments, summarized in Table IV-2, indicate the following:

- (1) Unacceptable taste and odor conditions developed upon exposure of butyl rubber, nordel, and viton to the iodinated solutions. For this reason these membranes were not subjected to further testing.
- (2) Substitution occurred at insignificant levels in the teflon control experiment and also with the polyurethane; the conversion reaction constants for polyurethane were about eight-times greater than those reported for silastic.
- (3) Sorption uptake occurred with silastic, polyisoprene, and polyurethane, and equilibrium sorption could be described by the Freundlich Isotherm for polyisoprene and by the Langmuir Isotherm for silastic. A sorption isotherm could not be developed for the polyurethane due to insufficient observations. On a relative scale, sorption was the least significant with the silastic and most significant with polyisoprene; sorption was the major factor causing iodine depletions both with the polyisoprene and polyurethane membranes.
- (4) Conversion reactions were observed with silastic, polyisoprene, and polyurethane, the relative ratios of the conversion reaction constants being 1:7.3:55 respectively.

The conclusions of the membrane studies are as follows:

- (1) Butyl rubber, Nardel, and Viton membrane materials are totally unacceptable on the basis of taste and odor development.
- (2) Silastic is the most acceptable membrane material in times of minimum iodine depletions over time as a result of sorption, conversion, and substitution phenomena.
- (3) Polyisoprene and polyurethane are the least acceptable membrane materials, primarily because of iodine depletions due to sorption, and secondarily because of iodine depletions due to conversion.

CHAPTER IV  
LIST OF REFERENCES

- IV-1 "Chemical Reaction Engineering", by Octave Levenspiel, John Wiley and Sons, New York, 1962.
- IV-2 "Diffusion in Elastomers", by G.J. Van Ameroneen, Rubber Chemistry and Technology, Volume 37, Number 5, December 1964.
- IV-3 "Water Supply and Wastewater Disposal", by G.M. Fair and J.C. Geyer, John Wiley and Sons, New York, 1954.
- IV-4 "New Methods for the Colorimetric Determination of Halogen Residuals; Part I-Iodine, Iodide, Iodate", by A.P. Black and G.P. Whittle. Journal of the American Water Works Association, Volume 59, No.4.
- IV-5 "Standard Methods for the Examination of Water and Wastewater", Published by American Public Health Association, 12th Edition, 1965.

# DIFFUSION CELL

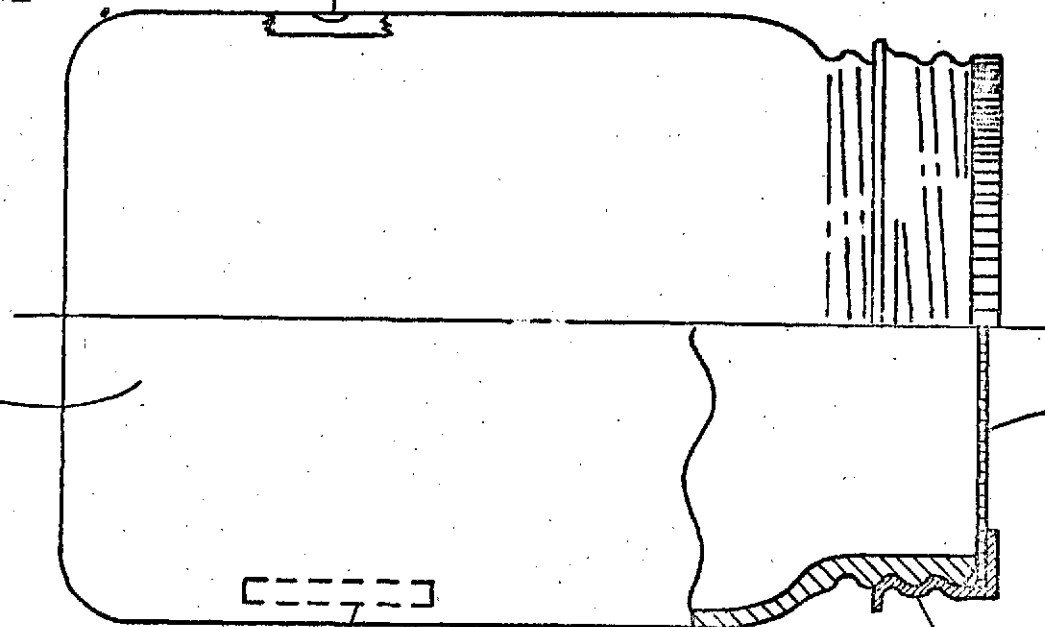
TEFLON TAPE COVERED  
APERTURE FOR ALIQUOT  
WITHDRAWAL

IODINE  
SOLUTION

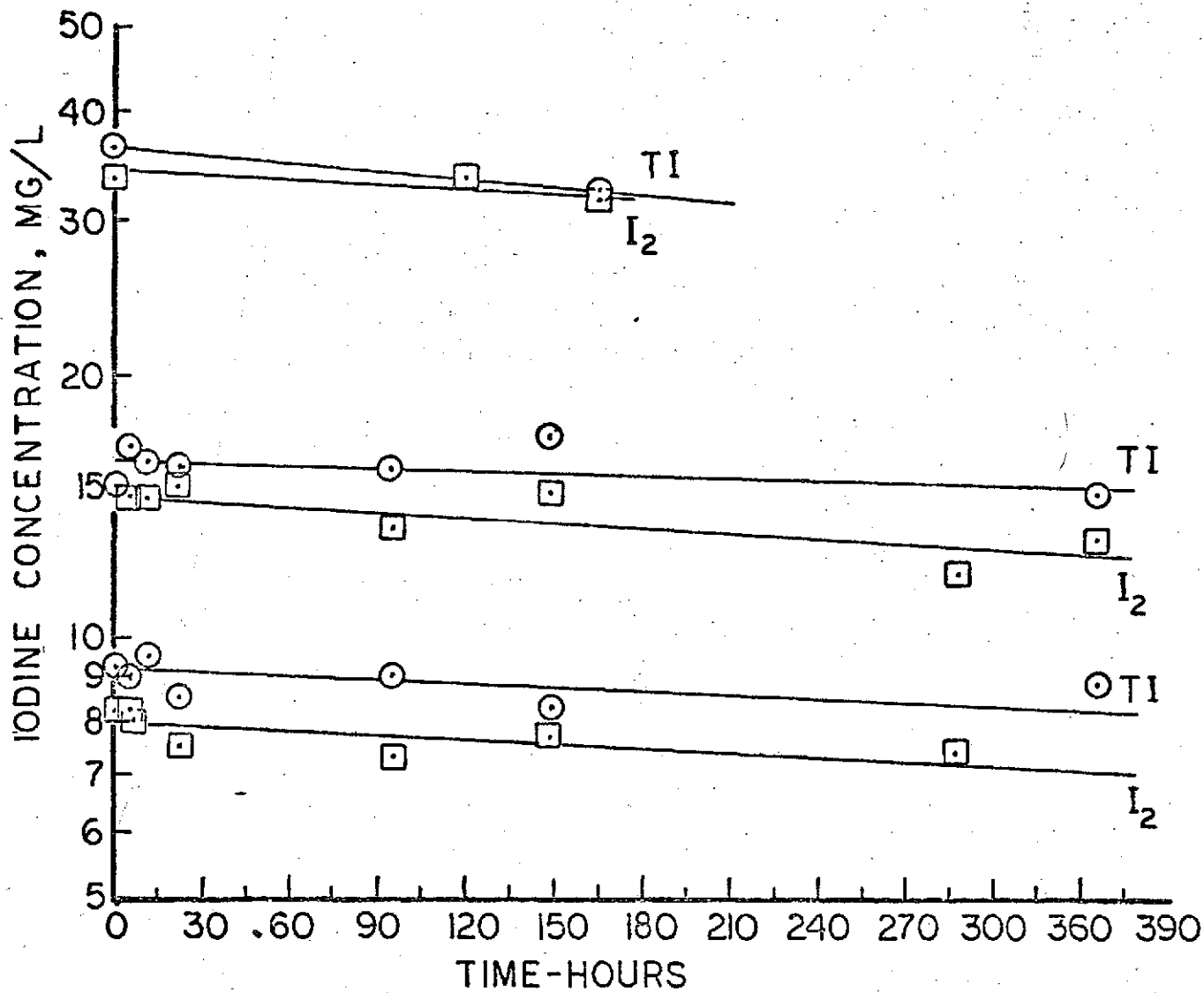
MEMBRANE MAT'L  
AND/OR TEFLON  
LID

MAGNET BAR  
STIRRER

METAL BAND  
GLASS JAR

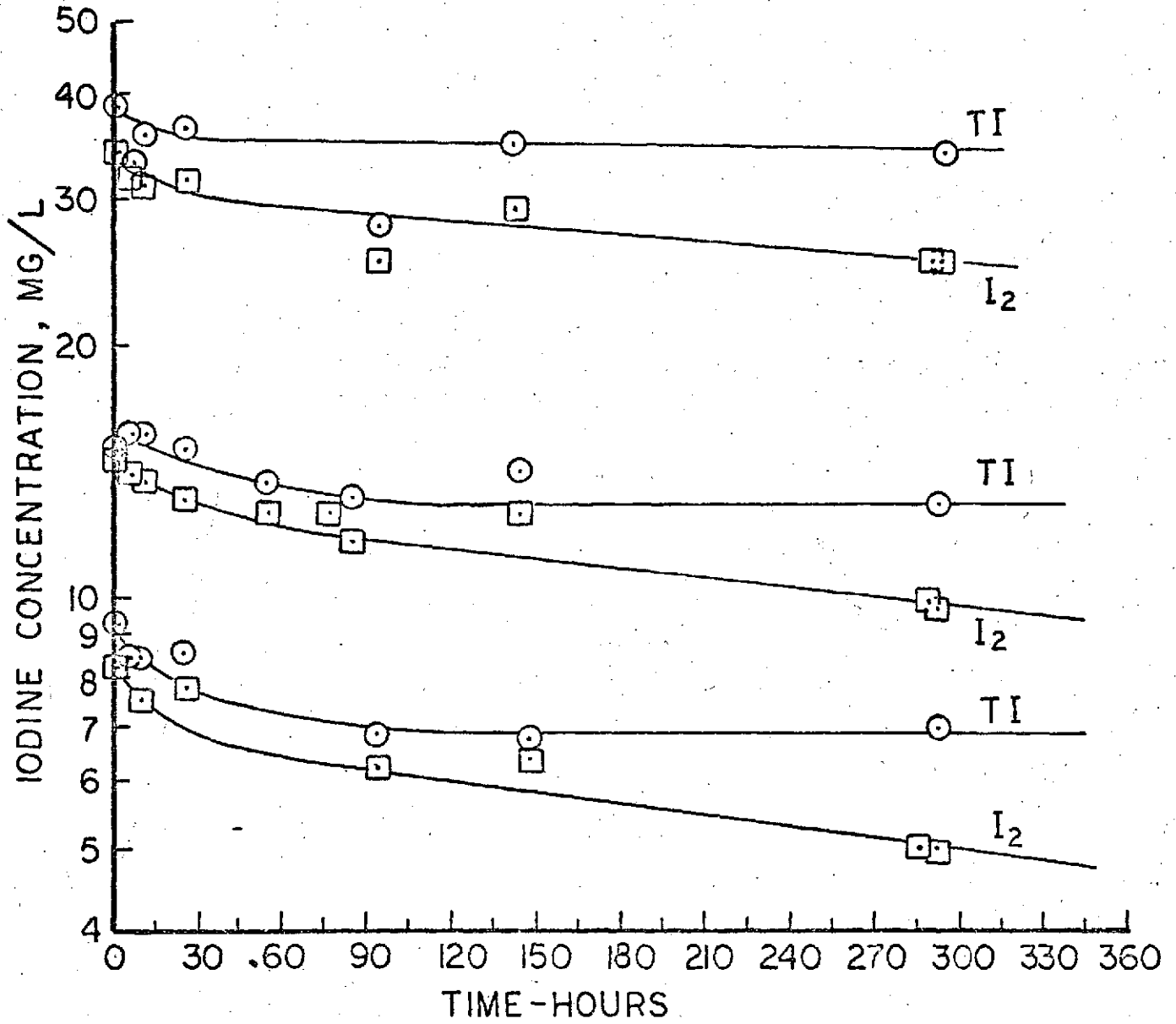


IODINE UPTAKE IN DIFFUSION  
 CELL APPARATUS WITH TEFLON  
 LIDS IN POSITION  
 (NO TEST MEMBRANE MATERIALS USED)



○ — TOTAL IODINE (TI)  
 □ — IODINE (I<sub>2</sub>)

IODINE UPTAKE-SILASTIC MEMBRANE  
 (TEFLON LID IN POSITION OVER  
 SILASTIC MEMBRANE)



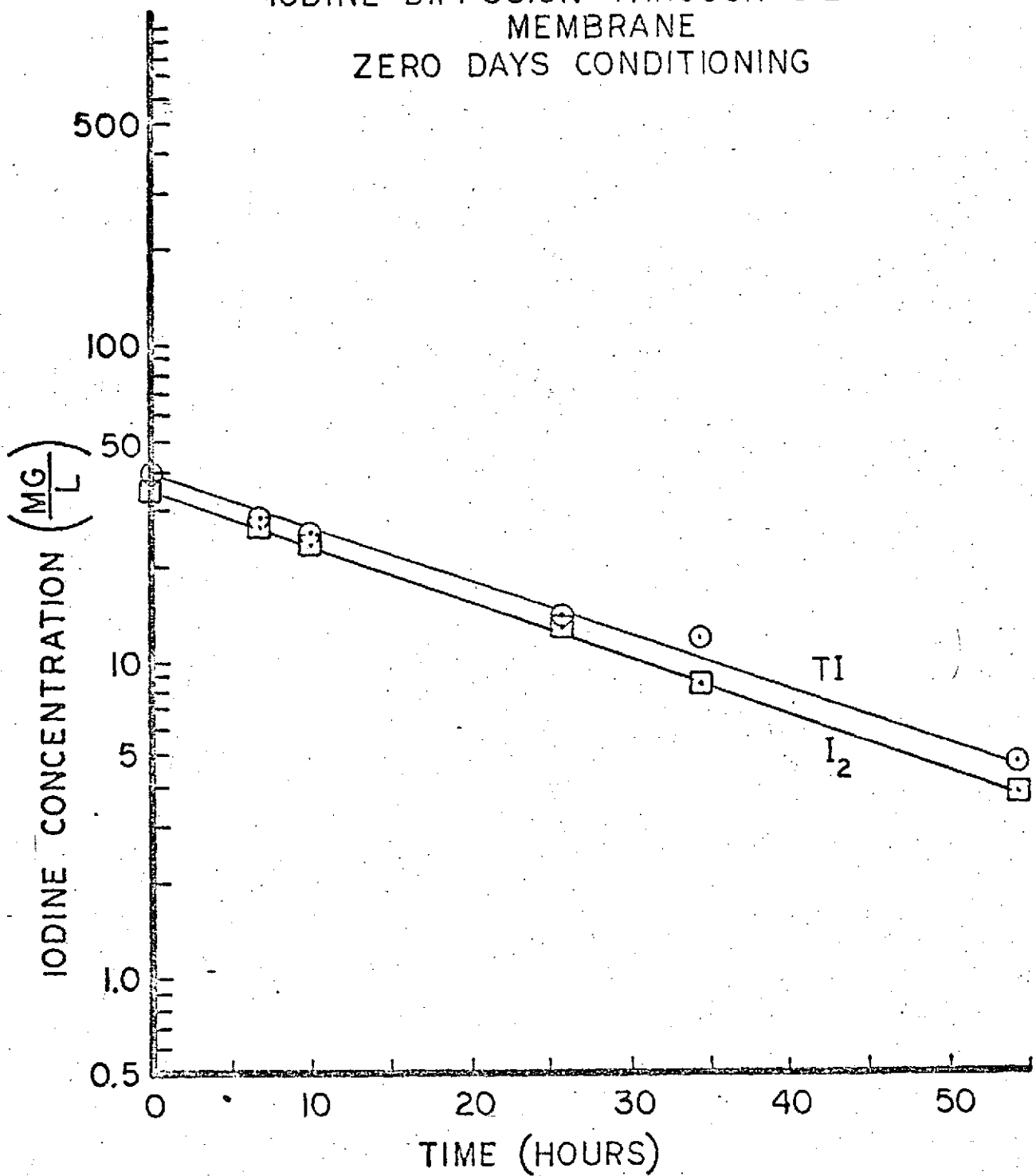
○ — TOTAL IODINE (TI)

□ — IODINE (I<sub>2</sub>)

DIFFUSION CELL : 970ML VOLUME

SILASTIC AREA : 29.4 SQ CM

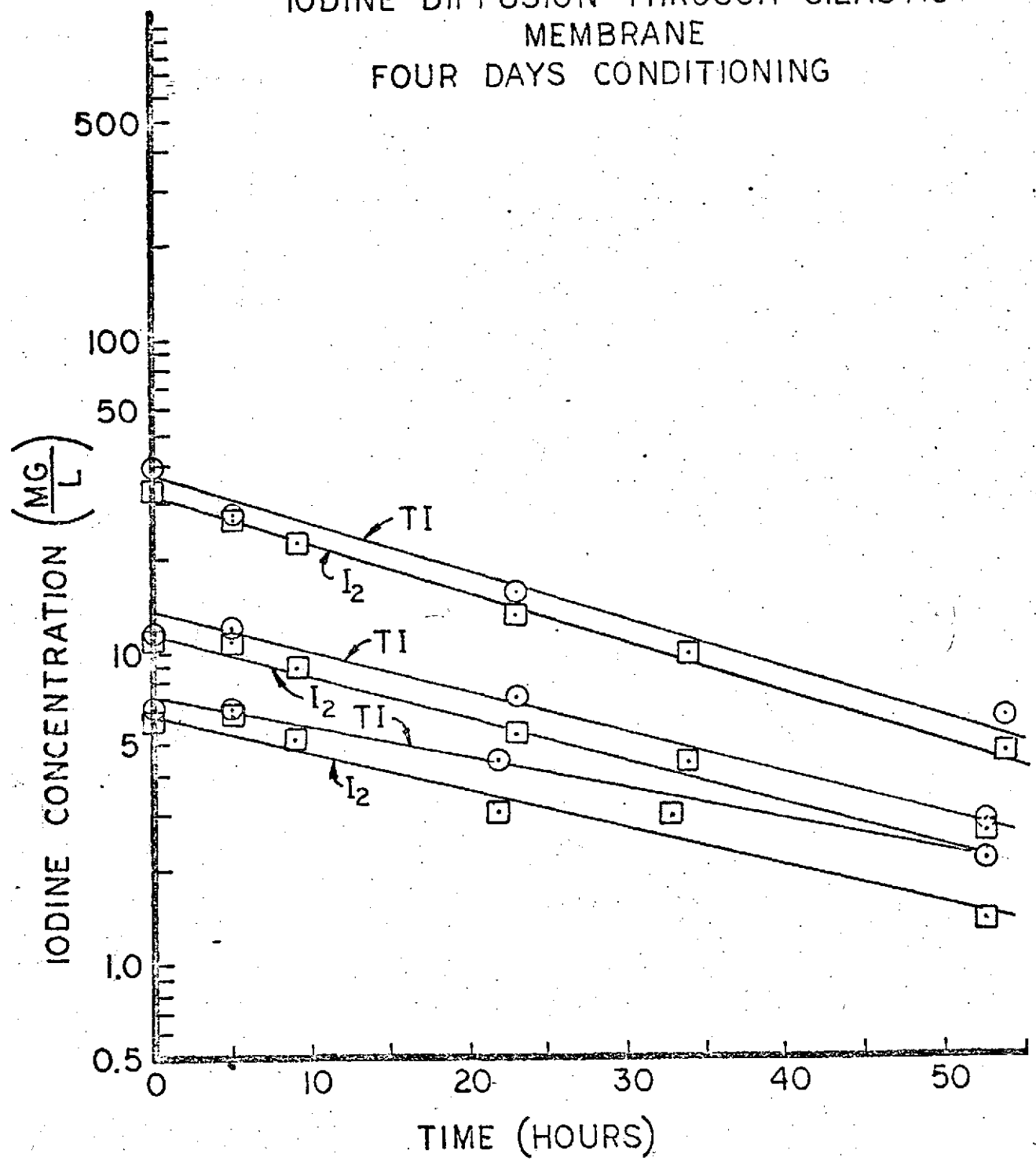
IODINE DIFFUSION THROUGH SILASTIC  
MEMBRANE  
ZERO DAYS CONDITIONING



○ = TOTAL IODINE (TI)  
□ = IODINE (I<sub>2</sub>)

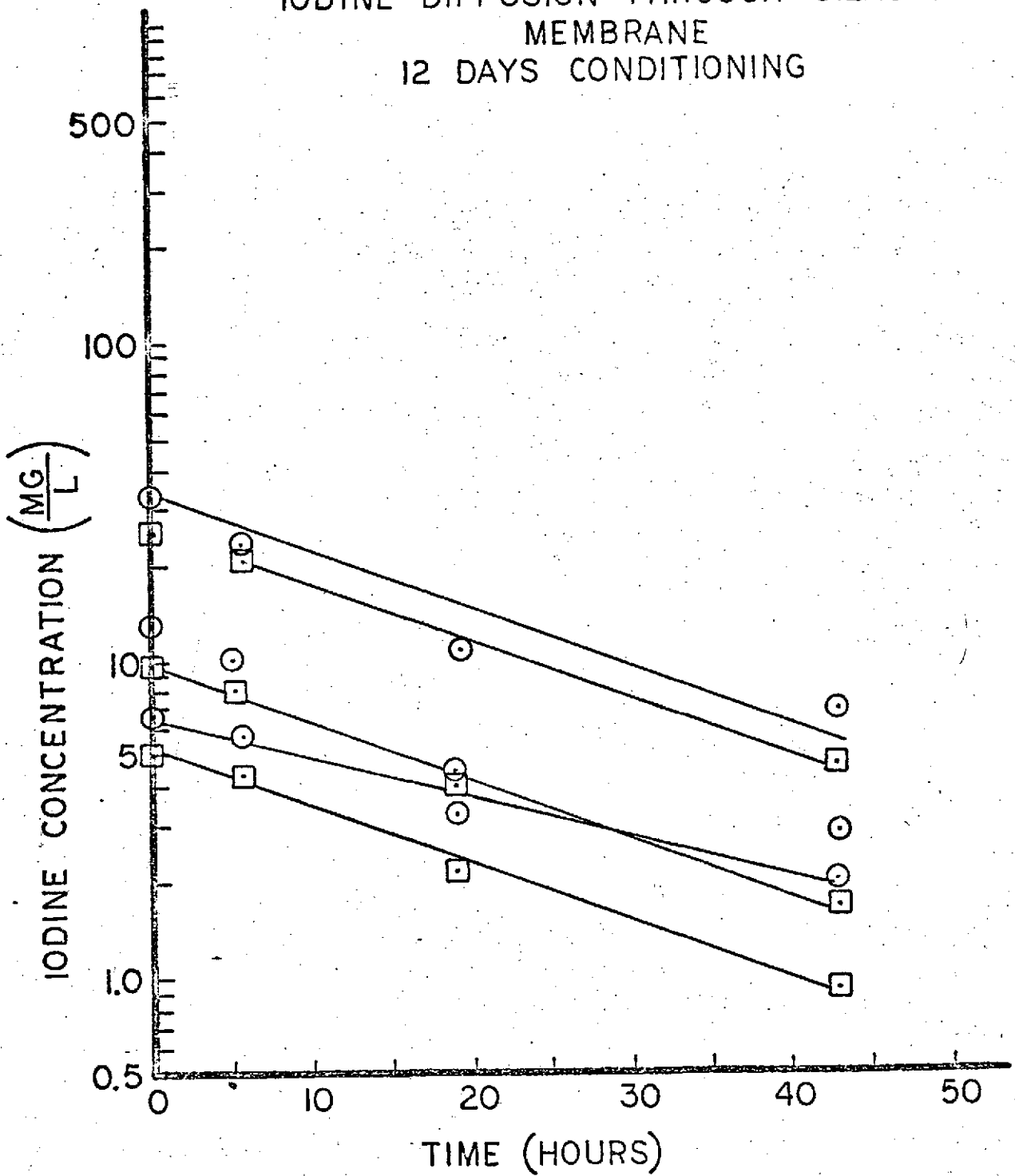


IODINE DIFFUSION THROUGH SILASTIC MEMBRANE  
FOUR DAYS CONDITIONING



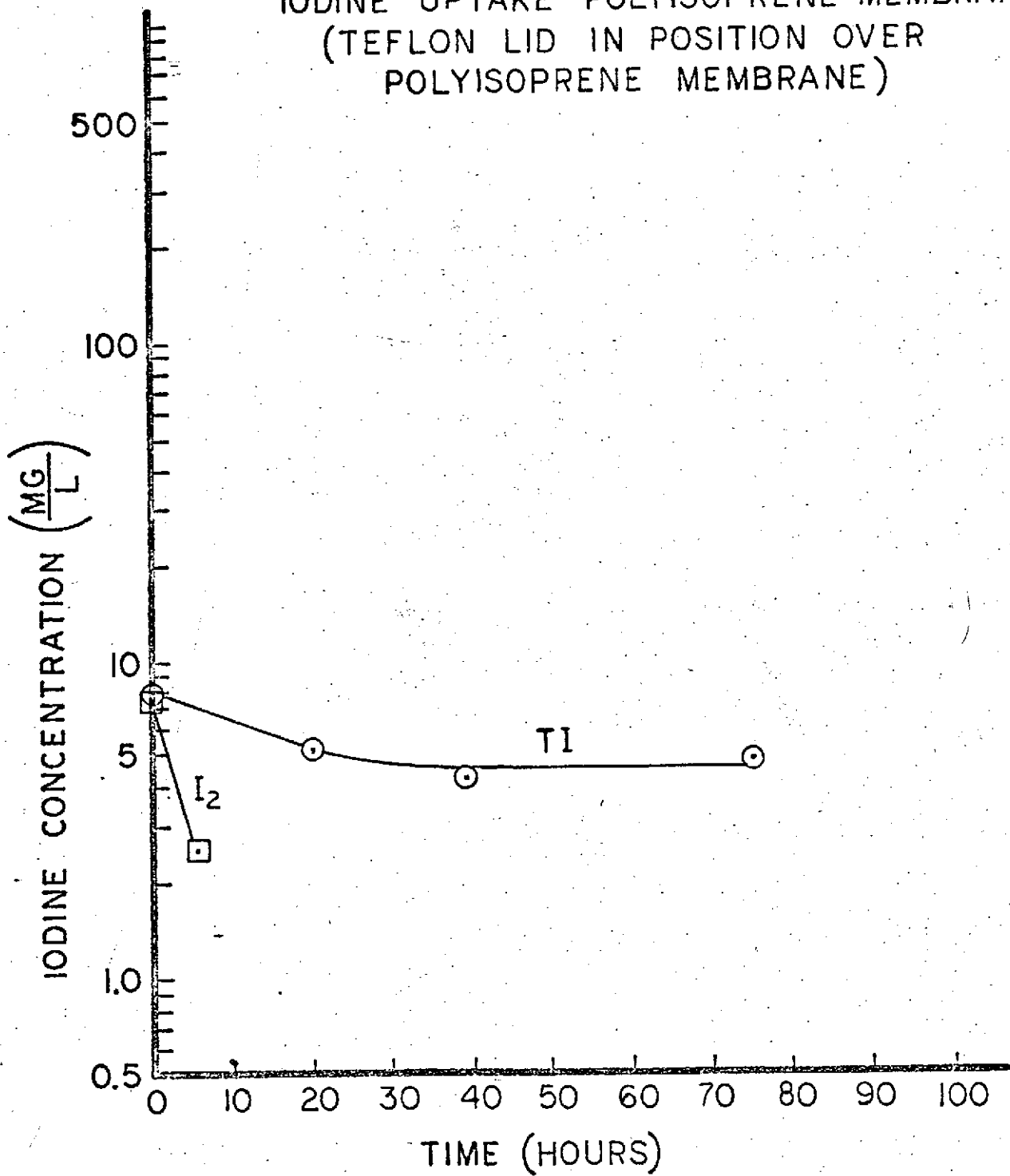
○ = TOTAL IODINE (TI)  
 □ = IODINE (I<sub>2</sub>)

### IODINE DIFFUSION THROUGH SILASTIC MEMBRANE 12 DAYS CONDITIONING



○ = TOTAL IODINE (TI)  
□ = IODINE (I<sub>2</sub>)

IODINE UPTAKE - POLYISOPRENE MEMBRANE  
 (TEFLON LID IN POSITION OVER  
 POLYISOPRENE MEMBRANE)

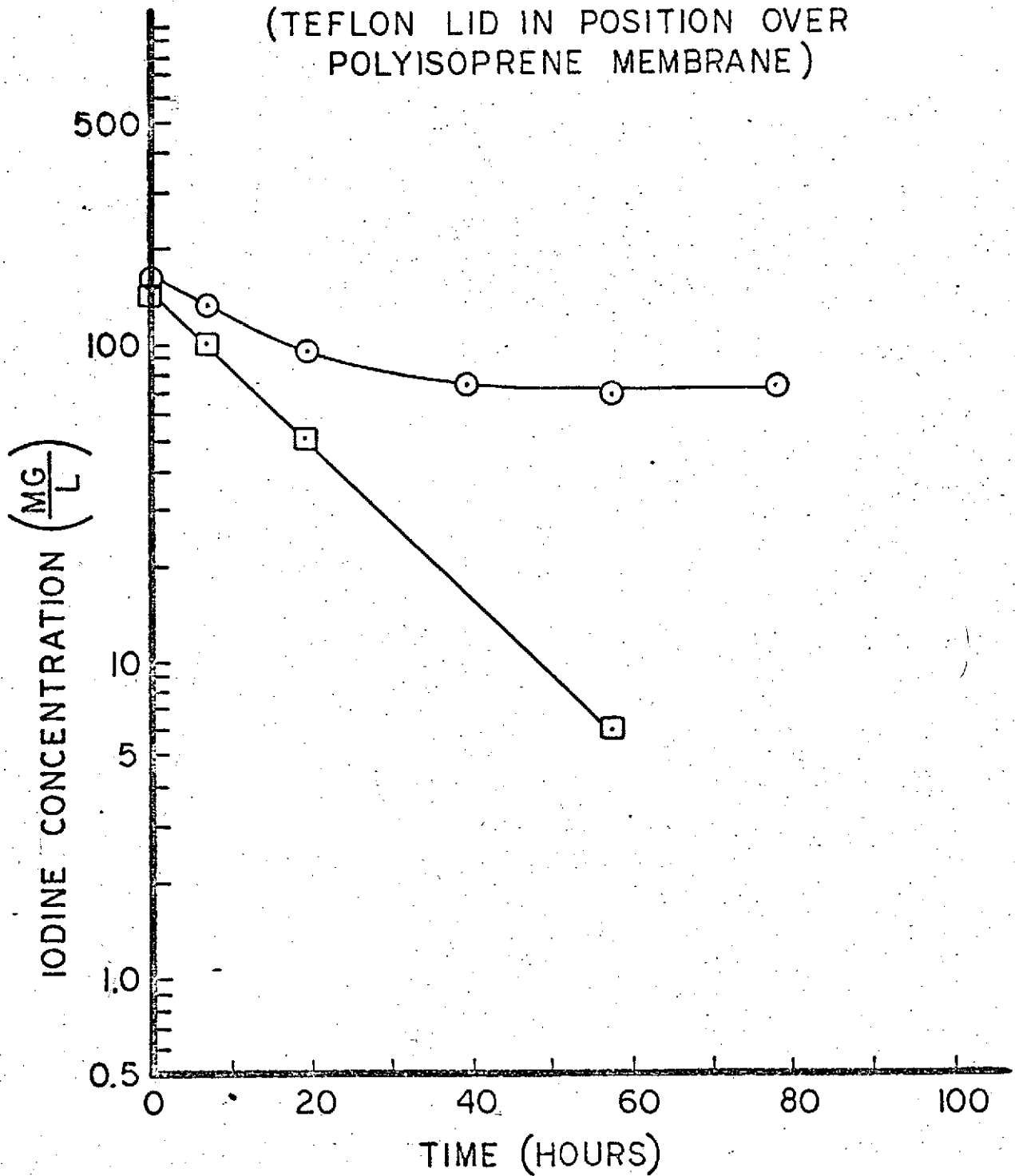


○ = TOTAL IODINE (TI)

□ = IODINE (I<sub>2</sub>)

INITIAL IODINE CONCENTRATION 7.4 MG/L

IODINE UPTAKE-POLYISOPRENE MEMBRANE  
(TEFLON LID IN POSITION OVER  
POLYISOPRENE MEMBRANE)

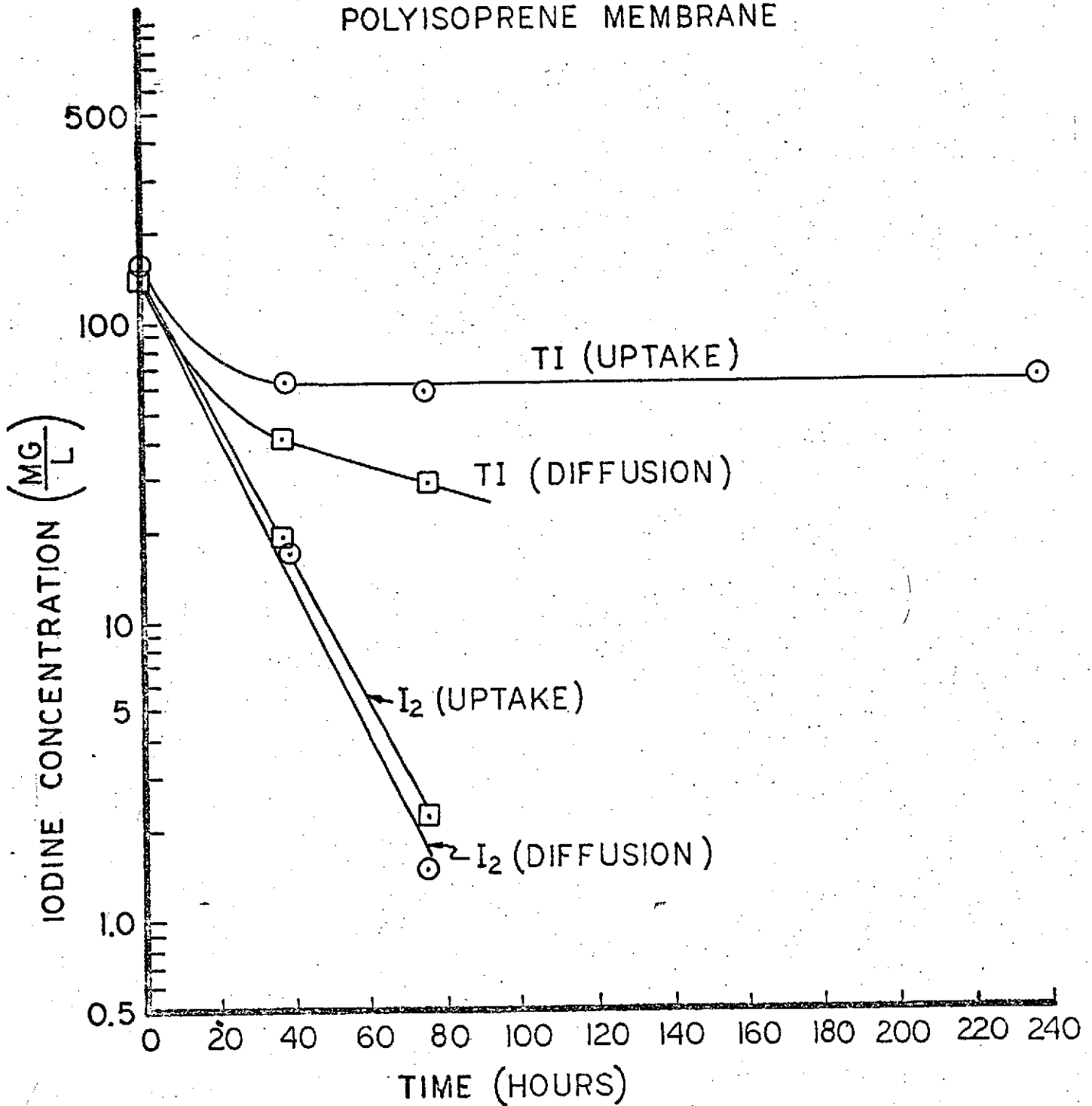


○ = TOTAL IODINE (TI)

□ = IODINE ( $\text{I}_2$ )

INITIAL IODINE CONCENTRATION 14.5 MG/L

IODINE UPTAKE AND DIFFUSION -  
POLYISOPRENE MEMBRANE

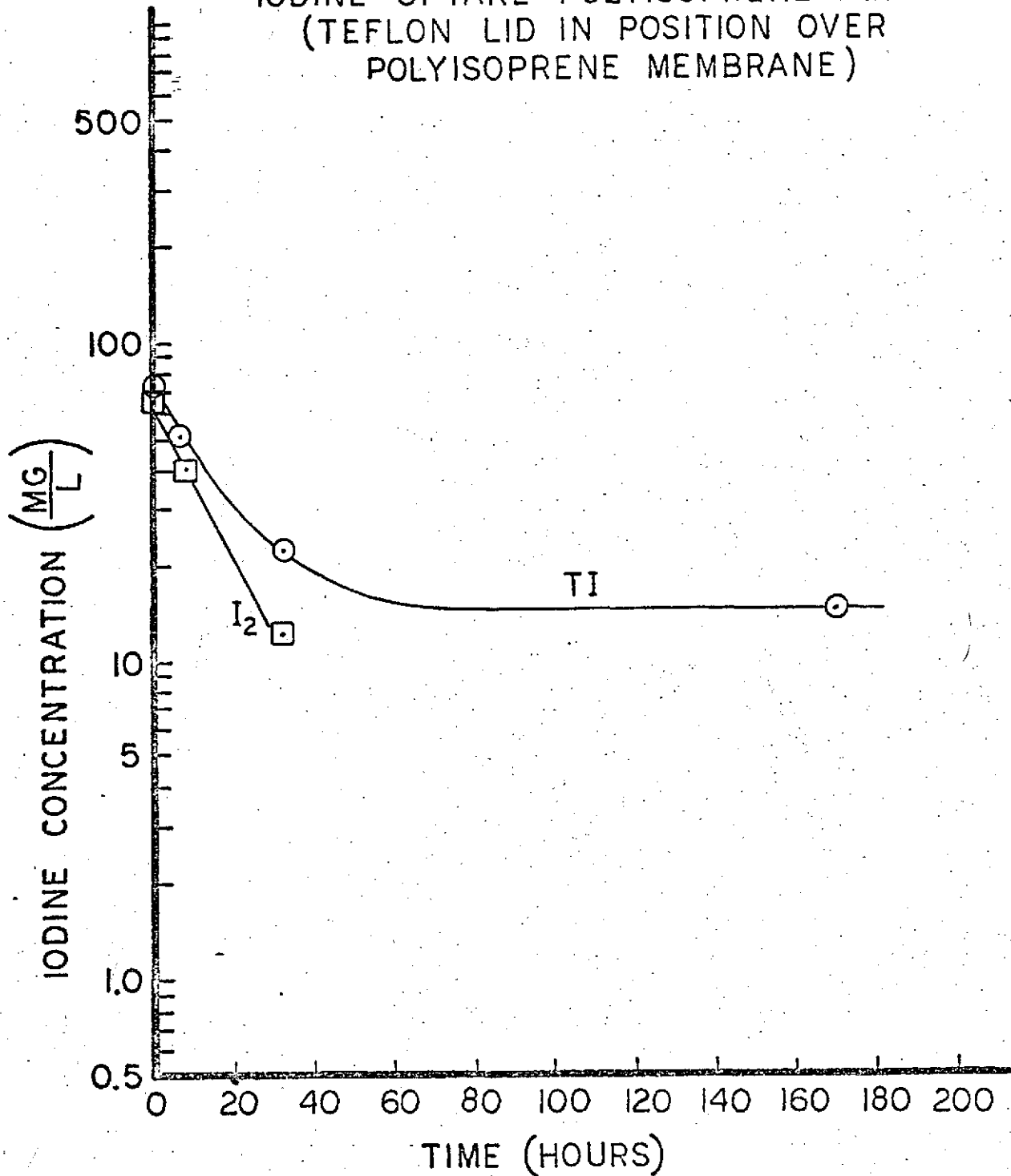


○ = TOTAL IODINE (TI)

□ = IODINE (I<sub>2</sub>)

TEFLON LID OVER POLYISOPRENE MEMBRANE  
FOR UPTAKE EXPERIMENT

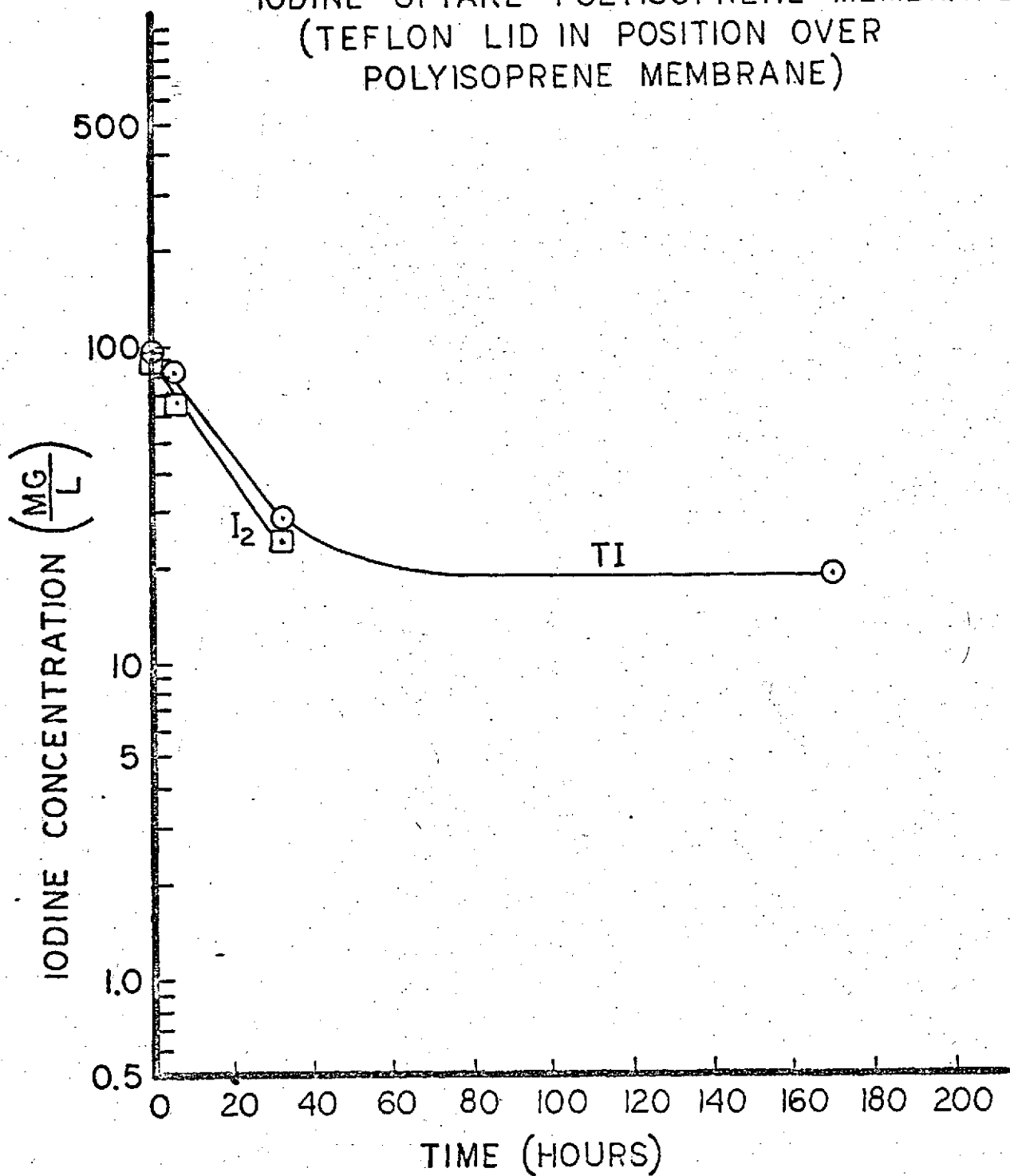
IODINE UPTAKE POLYISOPRENE MEMBRANE  
 (TEFLON LID IN POSITION OVER  
 POLYISOPRENE MEMBRANE)



○ = TOTAL IODINE (TI)

□ = IODINE (I<sub>2</sub>)

INITIAL IODINE CONCENTRATION 67 MG/L

IODINE UPTAKE POLYISOPRENE MEMBRANE  
(TEFLON LID IN POSITION OVER  
POLYISOPRENE MEMBRANE)

COMPARISON OF IODINE  
SORPTION ISOTHERMS

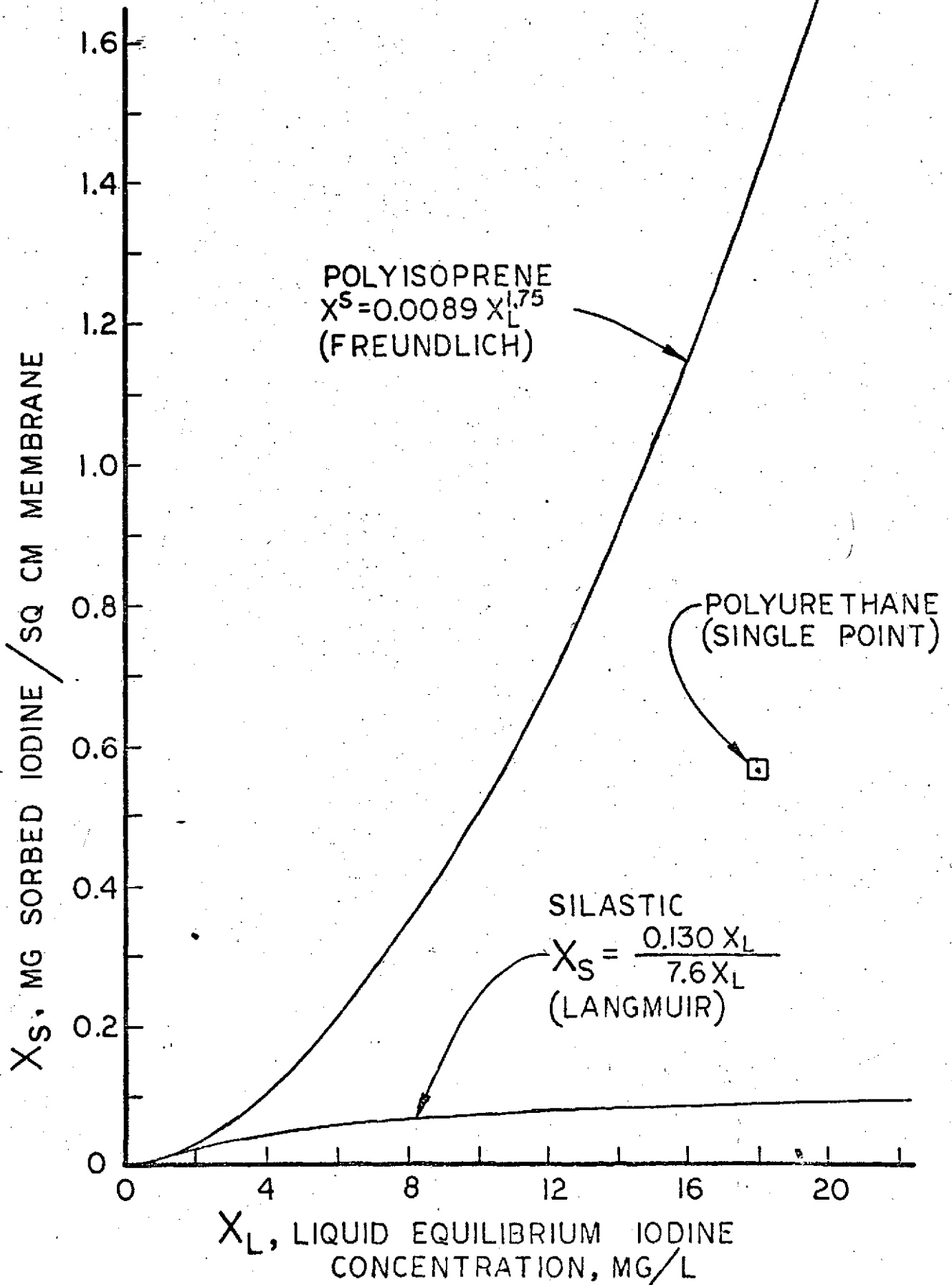




FIGURE IV-13  
 IODINE UPTAKE - VITON (TEFLON LID  
 OVER VITON MEMBRANE)

