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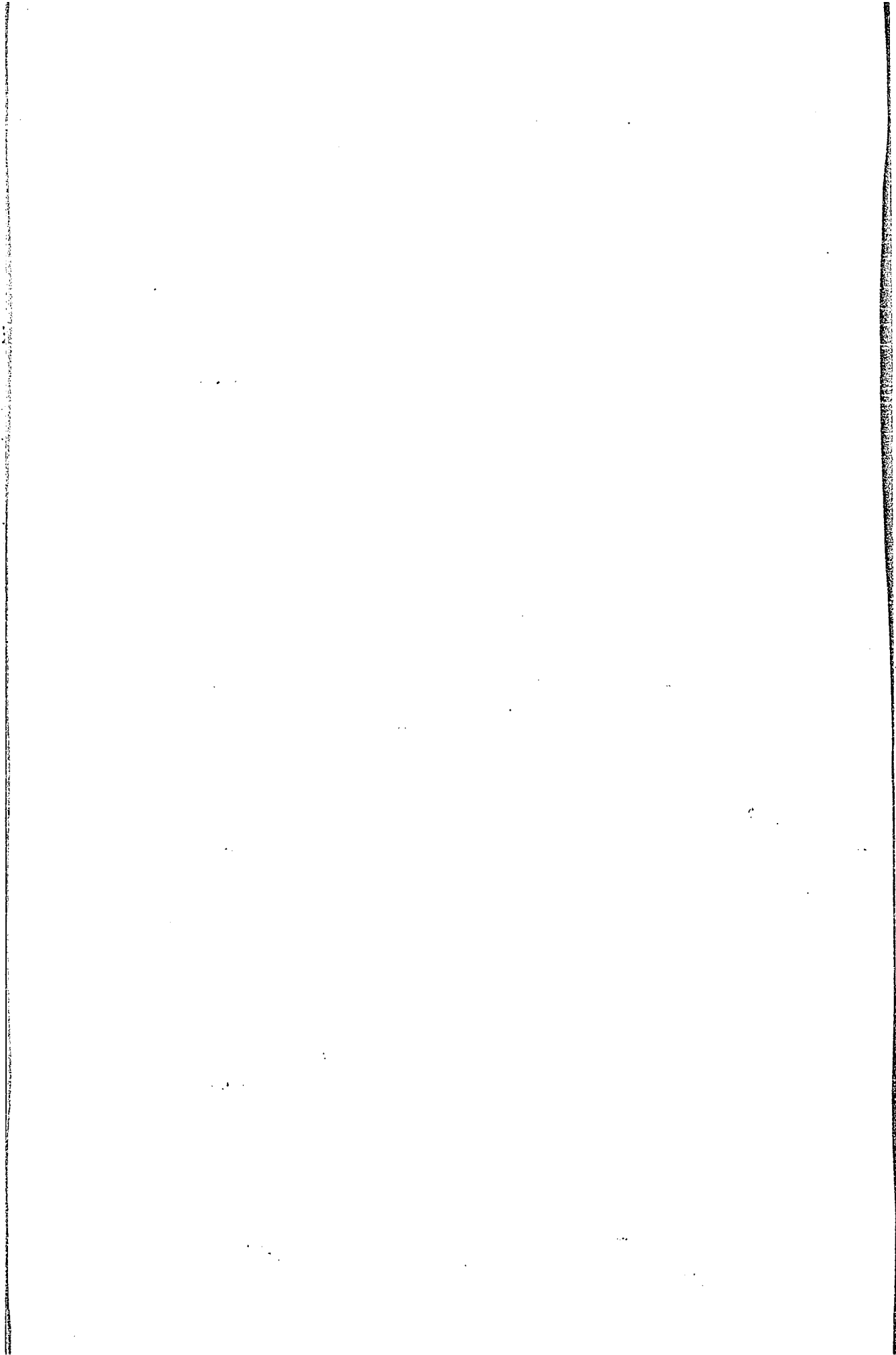
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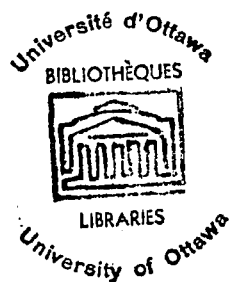
THE ELECTROCHEMICAL BEHAVIOUR OF
THE NICKEL OXIDE ELECTRODE

by

Pierre L. Bourgault

A thesis submitted in partial
fulfillment of the requirements
for the degree of Doctor of Philosophy
in the Department of Chemistry,
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PREFACE

Much previous work on batteries has been technological in nature and only recently have attempts been made to study the electrochemical processes at individual electrodes of batteries in distinction to examining the overall performance of the combination of positive and negative plates in an operating cell. These comments apply in a large measure to the work on nickel-cadmium or nickel-iron batteries although there have been some notable exceptions which are referred to in more detail in the text below.

In the present work, it has been the aim to examine the behaviour of the positive plate (the nickel oxide electrode) of the nickel-cadmium battery by modern experimental and theoretical electrochemical methods and deduce the kinetics of the processes involved in the charging, overcharging (oxygen evolution) and discharging of the nickel oxide electrode and in particular to examine the mechanism of the self-discharge which occurs on open-circuit with evolution of oxygen. The studies have also led to some new theoretical conclusions of general interest, concerning the interpretation of rates of E.M.F. decay on open-circuit and their relation to the mechanisms of the reactions concerned.

In addition to the kinetic studies, an attempt has been made to evaluate for the first time the true thermo-

dynamic reversible potentials of the semi-charged nickel oxide electrode at a formal state of oxidation $\text{NiO}_{1.25}$. In order to distinguish these potentials from open-circuit mixed potentials which arise from self-discharge effects, it has been necessary to make a "kinetic" approach to the study of these thermodynamic potentials.

For the purpose of providing a basis for the discussion of the results obtained in the present work, a number of topics which have special relevance to the interpretation of the data are reviewed in the Introduction to this Thesis.

The work carried out, although entirely fundamental in nature, has led to a number of conclusions of practical and technological interest and these are summarised in an Appendix.

Part of the work described in this thesis has been published in three papers entitled:

- (i) Electrochemical Behaviour of the Nickel-Oxide Electrode, Part I. Kinetics of Self-Discharge (Can. J. Chem., 37, 292 (1959)).
- (ii) Electrochemical Behaviour of the Nickel-Oxide Electrode, Part II, Quasi-equilibrium Behaviour (Can. J. Chem., 38, 1557 (1960)).
- (iii) An Automatic Recording Constant Pressure Gas Coulometer, (J. Electroanalytical Chem., 1, 8, (1959)).

Two other papers have been submitted for publication and are entitled:

- (iv) Interpretation of E.M.F. Decay on Open-circuit:
Applications to the Nickel-Oxide Electrode (Trans. Faraday Soc.; now accepted for publication).
- (v) Electrochemical Behaviour of the Nickel Oxide Electrode
III. Kinetics of Self-Discharge and Oxygen Evolution
at various Temperatures.

In the first Chapter, a number of basic topics are reviewed in order to provide the necessary background for the discussion of results obtained in kinetic studies of the behaviour of the nickel oxide electrode which have been carried out in the present work. No attempt has been made to give a comprehensive review of these matters, e.g. of electrode kinetics, since adequate accounts of these fields have been recently published elsewhere. Only those aspects of these fields which are necessary for the interpretation of the experimental data are examined in any critical detail. Further discussion of some of these matters, where new theoretical ideas are formulated, is given in the "Discussion" section (Chapter IV). Since much of the work has been concerned with examining the polarization of nickel oxide electrodes and interpreting the behaviour observed in terms of consistent and plausible mechanisms, we first discuss briefly the general theory of electrode processes in relation to diagnosis of reaction mechanisms in anodic oxygen evolution.

TABLE OF CONTENTS

	<u>Page</u>
PREFACE	i
TABLE OF CONTENTS	iv
LIST OF FIGURES	xiii
LIST OF TABLES	xxiii
ACKNOWLEDGMENT	xxiv
ABSTRACT	xxv

CHAPTER I - INTRODUCTION

1. THEORY OF ELECTRODE PROCESSES

a) General Kinetic Equations	1
b) Significance of Tafel Slopes	5
(i) General	5
(ii) Christiansen Method for Derivation of Tafel Slopes	7
(iii) Quasi-equilibrium Treatment	12
c) Tafel Slopes from E.M.F. Decay Measurements	14
(i) General	14
(ii) E.M.F. Decay from High Overpotential	15

	<u>Page</u>
(iii) E.M.F. Decay Near the Reversible Potential	17
d) Consecutive and Alternate Reactions: Changes of Mechanism	18
e) Simultaneous Anodic and Cathodic Processes	21
 2. ELECTROCHEMICAL OXYGEN EVOLUTION	
a) Behaviour at Electrodes other than Nickel Oxide	24
b) Oxygen Evolution at Nickel Oxide	27
 3. THE NICKEL OXIDE ELECTRODE	
a) Nature of the Nickel Oxide Electrode	31
b) Oxides of Nickel	33
c) Electrochemical Behaviour of the Nickel Oxide Electrode	37
(i) Stoichiometry of the Oxidation Reduction Reaction	37
(ii) Mechanism of Electrolytic Oxidation and Reduction of Nickel Oxide	41

	<u>Page</u>
(iii) Previous Work on the Process of Self-Discharge	43
 <u>CHAPTER II - EXPERIMENTAL</u>	
 1. SOLUTIONS	
a) Standard Purification Technique	48
(1) Potassium Hydroxide	48
(ii) Nickel Nitrate	48
b) High Purification Technique	49
(1) Potassium Hydroxide	49
(ii) Nickel Nitrate	51
c) Potassium Deuterioxide in Heavy Water	52
c) Solutions of Nickel Sulfate in Heavy Water	52
2. ELECTRODES	53
a) General	53
b) Sintered Plaques	53
c) Impregnation of Sintered Plaques	54
3. OXYGEN PURIFICATION	56
4. CELLS	56
5. REFERENCE ELECTRODES	59

	<u>Page</u>
6. CURRENT SUPPLY AND ELECTRICAL MEASUREMENTS	61
a) Constant Current Supply	61
b) Current Measurement	61
c) E.M.F. Measurements	62
7. OXYGEN VOLUME MEASUREMENTS	62
a) Design of the Apparatus	63
b) Sensitivity and Accuracy	66
c) Results	67
8. TEMPERATURE CONTROL	69
9. EXPERIMENTAL PROCEDURES	71
a) Fully Charged Electrodes	71
(i) Polarization Decay and Oxygen Evolution Measurements	71
(ii) Steady State Current-Potential Behaviour of Fully Charged Electrodes	75
b) Polarization Decay at Partially Charged Electrodes	78
c) Quasi-Equilibrium Potentials	79
 <u>CHAPTER III - RESULTS</u>	
1. BEHAVIOUR OF FULLY OXIDIZED ELECTRODES	82
a) Open-Circuit Behaviour	82

	<u>Page</u>
(i) General	82
(ii) Decay of E.M.F. with Time	82
(iii) Oxygen Evolution on Open-circuit	83
(iv) Decay of E.M.F. in Potassium Deuterioxide Solutions in D ₂ O	95
(v) Effect of High Purification and Preelectrolysis on the Kinetics of E.M.F. Decay	98
b) Steady State E.M.F. under Anodic Polarization: Tafel Lines	100
(i) Nickel Oxide Electrodes in Aqueous KOH Solutions	100
(ii) Nickel Metal in Ordinary Aqueous and in Deuterium Oxide Solutions	101
2. BEHAVIOUR OF PARTIALLY OXIDIZED ELECTRODES	
a) Decay from Anodic and Cathodic Polarization in Aqueous KOH	105
b) Decay from Anodic and Cathodic Polarization in Potassium Deuterioxide Solution	111
c) Quasi-Equilibrium and Reversible E.M.F. Values	113

	<u>Page</u>
(i) Reversible E.M.F. from Anodic and Cathodic Decay Lines	113
(ii) Quasi-Equilibrium or Mixed Potentials at Long Times	115
3. SURFACE CAPACITANCE OF THE NICKEL OXIDE ELECTRODE	
a) Definition	118
b) Origin of the Surface or Pseudo- Capacitance	120
c) Evaluations of Surface Capacitance	
(i) Capacitance of the Electrode from the Quantity θ	122
(ii) Capacitance from Charging Curves at Oxidized Electrodes	130
(iii) Capacitance from Simultaneous Measurements of E.M.F. and Volumes of Oxygen Evolved	133

CHAPTER IV - DISCUSSION

1. KINETICS OF SELF-DISCHARGE

a) Nature of the Self-Discharge Process	142
b) Significance of E.M.F. Decay Lines	145
(i) Origin of the Decay Law and the Assumptions Involved	145
(ii) Critical Examination of the First Assumption	146
(iii) Critical Examination of the Second Assumption	151
(iv) Relation between E.M.F. Decay Slopes and Oxygen Evolution Slopes	156
(v) Significance of E.M.F. Decay Measurements at Partially Charged Electrodes	175
c) Electrical Analogue to the Processes of Charging and Oxygen Evolution	178
d) The Rate-Determining Process	180

	<u>Page</u>
(i) Identity of the Rate-	
Determining Process	180
(ii) Tafel Slopes	183
(iii) Effects of Concentration	
on Rate	185
(iv) Effects of Temperature	
on Rates	192
(v) H-D Isotope Effects	193
(vi) Reaction Mechanism in the	
Oxygen Evolution Process	196
 2. THERMODYNAMICS OF SEMI-CHARGED ELECTRODES	
a) Introduction	202
b) Nature of the Electrode Processes	202
c) Form of the Decay Lines	205
(i) Oxygen Evolution on	
Partially Charged Electrodes	205
(ii) Diffusion Effects	209
(iii) Mixed Potentials	214
d) Assignment of Reversible Potentials	215
e) The Nernst Equation for the	
Electrode	215

	<u>Page</u>
APPENDIX	
CONSIDERATIONS OF PRACTICAL INTEREST IN	
RELATION TO BATTERY PERFORMANCE	221
1. GENERAL	221
2. THE EFFECTS OF KOH CONCENTRATION ON THE	
STABILITY OF THE HIGHER OXIDE	221
3. CHARGE AND DISCHARGE CHARACTERISTICS	223
4. EFFECTS OF RATES OF CHARGE	225
5. THE (POSSIBLE) EFFECTS OF CYCLING,	
IMPURITIES AND ADDITIVES	226
6. DEDUCTION OF RATES OF SELF-DISCHARGE	227
7. CORROSION OF THE NICKEL METAL IN THE	
OXIDE ELECTRODES	228
CLAIMS TO ORIGINAL RESEARCH	230
BIBLIOGRAPHY	233

LIST OF FIGURES

		<u>Page</u>
Figure I	- a) Change of mechanism for the case of consecutive reactions	
	b) Change of mechanism for the case of alternative reactions	20
II	- a) The mixed potential when the anodic and cathodic processes have comparable exchange currents	
	b) The mixed potential when the cathodic process has a much larger exchange current than the anodic process.	
	c) The steady state potential is determined solely by the much faster cathodic current process.	22
III	- Electrolysis vessel used for formation of potassium amalgam.	50
IV	- Experimental cell used in oxygen evolution and e.m.f. decay measurements.	57

		<u>Page</u>
Figure V	- a) Apparatus for the automatic measurement of oxygen volume.	
	b) Electrical circuit for the apparatus shown in Figure Va.	64
VI	- a) Recorder trace showing linearity of response in the case of a uniform rate of change of volume of gas in the burette. Upper line: increasing volume with time. Lower line; decreasing volume with time.	68
	b) Recorder trace of oxygen evolution during self-discharge of a nickel-oxide electrode	68
VII	- Photograph of air thermostat containing apparatus for measurement of volumes of oxygen evolved.	70
VIII	- Photograph of Experimental cell.	72

Figure IX	- Charging and discharging cycle used in polarization decay studies of partially charged nickel-oxide electrodes.	81
X	- Decay of e.m.f. on open-circuit at -25°C in 4.5, 8.2 and 11.8 molar KOH solution.	84
XI	- a), b) Decay of e.m.f. on open-circuit at 1.0°C .	85
XII	- a), b) Decay of e.m.f. on open-circuit at 25°C .	86
XIII	- a), b) Decay of e.m.f. on open-circuit at 60.5°C .	87
XIV	- Rates of evolution of oxygen on open-circuit as a function of e.m.f. at -25°C in 4.5, 8.2 and 11.8 molar KOH solutions.	89
XV	- a), b) Rates of evolution of oxygen on open-circuit as a function of e.m.f. at 1.0°C .	90
XVI	- a) Rates of evolution of oxygen on open-circuit as a function of e.m.f. at 25°C in 0.015, 0.15 and 2.9 molar KOH solutions.	91

	<u>Page</u>
Figure XVI - b) Rates of evolution of oxygen on open-circuit as a function of e.m.f. at 25° C in 7.1, 9.4 and 14.6 molar KOH solutions.	92
XVII - a) Rates of evolution of oxygen on open-circuit as a function of e.m.f. at 60.5° C in 0.15, 1.0 and 1.5 molar KOH solutions.	93
- b) Rates of evolution of oxygen on open-circuit as a function of e.m.f. at 60.5° C in 7.0 and 14.4 molar KOH solutions.	94
XVIII - Decay of e.m.f. on open-circuit in D ₂ O solution 0.93 molar in KOD compared with a control in H ₂ O solution.	97
XIX - Effect of ultra-purification and pre-electrolysis on the e.m.f. decay of nickel oxide electrode in 0.92 molar KOH solution.	99
XX - Tafel lines for oxygen evolution on nickel oxide at 1.8, 11, 25, 40 and 60.5° C.	102

	<u>Page</u>
Figure XXI - Steady state polarization measurements (Tafel Lines) on plain nickel wires in D_2O and H_2O solutions.	104
XXII - Decay of e.m.f. on open-circuit on a plain nickel wire electrode.	106
XXIII - a), b), c), d). Decay of e.m.f. from anodic and cathodic polarization on partially-charged electrodes (0.01 to 7.3 molar KOH).	108
XXIV - a), b) Decay of e.m.f. from anodic and cathodic polarization on partially-charged electrodes. (14.6 M KOH and KOH/KF mixed electrolyte).	109
XXV - Decay of e.m.f. from anodic and cathodic polarization on partially charged electrodes in KOD and D_2O solution compared with a control electrode in ordinary aqueous solution.	112

Page

- Figure XXVI - Reversibility of e.m.f. of the nickel oxide electrode with successive changes of concentration. Arrows indicate sequence of changes for electrode initially put in strongest solution after being maintained in 0.001 molar KOH 117
- XXVII - Comparison of e.m.f. values obtained from "stationary" potential measurements (crosses) and from appropriate extrapolation of logarithmic decay lines (circles). 119
- XXVIII - Comparison of a plot of e.m.f. vs $\log t$ with that of e.m.f. vs $\log (t + \theta)$ for a typical nickel oxide electrodes. 124
- XXIX - Plot of e.m.f. vs logarithm of the interval of time required for each 4.0 millivolt drop of e.m.f. during self-discharge on open-circuit. 126

	<u>Page</u>
Figure XXX - Test for condition a- The slopes and intercepts of e.m.f. decay lines are independent of current density.	128
XXXI - Test for condition b- The quantity θ is linear with the reciprocal of the initial polarizing current.	129
XXXII - Charging of the surface on nominally "charged" nickel oxide electrodes.	132
XXXIII - Volume of oxygen evolved on open-circuit as a function of electrode e.m.f. at -25° C.	135
XXXIV - Volume of oxygen evolved on open-circuit as a function of electrode e.m.f. at 1.0° C.	136
XXXV - Volume of oxygen evolved on open-circuit as a function of electrode potential at 25° C.	137
XXXVI - Volume of oxygen evolved on open-circuit as a function of electrode e.m.f. at 60.5° C.	138

	<u>Page</u>
Figure XXXVII - Rates of self-discharge obtained by measurements of oxygen evolution on open- circuit compared with the results of steady state polarization.	149
XXXVIII - E.M.F. decay line compared with the true Tafel line for an electrode in 8.2 molar KOH solution at -25° C.	153
XXXIX - E.M.F. decay line compared with the true Tafel line for an electrode in 0.15 molar KOH solution at 25° C.	155
XL - Logarithmic plots of volume of oxygen liberated on open-circuit as a function of E.M.F. of the electrode.	157
XLI - Schematic diagram of the course of q_{MOH} and C_{MOH} with increase of potential .	167
XLII - Estimation of the surface capacity of partially charged electrodes by constant current charging and discharging near the steady-state potential.	176

	<u>Page</u>
Figure XLIII - Electrical analogue to the nickel oxide electrode.	179
XLIV - Log exchange current i_0 versus log activity of KOH for the oxygen evolution process.	188
XLV - Log rate of oxygen evolution versus log activity of KOH for region II of the Tafel lines at 25° C.	189
XLVI - Log rate of oxygen evolution versus log activity of KOH for region III of the Tafel lines at 25° C.	190
XLVII - Log rate of oxygen evolution versus log activity of KOH at 1.0° C and -25° C.	191
XLVIII - Activation energy plots based on (a) rates of self-discharge in region II from oxygen evolution measurements, (b) direct current polarization measurements.	194
XLIX - (a) Tafel lines for anodic oxidation of the semi-charged electrode and for O ₂ evolution (0.1 MKOH).	207

	<u>Page</u>
Figure XLIX - b) E.M.F. decay lines corresponding to rates of anodic charging and O_2 evolution.	207
L - a) Tafel lines for anodic oxidation of the semi-charged electrode and for O_2 evolution (7.3 M KOH). - b) E.M.F. decay lines corresponding to rates of anodic charging and O_2 evolution.	208
LI - Polarization lines for the partial reactions in the "corrosion" or self-discharge of the nickel oxide electrode in 7.3 M KOH.	216

LIST OF TABLES

		<u>Page</u>
Table I	Surface capacitance and active oxygen content of electrodes as a function of temperature and KOH concentration.	140
II	Tafel slopes b_3 and E.M.F. decay slopes b_1 in the various potential regions.	162
III	Relationship between b_1 and b_3 when C is not constant with E.	165
IV	Exchange currents in amps per gram from extrapolation of E.M.F.-log [rate of oxygen evolution] lines.	186

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ABSTRACT

The nickel oxide electrode and its electrochemical properties have, for the most part, been ill characterized largely due to a lack of appreciation of the variable stoichiometry of the oxidized material and of the nature of the electrode processes occurring at the nickel oxide interface. In the present work a systematic attempt has been made to elucidate, using modern approaches in electrode kinetics: (a) the mechanism of oxygen evolution both on anodic polarization and open-circuit self-discharge; (b) the quantitative nature of the self-discharge process as an example of a mixed electrode reaction system analogous to corrosion; (c) the true thermodynamic reversible potentials of the nickel oxide electrode in a formal state of oxidation $\text{NiO}_{1.25}$ as a function of activities of KOH and water in the electrolyte.

The measurement of true rates of self-discharge on open-circuit has necessitated the development of a new technique for the microvolumetric determination of oxygen evolution rates. Measurements have also been made of e.m.f. decay on open-circuit and these measurements in conjunction with true self-discharge rates obtained by microvolumetric techniques have permitted a critical examination of the

significance of e.m.f. decay rates. It has been shown that the simple theory previously proposed is inadequate to explain the open-circuit e.m.f. behavior of the nickel oxide electrode. A general discussion of e.m.f. decay kinetics is given. Also the nature and the significance of the surface or pseudo-capacitance of the nickel oxide electrode is discussed in relation to the e.m.f. decay behavior of the electrode.

A detailed analysis of the self-discharge of nickel oxide has been made and it has been shown that a mixed electrode process, consisting of an anodic and a cathodic partial process, is involved in self-discharge on open-circuit. Of the two processes, the anodic partial process is the slower and may be considered rate-controlling, at least in the early stages of self-discharge. A mechanism for this partial process has been given and it has been shown that within this partial process two possible electrochemical radical desorption steps can be rate-controlling depending upon (a) the electrode potential, (b) the electrolyte concentration and (c) the temperature.

In the thermodynamic part of the work a "kinetic" ^{the} approach has been made to/quantitative elucidation of oxidation-reduction mixed potentials which are observed on open-circuit and this approach has enabled the true reversible potentials of a nickel oxide electrode in the

semicharged state to be evaluated for the first time as a function of KOH and water activities. It has been shown that previously recorded potentials are not true reversible values and that they do not in fact refer to the species claimed, viz. "NiO₂".

Detailed analysis of the open-circuit e.m.f.-time behavior following brief anodic and cathodic polarization of the semicharged electrode has enabled an evaluation to be made of the kinetic parameters governing the Ni^{II}-Ni^{III} redox reaction. The results are complicated in the anodic reaction by alternative anodic O₂ evolution which can proceed in parallel with the Ni^{II} → Ni^{III} electrochemical oxidation. These considerations lead to a model for electrochemical charging and discharging of nickel oxide which represents the electrical behavior of this electrode.

CHAPTER I

INTRODUCTION

1. THEORY OF ELECTRODE PROCESSES

a) General Kinetic Equations

In conventional kinetics the velocity of a reaction in the forward direction is given by

$$\vec{v} = \gamma \frac{kT}{h} \pi[a_1] \exp. [-\Delta G^{\ddagger}/RT] \quad [1]$$

where $\pi[a_1]$ is the product of the activities of the reacting species at the electrode interface, γ is the transmission coefficient, $\Delta G^{\ddagger}$ is the standard free energy of activation for the process and the other terms have their usual significance.

In the formulation of kinetic equations for electrochemical processes at interfaces, certain modifications of this basic equation are necessary. Thus the forward velocity of the reaction can be expressed in terms of current density* as

$$\vec{i} = \lambda \gamma_F \frac{kT}{h} \pi[a_1] \exp. [-\Delta G^{\ddagger}/RT] \quad [2]$$

* This equation may also be written in the alternative form

$$\vec{i} = \frac{nF}{\nu} \gamma \frac{kT}{h} \pi[a_1] \exp [-\Delta G^{\ddagger}/RT]$$

where n is the number of electrons involved in the overall reaction and ν is the so-called stoichiometric number (1) determining the number of acts of the rate-determining step required for one act of the overall process.

where F is the Faraday and λ the "electron number" (10) corresponds to the number of electrons required for one act of the rate-controlling step; $\Delta G^{\ddagger}$ is now the standard "electrochemical" free energy of activation, so-called because the reactants in approaching the transition state can suffer a change of "electrical" as well as "chemical" free energy. We can therefore speak of a change of electrochemical potential [cf. Butler (2), Guggenheim (3)] rather than only chemical potential in the activation process. When a potential difference $\Delta\phi$ exists between the electrode and the reacting ions, the value of $\Delta G^{\ddagger}$ will be changed from its hypothetical value when no potential difference exists at the interface by an amount* $azF\Delta\phi$ where a , the "transfer coefficient", determines the dependence of rate upon potential.** The transfer coefficient a is usually not a function of potential and its magnitude will depend upon the actual mechanism involved in the overall reaction. In section [b] below it will be shown how the experimentally determined value of a may be used to distinguish possible reaction mechanisms.

* In order to conform with the practice of giving a as a positive quantity for both cation and anion discharge, z should include the sign as well as the numerical value of the ionic charge.

** Here we have presented the essential significance of a in terms of $\Delta\phi$ and $\Delta G^{\ddagger}$. A general and detailed treatment of this matter has been given elsewhere by Bockris (4).

If $\Delta \bar{G}_r^{\circ \neq}$ is defined as the electrochemical free energy of activation at the reversible potential ϕ_r of the system, then $\Delta \bar{G}_r^{\circ \neq}$ may be written as

$$\Delta \bar{G}_r^{\circ \neq} = \Delta \bar{G}_r^{\circ \neq} - azF (\phi - \phi_r) \quad [3a]$$

or

$$\Delta \bar{G}_r^{\circ \neq} = \Delta \bar{G}_r^{\circ \neq} - a\eta zF \quad [3b]$$

where

$\eta = \phi - \phi_r$ is termed the overpotential.

Equation [2] may now be written as

$$\vec{i} = \lambda \gamma F \frac{kT}{h} \pi[a_1] \exp [-\Delta \bar{G}_r^{\circ \neq}/RT] \exp [-azF \eta/RT] \quad [4a]$$

By a similar argument the current for the back reaction may be written:

$$\overleftarrow{i} = \lambda \gamma F \frac{kT}{h} \pi[a_p] \exp [-\Delta \bar{G}_r^{\circ \neq}/RT] \exp [azF \eta/RT] \quad [4b]$$

where $\pi[a_p]$ is the product of activities of reaction products at the interface. At $\eta = 0$ the reaction is at equilibrium, so that

$$\vec{i} = \overleftarrow{i} = i_0 \quad [5]$$

where i_0 , the exchange current density, is the current passing reversibly per cm^2 in the forward and backward directions at zero overpotential.

Equations [4] and [4b] may now be simplified as

$$\vec{i} = i_0 \exp [-azF \eta/RT] \quad [6a]$$

and

$$\overleftarrow{i} = i_0 \exp [azF\eta/RT] \quad [6b]$$

The net current density in the forward direction for an anodic process (we choose this example since most of the present work refers to anodic reactions) will be given by

$$i_a = \overrightarrow{i} - \overleftarrow{i} = i_0 [\exp [\overrightarrow{azF\eta}/RT] - \exp [\overleftarrow{azF\eta}/RT]] \quad [7]$$

At overpotentials greater than about $\frac{50}{az}$ m.v. (i.e. $azF\eta \gg RT$) the second exponential term in equation [7] may be neglected so that

$$i_a = i_0 \exp [\overrightarrow{azF\eta}/RT] \quad [8]$$

Taking logarithms and rearranging, this yields

$$\eta = \frac{RT}{azF} \ln i_0 - \frac{RT}{azF} \ln i_a \quad [9a]$$

or

$$\eta = a + b \log i_a \quad [9b]$$

which is the familiar form of Tafel's equation relating anodic current density to overpotential.* Since a and b are experimentally determinable, it is possible from a plot of

η vs. $\log i$, to determine the parameters i_0 and a in equation [9a]. As seen from equations [4a] and [4b] in relation to [5], i_0 contains terms in reactant activities as well as in

* In the case of anodic reactions z, the charge on the ion, is negative so that the preexponential term b will be a positive quantity. For this reason, the Tafel equation is written as $\eta = a + b \log i$ rather than in the form $\eta = a - b \log i$ used when dealing with cathodic reactions.

entropy and heat of activation but not in overpotential although of course it still contains terms in absolute metal-solution potential difference (the ϕ_r in equation 3a); thus its significance is analogous to that of a rate for a surface catalyzed reaction in solution. The value of α will be characteristic (but not necessarily uniquely so) of the reaction mechanism. Its significance will now be discussed.

b) Significance of Tafel Slopes

(1) General

It has been mentioned above that for most electrode reactions the overpotential η and the current density i are related by an expression of the general form

$$i = i_0 \exp [-\alpha z F \eta / RT]$$

where i_0 and α are independent of potential for a given reaction mechanism.

The constant α is of particular interest since values of it may be used in some cases as a diagnostic criterion in determining the mechanism of the overall electrode reaction. For the simplest case, where the overall rate is determined solely by the slow discharge of a univalent ionic species, α will have a value 1/2 provided the energy barrier for the discharge reaction is a symmetrical one. If the Morse curve representing the potential energy of the ion about to be

discharged and that representing the discharged radical on the surface have equal and opposite slopes at their point of intersection, it can readily be shown that a change of potential difference $\Delta\phi$ between the electrode and the solution (corresponding to a change of energy of $z\Delta\phi F$) will produce a corresponding change of $1/2 z\Delta\phi F$ in the energy at the position of the activated complex (viz. the point of intersection of the Morse curves) for species having a charge of zF per mole. This will have the effect of lowering (or raising) the energy of activation by an amount $1/2 \Delta\phi zF$.

From the definition of η it follows that under these conditions

$$i = i_0 \exp [-1/2 zF\eta / RT] \quad [10]$$

and

$$d\eta / d \ln i = \frac{2RT}{F} \quad \text{for monovalent anions} \quad [11]$$

or

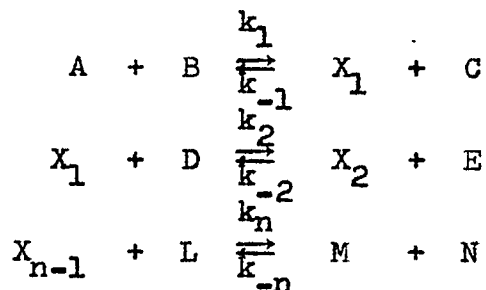
$$\alpha = 1/2.$$

If the overall reaction consists of a series of consecutive reactions the problem is somewhat more complex. It is possible, however, to calculate for a given mechanism involving a series of consecutive reactions, which Tafel slopes can be expected under certain limiting conditions. In general, a simple exponential relationship between overpotential and current density is predicted only under limiting conditions of

surface coverage by intermediates and by assuming one of the steps in the overall process to be much slower than the others. The most elegant method of arriving at the possible limiting slopes for a given mechanism is based on the Christiansen treatment for consecutive reactions. This method, which has been examined in detail by Bockris (5), will be discussed briefly, since it is applied later in this thesis to the experimental results.

(ii) Christiansen Method for Derivation of Tafel Slopes

Consider the series of reactions



where X_1 X_2 --- X_n are unstable intermediates.

We may write

$$v_1 = k_1 [A] [B] \quad [12a]$$

$$v_{-1} = k_{-1} [X_1] [C] \quad [12b]$$

$$v_2 = k_2 [X_1] [D] \text{ etc.,}$$

and if quantities w_1 , w_{-1} , w_2 --- w_n etc. are defined as the velocities of the corresponding elementary steps divided by

the concentrations of the respective unstable intermediates, we have

$$w_{-1} = \frac{v_{-1}}{[X_1]} \quad [13a]$$

$$w_1 = v_1 \quad [13b]$$

The net rate of the first step may now be written

$$v = w_1 - w_{-1} [X_1]$$

and for the second step

$$v = w_2 [X_1] - w_{-2} [X_2]$$

For the steady state condition in the reaction, we therefore have

$$v = w_1 - w_{-1} [X_1] = w_2 [X_1] - w_{-2} [X_2] = w_3 [X_3] - w_{-3} [X_3] = \dots w_n \text{ etc.}$$

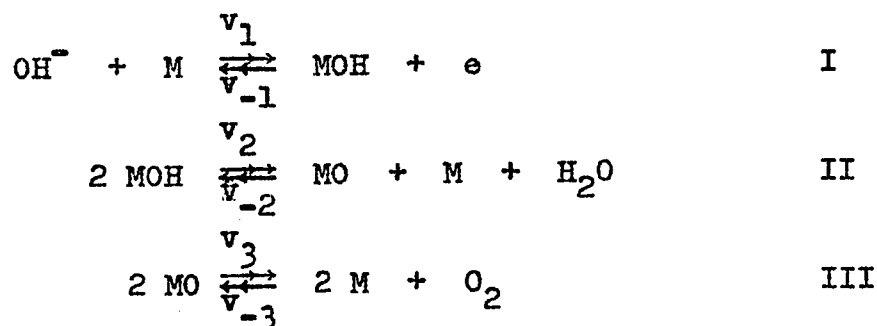
From this series of n simultaneous equations we may eliminate the terms for the $(n - 1)$ unstable intermediates and obtain a solution in terms of velocity. The result expressed in terms of v_+ , the velocity of the forward reaction, and v_- , that of the reverse reaction, is

$$\frac{1}{v_+} = \frac{1}{w_1} + \frac{w_{-1}}{w_1 w_2} + \dots \frac{w_{-1} \dots w_{-(n-1)}}{w_1 w_2 \dots w_n} \quad [14a]$$

$$\frac{1}{v_-} = \frac{1}{w_{-n}} + \frac{w_n}{w_{-n} w_{-(n-1)}} \dots \frac{w_n w_{n-1} \dots w_2}{w_{-n} w_{-(n-1)} \dots w_{-2} w_{-1}} \quad [14b]$$

The application of this method to electrolytic oxygen evolution is best illustrated by considering the example below.

Let the following mechanism be operative for oxygen evolution on a metal



Let it also be postulated that MOH recombination is rate-controlling. If θ represents the fraction of the surface covered with MOH and the concentration of MO is negligible, the fraction of surface which is bare will be $1 - \theta$. We may now write

$$\begin{aligned}
 v_1 &= k_1 [\text{OH}^-] (1 - \theta) \exp [F\eta/2RT]^* \\
 v_{-1} &= k_{-1} [\text{MOH}] \exp [-F\eta/2RT] \\
 v_2 &= k_2 [\text{MOH}]^2 \\
 v_{-2} &= k_{-2} [\text{MO}] [\text{H}_2\text{O}] \\
 v_3 &= k_3 [\text{MO}]^2 \\
 v_{-3} &= k_{-3} [\text{O}_2]
 \end{aligned}$$

* The assumption is made here that the energy barrier for discharge of OH^- is symmetrical. Experimental evidence for this is found in the observation of oxygen evolution slopes of 0.12 (i.e. $2.3 \frac{2RT}{F}$) at various metals under certain conditions (6).

Expressing these equations in terms of the quantity w we have

$$w_2 = k_2 [\text{MOH}]$$

$$w_{-2} = k_{-2}$$

$$w_3 = k_3 [\text{MO}]$$

$$w_{-3} = k_{-3}$$

The terms w_1 and w_{-1} offer an added difficulty because of the appearance in the expression of the term for surface coverage. This is resolved by Bockris (5) in the following manner.

$$\text{Let } \theta = k' [\text{MOH}]$$

Substituting in the expression for v_1 above

$$v_1 = k_1 [\text{OH}^-] \exp [F\eta/2RT] - k_{-1} k' [\text{OH}^-] [\text{MOH}] \exp [F\eta/2RT]$$

and

$$v = w_1 - w_{-1} = k_1 [\text{OH}^-] \exp [F\eta/2RT] - k_{-1} k' [\text{OH}^-] [\text{MOH}] \exp [F\eta/2RT] - k_{-1} [\text{MOH}] \exp [-F\eta/2RT]$$

$$w_1 = k_1 [\text{OH}^-] \exp [F\eta/2RT]$$

$$w_{-1} = k_{-1} k' [\text{OH}^-] \exp [F\eta/2RT] + k_{-1} \exp [-F\eta/2RT]$$

Substituting these values into the Christiansen expression for the overall rate of the forward reaction, equation [14a] and rearranging we have

$$v = \frac{k_1 k_2 k_3 [\text{MOH}][\text{OH}][\text{MO}] \exp[F\eta/2RT]}{k_2 k_3 [\text{MOH}][\text{MO}] + k_1 k' k_3 [\text{OH}^-][\text{MO}] \exp[F\eta/2RT] + k_{-1} k_3 [\text{MO}] \exp[-F\eta/2RT] + k_1 k_{-2} k' [\text{OH}^-] \exp[F\eta/2RT] + k_{-1} k_{-2} \exp[-F\eta/2RT]}$$

Since recombination of [MOH] has been assumed to be rate-controlling, $k_2 > k_{-2}$ and $k_2 \ll k_1$ and the expression simplifies to

$$v = \frac{k_1 k_2 [\text{MOH}] [\text{OH}^-] \exp [-F\eta/2RT]}{k_1 k' [\text{OH}^-] \exp [F\eta/2RT] + k_{-1} \exp [-F\eta/2RT]} \quad [15]$$

(a) Condition of low coverage of the surface by MOH: $\theta \ll 1$

Under these conditions, the first step I may be regarded as being in equilibrium so that

$$[\text{MOH}] = [\text{OH}^-] \frac{k_1}{k_{-1}} \exp [F\eta/RT] = [\text{OH}^-] K_1 \exp [F\eta/RT]$$

and if

$$k_1 k' [\text{OH}^-] \exp [F\eta/2RT] \ll k_{-1} \exp [-F\eta/2RT]$$

Hence

$$v = k_2 k_1^2 [\text{OH}^-]^2 \exp [2F\eta/RT] \quad [16]$$

and

$$i = K' \exp [2F\eta/RT]$$

and

$$d\eta/d\ln i = \frac{RT}{2F}$$

and

$$\alpha = 2.$$

(β) Condition of high surface coverage by MOH: $\theta \rightarrow 1$

This could be the condition obtaining under a larger applied overpotential η .

In this case

$$k_{-1} \exp [-F\eta/2RT] \ll k_1 k' [\text{OH}^-] \exp [F\eta/2RT]$$

Also the equilibrium expression for [MOH] is no longer valid so that neglecting the term $k_{-1} \exp [-F\eta/2RT]$ in equation [15] and simplifying we find

$$\begin{aligned} v &= \frac{k_2}{k_1} [\text{MOH}] \\ i &= K'' [\text{MOH}] \end{aligned} \quad [17]$$

which is an activation controlled limiting current when $[\text{MOH}] \rightarrow [\text{MOH}]_{\text{sat.}}$ for the completely covered surface.

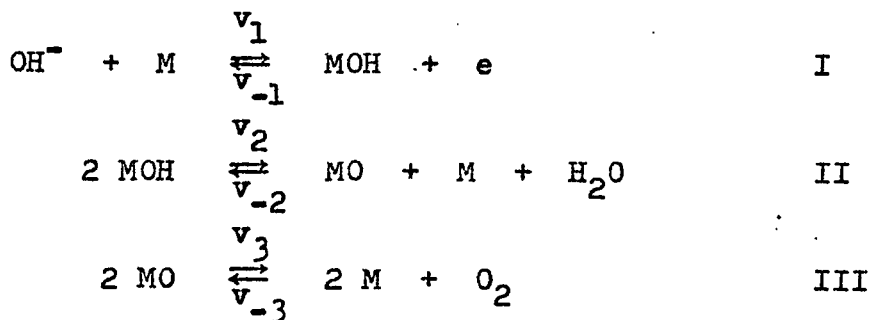
Other possible α values for the particular mechanism proposed above are $\alpha = 1/2$ for step 1 rate-controlling and $\alpha = 4$ for step 3 rate-controlling. In this way the Tafel slopes for most of the plausible mechanisms of oxygen evolution under certain limiting conditions have been calculated and tabulated (5). In some cases two or more mechanisms may exhibit the same Tafel slopes and further criteria for differentiation of the mechanism must be obtained by some other means.

(iii) Quasi-equilibrium Treatment for Derivation of Tafel Slopes

It is possible to calculate, as pointed out originally

by Parsons (7), the limiting Tafel slope values for any given mechanism simply by assuming that all steps preceding the rate-controlling step are almost in equilibrium. This latter method is more rapid and can yield limiting results identical with the Christiansen method in most cases. In fact, the assumptions required to simplify the complete Christiansen expression into one of a simple exponential relationship are equivalent to regarding all the steps preceding the rate-controlling step as effectively in equilibrium.

This method may be applied to the reaction scheme already discussed as follows



Recombination of MOH is again assumed to be rate-controlling.

The overall forward velocity may thus be written

$$\vec{v} = v_2 = k_2[\text{MOH}]^2$$

If reaction [I] is assumed to be in equilibrium

$$[\text{MOH}] = \frac{k_1}{k_{-1}} [\text{OH}^-] [\text{M}] \exp [F\eta/RT]$$

and if the surface is sparsely covered, $\theta \ll 1$

$$[\text{MOH}] = K_1 [\text{OH}^-] \exp [F\eta / RT]$$

where K_1 is an equilibrium constant.

Therefore

$$v = k_2 K_1^2 [\text{OH}^-]^2 \exp [2F\eta / RT] \quad [18]$$

which is identical with equation [16].

However, since one cannot arrive at the exact general rate expression in this way, the effects of surface coverage are not as readily recognized (e.g. cases of activation controlled limiting currents can arise) as they are with the more elaborate Christiansen treatment:

(c) Tafel Slopes from E.M.F. Decay Measurements

(1) General

The most direct method of evaluating the Tafel slope b , and thus the transfer coefficient α , is to measure the electrode potential as a function of current density under direct d.c. polarization. This method, although satisfactory in many cases, is subject to possible errors due to concentration polarization, IR drop in solution, local heating in the solution etc., as well as to more fundamental difficulties which arise when the surface condition of the electrode can change with time due to build up of surface films; this is particularly the case in anodic processes where oxide films can be formed and both the potential of the electrode and the reaction mechanism

may depend on the degree of oxidation. Such examples are discussed later in this thesis with reference to anodic processes at the nickel oxide electrode.

An alternative method for obtaining b , which largely eliminates these undesirable side effects, involves measuring the rate of decay of e.m.f. following interruption of a polarizing current (8,9,10).

(11) E.M.F. Decay from High Overpotential

We consider here the case of ions being discharged at an electrode solution interface by a polarizing current: Following interruption of the current, the potential difference across the interface will tend to be maintained by the capacitance of the electrical double-layer and ions will continue to be discharged. The rate of passage of ions across the interface at appreciable overpotentials is given by an expression of the form

$$i = i_0 \exp [-azF\eta/RT] \quad [19]$$

From elementary electrostatics we may also write

$$-C \frac{d\eta}{dt} = i \quad [20]$$

where C is the capacitance of the double-layer assumed in this derivation to be independent of potential (cases where it can be a function of potential are discussed in the "Discussion" section of this thesis). Since only the flow of ions

(i.e. of charge) can discharge the double-layer capacitance, we obtain from equations [19] and [20]

$$i_0 \exp [-azF\eta/RT] = -C \frac{d\eta}{dt}$$

$$- \frac{C}{i_0} \exp [azF\eta/RT] \cdot d\eta = dt$$

Integrating we have

$$- \frac{RT}{azF} \cdot \frac{C}{i_0} \exp [azF\eta/RT] = t + \theta \quad [21]$$

where θ is the constant of integration having the units of time.

For the boundary condition $t = 0$, let $\eta = \eta'$, the overpotential during polarization when the steady current was flowing.

Then

$$- \frac{RT}{azF} \cdot \frac{C}{i_0} \exp [azF\eta'/RT] = \theta$$

but

$$i_0 \exp [-azF\eta'/RT] = i'$$

the initial polarizing current.

Therefore

$$\theta = - \frac{RT}{azF} \cdot \frac{C}{i'} \quad [22]$$

Taking logarithms and rearranging equation [21] we have

$$\eta = - \frac{RT}{azF} \ln \frac{-RT C}{azF i_0} + \frac{RT}{azF} \ln \left[t - \frac{C}{i'} \frac{RT}{azF} \right] \quad [23]$$

From equations [9a] and [9b] - $\frac{2.3 RT}{azF} = b$ the Tafel slope,

therefore

$$\eta = a' - b \log \left[t + \frac{b C}{2.3 i'} \right] \quad [24a]$$

or

$$\eta = a' - b \log [t + \theta] \quad [24b]^*$$

We may hence expect that a plot of η versus $\log (t + \theta)$ will result in a straight line whose slope is equal in magnitude but opposite in sign to that of a conventional Tafel slope. Some of the advantages and limitations of this method for obtaining Tafel slopes will be discussed in the Discussion Section of this thesis.

(iii) E.M.F. Decay Near the Reversible Potential

As the reversible potential is approached (e.g. $\eta < 20$ mv.) the back reaction can no longer be neglected and one must write for the passage of ions across the interface

$$i = i_0 \left[\exp \left[\frac{-azF\eta}{RT} \right] - \exp \left[\frac{azF\eta}{RT} \right] \right] \quad [25]$$

From this equation it can be seen that i , the net forward current, will rapidly approach zero as η approaches zero

* Since η is a finite quantity when $t = 0$, i.e. when the steady polarizing current is still passing prior to interruption, it is seen that under these conditions the logarithmic term must be finite and equal to $\log [\theta]$, i.e. θ has the significance of that time required for the E.M.F. of the electrode to decay from a hypothetical infinite value to the value η' , the initial steady polarization immediately prior to interruption of the polarizing current.

and the electrode potential, as expected, can fall only as low as the thermodynamic reversible potential of the system. It will in fact approach the reversible potential asymptotically with time. The same, of course, must apply to an electrode recovering from a polarization applied in the other direction from the reversible potential.

(d) Consecutive and Alternative Reactions: Changes of Mechanism

Since different mechanisms for an overall electrode reaction usually have a different dependence of rate upon potential, the mechanism which is favored at one potential at a given electrode might no longer be favored at a different potential. In this way a change in the mechanism of an overall reaction may occur as the overpotential for the reaction is varied (10a). Such a change may occur in one of two ways:

- (i) the elementary steps in the overall reaction can remain the same with the rate-controlling step shifting from one elementary step to another ("series" change of mechanism);
- (ii) one or more of the elementary steps may become relatively less favored as the electrode potential is changed than an analogous step operating alternatively to it ("parallel" change of mechanism - these terms are used by analogy with the case of "series" or "parallel" combination of conductances). When a change of mechanism, series or parallel, occurs there will be

a change in the slope of the Tafel line for the reaction. This must occur since the change of mechanism arises because of the assumed difference of potential dependence (the Tafel slopes b) of the rates for the two mechanisms. If the change is a "series" change, the Tafel line will take on a higher slope at higher overpotentials while for a "parallel" change the slope will become lower at higher overpotentials. This is best seen by considering Figures Ia and Ib.

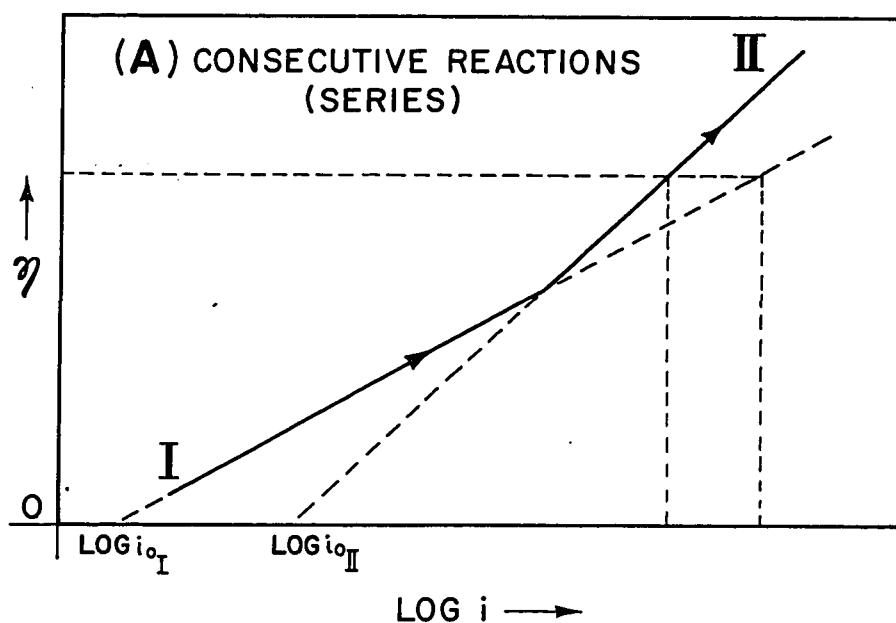
The lines I and II represent hypothetical Tafel lines for two different reactions in an overall electrode reaction. If these two reactions operate in "series" the overall rate will be governed by that of the slower reaction and the Tafel line for the overall rate, represented by the full line (Figure Ia) will have a "concave" inflexion with a higher slope at higher overpotential. If, on the other hand, these reactions operate in "parallel", the overall rate will be governed by the faster reaction, as indicated by the full line in Figure Ib, and the slope will be lower at the higher potentials, the line then exhibiting a "convex" inflexion. Thus when a change of Tafel slope is observed experimentally, it is immediately evident* whether the change of mechanism involves consecutive (series) or alternative (parallel) reactions.

* Under certain rather special conditions of surface coverage where the isotherm for the adsorbed intermediates passes from the Langmuir to the Temkin form due to interactions in the surface phase, changes of slope of Tafel lines for a given single mechanism have been predicted. However, in most cases either limitingly high or limitingly low surface coverages by intermediates are involved (11).

Figure 1a - Change of mechanism for the case of
consecutive reactions.

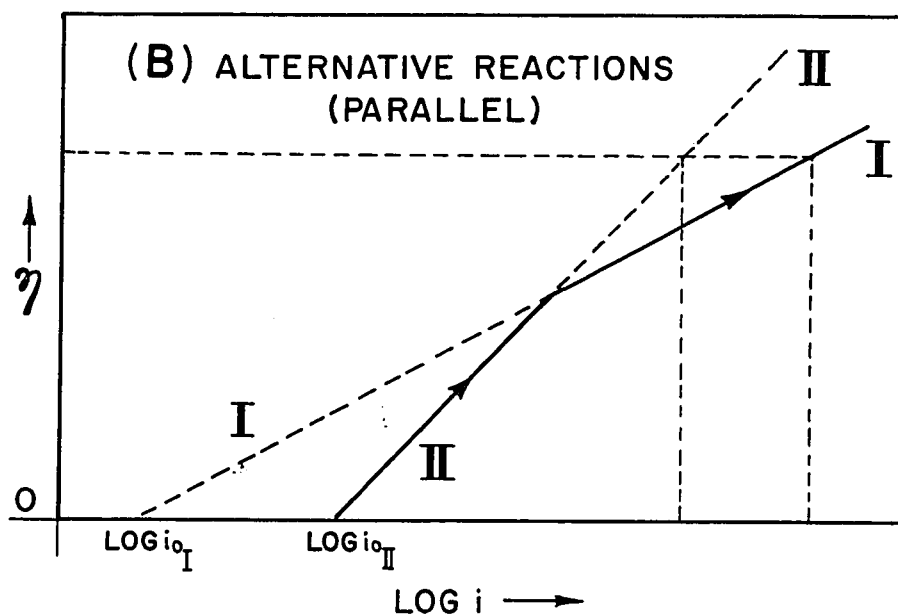
Figure 1b - Change of mechanism for the case of
alternative reactions.

CHANGES OF MECHANISM



Process I is slower than II but its rate depends more on potential than does that of II.

At high potentials II becomes rate-determining even though $i_{oII} > i_{oI}$.



At high potentials, if I and II are alternative, I passes more current than II even though $i_{oI} < i_{oII}$.

(e) Simultaneous Anodic and Cathodic Processes

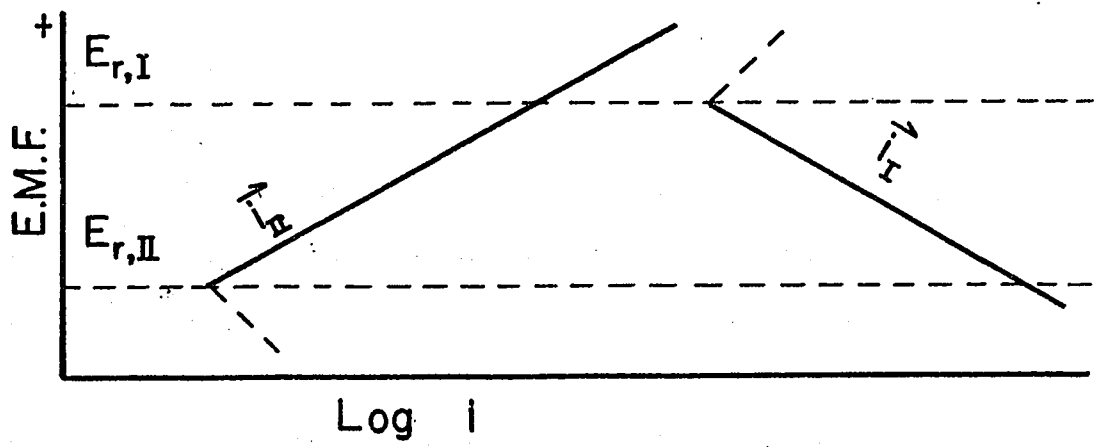
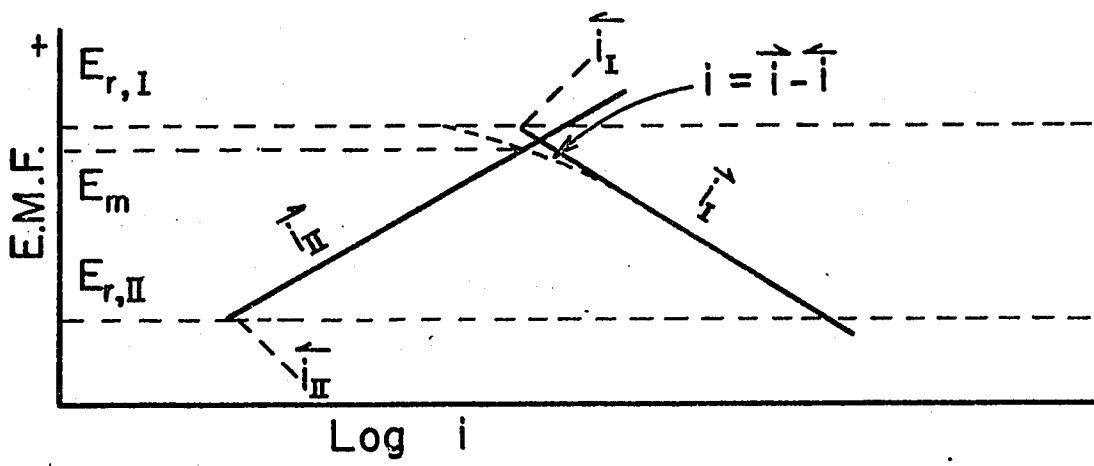
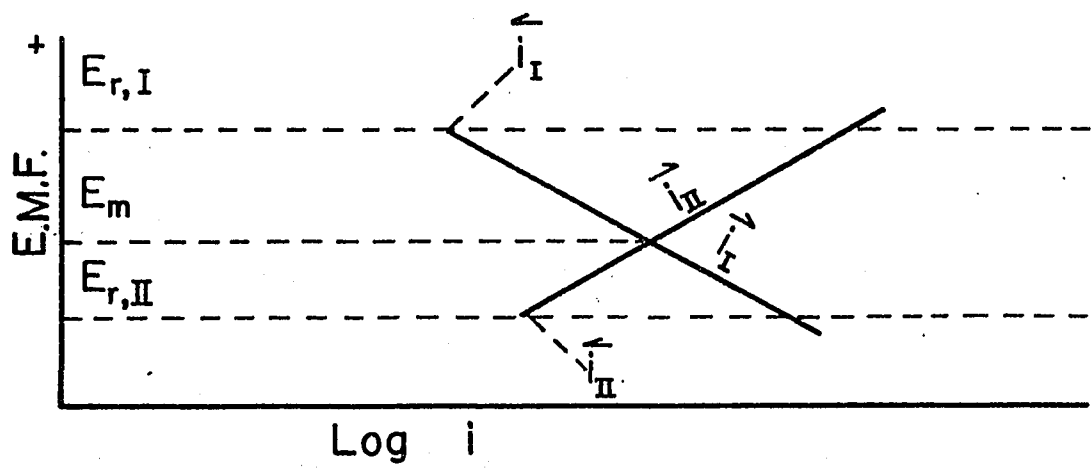
Hitherto, we have been concerned with processes occurring in one direction only at an electrode-solution interface. A number of electrode processes, however, such as metal dissolution, corrosion and the self-discharge of oxide electrodes such as the one studied in the present work, involve anodic and cathodic processes which occur simultaneously. In order to form a basis for quantitative discussion of self-discharge effects to be examined subsequently in the "Discussion" in relation to experimental results obtained in the present work, we shall briefly treat the behaviour of such electrode systems involving both anodic and cathodic processes. Of particular interest is the e.m.f. of such a system, under steady-state conditions, when no external current is applied, Under these conditions the overall cathodic reaction and the overall anodic reaction must occur at equal rates. The general treatment of processes under such conditions was first formulated quantitatively by Wagner and Traud (12).

