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ANODIC BEHAVIOR OF LITHIUM IN AQUEOUS ELECTROLYTES. IV. INFLUEN--ETC(U)
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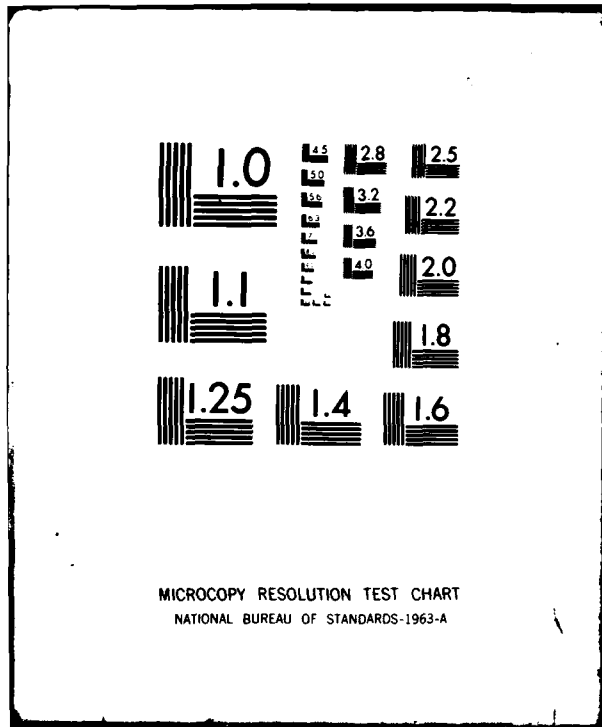
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ANODIC BEHAVIOR OF LITHIUM IN AQUEOUS ELECTROLYTES.

IV. INFLUENCE OF TEMPERATURE.

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INTRODUCTION

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The rapid dissolution of Li in alkaline aqueous solutions can be utilized electrochemically to produce very high rate batteries. In the $\text{Li-H}_2\text{O}$ system, the rate-limiting process is the oxidation of lithium rather than the reduction of H_2O at the cathode. A critical examination of the corrosion processes has revealed that the H_2 e.r. at the Li surface is rate determining, not the Li dissolution reaction ⁽¹⁾. Thus, unlike conventional battery systems, in $\text{Li-H}_2\text{O}$ cells the current efficiency is governed by the ratio of two competing reactions, namely, the anodic dissolution reaction and the parasitic self-corrosion reaction ⁽²⁾. The current efficiency increases as the electrode is polarized from its OCV, and it decreases at elevated temperatures where the corrosion reaction is stimulated. One of the most important features of the system is the fact that the maximum current (or limiting current) obtained during anodic polarization never exceeds the OCV corrosion rate. This unusual behavior and the impact of elevated temperature on the faradaic efficiency of the cell are examined in this paper.

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LOCKHEED PALO ALTO RESEARCH LABORATORY
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EXPERIMENTAL

Details of the electrochemical cell and support equipment have been given previously (1). In summary, the test cell housed a circular 11.4-cm² dia. anode support to which was bonded the lithium test specimen. The cathode comprised a wire screen spotwelded to a ribbed iron back plate. A needle point penetrometer was mounted on the cathode compartment such that on activation the platinum-plated steel needle could pass through the matrix and penetrate the anode surface. The penetrometer was instrumented with an impedance meter and linear motion transducer (3). Accuracy of the probe position was within $\pm 10^{-3}$ cm.

Electrolyte flow through the cathode matrix and across the anode face was provided by a micropump and was monitored with a rotameter. Electrolyte temperature was controlled to $\pm 0.1^{\circ}\text{C}$ by passing it from a reservoir to a constant temperature heat exchanger, and into the cell.

Real time hydrogen rate measurements were obtained using a wet test meter which was modified with an optical encoder connected to a digital/analog converter.

Lithium hydroxide solutions were prepared using reagent grade chemical and deionized water.

The experimental conditions for the sequence of tests reported here were:

LiOH concentration	:	4.5 M
Electrolyte flow rate	:	30 cm/s
Anode-cathode contact pressure	:	6.2×10^4 Pa
Electrolyte temperature:		18, 25, 35, 45, 55°C

Polarizations were performed potentiostatically, using a custom designed 0 - 10 A, 0 - 10 V instrument. Response time was 60 μsec (from no load),

input impedance was $1.5 \times 10^{12} \Omega$, and voltage stability was $\pm 2.5\%$.

Anode potentials were monitored with a cadmium (cadmium hydroxide) reference electrode ($E^\circ = -0.809 \text{ V vs NHE}$).

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RESULTS

The influence of temperature on the anodic polarization of Li in 4.5 M LiOH at a constant anode-cathode contact pressure, $P = 6.2 \times 10^4$ Pa and electrolyte flow velocity, $v = 30$ cm/s is shown in Fig. 1. The polarization curves possess two distinct regions, typified by the curve at 55°C. The initial portion of the curve depicted as a-c is linear. It represents IR drop across an essentially invariant protective oxide film layer. The highly polarized curved portion c-l has a configuration which is often characteristic of a limiting current. Over the entire span, a-c-l, it is assumed that the anodic film formation rate is balanced by the film dissolution rate because, as has previously been observed⁽³⁾, the film thickness is independent of the extent of polarization. Under the experimental conditions specified, it was noted that increasing temperature decreased the film's resistance and the maximum current depicted as I_l increased markedly with increasing temperature.