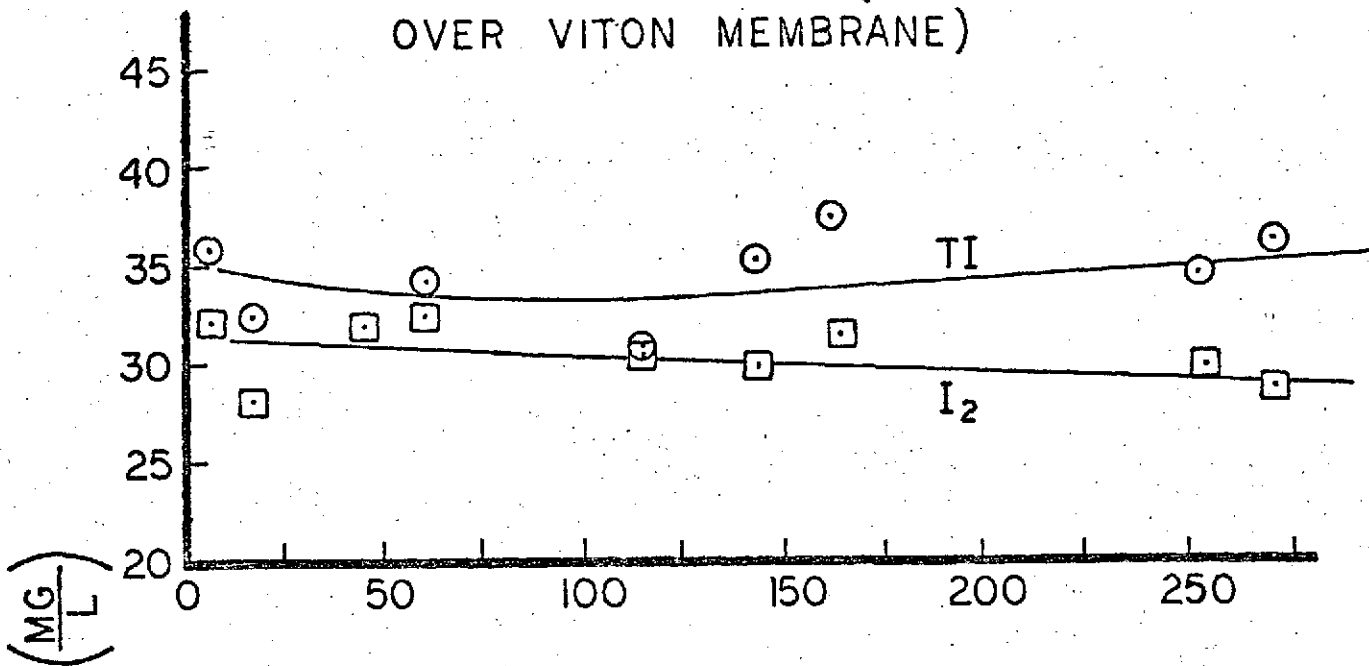
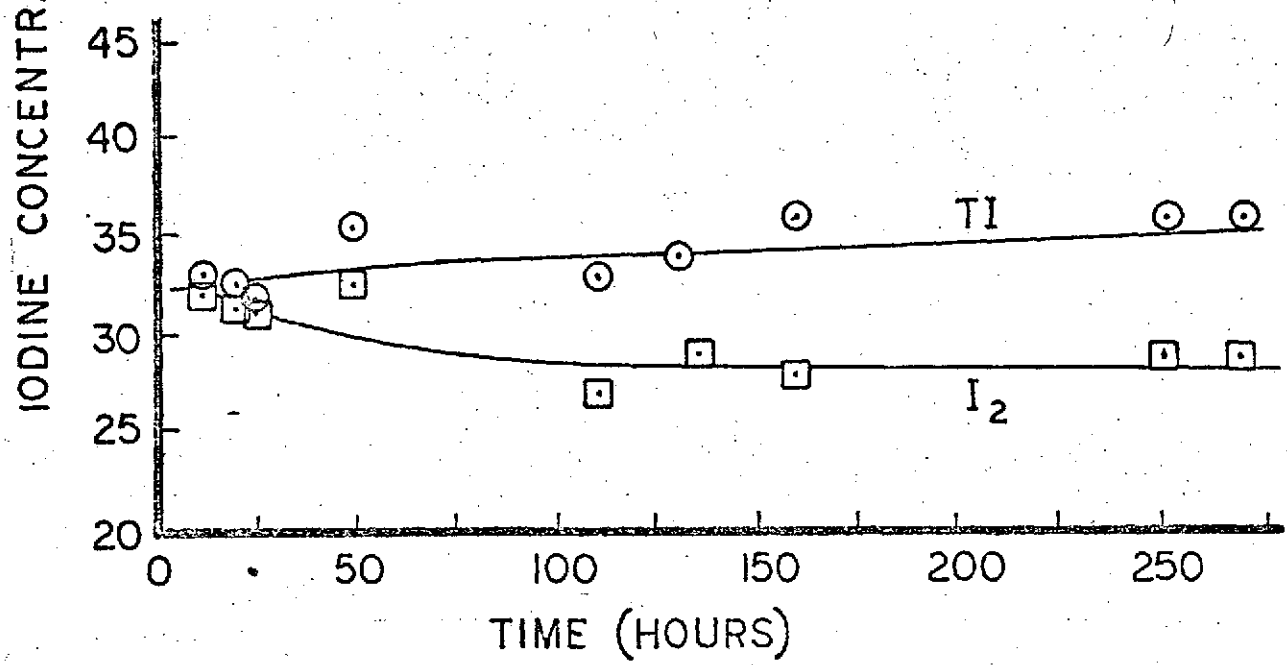
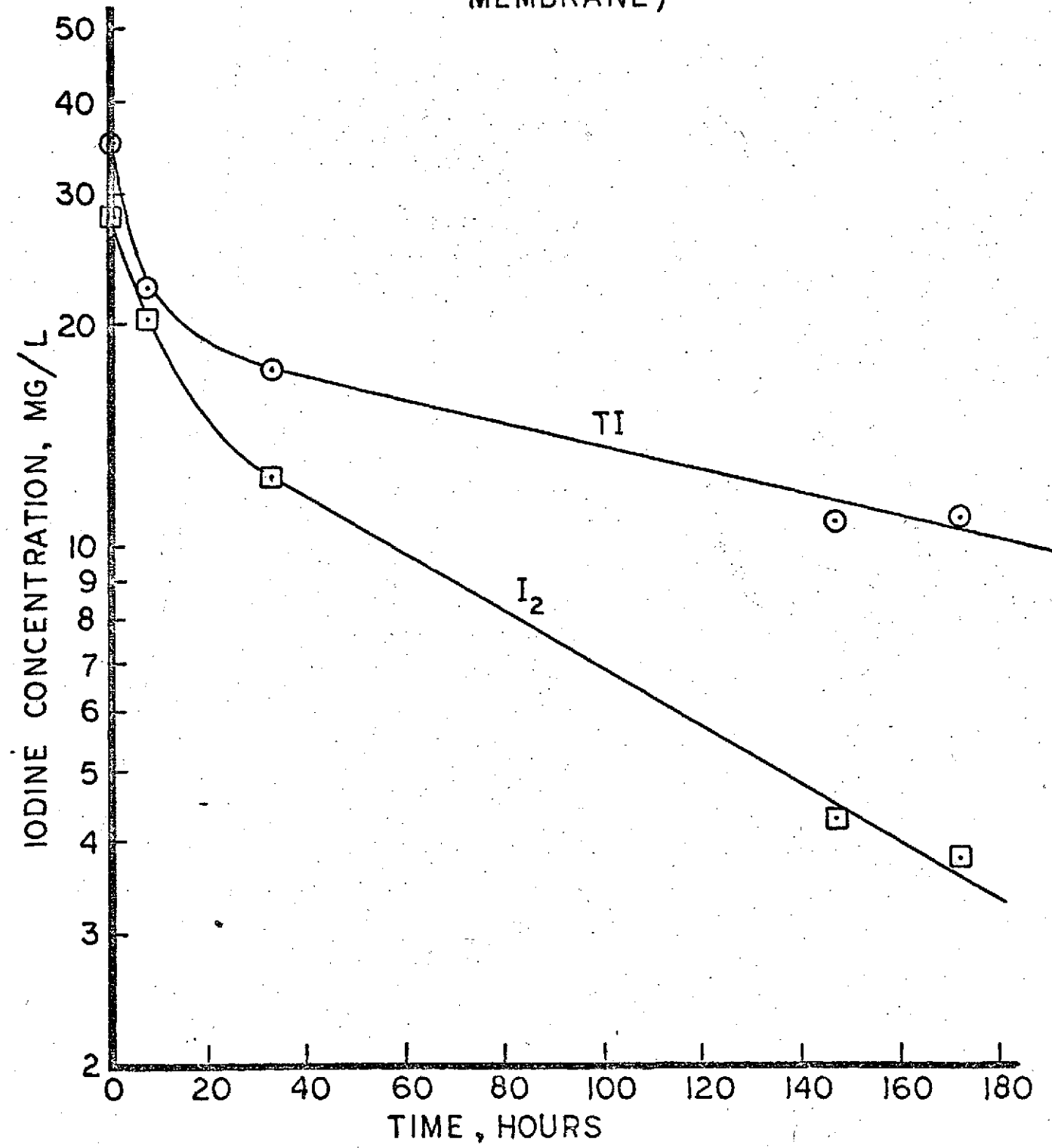


FIGURE IV-14  
 IODINE DIFFUSION THROUGH VITON



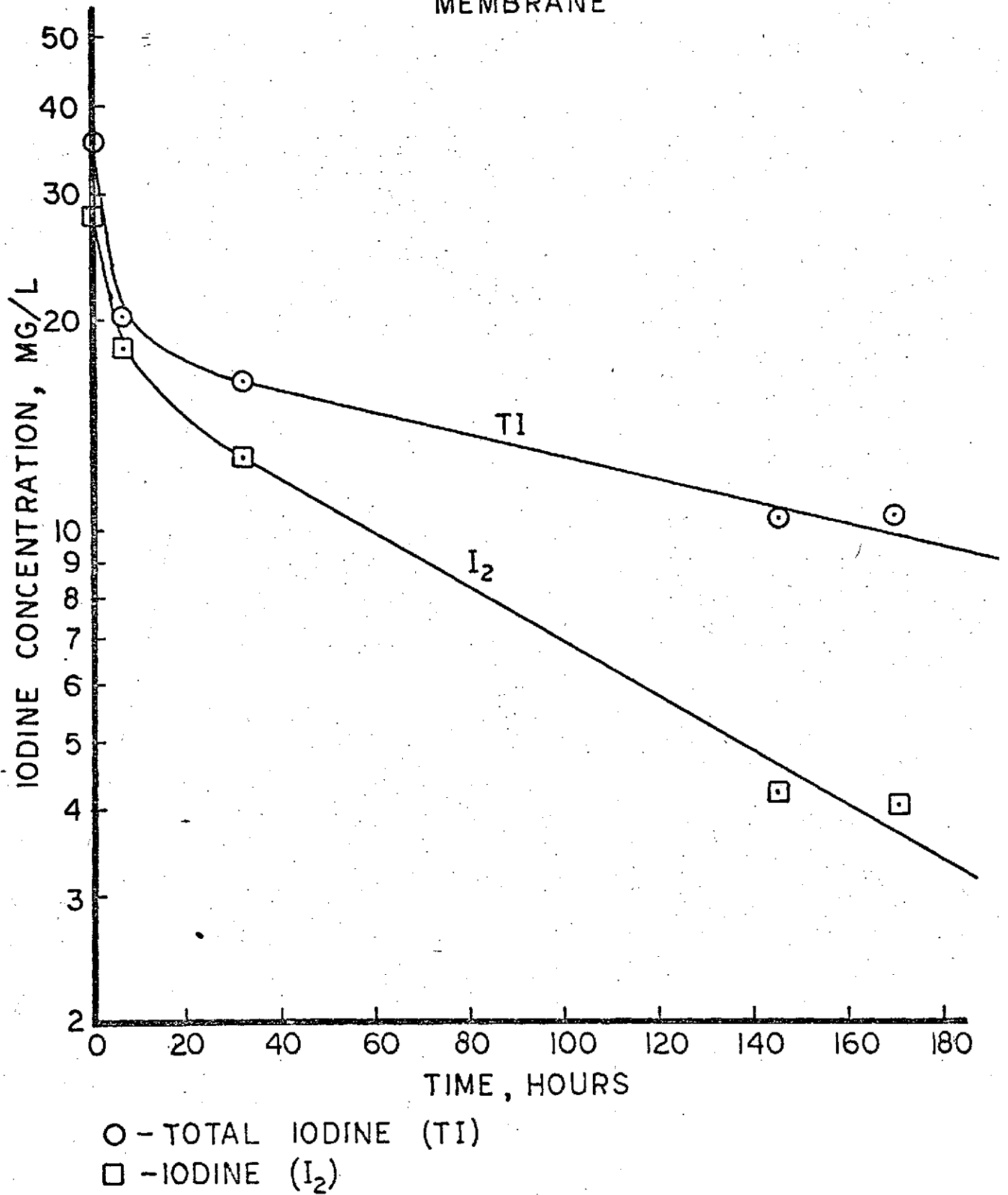
○ = TOTAL IODINE (TI)  
 □ = IODINE I<sub>2</sub>

IODINE UPTAKE-POLYURETHANE MEMBRANE  
(TEFLON LID OVER POLYURETHANE  
MEMBRANE)



○ - TOTAL IODINE (TI)  
□ - IODINE (I<sub>2</sub>)

IODINE DIFFUSION THROUGH POLYURETHANE MEMBRANE

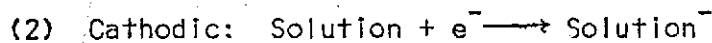
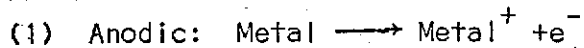


CHAPTER V  
CORROSION STUDIES

THEORY

Theoretical Considerations

It can be stated that corrosion is a natural process tending toward the conversion of a refined metal to its natural state. When the corrosion system is aqueous the process may be electrochemical as opposed to being purely chemical. Electrochemical corrosion occurs by anodic and cathodic processes at spatially separate areas because of electron mobility in the metal and ion mobility in the aqueous phase. The processes must be spatially (and temporally) discrete; with the reaction proceeding simultaneously on the same metal atom, the process becomes chemical corrosion. (Reference V-1). This separateness of the two processes allows anodic and cathodic reactions to take place where solution and metallic conditions are appropriate. Typical reactions can be conceptualized as:



With two reactions occurring at two separate areas and assuming complete electron mobility, a potential difference is created; the related E.M.F. is an indication of the driving force of the reactions. For this reason much of the theory of electrochemical corrosion is based upon the laws of galvanic corrosion cells.

Estimates of the rate and magnitude of the corrosion process may be easily determined from polarization curve characteristics of any electrochemical system. The corrosion parameters may be easily obtained from the slope of the current-voltage plot. This methodology is based upon the Butler equation of electrochemical kinetics and the empirical Tafel relationship.

The Butler equation can be written as:

$$i_p = i_o \left[ \exp\left(\frac{\alpha F \eta}{RT}\right) - \exp\left(-\frac{(1-\alpha) F \eta}{RT}\right) \right] \quad (V-1)$$

where:

$i_p$  = polarization current density

$i_o$  = exchange current density

$\alpha$  = charge transfer coefficient

$\eta$  = polarization overvoltage,  $E - E_{cor}$

F = Faraday constant

R = Universal gas constant

T = Temperature (absolute)

In the Butler equation, the exchange current density,  $i_o$ , represents the simultaneous cathodic and anodic reactions.

In the determination of corrosion rates from galvanostatic polarization curves, small values of  $i_p$  are applied so as to produce small changes in  $i_o$ , i.e., minimal corrosion surface perturbations. With this approach, the polarization overvoltage,  $\eta$ , can be kept small.

With small  $\eta$  values, Equation V-1 becomes:

$$i_p = i_o \left[ 1 + \frac{\alpha F}{RT} \eta - 1 + \frac{(1-\alpha) F}{RT} \eta \right] = \frac{i_o F}{RT} \eta \rightarrow 0 \quad (V-2)$$

By differentiation:

$$\left[ \frac{d\eta}{d i_p} \right]_{\eta \rightarrow 0} = \frac{RT}{F} \cdot \frac{1}{i_o} \quad (V-3)$$

A similar format is obtained if the empirical Tafel relationship is used. The equation derived is:

$$\left[ \frac{d\eta}{d i_p} \right]_{\eta \rightarrow 0} = \left[ \frac{1}{i_{cor}} \right] \frac{b_1 b_2}{2.3(b_1 + b_2)} \quad (V-4)$$

where:  $b_1$  and  $b_2$  are the anodic and cathodic exponential constants defined in the Tafel equations. The quantity  $\left[ \frac{d\eta}{d i} \right]_{\eta \rightarrow 0}$  is termed the corrosion resistance in ohms per square centimeter whose reciprocal is directly proportional to the corrosion current  $i_{cor}$ . Corrosion current is usually expressed as current density per millivolt per unit area.

By rearrangement of Equation V-4:

$$i_{cor} = k_c \frac{1}{\left( \frac{d\eta}{d i} \right)_{\eta \rightarrow 0}} \quad (V-5)$$

or:

$$\left[ \frac{d\eta}{d i} \right]_{\eta \rightarrow 0} = \frac{k_c}{i_{cor}} \quad (V-6)$$

where:

$$k_c = \frac{b_1 b_2}{2.3 (b_1 + b_2)}$$

## Application

The application of potentiometric techniques through use of the Mancy Corrosion Meter in obtaining corrosion measurements is based upon Equation V-5. In systems for which a value of the empirical constant,  $k_c$ , is known, the corrosion current can be computed directly. Unfortunately, a value for  $k_c$  applicable to either the stainless steel or aluminum electrodes used in this study is not available from the literature and its approximation is beyond the scope of this project. However, in the application of the Mancy potentiometric techniques, the change in potential is measured following induction of low current flow to the system. The slope of the potentiometric curve is linear as values approach zero and is directly proportional to the corrosion current  $i_{cor}$ . These rate estimates have been determined and used as comparative data in the present study.

In the above derivations, it should be noted that  $i_o$ , the exchange current, is replaced by  $i_{cor}$ , the corrosion current (a current produced by the differential between the cathodic and anodic processes). The corrosion current is equal to the net flux of material going into solution and directly proportional to the weight loss of the metal which is the classical (although less sensitive) method for determining corrosion rates.

## EXPERIMENTAL PROGRAM

The Mancy Corrosion Meter (Reference V-1) was employed in all corrosion experiments for the measurement of potential changes following the application of low current flows across the cells. The current was applied by a low amperage, high voltage Heathkit Model EUW-15 Universal Power Supply (Schlumberger Products Corporation, St. Joseph, Michigan). All potential measurements were obtained with a Beckman Model 76007 Expandomatic SS-2 pH meter.

### Cell Construction

The apparatus for obtaining relative corrosion rates by the electrochemical methods employed in this study is shown in Figure V-1. Six of these cells were run simultaneously in a stirred, thermostatically controlled ( $25.0 \pm 2^\circ\text{C}$ ) water bath constructed above six adjustable, motor driven magnetic stirrers.

The electrodes in the test cells consisted of either aluminum (A16061) or stainless steel (CRES 316L) materials obtained from commercial supplies. The electrode assembly pictured in Figure V-1 (Items G, H, I and J) was

constructed by soldering (in the case of aluminum) or brazing (in the case of stainless steel) Rod G to Sample H. Residual flux was removed from the assembly region and the exposed area of Sample (J) was carefully polished using extra fine flint paper. This abrasive was chosen to avoid the iron contamination produced by emery abrasives. After polishing, the electrodes were thoroughly washed in reagent acetone. Several coats of the protective coating (I) were then applied by dipping. A Carboline "series k" self-priming vinyl coating was found to be the coating least reactive and permeable to iodine. Other available products tested were:

- Insl-X Products Corporation (Yonkers, N.Y.) (insulating tool dip)
- Silicone adhesive backed Teflon (TFE) film - 0.005 in. thick
- Commercial epoxy paint
- Silicone coating

Inasmuch as the air-dried Carboline coating demonstrated a slight iodine uptake, efforts were directed at minimizing this effect. It was found that the covering material could be rendered completely inert by baking at 103°C for 12 hours.

All corrosion cell solutions were prepared from double deionized distilled water having a conductivity less than 0.8 Megohm/cm and free of color and odor. Some cells required minimal oxygen concentrations; oxygen was displaced from solution (to levels measured at  $\leq 1.0$  mg/l) by perfusion with purified nitrogen gas.

#### Cell Operation

After the cells were established as described above, appropriate test solutions were added. Samples were periodically removed by pipet via F (Figure V-1) and analyzed for iodine and chlorine residual. On the days of measurement, stopper (F) was removed and replaced by the electrode assembly illustrated in Figure V-2. This combined normal Ag-AgCl reference and platinum counter electrode was designed for minimum chemical perturbation of the cell solution; the micro-porous Vicor plug provided a conductive bridge without leaking salts into the cellular solution. The stability of this reference electrode was monitored by comparing it with a standard "leaky" saturated calomel electrode before each measurement.

After the combination electrode was inserted, the four metal samples in each cell were examined individually with a Beckman 76007 Expandomatic

SS-2 pH meter using the millivolt scale. The existing corrosion potential was first measured and the meter was then adjusted so that this potential read center-zero. Then a small positive current was applied through the counterelectrode to the test piece and the five minute equilibrium positive voltage perturbation ( $\eta_{\text{anodic}}$ ) was recorded. The polarity of the applied current was then reversed and a similar five minute equilibrium negative voltage perturbation ( $\eta_{\text{cathodic}}$ ) was recorded. This perturbation procedure with measurement of resultant over-voltages was repeated for higher current densities to give a sufficient number of points for accurate graphical interpretation of the corrosion rate. After all four electrodes were so measured, the combination electrode was removed and replaced with the glass stopper.

Throughout all experiments, the disinfectant residuals were monitored in order to track the anticipated reactant losses. Such losses were verified and measured. In order to maintain the proper experimental concentrations it was necessary to occasionally add appropriate amounts of the concentrated stock solutions (250-300 mg/l  $I_2$  and approximately 420 mg/l NaOCl).

#### Analytical Methods

The pertinent chemical methods applied in this study were those used to determine the concentrations of those disinfectant halogens of interest ( $Cl_2$  and  $I_2$ ).

Iodine: The thiosulfate titration of free iodine is a primary analytical method and, because of its universal acceptance, was the reference used for evaluating all other possible procedures. Because of volume considerations, the titration with thiosulfate to a starch endpoint could not be used in these studies. In order to obtain significant titration data, the thiosulfate titrant used in low level iodine titrations must be at dilute concentrations. Because of the inherent instability of sodium thiosulfate solutions, a lower concentration limit of around 0.0025 Normal exists for the production of adequate starch endpoints: a correction requiring rather large volumes (>50 mg/l) of sample to titrate the low levels of iodine with which we are concerned in the present studies. Most of the experimental volumes were 1.5 liters or less, necessitating the employment of a more sensitive colorimetric method. To satisfy these



requirements, analyses were conducted using the method developed by A. P. Black and G. P. Whittle (Reference IV-4). The use of this method demonstrated good reproducibility of the standard calibration curve. However, at low iodine levels a marked non-linearity was demonstrated for low iodine concentrations; such irregularity was related to impurities in the N,N-dimethyl aniline color reagent, which is easily purified by recrystallization. Irregularities in the calibration curve are believed to introduce errors not exceeding three percent in analytical results.

Chlorine: Difficulty in achieving reproducible color development obviated the use of the methodology of Black and Whittle (Reference V-1). For this reason it was necessary to utilize the iodometric method of analysis using 0.0025 N  $\text{Na}_2\text{S}_2\text{O}_3$  (Reference V-5) for chlorine determination.

## RESULTS

Two data sets have been accumulated in these corrosion rate studies. These data have included:

- (1) An evaluation of potentiometric curves; and
- (2) Estimates of the rate of iodine loss from the aqueous metal systems.

### Evaluation of Potentiometric Curves

All data in this phase of investigations were obtained from the potentiometric plots produced from the results of electrochemical cell perturbations. The cathodic curves derived from the data are illustrated in Appendix D and the complete data are recorded in Appendix E. The corrosion current values were obtained from the exponential portions of the curves approaching zero in accordance with the previously discussed theoretical formulations.

In all electrochemical measurements there existed a general decline in corrosion current generation with time. Because of this increased electrode stability with time, the measurements obtained after six to eight days were those utilized in all comparisons.

### Comparison of Aluminum Corrosion with Iodine and Chlorine

The first considerations in this initial phase consisted of an experimental design aimed at comparing the corrosive effects of iodine and chlorine on an aqueous aluminum system. In order to approximate the solution used in the NASA chlorination procedures, the chlorine was provided by the dissolution of sodium hypochlorite in a buffered solution.

A phosphate buffer (120 mg/l  $\text{Na}_2\text{HPO}_4$  @ pH6.5) was utilized in the chlorine system and no buffer was used in the iodine test cells; a buffer blank was included. The data for the solutions in these experimental cells, which were saturated with dissolved oxygen (8.4 mg/l at 25°C), are summarized in Table V-1. In general, the data demonstrated a significantly higher corrosion rate for the aluminum-chlorine system than for the aluminum-iodine system. The mean corrosion current for the aluminum-chlorine system was 17.5 nanno-amperes/cm<sup>2</sup>/mV. Even after consideration of the mean corrosion current values for the buffer blank of 3.15 nanno-amperes/cm<sup>2</sup>/mV, the average rate for the aluminum-iodine system (1.48 nanno-amperes/cm<sup>2</sup>/mV) is negligible in comparison with the aluminum-chlorine system.

#### Interaction of Iodine and Dissolved Oxygen

A factorial comparison was used to evaluate the effects of iodine and oxygen as well as any effects produced by the interaction between the two on the magnitude of the corrosion current. The results of these experiments are presented in Table V-2. An examination of these results indicates extreme differences in corrosion currents between those aluminum-iodine systems with differing oxygen levels. The mean corrosion currents varied from about 1.45 nanno-amperes/cm<sup>2</sup>/mV for the systems containing 8.4 mg/l dissolved oxygen to 3.84 nanno-amperes/cm<sup>2</sup>/mV for the Al - I<sub>2</sub> system (6 mg/l I<sub>2</sub>) and 14.17 nanno-amperes/cm<sup>2</sup>/mV for the Al - I<sub>2</sub> system (12 mg/l I<sub>2</sub>), each of the latter systems containing less than one mg/l dissolved oxygen. Thus, the magnitude of the corrosion current in the aluminum (Al 6061) system was essentially independent of the iodine concentration at a dissolved oxygen concentration of 8.4 mg/l, but was found to increase (as the dissolved oxygen concentration was decreased to less than one mg/l) approximately three-fold at test I<sub>2</sub> concentrations of 6 mg/l, and 10-fold at test I<sub>2</sub> concentrations of 12 mg/l.

In the experiments with the stainless steel (CRES 316L) - iodine system, conducted at a saturation dissolved oxygen concentration of 8.4 mg/l, the mean corrosion current decreased from 0.47 to 0.39 nanno-amperes/cm<sup>2</sup>/mV as the iodine concentration increased from 6 to 12 mg/l (or about 17 percent). Thus, as was the case with the aluminum systems at a dissolved oxygen concentration of 8.4 mg/l, the iodine concentration in the stainless steel systems was not a significant variable affecting the corrosion current at the above dissolved oxygen concentrations.

TABLE V-1

COMPARISON OF CORROSIVE EFFECTS OF CHLORINE AND IODINE  
ON ALUMINUM 6061

Composition of Experimental Cell	Electrode	Corrosion Current mu (nano) amperes/cm <sup>2</sup> /mV
NaH <sub>2</sub> PO <sub>4</sub> Buffer (120 ppm)	A	2.45
	C	3.48
	D	3.50
	Mean Observation	3.15
Al-Cl <sub>2</sub> (6 ppm), O <sub>2</sub> (saturated), and NaH <sub>2</sub> PO <sub>4</sub> Buffer (120 ppm)	A	16.66
	B	20.00
	C	16.66
	D	16.66
	Mean Observation	17.50
Al-I <sub>2</sub> (6 ppm), and O <sub>2</sub> (saturated)	A	1.56
	B	1.40
	Mean Observation	1.48

Note: Temperature @ 25<sup>+</sup>°C

B-V

TABLE V-2

COMPARISON OF CORROSIVE EFFECTS OF ALUMINUM  
AND STAINLESS STEEL IODINATION

Composition of Experimental Cell	Electrode	Corrosion Current $\mu$ (nano) amperes/cm <sup>2</sup> mV	
		Individual Observations	Mean of Observations
Aluminum - Iodine (6 mg/l) dissolved oxygen at saturation	A	1.56	1.48
	B	1.40	
Aluminum - Iodine (12 mg/l); dissolved oxygen at saturation	A	1.75	1.42
	B	1.50	
	C	1.00	
Aluminum - Iodine (6 mg/l); dissolved oxygen ( $\leq$ /mg/l)	B	4.00	3.84
	C	5.45	
	D	2.07	
Aluminum - Iodine (12 mg/l); dissolved oxygen ( $\leq$ /mg/l)	A	7.50	14.17
	C	15.00	
	D	20.00	
Stainless Steel - Iodine (6 mg/l); dissolved oxygen at saturation	A	0.48	0.47
	B	0.46	
	C	0.49	
	D	0.46	
Stainless Steel - Iodine (12 mg/l); dissolved oxygen at saturation	A	.43	0.39
	B	.34	
	C	.40	

- Notes: 1. Temperature @ 25<sup>±</sup>2°C  
 2. Saturation dissolved oxygen concentration  $\approx$  8.4 mg/l @ 25°C  
 3. Metal types: Al 6061 and Stainless Steel CRES 316L

The relative differences of iodination on stainless steel (CRES 316L) and aluminum (Al 6061) at a dissolved oxygen concentration of 8.4 mg/l are also evidenced by the magnitudes of the corrosion current for these systems reported in Table V-2. The current data for the stainless steel tests were developed at two iodine concentrations (6 and 12 mg/l), and the mean corrosion currents observed for these two systems ( $\sim 0.4$  nano-amperes/cm<sup>2</sup>/mV) are about one-third those observed for the aluminum-iodine systems under saturated dissolved oxygen conditions. On this basis, it is apparent that stainless steel is approximately three times more resistant to corrosion than is aluminum in iodinated solutions at saturation dissolved oxygen concentrations of 8.4 mg/l.

#### Iodine Depletion Kinetics

Graphical analysis was employed to evaluate the rates of I<sub>2</sub> depletion upon exposure of aluminum and stainless steel surfaces in iodinated solutions. Evidence presented subsequently indicates that the depletion process is due to the conversion of iodine to iodide rather than to sorption or substitution. The approach to evaluation of the iodine depletion kinetics across a metallic surface confined within a small, well-mixed reservoir consisted of estimating  $K_{C-A}^I$ , the rate of conversion of iodine to iodide, expressed as the total flux, N per unit of exposed surface area of the corroding metal, A. This relationship can be represented by:

$$AN = \frac{dX^I}{d\theta} = K_{C-A}^I X^I A \quad (V-7)$$

The most rational approach to a solution of the above relationship is graphical. However, this approach is impaired by the volume changes in the test solution incurred in the sampling and adding of I<sub>2</sub> to the test cells during the experiment. Corrections for such changes have been computed based upon the mathematical considerations presented in Appendix F and graphical analysis has been applied to the depletion data tabulated in Tables V-3 and 4 for the aluminum and stainless steel samples, respectively.

The data included in Tables V-3 and 4 were obtained from two completely-mixed experimental corrosion cells over a period of 14 days; the cells were constructed similarly to expose 16.0 sq cm of either aluminum or stainless steel to the disinfectant solutions in the absence of light. The test cells were maintained at dissolved oxygen levels of less than one mg/l and in the temperature range of 25<sup>±</sup>2°C. The depletion data, incorporating the cor-

TABLE V-3

ALUMINUM - IODINE SYSTEM  $I_2$  DEPLETION DATA (WITH GRAPHICAL CORRECTIONS)

Time From Start of Experiment (days)	Time Following Each Iodine Addition (days)	Volume (V) Before Sampling (liters)	$I_2$ Concentration $X^I$ (mg/l)	$X^I V$	Graphical Correction Log Cycles
0.00	0.00	1.19	12.4	19.5	
1.00	1.00	1.18	8.6	12.7	
1.77	1.77	1.17	7.3	10.2	0.0187
2.05	0.00	1.198	16.5	27.9	
2.77	0.72	1.188	13.1	21.2	
5.75	3.70	1.178	7.3	10.4	0.0112
6.72	4.67	1.143	6.5	8.5	0.0198
6.88	0.00	1.108	13.0	16.7	
7.77	0.89	1.098	11.4	14.5	
9.75	2.87	1.088	7.4	8.8	0.0106
9.81	0.00	1.104	11.8	15.0	
12.71	2.90	1.094	6.8	8.1	
12.81	0.00	1.112	12.0	15.5	
13.75	0.94	1.102	10.4	13.2	

TABLE V-4

ALUMINUM - IODINE SYSTEM I<sub>2</sub> DEPLETION DATA (WITH GRAPHICAL CORRECTIONS)

Time From Start of Experiment (days)	Time Following Each Iodine Addition (days)	Volume (V) Before Sampling (liters)	I <sub>2</sub> Concentration X <sup>I</sup> (mg/l)	X <sup>I</sup> V	Graphical Correction Log Cycles
0.00	0.00	1.190	12.4	19.5	
1.00	1.00	1.180	11.2	17.3	
1.77	1.77	1.17	11.0	16.5	0.0105
2.03	0.00	1.184	16.8	27.5	
2.77	0.74	1.174	16.5	27.0	
5.75	3.72	1.164	14.8	23.1	0.0218
6.75	4.72	1.129	12.8	17.7	0.0410
6.83	0.00	1.126	13.4	18.0	
7.80	0.97	1.116	13.2	17.8	
9.75	2.92	1.106	12.9	16.9	0.0112
9.80	2.97	1.101	12.7	16.5	0.0167
12.71	5.88	1.091	10.8	13.4	0.0279
12.79	0.00	1.102	13.0	16.0	
13.80	1.01	1.082	12.6	15.5	

reactions for test cell volume changes, are presented graphically in Figure V-3 for the aluminum-iodine system and in Figure V-4 for the stainless steel-iodine system. Each time interval between sampling/volume change has been treated as a discrete data set in the figures, the first-order conversion reaction constants for each time interval being a function of the slopes of the lines for each time interval.

As shown in Figure V-3, the rate of depletion of  $I_2$  in the aluminum system was greater during the initial 2.8 days of the experiment (dashed lines) than subsequent to 2.8 days (solid lines), after which the reaction constant approached a stable value for the time intervals to 6.72 days, 6.88 to 9.75 days, and 9.81 to 12.71 days as evidenced by the parallelism of the best-fit lines for the data of these time intervals. The average conversion reaction constant for  $I_2$  depletion during the time period of 2.80 to 12.71 days was:

$$K_{C-A}^A = 1.33 \times 10^{-2} \text{ l/sq cm} - \text{day}; \text{ equivalent to } 13.3 \text{ cm/day.}$$

The rate of depletion of  $I_2$  in the stainless steel system (Figure V-4) was greater during the initial day of the experiment (dashed line), after which (as indicated by the parallelism of the best-fit lines for the data of the subsequent time intervals) the reaction constant approached a stable value. The average conversion reaction during the time intervals after one day was:  $K_{C-A}^{SS} = 2.4 \times 10^{-3} \text{ l/sq cm} - \text{day}$ ; or 2.4 cm/day: on this basis the magnitude of the conversion reaction constant for stainless steel is about one-fifth that of the aluminum for the experimental conditions used in the determinations.

In both the aluminum and stainless steel systems, the conversion rates were greater during initial periods of the experiments (2.80 days for aluminum and one day for stainless steel) than during second phases in which stable first-order reaction constants were observed in each system. The factors associated with these observations could not be documented within the scope of study, and may have arisen as a result of iodine interaction with the apparatus, passivation reactions, or other factors.

#### SUMMARY AND CONCLUSIONS

Potentiometric methods were utilized in a comparative study of the relative corrosion potential of aluminum (Al 6061) and stainless steel (CRES 316L) under environmental conditions comparable to those associated



with spacecraft operation. The potentiometric methods employed were interpreted in terms of the corrosion current (a current produced by the differential between the cathodic and anodic processes and analogous to a corrosion rate measurement). This corrosion current,  $i_{cor}$ , is directly proportional to the classical but less sensitive methodology of monitoring metal weight loss.

Although the principal emphasis in these studies was directed to measurement of corrosion currents in aluminum-iodine, aluminum-chlorine, and stainless steel-iodine test systems, reaction constants for  $I_2$  depletion in aluminum and stainless steel systems were also determined under completely-mixed conditions.

The results of the experimental effort in each of the above areas are summarized as follows:

- (1) Under conditions of dissolved oxygen saturation at 25°C, a 12-fold greater relative corrosion rate (corrosion current) was observed in the aluminum-chlorine system (6 mg/l  $Cl_2$ ) than in the aluminum-iodine system (6 mg/l  $I_2$ ).
- (2) In aluminum-iodine systems at 25°C, the relative corrosion rate was found to be essentially independent of the iodine concentration at a dissolved oxygen saturation concentration of 8.4 mg/l, but was found to increase (as the dissolved oxygen concentration was decreased to less than one mg/l) approximately three-fold at test  $I_2$  concentrations of 6 mg/l, and 10-fold at test  $I_2$  concentrations of 12 mg/l.
- (3) Under conditions of dissolved oxygen saturation at 25°C, stainless steel was found to have a relative corrosion rate of about one-third that observed for aluminum.
- (4) The first-order conversion reaction constant for iodine depletion in aluminum systems is about five-fold greater than the constant for iodine depletion in stainless steel systems.

Based on the preceding observations, it is concluded that:

- (1) For any given set of disinfectant concentrations aluminum is less subject to corrosion in iodinated than in chlorinated solutions.
- (2) Corrosion in aluminum-iodine systems can be minimized by maintaining the dissolved oxygen concentration in the iodinated

solution at or near saturation levels.

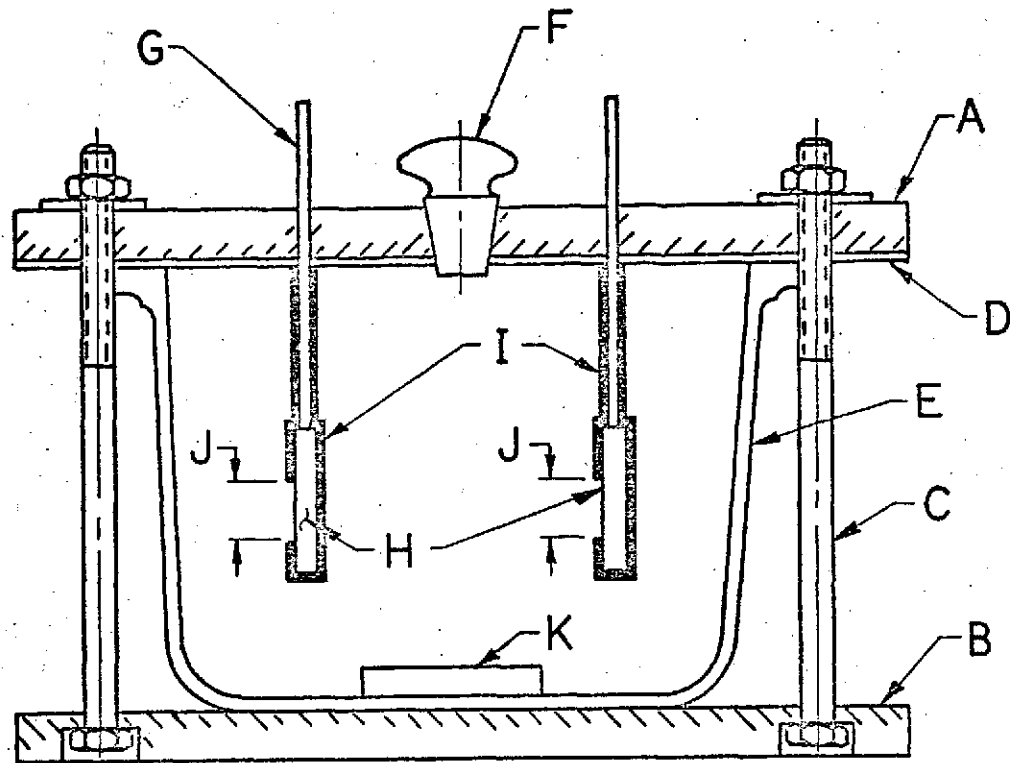
- (3) Stainless steel is much more desirable than aluminum for use in iodinated spacecraft water systems in terms of lower corrosivity, and, as a result of this, in terms of lower first-order rate constants for iodine conversion to iodide.

## CHAPTER V

### LIST OF REFERENCES

- V-1 "Dissolved Oxygen - A Corrosion Inhibitor as Promoted in Water Distribution Systems" by K. H. Mancy. Presented at National Association of Corrosion Engineers Meeting, Boston, October 17-19, 1960.
- V-2 "New Methods for the Colorimetric Determination of Halogen Residuals. Part II - Free and Total Chlorine" by A. P. Black and G. P. Whittle. Journal of the American Water Works Association, Volume 59, No. 5.