In Figure IIa are represented hypothetical Tafel lines for an anodic and a cathodic process having comparable currents and which are assumed to occur simultaneously at an electrode. In the steady-state, both processes must occur at equal rates given by the abscissa of the point of intersection of the two Tafel lines, and thus the potential will be fixed at a point intermediate between their reversible potentials.

Figure IIa - The mixed potential when the anodic and cathodic processes have comparable exchange currents.

Figure IIb - The mixed potential when the cathodic process has a much larger exchange current than the anodic process.

Figure IIc - The steady state potential is determined solely by the much faster cathodic process.



This steady-state potential is usually referred to as the "mixed potential" of the two processes.

In the foregoing case the respective reverse reactions for each of the anodic and the cathodic processes have been neglected since both are considered polarized well away from their reversible values. If, on the other hand, the exchange current for one process is much greater than that of the other it may be necessary to consider the reverse reaction of the former. Such a case is illustrated in Figure IIb. It is evident that the "mixed potential in Figure IIb will be at the point of intersection of the anodic Tafel line with the line (dotted) representing the net forward velocity of the cathodic process ($i = i_{\rightarrow} - i_{\leftarrow}$) and not with the line representing the forward reaction velocity only.

The case of one reaction having an exchange current overwhelmingly greater than the other is illustrated in Figure IIc. In this case the steady-state potential will essentially be the reversible potential of the reaction having the higher exchange current.

It will be shown in the "Discussion" section how mixed potentials can be set up at the nickel oxide electrode by simultaneous self-reduction of the higher valence oxide with liberation of oxygen at anodic sites; this situation is the converse of that existing when a metal dissolves, suffering oxidation with liberation of hydrogen as the cathodic process.

2. ELECTROCHEMICAL OXYGEN EVOLUTION

(a) Behaviour at Electrodes other than Nickel Oxide

The noble metals, because of their resistance to anodic dissolution and to oxidation (except for superficial oxide film formation), have been the most extensively used electrode materials for oxygen evolution studies (13-18). In recent years some of the baser metals have also received some attention; in particular Tafel slopes have been measured on the oxides or oxide covered surfaces of lead (19,20), iron (21), cobalt (18) and nickel (22-24). Many of the early workers in the field of electrochemical oxygen evolution did not fully realize the importance of adequate solution purification (16) and this, coupled with the time variation observed at many types of electrodes, has led to discrepant results.

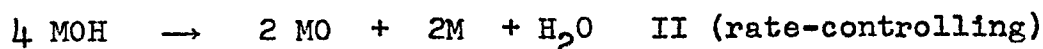
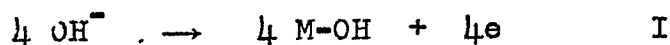
On Pt in H_2SO_4 solution, Tafel slopes $d\eta/d \log i$ ranging from 0.13 to 0.050 have been reported depending upon the experimental conditions. Low slopes, ($\ll 0.060$) however, appear not to be very reproducible on Pt in acid solution. Under conditions of ultra-purity the Tafel lines for anodic oxygen evolution become more reproducible giving a slope of approximately 0.10 (16). This value is characteristic of an ionic discharge step being rate-controlling; it can be shown that this step may be the initial discharge of H_2O or OH^- on

a sparsely covered surface or alternatively it may be a subsequent step occurring on a surface fully covered with the first intermediate of the overall reaction produced in the initial discharge step. From a determination of the stoichiometric number, Bockris and Huq have concluded that the initial discharge from H_2O (viz. $H_2O \rightarrow OH_{ads.} + H^+ + e$) on a sparsely covered surface must be rate-controlling on Pt in acid solution. Platinum in alkaline solution exhibits a lower Tafel slope of approximately 0.045 (15,18). This value has also been reported for oxygen evolution on gold (17) and iron (21) in alkaline solution. The only mechanism to be proposed in explanation of this value of 0.045 is one given by Hackerman for oxygen evolution on iron. This mechanism will be discussed further below. An analogous case of a slope of 2.3 RT/F (0.058) has been discussed by Bockris, Pentland and Sheldon (25) in relation to surface diffusion controlled radical recombination in hydrogen evolution. A first order surface recombination leading a slope of 2.3 RT/F was first discussed by Laidler (26) and examined further by Bockris, Pentland and Sheldon in the work mentioned above.

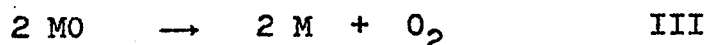
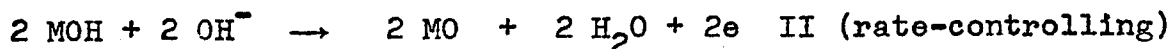
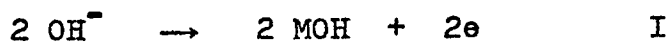
Wade and Hackerman report that on passivated iron good Tafel behaviour for anodic oxygen evolution is exhibited in both acid and alkaline solution (H_2SO_4 and NaOH). The values of b observed are 0.030 at pH 2.5, 0.040 at pH 4.0 and

0.054 at pH 14.5. The mechanisms proposed by these authors are the following:

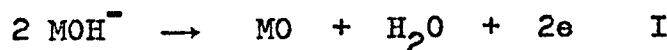
at pH 2.5 ($b = 0.030$)



at pH 4.0 ($b = 0.040$)



at pH 14.5 ($b = 0.054$)



This latter mechanism, for $b = 0.054$ involving simultaneous discharge and dehydration of two neighboring adsorbed ions bearing the same charge appears to the present author to be an unlikely path in oxygen evolution.

Lead dioxide in H_2SO_4 solution presents an interesting case in that on $\alpha\text{-PbO}_2$ a Tafel slope of 0.15 is observed while on $\beta\text{-PbO}_2$ the slope is 0.075 (20). No mechanisms have been proposed to explain these results but it would appear that the value 0.15 may be due to a slow discharge mechanism (theoretical 0.12). The value of 0.075 has no simple theoretical explanation.

Conway and MacDonald (27) have examined the kinetics of oxygen evolution at palladium-gold alloys in ultra-purified aqueous sulphuric acid and sodium hydroxide solutions and find slopes varying from 0.045 for gold (17) to 0.12 for palladium in the acid solutions depending on the alloy composition. In alkaline solutions the slopes at higher current densities are higher than $2.3 RT/F$ when non-ohmically conducting oxide film formation is occurring. Under those conditions, activation controlled electron or ion transport in the oxide film is probably involved and leads to anomalous high slopes as discussed by Thirsk (28). Such processes are, of course, well known in the behaviour of zirconium and tantalum oxide electrodes where the activation controlled charge transport in the oxide film leads to very high polarizations.

(b) Oxygen Evolution at Nickel Oxide

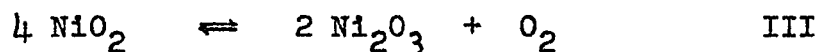
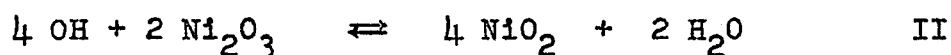
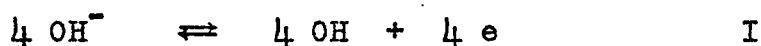
When nickel is polarized anodically in alkaline solution, an oxide layer is formed on its surface before oxygen can be liberated (22); thus anodic evolution of oxygen must be considered as occurring on an oxide of nickel rather than on the nickel metal itself. However, since both the state and extent of oxidation remain unchanged during prolonged polarization (i.e. at high current densities a passive film if formed), the oxide may be considered as simply a catalytic surface on which the process of oxygen evolution occurs. In

proposing mechanisms for anodic oxygen evolution on nickel, some authors have preferred this latter view (23) while others have written mechanisms involving the formation of unstable higher oxides of nickel which subsequently decompose (22,24). The distinction is somewhat academic, since an oxygen or a hydroxyl radical chemisorbed at a surface (e.g. on Pt,) can equally well be considered as constituting an oxidized state of the metal at that surface. Likewise, intermediates involved in the oxygen evolution reaction and adsorbed on nickel oxide may be considered as constituting a higher oxidation state of the surface or simply as adsorbed radicals.

The Tafel slopes reported by various workers for oxygen evolution on nickel oxide are in agreement only in so far as two Tafel regions of different slopes are found but the actual values are discrepant. At low current densities (10^{-6} to 10^{-3} am./cm²) slopes of from 0.027 to 0.040 are observed (22); at high current densities ($> 10^{-2}$ amp/cm²) values varying from 0.095 to 0.18 are reported (23). This latter slope is more difficult to measure accurately, since at the current densities required to obtain a region of sufficient length in logarithmic current density, ohmic potential drops in the solution and concentration polarization effects become appreciable. This will have the

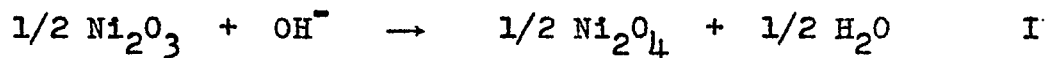
effect of making the slope appear greater than it really is.

For the lower slope, Fiseiski and Tur'yan have found a value of 0.027 volts for pure metallic nickel in 7.5 N. KOH solution. This they explain on the basis of the following mechanism



which, they state, predicts a limiting Tafel slope of 0.029 (2.3 RT/2F) for reaction II as the rate-controlling mechanism. A similar scheme has been proposed by Elina, Borissova and Zalkind (22), who have reported experimental Tafel slope values ranging from 0.035 to 0.040 volts.

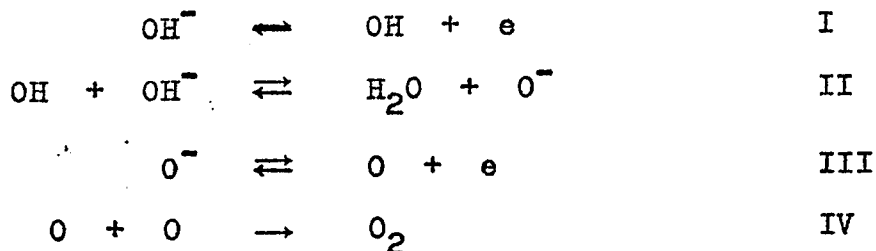
These latter authors write the following reaction scheme:



in which they assume the decomposition of Ni_2O_4 in reaction II to be rate-controlling. On this basis, they assert that the theoretical limiting slope will be 0.029 i.e. $2.3 \times \text{RT}/2\text{F}$ and that the experimental values of approximately 0.038 are in "adequate agreement" (sic). These conclusions appear to be oversimplified since reaction I cannot be considered as

elementary and involves the making and breaking of "bonds" in the oxide which cannot occur simultaneously with the passage of one ion across the electrode-solution interface. In any case the slope of 0.038 (viz. $2.3 [2/3] RT/F$ which arises in radical-ion desorption on a partially covered surface) is well authenticated and observed also in the present work. If the reaction mechanism is rewritten in a form where each step is elementary (i.e. writing reaction I as two separate elementary steps) then it can be readily shown that a slope of 0.015 (i.e. $2.3 RT/4F$) will result if the decomposition of " Ni_2O_4 " (path II above) is slow. The assumption of distinct stoichiometric chemical species such as " Ni_2O_4 " must in any case be regarded as unsatisfactory since the nickel oxide involved is probably (see below) a non-stoichiometric mixed valency oxide whose formal composition depends on its previous history and degree of electrochemical oxidation.

On the other hand, Volchkova and Krasil'shchov, who also report a slope of 0.038, propose the following scheme



and they assume reaction III to be rate-controlling. It is not entirely clear how these latter authors have arrived at

the conclusion that rate-controlling III will yield a theoretical value of 0.038 ($2.3 [2/3] RT/F$) for the Tafel slope; on the basis of the Christiansen treatment, a value of 0.023 ($2.3 [2/5] RT/F$) is predicted. If reaction II, however, is assumed to be rate-controlling, the experimentally observed value of 0.038 can in fact be predicted as suggested in the present work.

At higher current densities the experimentally observed slope of $2.3 2RT/F$ is characteristic of slow-discharge of OH^- ions. Unfortunately, when this is the case, on a bare surface or on one completely covered with the preceding intermediate e.g. MOH , it is not possible to make any further direct conclusions regarding the nature of the subsequent steps in the reaction. However, as discussed in a later section of the thesis, the analysis of E.M.F. decay curves can, under some conditions, lead to further information on the nature of the reaction path if adsorbed intermediates are involved in appreciable concentrations on the surface.

3. THE NICKEL OXIDE ELECTRODE

(a) Nature of the Nickel Oxide Electrode

In spite of the fact that the nickel oxide electrode has served as the positive plate in alkaline storage batteries since the turn of the century, much remains uncertain about both

the chemistry and the electrochemistry of the system. As used in alkaline storage batteries, the electrode consists of finely divided nickel oxide in intimate contact with a metallic conductor (usually nickel or graphite). An experimental model, having essentially the same characteristics as the battery electrode, may be prepared by anodically polarizing metallic nickel in alkaline solution, in the presence of hypochlorite or hypobromite (29). One of the major difficulties in this field has been that of identifying and characterizing the reaction products of the electrolytic oxidation reaction.

In the reduced state, the active material is presumed to be hydrated nickelous hydroxide Ni(OH)_2 in very finely divided, almost amorphous, form; in the oxidized state this becomes a higher valence hydrated oxide in which nickel has a mean formal valence of approximately three. A controversy concerning the stoichiometry of the electrolytic oxidation-reduction reaction was started in 1906 between Zedner (30,31,32) and Foerster (33,34,35) and, despite numerous papers since that time, there is still not complete agreement on the subject. Much of this lack of agreement is attributable to the nature of the higher oxides of nickel particularly those formed electrolytically, which are very ill-defined both in structure and composition, a fact which is also probably related to the discrepant electrode-kinetic results in the literature, referred to above.

(b) Oxides of Nickel

The divalent oxide and hydroxide of nickel are well known and well characterized. Nickel hydroxide $\text{Ni}(\text{OH})_2$, is readily prepared by precipitating divalent nickel from solution with ammonia or alkali hydroxide solution. In its freshly prepared form, nickel hydroxide may contain some loosely bonded water in excess of $\text{Ni}(\text{OH})_2$, ^{that corresponding to} but these water molecules are readily lost by oven drying above 100°C (36,37). Anhydrous nickel oxide NiO may be prepared in stoichiometric form (in vacuo) by the pyrolysis of $\text{Ni}(\text{OH})_2$ above 200°C in high vacuum (38). Thermal decomposition of nickel nitrate also yields the anhydrous oxide but when prepared in this way it contains oxygen in excess of the stoichiometric amount (39). Although reactions of the nickel oxide electrode are frequently written as though involving anhydrous nickel oxide NiO , this material is not electrochemically active (i.e., it cannot be oxidized or reduced electrolytically to any significant degree (40)). The hydroxide, on the other hand, can be oxidized electrolytically and, in fact, it is this material which is used as the active material in the (uncharged) positive plates of nickel-cadmium batteries.

The constitution of the higher oxides of nickel has been the subject of a great deal of controversy. Oxides in which nickel has a valence of three or more may be prepared

by a variety of methods including precipitation from nickel nitrate solutions with NaOCl or NaOBr in alkali (41), precipitation with $K_2S_2O_8$ in alkali (42), fusion of nickel with Na_2O_2 and electrolytic oxidation (43). The oxygen content of these oxides frequently exceeds that corresponding to an oxide of trivalent nickel, but it does not reach a composition corresponding to quadrivalent nickel. Reports that stoichiometric (or very nearly stoichiometric) NiO_2 had been prepared (44) have never been well substantiated (45,46).

A survey of the literature reveals that a considerable amount of work has been done in an attempt to elucidate the structure and composition of the various hydrates of nickel using analytical, calorimetric, X-ray diffraction and electron diffraction techniques (47-53). As a result of this work a variety of oxides of nickel have been reported some of which are listed below:

- NiO_2 - Evidence in calorimetric studies - also postulated because of the high oxygen content often encountered in oxides of nickel (as high as $NiO_{1.8}$).
- $\alpha-NiOOH$ - Identified by X-ray diffraction - prepared by precipitation $\begin{matrix} \text{from} \\ / \end{matrix} K_2Ni(CN)_4 \begin{matrix} \text{with} \\ / \end{matrix} K_2S_2O_8$ in alkali.

- β -NiOOH - Identified by X-ray diffraction - prepared by oxidation of $\text{Ni}(\text{OH})_2$ by NaOCl or NaOBr .
- γ -NiOOH - Identified by X-ray diffraction-prepared by fusion of Ni with Na_2O_2 , followed by careful hydrolysis.
- $\text{Ni}_2\text{O}_2(\text{OH})_4$ - Identified by X-ray diffraction - prepared by fusion of Ni with Na_2O_2 , followed by careful hydrolysis.

The formulae given for these various oxides must not be taken too literally since chemical analysis rarely supports such ideal stoichiometry. Usually there is found an excess or a deficiency of oxygen along with an excess of water. It has been the custom to ascribe these deviations from ideal stoichiometry to the presence of one or more other oxides of nickel but this does not appear entirely satisfactory. The results of X-ray diffraction work are likewise somewhat inconclusive since only a few diffuse lines appear. This is particularly true for oxides formed by electrolytic oxidation of nickel hydroxide where an almost structureless material is indicated. The lines that do appear indicate that, as electrolytic oxidation proceeds, the basic structure of nickel hydroxide (a hexagonal layer lattice) is distorted to accommodate the greater relative proportion of oxygen but no new well-ordered structure is formed. The modern consensus

of opinion appears to be that the hydroxide can be oxidized continuously without formation of definite intermediate compounds (e.g. Ni_3O_4 or $\text{Ni}_3\text{O}_2(\text{OH})_4$ in the modern formulation). The end product is generally assumed to be the β - NiOOH identified by Glemser and Einerhand but even this compound is probably not as simple as implied by the formula. Much of the difficulty is no doubt due to the almost amorphous nature of the material so that the composition of the surface phase, which may be different from that of the bulk, contributes measurably to the overall composition and properties of the electrochemically active material.

The kinetics of the decomposition of the higher oxides of nickel, formed by the action of alkaline NaOCl on NiSO_4 solution, have been studied by Howell (41). This author observed a high rate of oxygen loss in the initial stages of decomposition followed by a much slower rate at longer times. Howell has explained this behaviour by postulating the simultaneous decomposition of two oxides of nickel, NiO_2 and Ni_2O_3 , where the peroxide NiO_2 decomposes rapidly and the sesquioxide Ni_2O_3 evolves oxygen only slowly. He has further concluded from his results that NiO_2 decomposes directly to $\text{Ni}(\text{OH})_2$ and not to Ni_2O_3 ; also that the hydroxide is oxidized simultaneously to the sesquioxide and to the peroxide. Howell also maintains that the formation of the peroxide does not

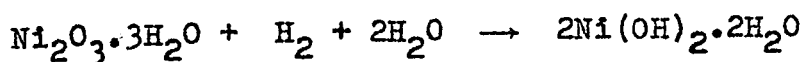
involve the sesquioxide as an intermediate and that NaOCl cannot, in fact, oxidize the sesquioxide to the peroxide. It has also been observed by this author that with increasing relative concentration of the alkali used for precipitation the amount of active oxygen in the precipitate increases and is proportional to the extent of adsorption of alkali by the precipitate. This latter observation is in qualitative agreement with the observed adsorption of KOH during electrolytic oxidation of nickel hydroxide (54) and with the known tendency for lower rates of self-discharge (with oxygen evolution) of nickel oxide electrodes in the presence of high concentrations of alkali (55).

(c) Electrochemical Behaviour of the Nickel Oxide Electrode

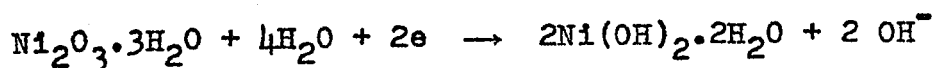
(1) Stoichiometry of the Oxidation-Reduction Reaction

Much of the early work on the nickel oxide electrode, in particular that of Zedner and Foerster, was concerned with establishing the stoichiometry of the oxidation and reduction reactions. These two authors, using mainly chemical analysis of reaction products and steady-state measurements of the dependence of e.m.f. on electrolyte concentration, arrived at rather different conclusions regarding the nature of the

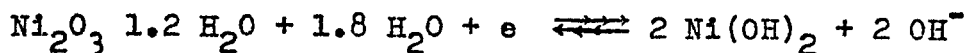
overall reaction. Both agreed that water was liberated during the oxidation reaction and consumed during electrolytic reduction but disagreed regarding the stoichiometric amount of water involved, as well as the degree of hydration of both the oxidation and reduction products. Using an isopiestic method, Zedner (31) determined the number of water molecules of hydration in the higher oxide and found that at 8°C the hydrate $\text{Ni}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was stable from 3 mm. Hg of H_2O down to the lowest vapor pressures that could be reached using H_2SO_4 . On the basis of e.m.f. measurements against a hydrogen electrode as a function of KOH concentration (and thus of H_2O activity), Zedner arrived at a value of 1.1 for the number of water molecules consumed per electron in the reduction of the higher oxide. From these two results he concluded that the overall reaction must be



which for the half-cell reaction gives



Foerster, on the other hand, from chemical analysis of the oxidized and the reduced active materials in the electrodes, as well as by studying concentration changes in the electrolyte of an Edison accumulator during charge and discharge, arrived at the following half-cell equation

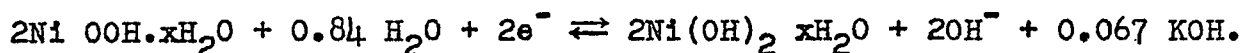


The experimental conditions used by Foerster in this work were quite different from those of Zedner, particularly in that Foerster worked with positive plates from Edison accumulators (containing 22% graphite) whereas Zedner used electrodes consisting of anodically formed nickel oxide on a platinum dish. In view of these differences of technique, it may be expected that the particle size of the active material in Foerster's and Zedner's electrodes might be different. It was later shown by Erschler and co-workers that this could affect the "apparent" consumption of water during electrolytic reduction (54).

The latter authors measured the concentration changes in the KOH electrolyte when a nickel oxide electrode was charged against nickel counter electrodes. They observed that the concentration of KOH decreased on charge as expected from Foerster's and Zedner's equations. However, no definite stoichiometric relationship could be found for the amount of water taking part in the reaction; the calculated quantity of water was found to depend upon initial KOH concentration (decreasing with increasing concentration) and it also depended upon particle size of the active material, being greater for finely divided material. These results led Erschler et al. to suppose that KOH was being adsorbed on the electrodes during

charging and released during discharging. In order to test this hypothesis, they conducted a number of experiments using, in addition to KOH, certain reference ions in the electrolyte (e.g. Cl^- , CO_3^{--}). These experiments did in fact confirm that KOH was adsorbed to an important degree during charging but their results lacked the precision necessary for a quantitative assessment of the effect. The fact that the reference ion might also be adsorbed (cf. effects at the Hg electrode) appears to have been overlooked by these workers.

More recently Kornfeil (56), essentially repeating the work of Erschler, made more precise determinations of reference ion and KOH concentration changes during charging and discharging of the nickel oxide electrode. From the results of this work, Kornfeil has proposed the following half-cell reaction:



Kornfeil claims that the variation of e.m.f. values of electrodes with KOH concentration, measured after long periods of time on open-circuit, is quite accurately predicted by the above equation based on analytical determinations of concentration changes during charge and discharge. However, the above equation does not agree with data obtained in the present work, nor with the results of Zedner, as will be

discussed further in Chapter IV of this thesis.

(ii) Mechanism of Electrolytic Oxidation
and Reduction of Nickel Oxide

In contrast to the case of the lead oxide electrode (57), there is strong evidence that the oxidation of nickel hydroxide occurs in the solid state. Thus Kuchinskii and Erschler (58) have shown that oxidation and reduction do not take place by solution of the oxide followed by reaction at the metal-solution interface and subsequent deposition of the product. A solid state mechanism of oxidation is further supported by the fact that only divalent nickel has been observed in solution: in fact the higher oxides are the only known simple compounds of nickel where a valence state greater than two is exhibited.

According to the views expressed by Foerster (33), nickel hydroxide is first oxidized to " NiO_2 " and this material subsequently reacts with more Ni(OH)_2 to give " Ni_2O_3 " or decomposes, with loss of oxygen, to form " Ni_2O_3 ". This mechanism was postulated by Foerster to account for the high anodic potentials, relative to the steady state potential of the electrode, which are necessary in order for oxidation to proceed at an appreciable rate.* Foerster did not consider, however, that " NiO_2 " was involved in the

* In terms of modern views, this observation simply implies an appreciable polarization in the charging reactions, as discussed in more detail below.

discharge reaction. More recently (40) it has been postulated that some oxidation to the Ni^{4+} state is necessary* in order to endow the oxide with electronically conducting properties so that oxidation can proceed within the bulk of the oxide. The work of Kuschinskii and Erschler (58), in which the oxidation and reduction of a single grain of nickel hydroxide was observed/under a microscope, has shown that the oxidation process begins at the $\text{Ni}(\text{OH})_2$ -metal contact point and from there proceeds into the bulk $\text{Ni}(\text{OH})_2$. It is clear that oxidation can proceed into the lattice only if the oxide is electronically conducting. Stoichiometric nickel hydroxide itself is a relatively good insulator but with the addition of excess oxygen its conductivity is readily increased (39,59). There is no firm evidence, however, that the quadrivalent state of nickel, proposed by Wynne-Jones, is necessary for good electronic conductivity (see footnote below).

Kuchinskii and Erschler also found that by using very rapid rates of discharge, it is possible to reduce the oxide completely to $\text{Ni}(\text{OH})_2$ near the metal contact while the bulk is still largely oxidized. In this way an insulating layer of $\text{Ni}(\text{OH})_2$ is interposed between the oxidized material and the metal contact and thus the remaining material is no longer available for discharge. While this effect is most

* It would appear to be equally possible to have electronic conduction in a mixed $\text{Ni}^{++}/\text{Ni}^{+++}$ oxide.

pronounced under conditions of high discharge rates, it occurs to some degree even at the lowest rates of discharge. Thus it is not possible to reduce the oxide to stoichiometric Ni(OH)_2 electrochemically once it has been oxidized beyond this state since it must be left with sufficient "excess" oxygen to make it conducting. This explains why cathodic reduction does not restore to the electrode the original green appearance of Ni(OH)_2 .

(iii) Previous Work on the Process of Self-Discharge

The first account of the self-discharge behaviour of the nickel oxide electrode is that of Foerster in 1906 (33). In this work Foerster observed that a fully charged nickel oxide electrode on open-circuit will continue to evolve oxygen at a visible rate for as long as 24 hours after cessation of charging. This loss of oxygen is accompanied by a fall in the e.m.f. of the electrode which is at first rapid, then slower, but which continues for many days before eventually becoming negligible. Although Foerster's electrodes were commercial battery plates of the day (1906) consisting of a mixture of nickel oxide and graphite held in "pockets" of nickel plated steel, his e.m.f. results are not substantially different from those obtained more recently by Pitman and Work (60-63) and by Conway and Bourgault (64) using more refined techniques. Foerster's measurements were made using a calomel reference

electrode and a KCl salt bridge. It was believed by Foerster that the initial drop of e.m.f. corresponded to the decomposition of NiO_2 , (cf. Howell, loc. cit.) present in small quantities at the end of charging, after which the e.m.f. became stabilized at the characteristic potential of Ni_2O_3 . This latter potential is given by Foerster as

$$E_H = 0.49 \text{ V.}$$

Foerster's measurements of oxygen evolution during self-discharge are unfortunately of little quantitative significance since they were made on complete nickel-iron battery units. Not only does the presence of hydrogen (liberated from the negative plates) complicate the measurements of the net quantity of oxygen evolved but also the presence of readily oxidizable iron makes it very doubtful that all the oxygen liberated could be actually collected. This is substantiated by the fact that Foerster himself reports that the loss of electrical charge, as measured coulombically by electrical discharge, was greater than could be accounted for on the basis of the oxygen collected. From a qualitative point of view it is interesting to note from Foerster's results that immediately after cessation of charging, the gas liberated in a battery consisted of about 50% hydrogen but after longer times the proportion of oxygen became relatively greater until at the end of one day it is about 90%. This indicates the practical importance of the self-discharge of

the nickel-oxide plate since it will be the limiting factor in "shelf-life" of a charged nickel-iron accumulator. At the end of three days oxygen was still being liberated at an appreciable rate (approximately three cc. per hour from a 75 ampere-hour battery).

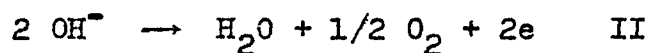
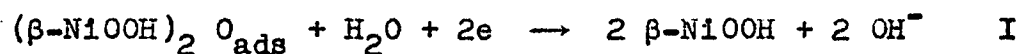
This work on oxygen evolution was carried out at one concentration of electrolyte only (2.8 M. KOH), so that no conclusions may be drawn regarding the effects of KOH or water activity on the rate of self-discharge.

More recently the kinetics of self-discharge of the nickel-oxide electrode have been studied by Pitman and Work (63). Using commercial nickel-cadmium batteries, these authors measured the rate of oxygen evolution on open-circuit (following polarization) as a function of electrolyte concentration. On the basis of their results, they concluded that the rate of self-discharge (in terms of oxygen evolved) was proportional to the square root of the water activity. This conclusion is not without ambiguity, however, since it was based on the total amount of oxygen evolved over a 12 hour period (from the first to the thirteenth hour) on open-circuit following polarization at a given fixed current density; no account was taken of the potential of the electrode or its state of oxidation at any time during this decay; nor was it realised, apparently, that the rate of self-discharge must vary

considerably during this period of time as the electrode potential falls. Under the conditions used, the rate of self-discharge is initially identical at all concentrations (being that of the imposed rate of anodic polarization). Thus what was measured, in fact, was the extent of decrease of rate of self-discharge after a given time as a function of electrolyte concentration. This cannot be taken as identical with the rate of self-discharge itself which is of course a function of electrode potential. The significant quantities determining the "rate of self-discharge" are the exchange current and the Tafel slope for the rate determining process in the self-discharge of the electrode.

Measurements of the e.m.f. decay of the nickel-oxide electrode on open-circuit by these same authors have shown the decay to be approximately logarithmic in time (61). They have also shown that if the log of the rate of oxygen evolution is plotted against e.m.f. E a plot consisting of two linear regions is observed. In aqueous KOH of specific gravity 1.4 (the only case given) the respective slopes $dE/d \log [\text{rate}]$ are 0.105 for the high potential region and 0.035 for the lower region. The value of 0.035 is in relatively good agreement with values found previously (22) for anodic oxygen evolution on nickel oxide. In spite of this important and relevant fact, however, they conclude that the oxygen evolution partial reaction is not rate-controlling in the self-discharge

process; rather they consider the evolution of oxygen on self-discharge to arise from oxygen adsorbed on β -NiOOH; this is lost by an electrochemical reduction mechanism which may be written as the sum of two reactions, the first of which is rate-controlling



It is not clear why the authors choose to regard reaction I as rate-controlling and it is obvious that its associated Tafel slope cannot be $0.035 \left(\div \frac{2}{3} \frac{RT}{F} \cdot 2.3 \right)$. Evidence is presented below from the present experimental work that the (anodic) oxygen evolution reaction is, in fact, the rate-controlling partial reaction in the mixed self-discharge process, analogous to electrochemical corrosion of a metal.

CHAPTER II

EXPERIMENTAL

1. SOLUTIONS

(a) Standard Purification Technique

(i) Potassium Hydroxide

Potassium hydroxide solutions used in a substantial part of this work were made up from the analytical grade material using water prepared by redistilling "distilled" water from alkaline permanganate in a still provided with three spray traps. Initial solutions of the potassium hydroxide slightly more than saturated at 25°C were prepared in a "seasoned" polyethylene bottle and left to stand, tightly sealed, at 25°C for the excess potassium hydroxide to crystallize from solution. Aliquots drawn from this solution were added to the doubly distilled water to provide solutions as required. Concentrations were checked after each run by titration against a standard solution of hydrochloric acid.

(ii) Nickel Nitrate

Saturated solutions of nickel nitrate used in the preparation of the electrodes (section II, 2) were made up from the recrystallized analytical grade (A.C.S.) reagent (specified "cobalt low") in the conductance water.

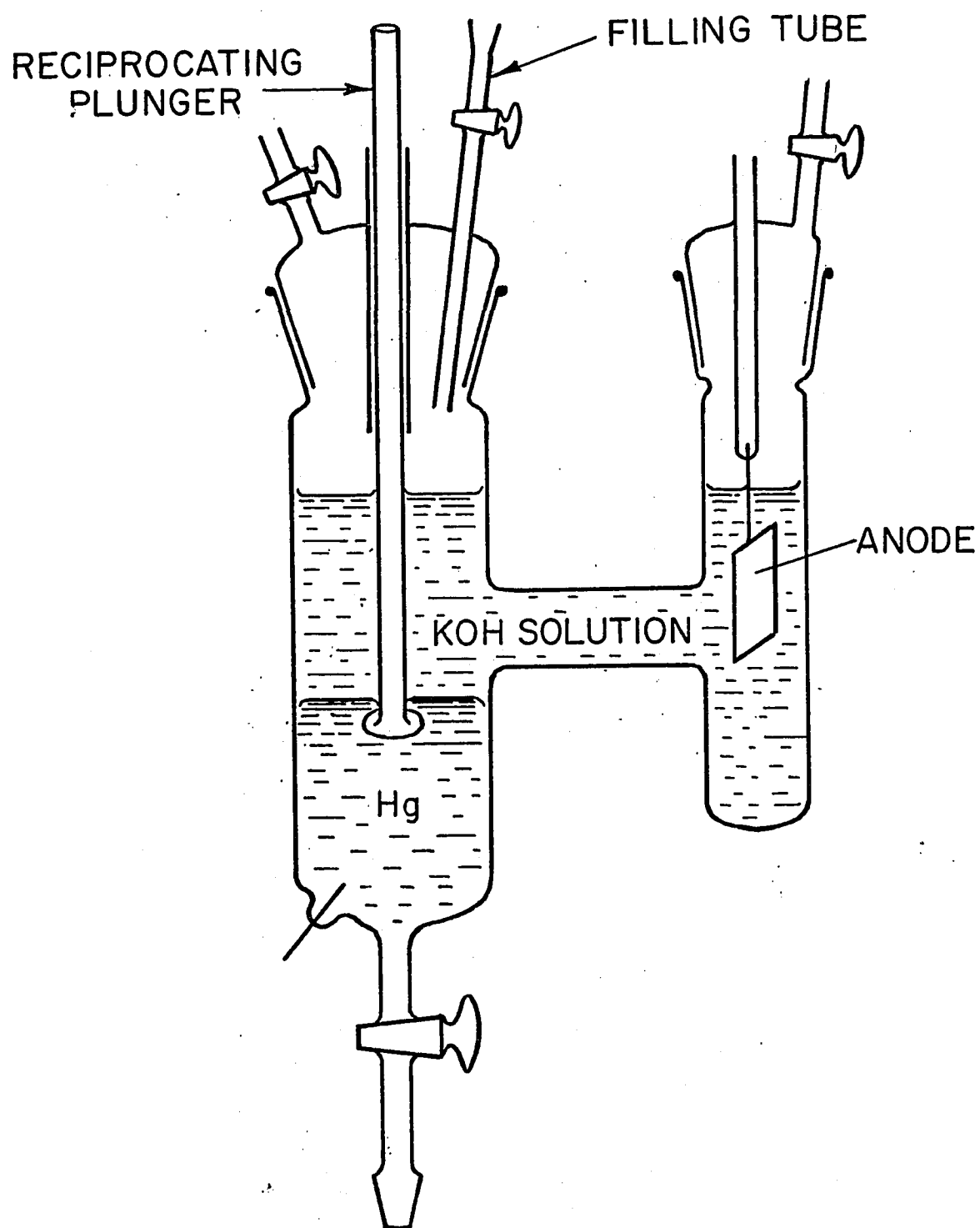
(b) High Purification Technique

In the early stages of the experimental work several runs were carried out under the most stringent conditions of purification in order to establish the role of possible trace impurities and to investigate the effects of high purification and preelectrolysis on the kinetic results. Experimental details are given below.

(1) Potassium Hydroxide

Analytical grade (A.C.S.) KOH was initially recrystallized at -20°C from a 15 M solution in conductance water in an all-glass vessel having a sintered glass bottom for filtering the solution out of contact with air. When an appreciable quantity of crystals had been precipitated at the low temperature, the mother liquor was forced out through the sintered disc under pressure of oxygen and conductance water was then distilled directly onto the crystals to form a solution approximately 8 to 10 molar in KOH. This solution was then run into an electrolysis vessel (Fig. 3) fitted with appropriate electrodes and containing triply distilled mercury in the cathode compartment. Potassium amalgam was then formed electrolytically at the mercury cathode using a current density of 0.25 a. cm^{-2} . Stirring of the amalgam was maintained during electrolysis by means of a reciprocating plunger. The amalgam thus formed was run into a third vessel

Figure III: Electrolysis vessel used for
 formation of potassium amalgam.



AMALGAM ELECTROLYSIS CELL

into which conductance water was redistilled in a stream of CO_2 -free nitrogen. In order to assist the decomposition of the amalgam, an external electrical connection was provided between the mercury and a platinized platinum electrode immersed in the solution.

Finally, this solution was passed into the experimental cell where it was pre-electrolyzed with a nickel anode, purified oxygen* being bubbled into the solution. In order to avoid the production of H_2 in the solution and consequent depolarization of the test anode, a charged (i.e. oxidized) nickel oxide electrode was made to serve as cathode during the pre-electrolysis treatment. A pre-electrolysis current density of 10^{-2} a. cm^2 (based on the apparent area of the anode) was passed for about 12 hours and the corresponding charge passed in this time was about 100 coulombs per ml. of solution.

(11) Nickel Nitrate

Nickel nitrate used in this part of the work was prepared by two recrystallizations of the analytical grade, "cobalt low", reagent from CO_2 -free conductance water. A sample of nickel nitrate was also prepared by dissolving a piece of spectroscopically-pure nickel in pure HNO_3 and twice recrystallizing the product. The results obtained

* For more details see "oxygen purification".

using this material were insignificantly different from those found with the nickel salt prepared as described above.

(c) Potassium Deuterioxide in Heavy Water

Solutions of KOD in D_2O were prepared by decomposing the potassium amalgam in D_2O (99.76% D_2O). The amalgam was prepared in the manner described above using aqueous KOH. The dried amalgam was then reacted with D_2O in a vessel suitably equipped with a drying tube to allow the escape of the liberated deuterium and yet protect the solution from any exchange with atmospheric water.

(d) Solutions of Nickel Sulfate in Heavy Water

For use in the preparation of plates (see below), solutions of $NiSO_4$ in D_2O were prepared as follows: analytical grade $NiSO_4 \cdot 6H_2O$ was dehydrated by heating at $600^\circ C$ to constant weight (about 54 hours). The loss of weight corresponded to apparent removal of more than 6 H_2O to an extent of about 5%. Since the initial hexahydrate was superficially dry, it was concluded that some SO_3 was lost on heating and the residual anhydrous salt hence contained traces of NiO . However, upon dissolution of the anhydrous salt in D_2O the residual NiO could be filtered off and a clear solution of the sulfate in D_2O resulted.

2. ELECTRODES

(a) General

All electrodes used in this work were similar to those employed in "sintered plate" nickel-cadmium batteries and consisted essentially of plaques of porous sintered nickel impregnated with chemically precipitated nickel hydroxide.

(b) Sintered plaques

The nickel hydroxide, which is the initial electro-chemically active material in these electrodes, is supported in plaques of sintered nickel powder having a real surface area* of about 0.12 meter² per gram, or 200 cm² per cm² of apparent surface. The nickel plaques are normally prepared by heating nickel powder, obtained by the Mond carbonyl process, to about 800°C for about 15 minutes in an atmosphere of hydrogen. The sintered plaques used in this work were obtained from two sources. For the study of the steady state current-potential behaviour of these electrodes, and for a few preliminary runs of e.m.f. decay and of oxygen evolution, plaques manufactured by the Clevite Corporation, and supplied through the courtesy of the Defence Research Chemical Laboratories, were used. The sintered nickel plaques were 1 mm. in thickness

* This measurement was kindly carried out by Dr. C. Amberg of the National Research Council using the B.E.T. (Nitrogen) method.

and had a porosity of about 80%. For the remainder of the work plaques of 2 mm. thickness and about the same porosity supplied by the Edison Corporation were used. For measurements of rates of open-circuit oxygen evolution, rectangular pieces 1" x 3" were cut out from the large plaques described above and given two cycles of impregnation as described in section (2c). In the case of experiments conducted in D_2O , plates 0.25"x0.5" were used. For the remainder of the work involving thermodynamic experiments, steady state polarization studies and for some control experiments, singly impregnated plates 0.5" x 1" were used.

(c) Impregnation of Sintered Plaques

Nickel hydroxide was introduced into the pores of the nickel sinter by the following procedure: the sinter was first placed in a pyrex vessel which was evacuated to below 1 mm. pressure of mercury. After closing a stopcock connection to the pump, aqueous nickel nitrate, prepared as described above, was allowed to flow from an upper bulb into the evacuated vessel until the sintered plaque was entirely submerged. The vessel was then opened to the atmosphere, thus allowing the externally applied atmospheric pressure to force the solution into the pores. After standing in the solution of nickel nitrate for 10 minutes, the sintered plaque was removed and placed in a 25% KOH solution at 70°C, and immediately polarized

cathodically at a current density of 0.1 amperes per apparent cm^2 of surface area. Plane sheets of pure nickel metal, on either side of the sintered plaque, were used as anodes. After about 20 minutes of this treatment, the potential across the electrodes was observed to rise quite sharply and hydrogen began to be evolved at an appreciable rate. Cathodic polarization at the same current density was then continued for an additional ten minutes. The electrode was then removed and washed in a bath of distilled water. Washing was continued with frequent changes of water until the water dripping from the electrodes showed no sign of alkalinity to litmus.

The electrode was then dried in an oven at 75°C for 4 hours. By heating at this temperature the initially partially hydrated $\text{Ni}(\text{OH})_2$ (possibly $\text{Ni}(\text{OH})_2 \cdot 1.5 \text{H}_2\text{O}$ (65)) becomes dehydrated to $\text{Ni}(\text{OH})_2$ as shown by Huttig and Peters (36). From the weight gained by the electrode during impregnation, the amount of $\text{Ni}(\text{OH})_2$ taken up could be evaluated.*

All electrodes used in conjunction with the highly purified solutions discussed previously were given surface

* The treatment employed up to this stage is based closely on that employed in the preparation of commercial battery plates and has been published previously (66,67). The purpose of the cathodic treatment during forming is to diminish diffusion of nickel ions out of the sintered electrode during precipitation of $\text{Ni}(\text{OH})_2$ which is not immediate owing to the finite time required for the KOH to diffuse in. Also, during the polarization, reduction of the nitrate to NH_3 (aq.) occurs and enhances the alkalinity inside the electrode.

cleaning treatment prior to impregnation. This consisted of washing the plaques in hot carbontetrachloride followed by acetone and alcoholic KOH and finally a thorough washing in distilled water. After drying at 75°C , these plaques were stored in a vacuum desiccator until required for impregnation.

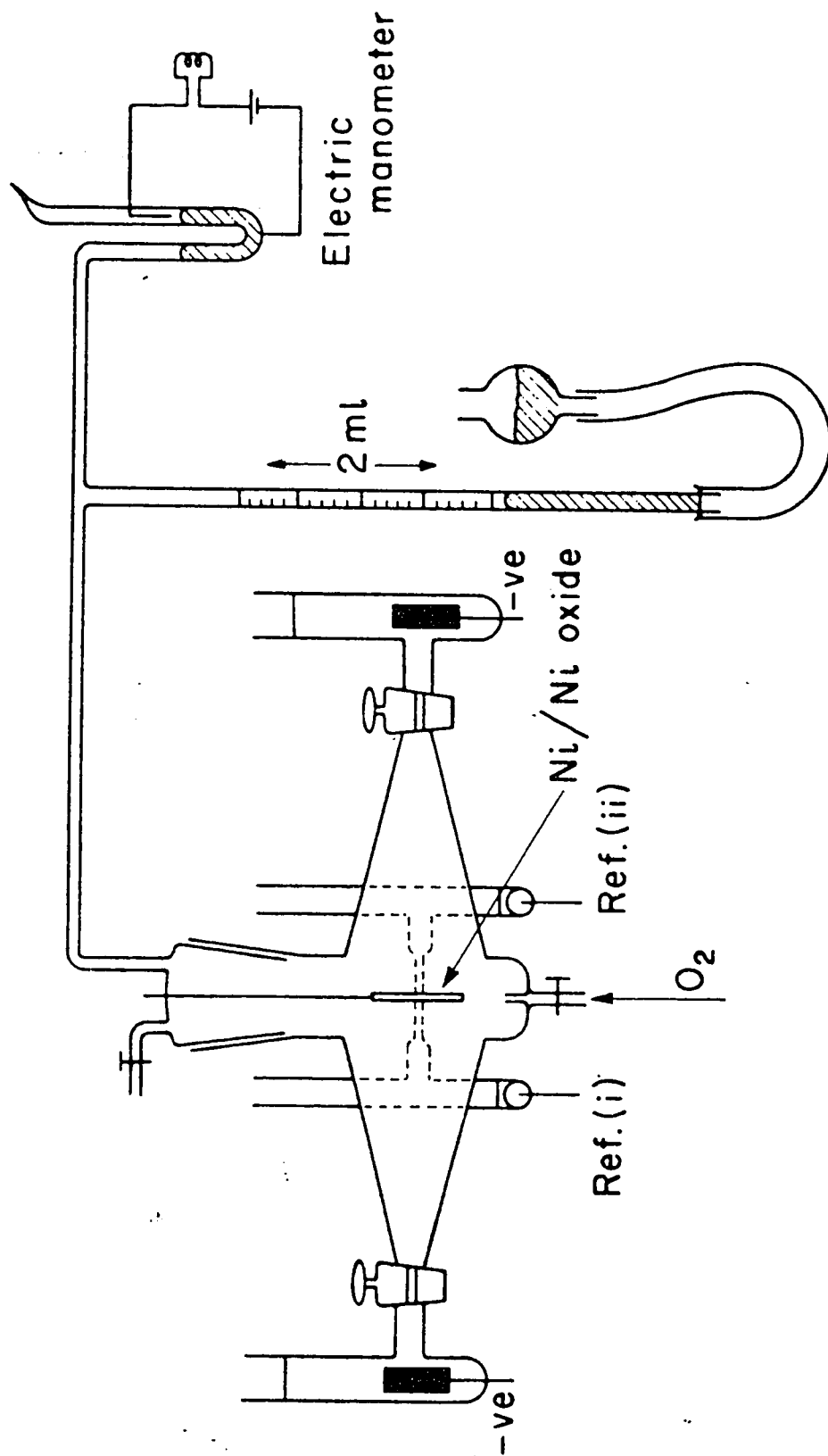
3. OXYGEN PURIFICATION

The oxygen used for stirring the solution was purified by bubbling through a solution of 12 molar KOH using a sintered disc bubbler. The gas was then passed through a drying column of crushed solid KOH, and finally through a trap cooled in a solid CO_2 -acetone mixture. In runs carried out under "standard purification" conditions, the cold trap was omitted. It will be shown in a later section [Chapter III] that no significant difference in the results were obtained when the "high purification" technique was replaced by the "standard" one.

4. CELLS

In order to insure uniform current density at the electrode surface in dilute solution, a cell constructed as illustrated in Figure IV was used for most of the work. The test electrode is situated, as indicated in the figure, at the center of the cell between the two conical portions, each of which communicates to a limb where the counter electrodes are located. Directly under the test electrode was located

Figure IV: Experimental cell used in oxygen
 evolution and e.m.f. decay
 measurements.

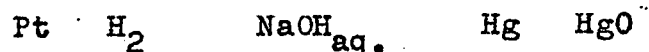


a bubbling tip through which oxygen was supplied both to saturate the solution with the gas and to provide a means of stirring the solution. Two reference electrodes with Luggin capillaries (68) were provided at either side of the cell and their tips were arranged so as to make contact with different parts of the electrode surface. Stopcocks were provided so that the portion of the cell containing the test electrode could be completely closed off during collection of oxygen through the exit tube when the electrode was on open-circuit. In preference to the use of conventional metal wires or plates as counter electrodes, it was considered desirable to use fully charged nickel oxide electrodes of excess capacity (see below) as cathodes. This allowed the test electrode to be polarized anodically for as long as necessary and yet keeping the entire system free of hydrogen, since the cathodic process at the counter electrodes was then only the reduction of Ni III to NiII in the oxide. In experiments involving D_2O , a cell of the same basic design was used except that it had a total volume of approximately 8 ml. as compared with 300 ml. for the oxygen collecting cell described above. In the case of solutions having a concentration greater than 1 M in KOH, it was found that a more conventional two limb cell with reference electrode, Luggin capillary and oxygen bubbler could be satisfactorily used. A number of

experiments in concentrated solutions were carried out in this type of cell.

5. REFERENCE ELECTRODES

All e.m.f. values were measured against a mercury-mercuric oxide electrode in the same solution as the experimental nickel oxide electrode. The reference electrodes were made up from purified redistilled mercury and yellow mercuric oxide (A.C.S. analytical grade). Use of the Hg/HgO system as a reference electrode has been criticised by Knobel (69) who claimed that a variation of e.m.f. with time of up to 6 millivolts can occur over a period of one week. This he attributed to a spontaneous conversion, in alkaline solution, of the red oxide to the more soluble yellow form. However, more recent work by Samuelson and Brown (70) has indicated that with very pure materials, a reproducibility of better than 0.1 millivolt is possible and, moreover, no appreciable time variation is then observed. These latter authors also report that by using standard "chemically pure" materials and red or yellow mercuric oxide obtained from various sources, potentials within ± 1.0 millivolts of those attained with electrodes of more highly purified materials could be measured. These results are in good agreement with the earlier work of Ming Chow^(70,a), who measured the e.m.f. E of the cell.



in solutions of NaOH from 0.3 molal to 0.001 molal, and found that E was constant* at 0.9264 volts over the entire range of concentrations, with a reproducibility of better than 0.1 millivolt.

In the present work it was found that using the red form of mercuric oxide the reproducibility between electrodes was within ± 0.5 millivolt. However, by using the yellow oxide, somewhat better reproducibility could be achieved; the agreement between electrodes was usually within 0.1 millivolt and it was never observed to exceed 0.5 millivolt. The constancy of any one given electrode was found to be within 0.1 millivolt over a period of a week.

The e.m.f. value measured against the hydrogen electrode in 1 molar KOH was found to be $0.9260 \pm .0005$ volts, which is in reasonable agreement with the theoretically calculated value of .9264 reported in the literature. This agreement is entirely adequate for electrode kinetic work where reproducibility of overpotential values rarely exceeds 10 mv., although it must be stated that with the present

* The expected dependence of E on water activity is too small to be of significance in this work since the activity of water in NaOH solutions is insignificantly different from unity in the dilute solutions studied by this worker.

large surface electrodes, overpotentials were often reproducible to better than 5 mv. (see Chapter III, section 1 a).

6. CURRENT SUPPLY AND ELECTRICAL MEASUREMENTS

(a) Constant Current Supply

As a source of current for anodic or cathodic polarization, a bank of storage batteries with a terminal voltage of 60 volts and an electrical "capacity" of about 75 ampere hours, was used in all instances. This insured that the source would give a stable pure d.c. Control of current was achieved entirely by series resistors, thus maintaining a maximum impedance in the circuit and minimizing the effect of any changes of back e.m.f. or of impedance which might occur during measurements or during charging of the electrode in the cell under study. With this arrangement, it was found that the current could be maintained to better than 1% with only an occasional manual adjustment.

(b) Current Measurement

Currents were measured with a "Sensitive Research Instrument Corporation" milliammeter having ranges from 10 microamps to 1 amp for full scale deflection. The guaranteed accuracy of the instrument based on the manufacturers calibrations was 0.5%.

(c) E.M.F. Measurements

Potential measurements were made using the following instruments: (i) A Philips high impedance recording electronic potentiometer especially equipped with ranges of 0-100, 100-200, -----, 500-600 millivolts full scale. The absolute accuracy of this instrument was better than 0.5 millivolt on all ranges. The major portion of the work was carried out using this instrument. (ii) A manual Tinsley potentiometer capable of reading to 0.1 millivolt (in the ranges of potential used in this work). This instrument was used to check the recording potentiometer and in the study of the reproducibility of the reference electrodes. It was itself calibrated by means of a Weston cadmium cell. (iii) A Hewlett-Packard cathode ray oscilloscope equipped with a Polaroid Land camera was used to obtain short period decay curves in studies of e.m.f. decay on open-circuit. (Long period decay curves were obtained on the recording potentiometer). The oscilloscope y-axis was calibrated by means of a standard cell.

7. OXYGEN VOLUME MEASUREMENTS

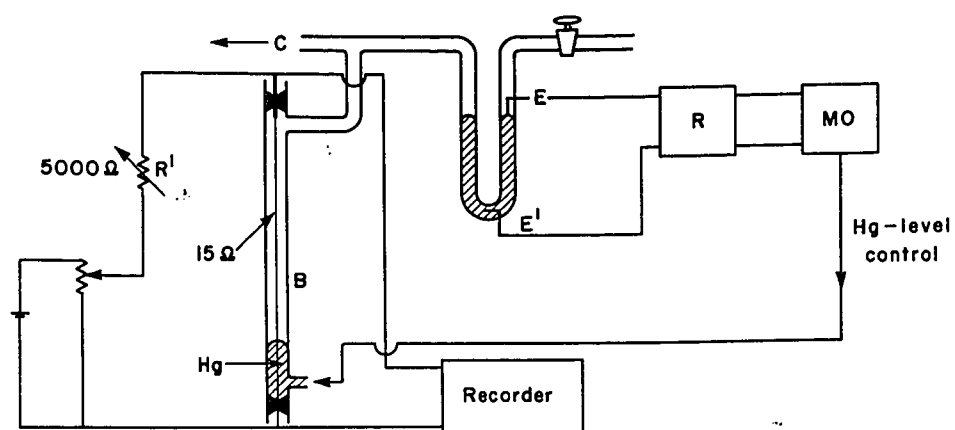
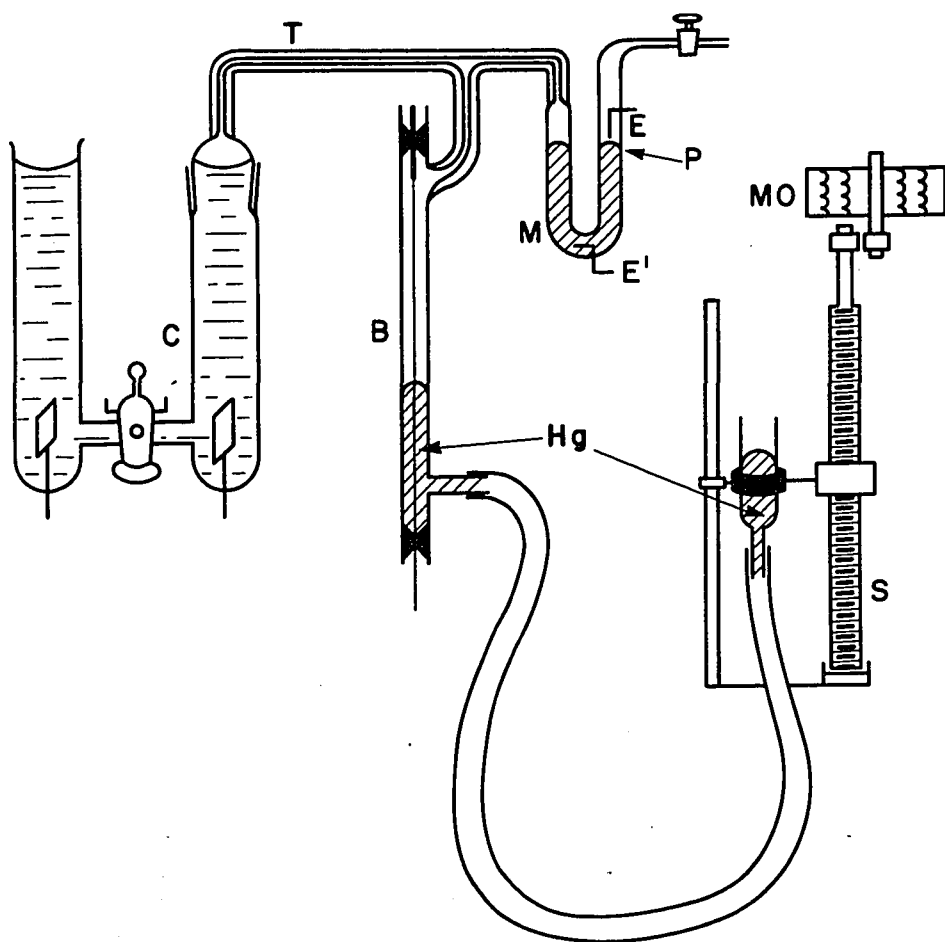
Rates of oxygen evolution on open-circuit were measured using an automatic recording constant pressure gas coulometer developed for this purpose. A detailed description of this instrument is given below.