From the slopes of the resistive polarization sections of the curves of Fig. 1, a plot of film resistance vs temperature may be obtained as shown in Fig. 2. Temperature dependence of the limiting current density, i_l , derived from Fig. 1, and of the measured corrosion rate at OCV, i_{cor} , are displayed in Fig. 3. i_{cor} increases significantly at elevated temperatures (i.e., $> 35^\circ\text{C}$) while i_l maintains a linear relationship with temperature over the range of this study.

Fig. 4 shows that the relationship between anode film thickness and temperature is nonlinear. The decrease of film thickness x_o with increasing temperature may be associated with the fact that the solubility of LiOH, which comprises the major portion of the oxide film, increases with increasing temperature⁽⁴⁾. Since the film thickness does not change with polarization⁽³⁾, it seems reasonable to assume that the solubility of LiOH at various temperatures

FIG. 1 ANODIC POLARIZATION OF LI IN 4.5
LiOH AT VARIOUS TEMPERATURES AT $P = 6.2 \times 10^5$
AND $v = 30 \text{ cm/s}$.

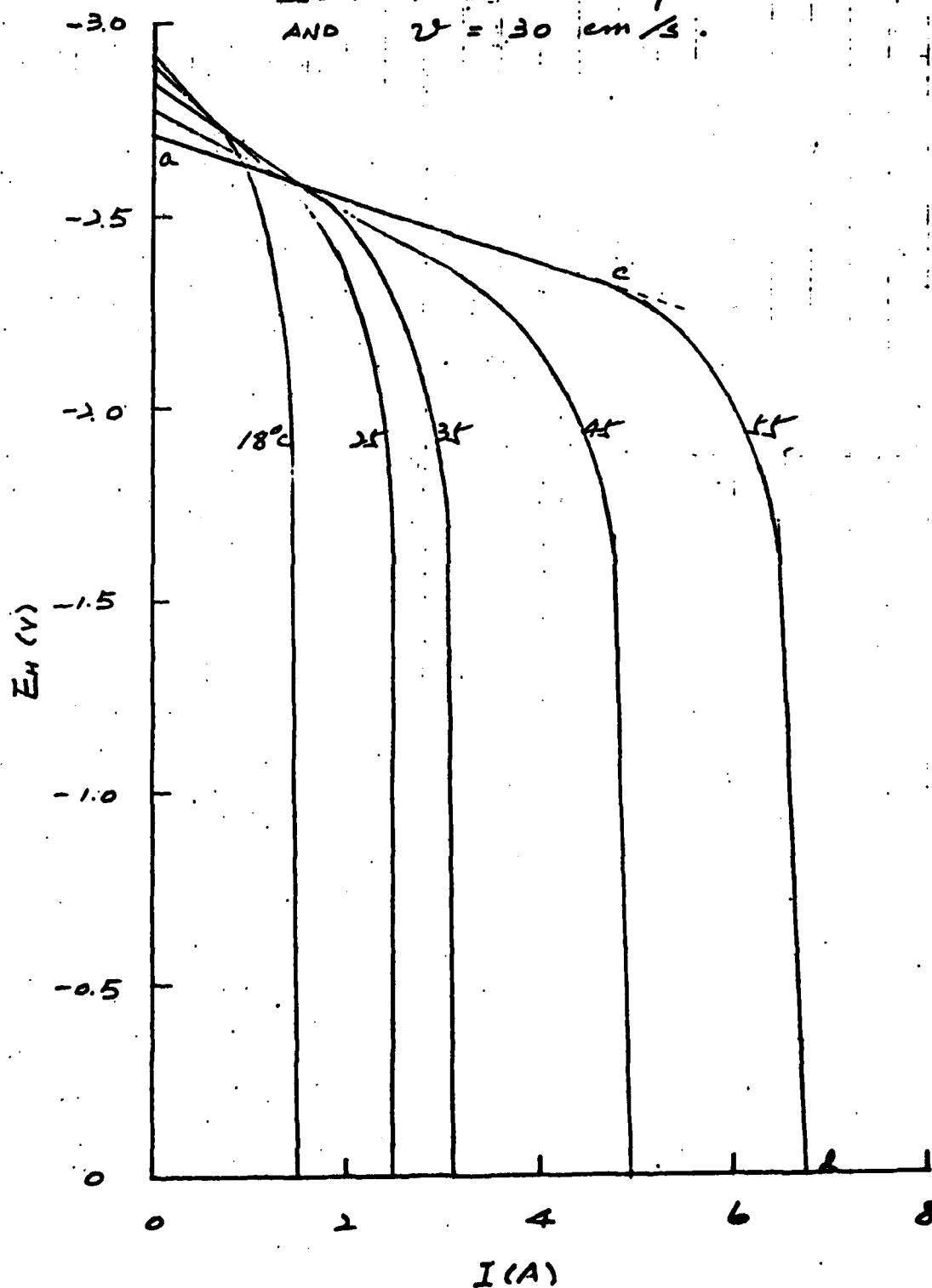


FIG. 2. INFLUENCE OF ELECTROLYTE TEMPERATURE ON ANODE FILM RESISTANCE IN 4.5M LiOH AT $P=6.2$ Pa AND $v = 30$ cm/s.