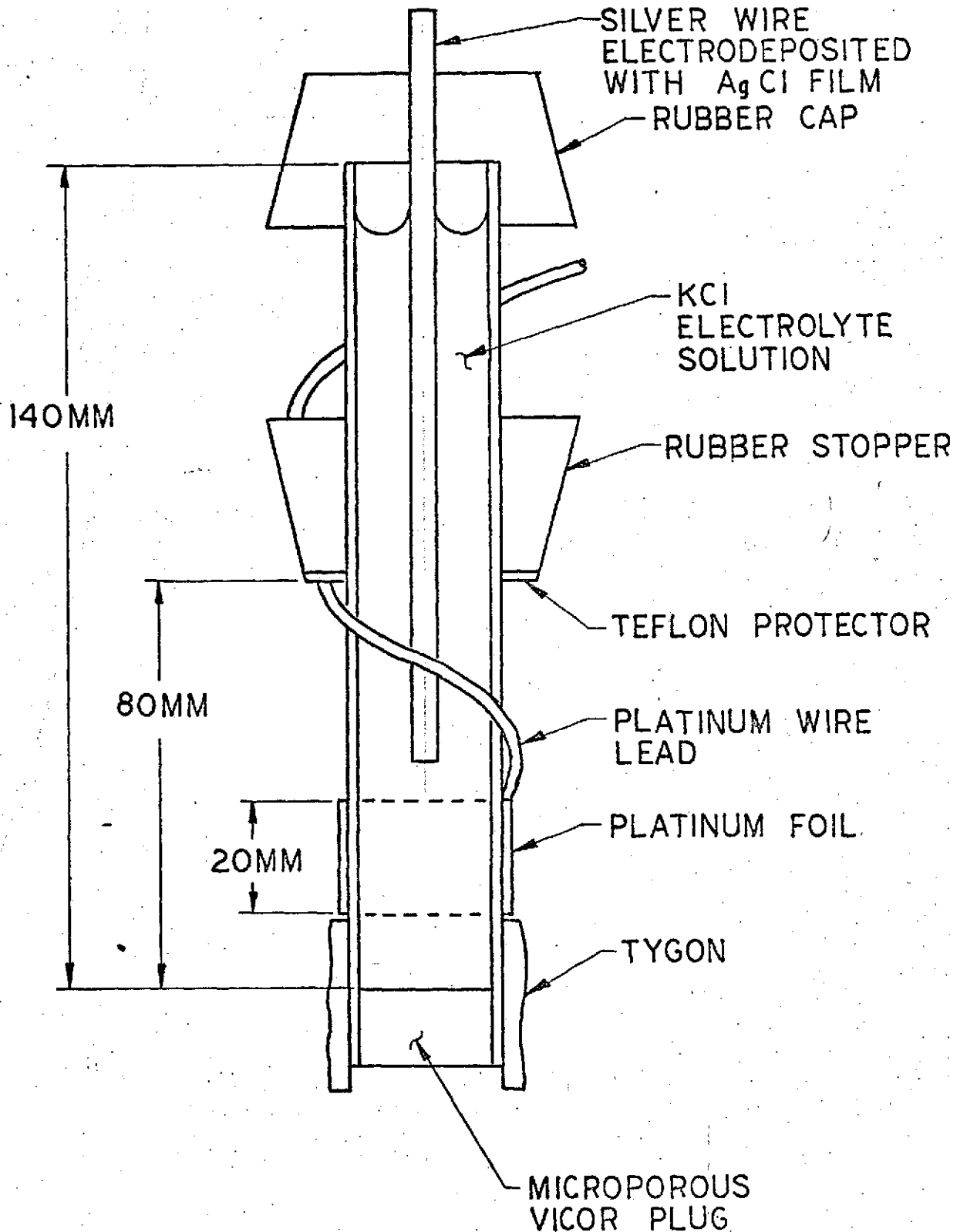
## SCHEMATIC OF TEST CELL CONSTRUCTION



## KEY:

- A - 0.5" Plexiglas top
- B - 0.5" Plexiglas bottom (counterbored for bolts)
- C - 3/8" x 6" steel bolts
- D - 1/16" Teflon sheet glued to (A)
- E - 1.5 liter glass jar with ground glass rim
- F - # 19 glass stopper fitted in reamed opening in (A) and (D)
- G - 3/32" brass support-conductive wire (brazed or soldered to (H))
- H - 1.5" x 1" x 1.25" Test metal coupon
- I - Carboline Series "K" self-priming vinyl coating
- J - Exposed area of metal sample for active corrosion
- K - 1.5" x 0.25" Teflon coated magnetic stir bar

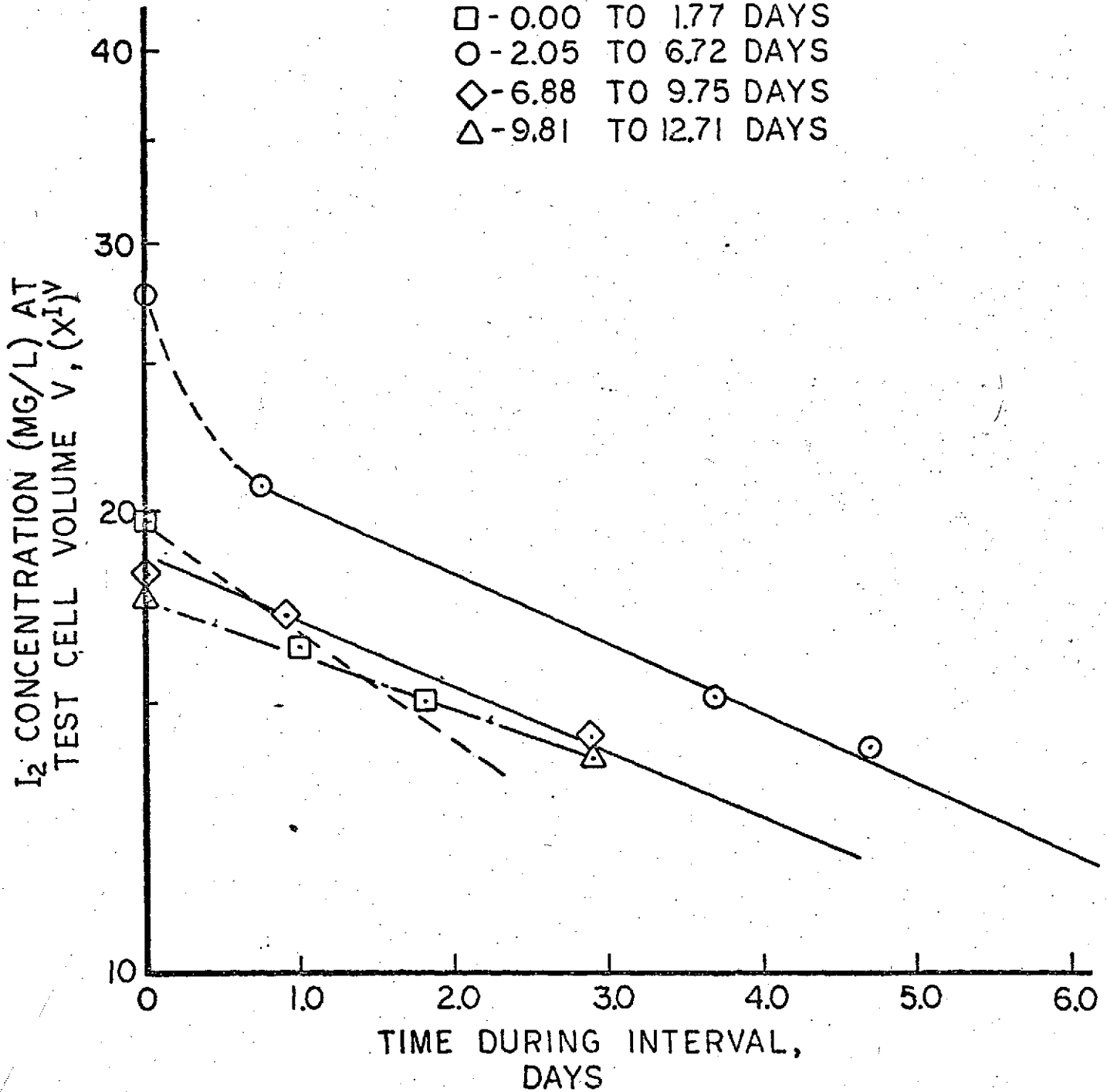
SCHEMATIC OF REFERENCE ELECTRODE



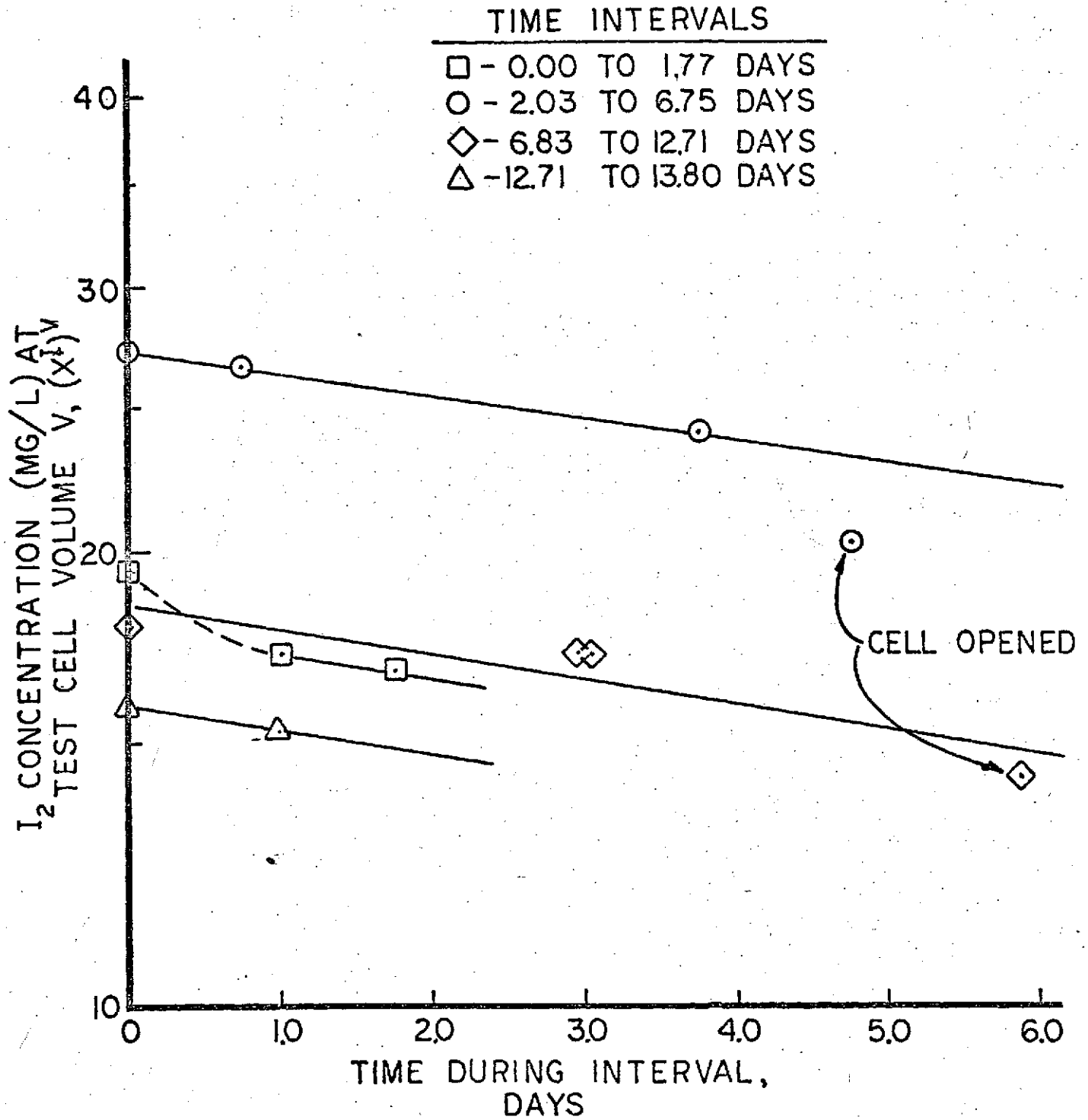
ALUMINUM (AL6061)-  
IODINE DEPLETION CURVES

TIME INTERVALS

- - 0.00 TO 1.77 DAYS
- - 2.05 TO 6.72 DAYS
- ◇ - 6.88 TO 9.75 DAYS
- △ - 9.81 TO 12.71 DAYS



STAINLESS STEEL (CRES 316L)  
IODINE DEPLETION CURVES



CHAPTER VI  
DISINFECTANT EVALUATION STUDIES

INTRODUCTION

Significantly high counts of bacteria have been obtained periodically in analyses of the drinking water supply of the CM spacecraft (Reference VI-1). Consequently, the possibility that bacterial concentrations may exceed U. S. Public Health Service Standards (Reference VI-2) has existed. These health (and aesthetic) considerations in the spacecraft water supply systems have prompted this study of disinfectant concentrations and contact times required to produce acceptable drinking water quality within the spacecraft.

Several considerations are pertinent in the laboratory elucidation of disinfectant-microbial interactions. Of primary concern are the nature of disinfectant, the microbial characteristics, the ambient temperature and the pH of the system in question. For the purposes of this study, the halogen disinfectants iodine and chlorine were chosen; other disinfecting agents were omitted from further consideration after the following qualities became evident:

- (1) Antibiotics may be related to the production of strain resistant microbial species and their continued use in drinking water supplies may produce gastrointestinal flora changes with attendant symptomatic results.
- (2) Metallic additives possess qualities incompatible for use within a metallic distribution system susceptible to corrosive activity or for continued human consumption.
- (3) Organics, such as phenol, quaternary amines, etc. possess the unsuitable characteristics of instability and reactivity within an aqueous-metallic-membrane system.

The bactericidal effects of chlorine and iodine are universal (Reference VI-3). One of the most striking features of disinfecting halogens is that the concentration necessary to disinfect does not vary greatly with different species of microorganisms. A number of theories regarding the mechanism whereby these halogens produce the death of cells have been advanced (Reference VI-4). It is generally agreed that the bactericidal effect of chlorine is due to its oxidative characteristics and its ability to inhibit certain enzyme systems. There is also some evidence that exposure



of cells to low levels of chlorine results in the destruction of the cell wall permeability. The ability of iodine to actually penetrate the cell wall seems to account for its effectiveness as a disinfectant. This evidence for the relationship of the universality of the disinfection powers of halogens to a disruption of cellular processes and/or constituents rather than enzymatic blockage (from which resistant species may develop), allows the use of general indicator organisms rather than specific species.

The United States Food and Drug Administration and the Public Health Department of the State of California have established disinfection standards defining an effective disinfectant as one which produces a 99.999 percent bacterial inactivation within 15 seconds of contact time. This standard will be used in the interpretation of the results obtained in this study in light of the levels of sterility as perceived by NASA; such a standard approach is the *theoretical limit of absolute sterility*.

#### EXPERIMENTAL PROGRAM

In this study the water disinfectants, iodine and chlorine, were evaluated under simulated spacecraft conditions; bacteria of sanitary and spacecraft significance were utilized as test organisms at an ambient temperature of 25°C (77°F), and solutions at pH 6 and pH 8 were employed in most experiments. The combinations of conditions investigated are listed in Table VI-1.

#### Test Organisms

The choice of organisms for investigation was based upon the specific nature of the spacecraft disinfection problems as well as the comparative disinfection effectiveness of iodine and chlorine for indicator organisms. The "universal" disinfection powers of iodine and chlorine justify concentration on two indicator organisms. The choice of Escherichia coli was made on the basis of its classical use as an indicator of fecal pollution. Alternatively, Flavobacter sp. was chosen because of its ubiquitous distribution in nature and its prior association with the spacecraft water supply. Follow-up studies have employed the use of the pathogen Staphylococcus aureus (a spacecraft contaminant organism), and the spore-former Bacillus subtilis as well as Pseudomonas aeruginosa which has previously exhibited a high degree of resistance to iodine (Reference VI-4).

#### Methodology

Organism cultures were maintained under the conditions described in

TABLE VI-1

ORGANISMS AND DISINFECTANTS USED IN DISINFECTION TESTS

Organism	pH	Disinfectant	Disinfectant Concentration ppm
<u>Escherichia coli</u> ATCC 1103	6	None	-
" "	"	Iodine	0.25
" "	"	"	0.8
" "	"	"	1.0
" "	"	Chlorine	0.6
" "	"	"	1.0
" "	8	None	-
<u>Flavobacter breve</u>	6	None	-
" "	"	Iodine	0.23
" "	"	"	0.77
" "	"	Chlorine	0.26
" "	"	"	0.78
" "	8	None	-
<u>Staphylococcus aureus</u> P209	6	Iodine	0.6
<u>Pseudomonas aeruginosa</u>	6	Iodine	0.96
<u>Bacillus subtilis var niger</u>	6	Iodine	0.6

Table VI-2. With the exceptions of Flavobacter breve and Pseudomonas aeruginosa the organisms were grown in a nutrient medium used in disinfection studies by the Association of Official Agricultural Chemists modified with 100 ppm sodium thiosulfate for iodine and chlorine inactivation ("Standard Methods", Reference IV-5). The specific growth requirements of Flavobacter breve and Pseudomonas aeruginosa necessitated the use of two percent Bacto-Casitone (Trypticase Soy Broth) as nutrient substrate. In all instances, 24-hour cultures were used; such cultures present the least inherent variation in resistance (Reference VI-6). All the disinfection tests were performed at 25°C in a laminar flow work bench under isolated clean room conditions designed for easy decontamination.

Cells from a 24-hour culture were centrifuged and washed in deionized water before introduction into the disinfectant solution to be tested. Cell concentrations were estimated on the basis of tube dilutions and plate counts.

All disinfection tests were initiated by the introduction of a known number of washed cells into an Erlenmeyer flask containing 200 ml of disinfectant solution. The flask was placed on a Mag-Mix and aliquots were

TABLE VI-2  
CULTURE CONDITIONS OF THE MICROORGANISMS  
USED IN DISINFECTION TESTS

Organism	Growth Medium	Incubation Temp. °C
<u>Escherichia coli</u> ATCC 1103	A.O.A.C. Nutrient Medium	35
<u>Flavobacter breve</u>	Bacto-Casitone	30
<u>Staphylococcus aureus</u> P209	A.O.A.C. Nutrient Medium	35
<u>Pseudomonas aeruginosa</u>	Nutrient Medium	35
<u>Bacillus subtilis</u> var <u>niger</u>	A.O.A.C. Nutrient Medium	35

removed at 15, 30, 60, 120, 300 and 600 seconds for tube dilutions and subsequent plate inoculations. Residual chlorine and iodine analysis were run immediately before and after test performance. The majority of the tubes and plates were incubated for 24 hours and then observed for organism presence or count; the exception, Flavobacter breve, required 48 hours of incubation.

## RESULTS

Data obtained from the disinfection tests described above are presented in Table VI-3. The data contained in Table VI-3 have been converted to percent survival units and plotted against time on a log-log scale. This form of data analysis is an established approach for such disinfection data. The lines of best fit were established for the data points and plotted in Figure VI-1 through VI-8. As a general rule the origins of these plots were at about 100 percent survival at one second; an expected observation inasmuch as the precision of such tests would detect little difference between 0 time and one second survival values. The slopes of these logarithmic die-away curves, (designated  $k_m$ , bacterial inactivation constant) represent an empirical relationship between organism survival and contact time and can be utilized to compare the relative efficacy of disinfectants at the pH and disinfectant levels as represented in Table VI-4. The  $k_m$  values presented in Table VI-4 can be used specifically to compare the organism inactivation rates on both inter-halogen and intra-halogen bases. As a reference inactivation rate, a line on the logarithmic plots utilized herein with a slope of -4.25 would represent a 99.999 percent bacterial inactivation after a 15-second contact time. The disinfectant concentrations required to produce such an inactivation rate for the test organisms are given in Table VI-5. These inactivation data are summarized in Figure VI-9 where the respective  $k_m$  values are plotted against the chlorine and iodine concentrations in contact with the test organisms used.

## DISCUSSION

In all instances, the 99.999 percent die-away rate has been produced within 15 seconds contact time with halogen levels considerably lower than the residuals anticipated in spacecraft water systems. Therefore the disinfecting halogens employed, chlorine and iodine, have been found to be effective agents for bacterial inactivation according to the criteria prescribed by the United States Food and Drug Administration and the Public Health Department of the State of California. In this set of studies, these effective disinfecting conditions have been defined by a bacterial inactivation constant,  $k_m = -4.25$ : the slope of the log-log plots of the die-away results.

Die-away curves obtained for Escherichia coli indicate that 1.7 ppm iodine at pH 6 would produce a  $k_m$  of -4.25; 1.2 ppm chlorine under similar

TABLE VI-3  
CELL CONCENTRATION VS. TIME OF EXPOSURE TO IODINE AND CHLORINE

Organism	Disinfectant	Disinfectant Concentration (mg/l)	pH	Cell Concentration (per ml) @ Time of Exposure (Seconds)						
				0	15	30	60	120	300	600
<u>Escherichia coli</u>	None	-	6	$10^7$	$10^7$	-	$10^7$	$10^7$	$10^7$	$10^6$
" "	"	-	8	$5 \times 10^7$	$10^8$	-	$10^8$	$10^8$	$10^8$	$10^7$
" "	Iodine	0.25	6	$4.5 \times 10^7$	-	-	-	$10^5$	-	$10^3$
" "	"	0.8	6	$4.5 \times 10^7$	$4.5 \times 10^3$	-	$10^2$	-	-	-
" "	"	1.0	6	$1.5 \times 10^7$	$1.5 \times 10^3$	-	-	1	-	-
" "	Chlorine	0.6	6	$1.3 \times 10^8$	-	-	$10^3$	$10^2$	20	-
" "	"	1.0	6	$4 \times 10^7$	-	$10^2$	-	-	-	-
<u>Flavobacter breve</u>	None	-	6	$3 \times 10^7$	-	-	-	-	$10^6$	-
" "	"	-	8	$2.8 \times 10^6$	$10^6$	$10^6$	$10^6$	-	$10^6$	$10^6$
" "	Iodine	0.23	6	$2 \times 10^6$	-	$2 \times 10^5$	$1.2 \times 10^5$	$9 \times 10^4$	$2.8 \times 10^4$	$2.0 \times 10^3$
" "	"	0.77	6	$5 \times 10^8$	$2.1 \times 10^{4a}$	$5.2 \times 10^{3b}$	$2.3 \times 10^3$	$7.5 \times 10^2$	-	-
" "	Chlorine	0.26	6	$4.5 \times 10^6$	-	$10^5$	-	$5 \times 10^4$	$4.2 \times 10^3$	-
" "	"	0.78	6	$1.5 \times 10^8$	-	$5 \times 10^4$	$3 \times 10^4$	-	9	$1.9 \times 10^2$
<u>Staph. aureus</u>	Iodine	0.6	6	$1.3 \times 10^7$	$3 \times 10^3$	$6 \times 10^2$	50	-	-	-
<u>Pseudomonas aeruginosa</u>	"	0.96	6	$2.2 \times 10^7$	$9 \times 10^4$	$7.5 \times 10^3$	$1.4 \times 10^3$	-	-	-
<u>Bacillus subtilis</u> <u>var niger</u>	"	0.6	6	$8.2 \times 10^5$	$6.1 \times 10^2$	-	-	-	-	-

Notes: a)  $\theta = 25$  seconds

b)  $\theta = 40$  seconds

TABLE VI-4

SUMMARY OF BACTERIAL INACTIVATION CONSTANTS FOR DIE-AWAY STUDIES

Organism	pH	Disinfectant	Disinfectant Concentration (ppm)	$k_m$
<u>Escherichia coli</u>	8	None	-	-0.268
" "	6	"	-	-0.268
" "	"	Chlorine	0.6	-2.84
" "	"	"	1.0	-3.89
" "	"	Iodine	0.25	-1.43
" "	"	"	0.8	-3.24
" "	"	"	1.0	-3.44
<u>Flavobacter breve</u>	8	None	-	-0.268
" "	6	"	-	-0.268
" "	"	Chlorine	0.26	-1.00
" "	"	"	0.78	-1.97
" "	"	Iodine	0.23	-0.698
" "	"	"	0.77	-2.30
<u>Staphylococcus aureus</u>	"	"	0.6	-2.38
<u>Pseudomonas aeruginosa</u>	"	"	0.96	-2.10
<u>Bacillus subtilis</u> <u>var niger</u>	"	"	0.6	-2.71

conditions would produce a comparable die-off rate for E. coli.

Flavobacter breve demonstrated a slightly greater resistance to both chlorine and iodine than did the strain of Escherichia coli tested. The Flavobacter breve die-away curves indicate that 3.3 ppm chlorine or 3.4 ppm iodine at pH 6 will produce a  $k_m$  value of -4.25.

Staphylococcus aureus, another indicator organism as well as a potential pathogen within the spacecraft water supply system, is less resistant to either chlorination or iodination than is the strain of Flavobacter breve

TABLE VI-5  
EFFECTIVE IODINE AND CHLORINE  
CONCENTRATIONS FOR DISINFECTION

Organism	Disinfectant	Disinfectant Concentration (mg/l) at pH 6 Required to Produce a $k_m$ of -4.25
<u>Escherichia coli</u>	Chlorine	1.2
" "	Iodine	1.7
<u>Flavobacter breve</u>	Chlorine	3.3
" "	Iodine	3.4
<u>Staphylococcus aureus</u>	"	2.3
<u>Pseudomonas aeruginosa</u>	"	4.8
<u>Bacillus subtilis</u> <u>var niger</u>	"	1.7

tested; S. aureus is, however, more resistant to iodination than E. coli. Projected values for S. aureus would indicate that a 2.3 ppm iodine solution at pH 6 would produce an acceptable  $k_m$ .

Vegetative cells of Bacillus subtilis var niger demonstrated the same resistance to iodine at pH 6 as did the strain of Escherichia coli tested. In the same light, predicted die-off for vegetative cells of B. subtilis indicate that a 1.7 ppm iodine solution at pH 6 would be needed to produce an acceptable  $k_m$  of -4.25.

As expected, Pseudomonas aeruginosa demonstrated a higher resistance to iodine and chlorine than did any other of the test organisms. Projections from the die-off curves indicate that an iodine level of 4.8 ppm would be required to effectively inactivate this organism if it should be found to be present in the spacecraft. Since Pseudomonas aeruginosa is

known for its high level of resistance to iodine, it can probably be assumed that a level of 4.8 ppm iodine would be more than sufficient to inactivate the bacterial flora that may find their way into the drinking water supply of the spacecraft.

#### SUMMARY

The inactivation of five genera of bacteria upon exposure to defined concentrations of chlorine and iodine at defined pH's and temperatures were studied. The organisms were chosen on the basis of their classical sanitary significance, representation of the organisms actually found in the spacecraft, and, in one case, on the basis of a known high degree of resistance to iodine. In all cases, the inactivation dynamics were defined in terms of die-off rates and contact times. The data were summarized so as to determine the disinfectant levels needed to produce a bacteriologically safe drinking water supply in the spacecraft.

#### CRITIQUE OF PRIOR STUDIES

A critique of several reports summarizing evaluation data on microbial contamination of spacecraft water systems is presented in Appendix G.



## CHAPTER VI

### LIST OF REFERENCES

- VI-1 "Documentation and Summary of Analytical Data From Apollo 10 CSM 106/LM-4 Potable Water", memorandum to R. L. Sauer from Sanitary Engineer, Contract NAS9-6568, S/D. J. Calley', 10 June 1969.
- VI-2 "Public Health Service Drinking Water Standards", 1962, U. S. Public Health Service Publication No. 956 (1963).
- VI-3 "Disinfection and Sterilization", McCulloch, E. C., Second Edition, 1945, Lea & Febizer, Philadelphia.
- VI-4 "Disinfection, Sterilization, Preservation"; Lawrence, Carl A., Black, S. E., Lea & Febizer, 1968.
- VI-5 "Iodine for Disinfection of Water"; Black, A. P., etal, Journal A.W.W.A., pp 69-83, 1968.
- VI-6 "Elemental Iodine as a Disinfectant for Drinking Water," Chang, S. L. and Morris, J. C., Ind. and Eng. Chemistry 45: 1009-1012, 1953.

INACTIVATION OF ESCHERICHIA COLI BY IODINE AT PH 6

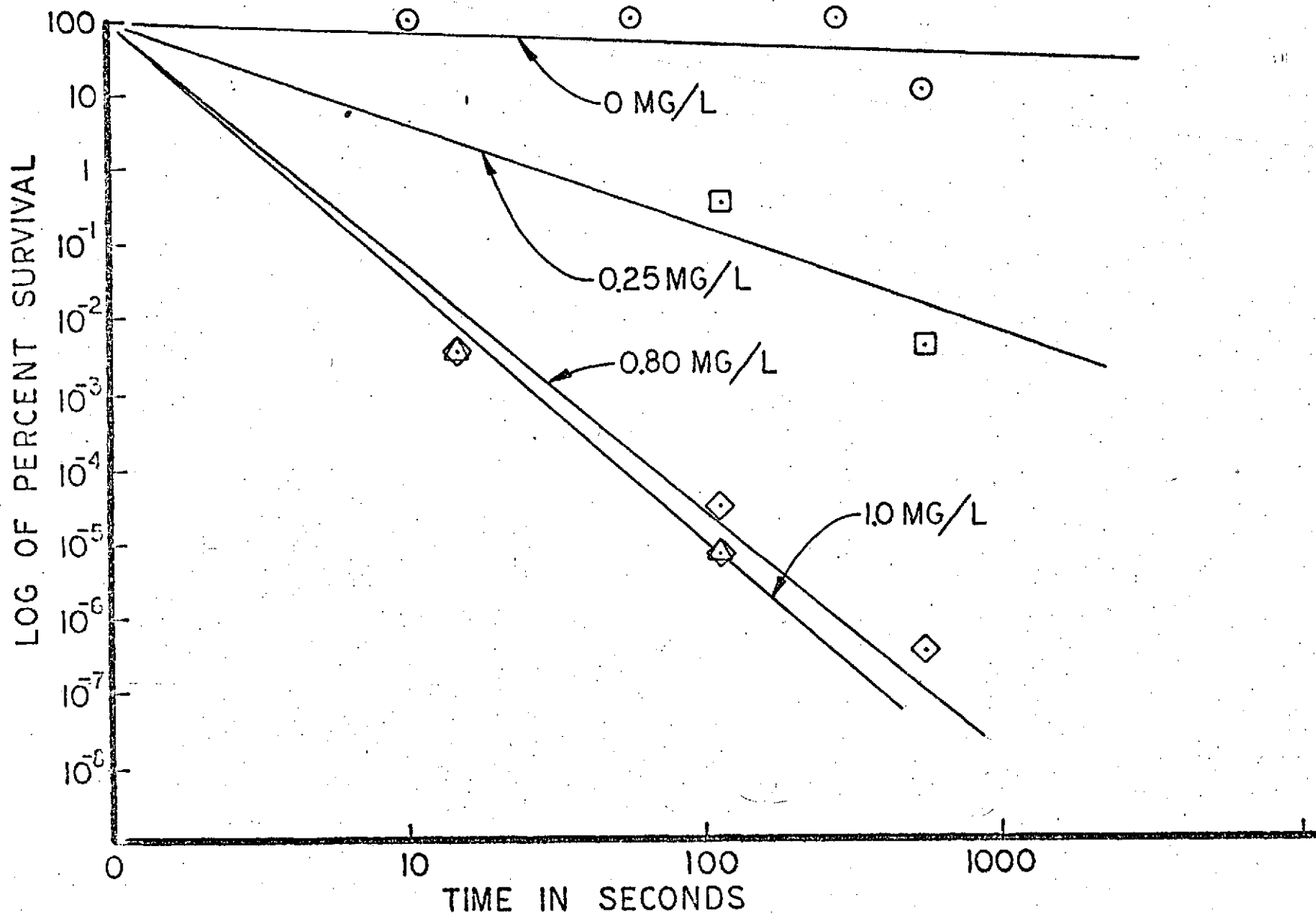
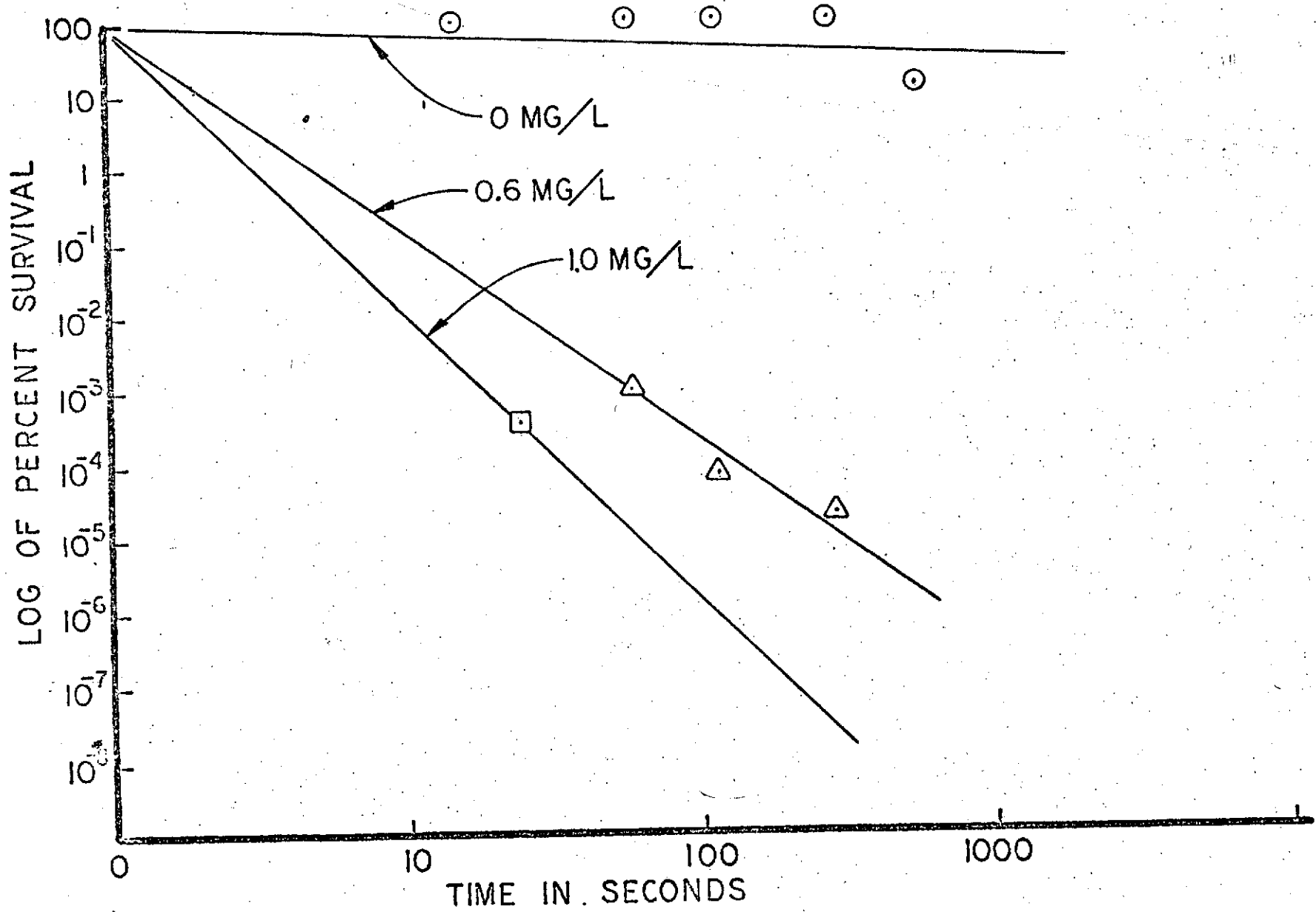
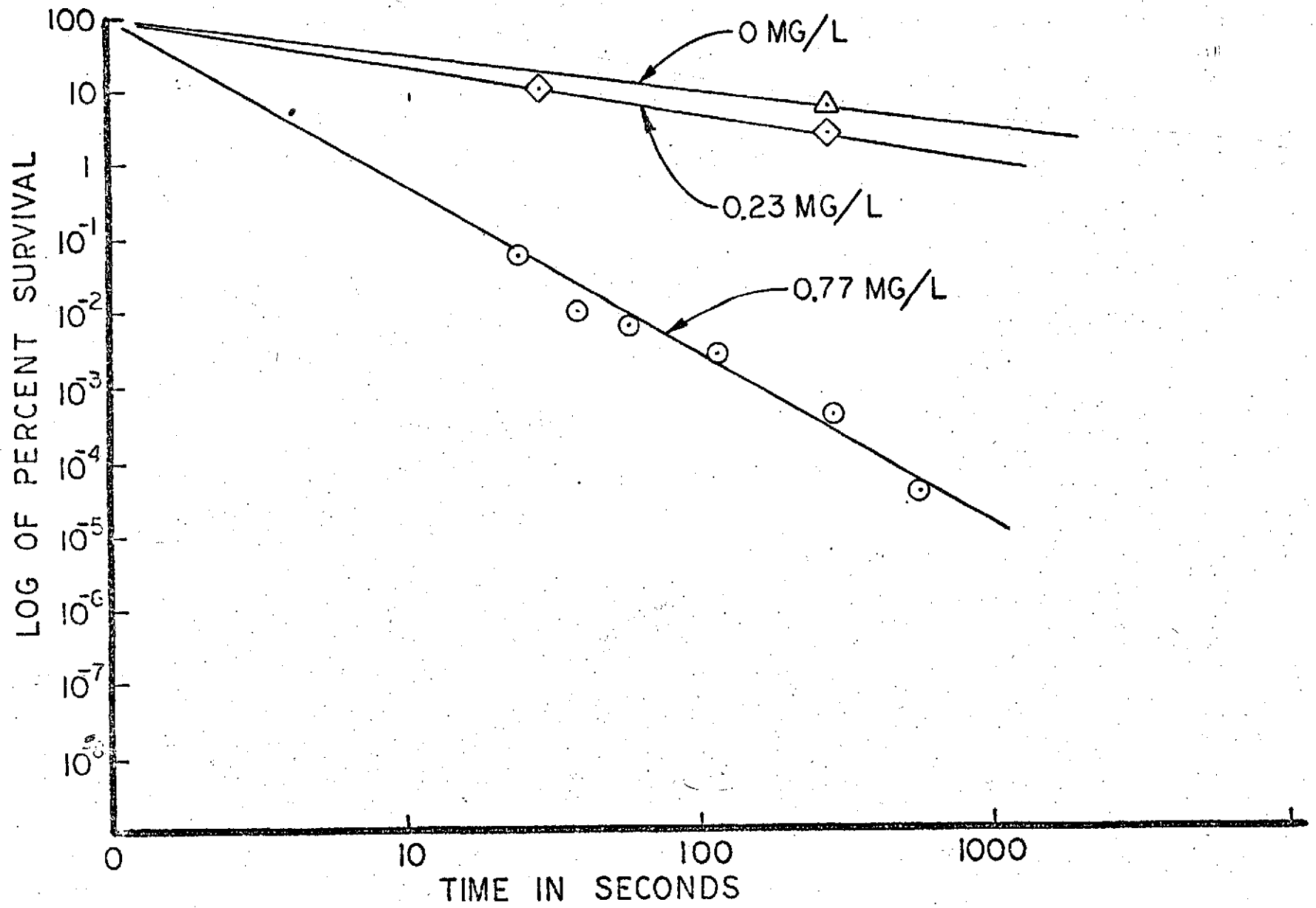


FIGURE VI-1

INACTIVATION OF ESCHERICHIA COLI BY CHLORINE AT PH 6



# INACTIVATION OF FLAVOBACTER BREVE BY IODINE AT PH 6



# INACTIVATION OF FLAVOBACTER BREVE BY CHLORINE AT PH 6

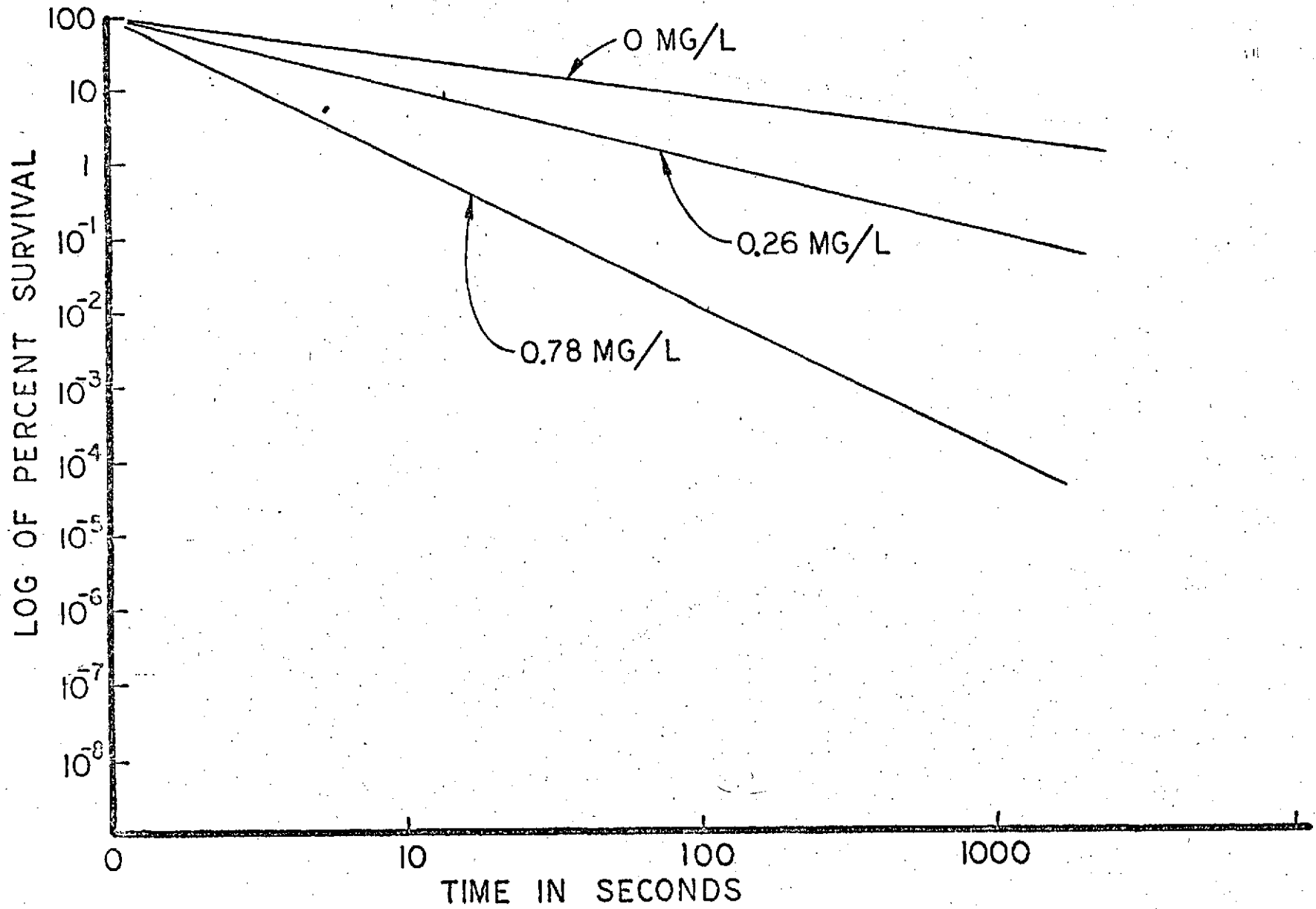


FIGURE VI-4

INACTIVATION OF ESCHERICHIA COLI & FLAVOBACTER BREVE  
AT PH.6 (NO DISINFECTANT)

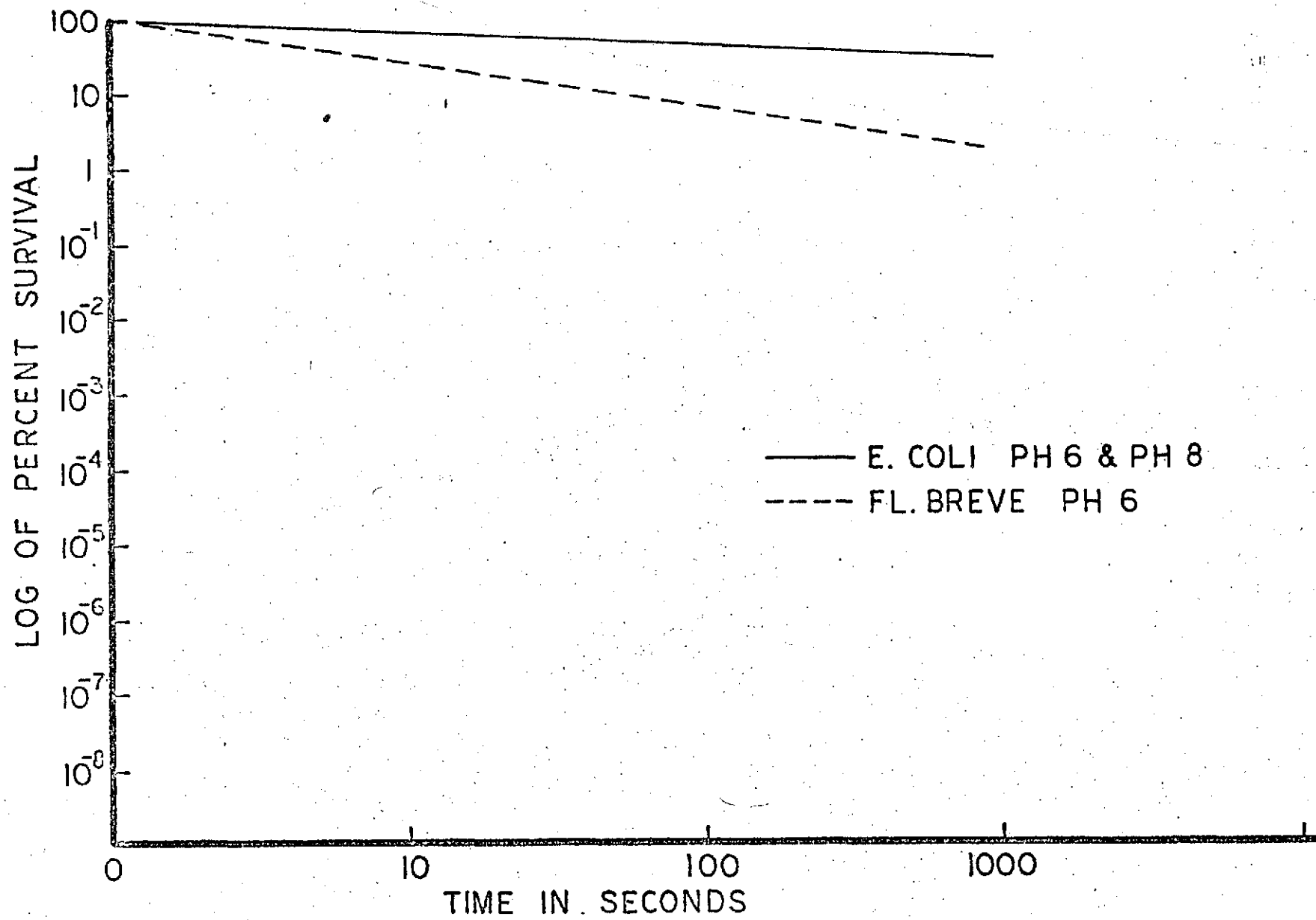


FIGURE VI-5

INACTIVATION OF STAPHYLOCOCCUS AUREUS  
BY 0.6MG/L IODINE AT PH 6

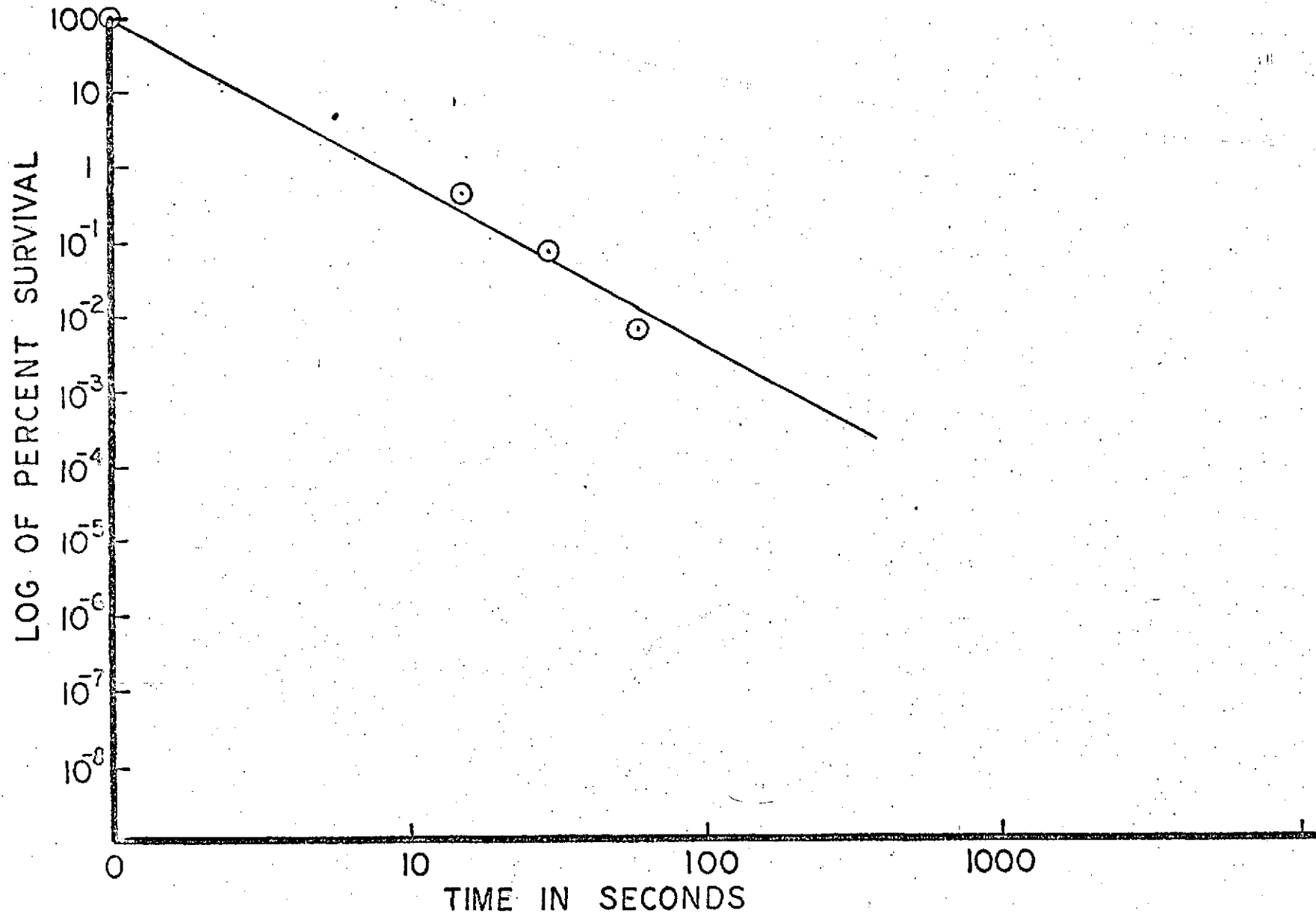


FIGURE VI-6

INACTIVATION OF BACILLUS SUBTILIS VAR NIGER  
BY 0.6 MG/L IODINE AT PH 6

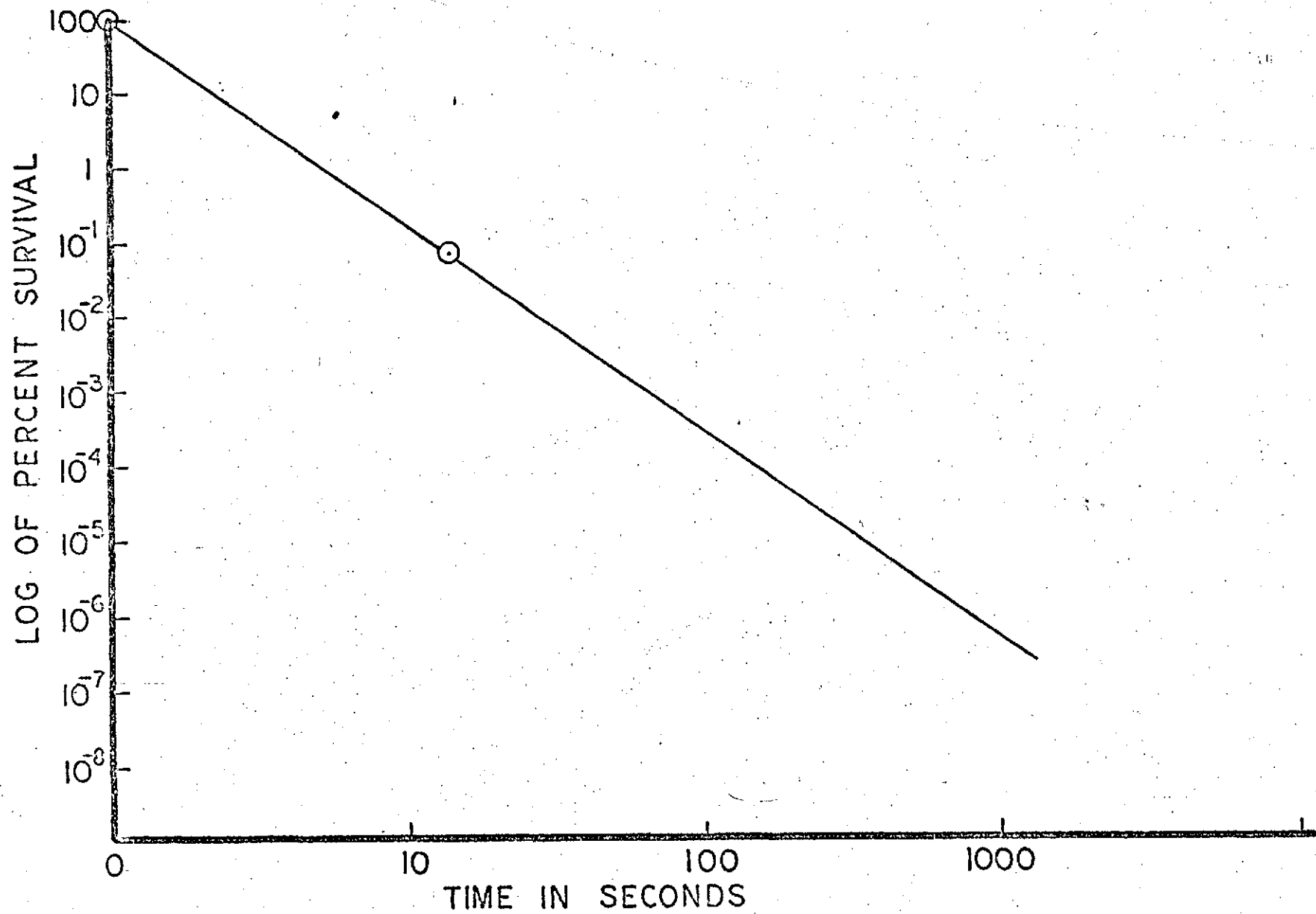
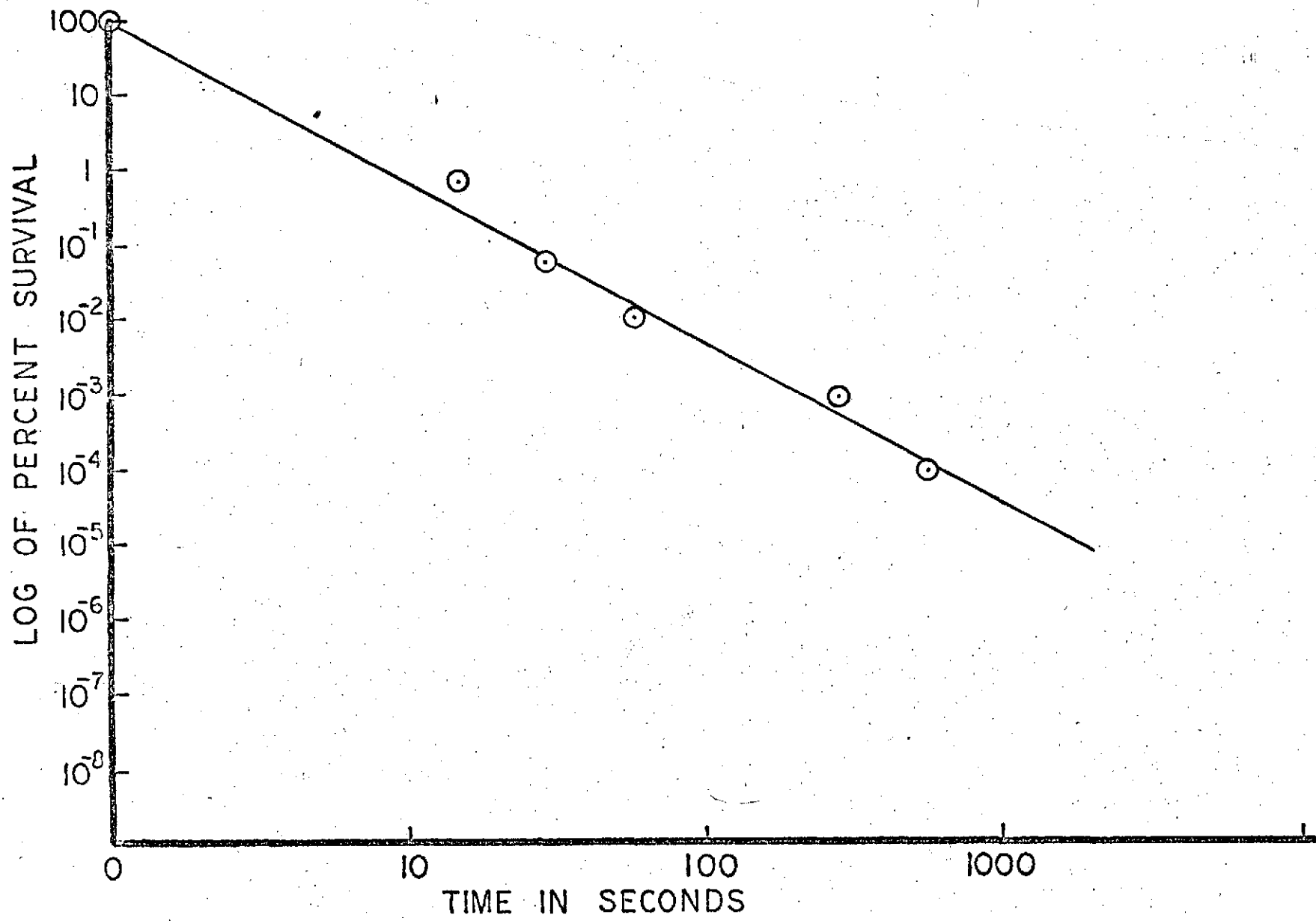