(a) Design of the Apparatus

The apparatus shown in Figure Va consisted of the electrochemical cell C provided with a capillary exit tube T which was joined by means of further capillary tubing to the measuring burette B and to a manometer M with electrical contacts E and E' which formed part of a feed-back circuit for maintenance of constant pressure. The right-hand side of the manometer M was closed at a known pressure with the mercury just making contact with the platinum probe P. A circuit was made between the probe P and the electrical contact E' through an electronic relay R as shown in Figure Vb. Upon closing the circuit by a rise of the mercury on the right-hand side of M, owing to build up of pressure in the apparatus C, the contact at P was closed and the relay R was activated and supplied current to a powerful small motor M0 which drove a screwed shaft S at a rate of about 1 r.p.m. The pitch of the thread on this shaft was about 0.5 mm. The shaft was provided with an accurately machined nut which carried, between guides, a clamp holding a small reservoir of mercury connected to the lower end of the gas burette B by means of small diameter pressure tubing. So long as there was excess gas pressure in the burette B, the manostatic circuit between the manometer and the motor provided a drive which decreased the height of mercury in B until a constant pressure was restored in B equal to that in the

Figure Va. Apparatus for the automatic measurement
of oxygen volumes.

Figure Vb. Electrical circuit for the apparatus
shown in Figure Va.



closed right-hand limb of M. The gas was therefore collected continuously at a constant pressure in B. The whole apparatus except the motor, shaft, and recorder was maintained in an air thermostat at $25 \pm 0.15^\circ$.

Automatic recording of the volume of gas in B was achieved as follows. A fine platinum wire (0.001 inch in diameter) was stretched longitudinally down the centre of the burette B and sealed at each end to the glass without contact with the glass at any point along its length except at the ends. The upper end was connected to about 0.5 inch of thick platinum wire of negligible resistance which completed the seal through the glass and eliminated end-effects. The fine platinum wire was connected in series with a 12-V battery and a 5000 ohms variable resistance. The fine platinum wire had a resistance of about 15 ohms, i.e. very small compared with the 5000 ohms with which it was in series. An electronic recording potentiometer was connected as shown in Figure Vb in parallel across the fine platinum wire in the burette. This wire then acted as a potential divider giving a potential difference proportional to the amount of wire exposed above the level of the meniscus of mercury in the burette. When the meniscus was moved automatically by the manostatic feed-back circuit as more gas was collected at constant pressure, the output potential difference across the wire gave a trace on the recorder.

Calibration of the burette and adjustment of the current in the circuit by the variable resistance R' then enabled the full-scale displacement (20 mV.) on the recorder to be made to correspond to the volume of the burette between the meniscus of mercury at its lowest level and the upper thick platinum contact.

(b) Sensitivity and Accuracy

The sensitivity of the instrument depended upon (i) the diameter of the burette i.e. upon the ratio $\Delta l/\Delta V$ where Δl was the length of wire in the burette corresponding to a volume ΔV ; (ii) the applied voltage v or the current passing in the circuit from the battery; (iii) the channel sensitivity on the recorder, i.e., the p.d. required to cause full-scale deflection of the pen; and (iv) the dead space in the apparatus. Magnification of any range of volumes to be measured in the burette could be readily achieved by increase of the voltage v or of the channel sensitivity. In the apparatus actually constructed, 2 ml. was the maximum volume measurable in the burette at full-scale on the recorder and changes in volume of 0.01 ml. could be detected and recorded. Burettes larger than 2 ml. could obviously be used in other applications. The dead space varied from about 4 to 6 ml. depending on the volume of gas collected.

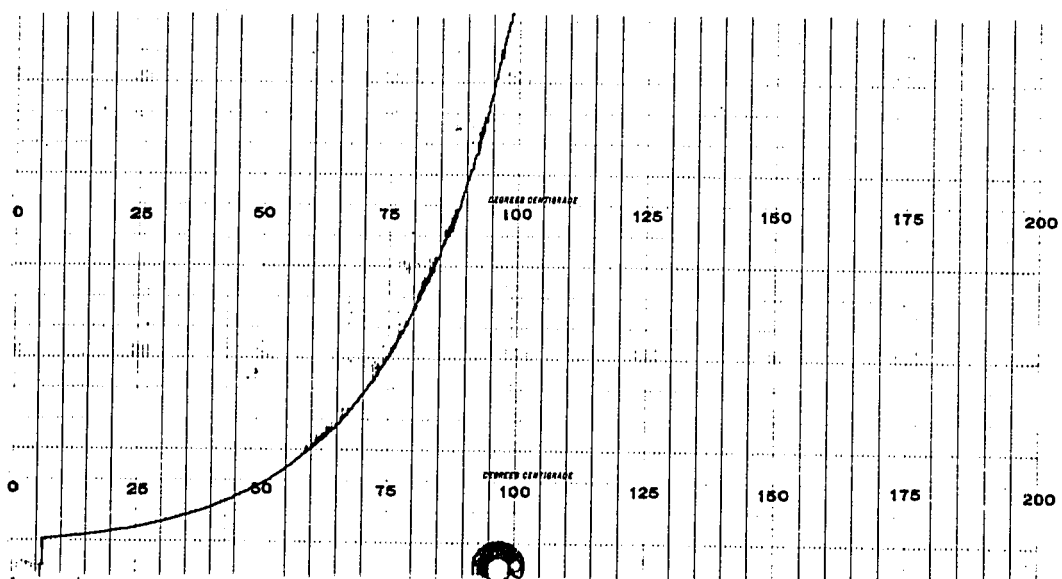
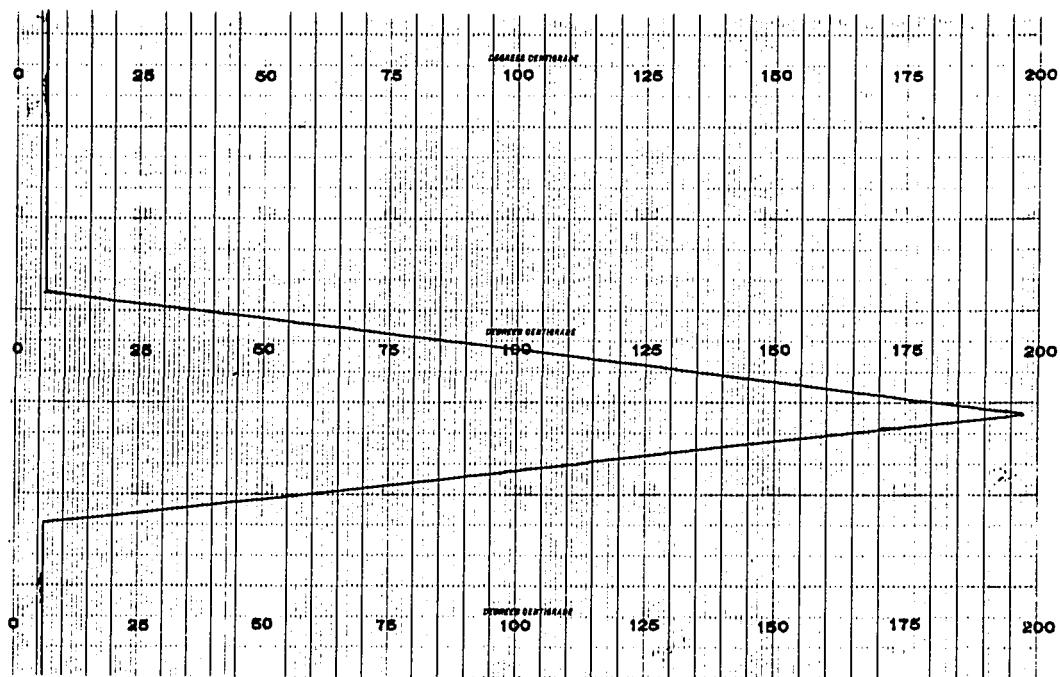
The accuracy of the instrument depended mainly on the closeness with which the pressure could be followed by the manostat and motor drive. The feed-back differential in the apparatus constructed was equivalent to about 0.005 to 0.01 ml. but could be decreased by use of a more sensitive magnifying manometer, for example, of the inclined type (71)

(c) Results

Some typical records of volume measurements and of the recorder response are shown in Figure VIa and VIb. Figure VIa, which is a reproduction of a recorder tracing, shows that very satisfactory linearity of response is achieved when there is a continuous linear increase in volume with time. This test was made by running the drive motor disconnected from the manostat so that the mercury in B fell at a constant rate. Figure VIb shows the response during an actual kinetic run in which oxygen was being evolved during self-discharge of a nickel-nickel oxide electrode on open-circuit (64). The halts in the response correspond to changes of volume somewhat less than 0.01 ml. The instrument could therefore record changes as low as 0.01 ml. of oxygen. Pre-saturation of the solution with the gas whose volume is being measured is of course necessary for the most accurate results and was carried out in the present work. However, if the electrolyte is concentrated (> 1 or 2 N) solubility of evolved gases is small owing to salting-out.

Figure VIa. Recorder trace showing linearity of response in the case of a uniform rate of change of volume of gas in the burette. Upper line: increasing volume with time. Lower line: decreasing volume with time.

Figure VIb. Recorder trace of oxygen evolution during self-discharge of a nickel oxide electrode.

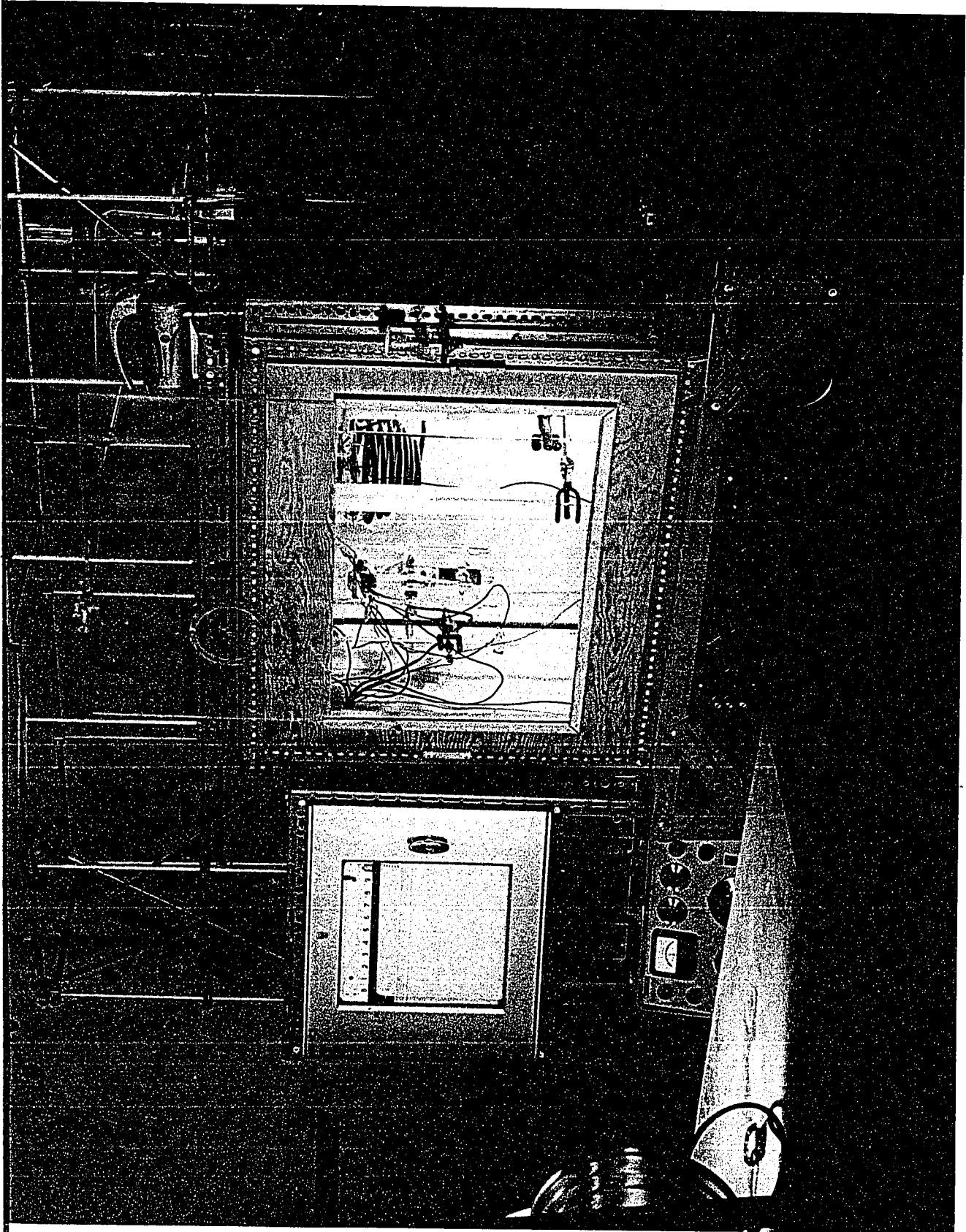


8. TEMPERATURE CONTROL

The apparatus for measurement of volumes of oxygen evolved was entirely contained in a large air thermostat illustrated in Figure VII. Temperature control was achieved using a mercury type thermoregulator connected to an electronic relay, which in turn controlled a hundred watt light bulb inside the air bath.

For runs done at high temperatures, (e.g. 60°C) some additional heating was supplied continuously by means of a large heating element made of nichrome wire. This element was loosely wound over insulated rods so as to cover the two end walls as well as the floor of the box, thus uniformly supplying heat over all regions of the box. Because of the large area for the heat exchange, a temperature of 60°C . could be easily maintained although the temperature of the element itself did not exceed 100°C . Circulation of the air was achieved using a five inch fan operating continuously.

In addition, a coil of copper tubing, through which cold water could be circulated, was located directly in front of the fan thus providing a means of cooling if necessary. With this arrangement a constancy of temperature of 0.1°C could be readily achieved at any given point in box with a maximum temperature variation with both time and location in the box of not more than 0.2°C .



In all experiments conducted at temperatures of 25°C or higher, the experimental cell shown in Figure VIII, was housed in this air thermostat and connected to the oxygen measuring device described above. For experiments carried out at temperatures lower than room temperature, the experimental cell was immersed in a thermostatted, refrigerated liquid bath. For oxygen evolution measurements at the lower temperatures, the evolved oxygen was conducted from the cell in the refrigerated bath to the measuring device in the air thermostat by means of a piece of fine capillary tubing about eight inches in length. The temperature of the refrigerated bath was maintained constant to better than 0.1°C.

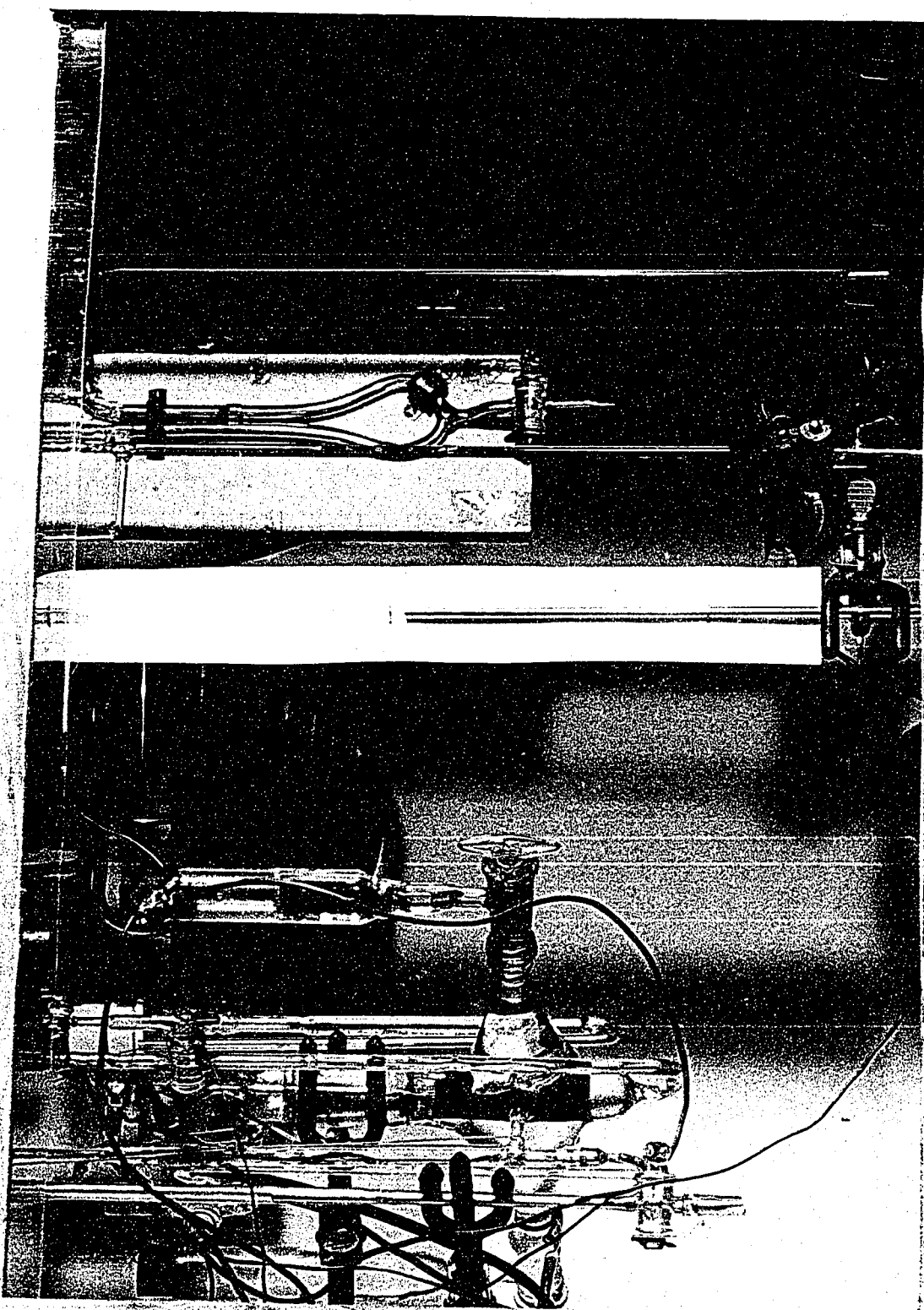
9. EXPERIMENTAL PROCEDURES

(a) Fully Charged Electrodes

(i) Polarization Decay and Oxygen Evolution Measurements

In this part of the work, the purpose was to study the rate of decay of e.m.f. and the corresponding rate of oxygen evolution on "fully" oxidized* nickel oxide electrodes following cessation of charging, i.e. anodic polarization. Measurements of rates of e.m.f. decay and oxygen evolution were made as a

* The degrees of oxidation achieved in the "fully" oxidized" electrodes referred to here are discussed in Chapter III and given in Table I.



function of alkali concentration and temperature.

A fully impregnated, dry electrode containing approximately one gram of $\text{Ni}(\text{OH})_2$ was placed in the anode compartment of the test cell. The two reference electrodes were freshly prepared and a potassium hydroxide solution of the appropriate concentration was added. In the two cathode compartments were placed two fully oxidized nickel oxide electrodes, each having about three times the electrochemical "capacity" of the test electrode. These counter electrodes had been charged previously in a separate vessel containing a potassium hydroxide solution of the same concentration and purity as that used in the experiment under consideration. The cell was then placed in the thermostatted bath and allowed to stand with oxygen bubbling continuously for 6 to 12 hours. Sufficient time was thus allowed for the solution to become saturated with oxygen, for the equilibrium to be attained and for the potentials of the reference electrodes to become stabilized.

The electrode was then charged for 30 hours at a rate sufficient to provide four times the quantity Q of electricity required to oxidize fully the $\text{Ni}(\text{OH})_2$ present; the quantity Q is calculated on the basis that the electrochemical reaction involves oxidation of the nickel in the hydroxide from the di- to the trivalent states; it is also assumed that the weight gain during impregnation corresponds to addition of stoichiometric

$\text{Ni}(\text{OH})_2$. The quantity of electricity $4Q$ corresponds to a current density of 38.5 milliamps per gram* of $\text{Ni}(\text{OH})_2$ passed for 30 hours. At the end of the 30 hour period, charging was discontinued and the anode compartment of the cell was completely sealed off except to the oxygen collecting apparatus by closing and opening appropriate stopcocks. Simultaneous measurements of volume of oxygen evolved and e.m.f. were then made automatically by means of the two separate recording electronic potentiometers. The first e.m.f. decay readings could be recorded after about 2 seconds following the cessation of charging; the oxygen volumes, however, were not obtainable at times shorter than about 30 seconds. This was due to the finite time required for manual closing of stopcocks and for initial establishment of pressure equilibrium in the oxygen measuring apparatus.

This decay of e.m.f. with simultaneous oxygen evolution was followed for about three days after which the

* Here and elsewhere the current density is expressed as current per "gram" of electrochemically active material as discussed in previous publications (55,64). The necessity of using these units arises from the uncertain real area of the surface of the wet hydrous nickel oxide in the sintered electrodes. B.E.T. area determinations made on the dried material showed a real surface area of about 40 meters² per gram of $\text{Ni}(\text{OH})_2$ [see Chapter III section 3b]. It is of course quite probable that the surface area changes somewhat during drying.

electrode was discharged at constant rate to zero volts with respect to the Hg/HgO reference electrode. The discharge rate was chosen such that the theoretical capacity (based on a state of oxidation " $\text{NiO}_{1.5}$ ") would be discharged in five hours. This rate will henceforth be referred to as a "five hour rate", a term familiar in battery technology.

(ii) Steady State Current-Potential Behaviour of Fully Charged Electrodes

In this part of the work, smaller electrodes containing approximately 0.05 gram of $\text{Ni}(\text{OH})_2$ were used. These were given three charging and discharging cycles at 25°C before being used for the polarization measurements. The first charging cycle was for 30 hours at a current of 38.5 mA. per gram of $\text{Ni}(\text{OH})_2$. After allowing the electrode to stand for about 24 hours, it was discharged at a "five hour rate" to zero potential with respect to the Hg/HgO reference electrode. The two subsequent cycles were carried out at the same "five hour rate" on both charge and discharge, using a charging time of 10 hours (i.e. with a five hour overcharge period) and discharging finally to zero volts. [This preliminary conditioning of the electrodes was found to improve the reproducibility of the current-potential behaviour (Tafel lines)]. These electrodes were then transferred to the experimental cell containing freshly prepared reference electrodes and KOH solution. They

were then polarized anodically, first at 38.5 mA./g. (to charge or oxidize the previously discharged electrode) for 30 hours, then at various higher and lower current densities; at each current sufficient time was allowed for the e.m.f. to reach a steady value.

The criterion of what constituted a "steady value" was dependent upon the current density involved. At high current densities (e.g. 300 mA. g.⁻¹) the e.m.f. was considered constant when it changed at a rate not greater than 10⁻² mV. per sec. However at current densities of 3 mA. g.⁻¹ a rate of change of e.m.f. of 10⁻⁴ millivolts per second can be quite significant. This arises from the following considerations: The total current, i_T , passing into the electrode may be considered as consisting of two distinguishable components. In going from a lower to a higher e.m.f. value, (i.e. increasing the current density) a portion of the current, i_{O_2} , will be consumed by oxygen evolution, and the remaining current, i_c , will go to charge the surface capacity (see Chapter III section 3) associated with the electrode.

Thus we may write

$$i_T = i_{O_2} + i_c$$

or

$$i_T = i_{O_2} + C \frac{dV}{dt}$$

The relevant quantity in an e.m.f. - log current density study is i_{O_2} ; what is measured experimentally is, of course, i_T . The experimentally measured current density i_T will be equal to i_{O_2} when the quantity $C \frac{dV}{dt}$ is negligible in comparison with i_{O_2} . From these considerations it can be readily appreciated that at low ^{current} densities (i.e. at small i_T) one must wait for a much greater constancy of e.m.f. with time (i.e. a low value of $\frac{dV}{dt}$) than would be the case at higher current densities.

At the highest current densities used, the value of $C \frac{dV}{dt}$ became negligible in comparison to i_T in a few minutes. At the lowest current densities, however, several days were required for the value of $C \frac{dV}{dt}$ to become less than 1% of i_T . In order to overcome this difficulty, the value of $C \frac{dV}{dt}$ was evaluated at various times and when it reached a value less than 10% of i_T this correction was applied ^{to} i_T thus giving the relevant quantity i_{O_2} . **

Several e.m.f. decay and oxygen evolution measurements were made for comparison on electrodes having the same

* The capacitance C of these electrodes is very large, (of the order of a few hundred farads) so that the potential must be quite constant in order for the quantity $C \frac{dV}{dt}$ to be negligible. Methods of evaluating C will be discussed in a later section.

** Allowing for a possible error of 10% in the evaluation of $C \frac{dV}{dt}$, the error introduced in the estimation of the value of i_{O_2} , when $i_c = i_T/10$, was 1%.

preliminary conditioning as those used for the above current-potential measurements.

(b) Polarization Decay at Partially Charged Electrodes

Here the decay of e.m.f. from anodic and cathodic polarization was studied on nickel oxide electrodes having a controlled formal state of oxidation corresponding to $\text{NiO}_{1.25}$ i.e. at a state of oxidation half way between Ni II and Ni III.

The electrodes were initially charged in solutions of KOH of various concentrations, at a rate 38.5 mA. per gram of Ni(OH)_2 for thirty hours at 25°C . The electrodes were then left to stand on open-circuit to allow the surface pseudo-capacity (see Chapter III section 3) to become discharged or reach a steady state of charge. The remaining bulk electrochemical capacity was then determined by discharging with constant current at the "five hour rate". The observed charge held by the electrodes agreed with that expected theoretically to within 10% (this deviation is not unexpected, since the higher oxide of nickel is known to be non-stoichiometric (40,49) and seldom corresponds exactly to the formal state of oxidation $\text{NiO}_{1.5}$). On the basis of this determination, a charging rate, i_c , was chosen such that the electrode would be oxidized to 50% Ni II - Ni III (i.e. $\text{NiO}_{1.25}$) in one hour. The charging was interrupted and the decay of potential was followed on open-circuit for 24 hours or more on a recording

potentiometer. The charging was resumed at the rate i_c for two hours; after decay on open-circuit for several hours (to again discharge the surface capacity associated with oxygen evolution), discharging was commenced at the rate $-i_c$ for one hour so that the electrode regained a state of oxidation of " $\text{NiO}_{1.25}$ ". The discharging current was interrupted and the potential decay from the cathodic polarization was followed for 24 hours, after which the remaining bulk electrochemical "capacity" was checked by complete discharge with the same current, $-i_c$.

This sequence of operations and the corresponding e.m.f.'s are shown schematically for a typical experiment (in 7.3 M KOH) in Figure IX.

(c) Quasi-Equilibrium Potentials

In this series of measurements, electrodes were allowed to stand on open-circuit in 0.001 M aqueous KOH until the degree of charge corresponded to an approximate state of oxidation of " $\text{NiO}_{1.25}$ ". The electrodes were then transferred to other potassium hydroxide solutions by the following three alternative procedures:

(a) Six electrodes were transferred directly into solutions 14.6, 11.0, 7.3, 3.7, 1.46, and 0.146 M in KOH, respectively, which were stirred by bubbling purified oxygen. The e.m.f. of the electrodes was followed as a function of time

(versus a Hg/HgO electrode) for one week.

(b) Six electrodes were transferred from the 0.001 M KOH to a solution of 14.6 M KOH where they were allowed to stand for about 24 hours; they were then transferred to solutions of 0.07, 0.146, 0.73, 1.46, 7.3, and 11 M KOH respectively and again the e.m.f. was recorded at regular intervals of time.

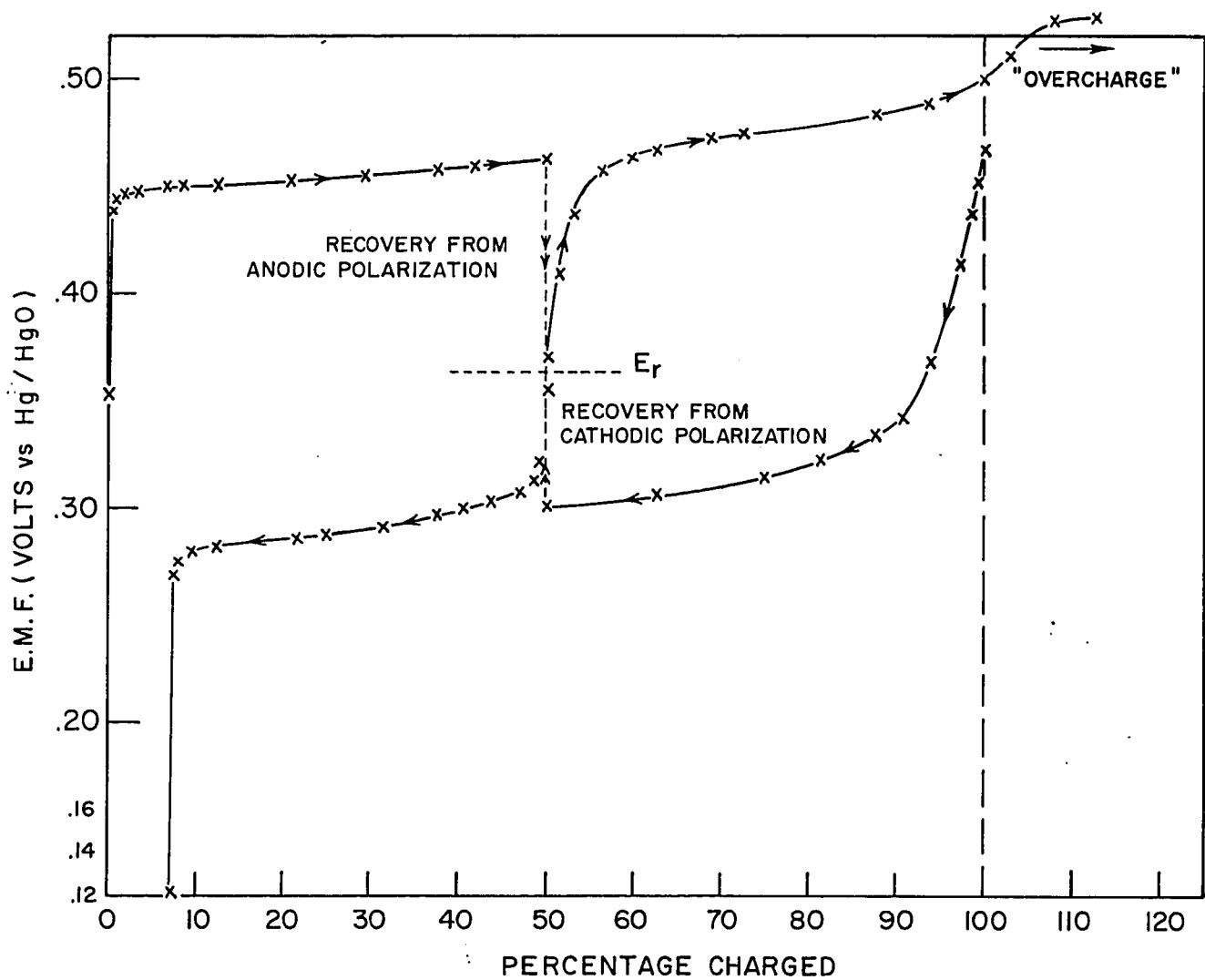
(c) (i) An electrode was taken from the 0.001 M KOH solution and then allowed successively to equilibrate in 0.07, 0.7, 3.65, 7.3, 11.0, and 14.6 M KOH solutions for periods of two hours during which the e.m.f. became constant to better than 0.5 mv per hour. A reverse series of measurements was then made by transferring the electrodes back from the concentrated to the more dilute solutions.

(ii) A similar series of e.m.f. values were obtained by transferring the electrode from the 0.001 M KOH directly to the strongest (14.6 M) solution and thence successively to the more dilute solutions and back again to the more concentrated ones.

From these measurements, the reversibility of the e.m.f. changes with changes of concentration could be judged.

The degree of oxidation of the electrodes was measured after the e.m.f. runs by discharging the electrodes at a controlled current.

Figure IX. Charging and discharging cycle used in
polarization decay studies of partially
charged nickel oxide electrodes.



CHAPTER III

RESULTS

1. BEHAVIOR OF FULLY OXIDIZED ELECTRODES

a) Open-circuit Behavior

(i) General

In order to study the mechanism and to determine the kinetics of the processes involved in the self-discharge of the initially fully oxidized nickel oxide electrode on open-circuit, the e.m.f. (vs. the Hg/HgO electrode) and the volume of oxygen evolved were simultaneously observed as a function of time after cessation of anodic polarization. Measurements were made at concentrations of KOH ranging from 0.01 to 15.4 molar and at temperatures of -25° , 1.0, 25 and 60.5° C. The experimental procedure used has been described in Chapter II.

(ii) Decay of E.M.F. with Time

The expected behavior of the e.m.f. with time after cessation of anodic polarization has been discussed previously in the Introduction section (l.c). Thus a plot of e.m.f. vs. $\log (\text{time} + \theta)$ (where θ is the semiempirical constant discussed previously) will normally result in a straight line for a given electrochemical mechanism of discharge of the double-layer or surface capacity. The slope of this line will

be identical in magnitude but opposite in sign to that of the Tafel slope for the rate-determining mechanism involved in the discharge of the double-layer or surface capacity, provided that this capacity is constant in the range of potentials over which the polarization decay occurs.

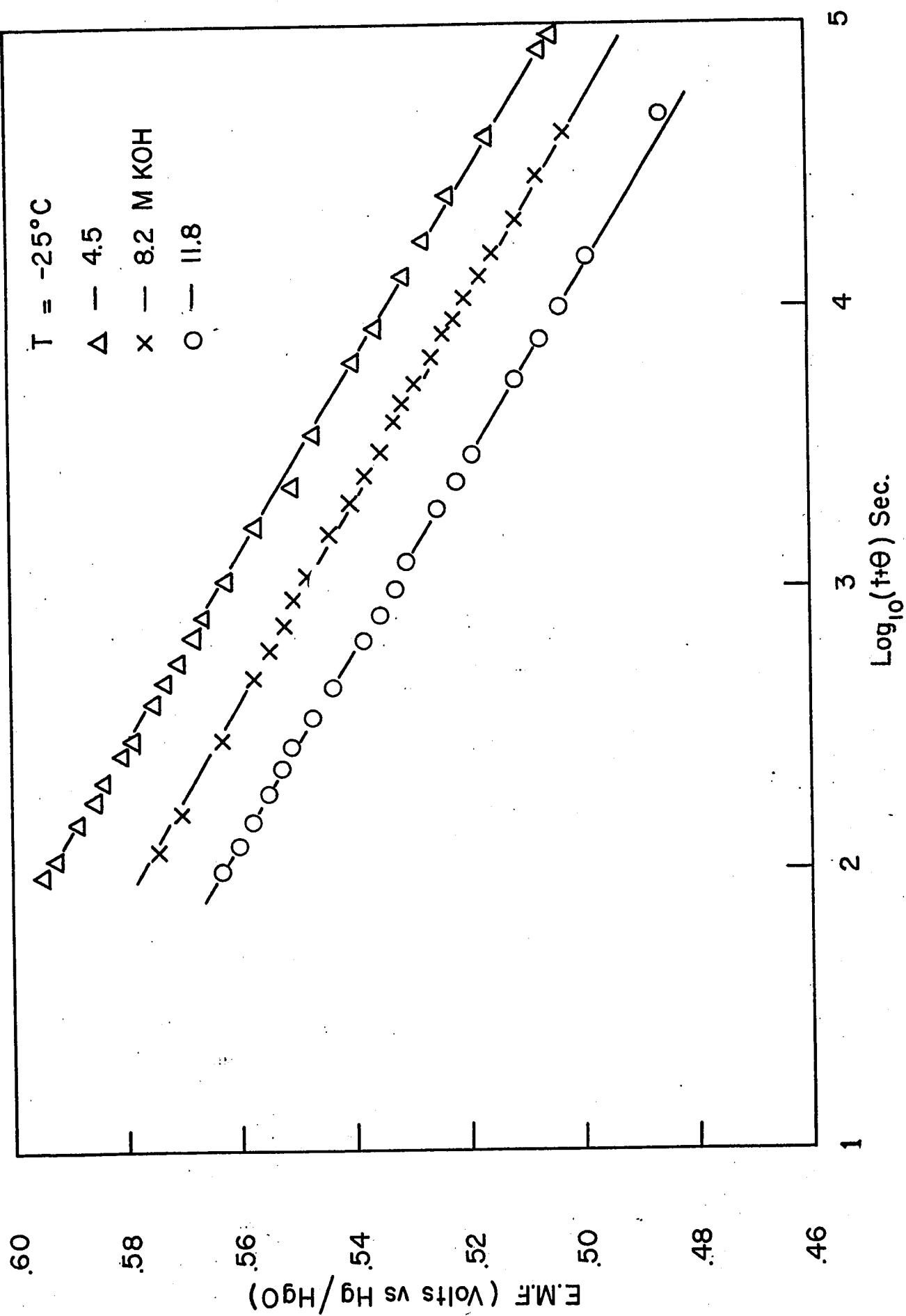
Results of such plots of e.m.f. vs. $\log (t + \theta)$ are shown in Figures X, XI, XII and XIII. It will be noted that a single straight line is observed for all concentrations of KOH at -25° C as well as in the more concentrated solutions at 1.0° and 25° C. However, in the more dilute solutions at 1.0° and 25° C, as well as at 60.5° C, a change of slope occurs in the semi-logarithmic e.m.f. decay lines, which then exhibit two distinct linear regions as shown in Figures XIIa and XIIIa. The position at which this change occurs depends markedly upon the KOH concentration, appearing at higher potentials and at shorter times for the more dilute solutions.

At 60.5° C the decay lines do not display the expected ideal Tafel behavior (viz. constant slope equal and opposite to that of the Tafel polarization equation) but show some curvature particularly in the more concentrated solutions (Figures XIIIb).

(iii) Oxygen Evolution on Open-circuit

From the experimentally determined volumes of gas liberated as a function of time on open-circuit, the true

Figure X - Decay of e.m.f. on open-circuit at
-25° C in 4.5, 8.2 and 11.8 molar
KOH solution.

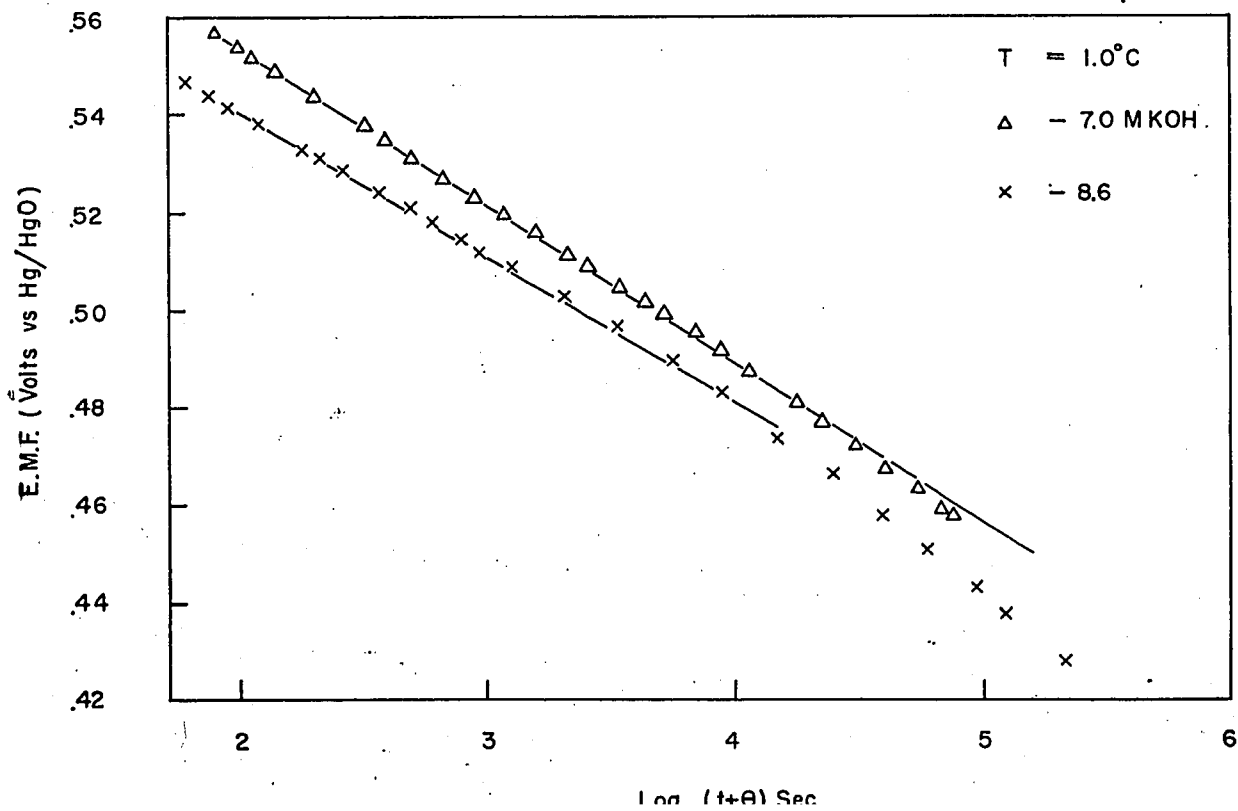
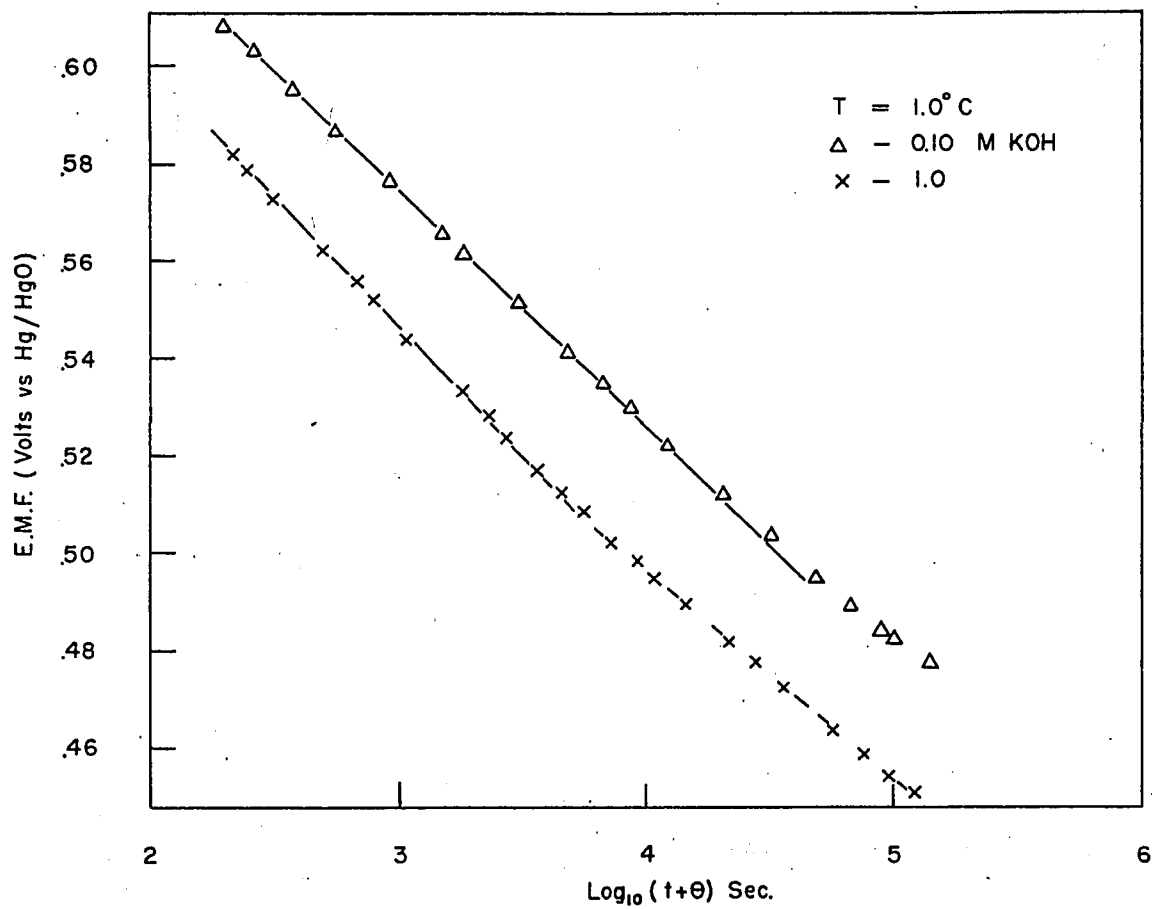


Figures XIa,

XIb, - Decay of e.m.f. on open-circuit at
1.0° C.

(a) 0.10 and 1.0 molar KOH

(b) 7.0 and 8.6 molar KOH.



Figures XII a,

XII b, - Decay of e.m.f. on open-circuit
at 25° C.

(a) 0.015, 0.15 and 2.9 molar KOH

(b) 7.1, 9.4 and 14.6 molar KOH.

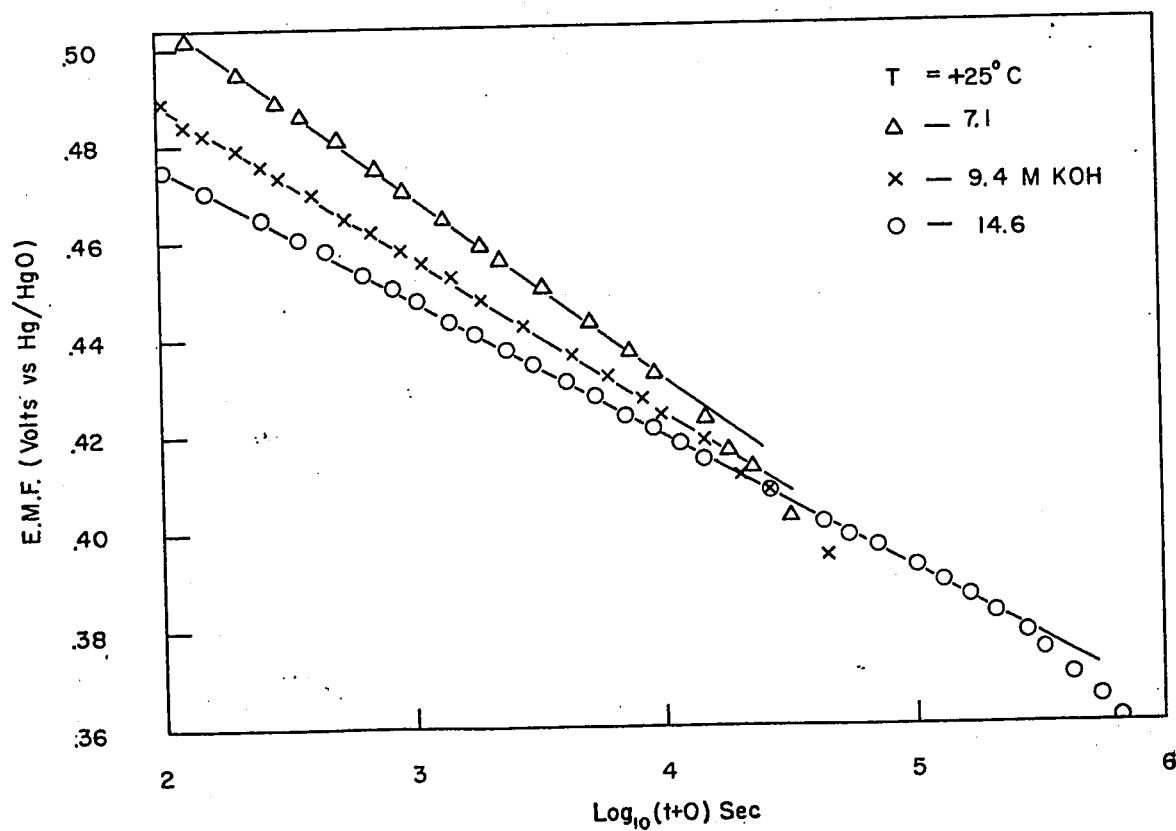
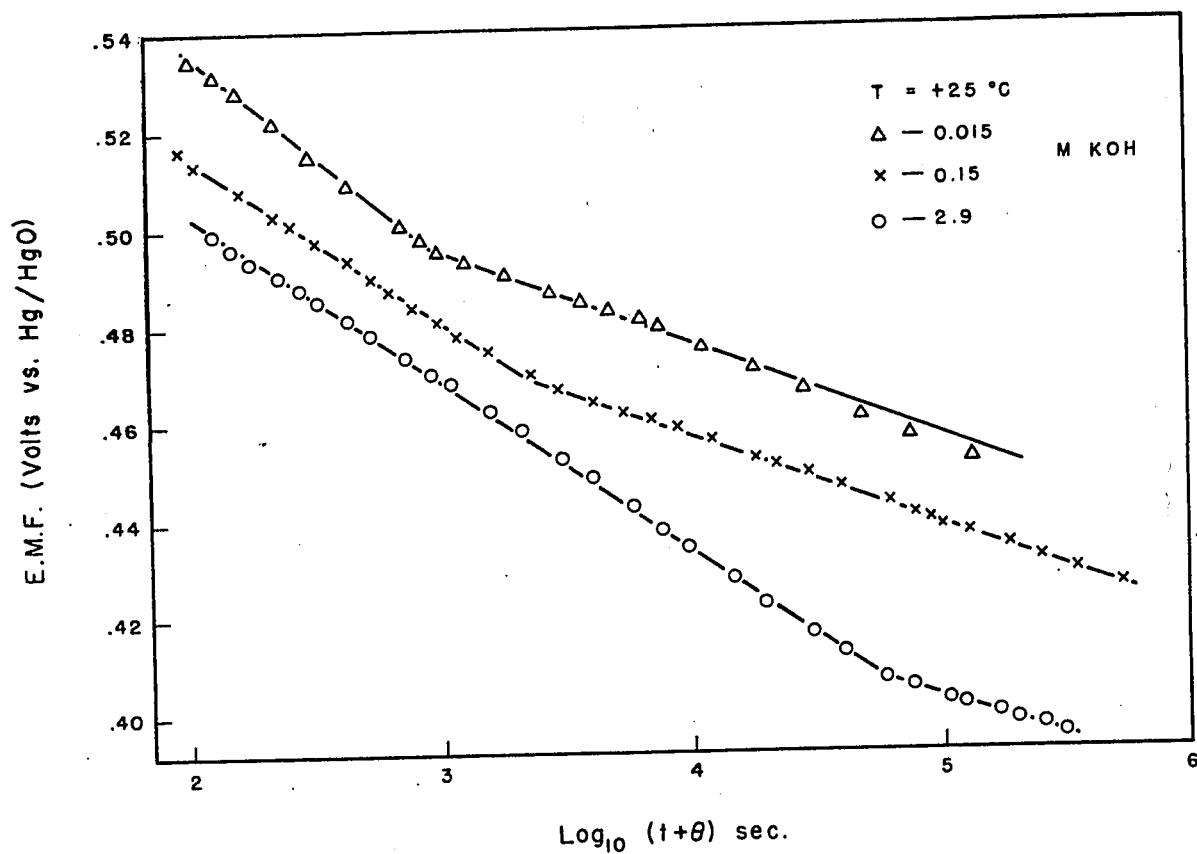
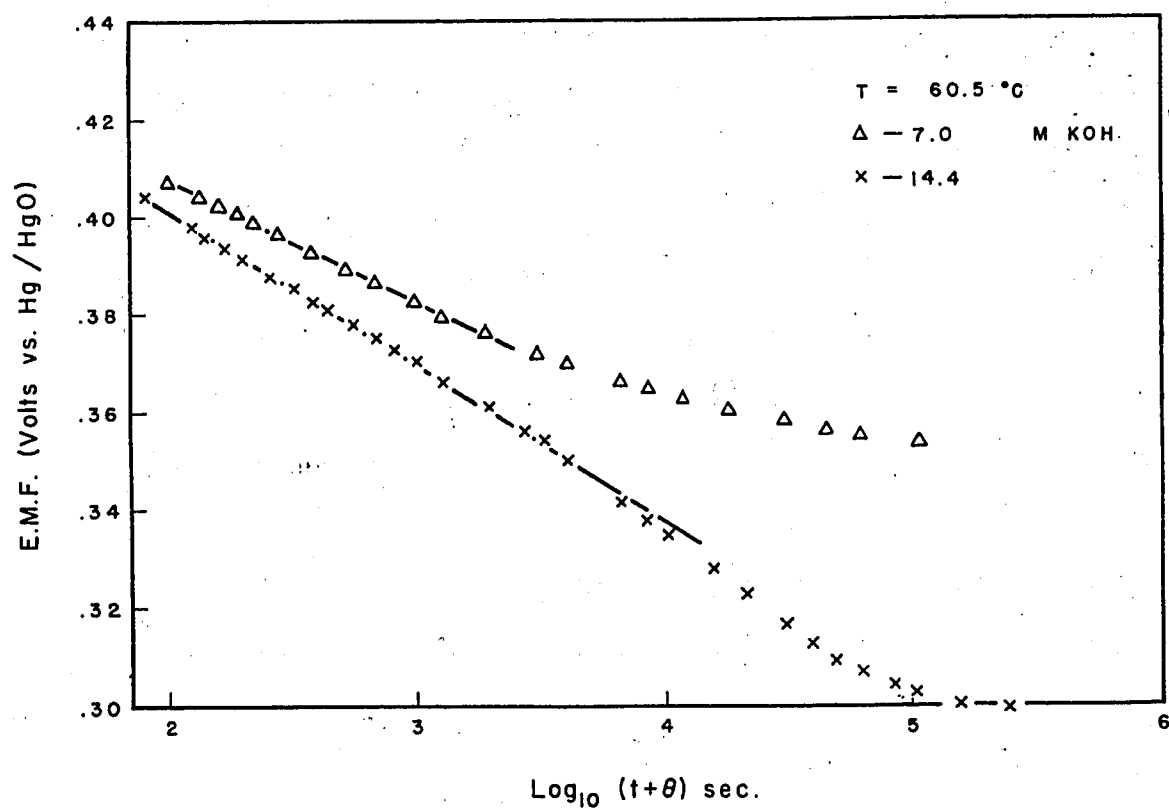
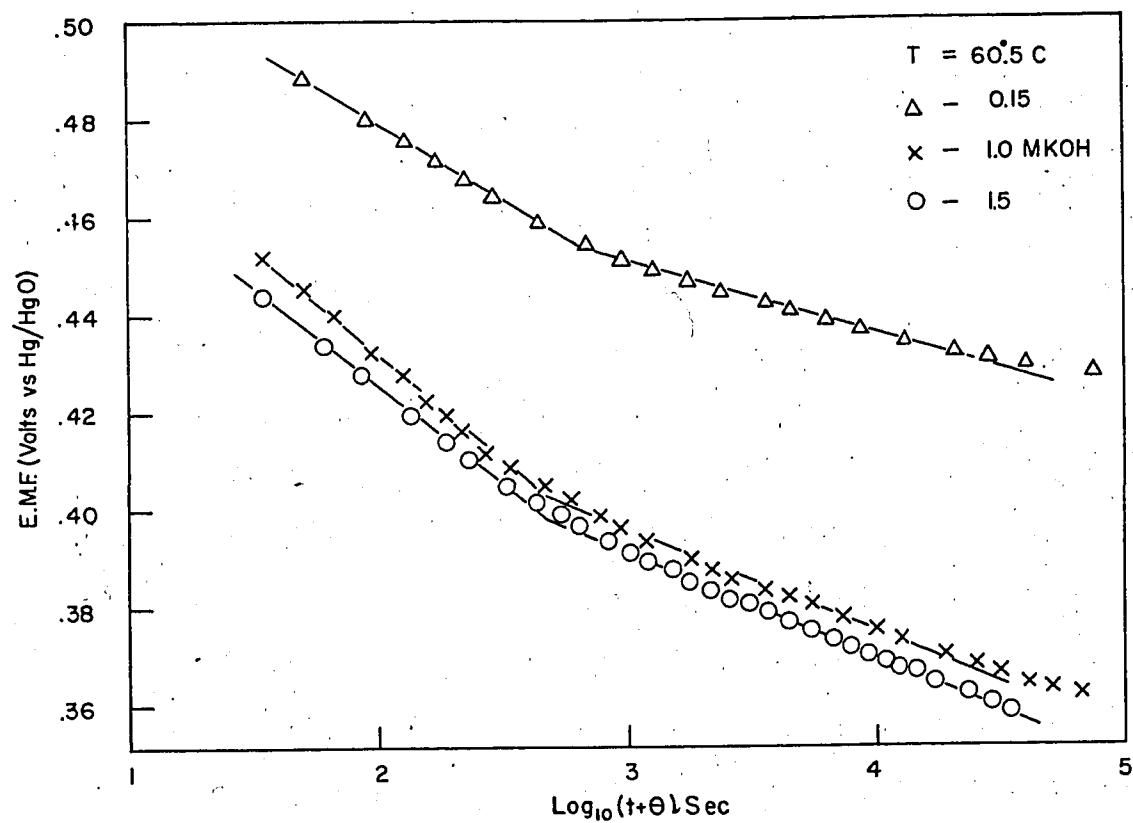


Figure XIII a,

XIII b, - Decay of e.m.f. on open-circuit
at 60.5° C.