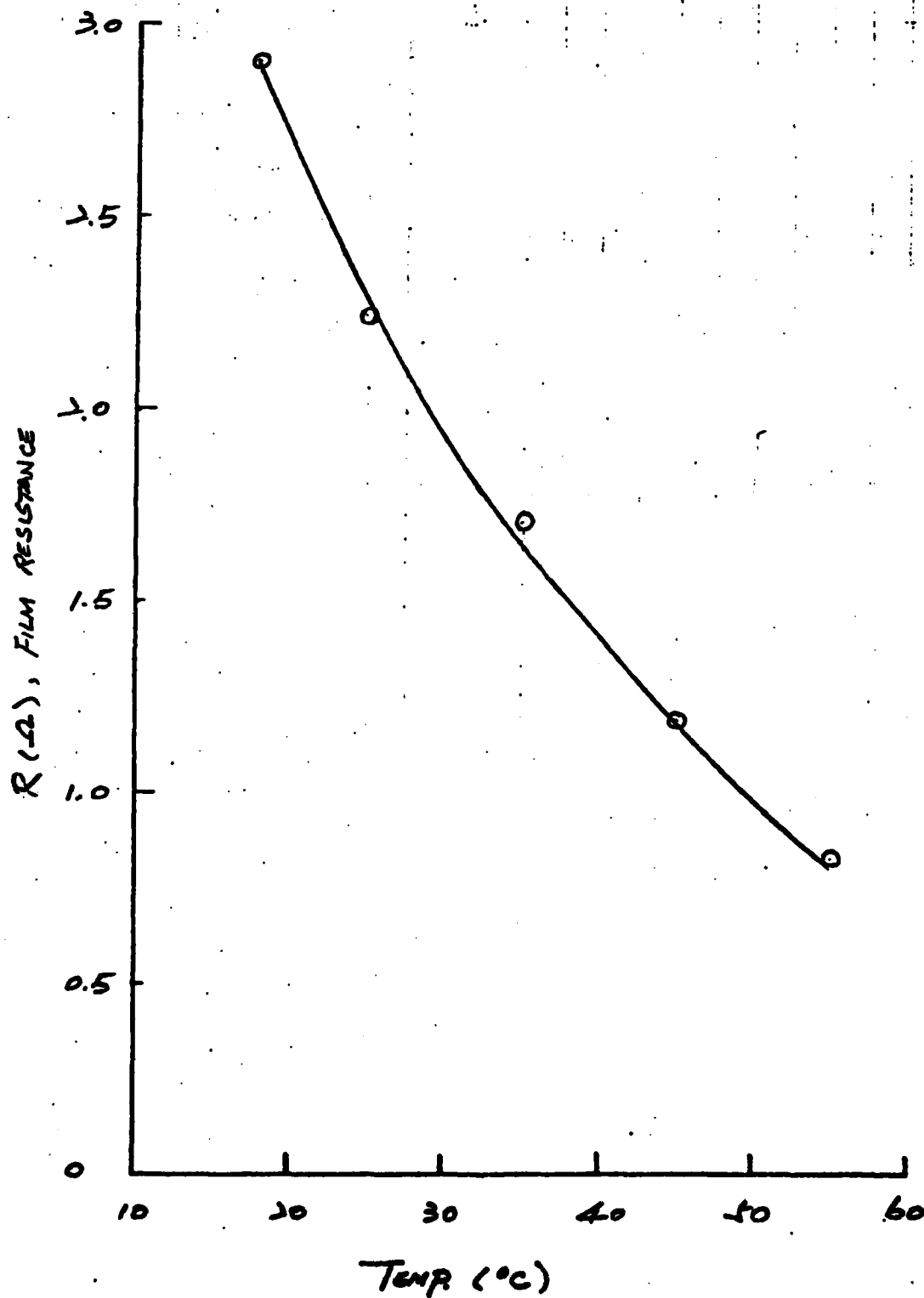


FIG. 3 INFLUENCE OF ELECTROLYTE TEMPERATURE ON THE CORROSION RATE AT OCV (i_{cor}) AND ANODIC LIMITING CURRENT DENSITY OF Li IN 4.5M LiOH AT $P=6.2 \times 10^5$ AND $v = 30 \text{ cm/s}$.