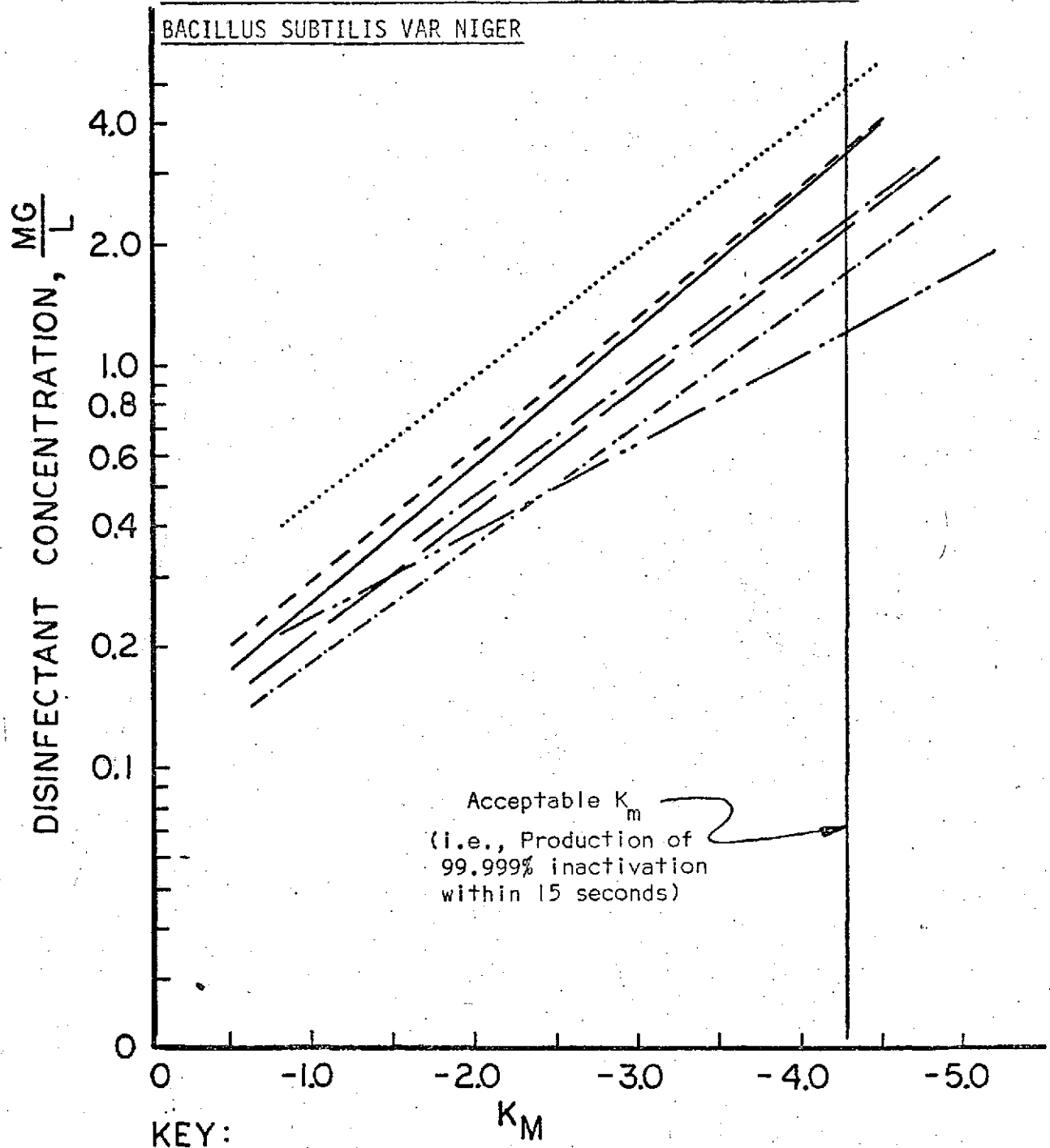
FIGURE VI-7



INACTIVATION OF PSEUDOMONAS AERGINOSA  
BY 0.96 MG/L IODINE AT PH 6



SLOPE OF INACTIVATION CURVES, K, VS. CHLORINE AND IODINE CONCENTRATIONS FOR ESCHERICHIA COLI, PSEUDOMONAS AEROGINOSA AND FLAVOBACTER BREVE AND STAPHYLOCOCCUS AUREUS AND BACILLUS SUBTILIS VAR NIGER



KEY:

- E. Coli, Chlorine
- ..... E. Coli, Iodine
- Flavobacter Breve, Chlorine
- Flavobacter Breve, Iodine
- · — · — Staphylococcus Aureus, Iodine
- ..... Pseudomonas aeroginosa, Iodine
- Bacillus subtilis var niger, Iodine

## CHAPTER VII

### ENGINEERING EVALUATION OF SPACECRAFT WATER SYSTEMS

#### INTRODUCTION

The foregoing studies on membrane sorption, conversion, substitution and diffusion phenomena, relative corrosivity, and disinfection kinetics have provided a knowledge of some of the basic interactions governing the behavior of components of the spacecraft water systems. There is a need to present in this report not only a perspective of how these defined interactions explain operational problems as described symptomatically elsewhere, but also to exemplify the predictive capability that can be developed from such fundamental information. In preparation of this chapter it has been necessary occasionally to draw upon information developed outside this study; information developed in other studies is acknowledged wherever used.

This chapter serves the following purposes:

- (1) Documentation of the physical, dimensional, and dynamic characteristics of water systems in the Command Module, Lunar Module, and Orbital Workshop (the latter as currently planned).
- (2) Identification of real or potential problem situations in the water systems and of the limitations of current understanding about these problems.
- (3) Prediction of septum behavior in the water systems as information permits.

At the onset of the study, the work planning effort was directed primarily to the water management systems of the Apollo Command and Service Module (CSM) and the Lunar Module (LM). As the study developed, it became expedient to include consideration in the study of the sanitary engineering aspects of planning for the Saturn V Orbital Workshop Program (OWS). For this reason, description and discussion in the following sections are directed to the CSM, LM, and OWS spacecraft water systems.

#### COMMAND AND SERVICE MODULE WATER SYSTEMS

##### Description

The components of the Apollo spacecraft interfacing with the water system are the Command and Service Modules (CM and SM, respectively). The CM, the control center of the spacecraft houses the three crewmen on the flight to and from the moon. The CM consists of a surrounding outer heat

shield and an inner crew compartment. The outer heat shield is composed of stainless-steel honeycomb between stainless-steel sheets and is covered on the outside with an ablative material (that is, a material which is burned away during reentry to dissipate the generated heat). The inner crew compartment is a pressure chamber constructed of aluminum honeycomb between aluminum-alloy sheets. This construction is designed to be as light as possible but strong enough to withstand the environment of space.

The cylindrical-shaped SM, which is approximately 13 feet in diameter and 22 feet in height, is constructed primarily of aluminum alloy. The SM contains the restartable propulsion engine and the propellant tanks used for translunar and transearth midcourse corrections and the systems required to support the CM and the crewmen. These systems include the electrical system (fuel cells), the reaction control system, and that part of the environmental control system not required during reentry.

Three basic functions occur in the water-supply system in the CM and SM: generation and storage of supply; transport of water to points of use for drinking and food-preparation purposes as well as for cabin cooling; and transport of humidity condensates to a waste-water storage and disposal facility for spacecraft cooling. The water supply of the CSM is by product water generated from operation of the fuel cell for power generation. Provisions are made for heating and cooling of the water supply, and the water supply can be used for supplemental or secondary cooling under emergency conditions.

A schematic drawing of the CM-SM water system is shown in Figure VII-1. The fuel cell is located in the SM (SM sector), and water enters the CM (CM sector) through a single line. After passing through a water-valve (control) panel, potable water is routed preferentially to the potable-water tank and then to the food preparation unit. If the potable-water tank is full, water is routed to the waste-water tank. Waste water from the humidity condensate is routed either to the waste-water tank or to an overboard dump.

#### Service Module Fuel Cell Assembly

The fuel cells are the only components interrelated with the water system which are located in the SM. Fuel cells consist of two chambers separated by porous nickel electrodes containing concentrated potassium hydroxide (KOH) liquid electrolyte. One of the chambers is filled with

oxygen (cathode), and the other is filled with hydrogen (anode); both chambers are held at a pressure of 60 psi. Oxygen is diffused through the electrode into the hydrogen-filled chamber where the two gases are combined to form water. This chemical reaction produces the electrical current used to meet the electrical-power requirements of the CSM. The fuel cells operate at a temperature of approximately 410° F and 60 psi and produce water at a nominal rate of 1.2 pounds per hour. The water production rate depends on the power drawn from the cells and may increase from the nominal rate to as much as 2.0 pounds per hour for short time periods. Before fuel-cell water is transferred to the CM, the water is cooled to 76° F and the system pressure is reduced to 25 psi.

Typical chemical analysis of water samples from three fuel cells are shown in Table VII-1. The chemical composition of fuel-cell by-product water is essentially that of distilled water and is saturated with hydrogen gas. The total dissolved solids of three samples described in Table VII-1 averaged 0.73 mg/l and the average pH was 5.6.

#### Command Module Water Systems

The water supply of the CM, adjusted to 25 psi and 76° F, is conveyed to a hydrogen separator and then to the water control panel (Figure VII-1). The separator consists of palladium-silver tubes through which hydrogen is diffused from the water and subsequently is vented to space. The main controls on the water panel are two water-shutoff valves, one each for the potable-water and waste-water systems; a shutoff valve which permits access to the waste-water system; the chlorine-injection assembly; a control valve to the overboard dump; and two pressure-relief controls. The system design permits both the potable-water tank and the waste-water tanks to be supplied with fuel-cell water and excess fuel-cell water to be dumped overboard if these tanks are filled. The potable-water system line (Line 1b, Figure VII-1) leads to the chlorine-injection assembly, to a check valve, and to the potable-water tank. Water flows out of the potable-water tank through a bypass line which has another check valve and can be transferred to the chiller, heater, waste-water tank, or overboard dump. The function of the chiller is to reduce the water temperature of 76° F to approximately 50° F. The food-preparation unit consists of a heater and two faucets, one for hot water and the other for chilled water. The heater can raise the water

TABLE VII-1

## ANALYSIS OF FUEL CELL WATER SAMPLES

Characteristics	Fuel Cell A	Fuel Cell B	Fuel Cell C
pH, 7.0-7.5 <sup>a</sup>			
Specific conductivity, μmho/cm (77° F)	.59	.59	.86
Total dissolved solids, mg/l	.69	.75	.76
Total suspended solids, mg/l	<.1	<.1	.2
Total solids, mg/l	<.79	<.85	.96
Total Organics, mg/l	.07	.06	.05
Nonvolatile solids, mg/l	<.62	<.79	.91
Taste and Odor	None	None	None
Turbidity, JTU <sup>b</sup>	.8	.8	.7
Color, true, color units	1.	1.	1.
Ionic species, mg/l			
Cadmium	<.01	<.01	<.01
Chromium	<.01	<.01	.02
Copper	.20	.23	.21
Iron	.04	.05	.05
Lead	<.01	<.01	<.01
Manganese	<.05	<.05	<.05
Mercury	<.005	<.005	<.005
Nickel	.03	.04	.04
Silver	<.01	<.01	<.01
Zinc	.15	.18	.26
Calcium	.4	.4	.3
Magnesium	<.1	<.1	<.1
Sodium	.25	.29	.82
Potassium	.1	.1	.1
Selenium	<.01	<.01	<.01
Aluminum	.9	1.1	.8

<sup>a</sup>Typical ranges of fuel cell water pH

<sup>b</sup>Jackson turbidity unit

Source: Reference VII-1

temperature to 150° F. A pressure of 25 psi is maintained in the potable-water system by oxygen applied to an expansion bladder in the potable-water tank.

#### Command Module Waste-Water System

The supply of fuel-cell water to the waste-water system can take place only if the potable-water tank is filled. Water can be transferred from the waste-water tank through a service line (Line 4, Figure VII-1) to the overboard dump or to two evaporators (Line 9), which are secondary heat exchangers for the glycol cooling system of the CSM. Evaporated water is discharged to space through a steam duct. The service line also receives humidity condensate from the astronauts' suits and from the breathing oxygen of the CM. The condensate serves as a second source of water to the waste-water system.

#### Command Module Functional Components

The following key functional components are used in the CM water management system.

- (1) Potable-water tank: The potable-water tank (PWT) serves as a storage container in case of fuel-cell failure and as an equalization tank to satisfy sudden demands at low continuous supply. The cylindrical vessel holds a maximum of 39 pounds of water, and the shell is fabricated of 6061 T6 aluminum alloy. An oxygen-filled polyisoprene (EMS-382) bladder maintains a pressure of 25 psi in the tank and throughout the system. The oxygen that keeps the bladder inflated is obtained from a common supply in the SM that also provides oxygen for breathing and power generation. Because free hydrogen in the water diffuses through the bladder material, a low-rate gas bleedoff is provided to prevent the buildup of diffused hydrogen and formation of an explosive hydrogen/oxygen mixture in the oxygen plenum. The physical dimensions of the PWT are as follows: volume, 17,700 cu cm; surface area of aluminum walls, 4,700 sq cm; surface area of polyisoprene membrane, 1,550 sq cm; residence time of one flow-through volume in tank at water production rate of 1.2 lb/hr, 32.7 hr. (The PWT is the subject of analysis subsequently).
- (2) Waste-water tank: The waste-water tank provides storage of water

to supply water evaporators in case of failure of the primary cooling-system radiators. This tank holds a maximum of 56 pounds of water and is similar in design and operation to the potable-water tank.

- (3) Water-chiller: The chiller, which has a storage capacity of 0.5 pound of water, reduces the temperature of the water for the drinking gun and food-preparation unit from 76° F to 50° F. The tubes of the heat exchanger in the chiller are fabricated of stainless steel Type 347, and the material of all other components is stainless steel CRES Type 316L. Chilling is provided by the spacecraft water-glycol cooling system.
- (4) Food-preparation unit: The food-preparation unit transfers hot or cold water in 1-ounce deliveries into dehydrated food packages. This unit includes a heater and two metering faucets. The heater holds 2.5 pounds of water and produces water at a temperature of 150° F. The heater consists mainly of a stainless steel CRES Type 347 reservoir shell with copper (ASTM B 152-58) baffles and tubes.
- (5) Drinking-water gun: A drinking-water gun is connected to the water system by 70 inches of viton hose.
- (6) Service Lines: All service lines in the system are fabricated from 1/4-inch or 3/16-inch diameter Type 6061 aluminum tubing. The physical characteristics of the service lines comprising the entire water system between the PWT, chlorine injection point, and hot and cold water ports, are as follows: length, 960 cm @ 1/4-inch diameter and 300 cm @ 3/16-inch diameter (Reference VII-2); volume, 341 cm; surface area, 2,160 sq cm.
- (7) Disinfectant: Sodium hypochlorite (NaOCl) has been used as disinfectant for the water-supply system of the CSM.

#### System Disinfection

Both preflight and inflight system disinfection procedures are used with the CM water system. Approximately five days before lift-off, the water system of the CM is filled with deionized water containing 12 mg/l of sodium hypochlorite as chlorine. After an exposure time of four hours, the system is drained and flushed with water which has been deionized through a Millipore Super Q Unit. After the flushing, the system is



filled with deionized water. Three hours before lift-off, 20-cubic-centimeter ampules of sodium hypochlorite (5,000 mg/l as chlorine) and sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) buffer (0.7 molar) are injected into the spacecraft system. These dosages are equivalent to the injection of 105 mg  $\text{NaOCl}$  and 1,695 mg  $\text{NaH}_2\text{PO}_4$ , or, in terms of the daily average water production of approximately 13 liters, equivalent to a salt increment of approximately 140 mg/l.

In-flight disinfection of the potable-water system of the CM is performed in the following steps.

- (1) If the potable-water tank is completely full, ullage is created in the potable-water tank by withdrawing water through the drinking gun or food-preparation unit. This step is required to permit a flow of fuel-cell water past the disinfectant injection point and into the potable-water tank.
- (2) A 20-cubic centimeter capsule of sodium hypochloride buffer solution containing 5000 mg/l sodium hypochlorite as chlorine is injected.
- (3) A 20-cubic-centimeter capsule of sodium dihydrogen phosphate buffer solution 0.7 molar is injected.
- (4) During a 10-minute contact time, the injected solutions are flushed in the flow of fuel-cell water past the point where the service line (Line 2, Figure VII-1) branches off the line to the potable-water tank (line 1b). Most of the disinfectant and buffer passes the branching point and is carried into the storage tank. However, a small fraction may remain in the injection tee or may diffuse into the service line. In a study by North American Rockwell Corporation (Reference VII-2) it was estimated that peak chlorine concentrations in excess of 80 mg/l could occur during the chlorine injection cycle.
- (5) After the 10-minute contact time, a capsule of water is withdrawn through the injection point. This withdrawal pulls any chlorine slugs in the service line back into the main line where the chlorine can be transferred into the storage tank by the fuel-cell water.
- (6) An additional 20-minute period is allowed to elapse before any water is used from the system to allow the disinfectant and buffer

to disperse in the potable-water tank.

- (7) The disinfected water is withdrawn for consumption through the drinking-gun and food-preparation service outlets.

### Problem Areas

The key problem areas experienced in the water systems of the CSM and LM have been related to (1) the transport of dissolved gases into, through, and out of the water system to points of use, and (2) the attrition of disinfectant levels caused by interaction with the system components.

#### Gas Transport

The physical design and operational characteristics of the CSM permits two gases to be transported through the system: hydrogen and oxygen. Fuel-cell byproduct water is saturated with hydrogen gas at 410° F and 60 psi as it leaves the cell. When byproduct water is adjusted to 76° F and 25 psi pressure, significant quantities of hydrogen gas are released from solution. In later Apollo flights, a palladium-silver hydrogen separator has been used to prevent gaseous hydrogen from reaching the PWT. In earlier Apollo flights, it was believed that hydrogen gas was transported to the PWT where upon dissolution it passed through the polyisoprene membrane into the oxygen-filled balancing plenum of the PWT. For this reason, the balancing plenum is purged constantly at a slow rate to prevent the development of an explosive hydrogen-oxygen gas mixture. Evidence developed by AiResearch Manufacturing Division (Reference VII-3) indicates that hydrogen can permeate through the polyisoprene membrane; a discussion of these data is presented in Appendix H.

Oxygen is transported into the water system by diffusion from the balancing plenum of the PWT (pressurized to 25 psi oxygen) into the water stored in the PWT and thence to the use ports. It is believed that this source of oxygen is the cause of degassing at the use ports as the water is transferred from the supply system at 25 psi to the cabin atmosphere at five psi. Degassing of water at the use ports has created problems during flight inasmuch as the amount of gas released in the water has formed bubbles of sufficient size to inhibit its direct use for drinking or food preparation. Techniques to effect gas-liquid separation under zero-gravity conditions, such as bagging and centrifugation, have not been effective. The hydrophobic-hydrophilic water-gas separator performed sat-

isfactorily on Apollo 11 mission and its use will continue. In addition, Apollo 12 and subsequent missions will use the silver-palladium hydrogen separator.

Evidence developed by the AiResearch Manufacturing Division (Reference VII-3) has shown that the polyisoprene membrane is highly permeable to oxygen. The raw data presented in the AiResearch study are analyzed in Appendix H. To date, no studies other than the AiResearch effort have been done to evaluate the dissolved oxygen level at various points in the aluminum service lines of the CM. This lack of information on dissolved oxygen levels becomes of immediate concern when considered relative to the findings of the corrosion experiments in this study, viz., that dissolved oxygen tension is a foremost factor in the relative corrosion rate of aluminum-halogen systems.

A third source of dissolved gases is water from the ground support equipment which is not totally degassed prior to loading into the CM. No information is available to quantitate how much dissolved gas is supplied to the CM from this source.

#### Corrosion

The initial occurrence of corrosion was found at three points in the CM: The inlet tube to the heater; the tube immediately in front of the connection to the hose of the drinking gun; and in the section of tubing between the chlorine-injection point and the potable-water tank. The continuing investigation revealed that a pitting-type corrosion was occurring throughout the system. These pits were found to occur at points of surface imperfections in the 6061 aluminum tubing. The corrosion has resulted in the presence of nickel, cadmium, and manganese in the water supply in levels in excess of the NASA Potable Water Specification.

It is believed that the corrosion is attributable primarily to the following:

- (1) The incompatibility of the biocide with the system (for example, the capability of chloride ion to penetrate the passivating oxide layer formed on aluminum tubing).
- (2) The selection of materials for system fabrication.
  - a. Dissimilar metals electrically connected (for example, the incompatibility of aluminum and copper based on the electrode potential difference of  $\approx 2$  volts between these elements).

- b. Surface imperfections in tubing used for system construction which provides sites for active localized corrosion.

Numerous studies have been carried out by NASA and NASA subcontractors to ascertain the interactions of aluminum corrosion rates and one or more of the following variables: ionic concentration, additives (including additives such as nitrate at concentrations less than 10 mg/l  $\text{NO}_3\text{-N}$ ), disinfectant concentrations, electrochemically incompatible metals, etc. These studies have shown that fuel-cell water containing sodium hypochlorite, sodium dihydrogen phosphate, and copper at concentration levels predicted or observed in the spacecraft produced considerable corrosive action on aluminum. As a result of corrosive activity and the deterioration of nickel-copper brazing and the aluminum-alloy tubing, there is a release of nickel, cadmium, manganese, and to a lesser extent, other metals, into the CM water supply. In addition to the problems that corrosion imposes on maintaining system integrity, corrosion also is a sink for disinfectant (chlorine) in the CM resulting in a loss of residual disinfectant.

While the above studies have produced large amounts of information, there is little evidence either that these efforts have produced knowledge of the fundamental relationships on how chlorine or its degradation product causes aluminum to corrode, or that the findings of these studies have generated a substantive engineering analysis of the corrosion problem. Data are not yet available to describe systematically:

- (1) Effects of varying of chlorine concentrations, ionic concentrations, and dissolved oxygen concentrations on the kinetics of aluminum corrosion in an aqueous chlorine solution.
- (2) Rates of conversion of chlorine to chloride associated with aluminum corrosion.
- (3) Rates of diffusion of chlorine in water at 76° F.
- (4) Engineering analysis of which of the above factors, diffusion of chlorine to an aluminum wall, conversion of chlorine in the immediate wall area, and ionic concentration, or dissolved oxygen tension, have the rate limiting role in the corrosion process.

Effort was made in this study to ascertain the relative rate of aluminum corrosion in a chlorine system relative to aluminum corrosion in an iodine system (at similar levels of dissolved oxygen). No work was done on the effect of oxygen concentration on the relative rate of aluminum

corrosion in the chlorine system; however the corrosion studies with iodine-aluminum systems were done over a range of dissolved oxygen concentration and did point out the significance of oxygen as a variable in aluminum corrosion.

#### Disinfectant Interaction With Membrane Material

The degree of interaction of chlorine with the polyisoprene membrane in the PWT, whether due to sorption, substitution, or diffusion/permeation process, is undocumented. The primary reason for the lack of information in this area is that depletion of chlorine residuals in the CM (the rate of which is unknown) has been offset by the daily procedure of slug injection of NaOCl solution. There is interaction between chlorine and the polyisoprene membrane, as evidenced by the detection of metal carbamate in the CM water systems which was found to be a curing agent used in the polyisoprene membrane. An earlier problem of interaction between the chlorine and the neoprene hose originally used to connect the drinking-water gun to the water system (resulting in generation of taste and odor problems) has been obviated by the substitution of Viton for neoprene in later Apollo spacecrafts.

#### Microbial Contamination

The problem of microbial contamination in the water system of the CM has been related almost totally to the preflight detection of aerobic organisms in the hot-water port and the drinking gun. Bacterial growth has been detected preflight during the interval prior to a final chlorination before lift-off.

Several types of organisms have been identified in cultures from the use ports: Flavobacterium sp., Staphylococcus epidemidis, Sarcinia sp., and Corynebacterium sp. The Flavobacterium sp. has been observed the most frequently and in the highest numbers. These organisms have been detected preflight prior to the preflight chlorine injection. Post-flight samples have consistently had negative bacterial counts at the drinking gun and either negative or nominal counts (< 20/100 ml) at the hot-water port. Test for coliforms, anaerobic bacteria, yeasts, and molds have been negative at all sample ports both in preflight and postflight monitoring. This has been attributed to the 24-hour inflight chlorination schedule.

A critique of the various reports summarizing the bacteriological studies from which the above observations were obtained is presented in Appendix G.

#### Summary of Problem Areas

The above review of problem areas and of information on hand to analyze and resolve these problem areas indicates the limited amount of fundamental information that is available to describe disinfection and corrosion phenomena taking place in the CM. The principal areas where information is available relate to corrosion and to gas transfer phenomena. An analysis of basic information on oxygen transfer in the CM, with the objective of predicting the oxygen concentrations in the delivered CM water supply, is presented below.

Oxygen Concentrations in Delivered Command Module Water Supply: The level of dissolved oxygen in the delivered water supply of the CM can be estimated with the following assumptions:

- (1) The mass inflow of oxygen through the polyisoprene membrane equals the mass outflow of dissolved oxygen from the potable-water tank.
- (2) The water is supplied to the potable-water tank from the fuel-cell at an average rate of 1.2 lb/hr (540 cc/hr) and is free of oxygen.
- (3) The contents of the potable-water tank are mixed completely.
- (4) The diffusion constant of  $0.0557 \text{ cm}^2/\text{hr}$  (oxygen) determined with Airesearch data (Appendix H; Reference VII-3) is applicable.

Based on these assumptions, the mass inflow and outflow of oxygen can be determined by the following equation:

$$N = \frac{DA}{t} (X_2^0 - X_L^0) = QX_L^0 \quad (\text{VII-1})$$

where:  $N$  = Oxygen flux rate, mg/hr

$D$  =  $0.0557 \text{ cm}^2/\text{hr}$

$A$  = 1,550 sq cm (area of polyisoprene membrane)

$t$  = 0.178 cm (thickness of polyisoprene membrane)

$Q$  = 540 cc/hr

$X_2^0$  = 70 mg/l, saturation concentration of dissolved oxygen at 25 psia  $O_2$  and  $76^\circ \text{ F}$ .

$X_L^0$  = Dissolved oxygen concentration in outflow from potable-water tank.

By substitution,

$$x_L^O \approx 69 \text{ mg/l}$$

The results of the above analysis indicate that the dissolved oxygen concentration in the delivered water supply is almost at saturation, i.e., at equilibrium with the oxygen pressure of 25 psia in the balancing plenum. The equilibrium dissolved oxygen concentration in the delivered supply is nearly an order of magnitude greater than attained in terrestrial waters, and is particularly noteworthy in that degasification of delivered water at the use port has been identified as a foremost problem area in both the CM and LM. The degasification of a water containing 69 mg/l oxygen at 76° F in an atmosphere of 5 psi oxygen would result in the release of 0.11 liter of oxygen per liter water. Hydrogen is the only other gas which can occur in the Command Module water system. If it is assumed that the palladium-silver hydrogen separator effectively removes fuel-cell hydrogen from the water supply, then oxygen is the primary, if not the sole cause, of the degasification problem in the Apollo Command Module.

The foregoing analysis, while accomplished under a number of assumptions, provides substantive evidence that oxygen transfer through the polyisoprene membrane is a significant factor in the water quality of the delivered supply. From a mechanistic viewpoint, evidence exists to indicate that the degree of corrosion of aluminum by halogens would be expected to decrease with increasing oxygen tension. On this basis it is probable that the high dissolved oxygen concentrations in the delivered water provided a measure of passivation against the corrosive environment resulting from chlorination.

#### Iodine Disinfection

The use of iodine in lieu of chlorine as a disinfectant in the CM water system would appear to be desirable from the standpoint that the relative corrosion rates in iodine-aluminum-high dissolved oxygen systems were found to be much less than in chlorine-aluminum systems. However, this advantage would also have to be considered relative to the interaction observed in the experimental program between iodine and polyisoprene membrane material. The study results indicate that iodine is sorbed into polyisoprene and reacted chemically with the membrane resulting in the

conversion of iodine to iodide. It was also observed that iodine diffused through polyisoprene although depletion by dilution was not observed to be as significant as by conversion. As discussed below, the loss of iodine by diffusion through the silastic membrane used in the LM water tank is a foremost problem area in the LM spacecraft water system. For the above reason iodine should not be used as disinfectant in the CM without careful evaluation at the prototype scale of the iodine uptake in, and diffusion losses through, polyisoprene.

## LUNAR MODULE

### Description

The water management system of the LM, which is shown in Figure VII-2 differs in several aspects from the CM system. The LM system is designed to provide for two sources of demand: drinking-water supply and sublimation cooling. The drinking gun provides water for drinking and food preparation for the astronauts. However, no provisions are made for either chilling or heating aboard the LM. The sublimation unit serves as a heat exchanger to chill the cooling fluid for various electrical components of the LM.

All water demands are supplied from three storage tanks that are filled with deionized water before lift-off. The large storage tank (Tank 1), which holds 400 pounds of water, is located in the descent stage of the LM. The descent tank supplies all water needs of the LM during the phase of descent from the orbiting CSM to the lunar surface and during the surface-exploration phase. During the ascent phase and the LM/CM rendezvous and linkup phases, all water requirements are met with the two 40-pound water-storage tanks (Tanks 2 and 3) in the ascent stage. The descent stage of the LM is separated before lift-off and left on the lunar surface. Storage Tank 2 is used exclusively to supply water to the sublimation unit. A check valve prevents the conveyance of water from Tank 2 to the drinking gun. Tank 3 provides drinking water, and if required, supplies water to the sublimation units. The water management system is essentially all alodine-treated aluminum; 1/4-inch-diameter tubing is used throughout the system.

The following key functional components are used in the LM water system.

- (1) Water-storage tanks: The three water tanks of the LM are made of aluminum. The LM water supply in these tanks is stored in



silastic bladders. The space between the bladders and the tank shell is pressurized with nitrogen at 45 psi. The physical dimension of one of the 40-pound water tanks are as follows: volume, 18,000 cu cm; surface area of membrane, 4,000 sq cm; and surface area of aluminum in tanks, nil.

- (2) Service lines: it is believed that the service lines in the LM are fabricated from 1/4-inch or 3/16-inch diameter Type 6061 aluminum tubing. The physical characteristics of the service lines used to move iodinated water are unknown; for discussion purposes it is assumed that the service lines for one PWT have a surface area of 1,000 sq cm.
- (3) Sublimation units: The sublimation units are heat exchangers which chill the water-glycol fluid for the various components of the LM. The units consist basically of sintered nickel plates which form a barrier between a water-ice phase at one side and a space on the other side. At the inner side of the plates a thin ice film develops which sublimates and passes through the plates to space.
- (4) Disinfectants: Iodine was selected as disinfectant for the water management system of the LM because chlorine was found to cause operating problems with the sublimation units used in the system. The potable-water specification of NASA calls for a minimum residual iodine concentration of 0.5 milligram per liter.

Only preflight disinfection procedures are used with the LM. Approximately seven days before lift-off, the water management system of the LM is filled with a 30 mg/l iodine solution. After 1 hour, the system is drained and refilled with deionized water (Millipore Super Q Unit) to which 10 mg/l iodine solution has been added. This final fill is left in the LM tanks and is used to supply water requirements during the lunar mission.

#### Problem Areas

The key problem areas found in the LM water system have been related to (1) attrition of iodine levels due primarily to the permeation of iodine through the silastic membrane and to a lesser extent, due to the interaction of iodine with the metallic components of the system, and (2) due to the

transport of dissolved gases into, through, and out of the system to points of use. The above problems, while similar to those in the CM, assume different priorities of importance in that the depletion of iodine by diffusion is the most significant identified problem in the LM whereas corrosion is the most serious identified problem in the CM.

#### Disinfectant Interaction With Membrane Material

The principal problem of disinfectant interaction with the silastic membrane in the LM has been identified as loss of iodine from the storage tanks by diffusion through the membrane. Evidence developed in the experimental program of this study indicates that the permeability of silastic varied randomly with an increasing time-concentration exposure history of the membrane to iodinated water. Other interactions of the silastic with iodine as defined in this study were: sorption of iodine into the membrane; and conversion of iodine to iodide on membrane surfaces and possibly elsewhere.

#### Corrosion

The interaction of iodine with aluminum has caused corrosion in the LM water system as evidenced by the presence of nickel in samples taken from the ascent tank use-port and of cadmium in samples from the descent-tank use port. Evidence presented in Chapter IV of this study substantiates the degree of corrosion which can occur in aluminum-iodine systems. The reaction constant for conversion of iodine to iodide on aluminum surfaces in mixed systems was found to be  $1.33 \times 10^{-2}$  liter/sq cm-day (Chapter V), or five-times greater than the conversion reaction constant for stainless steel.

Aside from information developed in the present study as well as several observations presented in a NASA report (Reference VII-4) there are no additional sources of information on iodine-aluminum interaction. Particularly lacking are data on rates of diffusion of iodine in water at 76° F; and data on the circulation and mixing (or non-mixing) regimes existing in the LM.

#### Microbial Contamination

Samples of the LM water supplies can be taken only during the pre-flight period inasmuch as the components of the LM are left on the lunar surface or in lunar orbit. Tests for coliforms, anaerobic bacteria, yeasts, and molds have been made. The aerobic organism Flavobacterium has been

found in a water supply prepared for transfer to the LM; after iodination, no organisms of any kind were found in this water supply prior to transfer or in the LM after transfer. In all instances, after iodination procedures have been completed preflight, no bacterial growth has been obtained from any samples.

#### Gas Transport

Similar problems of degassing have occurred at the use ports of the LM as have occurred in the CM. In the LM it is believed that the gases were nitrogen diffusing into the water supply from the balancing plenum of the potable-water tanks or dissolved air in the water supply added to the LM spacecraft.

#### Summary of Problem Areas

The foregoing review of the problem areas and information on hand indicates that the following problem areas can be evaluated:

- (1) Depletion rates of iodine from a storage tank due to diffusion through the silastic membrane.
- (2) Magnitude of iodine depletion by diffusion as compared with depletion by sorption to the silastic membrane.
- (3) An estimation of the iodine depletion due to conversion on the aluminum service lines.
- (4) An estimation of the amount of nitrogen dissolution (degassing at the use-ports).

#### Iodine Depletion

##### Depletion by Diffusion

The depletion of iodine from one of the 40-lb LM water storage tanks (Tank No. 3) can be estimated using the following equation:

$$\ln \frac{X_1^I}{X_2^I} = - \frac{DA}{tV} (\theta_2 - \theta_1) \quad (\text{VII-2})$$

where:  $X_1^I$  = initial iodine concentration, mg/l, at time  $t_1$

$X_2^I$  = final iodine concentration, mg/l, at time  $t_2$

$D$  =  $10 \times 10^{-2}$  sq cm/hr (average diffusion constant for completely mixed system from Chapter IV).

$A$  = 4,000 sq cm, area of silastic membrane.

$V$  = 18,000 cu cm, volume of tank.

$t$  = 0.080 cm, silastic thickness

By substitution,

$$\ln \frac{X_1^I}{X_2^I} = 0.278 (t_2 - t_1) \quad (\text{VII-3})$$

Equation VII-3 has been used to develop the curve in Figure VII-3, which is a relationship between  $X_2^I/X_1^I$  and time.

The relationship in Figure VII-3 indicates that, for an initial iodine concentration of 12 mg/l, less than 0.5 mg/l of iodine would remain after 12 hours. This rate of depletion is far in excess of the depletion rates observed by NASA (Reference VII-4) for the same initial concentration, viz., 6 mg/l after three days, and 2.5 mg/l after five days. These differences are sufficiently significant to indicate that iodine depletion by dilution through the silastic membrane is not the rate-limiting step in the depletion; rather, this analysis is strong evidence that iodine diffusion through the bulk fluid to the membrane is rate-limiting.

The NASA observation of an iodine concentration of 2.5 mg/l at five days (following an initial iodine concentration of 12 mg/l at time zero) was used to estimate an effective diffusion constant for the prototype. The effective diffusion constant was found to be 0.005 sq cm/hr observed in the laboratory studies. A curve has been plotted in Figure VII-3 using the effective diffusion constant.

The above analysis points to the sensitive relationship between the iodine residual in the LM and the mixing regime of the bulk fluid. It is unknown what effective degree of mixing of tank contents is effected by launch, maneuvering in space, lunar landing, etc., and consequently a prediction of the iodine depletion could be made only between the boundary conditions defined by the depletion curves in Figure VII-3. Another problem exists relative to the unmixed system, viz., that if the bulk diffusion of iodine is rate-limiting, then it is uncertain what concentration gradients exist in the tank and what iodine residuals may result in peripheral sectors of the tank as a result of these gradients. Thus, with the level of information currently available, it is apparent that both mixed and unmixed systems offer serious disadvantages from the viewpoint of maintaining iodine residuals deemed adequate for disinfection.

#### Depletion by Sorption

The sorption isotherm for silastic was presented in Chapter IV

(Table IV-2) is as below (unit area basis):

$$X_S = \frac{0.130 X_L}{7.6 + X_L} \quad (\text{VII-4})$$

where:  $X_S$  = sorbed concentration of iodine on silastic, mg/sq cm

$X_L$  = liquid equilibrium iodine concentration, mg/l

Equation VII-4 can be used to estimate the initial iodine uptake by the membrane, using the following assumptions:

- (1) Initial iodine concentration: 12 mg/l
- (2) Membrane area: 4,000 sq cm
- (3) Tank volume: 18,000 cu cm

The initial iodine demand equals  $(0.130)(12)(4,000)/(7.6 + 12)$ , or 319 mg iodine. The total mass of iodine in the tank, at an equilibrium concentration of 12 mg/l and a tank volume of 18 liters, is 216 mg, or less than the initial demand. From this analysis it can be reasoned the membrane has an extremely significant demand for iodine, that the pre-soak procedure used by NASA may satisfy some portion of the above demand, and that some level of equilibrium is set up between the bulk fluid and the membrane to which the initial iodine level adjusts.

#### Conversion on Aluminum Service Lines

The steady state rate of conversion of iodine to iodide on the aluminum service lines can be estimated for any residual iodine concentration level using the equation:

$$C = K_{C-A}^I AX^I \quad (\text{VII-5})$$

where:  $C$  = flux rate or conversion rate of iodine

$$K_C^I = 1.33 \times 10^{-2} \text{ liter/sq cm - day}$$

$A \cong 1,000$  sq cm (assumed surface area of service lines for one PWT)

By substitution, at  $X^I$  equals say 3 mg/l,

$$C = 40 \text{ mg/day}$$

The above calculation implies that the conditions exist in the system which permit steady-state conversion. Needless to say, such is not the case. However, the above calculation indicates that conversion can be a significant sink for iodine, even under conditions of declining rate conversion such as would occur in the LM water delivery system. The facts

that conversion does occur and that the water delivery system presents a significant surface area for conversion is strong evidence that little or no residual iodine exists in the water delivered to the use ports.

#### Summary

The implications of the above estimates of iodine depletion by diffusion, membrane sorption, and conversion on service lines are sufficient and weighty evidence to conclude that, over the extent of a lunar mission, the disinfection procedures used in the LM do not provide an iodine residual sufficient for protection against microbial contamination. The totally undefined, and perhaps unanswerable question, of what type of mixing regime exists in the water storage tanks, alone is sufficient question to raise serious doubts as to the efficacy of the current pre-flight disinfection procedure. The above concern over the currently unidentifiable adequacy of the disinfection approach is amplified by the fact that there is no way to monitor, at the end of a mission, the residual iodine concentration or the microbial population present in the delivered water.

#### Nitrogen Concentration in Delivered Lunar Module Water Supply

The level of dissolved nitrogen in the delivered supply of the LM can be estimated by assuming that, over the duration of a mission, the stored water supply achieves a dissolved nitrogen concentration in equilibrium with the nitrogen (45 psi) in the balancing plenum. The solubility of nitrogen in water at 76° F is 0.0144 liter N<sub>2</sub> at STP/liter water-atm N<sub>2</sub>. The cabin of the LM is pressurized at 5 psi oxygen; thus all the dissolved nitrogen will be released eventually. At 76° F (24.4°C), the volume of nitrogen gas released per liter of water delivered to the cabin will be:  $0.0144 \times \frac{45}{14.4} \times \frac{297}{273}$ , or 0.048 liter N<sub>2</sub>/liter water. Thus it is estimated 48 ml of nitrogen gas will be released per liter of delivered water in the LM.

#### ORBITAL WORKSHOP

##### Description

The Saturn V Orbital Workshop (OWS) water system consists basically of a series of 10 water storage tanks which will be used to supply sequentially and separately the water demands of a wardroom, head, and a portable system. The OWS total spacecraft concept is now in the design review stage, and the concerns, from a sanitary-engineering perspective, relate primarily to maintenance of a residual iodine level in the 10 water storage tanks

over a one-year period between launch and initial usage of the supply

Each of the 10 water storage containers (as well as the remainder of the system) will be fabricated from series 300 stainless steel and will consist of a cylindrical shell into which an expandible stainless steel bellows is fitted. When the tank is filled the bellows will be in a collapsed position and the capacity of the tank will be 315 liters (19,310 cu in) (Reference VII-5). The surface area of the tank and bellows will be 79,000 sq cm (Reference VII-5). Each container will have a water quantity indicator; bleed, use and service ports; an iodine injection port that provides access to the water for iodine injection (configuration unknown); a heater blanket to prevent the water from freezing during orbital storage; and other fittings (Reference VII-6). It is unknown what level of recirculation or mixing regime will be imposed on the contents of the 10 water storage containers.

The mode of operations currently planned for the OWS water system is that degassed water (specifications undefined) will be used to fill the water system prior to launch. It is planned that an iodine solution be added during ground servicing to provide an initial iodine level of 12 mg/l.

#### Potential Problem Areas

At the current level of design development the foremost questions of concern can be identified as:

- (1) What is the rate of corrosion of stainless steel in contact with iodinated water and what is the possibility of differential corrosion occurring on the continually flexing edges of the metal bellows?
- (2) A corollary question to Item (1) is what is the least corrosive type of stainless steel that can be selected?
- (3) Will iodine depletion occur due to conversion of iodine to iodide in conjunction with corrosion of the stainless steel, and will the extent of depletion preclude adequate disinfection?
- (4) What effect will a reduced level of dissolved oxygen associated with degassed water have on the corrosion rate, particularly as relative to finding of the present study?
- (5) What degree of mixing, or stratification, will be achieved in the OWS water system during launch, orbital maneuvering, etc.?

### Present Information Level

Other than the present study, the only source of information to even begin looking at the above problem areas is available in the raw data developed by McDonnell-Douglas Astronautics Laboratory (Reference VII-7). These studies were directed to an evaluation of iodine depletion over 15-day periods in four reduced-scale models of OWS water storage containers. Each container was made of a different type of series 300 stainless steel, viz., Types 304L, 316-13, 321, and 347; initial iodine levels of 7.3 to 7.6 mg/l were used.

An analysis and interpretation of the McDonnell-Douglas are presented in Appendix I. Several key points can be reiterated from discussion (in Appendix I) of the findings of Reference VII-7. First, no information was published in Reference VII-7 to indicate the level of dissolved oxygen in the test solutions, and the temperature of the test solutions during the depletion studies was not reported. Both of these variables have fundamental roles in the diffusion and corrosion process purportedly of concern. Second, no definition was made of the mixing regime. The above information gaps render the value of the McDonnell-Douglas data as minimal without many qualifications; it was necessary in using the data to make the following assumptions: zero mixing in the bulk fluid; and temperature at that level (unknown) to be maintained in the OWS.