(a) 0.15, 1.0 and 1.5 molar KOH

(b) 7.0 and 14.4 molar KOH.



volume of evolved dry oxygen at N.T.P. was calculated at various times. The vapor pressure of water over the solution at various concentrations of KOH at the various temperatures was calculated from the data of Akerlöf and Bender (72). A plot of these corrected volumes vs time was then made for each electrode, and rates of oxygen evolution were then calculated from tangents drawn to the volume-time curves at various times.

These values of rate of oxygen evolution expressed in ml. sec^{-1} , could then be converted to rates of self-discharge expressed in terms of amperes by multiplying by the factor zF/V_M where z is the number (four) of Faradays F required to liberate the gram molecular volume V_M of oxygen gas, where V_M is expressed in ml.

The e.m.f. values corresponding to these rates could be obtained readily from the e.m.f. - time measurements which were taken simultaneously as described above. In Figures XIV, XV, XVI and XVII are shown the logarithm of these rates of oxygen evolution, expressed in terms of amperes per gram of nickel hydroxide (see page 74), plotted against the corresponding e.m.f. These results were obtained simultaneously and on the same electrodes as those of e.m.f. decay shown in Figures X, XI, XII and XIII.

It will be noted that single straight logarithmic rate lines are observed wherever the e.m.f. - $\log$ [time] lines

Figure XIV - Rates of evolution of oxygen on open-circuit as a function of e.m.f. at -25°C in 4.5, 8.2 and 11.8 molar KOH solutions.

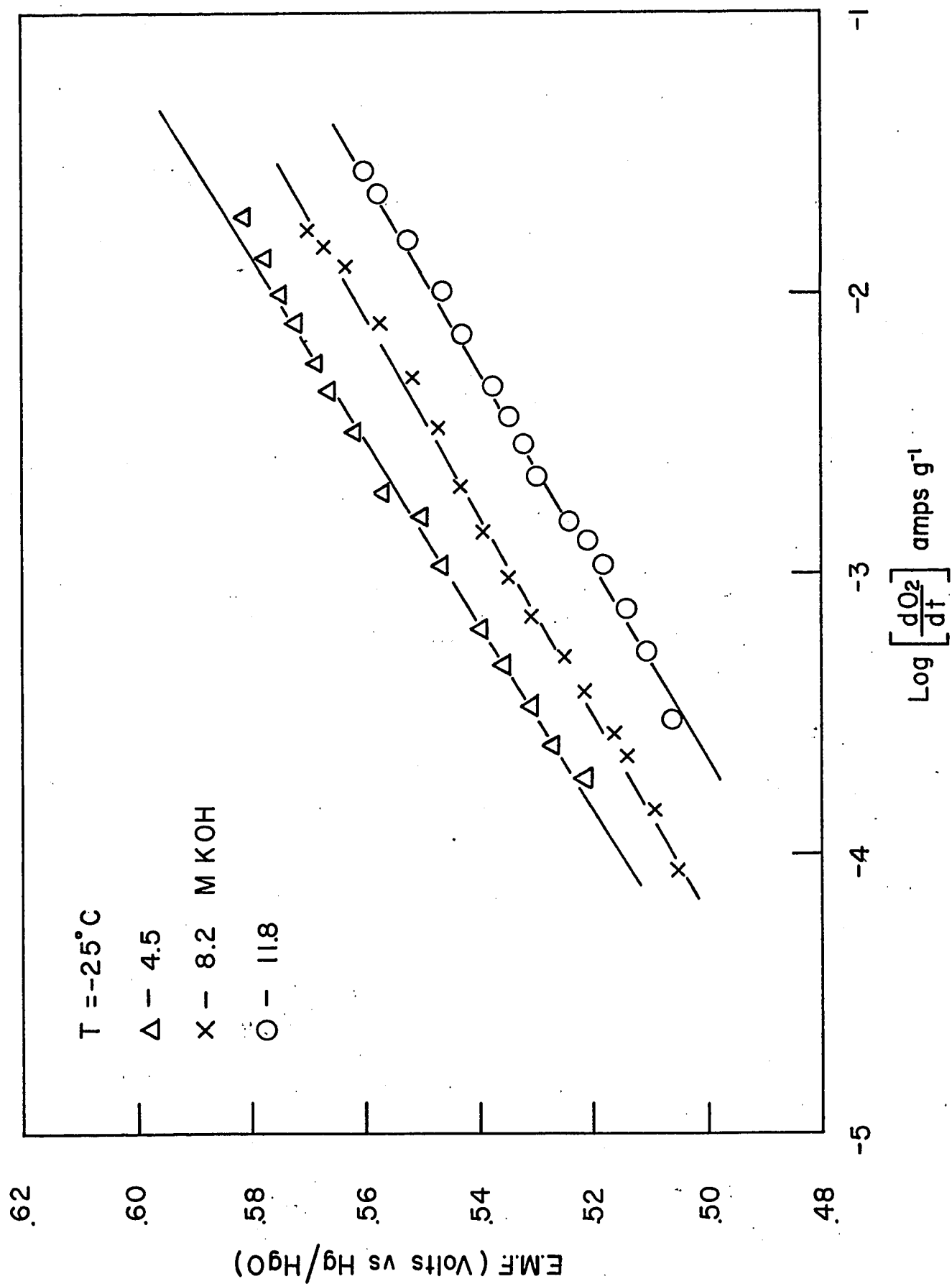


Figure XV a,

XV b, - Rates of evolution of oxygen on
open-circuit as a function of
e.m.f. at 1.0° C.

(a) 0.10 and 1.0 molar KOH

(b) 7.0 and 8.6 molar KOH.

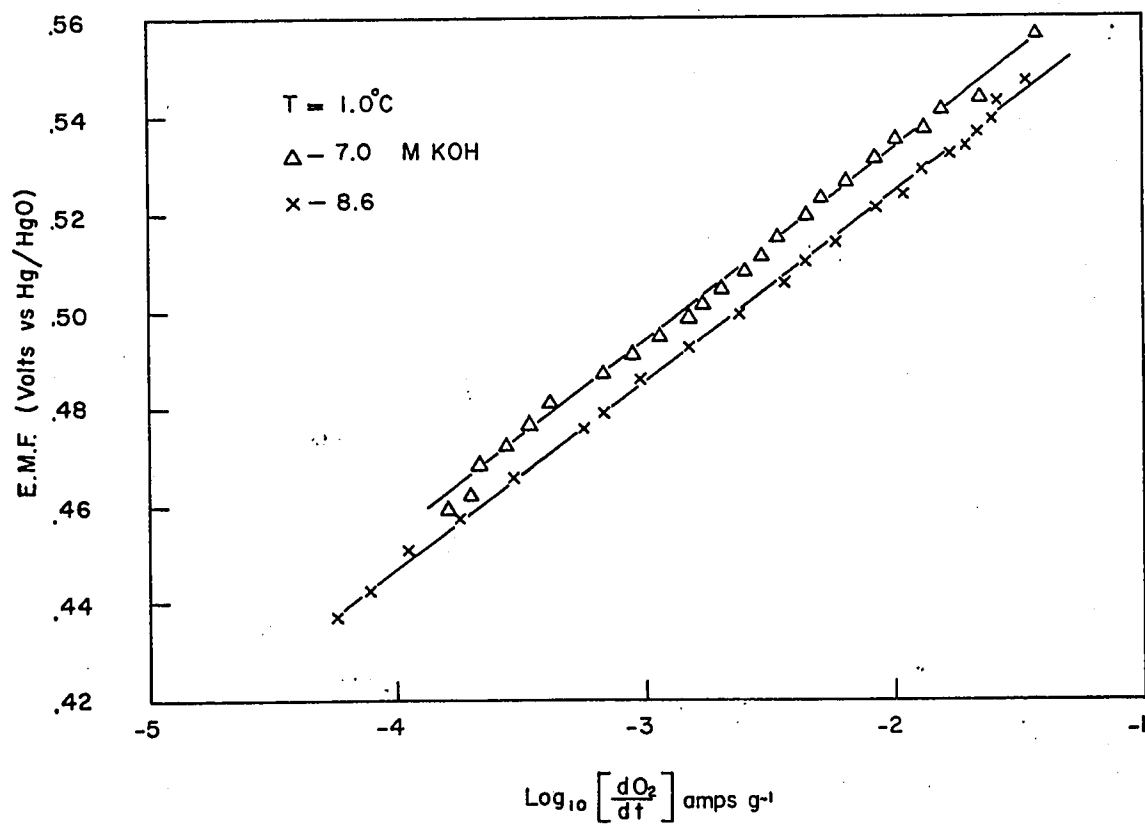
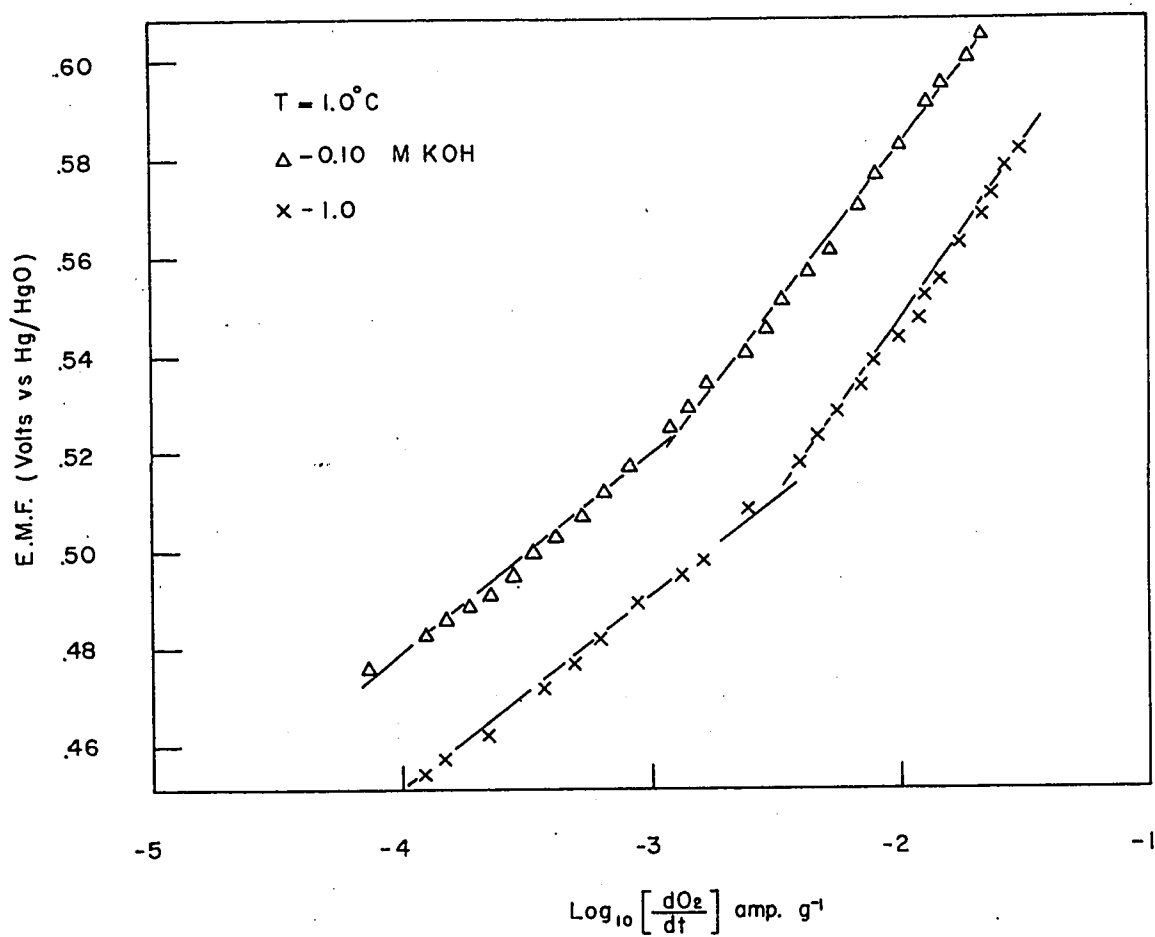


Figure XVI a - Rates of evolution of oxygen on open-circuit as a function of e.m.f. at 25° C in 0.015, 0.15 and 2.9 molar KOH solutions.

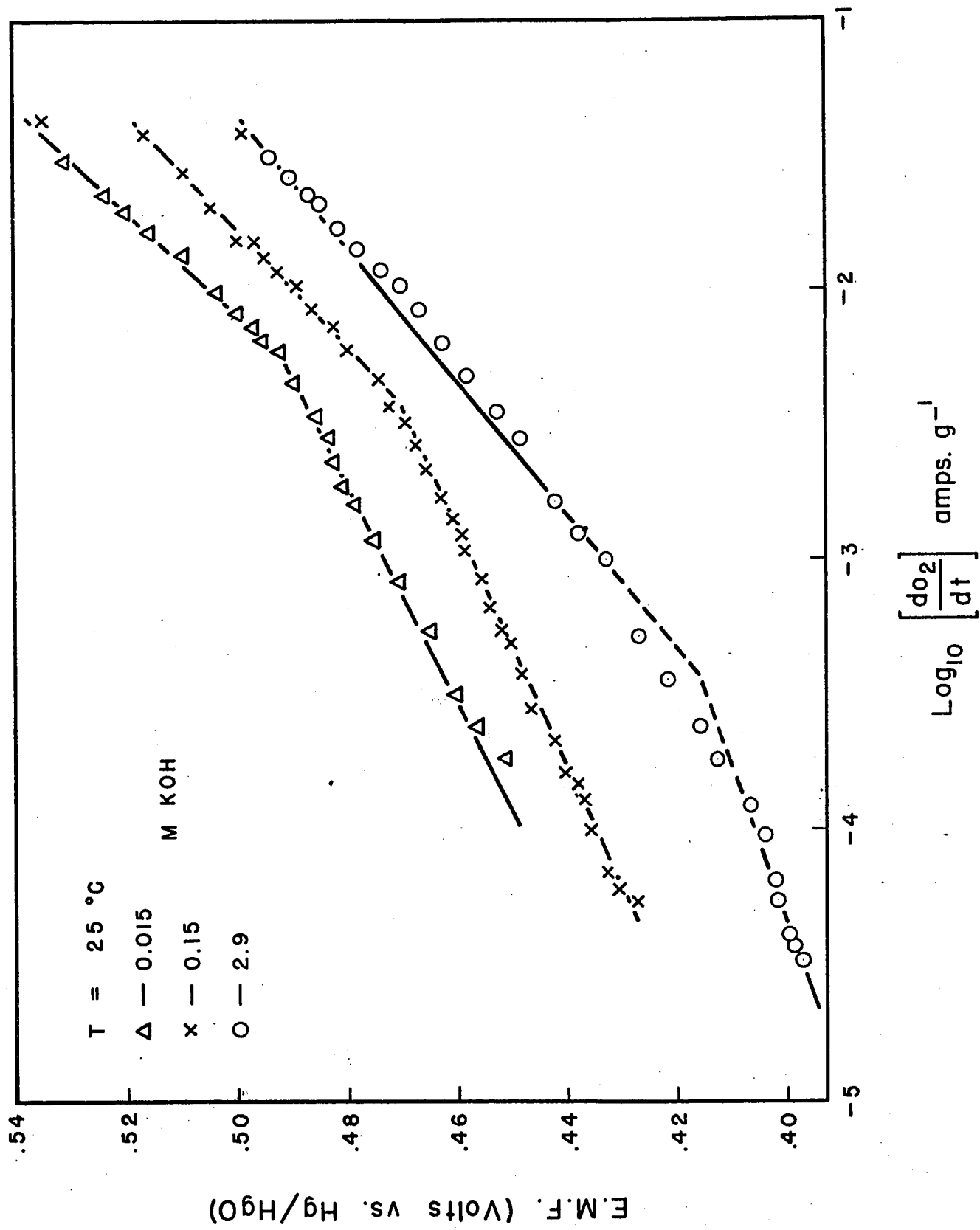


Figure XVI b - Rates of evolution of oxygen on
open-circuit as a function of e.m.f.
at 25° C in 7.1, 9.4 and 14.6 molar
KOH solutions.

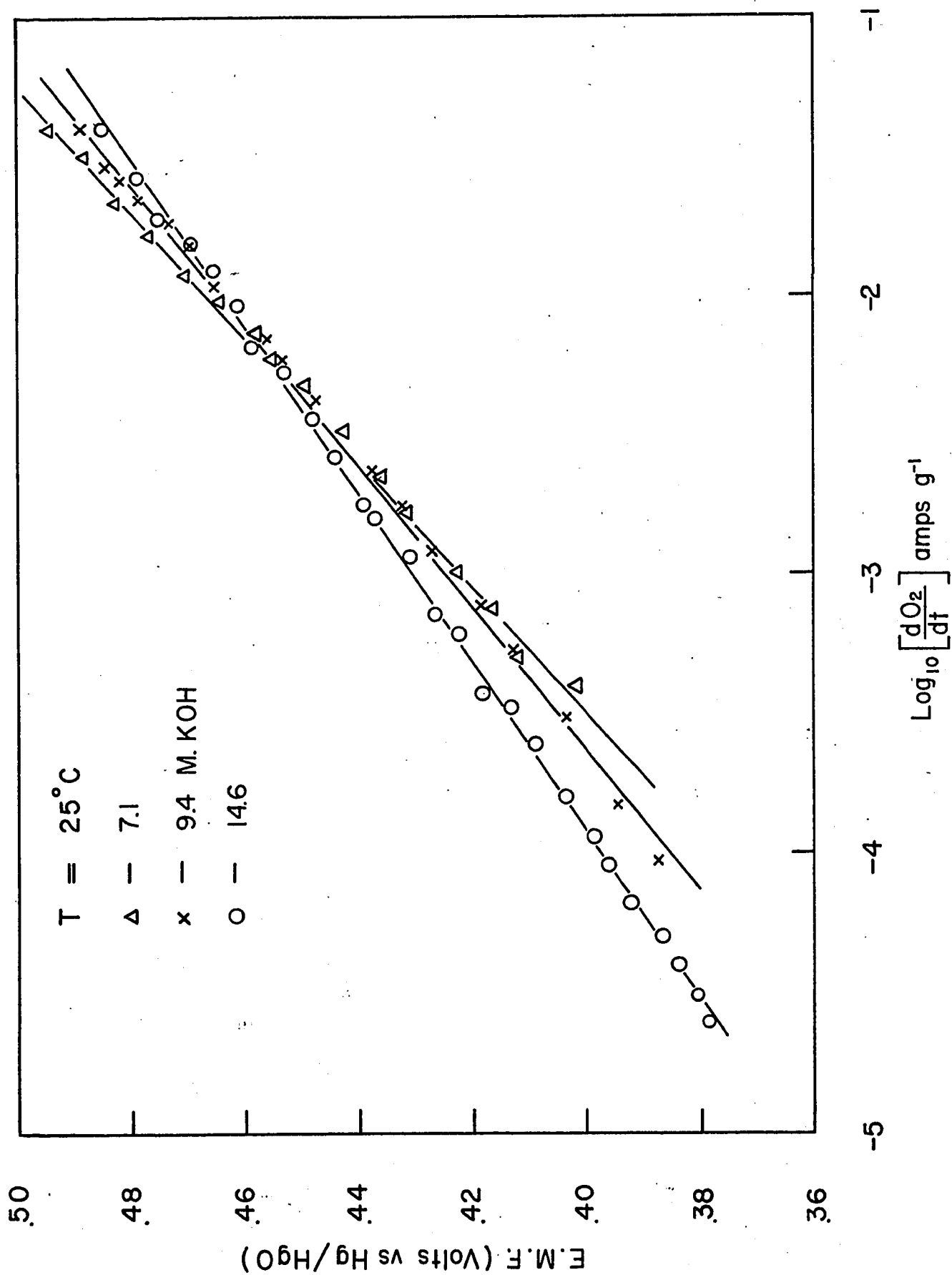


Figure XVII a - Rates of evolution of oxygen on open-circuit as a function of e.m.f. at 60.5° C in 0.15, 1.0 and 1.5 molar KOH solutions.

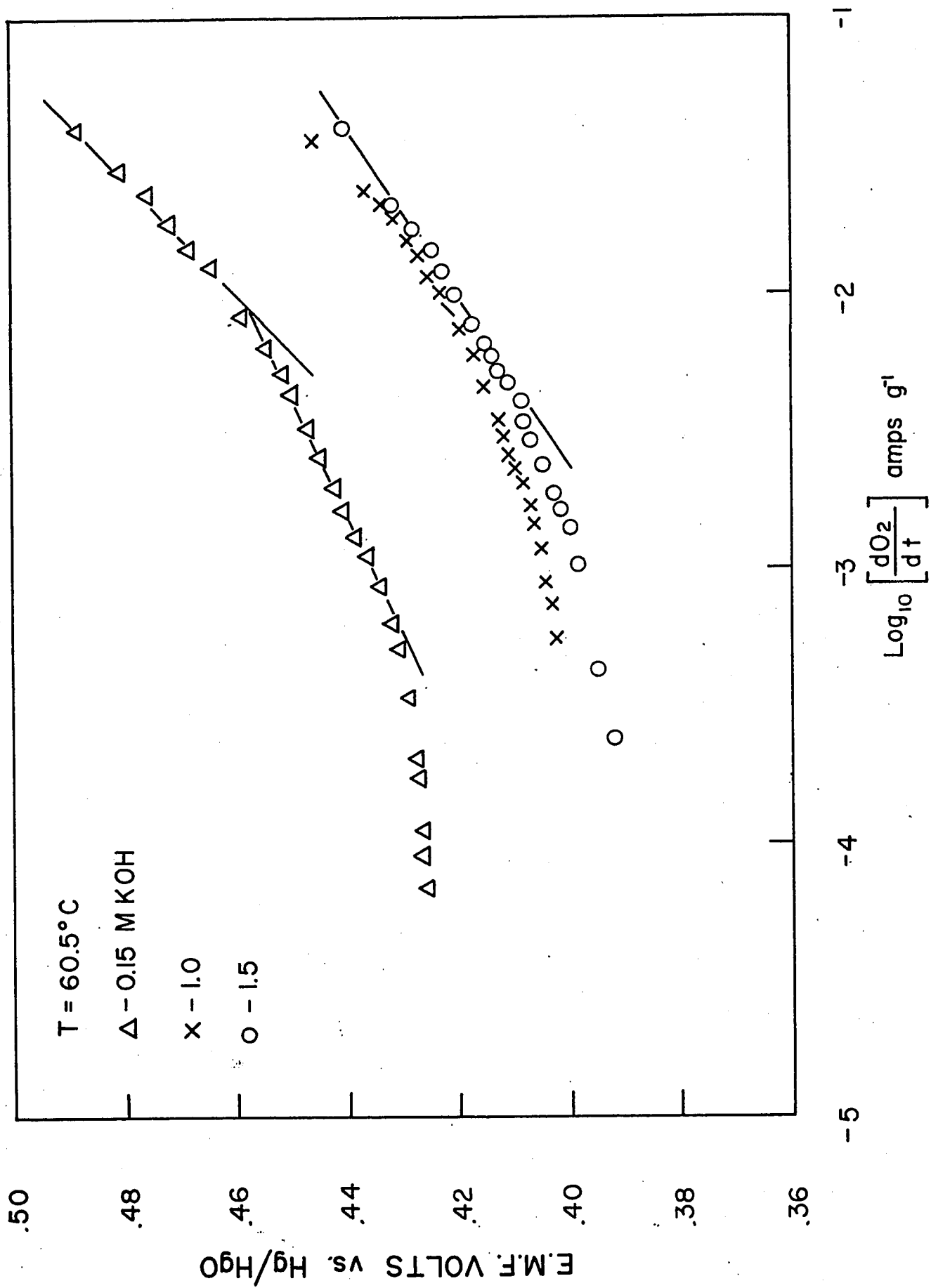
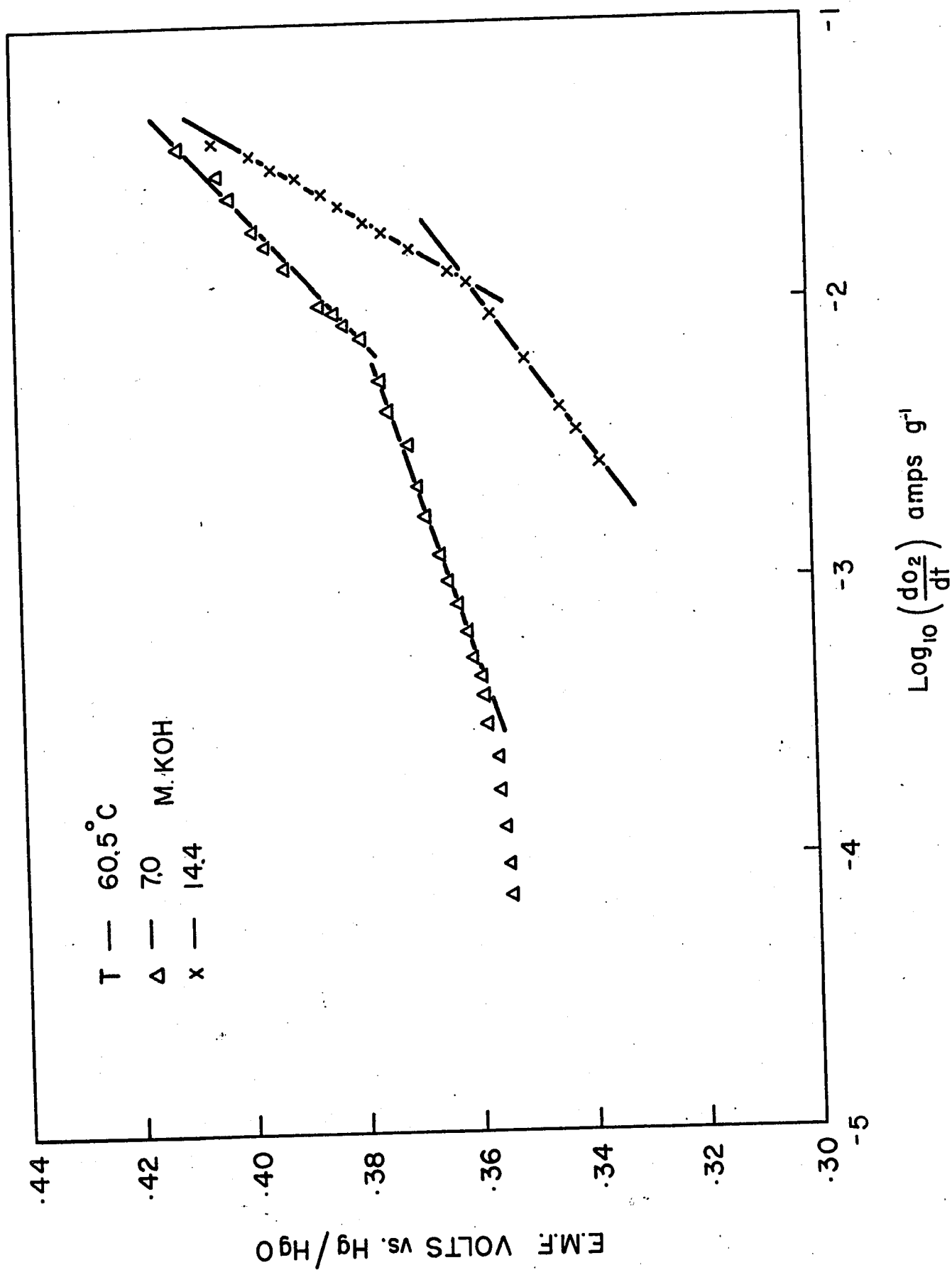


Figure XVII b - Rates of evolution of oxygen on
open-circuit as a function of e.m.f.
at 60.5° C in 7.0 and 14.4 molar
KOH solutions.



are also linear (i.e., at low temperatures at all concentrations as well as at high concentrations at 25° C). Moreover, the conditions that produce a change of slope in the e.m.f. decay lines likewise produce a change of slope in the plots of log rate of evolution of oxygen versus e.m.f. Contrary to the predictions of simple theory [Chapter I section 1, c], the slopes of the e.m.f. log rate lines do not, however, always have the same values as those for the e.m.f. decay lines. This difference arises from the fact that the "capacitance" associated with the electrode surface is in fact not always constant in the region over which the decay of e.m.f. occurs. This point will be discussed in more detail in Chapter IV (section 1, b).

(iv) Decay of E.M.F. in Potassium Deuterioxide

Solutions in D₂O

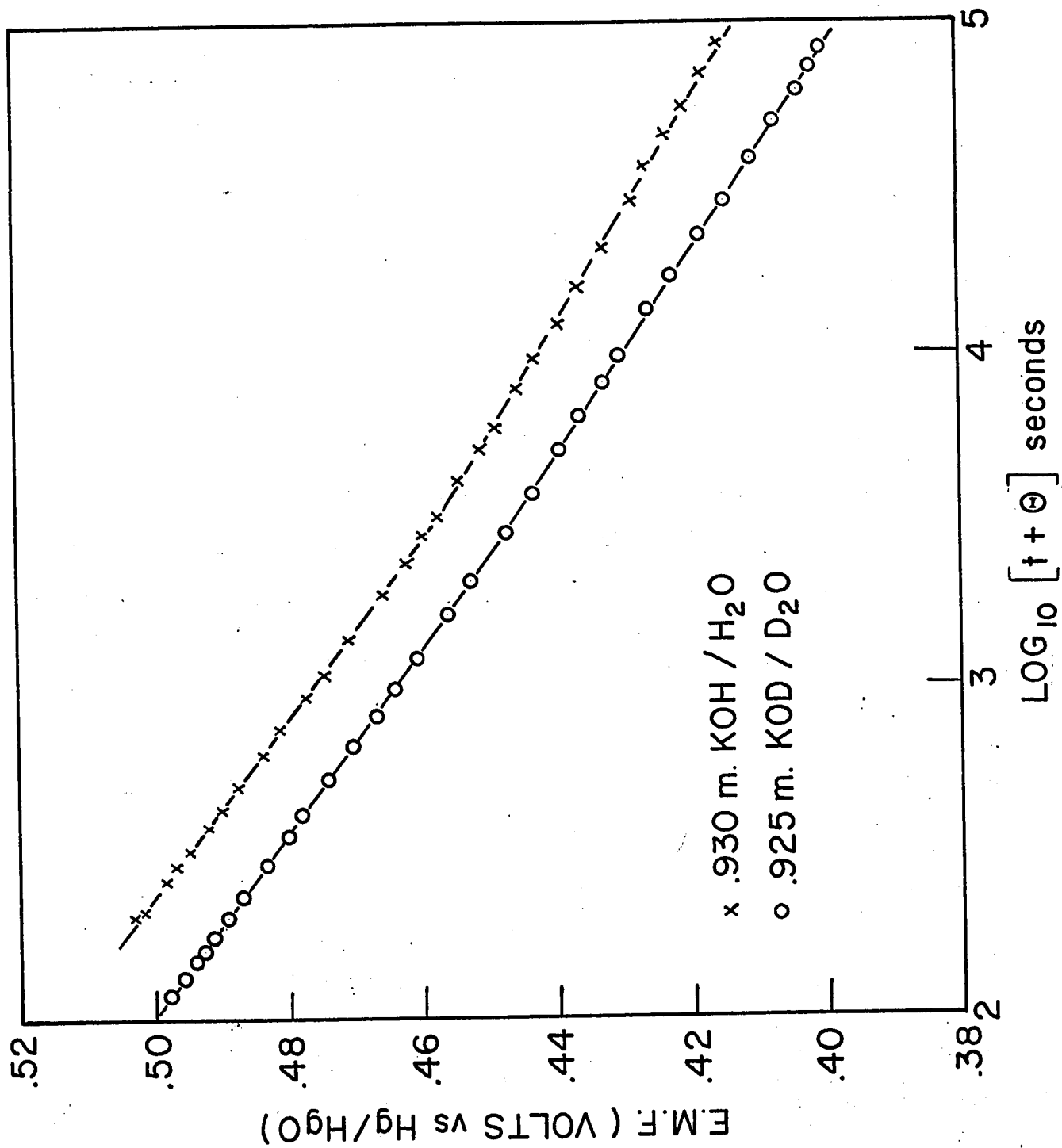
In order to obtain experimental criteria which may assist in the distinction between anodic oxygen evolution processes and cathodic proton transfer steps as rate limiting partial reactions in the overall process of self-discharge of the nickel oxide electrode, (i.e. to distinguish between "anodic control" or "cathodic control" in the corrosion type of reaction occurring) deuterium isotope effects were investigated.

Measurements of e.m.f. decay similar to those described above were hence also made using electrodes containing Ni(OD)_2 as the initial electrochemically active material and using KOD in D_2O as the electrolyte. In the preparation of electrodes for these experiments, nickel sulfate rather than nickel nitrate was used for impregnation as described above Chapter II (section 2, c). However, each experiment made in D_2O was duplicated by one in H_2O where all controllable conditions, including impregnation with nickel sulfate, were kept identical. Oxygen evolution measurements were not possible here since the use of D_2O required that the experiments be conducted on a much smaller scale where the oxygen liberated could not be measured with any degree of accuracy.

Results of the e.m.f. decay studies in D_2O solutions 0.93 molar in KOD are shown in Figure XVIII where they are compared with data from control experiments in H_2O solution. Each line is based on points which are average of data obtained in two experiments. It is seen that the slopes are almost the same in both cases and have the characteristic values normally observed at this concentration and temperature (cf. Figure XII a). The line for e.m.f. decay in D_2O , however, falls somewhat below (i.e. less anodic to the reversible oxygen potential*) that for H_2O . Since these decay lines are the

* Here it should be noted that under the conditions of measurement of e.m.f. using the Hg/HgO half-cell as a reference electrode the reversible oxygen potential measured with respect to this half-cell is independent of the isotopic nature of the solvent since the stoichiometric reaction is simply $\text{Hg} + 1/2 \text{O}_2 \rightleftharpoons \text{HgO}$ and hence does not involve H_2O or D_2O activity.

Figure XVIII - Decay of e.m.f. on open-circuit in D_2O solution 0.93 molar in KOD compared with a control in H_2O solution.



analogues of corresponding Tafel lines, this indicates a higher exchange current for oxygen evolution in the case of the deuterated material in D_2O solution than in the case of the analogous H-containing system.

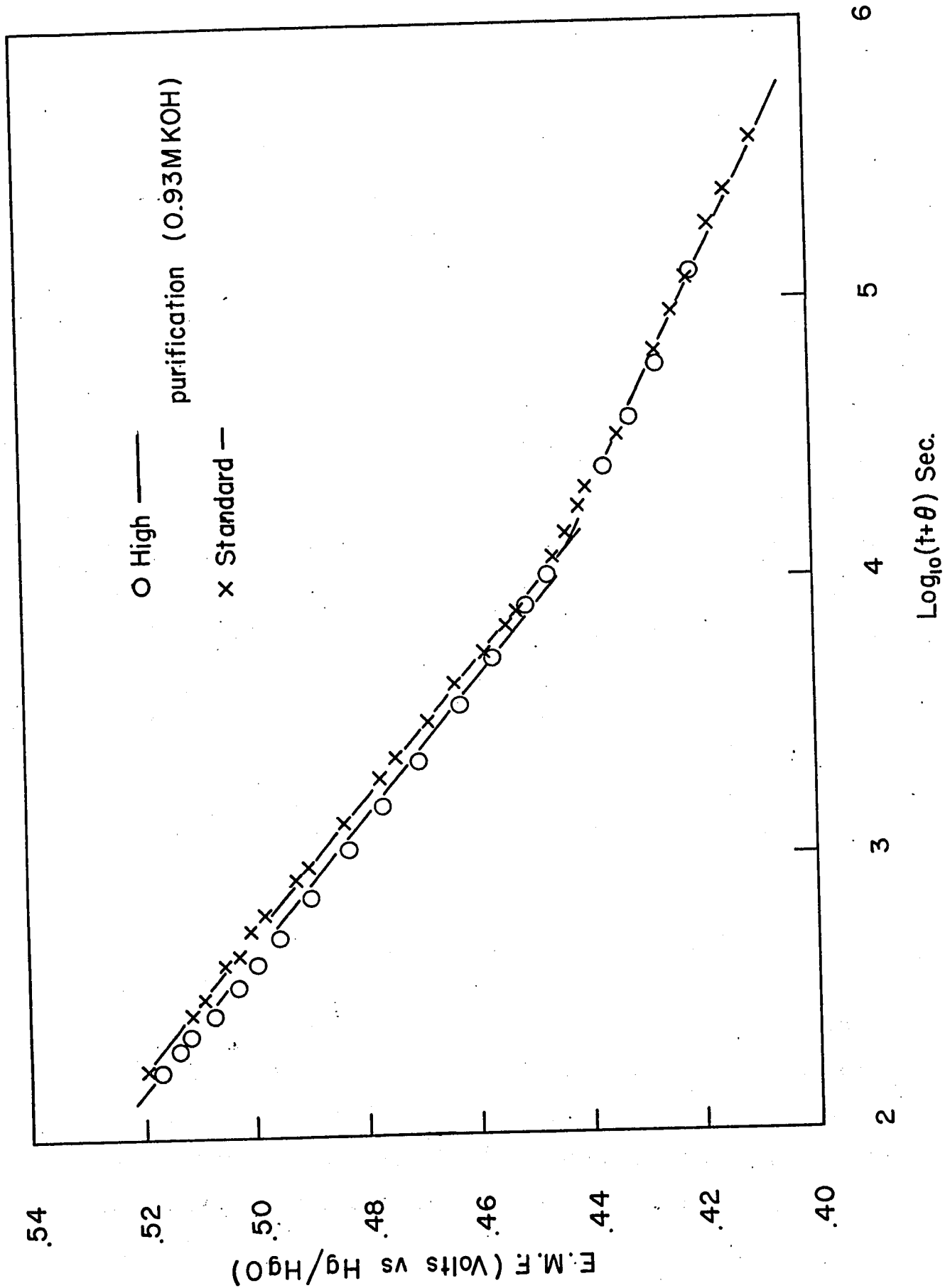
(v) Effects of High Purification and Pre-electrolysis on the Kinetics of E.M.F. Decay

The effects of high purification and pre-electrolysis on the kinetic parameters for oxygen evolution were examined in several experiments involving decay of e.m.f. after cessation of anodic polarization. The results obtained using the high purification techniques outlined in Chapter II section (1, b) were found to be insignificantly different from those obtained using the standard purification technique. In Figure XIX is shown a comparison of typical data obtained in runs made under the above two conditions of purification. The small difference observed (4-5 mV.) in Figure XIX is no greater than normal variation* (± 5 mV.) between runs done at the same degree of purification. Moreover, no definite trend of the results, due to ultra-purification, could be established since the highly purified solutions gave decay lines which showed

* It should be noted that in the present and other anodic studies (17,27) the degree of reproducibility of polarization results is substantially better than in analogous cathodic studies and moreover the results are also much less dependent on ultra-purification of solutions.

Figure XIX - Effect of ultra-purification and pre-electrolysis on the E.M.F. decay of the nickel oxide electrode in 0.92 molar KOH solution.





sometimes higher and sometimes lower polarization than the corresponding control runs made in the solutions prepared under the "standard conditions" of purification. The fact that high purification and pre-electrolysis has little or no effect on the kinetics of processes at these electrodes may be attributable to the very large real surface area existing in these electrodes. Furthermore, in an anodic process it would not necessarily be expected that the same large effects due to trace impurities which are found (73) in cathodic processes would be observed, since trace cations which can poison cathodes by electrodeposition cannot similarly affect anodes. Anionic impurities would not have the same tendency to deposit (and remain deposited) and thus poison (or activate) the surface and could presumably only act as depolarisers at low current densities.

b) Steady State E.M.F. under Anodic Polarization:

Tafel Lines

(1) Nickel Oxide Electrodes in Aqueous KOH

Solutions

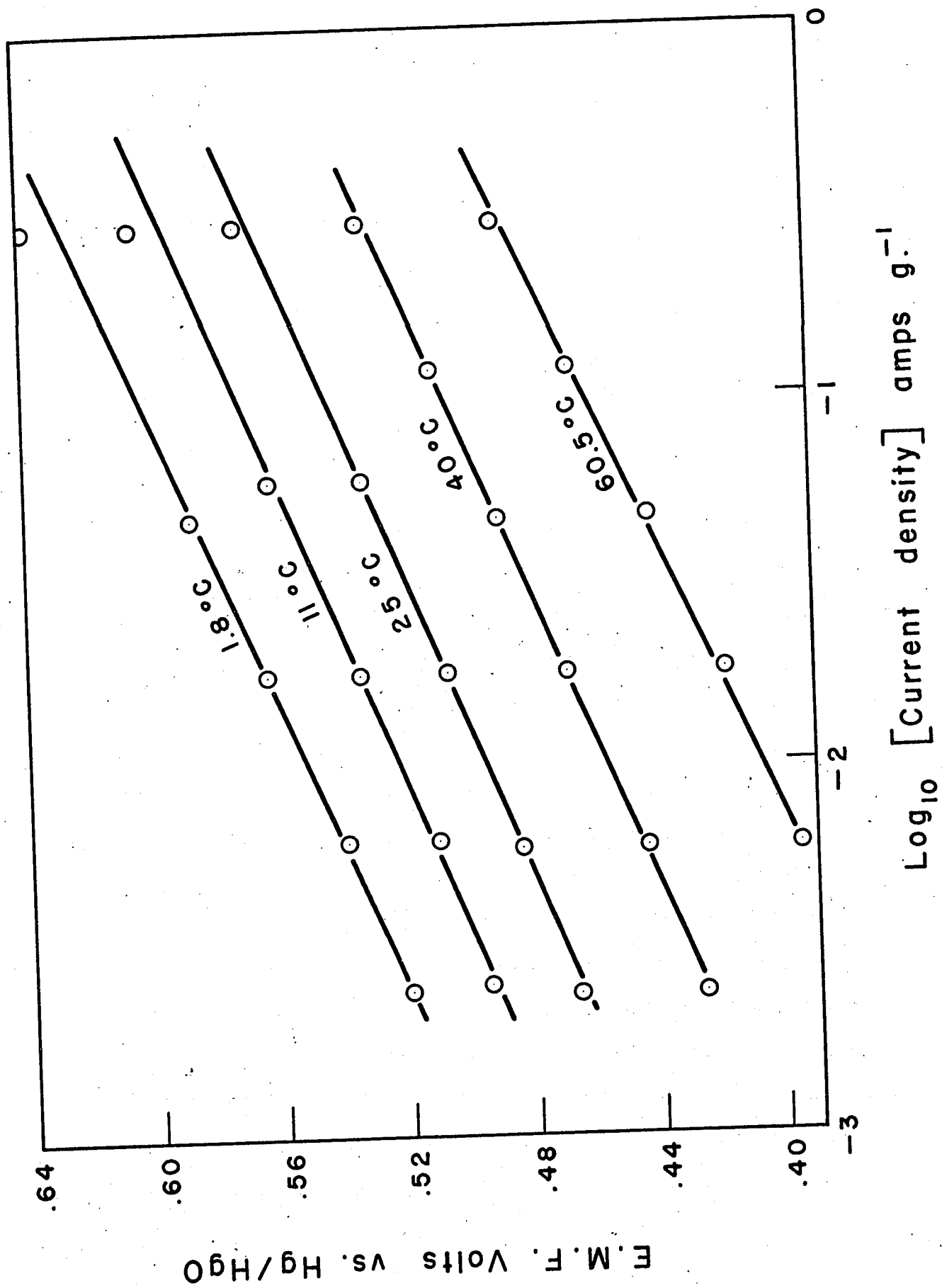
The steady state e.m.f. as a function of current density (i.e. the Tafel behavior) on nickel oxide electrodes was investigated at 5 temperatures, (1.8, 11, 25, 40 and 60.5° C) in 7 molar KOH solution. Plots of e.m.f. versus the logarithm of current density (in amp. g⁻¹; cf. p. 74) gave

good straight lines which are shown in Figure XX. The lines were found to be nearly parallel having decadic logarithmic slopes of approximately 0.049 V. at 25° C. These lines, of course, are not expected to be perfectly parallel at the different temperatures since the theoretical slope of each line will be temperature dependent, viz. $\frac{RT}{\alpha F}$. The "transfer coefficient", α , will depend upon the mechanism of the rate determining reaction as discussed above in Chapter I. If α is independent of temperature the slope will vary directly as the absolute temperature. Here, as seen in Figure XX, this is observed only qualitatively in so far as the polarization lines at higher temperatures have somewhat higher slopes.

(ii) Nickel Metal in Ordinary Aqueous and in Deuterium Oxide Solutions

As has been stated above, the exchange current for oxygen evolution on self-discharge of the nickel oxide electrode was shown to be greater in D₂O solutions. In order to complement the above mentioned results, steady state polarization measurements were made on plain nickel metal electrodes in the form of wires in H₂O and D₂O solutions of KOH and KOD respectively. The solutions used in these experiments were prepared from the potassium amalgam as described in Chapter II (section 1, b) and were pre-electrolysed using nickel oxide electrodes initially containing Ni(OH)₂ and Ni(OD)₂ respectively.

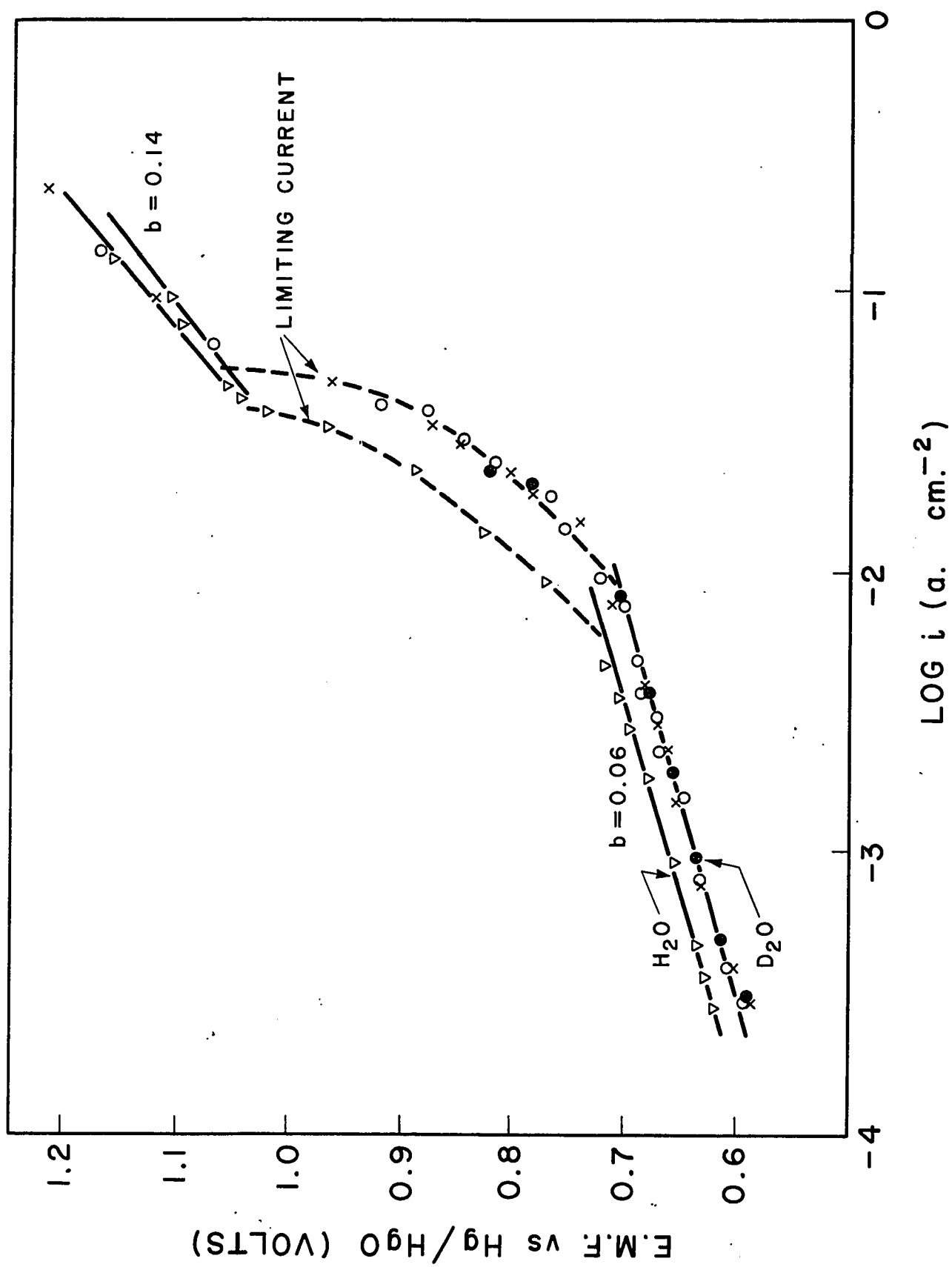
Figure XX - Tafel lines for oxygen evolution on nickel oxide at 1.8, 11, 25, 40 and 60.5° C.



[The high purification technique was used here in order to avoid possible contamination effects which could be more important on the small area (0.1 cm^2) wire electrodes used in this part of the work]. The results of these experiments are shown in Figure XXI. The reproducibility, which was equally good in H_2O and D_2O solutions, may be assessed by inspection of the three sets of points corresponding to three different experiments shown for the D_2O solution.

Owing to the much smaller real areas of these nickel wires as compared with those of the sintered nickel oxide electrodes used in the remainder of the work, the lowest current densities examined here corresponded approximately to the highest current densities used in self-discharge experiments. The slope of 0.06 observed here in the low current density region is somewhat higher than that found on the oxide electrode (approx. 0.045). However, it is clear that as in the case of self-discharge on open-circuit the exchange current is greater in the D_2O than in the H_2O solutions. There are also indications here of a limiting current at higher current densities followed by a second Tafel region at the highest current densities. However, since the examination of this effect was not the main object of this part of the work, no further attempt was made to characterize or to interpret these phenomena.

Figure XXI - Steady state polarization measurements
(Tafel lines) on plain nickel wires
in D_2O and H_2O solutions.



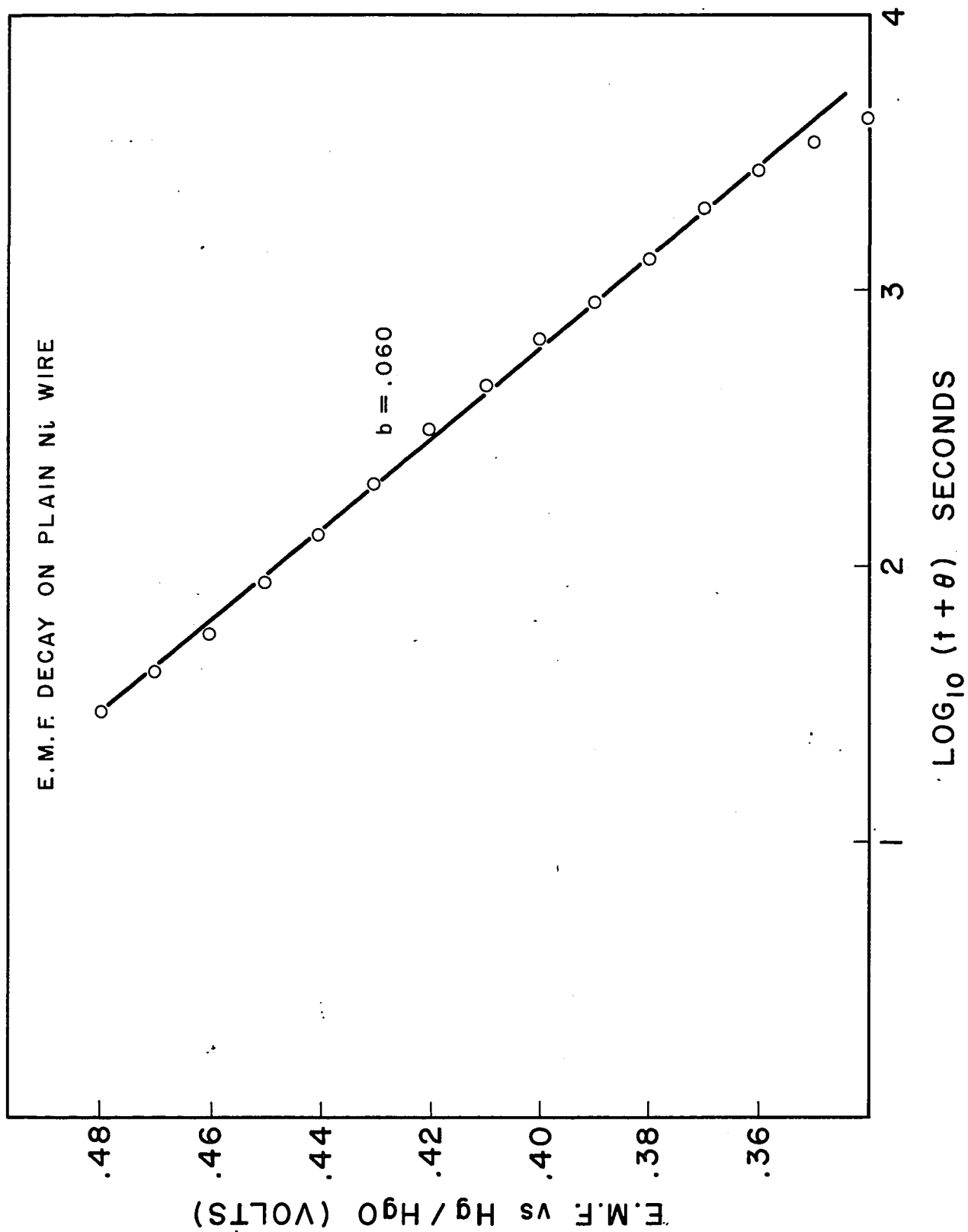
Measurements of e.m.f. decay on these nickel wire electrodes gave good straight lines when plotted semi-logarithmically in the usual manner. A typical decay curve is illustrated in Figure XXII. The slope is observed to be about 0.060 m.v. corresponding to the lower potential region of the Tafel lines obtained from d.c. polarization measurements. In these experiments with plain wire electrodes the e.m.f. decay from higher overpotentials (corresponding to the upper region in Figure XXI) was very rapid owing to the relatively high real current densities used and no attempt was made to study this region in detail.

2. BEHAVIOR OF PARTIALLY OXIDIZED ELECTRODES

a) Decay from Anodic and Cathodic Polarization in Aqueous Potassium Hydroxide

In Chapter I, section 1,c, it has been shown that when polarization of an electrode is interrupted the electrode process occurring prior to the interruption will continue for some time at a progressively diminishing rate. The current required for this continuation of the process is supplied by discharge of the double-layer or surface capacity associated with the electrode. In the semi-oxidized electrode at a state of oxidation " $\text{NiO}_{1.25}$ " the process occurring during anodic polarization is oxidation of $\text{Ni}(\text{OH})_2$ in the electrode itself. Conversely the process occurring during the cathodic polarization

Figure XXII - Decay of e.m.f. on open-circuit on
a plain nickel wire electrode.



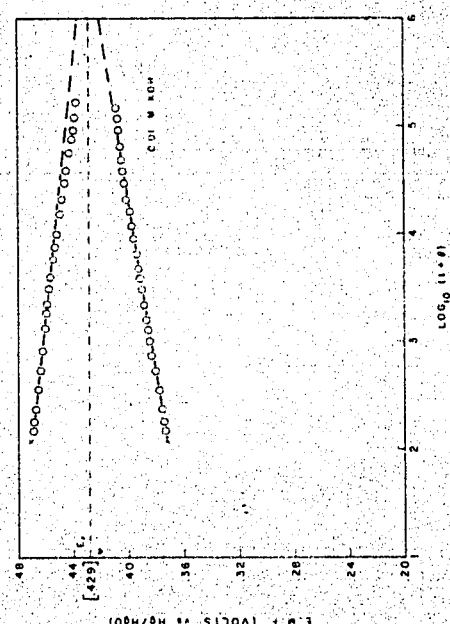
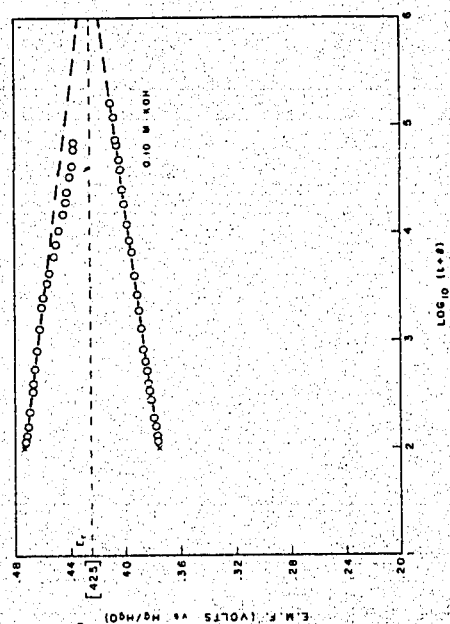
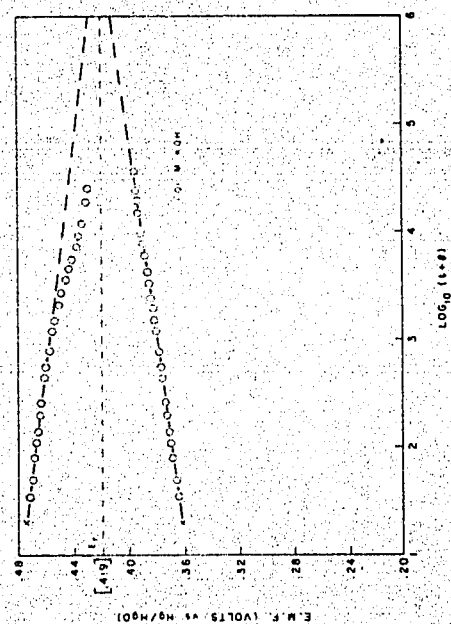
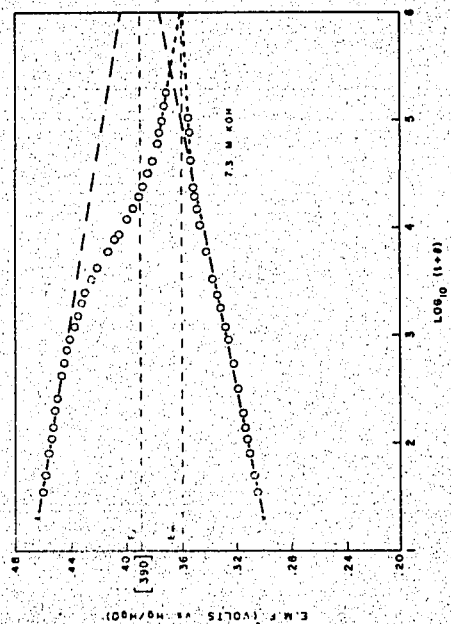
is reduction of the higher nickel oxide. Thus, by studying the kinetics of e.m.f. decay following the interruption of either anodic or cathodic polarization at a semi-charged electrode, it is possible to gain some insight into the kinetic parameters involved in the electrolytic oxidation and reduction of the nickel oxide electrode. The Tafel slopes for the oxidation and reduction processes cannot be obtained by the usual method of measuring the steady state e.m.f. as a function of current density, since at no time during the charging or discharging is the e.m.f. truly constant. During charging (i.e., anodic polarization at constant current), the e.m.f. rises continuously until complete oxidation is reached followed by oxygen evolution ("overcharge" region); likewise, during discharging (cathodic polarization) the e.m.f. falls continuously until the higher oxide is completely reduced. Thus e.m.f. decay measurements appeared to be the most satisfactory method of obtaining information on the kinetic parameters for oxidation and reduction of the nickel oxide species.