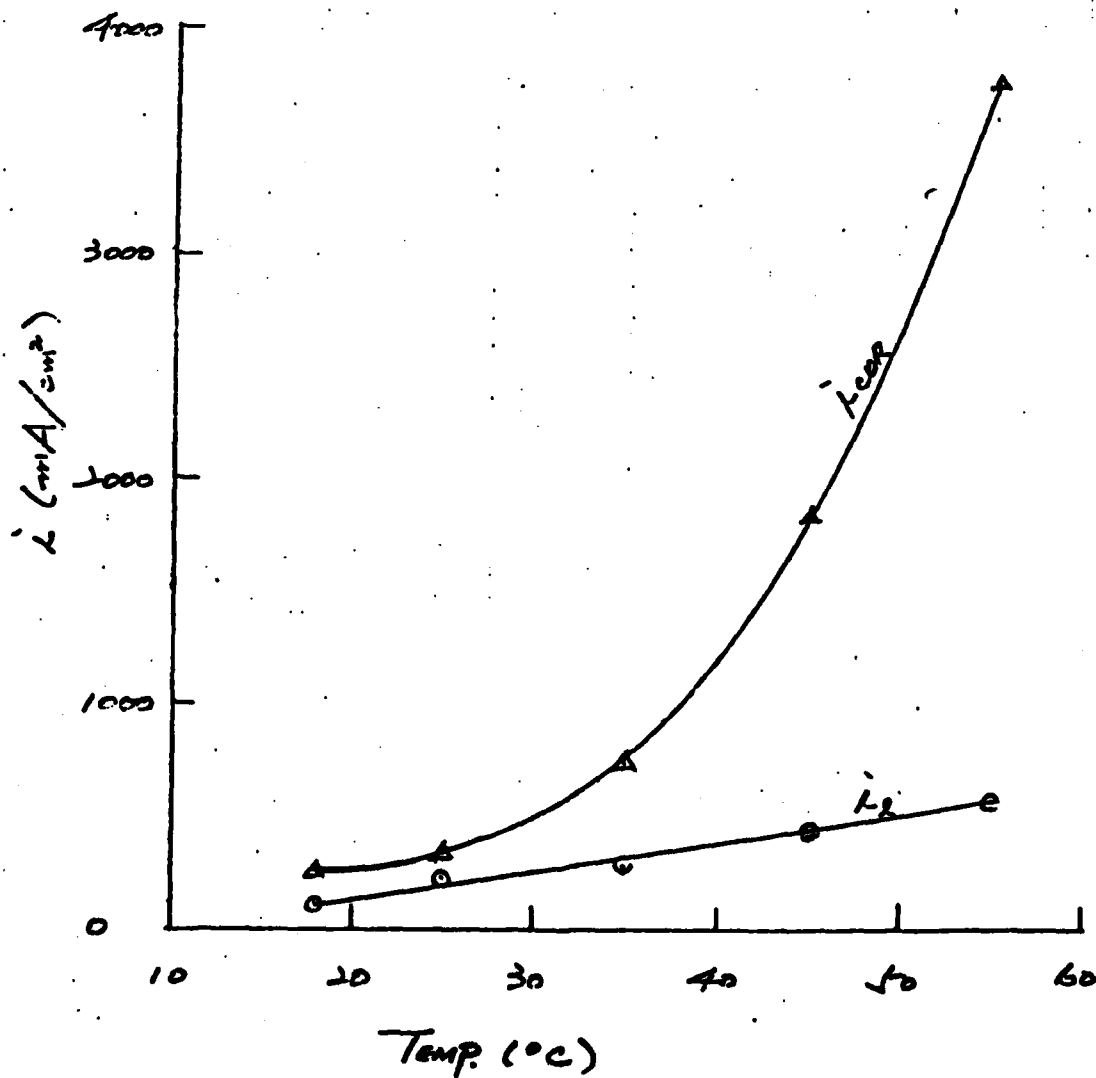
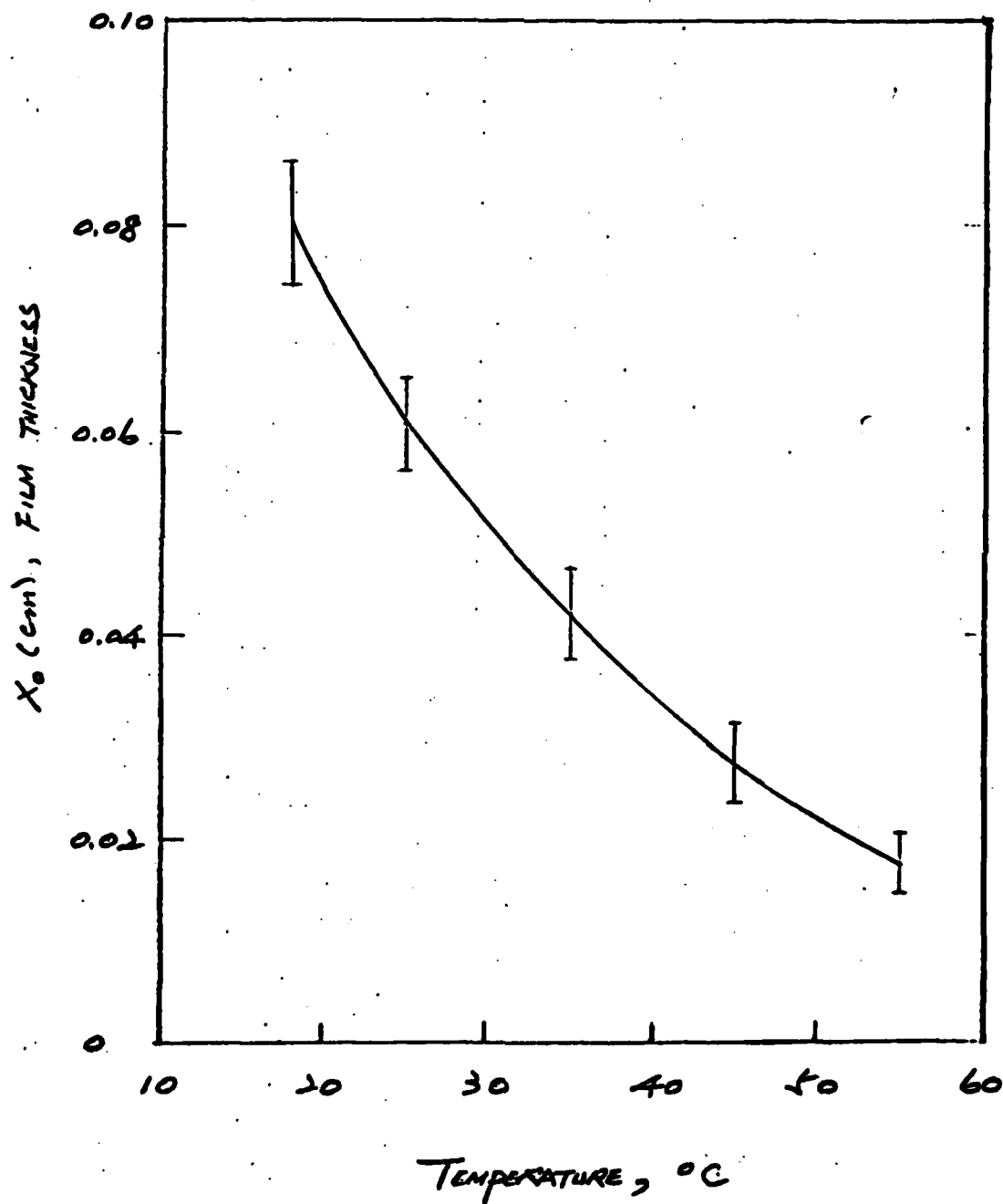