With the above qualifications, and with the added uncertainty in Reference VII-7 as to the validity of the analytical techniques, an analysis of the iodine depletion data (Appendix I) showed that the lowest reaction constant for the iodine conversion ( $1.98 \times 10^{-5}$  liter/sq cm-day) was in the Type 304 stainless steel tank. The highest reaction constant, ( $3.19 \times 10^{-5}$  liter/sq cm-day) was observed in the Type 347 stainless steel tank. It is noteworthy that the above depletion constants, assumed to be obtained in unmixed systems, are about two orders of magnitude less than the iodine-stainless steel constant of  $2.40 \times 10^{-3}$  liter/sq cm-day obtained in the completely-mixed corrosion experiments in this study.

A graphical comparison of iodine depletion by conversion using the McDonnell-Douglas constant and the constant developed in the present study is given in Figure VII-4. The relationships were developed using the following equations:



$$\ln \frac{X_1^I}{X_2^I} = \frac{K_{C-A}^I}{V} (\theta_2 - \theta_1) \quad (\text{VII-5})$$

where:  $A = 79,000$  sq cm  
 $V = 315$  liters

It is apparent from the curves in Figure VII-4 that the degree of mixing has a profound effect on the iodine depletion. In a completely stirred system at 76° F, the iodine level would equal less than 0.5 mg/l in less than five days. In the assumedly unmixed system, the residual iodine level is estimated to be 1.6 mg/l after one year, a level which meets the current NASA specification of 0.5 mg/l as a minimum level for disinfection. This analysis as well as that presented previously for the LM are weighty evidence that, unless the mixing regime is defined, there is no certainty that a residual iodine level associated with adequate disinfection can be maintained in the OWS water system over a one-year period. Moreover, there also exists the uncertainty in the unmixed system that iodine concentration gradients in the unmixed system will result in zones in the tankage wherein residual iodine concentration do not meet specifications for disinfection. Furthermore, because of the lack of fundamental information on bulk iodine diffusion coefficients, little can be said as to what levels will be maintained in the unmixed system, or what degree of mixing is necessary to effect a satisfactory tradeoff between maintaining adequate iodine levels for disinfection and minimizing the concentration-driven rate of conversion.

Another facet of the problem areas identified above relates to the decision to degas the water supply to be used in the OWS. The results of the corrosion study indicated that the relative rate of metal corrosion in iodinated waters increased as the dissolved oxygen level is decreased. Thus there is serious concern, from the standpoint of minimizing corrosion, that degasification of the supply is not appropriate. There is also concern, from a palatability standpoint, that degasification will not improve the quality of the water.

The above information answers but a few of the aspects in the five questions outlined above. To date, no information exists in several problem areas, the most overwhelming gaps being lack of definition of: the mixing regime; the effect of dissolved oxygen levels on the rate of corrosion; and the bulk diffusion constant of iodine. As has been demonstrated

in the calculations presented herein, each of the above areas is so fundamental to the process controlling the rate of iodine depletion that it is difficult to recommend consideration of other aspects of the problem without first defining these areas.

#### SUMMARY

The findings of the engineering evaluation presented in this chapter can be summarized as follows:

- (1) There exists no substantive data with which to describe systematically the following:
  - a. Effects of varying levels of ionic, disinfectant, and dissolved oxygen concentrations on the kinetics of aluminum corrosion by iodine.
  - b. Bulk diffusion constants for iodine and for chlorine in aqueous systems at 76° F.
  - c. Definition of the degree of mixing effected by the dynamics of spacecraft movement and throughput rates on water stored in spacecraft water systems.
- (2) Degasification is predicted to occur in both the LM and CM due to the significant solutions of gases which is permitted by the water system configuration.
  - a. In the CM, it is estimated that in excess of 100 ml of dissolved oxygen are released per liter of delivered water. There is evidence from the corrosion experimentation in the present report that the high dissolved oxygen concentrations in the CM water system effect a degree of passivation in the water system.
  - b. In the LM, it is estimated that about 50 ml of dissolved nitrogen are released per liter of delivered water.
- (3) From a corrosion standpoint, iodine is a less corrosive chemical than chlorine, yet possesses a similar level of disinfective capacity. If the use of iodine as a disinfectant in the CM were being considered, a detailed evaluation of the interaction between iodine and the polyisoprene membrane is needed before the efficacy of the use of iodine in the CM can be established.
- (4) In both the LM and OWS water systems bulk iodine diffusion rather than diffusion through a membrane (LM) or conversion at metal

surface (OWS) was implicated as the rate-limiting step in the depletion of iodine from these systems.

- (5) The mixing regime is the most significant undefined mechanism in spacecraft water systems, in that:
  - a. In the completely mixed system the rate of iodine depletion is several orders of magnitude greater than in the unmixed system; calculations presented in this chapter indicate that it is impossible to maintain an acceptable residual iodine concentration in the LM after a few hours and in the OWS after a few days.
  - b. It is assumed in the unmixed system that the bulk diffusion of iodine is rate-limiting in the iodine depletion process; the concentration gradient of iodine established under this condition may result in iodine concentrations in peripheral sectors of the tankage which are below minimum levels specified for disinfection.
  - c. For the above reasons both mixed and unmixed systems offer serious disadvantages from the viewpoint of maintaining iodine residuals adequate to effect disinfection.

## REFERENCES - CHAPTER VII

- VII-1 "Spacecraft Water Supply and Quality Management in the Apollo Program", by Richard L. Sauer and Timothy G. Shea, paper presented at the International Water Conference of the Engineer's Society of Western Pennsylvania, Pittsburg, October 28-30, 1969.
- VII-2 "Apollo CSM 101 Potable Water System Simulator", Report SD68-911, prepared by R. S. Pearce, Space Division, North American Rockwell Corporation, November, 1968.
- VII-3 "Development Test Data - Potable Water Tank Bladder Oxygen Permeability Tests", Memorandum, NR/SD Project Apollo, DTD-222, AIREsearch Manufacturing Division, Garrett Corporation, 26 August, 1969.
- VII-4 "Documentation and Summary of Analytical Data from Apollo 10 CSM 106/LM-4 Potable Water", Memorandum to R. L. Sauer from Sanitary Engineer, Contract NAS 9-6568, S/D.J. Colley, 10 June, 1969.
- VII-5 Personal Communication, R. L. Sauer, 14 January, 1970.
- VII-6 "Engineering Status Report - SVWS Water System", to T. A. Cook from Jack C. Temple, McDonnell-Douglas Astronautics Company, 27 October, 1969.
- VII-7 "OWS Water System Material Selection Tests", Memorandum to R. L. Sauer from Jack Temple, McDonnell-Douglas Astronautics Company, 9 January, 1970.

# COMMAND MODULE WATER SYSTEM SOURCE: REFERENCE VII-1

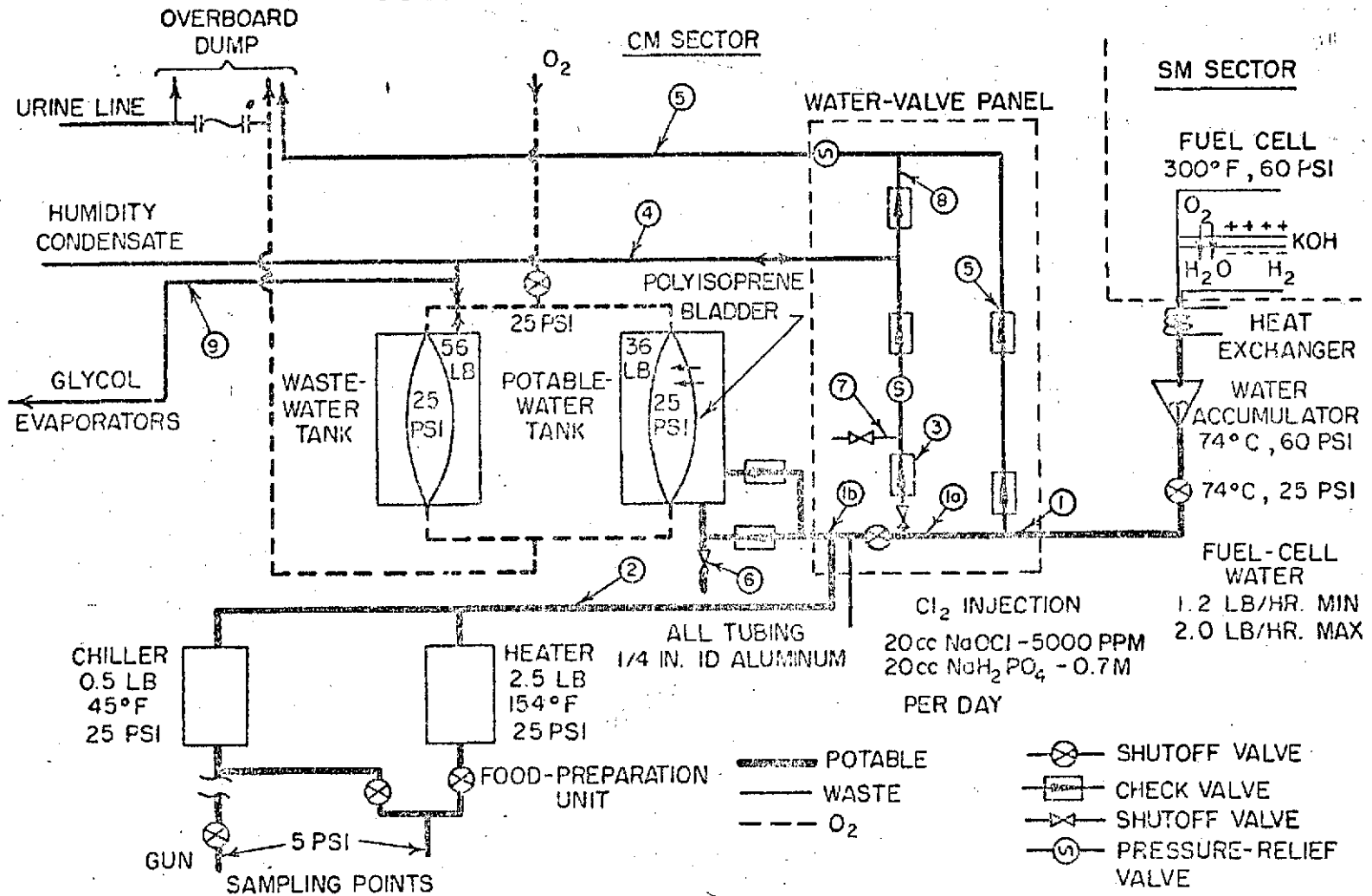


FIGURE VII-1

LUNAR MODULE WATER SYSTEM  
SOURCE: REFERENCE VII-1

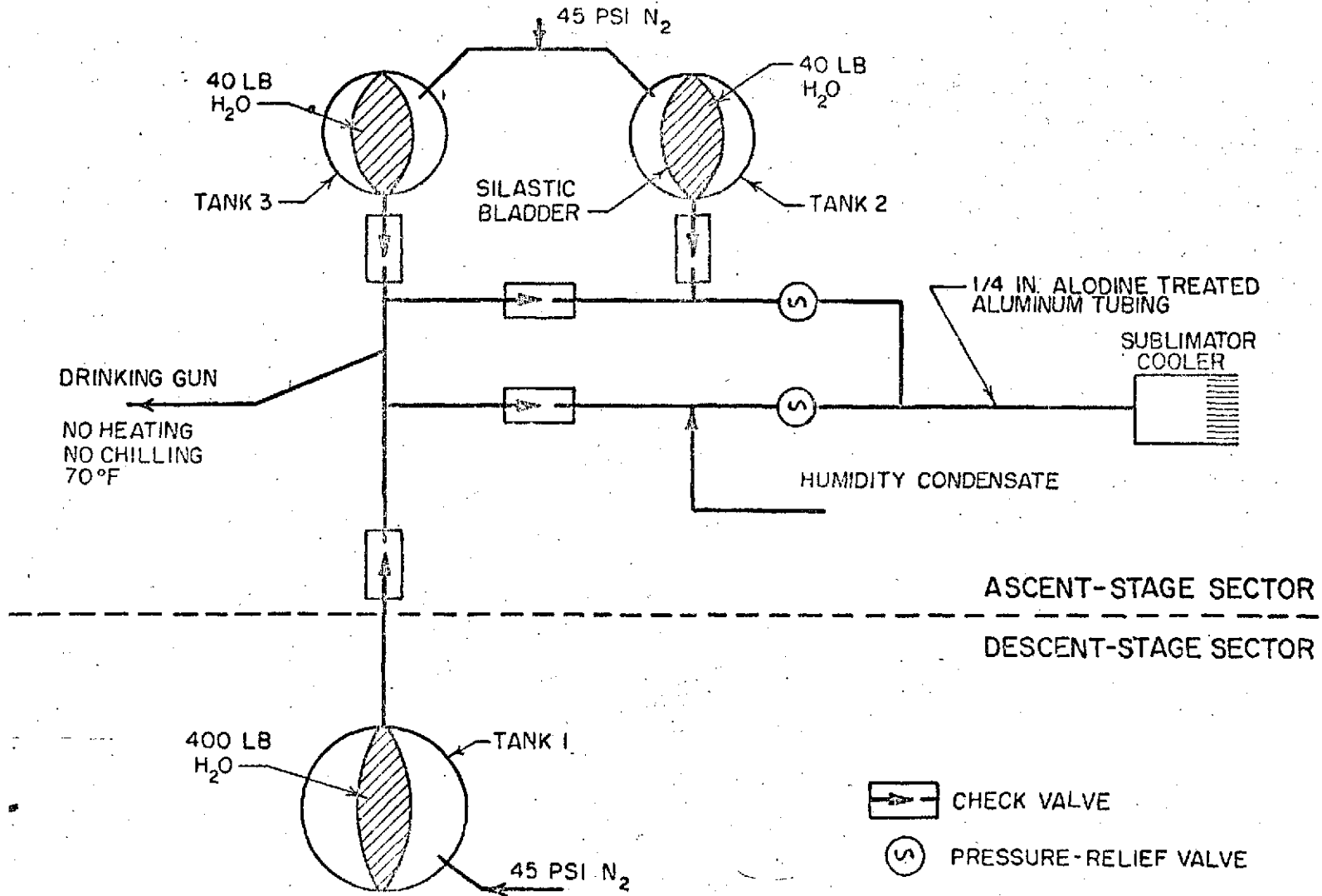


FIGURE VII-2

PREDICTED IODINE DEPLETION BY DIFFUSION THROUGH SILASTIC MEMBRANE  
 IN LUNAR ASCENT WATER TANK NO. 3

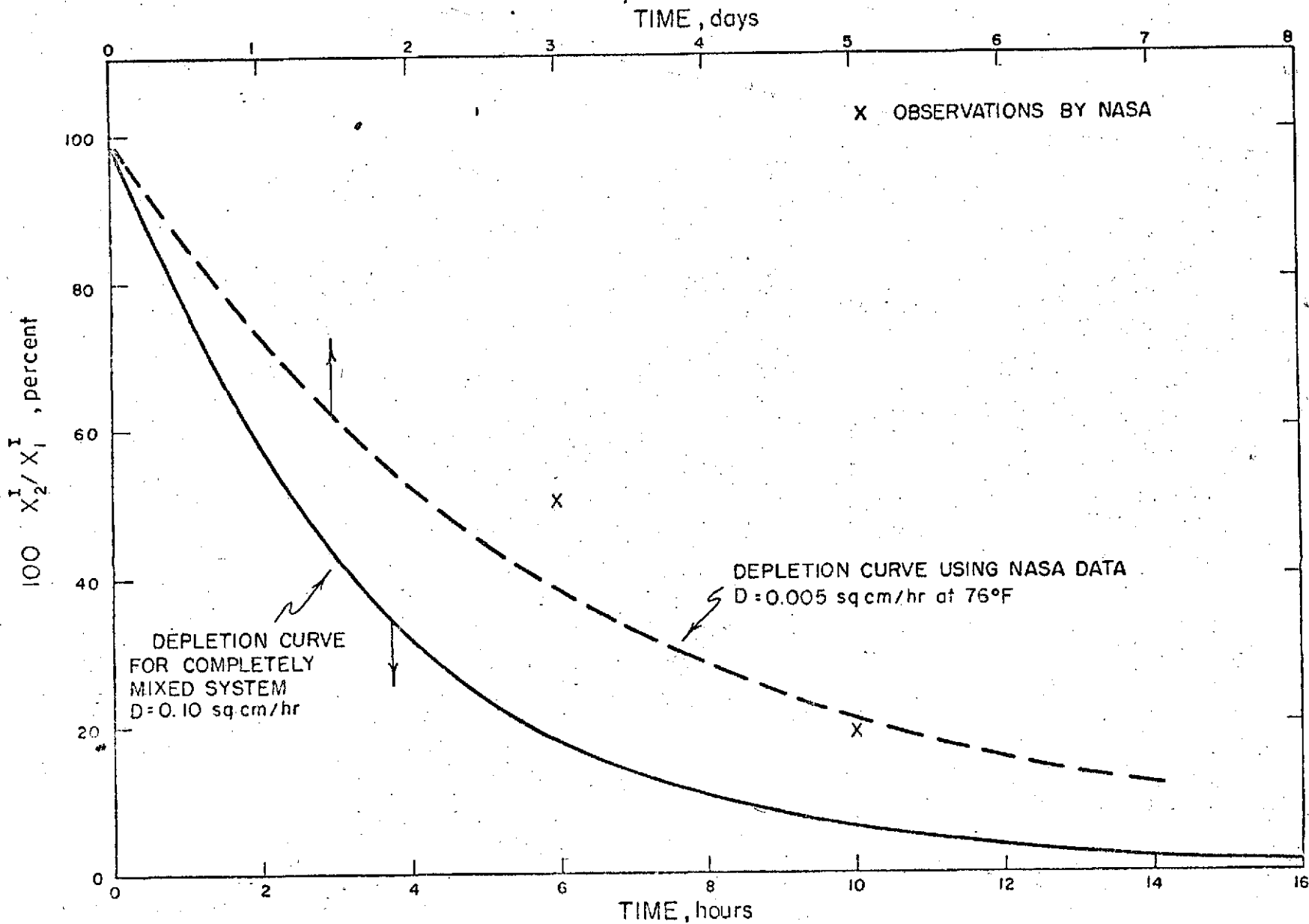


FIGURE VII-3

PREDICTED IODINE DEPLETION BY CONVERSION ORBITAL WORKSHOP  
WATER STORAGE TANKS

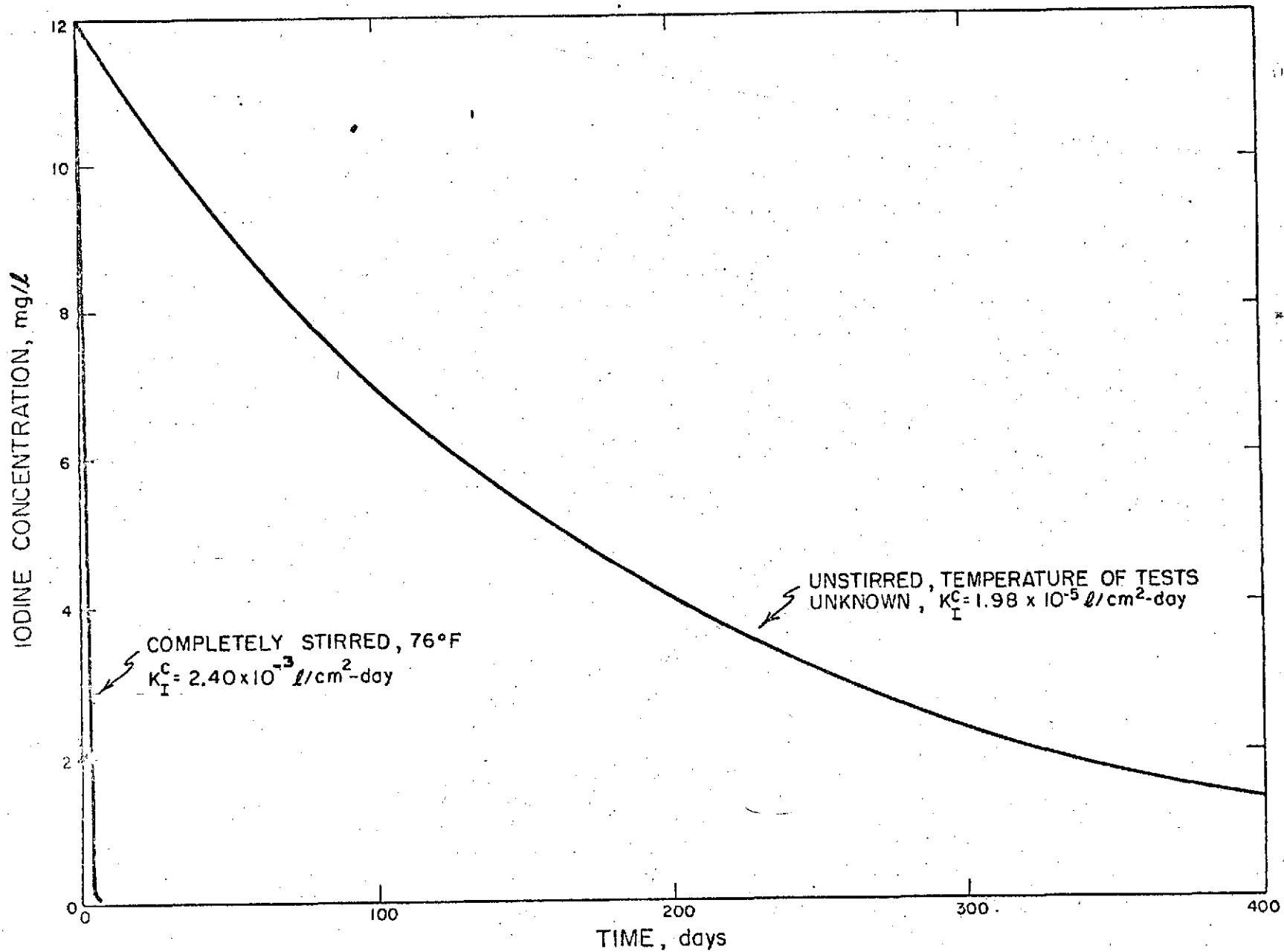


FIGURE VII-4



## CHAPTER VIII

### OBJECTIVES IN WATER SYSTEM MANAGEMENT

The basic driving forces in water system management are the objectives of the program, which, in turn, evolve from broader based policy statements. The successful operation of a water management system depends on the translation of the objectives into procedures which can be implemented. The success or failure of the implementation process, in turn, will eventually lead to a review of the policies guiding the program and, as necessary, a revision of policy to meet emerging needs in the program.

The common linkage between policy, objectives, and implementation is information, the overall impact of which on a water system management program is shown in Figure VIII-1. Information is required to provide a rational basis for development of policy such that all needs are recognized, and for development of objectives that are compatible with current technology as well as for documenting implementation. As a management program develops, there will exist a body of knowledge which defines and/or relates to various aspects of the characteristics, uses, and implications of the uses of the water system. The available information will have a strong effect on the delineation of objectives and establishment of procedures for a management program. This effect is indicated by the arrows indicating that "available information" has an effect on "objectives of water system management program" and "implementation procedures for program" as shown in Figure VIII-1.

The effects of information on the designers of a water system management program will be manifested in terms of defining those objectives and procedures which are possible or feasible based on the totality of information available in water-related fields as well as that which pertains specifically to a problem of immediate concern in the system. For example, at present an objective could be to adjust the concentration of dissolved oxygen in ground support water to reduce corrosion. Such an objective would not have been established a year ago because there was insufficient evidence to indicate the need for it.

The implementation procedures define the level of responsibility for decisions in a water system management program by delimiting the courses of action that can be taken and what is needed for an efficacious solution.

The available information is the factor defining the decision capacity which is resident in the agency. The sequence of elements, or feedback loop, leading from objectives through level of responsibility for decisions and ultimately, back to objectives. Another feedback loop exists from available information, through decision capacity, information collection and information, available information, and ultimately leading back to modification of objectives. If it is assumed that decision capacity is based on information and that other level of information are required for dealing with decision responsibilities, then the difference between the decision responsibilities and decision capacity can be used to define the additional information required to permit a water system management program to assume its decision responsibilities. Subsequent to the definition of information requirements the information can be acquired either through the in-house efforts of the program or through information and data acquisition programs resident in outside facilities. Depending on the size and scope of the program it may be desirable for the agency to expand a major portion of its effort in the evaluation of information relative to its own needs. The collection, completion, and evaluation of information increases the level of information available which, as shown in Figure VIII-1, permits modifications of the objectives and implementation procedures of the program. It is this cyclic process, driven off available information and resulting in continuous modifications of objectives and procedures, which is vital to a program if its decisions and actions are to be responsive and germane to the problems of water system management over time. Exogenous inputs, which are not part of the feedback loops, relate to information generated by other programs, policies, and research and development efforts relative to similar or different aspects of water system management.

The system in Figure VIII-1 shows that information should be obtained only when there is a defined need and the required information has been defined specifically. The acquisition of information because it is easily obtained cannot be justified by any program. An accountability should exist between what is obtained and what its utility is.

The cyclic processes defined in the decision responsibility and design capacity loops in Figure VIII-1 can function independent of each other, a process which occurs when perception does not exist of the dif-

ference between the decision responsibilities and decision capacity. This situation gives rise to the circumstance in which the information required to permit a program to operate at a level germane to its problems remains undefined, with the net effect that the decision capacity of the program is driven by available information rather than from defined information needs. Such a situation can be self-perpetuating in the sense that as the available information increases, and, because of the feedback loop in Figure VIII-1, it is possible to continue increasing decision capability without any required reference to objectives. However, because this process can proceed without a recognition of a growing gap in information needs for decision responsibility relative to decision capacity, it is totally fortuitous that the increase in decision capacity is relevant to that required to meet decision responsibility.

The above discussion is closely related to what appears to be the current situation in the water system management program at NASA. Chapter VII of this study is an evaluation of available information relative to defined data needs required to make fundamental decisions about how to accomplish disinfection and corrosion control. It is apparent in Chapter VII that there is a significant gap of information between what is now known about the spacecraft water systems in which disinfection and corrosion control must be implemented and what information is needed. The information gap exists in spite of significant information inputs from outside organizations and from other programs involved in water system management, as well as from data collection and evaluation process at NASA.

In order to eliminate the information gap that has arisen in the current management program at NASA, a positive redefinition of objectives and implementation procedures is needed. If such a redefinition is considered, it is recommended that the following be integrated into program policy at NASA.

(1) Policy

- a. No water system, the management of which is vested in one responsible division, should be approved for use in a spacecraft without the approval of the responsible division.
- b. All objectives and policy developed within the division at NASA responsible for water system management should be re-

viewed and approved by the entire NASA organization before becoming part of the body of policy of the responsible division. Planned actions on the part of any division impinging on water system management should be reviewed by the responsible division before being carried out.

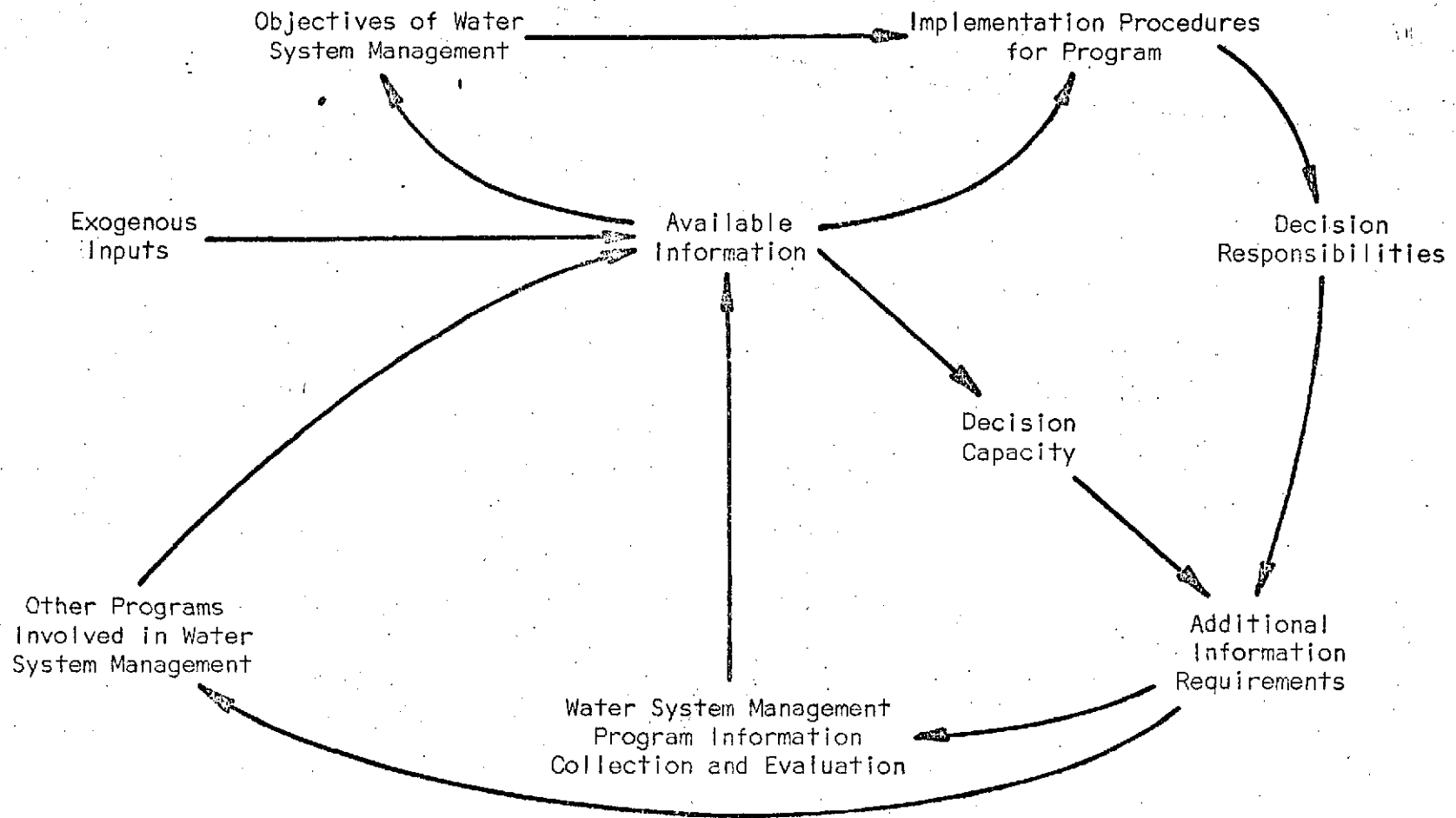
(2) General Objectives

- a. All water-oriented spacecraft systems should be planned, designed, and operated to maximize preservation of component integrity.
- b. The health of the crewman should be protected against infection or toxication to the extent that is accepted in the terrestrial environment.
- c. The aesthetic quality of the water supply should be protected at levels commensurate with the duration and type of mission.

(3) Specific Objectives

- a. A water system concept submitted to NASA for approval should be accompanied by the following documentation:
  1. Documentation of mass transfer and conversion processes operative in the system, including description of mechanisms of concern, relationships to be used in predicting system behavior, and calculations indicating that system performance is commensurate with water system standards of the responsible division.
  2. Documentation of the operating and monitoring requirements to achieve performance levels in the system commensurate with water system standards.
  3. Identification of areas where inadequate technology exists to define the mechanisms and relationships governing expected process behavior.
- b. A set of water system standards should be developed to ensure the protection of system integrity, health of astronauts, and aesthetic quality of the supply. The rationale and engineering, medical, toxicological, and other criteria for each standard should be documented; areas where information is inadequate to define the rationale for a standard should be identified.

- c. A statement of research and development priorities should be developed and updated as the cornerstone instrument for developing, through internal or external effort, the technology required to develop objective statements and implementation procedures for water system management.



OBJECTIVES AND INFORMATION IN  
WATER SYSTEM MANAGEMENT

APPENDIX A

GLOSSARY OF TERMS

## APPENDIX A

### GLOSSARY OF TERMS

<u>Symbol</u>	<u>Description and units (Length, Mass, Time)</u>
V	Volume of solution containing reactant ( $L^3$ )
A	Surface area of membrane or exposed metal ( $L^2$ )
X	Concentration
	(a) Subscripts
	$X_1$ - Initial concentration ( $M/L^3$ )
	$X_2$ - final concentration ( $M/L^3$ )
	$X_S$ - sorbed concentration per unit area of membrane ( $M/L^2$ )
	$X_A$ - sorbed concentration per unit volume of membrane ( $M/L^3$ )
	$X_L$ - liquid equilibrium concentration ( $M/L^3$ )
	(b) Subscripts
	$X^M$ = maximum value
	$X^I$ = iodine ( $I_2$ )
	$X^V$ = concentration at test cell volume V
	$X^O$ = oxygen ( $O_2$ )
K	Reaction Constant
	(a) Subscripts
	$K_{S-A}$ - Substitution reaction constant per unit area of membrane (1/T)
	$K_{S-V}$ - Substitution reaction constant per unit volume of membrane (1/T)
	$K_{C-A}$ - Conversion reaction constant per unit area of membrane (L/T)
	$K_{C-V}$ - Conversion reaction constant per unit volume of membrane (1/T)
	(b) Superscripts
	$K^S$ - silastic
	$K^P$ - polyisoprene
	$K^U$ - polyurethane
	$K^A$ - aluminum
	$K^{SS}$ - stainless steel



## APPENDIX A (Continued)

### GLOSSARY OF TERMS

<u>Symbol</u>	<u>Description and Units (Length, Mass, Time)</u>
$\theta$	Time (T)
	(a) Subscripts
	$\theta_1$ - initial time
	$\theta_2$ - final time
D	Diffusion Constant ( $L^2/T$ )
S	Saturation Constant ( $M/L^3$ )
t	Membrane Thickness (L)
$k_f, n_f$	Freundlich Isotherm Constants
$i_p$	Polarization current density
$i_o$	Exchange current density
$\alpha$	Charge transfer coefficient
$\eta$	Polarization overvoltage ( $E - E_{cor}$ )
F	Faraday constant
R	Universal gas constant
T	Temperature (absolute)
$b_1$	Anodic Tafel constant
$b_2$	Cathodic Tafel constant
$k_c$	Empirical corrosion constant
$i_{cor}$	Corrosion current
N	Flux rate ( $M/L^2 - T$ )
$k_m$	Bacterial inactivation constant
C	Conversion rate (M/T)

APPENDIX B

MEMBRANE TESTING BASIC DATA

TABLE B-1

UPTAKE DATA FOR BLANKS

Date	Time	θ Hrs	I <sub>2</sub> mg/l	TI mg/l	Notes
4/12/69	1:30 PM	0.00	8.2	9.2	
4/12/69	6:45 PM	5.25	8.3	9.0	
4/12/69	11:05 PM	9.58	8.0	9.5	
5/12/69	2:25 PM	24.92	7.5	8.5	
8/12/69	10:30 AM	93.00	7.3	9.0	
10/12/69	4:10 PM	147	7.7	8.3	
16/12/69	11:40 AM	286	7.30	-	
18/12/69	11:20 AM	334		8.80	
4/12/69	1:00 PM	0.00	14.8	15.0	
4/12/69	7:10 PM	6.17	14.5	16.6	
4/12/69	11:05 PM	10.08	14.6	16.0	
5/12/69	2:25 PM		14.8	15.6	
8/12/69	10:30 AM	93.5	13.2	15.6	
10/12/69	3:05 PM	146.0	14.8	1.0	
16/12/69	11:40 AM	286.0	11.6	-	
18/12/69	11:15 AM	334.0	12.8	14.5	
11/12/69	1:00 PM	0.00	33.5	36.5	
16/12/69	11:40 AM	119	33.4	-	
18/12/69	11:10 AM	166	31.4	32.0	

TABLE B-2

SILASTIC MASS TRANSFER TEST DATA:  
NO PRIOR IODINE CONTACT

Date	Time	θ Hrs	I <sub>2</sub> mg/l	TI mg/l	Notes
4/12/69	12:30 PM	0.00	34.0	<del>39.0</del>	Mass Transfer Begun
4/12/69	6:45 PM	6.25	26.7	28.3	
4/12/69	10:30 PM	10.00	22.7	25.0	
5/12/69	2:25 PM	26.0	12.6	13.3	
5/12/69	10:30 PM	34.0	8.6	12.0	
6/12/69	6:45 PM	54.25	3.7	4.8	
7/12/69	5:00 PM	76.5	1.45	-	
8/12/69	11:00 AM	94.5	0.5	2.0	
10/12/69	3:05 PM	147	0.300	2.07	

TABLE B-3

SILASTIC TEST DATA: FOUR DAYS  
UPTAKE PLUS MASS TRANSFER

Date	Time	$\theta$ Hrs	$I_2$ mg/l	TI mg/l	Notes
4/12/69	1:30 PM	0.00	8.2	9.2	
8/12/69	12:10 PM	94.67	5.8	6.8	Mass Transfer Begun
8/12/69	5:10 PM	99.67	6.2	6.5	
8/12/69	9:10 PM	104	5.2	-	
9/12/69	10:40 AM	117	3.1	4.5	
9/12/69	9:30 PM	128	3.0	-	
10/12/69	5:10 PM	148	1.4	2.1	
4/12/69	1:00 PM	0.00	14.8	15.0	
8/12/69	12:10 PM	95	11.2	11.6	Mass Transfer Begun
8/12/69	5:10 PM	100	10.8	12.0	
8/12/69	9:10 PM	104	8.9	-	
9/12/69	10:40 AM	118	5.4	7.0	
9/12/69	9:30 PM	129	4.4	-	
10/12/69	5:10 PM	148	2.6	2.9	
4/12/69	12:30 PM	0.00	34.0	39.0	
5/12/69	11:40 AM	23.17	32.0	36.5	
8/12/69	10:30 AM	94.0	29.3	33.0	
8/12/69	12:10 PM	95.67	34.5	40.0	Mass Transfer Begun
8/12/69	5:10 PM	101	27	28	
8/12/69	9:10 PM	105	22.6	-	

TABLE B-3 (Continued)

SILASTIC TEST DATA: FOUR DAYS  
UPTAKE PLUS MASS TRANSFER

<u>Date</u>	<u>Time</u>	<u><math>\theta</math> Hrs</u>	<u>I<sub>2</sub> mg/1</u>	<u>TI mg/1</u>	<u>Notes</u>
9/12/69	10:40 AM	118	13.4	15.6	
9/12/69	9:30 PM	129	9.9	-	
10/12/69	5:10 PM	149	4.8	6.3	

TABLE B-4

SILASTIC TEST DATA: TWELVE DAYS  
UPTAKE PLUS MASS TRANSFER

Date	Time	θ Hrs	I <sub>2</sub> mg/l	TI mg/l	Notes
4/12/69	1:30 PM	0.00	8.2	9.2	
4/12/69	6:10 PM	4.67	7.8	8.3	
4/12/69	10:30 PM	9.00	7.5	8.4	
5/12/69	1:45 PM	24.25	7.8	8.5	
8/12/69	10:30 AM	93	6.2	6.8	
10/12/69	4:10 PM	147	6.4	6.7	
16/12/69	11:35 AM	286	5.00	-	
16/12/69	4:45 PM	291	5.00	6.90	(291.25 Mass Transfer Begins) makeup added
16/12/69	10:15 PM	297	4.3	5.8	
17/12/69	11:30 AM	310	2.15	3.25	
18/12/69	11:20 AM	334	0.93	2.07	
4/12/69	1:00 PM	0.00	14.8	15.0	
4/12/69	7:10 PM	6.17	13.8	15.6	
4/12/69	11:05 PM	10.08	13.6	15.6	
5/12/69	2:25 PM	25.25	13.0	14.8	
6/12/69	6:45 PM	53.75	12.6	13.5	
7/12/69	5:00 PM	76.00	12.6	-	
8/12/69	10:30 AM	93.5	11.6	13.0	
10/12/69	12:05 PM	143	12.5	14.0	
16/12/69	11:35 AM	287	9.80	-	
16/12/69	4:45 PM	292	9.60	12.80	(291.75 Mass Transfer Begins) Makeup added.
16/12/69	10:15 PM	297	4.3	5.8	

TABLE B-4 (Continued)

SILASTIC TEST DATA: TWELVE DAYS  
UPTAKE PLUS MASS TRANSFER

Date	Time	$\theta$ Hrs	$I_2$ mg/l	TI mg/l	Notes
17/12/69	11:30 AM	311	4.0	4.5	
18/12/69	11:15 AM	334	1.7	2.9	
4/12/69	12:30 PM	0.00	34.0	39.0	
4/12/69	6:45 PM	6.25	31.3	32.7	
4/12/69	10:30 PM	10.00	30.7	35.0	
5/12/69	1:45 PM	25.25	31.5	36.0	
8/12/69	10:30 AM	94.0	25.0	27.3	
10/12/69	12:05 PM	144.0	28.8	34.6	
16/12/69	11:35 AM	287	25.00	-	
16/12/69	4:45 PM	292	25.00	33.40	292.25 Mass Transfer Begins
16/12/69	10:15 PM	298	20.6	23.4	
17/12/69	11:30 AM	311	10.8	10.8	
18/12/69	11:10 AM	335	4.5	7.0	



TABLE B-5

POLYISOPRENE UPTAKE TEST DATA

Date	Time	θ Hrs	I <sub>2</sub> mg/l	TI mg/l	Notes
23/12/69	3:40 PM	0	7.4	7.9	
23/12/69	10:15 PM	6.5	2.8	3.2	
24/12/69	10:30 AM	19.0	0.21		
19/12/69	12:00 PM	0	6.8		Co from 17/12/69
21/12/69	3:00 AM	39.0		4.5	
21/12/69	1:30 AM	37.5	0.3		
22/12/69	3:20 PM	75.	0	4.55	
23/12/69	3:40 PM	0	14.5	16.2	
23/12/69	10:15 PM	6.5	10.2		
24/12/69	10:30 AM	19.0	5.1		
25/12/69	7:00 PM	57.0	0.59	6.8	
19/12/69	12:00 PM	0	11.8	-	Co for 17/12/69
21/12/69	1:30 AM	37.5	0.3	-	
21/12/69	3:00 AM	39.0	-	7.04	
22/12/69	3:10 PM	75.	0.2	7.35	
19/12/69	12:00 PM	0	30.00	31.70	
21/12/69	1:30 AM	37.5	4.0	13.0	
22/12/69	3:10 PM	75.0	.46	12.0	
29/12/69	10:15 AM	238	0	13.5	

TABLE B-5 (Continued)  
POLYISOPRENE UPTAKE TEST DATA

Date	Time	$\theta$ Hrs	I <sub>2</sub> mg/l	TI mg/l	Notes
30/12/69	11:00 AM	0	28.0	35.0	
30/12/69	5:20 PM	6.5	15.0	24.0	
31/12/69	6:30 PM	31.5	2.90	-	
1/1/70	12:00 PM	170	0	14.3	
30/12/69	11:00 AM	0	67.0	73.0	
30/12/69	5:20 PM	6.5	42.2	51.5	
31/12/69		31.5	12.6	22.4	
6/1/70	12:00 PM	170	-		
6/1/70		170		14.3	
30/12/69	11:00 AM	0	90.	95.0	
30/12/69	5:20 PM	6.5	67.5	83.0	
31/12/69	-6:30 PM	31.5	14.4	29.0	
6/1/70	12:00 PM	170	0	19.0	

TABLE B-6

POLYISOPRENE MASS TRANSFER TEST DATA

Date	Time	θ Hrs	I <sub>2</sub> mg/l	TI mg/l	Notes
19/12/69	12:00 PM	0	30.00	31.70	
21/12/69	2:30 AM	38.5	3.40		
22/12/69	3:30 PM	75.0	0.30	6.0	

TABLE B-7

VITON UPTAKE TEST DATA

Date	Time	$\theta$ Hrs	I <sub>2</sub> mg/l	TI mg/l	Notes
23/12/69	3:45 PM	0.00			
23/12/69	10:15 PM	6.5	32.0	35.7	
24/12/69	10:30 PM	18.75	27.8	32.65	
25/12/69	7:00 PM	51.25	31.8	-	
26/12/69	4:00 PM	72.5	32.3	34.3	
29/12/69	10:15 AM	138.5	30.0	30.7	
5/1/70	11:30 AM	308	29.75	34.75	
6/1/70	11:00 AM	331	28.5	36.0	
30/12/69	5:20 PM	169.5	29.5	35.3	
31/12/69	6:30 PM	194.75	30.6	37.4	

TABLE B-8

VITON MASS TRANSFER TEST DATA

<u>Date</u>	<u>Time</u>	<u>θ Hrs</u>	<u>I<sub>2</sub> mg/l</u>	<u>TI mg/l</u>	<u>Notes</u>
23/12/69	3:45 PM	0			
23/12/69	10:15 PM	6.5	32.0	33.3	
24/12/69	10:30 AM	18.75	31.3	31.7	
26/12/69	4:00 PM	72.25	32.7	35.3	
24/12/69	10:15 AM	138.5	27.0	32.7	
5/1/70	11:30 AM	308	29.5	35.5	
6/1/70	11:00 AM	331	29.5	36.0	
30/12/69	5:20 PM	169.5	29.5	34.3	
31/12/69	6:00 PM	194.75	28.2	36.0	

TABLE B-9

POLYURETHENE UPTAKE TEST DATA

Date	Time	θ Hrs	I <sub>2</sub> mg/l	TI mg/l	Notes
30/12/69	11:00 AM	0	28.0	35.0	
30/12/69	5:20 PM	6.5	20.5	22.3	
31/12/69	6:30 PM	31.5	12.5	17.4	
5/1/70	11:30 AM	145	4.3	10.8	
6/1/70	11:00 AM	169	3.8	11.0	

TABLE B-10

POLYURETHANE MASS TRANSFER TEST DATA

Date	Time	$\theta$ Hrs	$I_2$ mg/l	TI mg/l	Notes
30/12/69		0	28.0	35.0	
30/12/69	5:20 PM	6.5	18.7	20.0	
31/12/69	6:30 PM	31/5	12.6	16.2	
5/1/70	11:30 AM	145	4.3	10.4	
6/1/70	11:00 AM	169	4.1	10.5	

APPENDIX C

CALCULATIONS FOR MEMBRANE STUDIES



TABLE C-1

ISOTHERM CALCULATIONS FOR SILASTIC SORPTION OF TOTAL IODINE

$X_1 - X_L$ (mg/l)	$X_S$ (mg/sq cm)	$\frac{1}{X_S}$	$X_L$ (mg/l)	$\frac{1}{X_L}$
3.5	.110	9.09	35	.0296
2.5	.0785	12.7	12.8	.0781
2.0	.0628	15.9	6.8	.147

Given:

$$\frac{1}{X_S} = \frac{1}{X_S^M} + \frac{S}{X_S^M X_L}$$

and:

$$A = 29.2 \text{ sq cm}$$

$$V = 0.92 \text{ L}$$

From Figure C-1, for the Langmuir Isotherm;

$$t: X_S^M = \frac{1}{7.7} = 0.130, \text{ mg/sq cm}$$

$$\text{and: } S = .130 \times 58.5 = 7.6 \text{ mg/l}$$

$$\text{then: } X_S^S = \frac{0.130 X_L}{7.6 + X_L}$$

Note: Data for  $X_1 - X_L$  from Figure IV-3

TABLE C-2

ISOTHERM CALCULATIONS FOR POLYISOPRENE SORPTION OF TOTAL IODINE

$X_L$ (mg/l)	$X_1 - X_L$ (mg/l)	$X_S$ (mg/sq cm)	$\frac{1}{X_L}$	$\frac{1}{X_S}$
4.3	3.6	0.113	0.233	8.84
7.2	9.0	0.282	0.139	3.53
13.2	18.5	0.582	0.0757	1.72
14.3	58.7	1.84	0.0700	0.542
19.0	76.0	2.38	0.0526	0.418