The decay of e.m.f. from anodic and cathodic polarization has been measured on semi-charged electrodes and the results are shown plotted semi-logarithmically in t plus θ for a number of KOH concentration in Figures XXIII and XXIV. The significance of θ , the semiempirical constant, has been discussed previously [p. 17]. In order to establish the effect

Figures XXIII a, XXIII b, XXIII c, XXIII d. -

Decay of e.m.f. from anodic and cathodic
polarization on partially charged electrodes.

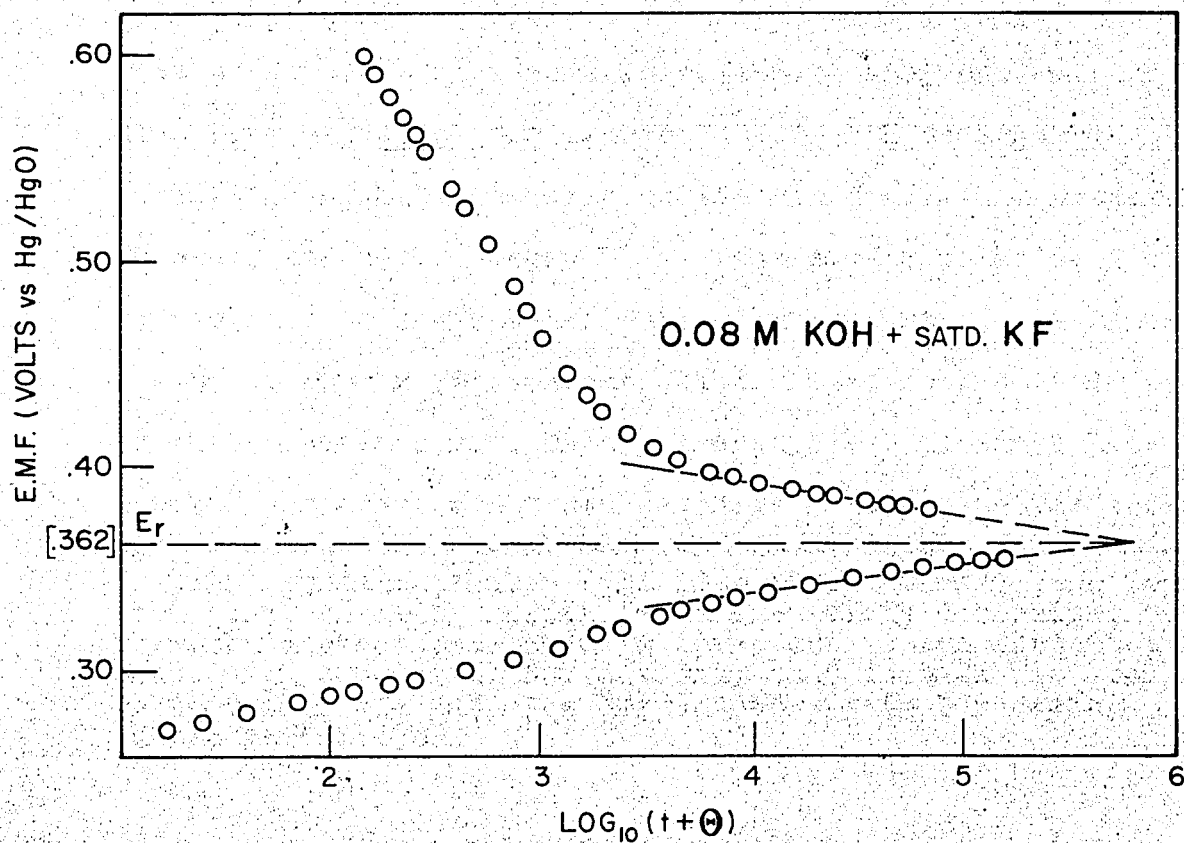
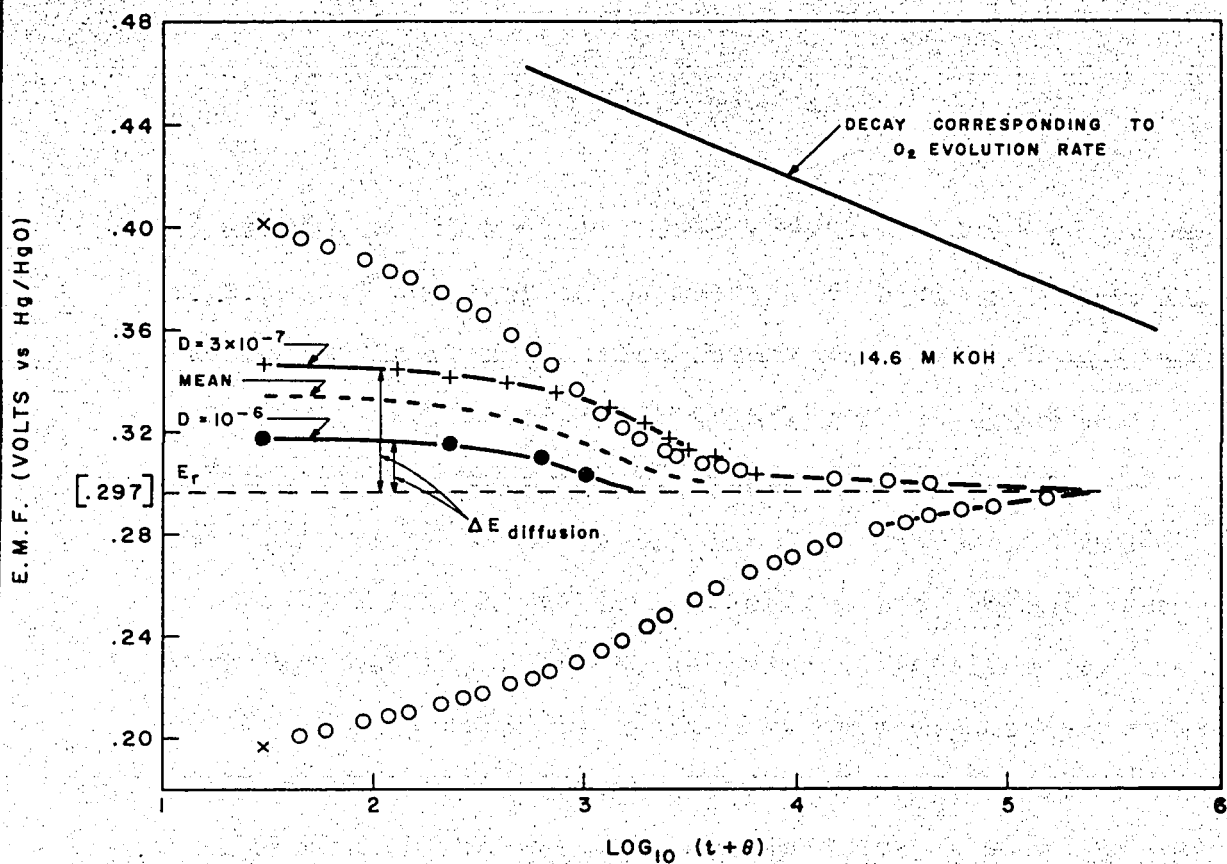
- (a) 0.01 molar KOH solution
- (b) 0.10 " " "
- (c) 1.01 " " "
- (d) 7.3 " " "



Figures XXIV a, XXIV b - Decay of e.m.f. from
anodic and cathodic polarization on
partially charged electrodes

(a) 14.6 molar KOH solution

(b) 0.08 molar KOH + saturated KF electrolyte.



of varying water activity at a constant KOH activity, one experiment, the results of which are shown in Figure XXIV b, was conducted in a solution saturated in KF and 0.08 molar in KOH. The water activity of this latter solution was determined by a differential vapor pressure measurement at 25° C and found to be 0.30. The activity of the 0.08 M KOH in the KF solution was estimated from its concentration by assuming that the relevant activity coefficient for the KOH was that for a solution of KOH having the same water activity (0.3) as that of the saturated KF solution.* The electrodes used for these measurements of e.m.f. decay were charged to a formal state of oxidation " $\text{NiO}_{1.25}$ " (i.e., 50% Ni^{II} - Ni^{III}) (cf. Chapter II section 9, b). Very good straight lines were observed for the semi-logarithmic decay of e.m.f. with time from cathodic polarization at all KOH concentrations except the highest and also in the mixed KF - KOH electrolyte. However, the e.m.f. decay lines from anodic polarization showed inflections in all but the most dilute solutions at times of the order of 3×10^3 seconds. The slopes in the early region of these latter e.m.f. decay lines, (i.e., at times less than 3×10^3 seconds) were taken as those relevant to the oxidation

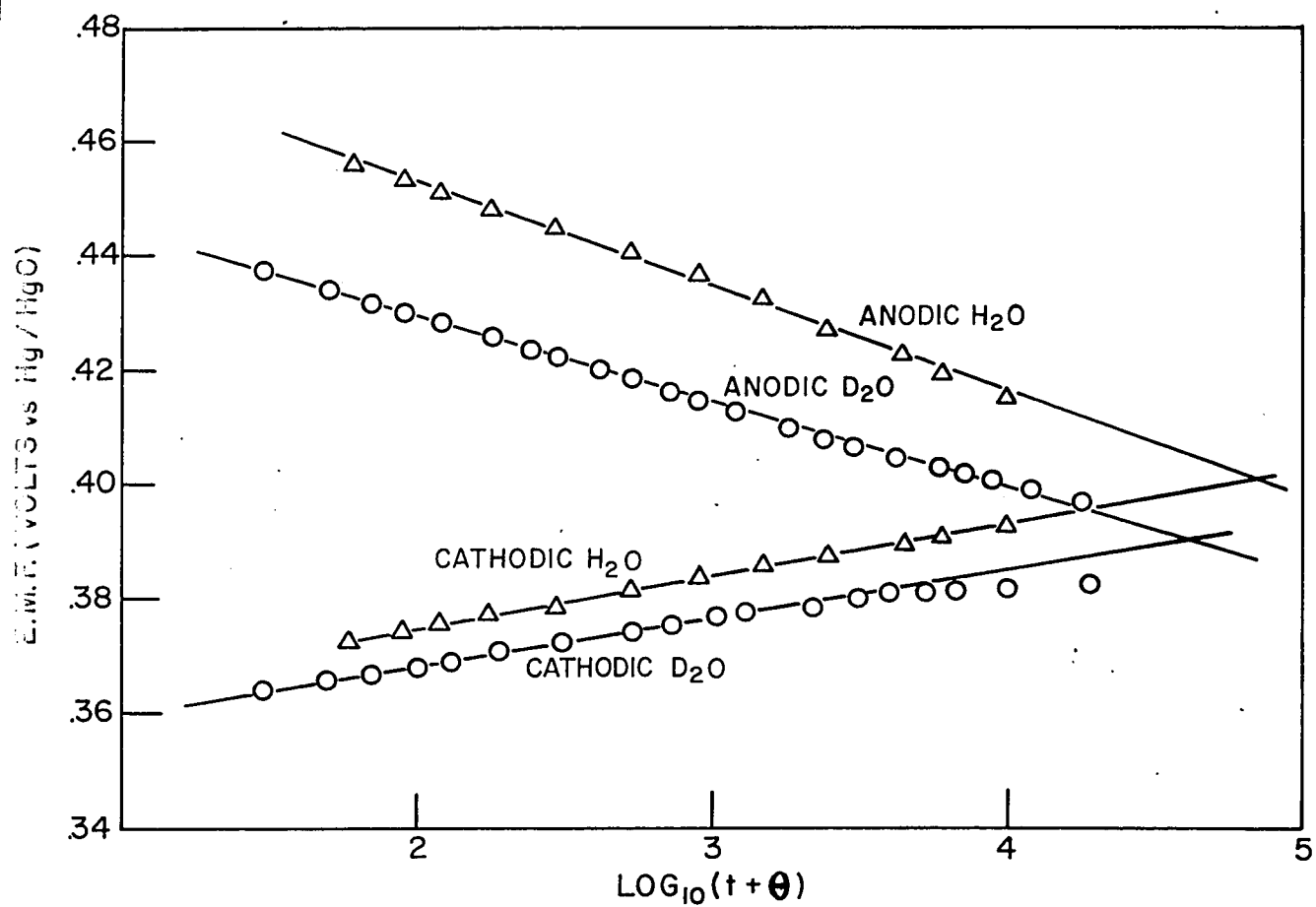
* This approximation is justified since at very high ionic strengths, activity coefficients are mainly determined by ion-solvent interaction. This is borne out by the fact that at these high concentrations activity coefficients are much greater than one and rise very rapidly with increasing concentration (70).

of the nickel in the oxide from the II to the III-valent states for reasons which will be discussed in detail in the following chapter, where it is shown that the inflection arises from kinetic competition between the oxygen evolution process and the electrochemical oxidation of Ni^{II} . This has the effect of making the e.m.f. fall more rapidly than it would if only the process corresponding to oxidation of Ni^{II} to Ni^{III} occurred. The results obtained from the experiments in very concentrated KOH and in the mixed $\text{KF} - \text{KOH}$ electrolyte, Figure XXIV b, present a somewhat different problem of interpretation. In these cases, changes in the relative concentrations of KOH and H_2O within the porous sintered electrode can be shown to cause the observed departure from the theoretically expected behavior. This point is treated in further detail in Chapter IV, (section 2,c, ii).

b) Decay from Anodic and Cathodic Polarization in Potassium Deuterioxide Solution

Anodic and cathodic e.m.f. decay measurements similar to those described in the previous section were made on Ni(OD)_2 electrodes in $\text{KOD-D}_2\text{O}$ solutions prepared as described in Chapter II, section 1,c. The results are shown in Figure XXV where they are compared with corresponding measurements on control electrodes in aqueous KOH solution.

Figure XXV - Decay of e.m.f. from anodic and cathodic polarization on partially charged electrodes in KOD in D_2O solution compared with a control electrode in ordinary aqueous solution.



Both the Ni(OD)_2 and the Ni(OH)_2 control electrodes used in these measurements differed from the electrodes used in the remainder of the work in that they were prepared from NiSO_4 rather than $\text{Ni(NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ and the density of Ni(OD)_2 and Ni(OH)_2 in the sinter was less by a factor of from five to ten than that in the regular $\text{Ni(NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ prepared electrodes. It will be noted that both the anodic decay and cathodic recovery lines are displaced to lower potentials in the deuterium containing electrodes and solutions as compared with the control Ni(OH)_2 electrodes in H_2O . The decay lines, however, show no significant difference of slope.

c) Quasi-Equilibrium and Reversible E.M.F. Values

(1) Reversible E.M.F. from Anodic and Cathodic Decay Lines

The anodic and cathodic decay lines discussed above cannot of course continue straight to infinite time but ideally will curve as the reversible electrode potential is approached becoming asymptotic to the reversible potential at very long times. This behavior is analogous to that for anodic and cathodic Tafel lines for a given electrode process where the intersection of the extrapolation of the straight regions of each line gives a point, the coordinates of which are the reversible potential and the logarithm of the exchange current. Thus, from the point of intersection of the extrapolated straight

regions of the anodic and cathodic decay lines shown in Figures (XXIII and XXIV), the reversible potentials at a state of oxidation $50\% \text{Ni}^{\text{II}} - \text{Ni}^{\text{III}}$ may be evaluated at the various concentrations. In the most concentrated solution (14.6 molar), concentration changes coupled with slow diffusion of water out of, and of KOH into, the electrode* cause distortions in the e.m.f. decay lines making an extrapolation from short times impossible. However, since in this case the e.m.f. E_f at long times tends to a value less anodic than the oxygen reversible potential, " E_f " may be taken as the reversible potential without the possibility of kinetic complications arising from simultaneous oxygen evolution which occurs in the more dilute solutions at the reversible ($\text{Ni}^{\text{II}} - \text{Ni}^{\text{III}}$) potential. This matter will be discussed in more detail in Chapter IV (section 2, c) where self-discharge effects and mixed potentials are discussed. In the $\text{KF} - \text{KOH}$ solution, concentration effects are also important, again making extrapolation from short times of doubtful significance. Moreover, the potential approached from anodic and cathodic polarization at long times is higher than the reversible oxygen potential so that the " E_f " value reached at very long times actually corresponds in this case to a mixed potential.

* For more details see Chapter IV, section 2, c.

However, from considerations to be discussed later (Chapter IV, section 2, c) it can be shown that the mixed potential in KF - KOH solution will be quite close to the true reversible potential for the electrode in that solution.

The above considerations in relation to the data in Figures XXIII and XXIV enable the true reversible potentials for the " $\text{NiO}_{1.25}$ " electrode to be expressed as function of KOH and water activity and hence allow a formal Nernst equation to be evaluated and a corresponding stoichiometric redox equation to be formulated. This is further discussed in Chapter IV where the theoretical aspects of this matter are examined more fully.

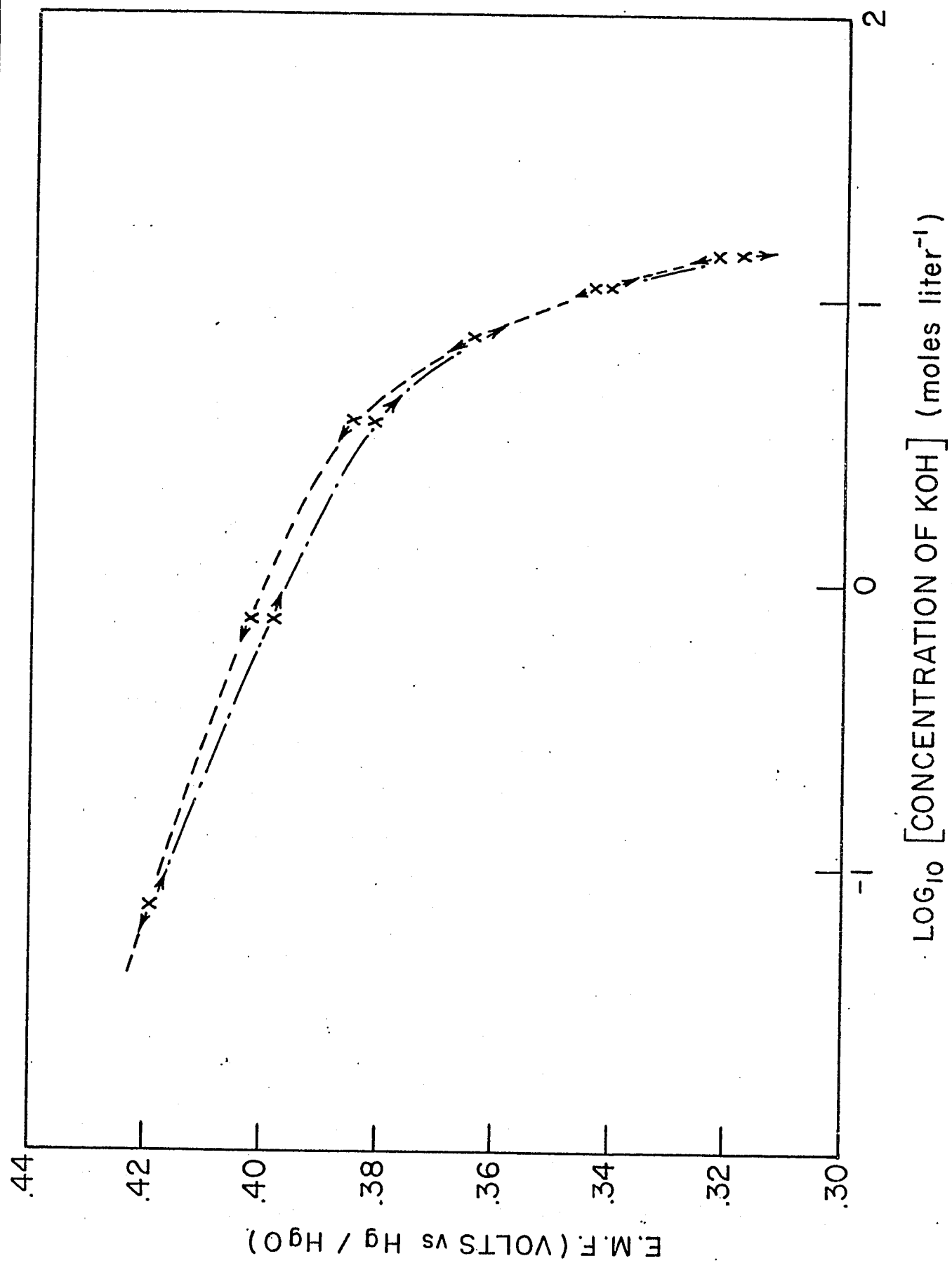
(ii) Quasi-Equilibrium or Mixed Potentials at Long Times

From the foregoing, it is clear that except in the strongest KOH solutions the potentials measured on open-circuit after long periods of standing will not be the true reversible potentials but rather steady state quasi-equilibrium or mixed potentials. In this section, these potentials determined after long periods of standing are related to KOH and water activities and compared with the true reversible potential of the electrode deduced by the kinetic analysis involving e.m.f. decay discussed above.

The potentials obtained by the procedure c, (ii) (p. 80), described in section 9 under "Experimental"

(i.e. after having been allowed to equilibrate, an electrode is transferred successively into KOH solutions of decreasing concentration, then successively back into more concentrated solutions each time measuring its equilibrium potential) are shown as a logarithmic function of molar concentration of KOH in Figure XXVI. The results obtained from "backward" successive immersions (dilute to strong) in various KOH solutions agreed satisfactorily with those obtained by "forward" immersion (strong to dilute) as shown in this Figure but some irreversibility occurred when the sequence of operations (procedure C, i, page 80) was carried out by immersing the electrode initially in the dilute solutions followed by successively more concentrated solutions and thence returning to the more dilute solutions. The values attained initially in the dilute solution were somewhat less positive than those reached upon "return" from the concentrated solutions. The latter values obtained upon return from the concentrated solutions were in good agreement with those obtained by procedure c, ii. Likewise values obtained by procedure b, (i.e. six electrodes initially transferred to the strongest solution and thence directly to solutions at six different KOH concentrations), were in good agreement with those obtained by procedure c, ii. Procedure a (p. 79) (i.e. six electrodes transferred directly from the 0.001 M KOH solution to solutions at six different KOH concentrations) gave potentials in agreement

Figure XXVI - Reversibility of e.m.f. of the nickel oxide electrode with successive changes of concentration. Arrows indicate sequence of changes for an electrode initially put in the strongest solution after being maintained in 0.001 M KOH.



with those obtained by the other methods in concentrated solutions but somewhat lower and less reproducible potentials in the dilute solutions.

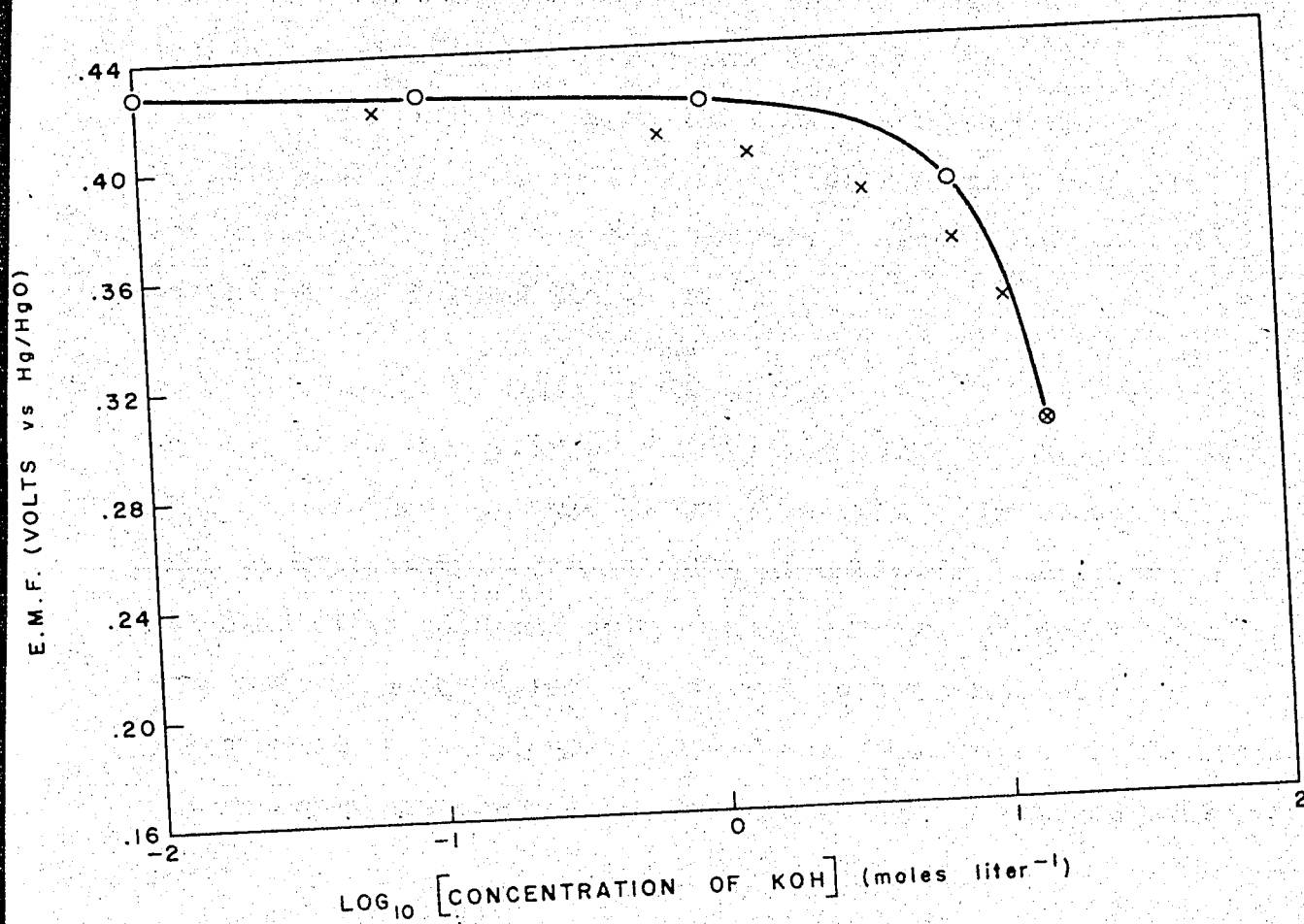
In Figure XXVII comparison is made between the data obtained by procedure b described in section 9 Chapter II (six electrodes transferred from the strongest solution to six different KOH concentrations) (crosses) and the polarization decay method (circles). It is seen that the polarization decay method gives values significantly more positive (ca. 15-30 mV.) to the Hg/HgO electrode than those obtained by procedure b. This is in fact to be expected since the values obtained by the latter procedure are the mixed potentials and will be depressed from the corresponding true reversible potentials by the small cathodic polarization impressed on the electrode by virtue of its finite rate of self-discharge by the corrosion - type of process discussed previously.

3. Surface Capacitance of the Nickel Oxide Electrode

a) Definition

When considering the nickel oxide and other similar electrodes, which are capable of storing energy electrochemically some care must be taken in the definition and use of the terms "capacitance" and "capacity". In battery technology the term "capacity" or "electrochemical capacity" conventionally refers to the quantity of electricity, expressed

Figure XXVII - Comparison of e.m.f. values obtained from "stationary" potential measurements (crosses) and from appropriate extrapolation of logarithmic decay lines (circles).



as the product of current and time, which can be drawn from the electrode on discharge or conversely, the quantity of electricity required to charge the electrode. The "capacity" used in this sense is usually expressed in units of ampere-hours or coulombs (ampere-seconds) and is hence not truly a "capacitance" in the electrostatic sense.

The capacitance, on the other hand, relates the potential of a system or body to the charge which has been communicated to it. The "differential" capacitance C of a system may be defined simply as

$$C = \frac{dq}{dE}$$

where q is the quantity of electricity and E is the potential. If q is measured in coulombs and V in volts, the capacitance will be expressed in farads. The capacitance C need not necessarily be constant over a range of E values and in fact this case is encountered with regard to the double-layer capacitance of an electrode interface. The origin of the ionic double-layer capacitance has been adequately discussed elsewhere (74).

b) Origin of Electrochemical Surface or Pseudo-Capacitance

At an ideal polarizable electrode (74) such as mercury, the potential of the electrode can be raised with corresponding change of net surface charge upon the metal and of ionic charge in the solution adjacent to the metal surface; during this

process, no net transfer of charge takes place across the interface. Under these conditions, the interface behaves electrically like a condenser and it is hence possible to speak of the "capacitance" of the double-layer of charges at the surface. In a similar way, electrodes at which a limited amount of pure species can be deposited on the surface to form an adsorbed film also behave like electrical condensers over a limited range of potentials. In this case, some charge transfer must occur to build up the film but this process is distinct from continuous electrolysis. It is usually found that these surface film capacitances are larger by a factor of 5-50 than that observed for the ionic double-layer capacitance at mercury although of course the value of this capacity depends on the electrode potential (75). In some cases, e.g. with regard to the surface film capacitance due to adsorbed H at Pt (76), these two types of capacitance can be distinguished but, depending on the potential at which the ad-species is formed or removed at the interface, this distinction may not always be possible or at least not facile (cf. Bockris and Devanathan, 76).

In the case of the nickel oxide electrode, high capacitances are observed (see below Table I). These large values have been attributed by Lukovtsev and Temerin (77) to a surface layer of adsorbed intermediates (e.g. OH or O radicals). This suggestion appears to be entirely plausible

since B.E.T. measurements* made on the dried materials, reveal a surface area of 40 m^2 per gram of active nickel oxide in the charged state and 32 m^2 per gram in the discharged state. Assuming the surface of the material in the original wet state to be at least of comparable magnitude, it is readily shown that less than a monolayer of O or OH radicals can account for the capacitance values observed.

(c) Evaluation of Surface Capacitance

(1) Capacitance of the Electrode from the Quantity θ

In Chapter I an expression was derived relating the e.m.f. of an electrode to the time elapsed from the moment of interruption of the polarizing current. It was shown that

$$E = a' - b \log (t + \theta)$$

where E is the potential at any time t and a' , b and θ are constants. It also has been shown (p. 16) that the constant θ , which has the units of time, is related to the capacitance, C, of the electrode by

$$\theta = \frac{bC}{2.3031}$$

* These measurements were carried out through the kindness of Dr. C. Amberg of the National Research Council.

where b is the slope of the e.m.f. decay line and i' is the polarizing current passing prior to the interruption of polarization. Since b , i' and θ are experimentally measurable quantities, C may be readily calculated. The evaluation of θ is usually made empirically from e.m.f. $\log$ (time) plots simply by adding to the measured time t that constant value of time, θ , which gives an initially (and continuously*) linear e.m.f. - $\log (t + \theta)$ plot. Such a plot is shown in Figure XXVIII. An alternative method of evaluating θ , which eliminates any arbitrariness, has also been used in this work in order to verify the accuracy of the empirical method just described. This alternative method is based on a relationship which may be derived as follows.

If the e.m.f. is related to the time by the expression

$$E = a' - b \log (t + \theta) \quad [26]$$

then differentiating

$$\frac{dE}{dt} = \frac{-b}{2.3 (t + \theta)} \quad [27]$$

and

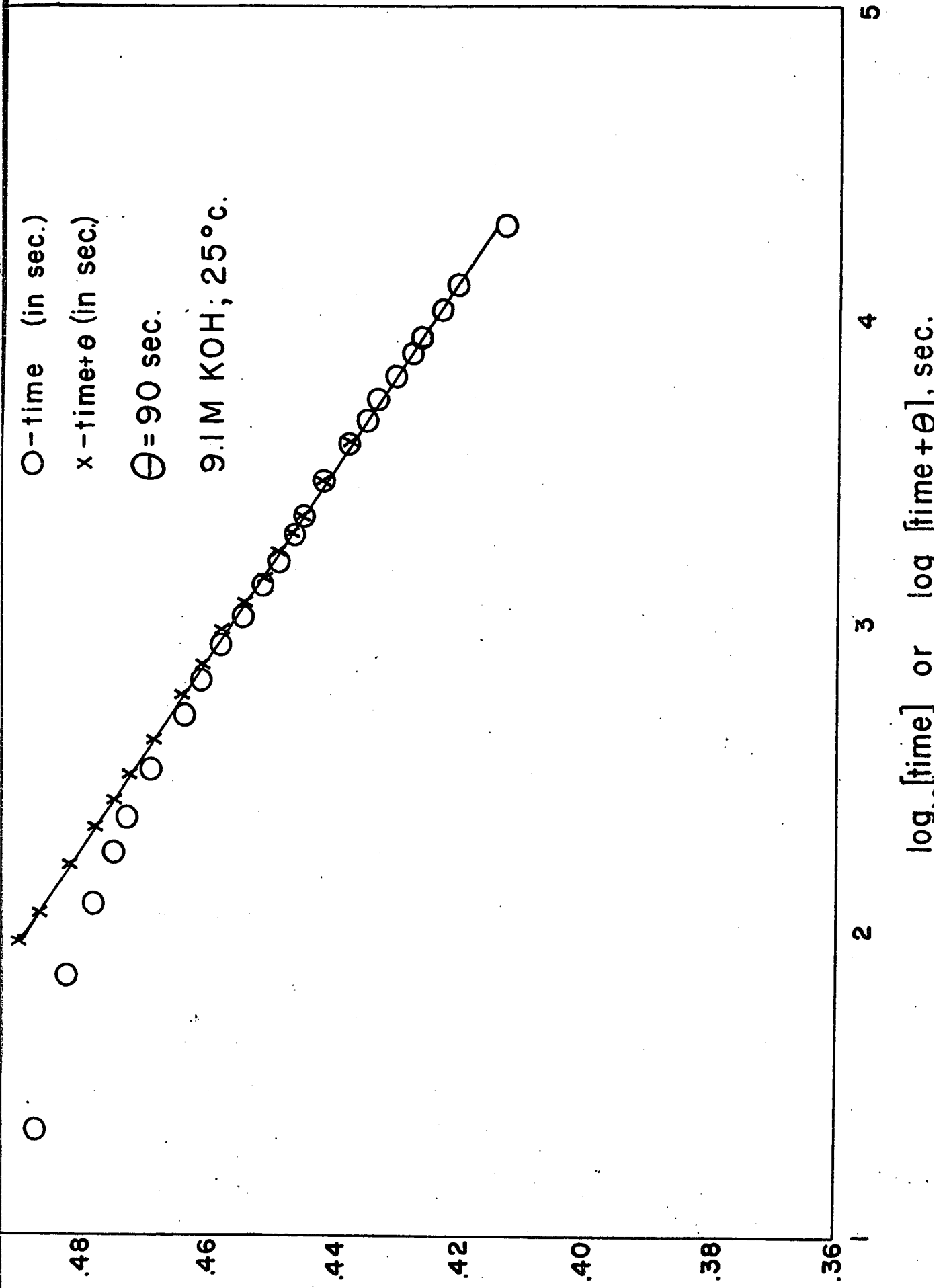
$$t + \theta = \frac{-b dt}{2.3 dE} \quad [28]$$

Substituting this value in equation [26] we have

$$E = a' - b \log \left[- \frac{b dt}{2.3 dE} \right] \quad [29]$$

* Except where changes of mechanism are involved as the potential falls.

Figure XXVIII - Comparison of a plot of e.m.f. vs
log (t) with that of e.m.f. vs
log (t + θ) for a typical nickel
oxide electrode.



which may be approximately written as

$$E = a' - b \log \left[-\frac{b}{2.3 \Delta E} \Delta t \right] \quad [30]$$

and for small, constant decrements of e.m.f. $-\Delta E$

$$E = a'' - b \log (\Delta t) \quad [31]$$

where the quantity Δt refers to the increments of time required for constant successive decrements of E.M.F. ΔE to occur during the overall decay of E.M.F. with time.

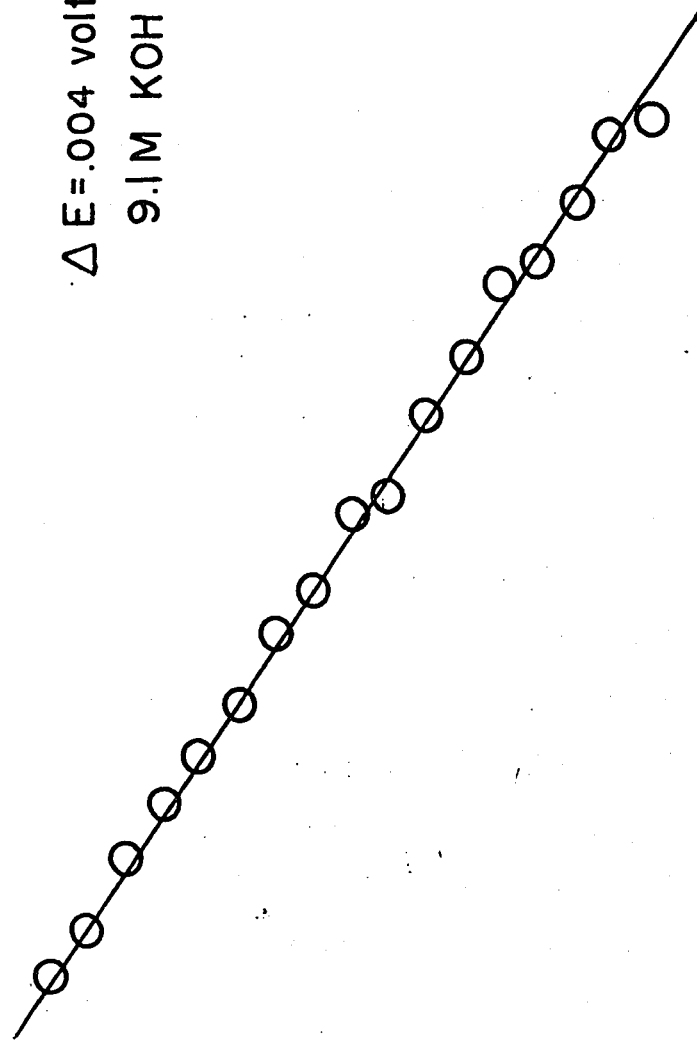
In Figure XXIX is shown such a plot of e.m.f. versus $\log \Delta t$ where Δt is the time required for a constant decrement of e.m.f. ΔE . In this way the slope of the e.m.f. decay line may be obtained independently of the value of θ . At long times (i.e. $t > 100 \theta$), t may be taken as approximately equal to $(t + \theta)$; hence, knowing the slope b as well as the coordinate of one point on the decay line at long times, it is possible to draw the line representing the expression

$$E = a' - b \log (t + \theta)$$

The value of θ may then be obtained graphically as the difference between the experimentally measured time at a given value of E and the corresponding value of $(t + \theta)$ at the same value of E . Values of θ determined in this way were not significantly different from those obtained by the empirical method ~~previously~~ described above. Moreover, no real gain in accuracy was

Figure XXIX - Plot of e.m.f. vs logarithm of the interval of time required for each 4.0 millivolt drop of e.m.f. during self-discharge on open circuit.
(Data is based on the same e.m.f. decay run as that referred to in Figure XXVIII).

$\Delta E = .004$ volt decrements.
9.1M KOH; 25°C.



achieved by using this more laborious method except in those cases when a change of slope, due to a change of mechanism, occurred after short times. The above method was hence used only as a check on the empirical method and in those cases where some difficulty was otherwise experienced in obtaining θ . The precision attainable by both methods was approximately $\pm 10\%$.

If the e.m.f. decay equation given previously is valid (viz. $E = a - b \log (t + \theta)$ where $\theta = \frac{bC}{2.3 i'}$), then two conditions will be fulfilled:

(a) the decay lines for various initial polarization currents on a given electrode will coincide although having different values of θ

(b) the values of θ should be inversely proportional to initial polarizing currents.

Figure XXX shows plots of e.m.f. vs $(t + \theta)$ for three successive decay runs on an electrode, where the initial polarizing currents i' were respectively 20, 3 and 1 milliampere. The small differences between these lines are due to the effects of ageing rather than to different i' values. In the example illustrated in Figure XXX the decay lines were taken on the same electrode in the order 3 M.A., 1 M.A and 20 M.A. for the initial polarizing currents i' .

Figure XXXI shows that θ is in fact satisfactorily linear with $1/i'$ and the line passes, as it should, through the origin,

Figure XXX - Test for condition (a): The slopes and intercepts of e.m.f. decay lines are independent of current density.

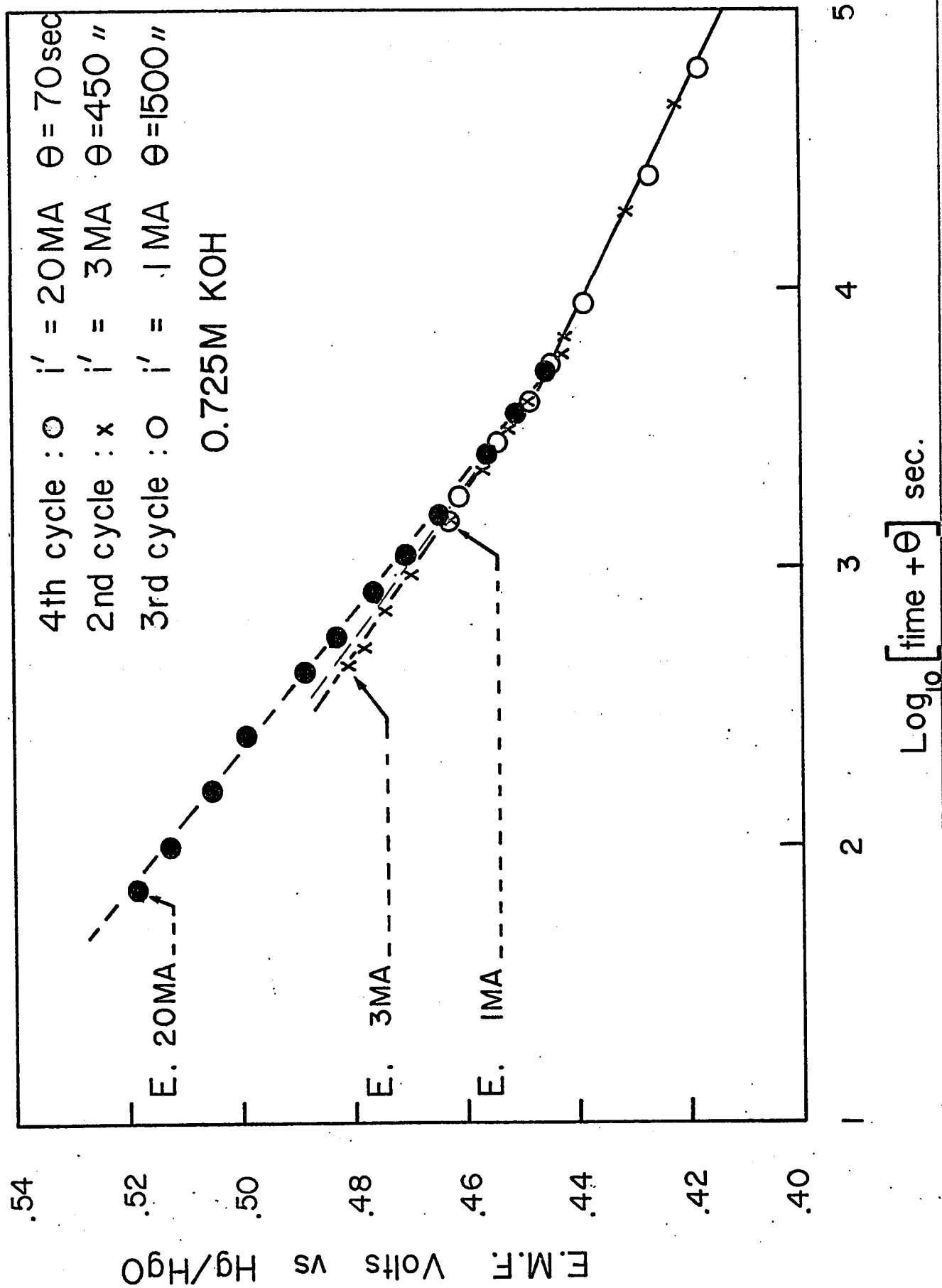
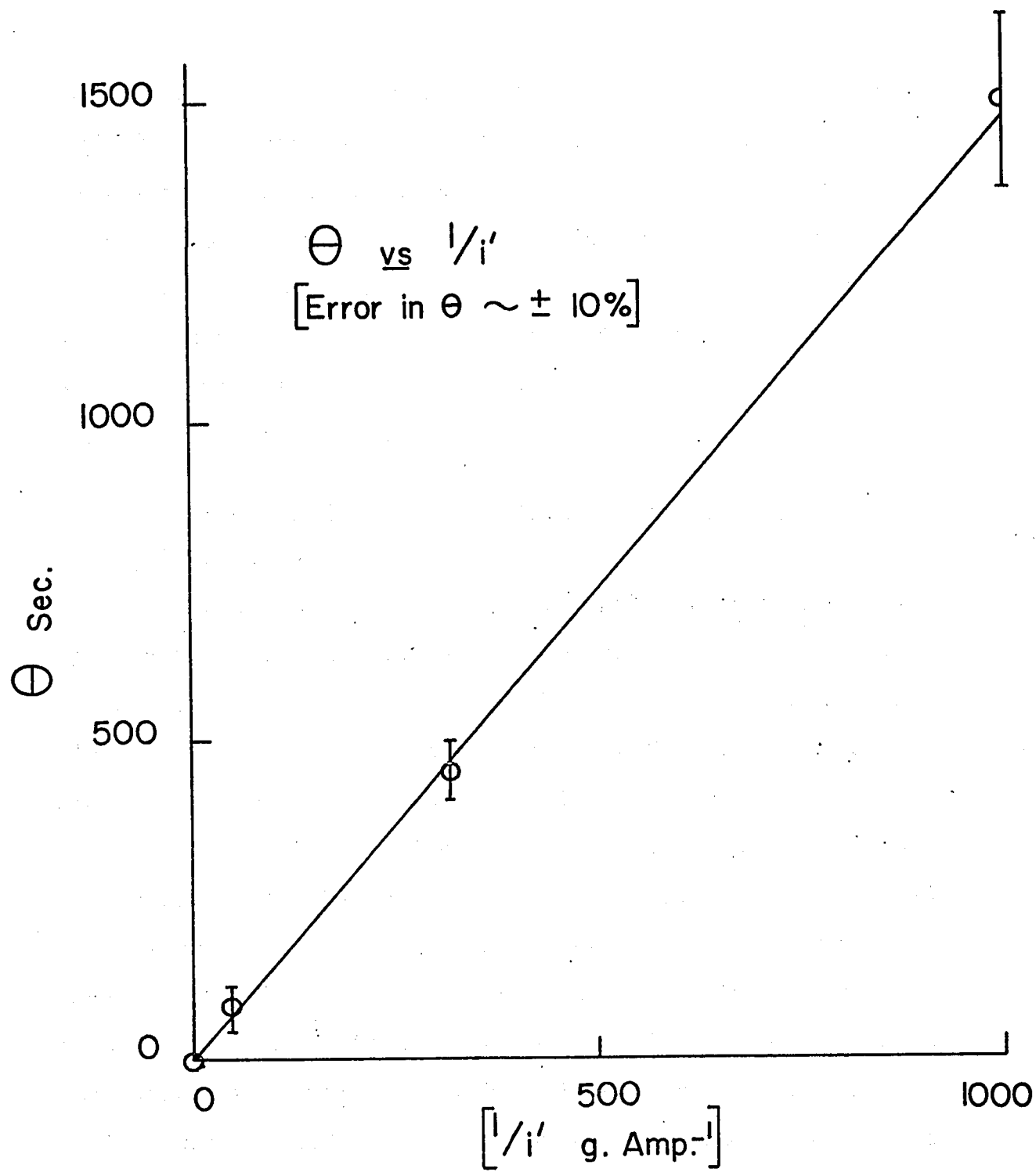


Figure XXXI - Test for condition (b): The quantity θ is linear with the reciprocal of the initial polarizing current.



i.e. condition (b) is likewise fulfilled. This serves as experimental proof that the analysis of e.m.f. decay is fundamentally correct and that the addition of θ to the time on open-circuit is legitimate and not just a device to straighten an otherwise curved line. (It may also be noted that θ has the significance of that time required for the electrode potential to fall from an initial hypothetical value of infinity to the actual starting potential.)

(ii) Capacitance from Charging Curves at Oxidized Electrodes

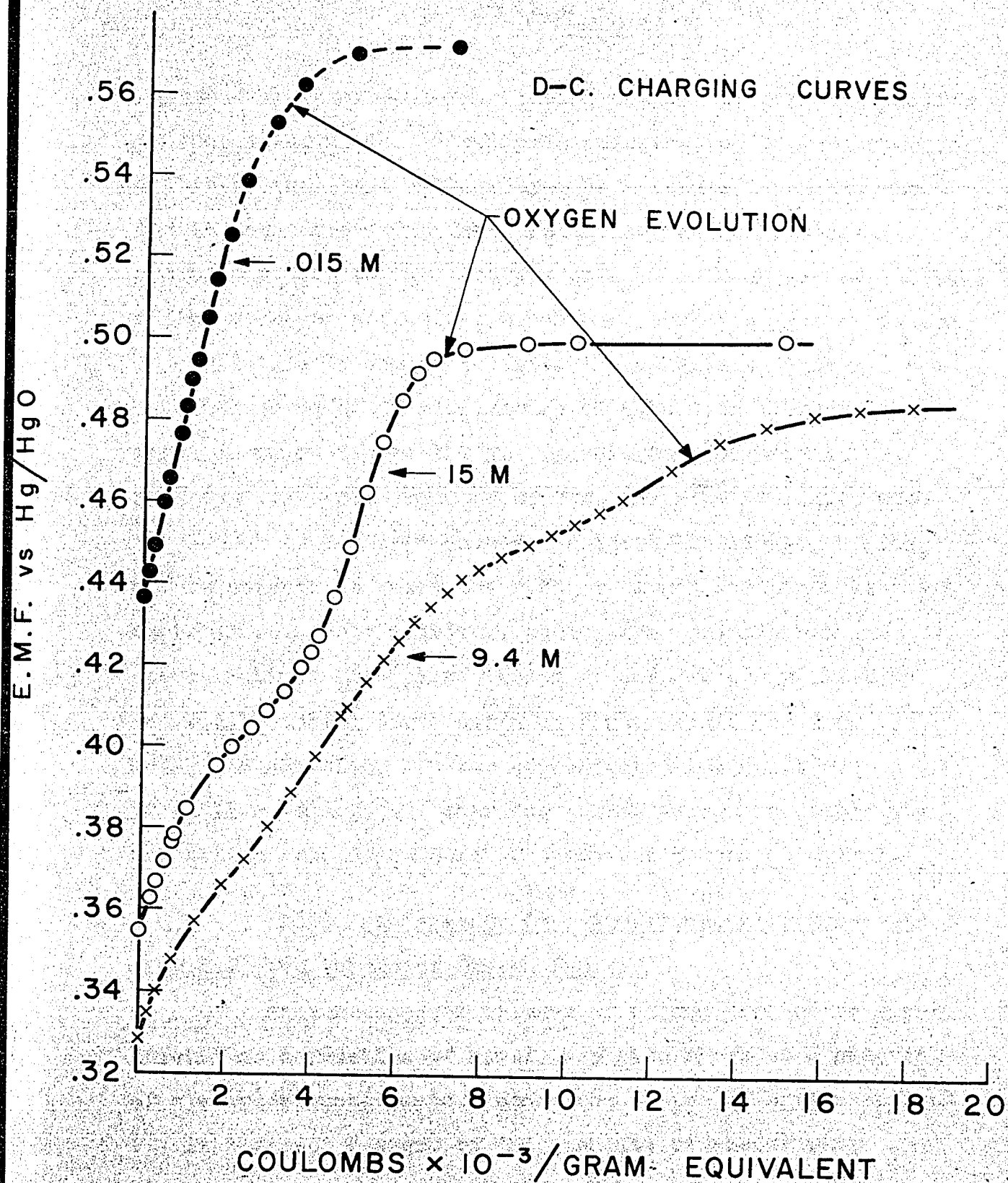
When an anodic or cathodic polarizing current is applied to a nickel oxide electrode, there is no instantaneous departure of the potential from the open-circuit value. The electrode potential, in fact, rises (or falls) relatively slowly from the initial open-circuit value in a manner analogous to the behavior of a condenser of abnormally large capacitance. When a partially charged nickel oxide electrode is polarized at constant current, the potential at first rises almost linearly and then curves into a region where the electrode potential is almost independent of quantity of charge passed and oxidation of the oxide takes place. When oxidation of the Ni(OH)_2 has proceeded to "completion" (i.e. approximately to the state " $\text{NiO}_{1.5}$ ") another sharper rise of potential is observed until a potential is reached where steady state anodic oxygen

evolution occurs at a rate corresponding to the whole polarizing current. Under these conditions, the potential then becomes constant. This behavior is illustrated by the upper (charging) curve in Figure IX. If, on the other hand, the electrode is initially in a state of oxidation corresponding to $\text{NiO}_{1.5}$, the potential, on anodic polarization, will rise directly to the potential for steady-state oxygen evolution. This behavior is illustrated in Figure XXXII. In these experiments, electrodes were fully charged and then left on open-circuit for about 24 hours in order to allow the potential to approach a steady value.* They were then anodically polarized at constant current and the e.m.f. was followed as a function of time by means of an electronic recording potentiometer. Initially, since the e.m.f. was too low for any appreciable oxygen evolution to occur, the current could be assumed to go almost entirely to charge the apparent capacitance of the electrode.

As higher potentials were reached, oxygen evolution did of course begin to occur at an appreciable rate taking up a progressively larger portion of the total polarizing current until finally the e.m.f. became constant with time and only

* The nature of these steady values, which are in fact mixed potentials, is discussed in a later section.

Figure XXXII - Charging of the surface on nominally
"charged" " $\text{NiO}_{1.5}$ " nickel-oxide
electrodes.



oxygen evolution occurred. [This behavior is formally similar to that observed in the cathodic polarization of mercury where initially the ionic double-layer capacitance is charged up and at high negative potentials the current corresponds almost entirely to the Faradaic process of hydrogen evolution.] In the range of potentials where the rate of oxygen evolution is negligible in comparison with the polarizing current, the capacitance dq/dE is directly obtainable from plots such as those shown in Figure XXXII. In solutions of low and intermediate concentrations of KOH, the rise of e.m.f. with the number of coulombs passed was initially linear, curving off at potentials where the rate of oxygen evolution became appreciable. This behavior, observed in solutions having concentrations less than 3 molar in KOH, is exemplified by the d.c. charging curve shown in Figure XXXII for a 0.015 molar KOH solution. In the concentrated KOH solutions (7 to 14.6 molar), the charging curves were more complicated exhibiting some dependence of capacitance upon potential.

(iii) Capacitance from Simultaneous Measurements of E.M.F. and Volume of Oxygen Evolved

Measurements of volumes of oxygen evolved on open-circuit as a function of e.m.f. may also serve as a measure of electrode capacitance. Since the volume of oxygen evolved V_{O_2} is a direct measure of the quantity of electricity

consumed (in self-discharge) over a given range of potential decay, we may write

$$-k \frac{dV_{O_2}}{dE} = \frac{dq}{dE} = C$$

where k is the factor $\frac{4F}{22400}$ for converting ml. of oxygen at N.T.P. to coulombs.

Plots of volumes of oxygen evolved corrected to N.T.P. and corrected for the partial vapor pressure of water over the solutions used, are shown in Figures XXXIII, XXXIV, XXXV and XXXVI. The corresponding capacitance at any given potential will be given by the reciprocals of the slopes of the lines multiplied by $\frac{4F}{22400}$. The capacitance at the beginning of the self-discharge process (i.e. at the highest anodic potentials) should be the same as that which gives rise to the quantity " θ " previously discussed. In fact, values of capacitance obtained from these oxygen volume measurements are in relatively good agreement with those calculated from θ and those obtained from the d.c. charging curves. A comparative summary of capacitance obtained by these methods at various temperatures and KOH concentrations is given in Table I. Also included in Table I is the state

Figure XXXIII - Volume of oxygen evolved on open-circuit as a function of electrode potential at -25° C. The electrode capacitance (inversely proportional to the slope) is observed to be quite constant in this region.