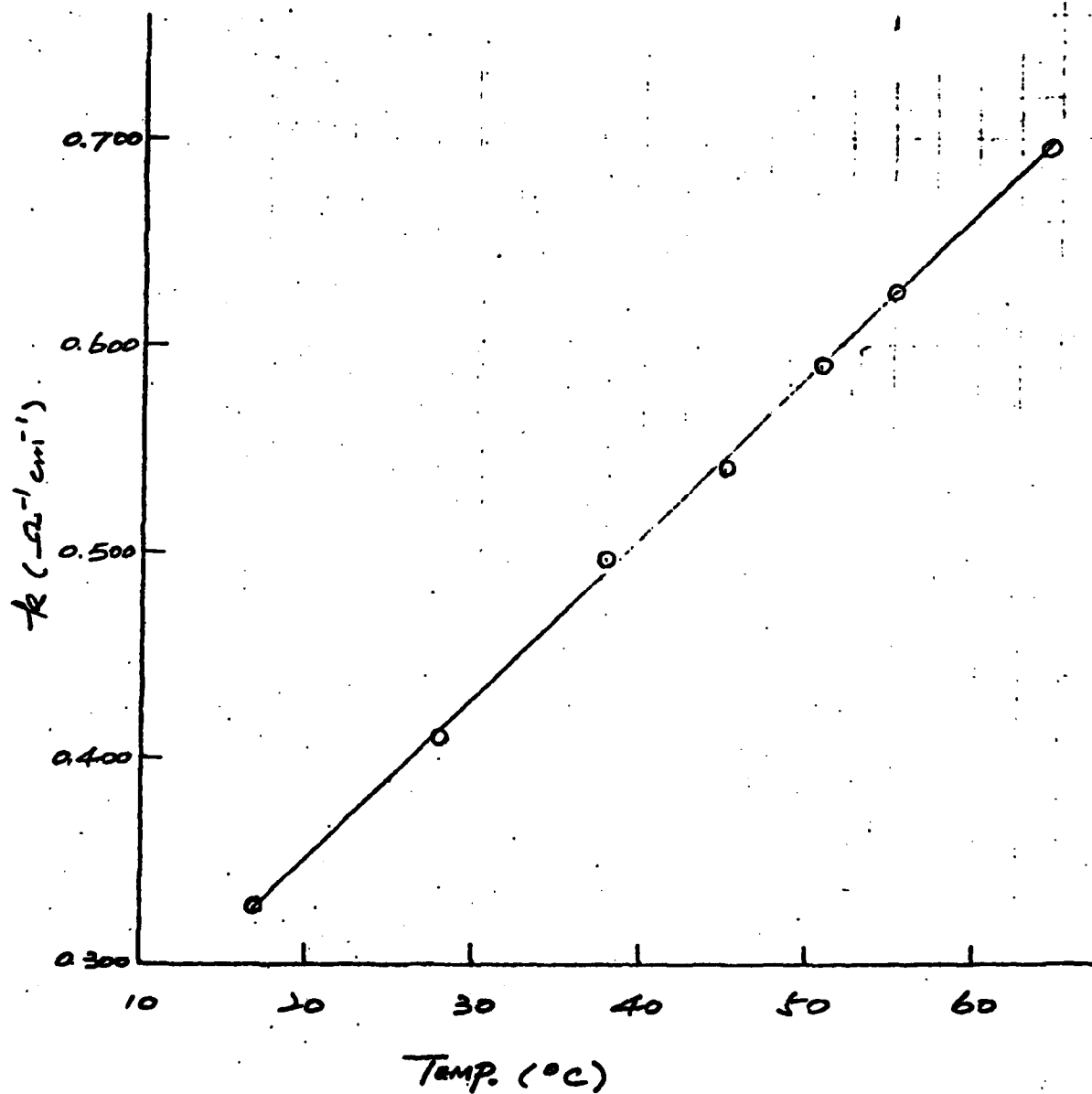
FIG. 4. INFLUENCE OF ELECTROLYTE TEMPERATURE ON ANODE FILM THICKNESS IN 4.5 M LiOH AT $P = 6.2 \times 10^4$ Pa AND $v = 30$ cm/s.