Given:

$$X_S = k_F X_L^{1/n_F}$$

and:

$$A = 29.2 \text{ sq cm}$$

$$V = 0.92 \text{ L}$$

From Figure C-3

$$1/n_F = 1.75$$

$$k_F = 0.0089$$

$$X^S = 0.0089 X_L^{1.75}$$

LANGMUIR ISOTHERM FOR SILASTIC  
SORPTION OF TOTAL IODINE

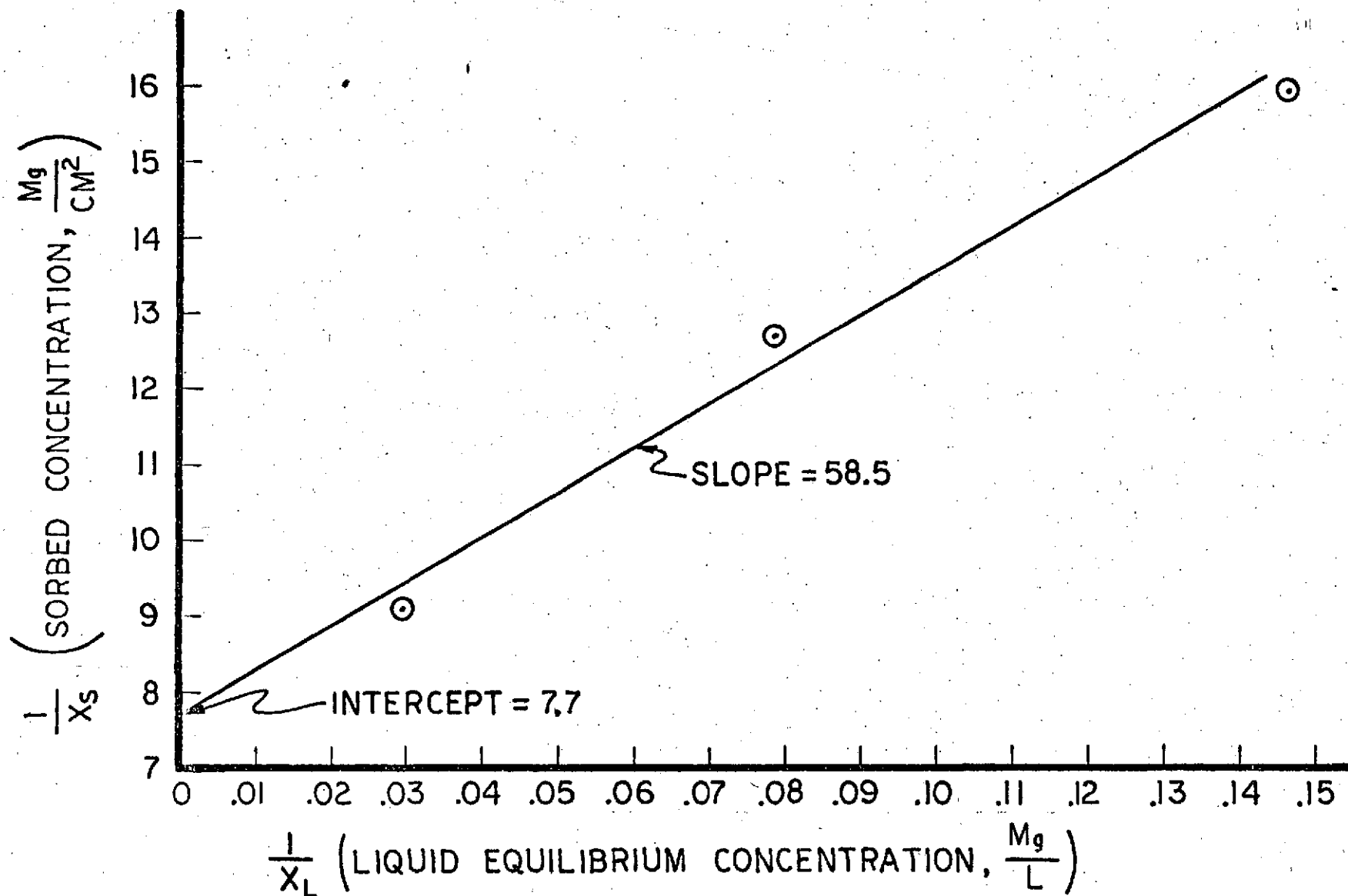
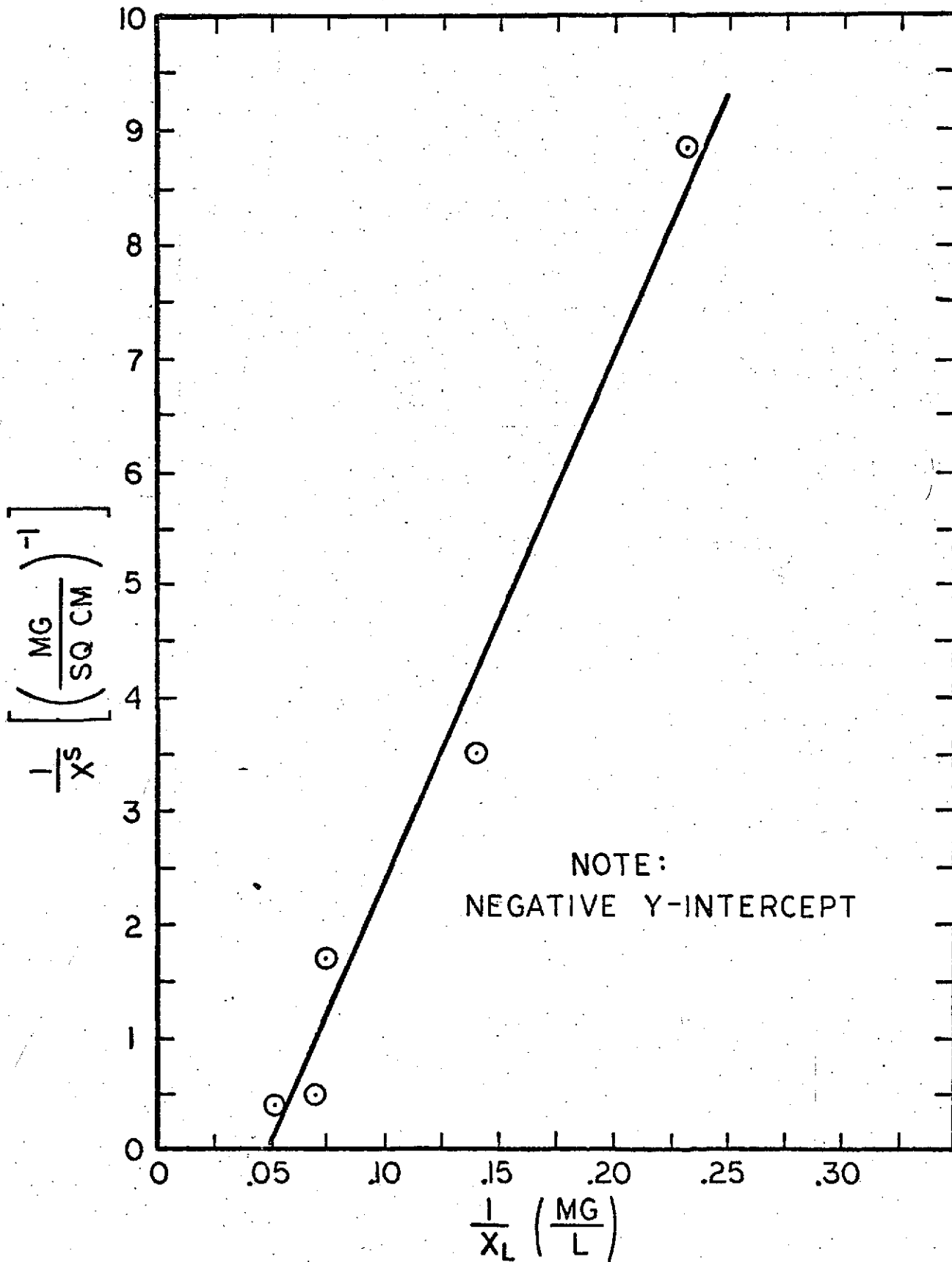
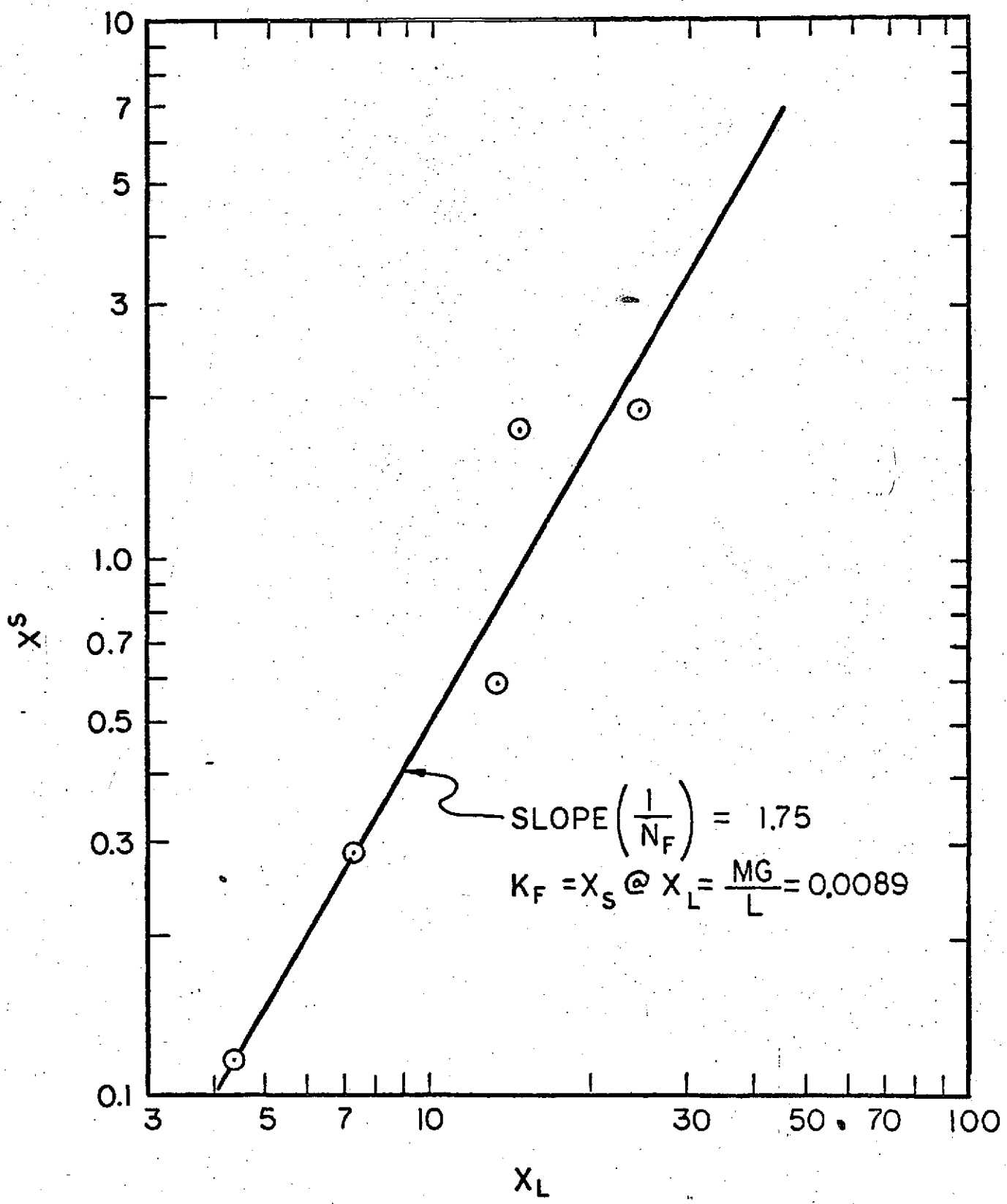


FIGURE C-1

LANGMUIR ISOTHERM FOR POLYISOPRENE  
SORPTION OF TOTAL IODINE



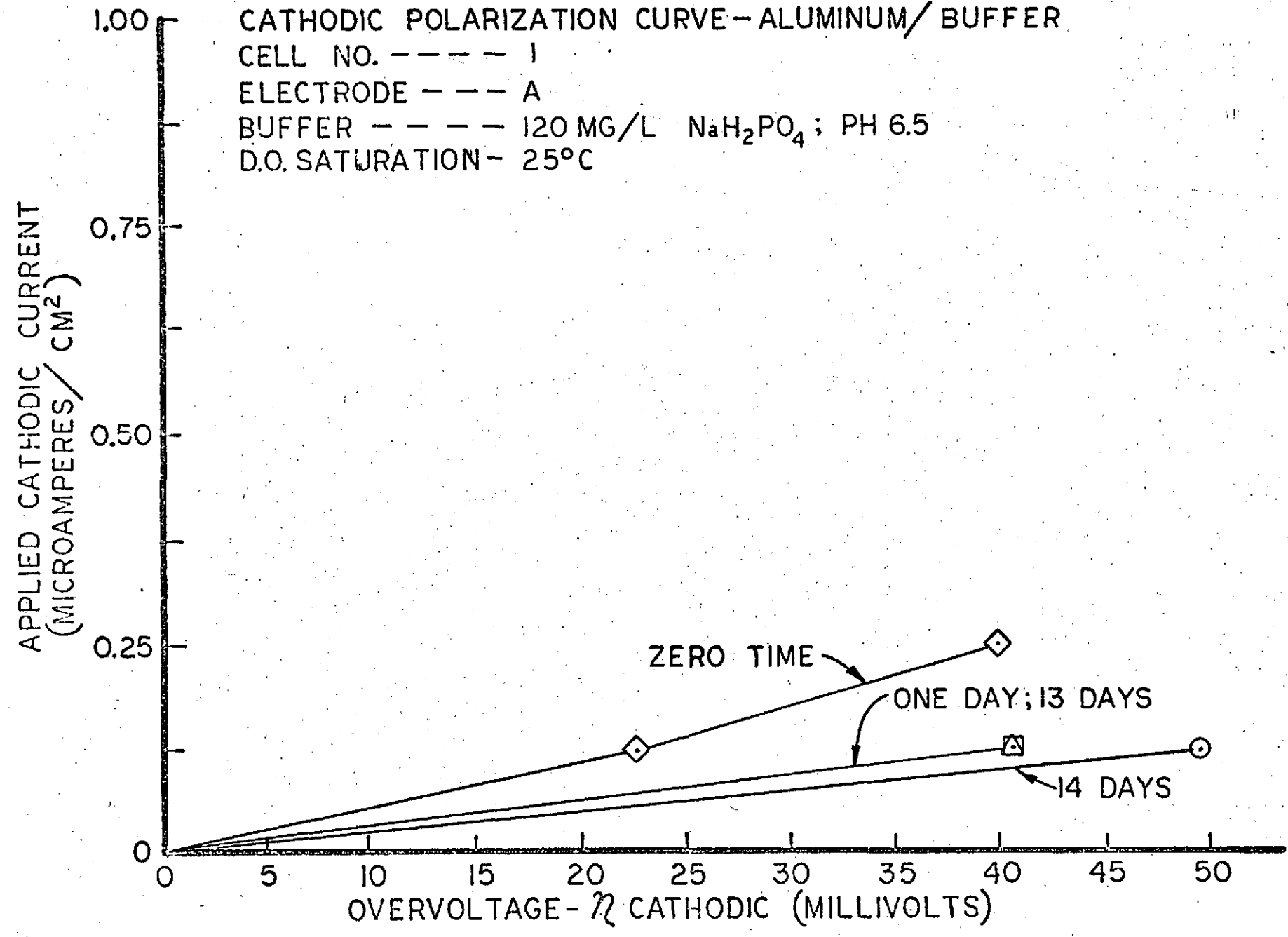
FREUNDLICH ISOTHERM FOR POLYISOPRENE  
SORPTION OF TOTAL IODINE



APPENDIX D

CATHODIC POTENTIOMETRIC CURVES

CATHODIC POLARIZATION CURVE - ALUMINUM / BUFFER  
CELL NO. --- 1  
ELECTRODE --- A  
BUFFER --- 120 MG/L  $\text{NaH}_2\text{PO}_4$ ; PH 6.5  
D.O. SATURATION - 25°C



CATHODIC POLARIZATION CURVE - ALUMINUM  
CELL NO. --- 1  
ELECTRODE --- C  
BUFFER --- 120 MG/L  $\text{NaH}_2\text{PO}_4$ ; PH 6.5  
D.O. SATURATION --- 25°C

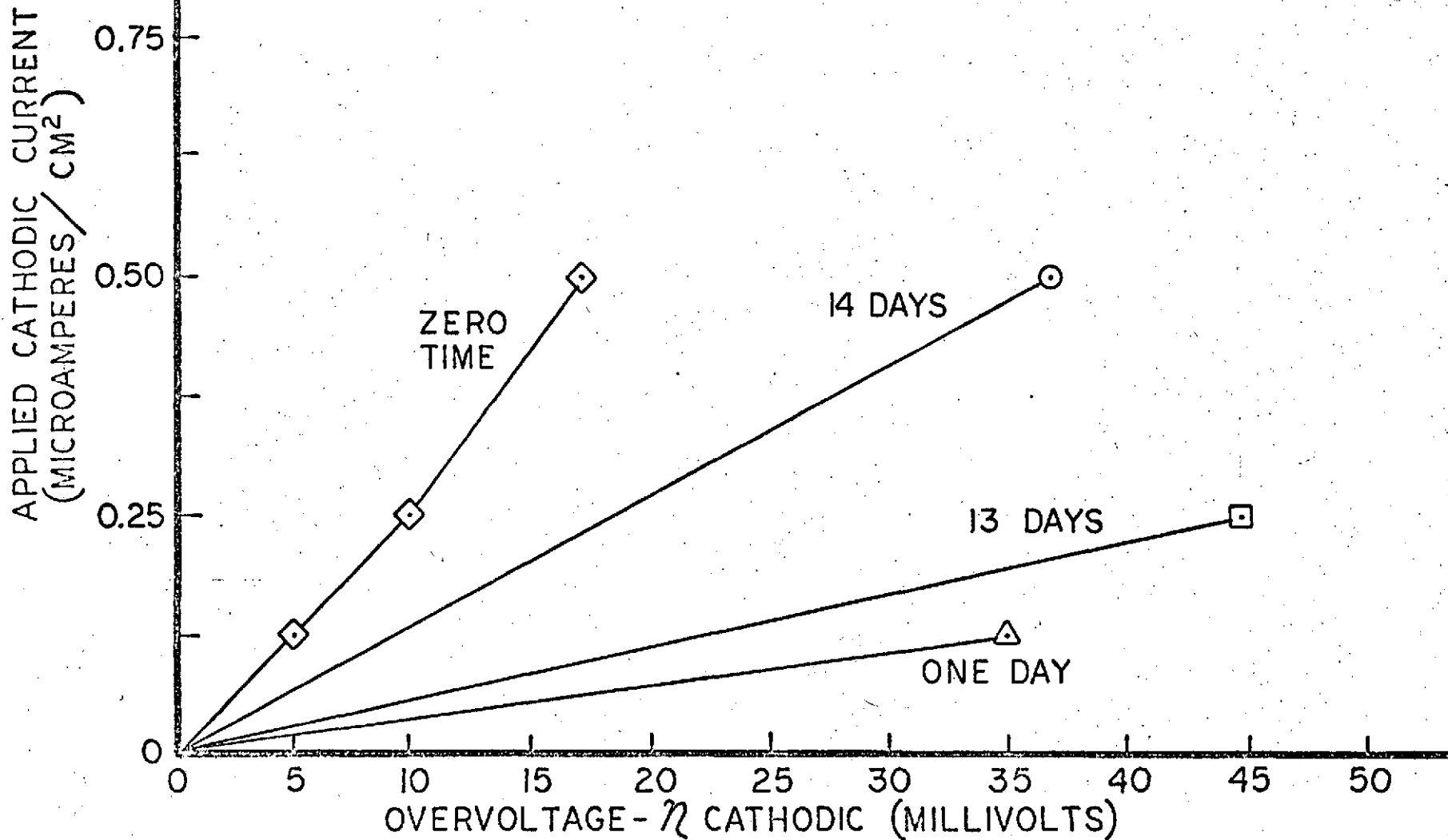


FIGURE D-2



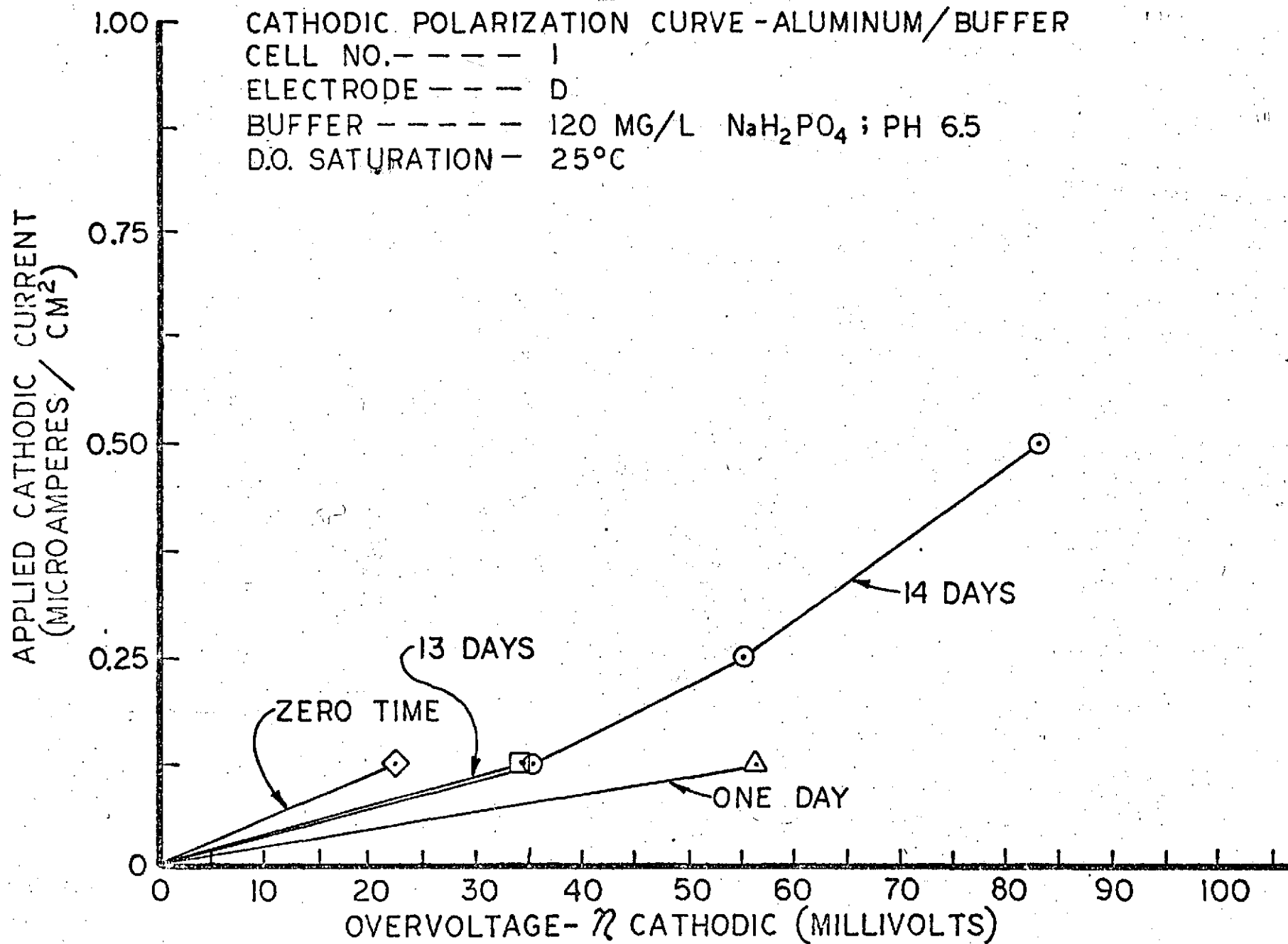
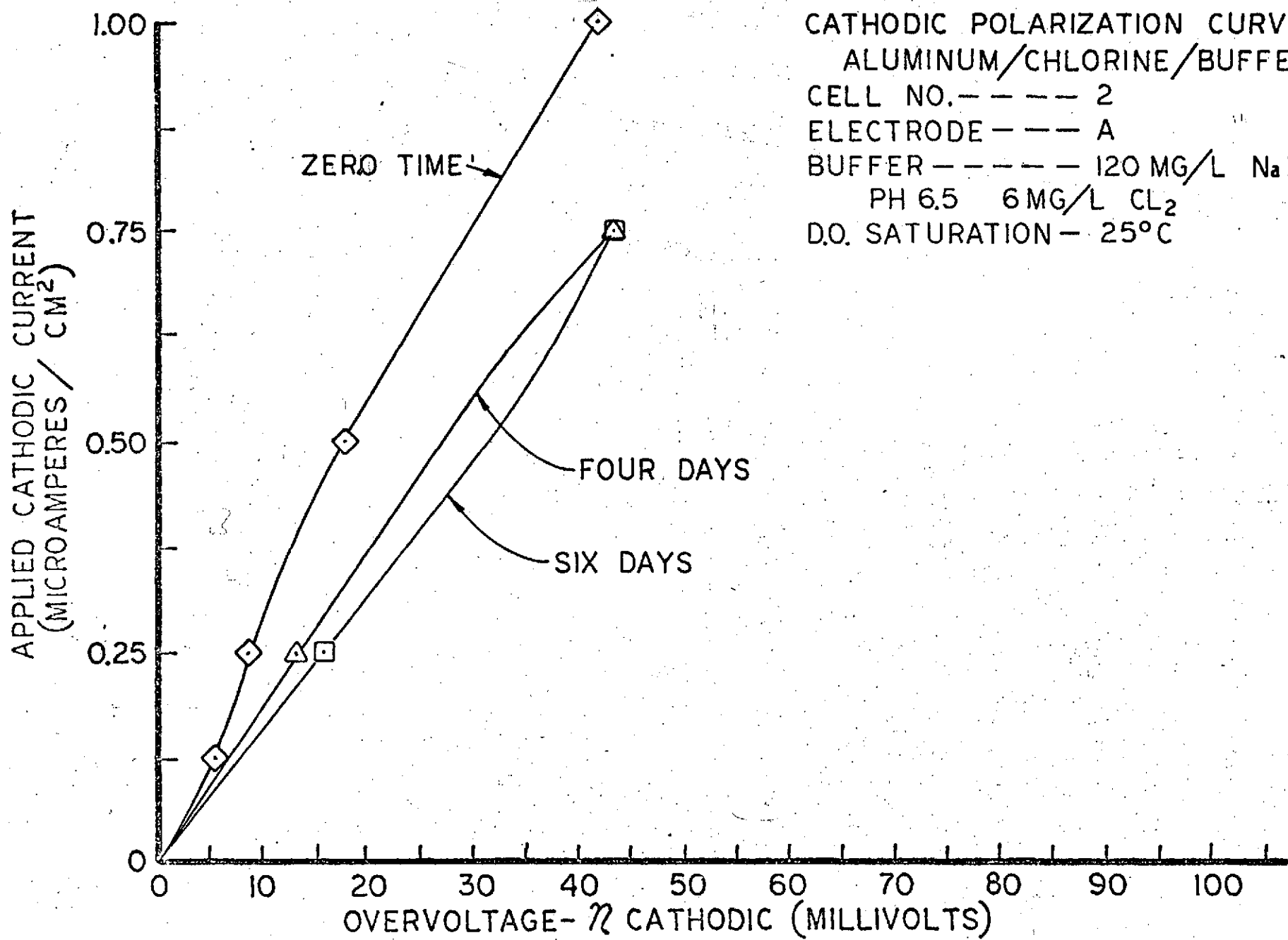


FIGURE D-3



CATHODIC POLARIZATION CURVE—  
 ALUMINUM/CHLORINE/BUFFER  
 CELL NO.— — — — 2  
 ELECTRODE — — — A  
 BUFFER — — — — 120 MG/L NaH<sub>2</sub>PO<sub>4</sub>;  
 PH 6.5 6 MG/L CL<sub>2</sub>  
 D.O. SATURATION — 25°C

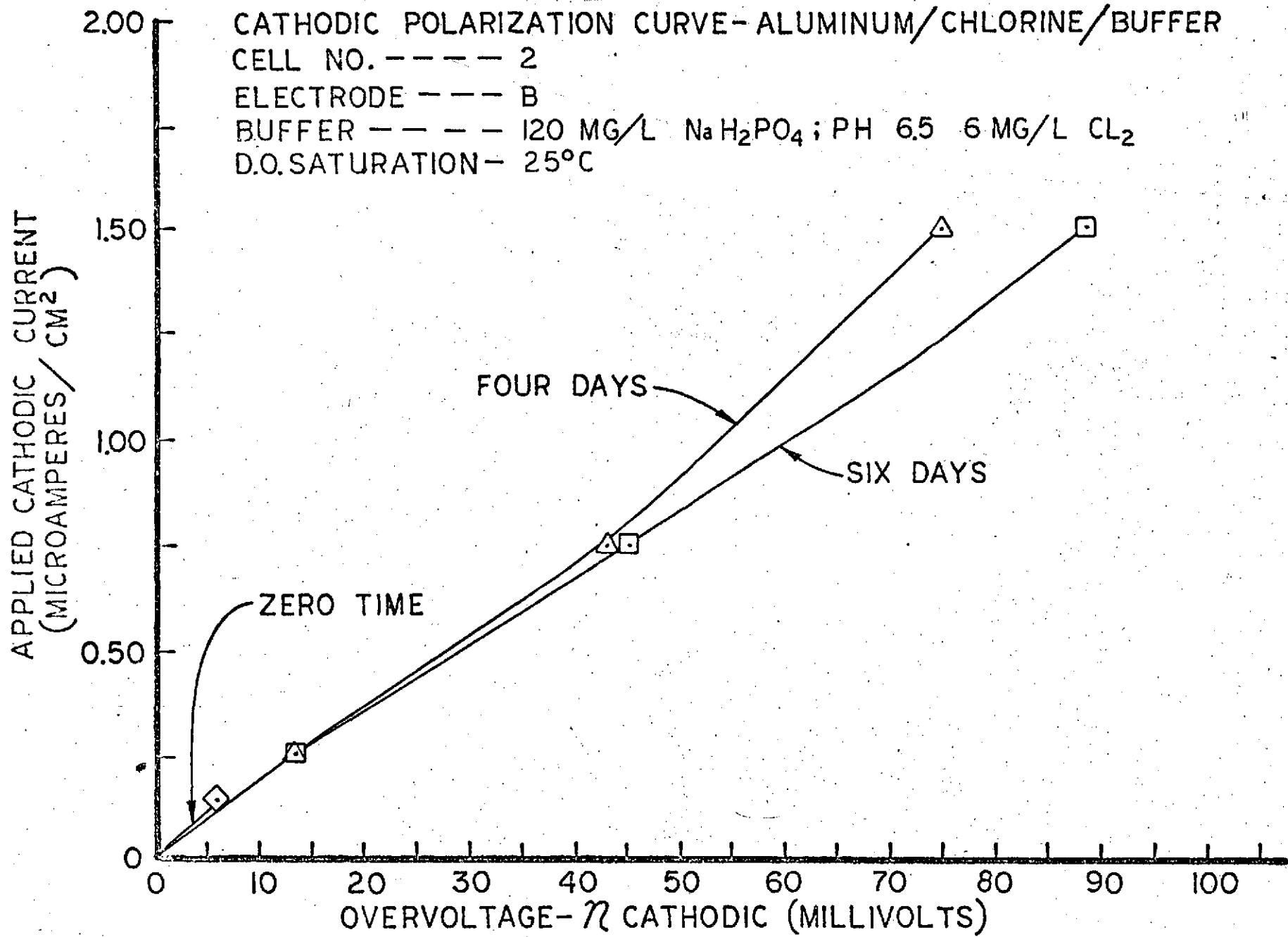


FIGURE D-5

CATHODIC POLARIZATION CURVE-ALUMINUM/CHLORINE/BUFFER  
CELL NO. --- 2  
ELECTRODE --- C  
BUFFER --- 120 MG/L  $\text{NaH}_2\text{PO}_4$  ; PH 6.5 6 MG/L  $\text{CL}_2$   
D.O. SATURATION  $\pm$  25°C

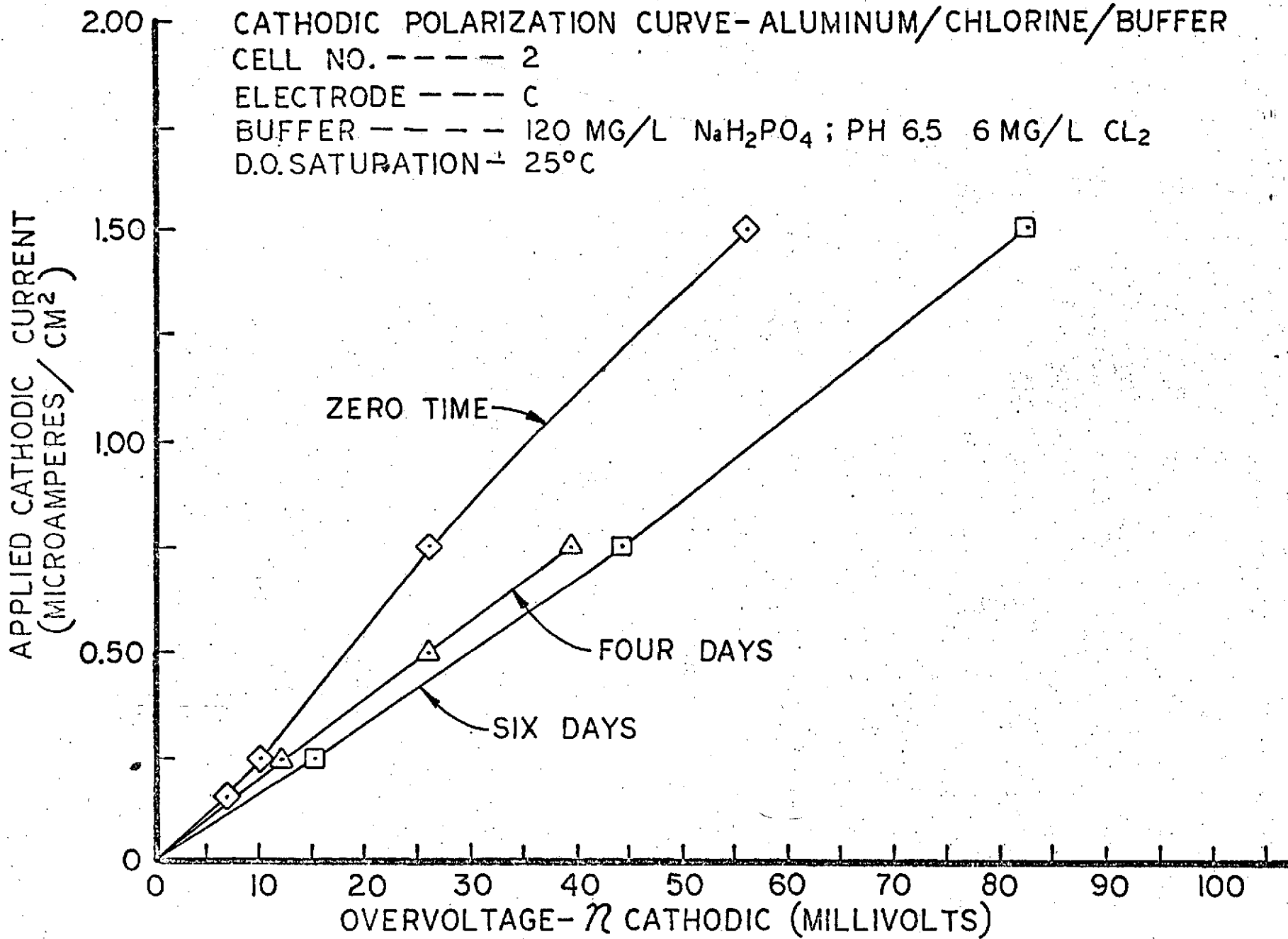


FIGURE D-6

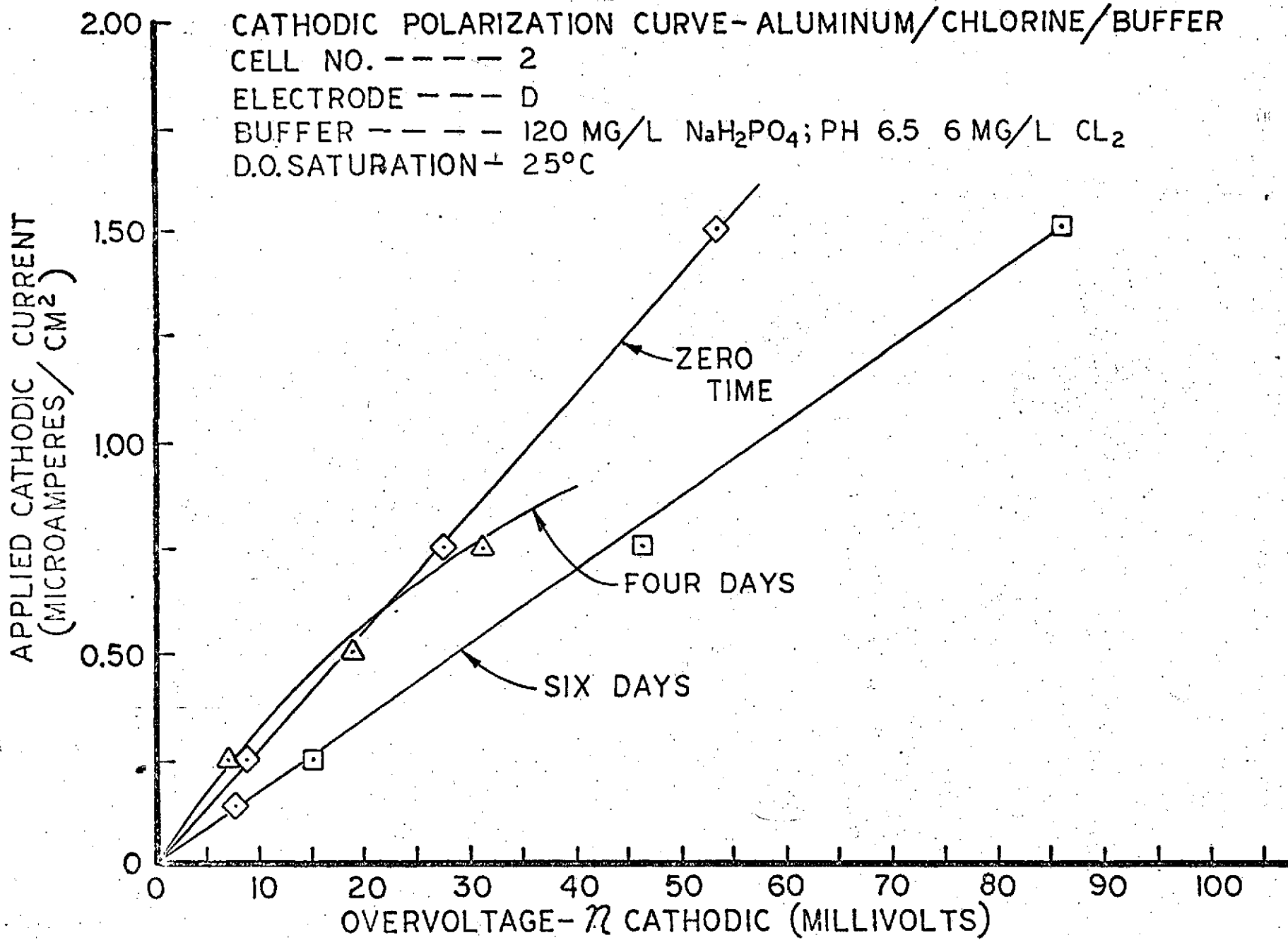


FIGURE D-7

CATHODIC POLARIZATION CURVE - ALUMINUM/IODINE  
 CELL NO. ----- 3  
 ELECTRODE ----- A  
 BUFFER ----- 12 MG/L I<sub>2</sub>  
 D.O. SATURATION - 25°C