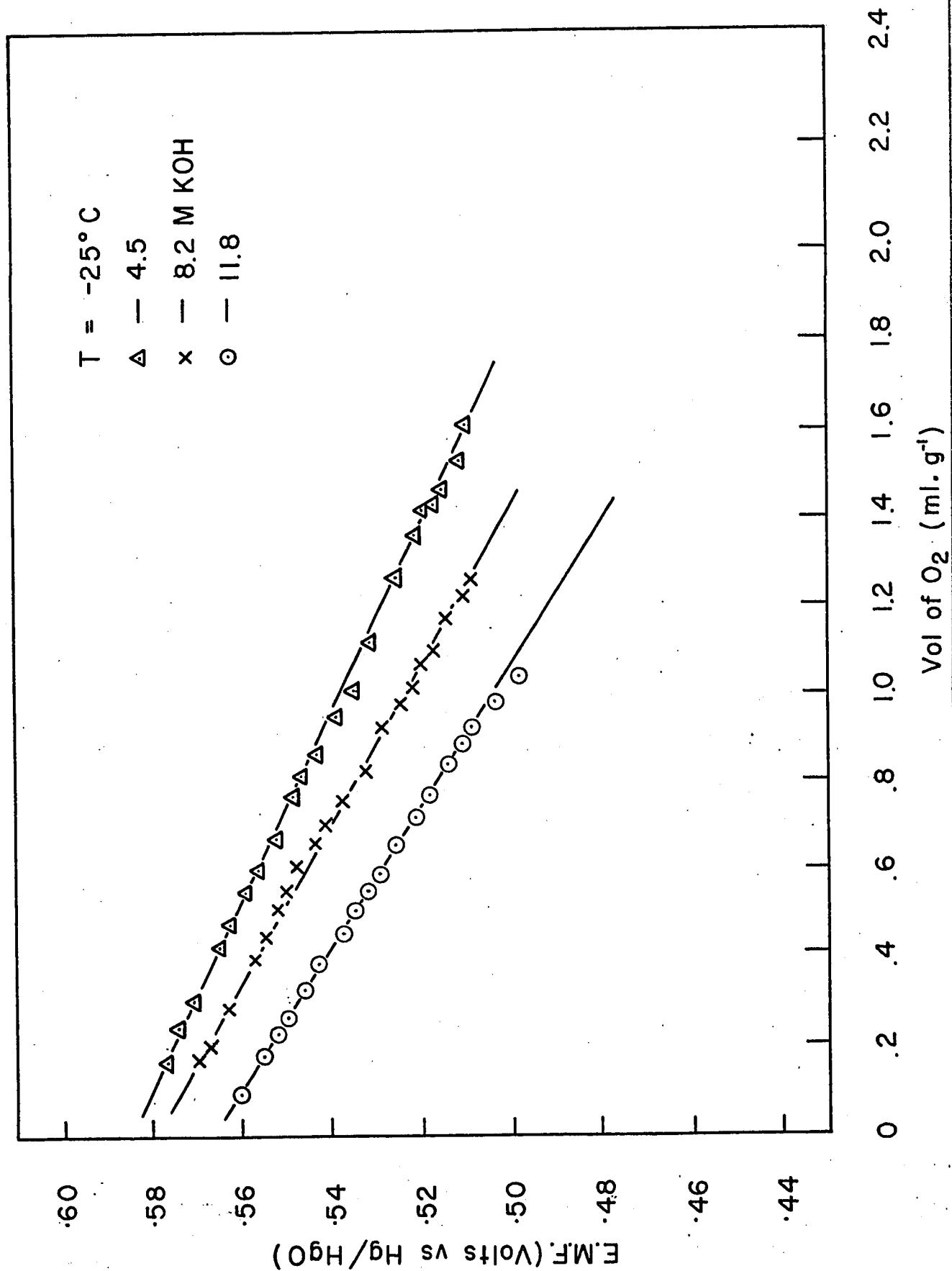


Figure XXXIV - Volume of oxygen evolved on open-circuit as a function of electrode potential at 1.0°C . Some dependence of capacitance on the electrode potential is evident.

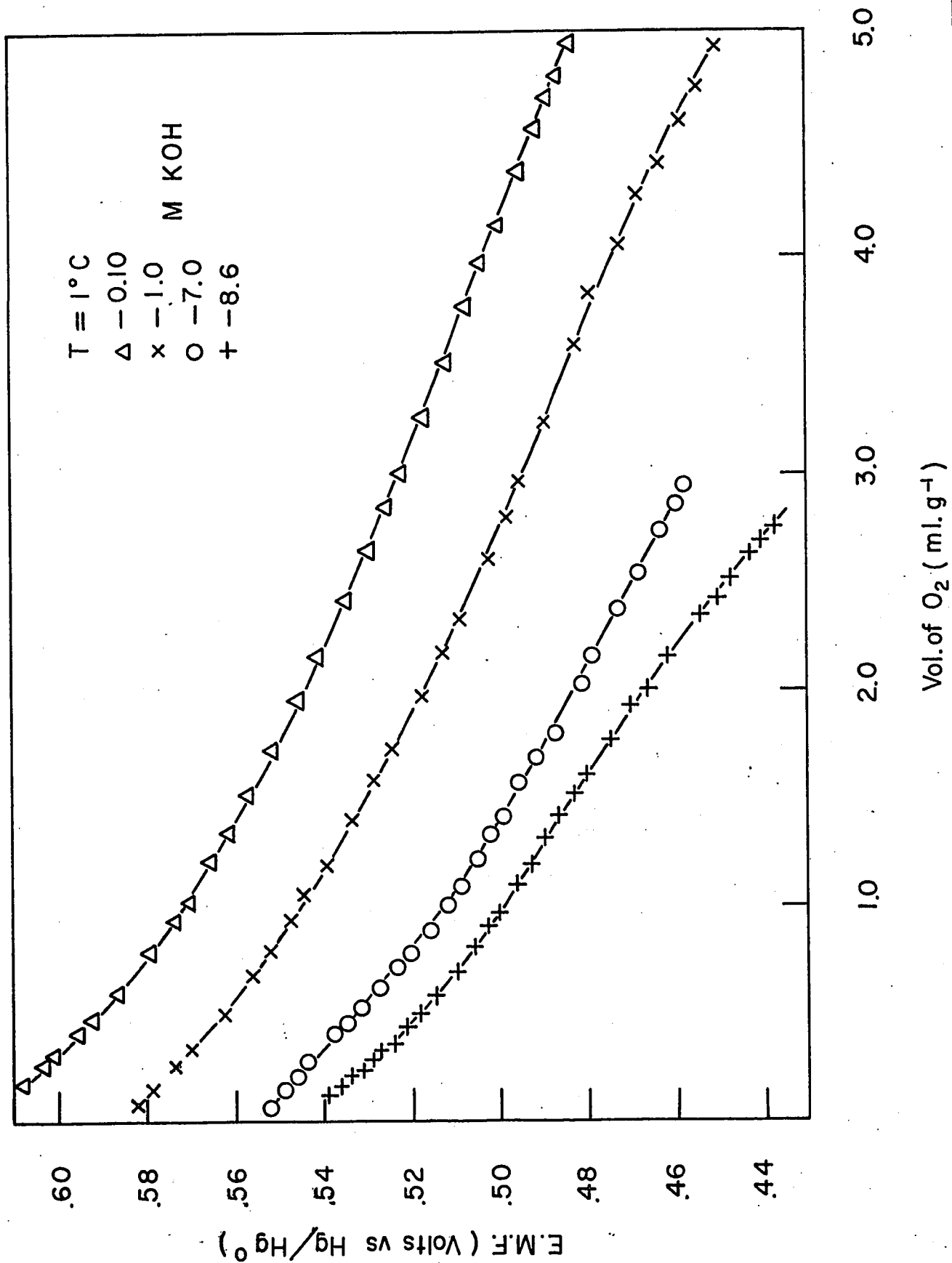


Figure XXXV - Volume of oxygen evolved on open-circuit as a function of electrode potential at 25° C. There is a very marked increase of capacitance as the electrode falls to lower potentials in the more dilute KOH solutions.

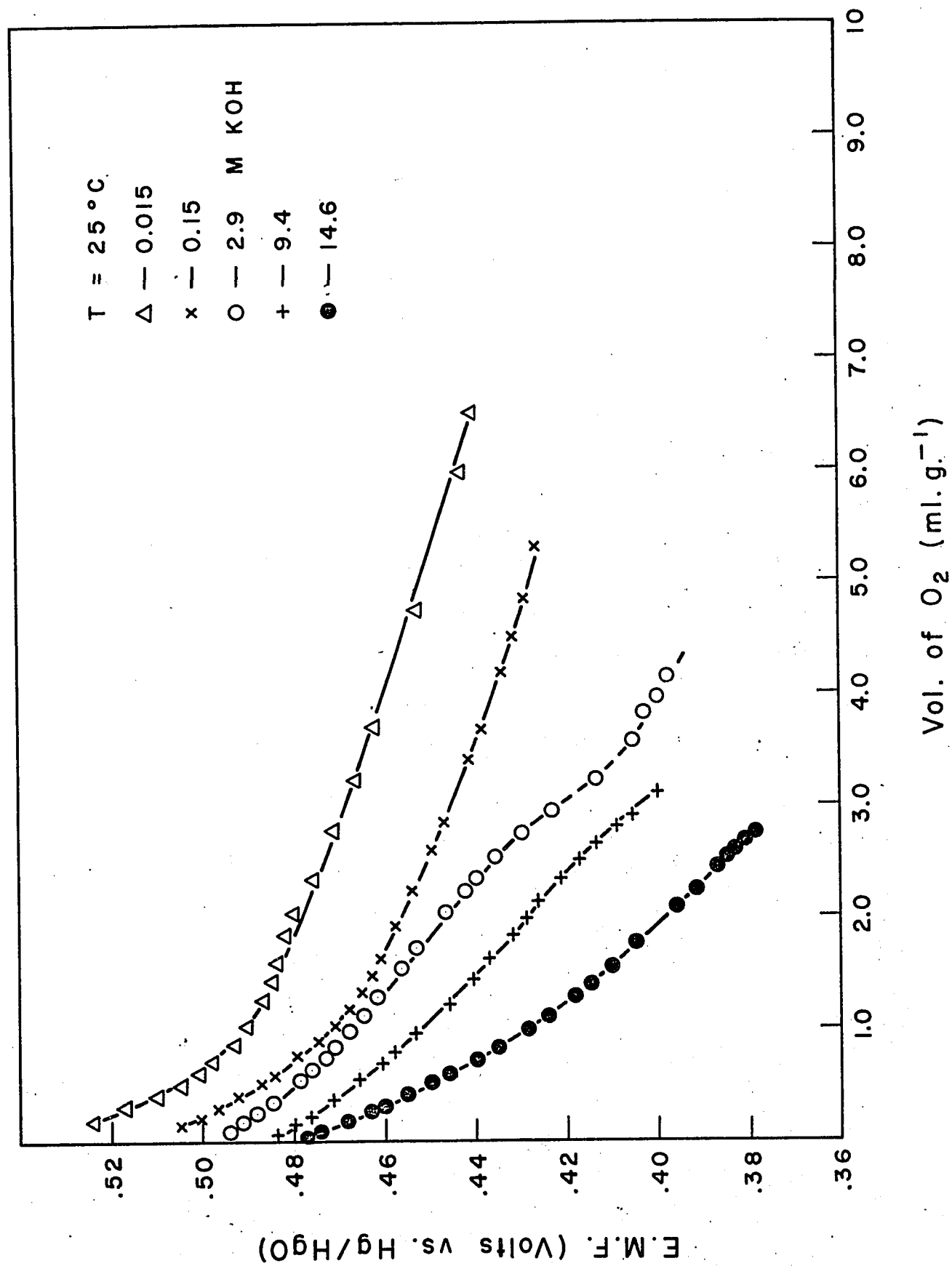
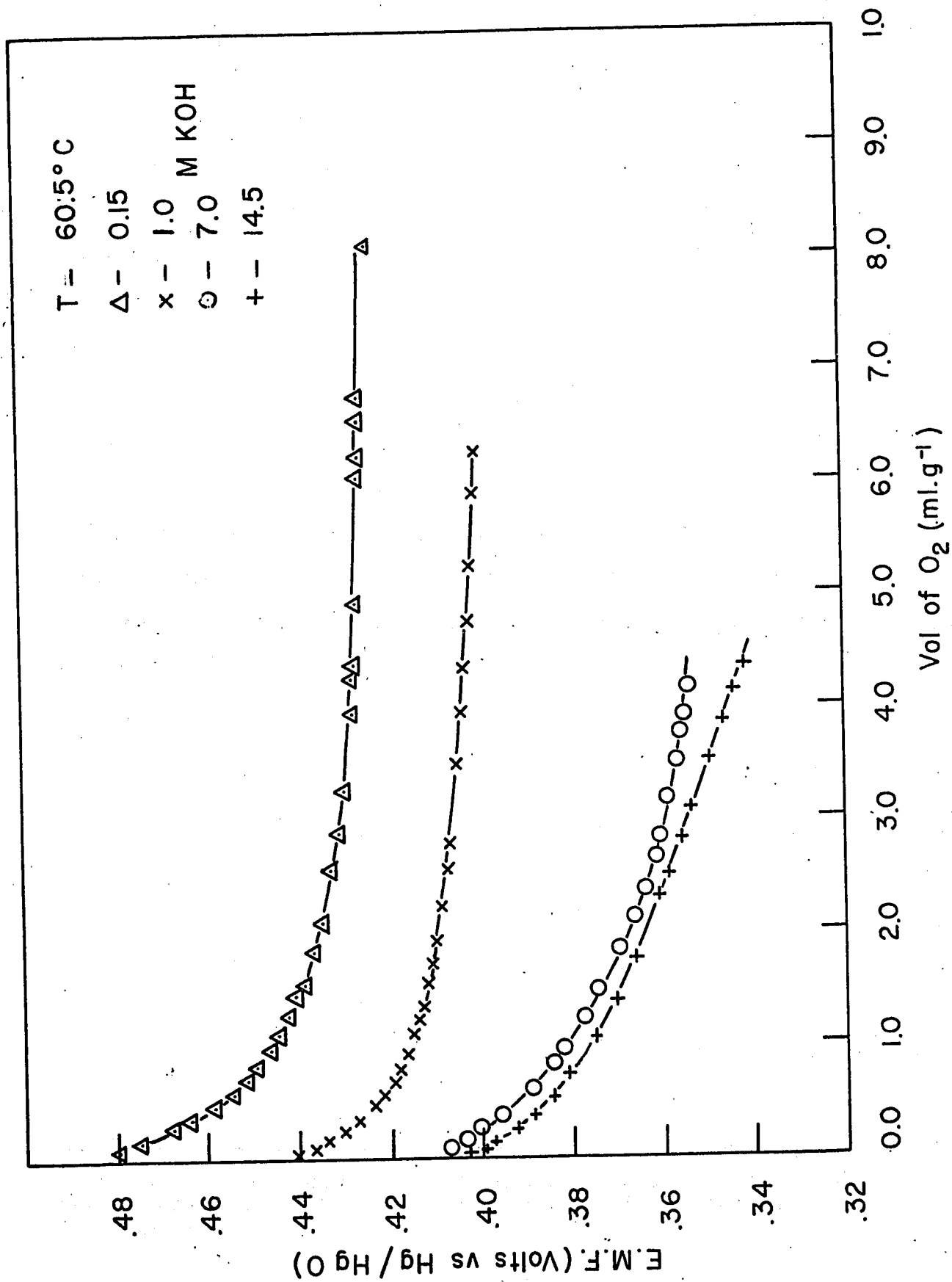


Figure XXXVI - Volume of oxygen evolved on open-circuit as a function of electrode potential at 60.5° C. Capacitance increases with falling potential at all concentrations of KOH.



of oxidation Q expressed as the ratio of electrochemically active oxygen* to nickel reached by the electrodes immediately after charging. Values of Q were determined by measuring the number of coulombs required, at constant current, to discharge the electrode to zero volts with respect to the potential of the Hg/HgO electrode. The last column in Table I refers to the quantity of charge, again expressed as a ratio of active oxygen to nickel, which is lost on self-discharge during the first 24 hours on open-circuit. The latter values are based on the measured volume of oxygen evolved from the electrode during this period.

* That is, the stoichiometric excess of O in the oxide above that corresponding to the formal composition "NiO" (cf. Forster, 33).

Table I

Surface Capacitance and Active Oxygen Content of Electrodes
as a Function of Temperature and KOH Concentration

<u>Temperature</u> °C	<u>Conc.</u> M/liter	<u>Surface Cap. F.g.⁻¹</u>		<u>Active Oxygen Atom</u> <u>per atom Ni</u>	
		<u>From θ</u> <u>($\pm 15\%$*)</u>	<u>From dE/dO_2^{**}</u> <u>($\pm 15\%$*)</u>	<u>Initial</u> <u>($\pm .03^*$)</u>	<u>Lost in</u> <u>first 24hr</u> <u>($\pm .005^*$)</u>
-25 °C	4.5	170	210	0.42	0.015
	8.2	170	130	0.42	0.010
	11.8	130	130	0.41	0.010
1.0 °C	0.10	300	210	0.43	0.030
	1.0	300	230	0.49	0.035
	7.0	230	400	0.46	0.022
	8.6	180	210	0.43	0.020
25 °C	0.015	320	230	0.41	0.035
	0.15	250	300	0.44	0.032
	0.93	400	600	0.43	0.035
	2.9	330	380	0.48	0.026
	7.0	330	480	0.52	0.028
	9.4	280	300	0.51	0.025
	14.6	180	240	0.57	0.020

Table I - continued.

60.5 °C	0.15	150	130	0.28	0.050
	1.5	160	160	0.39	0.035
	7.0	200	260	0.57	0.028
	14.4 -	220	240	0.67	0.035
	15.4	280	320	0.66	0.035

* The margins of error indicated are the maximum deviations from the mean values observed between replicate runs done under the same conditions of temperature and concentration.

** The values recorded here are of "initial" capacitance (cf. p. 133) at the highest anodic potential at the beginning of the E.M.F. decay. Substantially higher values arise at lower E.M.F.'s after the decay has proceeded for some time particularly in the more dilute solutions at higher temperatures.

CHAPTER IV

DISCUSSION

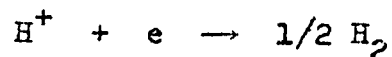
1. KINETICS OF SELF-DISCHARGE

a) Nature of the Self-Discharge Process

The oxidized nickel oxide electrode in aqueous solution must be considered as thermodynamically unstable since, as has been shown above, the electrode potential of the system $[Ni] Ni^{II} - Ni^{III}$ in alkaline solution is somewhat more positive than that of the reversible oxygen electrode in the same solution. The situation is analogous to that of a metal higher (i.e. less noble) than hydrogen in the electromotive series in aqueous solution. If, in the case of a metal, the half-cell potential for the process



is more negative (International Stockholm Convention) than the half-cell potential in the same solution for the reaction

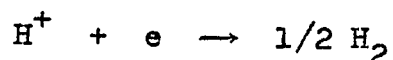


then dissolution or corrosion of the metal will tend to occur with evolution of hydrogen.

This dissolution or corrosion will proceed by an electrochemical mechanism; the anodic process

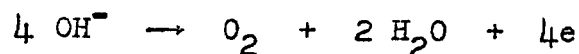


will supply electrons for the corresponding cathodic process



and the overall rate will be controlled mainly by the slower of either the anodic or the cathodic partial processes (12).

Similarly, an electrode system lying at a potential anodic to the reversible oxygen electrode (i.e., lower than oxygen in the electromotive series) will become reduced electrochemically with evolution of oxygen provided that two conditions are met. The first is that the anodic reaction



can occur at a finite rate on the electrode surface at the potential involved and the second is that a cathodic process can occur simultaneously that will take up the electrons liberated by the anodic process mentioned above.

The oxidized nickel oxide electrode can be quite readily discharged cathodically as demonstrated by its use as a battery electrode; thus the cathodic process required for a "corrosion" type mechanism of self-discharge is certainly possible. The anodic process of discharge of OH^- to liberate oxygen can likewise proceed without excessive activation polarization during "overcharge" (i.e., during anodic polarization after the electrode has become fully oxidized). Moreover, it is well known that the higher oxide of nickel

is more stable in the dry state than it is in contact with water (33). We must look therefore, for an electrochemical corrosion type of mechanism in the self-discharge of the nickel oxide electrode in aqueous solutions; it will be shown that the present work provides strong evidence for this viewpoint and allows a detailed electrochemical analysis of the processes occurring to be made. In this treatment of the corrosion type of process, we have therefore to decide from the observed kinetics: a) whether the anodic or the cathodic partial process is rate-determining and (b) having established this, determine what individual mechanism(s) in the net anodic or cathodic process determine its rate.

In order to obtain information which will enable the above mechanistic problems to be elucidated, the following techniques have been used, as described in detail above in Chapter II, section 9: (a) Steady-state polarization measurements (Tafel lines); (b) rates of self-discharge on open-circuit by oxygen evolution measurements and (c) rates of decay of e.m.f. on open-circuit using fully and partially charged electrodes.

The aims of the measurements have been: (a) to evaluate the rates of self-discharge and oxygen evolution as a function of KOH and water activity; (b) to establish, for the purpose of indicating reaction mechanism(s), the slopes of the

anodic and cathodic polarization lines; (c) to evaluate the mixed potentials; (d) to complement the above studies by determination of the direction of the H/D isotope effect in the self-discharge process.

Before we can make kinetic interpretations of polarization and e.m.f. decay slopes in terms of reaction mechanisms it will be necessary to examine the fundamental significance of the decay slopes and it will be shown that, for the present electrode systems, the simple analysis of such slopes published previously (8,9) are applicable only under certain limiting conditions.

b) Significance of E.M.F. Decay Lines

(1) Origin of the decay law and assumptions involved

In Chapter I the expression

$$\eta = a' - b \log (t + \theta)$$

was derived and it was shown that b , the semi-logarithmic slope, could be equal in magnitude but opposite in sign to the Tafel slope for the process. This e.m.f. decay method has, in fact, been suggested by a number of authors (8,9,78) as a convenient means of obtaining e.m.f.-log current density relationships (Tafel slopes) for electrode reactions. From data available from the present work, it is possible to examine critically this method of obtaining the Tafel slope and to determine some of the conditions under which it may or may

not be valid. The significance of applications to the nickel oxide will then be clear.

In the derivation of the above expression relating e.m.f. to $\log(t + \theta)$, two basic assumptions are made:

- (a) it is assumed that the same Faradaic process which was occurring prior to the interruption of polarization continues to occur on open-circuit at a diminishing rate determined by the potential difference across the interfacial double-layer;
- (b) the charge held in the electrode-solution interfacial capacitance is assumed to behave like that in an ideal condenser (i.e. the capacitance is independent of potential*).

(ii) Critical examination of the first assumption

The first assumption (that the same Faradaic process which was occurring prior to the interruption of polarization continues to occur on open-circuit) is unambiguous if the charge residing in the electrode-solution interface is purely "electrostatic" in nature (i.e. electrons in the metal and ions in the solution). If, on the other hand, the charge arises from chemisorbed intermediates on the electrode surface, it is no longer obvious that the process occurring on open-circuit is identical with that occurring during polarization. The intermediates already present on the surface may recombine or be otherwise desorbed (e.g. by an ionic mechanism) as they did during polarization but they need no longer be produced

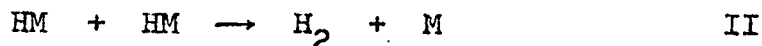
* That the capacitance could be a function of potential has been previously recognised (10) but the kinetic consequences of this possibility have not hitherto been developed explicitly.

in significant amounts* as was required during steady-state polarization. Thus the e.m.f. may fall owing to the disappearance of these intermediates (79), but now not all the steps in the overall process need occur in order to account for the observed decay of e.m.f.

This may be illustrated by reference to the following example concerning cathodic hydrogen evolution. Let us assume that^{ab} a metal, (e.g. Pt) the processes



and



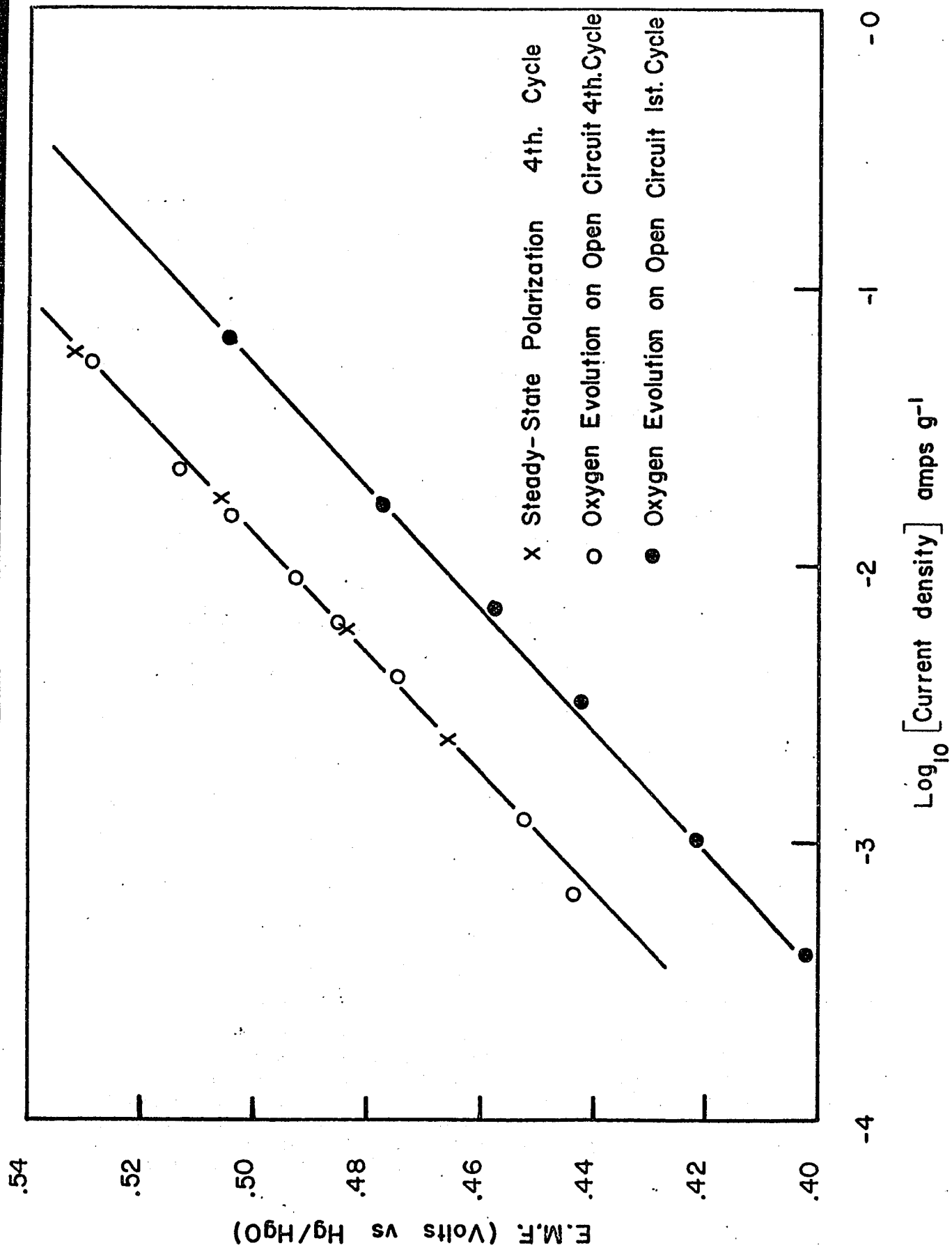
are occurring consecutively with II rate-determining during polarization ($b = 2.3 \text{ RT}/2\text{F}$). Upon interruption of the cathodic polarizing current, I and II will continue to occur at a diminishing rate as the double-layer capacitance is discharged. However, the capacitance due to charges in the double-layer (H_3O^+ on the solution side and electrons in the metal) will,

* We may note that owing to continuing discharge of the ionic double-layer on open-circuit, a small amount of ad-species will in fact continue to be formed. Since, however, the ionic double-layer capacity is usually 10-50 times smaller than the surface pseudo-capacity due to adsorbed films (75) the number of adsorbed species arising from continuing discharge of the ionic double-layer may be neglected in comparison with the number already present on the surface at the moment of interruption of the current.

in the case considered, be much smaller than that associated with H adsorbed on the metal. This latter pseudocapacity can, however, be effectively "discharged" simply by the recombination reaction II continuing to occur (without involving I and the "electronic" double-layer capacity) with an associated decrease of surface coverage by H and a consequent decrease of the potential difference across the double-layer. It is thus in this sense that when consecutive reactions involving chemisorbed intermediates are proceeding, the decay processes occurring on open-circuit do not necessarily involve the same overall process (viz. I followed by II in the present example) as that occurring during polarization.

In the present work, the rate of oxygen evolution observed during self-discharge measures unambiguously the true rate of the process occurring on open-circuit as a function of potential. It is in fact observed that if this rate, expressed in amperes per gram, is plotted logarithmically as a function of potential, straight line regions generally result (Figures XIV-XVII) and the slopes of these lines are identical with those obtained from results of steady-state polarization measurements. Thus, plots of results obtained by these two methods in 7.0 molar KOH solutions at 25° C are shown in Figure XXXVII. The lower line (full circles) representing the

Figure XXXVII: Rates of self-discharge obtained from (a) measurements of oxygen evolution on open-circuit (O), and (b) steady state polarization (X). [Similarity of Tafel parameters is strong evidence that the same process is rate-determining in the two cases].



rate of self-discharge on open-circuit was obtained from measurements of rates of oxygen evolution on a freshly prepared electrode after a single cycle of charging. The points represented by circles are from open-circuit measurements on a similar electrode which was given three previous charging and discharging cycles and finally the rate of oxygen evolution was followed after the fourth-charge. The points represented by crosses are from results of steady-state polarization measurements made on electrodes which had been given three prior charging and discharging cycles.* Results obtained from the steady-state polarization and the oxygen evolution measurements on open-circuit are in agreement to within 5 m.v. if the experiments are conducted under comparable conditions. This agreement is well within experimental error for work of this kind and must be regarded as quite satisfactory.

This result shows that the process occurring on open-circuit is kinetically indistinguishable from that occurring during steady-state anodic polarization and thus the first assumption made in the derivation of the decay

* In these series of measurements it was found that the electrodes which had been given several cycles of charging and discharging gave more reproducible results. This may be attributable to the opportunity thus provided for crystallites of the hydrated oxide to reach equilibrium states by processes analogous to those occurring during digestion of precipitates in gravimetric analysis.

equation is in fact experimentally justified. As we have shown above, this does not necessarily imply however, that the processes occurring during steady-state polarization and during open-circuit oxygen evolution are identical in all respects. The rate-controlling step must, of course, be the same but steps preceding it which are essentially in equilibrium need not proceed in a net forward direction (under the conditions assumed above for the surface capacity) in the case of open-circuit decay as they must during steady-state polarization.

(iii) Critical examination of the second assumption

As shown previously (Results section 1, (a) ii) the slopes of the e.m.f. decay lines are not always identical with those of the e.m.f. - $\log [dV_{O_2}/dt]$ lines. Since the rate of oxygen evolution measures directly the true rate of self-discharge, the potential dependence of the rate obtained by this procedure must be accepted as correct and corresponding to the true, kinetically significant, Tafel slope b . In the cases where the slope of the e.m.f. decay line and that of the oxygen evolution line are not in agreement, the origin of the discrepancy must therefore be sought in the assumptions involved in the e.m.f.-decay method.

We have mentioned above that the second assumption made in deriving the e.m.f. decay expression is that the

surface capacitance is constant over the full range of potentials covered during the decay of e.m.f. This implies that

$$- \frac{dq'}{dE} = \text{constant}$$

where q' is the quantity of electricity consumed during self-discharge and E is the varying electrode potential observed during open-circuit decay. Since (see also section 3, c, iii)

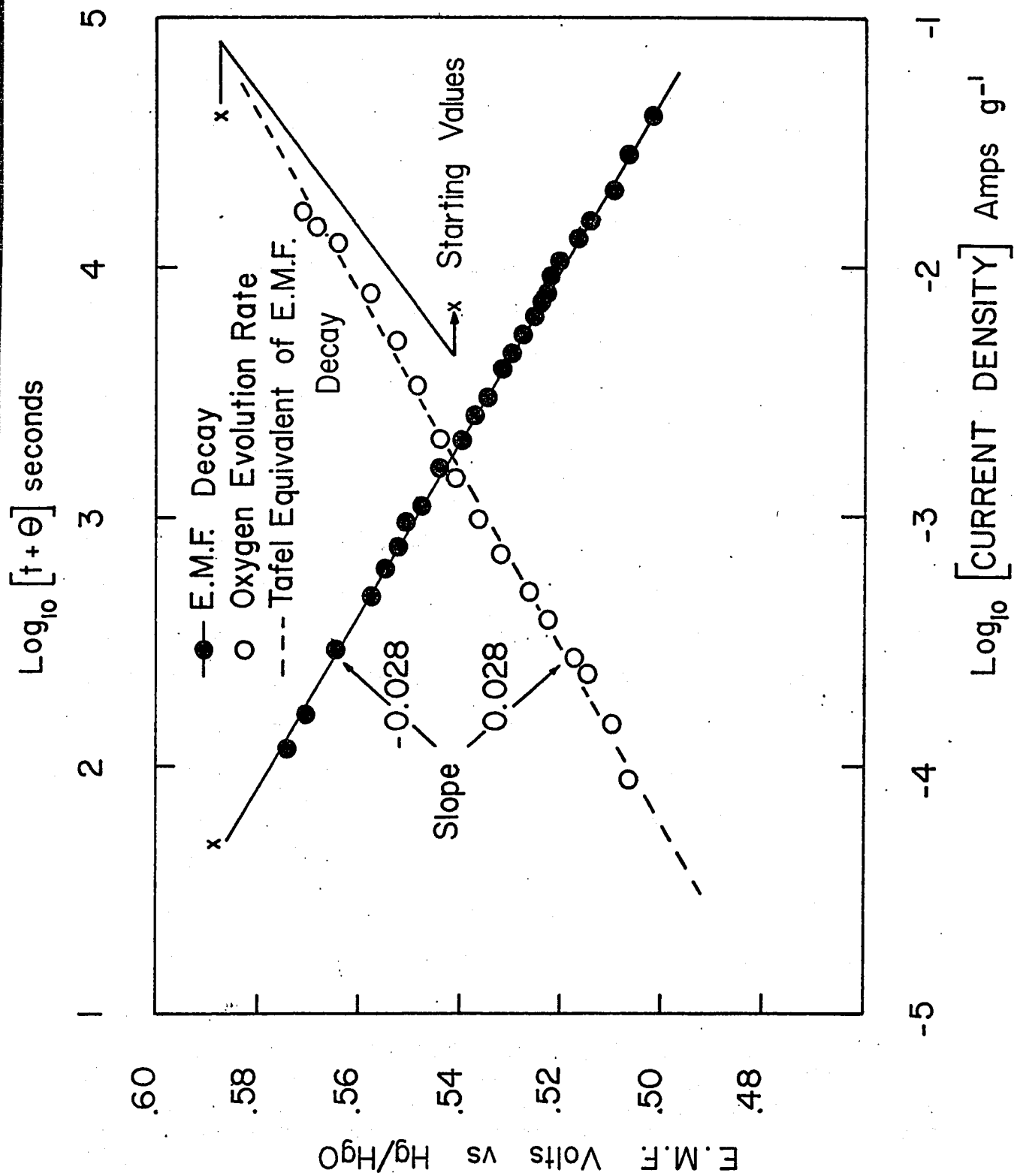
$$q' = k V_{O_2} \quad (k = 4F/22400)$$

where V_{O_2} is the volume of oxygen in ml. at N.T.P. evolved during a certain degree of decay of e.m.f. E , the assumption of constant capacitance leads to

$$\frac{dV_{O_2}}{dE} = \text{constant}$$

and thus a plot of e.m.f. vs. volume of oxygen evolved should be linear, the slope of this line then being inversely proportional to the capacitance. An examination of Figures XXXIII, XXXIV, XXXV and XXXVI shows that this behaviour is in fact observed only under certain conditions. Thus at -25°C , (Figure XXXIII) the e.m.f. is observed to be directly proportional to the quantity of oxygen evolved so that the capacitance is constant. We can therefore expect that the e.m.f.-log $(t + \theta)$ and the e.m.f.-log $[dV_{O_2}/dt]$ lines will have equal and opposite slopes. An examination of Figure XXXVIII

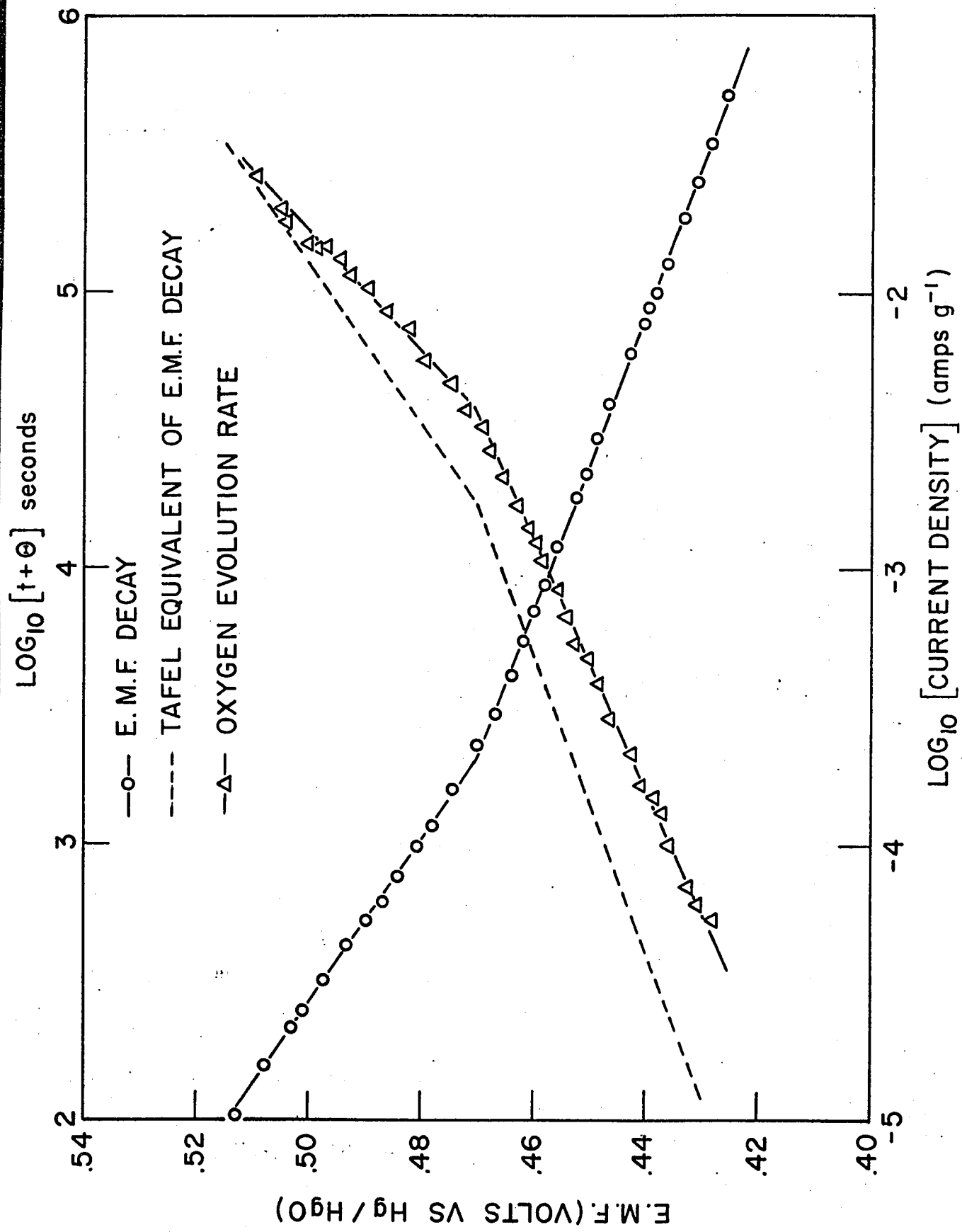
Figure XXXVIII: E.M.F. decay line compared with the true Tafel line (from oxygen evolution measurements) for an electrode in 8.2 molar KOH at -25° C. The dotted line represents the hypothetical Tafel line (Tafel analogue) which would be obtained from decay measurements assuming the decay slope to be numerically identical with the Tafel slope.



shows this to be true. In Figure XXXVIII these two lines are represented, together with the Tafel analogue* of the e.m.f. decay slope (shown by a dotted line) for the case of an 8.2 molar solution at -25° C. It is in fact observed that the slopes of the e.m.f.-log $(t + \theta)$ and that of e.m.f.-log $[dV_{O_2}/dt]$ have numerically equal slopes in this case. At other temperatures, however, the capacitance is observed to increase as the e.m.f. decays to lower values (cf. Figures XXXIV, XXXV and XXXVI). Under these conditions, we can no longer expect that the slopes of the e.m.f.-log $[t + \theta]$ and of e.m.f.-log $[dV_{O_2}/dt]$ plots will be equal in magnitude since the assumption of constant capacitance no longer holds. Experimentally it is found that in these cases the slopes are in fact different. An examination of Figure XXXV shows that the capacitance in the 0.15 molar solution at $+25^{\circ}$ C is a function of potential and when the e.m.f.-log $[t + \theta]$ and the e.m.f.-log $[dV_{O_2}/dt]$ slopes are compared for this case (see Figure XXXIX) they are seen to be significantly different. The slope of the e.m.f.-log $[t + \theta]$ line is lower than that of the corresponding e.m.f.-log $[dV_{O_2}/dt]$ line. This is the

* We refer here to the "Tafel analogue" of the e.m.f. decay slope as that Tafel line whose parameters i_0 and b are the same as those determining the slope and position of the decay line whose double layer or surface capacitance is independent of potential.

Figure XXXIX: E.M.F. decay line and its Tafel
analogue compared with the true Tafel
line (from oxygen evolution measurements)
for an electrode in 0.15 molar KOH
solution at 25° C.



direction expected for an increase of capacitance with decreasing e.m.f.; thus, for a given rate of self-discharge, the e.m.f. will fall less rapidly if the capacitance gets progressively larger, than it would if the capacitance remained constant. A quantitative examination of the effect of varying surface capacitance is given below.

(iv) Relation between E.M.F. decay slopes and oxygen evolution slopes

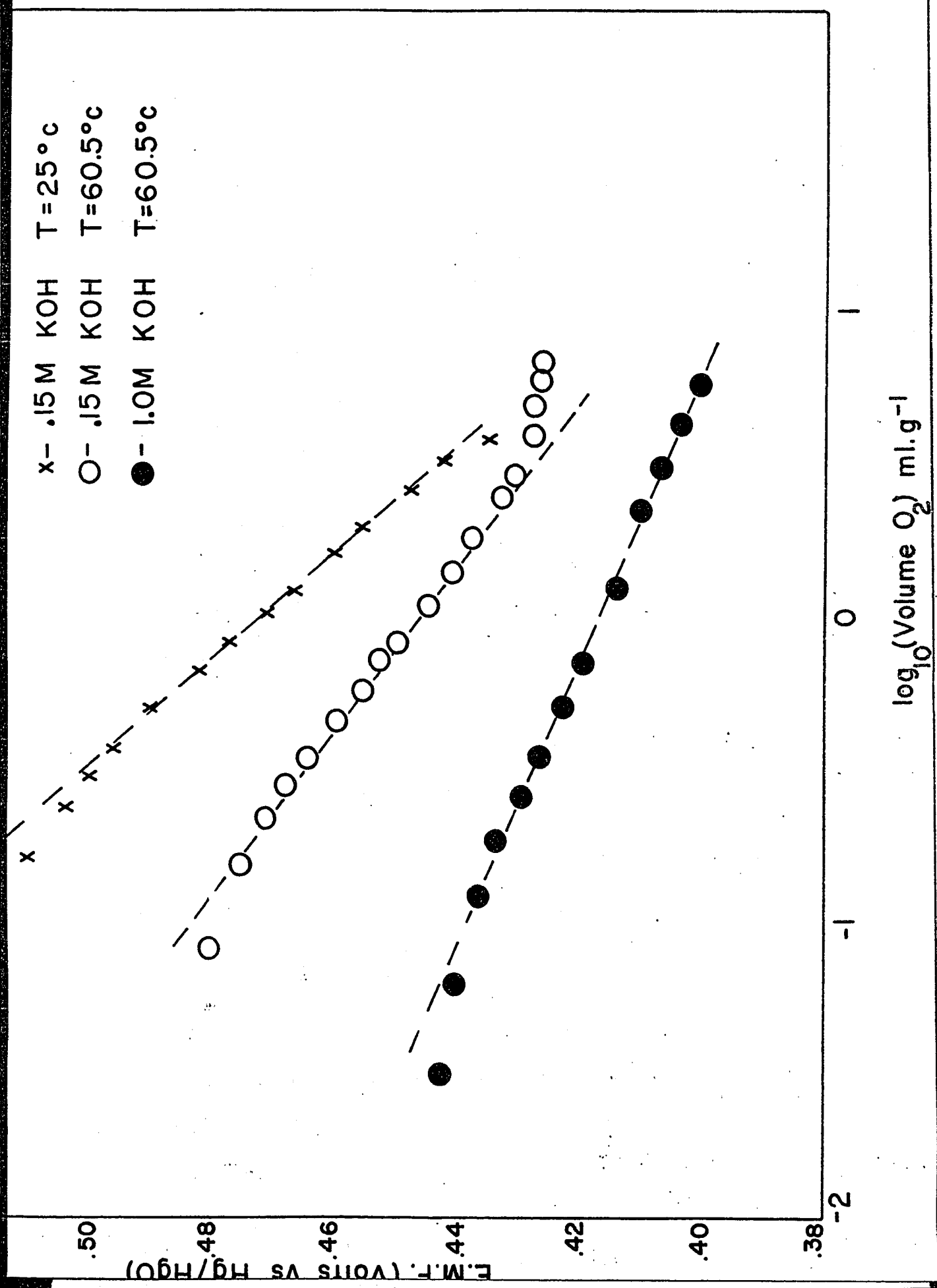
In those cases where the capacitance involved in the e.m.f. decay is not constant, it is frequently found that an exponential relationship exists between the volume of oxygen evolved V_{O_2} and the electrode potential E . Such is seen to be the case for the results shown in Figure (XL), where the e.m.f. is plotted against the logarithm of the volume of oxygen evolved for three experiments at different concentrations and temperatures.

The theoretically predicted open-circuit e.m.f. decay behavior under these conditions may be arrived at from the following considerations. If the charge q lost during a decrease of potential of an electrode is an exponential function of the potential E , being of the form

$$q = A e^{E/b_2} \quad [32]$$

where A and b_2 are empirical constants, and b_2 may have a

Figure XL: Plots of the logarithm of the volume of oxygen liberated on open-circuit as a function of the E.M.F. of the electrode.



positive or a negative value, then we can express the discharge rate in terms of η as

$$i = \frac{dq}{dt} = \frac{A}{b_2} \exp [\eta / b_2] d\eta / dt \quad [33]$$

Moreover, we have from equation [8] (Chapter I) that

$$i = i_0 \exp [\eta / b_3] \quad [34]$$

where b_3 is the Tafel slope $[-azF/RT]$ for the rate-determining process.

Equating [33] and [34]

$$\frac{A}{b_2} \exp [\eta / b_2] \frac{d\eta}{dt} = i_0 \exp [\eta / b_3]$$

which upon integration leads to

$$\frac{A}{b_2 i_0} \frac{b_2 b_3}{b_3 - b_2} \exp \left[\eta \left(\frac{b_3 - b_2}{b_2 b_3} \right) \right] = t + \theta \quad [35]$$

Taking logarithms and rearranging [35] gives

$$\eta = A' + \frac{b_2 b_3}{b_3 - b_2} \ln (t + \theta) \quad [36]$$

The e.m.f. decay slope (b_1) is thus given as

$$b_1 = \frac{b_2 b_3}{b_3 - b_2} \quad [37]$$

For the boundary condition $t = 0$, η will equal η' the initial overpotential and i will equal i' the initial polarizing current. Therefore

$$\theta = \frac{A}{b_2^1} \frac{b_2 b_3}{b_3 - b_2} \exp \left[\frac{\gamma' (b_3 - b_2)}{b_2 b_3} \right] \quad [38]$$

but

$$q = A \exp [\gamma/b_2]$$

and

$$\frac{dq}{d\gamma} = C = \frac{A}{b_2} \exp [\gamma/b_2] \quad [39]$$

Combining equations [34], [38] and [39]

$$\theta = \frac{C'}{1} \cdot \frac{b_2 b_3}{b_3 - b_2} \quad [40]$$

where C' is the capacitance involved in the self-discharge process at $t = 0$. It will be noted that evaluation of θ for a range of potentials (and hence initial current densities) could lead to a means of determining C as a function of potential.

In form, equation [36] is basically the same as one derived by Lukovtsev and Temerin (77) who assumed the electrode potential E to be related to the degree of oxidation or charging of the bulk oxide by the Nernst expression

$$E = E^0 + b_2 \log \frac{q_{ox}}{q_{red}} \quad [41]$$

where q_{ox} and q_{red} are the degrees of oxidation and reduction, respectively of the bulk oxide. We have suggested above that a surface pseudo-capacity* arises from adsorbed O-containing radicals. In order to affect

* Footnote: see over.

* The evidence in support of the view that the self-discharge effects and the capacitance involved refer to the surface phase rather than to the bulk may be summarised as follows:

a) The volumes of oxygen evolved on open-circuit up to quite long times, e.g. 7 days, are from 2 to 5 ml. at N.T.P. and with the B.E.T. surface area of the dry material of $40 \text{ m}^2 \text{ g}^{-1}$ of active "nickel III" oxide, these volumes correspond to coverage of less than a monolayer of O or OH on the nickel oxide particles. We believe we are hence justified in speaking of the "surface pseudo-capacitance".

b) The volumes of oxygen evolved on self-discharge over a potential range of ca. 150 mV. correspond only to 5-8% of the total "active oxygen" in the bulk material;

c) The dependence of E.M.F. upon the logarithm of the volume of oxygen evolved on self-discharge is determined by an apparent Nernst coefficient which is no simple fraction of RT/F (see Fig. XL) and varies with KOH concentration and temperature as might be expected for a non-stoichiometric surface phase and as discussed by Ruetschi for electrochemically adsorbed H and O bearing partial charges (79).

c) The variation of polarisation with time during a long galvanostatic pulse is quite extended both at the fully and the semicharged electrodes, indicating the presence of an effective capacitance in parallel with the current input to the bulk material as discussed previously (5). This capacitance is of the same magnitude as that deduced from θ and from the slopes of the E.M.F.- O_2 volume plots but is much less than the mean capacity associated with the bulk material.

charging of the bulk, or oxygen evolution, this capacity must first be charged up and it is this capacity (in parallel with the smaller ionic double-layer capacity) which is involved in the processes leading to decay of e.m.f. on open-circuit. Hence, we require for the interpretation of e.m.f. decay behavior, when C is not constant, a relation such as equation [41] between E and q_{ox} for the surface layer rather than for the bulk. As we have seen above, it is experimentally found that E under certain conditions is a linear function of V_{O_2} the volume of oxygen evolved (see Figure XXXII) whilst under other conditions the relationship between E and V_{O_2} is more nearly an exponential one (Figure XL). Since we can write $(V_{O_2})_t$ as proportional to $[(q_o)_s - (q_t)_s]$, the difference between the charge $(q_o)_s$ associated with a surface phase in a more highly oxidized condition at $t = 0$ (corresponding to a certain degree of coverage by adsorbed radicals) and the charge $(q_t)_s$ corresponding to some less covered or oxidized surface phase, it follows that under certain conditions (Figure XL)

$$E \propto \log [(q_o)_s - (q_t)_s] \quad [42]$$

and under other conditions (Figure XXXII)

$$E \propto [(q_o)_s - (q_t)_s] \quad [43]$$

When equation [43] holds, $-b_1$ and b_3 should be identical. This is found experimentally, for example as shown in Figure XXXVIII, where the Tafel line equivalent to the E.M.F. decay, assuming the same b values (dashed line), is identical with the line based on experimental points (circles) obtained from direct measurements of oxygen evolution rates during E.M.F. decay, i.e. from the true experimental Tafel line obtained during decay on open circuit. When equation [42] holds (dilute solutions and/or higher temperatures), $-b_1 \neq b_3$ and b_2 can be obtained empirically as the coefficient $dE/d \log [(q_o)_s - (q_t)_s]$. The slope b_1 can then be compared with $b_2 b_3 / b_3 - b_2$ (equation [37] as shown in Figure XXXIX where the experimental E.M.F. decay line is shown for 0.15 M KOH solution at 25° C, and compared with (a): its Tafel line equivalent based on the same b values for each part of the inflected line and also (b): the true experimental Tafel line determined during E.M.F. decay by kinetic microvolumetric oxygen measurements. It may be seen from Figure XXXIX that the lines for E.M.F. vs $\log (t + \theta)$ and for E.M.F. vs $\log$ [current density] (calculated from the open-circuit oxygen evolution rates) both show inflections at a more or less characteristic potential. The inflections in the E.M.F. decay lines are therefore not artifacts due, for example, to changes of capacity, and hence may legitimately be examined in terms of changes in rate-determining mechanism of oxygen evolution. However, since the

Table II

TAFEL SLOPES b_3 AND E.M.F. DECAY SLOPES b_1 IN

THE VARIOUS POTENTIAL REGIONS

Temp. °C	Conc. moles per litre	Region I		Region II		Region III	
		O_2 b_3	E.M.F. decay $-b_1$	O_2 b_3	E.M.F. decay $-b_1$	O_2 b_3	E.M.F. decay $-b_1$
				$\pm .004$	$\pm .002$	$\pm .004$	$\pm .002$
- 25	4.5 8.2* 11.8			0.035 0.038 0.035	0.034 0.034 0.036		
1.0°C	0.10* 1.0* 7.0 8.6	(0.071) (0.076)	(0.052) (0.058)	0.046 0.044 0.042 0.039	0.045 0.035 0.033		
25°C	0.015 0.15 0.93* 2.9* 7.0 9.4 14.6			0.053 0.045 0.040 0.045 0.041 0.035	0.042 0.034 0.039 0.034 0.037 0.032 0.028	0.025 0.022 0.018	0.020 0.017 0.022 0.016

(Table II, Continues on next page)

Table II (Continued)

Temp. °C	Conc. moles per litre	Region I		Region II		Region III	
		O ₂ evol. b ₃	E.M.F. decay -b ₁	O ₂ evol. b ₃	E.M.F. decay ± .002**	O ₂ evol. b ₃	E.M.F. decay -b ₁ ± .002**
60.5	0.15			0.051	0.035	0.027	0.018
	1.5			0.044	0.024	0.021	0.011
	7.0			0.048	0.028	0.021	0.016
	14.4 *	(0.093)	(0.035)	0.040			
	15.4 *	(0.092)	(0.041)	0.035			

* Only one experiment done under these sets of conditions. Others are average values from two to five experiments.

** Limits shown here are based on the mean reproducibility of b values for the cases where more than one run under a given set of conditions was carried out.

Values of b given in this Table have all been converted to equivalent values at 25° C in order to facilitate comparison of the values of the slopes at various temperatures in terms of possible reaction mechanisms. Thus, in general, the measured value of the slope at t° C, b_t, has been expressed as b_{25° C} by the relationship:

$$b_{25^{\circ}C} = b_t \times 298/T$$

This procedure is adopted only for convenience of presentation and comparison of data and does not imply that we assume that a is experimentally independent of temperature.

slopes of the E.M.F. decay lines are now (when C is $f(E)$) not identical with those of the kinetically significant true Tafel Lines based on oxygen evolution rates, mechanistic conclusions should strictly only be made from the slopes of the latter lines shown in the graphs in Figures XIV to XVII. This limitation will hold only when C is not a constant with varying potential.

Quantitative comparison between E.M.F. decay slopes and the "true" Tafel slopes based on rates of oxygen evolution on open-circuit are shown below in Table II for various experimental conditions of concentration and temperature. The slope data have been divided into three regions for convenience, corresponding to the three main ranges of values of slopes encountered under various conditions. In most cases, the changes of slope of E.M.F. decay lines are quite abrupt and experimentally unambiguous values of b_1 may be assigned to each region.

In those cases where E is a logarithmic function of volume of oxygen evolved Figure XL, evaluation of b_1 from b_2 and b_3 gives the values listed below in Table III.

Table III

Relationship between b_1 and b_3 when C is not constant with E

Conc./temp.	Region	$-b_2$	b_3	$-b_1$ (Calc.)	$-b_1$ (Obs.)
0.15M/25°C	II	0.06	0.045	0.026	0.034
0.15M/25°C	III	0.06	0.022	0.016	0.017
0.15/60.5°C	II	0.04	0.051	0.022	0.035
0.15/60.5°C	III	0.042	0.027	0.016	0.018
1.5/60.5°C	II	0.022	0.044	0.015	0.024
1.5/60.5	III	0.022	0.021	0.011	0.011
Mean deviation between calc. and obs. $-b_1$:					0.005(5)
Mean % deviation between calc. and obs. b_1 :					19%

It is not possible to test the relation between the slope constants b_1 , b_2 and b_3 over a very wide range of temperatures or concentrations since at lower temperatures or higher concentrations or both, E becomes linear with volume of oxygen evolved, i.e. C is constant with falling E.M.F. on open-circuit and $-b_1 = b_3$. (See Figure XXXVIII).