plays the predominant role in determining the film thickness.

Information on the conductivity of the electrolyte as a function of temperature is required for analysis of the experimental data. This data is presented in Fig. 5.

FIG. 5 TEMPERATURE DEPENDENCE OF CONDUCTIVITY
FOR 4.5 M LiOH



DISCUSSION

In strongly alkaline solution, the dissolution of Li, even when under anodic polarization, consists of two competing processes — an electron-producing electrochemical reaction as described by Eq. [1]



and a direct corrosion (parasitic) reaction as depicted by Eq. [2]



Strictly speaking, the overall corrosion reaction [2] is a coupling of [1] with the cathodic reduction of H_2O at adjacent sites on the anode surface. The nature of the local cell reactions has been reported previously (1).

Since the competing reactions [1 & 2] can occur at any polarization level at anode sites, it is not reasonable to assume that temperature has identical impact on each. Indeed, Fig. 3 clearly illustrates the difference. On one hand, at OCV where there is no external electron producing reaction, the corrosion rate i_{cor} follows an Arrhenius exponential dependence. On the other hand, when the corrosion reaction is suppressed to a negligible amount by polarizing the electrode, the rate of the electron-producing process, i_{e} , increases linearly with increasing temperature. Taking a typical polarization curve, such as that at 55°C in Fig. 1, i_{cor} and i_{e} represent the rates of Li dissolution at points a and b respectively. During normal operation of the Li- H_2O cell, the Li anode is polarized to a level between a-b and the current efficiency of the anodic reaction is always somewhat less than 100%. In an earlier paper, a rate equation for the general case of parasitic hydrogen evolution reaction at a polarized electrode was derived (1):

$$i_{\text{H}_2} = i_{\text{cor}} \exp \left(\frac{-\alpha F (E - E_c)}{RT} \right) \quad [3]$$

where E_c is the OCV of the Li at a given temperature; α , the transfer coefficient of H_2 e.r. on the Li surface = 0.14 (1), and the other terms have

their usual meaning. The current efficiency for the polarized Li anode is defined as

$$\epsilon(\%) = \frac{i}{i + i_{H_2}} \quad [4]$$

where i represents the rate of anodic reaction. Using Eq. [3] and the data of Table I, and Fig. 1, $\epsilon(\%)$ at different temperatures have been calculated and are shown in Fig. 6. Fig. 6 also includes experimental results obtained from the H_2 rate measurements. Although the two curves are not exactly identical, the similarity in their shapes seems to support the validity of the model which holds that the H_2 e.r. is the rate-determining step in the corrosion reactions of Li. It is also seen from this figure that, with sufficient polarization, near to 100% current efficiency is obtained. To illustrate the temperature dependence of $\epsilon(\%)$ at various polarization levels, Fig. 7 has been constructed. At elevated temperatures, i.e., $T \geq 55^\circ C$, $\epsilon(\%)$ is generally degraded due to the very high parasitic reaction rate. Thus, in order to operate the Li- H_2O system efficiently at elevated temperatures, a trade-off has to be taken in the form of additional polarization of the anode to achieve acceptable faradaic efficiency.

Over the span of the active polarization region (curve a-c-l in Fig. 1), steady-state conditions are observed. It is conceivable that in this region a quasi-equilibrium state exists between active and inactive sites. A simplified model of the system indicates that the fraction of active sites, $1 - \theta_o$, may be related to the film thickness (x_o), the average conductivity (k), film resistance (R), and the projected surface area (A) by the equation (3)

$$1 - \theta_o = \frac{x_o}{kA R} \quad [5]$$

where θ_o is the surface coverage by the oxide film. Coupling this equation and data of Table I, enables calculation of $(1 - \theta_o)$ at various temperatures. The results are listed in the last column of Table I. The decreasing trend of $(1 - \theta_o)$ with increasing temperature is an intriguing observation,

Table I Some Basic Parameters of the Li-H₂O System
in 4.5 M LiOH at $P = 6.2 \times 10^4$ Pa and $v = 30$ cm/s

Temp (°C)	k ($\Omega^{-1} \text{ cm}^{-1}$)	i_l (mA/cm ²)	i_{cor}^2 (mA/cm ²)	x_o (cm)	R (Ω)	$1 - \theta_o$
18	0.332	138	251	0.080	0.290	0.07
25	0.386	219	342	0.061	0.223	0.06
35	0.467	276	762	0.042	0.170	0.05
45	0.540	434	1830	0.027	0.118	0.04
55	0.623	591	3760	0.018	0.082	0.03