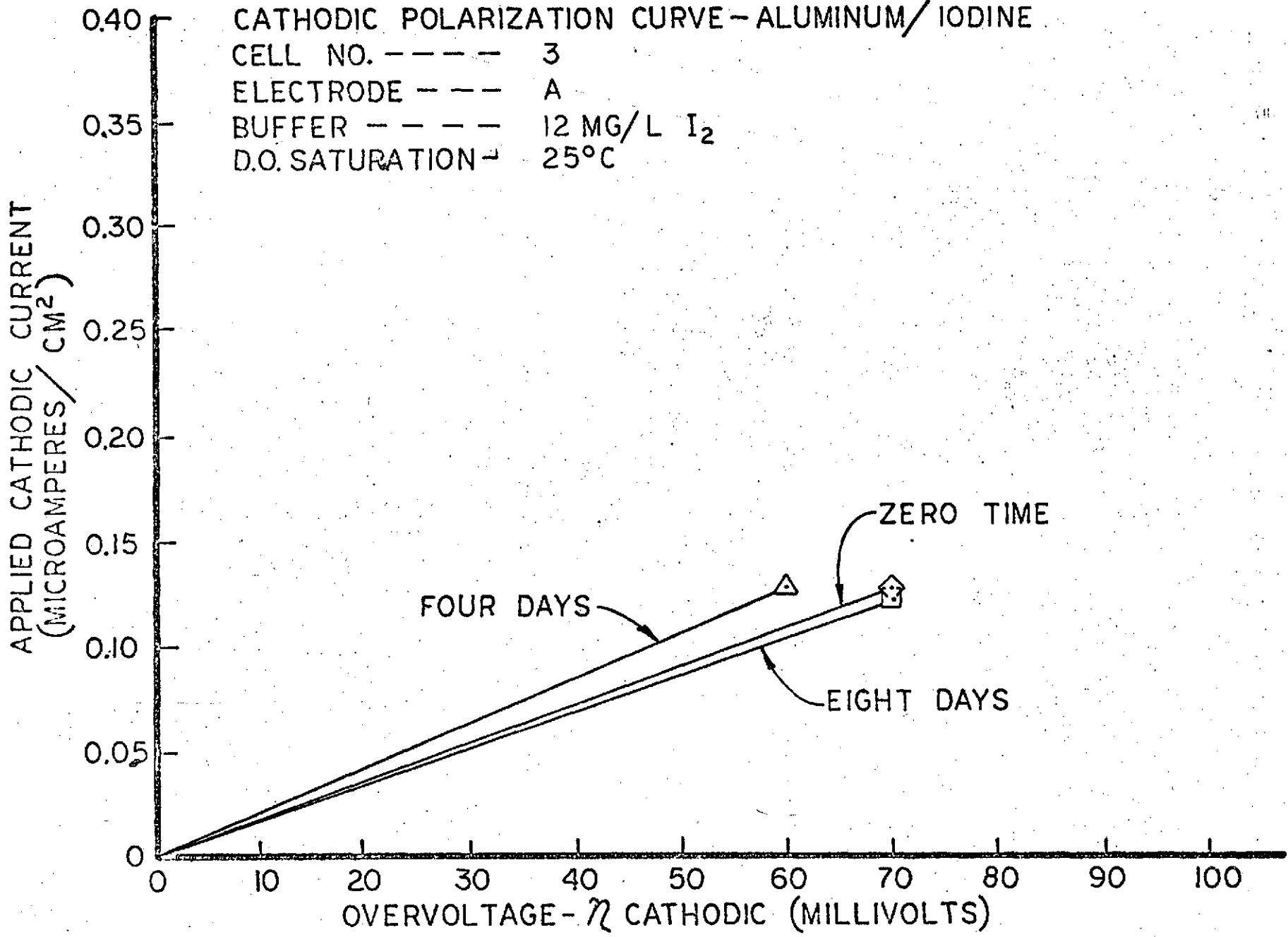


FIGURE D-8

CATHODIC POLARIZATION CURVE- ALUMINUM/IODINE

CELL NO. - - - - 3  
ELECTRODE - - - B  
BUFFER - - - - 12 MG/L I<sub>2</sub>  
D.O. SATURATION - 25°C

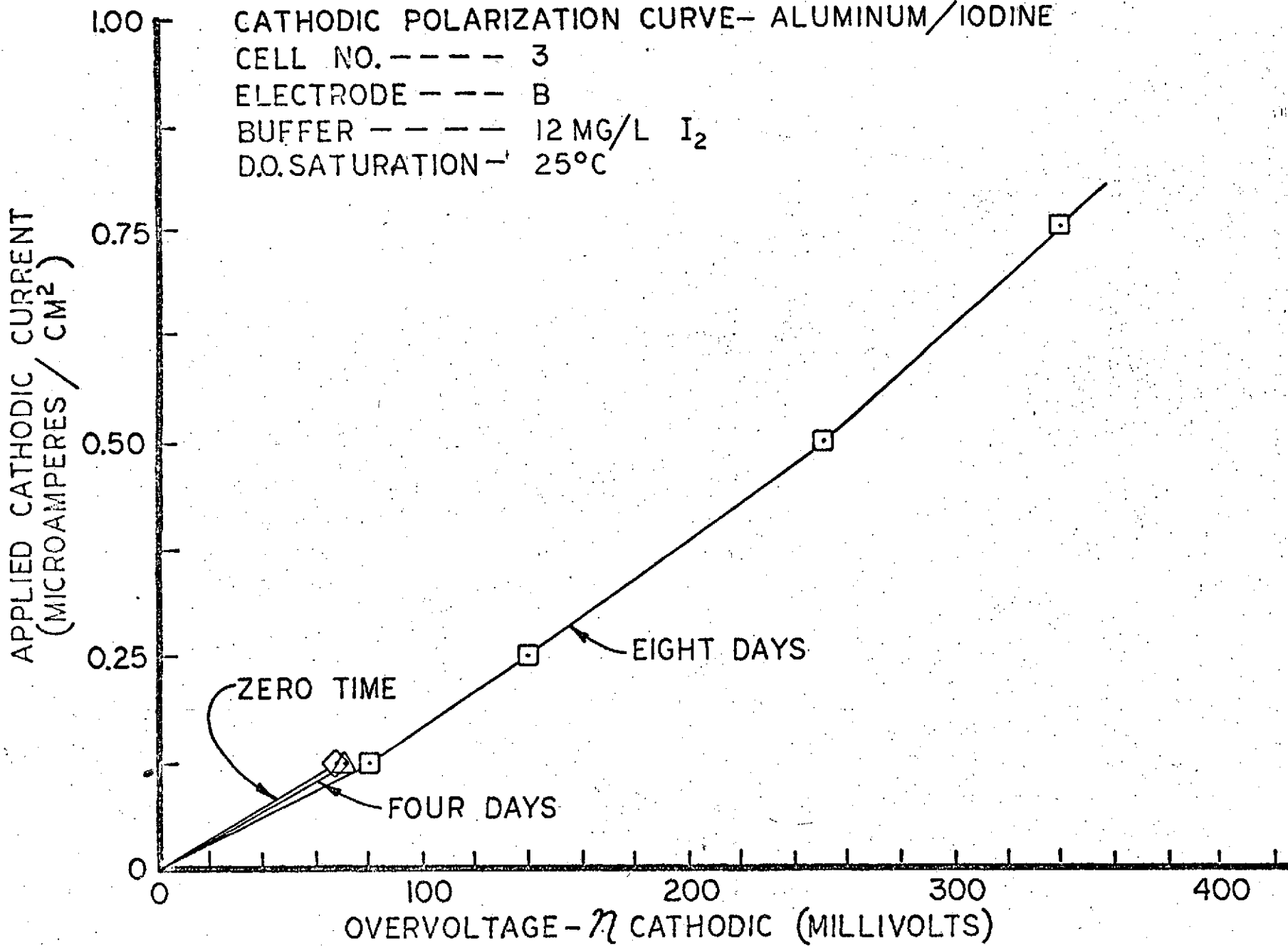


FIGURE D-9

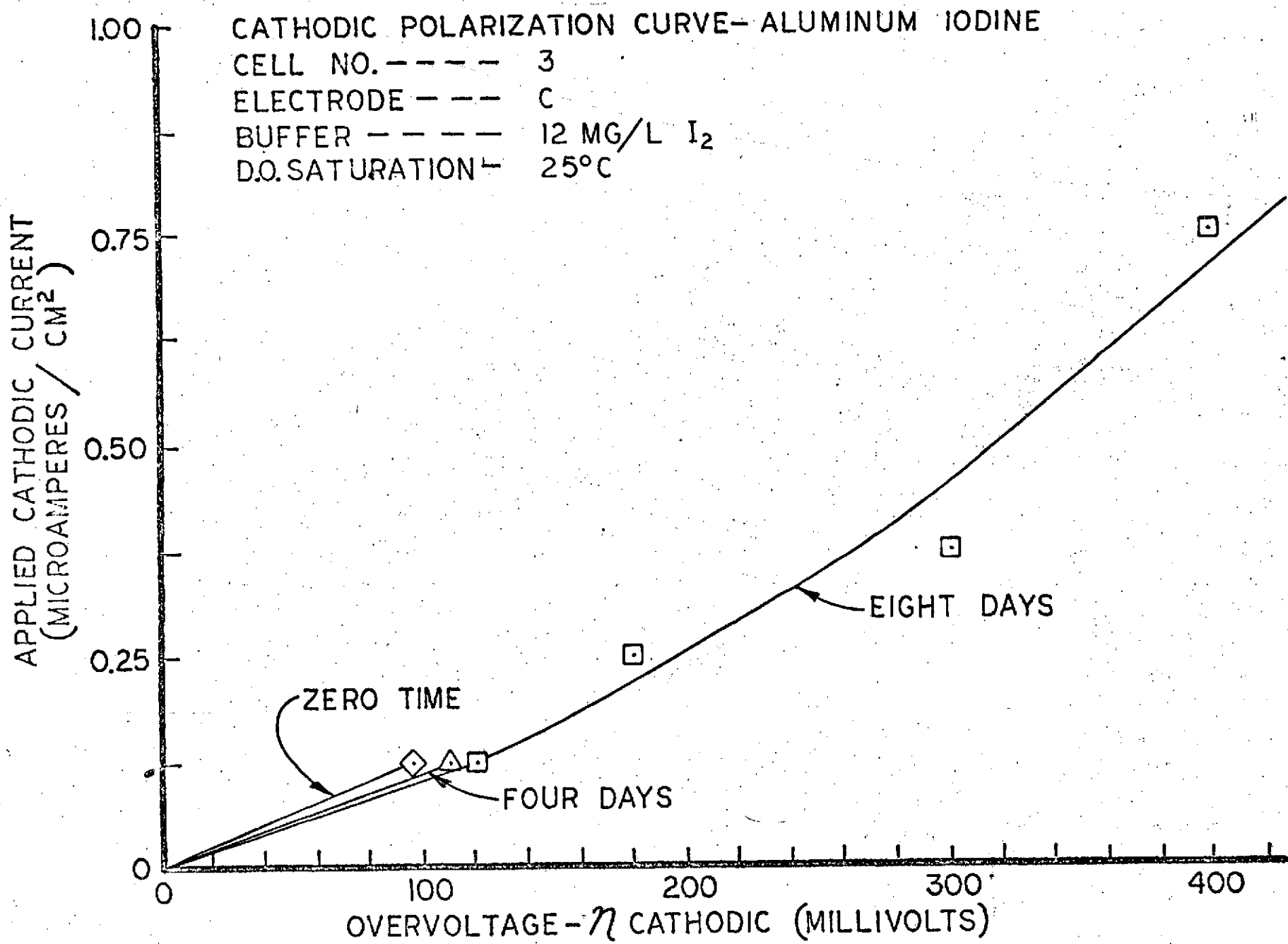


FIGURE D-10



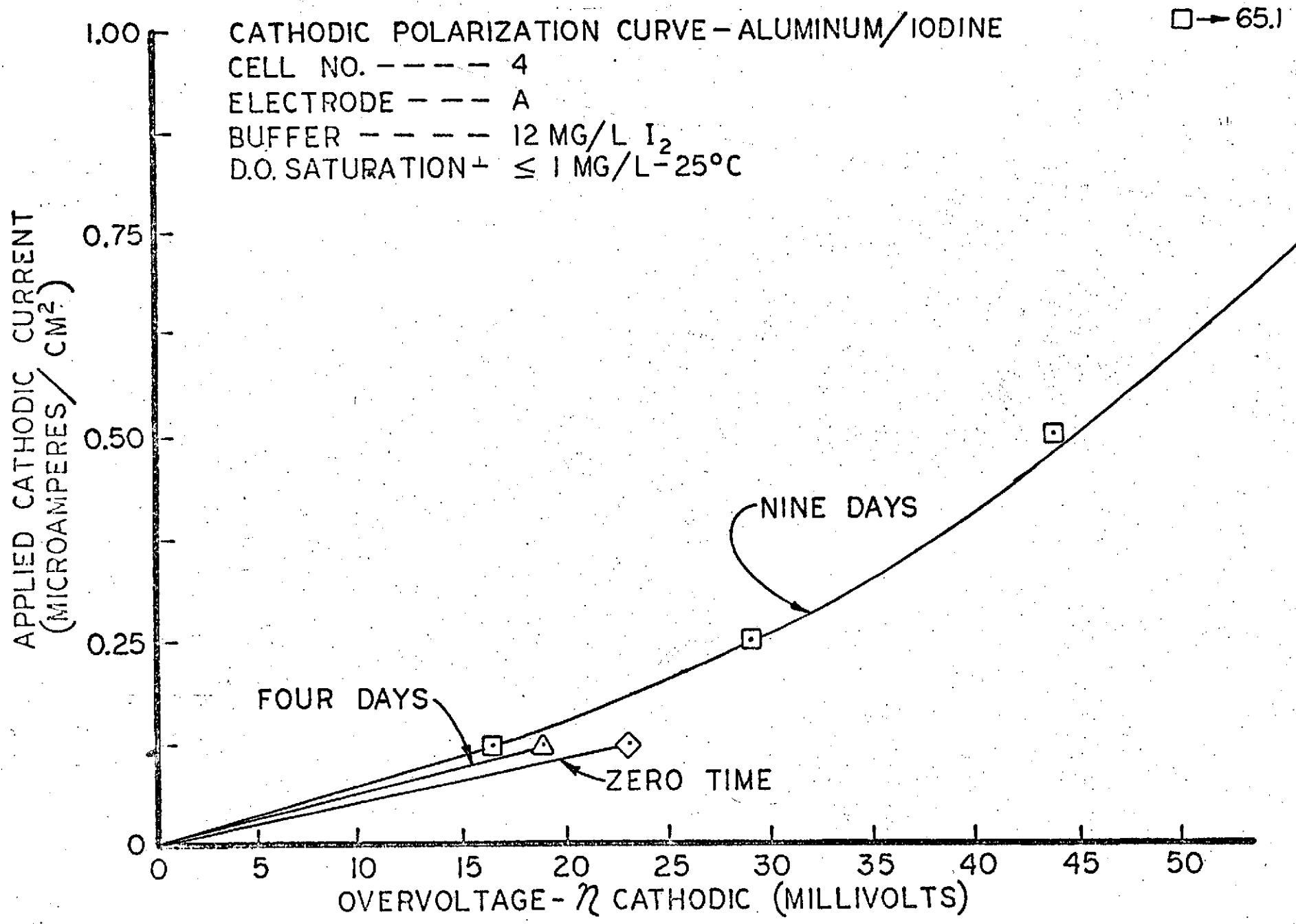


FIGURE D-11

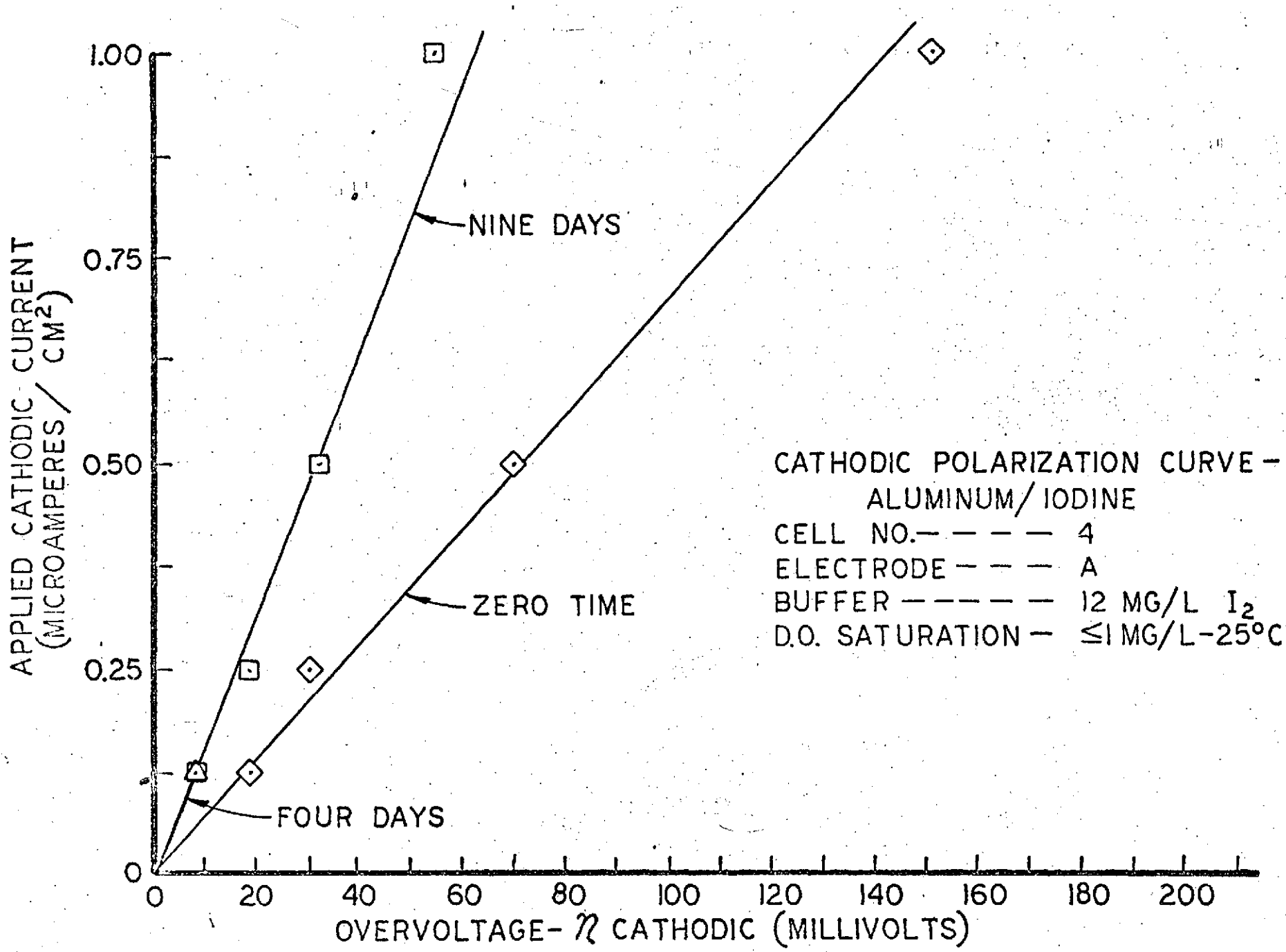
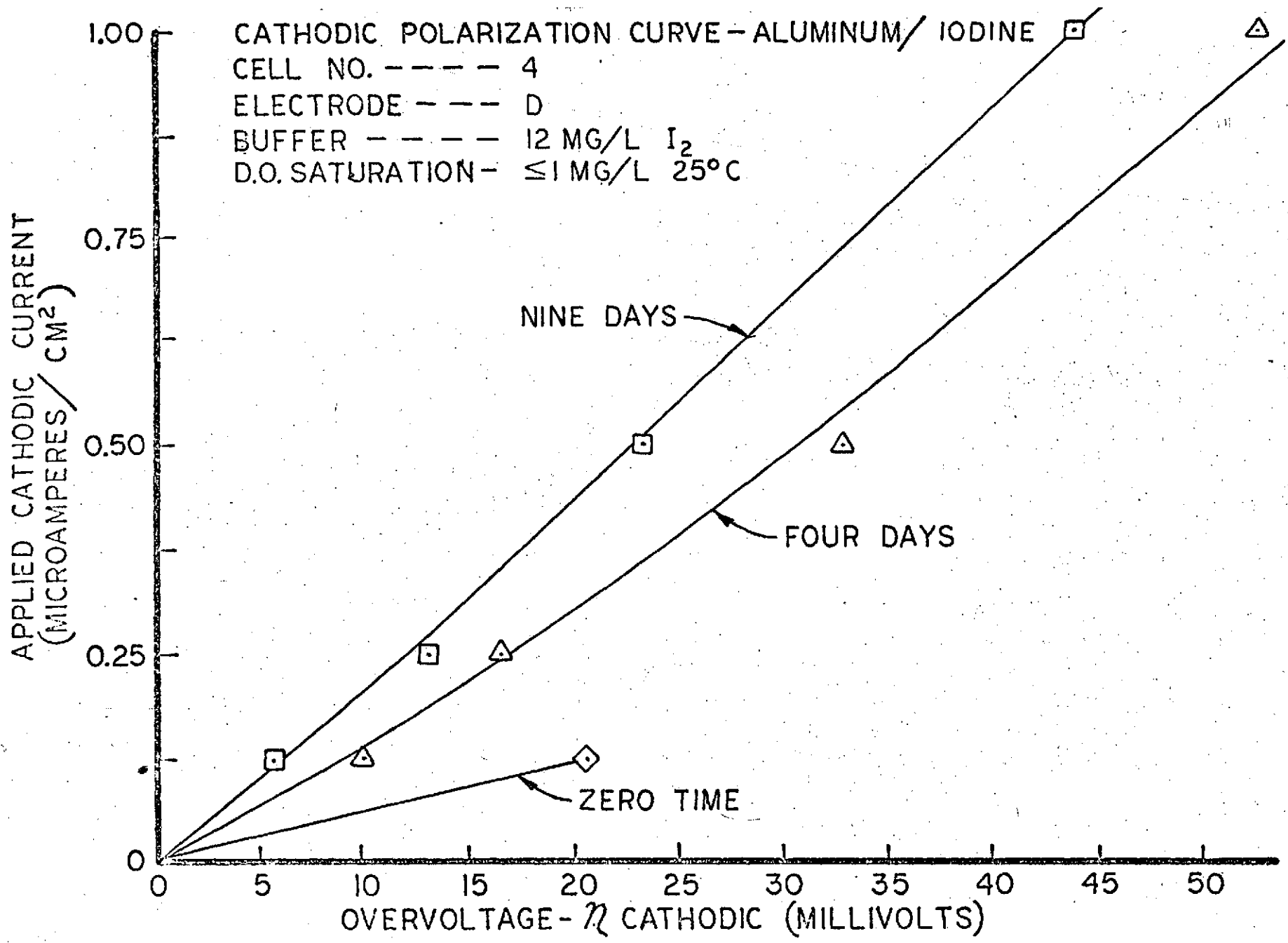


FIGURE D-12



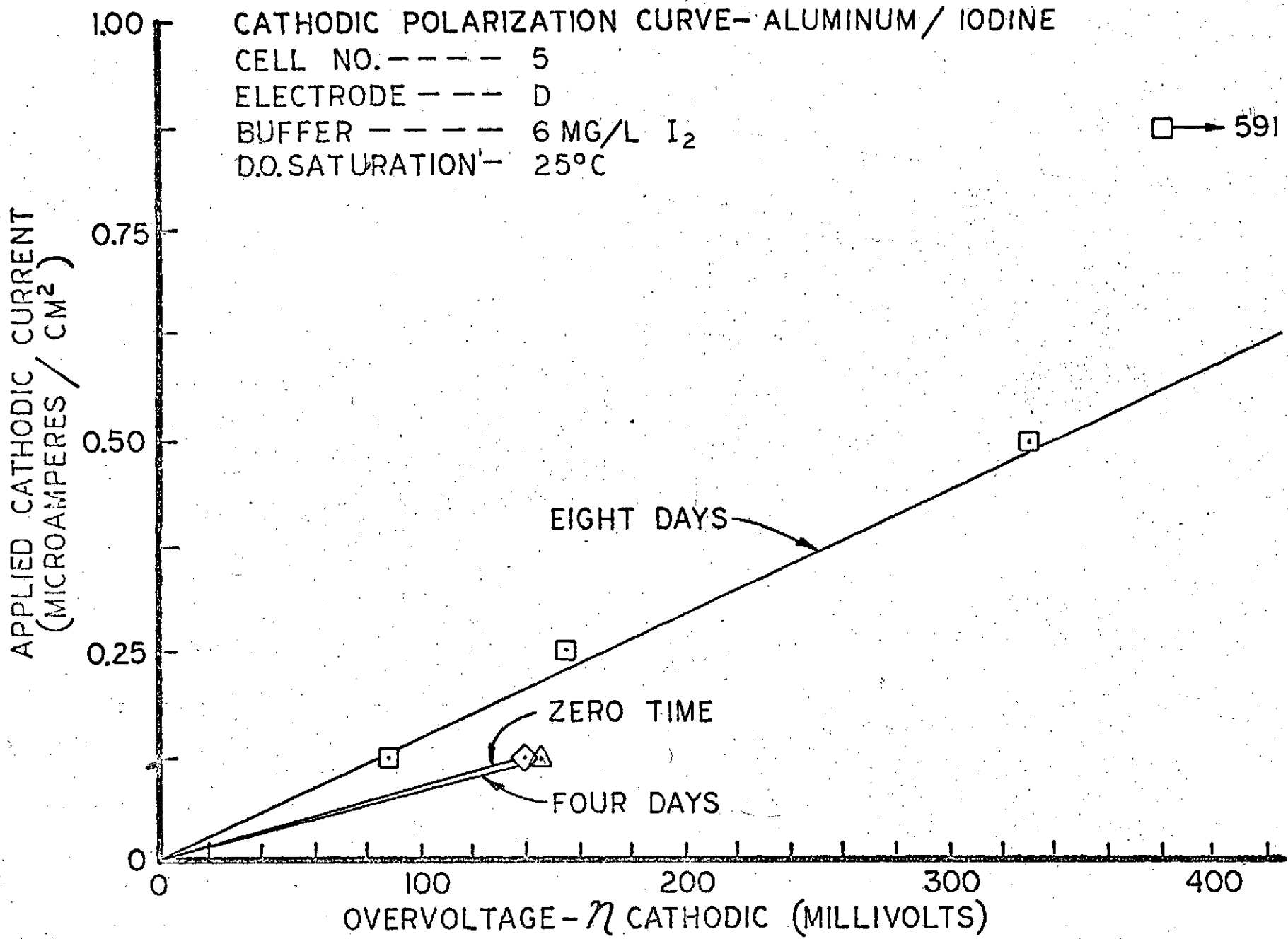


FIGURE D-14

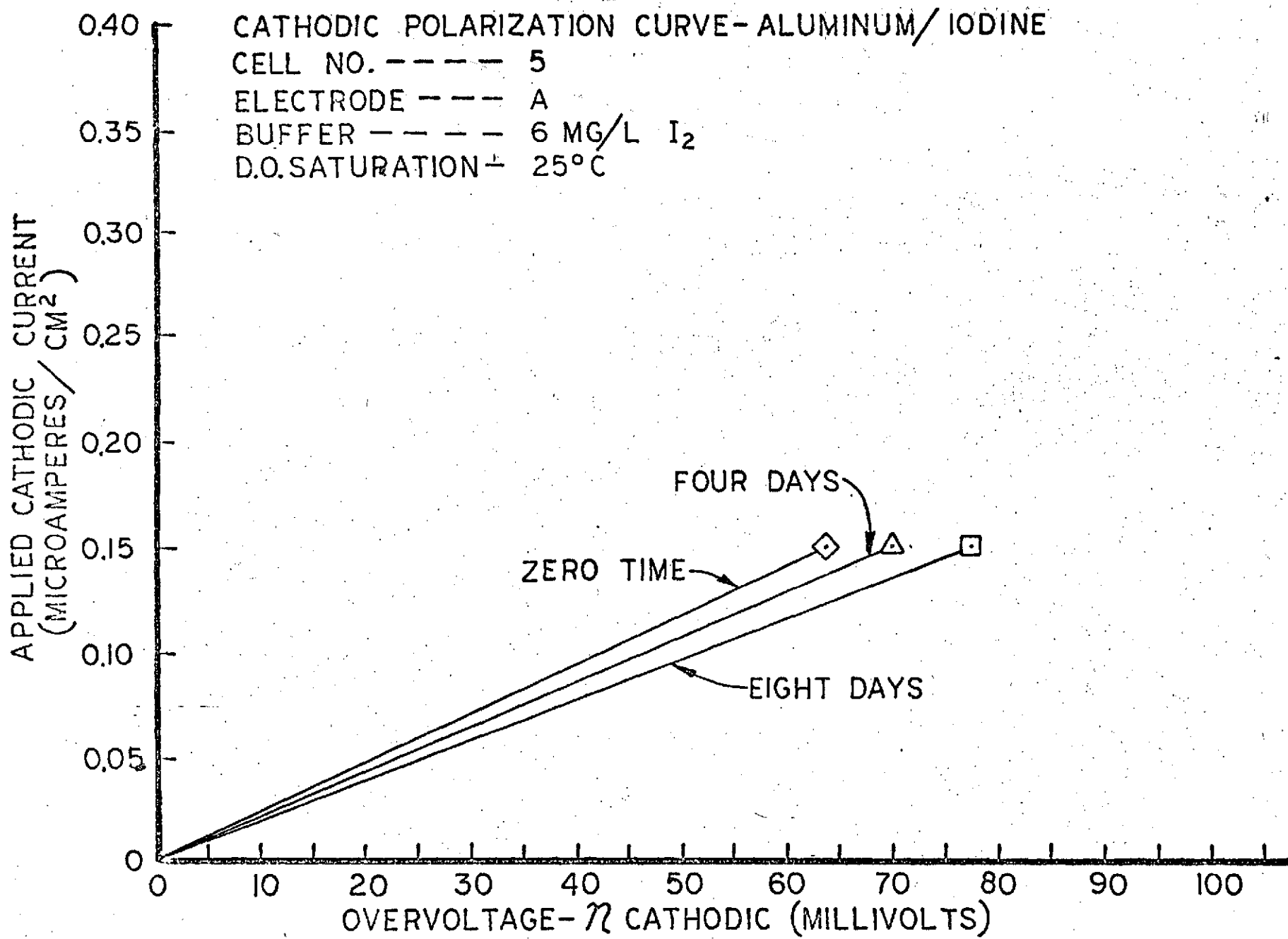


FIGURE D-15

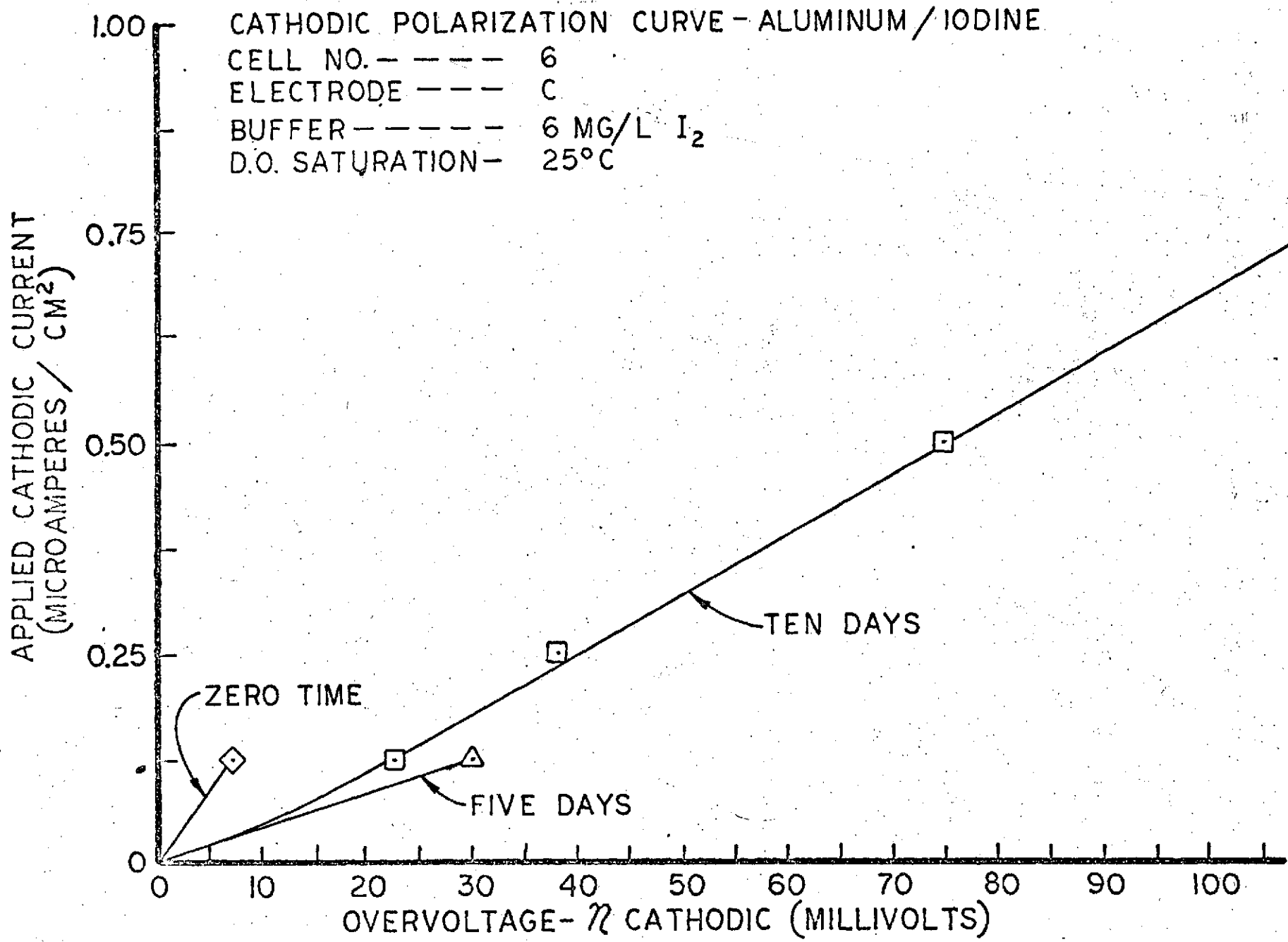


FIGURE D-16

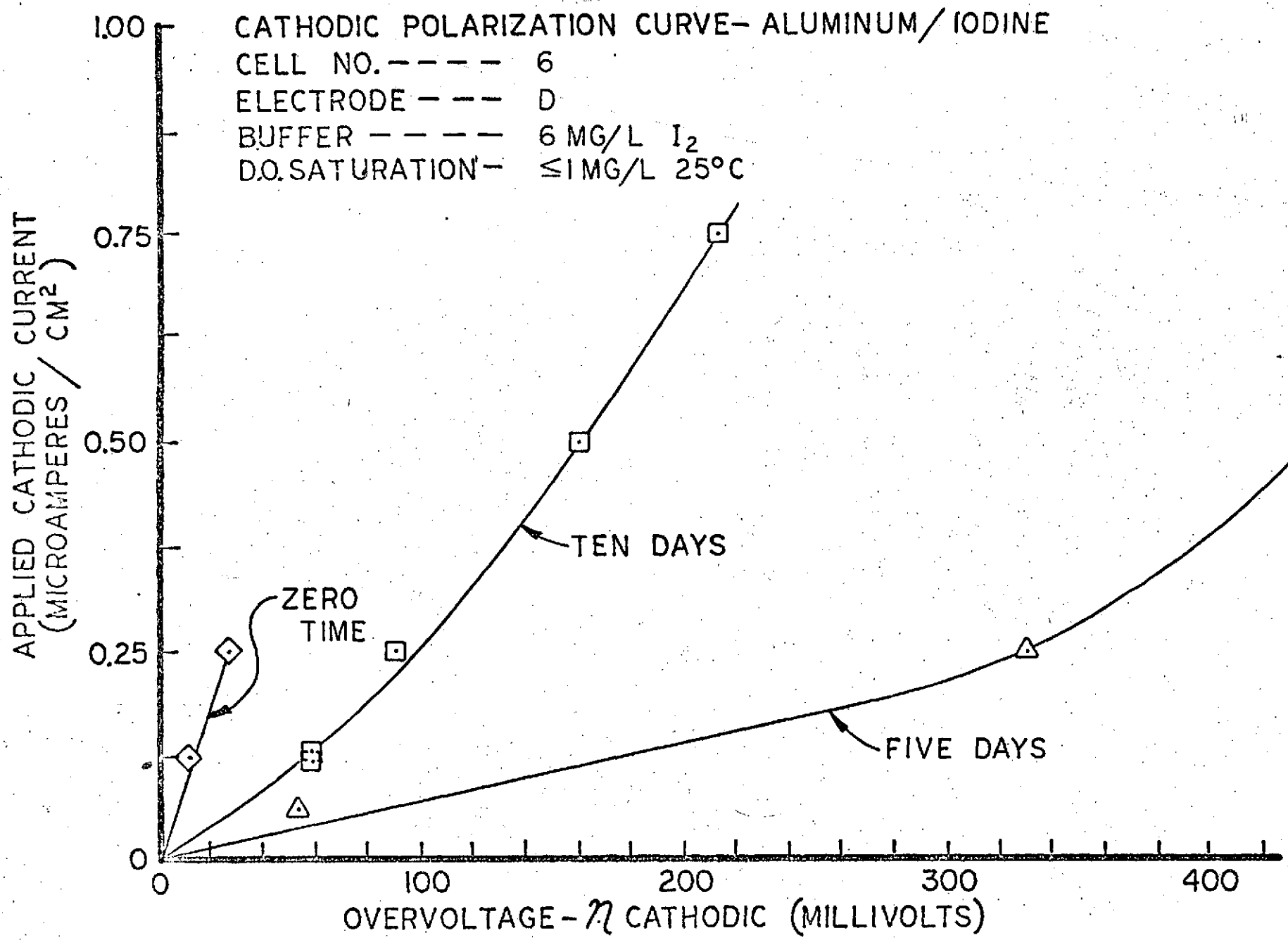
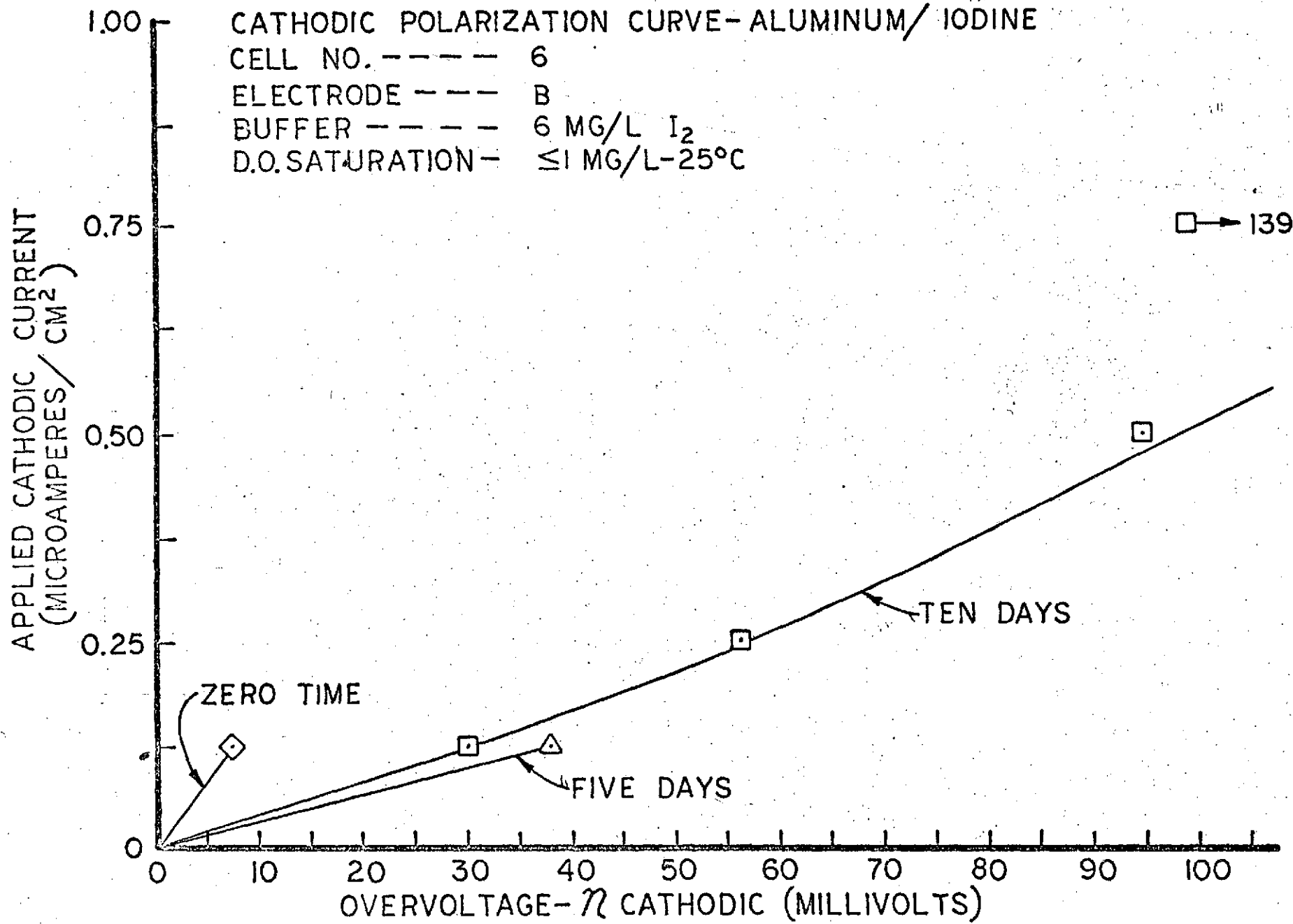


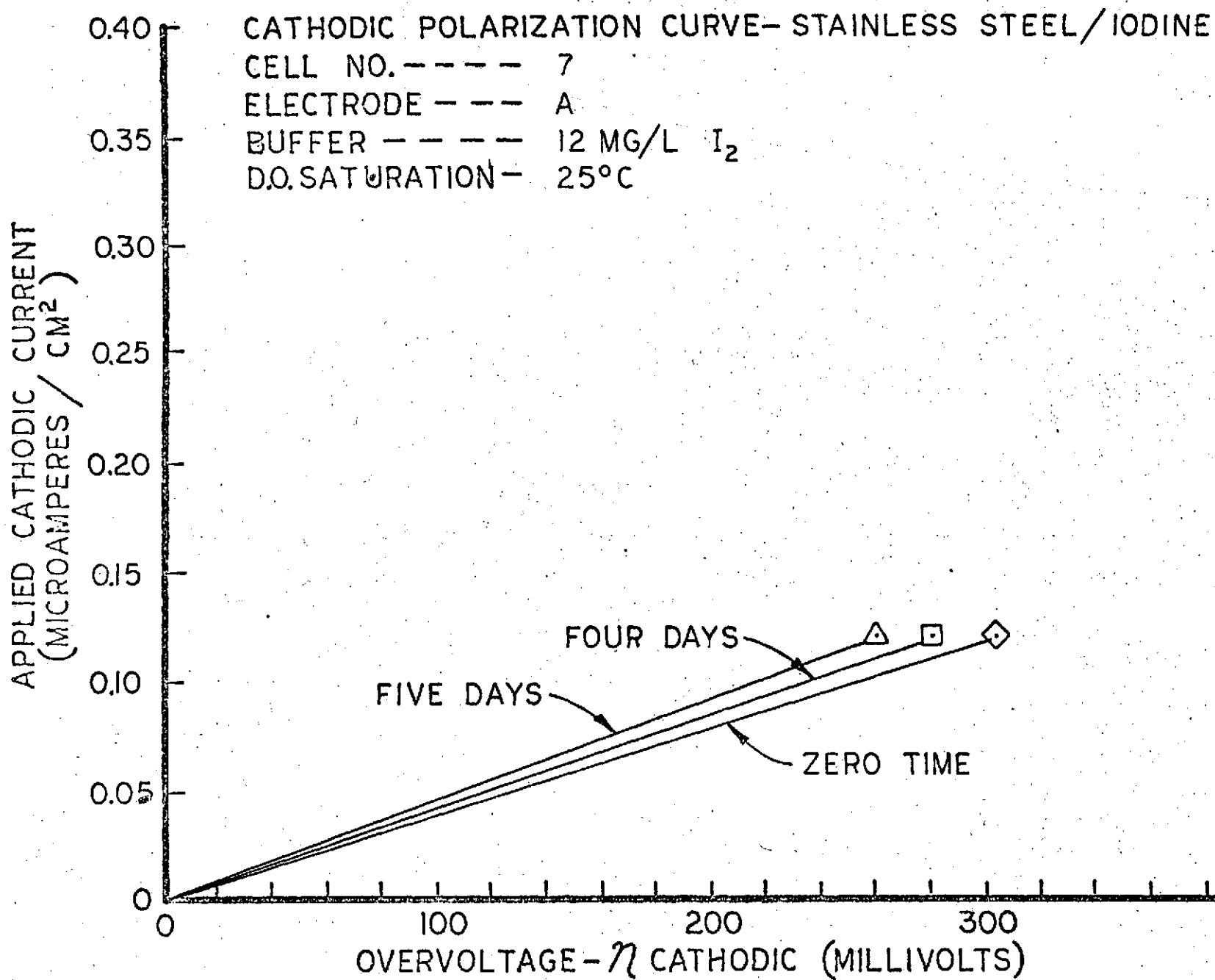
FIGURE D-17

CATHODIC POLARIZATION CURVE-ALUMINUM/ IODINE

CELL NO. - - - - 6  
ELECTRODE - - - - B  
BUFFER - - - - 6 MG/L I<sub>2</sub>  
D.O. SATURATION - ≤1 MG/L-25°C







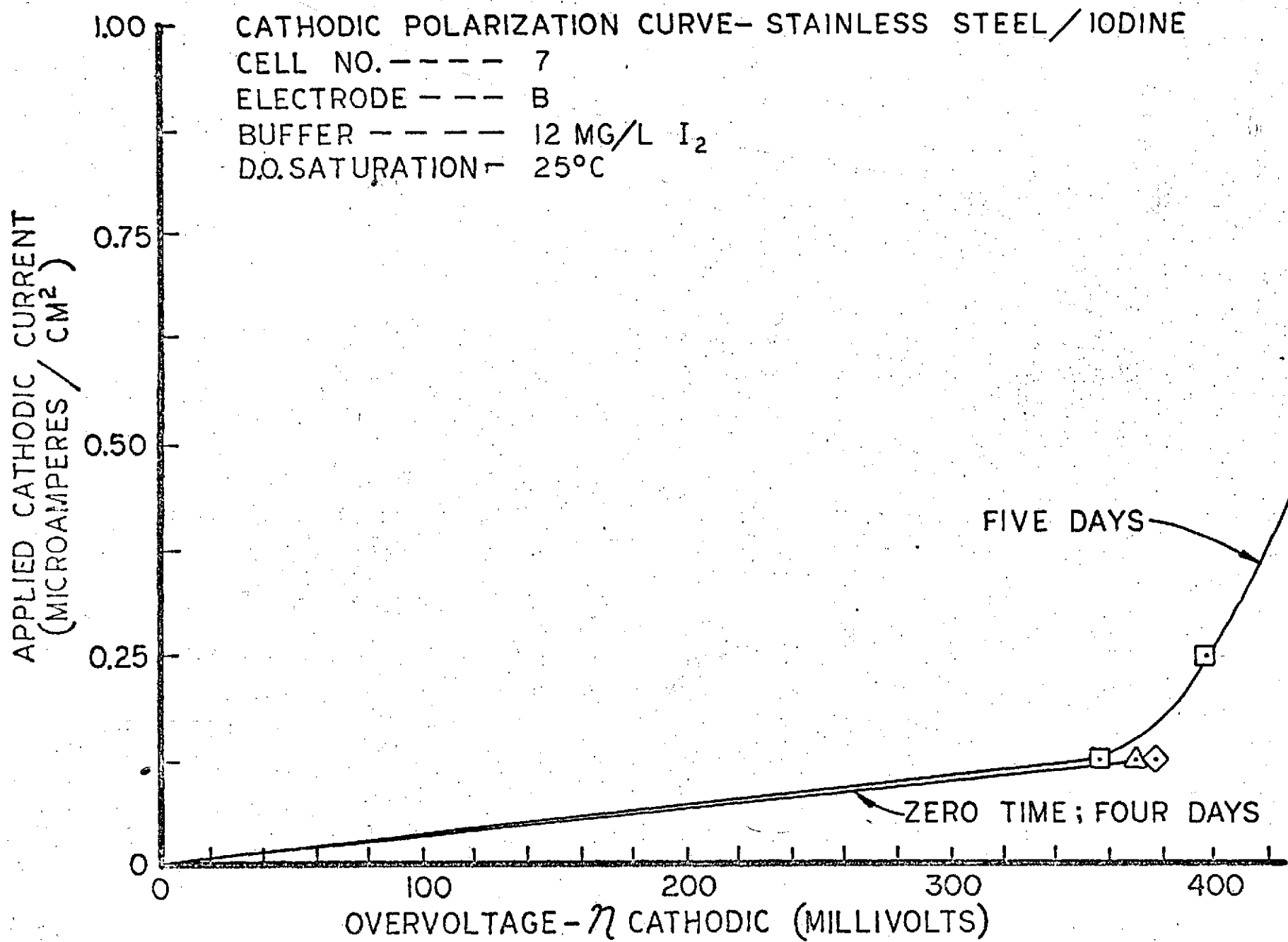


FIGURE D-20

CATHODIC POLARIZATION CURVE- STAINLESS STEEL/ IODINE

CELL NO. --- 7  
ELECTRODE --- C  
BUFFER --- 12 MG/L I<sub>2</sub>  
D.O. SATURATION --- 25°C

APPLIED CATHODIC CURRENT  
(MICROAMPERES / CM<sup>2</sup>)

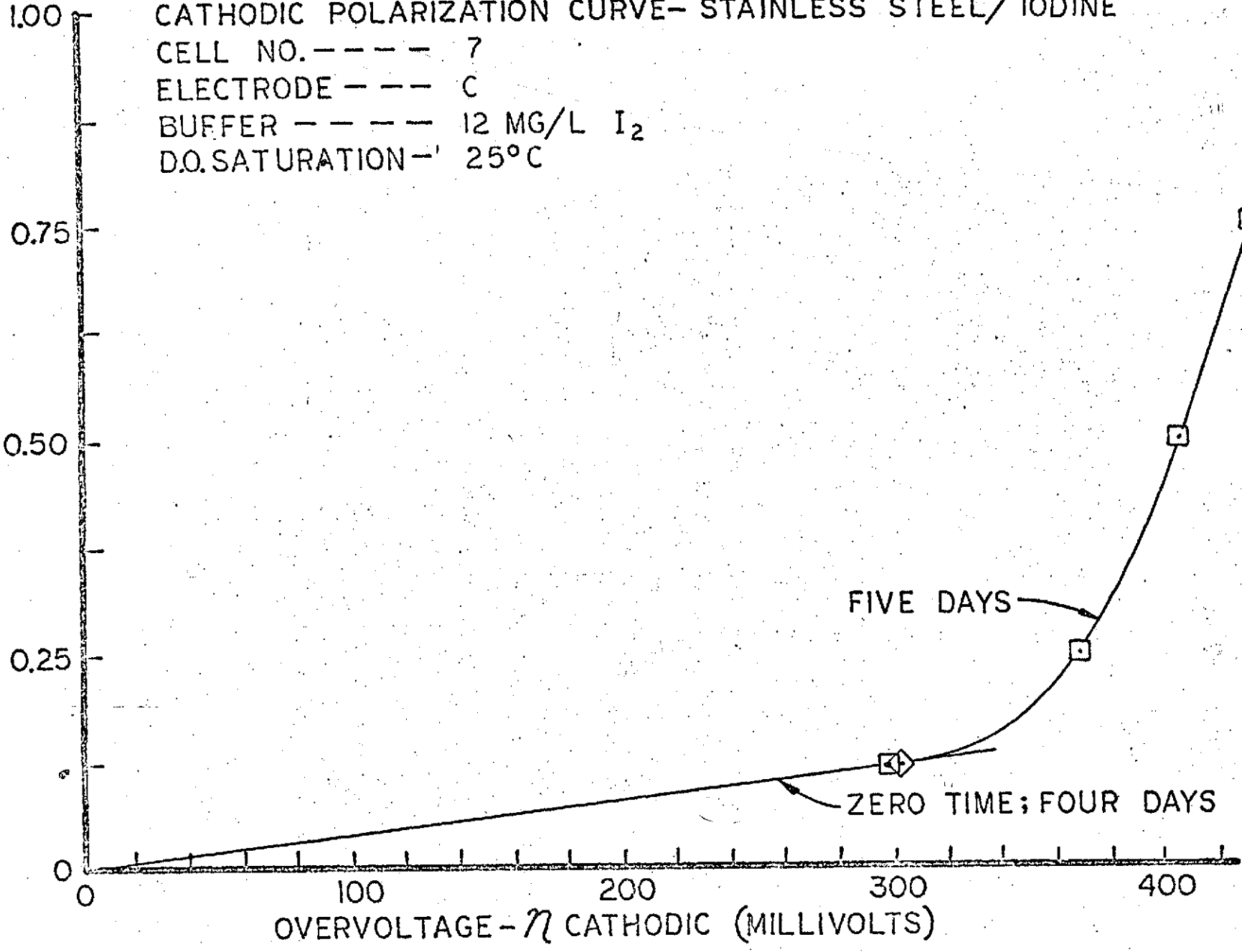


FIGURE D-21

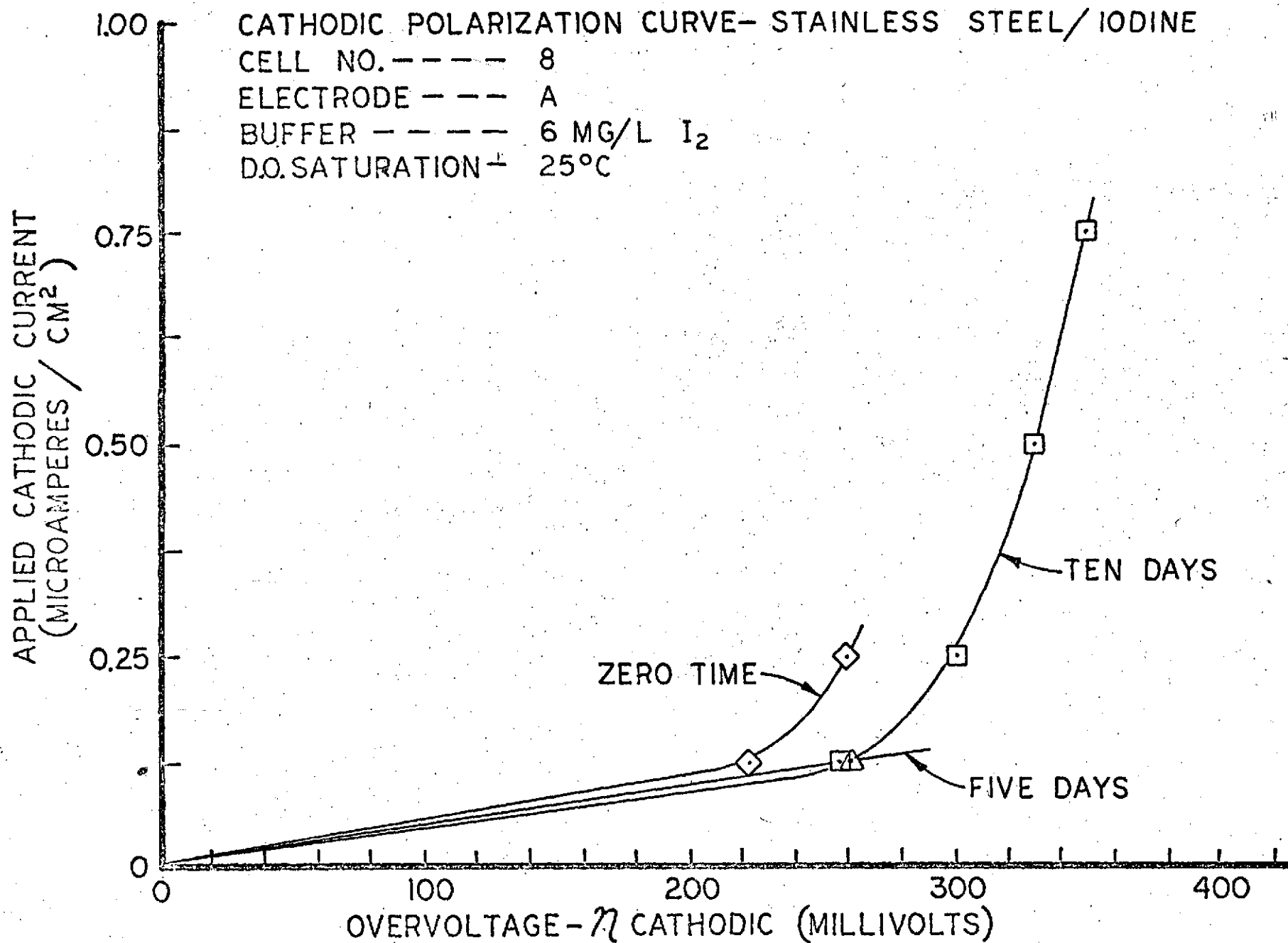
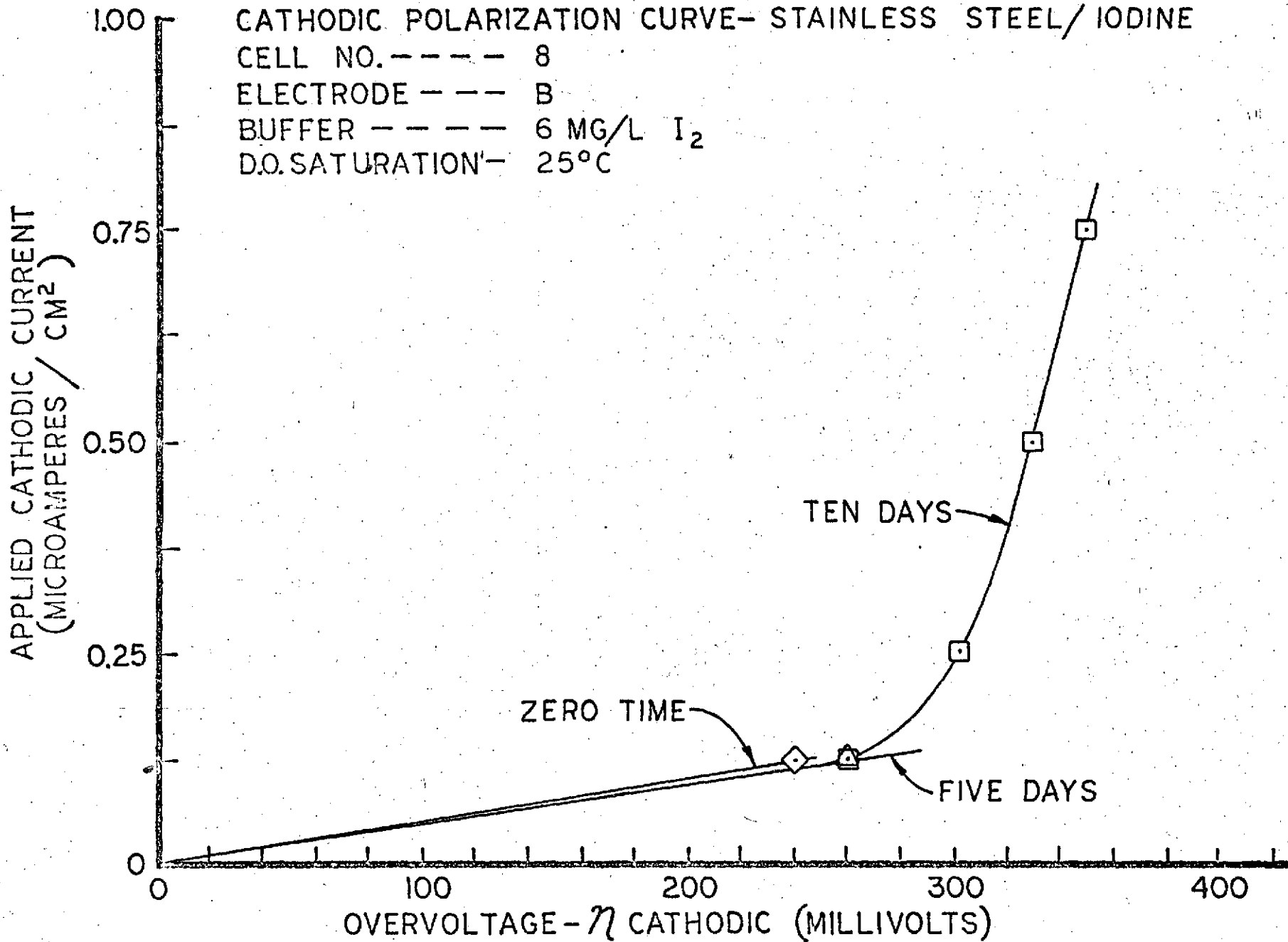