We may speculate that the origin of the variation of capacity with potential under some conditions, and its constancy under others, is connected with the degree of surface coverage θ of the oxide by adsorbed oxygen. The isotherm for

adsorption of oxygen can be written (cf. 80) as

$$\ln \left[\frac{\theta}{1-\theta} \right] = \ln [p_{O_2}]^{1/2} - \Delta G^0/RT - k'\theta \quad [44]$$

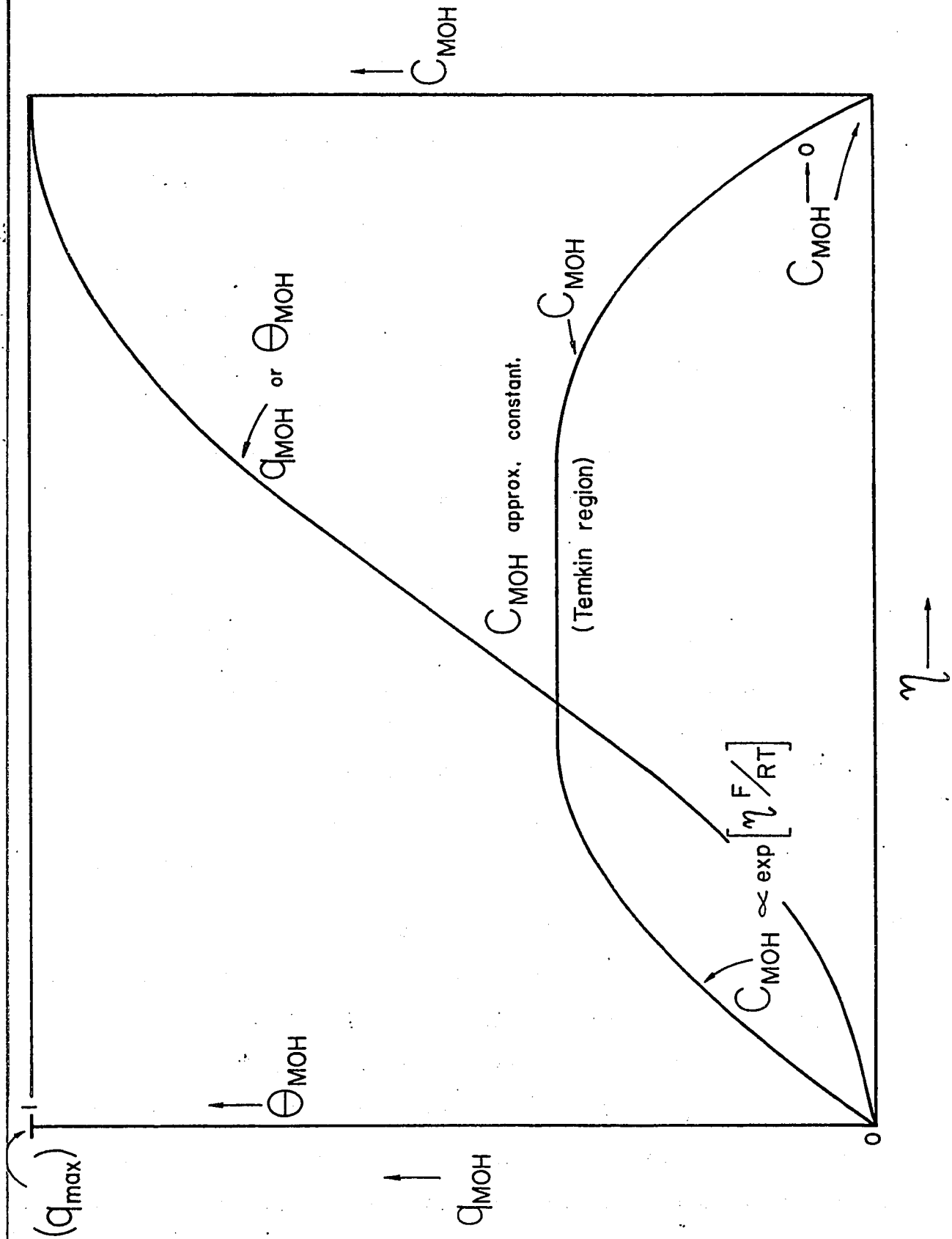
where $k'\theta$ represents an interaction term (cf. Temkin) corresponding to falling heat of adsorption with coverage θ , p_{O_2} is the pressure of molecular oxygen and ΔG^0 the standard free energy of adsorption.

At low or high coverage of electromotively active radicals, when the variation of the logarithmic term in θ with θ can exceed (cf. 80) that of the linear term with θ , (Langmuir behavior) equation [44] may be rewritten in terms of e.m.f. as

$$E = E_0 + b_2' \ln \left[\frac{\theta}{1-\theta} \right] \quad [45]$$

which is formally identical with the Lukovtsev and Temerin equation (equation 41) if we now regard the oxidized form as surface radicals and the reduced form as vacant surface sites. The degree of surface coverage θ will be directly proportional to q the charge required to deposit the O-containing radicals on the surface. It is clear, therefore, that the surface charge q will vary with the e.m.f. in the qualitative manner shown in Figure XLI. The associated surface capacitance dq/dE , also shown schematically in Figure XLI, will initially increase with increasing potential until at $\theta = 0.5$ it reaches its maximum value after which it declines. Three limiting cases of surface coverage may be considered:

Figure XLI: Schematic diagram of the course of
 q_{MOH} and C_{MOH} with increasing
potential .



Case (i) Surface completely covered or surface completely bare

For the extreme cases when the surface coverage is essentially complete, or alternately when the surface is essentially bare, the capacitance arising from adsorbed radicals tends to zero (see Figure XLI). Under these conditions the capacitance of the electrode is determined almost entirely by the ionic double-layer capacitance. In the e.m.f. regions corresponding to these conditions of coverage we can therefore expect the capacitance to be approximately constant and in general to be substantially smaller than in regions of intermediate coverage.

Case (ii) Low but significant coverage

In the region of coverage $0 < \theta < 0.5$ we can see from Figure XLI that the surface pseudo-capacitance increases with increasing e.m.f. For the region where $\theta \ll 1$ equation [45] approximates to

$$E = E_o' + b_2' \ln \theta \quad [46]$$

so that an exponential relationship is predicted between the e.m.f. and the quantity of charge needed to deposit the radicals on the surface. Under these conditions b_2 is a positive quantity and therefore $b_1 > b_3$. (see equation 37). Clearly this is not the situation encountered in the present work since in all cases b_1 was smaller than or equal to b_3 (see Table II).

Case (iii) High surface coverage

In the potential region where $0.5 < \theta < 1$ we have a surface capacitance which decreases with increasing e.m.f. (see Figure XLI). For the condition that $\theta \rightarrow 1$ equation [45] becomes

$$E = E_0 + b_2' \log \left[\frac{1}{1-\theta} \right] \quad [47a]$$

or

$$E = E_0 - b_2' \log [1-\theta] \quad [47b]$$

since we can write $\theta = k (q_t)_s$ where q_t is the quantity of charge associated with the surface radicals at any time t ,

$$E = E_0 - b_2' \log [1 - k (q_t)_s] \quad [48]$$

If at $t = 0$ the surface is almost completely covered so that $k (q_0)_s \doteq 1$ we may rewrite equation [48] as

$$E = E_0 - b_2' \log [k(q_0)_s - k(q_t)_s] \quad [49a]$$

or

$$E = E_0' - b_2' \log [(q_0)_s - (q_t)_s] \quad [49b]$$

$$= E_0'' - b_2' \log [V_{\theta_2}] \quad [49c]$$

which is the relationship corresponding to the conditions for which equation [32] applies. It will be noted, however, that $-b_2'$ in equation [49c] corresponds to b_2 in equation [32]. In this case b_1 (equation 37) will always be smaller than b_3 . It will be noted from the data given in Table II that the observed values of b_1 are always less than the corresponding b_3 values in all cases where C is not constant.

It is therefore reasonable to conclude that under those conditions where the surface capacitance of the nickel oxide electrode is not constant (i.e., for high temperatures and dilute KOH solutions), we are dealing with a surface which is initially nearly completely covered with adsorbed radicals. The region of constant capacitance observed at low temperatures (Figures XXXIII and XXXIV) is more difficult to explain in terms of surface coverage. In this region the capacitance is approximately the same as the initial capacitance (i.e. the capacitance at $t = 0$) for those cases of exponentially increasing capacitance (see Table I). Since, moreover, the region of constant capacitance occurs at the higher (more anodic) potentials, this lends support to the view that we are here in the region of "effective" full coverage and that the capacitance is no more than an ionic double-layer capacity as discussed above in case (i).

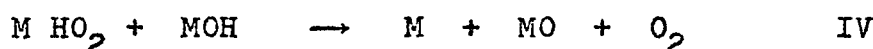
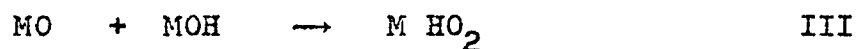
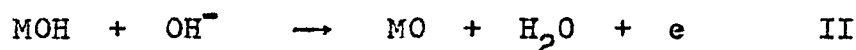
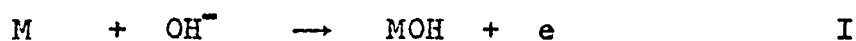
However, B.E.T. measurements of surface area on the charged material reveal a surface which is too small by nearly a power of ten to account for the magnitude of the capacitance observed. The effects of drying the material are, however, not known so that, in spite of the B.E.T. results, one cannot eliminate the possibility of having a surface large enough in the "wet" state to account for these results on the basis of a simple double-layer capacity. Alternately we must assume that the e.m.f. in this region is a linear function of

surface coverage. Cases of this nature have been reported by Ruetschi et al (79) and by Byrne and Rogers (81). These latter authors were dealing with a low surface coverage of silver on a gold electrode so that their case is probably not comparable to the present system where we have reason to suspect high coverage. The behavior reported by Ruetschi (79) for adsorbed radicals on lead and that observed in our own work imply Temkin adsorption behavior under these conditions (80). Under other conditions, when C varies with potential, we have Langmuir adsorption behavior. The reason for these different types of behavior by the adsorbed radicals under different sets of conditions is not clear.

Equation [44] becomes equivalent to a Temkin isotherm if $\theta \sim 0.5$ and variations of $\ln [\theta/1-\theta]$ with θ are less than those of $k'\theta$ with θ . Under these conditions the actual free energy of the surface phase (proportional to $\ln [p_{O_2}]^{1/2}$ for the pressure p_{O_2} of oxygen in equilibrium with it) and hence the associated electrode potential will be linear with θ . This could give rise to a constant capacity in a region where θ was neither tending to zero nor to unity. Analogous results may be obtained by a kinetic treatment as follows:

Case (i) Low surface coverage by intermediates

If the oxygen evolution process in self-discharge occurs e.g. by a mechanism such as the following:



with e.g. II rate-determining and significant coverage of M (the conducting particles of bulk nickel oxide) by adsorbed OH radical intermediates, it is readily shown by the usual steady state method (cf. 5) that at low coverage θ of MOH θ_{MOH} is given as a function of the overpotential η approximately by

$$\theta_{MOH} = K_1 [OH^-] \exp [\eta F/RT] \quad [50]$$

and

$$\theta_{MOH} = k q_{MOH} \quad [51]$$

where q_{MOH} is the associated charge required to remove or deposit MOH entities; the corresponding pseudo-capacity C_{MOH} is hence also an exponential function of η . The velocity v_2 of II is then (cf. 64)

$$\overrightarrow{v_2} = k_2 K_1 [OH^-]^2 \exp. (1 + \beta) \eta F/RT \quad [52]$$

When $\theta_{MOH} \ll 1$, I is in quasi-equilibrium and with

$$C_{MOH} = d(q_{MOH})/d\eta = d(\theta_{MOH})/kd\eta \quad [53]$$

and on open-circuit self-discharge of the pseudo-capacity

$$1 = 2F \overrightarrow{v_2} = - C_{MOH} \frac{d\eta}{dt} \quad [54]$$

so that

$$2F k_2 K_1 [\text{OH}^-]^2 \exp (1+\beta) \eta F/RT = - \frac{K_1}{k} [\text{OH}^-] \frac{F}{RT} \exp [\eta F/RT] \frac{d\eta}{dt} \quad [55]$$

and combining all constants into k'' (including constant $[\text{OH}]^-$ and T)

$$- k'' \exp. - [\beta \eta F/RT]. \quad d\eta = dt \quad [56]$$

Integrating and taking logarithms, we may obtain the E.M.F. decay slope $d\eta/d \log (t + \theta)$ as

$$d\eta/d \ln (t + \theta) = -RT/\beta F. \quad [\text{case I}] \quad [57]$$

i.e. a value different from the numerical value of the corresponding Tafel slope which, from equation [52], is $RT/(1 + \beta)F$ i.e. 0.038 with $\beta = 0.5$. In general, with

$$i_{\text{MOH}} = k e^{\eta/b_2} \quad [58]$$

where b_2 is some positive multiple or fraction of RT/F and b_3 is the Tafel slope of the rate-determining process (e.g. as in equation [58] above) in open-circuit decay, we then obtain the general decay law as

$$\ln [-k/i_o b_2] + \left(\frac{b_3 - b_2}{b_3 b_2}\right) \eta + \ln \left[\frac{b_2 b_3}{b_3 - b_2}\right] = \ln (t + \theta) \quad [59]$$

giving an E.M.F. decay slope b_1 of

$$b_1 = d\eta/d \ln (t + \theta) = b_2 b_3 / [b_3 - b_2] [\text{Case I}] \quad [60]$$

where θ is defined by

$$\theta = \frac{C'}{i'} \left(\frac{b_2 b_3}{b_3 - b_2} \right), \quad [61]$$

C' is the initial capacity at the starting potential in decay corresponding to an initial polarizing current density of i' .

Case (ii) Limiting case of full coverage by intermediates

When the surface is fully covered with MOH and reaction II then proceeds with a Tafel slope of $RT/\beta F$ (5), $C_{MOH} \rightarrow 0$, since q_{MOH} is independent of potential and the apparent electrode capacity is then simply the ionic double-layer capacity $C_{d.l.}$. The usual analysis (8,9) of E.M.F. decay rates then holds and the decay slope will be

$$d\eta/\ln(t + \theta) = -RT/\beta F \quad [\text{Case II}] \quad [62]$$

the same as the numerical value $RT/\beta F$ of the corresponding Tafel slope under these conditions, i.e. 0.116 with $\beta = 0.5$. Case II will hold over a range of potentials down to a potential where the adsorption capacitance begins to be comparable with the ionic double layer capacity. Below such a potential, case III (see below) will hold.

Case (iii) High, but not full coverage by intermediates

When θ_{MOH} approaches, but is less than unity, and is hence still a function of η , the C_{MOH} will decrease with increasing η in a complex way eventually becoming zero as

$\theta_{\text{MOH}} \rightarrow 1$ (the limiting case II) since θ_{MOH} is then given by

$$\theta_{\text{MOH}} = \frac{k_1 [\text{OH}^-] \exp [\beta \gamma F/RT]}{k_1 [\text{OH}^-] \exp [\beta \gamma F/RT] + k_{-1} \exp [-\beta \gamma F/RT] + k_2 \exp [\beta \gamma F/RT]}$$

and no simple decay law results from the kinetic treatment.

A more explicit result for this case follows from the quasi-thermodynamic treatment of adsorption isotherms already given above.

v) Significance of E.M.F. decay measurements at partially charged electrodes

For the purpose of evaluating the polarization parameters for electrodes in a state of partial charge (i.e. formal degree of oxidation lower than that corresponding to the formula " $\text{NiO}_{1.5}$ ") the normal method of measuring the dependence of rate on e.m.f. (viz. steady-state polarization studies) was not possible for the reasons previously discussed (section III, 2 a) and hence the e.m.f. decay method offered the only satisfactory alternative. The variation of surface capacitance* over the range of potentials involved in the decay of e.m.f. was checked by d.c. measurements and found to be small. In these experiments used to investigate the surface

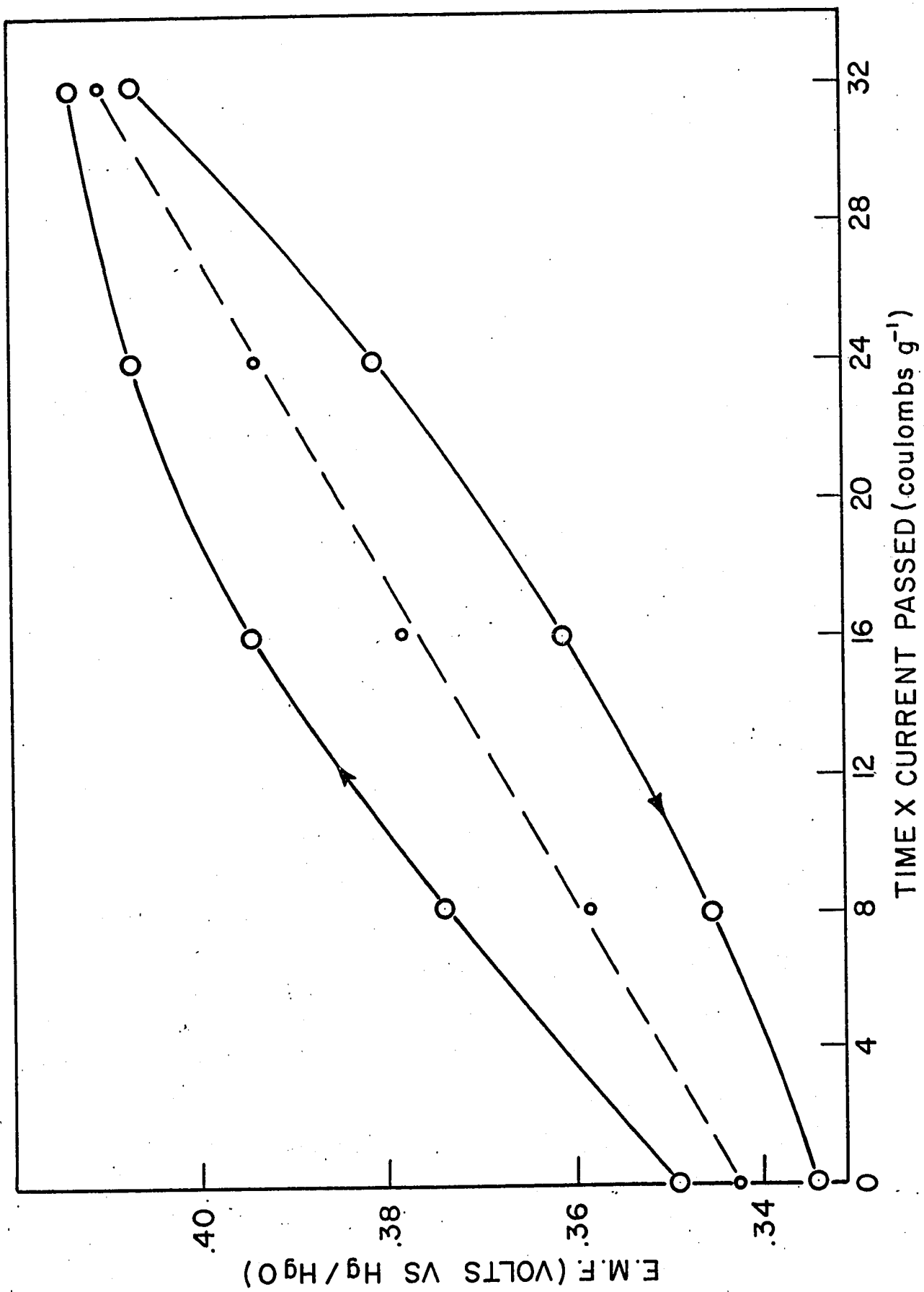
* The origin and nature of this concept of surface capacitance has been discussed in detail in Chapter III, 2 d (i).

capacitance, a constant polarizing current, anodic or cathodic, was applied to the electrode and the change of e.m.f. was followed as a function of time. When the e.m.f. reached a value such that the rate of oxidation or reduction* of the bulk material became comparable with the polarizing current, the direction of the current was reversed. Typical results of this type of measurement are shown in Figure XLII from which it is clear that the capacitance determined from the mean slope of the charge-potential curves is not greatly dependent upon the potential over a range of at least 70 mV.; it was not possible, however, to eliminate completely the oxidation or reduction of the bulk material while charging or discharging the surface capacitance. Part of the hysteresis observed in Figure XLII at high positive and negative potentials may be due to this leakage current (see p. 178 for full discussion of the significance of this current) corresponding to oxidation or reduction of the bulk material. However, even when this is taken into account[†] some curvature of the charge-

* The e.m.f. necessary for an appreciable rate of oxidation of the bulk may be estimated from charging curves (cf. Figure IX) at very low current densities.

† Here we anticipate the result (see p. 207) and estimate the leakage current at any given current density from a Tafel line drawn up from e.m.f. decay data on partially charged electrodes. The Tafel slope is obtained as the e.m.f. decay slope and the intercept is fixed from the known e.m.f. and corresponding current density at zero time.

Figure XLII: Estimation of the surface capacity on partially charged electrodes by constant current charging and discharging near the "steady-state" potential.



potential lines remains indicating that the charging and discharging of this surface capacitance is itself not a completely reversible process. This curvature does not imply that the capacitance is a function of potential since the curvature is convex in one direction of charging and concave in the opposite direction, thus indicating hysteresis. Moreover, the mean capacitance shown by the dotted line in Figure XLII is satisfactorily constant over the range of potentials investigated.

It can be seen that it is not possible to determine very accurately the surface capacitance of partially charged electrodes at any given potential; however, the measurements described here indicate that the capacitance does not change by more than a factor of about two over the range of potentials examined. In fact we can probably assume (see Figure XLII) that the variation is much less than this. Assuming this maximum variation of capacitance to be operative during the e.m.f. decay measurements, the value of the resulting e.m.f. decay slope would be in agreement with the corresponding theoretical true e.m.f. polarization slopes to within ten or fifteen percent. Although the certainty of these slopes is hence not as good as could be desired, it will be shown (section 2 c) that the values obtained do give some insight into the type of mechanism which is operative in the self-discharge of the nickel oxide electrode.

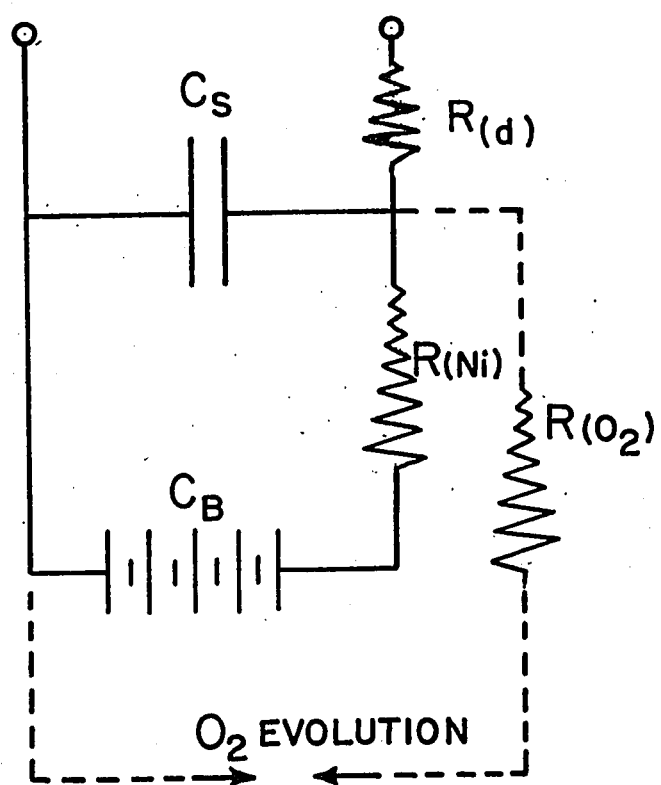
c) Electrical Analogue to the Processes of Charging and Oxygen Evolution: Relation between bulk charge-discharge processes and the self-discharge mechanism.

We have shown above that the nickel oxide electrode responds to a polarizing current as though a very large capacitor were in parallel with the current input. As current is passed into the electrode and the potential is disturbed, oxidation (or reduction) of the bulk material will occur and at slightly more anodic potentials oxygen evolution will (visibly) take place.* The overall electrochemical behavior of the nickel oxide electrode may hence be qualitatively represented by the electrical analogue shown in Figure XLIII where C_s is the surface capacitance, C_B the "electrochemical capacity" of the active bulk material, R_{O_2} the non-ohmic resistance corresponding to the reciprocal of the rate of electrochemical oxygen evolution and R_{Ni} that corresponding to the reciprocal of the rate of oxidation or reduction of the bulk material.

When constant current flows anodically into the system through the two schematic terminals at the top of the circuit (Figure XLIII), C_s is first charged and the potential across the terminals increases until the flow of charge through R_{Ni} and R_{O_2} becomes equal to the input current. If the bulk material is in the reduced state, charge will

* It must, of course, occur at a finite rate at any potential anodic to the oxygen reversible potential.

Figure XLIII: Electrical Analogue to Processes
occurring at the nickel oxide
electrode.



initially flow mainly through R_{Ni} , resulting in oxidation of $Ni(OH)_2$, with only a small leakage through R_{O_2} , giving oxygen evolution. When the bulk material has been fully oxidized (i.e. C_B can no longer accept significant charge) the potential must be raised in order to maintain flow of current which then passes entirely through the more difficult path, R_{O_2} , and steady-state oxygen evolution then occurs. If the input current is interrupted at this stage, current from C_s will continue to flow through R_{O_2} and the potential across the terminals will fall. When the potential has fallen to below the reversible potential of the nickel oxide system (i.e. when the potential across the terminals is lower than the potential of C_B) cathodic current will begin to flow from C_B through R_{Ni} thus tending to maintain the charge on C_s . Eventually a steady-state will be established and the cathodic current through R_{Ni} will become equal to the anodic current through R_{O_2} and this situation will correspond to the process of self-discharge with oxygen evolution on open-circuit which has been described above as a type of "corrosion" reaction.

d) The Rate-determining Process

(1) Identity of the rate-determining process

We have seen previously in section [1, b, ii] that the Tafel slope for self-discharge of the nickel oxide electrode

as measured by the rate of oxygen evolution is identical with that for steady-state oxygen evolution measured by d.c. polarization methods (cf. Figure XXXVII). This fact provides very strong evidence that the rate-controlling process for self-discharge is electrochemical evolution of oxygen on nickel oxide. Other experimental evidence that oxygen evolution is rate-controlling will be discussed more fully later but will be referred to briefly here. Summarily, the evidence is the following: (i) the activation energy for self-discharge is the same (see Fig. XLVIII) as that for steady state oxygen evolution; (ii) the deuterium isotope effect is in the same direction for the two processes (see Figs. XVIII and XXI). (iii) the variations of the oxygen evolution rate during steady polarization and on open-circuit with KOH concentration are in the same direction.

It should be noted, however, that these conclusions are strictly valid only in the region of potentials where the rate of oxygen evolution was measurable. Experimentally it was not found possible to measure accurately oxygen evolution rates at or near the mixed potential.

Thus we are led to the conclusion that, in the region of potentials concerned, the self-discharge of the nickel oxide electrode is electrochemical in nature and the anodic partial reaction is rate-controlling. In this potential region we are above the reversible potential of nickel oxide

(cf. this chapter, section 2,c) and thus the cathodic partial process must be the discharge of the surface capacitance (e.g. $\text{MOH} + e \rightarrow \text{M} + \text{OH}^-$). This reaction is a rapid one which proceeds with little activation polarization and thus it will make little if any contribution toward limiting the overall discharge rate. In terms of the electrical analogue, (Figure XLIII) oxygen evolution is maintained by the discharge of C_s through $R_{(O_2)}$, where $R_{(O_2)}$ is the non-ohmic resistance corresponding to the reciprocal of the rate of oxygen evolution. Since R_{O_2} is then the only barrier to the discharge of C_s , the rate of discharge will be governed simply by the kinetics of the oxygen evolution reaction.

However, when the potential has reached the mixed potential,* the cathodic process becomes (predominantly) the reduction of the bulk material as discussed in section III (1)c. This process exhibits appreciable polarization (e.g., see Figures XXIII, XXIV) and under these conditions both the

* We may note that, in principle, the mixed potential itself could vary with time owing to loss of charge of the electrode on open-circuit if the reversible potential of the nickel oxide electrode (see this chapter, section 2 d, p. 215) was sensitively dependent upon degree of oxidation (but see equation 41). For the small degrees of self-discharge involved in open-circuit measurements at room temperature, such variations of the mixed potential with time can, however, be shown to be insignificant.

cathodic and the anodic processes are simultaneously involved in determining the overall rate. In terms of the electrical analogue (Figure XLIII), charge coming from C_B must pass through both $R_{(Ni)}$ and $R_{(O_2)}$ in order for oxygen evolution to occur. If these two barriers are comparable in magnitude then both will be involved in limiting the overall rate. That they are comparable is evidenced by the fact that the steady state or mixed potential of these electrodes is not identical with the reversible e.m.f. of nickel oxide. This point is treated in some further detail in section 2 of this chapter. A detailed study of self-discharge at or near the mixed potential was not possible in the present work owing to the difficulties of obtaining sufficiently accurate oxygen-evolution rates after long periods of time on open-circuit (e.g. in 7 molar KOH one week or more is required to reach the mixed potential).

(ii) Tafel Slopes

As has been shown above, the rate-controlling process for self-discharge in the region of potentials studied is that of oxygen evolution. The Tafel slopes for this process, as determined from the rate of oxygen evolution on open-circuit, are given in Table II along with the corresponding semi-logarithmic slopes of e.m.f. decay lines. As shown in Figures XIV to XVII these Tafel lines exhibit a change of

slope under certain conditions of temperature and KOH concentration going, generally, from a region of high slope at high potentials to a region of lower slope at lower potentials. In Table II the data are listed in three columns according to the magnitude of the slopes and the order of their appearance starting at the highest potentials. The first group, region I, are however given in parenthesis and are included for the sake of completeness only, since these were observed in only a few instances and they are not sufficiently well characterized to be of any diagnostic value. Moreover, it is felt that in one of the two cases where these occur (i.e. dilute KOH solutions at 1.0°C) conditions are such that concentration polarization effects arising from inhomogeneity of concentration inside the sintered electrode brought about by the prior anodic polarization, may be significant.

Generally the Tafel slopes in the high overpotential region ranged from 0.035 to 0.050 depending upon temperature and concentration of KOH. In the less concentrated solutions and at the higher temperatures (less than 3 molar at 25°C and less than 7 molar at 60°C) the values of the slopes changed quite abruptly in the low overpotential region becoming approximately one half of those observed at higher overpotentials. The potential at which this change occurred was quite markedly dependent upon the concentration of KOH, appearing at the highest

potentials in the most dilute solutions. It is reasonable to assume that these lower slopes would also be observed at the lower temperatures if sufficient time were allowed for the e.m.f. to decay to the "transition" potential. At 1.0°C this would require from weeks to months depending upon the KOH concentration and an even longer time would be required at -25°C . In view of the existence of at least two distinct Tafel slopes it follows that the rate of the over-all oxygen evolution reaction may be controlled by either of two processes concerned, depending upon the electrode potential. The order of the appearance of these slopes, from a low to a higher slope with increasing potential, implies that these processes must operate in series in the over-all reaction scheme. [For a discussion of this point see Introduction, section 1,d].

(iii) Effects of Concentration on Rate

By extrapolating the linear portions of the experimental Tafel lines to the potential of the reversible oxygen electrode (0.303 w.r.t. Hg/HgO at 25°C), it is possible to obtain values for the exchange-currents of the rate-controlling processes. Values for the processes corresponding to the two commonly observed slopes (regions II and III) are given in Table IV. Owing to the long extrapolation necessary (which arises mainly from the low b values involved) to obtain

Table IV

Exchange Currents in Amps per gram from
Extrapolation of E.M.F.-Log Rate of Oxygen Evolution Lines

Temp.	Conc.	Region I	Region II	Region III
-25°C	4.5		5×10^{-10}	
	8.2		6×10^{-10}	
	11.8		3×10^{-10}	
1.0°C	0.10	$[8 \times 10^{-7}]^*$	1.4×10^{-8}	
	1.0	$[5 \times 10^{-6}]$	4.5×10^{-8}	
	7.0		2.7×10^{-8}	
	8.6		1.7×10^{-8}	
25°C	0.015		1.6×10^{-6}	1.5×10^{-10}
	0.15		7×10^{-7}	2.0×10^{-11}
	2.9		5.6×10^{-7}	2.2×10^{-10}
	7.0		2.7×10^{-6}	**
	9.4		1.2×10^{-6}	**
	14.6		2×10^{-7}	**
60.5°C	0.15		1.4×10^{-6}	
	1.5		5×10^{-6}	
	7.0		4×10^{-5}	
	14.4		8×10^{-5}	
	15.4		4×10^{-5}	

* These i_0 values correspond to the two values of b given for the same conditions in columns 3 and 4 of Table II.

** Values of i_0 for concentrations indicated by ** cannot be obtained since no second region of the oxygen evolution rate line appears. This is consistent with the e.m.f. decay behaviour (Figure XII).

these values of i_0 , and to some uncertainty in the exact value of the slopes, apparent differences of i_0 values for the same process at different concentrations but at a given temperature cannot be taken as significant, as shown in Figure XLIV. There is, however, at a given concentration and temperature a significant difference of exchange-current between the processes which are rate-determining in the higher and in the lower overpotential regions (Figure XLIV). The process which is rate-determining at the lower overpotential has, in fact, an exchange-current of the order of 10^3 times less than that of the process occurring at higher overpotentials. In order to eliminate some of the inherent error of a long extrapolation to zero overpotential, a comparison of rates was also made at constant finite overpotential as a function of concentration and temperature. The effect of KOH concentration on the rate of self-discharge at constant temperature and constant overpotential is shown in Figures XLV, XLVI and XLVII. The rate of oxygen evolution at a given overpotential is enhanced by increased activity of KOH in both the upper and the lower potential regions but with a considerably more pronounced effect in the lower region. In the upper region the rate is approximately proportional to $(a_{\text{KOH}})^{1/4}$ whilst in the lower region it is proportional to $(a_{\text{KOH}})^1$. It should be noted, however, that these relative rates, which have been calculated for comparative purposes

Figure XLIV: Log [exchange-current] versus log
[activity of KOH] for the oxygen
evolution process at nickel oxide
electrodes.

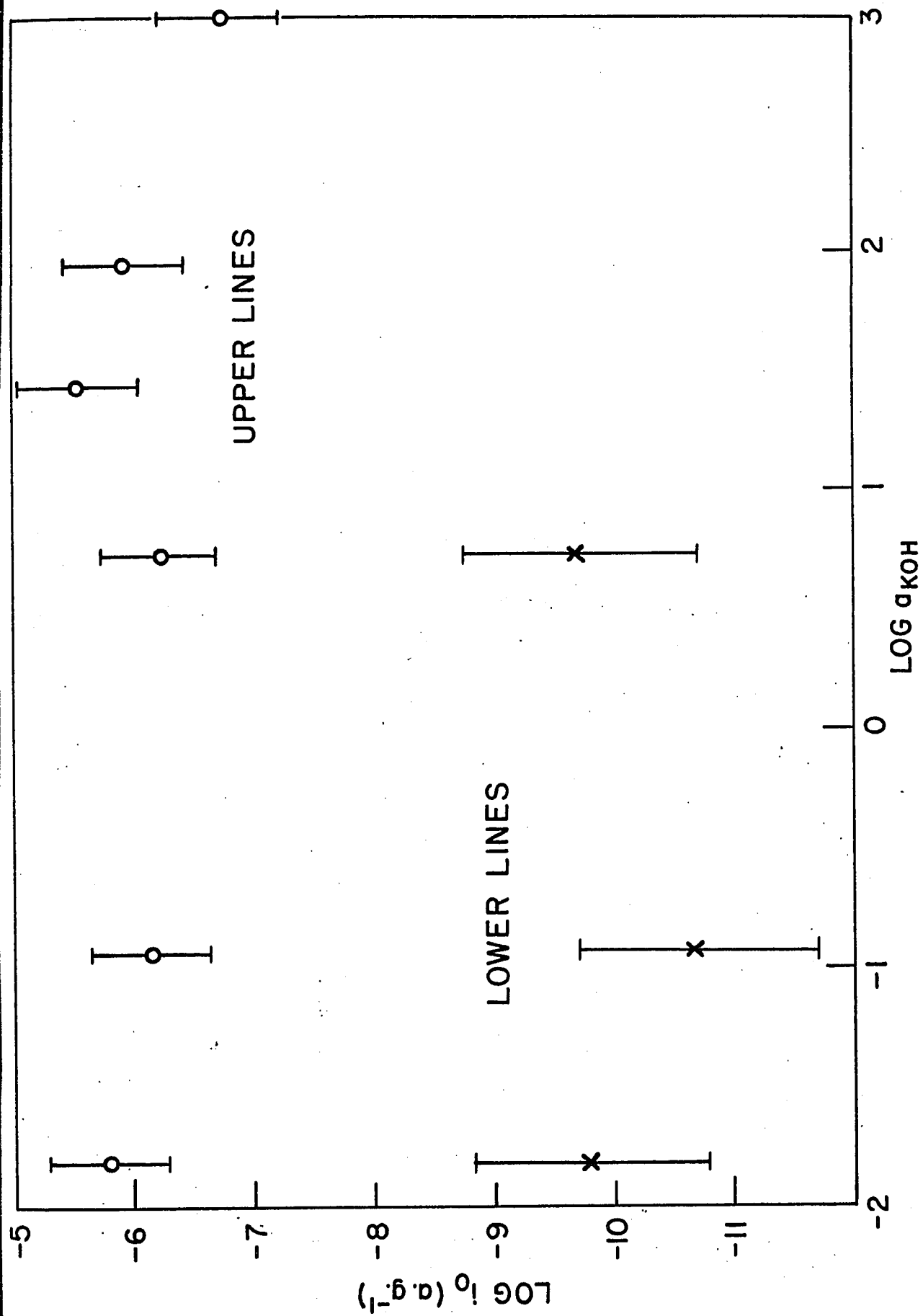


Figure XLV: Log [rate of oxygen evolution] versus
log [activity of KOH] for region II
of the Tafel lines at 25°C. Rates are
compared at constant overvoltage of
0.16 and 0.18 volts.

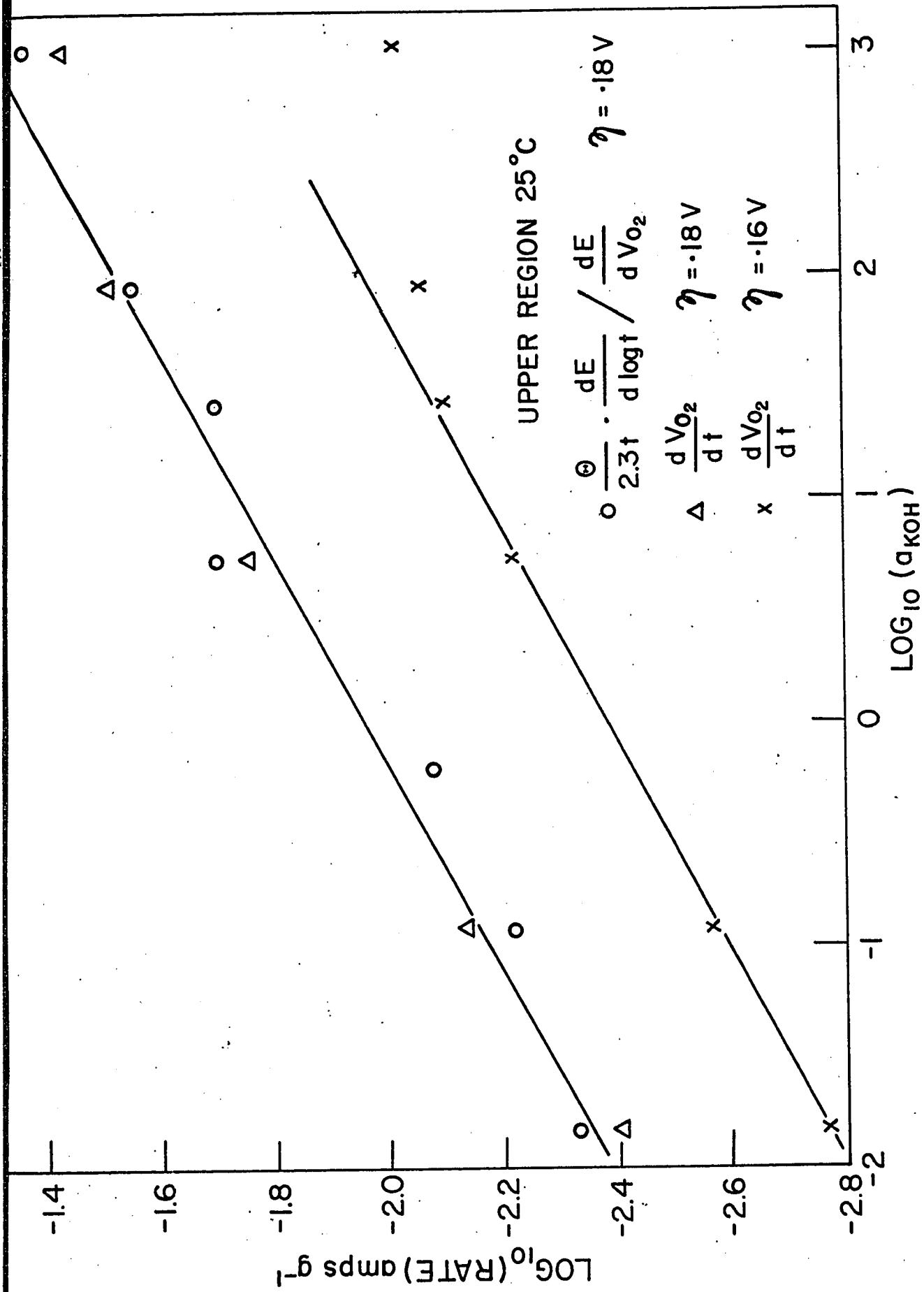


Figure XLVI: Log [rate of oxygen evolution] versus
log [activity of KOH] for region III
of the Tafel lines at 25°C.

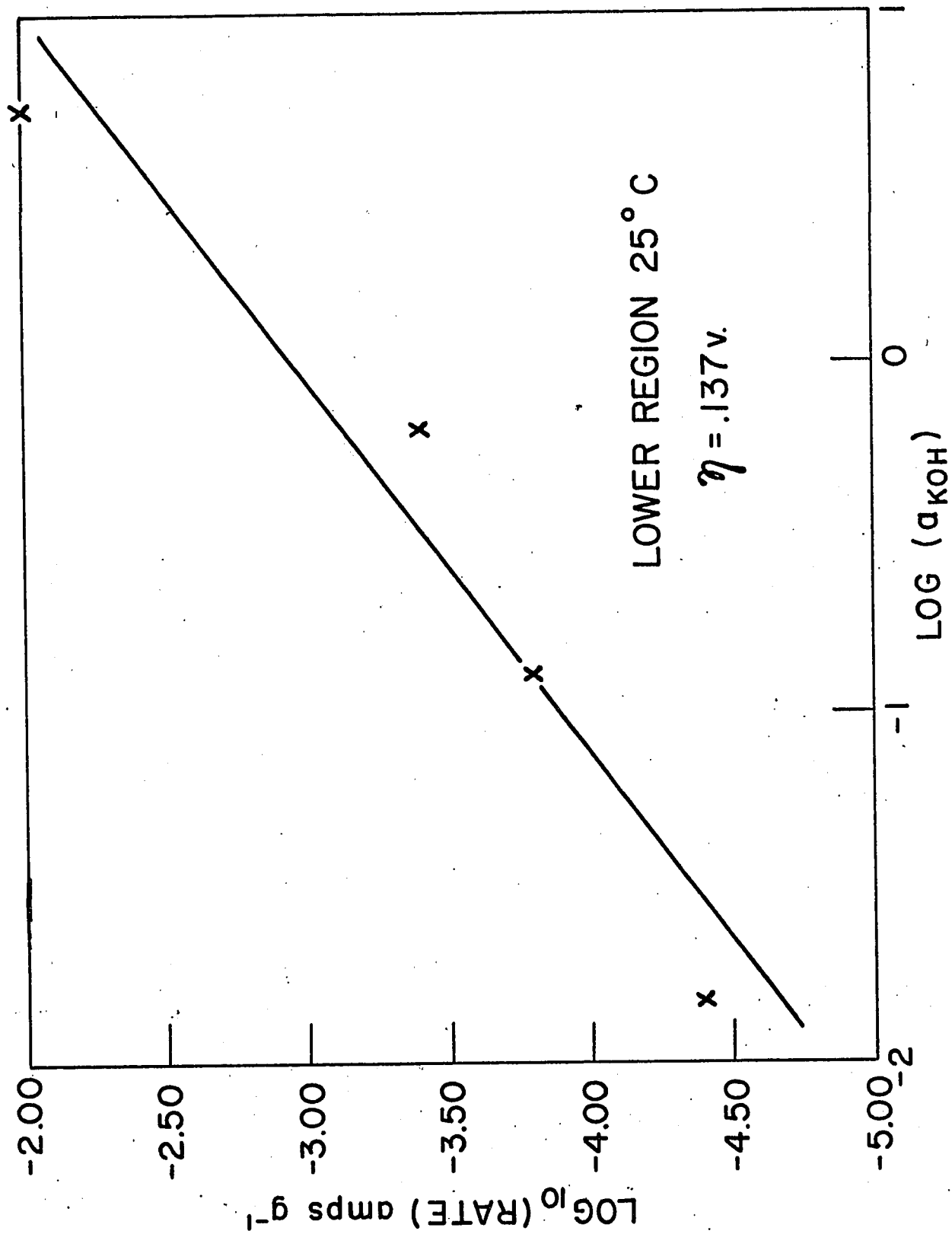
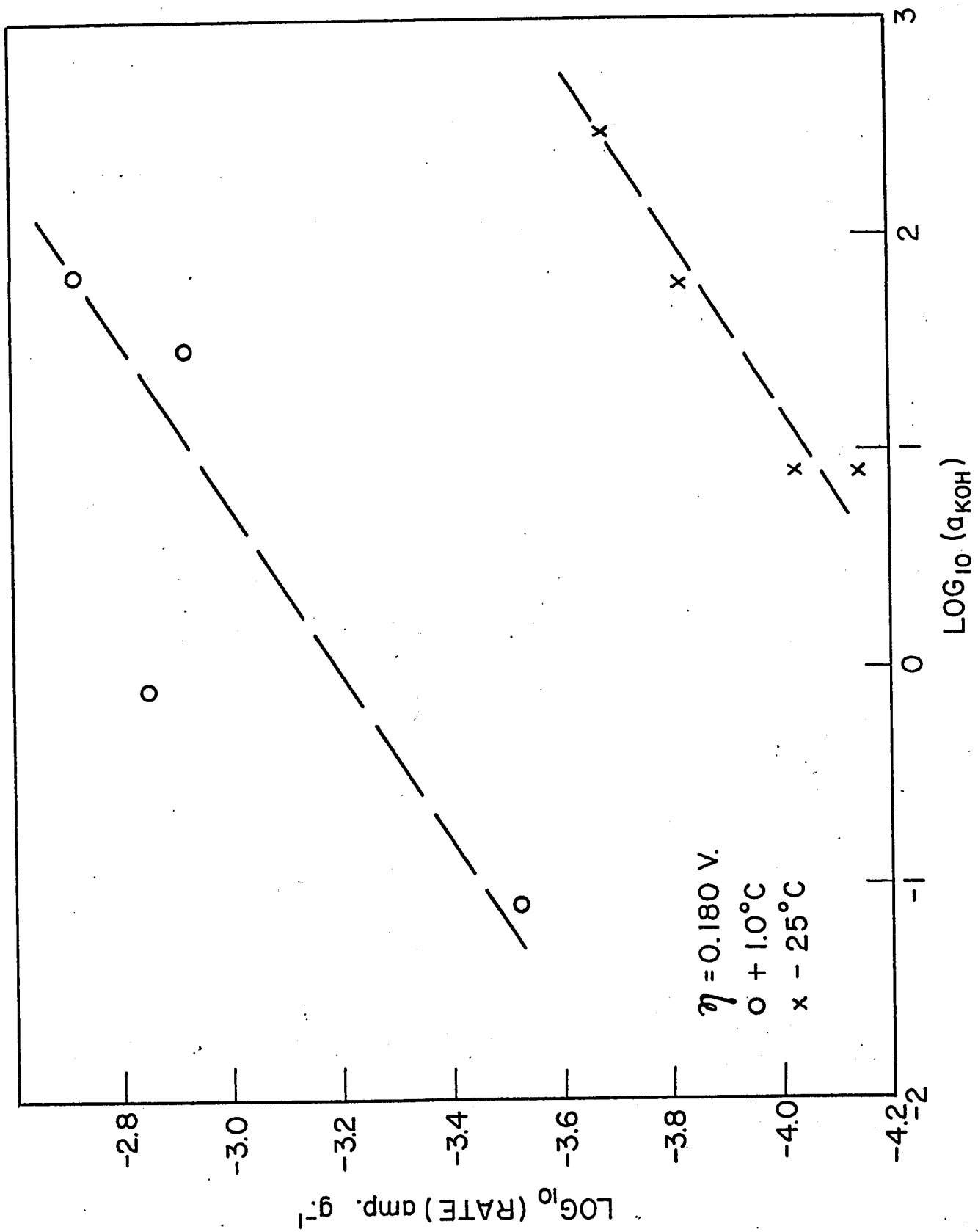


Figure XLVII: Log [rate of oxygen evolution] versus
log [activity of KOH] at 1.0°C and
-25°C.



only, will depend on variations of the slope b as well as of i_0 (which is, in fact, almost independent of concentration as we have discussed above, see Fig. XLIV) with KOH concentration. It must not, however, be concluded from the above results that the amount of self-discharge of an electrode in a concentrated solution will exceed that in dilute solution. In fact, owing to its lower (i.e. less "anodic") reversible potential (compared with that of the O_2 electrode in the same solution) in concentrated KOH solutions, an electrode at a given state of oxidation will actually decay the less rapidly the more concentrated the solution. This point will be discussed in more detail in a later section (see Appendix).

(iv) Effect of Temperature on Rates

The dependence of the rate of oxygen-evolution on temperature was evaluated for the upper potential region by comparing rates at a given constant overpotential* ($0.18 \text{ v. } E_{O_2}$) and constant concentration (7.0 M KOH) as a function of temperature. Log rates obtained by two independent procedures,

* Since the reference electrode was Hg/HgO a correction for the temperature coefficient dE/dT for the cell $Hg/HgO \text{ KOH}_{aq.}/O_2$ was necessary. (From the thermodynamic data given by Latimer (82) this was calculated to be -0.55×10^{-3} volts/degree C.)

(viz., d.c. polarization and rate of oxygen evolution on open-circuit) are shown plotted against $1/T$ in Figure XLVIII. From these data an apparent activation energy of 15.2 (± 1) kcal. mole⁻¹ was determined. This corresponds, with $b \doteq 2.3$ ($2/3 \cdot RT/F$), to a heat of activation at the reversible oxygen potential of 21.4 (± 1.6) kcal. mole⁻¹.

The fact that the rate of oxygen evolution on open-circuit and the rate under d.c. polarization have the same apparent activation energies is further proof that the rate-determining reaction during open-circuit decay is the anodic partial process of electrochemical evolution of oxygen on nickel oxide.

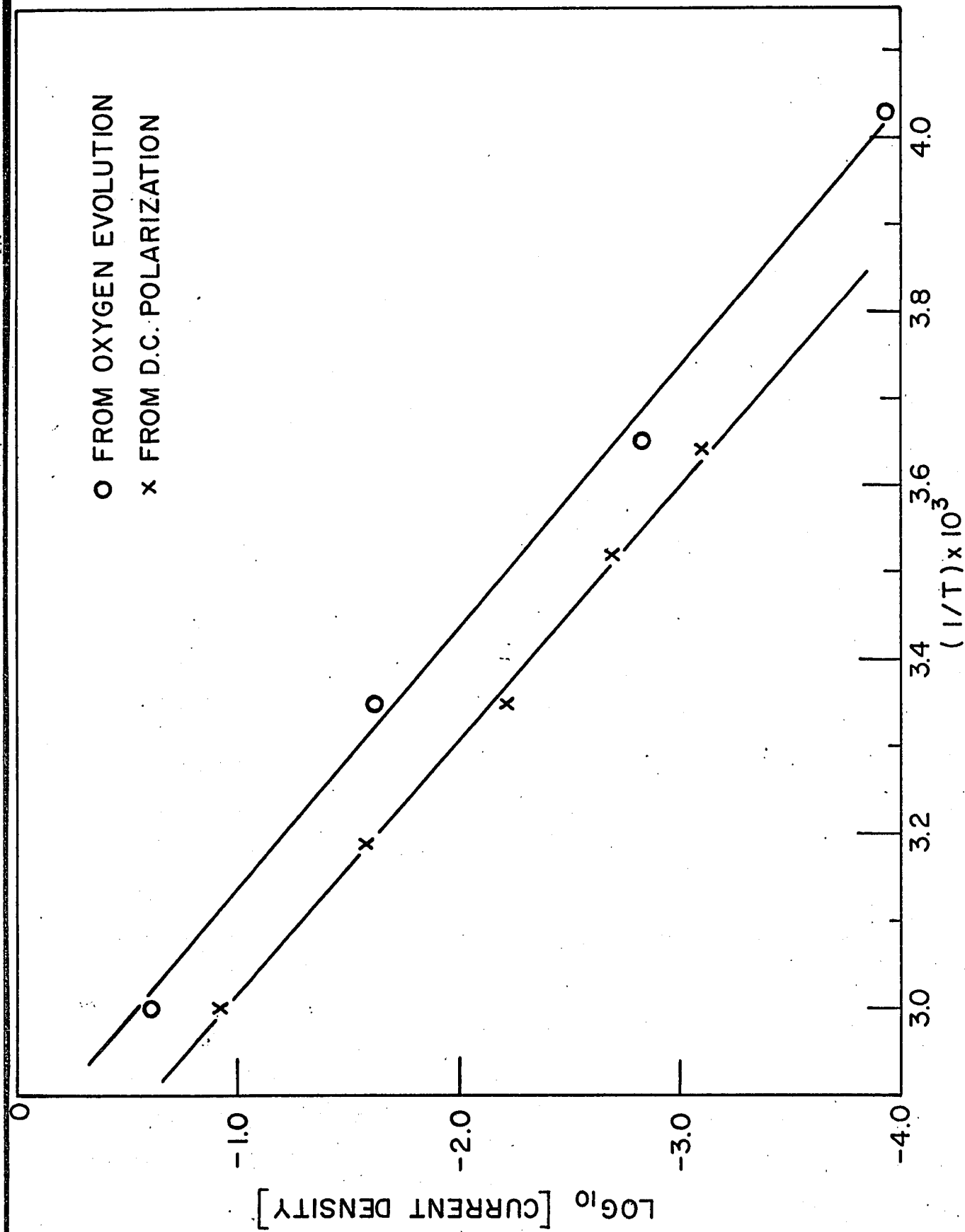
(v) H-D Isotope Effects

We have shown above that when the electrode potential of the nickel oxide electrode lies above the steady state mixed potential, the rate of the anodic partial reaction limits the rate of the overall self-discharge except within about 10 mV. of the mixed potential when the cathodic partial reaction will begin to influence the overall rate. The evidence for these conclusions was based on:

a) the identity of the slopes of the e.m.f.-oxygen evolution rate on open-circuit with the slope of the d.c. polarization lines under the same experimental conditions and

Figure XLVIII: Activation energy plots based on

- a) rates of self-discharge in
region II from oxygen evolution
measurements
and
- b) direct current polarization
measurements.



β) the identity of the apparent heats of activation for oxygen evolution on open-circuit and on steady state d.c. polarization.

A further method was employed which involved the determination of the direction of the kinetic H/D isotope effects on the rates of oxygen evolution measured by the rate of e.m.f. decay on open-circuit and by direct d.c. polarization studies. The results for the e.m.f. decay on open-circuit have been shown in Figure XVIII and those for the d.c. anodic oxygen evolution reaction at plain Ni wires in Figure XXI, both in aq. KOH and KOD in D₂O. It is clear that in both cases an inverse H-D isotope effect is observed. It may be noted that although the inverse isotope effect observed here is unusual, the reaction concerned is anodic evolution of oxygen from OH_{aq}^- and no proton transfer step (which would probably involve a normal isotope effect) occurs. The effect is therefore probably concerned with the relative stabilities of NiO.OH , H_2O and OH_{aq}^- compared with those of the corresponding D analogues. Were the process of self-discharge to involve rate-determining cathodic reduction with proton transfer it is probable that the isotope effect would have been in the normal direction as, in fact, found hitherto universally with electrochemical proton/deuteron transfer reactions (83).

(vi) Reaction Mechanism in the Oxygen Evolution

Process

The actual mechanism of oxygen evolution within the anodic partial process, indicated as rate-controlling by the above criteria, may now be considered by examining the magnitude of the observed true Tafel slopes.

On the basis of the theoretical considerations discussed previously (Introduction section 1 b) it is possible to write mechanisms for the oxygen evolution reaction which yield limiting Tafel b values of $0.015 [2.3 (RT/4F)]$, $0.020 [2.3 (RT/3F)]$, $0.024 [2.3(2RT/5F)]$, $0.029 [2.3 (RT/2F)]$, $0.038 [2.3 (2RT/3F)]$, $0.058 [2.3 (RT/F)]$ and $0.12 [2.3 (2RT/F)]$. Deviations from these limiting values may arise when assumptions concerning the surface coverage θ of the electrode by adsorbed intermediates (viz, θ is limitingly low or $\theta \rightarrow 1$) break down at intermediate coverage. Values of the slopes other than those given above will also arise if the potential barrier for the charge transfer step is asymmetrical (i.e. the symmetry factor β is not 0.5) but such cases are rare except when $\Delta H^\ddagger$ is small (< 5 kcal).