FIG. 6 CURRENT EFFICIENCY OF Li IN Li-H₂O SYSTEM AT
VARIOUS TEMPERATURES

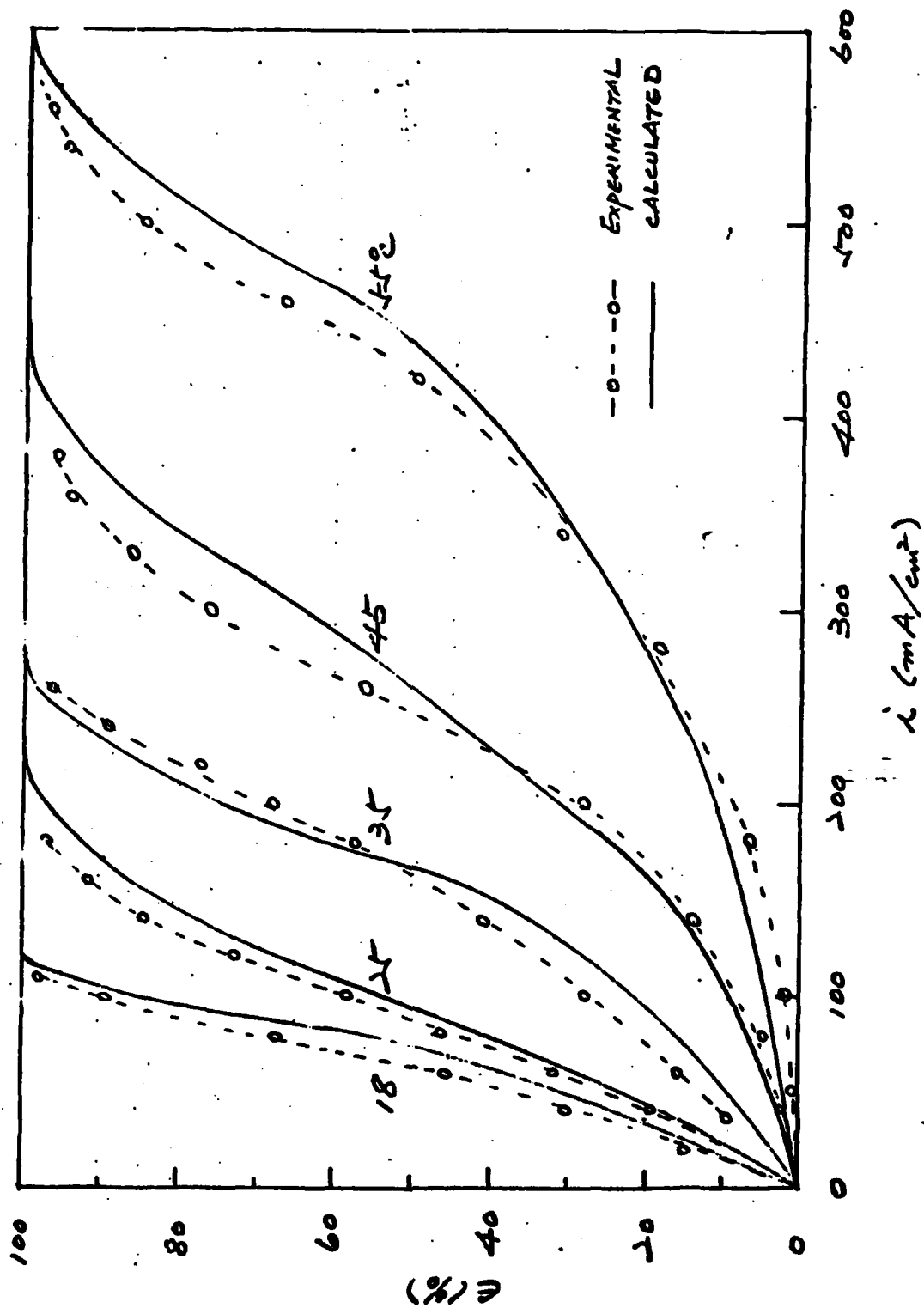
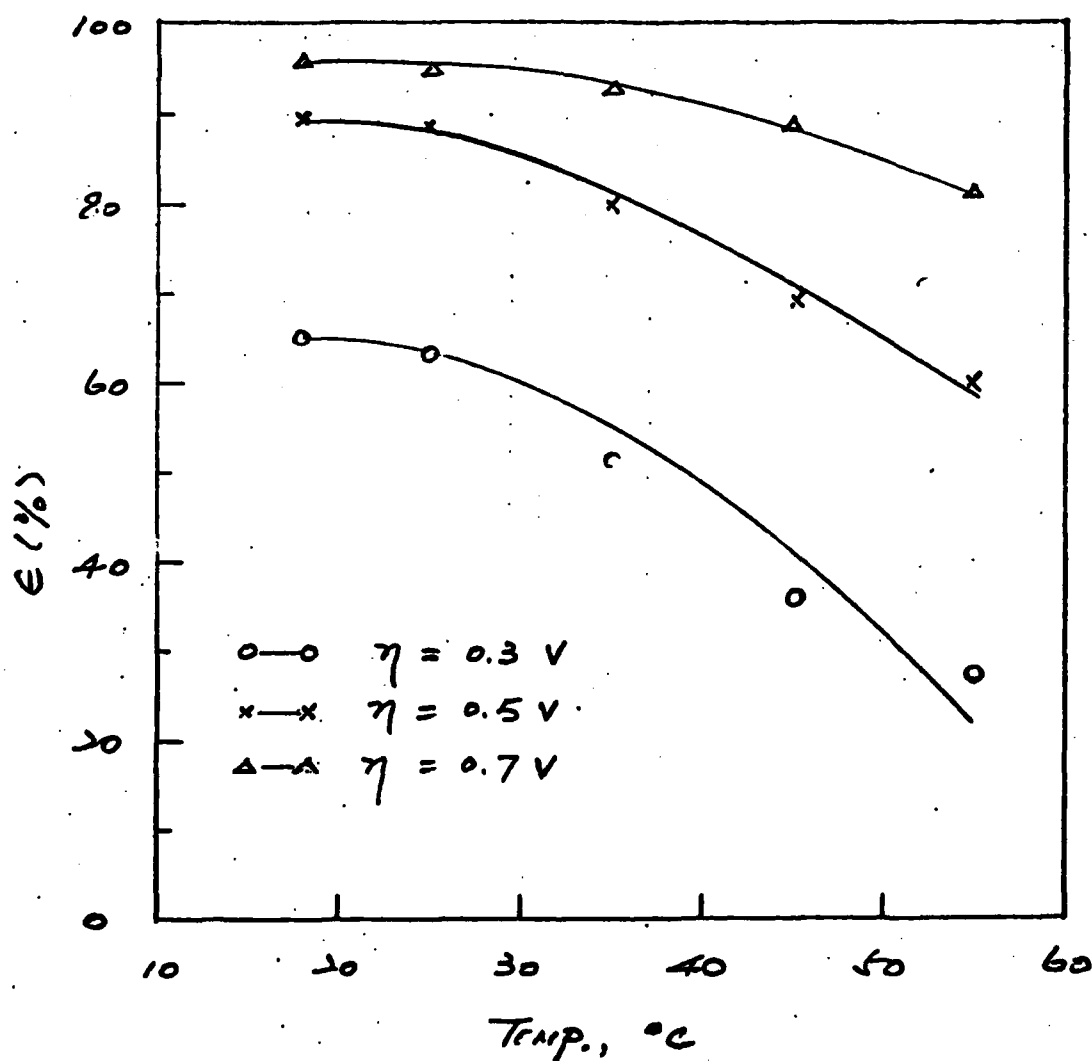