FIGURE D-22

CATHODIC POLARIZATION CURVE- STAINLESS STEEL/ IODINE

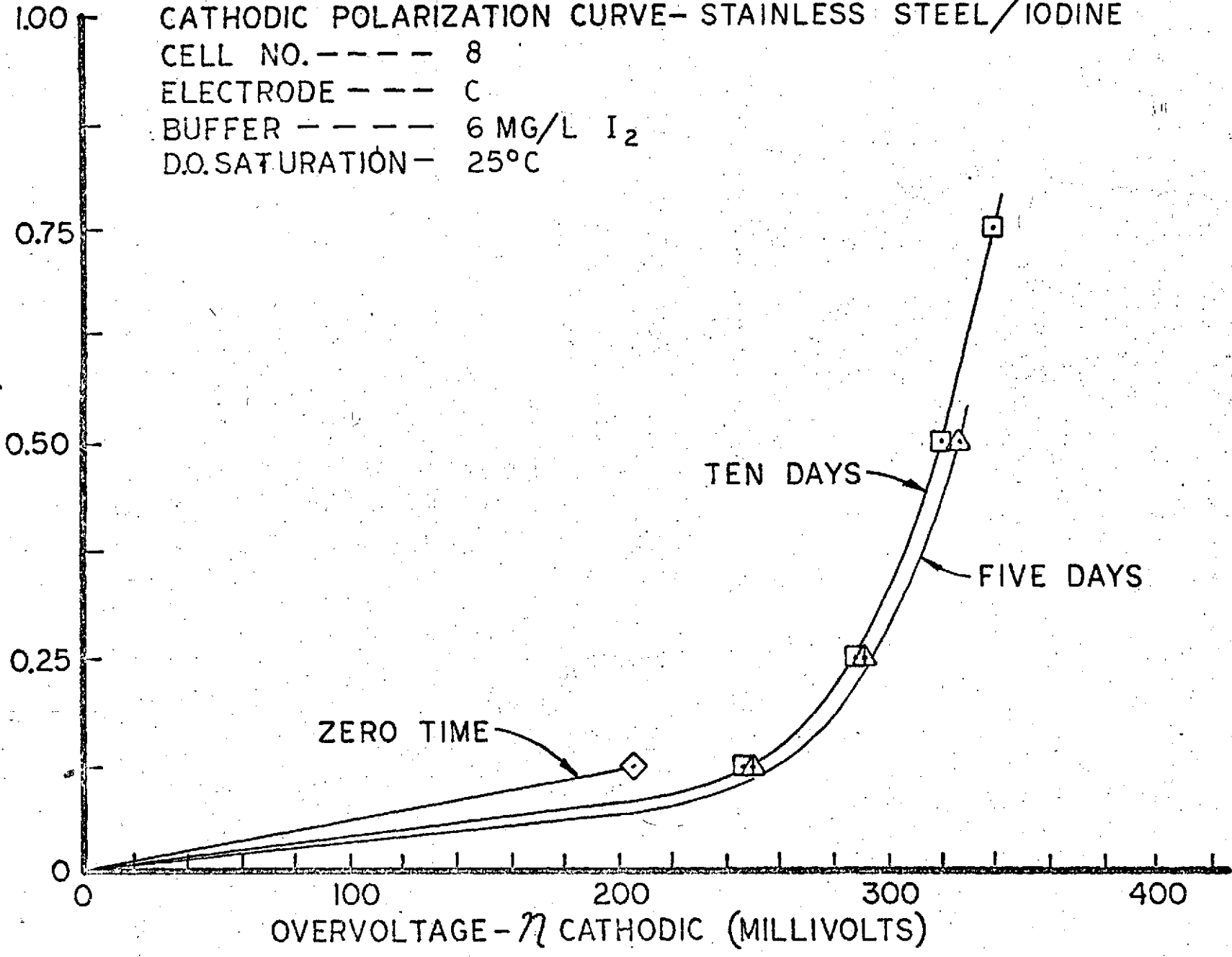
CELL NO. --- 8  
ELECTRODE --- B  
BUFFER --- 6 MG/L I<sub>2</sub>  
D.O. SATURATION --- 25°C



CATHODIC POLARIZATION CURVE- STAINLESS STEEL/IODINE

CELL NO. --- 8  
ELECTRODE --- C  
BUFFER --- 6 MG/L I<sub>2</sub>  
D.O. SATURATION --- 25°C

APPLIED CATHODIC CURRENT  
(MICROAMPERES / CM<sup>2</sup>)



CATHODIC POLARIZATION CURVE- STAINLESS STEEL/IODINE

CELL NO. --- 8  
ELECTRODE --- D  
BUFFER --- 6 MG/L I<sub>2</sub>  
D.O. SATURATION ± 25°C

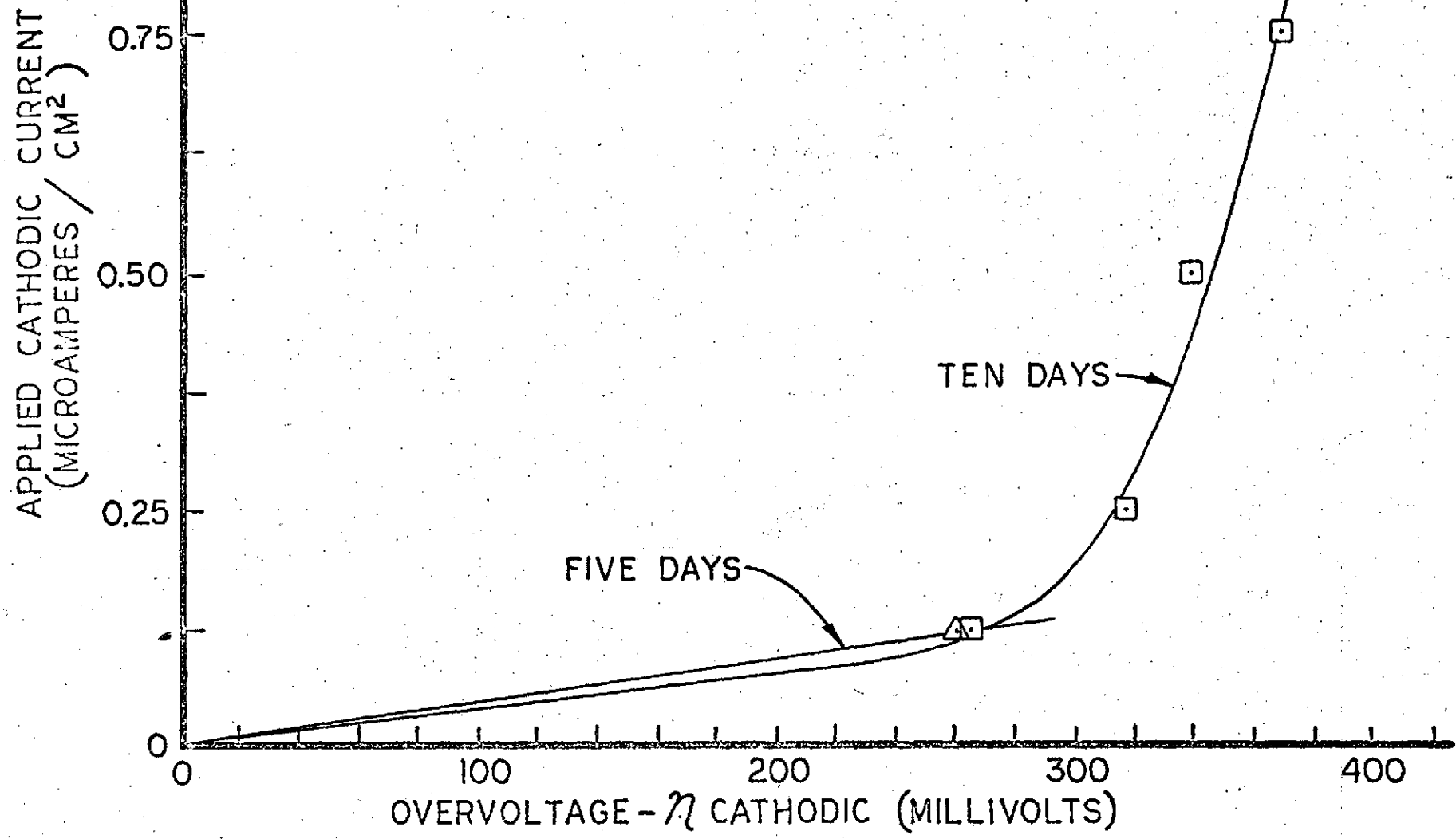


FIGURE D-25

APPENDIX E

CORROSION ELECTROCHEMICAL RAW DATA



TABLE E-1

CORROSION ELECTROCHEMICAL RAW DATA

Experimental Cell	Sampling Date	Electrode	Corrosion Potential (mV)	Applied (Current Ma)	a (mV)	c (mV)
#1 Al Blank Buffer	9 Dec	A	-508	0.5	8.2	22
				1.0	10.0	40
				2.0	25.1	-
		B	0.5	35.4	27.6	
			1.0	69.9	46.6	
			2.0	39.2	18.5	
	C	0.5	10.5	5.4		
		1.0	21.6	10.3		
		2.0	39.2	18.5		
	10 Dec.	D	-558	0.5	16.6	22.7
				1.0	21.6	10.3
				2.0	39.2	18.5
		A	-328	0.5	21.3	41.5
			-320	0.5	40.9	83.1
			-318	0.5	17.7	35.5
	22 Dec.	D	-362	0.5	32.4	56.7
				1.0	69.9	46.6
				2.0	39.2	18.5
A		-308	0.5	47.0	41.5	
		-301	0.5	33.0	35.0	
		-253	0.5	76.0	44.5	
23 Dec.	D	-308	0.5	55.4	34.6	
			1.0	107.0	36.0	
			2.0	159.0	83.0	
	A	-271	0.5	50.0	49.0	
		-330	0.5	25.0	22.0	
		-329	0.5	15.5	35.0	
C	-229	0.5	107.0	36.0		
		1.0	46.0	55.0		
		2.0	159.0	83.0		
D	-329	0.5	15.5	35.0		
		1.0	46.0	55.0		
		2.0	159.0	83.0		
A	-271	0.5	50.0	49.0		
		1.0	107.0	36.0		
		2.0	159.0	83.0		
B	-330	0.5	25.0	22.0		
		1.0	54.0	43.0		
		2.0	125.0	72.0		
C	-229	0.5	107.0	36.0		
		1.0	46.0	55.0		
		2.0	159.0	83.0		
D	-329	0.5	15.5	35.0		
		1.0	46.0	55.0		
		2.0	159.0	83.0		
A	-271	0.5	50.0	49.0		
		1.0	107.0	36.0		
		2.0	159.0	83.0		
B	-330	0.5	25.0	22.0		
		1.0	54.0	43.0		
		2.0	125.0	72.0		
C	-229	0.5	107.0	36.0		
		1.0	46.0	55.0		
		2.0	159.0	83.0		
D	-329	0.5	15.5	35.0		
		1.0	46.0	55.0		
		2.0	159.0	83.0		
A	-271	0.5	50.0	49.0		
		1.0	107.0	36.0		
		2.0	159.0	83.0		
B	-330	0.5	25.0	22.0		
		1.0	54.0	43.0		
		2.0	125.0	72.0		
C	-229	0.5	107.0	36.0		
		1.0	46.0	55.0		
		2.0	159.0	83.0		
D	-329	0.5	15.5	35.0		
		1.0	46.0	55.0		
		2.0	159.0	83.0		

TABLE E-2

CORROSION ELECTROCHEMICAL RAW DATA

Experimental Cell	Sampling Date	Electrode	Corrosion Potential (mV)	Applied (Current Ma)	a (mV)	c (mV)
#2 Al Cl <sub>2</sub> 6.0 mg/l NaOCl @ Cl <sub>2</sub> O <sub>2</sub> = 8.4 mg/l T = 25°C	9 Jan.	A	-392	0.5	5	5
				1.0	10	8
				2.0	14	17
				4.0	23	40
				0.6	6	6
		B	-396	0.6	4	7
				1.0	4	10
				3.0	20	26
				6.0	38	56
				10.0	58	95
		D	-406	0.6	3	7
				1.0	9	8
				3.0	18	27
				6.0	34	53
				10.0	52	91
13 Jan.	A	-460	1.0	10	12.5	
			3.0	32.5	41	
			6.0	53	72	
			10.0	74	117	
			15.0	99	169	
	B	-481	20.0	120	213	
			1.0	17	15	
			3.0	44	41	
			6.0	79	76	
			10.0	112	119	
				15.0	139	181
				20.0	150	236

TABLE E-2 (Con't)

CORROSION ELECTROCHEMICAL RAW DATA

Experimental Cell	Sampling Date	Electrode	Corrosion Potential (mV)	Applied (Current Ma)	a (mV)	c (mV)	
Al/Cl <sub>2</sub> Buffer 6.0 mg/l NaOCl @ Cl <sub>2</sub> O <sub>2</sub> = 8.4 mg/l T = 25°C	13 Jan.	C	-469	1.0	14	12	
				2.0	30	26	
				3.0	39	39	
				D	1.0	20	6.5
					2.0	35	19
	15 Jan.	A		-496	1.0	16	15
					3.0	43	41
					6.0	77	77
					10.0	110	121
					15.0	127	178
B				-540	1.0	16	13
					3.0	47	43
					6.0	100	85
					10.0	155	136
					15.0	186	209
C			-512	1.0	15	15	
				3.0	47	43	
				6.0	91	82	
				10.0	128	130	
				15.0			
D			-530	1.0	14	15	
				3.0	47	46	
				6.0	96	86	
				10.0	137	137	
				15.0	170	205	

TABLE E-3

CORROSION ELECTROCHEMICAL RAW DATA

Experimental Cell	Sampling Date	Electrode	Corrosion Potential (mV)	Applied (Current Ma)	a (mV)	c (mV)	
Al/I <sub>2</sub> 12 mg/l I <sub>2</sub> O <sub>2</sub> = 8.4 mg/l T = 25°C	19 Dec.	A	-572	0.5	-	-	
		B	-538	0.5	92.0	69.2	
		C	-558	0.5	125.0	95.0	
		D	-571	0.5	48.5	40.0	
	23 Dec.	A	-559	0.5	69.0	60.0	
		B	-568	0.5	108.0	71.0	
		C	-571	0.5	142.0	109.0	
		D	-577	0.5	62.0	39.0	
					1.0	80.0	72.0
					2.0	199.0	156.0
		27 Dec.	A	-619	0.5	76.0	69.0
			B	-623	0.5	95.0	80.0
					1.0	225.0	141.0
					2.0	478.0	247.0
					3.0	581.0	339.0
	C		-630	0.5	168.0	120.0	
				1.0	360.0	180.0	
				2.0	511.0	300.0	
				3.0	576.0	410.0	
	D	-687	0.5	43.0	37.0		
				1.0	107.0	71.0	
				2.0	248.0	131.0	
			3.0	390.0	170.0		

TABLE E-4

CORROSION ELECTROCHEMICAL RAW DATA

Experimental Cell	Sampling Date	Electrode	Corrosion Potential (mV)	Applied (Current Ma)	a (mV)	c (mV)	
Al/I <sub>2</sub> 12 mg/l I <sub>2</sub> O <sub>2</sub> < /mg/l T = 25°C	26 Dec.	A	-522	0.5	17	23	
		B	-514	0.5	17	19	
		C	-533	0.5	17	19	
				1.0	34	30	
				2.0	76	71	
				4.0	158	152	
	30 Dec.	D	-540	0.5	18	21	
		A	-496	0.53	9	18	
			B	-507	0.53	8	12
					1.0	18	20
				2.0	40	34	
			3.0	68	49		
4 Jan.	C	-448	0.53	14	8		
		D	-453	0.53	13	10	
				1.0	25	18	
				2.0	49	38	
				3.0	78	57	
		A	-438	0.5	2	16	
			1.0	-3	29		
			2.0	-1	44		
			4.0	14	70		
	B		-540	0.5	6	4	
				1.0	13	13	
			2.0	18	27		
		4.0	40	46			
C	-508	0.5	6	8			
		1.0	9	18			
		2.0	16	31			
		4.0	42	54			

TABLE E-4 (Con'd)

CORROSION ELECTROCHEMICAL RAW DATA

Experimental Cell	Sampling Date	Electrode	Corrosion Potential (mV)	Applied (Current Ma)	a (mV)	c (mV)
Al/I <sub>2</sub>	4 Jan.	D	-507	0.5	5	6
12 mg/l I <sub>2</sub>				1.0	8	12
O <sub>2</sub> </mg/l				2.0	18	23
T = 25°C				4.0	40	44

TABLE E-5

CORROSION ELECTROCHEMICAL RAW DATA

Experimental Cell	Sampling Date	Electrode	Corrosion Potential (mV)	Applied (Current Ma)	a (mV)	c (mV)		
#5 Al/I <sub>2</sub> 6.0 mg/l I <sub>2</sub> O <sub>2</sub> = 8.4 mg/l T = 25°C	19 Dec.	A	-567	0.5	81	64		
		B	-540	0.5	183	141		
		C	-458	0.5	39.7	74.5		
		D	-475	0.5	35.5	34		
	23 Dec.	A	-549	0.5	84	70		
		B	-511	0.5	180	146		
		C	-432	0.5	43	55		
		D	-481	0.5	28	32		
					1.0	58	49	
					2.0	119	101	
		27 Dec.	A	-529	0.5	90	77	
			B	-339	0.5	112	84	
						1.0	192	153
						2.0	279	331
						3.0	368	591
			C	-403	0.5	34	33	
					1.0	69	65	
					2.0	158	117	
	D	-498	0.5	22	16			
				1.0	43	37		
			2.0	98	95			
			3.0	131	101			

TABLE E-6

CORROSION ELECTROCHEMICAL RAW DATA

Experimental Cell	Sampling Date	Electrode	Corrosion Potential (mV)	Applied (Current Ma)	a (mV)	c (mV)		
#6 Al/I <sub>2</sub> 6.0 mg/l I <sub>2</sub> O <sub>2</sub> ≤ 1 mg/l T = 25°C	19 Dec.	A	-311	0.5	176	295		
		B	-222	0.5	8.9	7.0		
		C	-311	0.5	5.0	7.0		
		D	-290	0.5	5.0	12.0		
	24 Dec.				1.0	15.0	27.0	
			A	-481	0.5	59	46	
			B	-531	0.5	37	38	
			C	-551	0.5	29	30	
			D	-522	0.5	38	51	
						1.0	282	329
						2.0	417	433
	29 Dec.	A			0.5	98	70	
					1.0	210	117	
					2.0	447	201	
					3.0	585	143	
					0.5	43	30	
					1.0	83	56	
		B				2.0	187	94
						3.0	281	139
0.5						28	22	
1.0						64	38	
2.0						140	75	
3.0						218	118	
C				0.5	78	55		
				1.0	160	89		
				2.0	374	158		
				3.0	489	213		
				0.5				
				1.0				
D				2.0				
				3.0				
				0.5				
				1.0				
				2.0				
				3.0				



TABLE E-7

CORROSION ELECTROCHEMICAL RAW DATA

Experimental Cell	Sampling Date	Electrode	Corrosion Potential (mV)	Applied (Current Ma)	a (mV)	c (mV)		
S. Steel $I_2 = 12$ $O_2 = 8.4 \text{ mg/l}$ $T = 25^\circ\text{C}$	22 Dec.	A	+481	0.5	352	302		
		B	+548	0.5	349	377		
		C	+502	0.5	311	303		
		D	+516	0.5	315	312		
	26 Dec.	A	+477	0.5	343	272		
		B	+524	0.5	364	368		
		C	+501	0.5	319	299		
		D	-	-	-	-		
	27 Dec.	A			0.5	362	283	
					0.5	371	356	
		B				1.0	432	397
						2.0	512	436
						3.0	570	454
						0.5	324	298
						1.0	383	367
						2.0	449	405
C					3.0	501	432	
					0.5	316	310	
					1.0	368	369	
					2.0	422	419	
D				3.0	451	447		

TABLE E-8

CORROSION ELECTROCHEMICAL RAW DATA

Experimental Cell	Sampling Date	Electrode	Corrosion Potential (mV)	Applied (Current Ma)	a (mV)	c (mV)	
S. Steel/I <sub>2</sub> 6 mg/l I <sub>2</sub> O <sub>2</sub> = 8.4 mg/l T = 25°C	19 Dec.	A	+389	0.5	333	222	
				1.0	405	258	
		B	+419	0.5	312	239	
		C	+362	0.5	342	205	
			D	+402	0.5	325	-
	24 Dec.	A	+499	0.5	301	257	
		B	+479	0.5	273	262	
		C	+438	0.5	293	253	
				1.0	348	291	
				2.0	401	326	
		D	+442	0.5	288	260	
		29 Dec.	A	+451	0.5	321	255
					1.0	377	302
				2.0	419	332	
				3.0	447	353	
	B		+462	0.5	299	264	
				1.0	344	302	
				2.0	394	337	
				3.0	417	353	
	C		+421	0.5	325	249	
			1.0	373	286		
			2.0	419	320		
			3.0	441	341		
D	+442	0.5	305	263			
		1.0	359	317			
		2.0	400	341			
		3.0	431	369			

APPENDIX F

MATHEMATICAL BASIS FOR THE GRAPHICAL ANALYSIS  
EMPLOYED IN EVALUATING THE IODINE LOSS RATE ON  
ALUMINUM AND STAINLESS STEEL SURFACES

## APPENDIX F

### MATHEMATICAL BASIS FOR THE GRAPHICAL ANALYSIS EMPLOYED IN EVALUATING THE IODINE LOSS RATE ON ALUMINUM AND STAINLESS STEEL SURFACES

The disappearance of  $I_2$  upon reaction at the metal surface may be treated as though it represents a flux,  $N$  ( $mg/cm^2/day$ ), of  $I_2$  across the surface. At  $25^\circ C$  and atmospheric pressure,  $N$  is a function of:

- (1) General characteristics of the barrier including:
    - (a) substance
    - (b) surface preparation
    - (c) previous chemical exposure
- } reactant surface area,  $A$ .
- (2) The  $I_2$  concentration,  $X^I$
  - (3) The cell volume,  $V$ .

The cell volume is included in the above list since it is evident that the bulk transport of  $I_2$  to the metal surface could be dependent; dependency could be reduced by the small volumes and stirring utilized in these experiments. The simplest function to evaluate involving the above considerations include:

$$N = k X^I \quad (F-1)$$

where  $k$  is a rate constant embodying the thermodynamic activity coefficient for  $I_2$  as well as the barrier characteristics described above.

Experimentally,  $X^I$  is a time dependent variable whereas  $V$  is a step function (because of sample removal) over time.

Thus, from equation 1:

$$A \cdot N = \frac{dXV}{d\theta} \quad (F-2)$$

Combining Equations F-1 and F-2 and integrating over the interval  $\theta_1 = 0$  to  $\theta_2$ , with  $V_1$  constant:

$$\frac{k \cdot A}{2.303} = \frac{\log_{10} X_2^I - \log_{10} X_1^I}{\theta_2 - \theta_1} \quad (F-3)$$

Thus, as long as  $V$  is constant, a semilog plot of  $X^I$  vs  $\theta$  will be linear and the slope of this line will determine  $k$ . Since samples are periodically removed from the test cells, volume is a step function of time and a semilog plot of  $X^V$  vs.  $\theta$  is as schematically represented in Figure F-1 where:  $X_i^V$  denotes the test cell iodine concentration at a test cell volume of  $V_i$  and at time  $\theta_i$ .

Also presented in Figure F-1 are the correction factors for each step volume adjustment so that the best line of fit is represented by line, L.

Theoretically,  $k$  could be determined over each segment separately; variations in analytical precision produce large differences in  $k$  values determined individually. However, a plot of the sequence:

$$\theta_0, \log_{10} (V_0)^{V_1}$$

$$\theta_1, \log_{10} (X_1)^{V_0}$$

$$\theta_2, \log_{10} (X_2)^{V_1} + (V_0 - V_1) \log X_1$$

$$\theta_3, \log_{10} (X_3)^{V_2} + (V_0 - V_1) \log X_1 + (V_2 - V_1) \log X_2$$

will be precisely colinear. It should be noted that the correction terms become smaller with time.

SCHEMATIC OF  $X^V$  VARYING ON TIME WITH  
 $V$  CHANGING PREDICTABLY

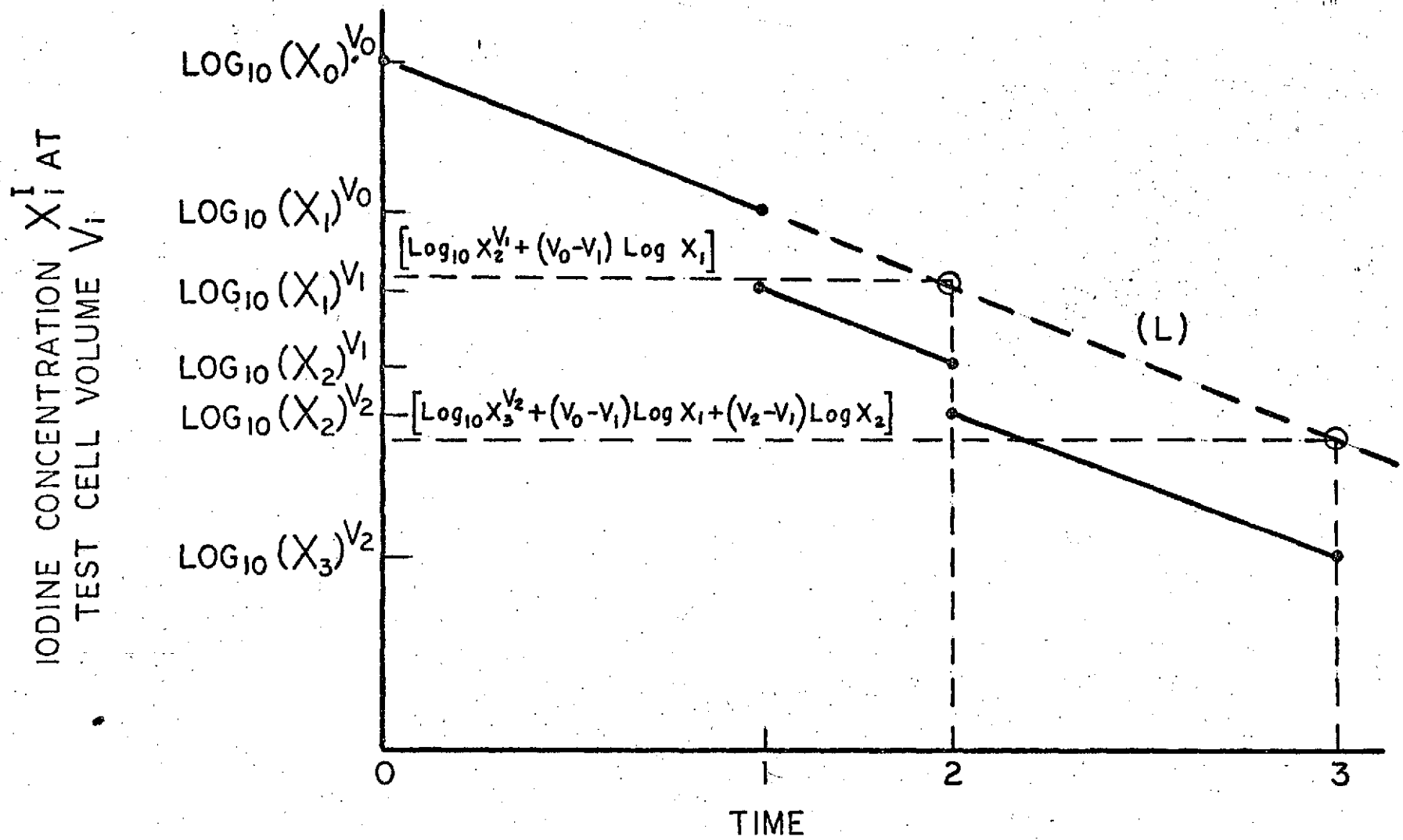


FIGURE F-1

APPENDIX G

CRITIQUE OF BACTERIOLOGICAL REPORTS

## APPENDIX G

### CRITIQUE OF BACTERIOLOGICAL REPORTS

(Prepared by Dr. R. C. Cooper)

**Title:** HAMILTON STANDARD (DIV. OF UNITED AIRCRAFT CORP.) - Report No. SUHSER 4741: Bactericidal Water Test of the Water Management Section of the Lunar Module Environmental Control System. September 1, 1967.

#### Brief Description

A model of the Waste Water Management Section of the Lunar Module was used in these tests. The test system was initially filled with a solution of 70% ethyl alcohol and allowed to stand for one hour. At the end of this contact time the system was flushed with SUP-114 water, a water simulating water used in the Apollo system. Water containing 4 mg/l iodine was added and the system allowed to stand for 27 days (pre-launch time). After this time the hardware was used for 50 hours, during which time a solution containing Bacillus subtilis was gradually infused into the water separation parts in order to simulate the input of suit condensate from the Astronauts.

This report indicates that the application of the 70% alcohol solution followed by the iodine treatment sterilized the system. It was also concluded that bacteria did not migrate from the waste water system to the potable supply. Iodine concentration changed from an initial concentration of 2.6 mg/l at the start of the 29 days to very low values by the end of the test period.

#### Critique

The bacteriology used in this series of tests was most elementary. The methods used did not really clarify the problem as to whether or not bacteria could migrate from the waste water section to the potable water system. No controls were run to determine whether the potable water was bacteria free because of the presence of iodine in the water or because no migration had taken place.

The word sterilization is used rather loosely. It was interesting to note that these investigators tested the alcohol and iodine solutions directly for the presence of bacteria. Apparently no attempt was made to neutralize the bactericidal properties of the disinfectant. For example, was sodium thiosulfate added to all samples containing iodine? In what form was the iodine added?



Why was B. subtilis chosen for these tests? I suspect because it is a spore forming organism and spores are noted for their resistance. In this report, however, it is obvious that no thought was given as to whether or not the organisms used were sporulating, and if so how much of the population if any was in this state.

In general, the bacteriology employed in these tests was very poor.

Title: HAMILTON STANDARD (DIV. OF UNITED AIRCRAFT CORP.) - Report No.

SVHSER 4741 Supplement #1: Bactericidal Water Test of the Water

Management Section of the Lunar Module Environmental Control System.

December 8, 1967.

#### Brief Description

This report is a continuation of the one previously described (SUHSER 4741-Sept. 1967). The procedures used were basically the same as described above.

It was concluded from this work that under the conditions of the test an initial concentration of 4 mg/l and never lower than 2.2 mg/l of iodine will maintain "bacteria free" water. It will also reduce the number of B. subtilis in the sublimator line but will not sterilize. No B. subtilis was found in the drinking water system either because none migrated through the system or any that did were killed by the residual iodine present.

#### Critique

The same criticism holds for this report as was stated concerning its predecessor.

Title: NORTH AMERICAN ROCKWELL CORPORATION - Report No. SD68-364: Bacteria

Migration in the Apollo Potable Water Supply System. April 26, 1968.

#### Brief Description

Tests were performed in a simulated Apollo water system to determine if bacterial migration was possible from the waste water system. A silver ion exchange unit was also tested for its efficacy as a sterilization method.

The test system was pretreated with exposure for six hours to a solution of 70% ethyl alcohol. At the end of this period the system was drained and purged with helium.

A five gallon carboy of water to which was added, daily, enough Escherichia coli to maintain a concentration of  $1 \times 10^6$  to  $1 \times 10^7$  organism per ml acted as a simulator of the suit heat exchanger and water separator

source. In addition, 2 ounces of human urine were added daily. Samples of this contaminated water were injected into the waste water system at regular intervals. One seven-day run was so conducted. The result was that no E. coli was detected at any site other than in the waste water supply; however, at the end of the second day there appeared a large number of bacteria tentatively identified as either Pseudomonas or Alcaligenes species.

A second run of three days duration was made in which the check valve between the potable and waste supply was opened; however, a silver ion unit was placed in between. Escherichia coli was quickly found in the potable supply indicating that the silver ion unit had failed. The failure was due to channeling in the unit. When a similar unit was placed at the drinking gun outlet it worked quite satisfactorily.

#### Critique

The results of these tests indicated that migration of bacteria from the waste system to the potable water supply was a remote possibility if the check valves are functioning properly. The silver ion unit can be effective in sanitizing the drinking water provided the resin bed is properly packed. This test run indicated that there is some risk of mechanical failure when using the silver ion device.

This test also indicated that the pretreatment of the system with alcohol and helium did not seem to "sterilize" the system. The resulting growth of the non-coliform gram negative organisms to levels of more than 5,000 per ml is not particularly unusual but would seem to be far beyond the NASA Water Quality Criterion that no virus, fungi or bacteria should be present in the water system. (Stated in Eng. Science Report to NASA, Sept. 1969).

This series of tests seems somewhat more conclusive concerning migration of microorganisms in the test configuration than the previous studies and did indicate that certain microorganisms will flourish in the potable system unless some continuous disinfecting process is used.

Title: BROWN AND ROOT-NORTHROP - Combined Test Plan and Test Report: Kill of Microorganisms in Sodium Acetate and Chlorine: LRL/BRN Test No. 68-193. December 13, 1968.

#### Brief Description:

The objective of the reported study was to determine the effectiveness of a combination of sodium acetate (40 mg/l) and chlorine (6 mg/l) in inhi-

biting the growth of six different genera of bacteria. These laboratory tests were conducted in a rather straightforward manner, by determining the ability of the test organism to grow after exposure of 15 minutes to two hours.

### Critique

In one-half of the cases the species of organism used were unknown. It would be much more informative and repeatable by others if the species used were described. The report is not at all specific concerning the cultural conditions of growth of the test organisms. It is important to know what phase of growth the organisms are in when tested, whether, in the case of spore formers, they are sporulating, and how the organisms were washed before use in the test. It is a well established fact that the cultural conditions just prior to exposure to adverse physical or chemical conditions have a significant effect on survival of bacteria.

This test series was not very well controlled and did not really evaluate the effect sodium acetate might have upon the efficacy of chlorine disinfection. No parallel tests were conducted with just chlorine and with just acetate alone. It was also not apparent whether any neutralizing solution was used to stop bactericidal action at the end of the various disinfection time periods.

Since the results were reported as either growth or no growth, it is difficult to understand why the investigators did not use broth tubes rather than "smear plates" with only 0.1 ml inoculum. Broth would have made the growth of the Clostridium sp. particularly easy and more accurate.

The whole test procedure would have produced more enlightening results if it had been done on a quantitative basis using pour plates and much shorter initial time intervals such as 15 seconds, 30 seconds, 45 seconds, and 1 minute.

APPENDIX H

ANALYSIS OF PERMEABILITY OF POLYISOPRENE  
TO HYDROGEN AND OXYGEN IN APOLLO  
COMMAND MODULE POTABLE WATER TANK

## APPENDIX H

### ANALYSIS OF PERMEABILITY OF POLYISOPRENE TO HYDROGEN AND OXYGEN IN APOLLO COMMAND MODULE POTABLE WATER TANK

#### INTRODUCTION

AiResearch Manufacturing Division has conducted tests to determine the permeability of polyisoprene membrane to hydrogen and oxygen in the simulated environment of the potable water tank of the Apollo Command Module. The results of the tests are reported in the document "Development Test Data - Potable Water Tank Bladder Oxygen Permeability Tests", NR/SD Project Apollo, DTD-222, AiResearch Manufacturing Division, dated 26 August 1969. This report was supplied to Engineering-Science, Inc. by the Project Officer; the basic information presented below was obtained from Figure 6 of the above-cited report.

It is noted that the AiResearch tests were conducted in batch systems rather than continuous flow systems. It is not possible to ascertain from the AiResearch report what degree of mixing was effected in their test system or what effort was made to simulate in the laboratory the degree of mixing achieved under prototype operating conditions of semi-continuous flow.

It is also noteworthy that the AiResearch report does not indicate the temperature at which the permeability experiments were conducted. Temperature is a foremost variable affecting both the diffusivity of dissolved gases in water and the permeation or diffusion of gases through a membrane. There is no reference, in the absence of specific temperature data, for application of the AiResearch data unless it is assumed that their experiments were performed at a laboratory temperature approximating the temperature realized in the prototype.

#### DATA ANALYSIS

Table H-1 summarizes four sets of concentration data each on the curves for oxygen saturation and hydrogen depletion taken from Figure 6 of the above-cited report. These data were analyzed assuming that the diffusion of oxygen and hydrogen can be modelled by the first order equation used elsewhere in this report, i.e.

$$\ln \frac{\Delta X_1}{\Delta X_2} = \frac{DA}{TV} \Delta \theta$$

TABLE H-1

OXYGEN SATURATION AND HYDROGEN DEPLETION DATA  
APOLLO COMMAND MODULE SIMULATION

Gas	Dissolved Gas Concentration Gradient (mg/l)		$\theta$ (hours)	$\ln \frac{\Delta X_1}{\Delta X_2}$	D (cm <sup>2</sup> /hr)	Average D (cm <sup>2</sup> /hr)
	Initial ( $\Delta C_1$ )	Final ( $\Delta C_2$ )				
Oxygen	62	34	25	0.600	0.0412	0.0557
	57.5	26	25	0.790	0.0543	
	57.5	18	30	1.16	0.0664	
	62	18	35	1.24	0.0607	
Hydrogen	3	0.4	60	2.02		
Hydrogen	3	0.4	60	2.02	0.0579	
	1.5	0.4	35	1.322	0.0650	
	2	0.3	55	1.895	0.0593	
	3	0.3	70	2.30	0.0566	
						0.0597

Notes: 1. Equation:  $\ln (\Delta X_1 / \Delta X_2) = (DA/L^2)\Delta\theta$

2.  $A/V = 1,550 / (15,000 \times 0.178) = 0.581 \text{ (cm)}^{-2}$

H-2

where:  $\Delta X_1$  = Initial concentration differential across membrane, mg/l  
 $\Delta X_2$  = Final concentration differential across membrane, mg/l  
 $D$  = Diffusion constant,  $\text{cm}^2/\text{hr}$   
 $A$  = Polysoprene membrane area, 1,550 sq cm  
 $V$  = Simulated potable water tank volume, 15,000 cu cm  
(33 lb  $\text{H}_2\text{O}$ )  
 $t$  = Membrane thickness, 0.178 cm

The concentration gradient for the oxygen saturation experiment was calculated using a saturation concentration of 70 mg/l (oxygen saturation level at 25 psia  $\text{O}_2$  and at 76°F). The concentration gradient for the hydrogen depletion curve was calculated using a zero hydrogen concentration. Diffusion constants were calculated for each of the four sets of points for each gas, and an average diffusion rate calculated for each gas from these data.

The average diffusion constant with polyisoprene as reported in Table H-1 are as follows: (1) Oxygen:  $0.0557 \text{ cm}^2/\text{hr}$ ; (2) Hydrogen:  $0.0597 \text{ cm}^2/\text{hr}$ .

APPENDIX I

ANALYSIS OF IODINE DEPLETION DATA  
FROM MC DONNELL-DOUGLAS ASTRONAUTICS COMPANY  
ORBITAL WORKSHOP REDUCED SCALE  
WATER STORAGE TANK



## APPENDIX I

### ANALYSIS OF IODINE DEPLETION DATA FROM MC DONNELL-DOUGLAS ASTRONAUTICS COMPANY ORBITAL WORKSHOP REDUCED-SCALE WATER STORAGE TANK

#### INTRODUCTION

A memorandum dated 9 January 1970 summarizing iodine depletion studies performed at McDonnell-Douglas Astronautics Company was transmitted to Engineering-Science, Inc. by the Project Officer on 14 January 1970. The studies described therein were carried out in four tanks, each sized at 8-in diameter and 14-in length and each fabricated from a different stainless steel alloy. The four alloys used were stainless steel types 304L, 316-13, 321, and 347, and the tank dimensions were set to simulate the surface area/volume ratios of the water storage tanks to be used in the OWS (Orbital Workshop Program). Tank contents were not stirred during the tests and the temperature of the test solutions was not reported. Iodine depletion tests were conducted over 15-day periods with each of the tanks using initial iodine concentrations of 7.3 to 7.6 mg/l.

#### DATA ANALYSIS

The raw data obtained in the depletion studies (from Figure I-1 of the subject memorandum) are summarized in Table I-1. These data, consisting of initial and final iodine concentrations, were analyzed assuming that the depletion of iodine can be modeled by the first order equation used previously in this report, viz.,

$$\ln \frac{X_1}{X_2} = \frac{K_{C-A} A}{V} \Delta \theta \quad (I-1)$$

where:  $X_1$  = Initial concentration, mg/l  
 $X_2$  = Final concentration, mg/l  
 $K_{C-A}$  = Reaction constant, conversion of iodine, liter/sq cm-day  
 $A$  = Surface area of vessel, sq cm  
 $V$  = Volume of vessel, liters  
 $\Delta \theta$  = Time, days

The  $K_{C-A}$  values obtained for each of the stainless steels is shown in Table I-1.  $K_{C-A}$  values varied from a minimum of  $1.98 \times 10^{-5}$  liter per sq cm-day for Type 304 to a maximum of  $3.19 \times 10^{-5}$  liter per sq cm-day for Type 347. Thus, Type 304 stainless steel exhibited the lowest iodine

TABLE I-1

IODINE DEPLETION DATA FOR  
ORBITAL WORKSHOP REDUCED-SCALE WATER STORAGE TANK

Stainless Steel Type	Iodine Concentrations (mg/l)		$\theta$ (days)	$\ln \frac{X_1}{X_2}$	$K_{C-A}$ (liter per sq cm-day)
	Initial	Final			
304	7.4	6.9	14	0.0697	$1.98 \times 10^{-5}$
316	7.3	6.8	13	0.0706	$2.15 \times 10^{-5}$
321	7.6	6.8	14	0.1107	$3.14 \times 10^{-5}$
347	7.5	6.8	13	0.1047	$3.19 \times 10^{-5}$

Notes: 1. Equation:

$$\ln \frac{X_1}{X_2} = \frac{K_{C-A} A \Delta \theta}{V}$$

$$\frac{A}{V} = \frac{2915 \text{ sq cm}}{11.6 \text{ liter}} = 252 \frac{\text{sq cm}}{\text{liter}}$$

2. Data from McDonnell-Douglas Astronautics Company
3. Tank contents unstirred
4. Oxygen concentration in tank contents not determined
5. Temperature of test solutions not determined

depletion rate of the four types which were tested. It is noteworthy that the above depletion constants, obtained in unmixed systems, are about two orders of magnitude less than the depletion constants determined for iodine in stainless steel in the corrosion studies ( $2.40 \times 10^{-3}$  liter/sq cm-day, Chapter V).

It is unknown whether McDonnell-Douglas Company has developed additional data from their studies. However, three points should be noted in interpretation of the above and additional data obtained from this study.

- (1) The dissolved oxygen concentration of the tank contents, which is believed to be a major factor in corrosion processes, was not determined. The statement that the stock solution was degassed has no meaning in this context, particularly when effort to adjust the dissolved oxygen concentration of the dilution water is not mentioned.
- (2) A comparison of the depletion rates estimated with the McDonnell-Douglas data (unmixed systems) and the depletion rates obtained in mixed cells in conjunction with the corrosion studies presents weighty evidence that mixing has a significant effect on depletion. The effect of mixing is to maintain a uniform concentration throughout the tank contents. It is apparent from the comparison that a factor other than iodine conversion at the metal surface is limiting, viz., iodine diffusion through the water mass. The implications of diffusion in the aqueous phase as the rate limiting step in iodine depletion are discussed in Chapter VII.
- (3) The temperature of the test solutions during the depletion studies was unknown. Both the rate of iodine conversion (corrosion rate) and the diffusion constant of iodine in aqueous solution are highly temperature dependent; thus, there is no reference in which the McDonnell-Douglas data can be used unless it is assumed that the work was done at a laboratory temperature approximating the temperature to be realized in the prototype.