The experimentally observed mean slopes in the higher overpotential region for the oxygen evolution process (viz, 0.042 ± 0.005 volts) appear to be associated with the same mechanism since they are either almost constant (at -25°C) or vary in a continuous manner with concentration between these

extremes (± 0.005 v.) at the three other temperatures investigated (see Table II). Clearly the theoretical value having mechanistic significance most nearly in agreement with these observed values is 0.038 i.e., $2.3 \frac{RT}{(1+\beta)F}$ when $\beta = 0.5$; the observed mean value of b which is 0.042 ± 0.005 would hence be obtained if β were 0.41 rather than 0.5 . Were the rate-controlling step in oxygen evolution one involving no charge transfer in that step (e.g. surface diffusion of radicals to recombination sites or the recombination process itself) the slope should then be an even fraction of RT/F , i.e. $2.3 RT/nF$ where n would be 1 or 2 for the two possible cases suggested above and the slopes would not involve the β whatever value it had for the charge transfer step. Whenever a charge transfer step is involved in the rate-determining step, the Tafel slope will have values of the form

$$b = 2.3 \frac{RT}{(n + \beta) F} \quad [49]$$

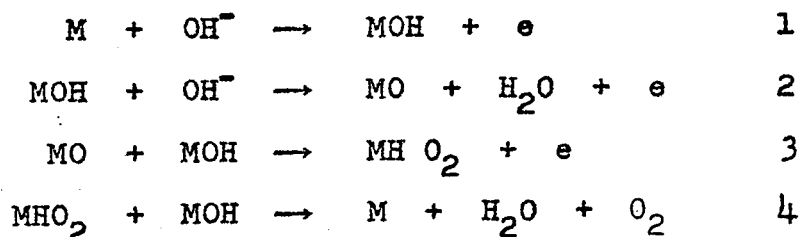
where n can now be 0 (primary discharge step rate-determining), 1 (desorption of 1st intermediate by an ion transfer mechanism) or two etc., and the coverage θ by the intermediates involved is potential dependent. The fact that for the upper over-potential region at the nickel oxide electrode the Tafel slope is

$$2.3 RT/2F < b < 2.3 RT/F \quad \text{and} \quad b \sim 2.3 \cdot \frac{2}{3} \frac{RT}{F}$$

leads to the conclusion, from the above arguments, that a process involving ion transfer in a desorption step is rate-determining and that deviations from the only slope deducible (viz. $2.3 RT/(1 + \beta)F$) having a value between $2.3 RT/2F$ and $2.3 RT/F$ must arise from the fact that β is less than 0.5; the value of 0.41 deduced above is not unreasonable since such deviations of β from 0.5 in simple ion transfer steps e.g. in hydrogen evolution are known (84,85).

The Tafel slope in the lower region is always very nearly one half (i.e., $2.3 RT/3F$) the value of the slope at higher potentials. However, it must be noted that the value $2.3 \cdot 2RT/5F$ (0.024, with $\beta=0.5$ and $n=2$ in equation [49]) is also in the range of the experimental data.

We thus require a mechanism having consecutive steps which can lead to Tafel slopes of $2.3 \cdot 2RT/3F$ and $2.3 RT/3F$ (or $2.3 \frac{2}{5} \frac{RT}{F}$) depending upon which step is rate-controlling under the particular set of circumstances. The following mechanism meets these requirements:



Here M signifies the interface of the electronically conducting bulk oxide and the indicated radicals e.g. OH, HO₂ are regarded

as adsorbed at the interface of the oxide at which oxygen evolution occurs. The scheme shown above is related to those discussed by Bockris (5) but is actually different from any one of his schemes in so far as the above series of reactions will be shown to lead to slopes of consecutive steps in the order $2.3 \frac{2}{3} \frac{RT}{F}$ followed by $2.3 RT/3F$ with decreasing potential, in a given reaction sequence. For the series of consecutive reactions (1) to (4) above the rates v are given by

$$v_1 = k_1 [OH^-] (1 - k' [MOH] - k'' [MO]) \exp [\eta F/2RT]^{\neq}$$

$$v_{-1} = k_{-1} [MOH] \exp [-\eta F/2RT]$$

$$v_2 = k_2 [MOH] [OH^-] \exp [\eta F/2RT]$$

$$v_{-2} = k_{-2} [MO] \exp [-\eta F/2RT]$$

$$v_3 = k_3 [MOH] [MO]$$

$$v_{-3} = k_{-3} [MHO_2]$$

$$v_4 = k_4 [MHO_2] [MOH]$$

where $[OH^-]$ is the concentration of hydroxyl ions in the double layer and k' and k'' are constants relating fractional

^{\neq} Here the usual assumption is made that, at moderate concentration, the overpotential η differs only by a constant from $\Delta\phi$, the potential difference between the electrode and the outer Helmholtz layer.

surface coverage by intermediates to their surface concentration. The symmetry factor for the charge-transfer steps is taken as 0.5 (cf. 87). In order to obtain the Tafel slopes for various rate-determining steps in the above scheme, we calculate the Christiansen coefficients for each step as

$$w_1 = k_1 [\text{OH}^-] \exp [\eta F/2RT]$$

$$w_{-1} = k_1 k' [\text{OH}^-] \exp [\eta F/2RT] + k_1 k'' [\text{OH}^-]^2 K_2 \exp [3 \eta F/2RT] + k_{-1} \exp [-\eta F/2RT]$$

if [MOH] and [MO] are both appreciable (i.e. if (3) is rate-determining); or if only [MOH] is appreciable (i.e. if (2) is rate-determining)

$$w_{-1} = k_1 k' [\text{OH}^-] \exp [\eta F/2RT] + k_{-1} \exp [-\eta F/RT]$$

K_2 is a quasi-equilibrium constant for (2) in the steady state if (3) is rate-determining. Other w values are

$$w_2 = k_2 [\text{OH}^-] \exp [\eta F/2RT]$$

$$w_{-2} = k_{-2} \exp [-\eta F/2RT]$$

$$w_3 = k_3 [\text{MOH}]$$

$$w_{-3} = k_{-3}$$

$$w_4 = k_4 [\text{MOH}].$$

If step (2) is rate-determining, the overall velocity is then

$$v = \frac{k_1 k_2 [\text{OH}^-]^2 \exp \eta F/RT}{k_1 k' [\text{OH}^-] \exp [\eta F/2RT] + k_{-1} \exp [\eta F/2RT] + k_2 [\text{OH}^-] \exp [\eta F/RT]}$$

which at relatively low potentials gives

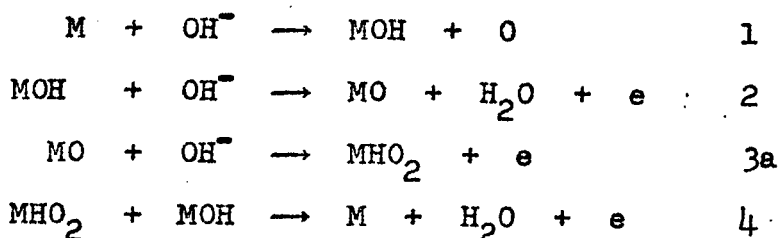
$$v = K_1 k_2 [\text{OH}^-]^2 \exp [3\eta F/2RT]$$

and if (3) is rate-determining, and at relatively low potentials

$$v = K_1^2 K_2 k_3 [\text{OH}^-]^3 \exp [3\eta F/RT]$$

where K_1 and K_2 are the quasi-equilibrium constants for (1) and (2) respectively. This will lead to a Tafel b constant of 2.3 (2RT/3F) for (2) rate-determining and 2.3 (RT/3F) for (3) rate-determining.

An alternative scheme of equations representing the overall reaction and giving rise to the sequence of slopes 2RT/3F and 2RT/5F may be formulated as follows:



If reaction 2 is rate-determining, a Tafel slope of 2.3 2RT/3F is again predicted. If reaction (3a) is however rate-controlling a slope of 2.3 2RT/5F will result from this scheme of reactions. Since the observed values of the slope in the lower potential region could correspond within the experimental error to either 2.3 2RT/5F or 2.3 RT/3F, is not possible to decide which of the above two similar schemes is to be preferred.

2. THERMODYNAMICS OF SEMI-CHARGED ELECTRODES*

a) Introduction

In this part of the Discussion, the aim will be to examine the results reported in section 2 on partially charged electrodes and consider the electrochemical behaviour of the electrodes under these conditions. It will be shown how information can be obtained on the kinetics of the electrochemical redox processes involved in the charge and discharge of the electrochemically active material and how the true reversible potentials of electrodes charged to a controlled state of oxidation of " $\text{NiO}_{1.25}$ " can be deduced and distinguished from mixed potentials exhibited on open-circuit. Previous work on so-called "reversible" potentials has been reviewed in the Introduction.

b) Nature of the Electrode Processes

In the polarization decay studies on partially charged electrodes (see sections 2,a) the aim was to disturb the equilibrium between reduced and oxidized forms of the nickel oxide by passing an anodic or a cathodic current and then observing the decay towards the "reversible" potential.

* This part of the work has been published almost in its entirety in a paper by Bourgault and Conway, Can. J. Chem., 1960.

However, from the foregoing discussion it is clear that the instantaneous effect of a current in either direction will be to change the concentration of the chemisorbed intermediate on the surface rather than to affect the oxidation state of the bulk oxide itself. These intermediates will subsequently proceed to combine with the bulk material with resulting oxidation or reduction of the latter. The process is best visualized by referring to the electrical analogue Figure XLIII discussed previously in this chapter, section 1c.

This time we are concerned with the case where polarization is interrupted whilst the bulk material is still in a partially reduced state, (i.e. C_B in Figure XLIII can still accept charge). Again, when anodic current initially flows into the system, charge is first absorbed by C_s with a resulting rise of potential across C_s and the input terminals. This, in turn, will result mainly in the passage of reacting particles (and hence current) over the barrier R_{N1} , with some leakage through R_{O2} producing respectively oxidation of the bulk material and oxygen evolution. On open-circuit, following anodic polarization the major portion of the excess charge on C_s passes through R_{N1} into C_B resulting in further oxidation of the bulk material. (A very small but at times quite significant amount of oxygen evolution also occurs.) This indirect mechanism of charging is supported by the direction of the H/D isotope effect on the polarization on charging and

discharging (Figure XXV), which is significantly less in D_2O than in H_2O . If H^+ or D^+ transfer steps (1,6) were rate-determining in the oxidation or reduction of the bulk oxide the reverse isotope effect would be expected (83). The faster rate in D_2O is connected with the expected lower heat of solvation of OD^- than that of OH^- - in the respective isotopic solvents (88).

Conversely, on cathodic polarization, C_s is discharged to potentials low enough for current to flow from C_B through R_{Ni} sufficient to maintain the current taken from the over-all system, the oxygen evolution rate then being negligible at these more cathodic potentials (it becomes significant in some cases only as the reversible or mixed potential is reached, e.g. in Figure XXIIIId). On open-circuit following cathodic polarization, C_s can be regarded as recharged by the current through R_{Ni} (less the small current corresponding to oxygen evolution) and this corresponds to the lower recovery lines shown in the Figures XXIIIa to XXIIIId and XXIVa.

At long times after cessation of anodic or cathodic polarization, the potential across C_s would become equal to that set up across C_B if no leakage occurred through R_{O_2} , i.e. if no self-discharge were taking place, and the reversible potential of the electrochemically active material constituting C_B would then be measured by the potential at which the

extrapolated logarithmic decay lines intersect. Inspection of the e.m.f. decay lines indicates, however, that in all but the most dilute solutions there are inflections in the anodic lines and at the highest concentrations (14.6 M) also in the cathodic line. This raises the problem of how the extrapolation should be carried out, i.e. by extension of the upper lines in the region of low times (i.e. $\log [t+\theta]$ in the range 1 to 3) or production of the lines after the longest periods of time (i.e. for $\log [t+\theta] > 4$). We therefore now consider possible reasons for these inflections in the decay lines.

c) Form of the Decay Lines

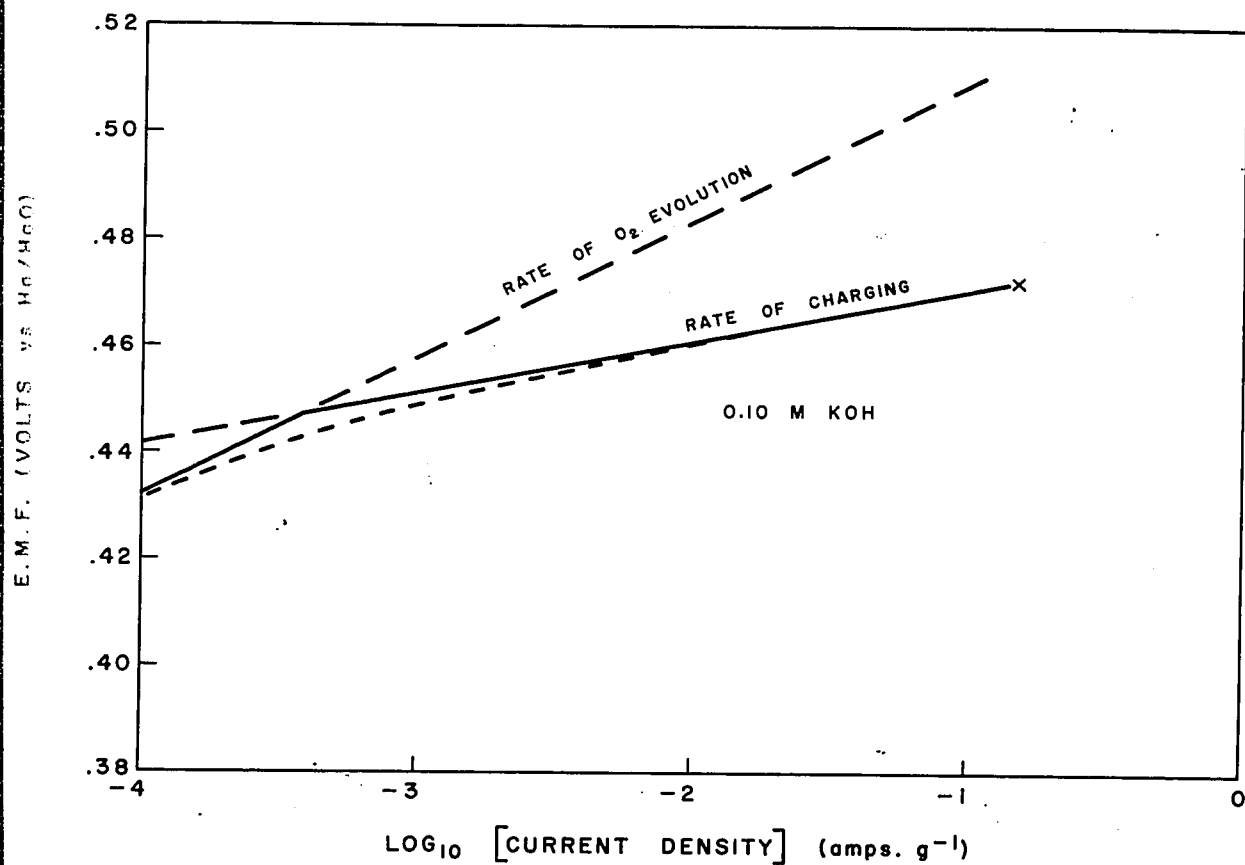
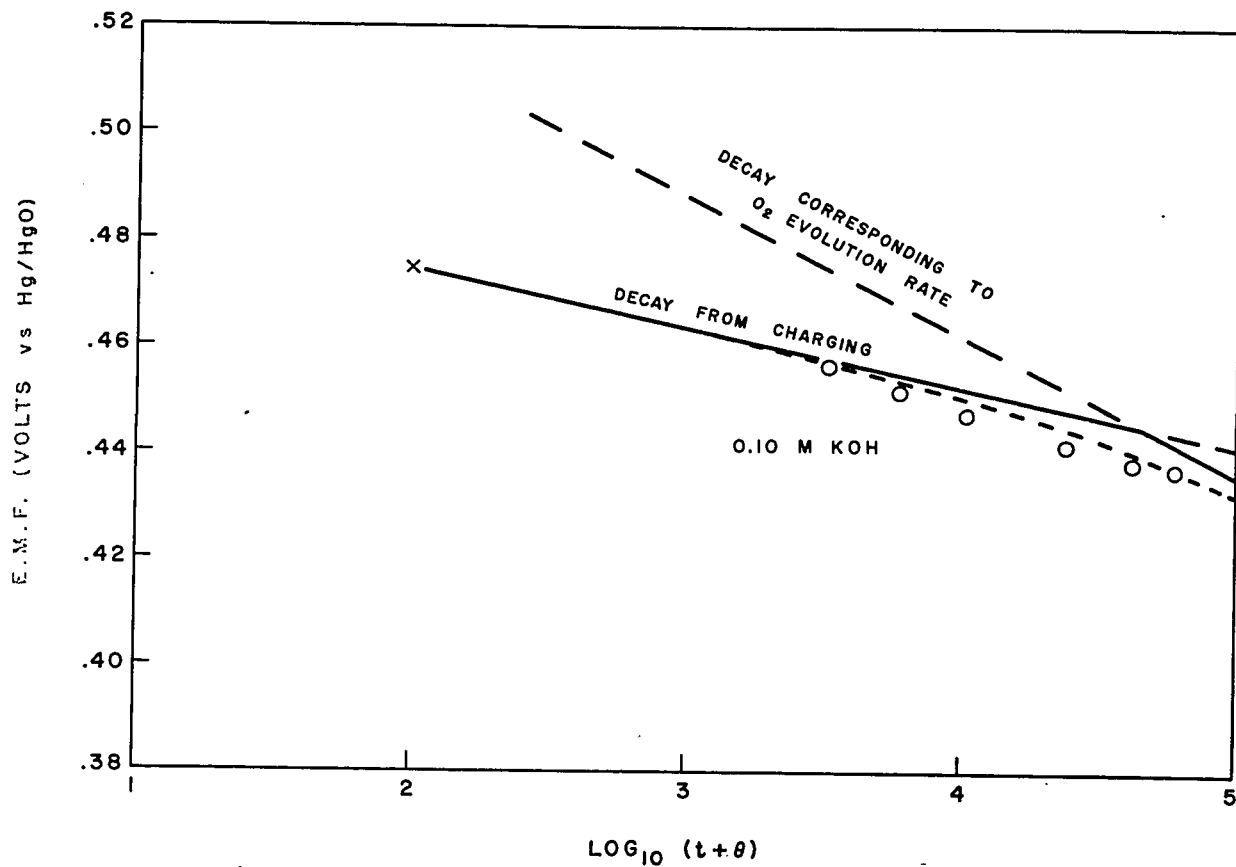
(1) Oxygen evolution on partially charged electrodes

The anodic decay lines for concentrations greater than 0.1 M KOH show an inflection from a low slope to a high slope with increasing time which is characteristic of alternative electrochemical reactions with different Tafel slopes as discussed by Parsons (10) (see Introduction, section 1 d). From the foregoing, it is evident that the process alternative to the one with the lower slope could be oxygen evolution. At higher anodic potentials we have examined the kinetics of oxygen evolution (cf. Figures XIV to XVII) and from these data it is possible to calculate what the rate of oxygen evolution will be in the range of potentials over which the polarization decay occurs at the semi-charged electrodes.

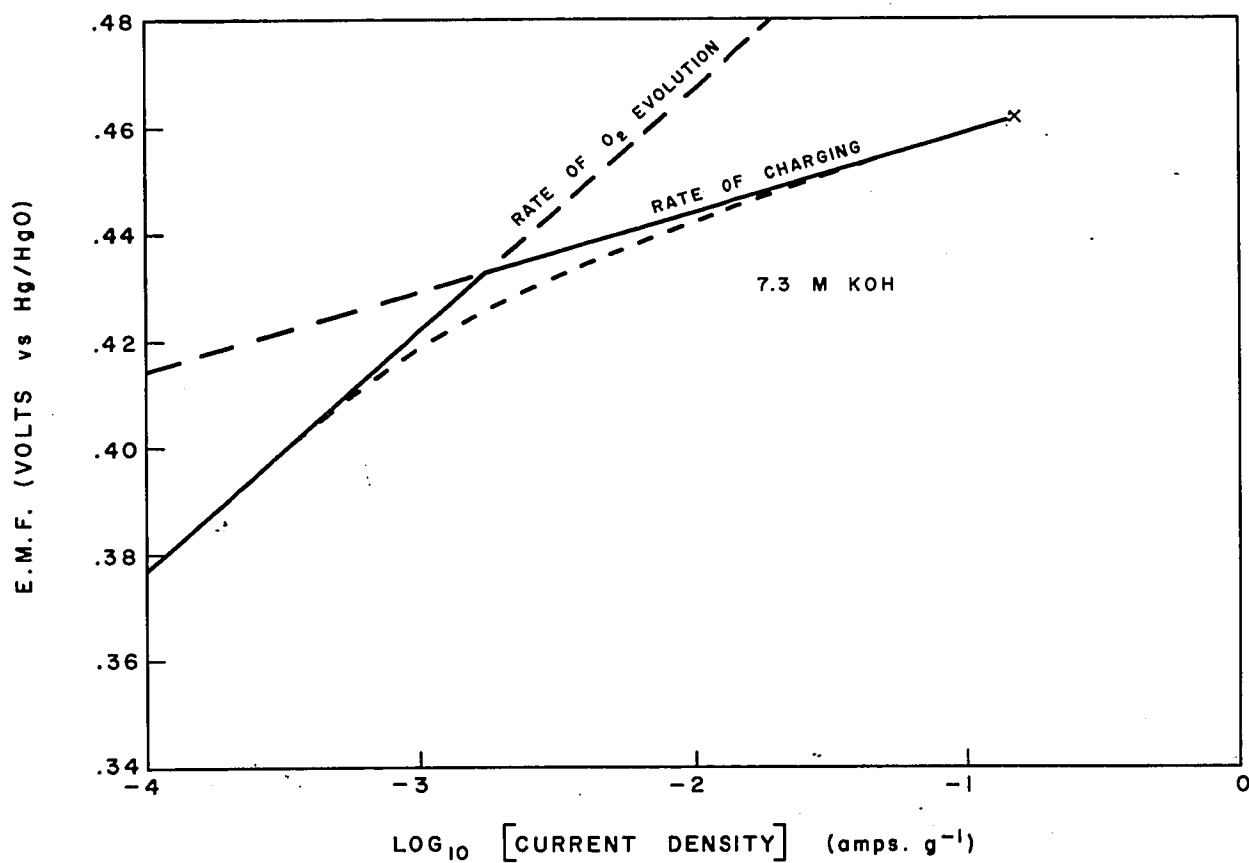
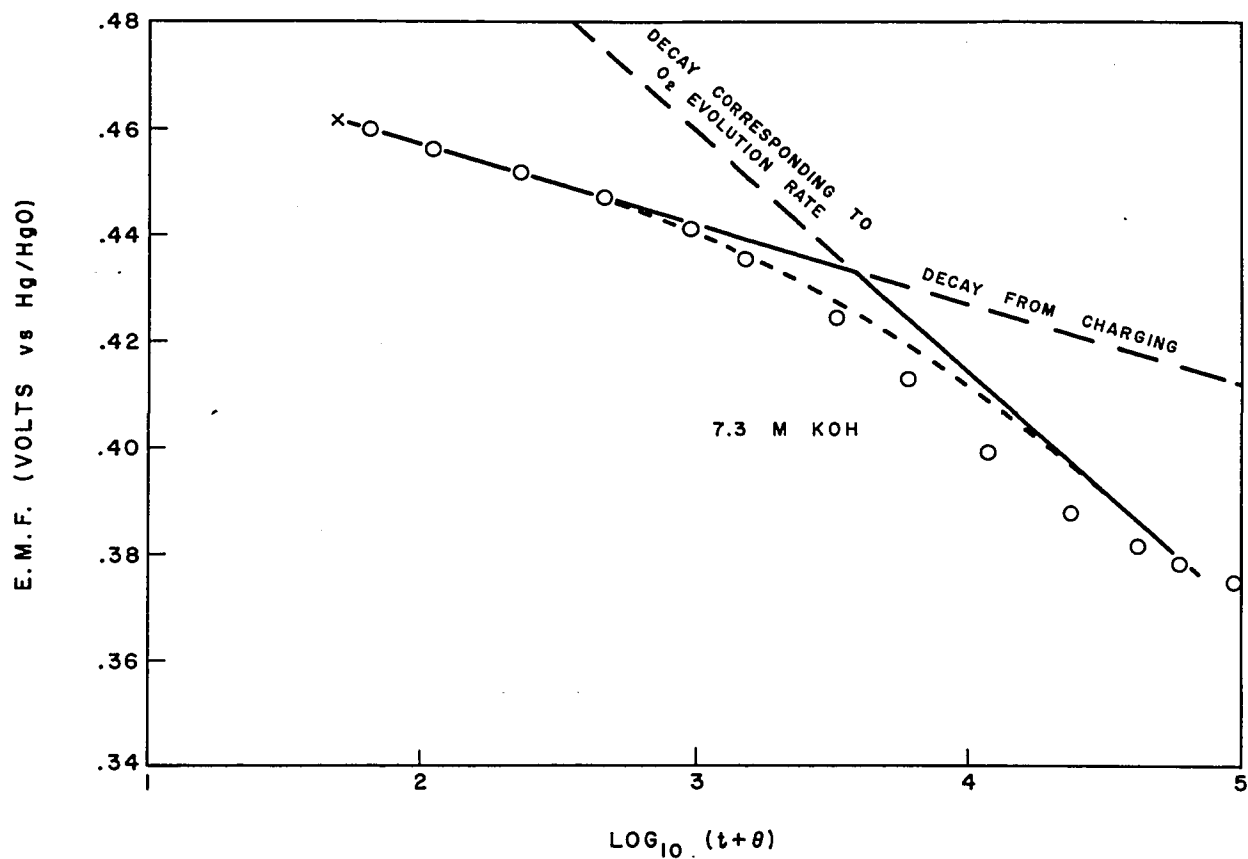
In Figures XLIXb and Lb are shown the Tafel lines for the anodic oxidation (I) of the semi-charged electrode and for oxygen evolution (II) in solutions of the same concentration. The solid lines show the polarization behavior based on i_0 and b values* for each of the alternative processes and the dotted line shows the calculated total rates over the potential range where I and II have comparable rates. Figures XLIXa and La show the same data plotted in terms of the e.m.f. decay lines, the dotted region corresponding to the total rate similarly drawn in Figures XLIXb and Lb and the points the actual e.m.f.'s obtained during an experimental decay run. It is clear from these figures that between 0.1 M and 7.3 M the inflections in the anodic decay lines are adequately accounted for by the alternative oxygen evolution process which becomes (because of its higher b value) the predominant process at low potentials. We may note that the cathodic lines in Figures XXIII a-d show no significant inflections; this would be expected since the alternative oxygen process is much slower at the more cathodic potentials. Calculations of the rates of the alternative oxygen evolution process indicate that the inflections in all the anodic decay plots up to 7.3 M KOH can be accounted for.

* The method of calculation of these parameters from the decay lines has been discussed previously (11, 1).

- Figure XLIX: (a) E.M.F. decay lines corresponding to rates of anodic charging and O_2 evolution: dotted line is resultant decay curve; circles represent experimental points (0.1 M KOH).
- (b) Tafel lines for anodic oxidation of the semi-charged electrode and for O_2 evolution (0.1 M KOH). Line for net current density is broken.



- Figure L: (a) E.M.F. decay lines corresponding to rates of anodic charging and O_2 evolution: dotted line is resultant decay curve; circles represent experimental points (7.3 M KOH).
- (b) Tafel lines for anodic oxidation of the semi-charged electrode and for O_2 evolution (7.3 M KOH). Line for net current density is broken.



(ii) Diffusion Effects

However, in the 14.6 M KOH solution and in some experiments carried out at 0° C, the oxygen evolution rate is too slow by a factor of about 100 to influence the decay, yet an inflection is observed (Figure XXIVa) and is also present now in the cathodic line. Furthermore, in the 14.6 M solution, the e.m.f. reached at long times is below the reversible oxygen potential to that the oxygen evolution process referred to above cannot be responsible for depressing the e.m.f. to this low value.

The electrochemical charging or discharging reaction causes changes of the relative concentrations of water and KOH in the sinter which can be shown to bring about a concentration polarization in the porous electrode which falls off with time on open-circuit owing to diffusion and gives rise to the inflection in Figure XXIVa.

These diffusion effects can arise in two ways:

- (i) from changes of e.m.f. of the electrode itself due to changes of KOH and water activity arising from Faradaic transport and the occurrence of the electrode reaction, and
- (ii) concentration polarization in the electrode arising secondarily from these concentration changes.

During charging, the water and KOH activities near the interface of the electrode material will be higher and

lower, respectively, than those in the bulk. After some time, a steady-state activity gradient of water and KOH will be set up in the electrode out towards the solution with a corresponding change in the electrode-solution potential difference. Upon termination of the charging, this activity gradient will fall to zero with attendant e.m.f. changes which will be superimposed on those arising from the "activation controlled" electrode processes discussed above.

It is of interest to make a semiquantitative calculation to establish if these effects could account for the observed inflection in the decay lines in 14.6 M KOH.

(a) Model: an infinite slab of thickness h is assumed (18) with homogenous solutions of concentration C_b at the two slab-solution interfaces. (The porous electrode approximates to this since its dimensions were 2.5 x 1.2 x 0.1 cm.) The integrated solution to the diffusion equation for this model is (89):

$$\frac{\bar{C} - C_b}{C_1 - C_b} = \frac{8}{\pi^2} \sum_{v=0}^{\infty} \frac{1}{(2v+1)^2} \exp \left[- \left(\frac{(2v+1)\pi}{h} \right)^2 Dt \right] \quad [63]$$

where $\bar{C}$ is the mean concentration of diffusing substance (diffusion constant D) at time t , C_1 the initial concentration (or in the present case, the mean steady state concentration of KOH during charging, prior to decay), and v the order of the terms required in the Fourier solution of the diffusion equation.

(b) Calculation of concentration changes with time: we cannot make a rigorous calculation of concentration changes with time owing to the complexity of the diffusion problem in a real electrode. However, the following method involving two successive approximations will enable an estimate of the magnitude of the changes of concentration with time to be calculated. Diffusion will occur as soon as any changes of concentration are brought about by the electrolytic charging. At the end of this process, the average concentration in the sinter will hence be less than that which would have arisen had there been no diffusion during charging.

As a first approximation, we assume hypothetically that the latter condition obtains and that this results in a change of mean concentration $\Delta \bar{C}$. The fall of $\Delta \bar{C}$ (with no current passing) with time is then calculated from equation [63] and from this plot rates of change of mean concentration $d\bar{C}/dt$ can be calculated at various times. As a second approximation, we then obtain that value of $d\bar{C}/dt$ from the values discussed above, which corresponds to the rates of production of water and removal of KOH, respectively, during charging. This value of $d\bar{C}/dt$ will then be relevant to that time at which the current is interrupted for decay measurements. In the first approximation treatment, this rate of change of concentration would have been reached after a time t' . The subsequent decay of $\Delta \bar{C}$ with time t after the actual termination of charging is

then calculated and plotted against t and this concentration change $\Delta \bar{C}$ after the times t would be equivalent to the same changes of concentration after times $t + t'$ in the first approximation calculation. This procedure will thereby allow approximately for the fact that during electrolysis some steady state change of concentration will tend to have been set up which will be less than that occurring if no diffusion took place. Two alternative values of D in equation [63] were taken as 10^{-6} and $3 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$ in order to place limits on the resulting e.m.f. variation which could arise from uncertainties in the value of D . The above values were estimated from data at low concentration (90) by correction for the relative viscosity (η_r) of 14.6 M KOH ($\eta_r = 12$) and after empirical allowance for the fact that, in the porous electrode, the diffusion path length will probably be somewhat longer than that corresponding to the free linear diffusion and the fact that the channel area available for diffusion out of the electrode will be less than the projected area of the electrode. The values of D taken are probably of the right order of magnitude but cannot be regarded as more precise than this.

From the changes of concentration calculated by the above procedure, the total change of e.m.f., ΔE_c , with time, due to diffusion effects, can be calculated using equation [51]

(see below section 2e) and the data given by Akerlöf and Bender (72) for concentration cells in KOH and water.

The calculated values of ΔE_c are shown for 14.6 M KOH in Figure XXIVa as a function of time during decay and it is seen that ΔE_c is comparable with the total anodic polarization observed and can hence account fairly well for the form of the inflected decay line in 14.6 M KOH. Similar considerations apply to the cathodic line where effects in an opposite direction will occur. It may be noted that no value of θ exists which can lead to linearity of the decay curve in Figures XXIVa or XXIVb.

We can therefore conclude that the potential to be taken as the reversible one in 14.6 M KOH (Figure XXIVa) is that corresponding to the intersection of the anodic and cathodic decay lines after the longest times. The same conclusions will apply to the results in saturated KF solution (Figure XXIVb).

Diffusion effects will be much less significant in the more dilute and less viscous solutions since it may readily be shown that ΔE_c values are much smaller and the times over which diffusion equilibration is occurring are much shorter (owing to the higher diffusion constants) than those for the 14.6 M solutions. For the more dilute solutions, the inflections arise, as discussed above, from the alternative

oxygen evolution process.

It can be shown that these effects in dilute solution are operative over periods of time comparable to θ (the time correction applied to allow for a finite charging rate). Thus diffusion effects are absorbed in the empirical assignment of θ . This will introduce some uncertainty in its value but will have no significant effect on the slope of the anodic and cathodic decay lines since θ in these cases is not larger than about 100 seconds.

(iii) Mixed Potentials

From the above, it is seen that the potentials reached at the intersection of the decay lines for solutions up to 7.3 M in KOH (or at very long times) must be the mixed potentials corresponding to a finite rate of oxygen evolution and self-discharge on open-circuit. These potentials will be less anodic than the true reversible potentials. From the present data (Figures XXIII a-d) and from the work described above (cf. this chapter section 1 b, iv and vi), we can obtain the polarization parameters i_0 and b for the cathodic and anodic partial "corrosion" reactions, respectively, in the self-discharge process; hence, the mixed potential and the net self-discharge rate at this potential may be calculated as shown in Figure LI for 7.3 M KOH solution. In this diagram, E_m is the steady-state mixed potential, E_r the ideal reversible

potential, and i_d the net rate of "corrosion" or self-discharge. It is clear that any e.m.f. measurements (cf. 30,33,56) taken on open-circuit at long periods of time, except in the most concentrated solutions and at low temperatures, will not give the true reversible potential E_r but the steady-state mixed potential E_m , which will be lower than E_r by 5-30 mv. Similar figures to LI may be drawn for the other concentrations of KOH and, except for the 14.6 M KOH solution, the extrapolated or long-time potentials will be E_m .

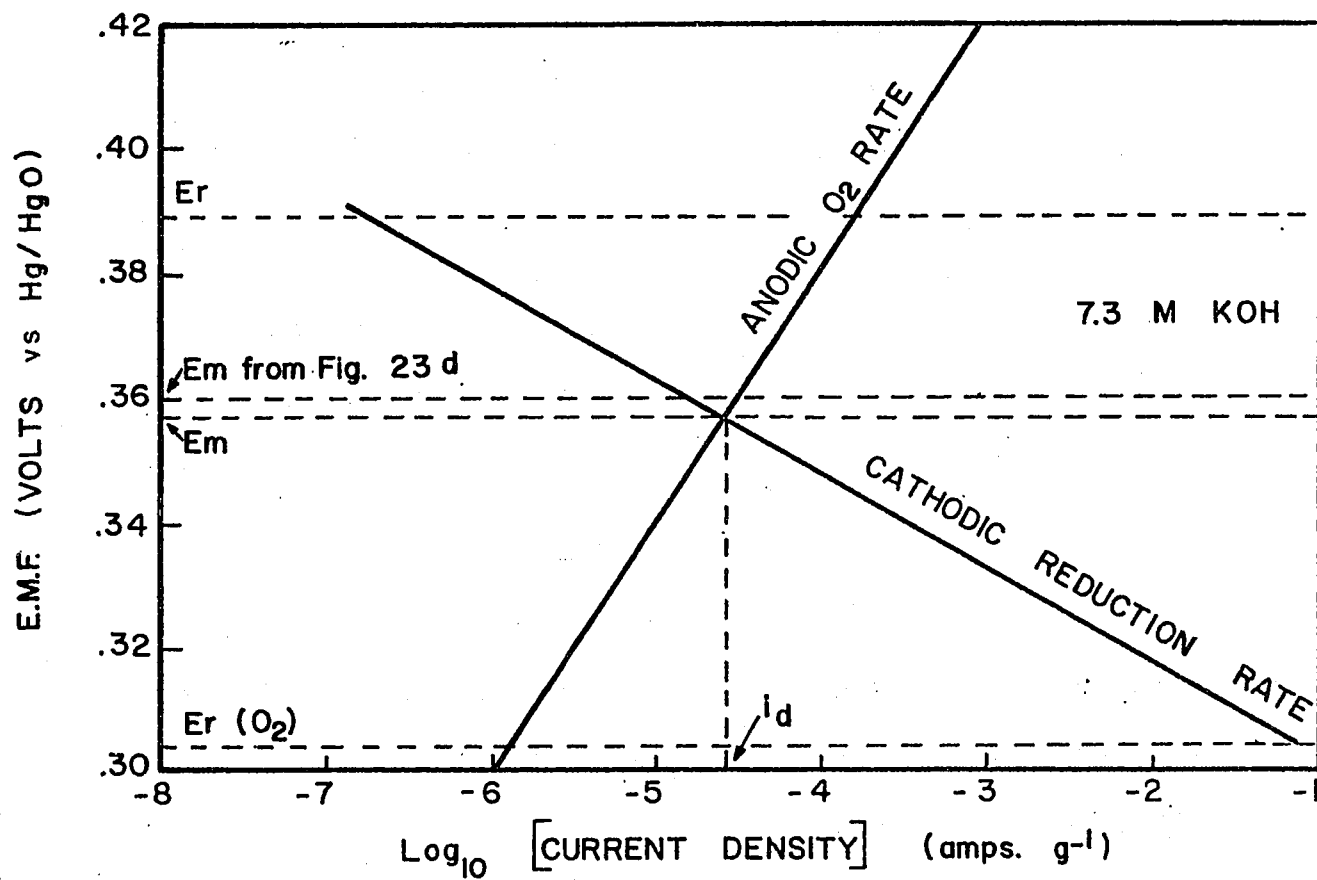
d) Assignment of Reversible Potentials

In solutions up to 7.3 M in KOH, the true reversible potentials E_r should be based on extrapolation of the whole region of the cathodic decay lines and that region of the anodic line before which oxygen evolution becomes a significant process, i.e. in the first 3.5 decades of $t + \theta$. The values of E_r thus obtained are shown as circles in Figure XXVII whilst the long-time values or those based on all the decay points (i.e. the E_m values) are indicated by crosses. They differ, as expected, by 5-30 mv. In the derivation of the Nernst equation for the electrode, it is clear that the E_r , and not the E_m values as usually used (30,33,56), must be considered.

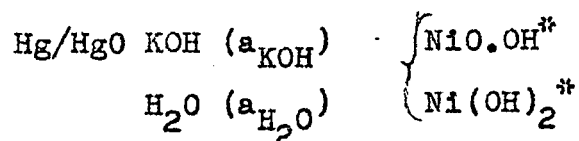
e) The Nernst Equation for the Electrode

From the above assignment of reversible potentials,

Figure LI: Polarization lines for the partial reactions in the "corrosion" or self-discharge of the nickel oxide electrode in 7.3 M KOH.



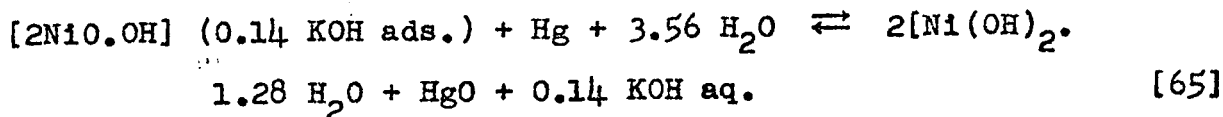
we obtain a series of E_r values at various KOH concentrations. Using the data of Akerlöf and Bender (72), these E_r values can be expressed as logarithmic functions of activity of KOH and water. Three unknowns are then involved in the Nernst equation for the potential-determining electrode process viz., E^0 , and the two coefficients of the logarithmic activity terms. Using the data shown in Figure XXVII for E_r , we may obtain three (or more) simultaneous equations in E_r (experimentally determined), E^0 , $\ln a_{H_2O}$, and $\ln a_{KOH}$, which give, upon numerical solution, the following Nernst equation at 25° C for the cell



where the * refers to unspecified and probably non-stoichiometric (22,23,24) quantities of associated water and adsorbed KOH:

$$E_r = 0.420 (\pm 0.002) - 0.004 (\pm 0.001) \log_{10}[a_{KOH}] + 0.105 (\pm 0.01) \log_{10}[a_{H_2O}], \quad [64]$$

which corresponds to the formal reaction



It will be noted that in this equation terms both in KOH and water activity are required to represent the results, i.e.

the dependence of E_r on KOH concentration cannot be quantitatively accounted for through the diminution of water activity with increasing KOH concentration. This residual dependence on KOH activity is consistent and in fair agreement with that deduced from previous work (56) and our own (see below) using a KOH/KF mixture. Chemically, adsorption of KOH at the higher oxide is not inconsistent with the general properties of higher oxides, which are usually more acidic than corresponding lower ones.

The dependence on water activity is, however, very much greater than that found in Kornfeil's work (56) and is moreover in the opposite direction to that found by him.

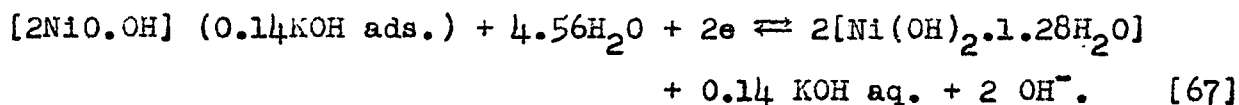
Our results are in qualitative agreement with those of Zedner (30,31) with regard to direction of the dependence of e.m.f. on water activity. It is unfortunate that Kornfeil's results are presented in an obscure fashion; thus, no absolute values of E_r as a function of concentration are stated and the dependence of e.m.f. upon concentration is expressed only as a fraction of the e.m.f. value for a 0.01 M KOH solution, i.e. E° is not stated. Kornfeil's equation

$$E = E^\circ - 0.029 (0.16 \log_{10} a_{H_2O} + 0.067 \log a_{KOH}) \quad [66]$$

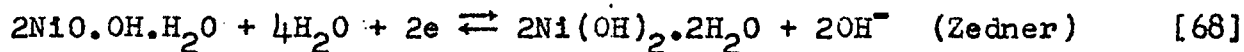
also predicts, using the data of Akerlöf and Bender (72), a minimum e.m.f. at 12 molal KOH, whereas in the present work and in that of Zedner (30,31) the e.m.f. continues to decrease

rapidly with increasing concentration at high concentrations of KOH. Since we have no knowledge of the actual e.m.f. values in Kornfeil's work, it is difficult to seek an explanation of his anomalous results. It may be remarked, however, that the procedure used in his work was different to that used here and involved analytical determinations of the change of KOH and water concentrations relative to that of ^a/KCl or KBr reference electrolyte. The interpretation of results obtained by this method may be complicated by variation of adsorption of KCl on the electrode with changing KOH concentration and electrode potential. Thus it is well known that Cl⁻ ions are specifically adsorbed at electrodes particularly at potentials anodic to the potential of zero charge (74).

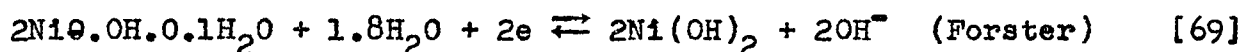
For the single electrode process at the nickel oxide electrode, equation [65] gives



Equations derived by other workers expressed in corresponding form (cf. 69) to that of equation [54] are



and



from which it is seen that apart from the KOH adsorption not

considered in the earlier work, our results with regard to dependence on water activity are in closest agreement with those of Zedner. Forster's results (33) differ from the above, possibly on account of the use of nickel oxide electrodes containing graphite. Kornfeil's equation $[2NiO.OH](0.067KOH \text{ ads.}) + 0.8H_2O + 2e \rightleftharpoons 2Ni(OH)_2^* + 2OH^- + 0.067KOH$ leads to an anomalously small role of water in the electrode process. Most of the above equations involve non-stoichiometric amounts of hydrate water and this is not inconsistent with available data (36,65,92) which indicate non-stoichiometric ranges of hydrate composition.

As an independent check on the validity of our equation [64], the measurements made (Figure XXIVb) in saturated KF containing 0.08 M KOH enabled a value of E_r to be obtained at a low KOH activity (1.3^*), and in which solution the water activity (determined directly by a differential vapor pressure measurement at $25^\circ C$) was also low at 0.30. The value of E_r observed experimentally in the KF/KOH mixture was 0.362 v whilst that calculated from equation [64] for the same conditions is 0.364 (the agreement is thus within the reproducibility claimed (see Results, Section 3)) in the present work.

* The activity coefficient for KOH in the mixed electrolyte was taken as that for a solution of pure KOH having the same water activity as that (0.3) in the KF solution. This approximation is justified since, at very high ionic strengths, the activity coefficient is determined to a large extent by ion-solvent interaction.

CHAPTER V

APPENDIX

CONSIDERATIONS OF PRACTICAL INTEREST IN RELATION
TO BATTERY PERFORMANCE

1. General

Considerable practical interest exists in the electrical behavior of the nickel oxide electrode owing to its use as the positive plate in the nickel-cadmium accumulator. In view of this, some aspects of the behavior discussed above are reviewed here in relation to their practical consequences:

2. The Effect of KOH Concentration on the Stability of the
Higher Oxide

The shelf-life of the charged nickel-cadmium battery is largely determined by the rate of loss of oxygen, or self-discharge, of the nickel oxide positive plate (93). This is evident from the fact that the gas evolved on open-circuit from a fully charged battery or positive plate electrode consists almost entirely of oxygen (33). Self-discharge of the cadmium plate through evolution of hydrogen is a much slower process, its rate being negligible in strongly alkaline

solutions at room temperature (82).^{*} In a practical battery most of the actual "self-discharge" of negative plates (i.e. oxidation of them) occurs indirectly through reaction with oxygen which is liberated from the positive plate and diffuses over to the negative plates.

This loss of oxygen from the higher nickel oxide has been studied in some detail in the present work and the dependence of its rate upon potential, temperature and concentration has been discussed. The effect of concentration, however, merits a few additional comments here. Concentration of the electrolyte affects the self-discharge rate in two distinct ways: (a) it will affect the kinetics of the oxygen evolution reaction; thus, at a given potential (w.r.t. Hg/HgO) a higher concentration of KOH would tend to result in a higher rate of self-discharge; (b) it will determine the reversible potential of the electrode for a given composition of the oxide. A higher KOH concentration will result in a lower (anodic) potential (at constant composition of the oxide) and thus, for this reason, will tend to lead to a decrease in the rate of self-discharge. These two effects are seen to

* The standard reversible potential for the reaction $2e + \text{Cd}(\text{OH})_2 \rightleftharpoons \text{Cd} + 2\text{OH}^-$ is -0.815 v. (Stockholm Convention). This compares with -0.828 for the standard hydrogen electrode in alkaline solution so that the cadmium electrode is thermodynamically stable in a solution saturated with hydrogen.

work in opposition to each other but an analysis of the results shows that the second of the two is dominant. This is particularly evident in the very concentrated solutions. It will in fact be noted that in a solution of 14.6 molar KOH the reversible potential at 25° C of an electrode 50% oxidized (i.e. "NiO_{1.25}") is lower than the reversible oxygen potential and thus the following important practical conclusion can be deduced, viz. that no self-discharge is possible under these conditions if the solution is saturated with oxygen. Very concentrated solutions (12 molar or more) could perhaps be profitably used where stability of the charged positive plate is of prime importance (e.g. where long periods of storage of charged batteries at elevated temperatures are necessary). This additional stability would however be obtained at the expense of a lower open-circuit e.m.f., of greater polarization during discharge (cf. Figures XXIII and XXIV) as well as a loss of the advantages characteristic of the battery at low operating temperatures, on account of crystallisation of the alkali hydrate.

3. Charge and Discharge Characteristics

It follows from the results of experiments on the decay from polarization at partially charged electrodes that the electrolytic oxidation and reduction of nickel oxide is by no means a reversible process in the thermodynamic sense.

In fact the exchange current is not particularly large (approximately 10^{-7} amps per gram) and it is in fact, only because the process exhibits a very strong dependence of rate upon overpotential (i.e. is associated with an unusually low Tafel slope) that the system is practicable as a battery electrode. In practical terms this very low Tafel slope means that the potential during discharge is not greatly dependent upon the rate of discharge; thus, changing the discharge rate by a factor of ten will only increase the polarization by 10 to 15 millivolts. Our results show that the Tafel slope for the discharge process is lowest in the more dilute KOH solutions, so that the rate of the discharge process will exhibit the least potential dependence under these conditions.*

In addition to having a low Tafel slope for electrolytic reduction, some internal polarization, due to the "corrosion type" mechanism of self-discharge referred to previously, is already impressed upon these electrodes on open-circuit and this tends to minimize even further the "apparent" polarization during discharge. The effect is

* This does not take into account any Ohmic IR drop in the solution which in fact may be quite significant in dilute solutions in a practical battery operating at high current drain.

best illustrated by considering the discharge of an electrode having typical values of exchange current, Tafel slope and self-discharge rate. Let these be, respectively, 10^{-7} amps per gram, 0.010 volts per current density decade and 10^{-5} amps per gram respectively. On open-circuit the steady-state potential will be displaced 20 millivolts below the true reversible potential due to self-discharge. On discharge at 10^{-1} amps per gram (approximately "3 hour" rate) the potential will be displaced 60 millivolts below the reversible potential. Thus the "apparent" polarization at a discharge rate of 10^{-1} amps per gram is only 40 millivolts. If, however, one charges the electrode at the same current-density the "apparent" polarization will be 80 millivolts. This accounts for the effect frequently observed experimentally (33,40) that a greater apparent polarization arises during charging than during discharging of nickel oxide electrodes.

It will be noted that this effect is significant even though the rate of self-discharge may be very small. In the case considered above the rate of self-discharge at 10^{-5} amps per gram is, for example, such that more than one year would be necessary to discharge the electrode.

4. Effects of Rate of Charge

The results of this work lead to the rather surprising conclusion that charging will be most efficient at the highest

potentials and consequently at the highest rates. During anodic polarization two alternate reactions may occur i.e. oxidation of Ni(OH)_2 to " NiOOH " and evolution of oxygen. The kinetic parameters of these two reactions are such that the latter is favored at low overpotential (potentials just slightly above the true reversible potential) whilst the former, oxidation of Ni(OH)_2 to " NiOOH ", is favored at higher overpotentials. This is most readily seen by considering Figures L. Here we have represented the Tafel lines for the Ni(OH)_2 oxidation process and for the oxygen evolution process in 7 M KOH. As may be seen from the diagram at potentials below about 0.430 volts (w.r.t. Hg/HgO) more than 50% of the total current goes toward oxygen evolution while at potentials greater than about 0.450 volts more than 90% goes toward oxidation of Ni(OH)_2 . In this particular case a current density of about 10^{-2} amps per gram can be shown to be required for 90% efficiency of charging.*

5. The (Possible) Effects of Cycling, Impurities and Additives

It has been mentioned previously (cf. Figure XXXVII) that subjecting an electrode to a number of charge and discharge cycles decreases the exchange current for the oxygen

* This figure applies to an electrode which is 50% charged; at a lower degree of charge the efficiency of charging would be higher and conversely at higher degrees of charge it would be less.

evolution process. In terms of the polarization diagram in Figure LI this may be indicated by shifting to the left the Tafel line for oxygen evolution. This will result in a lower rate of self-discharge and, assuming the kinetic parameters for the $\text{Ni}(\text{OH})_2$ oxidation process remain unchanged, a higher (i.e. a more positive) mixed potential. The higher mixed potential in turn will result in a greater "apparent" polarization during discharge and smaller "apparent" polarization during charge. The actual measured potential during charge and discharge will of course remain unchanged. Although this area has not been explored in this work it would appear possible that addition of chemical additives inhibitory to the oxygen evolution reaction could perhaps prove effective in further reducing the self-discharge rate. However, it must be kept in mind that the $\text{Ni}(\text{OH})_2$ oxidation reaction (probably) involves the same initial discharge steps as the oxygen evolution reaction and care must be taken not to inhibit the redox reaction involving $\text{Ni}(\text{OH})_2$. On the other hand, any additives that would facilitate the bulk oxidation and reduction reactions would improve the dynamic characteristics of the electrode. The effect on self-discharge would be to increase it slightly - other things being equal.

6. Deduction of Rates of Self-Discharge

At high degrees of charge the self-discharge rate can be directly determined micro-volumetrically by measurements of th

rate of oxygen evolution. For the "partially charged" electrode (degree of oxidation less than " $\text{NiO}_{1.5}$ ") this procedure cannot be used but the self-discharge rate can be deduced from a polarization diagram (Fig. LI) where the Tafel lines are plotted for the anodic and cathodic partial reactions which are proceeding during the self-discharge (this treatment is analogous to that used in deducing rates and potentials of corrosion of metals). From the e.m.f. decay and recovery lines determined at the partially charged electrodes and for the oxygen evolution rate lines (expressed in terms e.m.f.-log [rate]) determined at more highly charged electrodes we may construct (as we have shown above) the polarization diagram for self-discharge as shown in Fig. LI. The point of intersection of the cathodic and anodic partial current lines gives a point the coordinates of which give the self-discharge potential (a "mixed potential" as in corrosion of a metal) and the rate of self-discharge directly. Such diagrams are hence of considerable practical interest in evaluating shelf-life of battery electrodes and rates of self-discharge after charging.

7. Corrosion of the Nickel Metal in the Oxide Electrodes

During use of the micro-volumetric technique (see Chapter II, 7) for oxygen evolution measurements it was found that a consumption of oxygen could be detected when the

unimpregnated plaques were used in oxygen-containing KOH solutions at room and elevated temperatures. The extent of oxidation of the nickel amounts to about 5% of the capacity obtainable with the fully impregnated electrode based on a plaque of the same size. The spontaneous (and anodic) direct oxidation of the unimpregnated nickel plaque can be markedly accelerated by trace additions of chloride ions. Appreciable capacities can be generated in unimpregnated nickel plaques by this procedure but in all cases impregnation with Ni(OH)_2 still gave substantially higher electrochemical capacities.

CLAIMS TO ORIGINAL RESEARCH

1. The mechanism of self-discharge of the "fully charged" nickel oxide electrode has been elucidated quantitatively for the first time.
2. A new microvolumetric technique has been developed which has permitted the precise measurement of rates of oxygen evolution on open-circuit.
3. This microvolumetric technique has enabled the true kinetic parameters for open-circuit oxygen evolution on the nickel oxide electrode to be evaluated and it has been shown that self-discharge proceeds by an electrochemical mechanism involving anodic and cathodic partial processes.
4. Studies of (a) H-D isotope effects, (b) heats of activation and (c) comparison of the kinetic parameters for open-circuit oxygen evolution with those for steady state d.c. polarization has enabled the rate-controlling process in the self-discharge of the nickel oxide electrode to be identified as the anodic oxygen evolution reaction.
5. This oxygen evolution process has been shown to proceed by either of two distinguishable rate-controlling mechanisms depending upon potential, temperature and electrolyte concentration. Tafel slopes and exchange currents for these two mechanisms have been evaluated.

6. E.M.F. decay slopes on open-circuit have been measured and these have been compared with true Tafel slopes obtained from oxygen evolution studies. The theoretical significance of decay slopes has been examined and it has been shown that the values of these slopes will be identical to those of the corresponding true Tafel slopes only if the electrode has a constant capacitance over the potential range involved. Cases where the electrode capacitance varies with potential are discussed (see below). Comparison is made between theory and experiment for cases of potential dependent and potential independent capacitance and it is shown that the direction of variation of surface capacitance, i.e. its increase or decrease, with increasing potential can lead to information on the extent of surface coverage. Linear e.m.f. - $\log$ [time] lines also result when the capacitance is an exponential function of potential but under such conditions the e.m.f. decay slope will not be identical with the Tafel slope. It is shown, however, that true Tafel and mechanistically significant slopes can be deduced from such e.m.f. decay slopes if the relation between capacitance or surface charge and potential is known;

7. Techniques used to study the self-discharge process of the fully oxidized nickel oxide electrode ($\text{NiO}_{1.5}$) have been applied to the semicharged electrode ($\text{NiO}_{1.25}$) in order to elucidate the kinetics of oxidation and reduction of the bulk material involving Ni^{II} and Ni^{III} .
8. The true thermodynamic reversible potential of the nickel oxide electrode in a state of oxidation $\text{NiO}_{1.25}$ has been evaluated for the first time. Previously measured "equilibrium" potentials have been shown to be "mixed" potentials which, in fact, can differ from the true reversible value by 20 to 30 millivolts. Mixed potential diagrams have been obtained which quantitatively relate "mixed" or "steady state" potentials to true reversible potentials.
9. The stoichiometry of the oxidation-reduction reaction $\text{Ni}^{\text{II}} - \text{Ni}^{\text{III}}$ has been evaluated from the dependence of true reversible potentials upon water and KOH activity.

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