FIG. 7 EFFECT OF ANODIC POLARIZATION ON THE CURRENT EFFICIENCY OF Li AT VARIOUS TEMPERATURES



because earlier investigation on the influence of LiOH concentration on the fraction of the active sites revealed that $(1 - \theta_0)$ decreases markedly with increase in M LiOH, e.g., at 25°C, $(1 - \theta_0)$ ranged from 0.34 at 2.96 M to 0.05 at 4.84 M. Under steady-state conditions, the solubility of LiOH governs the dynamic balance between oxide film formation and dissolution. It seems reasonable to assume that the rapid increase in the dissolution rate of Li (see Fig.3) and its subsequent crystallization as LiOH on the electrode surface at elevated temperatures far exceeds the rate of increase of solubility of the salt as the temperature increases ⁽⁴⁾. This then results in a higher rate of film formation than dissolution. A parallel effect of this imbalance of rates is an increase in surface coverage at higher temperature, and this is reflected in decrease in $(1 - \theta_0)$. The implication of these observations is the realization that the Li-H₂O system is inherently stable even at elevated temperatures provided sufficient polarization is imposed on the anode.

CONCLUSIONS

This study has shed further light on the observation that polarization of the H_2 evolution reaction at the Li surface is the rate-limiting process rather than the anodic dissolution reaction. The rate equation which has not previously been tested for the H_2 e.r. at an anodically polarized Li surface serves successfully to predict the current efficiency at various temperatures. The investigation has also shown that, despite the fact that Li reacts rapidly with H_2O at elevated temperatures, the H_2 e.r. can be sufficiently inhibited under anodic polarization to permit good current efficiency to be obtained. The decreasing area of surface active sites with increasing temperatures reaffirms the stability of the Li- H_2O system in aqueous alkaline electrolytes.

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In reply refer to:
LMSC/D633746

30 January 1979

To: Naval Underwater Systems Center
Newport, Rhode Island 02840

Attn: Code 3632

Subj: Purchase Order N66604-78-M-8483, Final Report

Encl: Final Report, "Anodic Behavior of Lithium at Elevated Temperature,"
LMSD-D633746 (1 reproducible + 3 copies)

Gentlemen:

The enclosed report is submitted in accordance with the requirements of
subject purchase order.

With this submittal, the Contractor considers all obligations under subject
order to have been fulfilled.

LOCKHEED MISSILES & SPACE COMPANY, INC.
Advanced Systems Division

P. R. Bull

P. R. Bull
Contract Administration

PRB:mv

cc: Contracting Officer
Naval Underwater Systems Center
Newport, RI 02840 (w/o encl)

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